स्वाध्याय स्वमन्थन स्वावलम्बन

UTTAR PRADESH RAJARSHI TANDON OPEN UNIVERSITY

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UP Rajarshi Tandon Open University

UGCHE-05
Organic Chemistry-I

FIRST BLOCK : Fundamental Concept

SECOND BLOCK : Basic Skeleton : Hydrocarbons and Heterocycles

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UTTAR PRADESH
RAJARSHI TANDON OPEN UNIVERSITY

UGCHE - 05
Organic Chemistry - I

Block

1

FUNDAMENTAL CONCEPTS

UNIT 1

Bonding, Functional Group Classification and Nomenclature 9

UNIT 2

Stereochemistry – I 39

UNIT 3

Stereochemistry – II 61

UNIT 4

Effect of Molecular Architecture on Physical Properties 91

UNIT 5

Structure – Reactivity Relationships 121

ORGANIC CHEMISTRY

Organic Chemistry course is one of the elective courses for Bachelor's Degree Programme in Science. The concepts dealt with in this course will be useful in understanding the courses on "Organic Reaction Mechanism" and "Biochemistry"

The organic compounds and their reactions have been utilised by the people since the discovery of fire. The ancient Egyptians used organic compounds such as **indigo** and **alizarin** to dye cloth. The fermentation of grapes to yield alcohol and extraction of plants to yield medicines is known since thousands of years back. But, as a science, Organic Chemistry is less than 200 years old.

During the 1780s scientists began to distinguish between **organic compounds** and **inorganic compounds**. The study of substances derived from non-living matter was called **inorganic chemistry** while the study of matter obtained from living systems was called **organic chemistry**. The term organic chemistry was coined by Berzelius in 1807. Combustion studies established that the compounds obtained from living systems contained carbon and therefore, it led to a new definition of organic chemistry as the **chemistry of carbon compounds**. This definition is still used today. At that time, it was believed, that living systems possessed a *vital force* which was absent in non-living systems. This vital force was thought to be responsible for the synthesis of organic compounds. Thus, it was held that such a synthesis is possible only in living organisms and as a consequence, organic compounds could not be synthesised in laboratory.

This barrier between organic and inorganic chemistry was penetrated in 1828 by a German analyst, Wohler who in an attempt to synthesise ammonium cyanate (NH_4CNO) obtained urea ($NH_2\overset{O}{\overset{\|}{C}}NH_2$), an organic compound. The Wöhler's synthesis of an organic compound in the laboratory starting from inorganic constituents is a milestone in the history of organic chemistry, as it marked the beginning of an end of the 'vital force' theory.

Another important result of Wöhler's synthesis was the observation that both ammonium cyanate and urea have the same moleculer formula. Berzelius used the term **isomerism** to denote this phenomenon of existence of two or more compounds having the same elemental composition or molecular formula.

The concept of isomerism was vital in the development of the ideas of **structural theory** which was independently proposed by Kekulé, Couper and Butlerov between 1858 and 1861. They proposed that atoms of elements present in organic compounds can form a fixed number of bonds, called their *valence*. It was proposed that the carbon atom is always tetravalent and it can form bonds with other carbon atoms. The structural theory implied that a precise arrangement of atoms, i.e., its structure, uniquely defines a substance. The structural theory has been used to explain the physical architecture of many molecules.

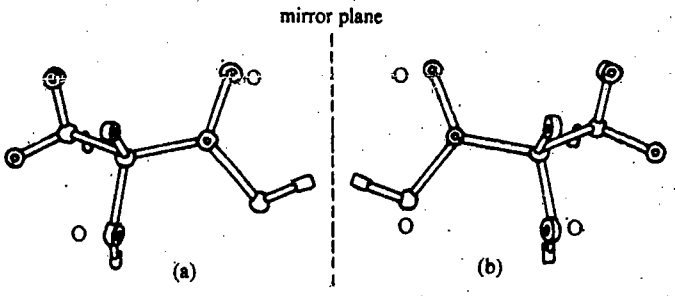
The properties, both physical and chemical, and reactivity of a molecule depend upon its structure. It is this idea which we will develop and study throughout this course. By understanding the relationship between the structure and reactions of molecules, you will be able to make predictions about the behaviour of new molecules and their reactions.

This course consists of four blocks. The first block contains the fundamental concepts or the nuts and bolts of organic chemistry. The concepts explained in this block will be used in understanding the ideas discussed in later blocks.

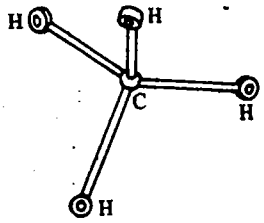
Block 2 deals with the Chemistry of hydrocarbons and heterocyclics which constitute the framework to which when various functional groups are attached, an enormous variety of organic compounds arises.

The functional derivatives of hydrocarbons will be discussed in Block 3 and Block 4. Block 3 includes the halogen derivatives, alcohols and phenols, ethers, sulphur analogs of alchols and ethers and carbonyl compounds. Block 4 deals with the

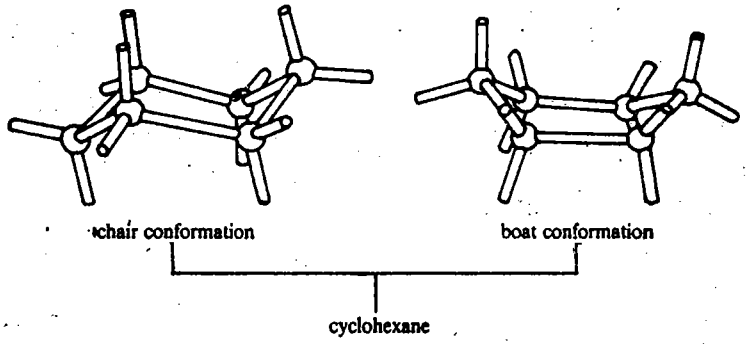
and *trans*-isomers. Similarly, you can make models for various other molecules, some of which are illustrated below:

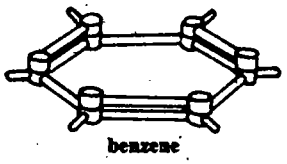


Enantiomers of Lactic acid



methane





benzene

BLOCK 1 FUNDAMENTAL CONCEPTS

In Block 1, we introduce the basic concepts of organic chemistry. There are five units in this block. In Unit 1, we explain the basic structural features such as bonding and hybridisation in organic molecules. As you progress in the study, you will come across with a large number of compounds; therefore, classification and nomenclature of compounds has also been discussed in this Unit.

Units 2 and 3 deal with Stereochemistry. It gives you an idea about the shapes of molecules in three-dimensions. Various activities using the models provided will be helpful in understanding the concepts explained in these units.

In Unit 4, the relationship between the molecular structure and physical properties of the molecules has been discussed. The spectral properties are also included as the spectroscopy has revolutionised the identification of organic compounds.

In Unit 5, we will explain the dependence of molecular reactivity on molecular structure. Here we will discuss various factors influencing the reactivity of the molecules.

You require to be patient and careful while studying the concepts described in this block.

The concepts which you will learn in this block will be useful in understanding the material of subsequent blocks.

Objectives

After studying this block, you should be able to:

- write the IUPAC name of a given compound from its structure and vice versa,
- write the possible isomers of a given compound,
- distinguish between geometrical isomers,
- assign the absolute configuration at the chiral centres in a molecule,
- draw the conformations of simple alkanes and cyclohexanes and comment on their stabilities,
- explain the gradation in the physical properties of a group of related molecules based on their molecular structure,
- compare the reactivities of various molecules on the basis of various factors such as structural, steric and solvent effects.

UNIT 1 BONDING, FUNCTIONAL GROUP CLASSIFICATION AND NOMENCLATURE

Structure

1.1 Introduction
Objectives
1.2 The Covalent Bond
1.3 Structural Formulas
1.4 Orbital Hybridisation
sp^3-Hybridisation
sp^2-Hybridisation
sp-Hybridisation
1.5 Functional Group Classification
1.6 Nomenclature of Organic Compounds
1.7 Summary
1.8 Terminal Questions
1.9 Answers

1.1 INTRODUCTION

Organic Chemistry is a highly organised discipline. It is the study of the relationship between the structures of molecules and their reactions. We will begin our study with the type of bonding and structural aspects of the molecules. You are already familiar from Unit 3, Block 1 of the Atoms and Molecules course that the compounds can be broadly divided into two classes, ionic and covalent. Ionic compounds are composed of positively and negatively charged ions which are held together by electrostatic forces. Since ions can be regarded as spheres having symmetrical distribution of charge, no particular direction can be assigned to such type of bonding. For example, in NaCl lattice, Na^+ and Cl^- ions are held together by electrostatic forces; no Na^+ ion can be regarded as bonded to a particular Cl^- ion. In other words, there is no such entity which can be called as NaCl molecule. In fact, the electrostatic forces operate between a particular ion (Na^+) and all its neighbouring ions (Cl^-) of opposite charge. On the other hand, in covalent compounds, molecules are the structural units. In contrast to the ionic compounds, in covalent compounds, the molecules are formed by the sharing of electron pair(s) between the constituent atoms. The bonds formed by sharing of pair(s) of electrons are called covalent bonds. Since in organic compounds, the bonds formed by carbon atom are covalent in nature, we will study some features of the covalent bonding in detail. We will then explain shapes of molecules using the concept of hybridisation. We shall also learn various types of functional groups present in organic compounds and classify these compounds into various classes on the basis of the functional groups. Finally, we will study, how to name the compounds belonging to various classes.

Objectives

After studying this unit, you should be able to :

- describe general features of a covalent bond,
- define bond length, bond angle and bond energy,
- explain various types of hybridisation of carbon compounds,
- identify the functional groups present in a molecule,
- give IUPAC names of various compounds belonging to different classes, and
- write the correct structure of a compound from its name.

1.2 THE COVALENT BOND

The sharing of electrons to form a covalent bond leads to an increase in electron

density in between the nuclei. In such an arrangement, the forces holding the atoms together are also electrostatic in nature; but this time the forces operate between the electrons of one atom and the nucleus of the other. Such a system has lower energy and is more stable as compared to the energy of isolated atoms. It is so because each electron is now attracted by two nuclei. As a result, the formation of the bond is accompanied by the release of the energy. The same amount of energy has to be supplied to break that particular bond. The amount of energy required to break a particular bond (expressed in terms of kJ mol^{-1}) is called its **bond dissociation energy**. You should not confuse **bond dissociation energy** with another term **bond energy** which is an **average** value for a particular bond. The difference in these two energies can be illustrated by taking the example of methane, CH_4. If the C–H bonds are successively broken as shown below, then the bond dissociation energy for each step is as indicated on the right hand side.

	Bond Dissociation Energy
$CH_4 \longrightarrow H\cdot + \cdot CH_3$	427 kJ mol^{-1}
$\cdot CH_3 \longrightarrow H\cdot + :CH_2$	460 kJ mol^{-1}
$:CH_2 \longrightarrow H\cdot + \cdot\dot{C}H$	435 kJ mol^{-1}
$\cdot\dot{C}H \longrightarrow H\cdot + \cdot\dot{C}\cdot$	339 kJ mol^{-1}

You can see from these values that the dissociation energies are **different** for each C–H bond breakage. On the other hand, **bond energy** is a single average value which can be obtained as,

$$\text{Bond energy of the C–H bond} = \frac{427+460+435+339}{4} \text{ kJ mol}^{-1}$$

$$= \frac{1661}{4} \text{ kJ mol}^{-1} = 415.25 \text{ kJ mol}^{-1}$$

Thus, the C–H bond energy in methane is one-fourth of the energy required for the following change.

$$CH_4 \longrightarrow \cdot\dot{C}\cdot + 4H\cdot$$

Clearly, if the molecule is diatomic, then bond dissociation energy and bond energy are the same. Generally, bond dissociation energy values are more useful. Table 1.1 lists the bond energies and bond dissociation energies for some bonds in kJ mol^{-1} (at 298 K and 1 atm. pressure).

Table 1.1 : Bond Energy and Bond Dissociation Energy Values in kJ mol^{-1}

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Dissociation Energy	Bond	Bond Dissociation Energy
H–H	436	N–N	163	CH_3–H	427	Ph–OH	431
F–F	158	N=N	409	CH_3CH_2–H	418	Ph–NH_2	381
Cl–Cl	242	N≡N	945	$CH_3CH_2CH_2$–H	410	Ph–F	485
Br–Br	193	O–H	463	$(CH_3)_2CH$–H	395.5	Ph–Cl	406
I–I	151	O–O	146	$(CH_3)_3C$–H	381	Ph–Br	301
H–F	565	O=O	497	CH_3–CH_3	368	Ph–I	272
H–Cl	426.8	C–O	334.7	CH_3–F	451		
H–Br	364	C=O	694.5	CH_3–Cl	349		
H–I	297.1	O=C=O	803.3	CH_3–Br	293		
C–H	414	C–N	284.5	CH_3–I	234		
C–F	484	C=N	615.1	HO–H	498		
C–Cl	338	C≡N	866.1	CH_3O–H	427		
C–Br	276	N–H	389.1	CH_3–OH	383		
C–I	238	N–O	200.8	Ph–H	431		
C–C	348	N=O	606.7	$PhCH_2$–H	356		
C=C	612	S–H	347.3	Ph–CH_3	389		
C≡C	813	S–S	225.9	PhO–H	356		
		S=O	497.9				

There are two more parameters associated with a covalent bond which determine the shape of a molecule and are known as **bond length** and **bond angle**. Bond length can be defined as the average distance between the nuclei of the atoms which are covalently bound together. Bond angle can be defined as the angle between the atoms, forming the bonds to the same atom. Table 1.2 gives the bond lengths for some of the bonds.

Table 1.2 : Bond lengths for some of the bonds

Bond	Bond length/pm	Bond	Bond length/pm
H-H	74	C-F	142
C-H	112	C-Cl	177
C-C	154	C-Br	191
C=C	134	C-I	213
C≡C	120	C-O	143
F-F	144	C=O	120
Cl-Cl	198	N-H	103
Br-Br	228	N-N	147
I-I	266	N=N	130
C-C in C_6H_6	139	C=N	130
O-H	97	C≡N	110

1 pm = 1 picometer
= 10^{-12} m

From these values of bond lengths, we can conclude that :

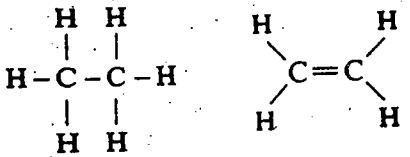
i) bond length decreases with the increase in multiplicity of the bond. Thus, the decreasing order for bond lengths for carbon – carbon bonds is
C-C > C=C > C≡C.

ii) bond lengths increase with the increasing size of the bonded atoms, i.e., the increasing order of bond lengths is C-H < C-F < C-Cl < C-Br < C-I.

We will study more about bond lengths and bond angles later in Sec. 1.4, when we discuss hybridisation. You will see in the later units in this course how important these parameters of a bond are in deciding the chemical reactivity of a compound. Before proceeding further, let us study something about how the structures for the organic compounds are written.

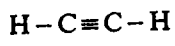
1.3 STRUCTURAL FORMULAS

Structural formula of a compound is its Lewis structure, which shows how various atoms are connected to each other. You are already familiar with Lewis structures of some of the compounds from your study of Unit 3, Block 1 of Atoms and Molecules course. Some examples are :



ethane

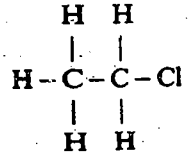
ethylene



acetylene

To save space and time, these structures are represented by **condensed formulas** which do not show the bonds. For example, the condensed formula for ethane can be written as CH_3CH_3.

Similarly, we can write condensed structural formula for

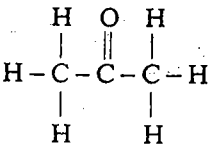


ethyl chloride

as CH_3CH_2Cl

Remember that all the representations of the formulas are in two dimensions but actually molecules are three-dimensional in nature. About this, you will study in Units 2 and 3 in detail.

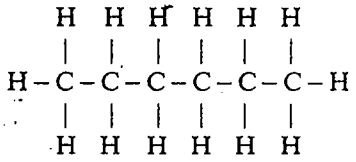
and for



as CH_3COCH_3.

acetone

Repeating units such as $(-CH_2-)$ in the structural formula can be enclosed in brackets and hence hexane



hexane

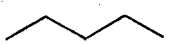
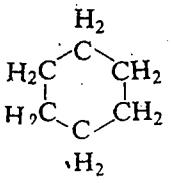
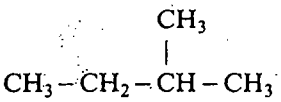
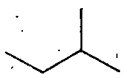
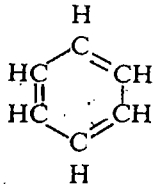
can be written as $CH_3(CH_2)_4CH_3$.

Condensed formulas for compounds having multiple bounds can be written as shown below:

$H_2C=CH_2$ ethylene $\quad$ $HC\equiv CH$ acetylene

For simple compounds, it is easy to write the condensed formulas. But, when the molecules are complex, these formulas look rather awkward and can be further abbreviated. These representations, are called **line** or **skeletal** structures. Here, the hydrogens are not shown and **each end** and **bends** represent the carbon atoms as shown below for some cases:

The skeletal structures or line structures show only the carbon-carbon bonds

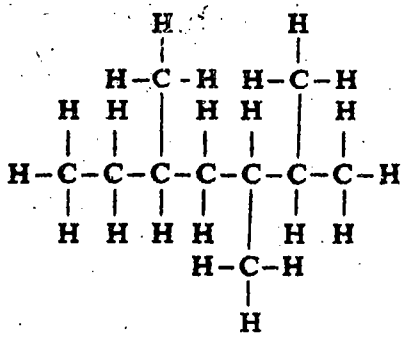
Compound	**Line structure**
$CH_3CH_2CH_2CH_2CH_3$ pentane	
 cyclohexane	
 2-methylbutane	
 benzene	

Having understood the above representations, answer the following SAQ.

SAQ 1

Write the condensed formulas for the following compounds:

a)



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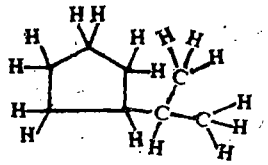
b)



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1.4 ORBITAL HYBRIDISATION

Properties and chemical reactions of most organic molecules can be easily explained by considering the molecules to be formed by sharing of electron pairs between the atoms. Another approach to formation of molecules which you studied in Unit 5 of Block 1 in Atoms and Molecules course, is the molecular orbital method. Organic chemists have for many years employed a bonding model that combines elements of molecular orbital theory with Lewis model of formation of covalent bond by electron sharing. This model was proposed by Pauling in 1930 and is based on the concept of **orbital hybridisation.** This model uses the terminology of molecular orbital theory but treats the bonds between the atoms as though they are localised, as in the case of diatomic molecules. In other words, it is a sort of **localised molecular orbital treatment of the bond.**

You have already studied in Unit 4, Block 1 of Atoms and Molecules course that various types of orbital hybridisation is possible depending upon the number and nature of the orbitals involved. In this unit, we will restrict our discussion to the hybridisation involving *s* and *p* orbitals. Let us now study each type of hybridisation involving *s* and *p* orbitals, in detail, to understand this concept and its use in explaining the formation of molecules.

Hybridisation is a theoretical concept which enables as realistic modelling of molecular structure as possible.

1.4.1 sp^3-Hybridisation

Let us consider the simplest organic compound, methane, having the molecular formula CH_4. You can recall that carbon has the electron configuration $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$. Since only two unpaired electrons are there, one may expect that it should form only two bonds with two hydrogens to forms CH_2. But actually it forms four bonds with four hydrogens to give CH_4. Pauling proposed that this could be explained by using orbital hybridisation. In this method, atomic orbitals are mixed to yield the new hybrid orbitals. In this case, in the first step one of the 2*s* electrons is promoted to the $2p_z$ orbital, electron configuration can then be written as $2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$. Bond formation with these pure atomic orbitals would lead to the situation where the bond formed by one 2*s* electron will be different from the bonds formed by three 2*p* electrons. But, in methane molecule, all the four bonds are equivalent. In order to explain this, the idea of orbital

The orbitals which undergo hybridisation, should not be energetically much different.

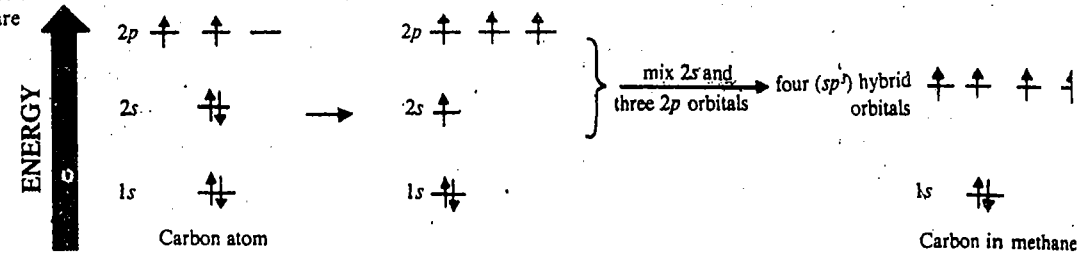
The number of hybrid orbitals generated is always equal to the number of atomic orbitals combined.

sp^3 is pronounced as *s*-*p*-three and not *sp* cube.

The hybrid orbitals are obtained by mathematical combinations of atomic orbitals.

Hybridisation may not always yield *equivalent* hybrid orbitals. You are already familiar from Unit 4 of Atoms and Molecules course that in sp^3d hybridisation two kinds of hybrid orbitals are obtained.

hybridisation was invoked. In this process, one 2*s* and three 2*p* orbitals on hybridisation yield a set of four new equivalent orbitals. These new orbitals are called **hybrid orbitals.** Since they are formed by combining **one *s* and three *p*** orbitals, they are called sp^3 hybrid orbitals. All the four sp^3 hybrid orbitals are of



equal energy and each one of them has 25% *s* character and 75% *p* character. These sp^3 hybrid orbitals are shown in Fig. 1.1. You can see in Fig. 1.1(a) that the

Like pure atomic orbitals, the hybrid orbitals also represent the region of space where there is some finite probability of finding an electron.

The tetrahedral shape is one of the most stable structures. This is reflected in case of diamond which is the hardest known substance. The structure of diamond (see Fig. 3.8, Sec. 3.4, Unit 3, Block 1 of Atoms and Molecules course) shows the tetrahedral carbon atoms linked together.

The tetrahedral concrete structures are used for checking sea-erosion as shown in the following picture:

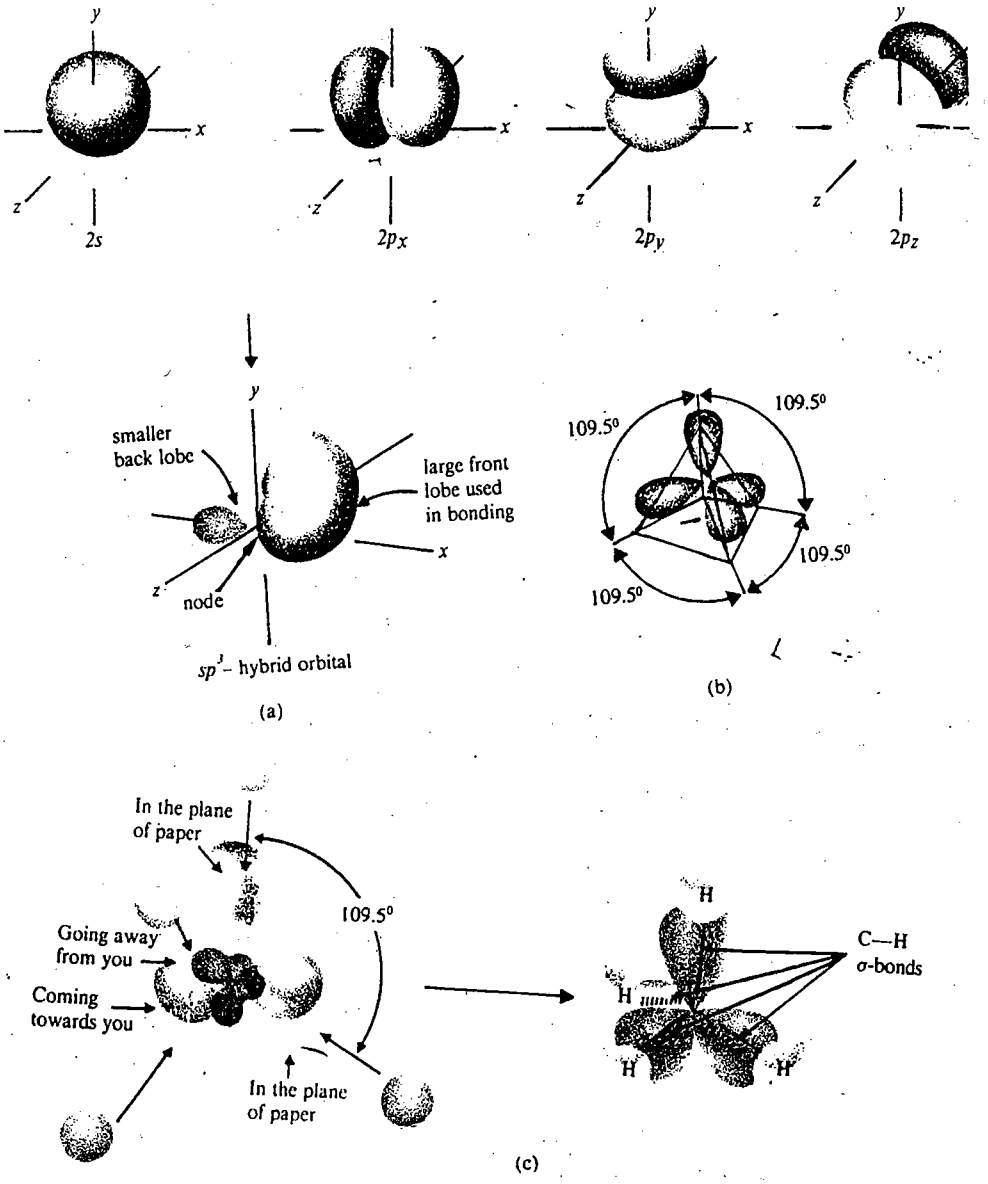


Fig. 1.1 : a) Hybridisation of one 2*s* and three 2*p* orbitals to yield four sp^3 hybrid orbitals, b) Four sp^3 hybrid orbitals directed towards the corners of a tetrahedrone; small back lobes are not shown c) Formation of methane molecule.

sp^3 hybrid orbital has two lobes of unequal size separated from each other by a node. This situation is similar to a p orbital but with the difference that here one lobe is very small and the other is very large. In other words, in sp^3 hybrid orbitals, the electron density is concentrated in one direction which leads to greater overlap as compared to pure atomic orbitals. Hence, the bonds formed by such orbitals will be stronger and more stable in comparison to those formed by using pure atomic orbitals. The spatial orientation of these orbitals is obtained by mathematical calculations and is shown in Fig. 1.1(b). This is in accordance with the VSEPR theory which you studied in Unit 3, Block 1 of Atoms and Molecules course. You can see in the figure that these orbitals are directed towards the corners of a tetrahedron and the bond angle between any two sp^3 hybrid orbitals is 109.5°. In methane molecule, each of the four sp^3 hybrid orbitals overlaps with 1s orbital of four hydrogens as shown in Fig. 1.1(c).

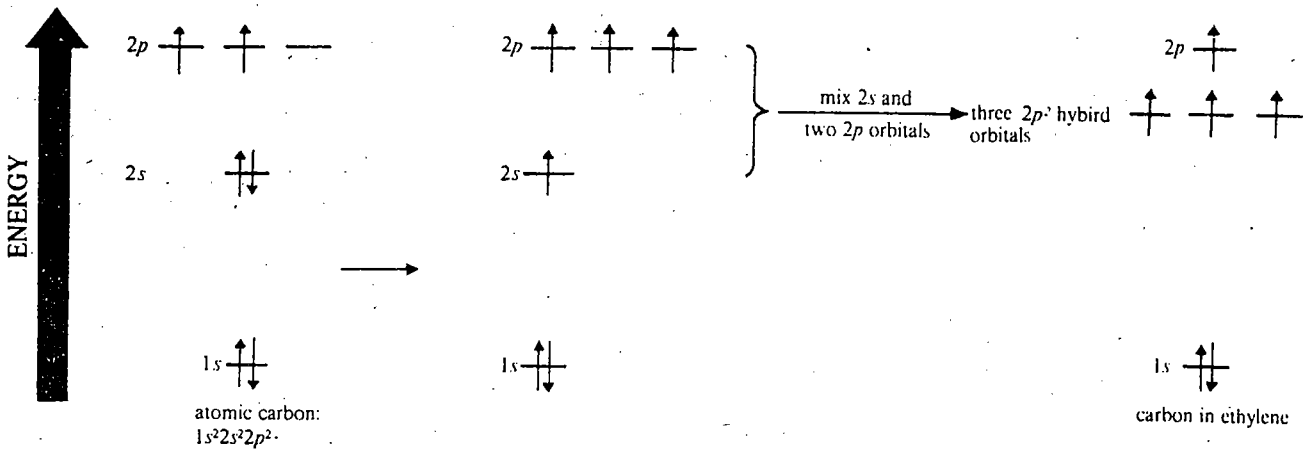
Remember that hybridisation involves mixing of orbitals of the one and the same atom and not the orbitals of different atoms.

Note that the bonds so formed, i.e., the C – H bonds, are σ (sigma) bonds. If instead of combining with hydrogens, the hybrid orbital forms a bond with the similar hybrid orbital of another carbon atom, then a C – C bond will result instead of the C – H bond. The C – C bond has a bond length of 154 pm and a bond energy of 348 kJ mol^{-1}. You will study more about the compounds involving sp^2 hybridisation in Unit 6 of Block 2 of this course.

1.4.2 sp^2-Hybridisation

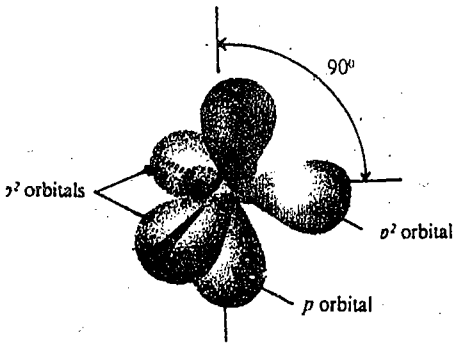
In a molecule like ethylene, where there are not enough hydrogens in the molecule to form six C – H bonds, another type of hybridisation has to be thought of.

In this type of hybridisation, as the name indicates, the 2s orbital of the carbon is hybridised with *only two* of the three available 2p orbitals, as shown below.

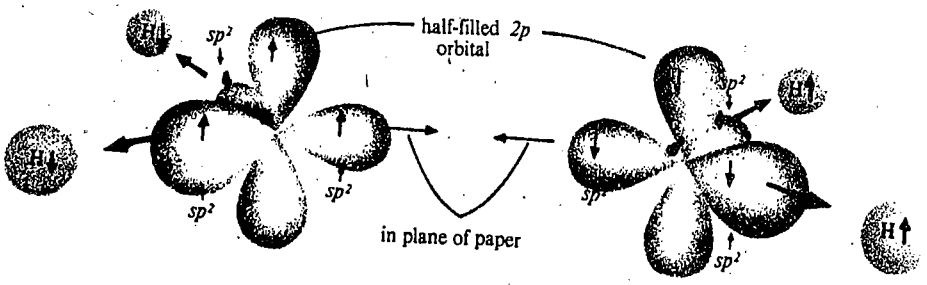


Since three orbitals are hybridised, three equivalent sp^2 hybrid orbitals are obtained. We shall now explain sp^2 hybridisation using ethylene as an example. According to the VSEPR theory, these orbitals are oriented in space making an angle of 120° with each other as shown in Fig. 1.2(a). Note that the three sp^2 hybrid orbitals are in one plane. The third p orbital which is not utilised for hybridisation is perpendicular to the sp^2 hybrid orbitals and is shown in colour in Fig. 1.2(a).

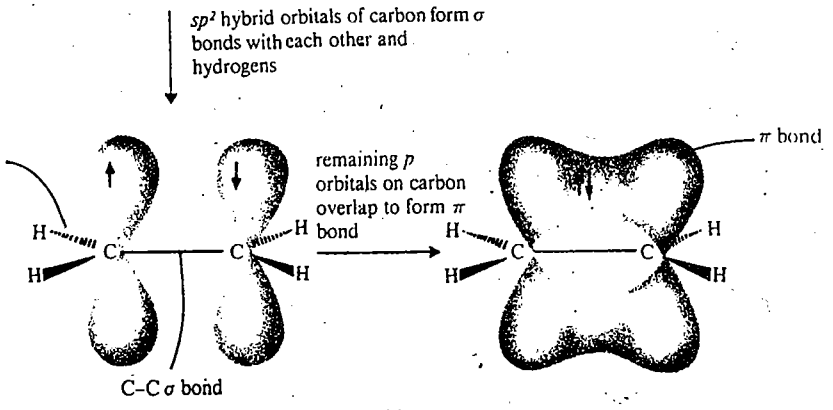
When two such sp^2 hybridised carbon atoms form a bond, the C – C bond formed is again a σ bond. If the rest of the sp^2 hybrid orbitals on each carbon atom overlap with 1s orbital of the two hydrogen atoms, then as shown in Fig. 1.2(b), the two unhybridised p orbitals on the two carbon atoms are parallel to each other. These p orbitals can overlap sideways to yield a second bond, known as π (pi) bond which is shown in Fig. 1.2(c). The C = C bond length for ethylene molecule so obtained is 134 pm. You can compare this value with C – C single bond length as given before in case of ethane. You will study in detail, the compounds having sp^2 hybridised carbon atoms such as **alkenes** and **dienes** in Unit 7 of Block 2.



(a)



(b)



(c)

Fig. 1.2 : a) sp^2 hybrid orbitals. b) Formation of C–C σ bond. c) Formation of a π bond in ethylene molecule.

You are aware that:
i) σ bonds are formed by the edge-on overlap of pure (*s* and *p*) or hybrid orbitals. The electron density in σ bonds is maximum along the internuclear axis.
ii) π bonds are formed by sideways overlap of *p* orbitals. π bonds have maximum electron density above and below the internuclear axis.

Activity

Make a model of ethylene molecule and convince yourself that it is flat in shape with the two carbons and their substituent hydrogens lying in one plane. However, the π bond is at right angles to this plane.

SAQ 2

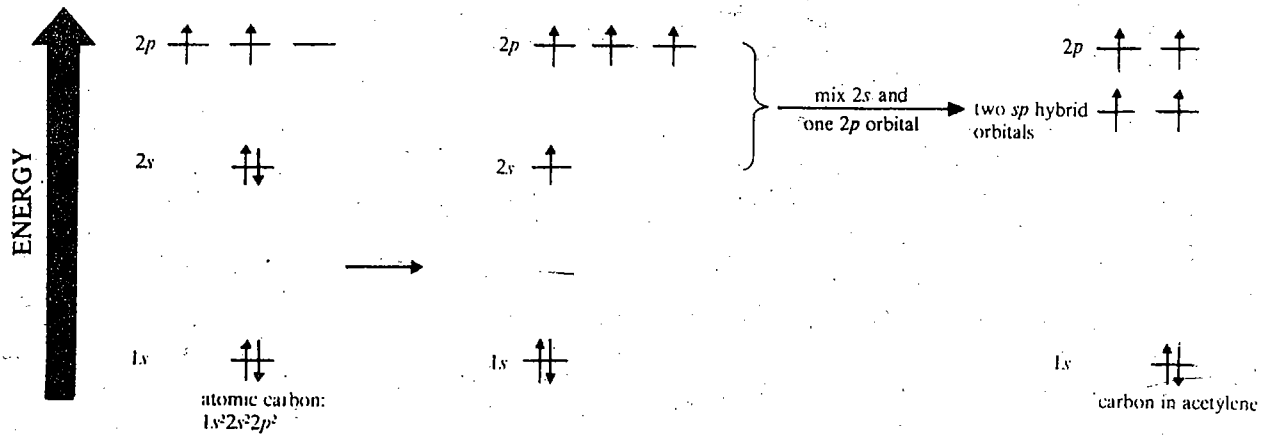
Predict the percentage of *s* and *p* character in sp^2 hybrid orbitals.

.....

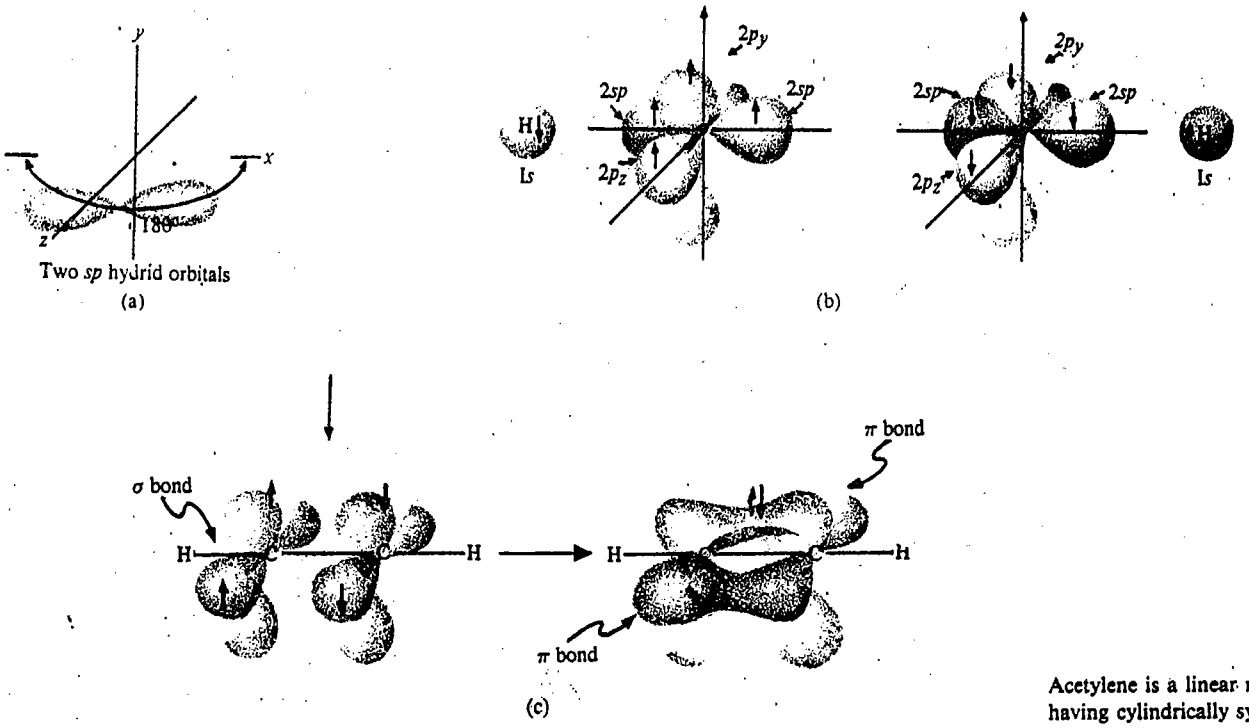
.....

1.4.3 *sp*-Hybridisation

Let us now consider the third type of hybridisation involving *s* and *p* orbitals in cases where a triple bond is stipulated. In carbon atom when 2*s* and *only one* of the three 2*p* orbitals hybridise as shown below, the hybridisation is known as *sp*-



hybridisation. This leads to two new equivalent *sp* hybrid orbitals as shown in Fig. 1.3(a). These two orbitals are oriented in space at an angle of 180° according



Acetylene is a linear molecule having cylindrically symmetrical π electron density about the internuclear axis.

Fig. 1.3 : a) Two *sp* hybrid orbitals. b) Formation of one σ (sigma) bond. c) Formation of two π bonds in acetylene molecule.

to the VSEPR theory. Let us study *sp*-hybridisation using acetylene as an example. When one of the two *sp* hybrid orbitals on each carbon atom combines with another, a C–C sigma bond is formed. The second *sp* hybrid orbital on each carbon forms a sigma bond with 1*s* orbitals of two hydrogens, as shown in Fig. 1.3(b). This leaves two *p* orbitals on each carbon atom which are not used in *sp* hybridisation. These *p* orbitals are perpendicular to each other and also to the sigma bond. These *p* orbitals can overlap laterally to give rise to two π bonds. Such a bond is called a triple bond and we get the acetylene moleculte, as shown in Fig. 1.3(c). The C=C bond in acetylene has a bond length of 120 pm and the H–C–C angle is 180° which shows that it is linear. Compounds having triple bond are called **alkynes** and will be dealt with in detail in Unit 8 of Block 2. We can sum up the above information as shown in Table 1.3.

Table 1.3 : Bond characteristics and hybridisation of carbon in simple molecules

Compound	Hybridisation of carbon atom	Bond length in pm	Bond angle	Nature of carbon – carbon bonds
Ethane	sp^3	154	109.5°	single
Ethylene	sp^2	134	120°	double
Acetylene	*sp*	120	180°	triple

From the data given in the Table 1.3 we can conclude that

i) in the hybrid orbitals, as the *s* character increases, bond length decreases.

ii) as the bond order increases, the bond length decreases.

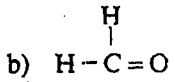
Before proceeding to the next section answer the following SAQ.

SAQ 3

Indicate the type of hybridisation for each of the carbon atoms in the following compounds:

a) $CH_3-C\equiv C-CH_2-CH_3$

.....

b) 

.....

c) $H_2C=C=CH-CH_3$

.....

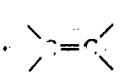
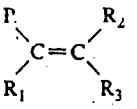
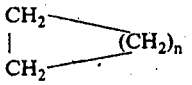
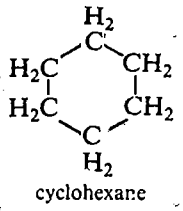
d) $CH_3-C\equiv C-C\equiv C-CH_3$

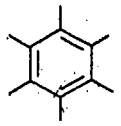
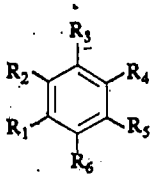
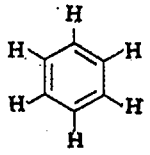
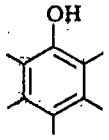
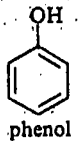
.....

1.5 FUNCTIONAL GROUP CLASSIFICATION

A systematic study of chemistry or for that matter any other branch of science, is not possible without arranging the subject matter in a logical manner when sufficient data has accumulated. In case of inorganic chemistry, formulation of the periodic table stimulated not only the search for missing elements but also led to the understanding of the periodic behaviour. In organic chemistry, as the number of known organic compounds runs into millions, it is very difficult to study each and every compound individually. Thus, by grouping similar compounds together in a class or a family, it is easier to understand their properties, reactions etc. One way of such classification is based on the **functional groups.** A *functional group* can be defined as an atom or a group of atoms in a molecule which exhibits characteristic chemical properties. Such chemical properties exhibited by the functional group are more or less constant for various compounds having different carbon chains. Indeed, many organic reactions involve transformation of the functional group and do not affect the rest of the molecule. The advantage of such a classification based on functional groups is that in addition to logically systematising the organic compounds, the properties of the compounds can be predicted just by looking at their structures, i.e., by knowing the type of functional group present. Table 1.4 lists a number of important functional groups. You will study each class of compounds in detail in the forthcoming blocks of this course.

Table 1.4 : Functional Groups

Class	Functional Group	General structural formula	Example	IUPAC suffix or prefix
Containing C and H only				
Alkane	none	R – H	CH_4 methane	-ane
Alkene			$H_2C=CH_2$ ethylene	-ene
Alkyne	$-C\equiv C-$	$R-C\equiv C-R_1$	$H-C\equiv C-H$ acetylene	-yne
Cycloalkane	none		 cyclohexane (n = 4)	cyclo– ··· –ane

Aromatic Compounds			 benzene	
Containing C, H and O				
Alcohol	$-OH$	$R-OH$	CH_3-OH methanol	-ol
Phenol		$Ar-OH$	 phenol	-ol
Ether	$-O-$	$R-O-R$	CH_3-O-CH_3 dimethyl ether	alkoxy-
Carbonyl compounds				
Aldehyde	$-C(=O)-H$	$RCHO$	CH_3CHO acetaldehyde	-al
Ketone	$-C(=O)-$	$R-C(=O)-R'$	$CH_3-C(=O)-CH_3$ acetone	-one
Carboxylic acid	$-C(=O)-OH$	$R-C(=O)-OH$	$CH_3-C(=O)-OH$ acetic acid	-oic acid
Ester	$-C(=O)-O-$	$R-C(=O)-OR'$	$CH_3-C(=O)-O-CH_3$ methyl acetate	-oate
Anhydride	$-C(=O)-O-C(=O)-$	$R-C(=O)-O-C(=O)-R'$	$CH_3-C(=O)-O-C(=O)-CH_3$ acetic anhydride	-oic anhydride
Containing C, H and N				
Amine	$-N<$	$R-NH_2$ (primary amine)	CH_3NH_2 methylamine	-amine or Amine
		$R-NH-R'$ (secondary amine)	$H_3C-NH-CH_3$ dimethylamine	
		$R-N(R')-R''$ (tertiary amine)	$H_3C-N(CH_3)-CH_3$ trimethylamine	
Imine	$-C(=N-)-$	$R-C(=N-R'')-R'$	$H_3C-C(=N-CH_3)-H$ *N*-ethylidene-methylamine	
Nitrile	$-C\equiv N$	$R-C\equiv N$	$CH_3-C\equiv N$ acetonitrile	-nitrile
Containing C, H, N and O				
Nitro Compounds	$-NO_2$	$R-NO_2$	CH_3-NO_2 nitromethane	Nitro-
Amide	$-C(=O)-N<$	$R-C(=O)-NH_2$	$CH_3-C(=O)-NH_2$ acetamide	-amide

Containing C, H and other elements				
Halide	$-X$	$R-X$	CH_3-Cl methyl chloride	Halo–
Acyl halide	$-\overset{O}{\overset{\|\|}{C}}-X$	$R-\overset{O}{\overset{\|\|}{C}}-X$	$CH_3-\overset{O}{\overset{\|\|}{C}}-Cl$ acetyl chloride	–oyl halide
Thiol	$-SH$	$R-SH$	CH_3-SH methanethiol	–thiol
Sulphonic acid	$-SO_2-OH$	$R-SO_2-OH$	CH_3-SO_2-OH methanesulphonic acid	–sulphonic acid

*Here, X stands for halogens (F, Cl, Br and I), R stands for the alkyl group and Ar stands for the aryl group.
*The names given in Column 4 are common names.
*At this stage, you should not worry about the last column of the table. We will refer back to this column while studying nomenclature of organic compounds in the next section.

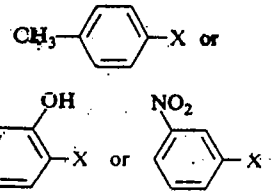
The compounds which are listed in the first category in Table 1.4 are the compounds which contain only carbon and hydrogen. These compounds are also called **hydrocarbons**. The hydrocarbons can be classified as **aliphatic, alicyclic** or **aromatic**. In the *aliphatic hydrocarbons*, the carbon atoms are linked to each other to form chains (straight or branched). The aliphatic hydrocarbons can be further classified as *saturated* or *unsaturated*. The saturated hydrocarbons contain the carbon and hydrogen atoms linked to each other by single bonds and are called **alkanes**. The unsaturated hydrocarbons are of two types: the one containing double bond as the functional group are named as **alkenes**; the other containing a triple bond as the functional group are known as **alkynes**.

In the *alicyclic hydrocarbons*, the carbon atoms are arranged in rings to yield cyclic structures. These compounds are also known as **cycloalkanes**.

The *aromatic hydrocarbons* include benzene and those compounds which resemble benzene in their properties.

In fact, the hydrocarbons provide a backbone to which various functional groups may be attached to yield an enormous variety of organic compounds.

The **alkyl** groups, generally represented by R, are derived from **alkanes** by removing one hydrogen. The simplest alkyl group is methyl group (CH_3-) which is derived from the alkane, methane (CH_4). Common alkyl groups are listed in Table 1.7. Similarly, **aryl** groups denoted by Ar, are obtained from benzene and its derivatives by removing one hydrogen. The simplest aryl group is **phenyl group** (C_6H_5- or ) and is abbreviated as Ph. In general, aryl halide (Ar – X) can refer to any of the following:



Let us now study about the structural features of some classes of aliphatic compounds. The compounds in which the carbon and oxygen atoms are linked by a single bond can be classified as **alcohols** or **ethers**, depending upon the number of alkyl groups attached to oxygen. In alcohols, oxygen is linked to only **one** alkyl group and one hydrogen; but in ethers, oxygen has **two** alkyl groups attached to it. The compounds containing carbon and oxygen linked by a double bond (i.e., $>C=O$), which is called **carbonyl group**, can be classified as **aldehydes** or **ketones**, depending on whether the number of alkyl groups attached to carbonyl carbon is **one** or **two**, respectively. If instead of an alkyl group, one hydroxyl (-OH) group is attached to the carbonyl group, a class of compounds known as **carboxylic acids** ($R-\overset{O}{\overset{\|\|}{C}}-OH$) is obtained. A number of carboxylic acid derivatives are obtained by replacing the hydroxyl group by halogens, $-NH_2$, $-O-\overset{O}{\overset{\|\|}{C}}-R$ or $-OR$ groups. Accordingly, these compounds are called **acid halides** ($R-\overset{O}{\overset{\|\|}{C}}-X$), **amides** ($R-\overset{O}{\overset{\|\|}{C}}-NH_2$), **anhydrides** ($R-\overset{O}{\overset{\|\|}{C}}-O-\overset{O}{\overset{\|\|}{C}}-R'$) and esters ($R-\overset{O}{\overset{\|\|}{C}}-OR'$). They are also called functional derivatives of carboxylic acids, as they are obtained by the changes in the functional group.

In a similar manner, compounds having carbon-nitrogen single bond are called **amines**. The amines can be of three types: **primary, secondary** and **tertiary** amines depending upon whether the number of alkyl groups attached to nitrogen is **one**,

two or **three**. The carbon-nitrogen double bond is characteristic of the class of compounds known as **imines** while compounds having carbon-nitrogen triple bond are called **nitriles**. Then we have **alkyl halides** which have their unique importance in the transformation of functional groups which you will realise when you study their reactions in the following blocks. The sulphur analogs of alcohols and carboxylic acids are known as **thiols** and **sulphonic acids**, respectively.

Parallel to the classes discussed above for aliphatic compounds, we have **aromatic compounds** in which benzene forms the backbone to which various functional groups mentioned above can be attached to yield similar classes of aromatic compounds, like aryl halides, arylamines, phenols, aromatic carbonyl compounds, aromatic acids and their derivatives, etc. As you have seen in Table 1.4, R is generally used to represent an **alkyl group**; the corresponding aromatic compounds are obtained by replacing R by Ar which denotes an aryl group; this is shown in Table 1.4 in case of alcohol and phenol. In the next section, we will study about the nomenclature of these compounds. Before that attempt the following SAQ to check your understanding about the functional groups.

The terms *primary*, *secondary* and *tertiary* as used for classification of branched alkyl substituents are explained under step 8 of nomenclature for branched chain alkanes in the next section

SAQ 4

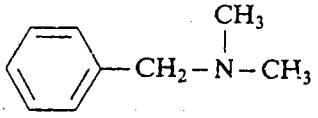
Encircle and name the functional groups present in the following compounds:

a) $CH_3-CH=CH-CH_2OH$

.....

b) $CH_3\overset{\overset{O}{\|}}{C}OCH_2CH_2-O-CH_3$

.....

c) 

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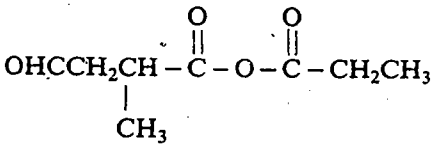
d) 

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1.6 NOMENCLATURE OF ORGANIC COMPOUNDS

The earliest attempts to name organic compounds were based either on their origin or on their properties. For example, citric acid was named so because of its occurrence in *citrus* fruits. The aromatic compounds were called so because of their characteristic odour (Greek: **aroma**, *fragrant smell*). Examples are oil of wintergreen and vanillin (a constituent of vanilla also used as a flavouring agent) which were called aromatic due to their characteristic fragrance. With the advancement and growth in the knowledge of chemistry, the number of known organic compounds has increased rapidly. Also, with the increase in the number of carbon atoms, the number of possible isomers for hydrocarbons (without any functional group) becomes very large (see Table 1.5).

Isomers are the compounds that have identical molecular formulas but differ in the ways in which the atoms are bonded to each other. For example, four carbons in a hydrocarbon having molecular formula C_4H_{10} can be arranged in the two different ways:

Straight chain

$H_3C-CH_2-CH_2-CH_3$

common name : normal butane or *n*-butane

Branched chain

$H_3C-\underset{\underset{CH_3}{|}}{CH}-CH_3$

common name : isobutane

Thus, *n*-butane and isobutane are isomers.

Table 1.5 : Possible Number of Isomers for Hydrocarbons

Number of carbon atoms in the hydrocarbon	4	5	6	7	8	9	10	12	15	20
Number of possible isomers	2	3	5	9	18	35	75	355	4,347	366,319

Having learnt about the variety of functional groups, you can imagine that the nature and position of functional groups present can raise these numbers many fold. Under such a situation, it is next to impossible to learn the names randomly assigned to the compounds, especially when there is no correlation of the name to the structure of the compound. This necessitated the need to have a **systematic nomenclature** for which the International Committee of Chemists met at Geneva in 1892. The work was carried on by the **International Union of Chemists (I.U.C.)** which gave its report in 1931, known as the I.U.C. system of nomenclature. As the nomenclature is always undergoing modifications and revisions, the latest rules which are widely accepted were recommended by the Commission on Nomenclature of Organic Chemistry of the **International Union of Pure and Applied Chemistry (I.U.P.A.C.)**. We will now study this system in detail.

Since the nomenclature of other classes of compounds is based on the nomenclature of alkanes, let us start the study of nomenclature with the alkanes. **Alkanes** are represented by the general formula C_nH_{2n+2} where n can be 1, 2, 3, 4... etc. The first four alkanes retain their original or nonsystematic names The names of alkanes higher than these start with a prefix (Greek or Latin words) which indicates the number of carbon atoms in the chain and end with suffix-**ane**. The IUPAC names for various alkanes having different chain lengths are given in Table 1.6. The unbranched alkanes have their common names as normal alkanes or *n*-alkanes.

Compounds that differ from each other in their molecular formulas by the unit $-CH_2-$ are called members of a homologous series. Thus, the compounds listed in Table 1.6 belong to a homologous series.

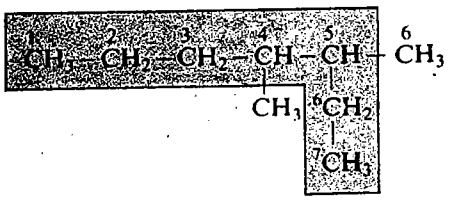
Table 1.6 : IUPAC Names of straight chain alkanes having general formula C_nH_{2n+2}

n	Formula	Name	n	Formula	Name
1	CH_4	methane	11	$CH_3(CH_2)_9CH_3$	undecane
2	CH_3CH_3	ethane	12	$CH_3(CH_2)_{10}CH_3$	dodecane
3	$CH_3CH_2CH_3$	propane	13	$CH_3(CH_2)_{11}CH_3$	tridecane
4	$CH_3(CH_2)_2CH_3$	butane	14	$CH_3(CH_2)_{12}CH_3$	tetradecane
5	$CH_3(CH_2)_3CH_3$	pentane	15	$CH_3(CH_2)_{13}CH_3$	pentadecane
6	$CH_3(CH_2)_4CH_3$	hexane	20	$CH_3(CH_2)_{18}CH_3$	*icosane
7	$CH_3(CH_2)_5CH_3$	heptane	30	$CH_3(CH_2)_{28}CH_3$	triacontane
8	$CH_3(CH_2)_6CH_3$	octane	40	$CH_3(CH_2)_{38}CH_3$	tetracontane
9	$CH_3(CH_2)_7CH_3$	nonane	50	$CH_3(CH_2)_{48}CH_3$	pentacontane
10	$CH_3(CH_2)_8CH_3$	decane	100	$CH_3(CH_2)_{98}CH_3$	hectane

*Prior to 1979 version of IUPAC rules, it was spelled as eicosane.

The branched chain alkanes are named by using the following steps:

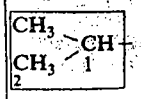
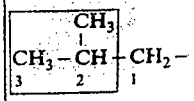
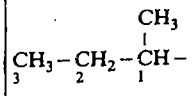
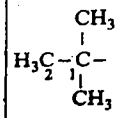
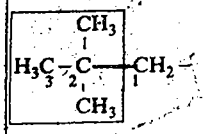
1. The longest continuous chain of carbon atoms is taken as the parent hydrocarbon. For example, in the compound shown below, the parent hydrocarbon is heptane and not the hexane.



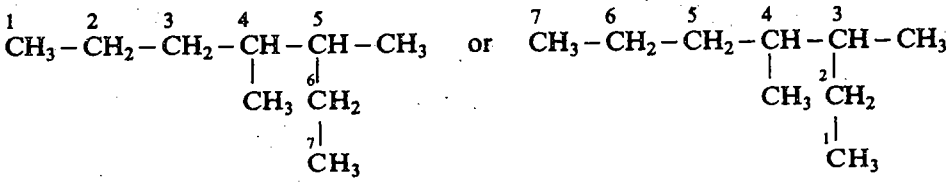
2. Identify the substituent alkyl groups attached to the parent chain. Some

common alkyl groups are listed in Table 1.7. You can locate that both the substituents in the example cited above are methyl groups.

Table 1.7 : Common Alkyl groups

Alkyl group	Common name	IUPAC name
CH_3	methyl	methyl
CH_3CH_2-	ethyl	ethyl
$CH_3CH_2CH_2-$	*n*-propyl	propyl
	iso propyl	1-methylethyl
$CH_3CH_2CH_2CH_2-$	*n*-butyl	butyl
	iso butyl	2-methylpropyl
	*sec*-butyl	1-methylpropyl
	*tert*-butyl	1, 1-dimethylethyl
	neo pentyl	2, 2-dimethylpropyl

3. The parent carbon chain is then numbered in such a way that the substituents get the lowest possible numbers. The carbon atoms in the above compound can be numbered as,



Can you guess which of the two numbering systems is correct? The first possibility locates the methyl groups at carbons 4 and 5 and the second way at carbons 3 and 4. Certainly, the second way of numbering the carbon chain is correct.

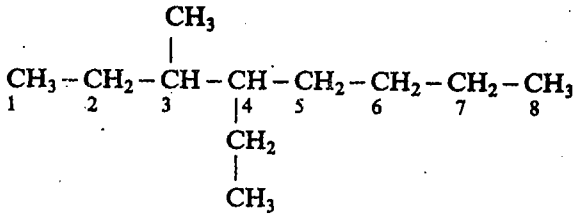
4. Perfixes *di, tri, tetra, penta* etc., are used when the substituents occur more than once. Since in the above compound the methyl substituent is occurring *twice,* the name is prefixed with *di* for the above compound.

5. The name of the compound is written by writing the location and name of the substituents followed by the name of the parent alkane. Thus, the above compound can be named as 3,4–dimethylheptane. Note that a comma is used to separate the two numbers and the numbers are separated from names of groups by a hyphen. Also note that there is no blank space between the name of the last substituent and the parent alkane.

6. When more than one type of alkyl groups are present, then they are cited in the name in the alphabetical order regardless of their location in the principal chain. The numerical prefixes *di, tri, tetra,* etc. and hyphenated prefixes such as *sec-, tert-* are not considered in determining the alphabetical order but prefixes iso, neo, cyclo are considered for alphabetising. To understand it, let us consider the examples given below:

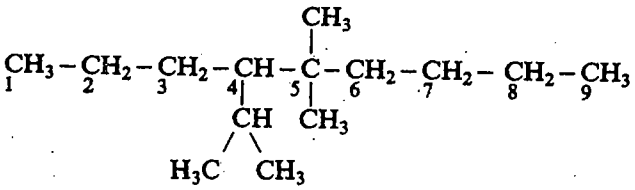
The IUPAC system of nomenclature has retained some of the older names for branched alkyl groups such as isopropyl, isobutyl, *sec*-butyl, *tert*-butyl and and neopentyl.

Note that the numbering of carbon atoms is from the point of attachment of the group to the parent chain.



4-ethyl-3-methyloctane

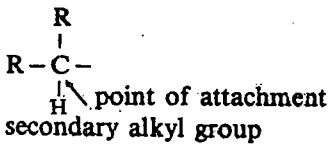
Note that here *ethyl* is cited before *methyl*, in spite of its higher location number Similarly, the compound shown below,



can be named as 4-isopropyl-5,5-dimethylnonane or 4-(1-methylethyl)-5, 5-dimethylnonane.

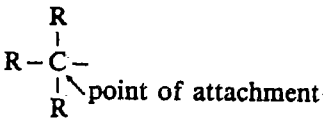
7. The branched chain substituents, such as 1-methylethyl shown in step 6, are numbered starting from the carbon attached directly to the parent chain. Table 1.7 shows the numbering for the branched substituents listed there. The longest carbon chain is selected and the substituents are named according to the rules listed above for compounds having unbranched substituents. Note that the name and numbering of branched substituent is written in brackets in order to separate it from the numbering of the main chain.

8. The alkyl substituents can be further classified as **primary, secondary** or **tertiary**. An alkyl group is called a *primary* alkyl group if the carbon atom at the point of attachment is bonded to only *one* other carbon. For example, $R-CH_2-$ is a primary alkyl group. Similarly, a *secondary* alkyl group has *two* alkyl groups bonded to the carbon atom taken as the point of attachment to the main chain. Thus, a secondary alkyl group can be written as shown below:



secondary alkyl group

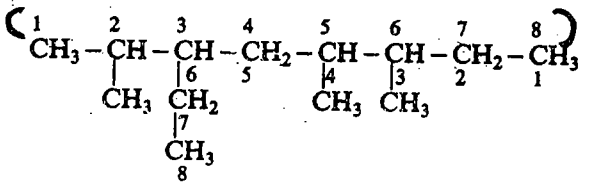
Similarly, a *tertiary* alkyl group has *three* carbon atoms bonded to the carbon atom taken as point of attachment. Thus, a tertiary alkyl group can be represented as shown below:



tertiary alkyl group

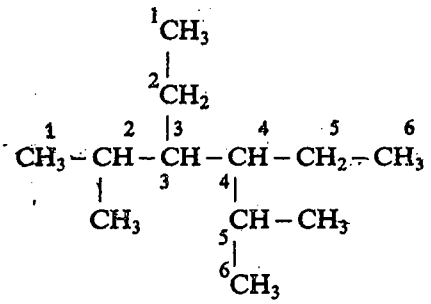
9. When more than one carbon chain of equal length are available, the numbering is done considering the following points:

   (a) The principal chain should have the greatest number of side chains. For example, in the compound shown below,



the chain having numbering in red colour has four side chains while the chain marked with numbers in black colour has three side chains. So the principal chain is the one which is marked in the red colour. Hence, the name is 3-ethyl-2,5,6-trimethyloctane.

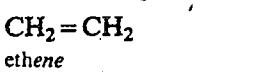
(b) The chain having the lowest number for substituents is chosen as the principal chain. In the compound shown below,



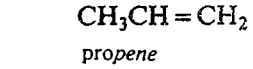
if the numbering is done as shown in black colour, the name would have substituents at positions 3, 4 and 5. But, if the carbon chain numbered in red colour is taken as the principal chain, then the substituents get the numbers 2, 3 and 4, which is obviously the correct choice.

Till now we were studying the nomenclature of alkanes. Let us now study how various compounds having different functional groups are named. In case of compounds which have a functional group, the functional group gets a precedence over the alkyl substituents. At this stage, you refer back to Table 1.4 where IUPAC prefixes and suffixes for various classes of compounds are given.

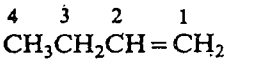
Alkenes: The suffix *ane* of the parent hydrocarbon is changed to *ene* and the functional group (a double bond in this case) is given the lowest possible number. Some examples are:



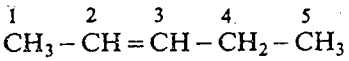
ethene
(Common name : ethylene)



propene

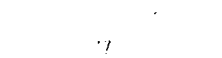


but-1-ene

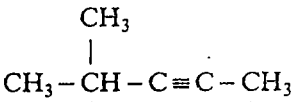


pent-2-ene

Alkynes: In this case suffix *ane* of the parent hydrocarbon is changed to *yne*. As expected, here also the functional group is given the lowest number.

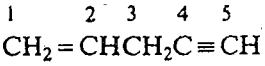


ethyne



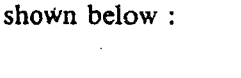
4-methylpent-2-yne

When both double and triple bonds are present, then the double bond gets the lower number. Thus, for the compound shown below,

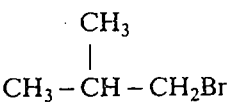


the correct name is pent-1-ene-4-yne.

Alkyl halides: The alkyl halides are the halogen derivatives of alkanes. The halogens present are usually F, Cl, Br and I. The common names are arrived at by writing the name of alkyl group followed by the name of the halide. Examples are shown below :



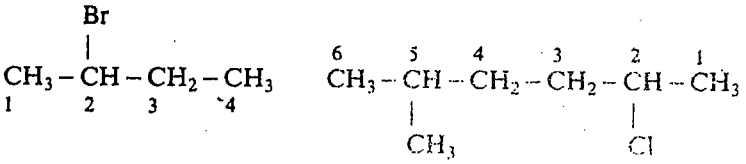
n-butyl chloride



isobutyl bromide

In the IUPAC system of nomenclature, prefix *halo-* (i.e., *fluoro-, chloro-, bromo-* or *iodo-*) is used and the carbon chain is so numbered to give the lowest number

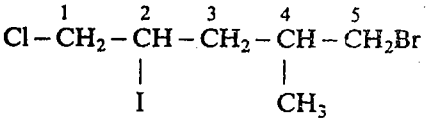
to the carbon atom to which the halogen is attached. For example, some halogen compounds are named below:



2-bromobutane

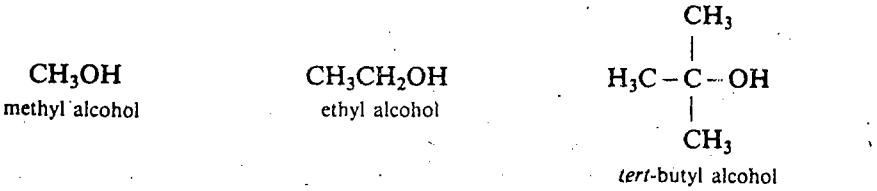
2-chloro-5-methylhexane

When more than one type of halogen atoms are present, their names are arranged in alphabetical order as shown in the next example.



5-bromo-1-chloro-2-iodo-4-methylpentane

Alcohols: Alcohols are the compounds having hydroxyl (−OH) group attached to the alkyl chain. The common names of the alcohols are written by specifying the alkyl group followed by the word alcohol, e.g.,

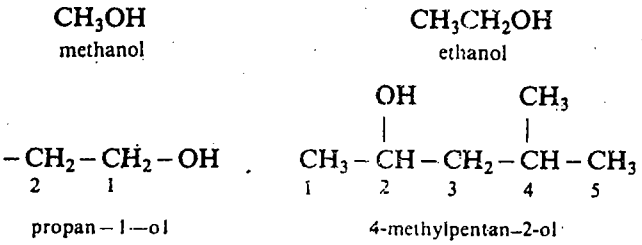


methyl alcohol

ethyl alcohol

tert-butyl alcohol

In the IUPAC nomenclature, suffix *ol* is used instead of final *e* of the parent hydrocarbon. The position of the hydroxyl group is given by assigning the lowest possible number to the carbon atom carrying it. Some examples are:



methanol

ethanol

propan−1−ol

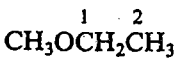
4-methylpentan-2-ol

Ethers: The common names for ethers are derived by naming the two alkyl groups in alphabetical order followed by the word ether. This is illustrated in the examples given below:

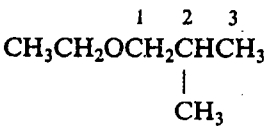
dimethyl ether

ethyl methyl ether

In the IUPAC system, ethers are named as **alkoxyalkanes.** The larger of the two alkyl groups is chosen as the hydrocarbon chain. For example, the compound,



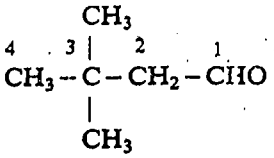
is named as 1-methoxyethane and not as ethoxymethane. Similarly, the compound,



has the name 1-ethoxy-2-methylpropane.

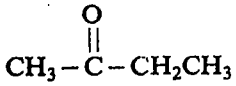
Aldehydes: Lower members of this class are commonly named after the acids that they form on oxidation. For example, HCHO, formaldehyde is named so because it forms formic acid (HCOOH) on oxidation.

In the IUPAC system of nomenclature, they are named as **alkanals.** The simplest aldehyde is methanal. Since the aldehyde group (−CHO) is always at the end of the chain, it is always numbered as C−1 in the chain, but this number is not specified in the name, i.e. the compound



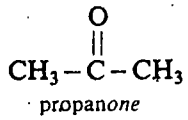
is named as 3, 3-dimethylbutanal.

Ketones: The common names for ketones are written similar to ethers, i.e. the two alkyl groups are written alphabetically followed by the word ketone. For example, the compound,

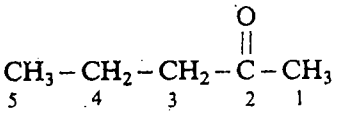


is commonly known as ethyl methyl ketone.

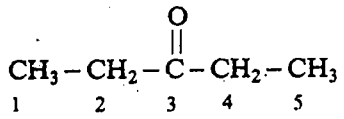
Thus, acetone, $CH_3\overset{\overset{O}{\|}}{C}CH_3$ is also known as dimethyl ketone. The IUPAC names for ketones are derived by using the suffix *one* instead of final *e* of the parent hydrocarbon. As usual, the position of the carbonyl group is indicated by the lowest possible number. A few examples are,



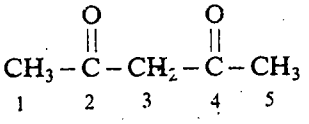
propan*one*



pentan-2-one



pentan-3-one

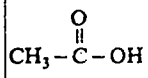
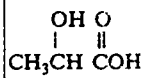
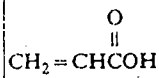
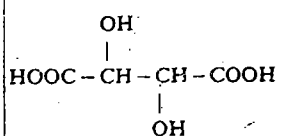


pentan-2, 4-dione

Carboxylic acids: Nowhere else in organic chemistry, the common names are so prevalent as they are among carboxylic acids. Some examples are listed in Table 1.8 along with both their common and IUPAC names. For monocarboxylic acids,

[i.e. acids having one carboxy ($-\overset{\overset{O}{\|}}{C}-OH$) group], the IUPAC names are derived

Table 1.8 : Some Carboxylic Acids

Structure	Common Name	IUPAC Name
	Formic acid	methanoic acid
	Acetic acid	ethanoic acid
	Lactic acid	2-hydroxypropanoic acid
$CH_3(CH_2)_{16}COOH$	Stearic acid	octadecanoic acid
HO_2C-CO_2H	Oxalic acid	ethanedioic acid
$HO_2C(CH_2)_4CO_2H$	Adipic acid	hexanedioic acid
	Acrylic acid	propenoic acid
	Tartaric acid	2,3-dihydroxybutanedioic acid

by replacing *e* ending of the alkane by *oic acid*. As for aldehydes, the carboxyl carbon is numbered 1. However, in case of the dicarboxylic acids, the final *e* of the hydrocarbon is not dropped.

Acyl halides: Acyl halides are commonly named by placing the names of the halide after the name of the acyl group. The acyl group is obtained from the carboxylic acid by removal of its hydroxyl portion, i.e. $R-\overset{O}{\overset{\|}{C}}-OH$ leads to $R-\overset{O}{\overset{\|}{C}}-$ acyl group. The acyl group is named by using *yl* as the ending instead of ending *ic* in the carboxylic acid. Some such examples are:

$CH_3\overset{O}{\overset{\|}{C}}-Cl$

(acetic + yl → acetyl)

acetyl chloride

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-I$

propanoyl iodide

IUPAC names for acyl groups use the ending *oyl* instead of ending *e* in the name of the corresponding hydrocarbon. The acetyl chloride has the IUPAC name ethanoyl chloride. Another example is $CH_3CH(CH_3)\overset{O}{\overset{\|}{C}}-Cl$ which is named as 2-methylpropanoyl chloride.

Acid amides: The common names for acid amides are derived by replacing the suffix *ic* or *oic* of the carboxylic acid by the suffix *amide* as shown below:

$CH_3\overset{O}{\overset{\|}{C}}-NH_2$

(acetic – acetamide)

The IUPAC name for an amide is derived by appending the suffix *amide* to the parent hydrocarbon with the final *e* dropped. Thus, acetamide has the IUPAC name **ethanamide**. Having done this, can you give common and IUPAC names for $H\overset{O}{\overset{\|}{C}}-NH_2$? These are formamide and methanamide, respectively.

Acid anhydrides: A symmetrical anhydride is named as anhydride of the parent acid. Thus, $CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$, the anhydride which is obtained from ethanoic acid (common name: acetic acid) is commonly known is acetic anhydride. The IUPAC name for this anhydride is ethanoic anhydride.

For mixed anhydrides, both the parent carboxylic acids are cited in alphabetical order, followed by the word anhydride, as illustrated below:

$H-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$

ethanoic methanoic anhydride

(common name : acetic formic anhydride)

Esters: As the esters contain alkyl and alkanoyl (acyl) groups, they are named as **alkyl alkanoates.** The alkyl groups is cited first, followed by the name of the alkanoyl (acyl) portion which is named by replacing the *ic* ending of the carboxylic acid by the suffix *ate*.

$CH_3\overset{O}{\overset{\|}{C}}O-CH_3$

methyl ethanoate

$CH_3\overset{O}{\overset{\|}{C}}O-CH_2CH_3$

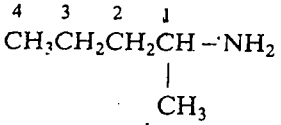
ethyl ethanoate

$CH_3CH_2\overset{O}{\overset{\|}{C}}O-CH_3$

methyl propanoate

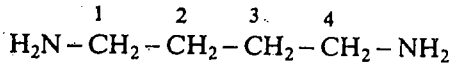
Amines: There are two systems of naming amines. One method names them as **alkylamines** and the other calls them as **alkanamines.** The alkanamine naming system was introduced by **Chemical Abstracts** and is easier to use as compared to the earlier IUPAC system of alkylamine names. The latest revision of IUPAC rules accepts both systems and examples below are named in both the ways.

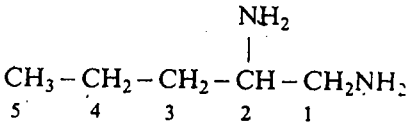
CH_3NH_2
methylamine
or methanamine


1-methylbutylamine
or 2-pentanamine

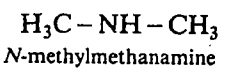
(Note that the numbering starts at the carbon and not at the nitrogen of the amine part).

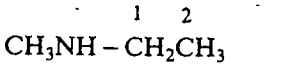
Primary diamines are named by using the suffix **diamine** after the name of the hydrocarbon.

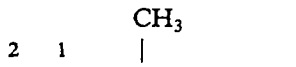

1,4-butanediamine

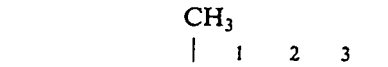

1,2-pentanediamine

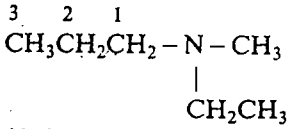
For the secondary and the tertiary amines, the longest alkyl group present is considered as the parent chain. The remaining alkyl groups are named as substituents attached to the nitrogen and a prefix *N*– is used with the name of the alkyl group.


N-methylmethanamine
(common name : dimethylamine)

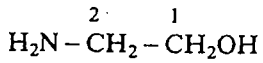

N-methylethanamine
(common name : ethylmethylamine)

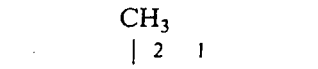

N,*N*-dimethylethanamine
(common name : ethyldimethylamine)


N,methyl-*N*-propylpropanamine
(common name : methyldipropylamine)


N-ethyl-*N*-methylpropanamine
(common name : ethylmethylpropylamine)

When used as a substituent, the $-NH_2$ group is named as **amino** and is prefixed with a number indicating the carbon atom to which it is attached.

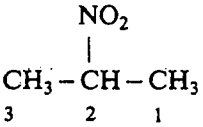

2-aminoethanol

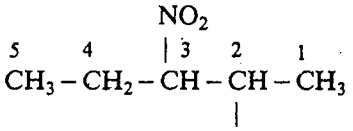

N,*N*-dimethylaminoethanoic acid

Nitro compounds: The nitro compounds are named as nitroderivatives of the corresponding hydrocarbons.

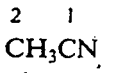
Examples being,

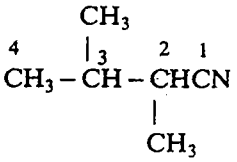
CH_3NO_2
nitromethane

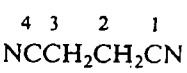

2-nitropropane


2,3-dinitropentane

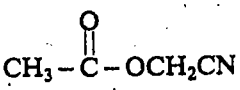
Nitriles: Nitriles are named in the IUPAC system by using the suffix **-nitrile** to the name of the hydrocarbon corresponding to the longest carbon chain. Note that here the carbon of the nitrile group is included in the numbering of carbon chain and is numbered as position 1. Some examples are given below:


ethanenitrile
(common name : acetonitrile)


2,3-dimethylbutanenitrile

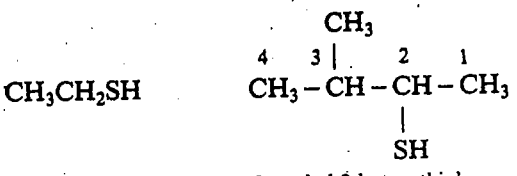

butanedinitrile

When named as a substituent, the –CN group is called a cyano group. For example, the compound



is named as cyanomethyl ethanoate.

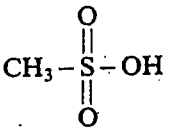
Thiols : In naming thiols, an ending *thiol* is used as a suffix to the name of the corresponding hydrocarbon; for example,



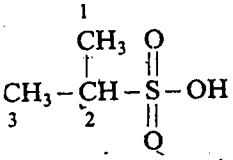
ethanethiol

3-methyl-2-butanethiol

Sulphonic acids: The names of sulphonic acids use the suffix *sulphonic acid* with the name of the corresponding hydrocarbon.



methanesulphonic acid



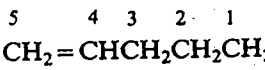
2-propanesulphonic acid

The order of priority for various functional groups is decided by considering the following points :
i) Functional groups that have an IUPAC **suffix** and terminate a carbon chain, have highest priority, e.g., carboxylic acids and their derivatives.
ii) Next are the groups that have a suffix and can be located at any position in the molecule, e.g., hydroxy and amino groups.
iii) Groups having no suffix and which are named as substituents, are given the lowest priority. Example being the halogens.

Till now, you have studied about the nomenclature of monofunctional compounds, i.e. the compounds which contain only one functional group. In polyfunctional compounds where more than one functional groups are present, one group is identified as the principal functional group and this principal functional group is used as a suffix in the name of the compound. The priorities for selection of principal functional group are given below in the order of decreasing precedence. The order is carboxylic acid, sulphonic acid, ester, acid anhydride, acyl halide, amide, nitrile, aldehyde, ketone, alcohol, thiol, amine, imine, alkyne, alkene, ethers, halides, nitro.

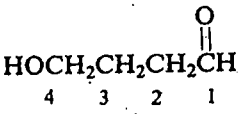
Let us study the examples given below which illustrate the nomenclature of polyfunctional compounds.

Example 1



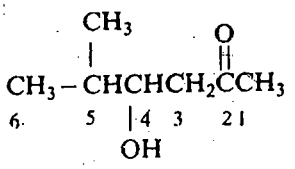
Here, the functional groups present are a hydroxyl group, (–OH) and a double bond. As per the order given above, the hydroxyl group is the principal functional group and hence the compound should be named as an alcohol (an not as an alkene). Hence, its name is pent-4-ene-1-ol.

Example 2



Now, in this case the carbonyl group or more specifically the aldehyde functional group (–CHO) is to be given priority over the hydroxyl group. Hence, this compound is named as 4-hydroxybutanal.

Example 3



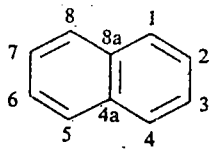
The principal functional group is the keto group. Hence, as shown in the structure, the numbering of the carbon-chain will be done so as to give this function the lowest number. Thus, the name of this compound will be 4-hydroxy-5-methyl-2-hexanone.

Let us next study the nomenclature of aromatic compounds. The aromatic compounds can have any of the following types of basic skeletones :

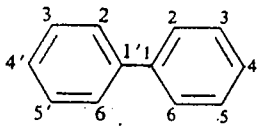
a) **Compounds containing one aromatic ring.** This class includes benzene and its derivatives. The derivatives of benzene include the compounds which can have any of the functional groups discussed before attached to the benzene ring.

benzene

b) **Compounds containing two aromatic rings.** Examples being naphthalene and biphenyl.

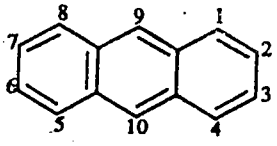


naphthalene

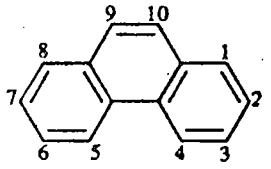


biphenyl

c) **Compounds having more than two aromatic rings.** Examples are,

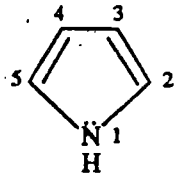


anthracene

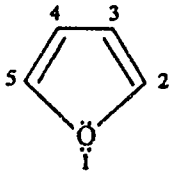


phenanthrene

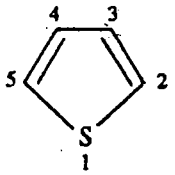
d) **Heterocyclic compounds:** Aromatic compounds containing heteroatoms such as O, N or S in the aromatic ring are called heterocyclic compounds. Some heterocyclic compounds are shown below:



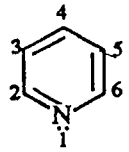
pyrrole



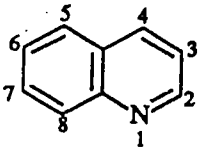
furan



thiophene



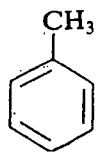
pyridine



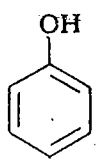
quinoline

At this stage we will study in detail the nomenclature of benzene and its derivatives only. Although the carbon skeletons for the type of compounds shown in the categories (b), (c) and (d) are numbered here, their nomenclature will be dealt at appropriate places in later units of this course.

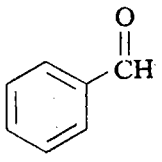
a) **Benzene and its derivatives:** A number of monosubstituted benzene derivatives are known by their special names. These names are in common use for long and hence are approved by IUPAC. Some examples of these compounds are given below along with their common and IUPAC names (in brackets).



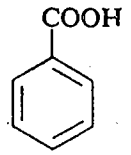
toluene
(methylbenzene)

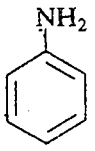


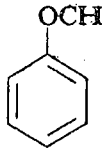
phenol
(benzenol)



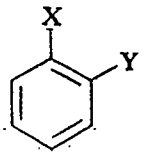
benzaldehyde
(benzenecarbaldehyde)

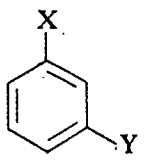

benzoic acid
(benzenecarboxylic acid)

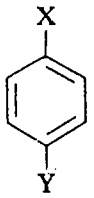

aniline
(benzenamine)


anisole
(methoxybenzene)

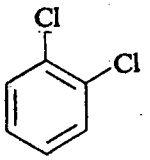
For disubstituted benzene derivatives, the following three arrangements of the substituents are possible.

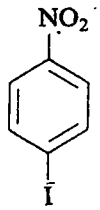

ortho-


meta-

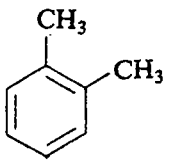

para-

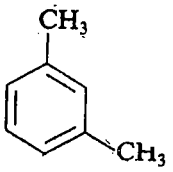
These arrangements are named using the Greek prefixes *ortho-*, *meta-* and *para-* which are abbreviated as *o-*, *m-* and *p-*. The substituents are then named in the alphabetical order. This is illustrated in the examples below.

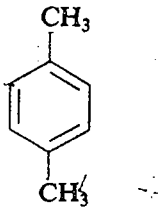

ortho-dichlorobenzene
or *o*-dichlorobenzene


p-iodonitrobenzene

Dimethyl derivatives of benzene are known as **xylenes**. The three xylenes are,

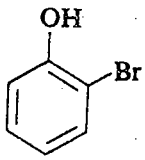

o-xylene
(1,2-dimethylbenzene)


m-xylene
(1,3-dimethylbenzene)

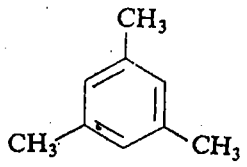

p-xylene
(1,4-dimethylbenzene)

When one substituent is such that it corresponds to the monosubstituted benzene that has a special name, then this substituent is called the principal functionality and the compound is named as a derivative of that parent functionality. For example,

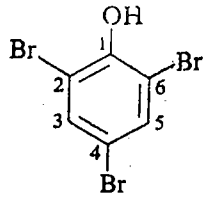

p-nitrotoluene


o-bromophenol

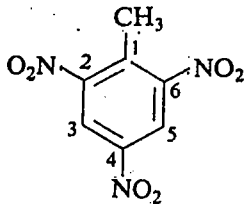
The polysubstituted benzenes are named by identifying the principal functions and then numbering is done such as to keep the principal function as number 1. The other substituents are then given the lowest possible numbers. This is illustrated in the following examples.



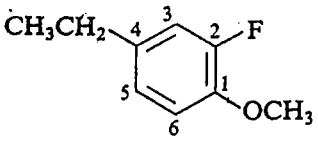
1,3,5-trimethylbenzene
(common name : mesitylene)



2,4,6-tribromophenol



2,4,6-trinitrotoluene (TNT)

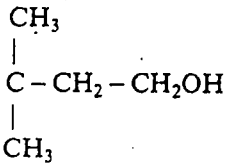


4-ethyl-2-fluoroanisole

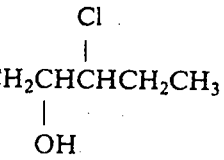
Having studied the nomenclature in detail, attempt the following SAQs to check your understanding about it.

SAQ 5

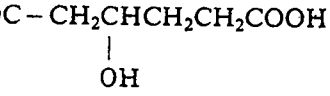
Name the following compounds according to IUPAC system of nomenclature.

a) 

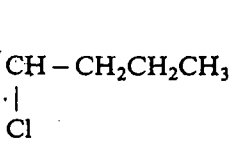
.....

b) 

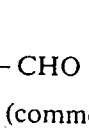
.....

c) 

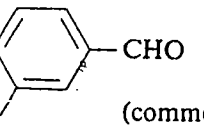
.....

d) 

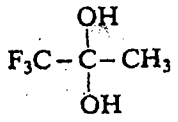
.....

e)  (common name: chloral)

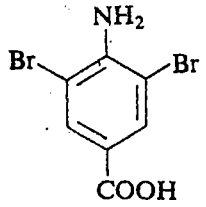
.....

f)  (common name: vanillin)

.....

g) 

.....

h) 

.....

SAQ 6

Given below are the names of some compounds. Write their structures.

a) 3-ethyl-3-pentanol

.....

b) 3-methyl-2-buten-1-ol

.....

c) 2-bromo-4-nitrotoluene

.....

d) 5-hexyn-2-one

.....

e) benzoic anhydride

.....

f) ethyl formate

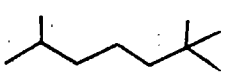
.....

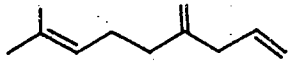
1.7 SUMMARY

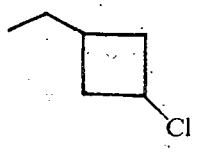
In this unit you have studied about the basic features of the covalent bond which is the bond occurring in all the compounds of carbon and is responsible for the formation of organic compounds. Then you have learnt how to write structures for these organic compounds. The formation of simple organic compounds is explained by using the concept of hybridisation. As these organic compounds are conveniently studied by grouping the similar compounds together in a class, classification of organic compounds has been dealt with in detail. The nomenclature of various classes of the organic compounds is also discussed using simple examples.

1.8 TERMINAL QUESTIONS

1. Expand the following line structures.

a) 

b) 

c) 

2. The structural formula for allene is shown below. Illustrate the formation of bonds in allene by showing the overlap of the orbitals using a diagram.

$H_2C=C=CH_2$
allene

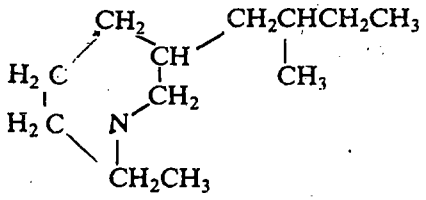
3. Many compounds isolated from natural sources often show more than one functional group. Given below are some such compounds. Identify the functional groups present in these compounds.

a) $CH_3CH(OH)-C(=O)-OH$
lactic acid

b) $CH_3CH(NH_2)-C(=O)-OH$
alanine

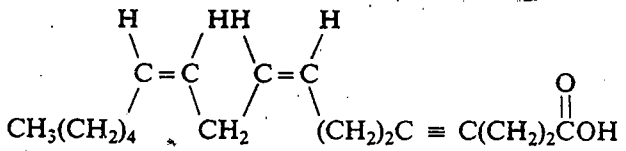
c) $HOCH_2CH(OH)-C(=O)-H$
glyceraldehyde

d)



a substance produced by a beetle to help it float on water.

e)



a metabolite of a seaweed that is poisonous to fish

4. For compounds having molecular formula, $C_3H_5Cl_3$, write structural formulas for all possible isomers and name them.

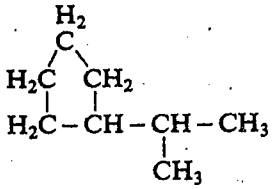
5. Write the structural formulas and IUPAC names for the following compounds:
   a) butanoic acid
   b) and its
      i) acid chloride
      ii) acid anhydride
      iii) acid amide
      iv) methyl ester

1.9 ANSWERS

Self Assessment Questions

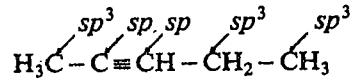
1. a) $CH_3-CH_2-CH(CH_3)-CH_2-CH(CH_3)-CH(CH_3)-CH_3$

b)

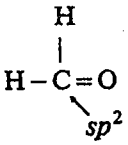


2. An sp^2 hybrid orbital has 33.33% *s* character and 66.67% *p* character.

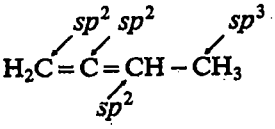
3. a)



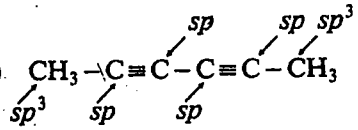
b)



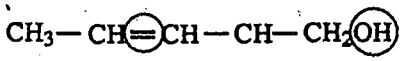
c)



d)

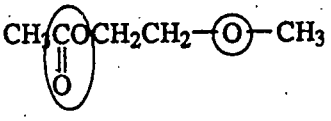


4. a)



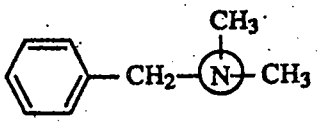
Double bond and hydroxyl group

b)



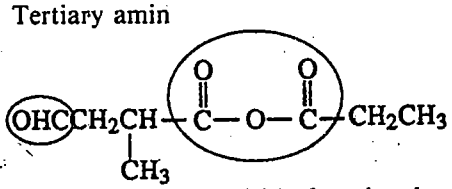
Ester and ether groups

c)



Tertiary amin

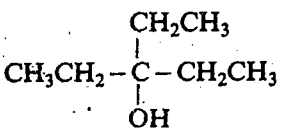
d)

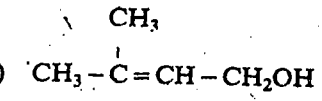


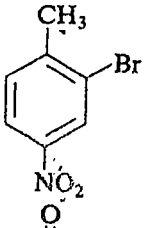
Aldehyde and anhydride functional groups.

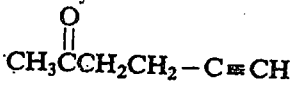
5. a) 3,3-dimethylbutanol
   b) 4-chloro-3-hexanol
   c) 3-hydroxyhexanedioic acid
   d) 2-chloropentanoyl chloride
   e) 2,2,2-trichloroethanal
   f) 4-hydroxy-3-methoxybenzaldehyde
   g) 1,1,1,3,3,3-hexafluoro-2,2-propanediol
   h) 4-amino-3,5-dibromobenzenecarboxylic acid

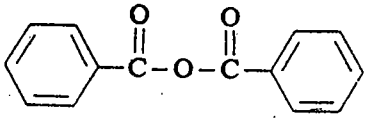
6. a)



b) 

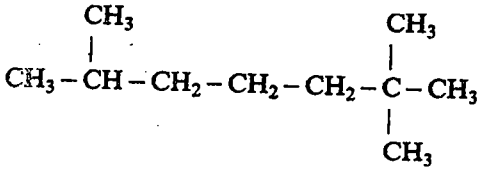
c) 

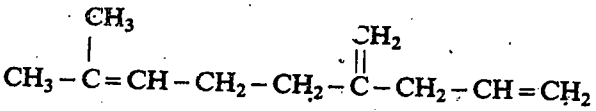
d) 

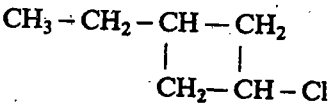
e) 

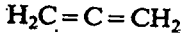
f) 

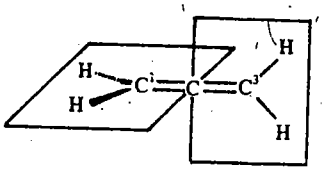
Terminal Questions

1. a) 

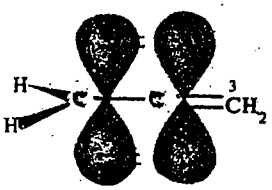
b) 

c) 

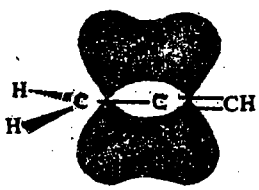
2. 



(a) Planes defined by H(C-1)H and H(C-3)H are mutually perpendicular

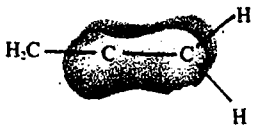


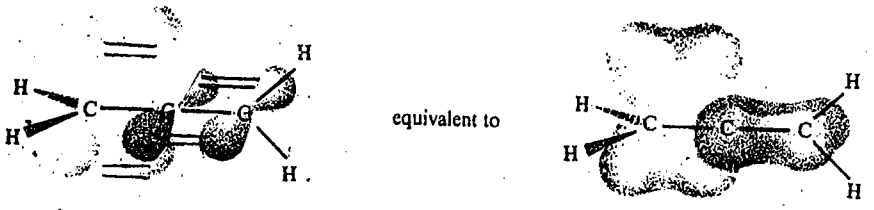
equivalent to



(b) The *p* orbital of C-1 and one of those of C-2 can overlap to form a π bond

equivalent to





(d) Allene has a linear carbon chain and two mutually perpendicuar π bonds

3. a) $-OH$ and $-COOH$ groups.
   b) $-NH_2$ and $-COOH$ groups
   c) Two $-OH$ groups (one primary and one secondary) and one $-CHO$ group..

d) $-N\lesseqgtr$ group.

e) Two double bonds, one triple bond and a $-COOH$ group.

4. a) $H_2C(Cl)-CH(Cl)-CH_2(Cl)$ — 1,2,3-trichloropropane

   b) $Cl-CH(Cl)-CH_2-CH_2(Cl)$ — 1,1,3-trichloropropane

   c) $Cl-CH(Cl)-CH(Cl)-CH_3$ — 1,1,2-trichloropropane

   d) $Cl-C(H)(Cl)-C(H)(Cl)-CH_3$ — 1,2,2-trichloropropane

   e) $CH_3-CH_2-C(Cl)(Cl)-Cl$ — 1,1,1-trichloropropane

5.

	Formula	IUPAC name
a)	$CH_3CH_2CH_2COOH$	butanoic acid
b)	$CH_3CH_2CH_2COCl$	butanoyl chloride
c)	$CH_3CH_2CH_2C(=O)-O-C(=O)CH_2CH_2CH_3$	butanoic anhydride
d)	$CH_3CH_2CH_2C(=O)NH_2$	butanamide
e)	$CH_3CH_2CH_2C(=O)-OCH_3$	methyl butanoate

UNIT 2 STEREOCHEMISTRY – I

Structure

2.1 Introduction
Objectives
2.2 Isomerism
2.3 Geometrical Isomerism
2.4 Characterisation of Geometrical Isomers
2.5 Optical Isomerism
Plane Polarised Light and Optical Activity
Origin of Optical Activity
Chirality
2.6 Chirality and Elements of Symmetry
2.7 Summary
2.8 Terminal Questions
2.9 Answers

2.1 INTRODUCTION

Although we are habituated to writing the structures of organic molecules in two dimensions but actually they have three-dimensional structures. The term **Stereochemistry** is coined from the Greek word **stereos** meaning "solid" and it deals with the chemistry in three dimensions. In addition to the study of the geometry of molecules which is referred to as **stereoisomerism,** stereochemistry is concerned also with the effect of molecular geometry (i.e., the three-dimensional structure of molecules) on chemical reactions and chemical equilibria. While these aspects will be dealt with in detail at appropriate places in this course and in the Organic Reaction Mechanism course, in this unit, we will confine our discussion mainly to stereoisomerism. We will begin with the concept of isomerism in general and then study geometrical and optical isomerism in detail.

While studying this Unit and Unit 3 which also deals with stereochemistry, you are advised to take help of the models. You can make models using the students set of models provided to you. Before using the models, go through the guidelines for using the models given in the study guide. For better understanding of the material, you should yourself do the various activities given in the margin.

Objectives

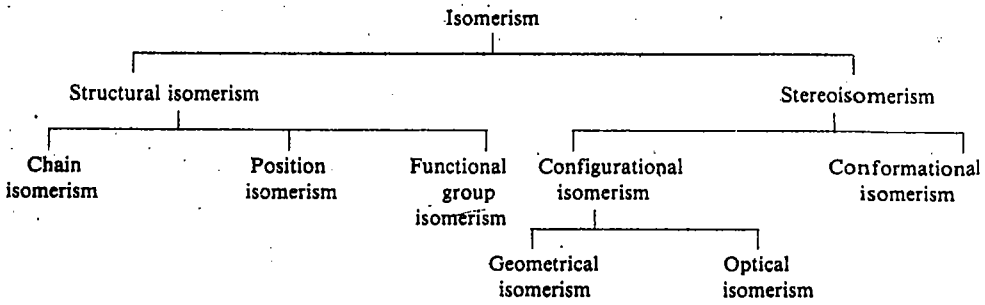
After studying this unit, you should be able to:

- list and define various types of isomerism,
- write geometrical isomers and designate them as *cis*- or *trans*- and *E* or *Z* isomers,
- predict whether a compound will show optical activity or not just by examining its structure,
- write the enantiomers for a given compound,
- differentiate between enantiomers and diastereoisomers,
- locate chiral centres in a molecule, and
- identify the elements of symmetry present in a molecule.

2.2 ISOMERISM

The phenomenon of existence of two or more compounds having the same molecular formula is known as **isomerism** and these compounds are individually referred to as **isomers.** Isomerism can be of various types. The different types of isomerism are represented below in a flow chart.

Isomers have same molecular formula but they differ from each other in their physical and chemical properties.



Let us now study each type of isomerism in detail.

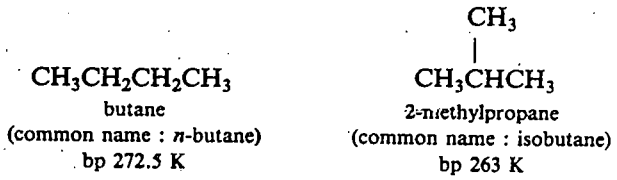
Isomerism, which is one of the important characteristics of organic compounds, arises because of the number and variety of ways in which carbon atoms, which form the back-bone of organic molecules can link with each other. On this is superimposed the position and linking of various heteroatoms like O,N,S, halogens etc., giving rise to a very large number of isomers. The number increases with the number and variety of atoms present in a molecule. So a study of the structure of the molecule is implicit and molecular formula alone is not enough.

1. **Structural Isomerism** arises due to differences in the structures of the molecules. These structural differences can be further classified into three types; accordingly, the three types of structural isomerism are as given below:

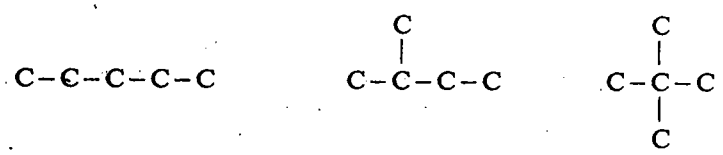
   a) **Chain Isomerism** is exhibited by the compounds which differ from each other in the way the carbon atoms form the basic skeleton. You have already studied such type of compounds in Unit 1, Sec. 1.6 where we considered that four carbon atoms can be linked to each other in two different ways to form either a straight chain of carbon atoms or a branched chain, as shown below :

These straight chain and branched chain carbon skeletons correspond to two different hydrocarbons having the molecular formula C_4H_{10}. These are commonly called *n*-butane and isobutane and are shown below.

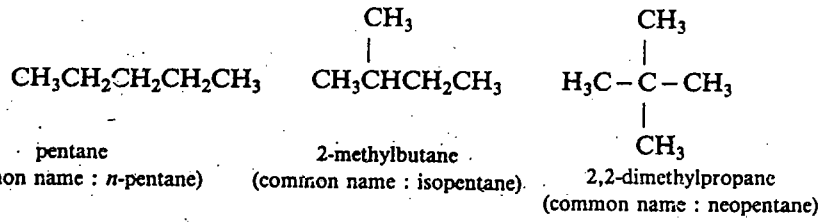
The two isomeric butanes are distinct entities having different boiling points.



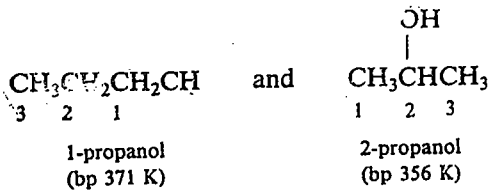
Thus, butane and 2-methylpropane exhibit chain isomerism. Similarly, five carbon atoms can have any of the following arrangements:



Corresponding to these arrangements, the isomeric hydrocarbons are shown below.



   b) **Position Isomerism** is different from chain isomerism in the sense that here the isomers have the same carbon skeleton but they differ from each other in the *position* of the substituent groups. For example, in a straight chain hydrocarbon having three carbon atoms, a substituent can be either at C-1 position or at C-2 position, i.e. if the substituent is a hydroxyl group, then the two position isomers are:



1-propanol (bp 371 K) and 2-propanol (bp 356 K)

c) **Functional Group Isomerism** is exhibited by compounds having the same molecular formula but different functional groups. For example, the molecular formula C_3H_6O corresponds to both propanone and propanal;

propanone propanal

Here, the functional group are the keto and the aldehyde groups, respectively. Such isomers thus belong to different classes.

2. **Stereoisomerism** is exhibited by compounds which have the **same** Lewis structure (or structural formula) but differ from each other in the spatial arrangement of the atoms or groups in their molecules. Such isomers are called **stereoisomers.** Stereoisomerism can be further classified into two types as given below:

   a) **Configurational Isomerism:** The absolute configuration of a compound can be defined as the actual orientation of the groups in space. This type of isomerism is exhibited by those stereoisomers which cannot be converted to each other without breaking of bonds. It can be further classified into geometrical isomerism and optical isomerism.

      i) **Geometrical isomerism** is caused by different arrangements of the groups around a rigid framework. This rigid framework can be a double bond or a cyclic structure around which the various groups are attached. Later, you will study that due to this rigid framework, interconversion of such isomers is not easily possible.

      ii) **Optical isomerism** arises due to molecular asymmetry and as the name indicates, this type of isomerism is manifested by the rotation of the plane of plane-polarised light. In this unit, you will study geometrical and optical isomerisms in detail.

   b) **Conformational Isomerism** arises due to different spatial arrangements of groups in a molecule which are obtained by rotation about single bonds. Each such arrangement is called a **conformation.** You will study more about conformations in Unit 3 of this block.

At this stage you check your understanding about various kinds of isomerism by answering the following SAQ.

SAQ 1

Write all possible structural isomers of C_3H_8O.

.....

.....

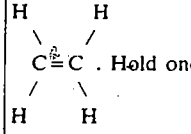
.....

2.3 GEOMETRICAL ISOMERISM

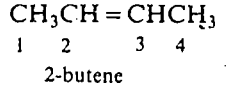
It was pointed out in the last section that geometrical isomerism is possible when groups are attached to a rigid framework like a double bond. You also studied earlier in Unit 1, Sec. 1.4, that a double bond is constituted by a *sigma* and a *pi* bond. Since the π bond is formed by the lateral overlap of *p* orbitals, rotation about the double bond is not possible without breaking it. You can verify this by making a model of ethene. Here you should be aware of the fact that the model of

ethene does not show the complete picture of the *pi* bond, as was illustrated in Fig. 1.2.

Activity

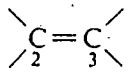
Make a model of ethene,  . Hold one of the carbon atomic centres and try to rotate the double bond. You will find that it is not possible to rotate one carbon atom with respect to the other without breaking one of the bonds.

Let us now study how geometrical isomerism arises when such a rigid framework is present. For this, consider the case of 2-butene. We can write its structure as shown below.

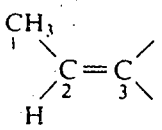


2-butene

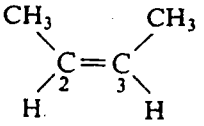
But actually two different compounds corresponding to this structure exist. You can yourself see this by writing the structural formulas for these two compounds. To do this start by writing the C-2 and C-3 carbon atoms of the carbon skeleton as:-



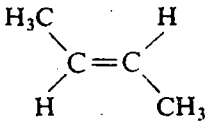
As shown in the structure of 2-butene, a methyl group and a hydrogen atom are linked to C-2 carbon; hence, attach a CH_3 group and a hydrogen to C-2 carbon as shown below:



Similarly, a $-CH_3$ group and a hydrogen atom are linked to the C-3 carbon atom. When you try to put this second methyl group at C-3 carbon, you have two possibilities:


cis-2-butene

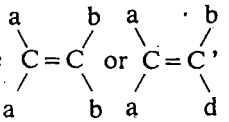
or


trans-2-butene

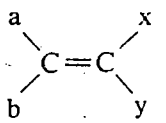
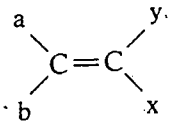
Activity

Make models of *cis*- and *trans*-2-butenes. Try to interconvert them by taking either of models of *cis*- or *trans*-isomer. To do this, try to rotate the substituents at one end of the double bond, keeping the substituents of the other end fixed. You will realise that by continuously applying the force for rotation of the substituents, you will break one bond of the double bond. So, *cis*- to *trans*- or *trans*- to *cis*- conversion is not possible by rotation about the double bond. Theoretically, the reason for this is that when we try to rotate the substituents around a double bond, the overlap of *p* orbitals forming the π bond decreases. The increasing rotation finally leads to no overlap between *p* orbitals, or breaking of π bond. Thus, *cis*- and *trans*- isomers are two different compounds which are capable of independent existence.

Clearly, in the first case, the two methyl groups are on the same side of the double bond and in the second structure one methyl group is on one side and the other methyl group is on the opposite side of the double bond. These two butenes are differentiated from each other by attaching the prefixes *cis*- (a Latin word meaning *on this side*) and *trans*-(a Latin word meaning *across*) in their names. Hence, these two butenes are named as *cis*-2-butene and *trans*-2-butene, respectively. Thus, *cis*- and *trans*-2-butenes exhibit geometrical isomerism and therefore, they are called geometrical isomers.

In other words, we can say that *cis-trans*-or geometrical isomers are the isomers of the type baC = Cab. Hence, in the molecules of the type  where the carbon atoms forming the double bond carry identical substituents, such an isomerism is not possible.

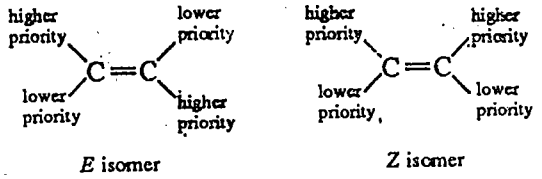
Let us now see what happens when all the four substituents around the double bond are different. For such a case, the following different arrangements of the groups are possible,


and


The question that immediately arises is how to differentiate these two compounds ? Can you designate them as *cis-* or *trans-?* The answer is **No** because the *cis- trans-* nomenclature does not provide clear guidelines about how to designate these isomers.

To designate such isomers, an unambiguous system of nomenclature, based on the sequence rules developed by **Cahn-Ingold and Prelog,** is used. In this system each of the two groups attached to same carbon atom of the double bond is assigned priority according to the sequence rules. This is done for both the carbon atoms forming the double bond. If the groups of higher priority are an opposite sides of the double bond, then the isomer is said to have *E* configuration. Otherwise, when the groups having higher priority are on the same side of the double bond, then the isomer is known as *Z* isomer. The letters *E* and *Z* are derived from the German words *entgegen* meaning **opposite** and *zusammen* meaning **together.** Thus, we can say that,

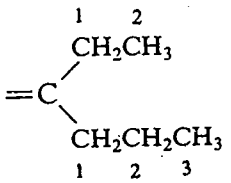
Although the Cahn-Ingold-Prelog sequence rules and the *E-Z* system have been sanctioned by IUPAC, use of *cis- trans-* nomenclature in the cases where it can be used unambiguously is allowed by IUPAC.



E isomer Z isomer

Let us now study the sequence rules used in Cahn-Ingold-Prelog system. These rules are given below:

1. Atoms of the higher atomic number have higher priority. For example, oxygen (At. No. 8) has higher priority than carbon (At. No. 6) which in turn has higher priority than hydrogen (At. No. 1).
2. When the priority is to be decided between the atoms which are isotopes of the same element, then the isotope of higher atomic mass has higher priority. Therefore, deuterium (^2_1H), an isotope of hydrogen has higher priority than hydrogen (^1_1H).
3. When the two groups attached to the carbon atom involved in the formation of double bond have the same atoms as points of attachment, then the priorities are assigned according to the first point of difference, applying the same considerations of atomic number and atomic mass. To understand this, consider that the two groups attached to the carbon atom involved in the formation of double bond are ethyl and propyl groups, as shown below:



Here both these groups are attached to the carbon atom forming the double bond by carbon atoms. To decide which of the two will have higher priority, look at the substituents on C-1 carbon atoms of the ethyl and propyl groups. You will find that in both the groups, two hydrogens are attached to the C-1 carbon atom. Let us move to the next carbon, C-2. In case of the ethyl group, there are three hydrogens attached to C-2 carbon while the propyl group has two hydrogens and one carbon attached to the C-2 carbon. Clearly, then this is the first point of difference where the C-2 carbon of propyl group has the substituents C, H, H while that of the ethyl group has the substituents H, H, H. Hence, the propyl group has priority over the ethyl group.

4. When we come across double or triple bonds while assigning the priorities, then these groups are visualised in such a way that the bonded atoms are duplicated or triplicated as the case may be. For example, in the group

$-HC=\overset{1}{C}H_2$, a carbon atom attached to another carbon atom by a double bond is considered to be bonded to two carbon atoms. Thus, this group can be regarded as $HC(-C)(-C)H_2$.

Similarly, the $-\overset{O}{\overset{\|}{C}}-H$ group is treated as equivalent to $-\overset{O-C}{\underset{O}{\overset{|}{C}}}-H$.

This is a kind of expansion of the groups in such a way that each atom is shown as linked to the other atom by a single bond. Thus, to write for the group shown below,

$$-\overset{1}{C}\equiv\overset{2}{C}-H$$

first expand at C-1 carbon which has all the three bonds linked to the carbon atom numbered as C-2. Thus, it is to be shown as if it is linked to three carbon atoms like this,

$$-\overset{1}{\underset{C}{\overset{C}{C}}}-\overset{2}{C}H$$

Now repeat the same for the C-2 carbon, which is expanded to yield,

$$-{}_1\overset{C}{\underset{C}{\overset{C}{C}}}-{}_2\overset{C}{\underset{C}{\overset{C}{C}}}-H$$

which is the equivalent form of $-C\equiv CH$ group considered for assigning the priority.

In the guidelines provided by these sequence rules, some commonly occurring groups can be arranged in the decreasing order of their priority as follows:

$$I->Br->Cl->HS->F->CH_3\overset{O}{\overset{\|}{C}}-O->H\overset{O}{\overset{\|}{C}}-O->CH_3CH_2O->$$

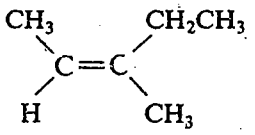
$$HO->H_2N->CH_3O\overset{O}{\overset{\|}{C}}->HO\overset{O}{\overset{\|}{C}}->CH_3\overset{O}{\overset{\|}{C}}->H-\overset{O}{\overset{\|}{C}}->HOCH_2->$$

$$(CH_3)_3C->CH_2=CH->(CH_3)_2CH->CH_3CH_2->CH_3->H.$$

Let us now study some examples which illustrate how a given compound is designated as *E* or *Z*, using the above sequence rules.

Example 1

higher priority higher priority

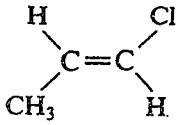


lower priority lower priority

In this compound, groups of higher priority are on same sides of the double bond, hence, it is the (*Z*)-isomer.

Example 2 :

lower priority higher priority

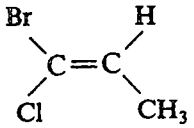


higher priority lower priority

In this case, groups of higher priority are on opposite sides of the double bond, hence, it is the (*E*)-isomer.

Similarly, the isomer shown below,

higher priority lower priority

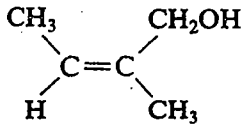


lower priority higher priority

is (*E*)-isomer and can be named as (*E*)-1-bromo-1-chloropropene.

And, the isomer

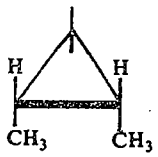
higher priority higher priority



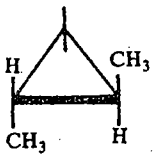
lower priority lower priority

is (*Z*)-isomer.

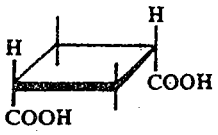
Similar to the geometrical isomerism exhibited about a double bond, the compounds having a cyclic rigid framework can also show geometrical isomerism. Some cyclic compounds which exhibit geometrical isomerism are shown below.



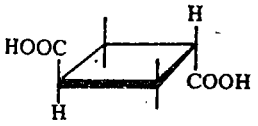
cis-1,2-dimethylcyclopropane



trans-1,2-dimethylcyclopropane



cis-1,3-cyclobutanedicarboxylic acid



trans-1,3-cyclobutanedicarboxylic acid

Activity

Make models for *cis*- and *trans*-isomers of 1,2-dimethylcyclopropane and convince yourself that all the three carbon atoms of the cyclopropane are in one plane and the methyl groups are located perpendicular to the plane of the ring. Thus, in the *cis*- isomer, both the methyl groups are either above or below the plane of the molecule but in the *trans*- isomer one methyl group is above the plane of the molecule and other is below the plane of the molecule.

You will study more about the stereochemistry of simple cyclic compounds such as cyclohexanes in the next unit. However, the general aspects of the chemistry of cycloalkanes will be dealt with in Unit 6 of Block 2 of this course.

Geometrical isomers vary widely in their physical properties. Physical properties of some geometrical isomers are listed in Table 2.1

Table 2.1: Physical properties of some geometrical isomers

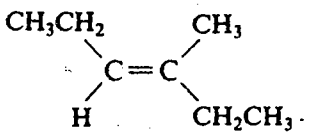
Compound	Melting point (K)	Boiling point (K)	Dipole moment / 10^{-30} (C m)
cis-2-butene	134	277	1.10
trans-2-butene	167	274	0
cis-1,2-dichloroethene	193	333	6.17
trans-1,2-dichloroethene	223	321	0
cis-1,2-dibromoethene	220	383	4.5
trans-1,2-dibromoethene	267	381	0
cis-1,2-diiodoethene	259	345	2.50
trans-1,2-diiodoethene	461	465	0

In the next section, we will use these physical properties to characterise geometrical isomers. But before that answer the following SAQ.

SAQ 2

Assign the configuration as *E* or *Z* to the following compounds.

i)



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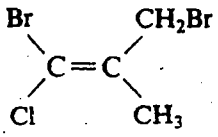
ii)



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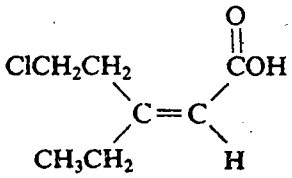
iii)



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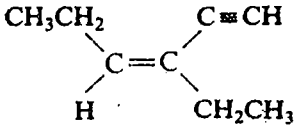
iv)



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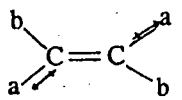
2.4 CHARACTERISATION OF GEOMETRICAL ISOMERS

There are several physical and chemical methods for differentiating between the

geometrical isomers. Let us first study the characterisation of geometrical isomers based on their physical properties and then we will study how chemical properties can be used for the characterisation of these isomers.

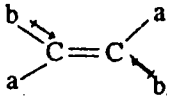
The geometrical isomers or the *cis* – *trans*– isomers differ from each other in their physical properties like melting point, boiling point, dipole moment and spectral characteristics. Table 2.1 clearly shows that the *trans*– isomer has a higher melting point than the corresponding *cis*– isomer. The reason for this is that the *trans*– isomer being more symmetrical, fits into the crystal lattice more easily and hence, has a higher melting point than the *cis*– isomer. However, the correlation of boiling points with configuration of the isomer is not as exact as is the case with melting points, because of its dependence on molecular volume. Hence, boiling points are not of much use for such determinations.

Another physical property useful for such differentiation is dipole moment. In geometrical isomers of the type abC = Cab, the *trans*– isomer has zero dipole moment. Some such examples are listed in Table 2.1. This is so because in the *trans*– isomer, the same substituents are located in the opposite directions and hence whatever be the magnitude of dipole moment due to one bond in one direction, it is cancelled by an equal moment operating in the opposite direction; thus, the resultant dipole moment is zero. Depending upon whether the substituents are electron-withdrawing or electron-donating, the directions of the dipole moments due to individual bonds for the *trans*– isomer are as given below.



(When group a is an electron-withdrawing group)

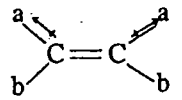
or



(When group b is an electron-donating group)

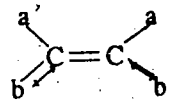
However, the resultant dipole moment, μ, for both the cases is zero.

But in the *cis* isomer, depending upon whether the groups are electron-donating or electron-withdrawing, the direction of individual bond moments is as shown below:



(When group a is an electron-withdrawing group)

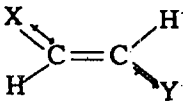
or



(When group b is an electron-donating group)

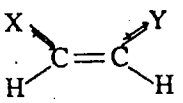
In both these situations, the individual dipole moments add vectorially leading to a definite resultant dipole moment. Hence, the molecule is said to have some dipole moment. You can check from Table 2.1 that the *cis*– compounds of this type always have some definite positive value for the dipole moment.

Let us next consider a molecule in which one substituent is electron-donating and the other is electron-withdrawing. Let X be an electron-donating substituent and Y be an electron-withdrawing substituent. The bond moments in the geometrical isomers of this type are shown below:



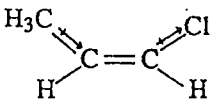
trans– isomer

or

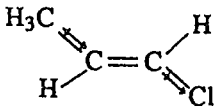


cis– isomer

In case of the *trans*– isomer, the bond moments add vectorially and reinforce each other leading to higher dipole moment for this isomer. The vectorial addition for the *cis*– isomer leads to a lower value for the resultant dipole moment. This is illustrated in the example given below.



cis- 1-chloro-1-propene
$\mu = 5.70 \times 10^{-30}$ C m

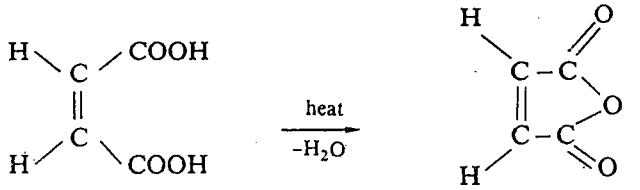


trans- 1-chloro-1-propene
$\mu = 6.56 \times 10^{-30}$ C m

The differentiation of geometrical isomers using spectral properties will be dealt with in Unit 7 of Block 2.

For a particular pair of geometrical isomers, the functional groups present are the same; hence, it is difficult to distinguish them on the basis of their chemical reactions. But there are some reactions which are possible with one isomer only because of the spatial arrangement of its groups. One such reaction is the formation of an anhydride by the maleic acid which is the *cis*- isomer of

An acid anhydride is formed by the elimination (or loss) of a water molecule from an acid. A dicarboxylic acid can lose a molecule of water and form an anhydride easily only if the carboxyl (–COOH) groups are on the same side of the molecule.



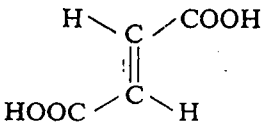
maleic acid
(*cis*-isomer)

maleic anhydride

but-2-ene-1,4-dioic acid. The two carboxyl (–COOH) groups are in close proximity in this isomer and hence can yield an anhydride by the elimination of a molecule of water. But, in the *trans*- isomer, i.e. in fumaric acid, since the two carboxyl groups are in opposite directions, such a reaction is not possible and hence it does

Activity

Make models of maleic acid (*cis*-but-2-ene-1,4-dioic acid) and fumaric acid (its *trans*- isomer) and convince yourself that the two carboxyl (–COOH) groups are close to each other in the *cis*-isomer whereas they are far apart in the *trans*- isomer.



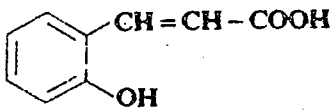
→ Anhydride formation is not possible

not form its own anhydride. However, when strongly heated, it forms the anhydride of maleic acid. Thus, we can differentiate between the *cis*-and the *trans*-isomers on the basis of chemical reactivity.

Before proceeding to the study of optical isomerism in the next section, you can check your understanding of geometrical isomerism by answering the following SAQ.

SAQ 3

a) Write the geometrical isomers of *o*-hydroxycinnamic acid having the following structure.



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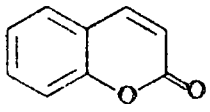
b) Which of the two isomers of *o*-hydroxycinnamic acid would undergo cyclisation easily to yield the following lactone:



coumarin

Give reason for your answer.

Hint: Note that the coumarin is formed by the loss of water; for removal of water, H and OH groups to be removed as water must remain spatially near to each other.

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2.5 OPTICAL ISOMERISM

As pointed out earlier, optical isomerism is manifested by the rotation of the plane of plane-polarised light. Let us first understand what is plane-polarised light and then see how it is used in the determination of optical activity.

2.5.1 Plane-polarised Light and Optical Activity

You are already familiar with the fact that light can be regarded as an electromagnetic radiation having oscillating electric and magnetic fields associated with it. The vectors describing these electric and magnetic fields are at right angles to each other (see Fig. 6.4, Unit 6, Block 2 of Atoms and Molecules course). Ordinary light consists of light waves of different wavelengths. A monochromatic light (light havin a single wavelength having λ = 589 nm, called sodium D line) obtained from the sodium lamp is used in the experiments. This monochromatic light still vibrates in many different planes as shown in Fig. 2.1 (a).

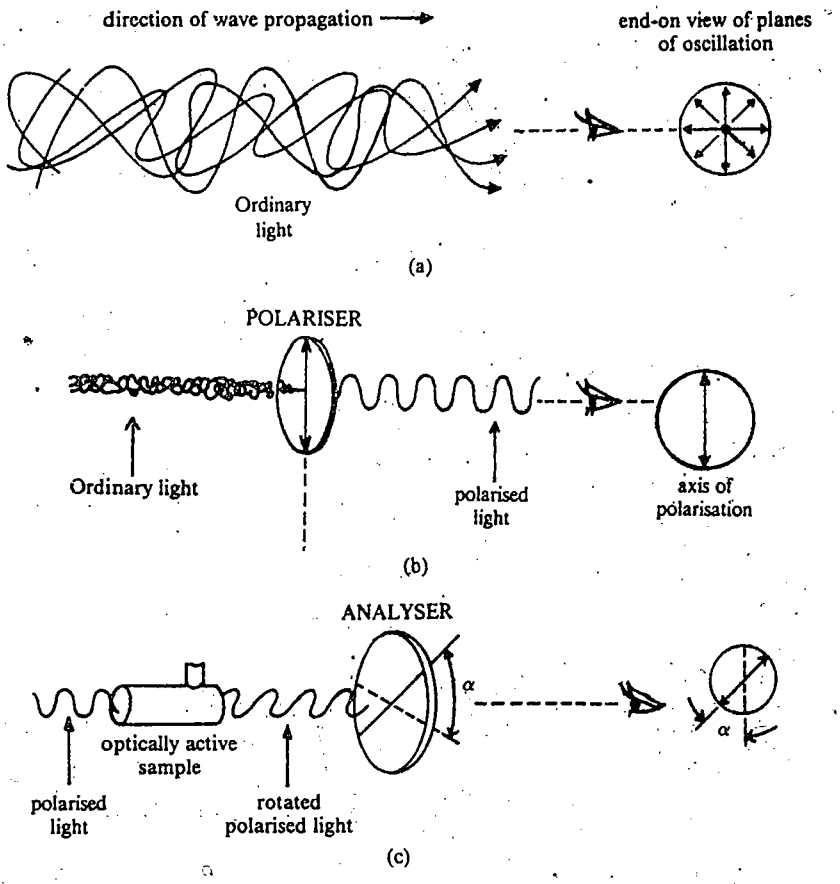


Fig. 2.1: a) Ordinary light. b) Plane-polarised light. c) Rotation of plane of plane-polarised light.

Such a light is called unpolarised light. When a beam of monochromatic light is passed through a polariser such as a polaroid lens or a device known as Nicol prism, the light, (i.e. its electric field) vibrating in **only one plane** is obtained. Such a light is called **plane-polarised light** [see Fig. 2.1. (b)]. It was observed that many substances such as quartz crystals and organic compounds like camphor and tartaric acid rotated the plane of plane-polarised light [Fig. 2.1 (c)]. Such substances are called **optically active.** The instrument used for the determination of optical activity is known as *polarimeter.*

Nicol prism, is named after its discoverer Nicol who passed ordinary light through a prism made by cementing two pieces of crystalline calcium carbonate, also known as Iceland spar, at specific angles to obtain plane-polarised light.

A schematic diagram of a polarimeter is shown in Fig. 2.2.

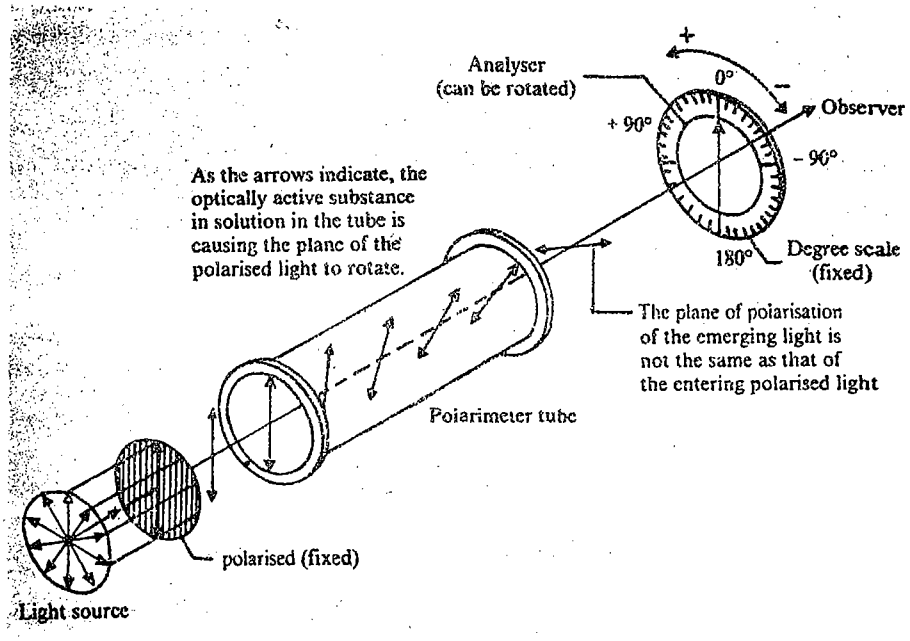


Fig. 2.2 : A schematic diagram of a polarimeter.

$1\ kg\ dm^{-3} = 1\ gm.ml^{-3}$

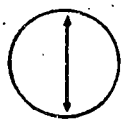
For an optically active compound, the extent of rotation, α, depends upon thickness of the sample (which is given by the length of the cell, l), its concentration (c), solvent, temperature and wavelength of the light used. When l is taken in decimetres and c is taken in kg dm^{-3}, then the rotation in degrees is termed as **specific rotation** and is denoted by $[\alpha]$. Thus, specific rotation can be calculated using the following expression,

$$[\alpha] = \frac{\alpha}{l \times c} \qquad \ldots(2.1)$$

electric vectors of a beam of unpolarised light

The temperature, t and the wavelength, λ, of the light used are specified as superscript and subscript, respectively. The solvent and the concentration of the solution are given in brackets. Hence, the specific rotation of a sample is expressed as,

$[\alpha]^{t}_{\lambda}$ (solvent, c)



direction of the electric vector of plane polarised light as it leaves the polariser

Thus, $[\alpha]^{293}_{D}$ denotes the specific rotation at the temperature 293 K when the measurement is done using the D line of sodium having λ = 589 nm.

The direction of rotation is specified as **dextrorotatory** or **levorotatory**. When a compound rotates the plane of polarised light in the clockwise direction, it is called **dextrorotatory** and this positive rotation is denoted by the plus (+) sign prefixed to the name of the compound. On the other hand, the compound rotating the plane of polarised light in the anticlockwise direction is called **levorotatory** and such a rotation is taken as rotation in the negative direction. Hence, it is indicated by prefixing a minus (−) sign to the name of the compound. Earlier the letters *d* and *l* were used to denote the dextrorotation and levorotation, respectively.

Dextrortation: plane of polarisation rotated clockwise: angle of rotation = + α

Levorotation: plane of polarisation rotated counterclockwise: angle of rotation = − α

Let us now study why some compounds are optically active and the others are not.

2.5.2 Origin of Optical Activity

The origin of optical activity can be traced back to the observations of the French physicist Biot who in 1813 discovered the existence of two types of quartz crystals (shown in Fig. 6.5, Unit 6, Block 2, Atoms and Molecules course). One type of crystals rotated the plane of polarised light to the left and the other type to the right. After two years, he observed that such optical activity is not restricted to the **crystalline structure** and some compounds such as camphor and tartaric acid exhibited optical activity even in **solution**. He also realised that optical activity in solution is due to some molecular property which is retained even in solution. Later Pasteur studied tartaric acid and its nineteen different salts and observed that

to certain faces and other being left-handed. These two types of crystals were mirror images of each other. Pasteur proposed that since the optical activity is retained in the solution phase also, it must be a property of the molecules themselves and just as the crystals of quartz are mirror images of each other, the molecules, of which these crystals are formed, are also mirror images of each other. This lead to the possibility of the existence of compounds whose molecules are mirror images of each other. These mirror image isomers being otherwise identical, exhibit identical physical properties; even the extent of rotation of the plane of polarised light is the same for such pairs. The only difference in their physical properties is in the direction of rotation of plane-polarised light: one isomer being dextrorotatory and the other being levorotatory.

Table 2.2 gives the physical properties for the mirror image isomers of 2-octanol.

Table 2.2 : Physical properties of isomeric 2-octanols

Physical property	(−)-2-Octanol	(+)-2-Octanol
Specific rotation $[\alpha]_D^{290}$	-9.9°	+9.9°
Boiling point (K)	448	448
Refractive index n^{298}	1.4254	1.4258
Specific gravity d^{293}	0.838	0.822

The next question that you may ask is: What kind of molecules are capable of existing as mirror image isomers? The answer is that the molecule and its mirror image isomer should be nonsuperimposable. Such nonsuperimposable mirror image isomers are called **enantiomers. Thus, for a compound to exist as two enantiomers, nonsuperimposability of mirror image structures is a condition.**

To decide whether the two given mirror image structures are enantiomers or are molecules of same isomer, try to superimpose one over the other. If they are superimposable, they are the molecules of the same isomer and if they are nonsuperimposable, they are enantiomers.

The most general example that helps to understand enantiomerism is the nonsuperimposability of our hands as shown in Fig. 2.3. You can see that the two hands are mirror images of each other but they are not superimposable on each other. This becomes more obvious if we try to put the right hand glove on the left hand and vice versa.

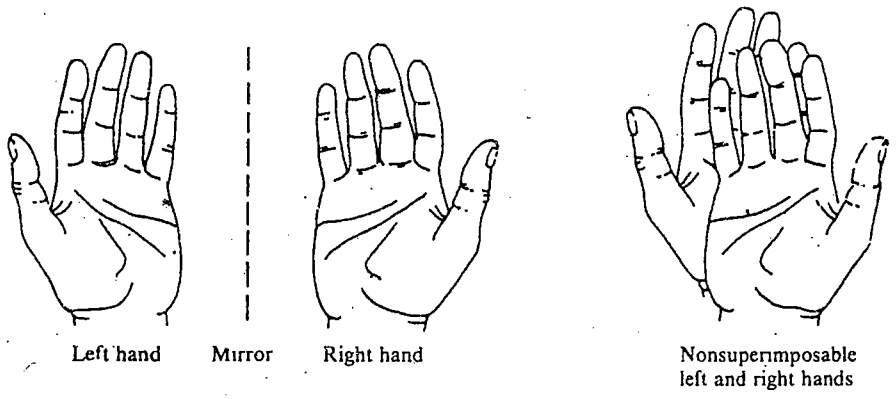


Fig. 2.3 : The nonsuperimposability and enantiomeric relationship of left and right hands.

In the Greek language the word **cheir** means *hand* and hence a molecule which is nonsuperimposable on its mirror image is said to be **chiral** and the term **chirality** means showing handedness. Thus, chirality is a necessary and sufficient condition for the existence of enantiomers. On the other hand, when a molecule is superimposable on its mirror image, it is said to be **achiral.** Let us now study some aspects of chirality in detail.

Chiral is pronounced as ki-rall

Handedness means existence of nonsuperimposable mirror image structures.

Only chiral molecules can exist as enantiomers.

The enantiomers have opposite chirality.

2.5.3 Chirality

The satisfactory explanation at the molecular level for the origin of optical activity (or existence of enantiomers) was given by van't Hoff and Le Bel simultaneously and independently in 1874. van't Hoff realised that it was necessary to think of molecular structures in three dimensions in order to solve the problem of isomers

The first Nobel Prize in Chemistry in 1901 was awarded to van't Hoff.

that were being discovered in the laboratory. He proposed that a carbon atom with four different substituents arranged tetrahedrally around it, would account for the existence of enantiomers. The tetrahedral arrangement of groups about the carbon atom makes it possible to have left-and right-handed structures (or isomers). The phenomenon of optical activity thus finds a satisfactory explanation in the tetrahedral geometry of saturated carbon compounds. Le Bel suggested that a carbon atom with four different substituents around it is the basis of optical activity but he did not specify the tetrahedral arrangement. Thus, in the case of lactic acid in which all the four substituents, i.e. H, CH_3, OH and COOH attached to the carbon atom, are different and are arranged tetrahedrally around it, two isomers are possible (see Fig. 2.4). These isomers being the nonsuperimposable mirror image isomers, are enantiomers.

Activity

Make models of the enantiomers of lactic acid and convince yourself that they are nonsuperimposable on each other.

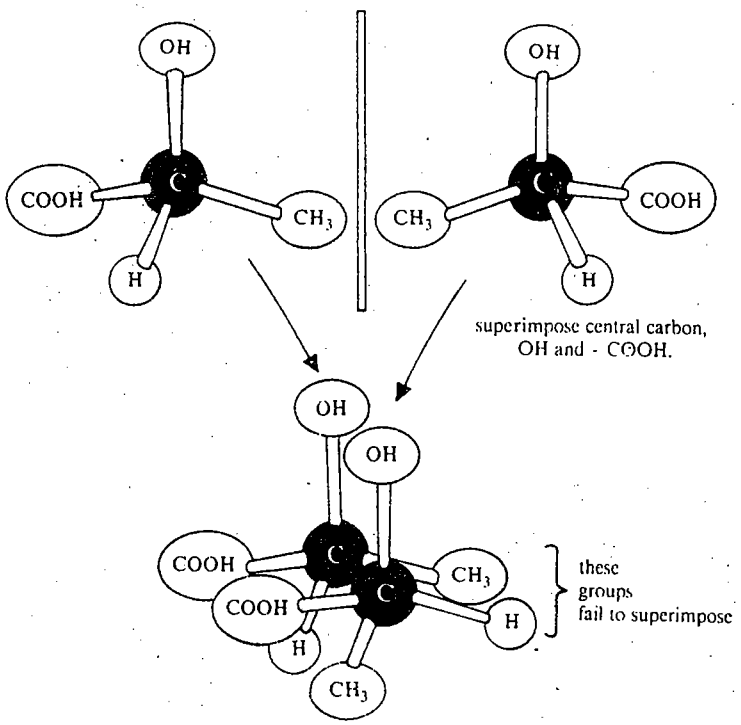
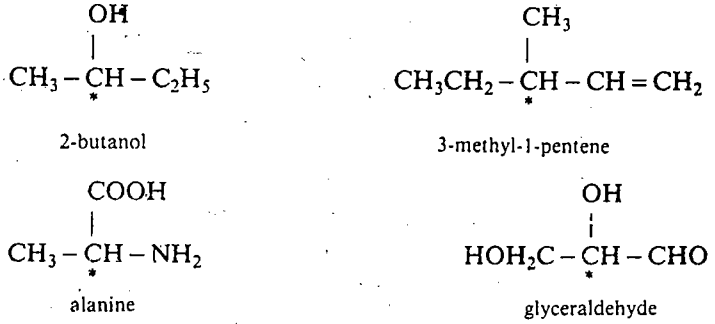


Fig. 2.4 : Enantiomers of lactic acid.

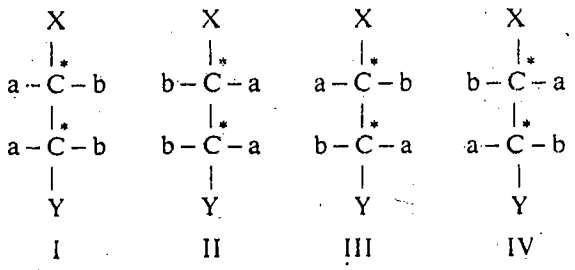
Hence, lactic acid is a chiral molecule and it is said to exhibit chirality. Such molecules which have four different substituents attached to a carbon atom are called **asymmetric**, i.e. they are without symmetry. To decide whether a given structure or a molecule has symmetry or not, we will study the elements of symmetry in the next section. The tetrahedral carbon atom bearing the four different substituents is variously referred to as a **asymmetric centre** or a **chiral centre**. Since it is the molecule itself which is chiral rather than one of its atoms, it has been suggested it is more correct to call the carbon atoms of this type as **stereocentres.** The IUPAC rules for stereochemical notation use the term chiral centre. Given below are some asymmetric compounds in which the chiral centre is shown by an asterisk (*) mark.

Remember that a carbon atom forming a double bond cannot be a chiral centre because it cannot have four different substituents.



Till now we were dealing with the compounds having only one chiral centre. Let us now study what happens when there is more than one chiral centre in a molecule.

For a molecule, abXC* – C*abY which has two chiral centres; the following four isomers are possible:



I II III IV

You can see that the isomers I and II are mirror image isomers. Similarly, III and IV are mirror image isomers. Since I and II are nonsuperimposable and so also are isomers III and IV. Hence, I and II, and III and IV are two enantiomeric pairs. But what is the relationship between the following pairs?

I and III,

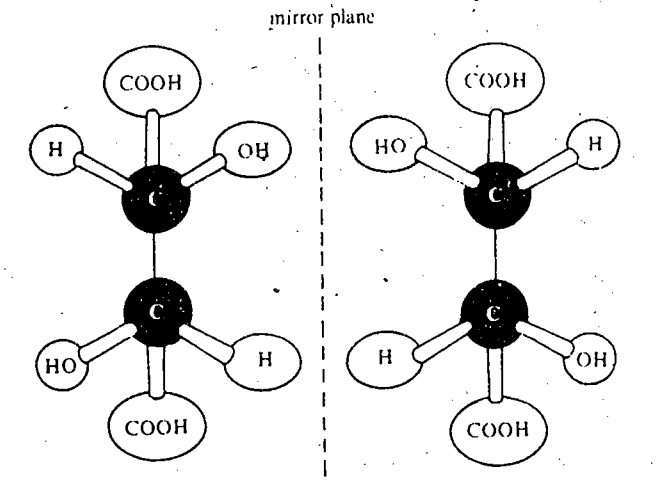
I and IV,

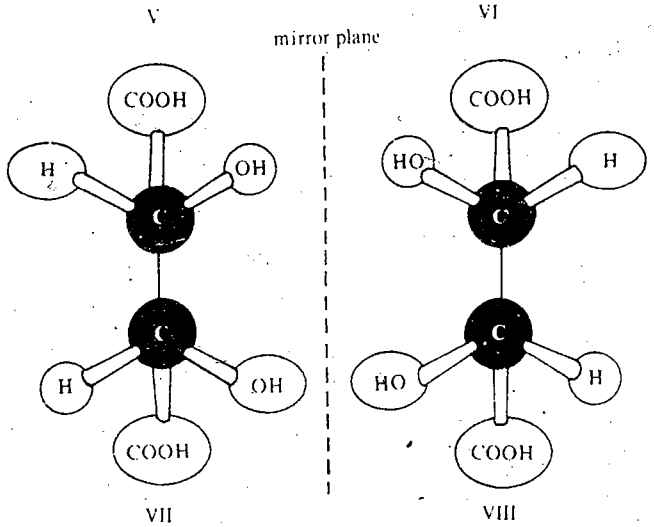
II and III, and

II and IV.

Certainly they are not mirror image isomers though they are isomeric. Stereoisomers which are not **enantiomers** are called **diastereoisomers** or **diastereomers.** Hence, I and III, and I and IV are diastereomers. Similarly, II and III, and II and IV are diastereomers.

Now let us take the specific example of tartaric acid. It has two chiral centres as shown below. The possible isomers of tartaric acid are given below as V, VI, VII and VIII.





Activity

Make models of V and VI and verify that they are nonsuperimposable.

Activity

Make models for VII and VIII and convince yourself that (i) they are mirror images of each other; (ii) they are convertible to each other by rotation of 180°; (iii) they are identical and represent two molecules of the same isomer.

Here, you can categorise V and VI as enantiomers. What about VII and VIII? Although they are mirror image isomers, but when we try to superimpose them, we

find that they are **superimposable.** Thus, they are not different but are identical; hence, **they represent the two molecules of the same isomer.** Thus, for tartaric acid we have only three isomers. In general for a compound having n chiral centres the number of possible stereoisomers is given by 2^n. Thus, for a molecule having 2 chiral centres, 4 stereoisomers are possible. But, in some cases (as in tartaric acid), when the chiral centres are equivalently substituted, (i.e. the substituents on the chiral centres are the same), fewer isomers than predicted by 2^n, exist. Of the above isomers, (V and VII) and (VI and VII) are diastereoisomers. Because the diastereoisomers are not mirror image isomers, hence, often they have different physical and chemical properties. Table 2.3 shows identical physical properties (except for the sign of rotation) for the enantiomers V and VI but their diastereomer VII (or VII) has physical properties different from those of V or VI.

Table 2.3 : Some physical properties for the isomers of tartaric acid.

Physical Property	V	VI	VII (or VIII)
Melting point/(K)	441 – 443	441 – 443	419 – 421
Density/(kg dm^{-3})	1.7598	1.7598	1.666
$[\alpha]_D^{293}$	+ 12	– 12	0

Table 2.3 shows that the compounds having structures V and VI are optically active but that corresponding to VII or VIII is not, although, it also has two chiral centres. Why is this so? You will find an answer to this question in the next section. But before studying that, answer the following SAQ.

SAQ 4

Write the stereoisomers for the compound $HOH_2CCHOHCHOHCHO$ and group them as enantiomers and diastereomers.

.....

.....

.....

.....

2.6 CHIRALITY AND ELEMENTS OF SYMMETRY

A general test of **chirality** which you learnt in the last section is the nonsuperimposability of the molecule and its mirror image. However, there is another simple way to examine the molecules for the **absence** of chirality. Molecules which are not chiral (or are **achiral**), possess one or more elements of symmetry. There are mainly three elements of symmetry, namely, plane of symmetry, centre of symmetry and alternating axis of symmetry. Let us study these elements of symmetry one by one.

Plane of Symmetry: A plane of symmetry is defined as an imaginary plane which divides the molecule into two halves which are mirror images of each other. Some objects having the plane of symmetry are shown in Fig. 2.5.

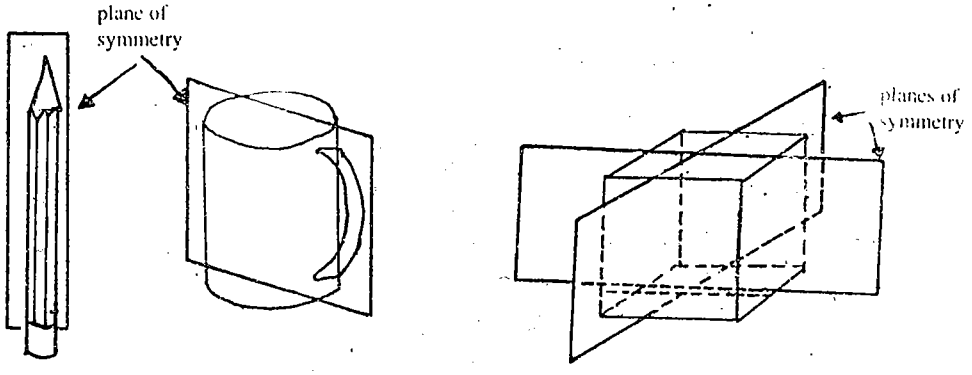


Fig. 2.5 : Plane of symmetry in some common objects.

Centre of symmetry: A centre of symmetry is a point such that any line drawn from this point to some other point (or group) in one direction, when extended at equal distance in the opposite direction, should find an identical point (or group). Such a centre of symmetry is shown in Fig. 2.6.

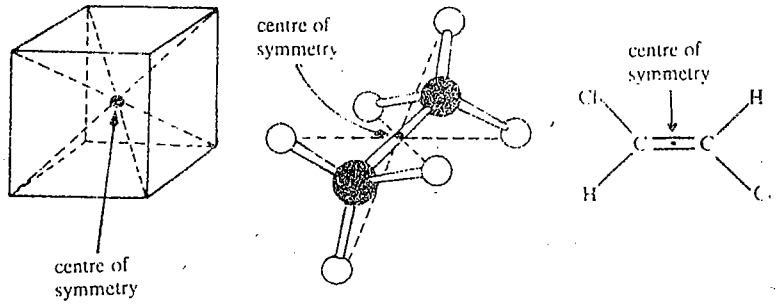
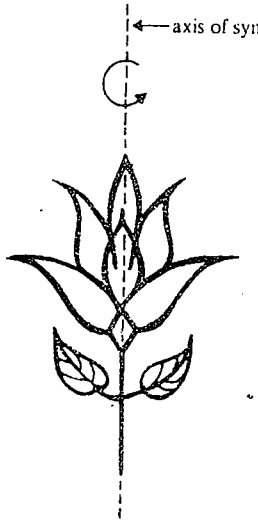
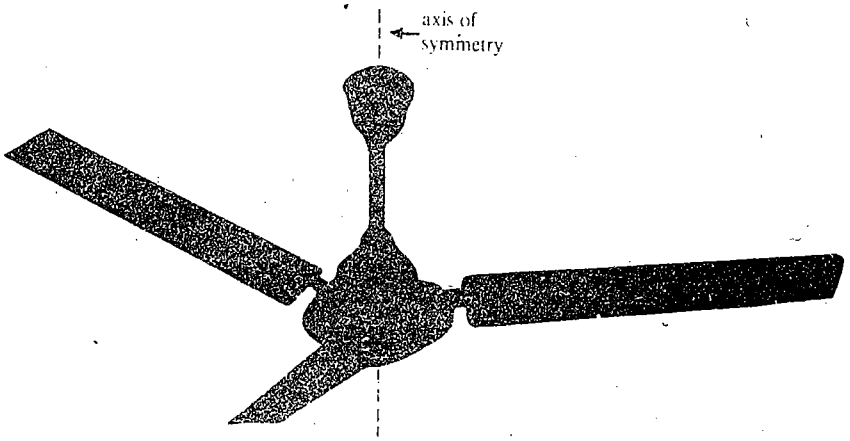


Fig. 2.6 : Centre of symmetry in (a) a cube; (b) ethane and (c) *trans*-1, 2-dichloroerthene.

Axis of symmetry: When a structure possessing this axis is rotated around this axis, another identical structure results In case the identical structures result twice on rotation of the molecule by 360°, the axis is called a **two-fold axis** of symmetry and when identical structures repeat three times, it is called a **three-fold axis** and so on. This is illustrated below:

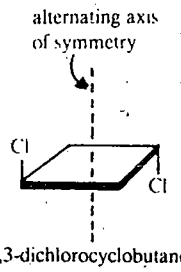


Two-fold axis of symmetry as the leaf appears twice on rotation by 360°



Three-fold axis of symmetry in a ceiling fan; the blades appear at equivalent positions thrice on a single rotation

When such identical points alternate around a plane or an axis, then the axis of symmetry is called an **alternating axis of symmetry**. For example, 1,3-dichlorocyclobutane has two fold alternating axis of symmetry and not the simple axis of symmetry, because when rotated around this axis although the Cl group appears twice, one of them appears **above** the plane of the molecule and the other appears **below** the plane.



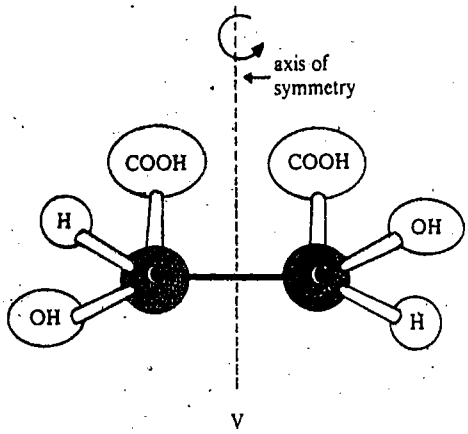
1,3-dichlorocyclobutane

A molecule having a plane of symmetry or a centre of symmetry or an alternating axis of symmetry is superimposable on its mirror image and, hence, is not chiral. Note that absence of alternating axis of symmetry is important and not just of the simple axis of symmetry. For example, a molecule having a simple axis of symmetry can show optical activity or chirality. Take models of the enantiomers of tartaric acid, shown in Sub-Sec 2.5.3 as structures V and VI (these models you have made earlier also) and convince yourself that both of them have a two-fold simple axis of symmetry but still they are optically active.

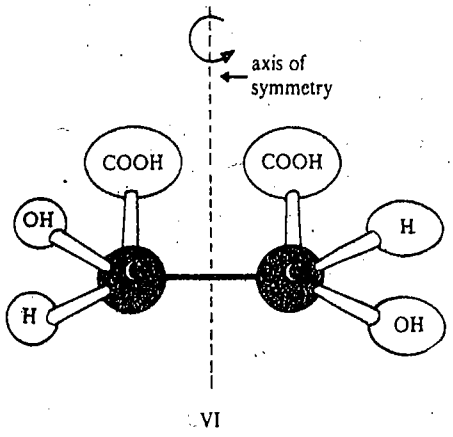
Let us now go back to the problem we left unanswered at the end of the last section. Since, the third isomer of tartaric acid, represented by structure VII, has a *plane of symmetry,* it is optically inactive. This plane can be easily visualised by looking at the model of structure VII. Such compounds in which one half of the molecule is the mirror image of the other half, are called *meso* compounds. Thus, *meso*-tartaric acid represented by structure VII (or VIII), has two chiral centres but as it has a plane of symmetry, the optical activity caused by one chiral centre

The word *meso* means middle or inbetween.

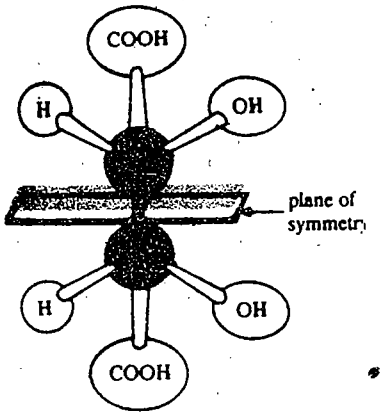
is **cancelled** by the other chiral centre. This is so because the two halves, being the mirror images of each other, have equal and opposite ro[illegible]. Hence, *meso* compounds are optically inactive.



V



VI



VII

A *meso* compound is optically inactive due to *internal compensation*; optical activity due to one half of the molecule is cancelled by that due to the other half.

In other words, if one half of the molecule causes a rotation of $+X°$ and the opposite half causes a rotation of $-X°$, then it leads to a zero rotation for the molecule or no optical activity. This type of cancellation is called *internal compensation*. There is another way in which compounds containing chiral centres can behave as optically inactive. You will study about this in the next unit You can apply your knowledge about the elements of symmetry in answering the following SAQ.

SAQ 5

Which of the following are chiral?

a) a shoe

.....

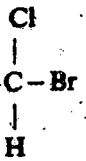
b) a book

.....

c) methane molecule

.....

d)



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2.7 SUMMARY

In this unit, we learnt that

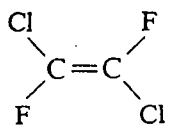
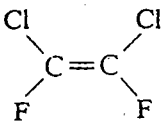
- Stereoisomers differ from each other in the arrangement of their atoms in space.
- Geometrical isomers can be named according to *cis*–, *trans*– or *E*, *Z* nomenclature.
- There are two types of optical isomers: enantiomers which are mirror image isomers and diastereoisomers which are stereoisomers other than enantiomers.
- Enantiomers have **identical** physical properties (except the direction of optical rotation) but diastereoisomers have different physical properties.
- Molecules having one chiral centre can exist as enantiomers. However, molecules having more than one chiral centre may or may not be optically active, e.g., *meso* compounds are optically inactive.
- The tetrahedral nature of carbon was postulated on the basis of the observations of optical activity.

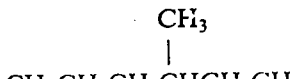
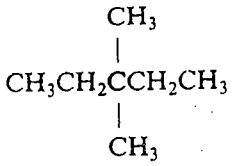
2.8 TERMINAL QUESTIONS

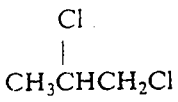
1. Write structural formulas for each of the following compounds. Be sure that you write the correct stereochemistry.

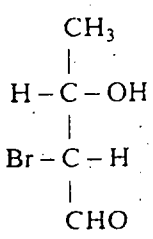
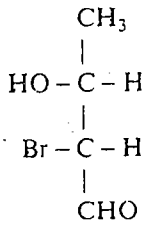
   a) (*Z*)-5-choloro-2-pentene
   b) *trans*-1,2-dimethylcyclopropane
   c) *meso*-2,3-dibromobutane
   d) *cis*-1,2-dichlorocyclopentane

2. Look at the following pairs of compounds carefully and state which type of isomerism they exhibit.

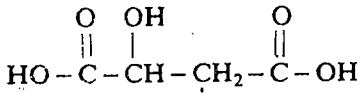
   a)  and 

   b)  and 

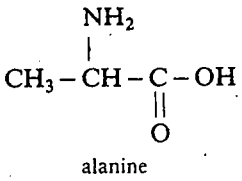
   c) $Cl_2CHCH_2CH_3$ and 

   d)  and 

3. a) Locate the chiral carbon atoms in the following compounds and mark them with asterisk.

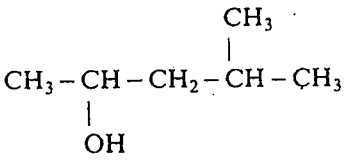
   i) 
   malic acid

ii)



alanine

iii)



b) Write the structures for the enantiomers of the compounds given in (a).

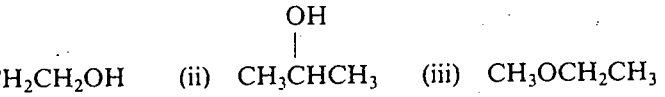
4. What elements of symmetry are present in the following?
   a) a ball b) a cube c) scissors
   d) letter X e) methane f) methylchloride.

5. How many *meso* stereoisomers are possible for 2,3,4-pentanetriol? Write their structures.

2.9 ANSWERS

Self Assessment Questions

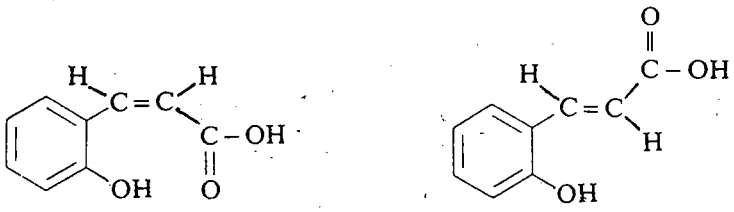
1. Structural isomers having molecular formula C_3H_8O are as given below.



(i) $CH_3CH_2CH_2OH$ (ii) CH_3CHCH_3 (iii) $CH_3OCH_2CH_3$

2. i) *E* ii) *Z* / iii) *Z* iv) *Z*

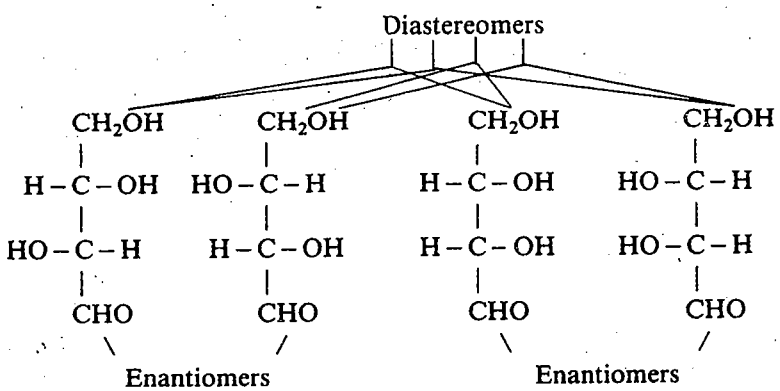
3.



cis-isomer *trans*-isomer

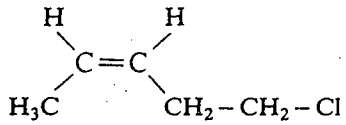
Since -OH and -COOH groups are in close proximity in *cis*-isomer, it can yield the required coumarin by loss of a water molecule.

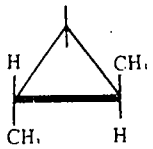
4.

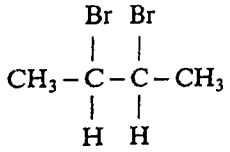


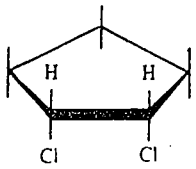
5. (a) and (b) are chiral.

Terminal Questions

1. (a) 

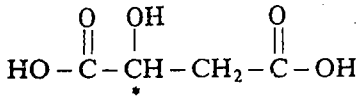
(b) 

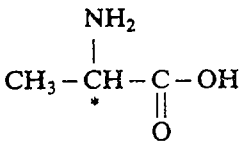
(c) 

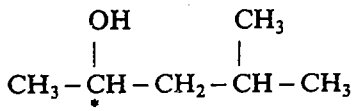
(d) 

2. (a) geometrical (b) chain
   (c) position (d) optical (diastereomers)

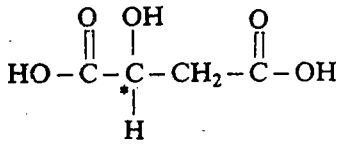
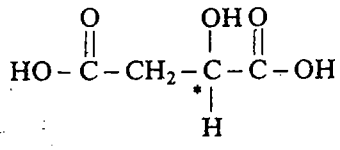
3. (a)

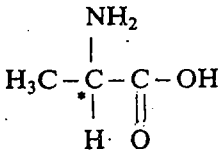
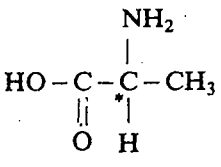
(i) 

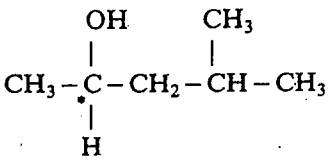
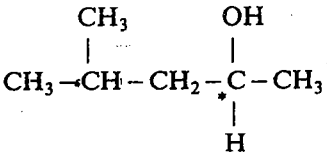
(ii) 

(iii) 

(b)

(i)  

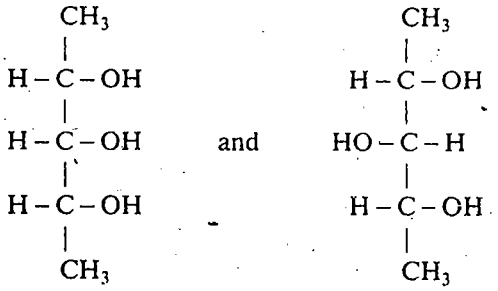
(ii)  

(iii)  

4. a) plane, centre and axis of symmetry
   b) plane, centre and axis of symmetry

c) plane of symmetry
d) plane, centre and axis of symmetry
e) plane and axis of symmetry
f) plane and axis of symmetry

5. The two *meso* stereoisomers of 2,3,4-pantanetriol are,



UNIT 3 STEREOCHEMISTRY – II

Structure

3.1 Introduction
Objectives
3.2 Configuration and Fischer Projection Formulas
3.3 Configurational Notations
3.4 Racemic Mixtures and their Resolution
3.5 Asymmetric Synthesis
3.6 Walden Inversion
3.7 Conformational Isomers and their Representation
3.8 Conformations of Ethane
3.9 Conformations of Butane
3.10 Conformations of Cyclic Systems
Conformations of Cyclohexane
Conformations of Monosubstituted Cyclohexane Derivatives
Conformations of Disubstituted Cyclohexane Derivatives
3.11 Summary
3.12 Terminal Questions
3.13 Answers

3.1 INTRODUCTION

In Unit 2, you studied the geometrical and optical isomerism. The arrangement of atoms or groups in space about a rigid framework was referred to as **'configuration'** in Unit 2. In geometrical isomerism you learnt that the geometrical isomers can be assigned the configuration as *cis*- or *trans*- and *E*- or *Z*-, depending upon the spatial arrangement of groups about the rigid framework. You also studied about the existence of optical isomers such as enantiomers and diastereomers. These optical isomers have different configurations.

In this unit, you will study how to designate the configuration of optical isomers. We will also discuss how configuration is affected in chemical reactions. Under the laboratory conditions, chemical reactions yield an equimolar mixture of the two enantiomers. Here, you will also learn how to separate these mixtures in order to obtain optically pure compounds.

Then we will shift the focus of our attention to conformational isomers and study the conformational isomerism of simple straight chain and cyclic hydrocarbons.

Objectives

After studying this unit, you should be able to:

- write Fischer projection formulas for simple organic compounds,
- assign the configuration as either *R* or *S* to the chiral centre in a compound,
- define a racemic mixture and give a method of resolution for such a mixture,
- define and give examples of asymmetric synthesis,
- describe Walden inversion,
- draw sawhorse and Newman projections for a given compound,
- illustrate the conformations for simple straight chain hydrocarbons like ethane and butane, and
- draw and compare the stabilities of the boat and chair forms of cyclohexane molecule and its derivatives.

3.2 CONFIGURATION AND FISCHER PROJECTION FORMULAS

The term *configuration* was used earlier in case of geometrical isomers to indicate the spatial arrangement of groups around a rigid framework. Similarly, the term

Emil Fischer
(Received Nobel Prize in 1902)

A Fischer projection formula is a standard way of depicting tetrahedral carbon atoms and their substituents in two dimensions.

configuration as applied to optical isomers indicates the spatial arrangement of atoms or groups around the chiral centre.

You know that the actual molecules are three-dimensional in nature. So, the spatial arrangement of groups in a molecule, i.e. its configuration, can be specified either by making its three-dimensional model or by writing the corresponding projection formulas. Also, to specify the configuration of a molecule having several chiral centres, the configuration at each chiral centre needs to be specified.

This specification of configuration for a molecule becomes more and more difficult as the number of chiral centres goes on increasing. Thus, a need was felt for a convention to represent the actual three-dimensional structure of molecules in two dimensions, (i.e. in the plane of the paper) in a simple and convenient way. The German chemist Fischer introduced such a convention. He called his representations as projection formulas. These representations are now known after his name as **Fischer projection formulas.**

Before proceeding to the study of Fischer projection formulas, it is necessary to familiarise you with another representation known as *perspective drawing.* Such a representation is used to represent three-dimensional structures of molecules in two dimensions. Fig. 3.1(a) illustrates such a perspective drawing. In a perspective drawing, a broken wedge represents the bond which is **behind** the plane of the paper and the solid wedge represents the bond which points **towards** the observer in front of the plane of the paper. The other two bonds which are represented by ordinary lines show the substituents which are **in** the plane of the paper.

Let us now learn how to write Fischer projection formula of the molecule whose perspective drawing is shown in Fig. 3.1(a). It is better if you take the help of the models supplied to you. Make a model of such a molecule by attaching four different substituents to a tetrahedral carbon atom. Now look at the model in such a way that the two substituents which point **towards** you are in the **horizontal plane** and the other two substituents which point **away from you** are in the **vertical plane,** as shown in Fig. 3.1(a). You can see in Fig. 3.1(b) that the angle between the horizontal and vertical planes is a right angle. Hence, the substituents in the horizontal plane are **at right angles** to the substituents in the vertical plane. We can represent these two sets of substituents at right angles to each other in one plane (obviously plane of paper), by drawing two lines at right angles to each other. Then, the substituents are written in the position they appear to the observer, i.e. the substituents which are at left and right of the observer are written at left and

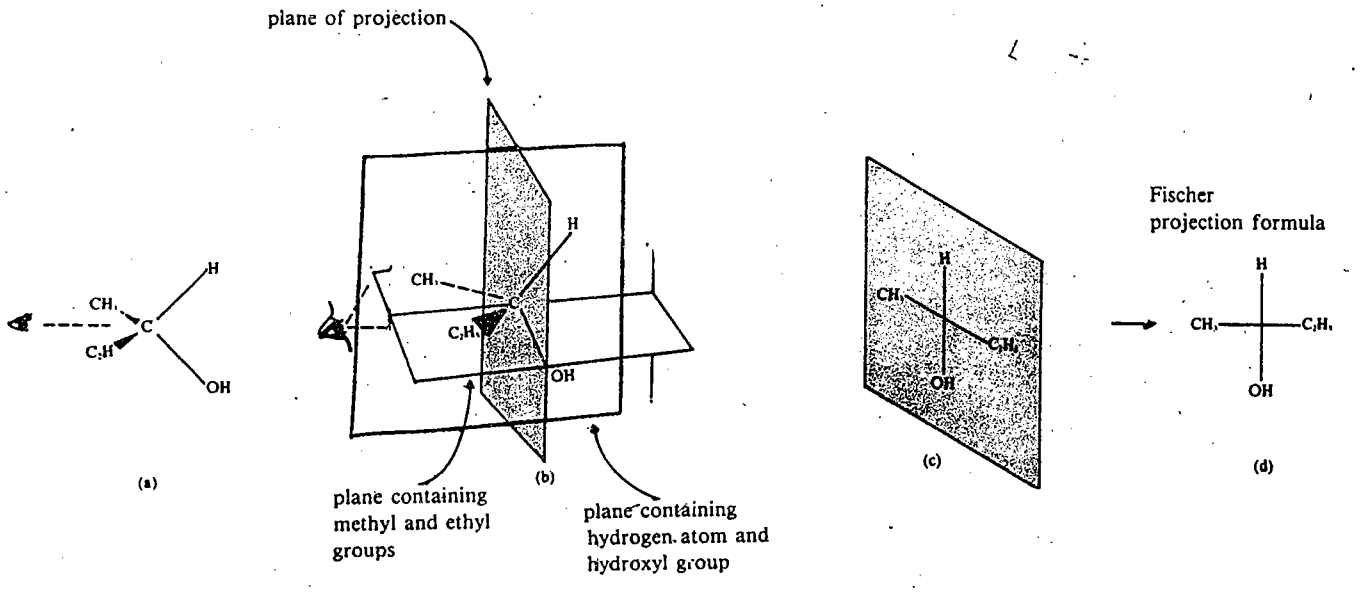


Fig. 3.1 : Writing Fischer projection formula for a molecule : (a) perspective drawing of a molecule having one chiral carbon atom; (b) two substituents each in horizontal and vertical planes at right angles to each other; (c) representation of molecule in plane of paper; and (d) the Fischer projection formula.

right, respectively, and the other two substituents which appear above and below are written at above and below positions, as shown in Fig. 3.1(c). Further, we can simplify Fig. 3.1(c) by removing the plane of paper shown in it and write the structure of the molecule as shown in Fig. 3.1 (d), which is nothing but the **Fischer projection formula** for the compound shown in Fig. 3.1(a). Note that the chiral centre is not shown in Fischer projections and it is assumed to be located at the point of intersection of the horizontal and vertical lines.

Similarly, the Fischer projection formula for one of the isomers of tartaric acid, shown in Fig. 3.2(a), can be written as shown in Fig. 3.2(b).

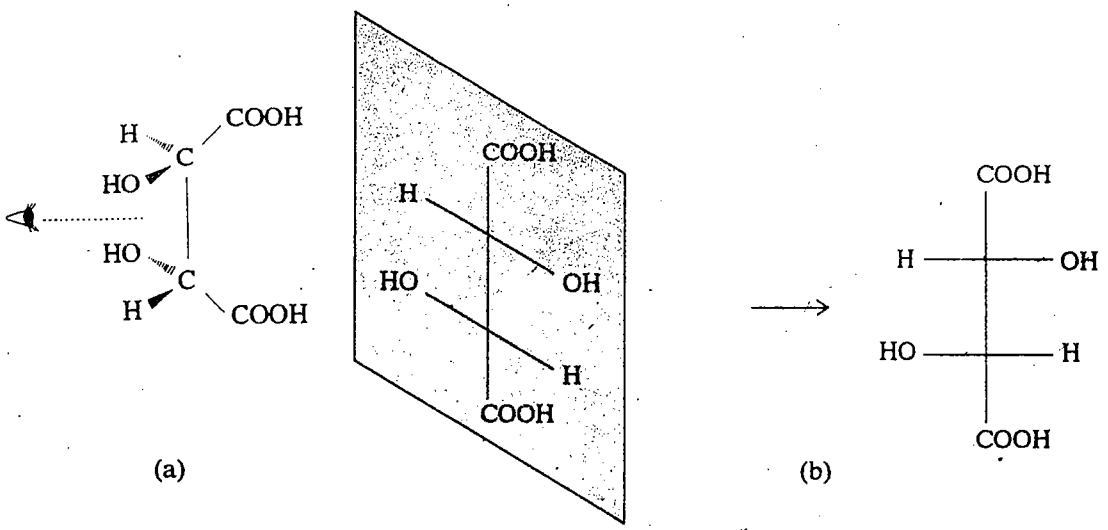
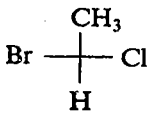


Fig. 3.2 : (a) An isomer of tartaric acid and (b) its Fischer projection formula.

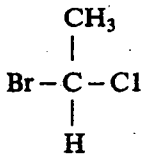
The Fischer projections are very useful in case of molecules having many chiral centres linked together to form a continuous chain. You will realise in Unit 20 of Block 4 of this course the importance of these projection formulas in writing the structures of carbohydrates.

Let us now learn the reverse of what we have done above, i.e. write the three-dimensional structure of a molecule from its Fischer projections. For this, we have to reverse the process we have just described. **Always remember that in a Fischer projection formula the vertical lines represent the bonds that point away from you and the horizontal lines represent the bonds that point towards you.** Let us start with a molecule having the Fischer projections as given below,

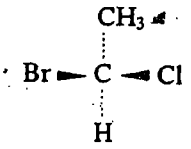


The three-dimensional structure for this molecule can be written by using the following steps:

i) Write a carbon atom at the intersection of the horizontal and vertical lines in Fischer projections, as shown below.

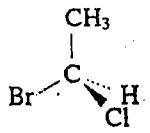


ii) Since the vertical lines represent the bonds away from the observer and the horizontal lines represent the bonds towards the observer, we can write the structure of the molecule shown in step (i) as,

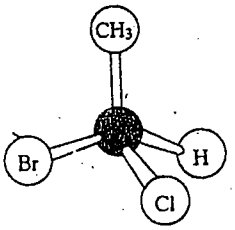


While studying step (ii), use models for writing the perspective formula.

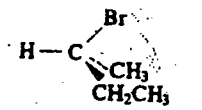
This can be translated into the perspective formula by viewing the molecule in such a way that the two substituents (say, CH_3 and Br) are parallel to the plane of the paper. In such a situation, H will appear behind the plane of the paper and Cl will appear projecting in front of the plane of the paper leading to the perspective drawing of the molecule as,

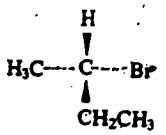


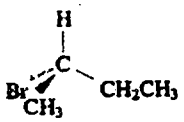
which leads to the following three-dimensional structure of the molecule.

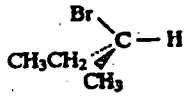


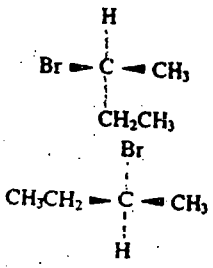
Different representations of (+)–2–bromobutane.





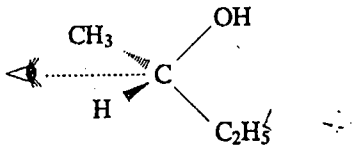




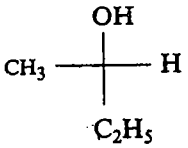


How to interconvert Fischer Projections while maintaining the Configuration

Since there are many ways in which a given molecule can be oriented depending upon which two substituents are chosen to point towards the observer; hence, several different Fischer projections can be written for the same molecule. Let us go back to Fig. 3.1 and instead of viewing the molecule as shown in Fig. 3.1(a), now let us view the molecule in such a way that the substituents CH_3 and H point towards the observer. Thus, the substituents will now appear as shown below.



For this orientation of the molecule, the Fischer projection formula can be written as,

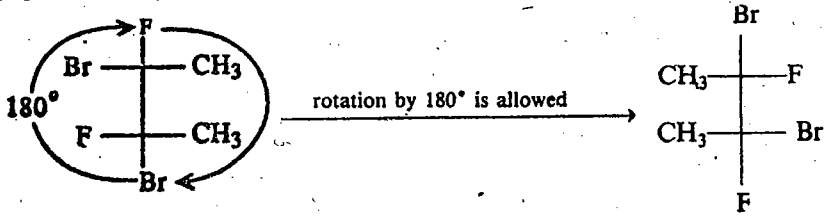


which is another Fischer projection formula for the same molecule as shown in Fig. 3.1(a). Because various Fischer projections are possible for a given molecule, you should have a clear understanding of writing different correct Fischer projections for a given molecule without going back and forth to the three-dimensional model. Therefore, you should be able to write different Fischer projections for the same molecule from its given Fischer projection formula. For this, there are some rules to be followed. These rules are as given below.

Activity

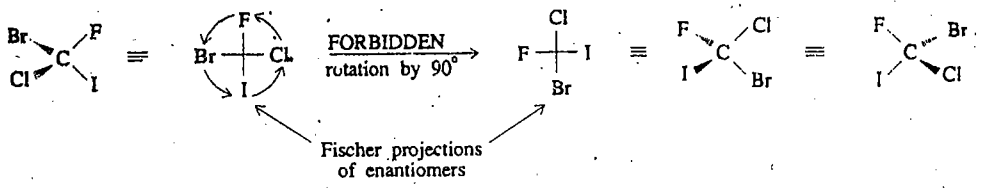
Make models of the molecules corresponding to the two Fischer projection formulas shown in rule 1. You can see that they represent the two Fischer projections of the same compound.

1. Rotation of the given Fischer projection formula by 180° in the plane of the paper yields another Fischer projection of the same molecule, i.e.,



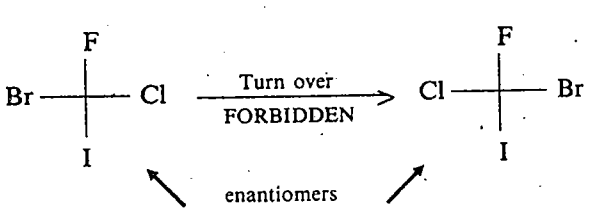
In other words, rotation of the Fischer projection in the plane of paper by 180° does not alter the configuration.

2. Rotation of a Fischer projection formula of a compound in the plane of the paper by 90° yields the Fischer projection formula of its enantiomer. It means that such a rotation leads to a change in the configuration at the chiral centre. This is illustrated in the following example.



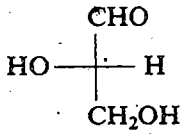
It is better to verify this rule with the help of the models.

3. A Fischer projection formula may **not** be lifted out of the plane of the paper and turned over as shown below.

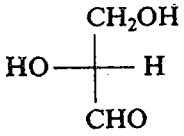


This turn over leads to the Fischer projection formula of the enantiomer. Thus, this operation on the Fischer projection changes the configuration at the chiral centre.

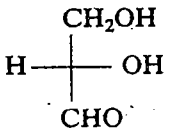
4. Interchange of two pairs of substituents leads to another Fischer projection of the same isomer. Hence, no change in configuration is observed by this operation. Let us understand this by the following example. If we have a molecule represented by the following Fischer projection,



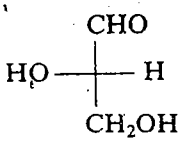
Interchange of one pair of substituents (i.e., $-CHO$ and $-CH_2OH$) leads to the Fischer projection,



Another interchange of second pair of substituents leads to the Fischer projection as



This when rotated by 180° yields

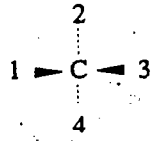


which is nothing but the same isomer we started with.

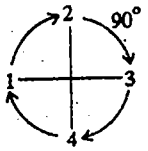
In the next section, you will learn about the specification of the configuration at a given chiral centre. Before that check your knowledge of Fischer projections, by answering the following SAQ

Activity

Make a model of a molecule having a chiral carbon atom linked to four different **substituents 1, 2, 3 and 4 as shown below:**

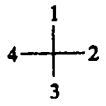


It has the following Fischer projections, given by (a)



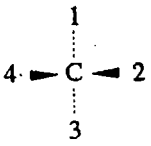
(a)

Rotate this Fischer projection by 90° to yield the following Fischer projections, shown as (b).



(b)

Make a model of the molecule corresponding to the Fischer projection formula shown in (b) as,



On comparing these two models, you will find that they represent the enantiomers.

SAQ 1

Study each of the following pairs of Fischer projections carefully and decide whether they represent the same isomer or an enantiomeric pair.

(a) 

.....

(b) 

.....

(c) 

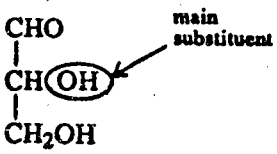
.....

(d) 

.....

3.3 CONFIGURATIONAL NOTATIONS

The existence of enantiomers poses special problem of their nomenclature. As the enantiomers differ from each other in their sign of rotation, prefixes *d* and *l* were used earlier to designate the dextrorotatory and levorotatory isomers, respectively. But it was realised that the sign of rotation does not tell about the absolute configuration of the compound. Thus, to define the structure of a compound completely, it was necessary to specify the configuration at each chiral centre.



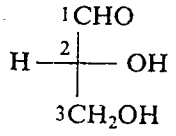
glyceraldehyde

There is also a convention that the longest carbon chain forms the vertical back bone of the Fischer projections with the most highly oxidised carbon (if any) at the top; and then the substituents are projected horizontally.

One of the earliest attempts to specify the configuration is that of Fischer which dates back to 1891. According to this system, the configuration at a particular carbon atom is designated by selecting a main chain in the molecule in the sense of the rules laid for nomenclature. The molecule is then oriented vertically in such a way that the carbon atom numbered 1 in the chain is at the top. Then, the main substituent attached to the chiral centre is looked for. For example, in glyceraldehyde, it is an -OH group. If in the Fischer projections of the compound the main substituent group is on the **right**, then the molecule is said to have D configuration and when this main substituent is on the **left**, then the molecule is said to have L configuration.

Do not confuse *d* and *l* with D and L. The lower-case *d* and *l* were used in many places in older literature to specify the direction of rotation (synonymously with '+' and '−'). But D and L are used to specify the configuration at the chiral centre.

Rosanoff (1906) suggested that a particular configuration be assigned to (+)-glyceraldehyde. The Fischer projection corresponding to this configuration is given below.



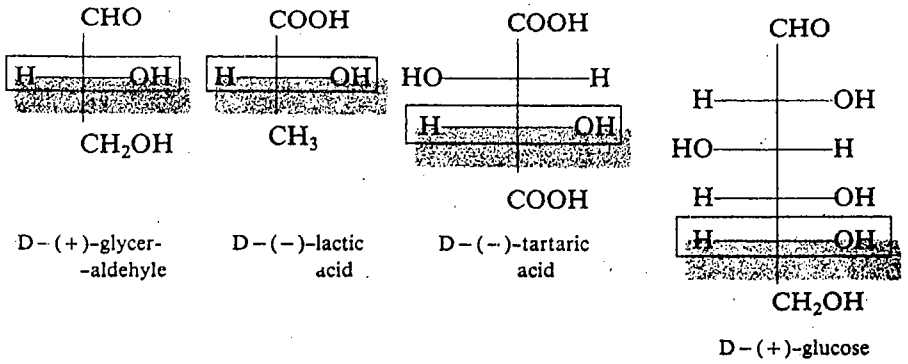
Thus, according to this system of designation of configuration as D or L. the carbon chain in (+)-glyceraldehyde can be numbered and oriented as shown above. Here, the substituent on the chiral centre is hydroxyl (-OH) group. Since it

; on the right side, hence, (+)-glyceraldehyde has D configuration. Similarly, the nantiomer of (+)-glyceraldehyde, i.e. (–)-glyceraldehyde will have L onfiguration. Thus, we can designate the two enantiomers as D-(+)-lyceraldehyde and L-(–)-glyceraldehyde. Also all compounds having an rrangement of atoms similar to that at the chiral centre of (+)-glyceraldehyde at ıe corresponding carbon atom are members of the D family. Similarly, we can :ate for the L family. Some examples of compounds belonging to D and L ımilies are listed below:

The D, L system is useful in specifying the configurations for carbohydrates and amino acids.

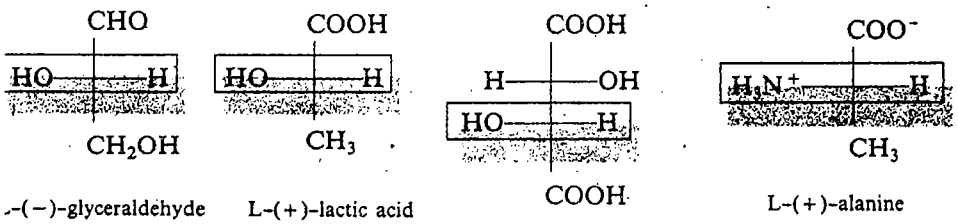
In the light of the fact that **the configuration of a chiral centre in a compound is not changed unless at least one bond at the chiral centre is broken**, chemists on the basis of the experimental evidences realised that the configurations of various optically active compounds can be related to each other even without knowing their absolute configurations. Thus, **relative configurations** of a large number of compounds could be determined.

D-family



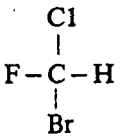
D–(+)-glycer-aldehyle | D–(–)-lactic acid | D–(–)-tartaric acid | D–(+)-glucose

L–family



-(–)-glyceraldehyde | L-(+)-lactic acid | L-(+)-tartaric acid | L-(+)-alanine

'he D, L system can be applied only when the main chain and the main ıbstituents can be unambiguously chosen; hence, in some cases, it is not possible ɔ assign the configuration by this system. For example, the molecules of the type



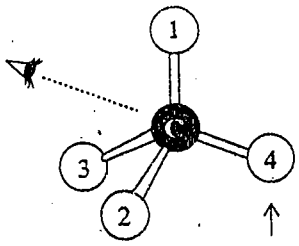
annot be assigned configuration according to this system. Also there are cases 'hen it is difficult to assign the configuration unambiguously to the molecules ɔntaining more than one chiral centre.

hus, a more systematic way of denoting configurations was needed. The system ıat emerged is called the *R*, *S* convention and is based on the actual three-imensional formula of the compound to be named. In this system, the ɔnfiguration at the chiral centre is assigned by assigning the order of precedence ɔ the groups attached to the chiral centre according to the specific set of rules. hese rules have been already listed as Cahn-Ingold-Prelog priority rules in Unit 2. ccording to this system, the configuration of a given chiral centre can be assigned sing the following steps:

Identify the four substituents attached to the carbon atom for which the configuration is to be assigned.

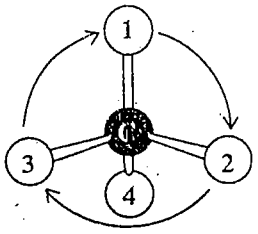
Arrange these substituents in the decreasing order of priority as $1 > 2 > 3 > 4$ which is determined by Cahn-Ingold-Prelog rules.

View the molecule in such a way that the substituent of lowest priority is away from the observer.



atom of lowest priority away from observer

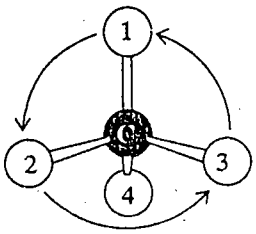
4. When the molecule is viewed in the way as suggested in step 3, the remaining substituents 1, 2 and 3 appear as spokes of a wheel, with the carbon atom at the centre of the wheel, as shown below.



clockwise: therefore *R*

Now, trace a path starting from the substituent of highest priority to the substituent next in order of priority, i.e., from 1 to 2 to 3. If this path is in clockwise direction, as in the case of arrangement shown above, then the chiral centre is said to have the *R* configuration (*R* from *rectus*, a Latin word meaning: **right**).

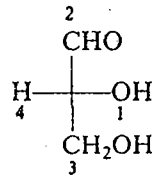
If this path from 1 to 2 to 3 has an anticlockwise direction, then the chiral centre is said to have the *S* configuration (*S* from *sinister*, a Latin word meaning: **left**), i.e.



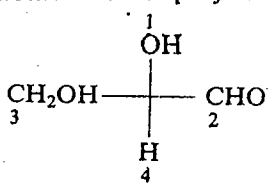
anticlockwise; therefore *S*

Since the assignment of *R* or *S* configuration to the molecule requires a specific orientation of the molecule in space, you should be able to write the three-dimensional orientation of a molecule from its Fischer projections and vice versa.

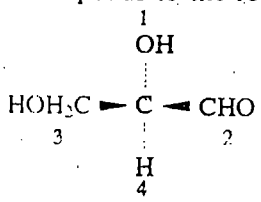
Let us now take the example of D-(+)-glyceraldehyde and see how the configuration at the chiral centre of a molecule can be assigned starting from its Fischer projection. The Fischer projection formula of D-(+)-glyceraldehyde can be written as



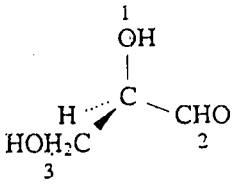
The four substituents attached to the chiral centre have the order of priorities as shown by the numbers 1 > 2 > 3 > 4. Now, the molecule is to be viewed in such a way that the substituent of lowest priority, numbered 4, which is a hydrogen in this case, is away from the viewer. In other words, in the Fischer projection formula, this substituent should find a place at the bottom end. Thus, we have to transform the above Fischer projection into another Fischer projection as shown below:



iis new Fischer projection corresponds to the following perspective drawing.

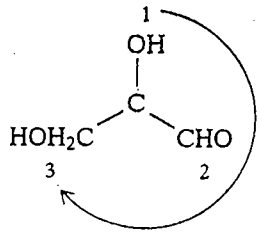


ıe molecule is then projected in such a way that H is at the back.



Use models to understand the transformations from perspective drawing to the assignment of configuration.

en, by overlooking this H, path from 1 — 2 — 3 is traced as illustrated below.

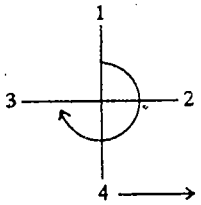


ıce this path is clockwise, hence, D-(+)-glyceraldehyde is assigned *R* nfiguration.

ere is another way which allows the assignment of configuration without having visualise the three-dimensional structure of the molecule. Let us study it.

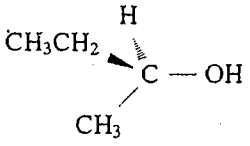
simple way to assign *R* or *S* Configuration using Fischer Projections

is a short cut method and requires that the Fischer projection is written in such way that the substituent of lowest priority is at bottom. Then, this substituent is glected and the configuration is assigned by tracing the path from 1 to 2 to 3, as ted before.



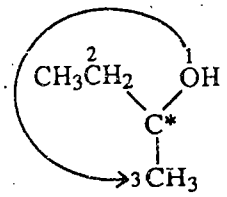
neglect it and trace the path from 1 to 2 to 3. Since this path is in clockwise direction, hence the configuration is *R*.

nilarly, in case of (+)-2-butanol,

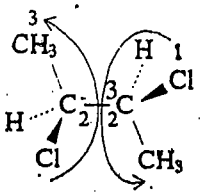


(+)-2-butanol

e order of priority of substituents is $\underset{1}{OH} > \underset{2}{CH_3CH_2} > \underset{3}{CH_3} > \underset{4}{H}$. If the olecule is viewed in such a way that the H is at the back, then the other ostituents appear as shown below:



ow trace the path from 1 to 2 to 3 which is anticlockwise in this case. Hence, the nfiguration of the carbon atom marked by asterisk (*) is *S*.



2,3-dichlorobutane

With the determination of absolute configuration of (+)-tartaric acid, the absolute configuration of its enantiomer (-)-tartaric acid was also established. The (-)- tartaric acid and (+)- glyceraldehyde were known to have the same relative configuration. Thus, the absolute configuration of (+)-glyceraldehyde was also established; and the configuration assigned earlier to (+)-glyceraldehyde arbitrarily was found to be correct.

In the compounds containing more than one chiral centre, the configuration is specified at each of these centres. For example, in case of 2,3 dichlorobutane, the priorities of substituents at the C-2 and C-3 chiral centres are Cl (1) > $-\underset{\underset{CH_3}{\diagdown}}{\overset{\overset{Cl}{\diagup}}{CH}}$ (2) > CH_3 (3) > H (4). Focusing our attention on C-2 carbon, the path from substituents 1 to 2 to 3 has anticlockwise direction; hence, it has *S* configuration. Similarly, at C-3 carbon also, the path from 1 to 2 to 3 is in anticlockwise direction. Hence, it also has *S* configuration. Thus, this isomer of 2,3-dichlorobutane is named as, (2*S*, 3*S*)-2,3-dichlorobutane.

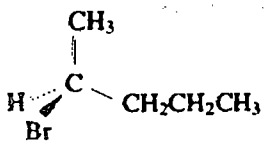
It is not difficult to decide whether a molecule has *R* or *S* configuration if the actual arrangement of the groups about the chiral centre is known. But, how to determine the actual arrangement of the groups? Until 1951, the absolute configuration of any optically active compound was not known. In 1951, Bijvoet determined the absolute configuration of (+)-tartaric acid using a sophisticated modification of X-ray diffraction called **anomalous dispersion.** Then, the absolute configurations of all other compounds whose configurations had been related to (+)-tartaric acid were also revealed.

To determine the configuration, one must have a pure sample of the compound. But this is not usually the case and most often in chemical reactions one gets a mixture of enantiomers. In the next section, we will study in detail about these mixtures and their separation into enantiomers. Before that answer the following SAQ.

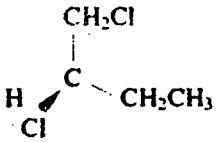
SAQ 2

Assign the configuration as *R* or *S* to each of the following compounds:

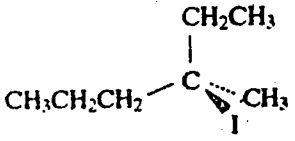
(a)



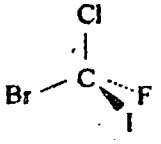
(b)



(c)



(d)



3.4 RACEMIC MIXTURES AND THEIR RESOLUTION

A mixture containing equal amount of each enantiomer of a compound is called a **racemic mixture** or a **racemic modification** or a **racemate.** A racemic mixture is indicated by the (±)-sign or just by the term racemic prefixed to the name of the compound.

The physical properties of a racemic mixture are different from those of the pure enantiomers. For example, the melting point of the either enantiomer of 2-hydroxypropanoic acid (lactic acid) is 326 K but the racemic 2-hydroxypropanoic acid (lactic acid) has a melting point of 291 K. Also, since a racemic mixture contains equal amounts of enantiomers, optical rotation of one enantiomer is cancelled by an equal and opposite rotation of the other enantiomer. Hence, a racemic mixture is **optically inactive** although its constituents are **optically active.**

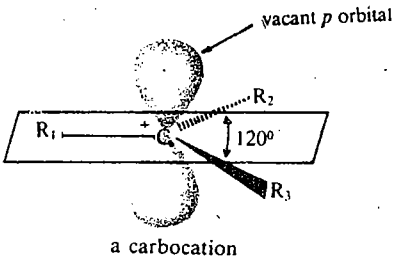
A racemic mixture can be obtained from a pure enantiomer by a process called **racemisation.** It can also be obtained by simply mixing two enantiomers in equal amounts. Racemic mixtures may also result from chemical reactions. One such kind of reactions is the *nucleophilic substitution reaction.* You will study about these reactions in detail in the Organic Reaction Mechanism course. But to give you an idea about how a racemic mixture results from them, one such reaction is illustrated in the box.

A **substitution reaction** can be defined as the reaction in which one group is substituted by another group. For example, in the reaction below,

$$\underset{\text{(substrate)}}{CH_3\text{-}I} + \underset{\text{(nucleophile)}}{OH^-} \longrightarrow \underset{\text{(product)}}{CH_3\text{-}OH} + \underset{\text{(leaving group)}}{I}$$

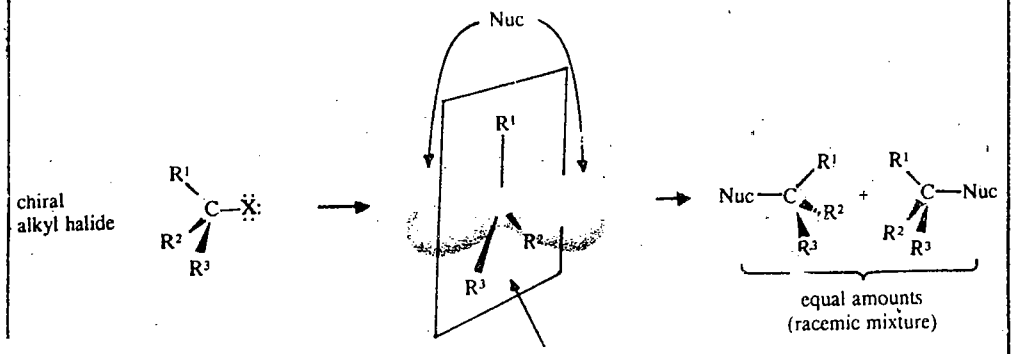
the iodide group is substituted by the hydroxide group. When the incoming group (OH^- group in this case) is a **nucleophile,** (means seeking a *nucleus;* obviously an electron rich species), then the reaction is called **nucleophilic substitution reaction.**

The nucleophilic substitution reactions can be **unimolecular** or **bimolecular,** depending upon the number of molecules involved in the rate-determining step of the reaction. When the rate-determining step involves a single molecule, the reaction is called a *unimolecular substitution reaction* and is denoted as S_N1. The S_N1 reactions involve a positively charged carbon atom as an intermediate which is called a **carbocation.** Such a carbocation is shown below.



a carbocation

This carbocation being planar, can be attacked by the incoming group or nucleophile from either side leading to the formation of both the enantiomers. If the attack is equally favourable from both the sides, then the enantiomers



S_N1
substitution unimolecular
nucleophilic

are formed in equal amounts and the product obtained is a racemic mixture.

The stereochemistry of *bimolecular substitution reactions* will be discussed in Sec. 3.6.

Once a racemic mixture is obtained, the next step is to separate this mixture into its pure components. The separation of a racemic mixture into the enantiomers is called **resolution.** The first resolution was that of tartaric acid by Pasteur in 1848. Tartaric acid was obtained as a by-product of wine making and was found almost always as its dextrorotatory 2*R*,3*R* stereoisomer. Occasionally, an optically inactive sample of tartaric acid was obtained.

One day Pasteur was viewing the crystals of sodium ammonium double salts of (+)-tartaric acid and inactive tartaric acid. He found that the crystals of the double salt of (+)-tartaric acid were hemihedral, (see Fig. 3.3a). But the crystals of the double salt of inactive acid were not the crystals of just one type, but a mixture of **two** types and these two types of crystals were mirror images of each other [see Fig. 3.3(a) and (b)]. He separated the two types of crystals with a pair of tweezers. These two types of crystals showed *equal and opposite optical rotation.* Thus, the inactive sample of tartaric acid was actually a **racemic mixture.** Pasteur had thus performed the first resolution by human hands! Before this the levorotatory form of tartaric acid was not known. It is now known that the double salt of racemic tartaric acid forms two types of crystals, as shown in Fig. 3.3(a) and (b), only at temperatures below 299 K. Had the temperature of Pasteur's laboratory been above this temperature, he would have obtained the crystals of the type shown in Fig. 3.3(c) and he would not have made this discovery.

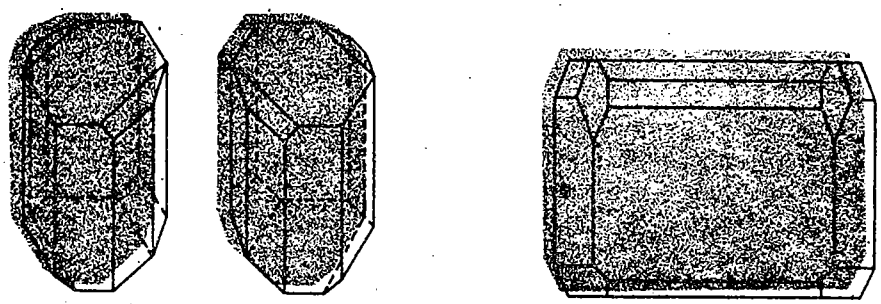


Fig. 3.3 : a) Dextrorotatory hemihedral crystals of sodium ammonium tartarate. b) Levorotatory crystals of sodium ammonium tartarate. c) Holohedral crystals of racemic sodium ammonium tatarate that crystallises at a higher temperature.

Resolution by ordinary physical methods like crystallisation, distillation, chromatography etc. is not possible because the physical properties of the two components, except the direction of rotation, are identical. Almost all methods of resolution make use of the fact that only under the influence of another chiral reagent, the enantiomers can be made to behave differently. Hence, the enantiomeric mixture is treated with a chiral substance to convert it into a mixture of diastereomers. Since the diastereomers have different physical properties, they can be separated using physical methods. The enantiomers are then regenerated from each diastereomer. The general scheme for resolution involving the formation of diastereomers is depicted in Fig. 3.4. The advantage of acid-base properties is also taken in obtaining the diastereomers. For example, if we want to resolve an acid A which is present as a mixture of the enantiomers (+)-A and (-)-A as shown in Fig. 3.4 (a); then we choose either of the enantiomers of base B, which is, say, (+)-B in this case. When the base (+)-B is added to the racemic mixture of acid A, diastereomers of the type (+)-A(+)-B and (-)-A(+)-B, as shown in Fig. 3.4(b), are obtained. These diastereomers can then be separated using physical methods, [see Fig. 3.4(c)].

The individual enantiomers of acid A are then regenerated from each of the above diastereomers by treatment with a mineral acid, Fig. 3.4 (d). Similarly, we can resolve a racemic mixture of a base using a chiral acid. The chiral reagents which are used for resolving a racemic mixture are called **resolving agents.** A number of

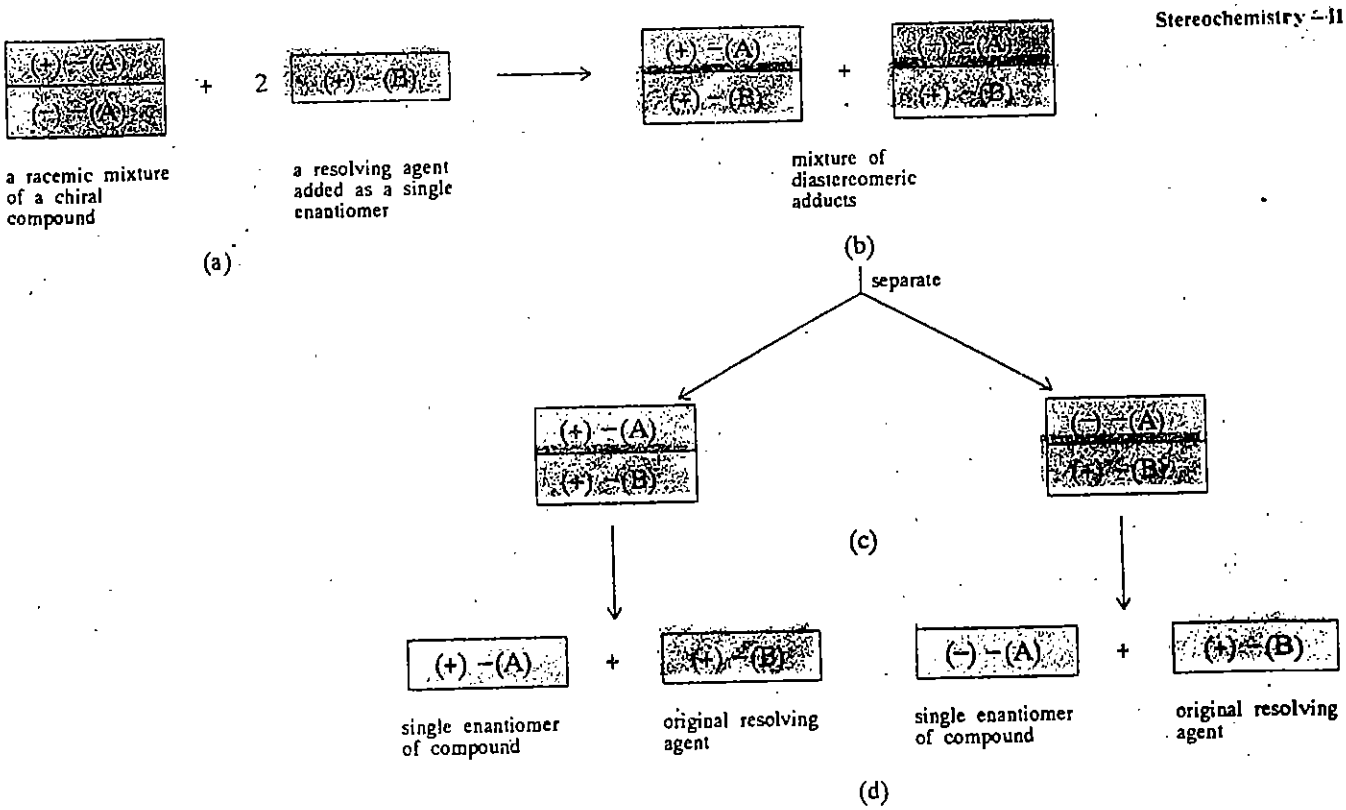
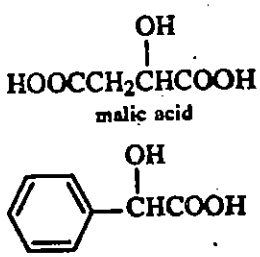


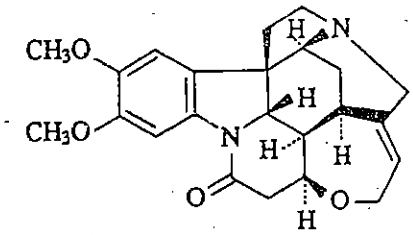
Fig. 3
c) Diastereomers separated. d) Enantiomers regenerated from diastereomers.

resolving agents are available, many of them are naturally occurring acids and bases. For example, chiral bases such as brucine, strychnine and quinine are used for resolution. On the other hand, chiral acids such as (+)-tartaric acid, (–)-malic acid and (–)-mandelic acid are used for resolution of racemic bases. Analogous methods for resolution of compounds containing other functional groups have also been developed.

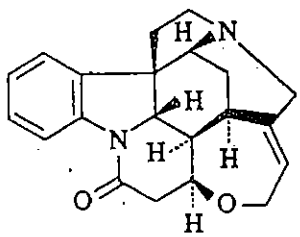


malic acid

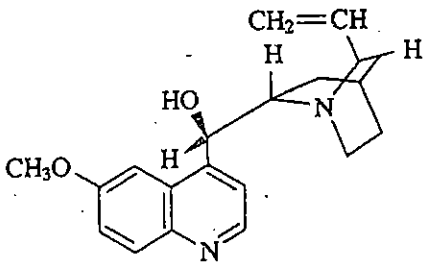
mandelic acid



brucine



strychnine



quinine (antimalarial drug)

Chromatographic methods for resolution using chiral adsorbents have also been developed. In such methods, one of the enantiomers gets adsorbed on the chiral

adsorbent more strongly than the other leading to their partial separation. The drawback with chromatographic resolution is that it is not quantitative.

As pointed out earlier, the resolution is effective only under a chiral influence. Such an influence can also be exerted using enzymes. The enzymes are highly selective with regard to stereochemistry of the compounds with which they interact. Hence, they can perform the resolution by metabolising only one enantiomer and rejecting the other. For example, the racemic ammonium tartarate when fermented using yeast or a mold (*Penicillium glaucum*), showed that the dextrorotatory isomer is consumed faster by the mold leaving behind the pure levorotatory isomer. A disadvantage of the resolutions of this type is that the more reactive enantiomer is usally not available and we get **only one** enantiomer at the end of the resolution.

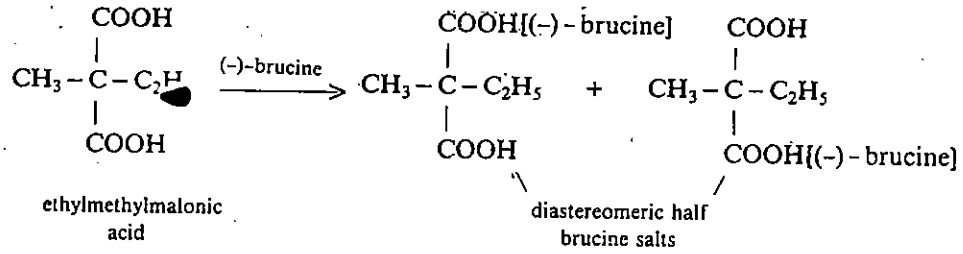
Pure enantiomers can also be obtained using synthetic methods, without the necessity of resolution. In the next section, you will study about these methods in detail.

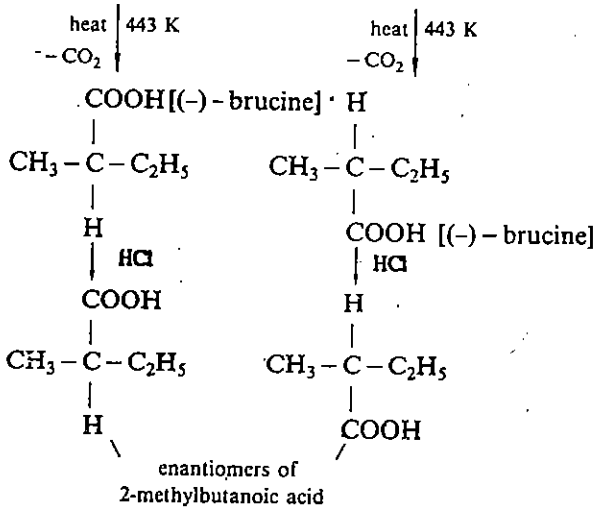
3.5 ASYMMETRIC SYNTHESIS

It is a general principle that *the optically inactive starting materials in a reaction yield optically inactive products.* To obtain an optically active product from an optically inactive starting material, it is necessary that in some way the reaction is so influenced that only one of the two enantiomers is selectively obtained. Such a synthesis is called **asymmetric synthesis** or **stereoselective synthesis.**

An asymmetric synthesis can be of two types: **partial asymmetric synthesis** and **absolute asymmetric synthesis.** In partial asymmetric synthesis, an optically active substrate or an optically active reagent is employed. Partial asymmetric synthesis can also be affected by using an optically active solvent or an optically active catalyst. On the other hand, an absolute asymmetric synthesis is the one which **does not** involve intermediate use of any optically active compound but is affected by 'physical reagents' such as **circularly polarised light.**

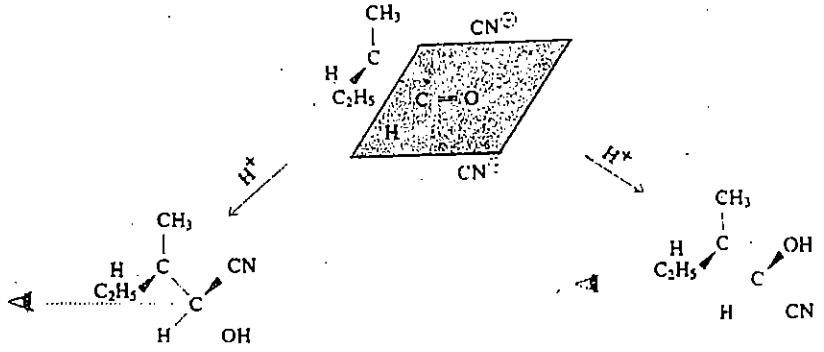
The first asymmetric synthesis was carried out by Marckwald in 1904 who obtained optically active (–)-2-methylbutanoic acid starting from ethylmethylmalonic acid. The scheme of reactions is shown below.



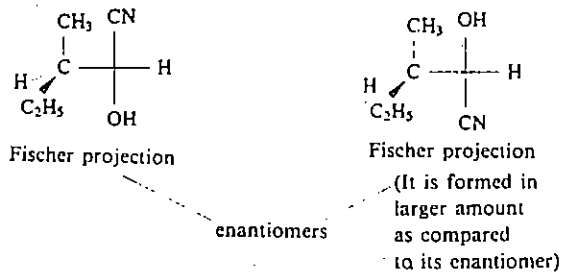


Since the two half brucine salts are diastereomeric, they yield the enantiomers of 2-methylbutanoic acid in different amounts, with the *levo* isomer predominating.

An example of partial asymmetric synthesis using optically active substrate is given below. Here, the attacking CN^- ion can approach the carbonyl carbon from two directions as shown, leading to the formation of enantiomeric products.



Use models to understand this example of partial asymmetric synthesis.



But, the approach of the reagent (CN^- anion) from the side of lesser steric hindrance (crowding) is preferred (i.e., from the downward direction) and we get the corresponding enantiomer in larger amount.

Many reactions of this type are known and in some of these reactions, the extent of stereoselectivity approaches 100%.

It was pointed out earlier that circularly polarised light can be used to achieve absolute asymmetric synthesis. The plane-polarised light is in fact a mixture of two forms of light which are called, respectively, *left-* and *right-* circularly polarised light. The electric fields of these light forms propagate through space as *left-*and *right-* handed helices as shown below in Fig. 3.5. You can see in the figure that

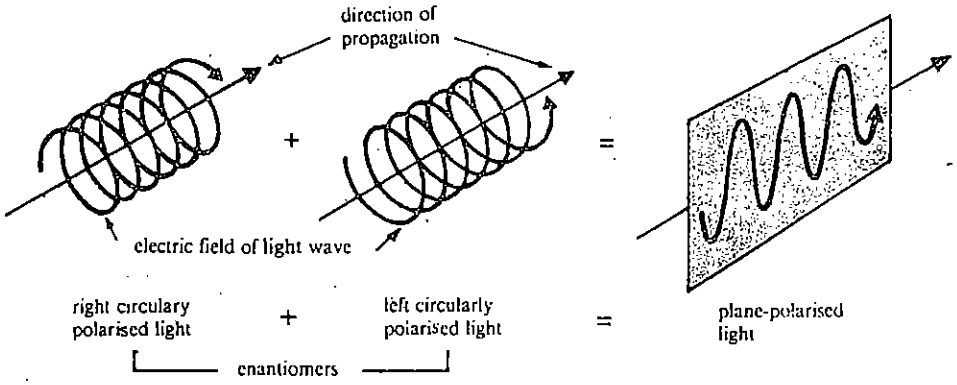
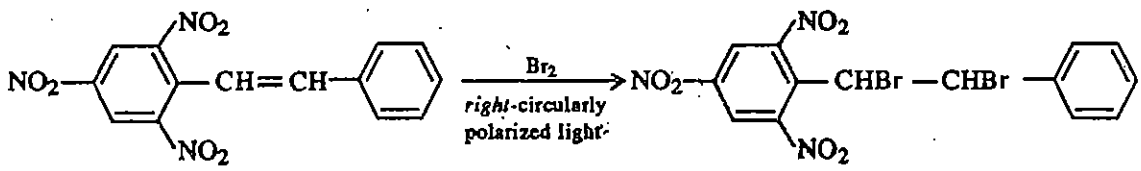


Fig. 3.5 : The electric fields of *right-* and *left-* circularly polarised light which add vectorially to give plane-polarised light.

The origin of chiral biolog[illegible] molecules is attributed to the effect of circularly polarised light in the early phases of evolution of life.

the two helices are enantiomeric. The vector addition of these two forms leads to plane-polarised light. Such *right*-circularly polarised light was used in the addition of bromine to 2,4,6-trinitrostilbene to yield the dextrorotatory product.

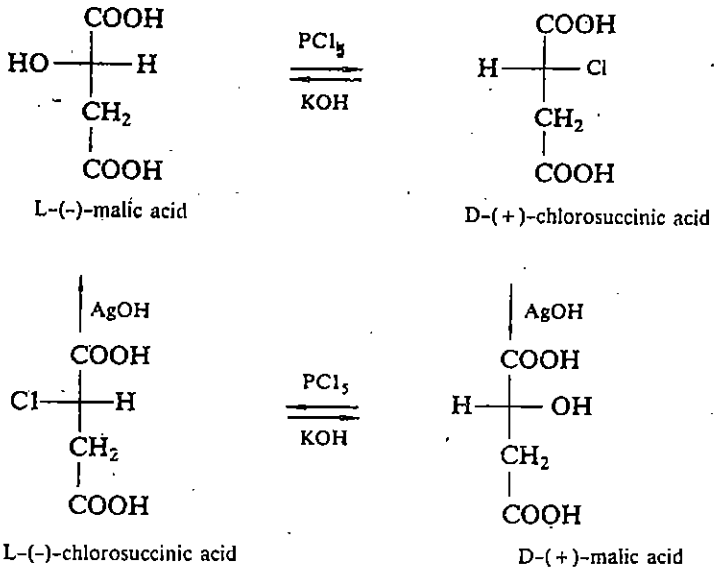


2,4,6-trinitrostilbene — dextrorotatory isomer

In this section, you have studied about how to obtain optically active compounds starting from optically inactive compounds. In the next section, you will study about the transformation of one enantiomer into another enantiomer which in fact involves the inversion of configuration. This phenomenon was first discovered by Walden and is known as *Walden Inversion*. Let us now study this phenomenon.

3.6 WALDEN INVERSION

Walden, in 1893, reported the following cycle of transformations.

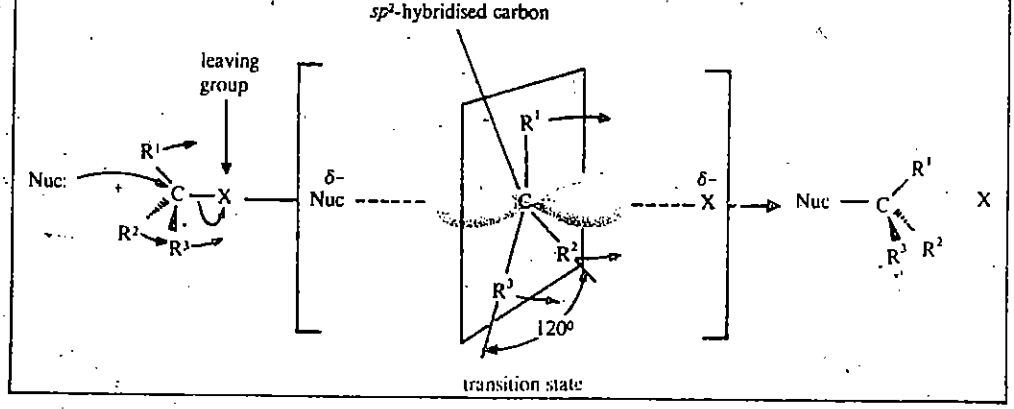


You can see that L-(-)-malic acid was converted to its enantiomer, D-(+)-malic acid in a two stage process. Similarly, L-(-)-chlorosuccinic acid was converted into its enantiomeric D-(+)-chlorosuccinic acid. Since an enantiomer is obtained, configuration at the chiral centre **must** have changed in **one** out of the **two** reaction stages. The step in which the inversion of configuration takes place is said to have undergone the **Walden inversion.** In some cases, the Walden inversion has been reported to be 100%. Note that the reactions in which the inversion is not complete, lead to racemisation.

S_N2 substitution nucleophilic bimolecular

The Walden inversion is a rule for bimolecular nucleophilic substitution reactions. The term **bimolecular** refers to the fact that **two** species undergo bonding changes in the transition state of the reaction. These reactions are represented in short as S_N2 reactions. The stereochemistry of one such reaction is shown in the box.

If in the S_N2 reaction, the attack of the nucleophile is from one side and the leaving group leaves from the opposite side simultaneously, as is shown in the transition state in the following example, then, such reactions proceed with the inversion of configuration. And, if the species that undergoes inversion has the same substituents on it before and after the inversion, the product obtained is the enantiomer of the starting compound, as was the case studied by Walden.



Thus, we can conclude that S_N1 type of reactions involve racemisation whereas S_N2 type of reactions are accompanied by inversion of configuration.

Till now you were studying about the configurational isomers in which the configuration at the chiral centre cannot be changed without breaking the bonds. Let us next study about those stereoisomers which are interconvertible without breaking the bonds between the atoms.

3.7 CONFORMATIONAL ISOMERS AND THEIR REPRESENTATION

The various spatial arrangements obtained by rotation about the single bonds are called **conformations.** Among the different conformations of a molecule, the stable ones are known as **conformers** or **conformational isomers.** The simplest molecule which shows these conformations is ethane. Before starting the study of conformations of various molecules, let us learn how to represent these conformations which are again three-dimensional spatial arrangements of a molecule, in two-dimensions. You have already learnt about the Fischer projections for representing the configuration of a compound. Two types of representations, namely, *Newman projections* and *Sawhorse projections* are used to show the conformations. We will first study the Newman projections.

Newman Projections

For writing the Newman projections of a molecule, it is viewed along the carbon-carbon bond as shown for ethane in Fig. 3.6(a). Here, the ethane molecule is shown in Wedge and dash drawing. In drawing the Newman projection, the carbon

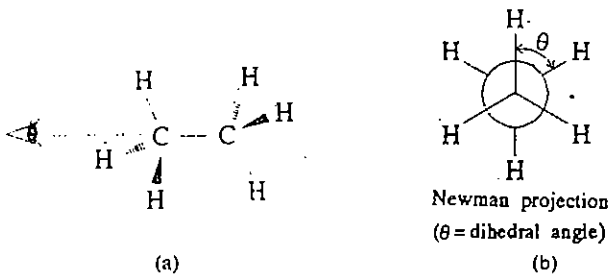


Fig. 3.6: a) Wedge and dash drawing of ethane; solid wedges show the bonds above the plane of paper and dash lines represent the bonds behind plane of the paper whereas the ordinary lines represent the bonds in plane of the paper. b) Newman projections of ethane.

atom nearer to the observer is represented by a point and the three groups attached to it are shown by three lines emerging from this point [Fig. 3.6(b)]. The rear carbon is shown by a circle and the three substituents attached to this carbon are shown by three lines emerging from the edge of the circle. The angle, θ, between the H – C – C plane and the C – C – H plane of an H – C – C – H unit is called the **dihedral angle.**

You are advised to use the models in understanding these representations.

Let us now understand how to write the sawhorse projections.

Sawhorse Projections

In this representation, the carbon-carbon single bond is represented by a line and is oriented diagonally backward, i.e., the left hand carbon projects towards the viewer and the right-hand carbon projects away from the viewer. This is illustrated in sawhorse projections for ethane in Fig. 3.7. Analogous to the Newman projections, here also the substituents on each carbon are shown by lines.

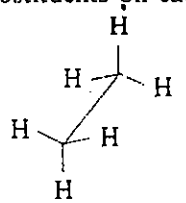


Fig. 3.7 : Sawhorse representation of ethane.

Remember that the four substituents attached to the carbon atoms in ethane are arranged in tetrahedral fashion

We now know how to represent a molecule in Newman or sawhorse projections. These projection formulas are useful in studying the conformations of simple molecules. Let us now study the conformations of ethane.

3.8 CONFORMATIONS OF ETHANE

A number of different conformations are possible for ethane molecule depending upon the value of the dihedral angle, θ. Fig. 3.8 shows the variation of potential energy for various conformations of ethane.

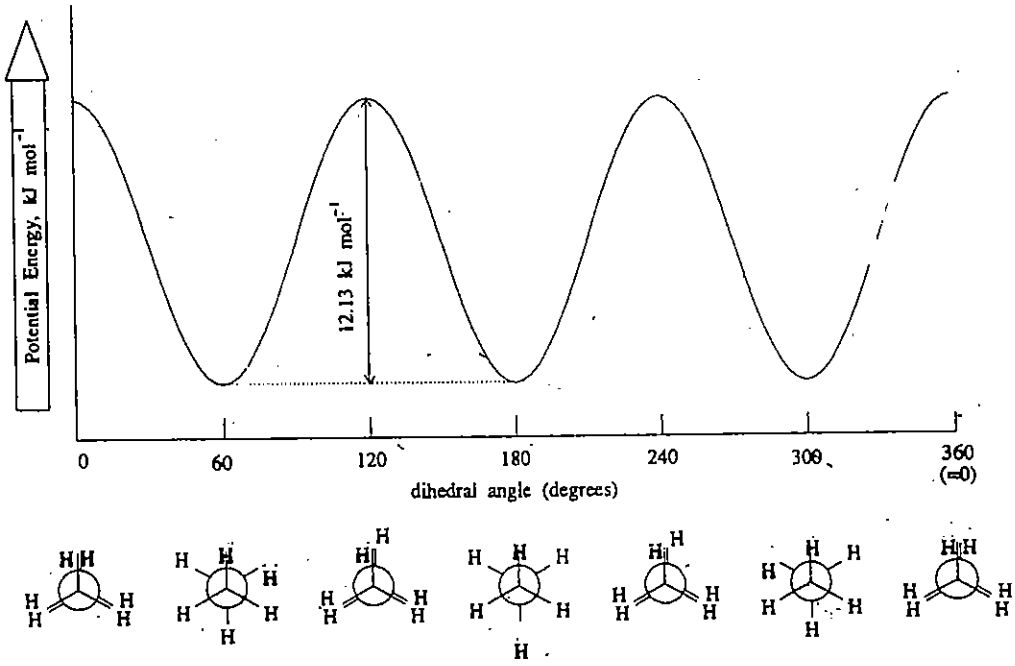
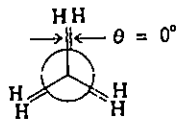


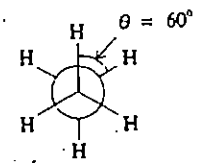
Fig. 3.8 : Variation of potential energy with dihedral angle. Here, to make it easy to visualise the dihedral angle, the two hydrogens on the two carbons are shown in the different colour

Activity

Make a model of ethane molecule in which one C – H bond on each carbon atom has a different colour. Rotate along the C – C single bond and try to make eclipsed and staggered conformations. Convince yourself that they have the dihedral angles as 0° and 60°, respectively.



eclipsed conformation of ethane



staggered conformation of ethane

When the dihedral angle is 0°, then the hydrogens on the two carbon atoms are parallel and the conformation is known as **eclipsed conformation.** The other limiting possibility is when the dihedral angle is 60°; this is called **staggered conformation.** Fig. 3.8 shows that there is an energy difference of 12.13 kJ mol^{-1} between the eclipsed and staggered conformations, with the staggered conformation having the lower energy. This can be explained in terms of the maximum separation of bonded electron pairs in the staggered conformation which leads to minimum repulsion between them. On the other hand, in the eclipsed conformation, the C-H bonds are closer and hence, there is a repulsion between the electrons forming these bonds. Thus, the staggered conformation is more stable than the eclipsed conformation. The energy difference of 12.13 kJ mol^{-1} between these two conformations is very small as compared to the kinetic energy of the molecule due to molecular motions and even at low temperatures a molecule can pass from one staggered conformation to another staggered conformation (although in between it has to pass through an eclipsed conformation) at the rate of about 10^{11} times per second! Thus, the interconversion of conformations is very rapid; nevertheless it is not strictly 'free' in the sense that there is an energy barrier of 12.13 kJ mol^{-1} to be overcome. Hence, the ethane molecule spends most of its time in its staggered forms, passing only transiently through its eclipsed forms. Before you proceed to study the conformations of another alkane, namely butane, answer the following SAQ.

SAQ 3

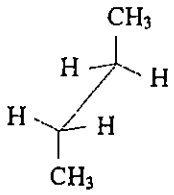
Draw the eclipsed and staggered conformations of ethane in sawhorse representation.

N... comparing the stability of various conformations, remember that the conformation having the least potential energy is the most stable conformation. Thus, ethane has one conformer which is the staggered conformation.

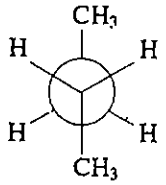
*The analysis of molecular conformations and their relative energies is called **conformational analysis.***

3.9 CONFORMATIONS OF BUTANE

The sawhorse and Newman projections of butane are represented below.



sawhorse projection



Newman projection

Similar to the case of ethane, various conformations of butane are possible due to rotation of the C–C bond formed by the carbon atoms numbered as 2 and 3. Fig. 3.9 shows the potential energy variation for various conformations of butane

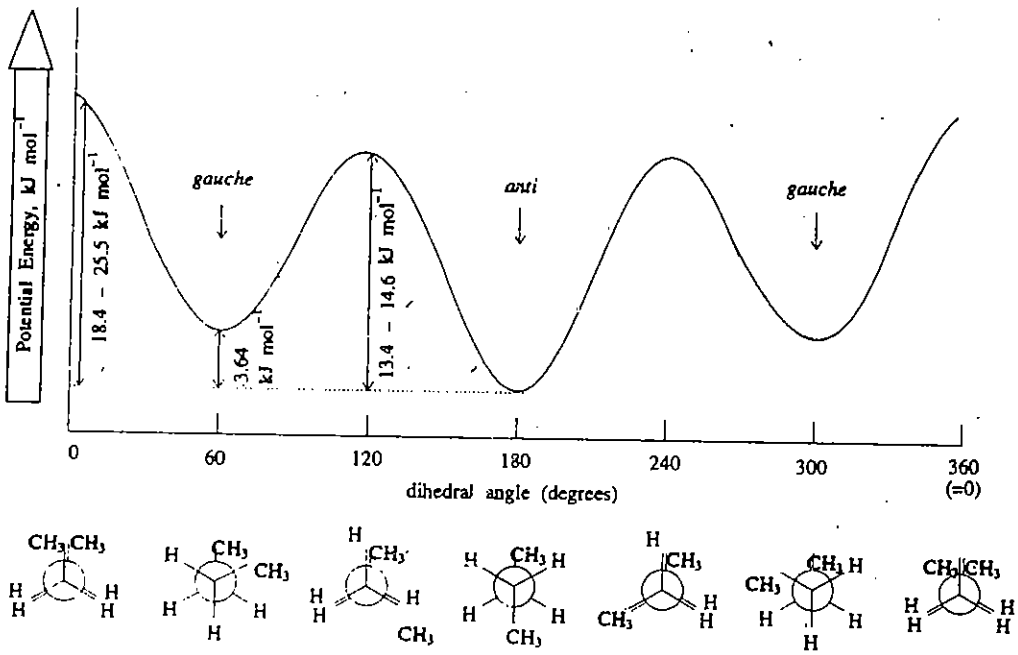


Fig. 39 : Potential energy diagram for the conformations of butane.

As the figure shows, when the dihedral angle is zero, the conformation is called **eclipsed conformation.** As the dihedral angle increases to 60°, we get another conformation which is called **gauche or skew conformation.** Further rotation of the C_2-C_3 bond yields another **eclipsed conformation** when the dihedral angle is 120° Note that in this conformation CH_3 *and* H *are eclipsed* whereas in the earlier eclipsed conformation **two methyl groups were eclipsed.** Hence, this eclipsed conformation is at a little lower energy level than the earlier eclipsed conformation. When the two methyl groups are maximum apart, i.e.. when the dihedral angle is 180°, then the conformation is known as **anti conformation.** Note that this is the most stable conformation of butane because it has the lowest energy value. On further rotation, another set of **eclipsed** and **gauche** conformations result. The difference in energy between the **anti** and **gauche** conformations is about 3.64 kJ mol^{-1}. At room temperature, butane is a mixture of 72% anti and 28%

Activity

Make a model of butane. Rotate along the $C_2 - C_3$ single bond. Try to make various conformations shown in Fig. 3.9 and study their dihedral angles.

Butane has two conformers, namely, *anti* and *gauche* conformations. The *anti* conformer is more stable as compared to the gauche, as shown in Fig. 3.9.

gauche conformations. Similar to ethane, in this case also, the interconversion of these conformations is rapid and if one wants to separate them, one has to make the interconversion slow by working at very low temperatures of about 43 K.

Hassel and Barton received Nobel Prize in Chemistry in 1969 for their contributions in the field of conformational analysis.

The study of conformations or **conformational analysis** is helpful in explaining the specificity of reactions; particularly, the reactions observed in living systems where such a specificity is exhibited by virtue of the particular conformations of the compounds.

At this stage, you can check your understanding about conformations of simple straight chain alkanes by answering the following SAQ.

SAQ 4

a) Write sawhorse projections for the two gauche conformations of butane.

.....

.....

b) What is the value of dihedral angle in these conformations?

.....

.....

c) What relationship do these two **gauche** conformations have with each other?

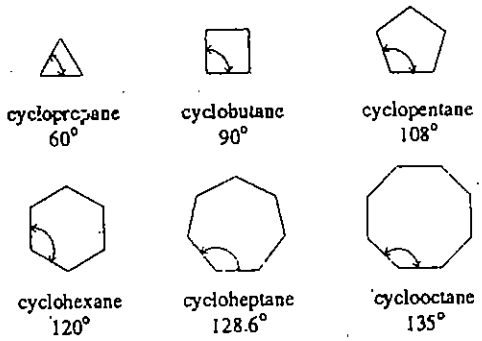
.....

.....

3.10 CONFORMATIONS OF CYCLIC SYSTEMS

During the nineteenth century, it was believed (erroneously, as we shall see in the subsequent discussion) that the cycloalkanes are planar. According to the German chemist Baeyer, the internal bond angles for cycloalkanes should be the same as those of the corresponding regular polygons. This is shown below.

The bond angle in a polygon having n sides is given by $\left(\frac{2n-4}{n}\right) \times 90°$. For example, in cyclopropane having n = 3, the bond angle $= \left(\frac{2\times3-4}{3}\right)\times 90°$ $= 60°$



In order to explain the fact that the cyclic compounds having rings containing fewer than five or more than six carbon atoms were less abundant in nature, he suggested that the stability of such compounds could be related to the tetrahedral bond angle of 109.5°. The deviation from this angle could cause a strain in the molecule leading to its decreased stability. This type of instability is called **angle strain.** According to this explanation, as the deviation from the tetrahedral value decreases, the stability should increase. Thus, the stability should increase from cyclopropane → cyclobutane → cyclopentane. As the deviation in angle from the tetrahedral angle of 109.5° is minimum in case of cyclopentane, Baeyer predicted it to be most stable. Cyclohexane and higher cycloalkanes according to him would be less stable than cyclopentane because the angles of larger polygons deviate more and more from the ideal tetrahedral angle.

The experimental values of heat of combustion per methylene group showed that the energies for the first three cycloalkanes are in the following order:

cyclopropane > cyclobutane > cyclopentane. This order is consistent with the predictions of the Baeyer's strain theory. But in case of cyclohexane, the heat of combustion is less indicating its greater stability. Further increase in the ring size does not affect the heat of combustion much, indicating a constant value of about 652.7 kJ mol^{-1} per methylene group in contradiction to the prediction of Baeyer Strain Theory that with the increase in the ring size, angle strain must increase.

Baeyer's theory failed because of the assumption that the cycloalkanes are planar. Of course, cyclopropane has to be planar because three carbons must lie in a single plane. But other larger cycloalkanes are **not planar and are puckered.** Puckering of rings relieves the angle strain. You will study about this in detail in case of cyclohexane in the following discussion.

General equation for combustion of alkanes is

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right) O_2 \longrightarrow$$

alkane oxygen

$$nCO_2 + (n+1)\,H_2O + \text{heat}$$

carbon dioxide water

The heat released on complete combustion of one mole of a substance is called its heat of combustion.

The heat of combustion data is useful in determining the relative energies of various molecules.

Higher the heat of combustion per methylene group, lower will be the stability.

3.10.1 Conformations of Cyclohexane

If you make a model of cyclohexane containing 6 sp^3 hybrid carbon atoms forming a regular hexagon, you will realise that in this molecule, in addition to the angle strain, the hydrogens on the adjacent carbon atoms have the eclipsed arrangement as depicted in Fig. 3.10.

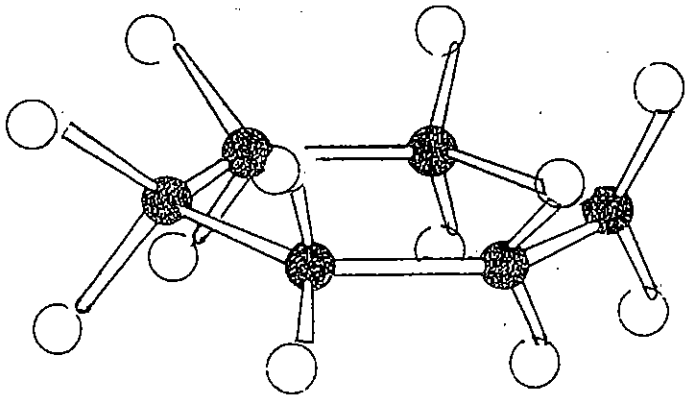


Fig. 3.10 : Strained planar conformation of cyclohexane showing eclipsed hydrogens.

Sachse in 1890 pointed out that two nonplanar models for cyclohexane are possible which are free from angle strain. These are called **chair** and **boat** conformations and are shown in Fig. 3.11.

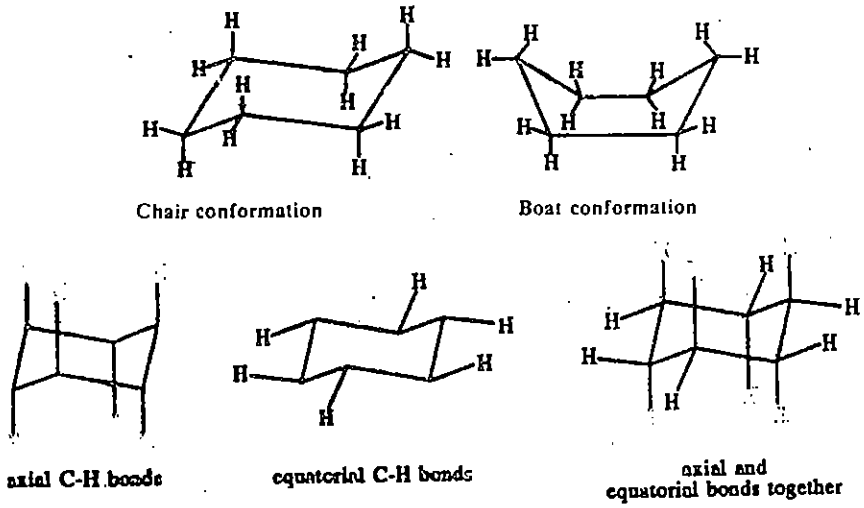
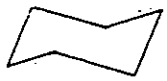


Fig. 3.11 : Chair and Boat conformation of cyclohexane.

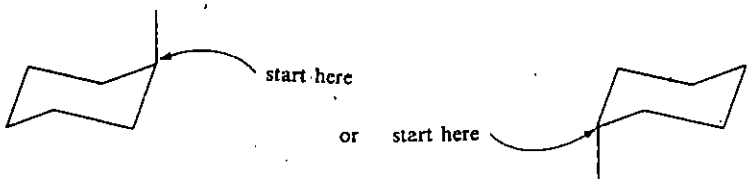
There are two types of hydrogens in the chair form of cyclohexane. The six hydrogens which are above and below the plane of the carbon ring are called **axial** hydrogens. Note that the axial bonds are alternately directed up and down on the adjacent carbon atoms. The second set of hydrogens is called **equatorial** hydrogens and are located approximately along the equator of the molecule. Given below are the steps to enable you to represent the axial and equatorial bonds correctly on the chair conformation of cyclohexane.

Steps

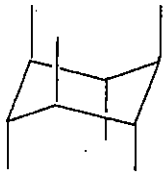
1) Draw the chair conformation of cyclohexane as,



2) Draw one axial bond as shown below,

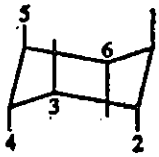


and then draw axial bonds alternately up and down as represented below.

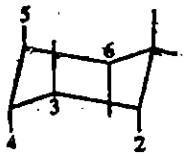


all axial bonds are parallel to each other

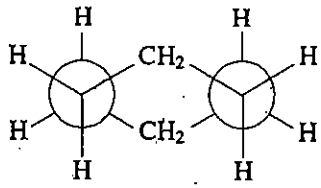
3) Draw equatorial bonds keeping in mind the tetrahedral arrangement at the carbon atoms. Draw an equatorial bond at C-1 in such a way that it is parallel to the carbon-carbon bond between C-2 and C-3 and then complete the other equatorial bonds as shown below.



Place equatorial bond at C-1 so that it is parallel to the bonds between C-2 and C-3, and between C-5 and C-6.

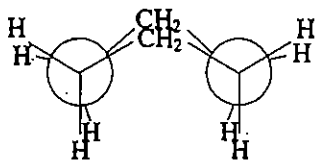


You can notice the sawhorse representation of the staggered bonds in the above chair conformation. This staggered nature of bonds can also be visualised in the Newman projections of the chair conformation of cyclohexane as shown below:



staggered arrangement of bonds in chair conformation of cyclohexane

However, a similar representation of the boat form of cyclohexane shows the eclipsed bonds.

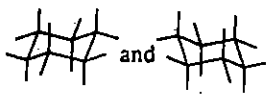


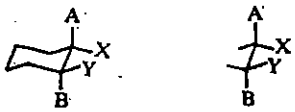
eclipsed bonds in boat conformation give it torsional strain

Further, in the boat conformation the two hydrogens, at the bow and stern of the boat, called **flagpole hydrogens** are 183 pm apart. This distance is significantly lesser than the sum of their van der Waal's radii (240 pm) and it results in a repulsion between them. These van der Waal's repulsions increase the energy of the boat form as compared to the chair form by about 27 kJ mol^{-1}.

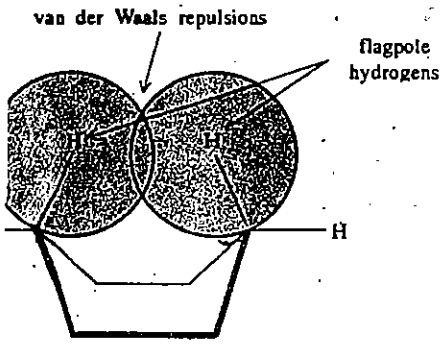
Activity

Practice drawing cyclohexane chairs oriented in either direction.





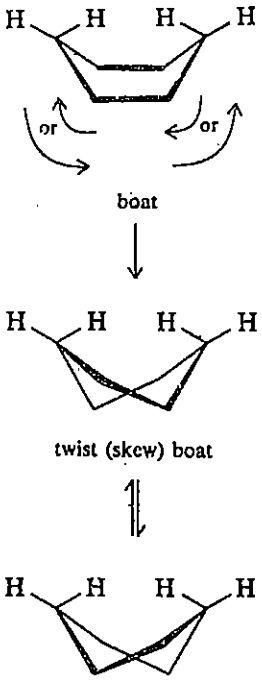
Chair cyclohexane drawings resemble sawhorse projections of staggered conformations of alkanes.



If the distance between two non-bonded atoms is less than the sum of their van der Waal's radii, there is repulsive interaction between the two-atoms. This is known as *van der Waal's repulsions.*

portion of the strain due to the flagpole interactions in the boat conformation is lieved in the **twist boat** (or **skew boat**) conformation, which is obtained by ghtly twisting the boat conformation as shown below:

The conversion of a boat into a twist-boat cyclohexane



he twist boat form is more stable than the boat conformation but is less stable an the chair conformation by about 2.51 kJ mol^{-1}. As the chair conformation is e most stable form, most of the molecules of cyclohexane exist in the chair rm. The available experimental data indicate that no more than one or two olecules per thousand exist in the skewboat conformation.

chair conformation is also convertible into another chair conformation by the ocess known as **ring flipping**. This interconversion, as shown in Fig. 3.12, occurs a the intermediate half-chair and skew-boat conformations. The energy profile r such an interconversion is shown in Fig. 3.12. The ring flipping requires an ergy of 45.18 kJ mol^{-1} and even at room temperature, this interconversion is ry fast.

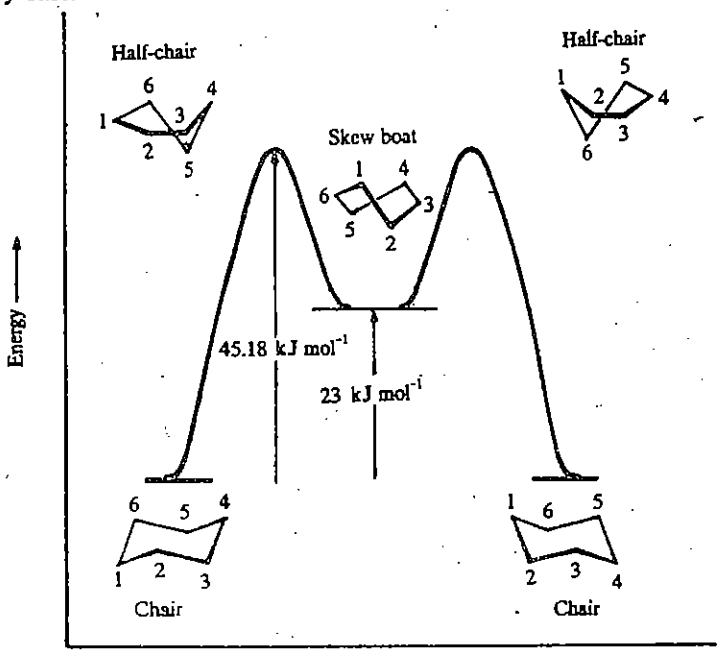


Fig. 3.12 : Energy profile associated with ring flipping.

n important consequence of the ring flipping is that the axial substituents in the iginal chair conformation become equatorial in the flipped chair conformation id vice versa. Note that this inversion does not involve any bond breaking or ond forming.

A detailed energy profile for various conformations of cyclohexane is shown in Fig. 3.13. Note that the boat form is a transition state for the interconversion of skew-boat conformations.

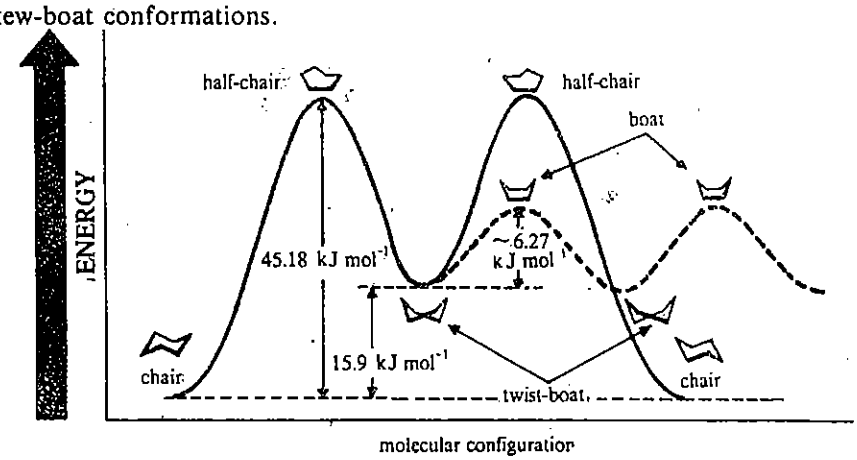
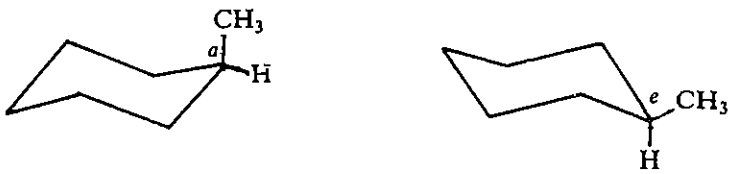


Fig. 3.13: Relative energies for various conformations of cyclohexane.

3.10.2 Conformations of Monosubstituted Cyclohexane Derivatives

Consider a monosubstituted cyclohexane, say, methylcyclohexane. In the chair conformation of methylcyclohexane, the methyl group ($-CH_3$) can occupy either axial or equatorial position as shown below.

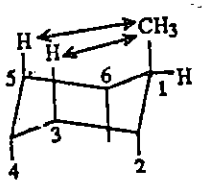


axial equatorial

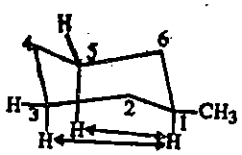
You are advised to use models while studying this section and the next section.

Remember that the ring flipping interconverts these two forms with the methyl group changing from axial to equatorial and vice versa. Also, since these two stereoisomers are not enantiomers, they are diastereomers. They have different energies or different stabilities. Let us now examine what happens when the methyl group occupies the axial position. In this position the methyl group is relatively close to the axial hydrogens at C-3 and C-5 carbon atoms. As the distance between the hydrogen of the methyl group and the C-3 or C-5 hydrogen atom is less than the sum of the van der Waal's radii for the two hydrogens; van der Waal's repulsions destabilise the axial conformation of methylcyclohexane.

Such a situation is avoided in the equatorial conformation in which the methyl group occupies equatorial position and hydrogen is axial. The axial hydrogen, being smaller in size as compared to methyl group, experiences smaller van der Waals repulsions. Thus, equatorial conformation of a monosubstituted



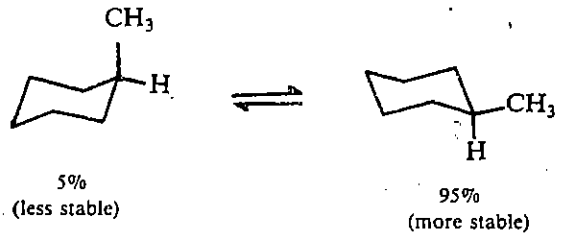
van der Waals repulsions between methyl and axial hydrogens at C-3 and C-5



smaller van der Waals repulsions between hydrogen at C-1 and axial hydrogens at C-3 and C-5

In 1960, Bush Weller was able to separate the equatorial conformation of chlorocyclohexane by cooling its solution in an inert solvent to 123 K.

cyclohexane is more stable as compared to the axial conformation. Since these two conformations are in rapid equilibrium, the relative amounts of the two conformations depend upon the size of the substituent. Thus, for larger substituents, the equilibrium may even be shifted completely to the equatorial conformation. This is illustrated below for some cases.

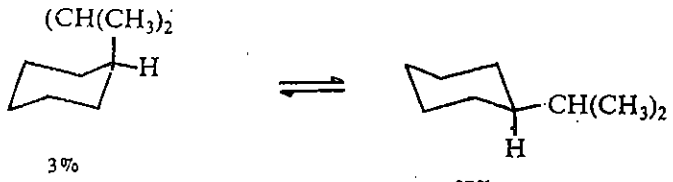


5%
(less stable)

95%
(more stable)

40%

60%



3%

97%

3.10.3 Conformations of Disubstituted Cyclohexane Derivatives

When we talk about disubstituted cyclohexanes, the possible patterns of substitution are 1,2-disubstituted, 1,3-disubstituted and 1,4-disubstituted derivatives. Let us study each of these patterns taking dimethylcyclohexane as the example.

1,2-Dimethylcyclohexane

Let one of the methyl groups occupy an axial position at C-1 carbon as shown here,

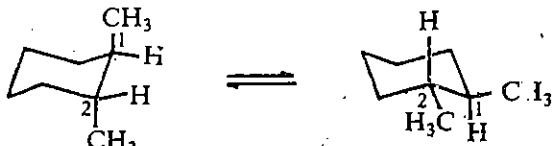
Activity

Use models to understand the interactions between the hydrogens of the methyl groups more clearly.

cis-1,2-dimethylcyclohexane

If the second methyl group occupies an equatorial position as represented above, then as both the methyl groups are on the same side, this arrangement is called *cis*. Since the two methyl groups are closer to each other, there is a crowding between the hydrogens of the two methyl groups. Ring flipping of the *cis* form changes it into another equivalent *cis* form. But this does not lead to any change as far as the interactions between the hydrogens of the two methyl groups are concerned.

Another possibility in which both the methyl groups occupy axial position lead to the *trans* arrangement of the groups. Note that this *trans* conformation is



(Both methyl groups are axial; less stable chair conformation)

(Both methyl groups are equatorial; more stable chair conformation)

trans-1,2-dimethylcyclohexane

convertible by ring flipping into another conformation in which both the methyl groups occupy equatorial positions. This arrangement is also *trans* because here

also the substituents have the up-down relationship. But these two *trans* arrangements are not equivalent.

Let us now study about the relative stability of these two *trans* arrangements. Note that the axial $-CH_3$ group at C-1 faces van der Waals repulsions by axial hydrogens at C-3 and C-5 carbon atoms. Similar repulsions for the axial C-2 methyl group with hydrogens at C-4 and C-6 carbon atoms, make this diaxial *trans* conformation less stable as compared to the diequatorial *trans* confirmation. Note that the equatorial positions are free from such interactions as the substituents project outward from the body of the molecule. Remember, **it is a general rule that any substituent is more stable in the equatorial position than in the axial one.**

Activity

Convince yourself using models that the two methyl groups at 1 and 2 positions have least van der Waals repulsions with the adjacent hydrogens when they occupy the equatorial positions.

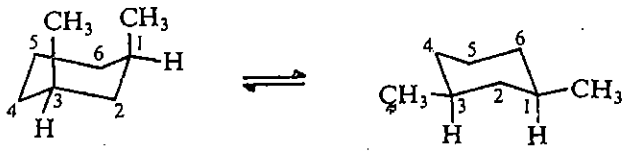
Thus, *trans* diequatorial conformation of 1,2-dimethylcyclohexane is more stable than the *trans* diaxial and *cis* forms.

1,3-Dimethylcyclohexane

Let the C-1 methyl group in this molecule occupy the axial position. Then, the C-3 methyl group can have either axial or equatorial position.

Let us now study each of these two possibilities one by one.

i) When the C-3 methyl group is **axial,**



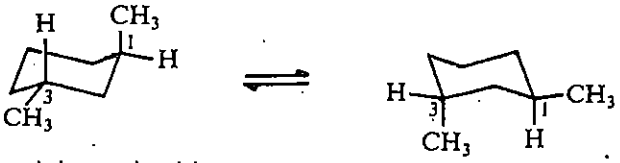
(Both methyl groups are axial; less stable chair conformation)

(Both methyl groups are equatorial; more stable chair conformation)

(Both methyl groups are up)
cis-1,3-dimethylcyclohexane

Then, both the methyl groups are on the same side and you can see that this arrangement is *cis*. Ring flipping of this *cis* conformation leads to another *cis* form in which both methyl groups occupy equatorial positions. (Do it yourself with the models.)

ii) When the C-3 methyl group is **equatorial,**



(One methyl group is axial, the other is equatorial)

(One methyl group is axial, the other is equatorial)

(One methyl group is up, the other is down)

trans-1,3-dimethylcyclohexane

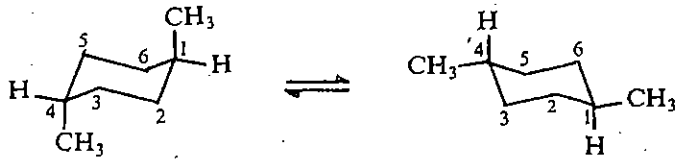
Then, the two methyl groups are said to be *trans* to each other. Ring flipping of this *trans* form yields another equivalent *trans* form. You can verify it using models.

The *trans* form has one methyl group in equatorial position and the other methyl group in the axial position whereas the *cis* form in its more stable conformation has both the methyl group oriented equatorially; therefore, in this case the *cis* form with diequatorial substituents is more stable than the *trans* form. Let us now apply the same considerations to 1,4-dimethylcyclohexane.

1,4-Dimethylcyclohexane

Let the C-1 methyl group occupy an axial position. The C-4 methyl group can be either axial or equatorial. Let us consider both these possibilities.

i) When the C-4 methyl group is axial, it leads to the *trans* arrangement of methyl groups. This chair conformation having the diaxial arrangement of methyl groups by ring flipping can change into chair form having diequatorial arrangement of methyl groups.



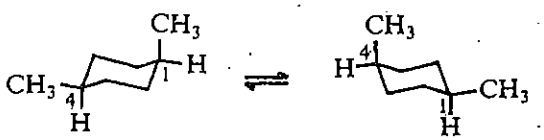
(Both methyl groups are axial: less stable chair conformation)

(Both methyl group are **equatorial**: more stable chair conformation)

(One methyl group is up, the other is down)

trans-1,4-dimethylcyclohexane

ii) When the C-4 methyl group is in equatorial position, we have *cis* arrangement of methyl groups. The two equivalent *chair* conformations shown below represent such an arrangement.



(One methyl group is axial, the other is equatorial)

(One methyl groups is axial, the other is equatorial)

(Both methyl groups are up)

cis-1,4-dimethylcyclohexane

Note that these two equivalent chair conformations have one axial and one equatorial methyl substituents.
A comparison of these *cis* and *trans* conformations shows that since the *trans* conformation permits both the methyl groups to occupy equatorial sites; hence, it is more stable as compared to the *cis* form which has one substituent each in the axial and equatorial positions.

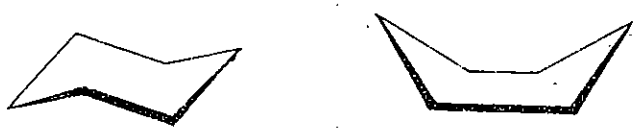
In other disubstituted cyclohexanes, when the two substituents are different, the stable isomer is the one in which the larger substituent occupies the equatorial position.

Using your knowledge of conformations of cyclohexane systems, answer the following SAQ.

SAQ 5

Which of the two isomers in each of the following pairs would be more stable?

i)

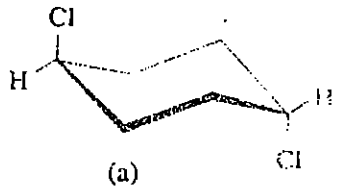


(a) (b)

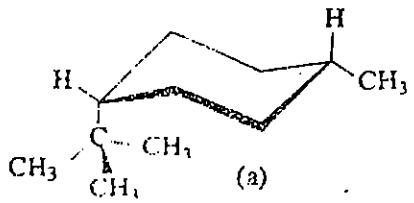
ii)

(a) (b)

iii)



iv)



3.11 SUMMARY

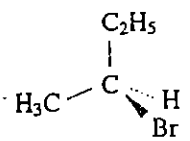
In this unit, you have learnt that

- The spatial arrangement of the atoms (or groups) in a molecule is known as the configuration.
- Fischer projection formulas are used for representing the configurations of the molecules in the two-dimensional plane of the paper.
- A chiral compound can be assigned an absolute configuration as either *R* or *S* using the Cahn-Ingold-Prelog sequence rules.
- Racemic mixtures can be resolved into optically active compounds via the formation of diastereomers.
- Optically active compounds can be synthesised from optically inactive compounds using asymmetric synthesis.
- Walden inversion involves the inversion of configuration.
- Rotation about carbon-carbon single bond leads to conformational isomers.
- Newman and sawhorse projections are used to represent the conformations of a molecule.
- Staggered conformation of ethane is more stable that its eclipsed conformation.
- Of the three conformations of cyclohexane, namely, chair, boat and skew-boat, the chair conformation is the most stable one.
- Substituents on a cyclohexane ring are more stable when they occupy equatorial position than when they are in axial position.

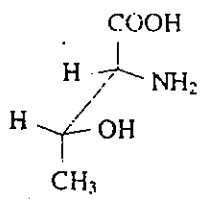
3.12 TERMINAL QUESTIONS

1. Draw Fischer projection formulas for the following compounds:

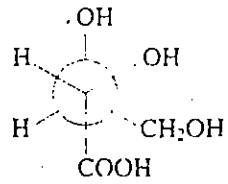
a)



b)



c)



2. a) Write the stereoisomers for tartaric acid (i.e., 2,3-dihydroxybutanedioic acid).
   b) Assign the configuration as *R* or *S* to the chiral centres in each of the stereoisomers in part (a).
   c) Which of the isomers of part (a) are optically active?

3. The resolution of 1-phenylethylamine using (–) malic acid, yielded the less soluble diastereomeric salt having the configuration (*R*)-1-phenylethylammonium (*S*)-malate. The other diastereomeric salt being more soluble remained in the solution. What is the configuration of this more soluble salt?

4. Substitued chiral ethanoic acid having the formula DHTC–$\overset{\overset{O}{\|}}{C}$–OH, in which two hydrogens of the CH_3 group have been substituted by deuterium, D, and tritium, T, can exist as enantiomers. Write the three dimensional structures for its *R* and *S* isomers.

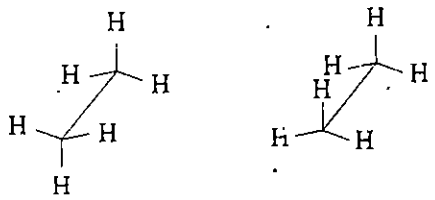
3.13 ANSWERS

Self Assessment Questions

1. (a) Same compound, Ist interchange – CH_3 and – OH
   IInd interchange – H and – C_3H_7.
   (b) Same compound, Ist interchange – COOH and – OH
   IInd interchange – OH and – H.
   (c) enantiomers, using rule 3.
   (d) enantiomers as they are interconvertible by rotation of 90°, (rule 2).

2. (a) *S* (b) *R* (c) *R* (d) *S*.

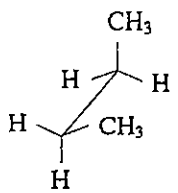
3.

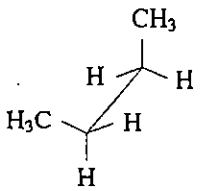


staggered conformation

eclipsed conformation

4. (a) Two gauche forms of butane in sawhorse projections:



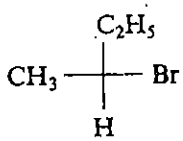


(b) 60°
(c) They are enantiomeric in nature.

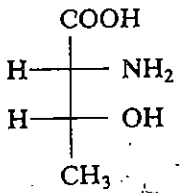
5. (i) a (ii) b (iii) b (iv) b

Terminal Questions

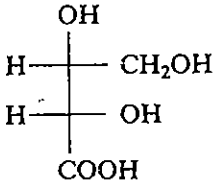
1. (a)



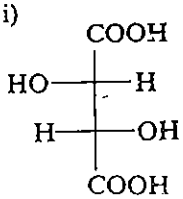
(b)



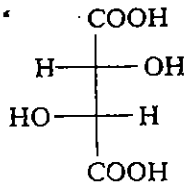
(c)



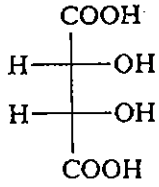
2. (a) i)



(ii)



(iii)

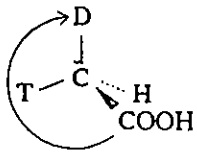


b) (i) 2*S*, 3*S* (ii) 2*R*, 3*R* (iii) 2*R*, 3*S*

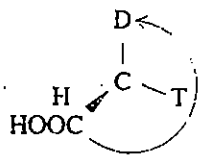
c) (i) and (ii) are optically active but (iii) being a *meso* compound, is optically inactive.

3. (*S*)-1-phenylethylammonium (*S*)-malate.

4.



R isomer



S isomer

UNIT 4 EFFECT OF MOLECULAR ARCHITECTURE ON PHYSICAL PROPERTIES

Structure

4.1 Introduction
Objectives

4.2 Molecular Architecture and Physical Properties
Intermolecular Forces
Melting Point
Boiling Point
Solubility

4.3 General Ideas about Spectroscopy

4.4 Ultraviolet Spectroscopy
Measurement of Ultraviolet Spectrum

4.5 Infrared Spectroscopy
Experimental Aspects of Infrared Spectroscopy

4.6 Nuclear Magnetic Resonance Spectroscopy
How to Obtain an NMR Spectrum
Interpretation of Proton NMR Spectrum

4.7 Mass Spectrometry

4.8 Summary

4.9 Terminal Questions

4.10 Answers

4.1 INTRODUCTION

In the preceding units we discussed some of the important aspects of bonding and the structures of organic molecules in detail. But have you thought about how we establish the identity and structure of a molecule?

One answer to this question could be comparing its physical and chemical properties with those of the known compounds. Earlier methods of identification involved the determination of physical properties such as melting point, boiling point, solubility and refractive index. The chemical methods used for identification involved, however, either the degradation of the molecule to simple compounds of known structure or its synthesis from the simple compounds of known structure In this unit, we will discuss the relationship between molecular structure and physical properties. The study of physical properties is also important in the purification of organic compounds.

Another possibility is that the compound under investigation may be a new compound which has never been studied before and for which no data for comparison is available. For such compounds other methods of structure determination are used. One such method involves the use of various forms of **spectroscopy.** The spectroscopic methods are based on the interaction of molecules with the electromagnetic radiation, their behaviour in a magnetic field or on impingement with high energy electrons. In this unit, you will study some spectroscopic methods such as *ultraviolet* (*uv*) *spectroscopy, infrared* (*ir*) *spectroscopy, nuclear magnetic resonance* (*nmr*) *spectroscopy ana mass spectrometry* (*ms*). Here, you will also learn how the information available from these methods can be used in determining the molecular structure.

However, the most complete method of structure determination is that of X-ray diffraction. This method provides a detailed picture of the spatial arrangement of various atoms in the molecule. Hence, it ena' les one to deduce bond lengths, bond angles and other geometrical features of the molecule.

Objectives

After studying this unit, you should be able to:

- define various kinds of intermolecular forces,
- explain the trends in physical properties such as melting point, boiling point, solubility etc. of molecules on the basis of intermolecular forces,
- correlate the physical properties of the molecules with the molecular structure,
- list various spectroscopic techniques used in the determination of molecular structure,
- predict the type of transitions possible in a molecule when it is subjected to ultraviolet radiation,
- state whether a molecule will show absorptions in the infrared spectrum or not and correlate the absorption bands in the infrared spectrum of a molecule to the functional groups present in it,
- predict the pattern of signals in the nmr spectrum of a given compound,
- write the fragmentation pattern for simple molecules and match it with the peaks obtained in their mass spectra, and
- predict the structure of a molecule from its physical properties and spectral data.

4.2 MOLECULAR ARCHITECTURE AND PHYSICAL PROPERTIES

The bonding and structural features of a compound are manifested in its physical properties. Thus, physical properties of a compound such as melting point, boiling point, solubility, etc., often give valuable clues about its structure. Conversely, if the structrue of a compound is known, its physical properties can be predicted. The physical properties of a compound depend upon the number and nature of atoms constituting its structural units and also on the nature of forces holding these units together. You know that in case of ionic compounds, the positive and negative ions are held together by strong electrostatic forces. Contrary to this, in covalent compounds, the molecules are held together by intermolecular forces. Let us now study briefly what these intermolecular forces are. Then, you will learn how these intermolecular forces affect the physical properties of the compounds.

4.2.1 Intermolecular Forces

The three important intermolecular forces are: (i) dipole-dipole interactions, (ii) London forces and (iii) hydrogen bonding. Let us now consider these intermolecular forces one by one.

i) **Dipole-dipole interactions** are defined as the interactions between the different molecules of a compound having permanent dipoles. Consider the example of chloromethane which has a permanent dipole. The molecules of chloromethane orient themselves in such a way that the positive end of one dipole points towards, and is thus attracted by, the negative end of the other dipole. These interactions, called dipole-dipole interactions are depicted in Fig. 4.1.

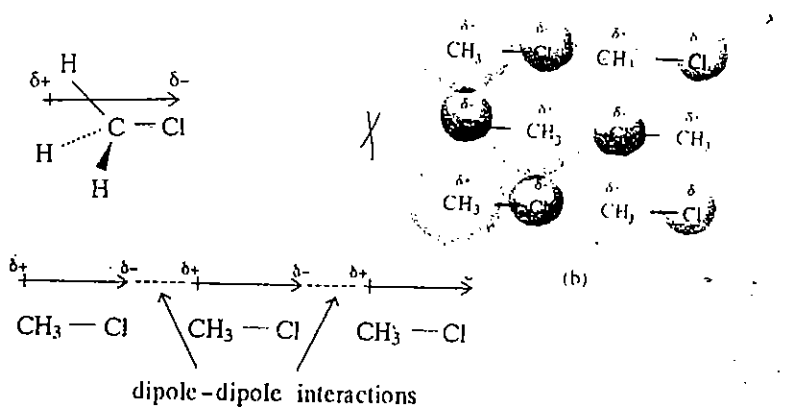


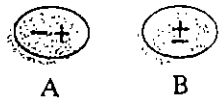
Fig. 4.1 : a) A polar chloromethane molecule showing positive and negative poles. b) Arrangement of chloromethane molecules and c) Dipole-dipole interactions between chloromethane molecules.

The dipole-dipole interactions are weak interactions and are of the order of 4 to 12 kJ mol^{-1} whereas the bond energy for an ordinary covalent bond ranges from 125 to 420 kJ mol^{-1}.

ii) **London forces**

The intermolecular interactions exist between nonpolar molecules also. Consider two nonpolar molecules A and B in which the centre of positive charge coincides with that of the negative charge.

When the molecules A and B approach each other, there is a distortion in the distribution of the charge resulting in a small and momentary dipole in one molecule. This small dipole can then create another dipole in the second molecule which is called **induced dipole.** Thus, if the momentary dipole of molecule A is as shown below;

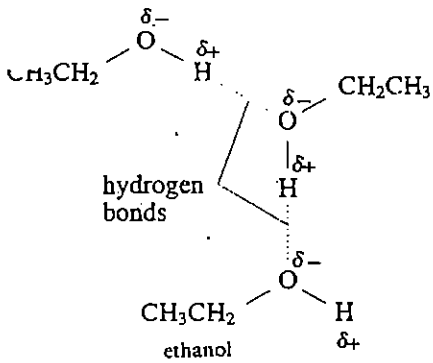


then, this leads to an induced dipole in molecule B as shown below:

Such a distribution of charge leads to mutual attraction between the molecules. These **induced dipole-induced dipole** interactions are also known as **London forces.** These interactions are weaker than the dipole-dipole interactions and are of the order of 4 kJ mol^{-1}. These forces vary with the distance between the molecules. If r is the distance between the two molecules, then the London forces are proportional to $1/r^6$.

London forces are the only forces of attraction possible between nonpolar molecules.

iii) **Hydrogen bonding** results when a hydrogen atom is covalently bonded to a strongly electronegative atom such as oxygen, nitrogen or fluorine. Such a hydrogen atom has a large affinity for the nonbonded electrons of oxygen (or nitrogen or fluorine) atom of the other molecule. This type of intermolecular interaction is known as hydrogen bonding. The hydrogen bonding in case of ethanol is represented below:



The hydrogen bonding is a special type of dipole-dipole interaction.

Note that the hydrogen bonds are indicated by the dash lines whereas the covalent bonds are represented by solid lines.

The hydrogen bonding is a stronger interaction as compared to the dipole-dipole interactions but it is weaker than a covalent bond. The strength of a hydrogen bond ranges from 10 to 40 kJ mol^{-1}. Hydrogen bonding has an important influence on physical properties such as melting point, boiling point and solubility of substances. This will be illustrated using examples in the following subsections.

The dipole-dipole, induced dipole-induced dipole etc. interactions are collectively known as **van der Waals forces.** Having understood the intermolecular forces, let us now study how the variation in molecular structure affects these intermolecular forces which in turn is reflected in the physical properties of the molecules.

Some authors prefer to give the name van der Waals forces only for London forces.

4.2.2 Melting Point

The **melting point** of a substance can be defined as the temperature at which it undergoes the transition from the solid to the liquid state.

Pure crystalline solids have sharp melting points and they melt over a temperature range of 1° or less. In contrast to this, impure crystalline solids melt over wider ranges of temperature.

Pure crystalline solids have **sharp** melting points. Thus, melting point is used as an important physical property both for the identification of organic compounds and for making the general assessment of the purity of these compounds. In a crystalline solid, the constituent ions or molecules are arranged in an orderly and rigid fashion. When such a solid is heated, the thermal energy of the molecules increases. This finally leads to the disintegration of the crystal structure and at the melting point a disorderly and random arrangement of particles, characteristic of a liquid, is obtained. Since the electrostatic forces holding the ions are very strong, they can be overcome only at high temperatures. Therefore, the ionic compounds generally have high melting points. For example, the melting point of sodium chloride is 1074 K and that of sodium ethanoate is 595 K. But, the **intermolecular** forces are very weak as compared to the **interionic** forces and hence, these can be overcome at lower temperatures leading to lower melting points for covalent compounds. The melting point of methane, a covalent compound, is only 90 K and the melting point of methanol, another covalent compound, is 179 K.

Let us now study the effect of molecular weight on the melting point. The relationship between molecular weight and melting point for alkanes is illustrated in Fig. 4.2.

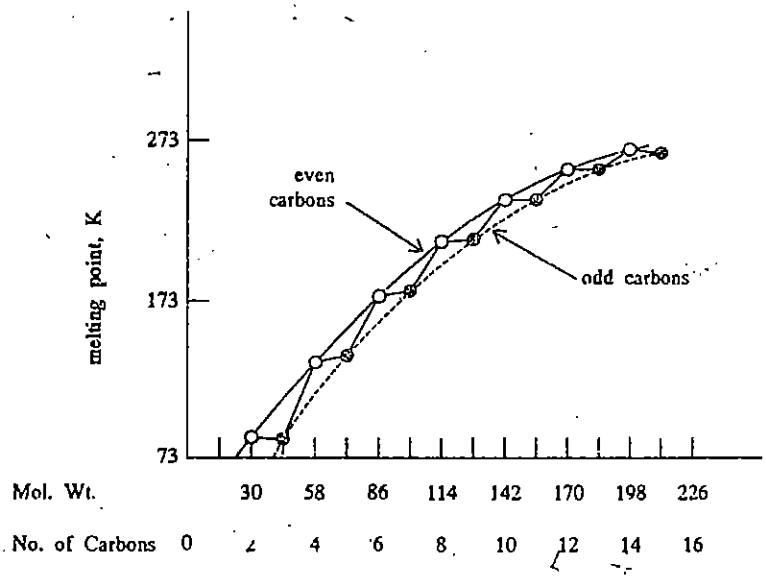


Fig. 4.2 : Plot of melting points of straight chain alkanes against the molecular weight; the number of carbon atoms present in alkane molecule are also indicated.

In a homologous series, the higher the molecular weight, the larger will be the molecules and the greater will be the 'area of contact' between the two molecules and hence the greater will be the London forces.

You can see in the figure that the melting point increases with the increase in the molecular weight. This can be explained due to increase in the London forces between the larger molecules of higher molecular weight. Thus, each additional methylene ($-CH_2$) unit contributes to the increase in melting point.

You must have noticed in Fig. 4.2, the alternating pattern of melting points for the alkanes having odd and even number of carbon atoms. It is also evident from the figure that the compounds having even number of carbon atoms lie on a higher curve as compared to the compounds having odd number of carbon atoms. This can be explained on the basis that in solid state, the London forces among the molecules having odd number of carbon atoms are weaker than those in the molecules having even number of carbon atoms. This is because the molecules of alkanes having odd number of carbon atoms do not fit well in the crystal lattice as compared to those of the alkanes having even number of carbon atoms.

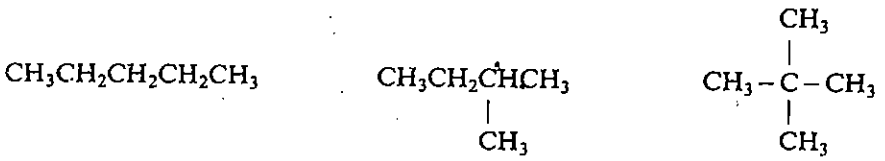
After studying the effect of molecular weight on melting point, let us now see how the isomeric compounds having the same molecular weight, show different melting points. The melting points of straight chain and branched chain isomers of butane are given below.

butane
m.p. 134 K
mol. wt. 58

2-methylpropane
m.p. 112.25 K
mol. wt. 58

The branching of the carbon chain interferes with the regular packing of the molecules in the crystal; hence, branched chain hydrocarbons tend to have lower melting points than their straight chain isomers.

But, in case, the branched molecule has a substantial symmetry, then its melting point is relatively high. This is clearly evident when we compare the melting points of isomeric pentanes which are as given below:



pentane
m.p. 143 K

2-methylbutane
m.p. 113 K

2,2-dimethylpropane
m.p. 257 K

The branching from pentane to 2-methylbutane lowers the melting point but further branching in 2,2-dimethylpropane increases the melting point. This can be explained by the fact that the symmetrical molecules fit together more easily in the crystal lattice and hence have higher melting points as compared to the less symmetrical molecules. Hence, higher melting point for 2,2-dimethylpropane is justified.

This is also reflected when we analyse the melting points of *cis*- and *trans*-isomers. The *trans*- isomer being **more** symmetrical, fits better in the crystal lattice than the less symmetrical *cis*- isomer. Hence, the *trans*- isomers generally have higher melting points, (see Table 2.1, Unit 2).

The nature of the functional groups present in a molecule also affects its physical properties. For example, when the functional group is such that it introduces polarity, and hence leads to a permanent dipole moment in the molecule; then, due to the dipole-dipole forces of attraction between the polar molecules, they show higher melting points than the nonpolar molecules of comparable molecular weights. For example, the melting point of propanone, a polar molecule having molecular weight of 58, is 178 K. You can compare it with the melting points of isomers of nonpolar butane (mol. wt. = 58) you have just studied above. This leads to the conclusion that the polar propanone has higher melting point than the nonpolar isomeric butanes.

The effect of hydrogen bonding on melting point is small. But, the hydrogen bonding has significant effect on the boiling point, about which you will study in the following subsection.

4.2.3 Boiling Point

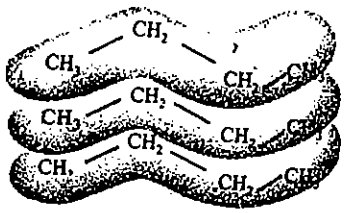
The **boiling point** of a substance is the temperature at which it changes from the liquid to the gaseous state. At the boiling point the vapour pressure of a liquid is equal to the external pressure. Thus, the boiling point depends on the external pressure and it increases with increase in the external pressure. Hence, while reporting the boiling point of a substance, external pressure must be specified. Normally, the boiling points are reported at atmospheric pressure.

Similar to the case of melting points, the boiling points are also used as constants for identification and characterisation of liquid substances. The knowledge of boiling points is also important in the purification of liquids. Let us now study some of the factors affecting the boiling point.

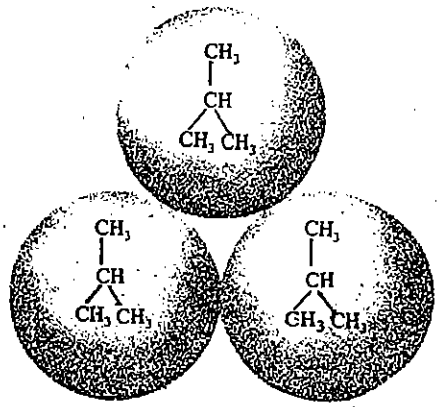
The boiling point of a substance depends on its molecular structure. In a homologous series, the boiling points of the compounds increase with the increase

in the number of carbon atoms. In other words, we can say that the boiling point increases with increase in molecular weight. Generally, this increase in boiling point amounts to 20–30° for the addition of each carbon atom in the molecule. The increase in boiling point with molecular weight can be again attributed to increased London forces of attraction between larger molecules.

Among isomeric molecules, since the unbranched isomer is linear and hence extended in shape, it has larger surface area as compared to the branched isomers. Therefore, the London forces are stronger in the unbranched isomer leading to higher boiling point for this isomer. This is illustrated in Fig. 4.3 for the isomers of butane.



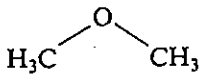
Interactions among elongated molecules b.p. 272.5 K



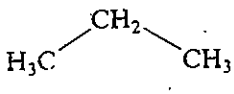
Interactions among spherical molecules b.p. 263 K

Fig. 4.3 : A comparison of intermolecular interactions for straight chain and branched chain isomers of butane.

The polarity of a compound also affects its boiling point. When we compare molecules having the same shape and size, the more polar molecule has the higher boiling point. Examples are,



Dimethyl ether

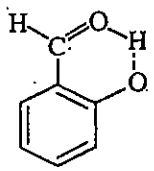


propane

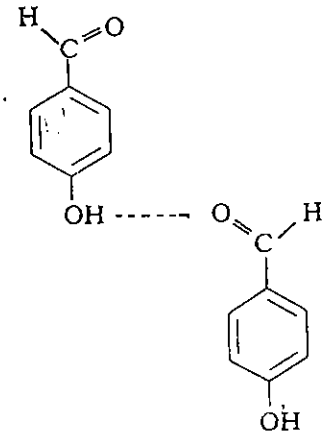
dipole moment	20.98×10^{-30} C m	– 0
boiling point	249.4 K	231 K
molecular weight	46	44

Alcohols have unusually high boiling points as compared to the other compounds of comparable molecular weight or size. For example, ethanol CH_3CH_2OH, which has the same molecular formula as that of dimethyl ether, has the boiling point 351 K. This can be explained due to hydrogen bonding. Hydrogen bonding for ethanol has been illustrated earlier in sub-Sec. 4.2.1. Thus, to vaporise such a compound, hydrogen bonds between the molecules must be broken. This requires energy which is manifested as the unusually high boiling point for such compounds.

The hydrogen bonding as shown for ethanol is known as **intermolecular hydrogen bonding** which means that the hydrogen bonds are present **between** the molecules.



2-hydroxybenzaldehyd
b.p. 470 K



4-hydroxybenzaldehyde
b.p. 523 K

Hydrogen bonding can also occur within the same molecule in which case it is called **intramolecular hydrogen bonding**. Thus, 2-hydroxybenzaldehyde shows **intramolecular** hydrogen bonding whereas its *p*-isomer, 4-hydroxybenzaldehyde can form only **intermolecular** hydrogen bonds.

The increased intermolecular attraction due to intermolecular hydrogen bonding is reflected in the higher boiling point for 4-hydroxybenzaldehyde as compared to 2-hydroxybenzaldehyde in which this intermolecular interaction is absent.

Hydrogen bonding is also important in other ways. As we shall see in the next subsection, hydrogen bonding plays an important role in the solubility of organic compounds.

4.2.4 Solubility

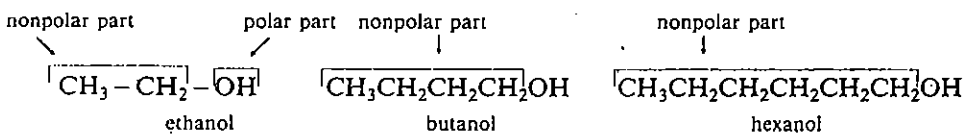
When any substance dissolves in a solvent, its constituent ions or molecules get separated from each other and the space between them is filled by solvent molecules. This is known as *solvation* and the amount of substance dissolved in a certain amount of solvent is referred to as its *solubility* in that solvent. Solubility, thus depends on the interactions between solute–solute, solute–solvent and solvent–solvent molecules. Clearly strong solute–solvent molecular interactions as compared to those of solute–solute or solvent–solvent molecules will lead to dissolution of the solute.

Similar to the processes of melting or boiling, dissolution of a substance also requires that the interionic or intermolecular forces of attraction between the ions or molecules must be overcome. The strong electrostatic forces between the ions of an ionic compound can be overcome by the solvents which have high dielectric constant. Thus, water which has a high dielectric constant of 80, dissolves ionic compounds readily whereas solvents like carbon tetrachloride (ϵ = 2.2) or ether (ϵ = 4.4) are extremely poor solvents for such compounds. Hence, ionic compounds have greater solubility in *polar* solvents.

The dielectric constant, ϵ, of a solvent measures its ability to separate the ions of the solute.

The term **polar** has double usage in organic chemistry. When we refer to a **polar** molecule, we mean that it has a significant dipole moment, μ. But, when we talk about a **polar solvent**, we understand that it has a high dielectric constant, ϵ. Thus, the dipole moment is the property of individual molecules whereas solvent polarity or dielectric constant is a property of many molecules acting together.

In determining the solubility of covalent compounds, the rule of thumb is **like-dissolves-like.** Since water is a polar compound, it is a good solvent for polar compounds, but is a poor solvent for hydrocarbons which are nonpolar in nature. Thus, the hydrocarbons readily dissolve in other hydrocarbons or in nonpolar solvents such as benzene, ether or tetrahydrofuran. As most organic compounds have both a polar and a nonpolar part, their solubility will depend upon the balance between the two parts. Consider the solubilities of three alcohols, ethanol, butanol and hexanol in water, as given below:



	ethanol	butanol	hexanol
Solubility :	miscible with water in all proportions	7.9 g in 1 dm^3 of water	5.9 g in 1 dm^3 of water

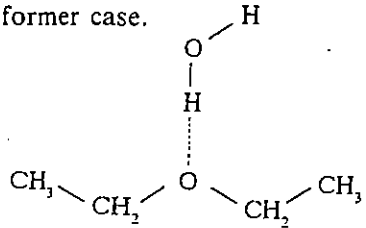
Solvent ether refers to diethyl ether.

Tetrahydrofuran, is abbreviated as THF.

1 dm^3 = 1 litre

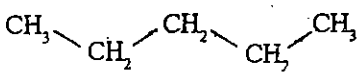
You can notice that as the size of the nonpolar portion of the molecule increases, its solubility in water decreases.

The solubility of organic compounds in water also depends on the extent of hydrogen bonding possible between the solute and the solvent (water) molecules. For example, the greater solubility of ether in water as compared to that of pentane (in water) can be accounted on the basis of hydrogen bonding present in the former case.



diethyl ether

solubility : 75 g in 1 dm^3 of water



pentane

0.36 g in 1 dm^3 of water

1 dm^3 = 1 litre

Since the olefinic, acetylenic or benzenoid character does not affect the polarity much, the solubility of unsaturated and aromatic hydrocarbons in water is similar to that of alkanes. In compounds like ethers, esters, aldehydes, ketones, alcohols, amides, acids and amines, solubility in water depends on the length of the alkyl chain and the members containing less than five carbon atoms in the molecules are soluble in water.

Polymers have high molecular weight.

Increase in the intermolecular forces in a solute, as a result of increase in the molecular weight, is also reflected in the low solubility of compounds having high molecular weight. For example, glucose is soluble in water but its polymer, starch is insoluble in water. Thus, in a homologous series, the solubility of the members decreases with the increase in molecular weight. However, branching of the carbon chain leads to a decrease in the intermolecular forces. Hence, the branched chain isomer is more soluble as compared to the straight chain isomer.

Apart from other factors discussed above, solubility of a compound in a given solvent generally increases with temperature.

Sometimes high solubility of a compound is observed due to a chemical reaction which acts as a driving force. One such category of reactions is acid-base reactions. For example, the higher solubility of aniline in aqueous acid is due to the formation of anilinium ion.

$$H_3O^+ + \underset{\text{aniline}}{C_6H_5NH_2} \rightleftharpoons \underset{\substack{\text{anilinium}\\ \text{ion}}}{C_6H_5\overset{+}{N}H_3} + H_2O$$

Although determination of the physical properties such as those discussed above helps in the identification of organic compounds, physical methods involving the use of spectroscopy allow determination of the molecular structure much more rapidly and nondestructively using small quantities of material. There are many kinds of spectroscopic methods available, but we will restrict our discussion only to **ultraviolet spectroscopy, infrared spectroscopy, nuclear magnetic resonance spectroscopy and mass spectrometry** because these are used most frequently in organic chemistry. In this unit, we will study each one of these in detail. But before studying the next section, answer the following SAQ to check your understanding about the relationship between the physical properties and molecular structure.

SAQ 1

Classify the following statements as **true** or **false.**

i) London forces are the only forces operating between polar molecules.

.....

ii) Within a homologous series, increase in molecular weight leads to decrease in the melting point.

.....

iii) Highly symmetrical molecules have unusually high melting points.

.....

iv) The shape of a molecule does not affect its boiling point.

.....

v) Polar compounds generally boil at higher temperatures as compared to the nonpolar compounds.

.....

vi) Hydrogen bonding increases the water solubility.

.....

4.3 GENERAL IDEAS ABOUT SPECTROSCOPY

Before studying the various kinds of spectroscopic techniques in detail, let us refresh our knowledge of some of the concepts you studied in Units 1, 7 and 8 of Atoms and Molecules course.

You are already aware that **spectroscopy** is the study of the interaction of matter and energy, or more generally, the electromagnetic radiation. You may recall that the **energy, frequency and wavelength** of electromagnetic radiation are related by the following expression:

$$E = h\nu = \frac{hc}{\lambda} \qquad \ldots(4.1)$$

Remember that
(i) the frequency is inversely proportional to the wavelength, and
(ii) the energy is proportional to the frequency.

where E is the energy, ν is the frequency and λ is the wavelength of electromagnetic radiation whereas h is Planck's constant and has the value 6.626×10^{-34}, Js. Here, c is the velocity of light and is equal to 2.998×10^{8} m s^{-1}

The total range of electromagnetic radiation is called the **electromagnetic spectrum.** There are various types of radiations within the electromagnetic spectrum which are shown in Fig. 4.4.

Description	Wavelength Range	*Wave Number* cm^{-1}	*Frequency* Hz	*Energy* kJ mol^{-1}
Radio frequency	3×10^{3} m	3.33×10^{-6}	10^{5}	3.98×10^{-8}
	0.30 m	0.0333	10^{9}	3.98×10^{-4}
Microwave	0.0006 m (600 μm)	16.6	4.98×10^{11}	0.191
Far infrared	30 μm	333	10^{13}	3.98
Near infrared	0.8 μm	1.25×10^{4}	3.75×10^{14}	149.8
Visible	(800 nm) 400 nm)	2.5×10^{4}	7.5×10^{14}	299.2
Ultraviolet	150 nm	6.66×10^{4}	19.98×10^{14}	795
Vacuum ultraviolet	5 nm	2×10^{6}	6×10^{16}	2.39×10^{4}
X rays and Y rays	10^{-4} nm	10^{11}	3×10^{21}	1.19×10^{9}

1 millimetre = 1 mm = 10^{-3} m

1 micrometre = 1 μm = 10^{-6} m

1 nanometre = 1 nm = 10^{-9} m

1 picometre = 1 pm = 10^{-12} m = 0.01 Angstrom Unit = 0.01 Å

Fig. 4.4 : The Electromagnetic Spectrum

The most common type of spectroscopy used for structure determination of organic compounds is **absorption spectroscopy.** You are already aware from Unit 7, Block 1 of Atoms and Molecules course that absorption spectroscopy is based on the absorption of energy from certain regions of electromagnetic radiation by molecules. Since the different regions of electromagnetic radiation have different energies, the absorption of energy from different regions of electromagnetic radiation leads to different forms of spectroscopy as is shown in Fig. 4.4. Such an absorption of energy can be determined using an instrument called a **spectrophotometer** and is expressed either in terms of wavelength or frequency or wavenumber. The components of such a spectrophotometer are shown in Fig. 4.5.

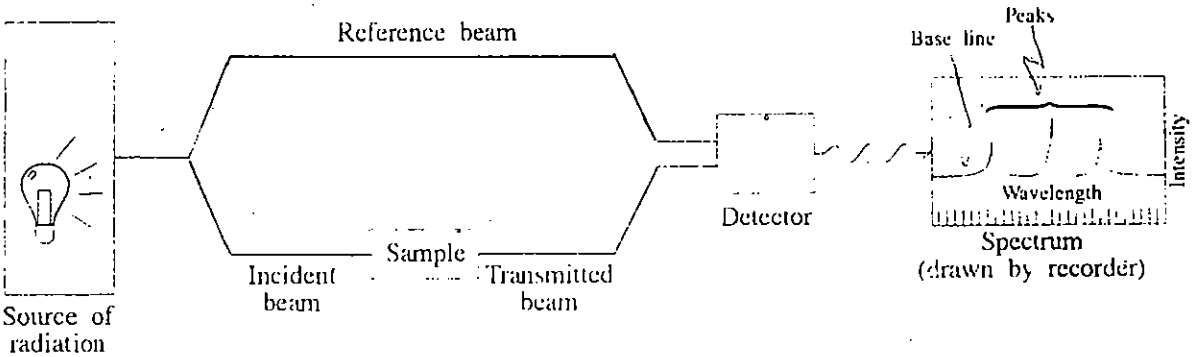


Fig. 4.5 : A schematic diagram of spectrophotometer.

Spectrum is a Latin word meaning *appearance* and it refers to the appearance of characteristic recorded lines.

As is illustrated in the figure, a source of electromagnetic radiation is required. The **sample** is placed in the radiation beam and the intensity of radiation absorbed by the sample is measured by the **detector.** Then, the wavelength (or frequency) of the radiation is varied and the radiation absorbed at each wavelength is recorded as a graph of either radiation transmitted or radiation absorbed versus the wavelength or the frequency. This graph is called the **spectrum** of the sample.

When a molecule is exposed to electromagnetic radiation, it absorbs energy corresponding to certain specific wavelengths, thereby passing from the lower energy level to the higher energy level. The particular quantity of energy absorbed by the molecule depends on the molecular structure and hence, it indicates the presence of a structural feature capable of absorbing that particular package of energy.

Many different kinds of excitations are possible in a molecule depending upon the amount of energy absorbed, which in turn is determined by the energy of the incident electromagnetic radiation. For example, the absorption of ultraviolet and visible radiation can move valence-shell electrons, particularly from a filled bonding molecular orbital to a vacant antibonding molecular orbital. Similarly, absorption of radiation from the infrared region can cause vibrational changes in the molecular framework. However, the absorption of radio waves can reorient nuclear spins and change the magnetic properties of certain atomic nuclei. This phenomenon forms the basis of nuclear magnetic resonance spectroscopy. The fourth kind of spectroscopic technique, i.e., mass spectrometry is fundamentally different from UV, IR and NMR spectroscopy in the sense that it is not an absorption spectroscopy.

As each of these methods yields a different kind of information about molecular structure, let us now study what the ultraviolet spectroscopy can tell us.

4.4 ULTRAVIOLET SPECTROSCOPY

Since the absorption of energy corresponding to the ultraviolet and visible regions of the electromagnetic spectrum results in the transitions between electronic energy levels of the molecule, the ultraviolet and visible spectroscopy is collectively also known as **electronic spectroscopy.**

The position of absorption in the uv and visible spectra is expressed in the units of 10^{-9} m or nanometer (nm).

The ultraviolet and visible regions range from the wavelength 200 nm to 400 nm and 400 nm to 800 nm, respectively. The absorption of energy in this region results in the transfer of electron(s) from bonding and nonbonding orbitals to antibonding orbitals. Hence, the wavelength of the light absorbed will depend upon the energy difference between the ground state and the excited state of the molecule. This difference will in turn indicate the energy difference between the orbitals of the molecule. For example, in saturated hydrocarbons which contain C-C and C-H single bonds, the possible electronic transitions are from σ bonding orbitals to σ^* antibonding orbitals. Since the energy required for these transitions is high, radiation of higher energy or very low wavelengths, i.e. below 200 nm are required for these transitions to take place. For recording the spectrum in this range of the electromagnetic spectrum, air has to be removed because it also absorbs radiation below 200 nm; therefore, this region is known as **extreme** or **vacuum ultraviolet spectral region.** On the other hand, molecules containing *pi* bonds can undergo $\pi \rightarrow \pi^*$ transitions, as shown in Fig. 4.6. Electronic transitions involving nonbonding electrons are also possible in which case the nonbonding electrons can be excited to σ^* and π^* higher energy states. The $n \rightarrow \pi^*$ transitions occur commonly in compounds containing double bonds involving the heteroatoms such as oxygen, sulphur and nitrogen. For example, the compounds containing the structural units such as >C=O, >C=S and >C=N show $n \rightarrow \pi^*$ transitions.

$\pi \rightarrow \pi^*$ is read as *pi* to *pi* star.

As is evident from Fig. 4.6, various transitions can be arranged in the decreasing order of their energy as shown below.

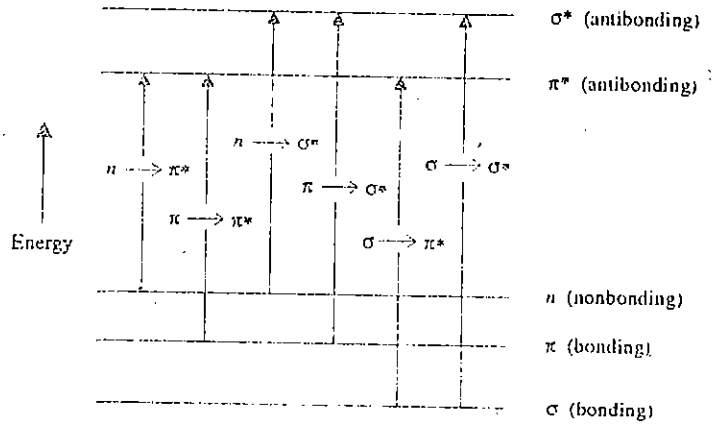


Fig. 4.6 : Energy changes associated with various possible electronic transitions in a molecule.

$$\sigma \rightarrow \sigma^* > \sigma \rightarrow \pi^* \sim \pi \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

The structrual units associated with these transitions are called **chromophores.** Some of the important chromophores include the unconjugated chromophores of the type, C=C, C≡C, C=O, C≡N and the conjugated ones such as C=C–C=C, C=C–C=O and benzene.

Originally, the term *chromophore* was used to denote the system responsible for imparting colour to a compound. In Greek, **chromophorous mean colour carrier.**

Here you may ask, is there any difference between the UV spectra of conjugated and unconjugated molecules and if there is a difference, what is the effect of conjugation on the wavelength of radiation absorbed? Before studying these aspects, it is necessary that you know how a UV spectrum looks like and what information about molecular structure is available from it. To understand this, look at the UV spectrum of 2-methyl-1,3-butadiene as shown in Fig. 4.7. You can see in the figure that the horizontal axis shows the **wavelength,** λ, of the ultraviolet

Multiple bonds which are separated from each other by a single bond are said to be *conjugated*. Compounds containing conjugated bonds have unique structures and chemical properties about which you will study in Units 7 and 9 of Block 2 of this course.

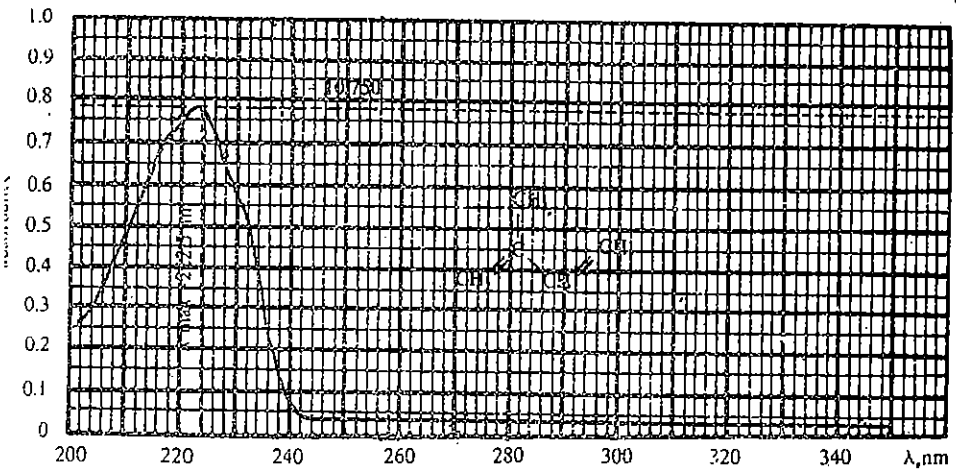


Fig. 4.7 : Ultraviolet spectrum of 2-methyl-1,3-butadiene in methanol.

radiation and the vertical axis shows **absorbance,** A. The absorbance is a measure of the amount of radiant energy absorbed. If a radiation having the intensity I_0 enters the sample and the radiation leaving the sample has the intensity, I, then the absorbance, A, is given by the log of the ratio I_0/I. Thus,

Absorbance is also known as optical density.

$$A = \log\left(\frac{I_0}{I}\right) \qquad \ldots(4.2)$$

Hence, the larger the ratio I_0/I, the greater is the absorbance and the more is the radiant energy absorbed. The wavelength at which the absorption is maximum is referred to as λ_{max} of the sample. As shown in Fig. 4.7, for 2-methyl-1,3-butadiene, λ_{max} is 222.5 nm.

λ_{max} **is read as lambda-max.**

As the absorbance at a given wavelength depends on the number of molecules present in the path of the radiation, it is proportional to the concentration, c expressed in moles dm^{-3}) of the solution multiplied by the path length, l, i.e.,

$$A \propto cl$$

or $A = \epsilon cl \qquad \ldots(4.3)$

where the constant of proportionality, ϵ, is called the **molar absorptivity** or **molar extinction coefficient.** It is a measure of the probability of the transition. The molar extinction coefficient has characteristic value for each absorption of the compound. Hence, quantitative determination of ultraviolet spectrum requires the specification of both λ_{max} and ϵ values. Since both λ_{max} and ϵ values are affected by the solvent, the solvent used for measurement is also to be indicated while reporting the ultraviolet spectral data. Hence, the description of the uv spectrum of 2-methyl-1,3-butadiene will be given as λ_{max} = 222.5 nm (ϵ = 10,750), in methanol.

Note that the ϵ has been used earlier to denote the dielectric constant also.

We are now in a position to interpret the uv spectral data for some alkenes given in Table 4.1.

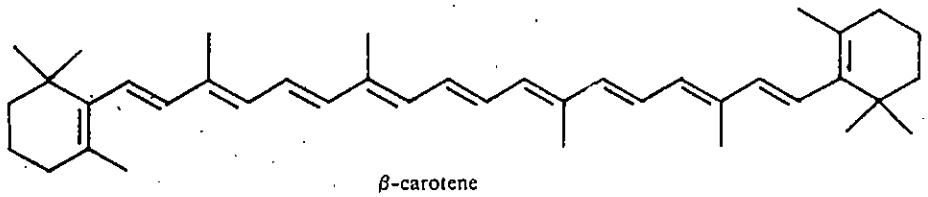
Substitution of A from Fig. 4.2 into Eq. 4.3 yields $\log (I_0/I) = \epsilon cl$ or $\epsilon = A/cl$ which is the expression for *Beer-Lambert law.* You can refer to Sec. 8.11 of Unit 8, Block 2 of Atoms and Molecules course where Beer-Lambert law was discussed in detail.

Table 4.1. : UV Absorptions for some alkenes.

Alkene	λ_{max}	$\epsilon/m^2\ mol^{-1}$
$CH_2=CH_2$	175	15,000
	178	not known
	217	21,000
	222.5	10,750
	268	34,600

The λ_{max} for ethene which has one double bond, was found to be 175 nm. You can compare the λ_{max} value of 1,4-pentadiene which is equal to 178 nm with that of 1,3-butadiene or 2-methyl-1,3-butadiene which have λ_{max} 217 nm and 222.5 nm, respectively. Note that all the three compounds have two double bonds which are isolated or nonconjugated in case of 1,4-pentadiene but are conjugated in 1,3-butadiene and 2-methyl-1,3-butadiene. Thus, conjugated molecules absorb at longer wavelengths as compared to the nonconjugated ones. Further extension of conjugation, as in 1,3,5-hexatriene leads to a λ_{max} value of 268. Hence, **the longer the conjugated system, the higher will be the λ_{max} value.** And, if in a molecule, the conjugation is large enough to yield a large λ_{max} value which lies in the visible region of the spectrum, then the compound will appear coloured. For example, β-carotene (which imparts red colour to carrots and is also a precursor of vitamin A) has 11 conjugated double bonds and λ_{max} value of 497 nm.

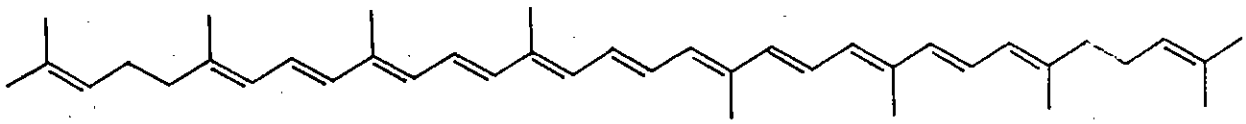
Conjugation increases wavelength of absorption by decreasing the energy difference between the ground and excited states.



β-carotene

In general, polyenes containing eight or more conjugated double bonds absorb light in the visible region of the spectrum.

Light of wavelength 497 nm has a blue-green colour and when this blue-green light is absorbed by β-carotene, we perceive the complementary colour of blue-green which is red-orange. Similarly, lycopene, a *red* pigment of ripe tomatoes which also has a conjugated system containing 11 double bonds shows λ_{max} = 505 nm which also lies in the visible region of the electromagnetic spectrum.



lycopene

When we are talking about the coloured compounds it is worthwhile to mention here about the **auxochromes.** An auxochrome can be defined as a group that can enhance the colour-imparting properties of a chromophore, although it is not a chromophore itself. Examples of auxochromes include groups of the type –OR, $-NH_2$, $-NR_2$, etc. where R denotes an alkyl group.

In addition to the conjugation, other factors such as the presence of substituent groups on the double bond and spatial arrangement of the double bonds also influence the λ_{max} value. You can see in Table 4.1 that the presence of methyl group in 2-methyl-1,3-butadiene increases the λ_{max} value by 5.5 nm as compared to that of 1,3-butadiene. Similarly, the presence of second alkyl group in 2,3-dimethyl-1,3-butadiene leads to an increase of 9 nm in λ_{max} value as compared to that of the unsubstituted compound.

4.4.1 Measurement of UV spectrum

The ultraviolet-visible spectrum of a compound can be recorded using an instrument called ultraviolet-visible spectrophotometer. The components of a UV-visible spectrophotometer are shown in Fig. 4.8 but here we will not go into the details of instrumentation. As the figure shows, the source of ultraviolet-visible

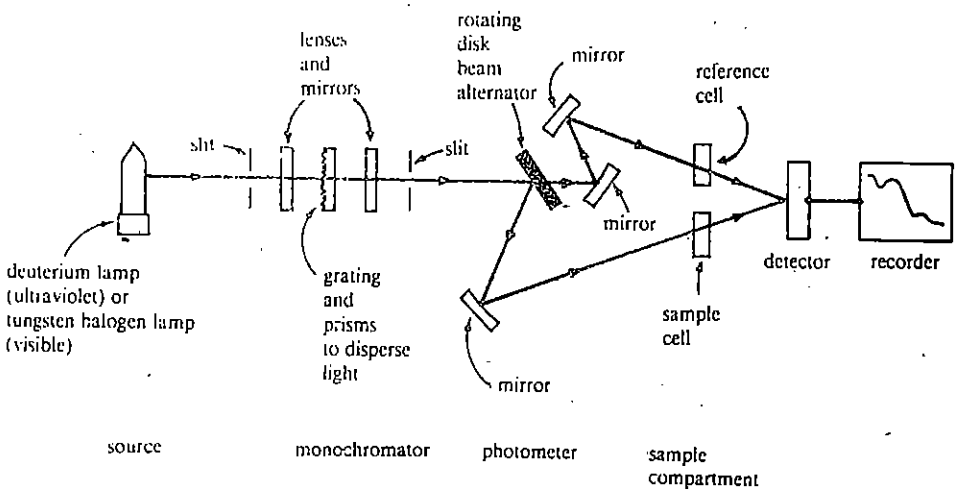


Fig. 4.8 : Schematic diagram of a typical ultraviolet-visible spectrophotometer.

spectrophotometer contains a tungsten filament lamp which gives the radiation having wavelength greater than 375 nm and a deuterium discharge lamp which yields the radiation of wavelengths below this value.

The spectrum is usually recorded using a very dilute solution of the sample. The sample solution is taken in cells which are made of quartz or silica. The cells of different path lengths, i.e., 0.1 cm, 1 cm and 10 cm are commercially available but for most of organic work, cells of 1 cm path length are employed. Two cells, one containing the sample solution and the other containing the pure solvent, are placed at appropriate places in the spectrophotometer. Two beams of equal intensity of uv radiation are passed through these cells. The intensities of the transmitted beams are then compared over the whole range of wavelength of the instrument which gives the absorbance at each wavelength. On most machines, the spectrum is automatically plotted by a recorder as absorbance versus wavelength.

While preparing the sample solution for recording the UV spectrum, the solvent must be so chosen that it should be transparent to the wavelength range being examined. Usually cyclohexane, 95% ethanol and 1,4 dioxane are used as solvents. Cyclohexane can be used for dissolving aromatic compounds particularly the polynuclear aromatic compounds. But when a polar solvent is required 95% ethanol or absolute ethanol is a good choice. Many **spectral grade** solvents are also commercially available.

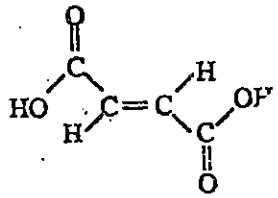
Absolute ethanol or anhydrous ethanol is a very pure alcohol and is obtained by further drying of the 95% ethanol.

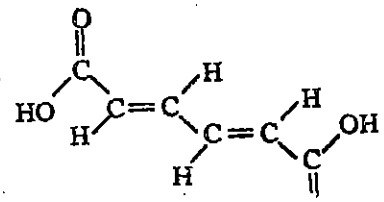
When the spectrum is recorded in different solvents, it may lead to a change in the position or in the intensity of the absorption band. This is known as **solvent effect.** When the shift is towards **longer** wavelength, it is known as **bathochromic shift or red shift.** When the shift is towards **shorter** wavelength, it is called **hypsochromic shift** or **blue shift.** Similarly, the increase in absorption intensity is called **hyperchromic effect** and the decrease in absorption intensity is known as **hypochromic effect.** The UV spectral data for various classes of compounds will be discussed in the respective units of this course.

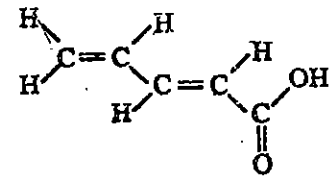
You can now check your understanding about ultraviolet spectroscopy by answering the following SAQ.

SAQ 2

Identify the chromophore present in the following compounds. Also predict which one of these will have the highest λ_{max} in uv spectra?

a) 

b) 

c) 

4.5 INFRARED SPECTROSCOPY

Infrared means beneath the red.

Wavenumber is denoted as $\bar{\nu}$.

Many scientists prefer to use the wavenumber convention because it is directly proportional to energy and frequency.

Wavenumber, $\bar{\nu}$, is inversely proportional to the wavelength, λ, and the relationship between the two can be expressed as,

$\bar{\nu} = 1/\lambda$ when λ is expressed in centimetres, and

$\bar{\nu} = \frac{10^4}{\lambda}$, when λ is expressed in micrometres.

The region of wavenumbers lower than 625 cm^{-1} is called **far infrared** and that of wavenumbers higher than 4000 cm^{-1} is called **near-infrared**.

The infrared region of the electromagnetic spectrum lies between the visible and the microwave region. Hence, it corresponds to the range of wavelength from about 10^{-4} to 10^{-6} m. But the portion of infrared spectral region which is most useful for structure determination, lies between 2.5×10^{-6} m and 16×10^{-6} m. The IR spectral data is usually expressed either in terms of **wavelength** of the radiation absorbed in micrometre units or in terms of **wavenumber.** Since one micrometre (μm) is equal to 10^{-6} m, the above region of infrared spectrum range from 2.5 to 16 μm. As wave number is the number of wavelengths contained in one centimetre therefore, wavenumbers are expressed in units of reciprocal centimetres (cm^{-1}). Hence, we can calculate the wavenumbers for the region of IR radiation we are interested in, as shown below:

For $\lambda = 2.5 \times 10^{-6}$ m or 2.5×10^{-4} cm, we get,

$$\text{wave number, } \bar{\nu} = \frac{1}{\lambda} = \frac{1}{2.5 \times 10^{-4}(\text{cm})} = \frac{1}{2.5} \times 10^4 \text{ cm}^{-1} = 4000 \text{ cm}^{-1}$$

Similarly, $\lambda = 16 \times 10^{-6}$ m or 16×10^{-4} cm yields $\bar{\nu} = \frac{1}{16 \times 10^{-4}\ (\text{cm})}$

$$= \frac{1000}{16} \text{ cm}^{-1}$$

$$= 625 \text{ cm}^{-1}.$$

Thus, we will be examining the infrared region between wavenumbers 625 cm^{-1} and 4000 cm^{-1}. An advantage of using wavenumbers is that they are directly proportional to the energy whereas the wavelength is inversely proportional to energy.

Let us now study the effect of absorption of IR radiation on molecular structure.

Atoms within a molecule are constantly vibrating about their average positions; such motions are referred to as **molecular vibrations.** The molecular vibrations can be of various types. One such vibration which produces changes in bond length is called a **stretching vibration.** The other type that changes bond angles is called a **bending vibration.** Fig. 4.9 shows various kinds of stretching and bending vibrations,

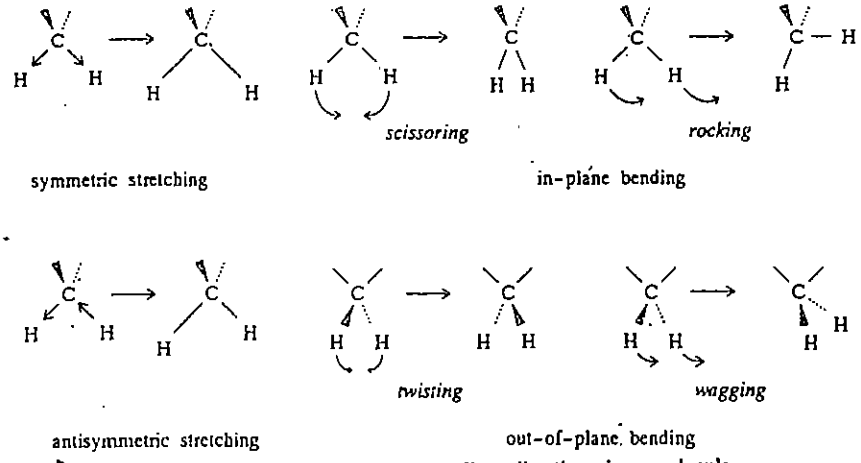
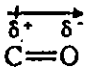


Fig. 4.9 : The stretching and bending vibrations in a molecule.

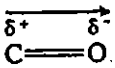
A nonlinear molecule having n number of atoms has $3n-6$ possible modes of vibration.

The absorption of infrared radiation leads to changes in the vibrational states of the molecule. A number of different vibrational states are possible for a molecule. When radiation having energy equal to the energy difference between molecular vibrational energy levels is absorbed, the amplitude of these vibrations increases and the molecule moves from the lower vibrational energy level to the higher vibrational energy level.

Not all molecules absorb the infrared radiation. Generally, the absorption of the infrared radiation, corresponding to a particular vibration, is observed only if the dipole moment of the molecule is different in the two vibrational states. This is because the variation of the dipole moment and a change in the interatomic distance due to vibration, results in an oscillating electric field which can interact with the oscillating electric field of the incident infrared radiation. Hence, a vibrational transition will be **infrared-active** only if it is accompanied by a change in the dipole moment. For example, in case of carbonyl functional group, the stretching vibration leads to an increase in dipole moment. Hence, it is infrared active and the carbonyl group absorbs radiation in the infrared region. On the other hand, vibrational transitions that do not result in a change of the dipole moment are not observed in the infrared spectrum and are said to be infrared-inactive. Hence, symmetrical molecules such as H_2, O_2 etc., do not absorb the infrared radiation.

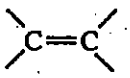


polar bond in carbonyl group

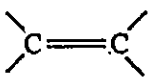


increase in dipole moment on stretching of bond in carbonyl group

intense absorption



nonpolar carbon-carbon double bond



small or no change in dipole moment on stretching the carbon-carbon double bond

absortion absent or weak

The vibrational changes of a diatomic molecule can be visualised using the vibrating spring as a model, as shown in Fig. 4.10.

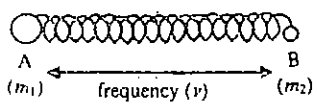


Fig. 4.10: A vibrating spring: a model for vibrational excitation of a bond in a diatomic molecule.

The two unequal weights on the spring are analogous to two atoms A and B held together by a bond (spring). The vibrational frequency for such a system depends upon the strength of the bond and masses of the atoms involved in the bond formation. The mathematical expression for vibrational frequency, as governed by Hooke's law is given below:

$$\nu = \frac{1}{2\pi}\sqrt{\left(\frac{k}{m_1 m_2/(m_1+m_2)}\right)} \qquad \ldots(4.4)$$

The higher the bond energy, the stronger the bond, and the greater is the force constant. The greater the force constant, the larger is the vibrational frequency.

where ν is the vibrational frequency, k is force constant and m_1 and m_2 are the masses of two atoms A and B, respectively.

Remember that
$E = h\nu = hc/\lambda = hc\bar{\nu}$
You have studied these relationships as Eq. 7.2 in Unit 7, Block 2 of Atoms and Molecules course.
Therefore, $h\nu = hc\bar{\nu}$ and
$\nu = c\bar{\nu}$ or $\bar{\nu} = \nu/c$

The quantity $\frac{m_1 m_2}{(m_1 + m_2)}$ is also known as the reduced mass, μ, of the system.

Substituting μ for $m_1 m_2/(m_1 + m_2)$ in Eq. 4.4 and expressing it in terms of wavenumber, $\bar{\nu}$, we get,

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \ldots(4.5)$$

where c is the velocity of light.

Since force constant varies with the bond strength, Eq. 4.5 leads us to expect that every individual bond in a molecule will show a specific absorption band in the infrared spectrum. Hence, different functional groups will absorb at different frequencies corresponding to the vibrations typical of that portion of a molecule. Thus, infrared spectral data can be used to identify various functional groups present in the molecule. The characteristic infrared absorption data for some common structural units are listed in Table 4.2. However, a detailed interpretation for the position of infrared absorptions for various classes of compounds will be given in the respective units dealing with them.

Table 4.2 : Characteristic Infrared Absorption Bands.

Bond Type	Stretching, cm^{-1}	Bending, cm^{-1}
C – H alkanes	2960 – 2850 (*s*)	1470 – 1350 (*s*)
C – H alkenes	3080 – 3020 (*m*)	1000 – 675 (*s*)
C – H aromatic	3100 – 3000 (*v*)	870 – 675 (*v*)
C – H aldehyde	2900, 2700 (*m*, 2 bands)	
C – H alkyne	3300 (*s*)	
C ≡ C alkyne	2260 – 2100 (*v*)	
C ≡ N nitrile	2260 – 2220 (*v*)	
C = C alkene	1680 – 1620 (*v*)	
C = C aromatic	1600 – 1450 (*v*)	
C = O ketone	1725 – 1705 (*s*)	
C = O aldehyde	1740 – 1720 (*s*)	
C = O α, β-unsaturated ketone	1685 – 1665 (*s*)	
C = O aryl ketone	1700 – 1680 (*s*)	
C = O ester	1750 – 1735 (*s*)	
C = O acid	1725 – 1700 (*s*)	
C = O amide	1690 – 1650 (*s*)	
O – H alcohols (not hydrogen bonded)	3650 – 3590 (*v*)	
O – H alcohols (hydrogen bonded)	3600 – 3200 (*s*, broad)	1620 – 1590 (*v*)
O – H acids	3000 – 2500 (*s*, broad)	1620 – 1590 (*v*)
N – H amines	3500 – 3300 (*m*)	
N – H amides	3500 – 3350 (*m*)	
C – O alcohols, ethers, esters	1300 – 1000 (*s*)	
C – N amines, alkyl	1220 – 1020 (*w*)	
C – N amines, aromatic	1360 – 1250 (*s*)	
NO_2 nitro	1560 – 1515 (*s*)	
	1385 – 1345 (*s*)	

s = strong absorption
m = medium absorption
w = weak absorption
v = variable absorption

Having studied the basic features of infrared spectroscopy, let us now learn how the infrared spectrum of a compound is recorded and how it really looks like.

4.5.1 Experimental Aspects of Infrared Spectroscopy

The details of an infrared spectrophotometer used for recording an infrared spectrum are shown in Fig. 4.11.

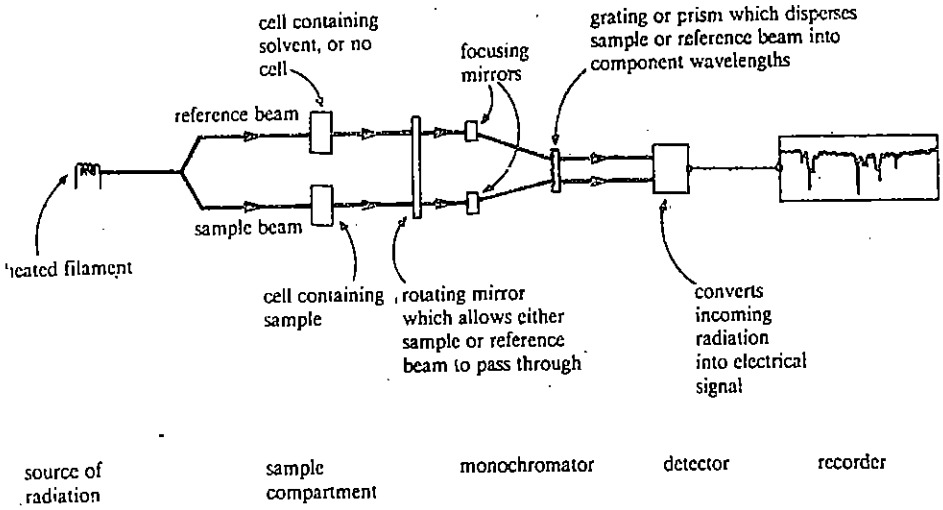


Fig. 4.11 : A schematic diagram of an infrared spectrophotometer.

Infrared radiation can be obtained by electrically heating the rods of the Nernst glower or Globar. The Nernst glower contains the oxides of zirconium, thorium and cerium while the Globar is a small rod of silicon carbide. Similar to the recording of the ultraviolet spectrum, here also the radiation is split into two equal beams, one of which passes through the sample and the other serves as a reference beam. The amount of radiation absorbed by the sample is recorded by the instrument in the form of a plot showing per cent transmittance on its vertical axis against wavenumbers plotted in cm^{-1} on the horizontal axis. The transmittance, T, of a sample is given by the ratio I/I_0 and is the per cent of the indicent radiation (i.e., radiation falling on the sample) that is transmitted to the detector. Clearly when all the radiation has been absorbed by the sample, the transmittance is 0%. On the contrary, 100% transmittance means no absorption of the radiation. Hence, the absorptions in the infrared spectrum are registered as downward deflections or the upside-down peaks. For example, the infrared spectrum of nonane as shown in Fig. 4.12 has absorptions at 2925, 1467, 1378 and 722 cm^{-1}.

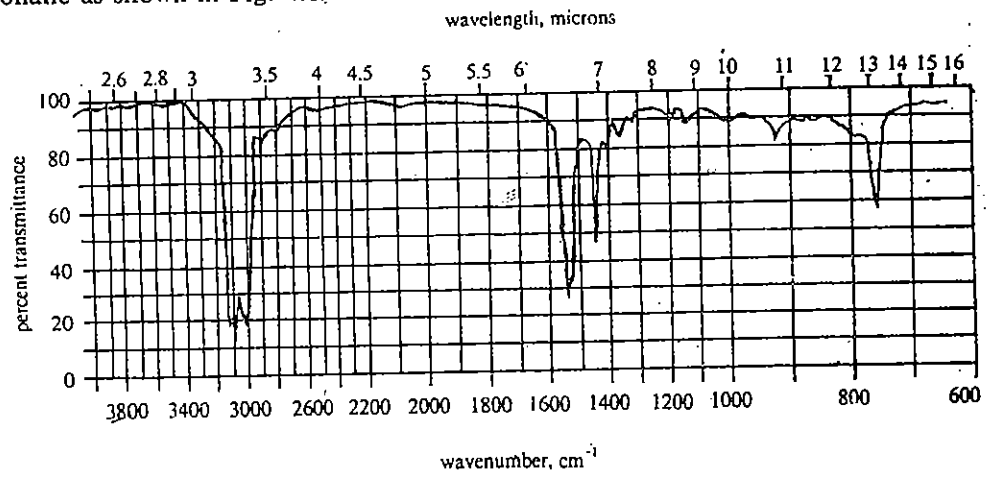
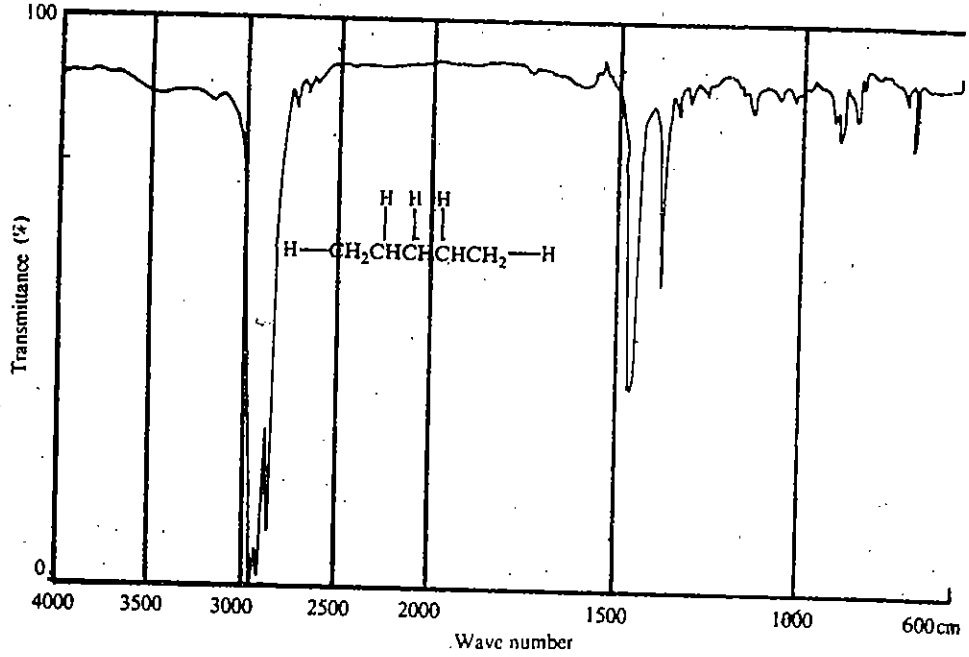
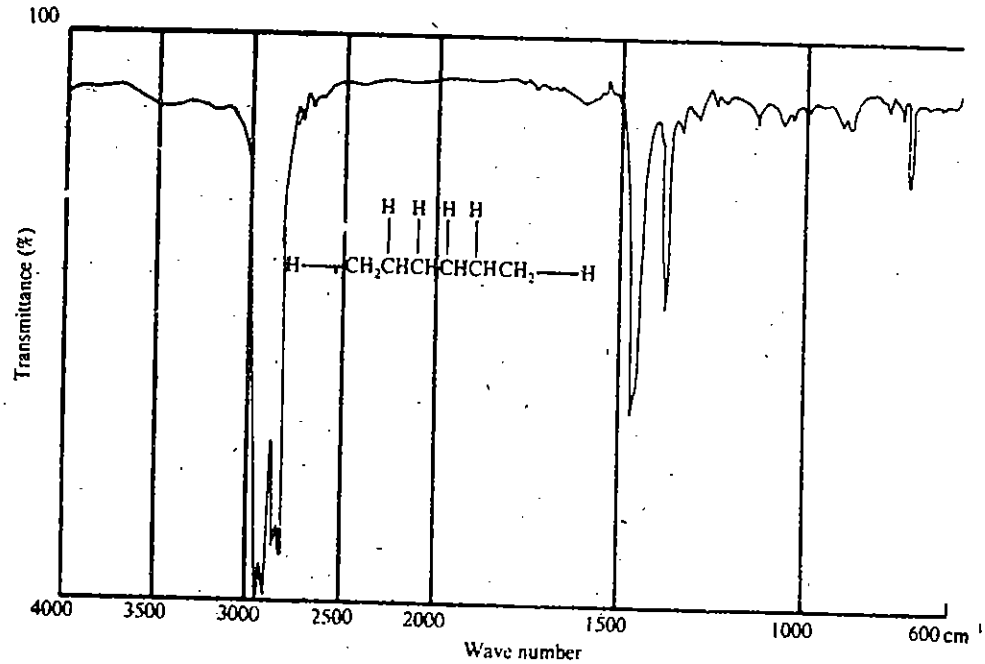


Fig. 4.12 : Infrared spectrum of nonane.

The region of infrared spectrum between 675 cm^{-1} and 1250 cm^{-1} is usually referred to as **fingerprint** region. This region shows absorptions which are quite characteristic of a particular molecule. Thus, this region is extremely useful in determining whether the given samples are identical or not. For example, the comparison of the infrared spectra for pentane and hexane (Fig. 4.13) shows that the pattern in the fingerprint region is quite different for the two compounds.

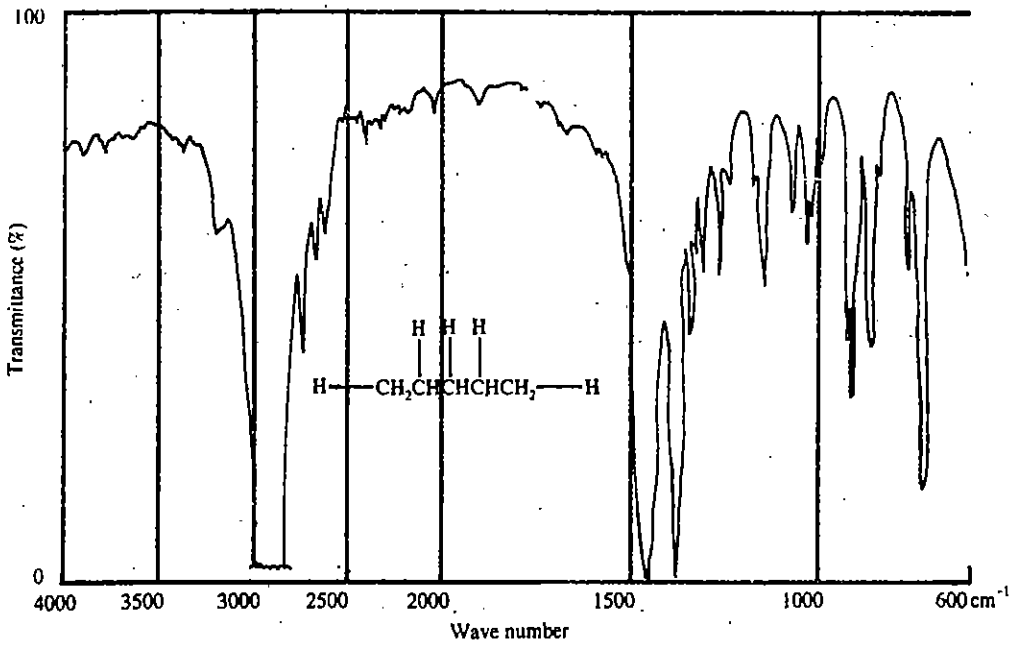


(a)

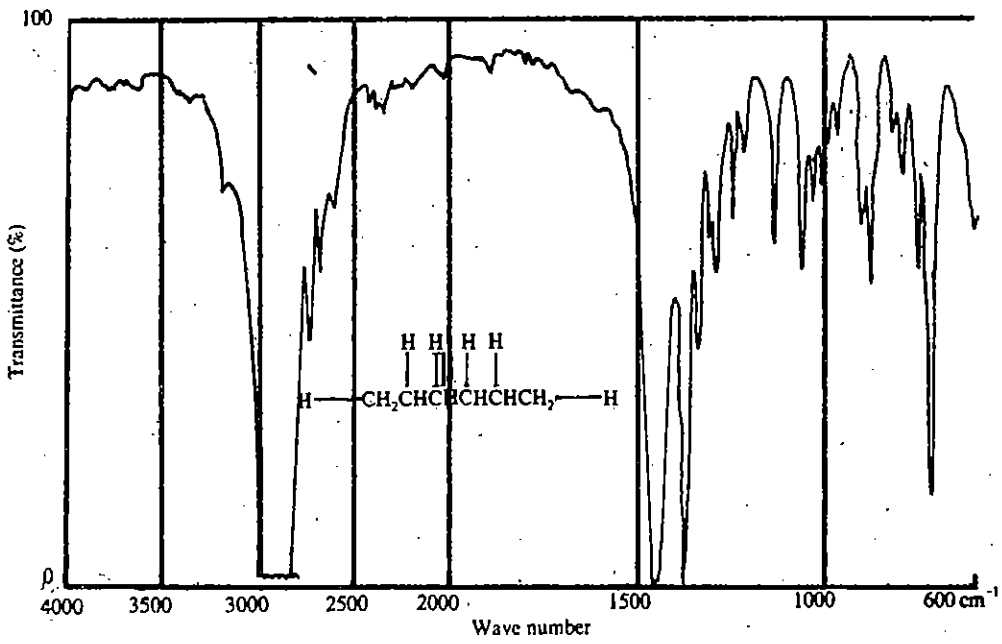


(b)

Fig. 4.13 : (a) IR spectrum of $\bar{\nu}_{\text{C-H stretch}}$ = 2960, 2930 and 2870 cm^{-1} $\bar{\nu}_{\text{C-H bend}}$ = 1460, 1380 and 730 cm^{-1} (b) IR spectrum of hexane. Note the similarly of the location of the major bands to those in the IR spectrum of pentane.



(c)



(d)

Fig. 4.13 : (c) IR spectrum of a sample of pentane at higher recorder sensitivity. Note that the fingerprint pattern is different from the pattern in the analogous spectrum of hexane. (d) IR spectrum of a sample of hexane at higher recorder sensitivity.

The infrared spectrum can be recorded on samples in solid, liquid, gaseous or solution state. For solid samples, generally, a Nujol mull or KBr disc is prepared. In case of liquid samples, a thin film of liquid is used between two infrared-transparent windows made of NaCl flats. For gases or low-boiling liquids, the spectrum can be obtained by using gas cells. The spectrum of a sample in the solution state is recorded by making 1–5% solution of the compound in solvents such as carbon tetrachloride, carbon disulphide or chloroform. These solvents have relatively few IR absorptions. Let us now end our discussion about IR spectroscopy. You will study the IR spectra of various compounds in the further blocks of this course.

Nujol is a high boiling petroleum oil.

KBr discs are prepared by grinding the sample (0.1–2% by weight) with dry KBr and processing it into a disc in a die.

KBr and NaCl do not absorb IR radiation.

Before proceeding to the next section which describes another type of spectroscopy, called nuclear magnetic resonance spectroscopy, answer the following SAQ.

SAQ 3

Which of the following vibrations will be infrared active and which would be infrared inactive?

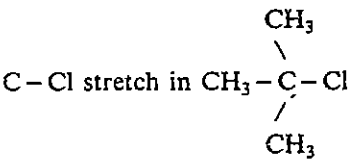
a) C=O stretch in $(CH_3)_2C=O$

.....

b) C≡C stretch in $C_2H_5-C\equiv C-C_2H_5$

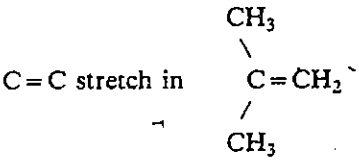
.....

d) C–Cl stretch in



.....

d) C=C stretch in



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4.6 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The physical significance of nuclear spin is that the nucleus acts like a tiny magnet and tends to become aligned in a magnetic field.

Nuclear magnetic resonance (nmr) spectroscopy is one of the most useful methods for structure elucidation. It was first observed in 1946 and is based on the magnetic properties exhibited by certain nuclei. Many atomic nuclei behave as if they are spinning and hence are said to have **nuclear spin.** The circulation or spinning of the nuclear charge generates a magnetic dipole whose magnitude is given by the nuclear magnetic moment. These magnetic properties occur in nuclei which have

i) odd atomic and odd mass numbers; examples being $^{1}_{1}H$, $^{15}_{7}N$, $^{19}_{9}F$ and $^{31}_{15}P$,

ii) odd atomic number and even mass number; for example, $^{2}_{1}H$ and $^{14}_{7}N$, and

iii) even atomic number and odd mass number as in $^{13}_{6}C$.

Similar to the electron spin, the nuclear spin is given by nuclear spin quantum number, I, which can have values 0, 1/2, 1, 3/2, 2, etc. The spin quantum number, I, has contributions both from the protons and the neutrons present in the nucleus. If the sum of the protons and neutrons is even then, I has zero or integral values, i.e., I = 0, 1, 2, ... etc. In case this sum is odd, then I has half integral values, i.e., 1/2, 3/2, 5/2 etc. But, when the number of both the protons and the neutrons is even, then, I is zero. Hence, the nuclei $^{12}_{6}C$ or $^{16}_{8}O$ do not show any resultant spin or magnetic moment and are, therefore, nonmagnetic. On the other hand, the nuclei, $^{1}_{1}H$, $^{19}_{9}F$, $^{13}_{6}C$, $^{15}_{7}N$ and $^{31}_{15}P$ have I = 1/2 and the nuclei $^{14}_{7}N$ and $^{2}_{1}H$ have I=1. The number of orientations which a nucleus may assume in the magnetic field is given by $2I + 1$. Hence, for the hydrogen nucleus, the number of possible orientations is $2\times1/2 + 1 = 2$. These two spin states are characterised by the values + 1/2 and -1/2 for the spin quantum number, I, in case of the hydrogen nucleus. Fig. 4.14 shows the two spin states of a proton.

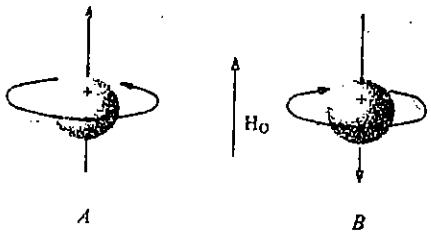


Fig. 4.14 : The nuclear spin states of a proton. Spin state A, in which the nuclear magnetic moment is parallel to the applied field H_0, is of lower energy than spin state B, in which the nuclear maganetic moment is antiparallel to the applied field.

These two spin states have the same energy in the absence of the magnetic field. However, a difference in energy between these spin states can be created by applying the magnetic field. This is illustrated in Fig. 4.15.

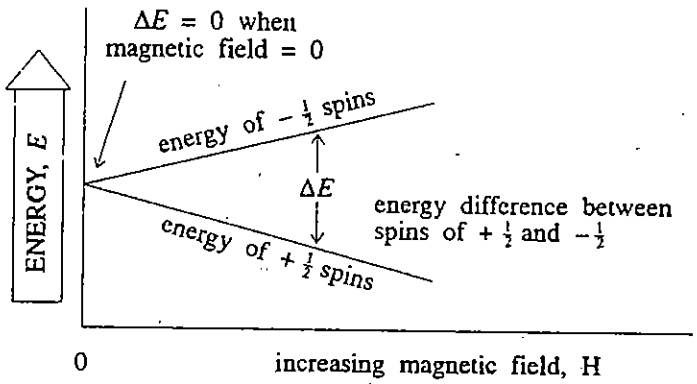


Fig. 4.15 : Effect of magnetic field on the energy difference of two nuclear spin states.

This energy difference is then detected by absorption of radiation of appropriate energy which corresponds to the radiofrequency region of the electromagnetic spectrum. The absorption of energy in this region causes these nuclei to invert or 'flip' their spins which involves a change from a lower energy state having $+1/2$ spin to higher energy state having $-1/2$ spin. When the energy of the source matches with the energy difference between the nuclear spin states, then the nuclei are said to be in **resonance** with the electromagnetic radiation.

Do not confuse this usage of the term *resonance* with the one which you will be studying in the next unit.

The energy difference between the two spin states, ΔE, can be quantitatively expressed as:

$$\Delta E = \frac{h\gamma}{2\pi} H \qquad \ldots(4.6)$$

Where h is Planck's constant, H is the magnetic field strength at the nucleus and γ is the magnetogyric ratio. Magnets varying in field strengths ranging from 1.4 τ to 7.1 τ are employed in various instruments. The corresponding frequency values needed to observe resonance lie between 60 MHz and 300 MHz. For hydrogen nuclei, when a magnetic field of 1.4 τ is applied, a radiation of frequency of 60 MHz is required. Similarly, for the magnetic field of 2.1 τ, a radiation of frequency 90 MHz is required. Since, almost all organic compounds contain hydrogens, the study of nmr spectroscopy of hydrogen nucleus is very useful to an organic chemist.

Magnetogyric ratio is the ratio of the angular momentum (due to rotating nuclear mass) and the magnetic moment (arising from the rotating nuclear charge). This ratio has a characteristic and different value for each nucleus.

The higher the applied field, the greater will be the energy difference between the two spin states of the nucleus. Therefore, the larger will be frequency of the radiation absorbed by the nuclei and hence larger will be the separation between the absorption signals leading to a higher resolution and more clear spectrum.

Before taking such an assignment, let us now learn about the instrumentation and experimental aspects of nmr spectroscopy.

4.6.1 How to Obtain an NMR Specturm?

Fig. 4.16 shows the schematic diagram of a typical nuclear magnetic resonance spectrometer. The sample to be studied is usually dissolved in a suitable solvent which itself does not absorb in the nmr range under investigation. For proton nmr, usually carbon tetrachloride or deuterated solvents such as $CDCl_3$ (deuteriochloroform), CD_3COCD_3 (hexadeuterioacetone) or C_6D_6 (hexadeuteriobenzene) are used. This solution is taken in an nmr sample tube (a cylindrical glass tube of 18 cm length and 5 mm diameter) and is placed between

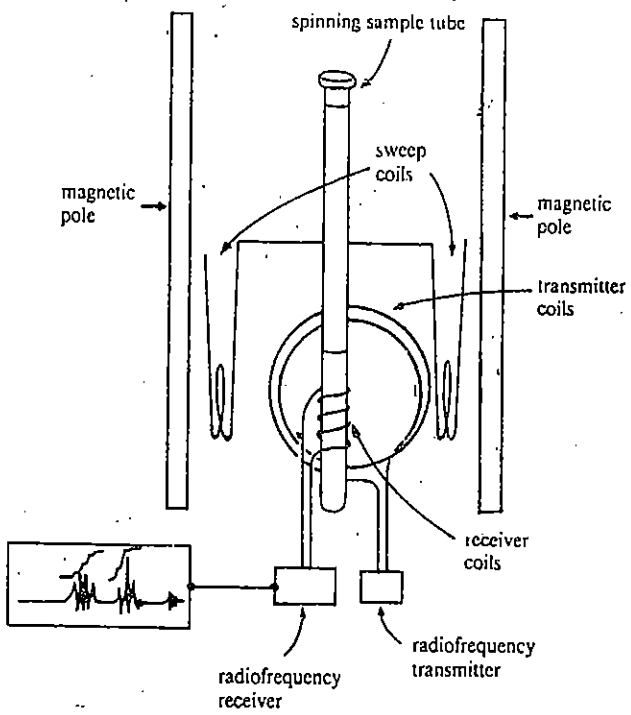
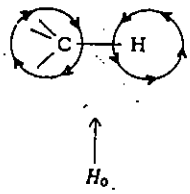


Fig. 4.16 : A schematic representation of the NMR spectrometer.

H^+
Bare proton

H — C

Proton in an organic molecule



The induced magnetic field of the electrons in the carbon-hydrogen bond opposes the external magnetic field. The resultant magnetic field experienced by the proton is slightly less than H_o.

the poles of the magnet (permanent or electromagnet). The sample is surrounded by a radio frequency source which irridiates it. Spectrometers using permanent magnets of fixed field strength involve a continuous variation of frequency of the source. When the energy of the source matches with the energy difference between the nuclear spin states, i.e., when the two are said to be in resonance with each other, then the frequency of the electromagnetic radiation which corresponds to this energy, is absorbed. The absorption of energy is detected by a radio frequency receiver and is shown as a peak in the nmr spectrum.

Nuclear magnetic resonance spectrometers which use electromagnets operate in a complementary manner. In these instruments, the frequency of the source is maintained at a constant value and the magnetic field strength is varied until the energy gap between the spin states matches with that of the source.

Let us now focus our attention on the proton nmr spectrum.

4.6.2 Interpretation of Proton NMR Spectrum

Till now, we discussed the two different spin states of a proton. But what is the actual situation in a molecule? In organic molecules, the hydrogen atom is bonded to another atom by a covalent bond. When an external magnetic field is applied, the electrons forming the covalent bond produce an induced magnetic field which opposes the applied magnetic field. Hence, the magnetic field 'felt' by the proton is less than the applied magnetic field. In other words, this hydrogen nucleus is said to be **shielded** by its electron cloud. The degree of shielding depends on the amount of electron density surrounding the nucleus. Hence, the increase in electron density around a proton results in its shielding while its decrease causes the **deshielding**. If the spectrum is recorded by keeping the radio frequency constant and varying the magnetic field, then for a shielded proton, higher magnetic field will be required to overcome the shielding effect. The protons in different electronic environments experience different amounts of shielding and hence will require different magnetic field strengths for their spin flipping. Thus, unique nmr signals will be observed for chemically different protons in a molecule. But chemically equivalent protons will appear at the same position in the nmr spectrum. The difference in the absorption position of a particular proton from the absorption position of a reference proton is called the **chemical shift** of that particular proton. Generally, the chemical shifts are recorded using the tetramethylsilane (TMS) as the reference compound. The signal due to the hydrogens of the methyl groups of TMS is set as zero while recording the nmr spectrum.

Chemically equivalent protons are those protons which are in exactly same environment. Therefore, they react exactly in the same manner with the chemical reagents. There are two sets of chemically equivalent protons in butane which are show below as a and b.

$CH_3CH_2CH_2CH_3$

a b b a

$CH_3-Si(CH_3)_3$

TMS

(Tetramethylsilane)

TMS is added to the sample solution as an internal standard.

Alternatively, when the spectrum is recorded at constant magnetic field by varying the frequency, then the higher the shielding, the lower will be effective magnetic field experienced by the proton and the lower will be the frequency required to reach the resonance condition.

Since the chemical shift values vary with the radiofrequency and magnetic field used in the instrument, a scale independent of the frequency or field strength applied is required to denote the chemical shift values. One such scale is δ (delta) scale and is defined by the ratio of chemical shift to the operating frequency of the instrument. Since the resulting number is small, it is multiplied by 10^6 so that it is convenient to handle. Hence, δ values are expressed in terms of parts per million (ppm). Using δ scale, chemical shifts are recorded downfield (i.e., to the left) from TMS signal which is set at zero delta value. This is shown below in Fig. 4.17. You can see in this figure that the δ values increase from right to left. Most of the protons in organic compounds appear in the range of δ between 0–10 ppm.

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\nu_{\text{used in instrument}}}$$

Another scale which is called tau (τ) scale is also used to represent the NMR signals. The τ scale is related to δ scale by the following expression.

$$\tau = 10 - \delta \qquad \ldots(4.7)$$

However, the δ scale is internationally preferred and we will also report the chemical shift in terms of δ values.

The nmr spectrum of ethanol is shown in Fig. 4.17. Using this spectrum as an example, let us now learn how the nmr spectrum of a compound can be correlated with its molecular structure.

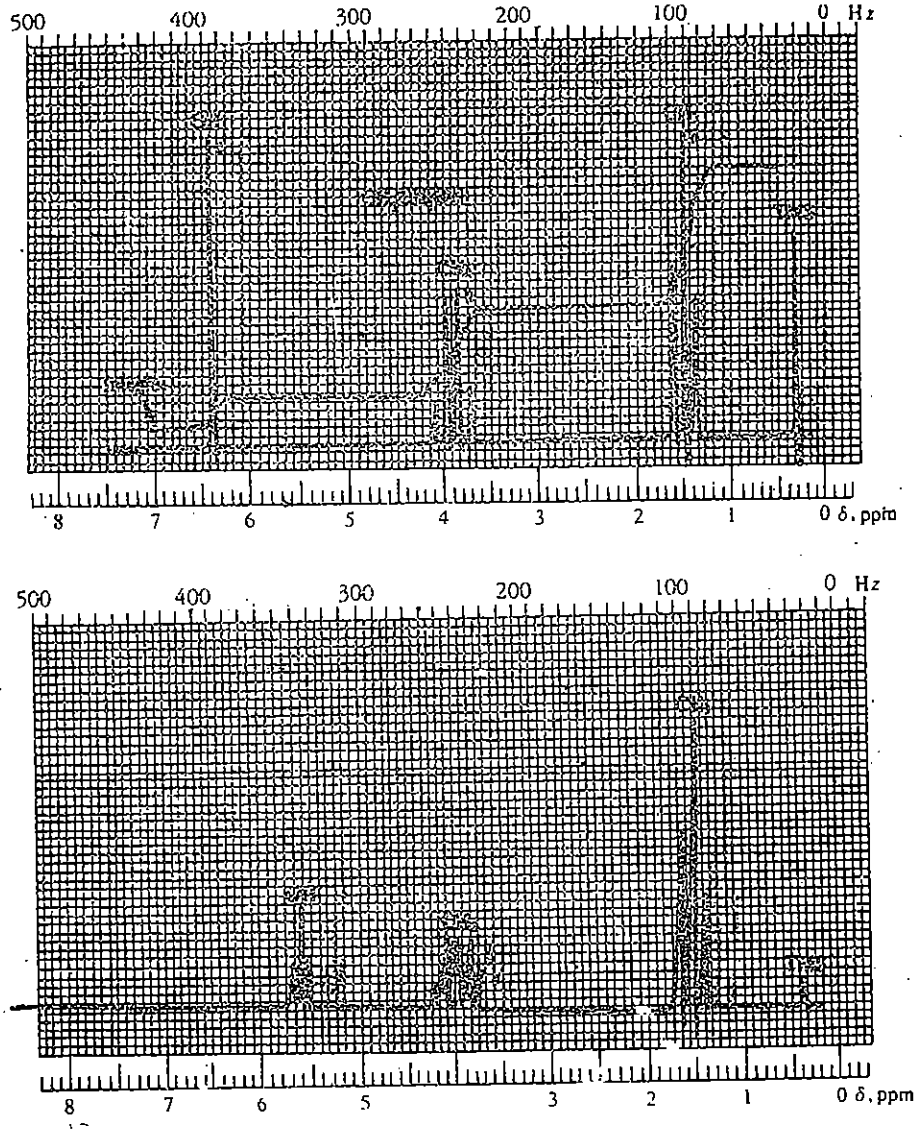


Fig. 4.17 : NMR spectrum of ethanol at 60 MHz : a) Commercial sample of ethanol and b) High resolution nmr spectrum of anhydrous sample of ethanol

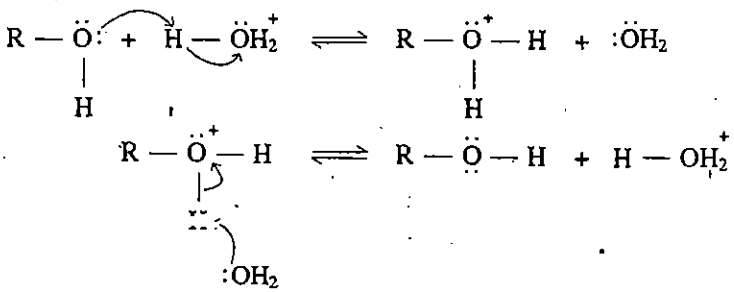
Although the Fig. 4.17 shows that the chart paper on which the spectrum is recorded is calibrated both in parts per million (ppm, at the bottom) and Hertz (at the top), but you need not worry about the calibration at the top. The chemically nonequivalent hydrogens in a molecule have different chemicals shift values and hence will appear at the different positions in the nmr spectrum; therefore, the presence of three sets of signals in the nmr spectrum of ethanol indicates the presence of three sets of non-equivalent portions. These are shown by a, b, c in the spectrum and structural formula of ethanol. Since the $-CH_2-$ group is linked to an -OH group, its hydrogen atoms are more deshielded as compared to those of the $-CH_3$ group. Therefore, the signal for $-CH_2-$ hydrogen atoms appear more downfield as compared to that of the $-CH_3$ group.

CH_3-CH_2-OH
a b c
ethanol

In Fig. 4.17, you must have also noticed the different intensities and patterns of the signals corresponding to the three sets of protons. The peak intensities are given by the total area under the peak which is determined by the mathematical integration of the peak. The nmr spectrometers are equipped with an integrating device which displays the integrals on each peak of the spectrum. The height of each integral is proportional to the area under the peak and is also proportional to the number of protons responsible for the peak. You can check that in the spectrum of ethanol, the heights of integrals for the peaks for CH_3-, CH_2- and -OH units are in the ratio 3:2:1 which is the ratio of number of hydrogen atoms attached to these units. The pattern of signals observed in Fig. 4.17(a) shows that the signal for the -OH proton appears as a single sharp peak which is called a **singlet.** But the signal for $-CH_3$ protons appears as a packet of three peaks which is called a **triplet.** Similarly, the signal for the $-CH_2-$ protons is called a **quartet** (a set of four peaks). This splitting of signals of chemically equivalent protons into doublets, triplets or quartets occurs due to the effect of one set of protons on the nmr signal of its neighbouring protons. Hence, the number of lines in the splitting pattern of a given set of chemically equivalent protons depends on the number of adjacent protons. This number can be determined using the n+1 rule which says that if n equivalent protons are adjacent to a set of equivalent protons, the signal for these equivalent protons will be split into n+1 lines. In accordance with this rule, the signal for $-CH_3$ group of ethanol is split into three peaks (a **triplet**) because it has two protons adjacent to it. What about the signal for $-CH_2-$ protons? The $-CH_2-$ group has three hydrogen atoms of $-CH_3$ group and one hydrogen atom of the -OH group adjacent to it; hence, its signal is split by both the sets of hydrogens. The three hydrogens of the $-CH_3$ group split the $-CH_2-$ signal into a *quartet* (3+1); each of the four peaks of this quartet are further split due to hydrogen of the -OH group into two peaks giving rise to an eight line pattern for the $-CH_2-$ signal.

No. of peaks in the nmr signal	Name for peak pattern	Abbreviation
1	singlet	*s*
2	doublet	*d*
3	triplet	*t*
4	quartet	*q*
5	quintet	*quin*
6	sextet	*sex*
7	septet	*sep*

The splitting of the signal of -OH proton is due to the two adjacent protons of the $-CH_2-$ group and hence it must be a triplet. Such a splitting is absent in the nmr spectrum of an ordinary commercial sample of ethanol. This is because the ordinary commercial sample of ethanol contains a trace of moisture which results in a **chemical exchange** of protons between the alcohol and water (or alcohol) molecules as shown below:



The spacing between the adjacent peaks of a splitting pattern, measured in Hz, is called the coupling constant and is denoted by *J*.

Two coupled protons have the same *J* value.

The presence of water, acid or base enhances **the chemical exchange.** Since, the chemical exchange is quite fast, the hydrogens of the -OH group do not spend enough time on a given molecule for the effective splitting to be recorded. Hence, no splitting due to -OH for such samples is obtained and the spectrum is obtained as shown in Fig. 4.17(a) which shows a singlet for -OH group, i.e., no splitting, and a quartet for $-CH_2-$ protons due to splitting only from methyl hydrogens. But such a splitting is observed in the nmr spectrum of pure anhydrous ethanol, as shown in Fig. 4.17(b). Hence, you can conclude that the nmr spectrum of a

compound can give important information about its structure. You will further appreciate the importance of nmr spectroscopy when you will study the nmr spectra of various compounds in the later units of this course.

At this stage, you have enough understanding of nmr spectroscopy to answer the following SAQ.

SAQ 4

Label the chemically equivalent protons in the following compounds by the letters a, b and c.

) $CH_3-CH(CH_3)-Cl$

.....

) $CH_3-C(CH_3)(CH_3)-CH_2-OH$

.....

) $CH_3OCH_2CH_2OCH_3$

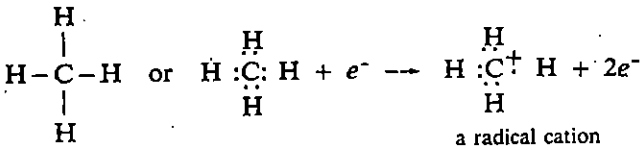
.....

) $CH_3CH_2-CH_2-Br$

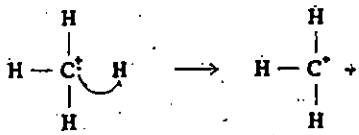
.....

4.7 MASS SPECTROMETRY

In constrast to the spectroscopic techniques discussed before, mass spectromerty does not involve the absorption of electromagnetic radiation. But, it involves the bombardment of the molecule with high energy electrons (i.e., having energy of the order 6700 kJ mol^{-1} or more). This energy is greater than the bond energies of chemical bonds and is hence sufficient to knock an electron out of the molecule, giving rise to a radical cation. For example, if methane is bombarded in this way, it loses an electron from one of the C–H bonds, as shown below.

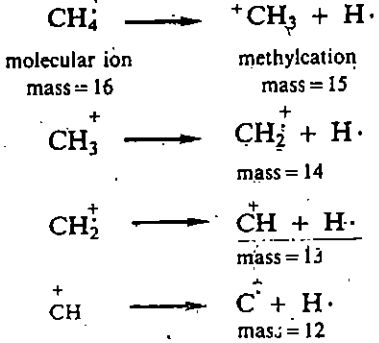


A radical cation is named so because it is both a radical and a cation and is denoted by +



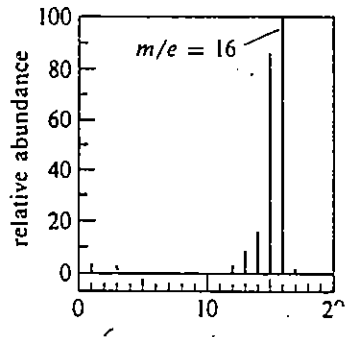
Note that a fishhook arrow is used to show the electron movement.

This radical cation which is formed from a molecule just by the loss of an electron is also called **molecular ion** and is commonly denoted as M^+ ion. This molecular ion can further undergo a series of **fragmentation reactions** to give other radical cations, carbocations and neutral molecules. This is illustrated below for the above radical cation.



Another possibility is the formation of a methyl radical and a proton, as shown below:

$$\underset{\text{mass = 16}}{CH_4^{+\cdot}} \longrightarrow \underset{\text{methyl radical}}{\cdot CH_3} + \underset{\text{mass = 1}}{H^+}$$



mass spectrum of methane

m/e	relative abundance
1	3.36
12	2.80
13	8.09
14	16.10
15	85.90
16	100.00
17	1.11

The radical cations so obtained are charged particles and hence can be accelerated by an electric field. These are then directed to an analyser surrounded by a magnet, see Fig. 4.18. This magnet deflects the ions from their original trajectory into a circular path whose radius depends on their mass to charge (m/z) ratio and the strength of the magnetic field. Hence, the ions having small m/z value are deflected more than those having larger m/z. By varying either the field strength or the degree of acceleration, ions of a particular m/z value can be counted by the detector of the spectrometer. Scanning of all m/z values gives the distribution of positive ions as the **mass spectrum.** The mass spectrum of a compound shows the relative amount of each ion (called the **relative abundance)** plotted on the vertical axis versus their m/z values plotted on the horizontal axis. Remember that only the ions are detected by mass spectrometer and not the neutral molecules or radicals.

Most ions obtained in the mass spectrometer have a single positive charge; hence, their separation is essentially done according to their mass.

Sophisticated mass spectrometers known as high resolution mass spectrometers can resolve ions which are different in their mass by only a few thousandths of a mass unit. For example CO^+ (m/z = 27.9940), N_2^+ (m/z = 28.0062) and $C_2H_4^+$ m/z = 28.0312) are distinguishable using high resolution mass spectrometer.

A very small amount of sample, i.e., about 10^{-6}g is required for recording the mass spectrum.

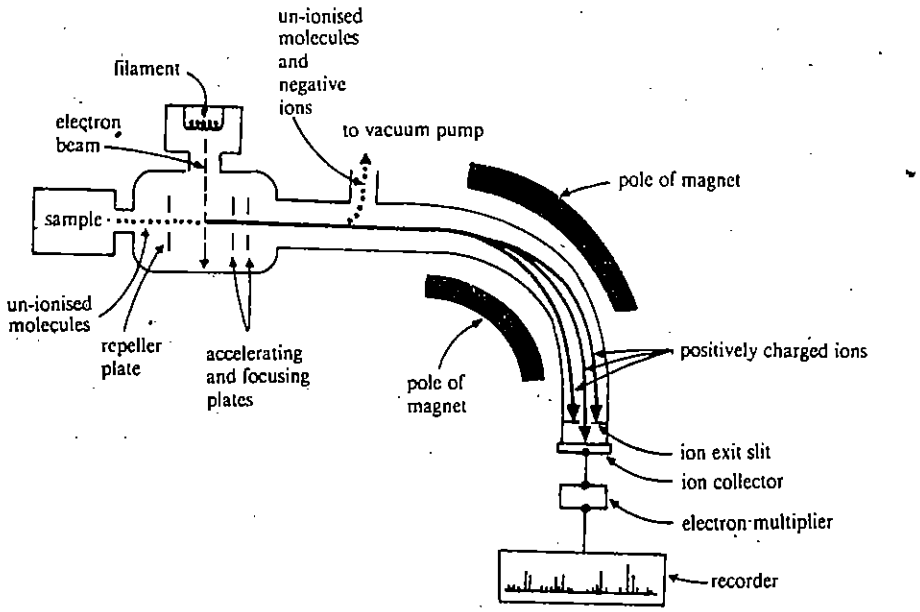


Fig. 4.18 : Schematic diagram of a typical mass spectrometer.

The mass spectrum of a compound can be used to determine its molecular weight by identifying the molecular ion peak in the spectrum. In addition to this, analysis of the fragment ions yields important information regarding the structure of the compound. Let us now analyse the mass spectrum of 2,2-dimethylpropane shown in Fig. 4.19. You can see a small molecular ion peak at m/z 72 in the spectrum.

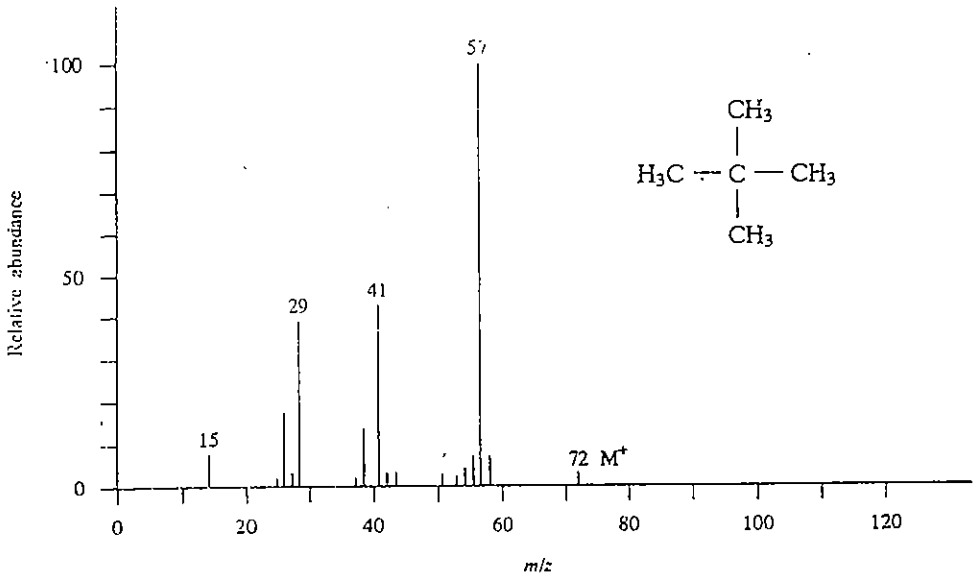
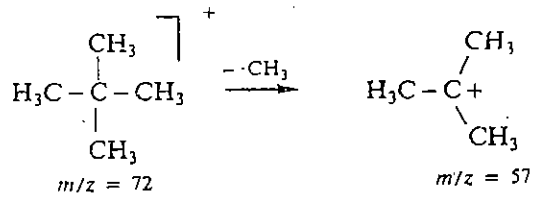
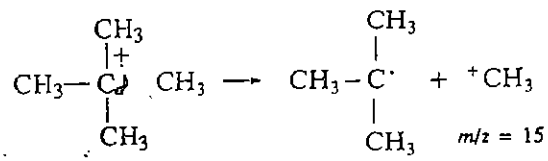


Fig. 4.19 : The mass spectrum of 2,2-dimethylpropane.

This molecular ion can further loss a $\cdot CH_3$ radical to yield another fragment having m/z 57, as shown below.



In this case, this fragment is the most abundant one and hence is called the **base peak**. The base peak is assigned the relative abundance of 100%. The abundance of the other ions is shown relative to this peak.



The peak having m/z = 15 is also observed in the spectrum but is less intense. The other prominent peaks observed are at m/z 41 and 29. This molecule cannot directly yield fragments such as $C_3H_5^+$ and $C_2H_5^+$, respectively, corresponding to the above m/z values. But, fragment ions of this type can result due to complex structural reorganisations which we will not discuss here.

In many compounds, the mass spectrum shows the presence of small M+1 and M+2 peaks. These peaks arise from the presence of isotopes of carbon, hydrogen, oxygen or halogens (like chlorine). For example, presence of $^{13}_{6}C$ in a compound will show an $(M+1)^+$ peak in its mass spectrum. The natural abundance of $^{13}_{6}C$ is 1.08% as compared to that of $^{12}_{6}C$. But, the natural abundance of the heavier isotopes of chlorine ($^{37}_{17}Cl$) is 32.5% as compared to $^{35}_{17}Cl$. Hence, a compound containing one chlorine atom will exhibit an M+2 peak which is of about one-third intensity as compared to the M^+ peak. However, the mass spectrum of chloroform having three chlorine atoms, will show M+2, M+4 and M+6 peaks depending upon the combination of isotopes of the chlorine present.

Thousands of compounds of known structure have been examined by mass spectrometry and the fragmentation patterns characteristic of various classes of compounds have been studied. Thus, a knowledge of these fragmentation patterns helps in identification of compounds.

Let us now sum up the contents of this unit.

4.8 SUMMARY

In this unit, you learnt that

- The physical properties of a compound such as its melting point, boiling point and solubility depend upon the intermolecular forces present between the molecules. The three types of intermolecular forces are:
  - i) dipole-dipole interactions
  - ii) London forces, and
  - iii) hydrogen bonding.
- The melting points increase with increasing molecular weight and molecular symmetry.
- The boiling point of a compound depends upon the intermolecular forces of attraction. An increase in molecular size increases London forces and hence it leads to an increase in the boiling point. On the other hand, branching reduces the total surface area leading to decrease in the boiling point.
- Intermolecular hydrogen bonding increases the boiling point and is also responsible for the higher water solubility of a compound.
- Absorption of energy from different regions of electromagnetic radiation leads to different kinds of spectroscopy.
- The absorption of ultraviolet radiation results in electronic excitations in the molecule. The wavelength of absorption increases with increasing conjugation and hence highly conjugated compounds are coloured.
- Infrared spectroscopy deals with the absorption of infrared radiation corresponding to characteristic molecular vibrations. The infrared spectrum provides information about various structural units and the functional groups present in the molecule.
- The three elements of NMR spectrum are **chemical shift** which provides information about the chemical environment of the particular nucleus, the **integral** which tells the relative number of the nuclei being observed; and the **splitting** which gives information about the number of nuclei on the adjacent atoms.
- The mass spectrum of a compound is a record of the m/z values of various fragments versus their relative abundance.

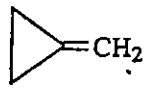
4.9 TERMINAL QUESTIONS

1. Match the following compounds with their melting points.
   Compounds: 2,2,3,3-tetramethylbutane and octane

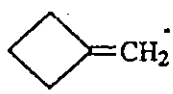
   m.p. : 374 K and 216 K

2. Arrange the following molecules in the increasing order of their boiling points.
   a) 2-Methylhexane
   b) Heptane
   c) 2,2-Dimethylpentane
   d) 2,2,3-Trimethylbutane

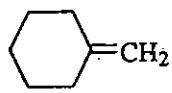
3. Given below are the C=C stretching absorptions for some compounds. Which one of these compounds has the strongest double bond? Why?

a) 

1781 cm^{-1}

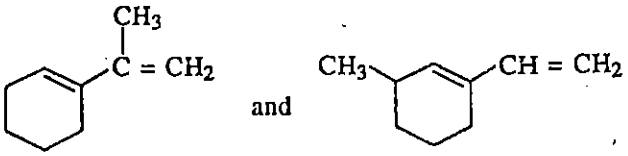
b) 

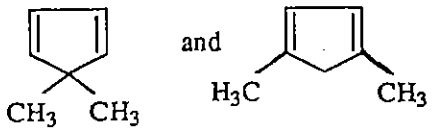
1672 cm^{-1}

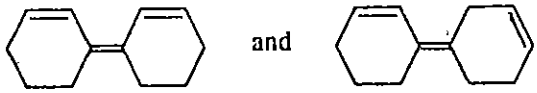
c) 

1650 cm^{-1}

4. Can you differentiate between the compounds of each of the following pairs. Name the spectroscopic technique you will use and give reason in support of your answer.

a) 

b) 

c) 

5. Predict the number of signals and their splitting pattern in the nmr spectra of the following compounds:

   a) CH_3-CH_2-Br

   b) $CH_3-CHI-CH_3$

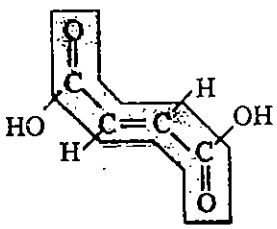
6. Two unknown compounds (a) and (b) containing C, H and O showed the molecular ion peaks at m/z (a) 46 and (b) 30. Give possible structures to these compounds.

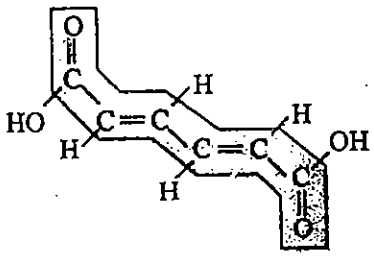
4.10 ANSWERS

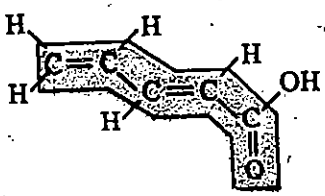
Self Assessment Questions

1. i) False ii) False iii) True
   iv) False v) True vi) True

2. a)

a) 

b) 

c) 

   b) will have longest wavelength of absorption.

3. a) active b) inactive c) active d) active.

4. a) $\overset{a}{CH_3}-\overset{b}{CH}(\overset{a}{CH_3})-Cl$

   b) $\overset{a}{CH_3}-\overset{a}{\underset{\overset{|}{CH_3}}{C}}-\overset{b}{CH_2}-\overset{c}{OH}$

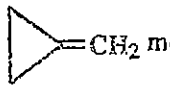
c) $\underset{a}{CH_3}\underset{b}{OCH_2}\underset{b}{CH_2}\underset{a}{OCH_3}$

d) $\underset{a}{CH_3}-\underset{b}{CH_2}-\underset{c}{CH_2}-Br$

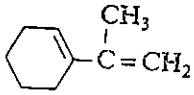
Terminal Questions

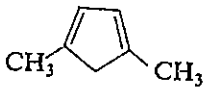
1. 2,2,3,3-Tetramethylbutane, 374 K.
   Octane, 216 K.

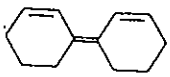
2. The boiling points are in the following order.
   (d) < (c) < (a) < (b).

3. The double bond in  molecule is the strongest one because it has the largest value of C=C stretching absorption.

4. Yes, the two compounds in each of the pairs can be differentiated. The UV spectroscopy can be used for such differentiation.

   a)  will absorb at longer wavelength due to greater substitution at the double bond.

   b)  will have larger λ_{max} due to the same reason as stated in part (a).

   c)  will have larger λ_{max} because all the three double bonds are in conjugation in this molecule.

5. a) two signals: i) a *triplet* for $-CH_3$ protons
      ii) a *quarter* for $-CH_2-$ protons.
   b) two signals: i) a *doublet* for $-CH_3$ protons.
      ii) a septet for $-CH-$ protons.

6. (a) having m/z = 46 can be CH_3OCH_3 or CH_3CH_2OH or $HC(=O)-OH$ and
   (b) having m/z = 30 can be HCHO.

UNIT 5 STRUCTURE – REACTIVITY RELATIONSHIPS

Structure

5.1 Introduction
Objectives
5.2 What are Acids and Bases?
5.3 Strengths of Acids and Bases
5.4 Factors Affecting the Strengths of Acids and Bases
Inductive Effect
Resonance Effect
Hyperconjugation
Hydrogen Bonding
Steric Effect
Solvent
5.5 Tautomerism
5.6 Summary
5.7 Terminal Questions
5.8 Answers

5.1 INTRODUCTION

In Unit 4, you studied about the relationship between molecular structure and physical properties including spectral properties. In this unit, you will study about the effect of molecular structure on the reactivity of the molecules. The *reactivity* of one substance towards another is measured by the rate at which the two substances react and the amount of the products formed.

Not all molecules are equally reactive. But, what makes some organic molecules more reactive than others? To find an answer to this question, we should have some idea of the nature of reactions that the organic molecules undergo. A large number of reactions that the organic molecules undergo can be readily understood as simple analogies of *acid-base reactions*. Therefore, it is important for us to know the basic features of acid-base reactions. We will begin this unit with a discussion on various ways in which the acids and bases can be defined. We will then familiarise you with the concept of acid-base equilibrium. Here, you will also study that the position of the acid-base equilibrium is a measure of molecular reactivity; further it is influenced by many factors. Although, the functional groups present in a molecule are of key importance in determining the molecular reactivity, it has been observed that various compounds containing the same functional groups differ in their reactivities. Thus, in addition to the presence of the functional groups, the nature and arrangement of atoms attached to the functional groups also control the molecular reactivity. These effects which are associated with the change in molecular structure, are called **structural effects**. In this unit, you will study various structural effects such as *inductive effect, resonance effect* and *steric effect,* and their influence on molecular reactivity.

In addition to the structural effects, we will also discuss solvent effects and hydrogen bonding which are also important factors affecting the rate and the extent of such reactions. Finally, you will study an interesting equilibrium involving a proton shift from one atom of a molecule to another, called **tautomerism.**

Objectives

After studying this unit, you should be able to:

- define acids and bases,
- classify the given compounds as acids or bases according to Bronsted – Lowry and Lewis definitions,
- define pK_a of an acid,

- predict the relative acidities and basicities of compounds from their pK_a values,
- list various factors affecting the strengths of acids and bases,
- explain the effect of structural changes on the acidic and basic behaviour of organic molecules,
- predict the relative reactivity of the molecules on the basis of inductive effect, resonance effect, steric effect, hydrogen bonding and hyperconjugation, etc.
- define tautomerism and give examples of various kinds of tautomerism.

5.2 WHAT ARE ACIDS AND BASES?

There are various ways of defining acids and bases. According to Arrhenius (1884), a Swedish chemist, an *acid* is a substance which ionises in aqueous solution to produce hydrogen ions (H^+), also known as *protons*. And, a *base* is a substance which ionises to produce hydroxide (OH^-) ions. Thus, Arrhenius theory assumes a simple dissociation such as,

Arrhenius received Nobel Prize in Chemistry in 1903.

Note that during dissociation, the covalent bond between H – A is broken and the electrons forming this bond shift on A as shown by the curved arrow.

$$\overset{\frown}{H-A} \rightleftharpoons H^+ + A^-$$

Arrhenius acid

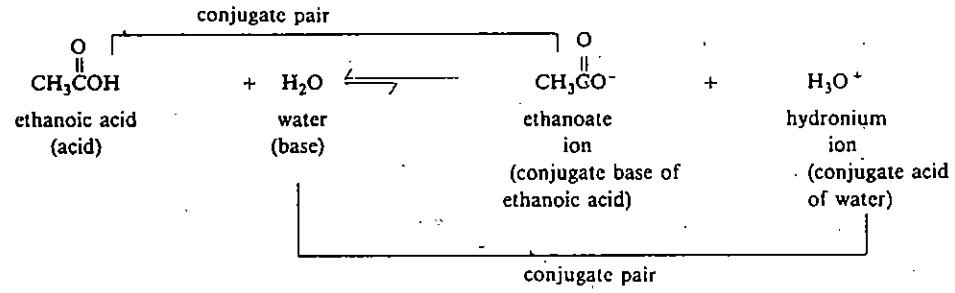
and

$$M-OH \rightleftharpoons M^+ + {}^-OH$$

Arrhenius base

Thus, HCl is an acid and NaOH is a base because on dissociation they yield H^+ and OH^- ions, respectively. Thus, the strength of these acids and bases is related to the degree of their dissociation. The mineral acids such as HCl, HI, HBr, H_2SO_4 and HNO_3 are strong acids because they are almost completely dissociated in aqueous solutions. Similarly, the strength of a base will also depend upon its degree of dissociation.

An alternative theory of acids and bases was devised independently by Brönsted and Lowry in 1923. According to the Brönsted-Lowry approach, **an acid is a proton donor and a base is a proton acceptor.** Since under ordinary reaction conditions a free proton cannot exist as a separate entity, when an acid in the Brönsted-Lowry sense is considered, a base must be present to accept the proton from the acid. Consider the following example,

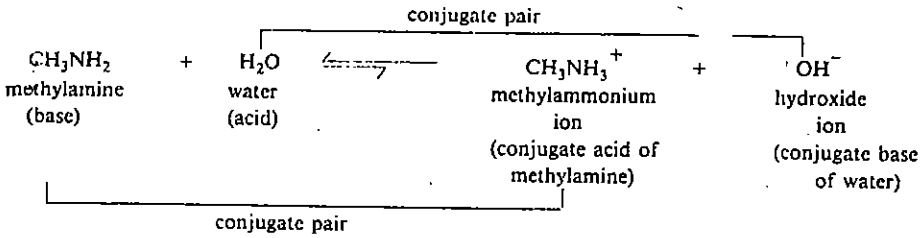


The Brönsted acids are also called **protic acids** because they react by the transfer of a *proton*.

The word **conjugate** has its origin from the Latin word **conjugatus** which means *joined together*.

Here, the ethanoic acid is an **acid** because it donates a proton to water which is a base because it accepts the proton. Similarly, the ethanoate ion, which is formed by the loss of a proton from ethanoic acid, functions as a **base** because it can accept a proton to become ethanoic acid again. Thus, ethanoate ion is called the **conjugate base** of ethanoic acid. Similarly, the hydronium ion is the **conjugate acid** of the base, water. This pair of a base and its conjugate acid or an acid and its conjugate base is also called **conjugate acid-base pair.**

Let us now consider an acid-base reaction involving methylamine which acts as a base and water which acts as an acid in this case, as shown below:



Note that water can act both as an acid as well as a base. It acts as an acid by donating a protion to yield the OH^- ion which is its conjugate base. It can also act as a base by accepting a proton to yield a hydronium ion which is its conjugate acid.

Although, we have illustrated both the above examples using water as one of the components, the scope of Brönsted-Lowry definition of acids and bases is not limited to aqueous solutions, as is the case in Arrhenius definition. The Brönsted-Lowry concept of acids and bases is more general and applies to any type of solvent.

Thus, according to this concept the general form of an acid-base reaction can be written as,

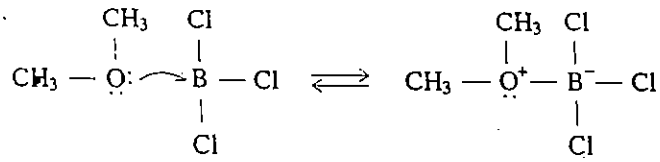
$$\underset{\text{acid}}{A_1} + \underset{\text{base}}{B_2} \rightleftharpoons \underset{\text{conjugate base of acid } A_1}{B_1} + \underset{\text{conjugate acid of base } B_2}{A_2}$$

where A_1–B_1 and A_2–B_2 are conjugate acid-base pairs.

The acid-base theory was further broadened by Lewis in 1938. He proposed that the *acids are the electron-pair acceptors* and *the bases are the electron-pair donors*. Hence, according to this idea any molecule or ion which can accommodate an electron pair is an acid. For example, a proton, H^+, is a Lewis acid because it can accept an electron pair.

A proton is only one of a large number of species that may act as a Lewis acid. The electron deficient species such as $AlCl_3$, BF_3, BCl_3, $ZnCl_2$, Mg^{2+} and carbocations are also Lewis acids. The electron deficient atoms in these species accept the electrons to complete their valence shell octets.

Similarly, any molecule or ion which has an unshared pair of electrons to donate can act as a base. Thus, dimethyl ether acts as a Lewis base towards boron trichloride which acts as a Lewis acid. This acid-base reaction is represented below



Note that the curved arrow shows the movement of a pair of electrons *from* their source *to* their destination.

You will agree that the bases are much the same in both the Lewis and the Brönsted-Lowry definitions because a Brönsted-Lowry base must possess a pair of electrons in order to accept a proton.

Having identified a substance as an acid or a base according to the above criteria, let us study how to determine the strength of an acid or a base.

Before that check your understanding of the above concepts by answering the following SAQ.

SAQ 1

Label the conjugate acid and the conjugate base in each of the following reactions.

(a) $CH_3-\overset{\overset{O}{\|}}{C}-OH + {}^{-}OH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O^{-} + H_2O$

.....

(b) $CH_3-\overset{\overset{O}{\|}}{C}-OH + H_2SO_4 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-\overset{+}{O}H_2 + HS\bar{O}_4$

.....

(c) $(CH_3)_3\overset{+}{N}H + CH_3O^{-} \longrightarrow (CH_3)_3N: + CH_3OH$

.....

(d) $\begin{matrix} CH_3 \\ \diagdown \\ \quad C=CH_2 \\ \diagup \\ CH_3 \end{matrix} + H_3O^{+} \longrightarrow \begin{matrix} \quad CH_3 \\ \quad | \\ CH_3-C^{+} \\ \quad | \\ \quad CH_3 \end{matrix} + H_2O$

.....

5.3 STRENGTHS OF ACIDS AND BASES

It is not possible to determine the strength of an acid or a base in absolute terms. Therefore, these strengths are always expressed in relative terms. The *relative strengths* of acids are determined by the extent to which they transfer a proton to a standard base. The standard base which is commonly used for such comparisons, is water. Hence, for an acid HA, the proton transfer can be represented by the following equilibrium :

$$HA + H_2O \rightleftharpoons :A^{-} + H_3O^{+}$$

The equilibrium constant, K_{eq}, for the above equilibrium can be written as,

$$K_{eq} = \frac{[:A^{-}]\,[H_3O^{+}]}{[HA]\,[H_2O]} \qquad ...(5.1)$$

where the quantities in brackets are the molar concentrations (expressed as moles dm^{-3}) of the species at equilibrium.

For dilute solutions, the concentration of water is large and is almost constant. Hence, the above expression for equilibrium constant can be rewritten in terms of a new constant, K_a, called the **acidity constant,** as given below:

$$K_{eq}\,[H_2O] = K_a = \frac{[:A^{-}]\,[H_3O^{+}]}{[HA]} \qquad ...(5.2)$$

The dissociation of an acid HA in solvents other than water can be generalised as,

$$HA + \text{solvent} \rightleftharpoons H^{+} - \text{solvent} + :A^{-}$$

The expression for acidity constant can then be written as follows:

$$K_a = \frac{[H^{+} - \text{solvent}]\,[:A^{-}]}{[HA]} \qquad ...(5.3)$$

The acidity constants of different acids have magnitudes ranging from 10^{14} to 10^{-50}. In order to avoid writing a wide range of powers of 10, K_a is generally expressed in terms of pK_a, where

$$pK_a = -\log_{10} K_a \qquad ...(5.4)$$

Table 5.1 shows the pK_a values for a variety of acids along with their conjugate bases.

Taking -log of Eq. 5.2 and rearranging, we get

$$-\log K_a = -\log [H_3O^{+}] + \log \frac{[HA]}{[:A^{-}]}$$

By definition,

$$-\log K_a = pK_a$$

and $-\log [H_3O^{+}] = pH$

Hence,

$$pK_a = pH + \log \frac{[HA]}{[:A^{-}]}$$

This expression relating the pK_a and pH is also known as **Henderson-Hasselbalch equation.**

Thus, when [HA] = [:A], then $pK_a = pH$.

Table 5.1 : p*K*a Values

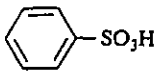
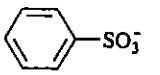
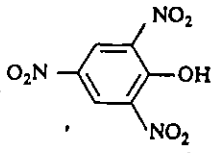
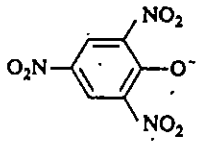
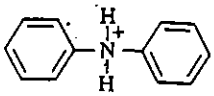
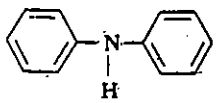
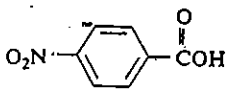
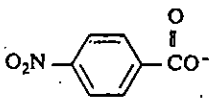
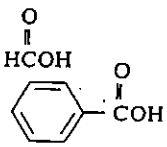
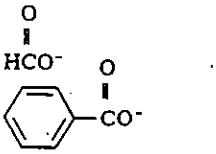
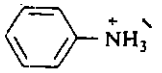
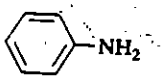
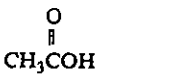
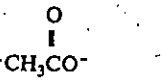
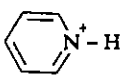
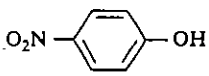
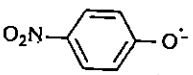
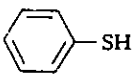
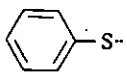
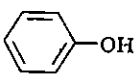
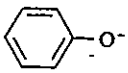
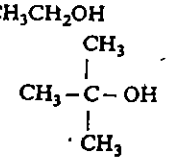
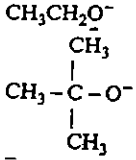
Acid	Base	p*K*a
H_2SO_4	HSO_4^-	−9
HCl	Cl^-	−7
H_3O^+	H_2O	−1.7
HNO_3	NO_3^-	−1.3
		−0.6
		0.25
		0.8
		3.4
		2.7 4.2
		4.6
		4.8
		5.2
		7.2
		7.8
NH_4^+	NH_3	9.4
$(CH_3)_3NH^+$	$(CH_3)_3N$	9.8
		10.0
CH_3CH_2SH	$CH_3CH_2S^-$	10.5
$CH_3NH_3^+$	CH_3NH_2	10.6
CH_3OH	CH_3O^-	15.5
H_2O	OH^-	15.7
CH_3CH_2OH	$CH_3CH_2O^-$	17
		19
$CHCl_3$	$\bar{C}Cl_3$	25
$HC{\equiv}CH$	$HC{\equiv}C^-$	26
NH_3	NH_2^-	36
$CH_2 = CH_2$	$CH_2{=}CH^-$	36
CH_4	CH_3^-	49

Table 5.1 shows that the acids which are listed at the top are strong acids. For strong acids such as H_2SO_4, the proton transfer to the base (i.e., water) is almost

complete and equilibrium lies towards the right. Thus, the stronger acids have larger K_a values. Therefore, it follows from Eq. 5.4 that the **stronger** the acid, the **smaller** the pK_a value. Thus, as Table 5.1 shows, the sulphonic acids and carboxylic acids are much more acidic as compared to phenol and alcohols.

The stronger the acid, the weaker is its conjugate base and vice versa.

Remember that the conjugate base of a strong acid will be a weak base and the conjugate base of a weak acid will be a strong base. Similarly, we can generalise for conjugate acids.

Note that Table 5.1 lists the pK_a values for protic acids or Brönsted acids only. A similar Table for the relative acidities of Lewis acids is not feasible because in these acids it is not possible to have a standard base as reference. But, an approximate order of the strengths of various Lewis acids is as given below :

Lewis acids such as boron trifluoride and aluminium chloride are important acid catalysts for certain organic reactions.

BF_3	>	$AlCl_3$	>	$FeCl_3$	>	$SbCl_3$	>	$ZnCl_2$	>	$HgCl_2$
Boron trifluoride		Aluminium chloride		Ferric chloride		Antimony chloride		Zinc chloride		Mercuric chloride

The Table of pK_a values can be used to predict the feasibility of an acid-base reaction. In general, an acid will transfer a proton to the conjugate base of any acid that is below it in the pK_a Table. Also, the larger the difference between the pK_a values (i.e., acidities) of the acid and the conjugate acid of the base, the more favourable will be the proton transfer from the acid to the base.

Many organic reactions are initiated by protonation or deprotonation of a reactant, therefore, the pK_a values are also helpful in choosing the appropriate acidic or basic reagents required for a particular reaction.

Similar to acids, an equilibrium for bases in water can be written as,

$$:A^- + HOH \rightleftharpoons HA^+ + OH^-$$

The equilibrium constant for such an equilibrium can be expressed as,

$$K_{eq} = \frac{[HA]\,[OH^-]}{[:A^-]\,[HOH]} \qquad \ldots(5.5)$$

where the quantities in brackets are molar concentrations of the respective species at equilibrium.

Since the reaction is carried out in aqueous solution, water is acting both as a solvent as well as an acid; hence, its concentration can be taken as almost constant. Thus, we can write Eq. 5.5 in terms of the basicity constant, K_b, as

In the expressions for K_a and K_b, the concentration of water is generally omitted and hence, K_a and K_b, have units of moles dm^{-3}

$$K_{eq}\,[H_2O] = K_b = \frac{[HA]\,[OH^-]}{[:A^-]} \qquad \ldots(5.6)$$

The self-ionisation of water can be represented as,

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

The concentration of the species H_3O^+ and OH^- in pure water is very low and is equal to 10^{-7} moles dm^{-3}. Therefore, the self-ionisation constant, K_w, of water is defined as,

$K_w = [H_3O^+]\,[OH^-]$
$= 10^{-7} \times 10^{-7}$ moles^2 dm^{-6}
$= 10^{-14}$ moles^2 dm^{-6}

The two constants K_a and K_b are related to each other as shown below :

$$K_a.K_b = \frac{[:A^-]\,[H_3O^+]}{[HA]} \cdot \frac{[HA]\,[OH^-]}{[:A^-]}$$
$$= [H_3O^+]\,[OH^-] = K_w = 10^{-14}$$

where K_w is the self-ionisation constant of water. Hence,

$$pK_a + pK_b = 14$$

Therefore, if we know the pK_a of acid HA, the pK_b of the base $:A^-$ can be obtained by using the above relation.

It is customary to express the strengths of organic bases not as K_b values but in terms of the K_a and pK_a values because it allows a single continuous scale for both acids and bases. As has been stated above the stronger the acid, the weaker will be its conjugate base and vice versa. In other words, the stronger the acid, the lower the pK_a, but, the stronger the base, the higher is the pK_a. This is also evident from Table 5.1 that whereas the acidity of the acids *decreases* from top to bottom, the basicity of the conjugate bases *increases* from top to bottom. You can see that NH_2^-, which comes almost at the bottom of this Table, is a very strong base (see

Table 5.1). A comparison of the pK_a values from Table 5.1 shows the following order of the basicities for some of the bases.

$$^-CH_3 > NH_2^- > RO^- > OH^- > RCOO^-$$

Note that the organic compounds which act as bases can be regarded as alkyl derivatives of either water or ammonia; for example, alcohols (R – O – H), ethers (R – O – R′) and amines RNH_2, R_2NH and R_3NH. The basic character of these compounds can be attributed to atoms such as nitrogen and oxygen which contain at least one lone pair or electrons.

Having discussed the strengths of acids and bases, let us now study the factors affecting the strength of acids and bases. But before proceeding to the study of next section which deals with these factors, answer the following SAQ.

SAQ 2

An acid HA_1 has $pK_a = 20$ and another acid HA_2 has $pK_a = 10$. (a) Which of these two acids is stronger? (b) If $Na^+A_1^-$ salt is added to acid HA_2, does any acid-base reaction take place? Explain.

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5.4 FACTORS AFFECTING THE STRENGTHS OF ACIDS AND BASES

The strengths of acids and bases depend upon many factors. It was mentioned before, that apart from the presence of functional groups, structural variations in molecules also influence their acidic or basic properties. We will now focus our attention on some effects which arise due to structural changes in the molecules. A change in molecular structure can affect the reactivity of the molecule by changing the *electron distribution* of the system, in which case it is called an **electronic effect**. Another possibility is that two or more groups or atoms may come close enough in space so that the London interactions between them become significant. The effects arising from such interactions are called **steric effects**.

We will begin our discussion with the study of an electronic effect, known as **inductive effect**.

5.4.1 Inductive Effect

You are already familiar with the fact that when two different atoms form a covalent bond, the shared pair of electrons is pulled more by the more electronegative atom. This unequal electron distribution results in partial separation of charge and we get a dipole in which one atom has a partial positive charge and another atom (the more electronegative one) has a partial negative charge. Such a polarisation of a bond can be felt by adjacent groups also. This phenomenon of the transmission of charge through a chain of atoms linked together by σ bonds is called **inductive effect**.

$\geq C^{\delta+} - X^{\delta-}$ (X is more electronegative than C)

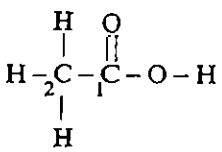
a dipole

$$C_3 - C_2 \rightarrow C_1 \gg X$$

Inductive effect of X

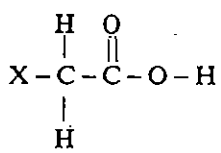
Note that the inductive effect is a permanent effect.

Let us now analyse how inductive effect causes a change in the acidity or basicity of a molecule. Let us take the example of ethanoic acid whose structure is shown below.



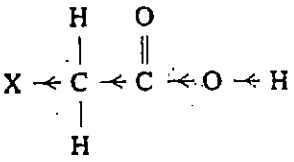
ethanoic acid

pK_a 4.76

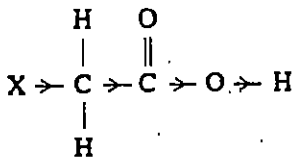


substituted ethanoic acid

i) When the substituent X is electron withdrawing, it decreases the electron density at H as shown below:



ii) When the substituent X is electron donating, it increases the electron density at H as represented below:



If we substitute one of the hydrogen atoms on the C-2 carbon atom with a substituent X, then, the nature of the substituent group may effect the electron density of the O – H bond resulting in a change in the acidity of the molecule. Depending upon whether the substituent X is electron-withdrawing or electron donating, the electron density will decrease or increase, respectively. If the electron density between the bond formed by O and H atoms *decreases*, then, the loss of H as H^+ ion is facilitated resulting in the *increased acidity* of the molecule. On the other hand, an *increase* in the electron density at the bond between O and H atoms will make the proton release difficult, thereby, *decreasing* the acidity.

The electron withdrawing substituents are said to have –I effect and the electron-donating substituents are said to have +I effect. Some examples of the substituents belonging to these two categories are listed in Table 5.2.

Table 5.2 : Inductive effect of various functional groups.

Electron-donating substituents (+I)	Electron-withdrawing substituents (-I)		
$-O^-$	$-F$	$-CO_2H$	
$-CH_3$	$-Cl$	$-CO_2R$	
$-CO_2-$	$-Br$		
	$-I$	$-C\equiv N$	
	$-OR$	$-NO_2$	
	$-OH$	$-SO_2-$	
			
	$-SR$		
	$-SH$	$-C\equiv C-$	

The effect of some of these substituents on the acidity of the substituted acids in terms of their pK_a values is shown in Table 5.3.

Table 5.3 : pK_a values for some substituted acids determined in water at 298 K.

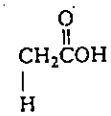
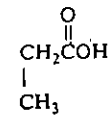
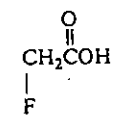
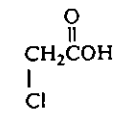
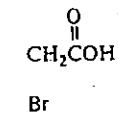
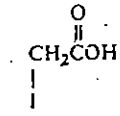
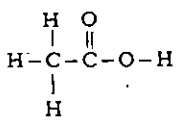
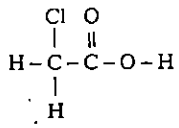
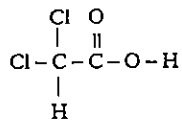
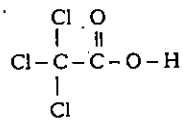
Name	Structure	pK_a
ethanoic acid		4.76
propanoic acid		4.87
fluoroethanoic acid		2.59
chloroethanoic acid		2.86
bromoethanoic acid		2.90
iodoethanoic acid		3.17

Table 5.3 shows the decreased acidity for propanoic acid (larger pK_a value) as compared to the ethanoic acid. Note that the propanoic acid has a methyl group in place of H in ethanoic acid. The methyl group is electron-donating in nature and, therefore, has a +I effect which results in the decrease in the acidity. But the acidity increases when the electron-withdrawing substituents such as F, Cl, Br and I are present. Note that the increase in acidity is in accordance with the electronegativity of these elements.

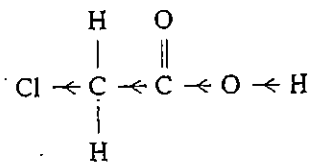
The inductive effect of these substituents is further enhanced with the increase in the number of these substituents. This is represented in Table 5.4.

Table 5.4 : Effect of increase in the number of chlorine sustituents on acidity of ethanoic acid.

Acid	Structure	pK_a
Ethanoic acid		4.76
Monochloroethanoic acid		2.86
Dichloroethanoic acid		1.30
Trichloroethanoic acid		0.65

In monochloroethanoic acid, one of the three hydrogen atoms in ethanoic acid has been replaced by an electron withdrawing chlorine atom. Hence, the electron pair constituting the C – Cl bond is drawn closer to the chlorine atom. This effect is transmitted through other atoms forming σ bonds to the OH bond of the

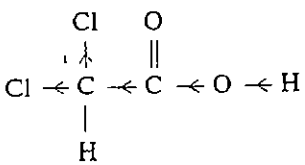
group. This results in a shift of the electrons constituting the O – H bond towards oxygen atom as shown below :



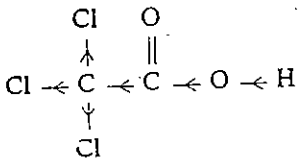
monochloroethanoic acid

Such an electron withdrawal by chlorine atom, thus, facilitates the departure of the proton and hence, increases the acidic character of monochloroethanoic acid as compared to ethanoic acid.

In the di- and trichloroethanoic acids, the presence of second and third chlorine



dichloroethanoic acid



trichloroethanoic acid

atoms results in more electron withdrawal away from hyd of the O – H bond and would, therefore, further increase the acidity of these compounds as compared to ethanoic acid or chloroethanoic acid. Therefore, we can arrange these acids in the increasing order of their acidities as ethanoic acid < chloroethanoic acid < dichloroethanoic acid < trichloroethanoic acid.

The position of electron-withdrawing substituents in a molecule also influences its acidic character. This is shown by the pK_a values of isomeric monochlorobutanoic acids given in Table 5.5.

Table 5.5 : Effect of position of substituent on acidity.

Name	Structure	pK_a
butanoic acid	$CH_3CH_2CH_2COH$ (O)	4.82
2-chlorobutanoic acid	CH_3CH_2CHCOH (O, Cl)	2.86
3-chlorobutanoic acid	CH_3CHCH_2COH (O, Cl)	4.05
4-chlorobutanoic acid	$CH_2CH_2CH_2COH$ (O, Cl)	4.52

It can be seen that although in each of these acids a chlorine atom has replaced a hydrogen atom but they show different acidities. Note that as the distance of the electron withdrawing chlorine atom from the reaction site (i.e., the O – H of the COOH group) increases, the acid strength decreases. Thus, the influence of the inductive effect on acid strength is greatest when the electron withdrawing chlorine atom is present on the carbon next to the carboxylic group and it diminishes quickly with increase in the distance. This effect is almost negligible after the fourth carbon atom in the chain.

A similar electron withdrawal occurs when a positively charged group is present in a molecule. A positive centre such as $(CH_3)_3\overset{+}{N}-$ (trimethyl ammonium) or $-\overset{+}{N}H_3$ (ammonium), eases the departure of proton by withdrawing electrons and hence, increases the acid character of the molecule. This is illustrated in the example given below

CH_3COOH (pK_a 4.76) $\qquad$ $(CH_3)_3\overset{+}{N}-CH_2COOH$ (pK_a 1.83) $\qquad$ $(CH_3)_3\overset{+}{N}CH_2CH_2CH_2CH_2COOH$ (pK_a 4.27)

Note that here also with the increase in the distance between the positively charged group and the carboxyl group, the inductive effect decreases.

If the presence of a positively charged group increases the acidity of a molecule, then a negatively charged group should decrease the acidity. Consider the dissociation of propanedioic acid, as given below:

$$COOHCH_2COOH \overset{K_{a_1}}{\rightleftharpoons} HOOCCH_2COO^- + H^+$$

propanedioic acid
$pK_{a_1} = 2.83$

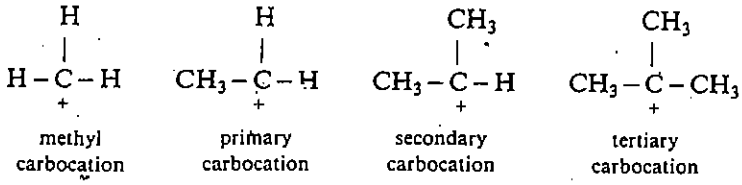
where K_{a_1} is the first dissociation constant.

Here, a proton is lost from one of the two carboxyl groups of the molecule. The dissociation constant for this dissociation is called the first dissociation constant and is represented by K_{a_1}. Further dissociation of the anion obtained in the above dissociation is difficult because it involves the removal of the proton from a negatively charged species. Therefore, this step has a pK_a value equal to 5.69. This is called pK_{a_2} because K_{a_2} represents the second dissociation constant.

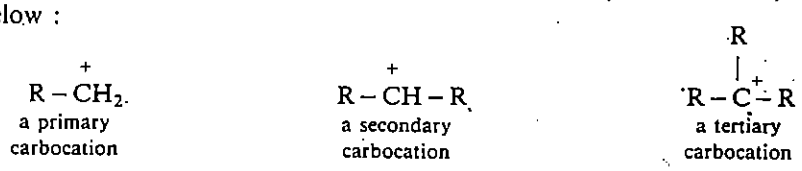
Always remember that K_{a_1} is larger than K_{a_2} for a dicarboxylic acid. Therefore, for these acids pK_{a_1} is lower than pK_{a_2}.

From the above discussion, we can say that the substituents having -I effect increase the acidity while the substituents having +I effect decrease the acidity. On this basis, let us now analyse the stability of carbocations which are reactive intermediates formed during the chemical reactions. You are already familiar with the shape of the carbocations which you studied in Unit 3 under the stereochemistry of S_N1 reactions. Look at the following examples of carbocations:

Carbocations contain a positively charged carbon atom.

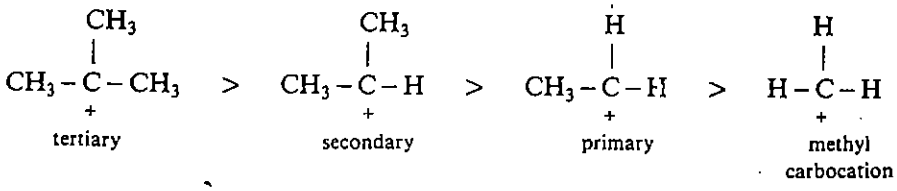


The carbocations are classified by the degree of alkyl substitution at the positively charged carbon atom as primary, secondary or tertiary carbocations, as shown below :

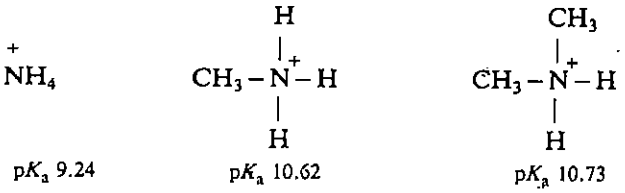


where R is the alkyl group.

Since the alkyl groups are electron donating in nature, the +I effect increases with the increase in the number of alkyl groups. Thus, the increase in the number of alkyl groups in a carbocation helps in the dispersal of its positive charge. Therefore, a tertiary carbocation is more stable than a secondary carbocation ion which is, in turn, more stable than a primary carbocation. Hence, we can arrange the above carbocations in the following order of their stabilities:



Since the substituents having +I effect decrease the acidity, their presence should also increase the basicity. This is what is actually observed when the hydrogen atoms of ammonia are successively replaced by methyl groups to give methylamine and dimethylamine whose basicities increase with the increase in the number of methyl groups, as shown below by the pK_a values of their conjugate acids.



The basicity of tertiary amines will be discussed in sub-Sec. 5.4.5

Till now, you have been studying the inductive effect of various substituents on the acidities and basicities of molecules. In fact, the inductive effect influences the electron density of the H – A bond. Another factor which affects the release of protons from the acid HA is the stability of the anion, A^-, formed by the loss of proton from the acid HA. This you will be studying in the next section.

At this stage, it would be helpful to answer the following SAQ.

SAQ 3

(a) Arrange the following compounds in the decreasing order of their acid strengths. Also, give reasons in support of your answer.

i) CH_3COOH, $NCCH_2COOH$, $NCCH_2CH_2CH_2COOH$

.....

.....

ii) CH_3NO_2, $CH_2(NO_2)_2$, $CH(NO_2)_3$

.....

.....

iii) CH_3COOH, $HOOCCOOH$, $^-OOCCOOH$

.....

.....

(b) Arrange the following compounds in the decreasing order of their **base** strength. Support your answer with reasons.

i) aniline, *N*-methylaniline, *N*, *N*-dimethylaniline

.....

.....

ii) NH_3, NH_2CH_3, NH_2OH

.....

.....

5.4.2 Resonance Effect

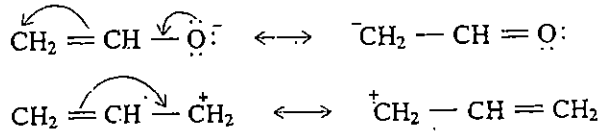
One of the factors which stabilises the A^- anion with respect to the acid HA, is *resonance effect*. Let us first revise the basic ideas about resonance which you have learnt earlier in Unit 4, Block 1 of Atoms and Molecules course and then we will discuss the effect of resonance on the acidity and basicity of molecules.

Resonance

You are already familiar with the fact that some covalent molecules or ions cannot be represented satisfactorily by a single Lewis structure. Therefore, for such species, more than one Lewis structure is possible. These Lewis structures are called **resonance structures** or **resonance contributors** and the actual molecule or ion is said to be a **resonance hybrid** of these resonance structures. Since we will be dealing with the resonance structures of various molecules in explaining their reactivity, we should be able to write all the possible resonance structures of a molecule. For this purpose, certain rules are to be followed. These rules are as listed below:

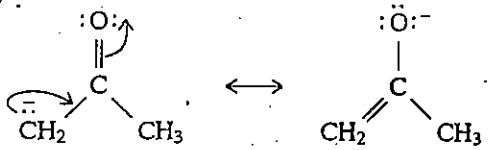
Not that a double headed arrow (⟷) is used to represent the resonance contributors. It should be clear to you that it does not mean that the resonance contributors are in rapid equilibrium but it implies that the actual molecule has one structure which has the contribution from various resonance contributors.

1. Only nonbonding electrons and electrons constituting the multiple bonds change locations from one resonance contributor to another. The electrons in single covalent bonds are not involved. This is shown in the examples below:



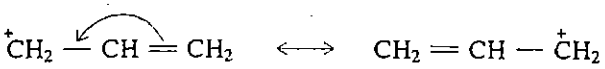
2. The nuclei of various atoms in different resonance contributors are in the same position. Hence, the structures which are shown below are not resonance structures because the location of the chlorine atom is different in them.

3. All resonance contributors must have the same number of paired and unpaired electrons. This is illustrated below :

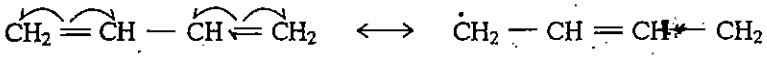


It is important to understand that the individual resonance structures have no reality and the actual compound is not a mixture of the various resonance contributors, but it is a **weighted average** of these structures. When we use the words **weighted average**, it is implied that some resonance structures are more important than the others and therefore, contribute more to the hybrid structure. But, how to know which structure is more important than the others. To evaluate the relative importance of various resonance structures, their stabilities are compared by considering each structure as a separate entity or species. In other words, we assume each resonance structure to be real. Thus, the most stable structures are the most important ones. Given below are some guidelines to enable you to assess the relative importance of resonance structures.

1. *Identical resonance structures are equally important and contribute equally towards the actual structure of a molecule.* For example, the following resonance structures contribute equally to the actual structure of the molecule.



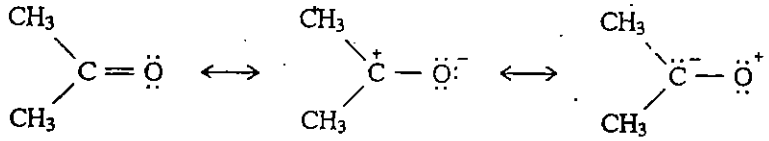
2. *Resonance contributors having greater number of bonds are more important.* Thus, in the following resonance structures, the one on the left hand side is more important.



more important

Single headed arrow denotes the movement of an electron.

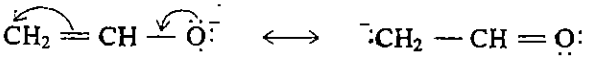
3. *Resonance contributors with little or no charge separation are more important than those having the large separation of charge.* Therefore, among the three resonance structures shown below, the first one is the most important.



most important

4. *In case of resonance contributors having separation of charge, the resonance contributor having the negative charge on the more electronegative atom is more important.*

Hence, in the following two resonance structures, the one in which the more electronegative oxygen atom carries the negative charge is more important.



more important

5. *Resonance structures in which the atoms of elements from the second period of the periodic table have eight electrons around them are more important than those in which these atoms have less than eight electrons.*

6. *Resonance structures that help in delocalisation of charge or of unpaired electrons are important.*

Having understood how to assign the relative importance to various resonance structures, let us now consider why resonance structures are important in deciding the stability of a molecule. Since the resonance structures of a molecule are symbolic representations of the additional bonding associated with the orbital overlap, *the greater the number of important resonance structures, the greater is the stability of the actual molecule.* This stabilisation due to resonance is measured in terms of the **resonance energy** which is the energy difference between the actual molecule and its best resonance structure.

Table 5.6 lists various groups which donate or withdraw electrons due to resonance. Groups which donate electrons by resonance are called +R groups. Some examples of the +R groups being the hydroxy (-OH), amino ($-NH_2$), alkoxy (-OR), halogens (-X) and alkylamino (-NHR and $-NR_2$) groups. On the other hand, the groups which withdraw electrons by resonance are called -R groups. The examples of -R groups are nitro ($-NO_2$), cyano ($-C\equiv N$), carbonyl ($>C=O$), and sulphonic ($-SO_3H$) groups.

Table 5.6 : Resonance effects of various groups.

Electron donating +R groups	Electrons withdrawing −R groups
−F	$-C\equiv N$
−Cl	$-\overset{\overset{O}{\|\|}}{C}-$
−Br	$-SO_2-$
−I	$-NO_2$
$-O^-$	
−OR	
−OH	
$-O-\overset{\overset{O}{\|\|}}{C}-R$	
$-N<$	
−SR	
−SH	
$-CH_3$	

Let us now study how resonance affects the acidity and basicity of various molecules. Consider the pK_a values for ethanoic acid and ethanol as given below:

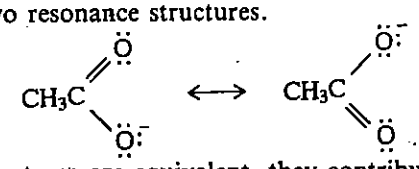
$CH_3\overset{\overset{O}{\|\|}}{C}-OH$ ethanoic acid pK_a 4.76 $\qquad$ CH_3CH_2OH ethanol pK_a 17

Consider the dissociation of these compounds as shown below:

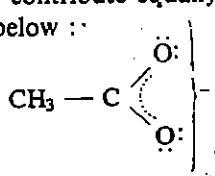
$$CH_3\overset{\overset{O}{\|\|}}{C}-OH + H_2O \rightleftharpoons CH_3-\overset{\overset{O}{\|\|}}{C}-O^- + H_3O^+$$
ethanoate ion

$$CH_3CH_2OH + H_2O \rightleftharpoons CH_3CH_2O^- + H_3O^+$$
ethoxide ion

We find that the anion of ethanoic acid can be represented as a resonance hybrid of the following two resonance structures.



Since these two structures are equivalent, they contribute equally to the actual structure which can be represented as shown below :



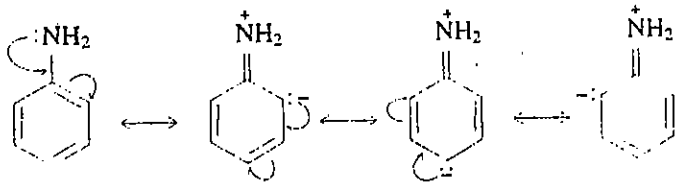
Thus, we can say that in the ethanoate anion the charge is not localised on any one of the oxygen atoms but is distributed equally, or is delocalised, over both the oxygen atoms. This dispersal of charge resulting from the delocalisation stabilises this anion. But, the delocalisation of charge reduces the availability of electrons, thereby resulting in the decrease in the basicity of the anion. Hence, the equilibrium lies in the forward direction resulting in the dissociation of the acid.

Similar resonance stabilisation is not possible for the ethoxide ion because such a stabilisation is possible only if the system has π electrons. Because of the absence of resonance stabilisation of the ethoxide anion, ethanol is less acidic as compared to ethanoic acid.

Resonance structures discussed in this section involve π electrons and in some cases nonbonded electrons. In the next section, you will study hyperconjugation which involves π and σ electrons.

The acidity of phenols can also be explained using the resonance phenomenon about which you will study in Unit 12. However, you will study the effect of resonance on the reactivity of aromatic compounds in Unit 9.

Similar to acidity, the basicity of compounds is also affected by the resonance. For example, in case benzenamine (aniline), in addition to the electron withdrawing nature (-I effect) of the aryl group, the following resonance structure are possible.



benzenamine (aniline)

These resonance structures clearly show that the nonbonding electrons of the nitrogen atom are delocalised over the aromatic ring. Thus, the electron density at the nitrogen atom decreases which results in the lower basicity of aniline as compared to ammonia.

You can check your knowledge of resonance by answering the following SAQ.

SAQ 4

Draw resonance structures for the following species to rationalise the facts given with them.

a) $H_2C=\overset{+}{O}-H$ is the conjugate acid of methanal (formaldehyde) and has a substantial positive charge on carbon.

.....

.....

.....

b) In acetonitrile oxide, $H_3C-C\equiv\overset{+}{N}-\ddot{O}:^-$, the inner carbon can act as a Lewis acid.

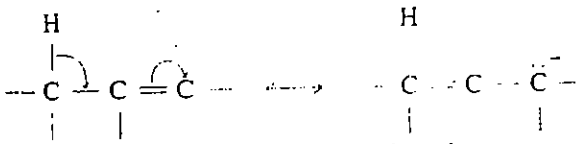
.....

.....

We will not study a special case of resonance which is known as **hyperconjugation.**

5.4.3 Hyperconjugation

Hyperconjugation involves the conjugation of *sigma* electrons with adjacent *pi* electrons, as shown below:



This is also known as $\sigma - \pi$ conjugation.

This type of delocalisation leads to a situation where there is *no bond* between the hydrogen and the carbon atom of the molecule. Therefore, it is also known as **no-bond resonance**. Remember that the proton does not leave its position and since the nuclei or the atoms do not change their positions, therefore, the hyperconjugation becomes similar to resonance. Hyperconjugation also results in the delocalisation of charge, as you will now study in case of carbocations. The

Hyperconjugation involving hydrogens is the most common.

Activity

Make a model of this carbocation and convince yourself about the overlap as shown here.

stability of carbocations has been earlier explained on the basis of inductive effect of the alkyl groups. Let us consider again a primary carbocation, such as the one shown below in Fig. 5.1.

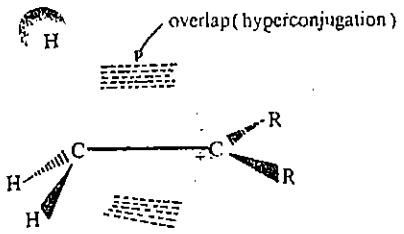
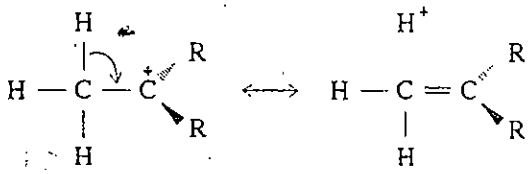


Fig. 5.1 : The hyperconjugation in a carbocation.

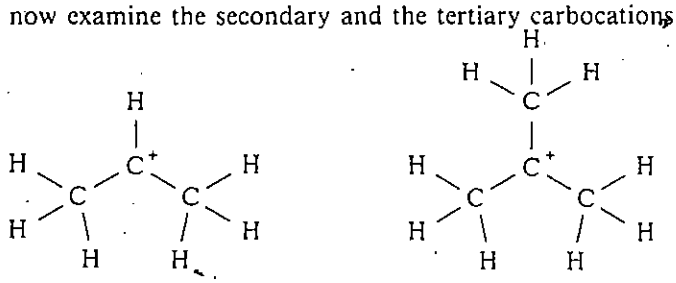
The C – H bond adjacent to the >C = C< or a carbocation is referred here as α-C–H bond.

It is clear from the above structure that the electrons forming the α-C – H bond can overlap, or spill over, into the empty *p* orbital of the carbon atom carrying the positive charge. The resulting hyperconjugation can be represented as illustrated below:



Note that hyperconjugation produces some additional bonding between the electron-deficient carbon and the adjacent carbon atom. Hence, hyperconjugation results in the stabilisation of carbocation by delocalising the positive charge. Obviously, the more the number α-C – H bonds which can participate in hyperconjugation, the more stable will be the carbocation. You can see that in case of the primary carbocation shown above, there are three such α-C – H bonds. Let us now examine the secondary and the tertiary carbocations.

For hyperconjugation to occur, the substituent next to the positively charged carbon must have a filled σ orbital available to overlap with vacant *p* orbital of the carbon atom carrying the positive charge.

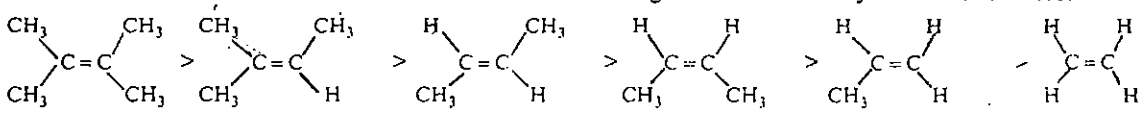


secondary carbocation
6 α – C – H bonds

tertiary carbocation
9 α – C – H bonds

The secondary carbocation has 6 α-C – H bonds which can participate in hyperconjugation whereas the tertiary carbocation has 9 α-C – H bonds. Certainly, more delocalisation of charge is possible in case of a tertiary carbocation than in a secondary carbocation which is in turn more than that possible in a primary carbocation. Therefore, the tertiary carbocation is more stable than the secondary carbocation which is more stable than the primary carbocation.

Hyperconjugation has also been used to explain the relative stabilities of substituted alkenes. Consider the following order of stability of some alkenes.



12 α-C – H bonds — *tetrasubstituted*

9 α-C – H bonds — *trisubstituted*

trans – 6 α-C – H bonds — *disubstituted*

cis – 6 α-C – H bonds — *disubstituted*

3 α-C – H bonds — *monosubstituted*

no α-C – H bonds — *no hyperconjugation* — *unsubstituted*

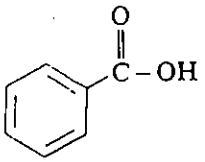
You can see that, in an alkene, the more the number of α-C – H bonds which can participate in hyperconjugation, the higher is its stability.

In spite of the fact that hyperconjugation can be used to explain many otherwise unconnected phenomena, it is controversial as it involves the formation a weaker *pi* bond at the expense of a strong *sigma* bond.

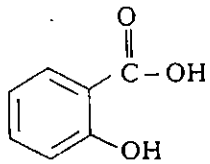
In addition to the resonance, another factor which contributes to the stability of the anion, A^-, is hydrogen bonding which you will now study.

5.4.4 Hydrogen Bonding

You are already familiar with the concept of hydrogen bonding from Unit 4 of this Block. If you analyse the pK_a values of benzenecarboxylic acid and 2-hydroxy-benzenecarboxylic acid, as given below, then you will conclude that



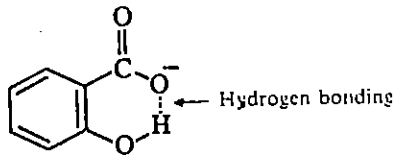
benezenecarboxylic acid
pK_a 4.2



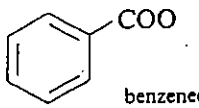
2-hydroxy benezenecarboxylic acid.
pK_a 2.98

2-hydroxy benzenecarboxylic acid is much more acidic than benzenecarboxylic acid. This is because the anion formed from 2-hydroxy-benzenecarboxylic acid is stabilised by hydrogen bonding, as shown below:

Hydrogen bonding stabilises the anion by delocalising the charge.



No similar stabilisation is possible for the benzenecarboxylate anion; therefore, benzenecarboxylic acid is less acidic than 2-hydroxy-benzenecarboxylic acid.

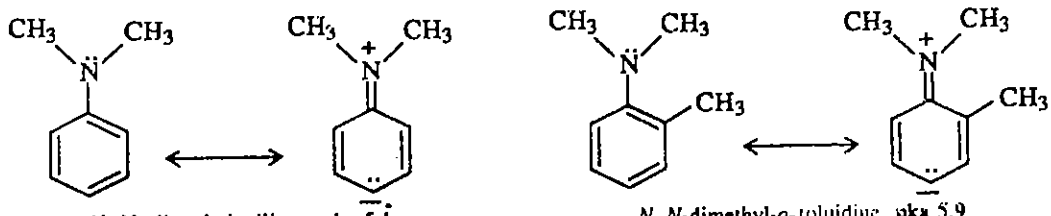


benzenecarboxylate anion

In the next section, you will study the steric effect on molecular reactivity.

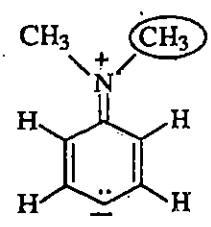
5.4.5 Steric Effect

The effect arising from the spatial interactions between the groups is called the **steric effect**. You have already studied the effect of such interactions on the stability of geometrical isomers, (in Unit 2 where you studied that the *trans-* isomer is more stable than the *cis-* isomer) and conformational isomers, (in Unit 3 where you studied that the staggered conformation is more stable than the eclipsed conformation). As the acid-base behaviour or the molecular reactivity is related to the availability of the electrons, steric factors may also influence the molecular reactivity. For example, they can inhibit the delocalisation of charge, as is observed in case of *N,N*-dimethyl-*o*-toluidine. The delocalisation of the nonbonded electron pair on nitrogen, as shown in the structure of *N,N*-dimethylaniline in Fig. 5.2(a),



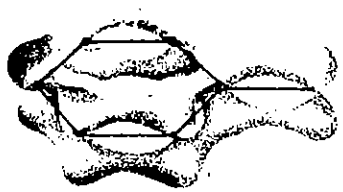
N, N- dimethylaniline pka 5.1

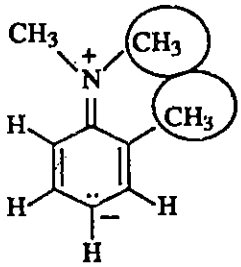
N, N-dimethyl-*o*-toluidine. pka 5.9



sterically feasible

(a)





not sterically feasible

(b)

Fig. 5.2 : a) Delocalisation of nonbonded electrons on nitrogen into aromatic ring in *N,N*-dimethylaniline. b) Such a delocalisation in not possible in *N,N*-demethyl-*o*-toluidine.

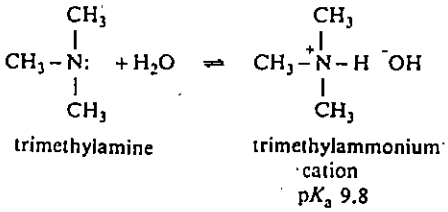
requires that the *p*-orbital of nitrogen and those of the aromati ring should be coplanar. Such coplanarity is inhibited in the case of *N,N*-dimethyl-*o*-toluidine due to the presence of the *ortho* methyl group, as shown in Fig. 5.2(b). Therefore, in this molecule the electron pair is not delocalised but is available for bonding with the proton which makes this molecule more basic than *N,N*-dimethylaniline. This type of steric effect is known as *steric inhibition of resonance.*

Remember that the *steric hindrance* affects the molecular reactivity not by increasing or decreasing the electron availability but due to spatial congestion. Therefore, it is different from electronic effects.

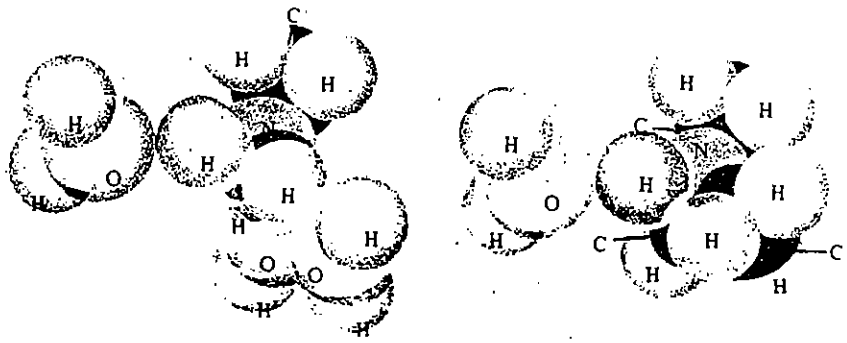
The most common steric effect is, however, the *steric hindrance* where the presence of the bulky groups makes the approach of the reagent to the reaction site difficult. Such steric hindrance can account for the lower basicity of tertiary amines as compared to secondary amines. The three alkyl groups attached to the nitrogen atom of the tertiary amine give rise to steric hindrance and interfere with the solvation (see next subsection) of its conjugate acid. Thus, as shown in Fig. 5.3, the trimethylammonium cation, i.e. the conjugate acid of trimethylamine, is sterically the most hindered.

Activity

Make models of primary, secondary and tertiary amines and compare the steric hindrance observed in these molecules.



trimethylamine — trimethylammonium cation, pK_a 9.8



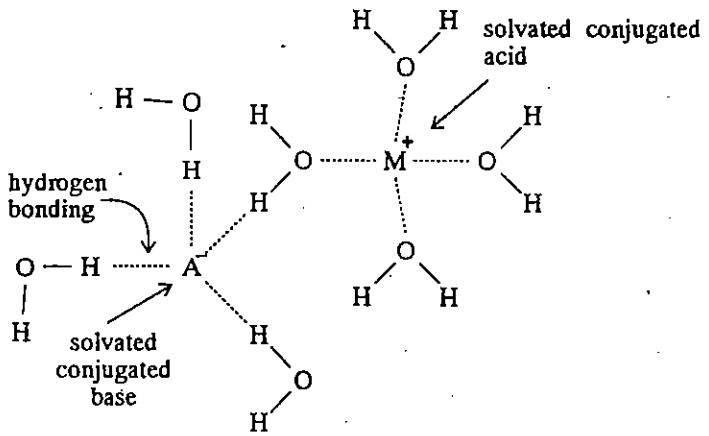
methylammonium ion hydrogen bonding with three water molecules

trimethylammonium ion hydrogen bonding with only one water molecule

Fig. 5.3 : A comparison of the solvation of trimethylammonium and methylammonium ions.

It is thus least stabilised by solvation, leading to the lower basicity of sterically the most hindered. It is thus least stabilised by solvation, leading to the lower basicity of trimethylamine in water as compared to dimethylamine and methylamine. However, in the gas phase or monaqueous media the electron-donating inductive effect of a methyl group makes frimethylamine the most basic among methylamines. Let us now study what is solvation and the role of solvent on the reactivity of the molecules.

The presence of a solvent in acid-base reactions leads to the solvation of the ionised species which are the conjugate acid and the conjugate base when we are dealing with Brönsted acids and bases. Solvation refers to the interaction of the dissolved species and solvent molecules wherein several solvent molecules surround the dissolved species by forming a **solvent shell** or **solvent cage** around it, as shown below:



The greater the solvation, the greater is the delocalisation of the charge on the species. Thus, increased solvation increases the dissociation of an acid or a base by increasing the stability of the ions.

These interactions are particularly important when water is used as a solvent where

the hydrogen bonding plays an important role in solvating the anions. The high dielectric constant of water also helps in the dissociation of the acids. Thus, the ionisation and the acidity of a substance increases with the increase in the dielectric constant of the solvent. This is illustrated in Table 5.7.

Table 5.7 : Effect of solvent on pK_a of ethanoic acid at 298 K.

Solvent	pK_a
Benzene	almost unionised
82% Dioxane – 18% Water	10.14
70% Dioxane – 30% Water	8.32
45% Dioxane – 55% Water	6.31
20% Dioxane – 80% Water	5.29
Water	4.76

Thus, as the percentage of water in the solvent system increases, the pK_a value of the acid decreases.

Water is a peculiar solvent as it can behave both as an acid as well as a base. But its use has a limitation in the sense that some organic compounds are not soluble in it.

Having discussed the various aspects of acids and bases, let us now focus our attention on an internal acid-base process called *tautomerism*.

5.5 TAUTOMERISM

The term *tautomerism* designates a rapid and reversible interconversion of isomers which are related to each other with the actual movement of electrons as well as of one or more atoms. Such isomers are called **tautomers**. Thus, tautomerism is a chemical reaction and is to be differentiated from resonance in which the nuclei do not move. It is, therefore, represented by the equilibrium sign (⇌) between the tautomers. Tautomers which differ from each other only in the location of a hydrogen atom and a double bond are called **proton tautomers**. Table 5.8 shows some examples of proton tautomers.

Table 5.8 : Some examples of Proton tautomers.

R, H, –O, –N –C(=O:)–CH– Carbonyl*	⇌	–C(–OH)=C– Enol	Keto-enol tautomerism occurs with all carbonyl-containing functional groups (esters, amides, etc.)
–N= –C–CH– Imine	⇌	–NH– –C=C– Enamine*	
:O: :N–CH– Nitroso	⇌	:OH :N=C– Oxime*	
:O: :O: N–CH– Nitro*	⇌	HO N=C– :O: *aci*-Nitro	(* = more stable tautomer)
:N≡C–CH– Nitrile*	⇌	HN=C=C–	

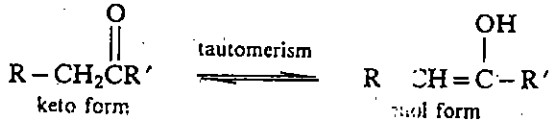
In contrast to resonance structures, tautomers are real compounds and are capable of independent existance.

enol has its origin from *ene+ol.*

In *keto-enol tautomers,* the *keto* form is usually the more stable form and, therefore, it predominates at equilibrium.

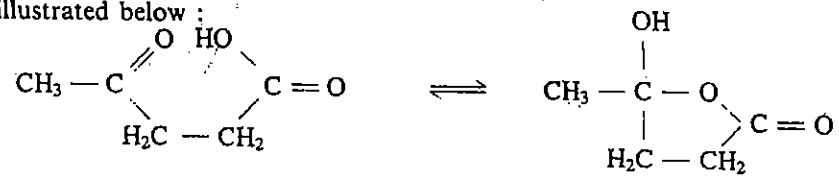
The mechanism of *enolisation* involves solvent mediated proton transfer steps rather than a direct intramolecular jump of the proton from carbon to oxygen.

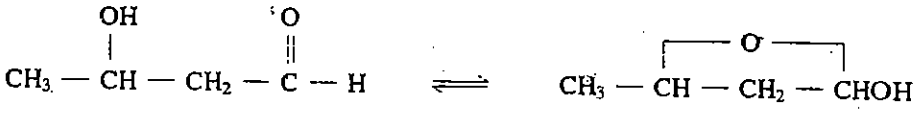
A particular example of tautomerism involving the ketones as carbonyl compounds is called **keto-enol** tautomerism and is represented below :



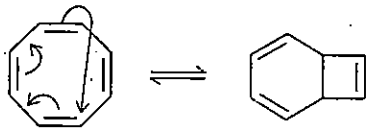
The keto-enol tautomerism is of enormous importance as you will study later in this course and also in the Organic Reactions Mechanism course.

Proton tautomerism in some cases leads to the formation of a ring in one of the tautomers. Such a tautomerism is called as **ring-chain tautomerism** and is illustrated below :





Another kind of tautomerism, known as **valence tautomerism** involves a shift in interatomic distances within a molecule, without the separation of any atom from the rest of the molecule, as an intermediate stage. This kind of tautomerism occurs as a result of movement of valence electrons of the molecule. An example of valence tautomerism is shown below :



cyclooctatetraene

The valence tautomerism may appear similar to resonance but remember that the two are different. The difference is that the valence tautomerism involves making and breaking of σ and π bonds while, in resonance only the π electrons or the nonbonding electrons shift and the σ framework of the molecule is not disturbed. Some other differences between tautomerism and resonance are as follows:

i) Tautomerism may involve a change in the hybridisation of atoms which may result in a change in the shape of the molecule. While in resonance there is no such change in the hybridisation and geometry of the molecule.

ii) The tautomers have a physical reality while the resonance structures are imaginary.

iii) Tautomerism involves an equilibrium between two or more tautomers. On the other hand, the resonance implies that the actual structure of the molecule is the *weighted average* of various resonance contributors and not a mixture of them.

5.6 SUMMARY

In this unit, you studied that,

- Many reactions of organic compounds can be classified as acid-base reactions. Therefore, the study of acids and bases is important for understanding the organic reactions.
- According to Brönsted-Lowry definition, an acid is a proton donor and a base is a proton acceptor.
- Lewis definition classifies acids as electron pair acceptors and bases as electron pair donors.
- The acidities of Brönsted acids can be expressed in terms of their pK_a values.
- A strong acid has a weak conjugate base and a weak acid has a strong conjugate base and vice versa.

- Structural changes can bring about marked differences in the acidic and basic behaviour of a molecule which can be explained on the basis of inductive, resonance and steric effects and on the basis of hydrogen bonding.
- The inductive effects operate through *sigma* bonds and decrease rapidly with increase in the distance between the substituent and the reaction site. As a consequence of the fact that inductive effect increases with the number of substituents present, a tertiary carbocation is more stable than a secondary carbocation which is more stable than a primary carbocation.
- Resonance stabilisation of an anion (or the conjugate base) favours dissociation of the acid.
- The steric effect operates due to the presence of the bulky groups near the reaction site which prevent the approach of the reagent to the reaction site. The steric requirements for Brönsted acids are usually negligible because of the small size of the proton but are important in case of Lewis acids.
- In addition to the structural changes mentioned above, the nature of the solvent also plays an important role in the acid-base equilibrium.

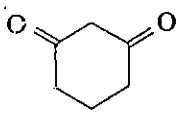
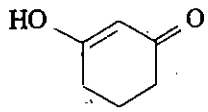
5.7 TERMINAL QUESTIONS

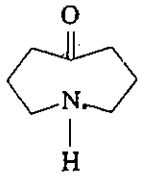
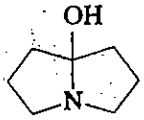
1. Explain the acidic nature of 2,2,2-trifluoroethanol as compared to ethanol.
2. Explain the difference between pK_{a_1} (4.16) and pK_{a_2} (5.61) of butanedioic acid
3. Draw resonance structures for the following:
   (i) chlorobenzene ii) acetonitrile
   iii) pyrrole,

4. Ethylamine and aniline react with aq. HCl. Write the equations for these reactions.
5. Are the following pairs of compounds tautomers or resonance forms?

(a) $CH_3-\overset{OCH_3}{\overset{|}{C}}=\overset{+}{N}(CH_3)_2$ and $CH_3-\overset{\overset{+}{O}CH_3}{\overset{||}{C}}-N(CH_3)_2$

(b) $CH_3-\overset{OCH_3}{\overset{|}{C}}=NCH_3$ and $CH_3-\overset{O}{\overset{||}{C}}-N(CH_3)_2$

(c)  and 

(d)  and 

5.8 ANSWERS

Self-assessment Questions

1. a) $\underset{\text{acid}}{CH_3-\overset{O}{\overset{||}{C}}-OH} + \underset{\text{base}}{^-OH} \rightarrow \underset{\text{conjugate base}}{CH_3-\overset{O}{\overset{||}{C}}-O^-} + \underset{\text{conjugate acid}}{H_2O}$

a) $CH_3-\overset{\overset{\large O}{\|}}{C}-OH + H_2SO_4 \rightarrow CH_3-\overset{\overset{\large O}{\|}}{C}-\overset{+}{O}H_2 + HSO_4^-$

base — acid — conjugate acid — conjugate base

c) $(CH_3)_3\overset{+}{N}H + CH_3O^- \rightarrow (CH_3)_3N: + CH_3OH$

acid — base — conjugate base — conjugate acid

d) $\begin{matrix} CH_3 \\ \ \ \diagdown \\ \quad C=CH_2 \\ \ \ \diagup \\ CH_3 \end{matrix} + H_3\overset{+}{O} \rightarrow \begin{matrix} CH_3 \\ \ \ \diagdown^{+} \\ \quad C-CH_3 \\ \ \ \diagup \\ CH_3 \end{matrix} + H_2O$

base — acid — conjugate acid — conjugate base

2. a) Acid HA_2 having the lower pK_a value is stronger than acid HA_1 having higher pK_a value.

b) Since HA_2 is stronger acid, therefore, A_2^- is the weaker base as compared to A_1^-. Thus, in an acid-base reaction between $Na^+A_1^-$ and HA_2 which is shown below;

$$Na^+A_1^- + HA_2 \rightleftharpoons HA_1 + Na^+A_2^-$$

the stronger base A_1^- will abstract the proton from the acid HA_2 and the equilibrium will lie towards the right to yield HA_1 and $Na^+A_2^-$.

3. a) The decreasing order of acidities is,

i) $NCCH_2COOH > NCCH_2CH_2CH_2COOH > CH_3COOH$. Since the $-CN$ group has $-I$ effect which increases the acidity of $NCCH_2COOH$ and $NCCH_2CH_2CH_2COOH$ as compared to ethanoic acid. But the $-I$ effect of the $-CN$ group decreases with the distance, therefore, $NCCH_2CH_2CH_2COOH$ is less acidic than $NCCH_2COOH$.

ii) The compounds have the following order of the acidities:

$$CH(NO_2)_3 > CH_2(NO_2)_2 > CH_3NO_2$$

As the $-NO_2$ group is strongly electron withdrawing, the acidity increases with the increase in the number of these substituents.

iii) $\underset{1}{HOOCCOOH} > \underset{2}{CH_3COOH} > \underset{3}{^-OOCCOOH}$

The COOH group is $-I$ type. Hence, it increases the acidity in case of HOOCCOOH as compared to CH_3COOH. But, in case of $^-OOCCOOH$, the removal of a proton is difficult because it is a negatively charged species. Hence, it is less acidic as compared to CH_3COOH.

b) i) The basicities decrease in the following order:

N,N-dimethylaniline > *N*-methylaniline > aniline

As the methyl group is electron donating, it increases the basicity in case of *N*-methylaniline as compared to aniline. The basicity further increases in *N,N*-dimethylaniline due to the increase in the number of methyl groups.

ii) The decreasing order of basicities is as shown below:

$$CH_3NH_2 > NH_3 > NH_2OH$$

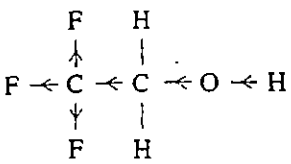
Since the methyl group has + I effect, it increases the basicity of CH_3NH_2 as compared to NH_3. But, the substitution of an $-OH$ group in NH_3 decreases its basicity because it has $-I$ effect.

4. (a) $H_2C=\overset{\curvearrowright}{O}-H \longleftrightarrow H_2\overset{+}{C}-O-H$

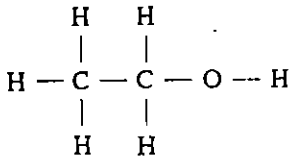
(b) $H_3C-C\equiv\overset{\curvearrowright}{N}-\ddot{O}:^- \longleftrightarrow H_3C-\overset{+}{C}=N-\ddot{O}:^-$

Terminal Questions

1.



2,2,2-trifluoroethanol



ethanol

The three strong electron withdrawing fluorine atoms (–I groups) increase the acidity of 2,2,2-trifluoroethanol as compared to ethanol.

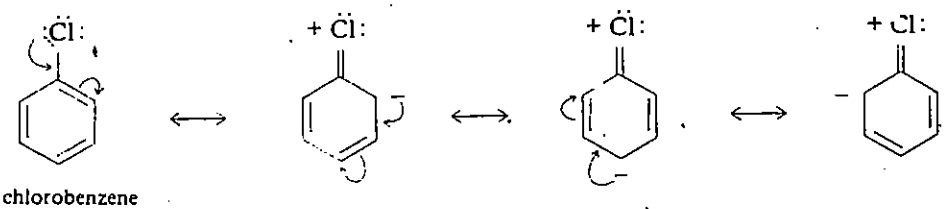
2. $CH_2-COOH \underset{\text{fast}}{\overset{\text{Base}}{\rightleftharpoons}} CH_2-C(=O)-O^-$ (anion) The first ionisation is fast because this anion is resonance stabilised.

$CH_2-COOH \qquad\qquad CH_2-COOH$

$CH_2-COO^- \underset{\text{slow}}{\overset{\text{Base}}{\rightleftharpoons}} CH_2COO^-$ The anion formed in the first step slows down further ionisation because it is difficult to remove a proton from a negatively charged species.

$CH_2-COOH \qquad\qquad CH_2COO^-$

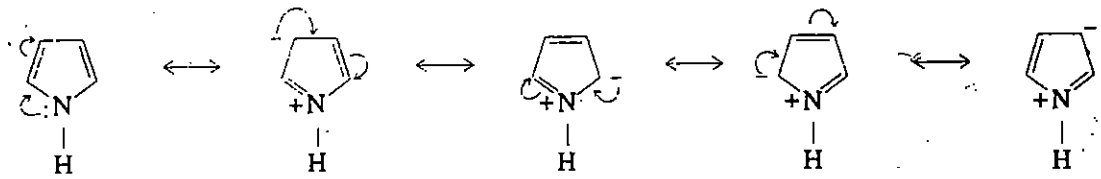
3. (i)



chlorobenzene

(ii) $CH_3-C\equiv\overset{\curvearrowright}{N} \longleftrightarrow CH_3-\overset{+}{C}=\overset{-}{N}$

acetonitrile



pyrrole

4. $C_2H_5NH_2 + HCl \rightleftharpoons C_2H_5\overset{+}{N}H_3\ Cl^-$

ethylamine

$C_6H_5NH_2 + HCl \rightleftharpoons C_6H_5\overset{+}{N}H_3\ Cl^-$

aniline

5. Only (a) shows resonance structures; (b), (c) and (d) are tautomers.

Further Reading

1. *Organic Chemistry, 6th* Ed., By R.T. Morrison and R.N. Boyd, Prentice-Hall of India Pvt. Ltd.
2. *Text book of Organic Chemistry,* 2nd Ed., By Lloyd N. Ferguson, Affiliated East-West Press Pvt. Ltd.
3. *Organic Chemistry*, Vol. I and II By S.M. Mukherji, S.P. Singh and R.P. Kapoor, Wiley Eastern Ltd.
4. *Text book of Organic Chemistry,* 24th Ed., By P.L. Soni and H.M. Chawla, Sultan Chand and Sons.

NOTES

UTTAR PRADESH
RAJARSHI TANDON OPEN UNIVERSITY

UGCHE - 05
Organic Chemistry - I

Block

2

BASIC SKELETON : HYDROCARBONS AND HETEROCYCLES

UNIT 6

Alkanes 5

UNIT 7

Alkenes 20

UNIT 8

Alkynes 37

UNIT 9

Aromatic Hydrocarbons and Polynuclear Aromatics 52

UNIT 10

Heterocyclic Compounds 81

BLOCK 2 BASIC SKELETON : HYDROCARBONS AND HETEROCYCLES

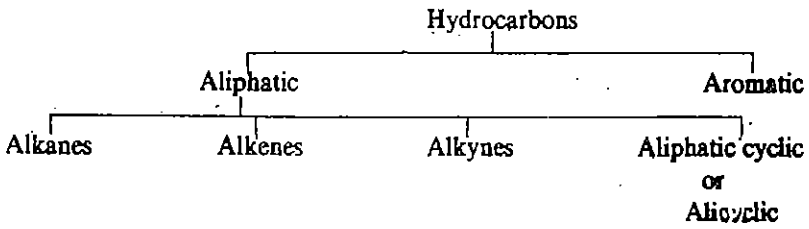
In Block 1, you have studied the fundamental concepts like :

- bonding,
- classification of organic compounds based on functional groups,
- nomenclature,
- stereochemistry,
- effects of molecular architecture on physical properties, and
- structure-reactivity relationships.

In this block, you will learn about the hydrocarbons and heterocyclic compounds. These compounds provide the skeleton for all organic compounds.

The term **hydrocarbon** is used to designate organic compound of carbon and hydrogen. On the basis of structure, the hydrocarbons can be divided into two main categories : aliphatic and aromatic.

The aliphatic hydrocarbons can be further divided into four families : alkanes, alkenes, alkynes and their cyclic analogues. Alkanes are saturated aliphatic hydrocarbons. Alkenes and alkynes are unsaturated aliphatic hydrocarbons.



This block contains five units. In Unit 6, which is the first unit of this block, we shall discuss chemistry of alkanes. Alkanes are saturated open or branched chain hydrocarbons. Alkanes can be prepared from alkenes, alkynes, alkyl halides or carboxylic acids. These compounds are generally unreactive. Alkanes undergo mainly substitution reaction, and that too at a high temperature or in the pressure of UV light. In addition to this, you will study about the petroleum and its refining.

In Unit 7, you will study the characteristic features of alkenes. Open or branched chain hydrocarbons containing one or more carbon-carbon double bond(s) are known as alkenes. Alkenes can be prepared from alkyl halides, alcohols and ketones. The characteristic reactions of alkenes involve addition to C=C bond. Addition reaction may be initiated by an electrophile or a free radical.

In Unit 8, you will learn another kind of hydrocarbons, known as alkynes, which contain carbon-carbon triple bond. Alkynes can be prepared by the alkylation of terminal alkynes or by two-fold elimination of HX from dihalides or dehalogenation of tetrahalides. Alky react with electrophilic reagents in a manner similar to that of alkenes. In addition to electrophilic reactions, alkynes undergo reduction and oxidation reactions. In this unit, you will also study the acidity of terminal alkynes which is the most unique aspect of chemistry of alkynes.

Unit 9 deals with the aromatic and polynuclear hydrocarbons. In this unit, you will study the isolation, properties and structure of benzene. We shall see that the characteristic reactions of aromatic hydrocarbons involve substitution, in which the resonance-stabilised ring system is preserved. In addition to substitution, these compounds undergo addition.

In the last unit, we shall discuss the heterocyclic hydrocarbons, i.e., rings containing another element in addition to carbon atom. The presence of lone pair of electrons on nitrogen and

other hetero atoms accounts for the difference in properties between heterocyclic and carbocyclic aromatic hydrocarbons. For example, unlike benzene, pyridine undergoes nucleophilic substitution, yet it resembles benzene in giving rise to electrophilic substitution. We shall study the isolation and preparation of furan, pyrrole, thiophene and pyridine from natural sources. We shall also discuss the chemical characteristics of these compounds. In first four units, the spectral characteristics of the concerned class of compounds have also been discussed.

Objectives

After studying this block, you should be able to :

- classify the types of hydrocarbons,
- list the physical and spectral properties of hydrocarbons,
- discuss the different methods for preparation of hydrocarbons and heterocyclic compounds, and
- discuss the important chemical reactions of hydrocarbons and heterocyclic compounds.

JNIT 6 ALKANES

tructure

.1 Introduction
Objectives

.2 Petroleum: A Source of Alkanes
Composition
Fractionation of Petroleum
Synthetic Petroleum
Octane Number
Cetane Number

3 Physical Properties

4 Spectral Properties

5 Preparation of Alkanes and Cycloalkanes
Wurtz Reaction
Kolbe's Electrolytic Method
Hydrogenation of Unsaturated Hydrocarbons
Reduction of Alkyl Halides
Decarboxylation of the Carboxylic Acids
Preparation of Cycloalkanes

6 Reactions of Alkanes
Halogenation
Nitration
Isomerisation
Aromatisation
Pyrolysis
Combustion
Reactions of Small Ring Compounds

7 Summary

8 Terminal Questions

9 Answers

.1 INTRODUCTION

lkanes are saturated aliphatic hydrocarbons. You have already learnt in your previous asses that the saturated aliphatic hydrocarbons have the general formula, C_nH_{2n+2}, Because their zig-zag patterns due to the tetrahedral geometry of sp^3 hybridised carbon, carbon oms which are close together often join up with expulsion of two hydrogen atoms to form ring. Such ring compounds are referred to as cyclic aliphatic hydrocarbons, also called icyclic hydrocarbons or cycloalkanes which have the general formula, C_nH_{2n}.

lkanes are also known as **paraffins**. The name paraffin comes from two Latin words, 'araum and affinis", which mean "little affinity". This name was suggested because these 'drocarbons were apparently unreactive. It is observed that, under ordinary conditions, kanes are inert toward reagents such as acids, alkalies oxidising agents and reducing ents. However, under suitable conditions, alkanes undergo different types of reactions like logenation, pyrolysis, aromatisation, etc. Many of these reactions proceed through the rmation of highly reactive free radicals.

this unit, first we shall discuss composition and fractionation of petroleum, as it is the ain source of alkanes. Then we shall discuss the preparation, physical properties and ectral properties of alkenes. Finally, we shall study some chemical reactions of alkanes d cycloalkanes.

bjectives

fter studying this unit, you should be able to :

- describe the composition and fractionation of petroleum,
- define octane number and cetane number,

- discuss the physical properties of alkanes,
- list the characteristic spectral peaks of alkanes in uv, ir, nmr and mass spectra,
- list the methods for preparation of alkanes and cycloalkanes,
- discuss the important chemical reactions of alkanes and cycloalkanes.

6.2 PETROLEUM : A SOURCE OF ALKANES

Petroleum is the chief source of many acyclic as well as cyclic alkanes. This complex mixture of alkanes occurs abundantly in various natural deposits in the earth.

The biggest oil-producing country of the world is the USA. The other major oil producing countries are Russia, Venezuela, Iran, Gulf countries, Romania, Nyammar, Pakistan and India.

Petroleum is an oily, thick inflammable and usually dark coloured liquid. The origin of the word petroleum is from the Latin words petra (rock) and oleum (oil), as it is found in abundance near the surface of the earth trapped by rock structure.

Petroleum industry in India has made headway only after independence. In the last 30 years, petroleum production and refining levels have increased by more than 100 times whereas the consumption has increased by around 15 times. It is worth mentioning that even with this increased productivity, only two-thirds of our needs are satisfied.

Petroleum can be separated into various fractions known as gasoline, naphtha, kerosene, etc. In the following section, we will study the composition of petroleum in detail.

6.2.1 Composition

Liquefied petroleum gas (LPG) contains a mixture of propane and butane.

The composition of petroleum varies with the locality of its occurrence but all samples contain mixtures of alkanes ranging in size from methane with only one carbon atom to long chain hydrocarbon containing upto 40 carbon atoms. Cyclohexane, naphthalenes and other aromatic hydrocarbons are also present in small amounts. In addition to hydrocarbons, oxygen, nitrogen and sulphur containing compounds as well as metallic constituents may also be present. In fact, as many as 500 compounds have sometimes been detected in a single sample of petroleum.

Natural gas is found along with petroleum whose major components are methane (80%) and ethane (10%). The remaining 10% being a mixture of higher hydrocarbons. Besides hydrocarbons, natural gas also contains carbon dioxide and nitrogen.

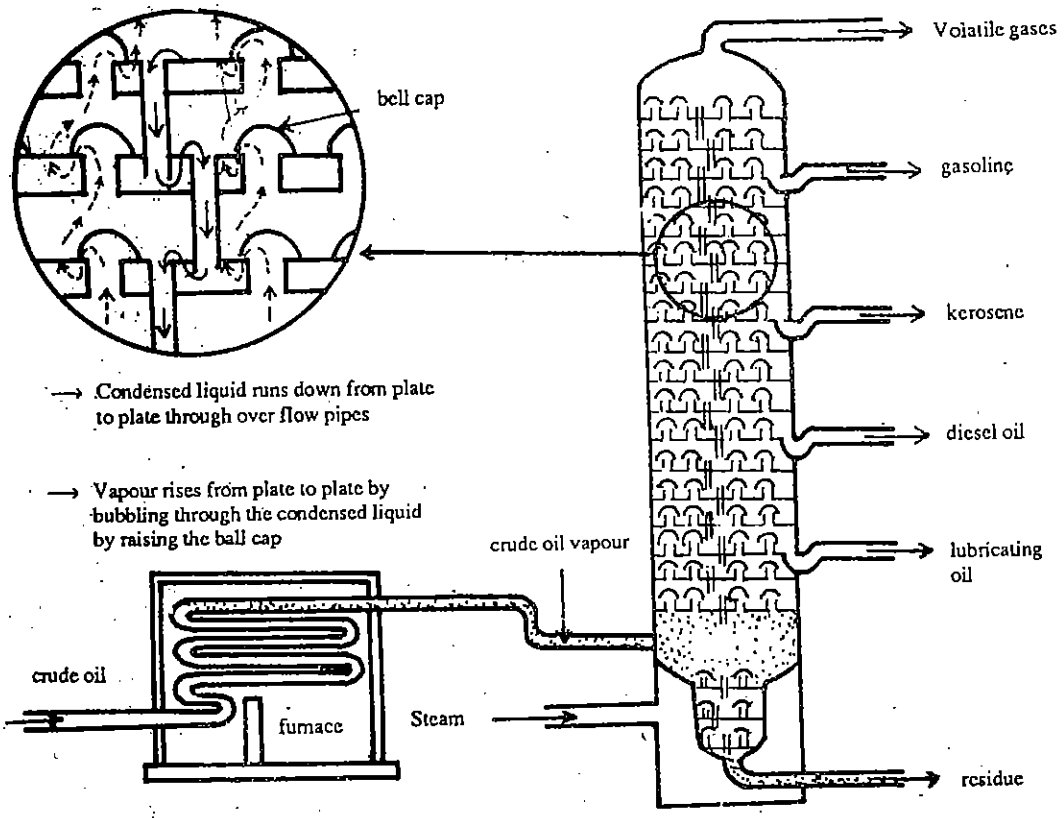


Fig. 6.1 : Fractionation of Petroleum

The petroleum obtained directly from the ground is not readily usable, since it is a mixture of many compounds. Separating the crude petroleum into useful components is called **refining**. The first step in refining is fractional distillation.

6.2.2 Fractionation of Petroleum

The first step in the refining of petroleum involves its separation into fractions of different boiling ranges by fractional distillation. Crude petroleum is heated in a furnace at 650 K and the hot liquid is then passed through a flash chamber where the low boiling fractions are volatilised by lowering the pressure. The vapours are then passed through a tall bubble tower. This tower is filled with horizontal stainless steel trays. Each tray is provided with chimneys covered with a loose cap called **bell cap** (Fig. 6.1). As the vapours ascend, they become gradually cooler and, therefore, various fractions condense at different heights. The higher boiling fractions condense in the lower portion of the tower. This permits the separation of crude petroleum vapours into a number of fractions, each condensing within a definite temperature range. Each fraction is a mixture of different hydrocarbons. Therefore, it has to be purified prior to use.

The important petroleum fractions along with their boiling ranges and chief uses are given in Table 6.1.

Tube 6.1 : Fractionation of Petroleum

Name	B.P. (K)	Approximate composition	Uses
Natural gas		C_1-C_4	Refinery and domestic fuel
Light petrol	293-373	C_5-C_7	Solvent
Benzine	343-363	C_6-C_7	Dry cleaning
Ligroin	353-393	C_6-C_8	Solvent
Petrol (gasoline)	343-473	C_6-C_{11}	Motor fuel
Kerosene (paraffin oil)	473-573	C_{12}-C_{16}	Lighting
Gas oil (heavy oil)	above 573	C_{13}-C_{18}	Fuel oil
Lubricating oil (mineral oil)	above 573	C_{16}-C_{20}	Lubricants
Greases, Vaseline, Petroleum	above 573	C_{18}-C_{22}	Pharmaceutical preparations
Paraffin wax (hard wax)	above 573	C_{20}-C_{30}	Candles, waxed paper, etc.
Residue (asphaltic bitumen)	above 573	C_{30}-C_{40}	Asphalt tar, petroleum coke

6.2.3 Synthetic Petroleum

With the development of civilization and the growth of industry, the demand of gasoline and petroleum products is increasing day by day. The natural resources are limited and it is feared that they will soon be exhausted. Keeping this in mind, the chemists have tried different methods of manufacturing synthetic fuels. Following processes have shown some promise.

Bergius Process. In this process, finely powdered coal is hydrogenated in presence of catalysts, such as tin and lead to give a mixture of liquid hydrocarbons. During this process, the carbon rings in coal undergo fission to give smaller fragments which are then hydrogenated to open chain and cyclic hydrocarbons. Gasoline (bp upto 473 K) and kerosene (bp upto 573 K) are obtained on fractional distillation of hydrogenation products.

Fischer-Tropsch Process. This method was developed in 1923 by two German chemists, Franz Fischer and Hans Tropsch. Water gas, which is a mixture of carbon monoxide and hydrogen, is obtained by the reaction of steam with red hot coke. The water gas is mixed with half its volume of hydrogen and the catalyst used in the process is a mixture of cobalt (100 parts), thoria (5 parts), magnesia (8 parts) and kieselguar (100 parts). This water gas when hydrogenated and passed over a catalyst at 470-870 K under 1-10 atm pressure yields crude petroleum.

$$n\text{CO} + m\text{H}_2 \longrightarrow \text{Mixture of hydrocarbons} + \text{H}_2\text{O}$$

The crude oil obtained is refined by the fractional distillation process as described earlier.

6.2.4 Octane Number

The most commonly used fuel for automobiles is gasoline. Not all fuel are equally good. Let us see how we can differentiate between good quality and bad quality fuels. This can be done by comparing their octane numbers. Octane number is a measure of the quality of gasoline : the higher the octane number, the better the fuel.

The 2, 2, 4-trimethylpentane (iso-octane), which is considered a good fuel, is given an octane number of 100 whereas *n*-heptane, a very poor fuel, is given an octane number of zero. Mixture of these two compounds are used to define octane numbers between 0 and 100. Octane number is the percentage of 2, 2, 4-trimethylpentane present in a mixture of 2, 2, 4-trimethylpentane and *n*-heptane which has similar ignition properties as the fuel under examination. For example, a fuel that performs as well as a 1 : 1 mixture of 2, 2, 4-trimethylpentane and *n*-heptane has an octane number 50. Commercial gasoline has octane number 81, 74 and 65 for the premium, regular and third grade gasoline. Good quality motor fuels used in modern automobiles have octane number in the 87-95 range.

It has been observed that :

- branching of the hydrocarbon chain increases octane number
- octane number decreases as the chain length increases
- unsaturated hydrocarbons have higher octane number than saturated hydrocarbons
- cycloalkanes have higher octane number than the corresponding acyclic alkanes.

Various additives, such as tetraethyllead, $(C_2H_5)_4Pb$ and *tert*-butyl methyl ether, $(CH_3)_3COCH_3$, are used to boost the octane number of gasoline. The use of tetraethyllead is being curtailed for environmental reasons.

6.2.5 Cetane Number

The working of diesel engine differs from that of gasoline engine. In diesel engines, fuels having a lower octane number are much more useful than those having a higher octane number. In other words, the straight chain hydrocarbons constitute a superior fuel than the branched chain hydrocarbons. Quality of diesel fuel is expressed in terms of a number called **cetane number**.

The hexadecane (cetane, $C_{16}H_{34}$), considered a good fuel, is given a cetane number 100 whereas α-methylnaphthalene, a very poor fuel, is given a cetane number zero. Cetane number is defined as the percentage of hexadecane in a mixture of hexadecane and α- methylnaphthalene which has similar ignition properties as the fuel under examination. Good quality diesel fuel required for modern diesel engine have cetane number greater than 45.

SAQ 1

State which compound has best octane rating in each of the following pairs.

a) $CH_3(CH_2)_4CH_3$; $CH_3CH_2CH_2CH_3$

b) $CH_3CH(CH_3)CH_3$; $CH_3(CH_2)_4CH_3$

c) $CH_2=CHCH_2CH_3$; $CH_3CH_2CH_2CH_3$

d) $CH_3C(CH_3)=CHCH_3$; $CH_3CH(CH_3)CH_2CH_3$

6.3 PHYSICAL PROPERTIES

Covalent bonds of an alkane molecule are either carbon-carbon bonds or bonds between carbon and hydrogen atoms that differ very little in electronegativity. Therefore, the alkane

molecule is either nonpolar or very weakly polar. Their physical constants like boiling points, densities, etc., increase with increase in the number of carbon atoms. Except for the first few members, the boiling point increases by 20 to 30 degrees for each CH_2 unit that is added to the chain. Boiling point of a covalent substance depends upon the intermolecular forces. Intermolecular forces, in turn, depend upon the number of electrons, surface area of the molecule and its dipole moment. The intermolecular forces increase with the increase in the number of electrons or in the value of the dipole moment and surface. area. The stronger the intermolecular forces, the higher the boiling point. In a particular series, with the increase in the number of carbon atoms, the surface area increases and hence, the intermolecular forces and boiling points also increase. Branching in a chain reduces the surface area and, therefore, decreases the boiling point.

	$CH_3CH_2CH_2CH_3$ butane	$CH_3(CH_2)_3CH_3$ pentane
BP (K)	273	309

	CH_3CHCH_3 | CH_3 2-methyl propane	$CH_3CHCH_2CH_3$ | CH_3 2-methyl butane	CH_3CCH_3 | | CH_3 CH_3 2, 2-dimethyl propane
BP (K)	261	245	276.5

Unlike boiling points, the melting points of alkanes do not show a regular increase. It has been found that molecules with an odd number of carbon atoms have lower melting point than those with an even number of carbon atoms. A possible explanation is given here. The carbon atoms in alkanes are sp^3 hybridised state with a bond angle of 109°28′. The terminal carbon atoms in a carbon chain with an odd number of carbon atoms lie on the same side, whereas those in a carbon chain with an even number of carbon atoms lie on the opposite site. This means that the packing efficiency and the interaction between the molecules in the solid state is less in alkanes containing an odd number of carbon atoms as compared to those with an even number of carbon atoms. This is reflected in the lower melting points of alkanes with odd number of carbon atoms. The maximum density of alkane is about 0.8, thus, all alkanes are lighter than water. Alkanes are soluble in nonpolar solvents but insoluble in polar solvents.

Terminal carbon atoms in a carbon chain with 5 carbon atoms (odd numbered) lying on the same side.

Terminal carbon atoms in a carbon chain with 4 carbon atoms (even numbered) lying on the opposite side.

SAQ 2

Fill in the blanks :

a) Alkane molecules are very weakly polar or nonpolar because there is very little ..... difference between the carbon and hydrogen atoms.

b) Boiling point of alkanes ..... with the increase in the length of the carbon chain.

c) Branching in the carbon chain ..... the boiling point.

d) Alkanes are soluble in ..... solvents.

6.4 SPECTRAL PROPERTIES

Uv spectroscopy is not of much help in the characterisation of alkanes, since the alkanes do not show any absorption band above 200 nm.

In the infrared (ir) spectra of alkanes, the position of C-H stretching band depends on whether the hydrogen atom is attached to a primary, secondary or tertiary carbon atom. Thus, we have the following regions :

$-\overset{|}{CH_3}$ 2975-2950 and 2885-2860 cm^{-1}

$-\overset{|}{CH_2}$ 2940-2915 and 2870-2845 cm^{-1}

$-\overset{|}{CH}$ 2900-2880 cm^{-1}

Some C—H deformation absorption frequencies are $-CH_3$, 1470-1435 and 1385-1370 cm^{-1}

and $>CH_2$, 1480-1440 cm^{-1}. Two useful skeletal vibrations are : $(CH_3)_2CH$-, 1175-1165 cm^{-1} and $(CH_3)_3C$-, 1255-1245 cm^{-1}. It is thus possible to detect the presence of these groups in a molecule.

The nmr spectra of alkanes give characteristic signals at, δ 0.9 (CH_3), δ 1.4 ($-\overset{|}{C}H_2$) and δ 1.5 ($-\overset{|}{\underset{|}{C}}H$).

Let us now examine the mass spectra of alkanes. The stability of the radical ions can also be presumed in the order *tert* > *sec* > *p*, hence, the fission of bonds in alkanes occurs preferentially at the branched carbon atom. When alternative fissions can occur, it is the heaviest side chain that is eliminated preferentially. Since alkyl radical ions are formed, all those with ^1H and ^{12}C will give peaks of odd masses in their mass spectra. In particular, alkanes give a series of peaks separated by 14 mass units (CH_2). The relative abundances of these peaks is usually the greatest for $C_3H_7^+$(43), $C_4H_9^+$(57) and $C_5H_{11}^+$(71), and decreases fairly regularly for the larger masses.

6.5 PREPARATION OF ALKANES AND CYCLOALKANES

Alkanes are generally obtained from natural sources : petroleum and natural gas. However, synthetic methods are more practical when a pure alkane is required. Alkanes can be prepared from : (a) alkenes or alkynes, (b) alkyl halides, and (c) carboxylic acids. You have already studied about the preparation of alkanes and cycloalkanes in your earlier classes. Here we recall only the important methods. General methods for the preparation of alkanes and cycloalkanes are summarised in Table 6.2.

Table 6.2 : Reaction for the preparation of alkane and cycloalkanes

ALKANES

Wurtz reaction

$2RX + 2Na \longrightarrow RR + 2NaX$

Kolbe's electrolytic method

$R'COOK + RCOOK \longrightarrow \underbrace{R'R + 2CO_2}_{\text{at anode}} + \underbrace{H_2 + 2KOH}_{\text{at cathode}}$

Hydrogenation of unsaturated hydrocarbons

$RCH=CHR + H_2 \xrightarrow{\text{catalyst}} RCH_2CH_2R$

Reduction of alkyl halides

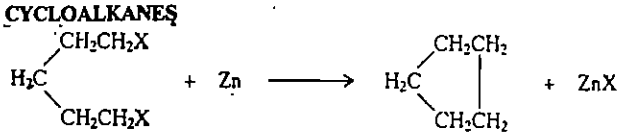
$RX \xrightarrow[\text{agent}]{\text{reducing}} RH$

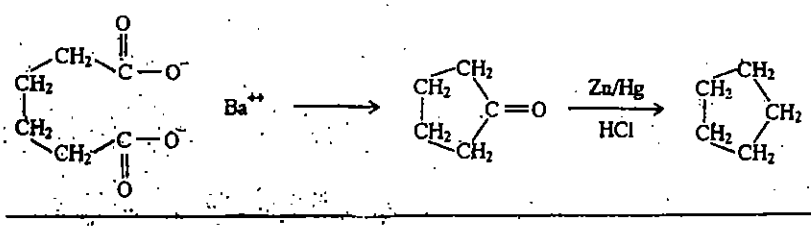
$RX + Mg \xrightarrow{\text{ether}} RMgX \xrightarrow[H_2O]{H^+} RH + Mg(OH)X$

Decarboxylation of carboxylic acids

$RCOONa + NaOH \longrightarrow RH + Na_2CO_3$

CYCLOALKANES





Now let us study these methods in brief.

6.5.1 Wurtz Reaction

In the Wurtz reaction, an alkyl halide is treated with sodium in the presence of dry ether. The result is the joining of the two alkyl groups from two molecules of alkyl halide with the loss of halogens.

$$2RX + 2Na \longrightarrow RR + 2NaX$$

This reaction is useful only when two identical alkyl halide molecules are used. When a mixture of two different alkyl halides is used, a mixture of three different alkane is obtained. For example, if you take a mixture of bromomethane and bromoethane, you will get three different products, viz.,

$$CH_3Br + C_2H_5Br + 2Na \longrightarrow CH_3\text{-}C_2H_5 + 2NaBr$$
$$CH_3Br + CH_3Br + 2Na \longrightarrow CH_3\text{-}CH_3 + 2NaBr$$
$$C_2H_5Br + C_2H_5Br + 2Na \longrightarrow C_2H_5\text{-}C_2H_5 + 2NaBr$$

The separation of such a mixture into individual alkane is quite difficult. Thus, the Wurtz reaction between two different alkyl halides is normally useless in practice. When a single alkyl halide is used, the synthesised hydrocarbon contains an even number of carbon atoms. In other words, we can say that Wurtz reaction is suitable for the preparation of only those alkanes which contain an even number of carbon atoms. As shown above, the main difficulty with the Wurtz reaction is the formation of many side products when an alkane with odd number of carbon atoms is desired.

6.5.2 Kolbe's Electrolytic Method

When a concentrated solution of sodium or potassium salt of a carboxylic acid is electrolysed, an alkane is formed. The method is known as Kolbe's electrolytic method.

$$RCOOK + RCOOK + H_2O \longrightarrow \underset{\text{at anode}}{RR} + 2CO_2 + \underset{\text{at cathode}}{H_2} + 2KOH$$

The following mechanistic pathway illustrates this method :

$$CH_3COOK \longrightarrow CH_3COO^- + K^+$$

at cathode

$$CH_3\overset{\overset{O}{\|}}{C}\!-\!O^- \xrightarrow{-e} \underset{\text{acetoxy radical}}{CH_3\overset{\overset{O}{\|}}{C}\!-\!O}$$

$$CH_3\overset{\overset{O}{\|}}{C}\!-\!O \longrightarrow CH_3 + CO_2$$

$$CH_3 + CH_3 \longrightarrow CH_3 - CH_3$$

At cathode

$$2Na^+ \xrightarrow{+2e} 2Na \xrightarrow{2H_2O} 2NaOH + H_2$$

$$2H_2O + 2\bar{e} \longrightarrow H_2 + 2\bar{O}H$$

In case a mixture of salts of two carboxylic acids is electrolysed, a mixture of alkanes is formed :

$$R'COOK + R''COOK \longrightarrow \begin{matrix} R'R' \\ R'R'' \\ R''R'' \end{matrix} + CO_2 + H_2 + KOH$$

This reaction has limited synthetic applications because of the formation of many side products as a result of other reactions of the free radicals formed.

6.5.3 Hydrogenation of Unsaturated Hydrocarbons

Alkanes or cycloalkanes can be prepared by hydrogenation of unsaturated hydrocarbons using platinum or palladium as a catalysts. The general reaction for the reduction of alkene is :

$$\underset{\text{alkane}}{RCH{=}CHR} + H_2 \xrightarrow{\text{Pt or Pd}} \underset{\text{alkane}}{RCH_2CH_2R'}$$

$$\underset{\text{alkyne}}{RC{\equiv}CR} + 2H_2 \xrightarrow{\text{Pt or Pd}} \underset{\text{alkene}}{RCH_2CH_2R}$$

Hydrogenation of an alkene can also be carried out by using nickel catalyst but relatively higher temperature and pressure are required for this reaction. This reaction is called **Sabatier-Senderen's reaction.** An example is given below :

$$\underset{\text{1-propene}}{CH_3CH{=}CH_2} + H_2 \xrightarrow{Ni} \underset{\text{propane}}{CH_3CH_2CH_3}$$

This is a very useful synthetic method and the yield is nearly 100%.

6.5.4 Reduction of Alkyl Halides

Alkanes can also be prepared by the reduction of alkyl halides by various methods. Reducing agents like zinc and acetic acid and zinc-copper couple give good yields of alkanes.

$$RX \xrightarrow[\text{agent}]{\text{Reducing}} RH$$

Lithium aluminium hydride, $LiAlH_4$, is an excellent reducing agent. Though it reduces many unsaturated functional groups, such as CO, C≡N, etc., it does not attack isolated double bond or triple bond. Dry ether is the commonly used solvent. For example,

$$\underset{\text{3-chloropropene}}{CH_2{=}\overset{\overset{Cl}{|}}{C}HCH_2} \xrightarrow{LiAlH_4} \underset{\text{propene}}{CH_2{=}CHCH_3} + LiCl + AlCl_3$$

Alkyl halide in ether reacts with magnesium to form alkylmagnesium halide (Grignard reagent) which, on treatment with water or dilute acid, decomposes to give alkanes. We will take up the preparation and properties of Grignard reagents in Unit 11 of this course.

$$RX + Mg \xrightarrow{\text{ether}} \underset{\text{Grignard reagent}}{RMgX} \xrightarrow[H_2O]{H^+} RH + Mg(OH)X$$

6.5.5 Decarboxylation of the Carboxylic Acids

Soda lime is a mixture of NaOH and CaO. The active ingredient is NaOH, CaO helps in keeping the reaction mixture porous.

Alkanes may be prepared through decarboxylation of carboxylic acids by heating a mixture of the sodium salt of a carboxylic acid with soda lime.

$$RCOONa + NaOH \longrightarrow RH + Na_2CO_3$$

This process of eliminating CO_2 from a carboxylic acid is known as decarboxylation. The alkanes so produced contain one carbon atom less than the original acid. The new hydrogen atom in the product is derived from soda lime.

Although methane is obtained from ethanoic acid in good yield, other acids give only 10-20% of the corresponding hydrocarbon.

Sometimes decarboxylation of the acid itself is more effective than that of its salt. The direct decarboxylation of a carboxylic acid can be carried out by heating it with an organic base, such as pyridine using copper chromite ($CuO.Cr_2O_3$) as catalyst.

$$\underset{\substack{\text{propanoic}\\\text{acid}}}{CH_3CH_2COOH} + \underset{\text{pyridine}}{C_5H_5N} \xrightarrow{CuO.Cr_2O_3} \underset{\text{ethane}}{CH_3CH_3} + CO_2$$

Next we discuss two methods of preparation of cycloalkanes.

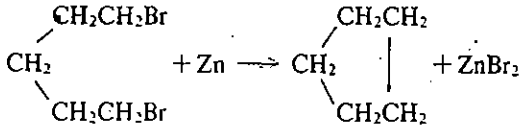
In common names Greek letters have long been used to designate position on a carbon skeleton, relative to a functional group.

$$\underset{\omega}{CH}\underset{\delta}{H_2}\underset{\gamma}{CH}\underset{\beta}{H_2}\underset{\alpha}{CH}$$
$$\underset{Br}{|}\qquad\qquad\qquad\qquad\underset{Br}{|}$$

1, 5-dibromopentane (α, ω-dibromopentane)

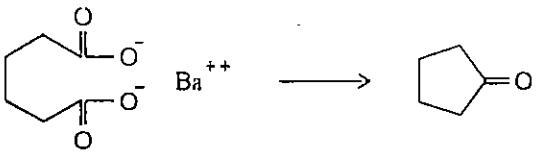
6.5.6 Preparation of Cycloalkanes

i) When 1, 5-dihalogen derivatives of alkanes are treated with sodium or zinc, the corresponding cycloalkane is formed, e.g., 1, 5-dibromopentane would form the cyclopentane :



1, 5-dibromopentane cyclopentane

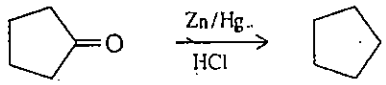
ii) When the calcium or barium salt of a dicarboxylic acid is distilled, a cyclic ketone is formed, e.g., barium adipate gives cyclopentanone



Salt of dicarboxylic acid

cyclopentanone

A cyclic ketone can be reduced into the corresponding cycloalkane using zinc amalgam and concentrated hydrochloric acid (Clemmenson reduction). You will study Clemmenson reduction in detail in Unit 14.



cyclopentanone

cyclopentane

SAQ 3

Write the equation showing synthesis of the following alkanes from the starting materials indicated. Write your answer in the space given below :

a) Cyclohexane from cyclohexene

.....

.....

b) Undecane from the sodium salt of dodecanoic acid, $CH_3(CH_2)_{10}COOH$

.....

.....

c) Cyclopropane from 1, 3-dibromopropane

.....

.....

d) Butane from 1-chlorobutane

.....

.....

6.6 REACTIONS OF ALKANES

Alkanes are relatively unreactive to most of the common reagents. It is difficult to define the terms "reactive" and "unreactive", since a compound may be reactive under one set of conditions and unreactive under another. This reactivity or unreactivity may be explained by considering the nature of C—C and C—H bonds present in their molecules. Since the electronegativities of carbon and hydrogen do not differ appreciably, the bonded electrons in C—H are more or less equally shared between them. Thus, C—H bonds encountered in alkanes are almost nonpolar and the same is true of C—C bonds. Thus, polar and ionic reagent find no sites to attack an alkane molecule. Alkanes undergo mainly substitution reactions, which can be explained using free radical chain mechanism. These reactions take place in the presence of uv light or at a high temperature or in the presence of certain free radical initiators such as peroxides. In substitution reactions, one or more of the H atom(s) of alkanes are substituted by halogen or some other groups. Some important reactions of alkanes are given in Table 6.3.

The chemical reactions which take place in the presence of light are called photochemical reactions.

Table 6.3 : Reactions of alkanes

Halogenation

$$RH + X_2 \xrightarrow[\text{or } \Delta]{h\nu} RX + HX$$

Nitration

$$RH + HNO_3 \longrightarrow RNO_2 + H_2O$$

Isomerisation

$$CH_3CH_2CH_2CH_3 \xrightarrow{AlCl_3-HCl} CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$$

Aromatisation

$$CH_3(CH_2)_4CH_3 \xrightarrow[775\ K]{Cr_2O_3 / Al_2O_3} \text{C}_6\text{H}_6 + 4H_2$$

Pyrolysis

$$CH_3CH_2CH_3 \longrightarrow CH_4 + CH_2=CH_2$$

$$\downarrow$$

$$CH_3CH=CH_2 + H_2$$

Combustion

$$CH_3CH_2CH_2CH_2CH_3 + 8O_2 \longrightarrow 5CO_2 + 6H_2O + 2549\ kJ\ mol^{-1}$$

Let us discuss these reaction in detail.

6.6.1 Halogenation

Halogenation of alkane is one of the most important reaction of alkanes. It is defined as the replacement of hydrogen atom(s), from an alkane molecule, by halogen atom(s).

$$RH + X_2 \xrightarrow{\Delta/h\nu} RX + HX$$

The reaction does not take place in dark but a vigorous reaction occurs when the mixture of alkane and halogen is exposed to light or heated to a high temperature. But in most cases, the reaction is of limited synthetic value because a mixture of products is obtained. Multiple substitutions may occur. For example, chlorination of methane produces a mixture of chloromethane, dichloromethane, trichloromethane and tetrachloromethane.

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{chloromethane}}{CH_3Cl}$$

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} \underset{\text{dichloromethane}}{CH_2Cl_2}$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} \underset{\text{trichloromethane}}{CHCl_3}$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} \underset{\text{tetrachloromethane}}{CCl_4}$$

The yield of the monosubstituted product may increase by using an excess of alkane.

Similarly, a cycloalkane reacts with halogen to give halocycloalkane, e.g.,

cyclopentane halocyclopentane

The mechanism of halogenation is supposed to involve the following steps :

In the first step, the halogen molecule undergoes homolysis forming free-radicals. This step is called chain initiation :

i) $X_2 \xrightarrow{h\nu/\Delta} 2X^{\cdot}$

In the next step, the halogen atom abstracts a hydrogen atom from the alkane molecule thereby producing an alkyl radical.

ii) $RH + \dot{X} \longrightarrow HX + \dot{R}$

The alkyl radical on collision with another molecule of halogen abstracts a halogen atom from it generating a molecule of the alkyl halide and a halogen atom. These two steps are called propagation. They are repeated in sequence till the reactants are consumed.

iii) $X_2 + \dot{R} \longrightarrow RX + \dot{X}$

Finally, the above chain may be terminated by coupling of any two radicals. This step is known as termination.

iv) $\dot{X} + \dot{X} \longrightarrow XX$
$\dot{R} + \dot{X} \longrightarrow RX$
$\dot{R} + \dot{R} \longrightarrow RR$

The order of reactivity of halogen in halogenation of alkanes is :

$F_2 > Cl_2 > Br > I_2$

However, the flourination reaction is too violent to be practical, and iodine actually does not react at all.

6.6.2 Nitration

Alkanes, especially the higher member, can be nitrated with nitric acid at a temperature of 675-775 K. Like halogenation, it is also free radical reaction.

$RH + HNO_3 \longrightarrow RNO_2 + H_2O$

In this reaction, the product is usually a mixture of nitroalkanes including those with smaller carbon chain than the parent alkane.

$$\underset{\text{propane}}{CH_3CH_2CH_3} \xrightarrow{HNO_3} \underset{\text{1-nitropropane}}{CH_3CH_2CH_2NO_2} + \underset{\text{2-nitropropane}}{CH_3\overset{\overset{NO_2}{|}}{C}HCH_3} + \underset{\text{nitroethane}}{CH_3CH_2NO_2} + \underset{\text{nitromethane}}{CH_3NO_2}$$

6.6.3 Isomerisation

The molecular rearrangement of one compound into another compound or into more than one compounds is called isomerisation. The straight chain alkanes are converted into branched chain isomers in the presence of aluminium chloride and hydrogen chloride.

$$\underset{\text{butane}}{CH_3CH_2CH_2CH_3} \xrightarrow{AlCl_3-HCl} \underset{\text{2-methylpropane}}{CH_3\overset{\overset{CH_3}{|}}{C}HCH_3}$$

Similarly, other less branched alkanes isomerise to more branched ones. Thus,

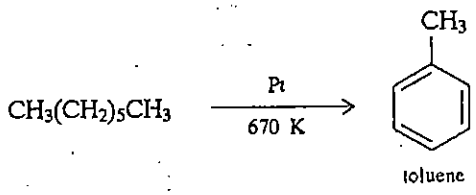
$$\underset{\text{2-methylpentane}}{CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_3} \longrightarrow \underset{\text{2, 3-dimethylbutane}}{CH_3\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}HCH_3}$$

Isomerisation is used to increase the branched chain content of lower alkanes produced by cracking; you have studied in subsec. 6.2.4 that branched chain alkanes are more valuable than straight chain alkanes as motor fuel.

6.6.4 Aromatisation

This is a process of converting aliphatic or alicyclic compounds to aromatic hydrocarbons. Alkanes with six or more carbon atoms, when heated strongly under pressure in the presence of a catalyst, give aromatic hydrocarbons. This process involves cyclisation, isomerisation and dehydrogenation. Aromatisation of gasoline increases their octane number from 40 to 95 because unsaturated hydrocarbons are better fuels.

$$\underset{\text{hexane}}{CH_3(CH_2)_4CH_3} \xrightarrow[775\ K.]{Cr_2O_3\ /\ Al_2O_3} \underset{\text{benzene}}{\text{C}_6\text{H}_6} + 4H_2$$



Catalytic aromatisation in the presence of platinum is sometimes referred to as platforming or hydroforming. This process also constitutes a valuable method for commercial production of these hydrocarbons.

6.6.5 Pyrolysis

This is a process of decomposing an organic substance by heating it to high temperature in the absence of oxygen. The word **pyrolysis** is taken from the Greek words **pyro** (fire) and **lysis** (disintegration). The pyrolysis of alkanes, particularly where petroleum is concerned, is known as **cracking**. When an alkane is heated to about 775-875 K, it decomposes into smaller molecules. For example, on cracking propane, the possible products are :

$$\underset{\text{propene}}{CH_3CH{=}CH_2} + H_2 \longleftarrow \underset{\text{propane}}{CH_3CH_2CH_3} \longrightarrow \underset{\text{methane}}{CH_4} + \underset{\text{ethene}}{CH_2{=}CH_2}$$

Large quantities of high boiling fractions of petroleum are converted into low boiling gasoline by cracking. Propene and hydrogen are produced from propane as a result of fission of C – H linkages. In the case of higher alkanes, fission of C –C linkages occurs more readily. The presence of catalysts like oxides of chromium, vanadium and molybdenum, however, accelerates the fission of C –H linkage. Pyrolysis in the presence of a catalyst is used in the manufacture of alkenes.

The mechanism of cracking is still obscure, but it is believed to be a **free radical** as illustrated below

$$CH_3CH_2CH_3 \longrightarrow CH_3CH_2CH_2 + H \longrightarrow CH_3CH{=}CH_2 + H_2$$

$$\downarrow$$

$$CH_3CH_2 + CH_3 \longrightarrow CH_2{=}CH_2 + CH_4$$

The products formed during cracking of alkanes depends upon : (i) the structure of alkane, (ii) the pressure employed, and (iii) the presence or absence of a catalyst.

6.6.6 Combustion

Alkanes burn in excess of air or oxygen to give carbondioxide and water. This reaction is known as combustion and is the most important of all their reactions. Combustion is highly exothermic and accounts for their use as valuable fuels. It is a free radical chain reaction and requires a very high temperature for its initiation. Once the reaction is started, the subsequent chain-carrying steps proceed readily with the evolution of a large amount of energy. For example, the heat of combustion of pentane is 2549 kJ mol^{-1}.

$$CH_3CH_2CH_2CH_2CH_3 + 8O_2 \longrightarrow 5CO_2 + 6H_2O + 2549 \text{ kJ mol}^{-1}$$

The large quantity of heat evolved can be a source of extensive power. Hence the use of petrol, diesel etc., as fuels in internal combustion engines. The burning of alkanes also produces **carbon black**, which is used in the manufacture of Indian ink, printer's ink, black pigments and as a filler in rubber compounding.

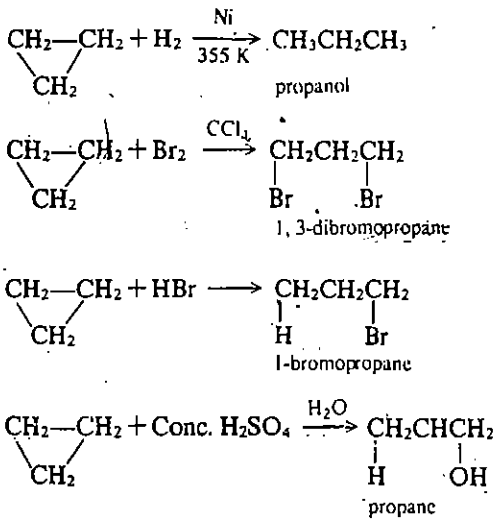
6.6.7 Reactions of Small Ring Compounds

Let us now study the reactions characteristic of small ring compounds, such as cyclopropane and cyclobutane.

Besides, the free radical substitution reactions that are characteristic of cycloalkanes and of alkanes, in general, cyclopropane and, to some extent, cyclobutane undergo certain addition reactions. You will recall from your previous classes that the bonding in cyclopropane and cyclobutane is not as strong as that in higher homologues. Hence, the bonds in cyclopropane and cyclobutane are vulnerable to attack by certain reagents. These addition reactions destroy

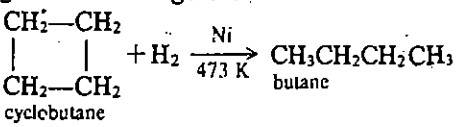
The sp^3 orbitals of the carbon atoms in cyclopropane cannot undergo complete overlap with each other because the angles between the carbon atoms of cyclopropane are geometrically required to be 60°. The ring sigma bonds of cyclopropane are, therefore, less stable than sp^3 sigma bonds that have the normal tetrahedral angle.

the cyclopropane and cyclobutane ring system, and yield open chain products. Some examples are given below :



In each of these reactions, a carbon-carbon bond is broken and the two atoms of the reagent appear at the terminal carbon atoms.

Cyclobutane does not undergo most of the ring opening reactions of cyclopropane; it gets hydrogenated under vigorous conditions.



So you can see that cyclobutane undergoes addition reactions less readily than cyclopropane,

SAQ 4

Complete the following reactions :

) $CH_3CH_3 + Cl_2 \xrightarrow{h\nu}$ .....

) $CH_3CH_3 + HNO_3 \longrightarrow$ .....

) $CH_2—CH_2 + \text{Conc. } H_2SO_4 \longrightarrow$ .....
$\quad\quad\ \ CH_2$

) $CH_3(CH_2)_5CH_3 \xrightarrow[670\,K]{Pt}$ .....

6.7 SUMMARY

In this unit you have learnt that :

- Alkanes are compounds of the general formula C_nH_{2n+2}. Cycloalkanes contain a ring of carbon atoms and have the general formula C_nH_{2n}.
- The chief source of alkanes is petroleum.
- The performance of gasoline for internal combustion engines is rated by octane number. Cetane number is a measure of the quality of diesel.
- Alkanes are nonpolar compounds. Their physical constants like boiling point, density, etc., increase with increase in the number of carbon atoms. Branching in the chain decreases the boiling point.
- Alkanes are prepared by : (i) Wurtz reaction, (ii) Kolbe's electrolytic method, (iii) hydrogenation of unsaturated hydrocarbons, (iv) decarboxylation of carboxylic acids, (v) reduction of alkyl halides, and (vi) hydrolysis of Grignard reagents.
- The main reaction of alkanes is combustion, heat for power production is its chief outcome.

- Halogenation of alkanes gives multiple substitution. The order of reactivity of halogens is $F_2 > Cl_2 > Br_2$. Iodine does not react at all.
- An alkane can be converted into its corresponding branched chain isomer in the presence of aluminium chloride and hydrogen chloride.
- When an alkane is heated to a high temperature (at about 875 K), it decomposes into small molecules. This process is known as pyrolysis.
- When alkanes with six or more carbon atoms are heated under pressure in the presence of a catalyst, aromatic hydrocarbons are produced.

6.8 TERMINAL QUESTIONS

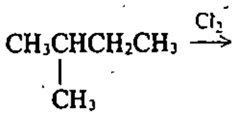
1) Give the products of the following reactions :

   a) $CH_3CH_2Br + CH_3CH_2Br \xrightarrow{Na}$

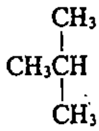
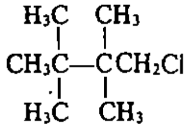
   b) $CH_3CH_2CH_3 \xrightarrow{LiAlH_4}$

   c) $CH_3CH{=}CHCH_2Cl \xrightarrow{H_2/Pt}$

   d) $CH_3CH_3 + Cl_2 \xrightarrow{h\nu}$

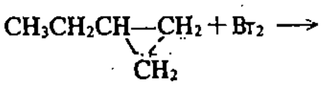
   e) 

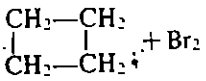
2) Starting with $CH_2{=}CHCH_2Br$ or $(CH_3)_3CCl$, how would you prepare the following compounds:

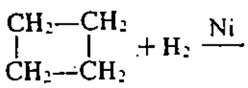
   a)  b) $CH_3(CH_2)_4CH_3$ c) 

3) Write the equation to show Wurtz reaction :

4) Complete the following equations:

   a) 

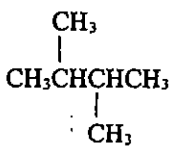
   b) 

   c) 

6.9 ANSWERS

Self Assessment Questions

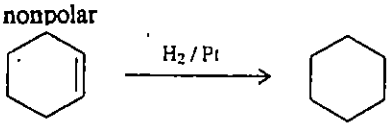
1) a) $CH_3CH_2CH_2CH_3$

   b) 

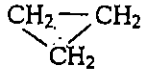
   c) $CH_2{=}CHCH_2CH_3$

d) $CH_3C(CH_3)=CHCH_2CH_3$

2) a) electronegativity
b) increases
c) decreases
d) nonpolar

3) a) 

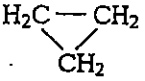
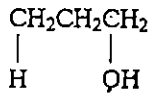
b) $CH_3(CH_2)_{10}COOH + C_5H_5N \xrightarrow{CuO.Cr_2O_3} CH_3(CH_2)_9CH_3$

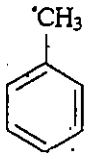
c) $BrCH_2CH_2CH_2Br + Zn \longrightarrow$  $+ ZnBr_2$

d) $CH_3CH_2CH_2Cl \xrightarrow{LiAlH_4} CH_3CH_2CH_3$

4) a) $CH_3CH_3 + Cl_2 \xrightarrow{h\nu} CH_3CH_2Cl$

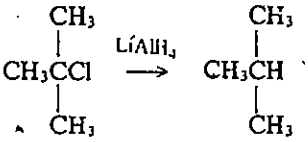
b) $CH_3CH_3 + HNO_3 \longrightarrow CH_3CH_2NO_2$

c)  + Conc. $H_2SO_4 \longrightarrow$ 

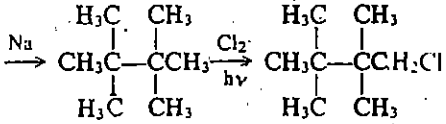
d) $CH_3(CH_2)_5CH_3 \xrightarrow[670\ K]{Pt}$ 

Terminal Questions

1) a) $CH_3CH_2CH_2CH_3$
b) No reaction
c) $CH_3CH_2CH_2CH_2Cl$
d) CH_3CH_2Cl
e) No reaction

2) a) 

b) $CH_2=CHCH_2Br + CH_2=CHCH_2Br \xrightarrow{Na} CH_2=CHCH_2CH_2CH=CH_2$
$\xrightarrow{H_2/Pt} CH_3(CH_2)_4CH_3$

c) 

3) $CH_3Br + CH_3Br \xrightarrow{2Na} CH_3CH_3 + 2NaBr.$

4) a) $CH_3CH_2CHCH_2$ (Br, Br)
b) No reaction
c) $CH_3CH_2CH_2CH_3$

UNIT 7 ALKENES

Structure

7.1 Introduction
Objectives

7.2 Classification of Alkenes

7.3 Physical Properties

7.4 Spectral Properties

7.5 Preparation of Alkenes
Dehydrohalogenation of Alkyl Halides
Dehydration of Alcohols
Wittig Reaction
Preparation of Dienes

7.6 Reactions of Alkenes
Addition of Halogens
Hydrohalogenation
Addition of Water
Hydroboration
Ozonolysis
Hydroxylation
Epoxidation
Addition to Conjugated Diene
Diels-Alder Reaction

7.7 Summary

7.8 Terminal Question

7.9 Answers

7.1 INTRODUCTION

In Unit 1, we mentioned briefly about the alkenes. In this unit, we shall discuss their chemistry in detail. Ethene, the simplest alkene, was known to chemists in the eighteenth century and was obtained in pure form in 1795. Alkenes, also called olefins, are hydrocarbons which contain one or more carbon-carbon double bond(s). Since alkenes evidently contain less than the maximum number of hydrogen atoms, they are referred to as **unsaturated hydrocarbons**.

Alkenes are often found as plant products and in petroleum. Many alkenes are biologically active compounds. For example, ethene induces ripening in fruit.

In this unit, we will discuss structure of alkenes, their spectral and physical properties, different methods for their preparation and finally, we will study their important chemical reactions.

Objectives

After studying this unit, you should be able to :

- classify the types of alkenes,
- explain the structure of monoenes and dienes,
- list their spectral and physical properties,
- list the different methods for their preparation, and
- write down the important chemical reactions of alkenes.

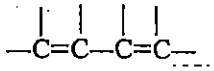
7.2 CLASSIFICATION OF ALKENES

Alkenes can be classified on the basis of the number of double bonds present in the molecule. Hydrocarbons containing one carbon-carbon double bond are called monoenes. The monoenes have the general formula C_nH_{2n}.

Hydrocarbons containing two double bonds are called diolefins or alkadienes or dienes. They have the general formula C_nH_{2n-2} and are isomeric with alkynes. Trienes have three double

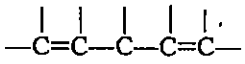
bonds and tetraenes have four double bonds. The term polyene is used for hydrocarbons containing more than four double bonds.

Dienes are divided into three main classes depending on the relative positions of the two double bonds in the molecule : isolated or non-conjugated dienes, conjugated dienes and cumulated dienes. In conjugated dienes, the two double bonds are separated by a single bond. A typical conjugated diene skeleton is given below :

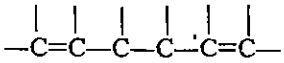


conjugated diene

In isolated dienes, the two double bonds are separated by at least two single bonds for which two typical skeletons are given below :

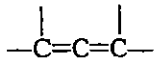


isolated diene
(two single bonds between two double bonds)



isolated diene
(three single bonds between two double bonds)

In cumulated dienes, there are two double bonds around the same carbon atom; a typical skeleton is given below :



cumulated diene (allene)

Compounds that contain cumulated double bonds are known but are very uncommon. The conjugated dienes are the most important among the dienes. They show certain reactions that are not shown by monoenes or other dienes. Thus, in this unit, we shall concentrate our attention on monoenes and conjugated dienes.

Structure of Monoenes and Dienes

The carbon-carbon double bond is both an important structural unit and an important functional group in organic chemistry. The shape of the organic molecule is influenced by the presence of the double bond which is also the site of most of the chemical reactions that alkenes undergo. So it is necessary to understand the structure of these molecules.

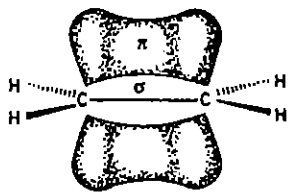


Fig. 7.1 : Orbital picture of ethene.

Carbon-carbon double bond is the distinguishing feature of the monoenes and dienes. You have already studied about the bonding of monoenes in Unit 1 of this course and learnt that the carbon atoms involved in double bond formation are sp^2 hybridised. The bond angle around the sp^2 hybridised carbon atoms is 120° (Fig. 7.1). Bonding in dienes with isolated double bonds is similar to monoenes. Thus here we shall discuss π bonds in conjugate and cumulated systems.

Let us consider 1, 3-butadiene as an example of a conjugated diene,

$CH_2=CHCH=CH_2$

1, 3-butadiene

Each of the four carbon atoms of butadiene contains an unhybridised p-orbital. The sideways overlap of unhybridised p-orbitals gives rise to two localised π bonds, i.e., the bonds between C_1 and C_2 and C_3 and C_4 (Fig. 7.2). The four carbon atoms and the six hydrogen atoms of butadiene lie in the same plane so that there is a certain amount of overlapping between the electron clouds of the p-orbitals of C_2 and C_3. This give rise to completely delocalised π-orbitals spread over all the four carbon atoms. It is this delocalisation of π electrons which imparts stability to 1, 3-butadiene.

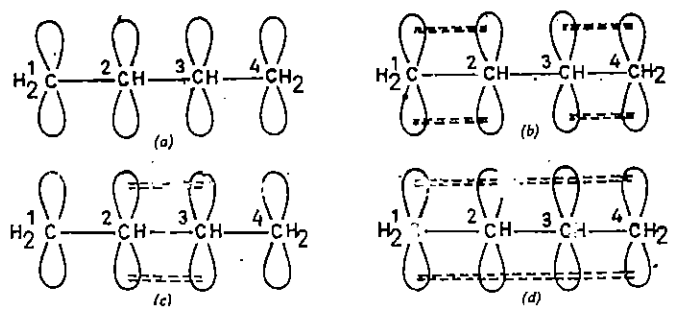


Fig. 7.2 : Orbital structure of 1, 3-butadiene

In the allene molecule, the central carbon atom is *sp* hybridised while the terminal carbon atoms are sp^2 hybridised. The central carbon atom forms a σ bond with each of the terminal sp^2 hybridised carbon atom. The remaining two *p*-orbitals of this carbon form two π bonds by sideways overlapping with the *p*-orbitals of the terminal carbon atoms (Fig. 7.3).

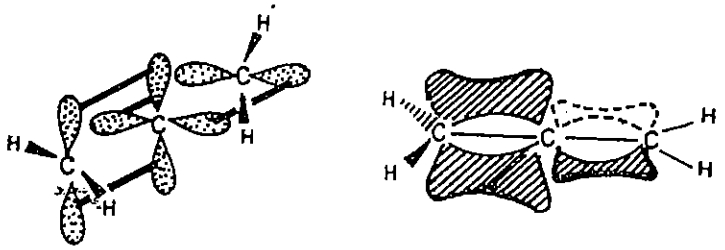


Fig. 7.3 : Molecular orbital picture of allene.

SAQ 1

Fill in the blank in the spaces given below :

a) Dienes are isomeric with .....

b) Polyenes contain more than ..... double bonds.

c) Double bonds that alternate with single bond are ..... dienes.

d) In allene the central atom is ..... hybridised and the terminal atoms are ..... hybridised.

7.3 PHYSICAL PROPERTIES

In general, the physical properties of alkenes are similar to those of the corresponding alkanes. Like alkanes, the boiling points of a homologous series of alkenes increase 20-30 K per CH_2 group except for the very small homologues. Like alkanes, branching in an alkene also lowers the boiling point. Lower alkenes, from ethene to butene, are colourless gases, higher ones, from C_5-C_{15}, are liquids and the rest are solids at room temperature.

Alkenes are slightly more soluble in water than the corresponding alkanes because the π-electrons are attracted to the partially positive hydrogen of the water molecules.

7.4 SPECTRAL PROPERTIES

In the uv spectrum, although the ethylenic chromophore shows an absorption band below 200 nm, yet it is not of much practical value as measurement of uv spectrum in this region is influenced by the absorption of air and solvent molecules.

The ir spectra are quite useful for structure determination of alkenes. The unsymmetrical alkenes are polar and absorb in the region between 1600 and 1700 cm^{-1}, whereas the symmetrical ones, being nonpolar, do not absorb in this region. Further, depending upon the substituent, one or more bands of medium intensity appear in the region between 3000 and 3100 cm^{-1} for >C=C—H stretching. The *cis*- and *trans*-isomers of the type RCH=CHR may be distinguished by C—H deformation frequencies. The *cis*-isomer absorbs at 675-730 cm^{-1} and the *trans*-isomer at 960-975 cm^{-1}

In the ir spectra of allenes, a band near 1950 cm^{-1} appears for the C=C stretching vibration. The strong band at 850 cm^{-1} arises from >C=CH_2 wagging and is characteristic of allene. The characteristic —C=C— stretching frequencies in conjugated systems is lower and appears around 1600 cm^{-1}

In the nmr spectra, the chemical shifts of olefinic protons are shifted towards lower field than those of alkane protons. The exact position of absorption depends on the location of the

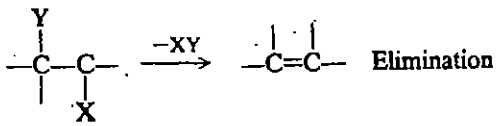
double bond in the hydrocarbon chain. In general, proton on the terminal alkenyl carbon absorb near δ 4.7 ppm, while the protons on the nonterminal carbon absorb slightly farther downfield at δ 5.3 ppm. The protons α to a double bond ($CH_2CH = CHCH_2$) appear at δ 2.06 ppm.

In conjugated dienes, the olefinic protons are more deshielded and consequently resonance due to these protons occurs downfield. In conjugated dienes, the signal due to $CH_2=$ protons appears at δ 5.3-5.7 ppm and that due to H—C=C proton at δ 6.0-6.5 ppm. In the nmr spectra of the allenes, the alkene hydrogen give rise to signals at δ 5.7-4.7 ppm.

In the mass spectra of alkenes, the molecular ion peak is usually distinct. The fragmentation of interest for alkenes is the allylic cleavage.

7.5 · PREPARATION OF ALKENES.

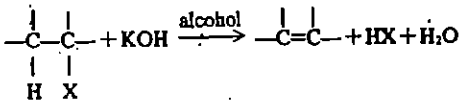
Synthetically, alkenes are prepared by introducing a double bond in saturated hydrocarbons through elimination of atoms or groups from two adjacent carbon atoms. The result is the formation of a double bond between these two carbon atoms.



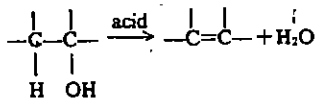
Alkenes can be prepared from alkyl halides, alcohol and ketones and through cleavage reactions. Some important methods for the preparation of alkenes are summarised in Table 7.1.

Table 7.1 : Preparation of alkenes

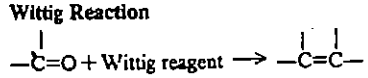
Dehydrohalogenation of Alkyl Halides



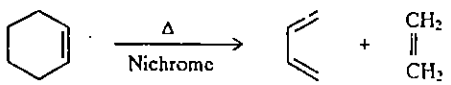
Dehydration of Alcohols



Wittig Reaction



Retro Diels-Alder Reaction



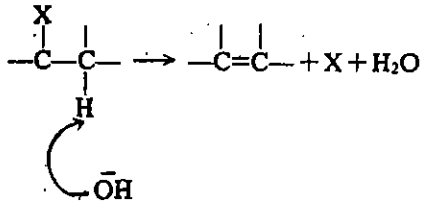
Let us discuss each method in detail.

7.5.1 Dehydrohalogenation of Alkyl Halides

Alkyl halides are converted into alkenes by dehydrohalogenation. Dehydrohalogenation involves elimination of the halogen atom together with a hydrogen atom from an adjacent carbon atom. The elimination is brought about by treating the alkyl halide with a strong base. Thus, bromoethane yields ethene when treated with potassium hydroxide in alcoholic solution.

$$\underset{\text{bromoethane}}{CH_3CH_2Br} \xrightarrow[C_2H_5OH]{KOH} \underset{\text{ethane}}{CH_2=CH_2} + HBr + H_2O$$

The function of hydroxide ion is to abstract hydrogen from the carbon atom next to the halogen bearing carbon. The carbon halogen bond then cleaves resulting in double bond formation.



Ease of hydrohalogenation of alkyl halides is : *tert* >*sec* >*p*

The alkyl halides, in which halogen is attached to a terminal carbon, yield a single alkene but alkyl halides in which the halogen atom is attached to a nonterminal carbon atom and both adjacent position have hydrogen atoms yield a mixture of alkenes.

$$\underset{\text{chlorobutane}}{CH_3CH_2CH_2CH_2Cl} \xrightarrow{KOH\ (alc)} \underset{\text{1-butene}}{CH_3CH_2CH=CH_2}$$

$$\underset{\text{2-chlorobutane}}{CH_3CH_2\overset{Cl}{\overset{|}{C}}HCH_3} \xrightarrow{KOH\ (alc)} \underset{\substack{\text{2-butene}\\(\text{major})}}{CH_3CH=CHCH_3} + \underset{\substack{\text{1-butene}\\(\text{minor})}}{CH_3CH_2CH=CH_2}$$

In the first reaction, chlorobutane can lose hydrogen only from C_2; therefore, it gives only one product, i.e., 1-butene. However, in the second reaction, 2-chlorobutene can lose hydrogen from any of the two-β-carbon atoms and, hence, it gives a mixture of 2-butene (80%) and 1-butene (20%). Now you may ask why 2-butene is the major product. Dehydrohalogenation follows **Saytzeff rule** which says that the more highly substituted alkene is the dominant product. You will study Saytzeff rule in detail in Unit 11.

7.5.2 Dehydration of Alcohols

An alcohol is converted into an alkene by dehydration, i.e., elimination of a molecule of water. Dehydration requires the presence of an acid and the application of heat. The alcohol is heated with sulphuric or phosphoric acid to a temperature as high as 475 K. Dehydration is also brought about by passing the alcohol vapour over alumina (Al_2O_3) at 625-675 K, e.g.,

$$\underset{\text{ethanol}}{CH_3CH_2OH} \xrightarrow[475\ K]{95\%\ H_2SO_4} \underset{\text{ethene}}{CH_2=CH_2}$$

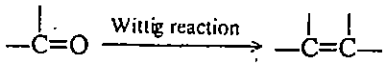
In the case of secondary and tertiary alcohols other than 2-propanol, there exists the possibility of the formation of more than one alkenes. For example, in 2-butanol, hydrogen elimination can occur either from C_1 or C_2. The direction and the rate of reaction again follow the Saytzeff rule and hence 2-butene, the more substituted alkene, is the major product and 1-butene the minor one.

$$\underset{\text{2-butanol}}{CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_3} \xrightarrow[H_2O]{H} \underset{\text{2-butene (major)}}{CH_3CH=CHCH_3} + \underset{\text{1-butene (minor)}}{CH_3CH_2CH=CH_2}$$

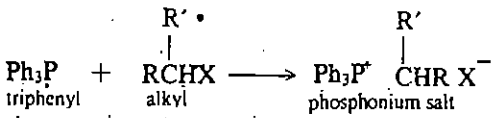
The ease of dehydration of various alcohols has been found to follow the order :
tert >*sec* >*p*

7.5.3 Wittig Reaction

In 1954, George Wittig reported a method of synthesising alkenes from carbonyl compounds. This reaction is applicable to aldehyde and ketones and leads to replacement of carbonyl oxygen by the group=CRR′ (where R ane R′ are hydrogen or alkyl group).



There are two main steps in Wittig reaction. In the first step, the nucleophilic reagent triphenylphosphine reacts with primary or secondary alkyl halide to give phosphonium salt.



This phosphonium salt further reacts with a strong base, which abstracts a weakly acidic α-hydrogen to give alkylidenetriphenylphosphorane (the phosphorous ylide) commonly known as the **Wittig reagent**.

$$Ph_3P^+-\underset{\displaystyle R'}{\underset{|}{C}}HR\ \bar{X} + C_6H_5Li \longrightarrow \underset{\text{(ylide)}}{Ph_3P=\underset{\displaystyle R'}{\underset{|}{C}}R} + C_6H_6 + LiX$$

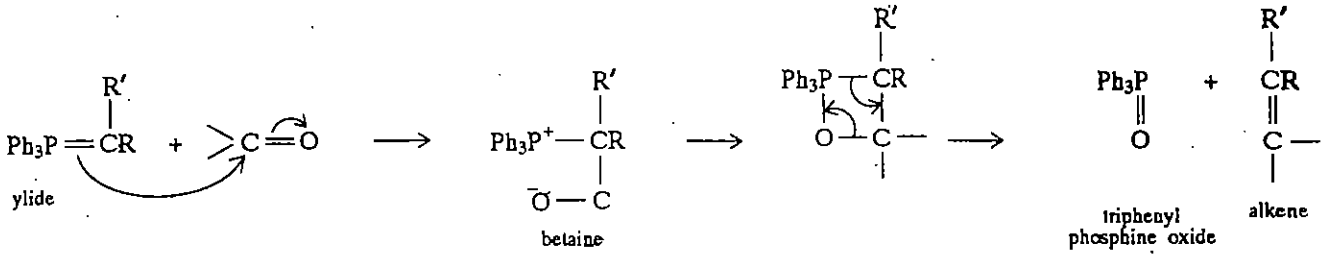
The phosphorous ylide has a hybrid structure and it is the negative charge on carbon that is responsible for their characteristic reactions.

$$Ph_3P=\underset{\displaystyle R'}{\underset{|}{C}}R \longleftrightarrow Ph_3P-\underset{\displaystyle R'}{\underset{|}{\bar{C}}}R$$

The resulting phosphorous ylide attacks the carbonyl carbon to form **betaine** which often undergoes elimination spontaneously to yield alkene.

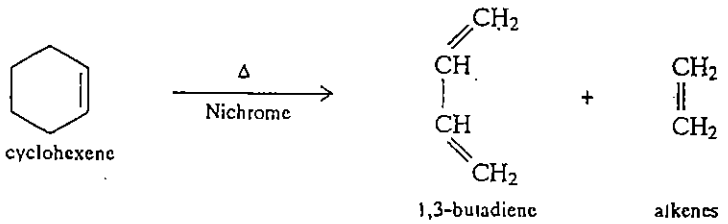
Betaine :
A molecule having non-adjacent oppite charges.

The mechanism of Wittig reaction has been the subject of much discussion, but evidence is now strongly in favour of formation of an intermediate betaine followed by ring closure and then fission.



7.5.4 Preparation of Dienes

Retro Diels-Alder Reaction : Dienes are usually prepared by the adaptation of the methods used to make simple alkenes. However, 1, 3-butadiene is prepared by passing vapours of cyclohexene over heated nichrome (Ni-Cr-Fe) alloy.

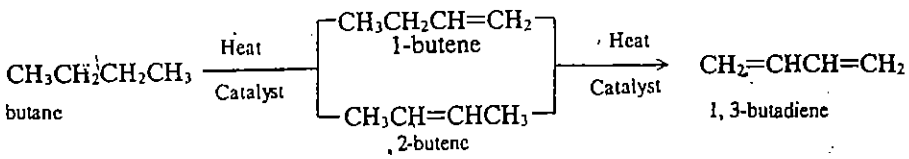


This reaction is also known as the retro Diels-Alder reaction as it is the reversal of the Diels-Alder reaction which you will study in section 7.6.9.

Other Methods for Preparation of Dienes : As stated above, dienes are usually prepared by adaptation of the method used to make simple alkenes. For example, 1, 4-dihydroxybutane on treatment with sulphuric acid gives 1, 3-butadiene.

$$\underset{\text{1, 4-dihydroxybutane}}{CH_2CH_2CH_2CH_2(OH)(OH)} \longrightarrow \underset{\text{1, 3-butadiene}}{CH_2=CHCH=CH_2}$$

1, 3-Butadiene can also be prepared from butane by the cracking process using Cr_2O_3 as illustrated below :



SAQ 2

Write equations for the preparation of alkene from the following starting material. If there is more than one product indicate the major one.

a) $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$

.....

b) $CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}(\overset{\displaystyle OH}{\overset{|}{C}})CH_2CH_3$

.....

c) $(CH_3)_2C{=}O$

.....

7.6 REACTIONS OF ALKENES

The double bond consists of a strong σ bond and a weak π bond; so most of the reactions of alkenes would involve the breaking of this weaker bond.

$$-\overset{|}{C}=\overset{|}{C}- + YZ \longrightarrow -\underset{\displaystyle Y}{\overset{|}{C}}-\underset{\displaystyle Z}{\overset{|}{C}}-$$

In addition reactions of alkene, the π-bond is broken and the electron pair comprising it is used in the formation of two new σ bonds. Thus, two sp^2 hybridised carbon atoms are rehybridised to sp^3 carbons. Compounds containing π bonds are usually of higher energy than those having σ bonds. Consequently, addition reactions are usually exothermic processes.

In the region of the double bond, there is a cloud of electrons above and below the plane of bonded atoms. The π electrons are loosely held by the nuclei and are thus easily available to electron-seeking reagent. Such reagents are called electrophilic reagents or electrophiles and the typical reaction of an alkene is the electrophilic addition. Some important reactions of alkenes are given in Table 7.2 and discussed below :

Table 7.2 : Reaction of alkenes

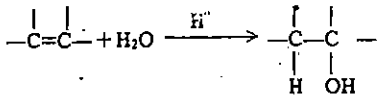
Halogenation

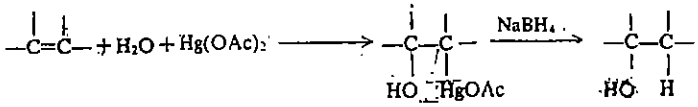
$$-\overset{|}{C}=\overset{|}{C}- + X_2 \longrightarrow -\underset{\displaystyle X}{\overset{|}{C}}-\underset{\displaystyle X}{\overset{|}{C}}-$$

Addition of hydrogen halide

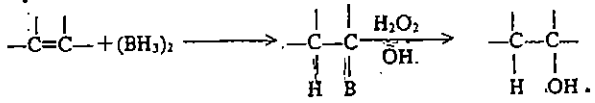
$$-\overset{|}{C}=\overset{|}{C}- + HX \longrightarrow -\underset{\displaystyle H}{\overset{|}{C}}-\underset{\displaystyle X}{\overset{|}{C}}-$$

Addition of water

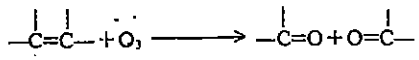




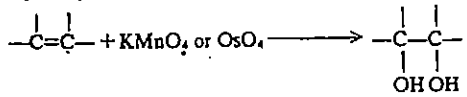
Hydroboration



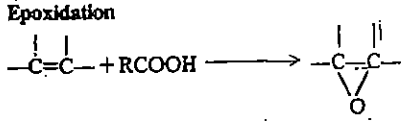
Ozonolysis



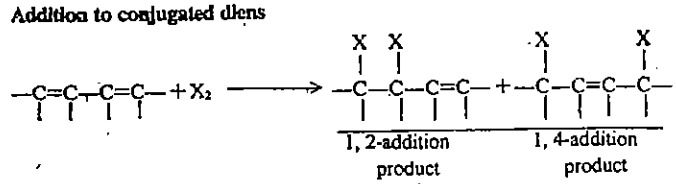
Hydroxylation



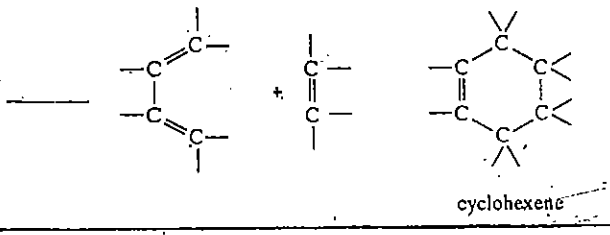
Epoxidation



Addition to conjugated dienes

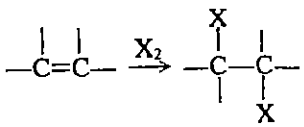


Diels-Alder Reaction



7.6.1 Addition of Halogens

Halogens are quite reactive towards alkenes. Treatment of alkenes with halogens gives 1, 2-dihalogenated alkenes.

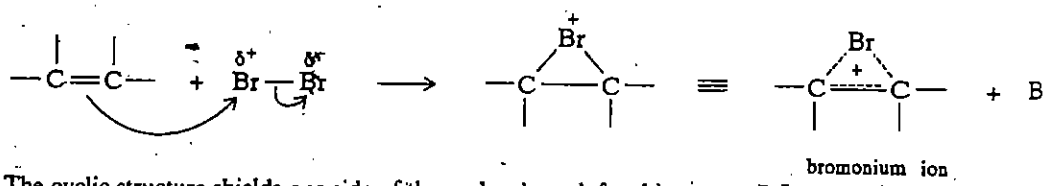


Bromine and chlorine are particularly effective electrophilic addition reagents. Fluorine tends to be too reactive and difficult to control for most laboratory procedures and iodine does not react with alkenes.

Mechanism

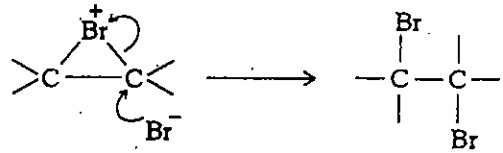
Although bromine is non-polar, it is nevertheless highly polarisable and, in the vicinity of the nucleophilic double bond, the bromine molecule becomes polarised and hence a partial positive charge (δ^+) develops on one bromine atom and a partial negative charge (δ^-) on the other. The π electrons of alkene attack the positive end of the polarised bromine molecule,

displacing bromide ion and forming a cyclic bromonium ion.



bromonium ion

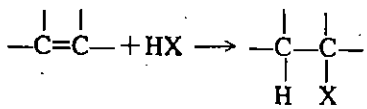
The cyclic structure shields one side of the molecule and, for this reason, Br^- attacks from the opposite side of the erstwhile double bond to give *trans* product. This process is known as *trans* addition. This steric course of the reaction is important in case of alkenes which can give rise to different isomeric products.



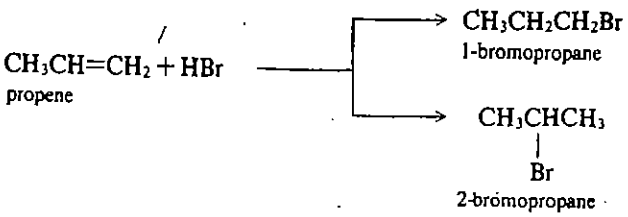
Addition of bromine is extremely useful for detection of carbon-carbon double bond. Rapid decolourisation of bromine solution serves as a test for the presence of the carbon-carbon double bond in a compound.

7.6.2 Hydrohalogenation

An alkene is converted by hydrogen halide (halogen acid) into the corresponding alkyl halide,



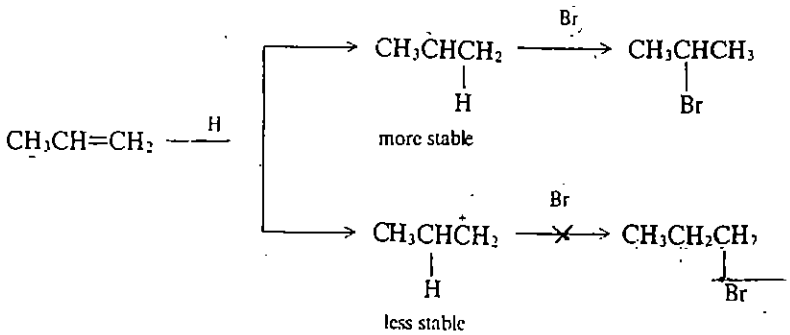
As long as the alkene is symmetrical, we get only one product. In case of unsymmetrical alkene, the position of attachment of nucleophile is governed by the nature of substituents. Addition of HBr to propene should give two products, i.e., 1-bromopropane and 2-bromopropane.



However, only one product, 2-bromopropane, is produced. Such reactions are called **regiospecific** reactions. To explain the exclusive formation of the product, the Russian chemist Markownikoff formulated a rule know after him as Markownikoff's rule, which states that addition of a hydrogen halide to an unsymmetrical alkene takes place in such a way that the negative part of the reagent goes to that carbon atom of the alkene which carries the lesser number of hydrogen atoms.

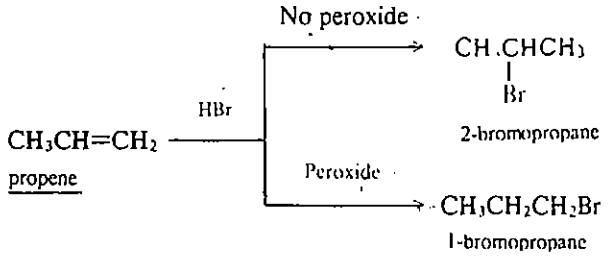
Regiospecific : Only one of the two direction of addition is observed.

Markownikoff's rule can be explained on the basis of the relative stabilities of carbocations which are of the order of tertiary, > secondary > primary. Accordingly, the more substituted carbocation is formed as an intermediate in preference to the less substituted one. For example, in the addition of H^+ to propene, there exists the possibility of the formation of either a primary or a secondary carbocation. Since, the secondary carbocation is more stable, addition of H^+ gives exclusively 2-bromopropane via the more stable intermediate.



Peroxide effect

You must be under the impression that addition to alkene always give Markownikoff's product. But it is not so. After an extensive study of the mechanism of addition of HBr to alkene, Kharasch and Mayo found that in the presence of peroxide the product obtained was not the one predicted by Markownikoff's rule but it was contrary to the Markownikoff's rule. Such additions are sometimes referred to as anti-Markownikoff additions. Since the reversal of the addition reaction is brought about in the presence of peroxides, it is known as the peroxide effect. For example, the addition of hydrogen bromide to propene in the presence of peroxides give 1-bromopropane rather than 2-bromopropane.



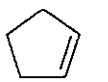
The reaction intermediate in such additions is a free radical rather than a carbocation. The mechanism is somewhat similar to that of halogenation of an alkane, which will be dealt in the "Organic Reaction Mechanism" course.

SAQ 3

Complete the following reaction

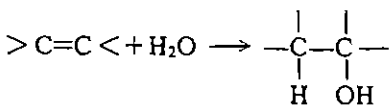
a) $CH_3CH_2CH{=}CH_2 + HCl \longrightarrow$ .....

b) $CH_3CH(CH_3){=}CH_2 + HBr \xrightarrow{\text{Peroxide}}$ .....

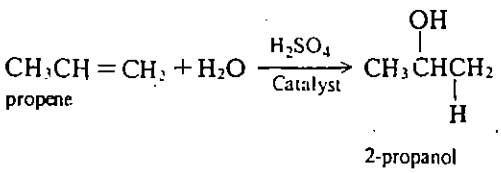
c)  + $Br_2 \longrightarrow$ ----------

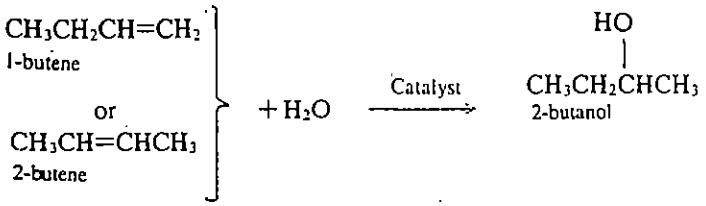
7.6.3 Addition of Water

Addition of H_2O to alkene is known as hydration of alkene. Hydration reaction occur when H_2O, adds to alkenes in the presence of an acid catalyst to yield an alcohol,

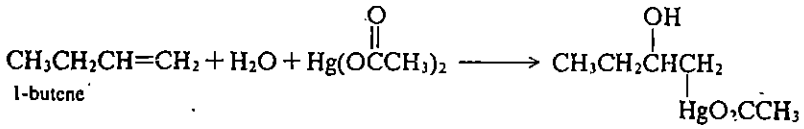


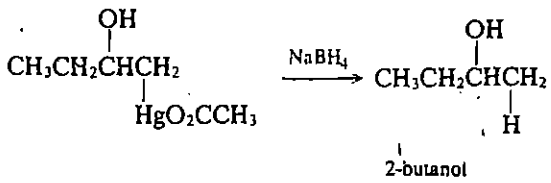
Like hydrogenation, addition of H_2O to unsymmetrical alkene follows Markownikoff's rule :





Another method used to accomplish Markownikoff's hydration of an alkene is **oxymercuration-demercuration.** Alkene reacts with mercuric acetate in the presence of water to give hydroxy-mercurial compounds which on reduction accomplishes demercuration and produces an alcohol. The product of oxymercuration is usually reduced with sodium borohydride ($NaBH_4$). Oxymercuration-demercuration reaction usually give better yield of alcohols than the addition of water with H_2SO_4.

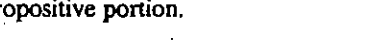




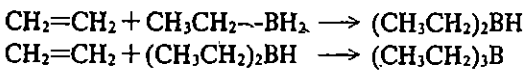
7.6.4 Hydroboration

When an alkene reacts with borane, addition to the carbon-carbon double bond takes place to yield an organoborane-- a compound with a carbon-boron bond. The reaction is known as **hydroboration**. This reaction is very facile and requires only few seconds for completion at 273 K and gives organoboranes in very high yield.

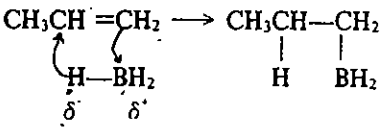
Borane (BH_3) itself is unknown but its dimer, diborane (B_2H_6) behaves as if it were the hypothetical monomer $(BH_3)_2$.



Since BH_3 has three hydrogen, addition occurs three times to produce trialkylborane product e.g.

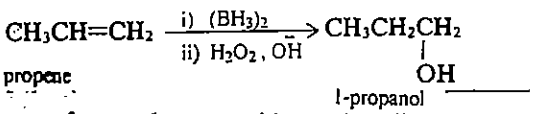


Hydroboration reaction is described as anti-Markownikoff's addition. This is true only in literal sense, because hydrogen is the electronegative portion of the molecule instead of the electropositive portion.

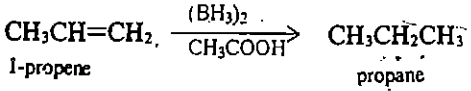


As shown above the hydrogen (as a hydride ion, H^-) goes to more substituted carbon. The result appears to be anti-Markownikoff's addition.

Organoborane are generally not isolated but are instead used directly as reactive intermediates for further synthetic reaction. For example, oxidation of organoborane by alkaline H_2O_2 gives corresponding alcohol.



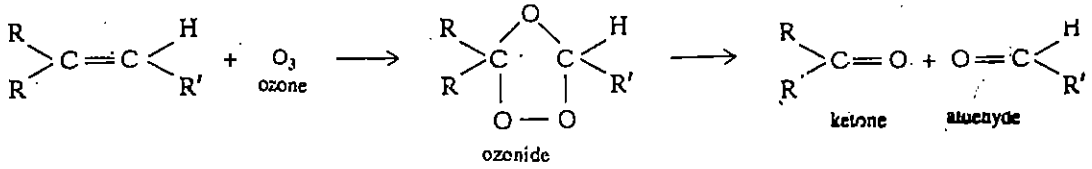
Treatment of organoboranes with a carboxylic acid leads to alkane,



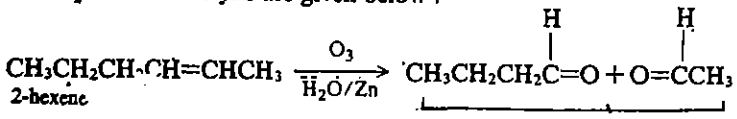
7.6.5 Ozonolysis

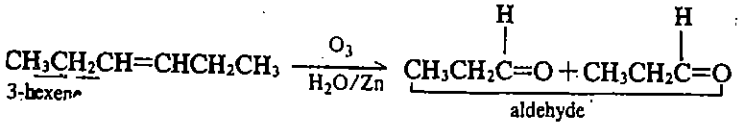
In all the reactions of alkenes studied so far, the carbon skeleton of the starting material was left intact. We have seen the conversion of the carbon-carbon double bond into new functional groups (halide, alcohol, etc.) by adding different reagents, but the carbon skeleton was not broken or rearranged. Ozonolysis is a cleavage reaction, i.e. a reaction in which the double bond is completely broken and alkene molecule is converted into two smaller molecules.

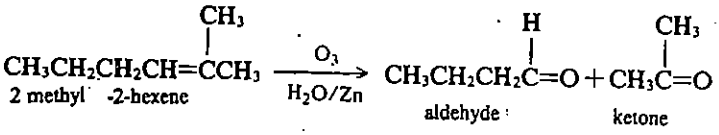
Ozonolysis consists of two separate reactions, the first is oxidation of alkene by ozone to give an ozonide; and the second is reduction of the ozonide to yield cleavage product.



Some examples of ozonolysis are given below :

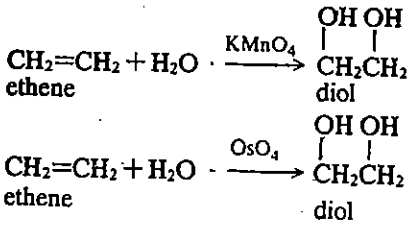






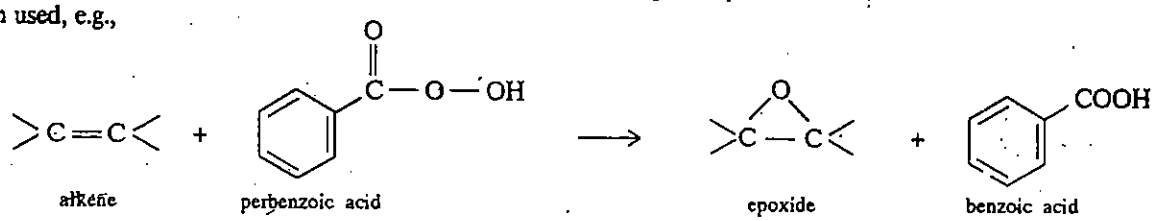
7.6.6 Hydroxylation

Alkenes are readily hydroxylated (addition of hydroxyl groups) to form a dihydroxy compound (diol) known as glycols. The most popular reagent used to convert an alkene to diol is cold alkaline aqueous solution of potassium permanganate or osmium tetroxide.



7.6.7 Epoxidation

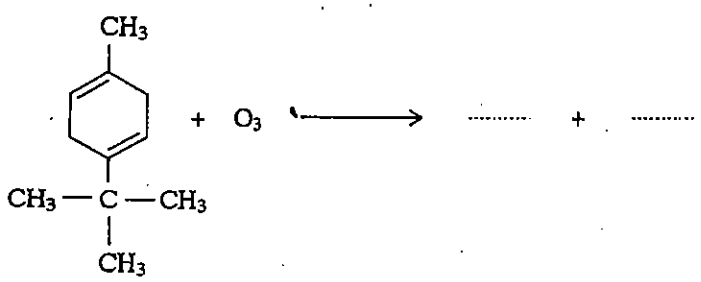
The double bond in alkene is converted into epoxide by means of peracids. Perbenzoic acid ($C_6H_5COO_2H$), monoperphthalic acid ($HO_2CC_6H_4COO_2H$) and *p*-nitroperbenzoic acid have been used, e.g.,



SAQ 4

Predict the products of the following reactions :

a)

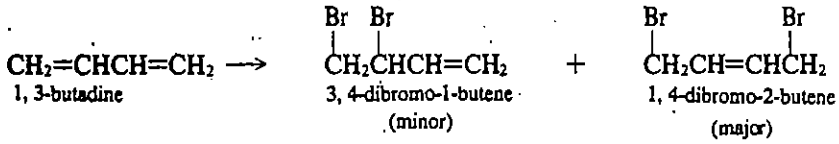


b) $CH_3C(CH_3)=CH_2 + CH_3COOH \longrightarrow$ .....

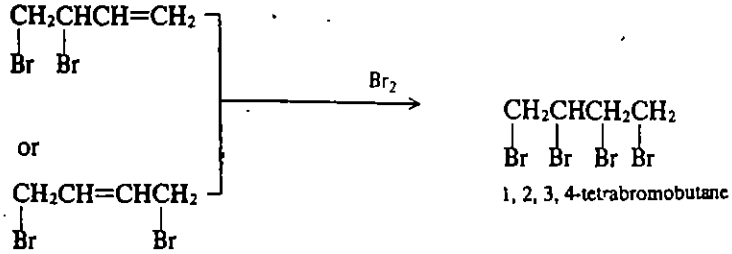
c) $CH_3CH=CH_2 \xrightarrow[H_2O]{KMnO_4}$ .....

7.6.8 Addition to Conjugated Diene

Alkadienes with conjugated system of double bonds undergo abnormal addition reactions, e.g., when 1, 3-butadiene is treated with bromine, two dibromo derivatives are obtained. One of these is 3, 4-dibromo-1-butene (due to 1:2 addition) and the other is 1, 4-dibromo-2-butene (due to 1:4 addition), a major product.

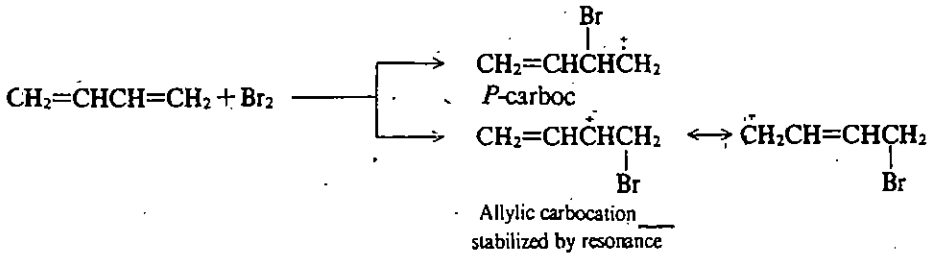


With excess of bromine, the 1, 4 addition as well as the 1, 2-addition products would yield the same 1, 2, 3, 4-tetrabromobutane.

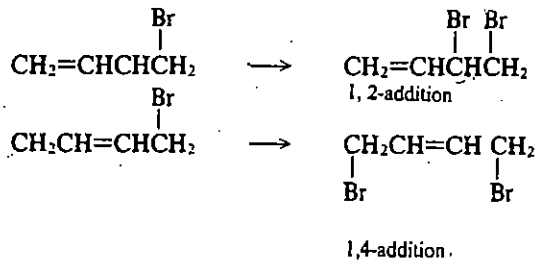


Mechanism

The mechanism of halogenation of 1, 3-butadiene is illustrated below :



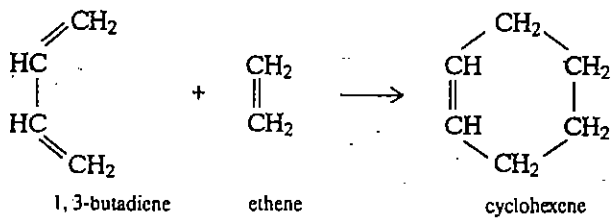
Bromine may attach itself to either C_1 or C_2. The addition of the bromine atom at C_2 would give rise to an unstable primary localized carbocation. But the bromine addition at C_1 results in the formation of resonance stabilized allylic cation. This also explains the enhanced reactivity of dienes over isolated ethylenic double bonds. When the allylic, carbocation is attacked by bromine ion (Br^-) to complete the electrophilic addition reaction, the attack can occur at either C_1 or C_3, since both share the positive charge. The result is a mixture of 1, 2- and 1, 4-addition products, the latter formed in excess since it has the more highly substituted double bond and is hence more stable.



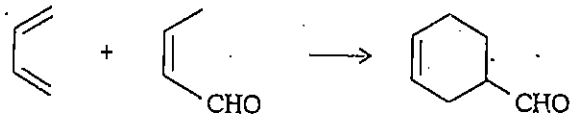
7.6.9 Diels-Alder Reaction

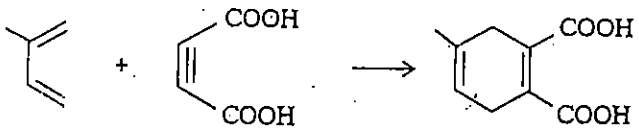
Diels and Alder jointly received the 1950 Noble prize for their work in this area.

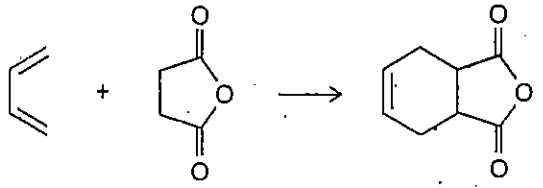
In Diels-Alder reaction, a conjugated diene is treated with an unsaturated compound called the dienophile (diene-lover) to yield a cyclic system. This reaction is named after the German chemists, Diel and Alder. It is a very useful reaction for synthesising cyclic systems. The simplest Diels-Alder reaction is the reaction of 1, 3-butadiene with ethene to yield cyclohexene. The resulting product (here cyclohexene) is called the adduct.



This is a very slow reaction and it occurs only under conditions of heat and pressure. Diels-Alder additions take place most rapidly and give the highest yield if the alkene component has electron withdrawing groups or the diene has electron donating groups. The reaction has wide scope because triple bonded systems also may be used as dienophiles. Some important examples of Diels-Alder reaction are given below :

i) 

ii) 

iii) 

SAQ 5

a) Write the structure of all possible carbocation intermediates in the addition of HI to 2, 4-hexadiene.

.....

b) Which carbocation, of the above problem, would you expect to be more stable?

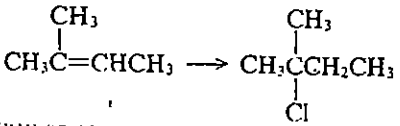
.....

7.7 SUMMARY

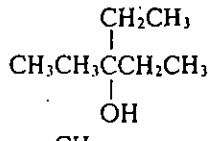
- Hydrocarbons containing one carbon-carbon double bond are known as monoene or olefins. Hydrocarbons containing two double bonds are known as alkedienes or dienes. Dienes are divided into three classes, i.e., conjugated dienes, isolated dienes and cumulated dienes.
- In general, the physical properties of alkenes are similar to the corresponding alkanes.
- Alkenes are generally prepared by the elimination of atoms or groups from the adjacent carbon atoms. Two such reactions are dehydrohalogenation of alkyl halides and dehydration of alcohols. The ease of dehydrohalogenation of alkyl halide or dehydration of alcohol is :
  tert > *sec* > *p*
- Alkenes can also be prepared from aldehydes or ketones by Wittig reactions.
- Dienes are prepared by retro Diels-Alder reactions.
- The main reactions of alkenes are electrophilic addition reactions. These reactions include addition of halogen, addition of alkyl halide, addition of water, etc.
- Alkenes can be oxidised by ozone, permanganate and osmium tetroxide. Alkenes on ozonolysis give aldehydes or ketones and on oxidation give 1, 2-diol.
- Addition of halogen to conjugated dienes give normal 1, 2-addition product as a minor product and abnormal 1, 4-addition product as a major product.
- Alkenes undergo Diels-Alder reaction.

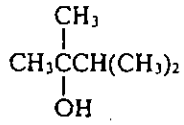
7.8 TERMINAL QUESTIONS

1) Give a structural formula for the carbocation intermediate that leads to the principle product in following reaction :



2) Identify the alkene obtained on hydration/dehydrohalogenation of each of the following compounds:

a) 

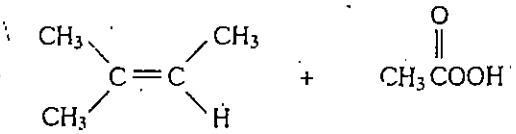
b) 

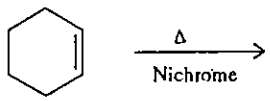
c) $CH_3CH_2CH_2Br$

3) Give the product formed when HBr react with 2-methyl-2-butene in presence of peroxide and in absence of peroxide.

4) Arrange the following alkenes in order of decreasing stability.
$R_2C{=}CR_2$; $R_2C{=}CH_2$; $CH_2{=}CH_2$; $R_2C{=}CHR$; $RHC{=}CHR$; $RCH{=}CH_2$.

5) Complete the following reactions :

a) 

b) 

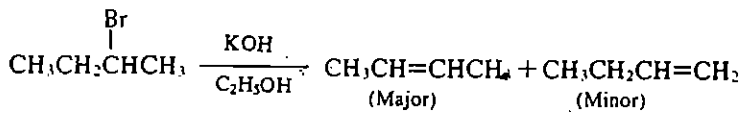
c) $CH_3CH{=}CH_2 + H_2O \xrightarrow[273\ K]{KMnO_4}$

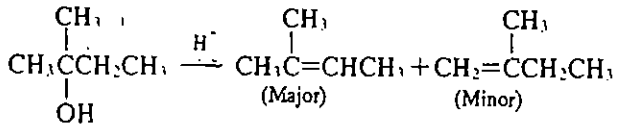
d) $CH_2{=}CHCH{=}CH_2 + HBr \longrightarrow$

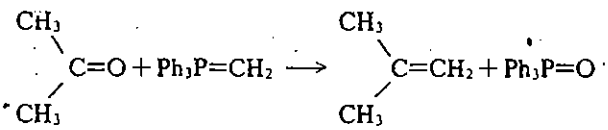
7.9 ANSWERS

Self Assessment Questions

1) a) alkyne
b) four
c) conjugated
d) sp; sp^2

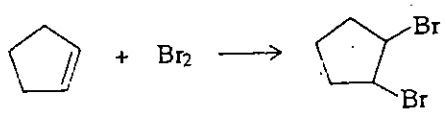
2) a) 

b) 

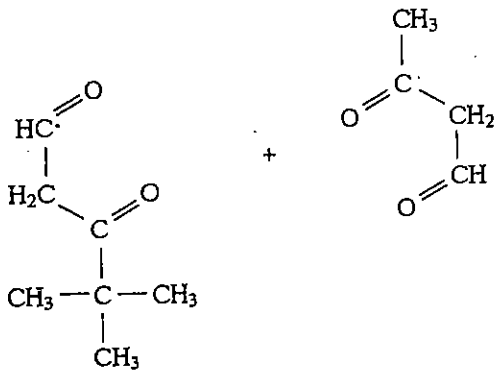
c) 

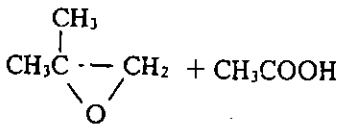
3) a) $CH_3CH_2CH{=}CH_2 + HCl \longrightarrow CH_3CH_2\underset{Cl}{\underset{|}{C}}HCH_3$

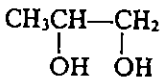
b) $CH_3\underset{CH_3}{\underset{|}{C}}H{=}CH_2 + HBr \xrightarrow{Peroxide} CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH_2Br$

c) 

4) a)



b) 

c) 

) a) $CH_3CH{=}CHCH{=}CHCH_3 \xrightarrow{H^+} CH_3CH_2\dot{C}HCH{=}CHCH_3 + CH_3\dot{C}HCH_2CH{=}CHCH_3$

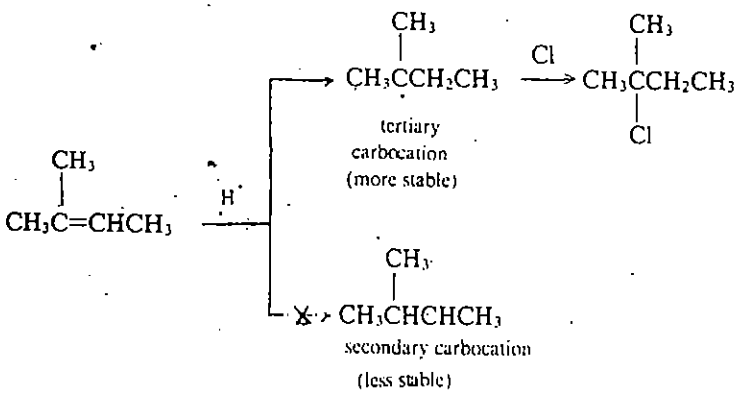
(Addition of H^+ to the other double bond gives identical intermediate)

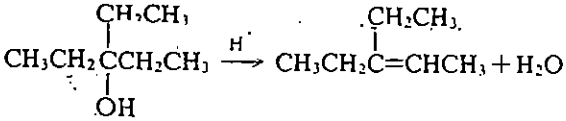
b) The first carbocation shown would be more stable because it is resonance stabilized allytic carbocation, i.e.,

$CH_3CH_2\dot{C}H{-}CH{=}CHCH_3 \longleftrightarrow CH_3CH_2CH{=}CH{-}\dot{C}HCH_3$

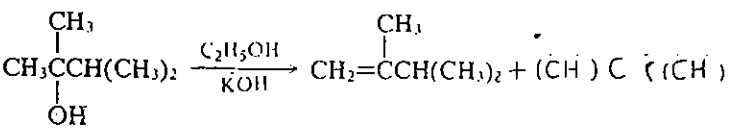
erminal Questions

)



a) 

The hydroxyl group is located on carbon that bear three equivalent ethyl substituents in the starting alcohol. Elimination can occur in either of the three equivalent direction to give same alkene.

b) 

c) $CH_3CH_2CH_2Br \xrightarrow[C_2H_5OH]{KOH} CH_3CH{=}CH_2$

3) The addition of HBr in absence of peroxide gives Markownikoff's product,

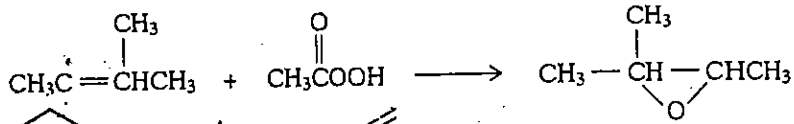
$CH_3C(CH_3){=}CHCH_3 + HBr \longrightarrow CH_3C(CH_3)(Br)CH_2CH_3$

The addition of HBr in the presence of peroxide gives anti-Markownikoff's product, i.e.:

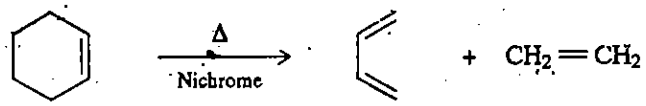
$CH_3C(CH_3){=}CHCH_3 + HBr \xrightarrow{Peroxide} CH_3CH(CH_3)CH(Br)CH_3$

4) $R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2,\ RCH{=}CHR > RCH{=}CH_2 > CH_2{=}CH_2$

5) a)



b)



c) $CH_3CH{=}CH_2 + H_2O \xrightarrow[275\ K]{KMnO_4} CH_3CH(OH)CH_2(OH)$

d) $CH_2{=}CHCH{=}CH_2 + HBr \longrightarrow CH_2(H)CH{=}CHCH_2Br + CH_2(H)CH(Br)CH{=}CH_2$

(major) (minor)

UNIT 3 ALKYNES

Structure

1 Introduction
Objectives

2 Types of Alkynes

3 Physical Properties

4 Spectral Properties

5 Preparation
Dehydrohalogenation of Dihalides
Dehalogenation of Tetrahalides
Alkylation of Ethyne

6 Acidity of Alkynes

7 Reactions of Alkynes
Electrophilic Addition
Reduction
Oxidation

8 Summary

9 Terminal Questions

10 Answers

1 INTRODUCTION

he previous two units, you have studied the chemistry of alkanes and alkenes. We shall y study another kind of hydrocarbon known as alkynes which contain carbon-carbon triple d.

yne, CH≡CH, the simplest alkyne, was burnt in the miners' lamps before electric lamps e developed. It is used in oxyacetylene torches for cutting and welding metals. It is nsively used as a fuel gas. In industry, it is the starting material for the preparation of many ortant chemicals, e.g., ethanoic acid, chloroethene (vinyl chloride), propanone, butanol, nol, etc.

rge number of naturally occurring compounds containing triple bonds have been isolated n plant kingdom. For example, a triyne from safflower has considerable activity against atodes and evidently forms part of the plant's chemical **defence against infestation**.

will see in this unit that the carbon-carbon triple bond reacts with many of the reagents reacts with alkenes. You will also study the most unique aspect of the chemistry of nes, the acidity of terminal alkynes.

jectives

r studying this unit, you should be able to :

list the various kinds of alkynes,

list the physical and spectral properties of alkynes,

explain the various methods for the preparation of alkynes,

explain the acidity of terminal alkynes.

explain the chemical reactions of alkynes.

2 TYPES OF ALKYNES

nes, also known as acetylenes, constitute the homogenous series of open chain urated hydrocarbons that contain one or more carbon-carbon triple bond. Alkynes may

be of two types : terminal and internal. In the terminal alkynes, the triple bond lies at the end of the carbon chain and in the internal alkynes, the triple bond lies anywhere except at the terminal position.

$CH_3C{\equiv}CH$	$CH_3CH_2C{\equiv}CCH_2CH_3$	$CH_3C{\equiv}CC{\equiv}CCH_3$
1-propyne (terminal alkyne)	3-hexyne (internal alkyne)	2,4-hexadiyne (internal alkyne)

8.3 PHYSICAL PROPERTIES

The increase in boiling point with increase in molecular weight is due to increased London forces, as discussed in Block 1 of this course.

Fractional distillation is the method of separating the components in a liquid mixture using the difference in their boiling points.

The pnysical properties of alkynes are similar to those of corresponding alkenes. They are all colourless and odourless (except ethyne). The first three members, i.e., ethyne, propyne and 1-butyne, are gases at room temperature; the next eight members are liquids and the higher members are solids. The physical constants like melting points, boiling points and densities increase gradually with the increase in molecular weight. Alkynes have slightly higher boiling points than the corresponding alkenes and alkanes. Terminal alkynes have lower boiling points than the isomeric internal alkynes and can be separated by careful fractional distillation. Alkynes share with alkanes and alkenes the properties of low density and low water solubility. They are nonpolar and dissolve readily in typical organic solvents, such as diethyl ether, chlorinated hydrocarbons, etc.

8.4 SPECTRAL PROPERTIES

The alkynyl chromophore absorbs below 200 nm (π-π^* transition) in uv region which is often difficult to detect. Conjugation with a multiple bond, however, results in a bathochromic shift.

The ir absorption region of compounds with a triple bond depends on whether they contain alkyne hydrogen or not. Thus, in terminal alkynes, RC≡CH, there is one absorption band in the region of 3300-3100 cm^{-1} due to the C≡CH stretching, and another in the region of 2140-2100 cm^{-1} due to —C≡C— stretch. In the internal alkynes RC≡CR, there is absorption in the region of 2260-2190 cm^{-1} corresponding to the —C≡C— stretching.

The internal alkynes, RC≡CR, have no alkynyl hydrogen, therefore, they have no nmr absorption characteristics of alkynyl hydrogen. The terminal alkynes, RC≡CH, give an absorption signal between δ 2 and 3, characteristic of alkynyl proton. Thus, value for alkynyl proton is less than the value of alkenyl protons. Let us suggest an explanation for this.

The chemical shift of a particular proton depends on the magnetic field felt by it. As you know, the chemical shift as well as the magnetic field felt by a particular proton depends on :

- the electronegativity of the carbon atom to which the proton is attached,
- the way the proton is oriented to the neighbouring π electron cloud, if any.

The *sp* hybridised carbon in alkynes is more electronegative than the sp^2 hybridized carbon in alkenes. Hence, we could expect higher δ value for alkynyl protons than for alkenyl protons. But the orientation of the alkynyl proton to the π electron cloud is unfavourable for higher δ values, as compared to the alkenyl protons.

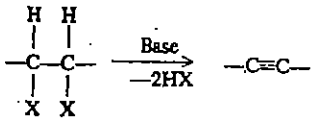
The mass spectra of an alkyne gives distinct molecular ion peak. However, the fragmentation is often complex and not easily interpreted.

8.5 PREPARATION

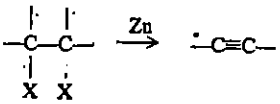
Organic synthesis makes use of two major reaction types : one is functional group transformation and the other is carbon-carbon bond forming reaction. Both these strategies are applied to the preparation of alkynes. In this unit, we shall discuss how alkynes are prepared by elimination reactions and by adding alkyl group(s) to the smaller ethyne unit. Some important methods of preparation of alkynes are outlined in Table 8.1.

Table 8.1 : Preparation of alkynes

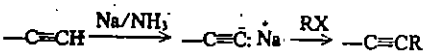
Dehydrohalogenation of dihalide



Dehalogenation of tetrahalide



Alkylation of ethyne

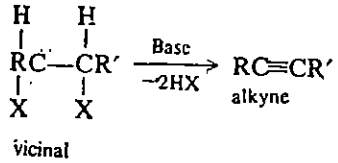


8.5.1 Dehydrohalogenation of Dihalides

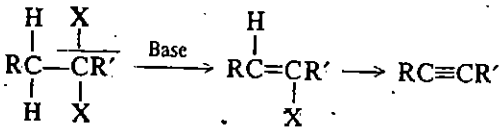
You have already seen in Unit 7 that an alkene can be prepared by the elimination of HX from an alkyl halide. Similarly, an alkyne can be prepared by the elimination of two molecules of HX from a dihalide. The dihalide may be of the geminal or vicinal type.

Geminal dihalide : One in which both the halogen atoms are substituted on the same carbon atom.

Vicinal dihalide : One in which halogen atoms are substituted on adjacent carbon atoms.

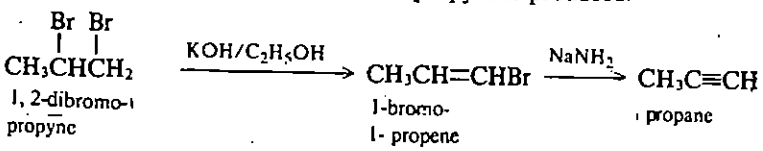


vicinal dihalide



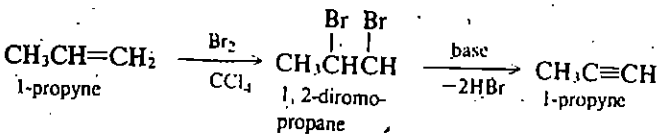
geminal dihalide — alkenyl halide — alkyne

Since an alkyne contains a triple bond as compared to the double bond in alkenes, two molecules of HX must be eliminated. Therefore, stronger conditions are required to remove the second HX molecule. For example, when 1, 2-dibromopropane reacts with a strong base, a two-fold elimination occurs and as a result a propyne is produced.



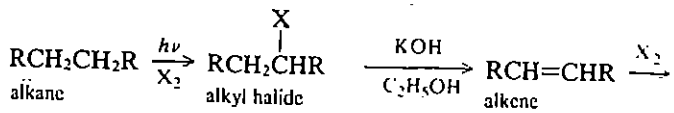
1, 2-dibromo-propyne — 1-bromo-1- propene — propane

You have studied in Unit 7 that dihalides are prepared by the addition of halogen to an alkene. Thus, the overall sequence of halogenation-dehydrohalogenation provides an excellent method for going from an alkene to an alkyne, e.g.,

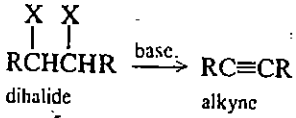


1-propyne — 1, 2-diromo-propane — 1-propyne

You may recall that alkenes can be prepared by elimination reactions of alkyl halides, which again, can be obtained from alkanes. Thus, we can say that alkane can serve as a starting material for the preparations of alkynes.



alkane — alkyl halide — alkene



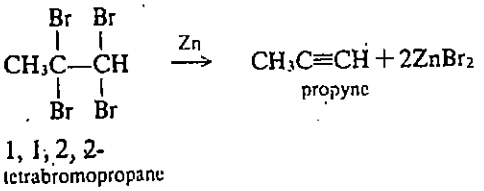
dihalide — alkyne

Different bases can be used for dehydrohalogenation; sodium amide is preferred, since it usually gives a higher yield.

The two-fold dehydrohalogenation follows the same mechanism as the dehydrohalogenation of alkyl halide to alkenes mentioned in Unit 7.

8.5.2 Dehalogenation of Tetrahalides

Alkyne can also be prepared by dehalogenation of tetrahalides. For example, propyne is formed when the vapours of 1, 1, 2, 2-tetrabromopropane are passed over heated zinc.



1, 1, 2, 2-tetrabromopropane

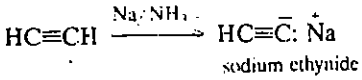
propyne

This reaction does not have any synthetic importance, since the tetrahalides themselves are usually prepared from alkynes. However, it provides a method for the purification of alkynes.

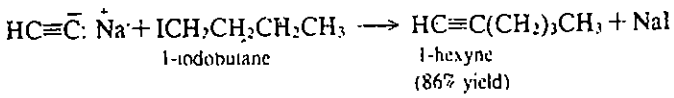
8.5.3 Alkylation of Ethyne

Reactions that lead to the attachment of an alkyl group to a molecular fragment are called alkylation.

In this sub-section, we shall see how alkynes are prepared by combining smaller units to build larger carbon chains. One of these structural units is ethyne itself. By attaching alkyl group to ethyne, more complex alkynes can be prepared. For example,



sodium ethynide



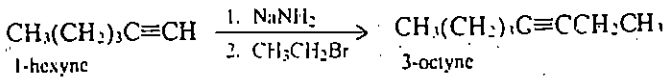
1-iodobutane

1-hexyne (86% yield)

Alkylation is a two-step process. In the first step, ethyne reacts with sodium amide to give an sodium ethynide ion, the conjugated base of ethyne.

In the second step, sodium ethynide ion attacks the C-1 carbon atom of 1-iodobutane and pushes out the iodine ion, yielding the terminal alkyne, 1-hexyne, giving an overall 86% yield.

Again, 1-hexyne can itself be converted into an alkynide anion, and can be alkylated a second time to yield an internal alkyne. A different alkyl halide can be used this time.

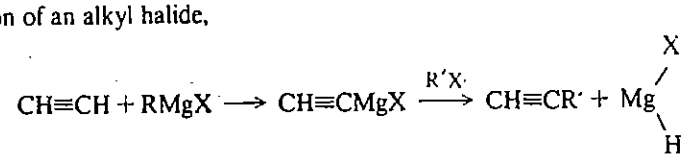


1-hexyne

3-octyne

This reaction gives good yields of alkyne only with primary alkyl bromides and iodides.

Alkylation can also be carried out by reacting ethyne and Grignard reagent, followed by the action of an alkyl halide,



SAQ 1

Suggest a method for preparation of the following alkynes starting with ethyne. Use any alkyl halide needed.

a) 2-Heptyne

.....

b) 3-Heptyne

.....

8.6 ACIDITY OF ALKYNES

You have already studied the Bronsted-Lowry theory of acids and bases in Unit 5 of this course. According to Bronsted and Lowry, an acid is a species that donates H^+. In fact, any compound containing a hydrogen atom can act as an acid under suitable conditions. Acid strength can be measured by measuring dissociation constants and expressing the results as values. Strong acids have lower pK_a values than weak acids.

Hydrocarbons are usually not regarded as acids. Nevertheless, we can consider the removal of a proton from a hydrocarbon by a very strong base.

$$\geq CH + B^- \longrightarrow \geq \bar{C}: + BH$$

In this equation, the hydrocarbon acts as a Bronsted acid and the conjugated base is a **carbon anion** or **carbanion**.

Approximate acidities of different types of aliphatic hydrocarbons have been measured and their pK_a values are given in Table 8.2.

Table 8.2 : Acidities of some hydrocarbons

Type	Example	pK_a
Alkane	$CH_4 \rightleftharpoons \bar{C}H_3 + H^+$	49
Alkene	$CH_2{=}CH_2 \rightleftharpoons CH_2{=}\bar{C}H + H^+$	44
Alkyne	$HC{\equiv}CH \rightleftharpoons HC{\equiv}\bar{C} + H^+$	25

From the data given in Table 8.2, we can see that there is a significant difference in the acidity of alkynes and other hydrocarbons. The order of acid strength of these hydrocarbons is :

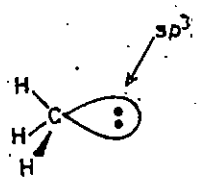
$$CH{\equiv}CH > CH_2{=}CH_2 > CH_3CH_3$$

Conversely, the decreasing order of basic strength of the conjugate anions resulting from these hydrocarbons should be :

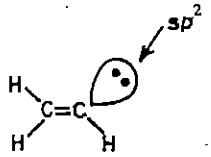
$$\underset{\text{alkanide anion}}{CH_3\bar{C}H_2} > \underset{\text{alkenide anion}}{CH_2{=}\bar{C}H} > \underset{\text{alkynide anion}}{CH{\equiv}\bar{C}}$$

This decreasing order of acidities and basicities of hydrocarbons can be explained as follows :

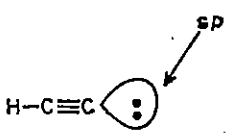
Conjugated bases of alkanes, alkenes and alkynes have an electron pair in sp^3, sp^2 and sp orbitals, respectively, i.e.,



alkanide anion



alkenide anion



alkynide anion

As we proceed from the alkanide anion to alkynide anion, the *s* character of the hybrid orbital increases and *p* character decreases. The alkanide anion (sp^3 hybridised) has 25% *s* character and 75% *p* character; alkenide anion (sp^2 hybridised) has 33.3% *s* character and 66.6% *p* character; and alkynide anion (*sp* hybridised) has 50% *s* character and 50% *p* character. You have already studied in your earlier classes that electrons in *s* orbital are closer to the nucleus than those in *p* orbitals. Since *s* character is maximum in alkynide anion and minimum in alkanide anion, the electron pair should be held most tightly in alkynide anion and most loosely in alkanide anion. Alkenide anion lies in between. In other words, the electron pair in alkynide anion should be least available for protonation. As you know, the basic strength is more if the electron pair is easily available for protonation.

Therefore, in the above series, alkynide anion is the weakest base and alkanide anion is the strongest base. Conversely, alkyne is the strongest acid and alkane the weakest acid.

This can be explained in another way also. On the basis of the above discussion, we can say that the *sp* hybridised carbon would attract the electrons pair constituting the C—H bond of an alkyne more than the sp^2 and sp^3 hybridised carbons in alkene and alkane; respectively. This implies that C—H bond in an alkyne would be more ionic and has a tendency to donate a proton (H^+). Hence, ethyne would be more acidic as compared to ethene or ethane.

Let us now compare its acidity with ammonia and water.

Addition of ethyne to sodamide in ether yields ammonia and sodium ethynide.

$$\underset{\text{stronger acid}}{HC{\equiv}CH} + \underset{\text{stronger base}}{\bar{N}H_2} \rightleftharpoons \underset{\text{weaker acid}}{H{-}NH_2} + \underset{\text{weaker base}}{HC{\equiv}\bar{C}}$$

$HA \rightleftharpoons H^+ + A$
Acid — conjugate base

The stronger the conjugate base, the weaker the acid and *vice-versa*.

The weaker acid, $H-NH_2$, is displaced from its salt by the stronger acid, HC≡CH. In other words, the stronger base, $\bar{N}H_2$ pulls the hydrogen ion away from ethyne to yield a weaker conjugate base, $HC{\equiv}\bar{C}$, since $\bar{N}H_2$ holds the hydrogen ion more tightly than $HC{\equiv}\bar{C}$, ammonia must necessarily be a weaker acid than ethyne.

Addition of water to sodium ethynide forms sodium hydroxide and regenerates ethyne.

$$\underset{\text{stronger acid}}{H{-}OH} + \underset{\text{stronger base}}{HC{\equiv}\bar{C}:\,\overset{+}{N}a} \longrightarrow \underset{\text{weaker acid}}{HC{\equiv}C{-}H} + \underset{\text{weak base}}{NaOH}$$

Many of the organic bases (R^-, $CH_2{=}CH^-$, $HC{\equiv}\bar{C}$, $\bar{O}C_2H_5$ etc.) are stronger than $\bar{O}C_2H_5$

The weaker acid, ethyne, is displaced from its salt by the stronger acid, H_2O. Thus, ethyne is a stronger acid than ammonia, but a weaker acid than water, i.e., the three compounds have the following order of acid strength :

$$H_2O > HC{\equiv}CH > NH_3$$

SAQ 2

Arrange the following bases in the increasing order of basic strength

$HC{\equiv}\bar{C}$, $\bar{O}H$, $\bar{N}H_2$

8.7 REACTIONS OF ALKYNES

Due to the presence of loosely held π electrons, alkynes undergo reactions similar to those of alkenes. You will see in this unit that some of the chemical characteristics of alkynes are similar to those of alkenes. Characteristic reactions of alkynes include electrophilic additions, reduction and oxidation. Some important reactions of alkynes are summarised in Table 8.3.

Table 8.3 : Reactions of alkynes

Electrophilic addition reactions

i) $RC{\equiv}CR \xrightarrow{HBr} RC(H)=C(Br)R \xrightarrow{HBr} RC(H)(Br)-C(H)(Br)R$

ii) $RC{\equiv}CR \xrightarrow{Br_2} RC(Br)=C(Br)R \xrightarrow{Br_2} RC(Br)(Br)-C(Br)(Br)R$

iii) $RC{\equiv}CR \xrightarrow[\text{catalyst}]{H_2O} RC(OH)=CHR \rightleftharpoons RCH_2COR$

iv) $RC{\equiv}CR \xrightarrow{(BH_3)_2} RC(OH)=CH(H) \rightleftharpoons RCCH_2R$ (O)

Reduction

i) $RC{\equiv}CR \xrightarrow[Pd-C/BaSO_4]{Lindlar\ pyridim,\ H_2} RC(H)=C(H)R$

ii) $RC{\equiv}CR \xrightarrow[No\ Poison]{Pd-C/H_2} RC(H,H)-C(H,H)R$

Oxidation

$RC{\equiv}CR \xrightarrow{O_3} RCOOH + HOOCR$

If one of the carbon atoms involved in double bond formation (with another carbon atom) carries a positive charge, then the species is called alkenyl cation.

8.7.1 Electrophilic Addition

Electrophilic addition reactions are characteristic of alkynes. Some common electrophilic addition reactions are discussed below.

i) Hydrohalogenation

Alkynes can add on the halogen acid (HX). The addition of halogen acid cannot take place in the dark, but is catalysed by light or metallic halides. Like alkenes, the addition is in accordance with Markownikoff's rule; for example, ethyne combines with hydrogen bromide to form first 1-bromoethene and then 1, 1-dibromoethane

$$\underset{\text{ethyne}}{HC{\equiv}CH} \xrightarrow{HBr} \underset{\text{1-bromo-ethene}}{HC(H)=CH(Br)} \xrightarrow{HBr} \underset{\text{1, 1-dibromoethane}}{HC(H,Br)-CH(H,Br)}$$

The mechanism of these reactions is the same as in the hydrohalogenation of alkenes, i.e.,

$$CH{\equiv}CH + \overset{\delta^+}{H}{-}\overset{\delta^-}{Br} \longrightarrow \overset{H}{\overset{|}{CH}}{=}CH + Br^-$$

$$\overset{+}{C}H{=}CH_2 \xrightarrow{Br^-} BrCH{=}CH_2$$

Addition of another molecule of hydrogen bromide could give either $CH_3\overset{+}{C}HBr$ (a secondary carbocation) or $\overset{+}{C}H_2CH_2Br$ (a primary carbocation). Since the secondary carbocation is more stable than the primary carbocation, the reaction proceeds via the secondary carbocation to form 1, 1-dibromoethane. Thus

$$CH_2{=}CHBr + \overset{\delta^+}{H}{-}\overset{\delta^-}{Br} \longrightarrow \overset{H}{\overset{|}{CH_2}}{-}\overset{+}{C}HBr + Br^-$$

$$CH_3{-}\overset{+}{C}HBr \xrightarrow{Br} CH_3{-}\underset{Br}{\overset{|}{CHBr}}$$

Because of the electron-withdrawing nature of bromine atom, the availability of π electrons in 1-bromoethene is less than that in ethene. Hence, the electrophilic addition (of HBr) to 1-bromoethene is much slower than that to ethene.

You may be aware that bromine atom is grouped as —I group. Recall what you have studied under inductive effect in Block 1

In the presence of free radical initiators such as peroxides, anti-Markownikoff addition of HBr is observed as with alkenes. For example, addition of HBr in the presence of peroxides to 1-butyne gives 1, 2-dibromobutane as shown below :

$$\underset{\text{1-butyne}}{CH_3CH_2C{\equiv}CH} \xrightarrow[HBr]{Peroxide} CH_3CH_2C(H)=CH(Br)$$

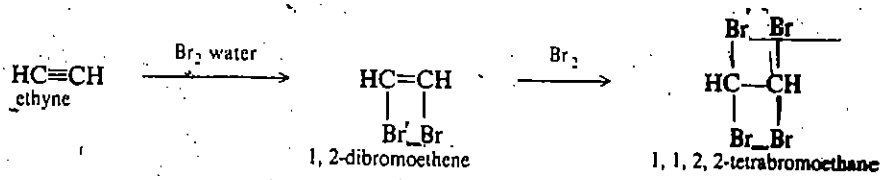
1-bromobutene

$$\underset{\text{1-bromobutene}}{CH_3CH_2CH=CHBr} \xrightarrow[HBr]{Peroxide} CH_3CH_2CH(Br)CH_2Br$$

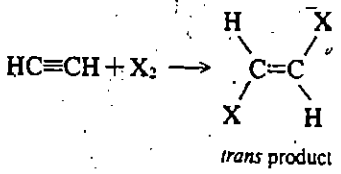
1, 2-dibromobutane

ii) Halogenation

Alkynes react with chlorine and bromine to yield tetrahaloalkanes. Two molecules of halogen add to the triple bond. A dihaloalkene is an intermediate and can be isolated using proper reaction conditions. Ethyne, for instance, on treatment with bromine water gives only 1, 2-dibromoethene whereas with bromine alone, it forms 1, 1, 2, 2-tetrabromoethane.



The addition of halogens to ethyne is stereoselective; the predominant product is the *trans* isomer.



SAQ 3

Write chemical equation for the reaction of propyne with each of the following reagents.

a) HCl

.....

b) Cl_2

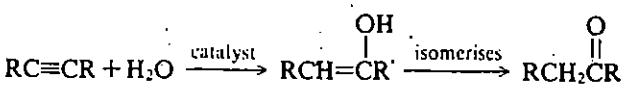
.....

c) HBr (in presence of peroxide)

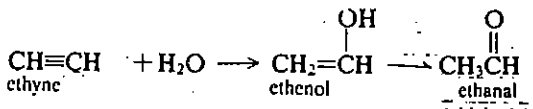
.....

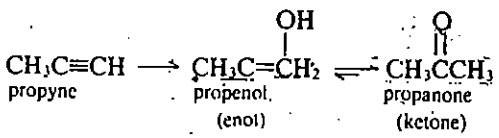
iii) Hydration

You have seen in Unit 7 that addition of a water molecule to an alkene gives an alcohol. Similarly, addition of a water molecule to an alkyne gives an enol. An enol has the —OH group attached to a double-bonded carbon atom.



In fact, enols are very unstable and they isomerise (or tautomerise) to give aldehyde or ketones. The process by which enols are converted into aldehydes or ketones is called keto-enol isomerism or keto-enol tautomerism. For example, when ethyne undergoes hydration, it gives an aldehyde, i.e., ethanal; while, propyne gives a ketone, i.e., propanone.



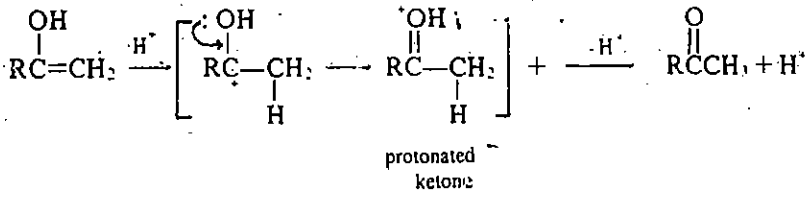


The arrow is longer towards aldehyde or ketone side showing the direction in which the equilibrium is favoured.

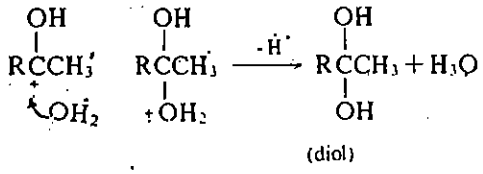
In case of unsymmetrical alkynes, addition of water takes place in accordance with Markownikoff's rule.

Enol is converted into an aldehyde or a ketone by a mechanism similar to the hydration of a double bond. The enol double-bond is protonated to give a carbocation. The carbocation in

the example shown below is a protonated ketone. Instead of adding water, this ion loses a proton to give ketone.



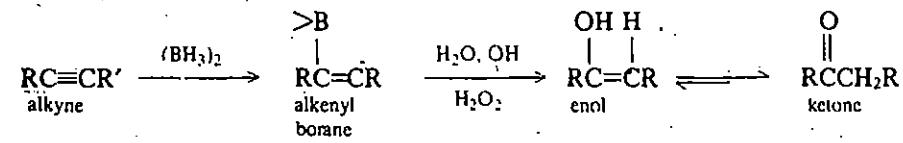
Now you may ask why carbocation is not attacked by water molecule to give a diol, i.e.,



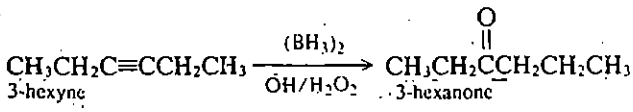
This reaction does not occur, because it is reversible, and the equilibrium between the ketone and the corresponding diol in most cases favours formation of the ketone.

iv) Hydroboration

Addition of borane to alkynes gives alkenyl boranes, which can be oxidised by basic hydrogen peroxide to ketones via their enol.

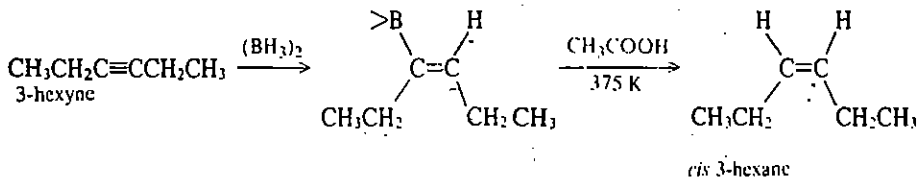


The symmetrical internal alkynes give a single product while unsymmetrical internal alkynes give a mixture of both the possible ketones. For example, 3-hexyne gives 3-hexanone while 2-hexyne gives a mixture of 2-hexanone and 3-hexanone.



The terminal alkynes on hydroboration give aldehydes.

Another reaction of organoboranes is **protonolysis**. That is, the alkenyl boranes, formed after the addition of borane to alkynes, on treatment with ethanoic acid yield *cis*-alkenes. This reaction sequence provides another method of converting alkynes to *cis*-alkenes.



SAQ 4

Give the equation for hydroboration of a terminal alkyne.

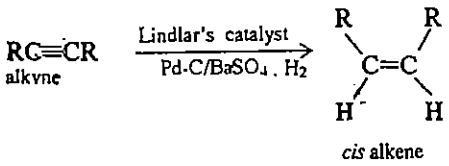
.....

.....

8.7.2 Reduction

A catalyst mixed with a selective inhibiting agent is called a poisoned catalyst.

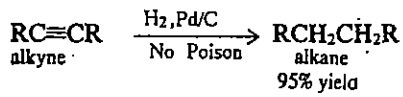
Like alkenes, alkynes undergo catalytic hydrogenation. The addition of hydrogen to an alkyne takes place in two steps. First addition results in the formation of an alkene; since an alkene can also undergo catalytic hydrogenation, the second addition gives an alkane. By using a calculated amount of hydrogen and a poisoned catalyst, hydrogenation can be stopped at the alkene stage. These catalysts selectively block the hydrogenation of alkenes.



cis alkene

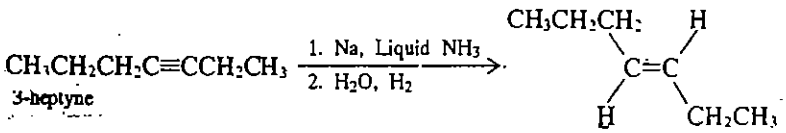
Stereoselective reaction is a reaction which yield predominantly one isomer.

This is a stereoselective addition reaction giving predominantly *cis* alkenes. In the absence of a poison, catalytic hydrogenation of an alkyne gives the alkane.



Now you can ask : can we modify the reduction of alkynes so as to get only *trans* alkenes. The answer is yes; we can get only *trans* products, but with a different reducing agent and through a different mechanism.

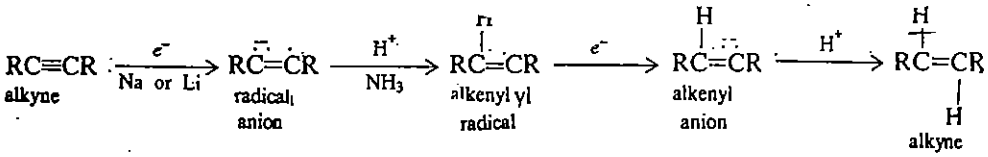
If we carry out the reduction of an alkyne with sodium metal or lithium metal in liquid ammonia, *trans* alkene is almost an exclusive product. For example, 3-heptyne is reduced to *trans* 3-heptene in the following way :



trans-3-heptene (86%)

In the first step of this mechanism, the alkyne accepts one electron to give a radical anion. The radical anion is protonated by ammonia solvent to give an alkenyl radical; which gets further reduced by accepting another electron to give an alkenyl anion. This species is again protonated to give the alkene.

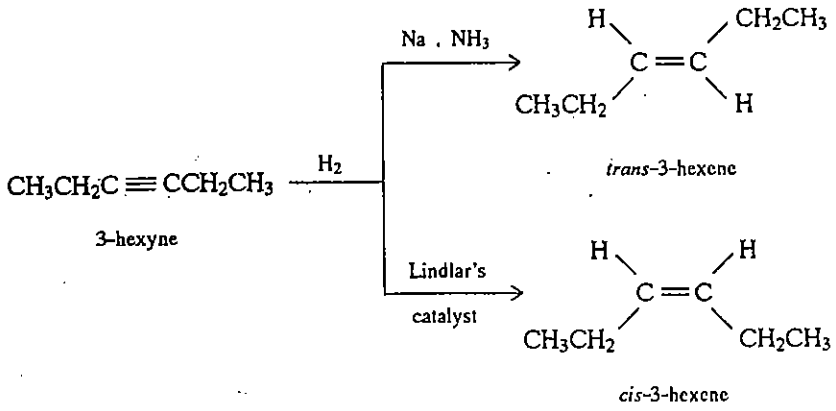
A radical anion has one centre with a negative charge and another, with an unpaired electron.



Formation of the *trans* alkene is due to the rapid equilibration of the intermediate alkenyl radical between the *cis*-and *trans*-forms. The equilibrium lies on the side of the more stable *trans* species.

cis radical (less stable) — *trans* radical (more stable)

In other words, we can say reduction of alkyne to double bond can yield either *cis*-alkene or *trans*-alkene, depending upon the choice of the reducing agent.



SAQ 5

Suggest a method for the synthesis of the following compounds from 2-hexyne :

a) *cis*-2-hexene

.....

.....

b) *trans*-2-hexene

.....

.....

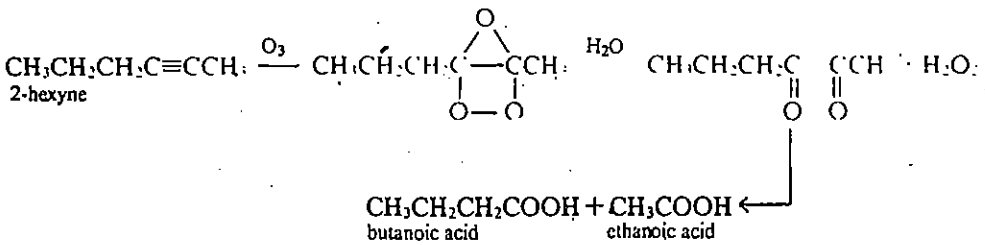
c) hexane

.....

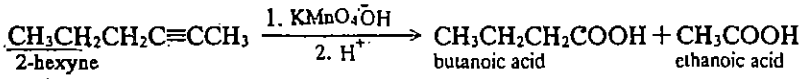
.....

8.7.3 Oxidation

Reagents and reactions that lead to oxidative cleavage of alkenes also lead to cleavage of alkynes. Addition of ozone to an alkyne produces the ozonide. The ozonides on hydrolysis give 1,2-dicarbonyl compounds, which undergo oxidative cleavage to carboxylic acids by hydrogen peroxide formed in the reaction. For example, 2-hexyne on ozonolysis gives butanoic and ethanoic acids.



Same products are obtained when alkynes are oxidised by alkaline permanganate and then hydrolysed using mineral acid.

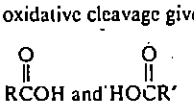


Oxidative cleavage reactions are used as a tool in structure determination. The carboxylic acids formed would tell us which of the carbon atoms were linked through the triple bond in the original alkyne.

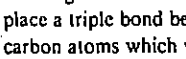
In this context, by carbonyl components, we specifically refer to aldehydes or ketones or compounds having both the functional groups. In general, a carbonyl compound means aldehyde ketone, acid, ester or any of acid derivatives.

The steps for arriving at the structure of an alkyne using oxidation cleavage are given below :

* First write down the formulae of the acids side by side, such that —C—OH groups face each other, e.g., let us propose the structure of the alkyne which on oxidative cleavage gives :

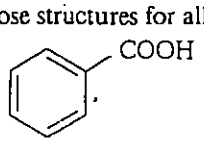


*combine the carbon chains omitting =O and —OH groups; place a triple bond between the carbon atoms which were earlier part of the carboxylic groups.



SAQ 6

Propose structures for alkynes that give the following products on oxidative cleavage :

a) 

+ CH_3COOH

.....

b) $CH_3(CH_2)_7COOH + HOOC(CH_2)_7COOH$

c) $2CH_3CH_2COOH$

8.8 SUMMARY

- Alkynes are the hydrocarbons with one or more carbon-carbon triple bond.
- Alkynes may be of two type, i.e., terminal or internal.
- Physical properties of alkynes are more or less similar to alkenes.
- Alkynes are prepared by alkylation of terminal alkynes or by a two-fold elimination of HX from dihalide or by dehalogenation of tetrahalides.
- Terminal alkynes are more acidic than alkanes or alkenes.
- Hydrohalogenation follows Markownikoff's rule.
- Halogens add to alkynes to give tetrahaloalkanes. Using proper reaction conditions dihaloalkene can be isolated.
- Hydration of an alkyne gives an unstable enol which tautomerises to give an aldehyde or a ketone.
- Hydroboration of alkynes may give ketones or aldehydes, depending on reaction conditions and the type of the alkyne.
- Hydrogenation of an alkyne in the presence of Pd, Pt or Ni catalyst yields an alkane. By using poisoned catalyst, the intermediate *cis*-alkene can be obtained. Reduction of an alkyne with sodium or lithium in liquid ammonia gives the *trans*-alkene.
- Ozonolysis of alkynes give carboxylic acids.

8.9 TERMINAL QUESTIONS

1) How would you carry out the following reactions :

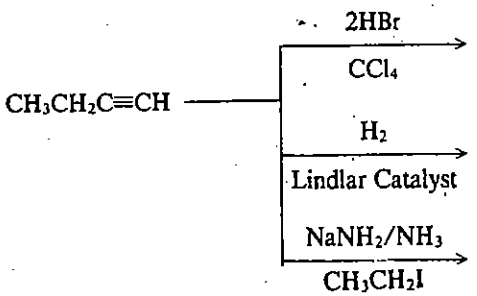
a) $CH_3CH_2C{\equiv}CH \xrightarrow{?} CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$

b) $CH_3CH_2C{\equiv}CH \xrightarrow{?} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H$

c) $CH_3CH_2C{\equiv}CHCH_3 \xrightarrow{?} CH_3CH_2COOH + CH_3COOH$

d) $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow{?} CH_3CH_2CH_2C{\equiv}CH$

2) Predict the product of the following reactions of 1-butyne :



3) How will you convert
   a) 2-Bromopropane to propyne
   b) 1-Bromopropane to 2-hexyne.

4) Suggest steps for the following transformations :
   a) 2, 3-dibromopentane to *trans*-2-pentene
   b) 3-methyl-1-butyne to *trans*-2-methyl-3-heptene

5) Show, by writing appropriate chemical equations, how each of the following compounds could be converted to 1-hexyne :
   a) 1, 2-Dibromohexane
   b) 1-Hexene
   c) Hexane

8.10 ANSWERS

Self Assessment Questions

1) a) $CH{\equiv}CH \xrightarrow{NaNH_2\,.\,NH_3} HC{\equiv}\bar{C}\,\overset{+}{N}a$

$HC{\equiv}\bar{C}\,\overset{+}{N}a + CH_3(CH_2)_3Br \longrightarrow HC{\equiv}C(CH_2)_3CH_3$

$HC{\equiv}C(CH_2)_3CH_3 \xrightarrow{NaNH_2\,.\,NH_3} \overset{+}{N}a\,\bar{C}{\equiv}C(CH_2)_3CH_3$

$\overset{+}{N}a\,\bar{C}{\equiv}C(CH_2)_3CH_3 + CH_3Br \longrightarrow CH_3C{\equiv}C(CH_2)_3CH_3$

b) $HC{\equiv}CH \xrightarrow[2.\ CH_3(CH_2)_2Br]{1.\ NaNH_2\,.\,NH_3} CH{\equiv}C(CH_2)_2CH_3$

$CH{\equiv}C(CH_2)_2CH_3 \xrightarrow[NH_3]{NaNH_2} \overset{+}{N}a\,\bar{C}{\equiv}C(CH_2)_2CH_3$

$\overset{+}{N}a\,\bar{C}{\equiv}C(CH_2)_2CH_3 + CH_3CH_2Br \longrightarrow CH_3CH_2C{\equiv}C(CH_2)_2CH_3$

2) $\bar{O}H < HC{\equiv}\bar{C} < \bar{N}H_2$

3) a) $CH_3C{\equiv}CH + HCl \longrightarrow CH_3\overset{Cl\ H}{\overset{|\ \ |}{C}}{=}CH \xrightarrow{HCl} CH_3\overset{Cl\ H}{\overset{|\ \ |}{C}}{-}\overset{Cl\ H}{\overset{|\ \ |}{C}}H$

b) $CH_3C{\equiv}CH + Cl_2 \longrightarrow CH_3\overset{Cl\ Cl}{\overset{|\ \ |}{C}}{=}CH \xrightarrow{Cl_2} CH_3\overset{Cl\ Cl}{\overset{|\ \ |}{C}}{-}\overset{Cl\ Cl}{\overset{|\ \ |}{C}}H$

c) $CH_3C{\equiv}CH + HBr \xrightarrow{Peroxide} CH_3\overset{Br}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}H$

$\xrightarrow[Peroxide]{HBr} CH_3\overset{H\ Br}{\overset{|\ \ |}{C}}{-}\overset{H\ Br}{\overset{|\ \ |}{C}}H$

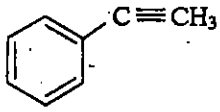
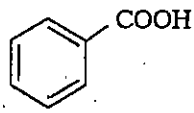
4) $CH_3CH_2C{\equiv}CH \xrightarrow{H\bar{B}<} CH_3CH_2\overset{\bar{H}\ B<}{\overset{|\ \ |}{C}}{=}CH \xrightarrow{H_2O_2\,,\,\bar{O}H}$

$CH_3CH_2\overset{H\ OH}{\overset{|\ \ |}{C}}{=}CH \rightleftharpoons CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H$

5) a) $CH_3CH_2CH_2C \equiv CCH_3 \xrightarrow[NH_3]{\bar{H}_2,\ Na} \begin{matrix} CH_3CH_2CH_2 & & H \\ & C=C & \\ H & & CH_3 \end{matrix}$

b) $CH_3CH_2CH_2C \equiv CCH_3 \xrightarrow[\text{catalyst}]{H_2} \begin{matrix} CH_3CH_2CH_2 & & CH_3 \\ & C=C & \\ H & & H \end{matrix}$

c) $CH_3CH_2CH_2C{\equiv}CCH_3 \xrightarrow{Pd/H_2} CH_3(CH_2)_4CH_3$

6) a)  $\xrightarrow[\text{or } KMnO_4]{O_3}$  + CH_3COOH

b) $CH_3(CH_2)_7C{\equiv}C(CH_2)_7COOH \xrightarrow[KMnO_4]{O_3 \text{ or}} CH_3(CH_2)_7COOH + HOOC(CH_2)_7COOH$

c) $CH_3CH_2C{\equiv}CCH_2CH_3 \xrightarrow[\text{or } KMnO_4]{O_3} CH_3CH_2COOH + CH_3CH_2COOH$

Answers to Terminal Questions

1) a) $CH_3CH_2C{\equiv}CH + H_2O \longrightarrow CH_3CH_2\overset{OH}{\overset{|}{C}}{=}CH_2 \rightleftharpoons CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$

b) $CH_3CH_2C{\equiv}CH \xrightarrow{HB<} CH_3CH_2\overset{H}{\overset{|}{C}}{=}CH \xrightarrow{H_2O,\ \bar{O}H}$

$CH_3CH_2CH{=}\overset{OH}{\overset{|}{C}}H \rightleftharpoons CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H$

c) $CH_3CH_2CH_2C{\equiv}CCH_3 \xrightarrow[\text{or } KMnO_4]{O_3} CH_3CH_2COOH + CH_3COOH$

d) $CH_3CH_2CH_2CH{=}CH_2 \xrightarrow[CCl_4]{Br_2} CH_3CH_2CH_2\overset{Br}{\overset{|}{C}}HCH_2\overset{Br}{\overset{|}{}} \xrightarrow[-2HBr]{NaNH_2} CH_3CH_2CH_2C{\equiv}CH$

2) $CH_3CH_2C{\equiv}CH$ —
- $\xrightarrow[CCl_4]{2HBr}$ $CH_3CH_2CH_2\overset{Br}{\overset{|}{C}}H\overset{Br}{\overset{|}{}}$
- $\xrightarrow[\text{Lindlar Catalyst}]{H_2}$ $CH_3CH_2CH{=}CH_2$
- $\xrightarrow[CH_3CH_2-I]{NaNH_2/NH_3}$ $CH_3CH_2C{\equiv}CCH_2CH_3$

3) a) $CH_3\overset{Br}{\overset{|}{C}}HCH_3 + KOH \xrightarrow[-HBr]{CH_3CH_2OH} CH_3CH{=}CH_2 \xrightarrow{Br_2}$

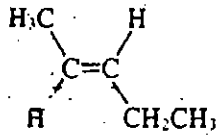
$CH_3\overset{Br}{\overset{|}{C}}H\overset{Br}{\overset{|}{C}}H_2 \xrightarrow[H_2O]{NaNH_2,\ NH_3} CH_3C{\equiv}CH$

b) $CH_3CH_2\overset{Br}{\overset{|}{C}}H_2 \xrightarrow[-HBr]{C_2H_5OH,\ KOH} CH_3CH{=}CH_2 \xrightarrow{Br_2} CH_3\overset{Br}{\overset{|}{C}}H\overset{Br}{\overset{|}{C}}H_2$

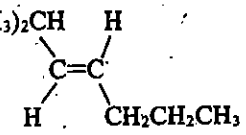
$\xrightarrow[H_2O]{NaNH_2,\ NH_3} CH_3C{\equiv}CH \xrightarrow{NaNH_2} CH_3C{\equiv}\bar{C}\ \overset{+}{N}a \xrightarrow{ICH_2CH_2CH_3}$

$CH_3C{\equiv}CCH_2CH_2CH_3$

4) a) $CH_3\overset{Br}{\overset{|}{C}}H-\overset{Br}{\overset{|}{C}}HCH_2CH_3 \xrightarrow[H2O]{NaNH_2} CH_3C{\equiv}CCH_2CH_3 \xrightarrow{NaNH_2}$



b) $(CH_3)_2CHC{\equiv}CH \xrightarrow{NaNH_2/NH_3} (CH_3)_2CHC{\equiv}CNa^+ \xrightarrow{BrCH_2CH_2CH_3}$

$(CH_3)_2CHC{\equiv}CCH_2CH_2CH_3 \xrightarrow{Li/NH_3}$ 

5) a) $CH_3(CH_2)_3\underset{\displaystyle Br}{\overset{\displaystyle Br}{CH}}CH_2 \xrightarrow[H_2O]{NaNH_2,\ NH_3} CH_3(CH_2)_3C{\equiv}CH$

b) $CH_3(CH_2)_3CH{=}CH_2 \xrightarrow{Br_2} CH_3(CH_2)_3\underset{\displaystyle Br}{\overset{\displaystyle Br}{CH}}CH_2$

$\xrightarrow[H_2O]{NaNH_2,\ NH_3} CH_3(CH_2)_3C{\equiv}CH$

c) $CH_3(CH_2)_4CH_3 \xrightarrow[Br_2]{h\nu} CH_3(CH_2)_3\overset{\displaystyle Br}{\underset{|}{C}}H_2CH_2$

$\xrightarrow[-HBr]{KOH,\ C_2H_5OH} CH_3(CH_2)_3CH{=}CH_2 \xrightarrow{Br_2}$

$CH_3(CH_2)_3\underset{\displaystyle Br}{\overset{\displaystyle Br}{CH}}CH_2 \xrightarrow[-HBr]{KOH,\ C_2H_5OH} CH_3(CH_2)_3C{\equiv}CH$

UNIT 9 AROMATIC HYDROCARBONS AND POLYNUCLEAR AROMATICS

Structure

9.1 Introduction
Objectives

9.2 Isolation of Benzene

9.3 Spectral Properties

9.4 Structure of Benzene

9.5 Resonance and Aromaticity

9.6 Reactions of Aromatic Compounds
Nitration
Halogenation
Sulphonation
Friedel-Crafts Alkylation
Friedel-Crafts Acylation
Mechanism of Electrophilic Substitution

9.7 Effect of Substituents on Reactivity and Orientation
Effect of Substituents on Reactivity
Effect of Substituents on Orientation

9.8 Addition Reactions of Benzene

9.9 Reduction

9.10 Reactions of Side Chain
Substitution in Side Chain
Oxidation of Side Chain

9.11 Polynuclear Hydrocarbons
Naphthalene

9.12 Summary

9.13 Terminal Questions

9.14 Answers

9.1 INTRODUCTION

In the last three Units, we have discussed the chemistry of aliphatic hydrocarbons. Now we come to another class of compounds, namely, aromatic hydrocarbons.

Early in the development of organic chemistry, organic compounds were arbitrarily classified as either aliphatic or aromatic. The meaning of word "aliphatic" means fatty. The aliphatic compounds were so named because the first members of this class to be studied were the fatty acids. In addition to the aliphatic compounds, there were a large number of another type of compounds, which were also obtained from natural sources, e.g., resins, balsams, aromatic oils, etc. The structure of these compounds was unknown but they had one thing in common, a pleasant odour. Thus, these compounds were arbitrarily classified as aromatic compounds (Greek : **aroma** 'fragrant smell'). Now the word aromatic is used for benzene and related compounds. So the original meaning of the word aromatic (fragrant) has no longer any significance.

Benzene, the simplest of the aromatic compounds, was isolated by Michael Faraday in 1825 from the gas obtained by pyrolysis of whale oil. Later, in 1845, Holman discovered benzene in

coal tar, which contains benzene and many of its derivatives.

Many compounds isolated from natural sources and many synthetic drugs are aromatic in nature. The local anaesthetic procaine and the tranquiliser diazepam (valium) are a few examples.

Benzene is carcinogenic and injurious to health. Prolonged exposure leads to bone-marrow depression. Benzene as a solvent should, therefore, be used carefully, avoiding evaporation in the open or inhaling its vapour.

Keeping in view the importance of aromatic compounds, we shall study the chemistry of benzene and its derivatives in this unit.

Objectives

After studying this unit, you should be able to:

- describe the isolation of benzene,
- list the important spectral peaks of benzene and its derivatives,
- explain the resonance energy of aromatic compounds,
- discuss the important reactions of aromatic compounds,
- explain the polynuclear hydrocarbons, and
- list the important reactions of polynuclear hydrocarbons.

9.2 ISOLATION OF BENZENE

Coaltar was once the chief source of benzene and its derivatives. Today, benzene and its derivatives can be extracted from petroleum in which they occur naturally. They are also prepared from the non-aromatic constituents of petroleum, which is now the main source. The most important such method is hydroforming or catalytic reforming.

Hydroforming or Catalytic Reforming

This method is based on dehydrogenation, cyclisation and isomerisation reactions. The aromatic compounds so obtained contain the same number of carbon atoms as the aliphatic starting materials. Hydroforming is carried out under high pressure and at temperatures of around 750-820 K in the presence of platinum catalyst. Following are some important examples of hydroforming :

$$\underset{\text{hexane}}{CH_3(CH_2)_4CH_3} \xrightarrow{\Delta} \underset{\text{benzene}}{C_6H_6} + 4H_2$$

$$\underset{\text{heptane}}{CH_3(CH_2)_5CH_3} \xrightarrow{\Delta} \underset{\text{toluene}}{C_6H_5CH_3} + 4H_2$$

Note that a mixture *o*−, *m*− and *p*−xylenes is referred to as xylenes.

$$\underset{\text{octane}}{CH_3(CH_2)_6CH_3} \xrightarrow{\Delta} \underset{\text{xylenes}}{C_6H_4(CH_3)_2} + \underset{\text{ethyl benzene}}{C_6H_5C_2H_5}$$

Various hydrocarbons are separated by a selective solvent process, but since, benzene is obtained in much smaller amount than toluene and the xylenes, these are converted into benzene by heating with hydrogen under pressure in the presence of a metal oxide catalyst. This process is called hydrodealkylation.

$$\underset{\text{toluene}}{C_6H_5CH_3} + H_2 \xrightarrow{\text{Catalyst}} \underset{\text{benzene}}{C_6H_6} + \underset{\text{methane}}{CH_4}$$

9.3 SPECTRAL PROPERTIES

The presence of an aromatic ring in a compound is detectable by uv spectroscopy. Aromatic compounds show a series of absorption bands with fairly intense absorption near 205 nm and a less intense absorption in the 255-275 nm range. As the conjugation increases, λ_{max} also increases.

The ir spectrum is quite useful for recognising the presence of aromatic compounds. The ir spectrum gives a weak absorption band near 3030 cm^{-1} for aryl C—H stretching vibration. Absorption due to C=C stretching in benzene gives a series of four bands, generally between 1450 and 1600 cm^{-1}.

Because of a great deal of overlapping of the various bands in the region of 1225-970 cm^{-1}, this region is not very useful for identification purposes.

The nmr spectrum is a useful tool for the structure determination of benzene and its derivatives. Since all the six hydrogen atoms in benzene are equivalent, the nmr spectrum gives only one singlet at δ 7.27 ppm. Recall that olefinic protons appear at higher field values, generally at about δ 5.0 ppm. Electron-withdrawing substituents on the ring shift the absorption of adjacent protons further downfield, while electron-releasing groups shift absorption upfield from that of the unsubstituted benzene.

The mass spectrum of benzene gives prominent molecular ion peak (M^+). Also M + 1 and M + 2 peaks, due to ^{13}C and ^2H are observed. Benzene shows prominent peaks at m/z 78 $(C_6H_6)^+$, m/z 77 $(C_6H_5)^+$, m/z 53 $(C_4H_5)^+$, m/z 51 $(C_4H_3)^+$, m/z 50 $(C_4H_2)^+$ and m/z 39 $(C_3H_3)^+$. All these also occur in the mass spectra of nearly all benzene derivatives.

9.4 STRUCTURE OF BENZENE

Molecular Orbital Theory provides a description of benzene. According to this theory, benzene is a planar flat symmetrical molecule having the shape of a regular hexagon. The C—C—C bond angle has a value of 120°. Each carbon atom in the molecule is sp^2 hybridised. Two orbitals of the sp^2 hybridised carbon atom overlap with the other two orbitals of the adjacent carbon atom resulting in the formation of two σ bonds. The third orbital of each carbon atom overlaps and forms a σ bond with 1*s* orbital of hydrogen atom. Thus six carbon-carbon σ bonds are formed. Each carbon atom still has a *p* orbital perpendicular to the plane of the ring. The *p* orbital has two lobes one above and the other below the plane of the ring and because all *p* orbitals are equivalent, they overlap equally well with both the neighbouring *p* orbitals resulting in a delocalised doughnut shaped π orbital cloud above and below the ring. The picture that emerges out of this discussion is given below in Fig. 9.1.

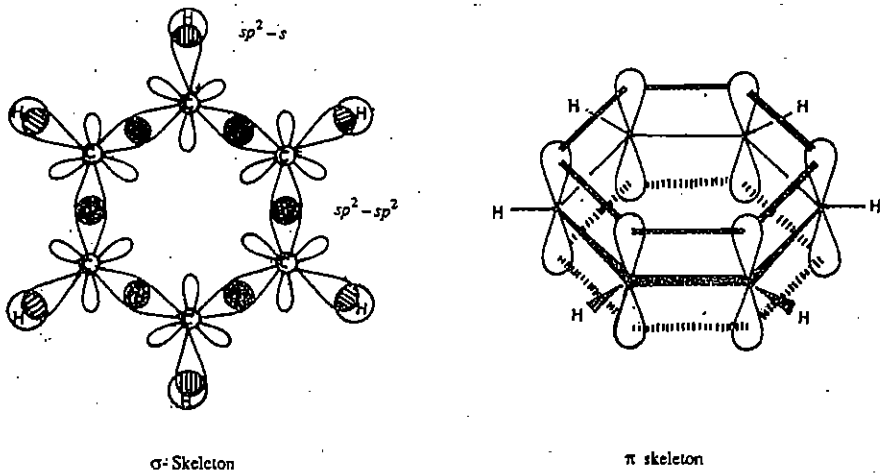


Fig 9.1 : σ and π skeleton of benzene

The benzene ring is a cyclic conjugated system and is usually represented as a regular hexagon with a circle inside the ring. This gives an idea of delocalisation of π-electrons.

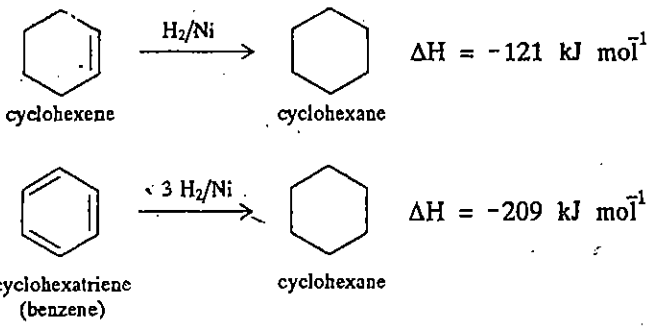
9.5 RESONANCE AND AROMATICITY

You have already studied the basic concept of resonance in Unit 5 of this course. Here, we will discuss the resonance effect in aromatic compounds. The structures of a large number of organic compounds can be written with the help of simple bond diagrams, e.g., ethene as $CH_2=CH_2$ ethyne as HC ≡ CH, etc. There are, however, many compounds for which

simple bond diagrams do not accurately describe these molecules, one of the examples being benzene. The structure of benzene (Fig 9.1) gives the impression that it is a cyclic compound of six carbon atoms containing three single and three double bonds. If this were so, you would expect two values of carbon-carbon bond lengths, viz., one for single bonds (nearly 154 pm as in ethane) and the other for double bonds (nearly 133 pm as in ethene). Experimental evidence through X-ray diffraction studies shows that all the six carbon-carbon bonds in benzene are equal and have a length of 139 pm, which is in between 133 and 154 pm. The explanation of this is as follows :

X-ray studies give the bond lengths and bond angle.

The heats of hydrogenation of cyclohexene and benzene determined experimentally are given below :



The heat evolved when hydrogen is added to cyclohexene (having one C = C bond) is 121 kJ mol^{-1}. The expected value of the heat evolved when hydrogen is added to benzene (having three C=C bonds) should be 3×121 kJ mol^{-1} = 363 kJ mol^{-1}, but the experimental value is 209 kJ mol^{-1}. We can infer that benzene is more stable (having lower energy content) than the hypothetical molecule containing three isolated C=C bonds by 363—209 = 154 kJ mol^{-1}. This energy difference is called the resonance energy and is responsible for the stability of benzene compared to other unsaturated compounds which lack resonance stabilisation.

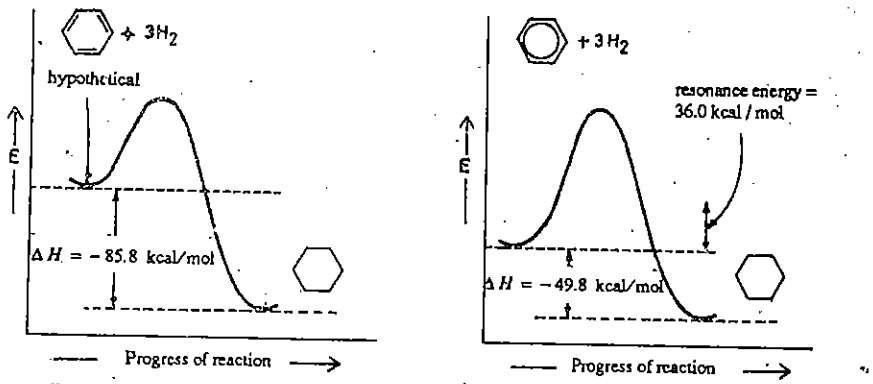
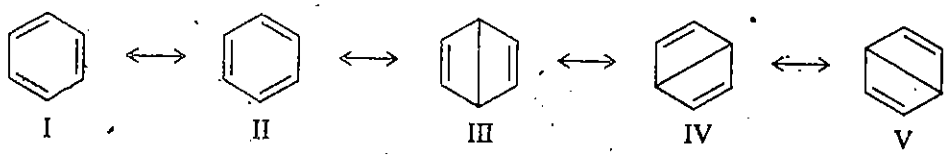


Fig. 9.2 Energy diagrams for the hydrogenation of cyclohexatriene (hypothetical) and benzene

We cannot write down a single structure for benzene which would encompass all its properties rather it is considered to be the resonance "hybrid" of the following hypothetical structures I-V



These structures are called resonance structures or contributors or canonical forms. The two "Kekule" forms, I and II, are of lower energy (more stable) than the three "Dewar" forms, III to V. Structures I and II could be expected to "contribute" more to the hybrid than either III, IV or V, hence, the properties of benzene would be expected to resemble more closely to either I or II than to III, IV or V. Since I and II have same energy, each would contribute to the hybrid by the same amount. The symbol of resonance, double-headed arrow (⟷) does not indicate an equilibrium. The canonical structures I-V are hypothetical and do not have any physical existence. These structures differ in their electronic arrangement and switch due to shift of π electrons within the molecule.

Aromaticity

Perhaps you have been wondering whether other cyclic compounds with π electron might also be considered aromatic, some of these systems are indeed aromatic, but not all of them. What structural features are necessary for a molecule to be aromatic.

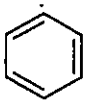
A German Physicist, Erich Hückel in 1931, proposed the Hückels rule. According to this rule, an aromatic molecule must be a cyclic conjugated species having $(4n + 2)$ π-electrons where n is an integer ($n = 0, 1, 2, 3$ .....). This means that only the ring with 2, 6, 10, 14, ... electrons may be aromatic but a ring with 4, 8 or 12 π electrons may not be aromatic. Hückel rule is also applicable to ionic species. Let us look at some of the evidence supporting the Hückel rule.

1) Cyclobutadiene

no. of π-electrons = 4

$4n + 2$ π-electrons are required for aromaticity. Cyclobutadiene has 4 π-electrons, hence cyclobutadiene is not aromatic as it has 4 π-electrons and is highly unstable.

2) Benzene



no. of π-electrons = 6

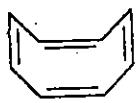
Here the $4n + 2\pi$ rule can be applied as it has 6 π-electrons which are required for a single ring system. It is an excellent example of an aromatic system.

3) Cyclooctatetraene

no. of π-electrons = 8

It does not have $4n + 2$ π-electrons and thus is not aromatic.

Another reason why cyclooctatetraene is not aromatic is that it is not even fully conjugated. It is a tub shaped molecule and the neighbouring orbitals containing the π-electron do not have the necessary geometry for proper overlap.

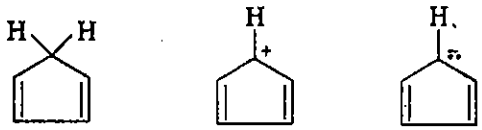


cyclooctatetrane

From the above example, it is clear that a flat planar geometry is required for proper overla resulting in delocalisation of π-electrons which is a necessary condition for aromaticity.

SAQ 1

Which of the following compound is aromatic?



9.6 REACTIONS OF AROMATIC COMPOUNDS

Characteristic reactions of benzene involve substitution, in which the resonance-stabilised ring system is preserved. Why is this so? You may answer by saying that this is due to the resonance stabilisation of the benzene. But then the question arises, why then benzene enters

into reactions at all, why is it not inert? This dual behaviour, the coexistence of stability and reactivity is due to the presence of the circulating π electrons in the benzene ring which, on one hand, keeps the carbon nuclei within bonding distance and, on the other, offers a site of attack to positively charged species. This explains the electrophilic reactivity of benzene.

Electrophilic substitution includes a wide variety of reactions, such as nitration, halogenation, sulphonation and the Friedel-Crafts reactions undergone by nearly all aromatic rings. Some important reactions are summarised in Table 9.1.

Table 9.1 Electrophilic aromatic substitution reactions

1) **Nitration**

$$ArH + HNO_3 \xrightarrow{H_2SO_4} ArNO_2 + H_2O$$

2) **Halogenation**

$$ArH + X_2 \xrightarrow{Fe} ArX + HX$$

3) **Suphonation**

$$ArH + SO_3 \xrightarrow{H_2SO_4} ArSO_3H + H_2O$$

4) **Friedel-Crafts alkylation**

$$ArH + RCl \xrightarrow{AlCl_3} ArR + HCl$$

5) **Friedel-Crafts acylation**

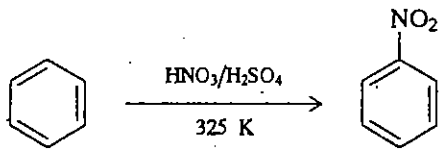
$$ArH + RCOCl \xrightarrow{AlCl_3} ArCOR + HCl$$

Note : Ar = C_6H_5

9.6.1 Nitration

Replacement of hydrogen by the nitro-group is known as **"Nitration"**.

Nitration of benzene can be carried out by the reaction of benzene with a mixture of concentrated nitric and sulphuric acids



benzene nitrobenzene

The electrophile in this reaction is the nitronium ion, NO_2^+. It is generated by the reaction of H_2SO_4 with HNO_3.

$$H_2SO_4 + HONO_2 \rightleftharpoons \overset{H}{\underset{+}{HO}}NO_2 + HSO_4$$

$$\overset{H}{\underset{+}{HO}}NO_2 \rightleftharpoons H_2O + \underset{\text{nitronium ion}}{NO_2^+}$$

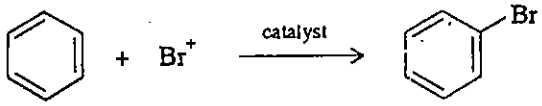
Further evidence for the participation of the nitronium ion comes from the fact that other species capable of producing nitronium ion, such as NO_2BF_4, NO_2NO_3 and NO_2ClO_4 also nitrate benzenoid compounds.

Nitration of benzene is an important reaction because the nitro group can be converted into other functional groups. We will discuss this in Unit 18 of Block IV.

9.6.2 Halogenation

Benzene reacts with halogens in the presence of a catalyst ($FeBr_3$, $FeCl_3$) to yield halogen substituted products, i.e., aryl halides.

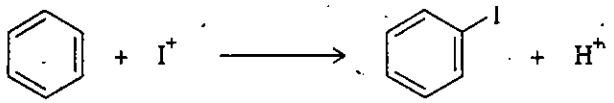
The main function of the catalyst is to partially or completely polarise the halogen-halogen bond, e.g.,



bromobenzene

A typical reaction of aromatic halogenation is the bromination of benzene. As a general rule, fluorine is too reactive and a poor yield of fluorobenzene is obtained. Chlorine reacts smoothly and gives an excellent yield of chlorobenzene. Iodine itself is unreactive; however, iodination of benzene is carried out in the presence of oxidising agent such as hydrogen peroxide, H_2O_2, or copper salt such as $CuCl_2$. This oxidising agent oxidises molecular iodine to an electrophile I^+

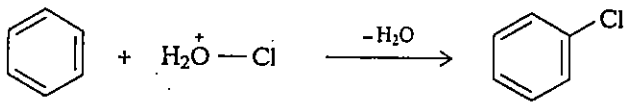
$$I_2 + 2\,Cu^{++} \longrightarrow 2\,I^+ + 2\,Cu^+$$



iodobenzene

Halogenation can also be affected by other reagents, such as hypochlorous or hypobromous acids in presence of strong acids.

$$H{-}O{-}Cl + H^+ \longrightarrow H_2O^+{-}Cl$$

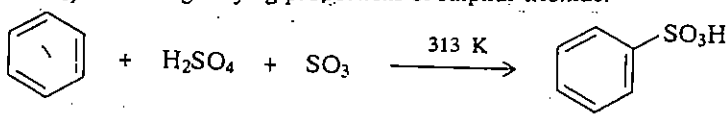


chlorobenzene

9.6.3 Sulphonation

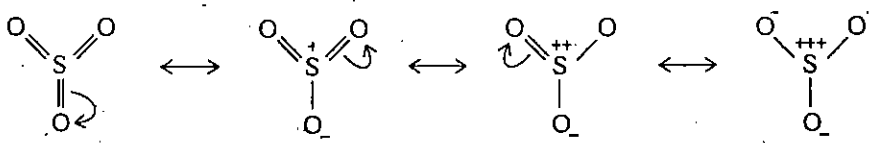
Aromatic compounds in which the sulphonic group ($-SO_3H$) is directly attached to the benzene ring are called aromatic sulphonic acids. Replacement of hydrogen from benzene by the sulphonic group is called sulphonation. It is another example of electrophilic substitution reaction. Sulphonation is usually accomplished using sulphuric acid or fuming sulphuric acid ($H_2SO_4 + SO_3$) containing varying proportions of sulphur trioxide.

$2H_2SO_4 \longrightarrow SO_3 + HSO_4^- + H_3O^+$



sulphonic acid

The reactive electrophile is neutral SO_3, as is evident from its structure given below:



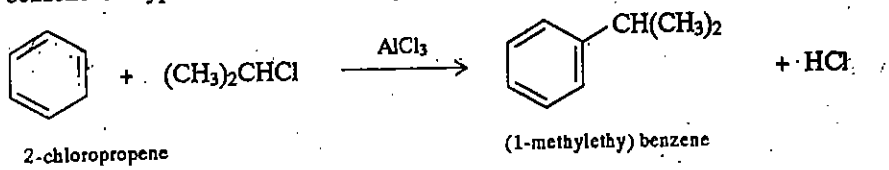
Unlike the other electrophilic substitution reaction of benzene, sulphonation is a highly reversible reaction and the direction depends on the reaction conditions. Sulphonation is favoured in the presence of concentrated or fuming sulphuric acid, desulphonation in hot, dilute aqueous acids.

9.6.4 Friedel-Crafts Alkylation

Complex substituted aromatic compounds are almost always synthesised from the simpler, readily available aromatic compounds. Since benzene is very common and easily available, chemists use it as starting material and introduce the desired substituents. You have already studied the substitution of halogen, nitrogen and sulphur-based functional groups to the aromatic ring. Now you will study another important reaction, i.e., alkylation of aromatic ring.

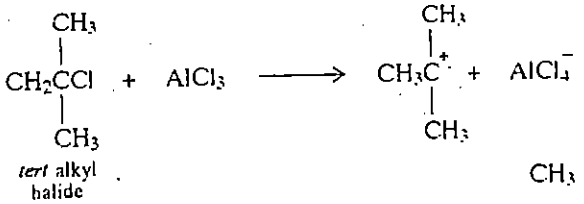
Alkylation of benzene is the substitution of a ring hydrogen by an alkyl group in the ring. Reaction of the aromatic compounds with alkyl halides in the presence of anhydrous $AlCl_3$, as the catalyst gives alkylated products. This reaction is known as Friedel-Crafts alkylation. The reaction of 2-chloropropane with benzene in the presence of $AlCl_3$ to yield (1-methyl ethyl) benzene is a typical Friedel-Crafts alkylation reaction.

Friedel, a French chemist, and Crafts an American chemist developed this reaction in 1877.

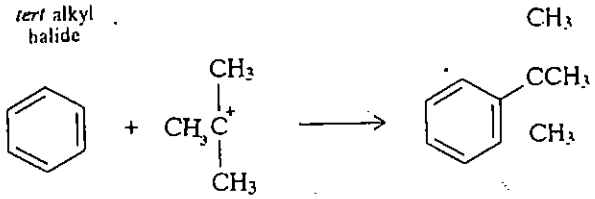


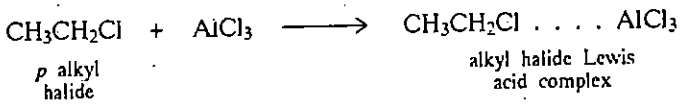
2-chloropropene (1-methylethy) benzene

The electrophile in the Friedel-Crafts reaction is R^+. This ion is formed when an alkyl halide reacts with a Lewis acid. Lewis acids such as $AlCl_3$, $FeCl_3$, $ZnCl_2$, $AlBr_3$, BF_3 etc. are used in Friedel-Crafts alkylation. In case of alkylation with tertiary alkyl halides, the electrophilic species is a free carbocation. However, in primary and secondary alkyl halides, it appears that instead of free carbocations, the electrophilic species is an alkyl halide-Lewis acid complex with positively polarised carbon.

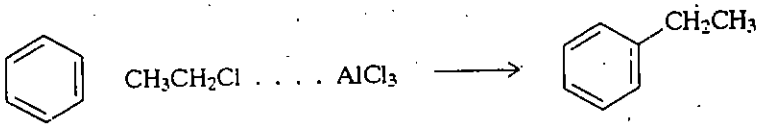


tert alkyl halide



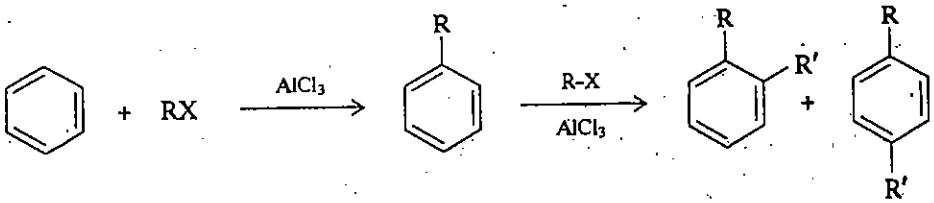


p alkyl halide — alkyl halide Lewis acid complex



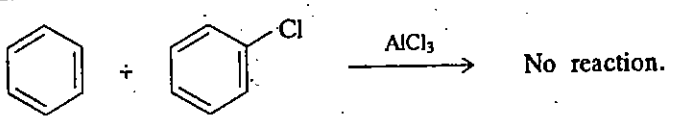
Though the Friedel-Crafts reaction is widely applicable in organic synthesis, it has some limitations as given below:

i) The main difficulty with the Friedel-Crafts alkylation is that the substitution of the first alkyl group activates the ring towards further substitution. We will discuss activation and deactivation in Sec. 9.7.2.

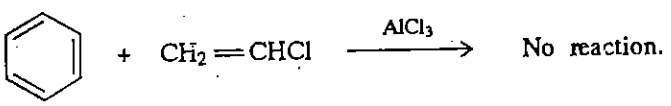


The best way of avoiding this second reaction is to use an excess of aromatic compound.

ii) Friedel-Crafts alkylations are limited to alkyl halides; aryl halides and alkenyl halides do not react. Aryl and alkenyl carbocations are too unstable to form under Friedel-Crafts reaction conditions.

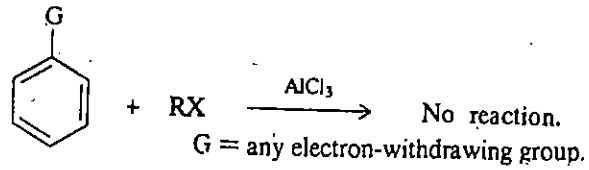


aryl halide



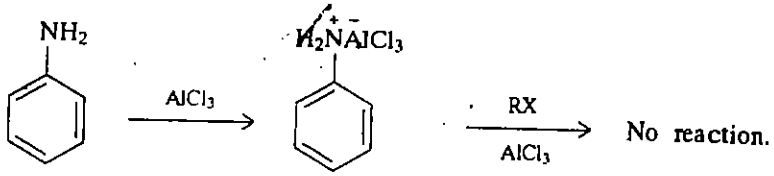
alkenyl halide

iii) If the aromatic compound has an electron withdrawing substituent, it does not undergo Friedel-Crafts alkylation; the deactivated ring is not reactive to attack carbocations.



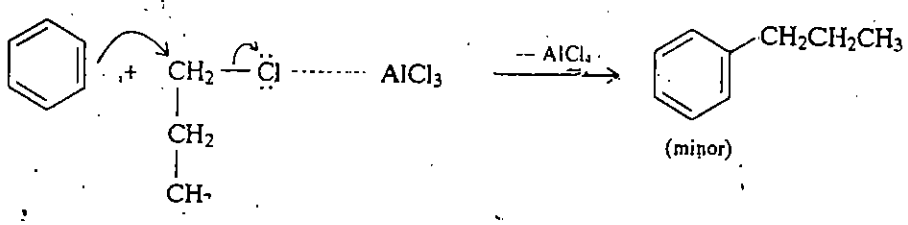
G = any electron-withdrawing group.

iv) Aromatic amines fail to undergo alkylation, probably because amino group forms a complex with Lewis acid. Since this complex has a positive charge on nitrogen, it deactivates the aromatic ring for electrophilic substitution.

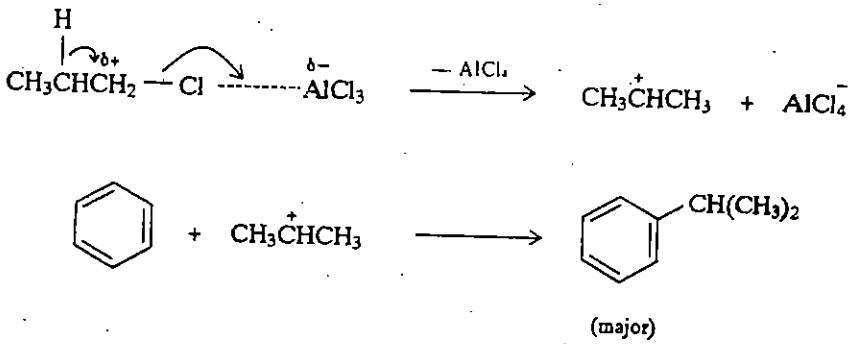


v) Sometimes during alkylation, the attacking electrophile undergoes rearrangement by 1, 2 shift of H or R. For example, the alkylation of benzene with chloropropane leads to a mixture of propylbenzene and (1-methylethyl) benzene.

No rearrangement



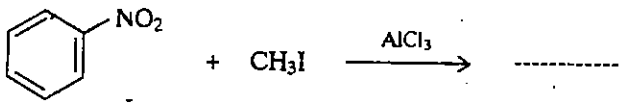
Rearrangement

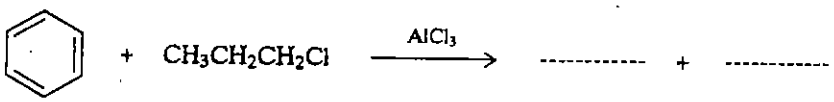


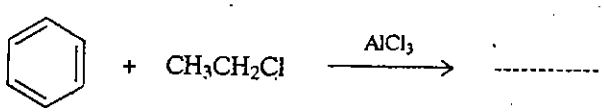
The mechanism is similar to alkylation with an alkyl halide and this reaction proceeds through the more stable carbocation intermediate.

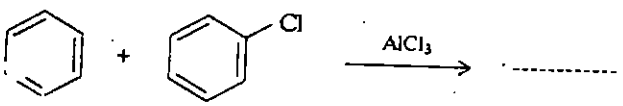
SAQ 2

Give the product(s) of the following reactions:

a) 

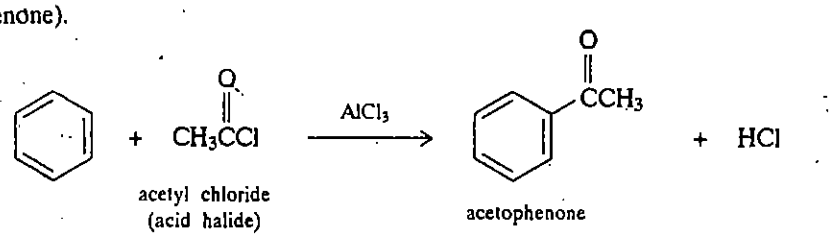
b) 

c) 

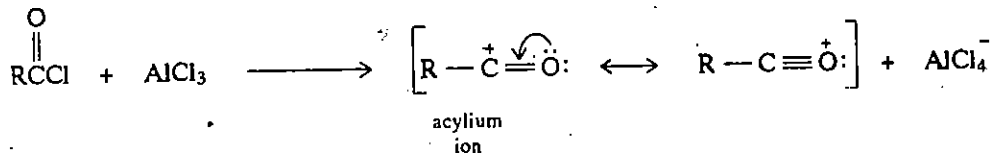
d) 

9.6.5 Friedel-Crafts Acylation

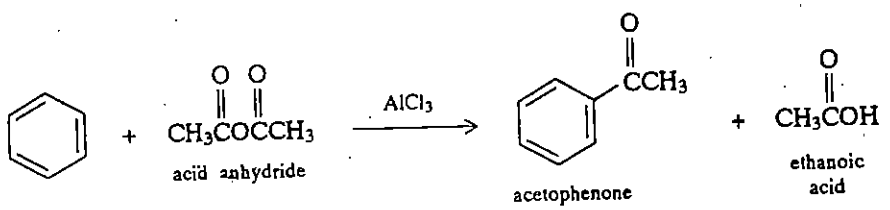
The $RC(=O)-$group or $ArC(=O)-$group is called an acyl group. Substitution of an acyl group into an aromatic ring by the reaction with an acid chlorides in the presence of Lewis acid as catalyst is called an aromatic acylation reaction or Friedel-Crafts acylation. For example, the reaction of benzene with ethanoylchloride (acetyl chloride) gives the ketone, phenylethanone (acetophenone).



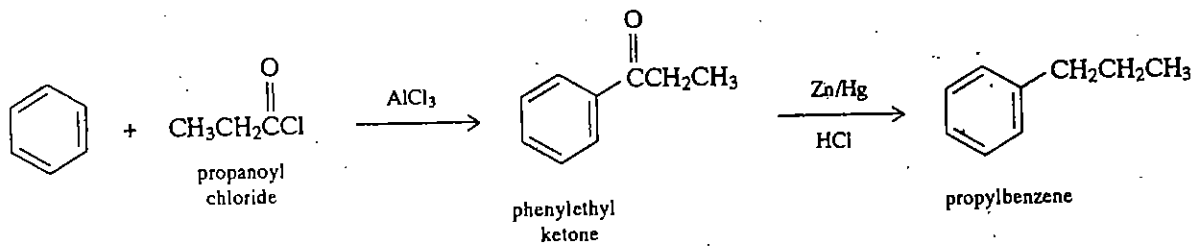
The mechanism of Friedel-Crafts acylation is similar to that of the other electrophilic aromatic substitution reactions The electrophile in this reaction is the resonance-stabilized carbocation, **acylium ion**. This ion is formed when the acid chloride reacts with the Lewis acid, $AlCl_3$.



Carboxylic acid anhydride can be used as alternative to acid chloride for the Friedel-Crafts acylation reaction.



Friedel-Crafts acylation reaction is a synthetically useful reaction. For example, the carbonyl group of the ketone produced by Friedel-Crafts acylation can be reduced to $> CH_2$ group by using zinc amalgam and hydrochloric acid. This method of reduction is known as Clemmensen reduction. By the combination of Friedel-Crafts acylation and Clemmensen reduction, an alkylbenzene may be prepared.

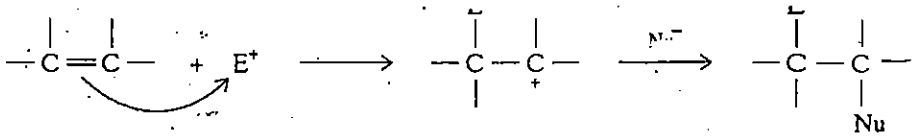


Unlike Friedel-Crafts alkylation, Friedel-Crafts acylation reactions are not accompanied by rearrangements within the acyl group. Moreover, there is no polysubstitution as the aromatic ring is deactivated after the introduction of the first acyl group.

9.6.6 Mechanism of Electrophilic Substitution

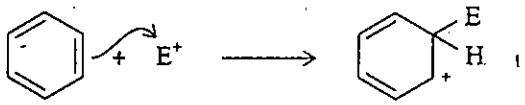
There are reasons to believe that the electrophilic substitution reactions take place by similar mechanism. It is necessary to understand the principles of this mechanism. Thus, we will discuss the general electrophilic substitution mechanism by using E^+ for electrophiles.

Before studying detailed mechanism, let us briefly recall what we have learnt about electrophilic addition to alkenes. Electrophilic attack on C=C gives carbocation intermediate which is then attacked by nucleophile to yield addition product.

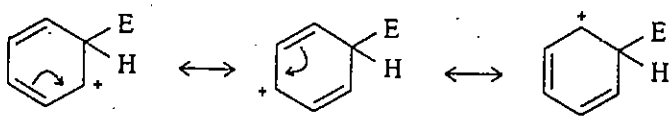


If a reaction takes place through a series of steps, the slowest step is called the rate-determining step (RDS).

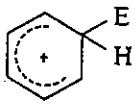
An electrophilic aromatic substitution reaction begins in a similar way. The π electrons of the ring attack on electrophile E^+, forming a σ bond with electrophile. In this process, the positive charge of the electrophile is to be transferred to the adjacent ring carbon atom which is called carbocation. This is a slow step and is, therefore, the rate determining step.



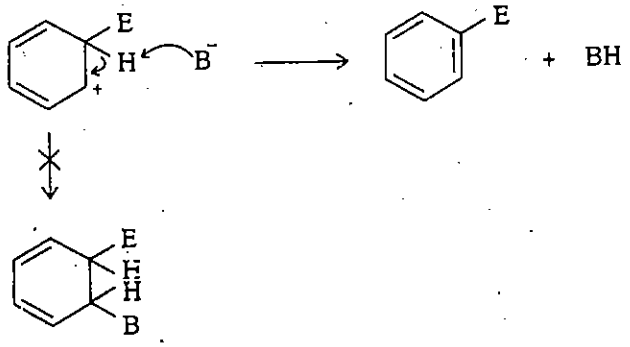
This carbocation is stabilized by resonance as shown below:



These three resonance structures of the intermediate are often combined and represented as follows:



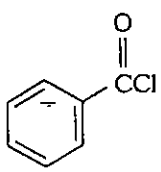
In the case of alkenes, you have seen that nucleophile attacks the carbocation to yield the addition product. Since, in the present case, the addition of the nucleophile would destroy the aromatic stabilisation of the benzene ring, this type of addition does not take place in aromatic carbocation. Instead, nucleophile acts as base and abstracts a ring proton yielding substituted aromatic product.



SAQ 3

Give the structure of the product expected from the reaction of each of the following compounds with benzene in the presence of $AlCl_3$.

a) $(CH_3)_2CHCCl$ (O)

b) 

c) $C_2H_5COCC_2H_5$ (O O)

SAQ 4

Write the mechanism of sulphonation of benzene using SO_3 as electrophile.

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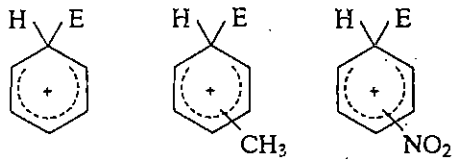
9.7 EFFECT OF SUBSTITUENTS ON REACTIVITY AND ORIENTATION

Benzene forms only one monosubstituted product by the electrophilic substitution. Let us see what happens when we carry out an electrophilic substitution on a substituted benzene. Studies have shown that the substituents affect the reactivity and the orientation of the benzene ring. Three possible disubstituted products, viz., *ortho, para* and *meta* can result. These three products are not formed at random; rather, a given substituent already attached to the benzene ring usually directs the position of the second substituent.

There are two types of substituents—one is electron-donating group, such as $-NR_2$, $-OH$, $-OR$, $-NHCOR$, and alkyl group, other is electron-withdrawing group which includes halogens $-\overset{O}{\overset{\|}{C}}H$, $-\overset{O}{\overset{\|}{C}}R$, $-\overset{O}{\overset{\|}{C}}OR$, $-CN$, $-\overset{+}{N}O_2$, $-NR_3$. Now we will study the effect of substituents on reactivity and orientation.

9.7.1 Effect of Substituents on Reactivity

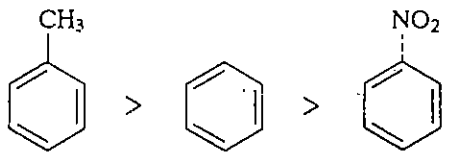
To compare the rates of electrophilic substitution in benzene, methyl substituted benzene (methyl benzene or toluene) and nitro substituted benzene (nitrobenzene) are compared in a reaction, say nitration. It is found that nitration of methyl benzene (toluene) is more facile than benzene whereas nitration of nitrobenzene is more difficult. In other words, benzene ring seems to be activated in toluene and deactivated in nitrobenzene. Let us see if we can explain this on the basis of intermediate carbocation formed.



I II III

In the case of methylbenzene (II), the methyl group, which is an electron-donating group, tends to neutralise the charge on the carbocation, this dispersal of the charge stabilises the carbocation thus leading to faster reaction than benzene.

In case of nitrobenzene (III), the NO_2 group which is an electron-withdrawing group, tends to intensify the positive charge and destabilise the carbocation. Due to this effect, the rate of the reaction is slower than in benzene. Reactivity in electrophilic aromatic substitution depends, then, upon the tendency of a substituent group to release or withdraw electrons. A group that releases electrons activates the ring; a group that withdraws electrons deactivates the ring. Hence, the order of reactivity of the above compounds towards electrophilic substitution reaction is:



SAQ 5

Which compound would you expect to undergo aromatic nitration more readily, $C_6H_5-CH_3$ or $C_6H_5-CCl_3$? And why ?

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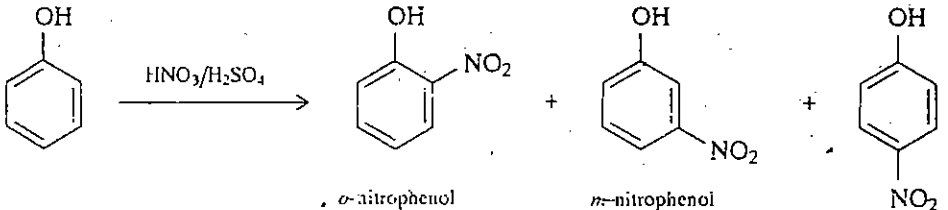
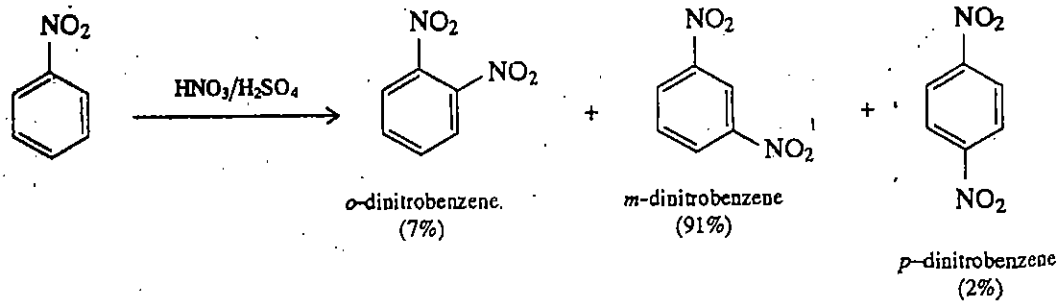
9.7.2 Effect of Substituents on Orientation

The second effect of a substituent is to direct the position of the incoming substituent. Thus, for instance, nitration of phenol gives *ortho* and *para*-nitrophenol as major products.



On the other hand, nitration of nitrobenzene yields *meta* dinitrobenzene as a major product, i.e.,



o-dinitrobenzene. (7%) + *m*-dinitrobenzene (91%) + *p*-dinitrobenzene (2%)

This shows that different substituents have different effect on substitution reaction. Thus substituents can be classified into three groups, i.e.,

- *ortho* and *para*-directing activator
- *meta*-directing deactivator
- *ortho* and *para*-directing deactivator

No meta directing activators are known.

Table 9.2 lists some of the groups in each category.

Table 9.2 : Classification of directing effects for some common substituents

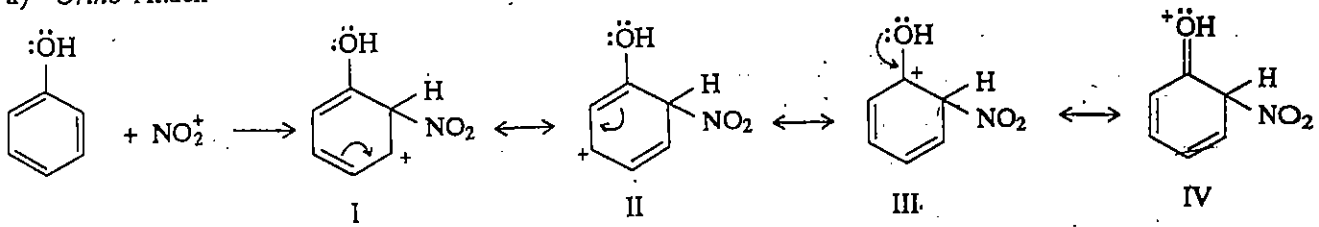
Ortho-and *para*-directing activators	*Ortho*- and *para*-directing deactivators	*Meta*-directing deactivators
$-NH_2$	$-I$	$-N^+(CH_3)_3$
$-OH$	$-Br$	$-NO_2$
$-OCH_3$	$-Cl$	$-CN$
$-NHCOCH_3$	$-F$	$-CCH_3$ (O)
 $-CH_3$		$-COCH_3$ (O)
		$-COH$ (O)
		$-CH$ (O)

Before we try to account for the orientation in electrophilic substitution, we should clarify our definitions of activating and deactivating. Activating groups activate all the positions of the ring. They are *ortho* and *para* directors because they activate *ortho* and *para* position much more than they do the *meta* position. Similarly, deactivating groups deactivates all position in the ring. They are *meta* directors because they deactivate the *ortho* and *para* position more than they deactivate the *meta* position. Thus, the effect of any group, whether activating or deactivating, is strongest at the *ortho* and *para* positions.

***Ortho* and *para*-directing activator :** To understand the orientation effect of the substituents, we have to first write all the possible resonance forms of the charged intermediates for each of the three possible reaction courses.

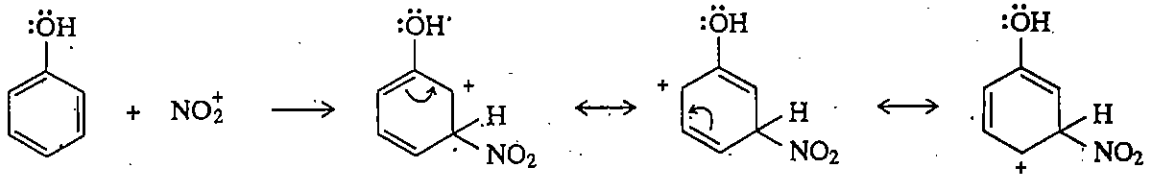
Reactions of NO_2^+ at the *para*, *meta* and *ortho* positions of phenol give the intermediates with the following resonance structures.

a) *Ortho*–Attack



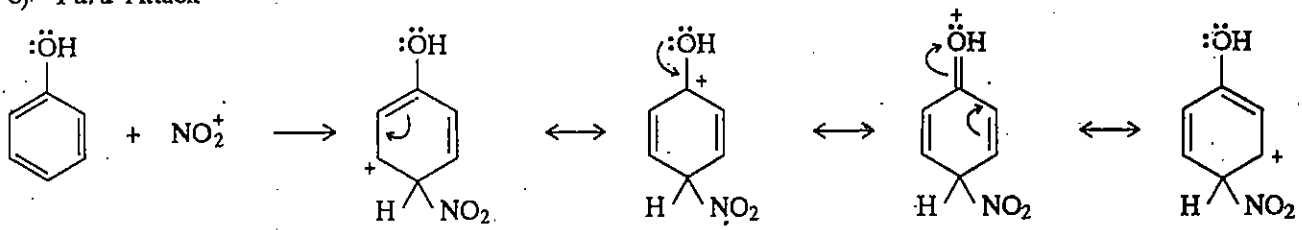
I II III IV

b) *Meta*–Attack



V VI VII

c) *Para*–Attack

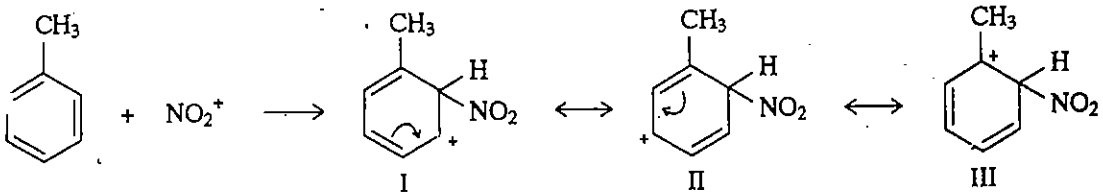


VIII IX X XI

In case of *ortho* and *para* attacks, structures IV and X respectively show that the unshared electron pair of oxygen delocalize the positive charge on the carbocation and, hence, four resonance structures are possible. In the case of *meta* attack, since the charge cannot be delocalised onto the $-\ddot{O}H$ group, the carbocation that is formed has only three resonance structures. Hence, carbocation formed by *ortho* and *para* attacks are more stable and, therefore, *ortho* and *para* nitrophenols are the major products.

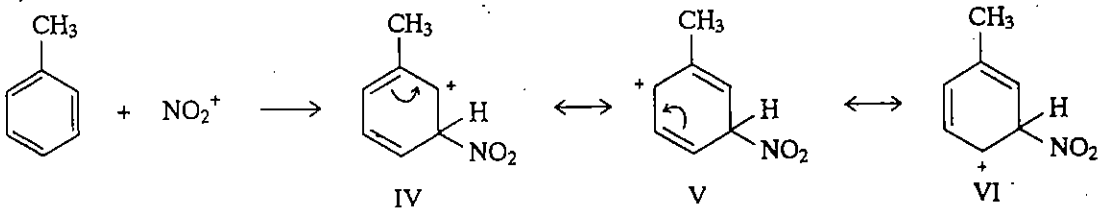
Now take the example of electrophilic aromatic substitution on alkyl substituted benzene ring. Let us inspect the possible resonance structures of carbocation formed by the attack of the electrophile, $N\dot{O}_2$, on toluene.

a) *Ortho*–Attack



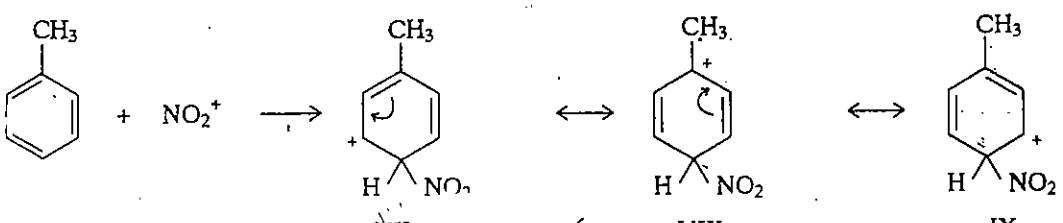
I II III

b) *Meta*–Attack



IV V VI

c) *Para*–Attack



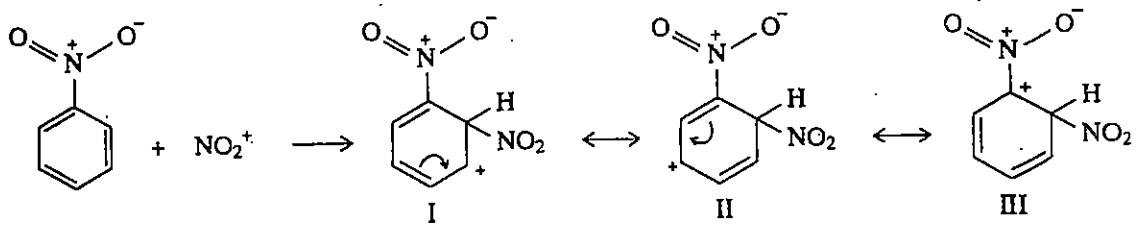
VII VIII IX

As indicated above, in structures III and VIII, resulting from *ortho* and *para* attack respectively, the positive charge is located on the carbon atom to which the methyl group is attached. Because that structure has tertiary carbocation character, it is more stable than the others, in which the positive charge is at a secondary carbocation. On the other hand, *meta* attack produces an intermediate in which none of the resonance structures benefits from such tertiary carbocation stabilisation. Thus, electrophilic attack on a carbon located *ortho* or *para* to methyl group leads to a cationic intermediate that is more stable than the one derived by attack at the *meta* carbon. Substitution at *ortho*-and *para*-position is, therefore, preferred to *meta*-substitution.

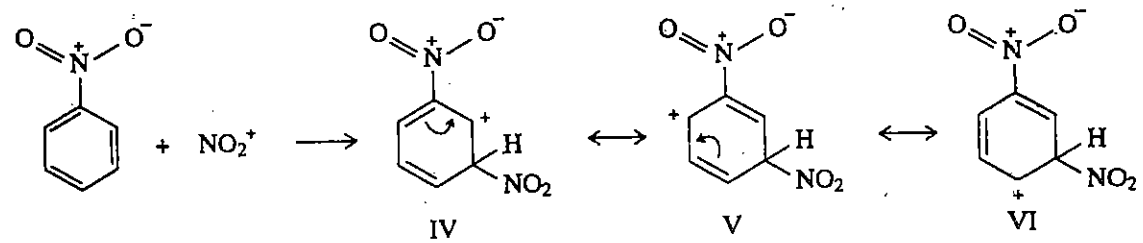
This can also be explained on the basis of inductive effect. The carbocation III and VIII formed by the *ortho*-and *para*-attack respectively, are stabilised by inductive effect of methyl group and, therefore, formed in major amount.

Meta-directing deactivators : We can apply similar arguments to *meta*-directing groups. These groups are all electronegative groups without an unshared electron pair on an atom adjacent to the benzene ring. In all these cases, the benzene ring would be deactivated. Let us take the example of nitration of nitrobenzene. The possible resonance structures of the carbocation formed are :

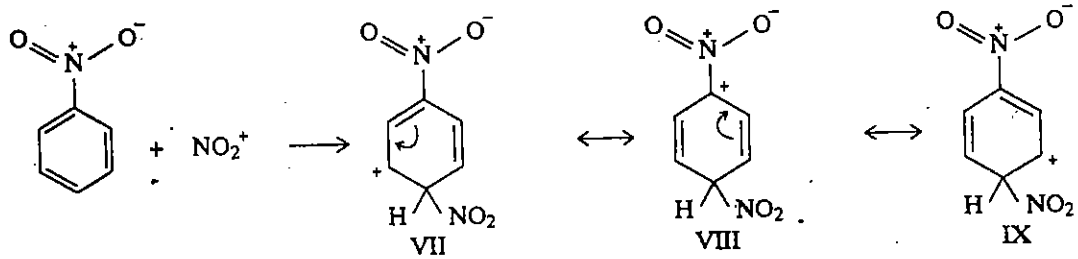
a) *Ortho*–Attack



b) *Meta*–Attack



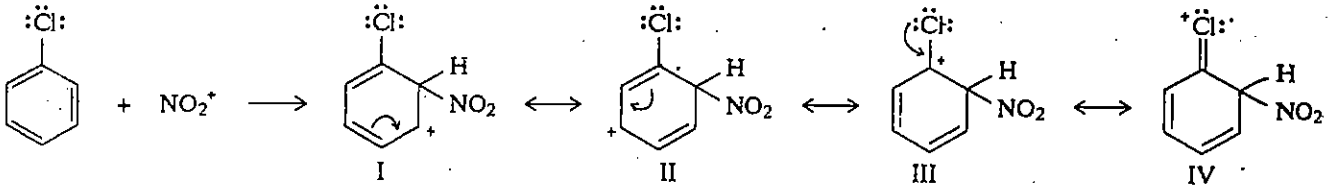
c) *Para*–Attack



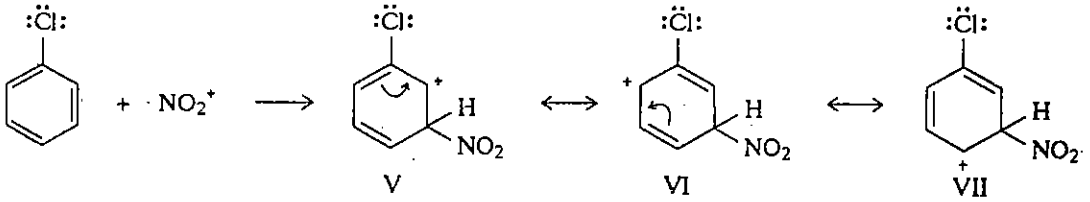
In all the three cases, carbocations formed have three resonance structures. But the structure III and VIII resulting from *ortho* and *para* respectively, are very unfavourable because the positive charge is placed directly on the carbon carrying the electron withdrawing group. A severe electrostatic repulsive interaction between the carbocation and the positive end of the $\overset{+}{N}O_2$ group strongly disfavours this carbocation. The carbocations formed by *meta* attack, have no such form with similar charges on adjacent atoms. Therefore, its transition state is the most stable, and attack at *meta*-position is preferred.

***Ortho* and *para* directing deactivator** : Halogens are unusual in their effect on electrophilic aromatic substitution. They are deactivating yet *ortho* and *para* directing. For understanding the orientation, consider the attack of electrophile at *ortho, meta* and *para* positions of chlorobenzene.

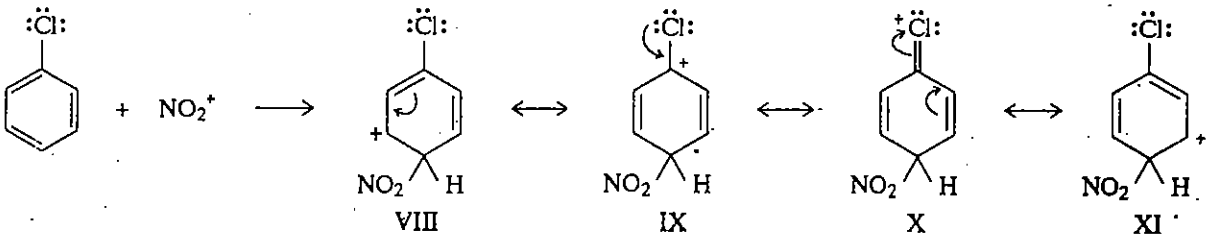
a) *Ortho*-Attack



b) *Meta*-Attack



c) *Para*-Attack



In structures III and IX, resulting from *ortho* and *para* attack, there is a positive charge on carbon bearing the halogen atom. Through its inductive effect, chlorine withdraws electrons, making this structure unstable. But there is another factor that one should not forget. It is known that halogen can share a lone pair of electrons and accommodate the positive charge, as shown in structures IV and X, for *ortho* and *para* attack, respectively. These structures are comparatively stable. No such structure is possible when the electrophile attack on *meta* position. Structures IV (in *ortho* attack) and X (in *para* attack) outweigh the instability rendered by structures III and IX. Therefore, attack at *ortho* and *para* position is prepared.

SAQ 6

Predict the major and minor products of the following:

a) Nitration of bromobenzene

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b) Nitration of nitrobenzene

.....

c) Bromination of nitrobenzene

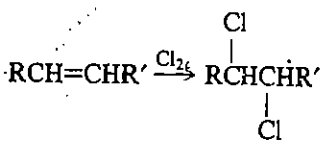
.....

d) Chlorination of phenol

.....

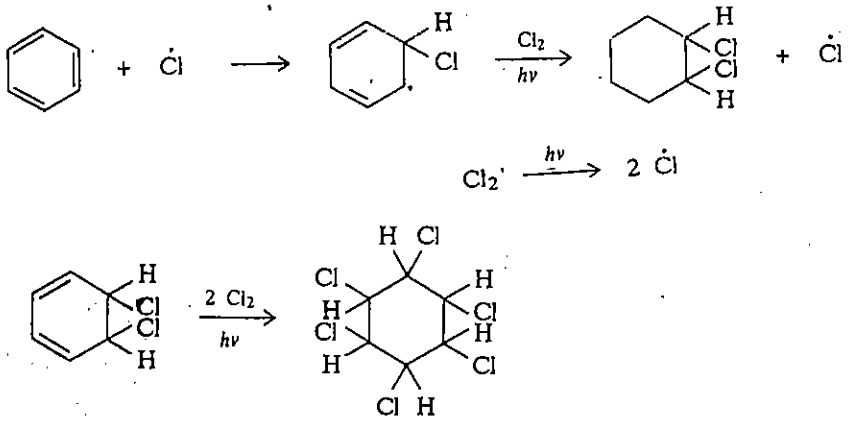
9.8 ADDITION REACTIONS OF BENZENE

You have already studied in Unit 7 that the chlorination of an alkene gives 1, 2-dichloroalkane.



In contrast to this, the addition of chlorine to benzene takes place with some difficulty and produces several isomers of 1, 2, 3, 4, 5, 6-hexachlorocyclohexanes. When treated with

chlorine or bromine in the presence of sunlight, benzene forms the hexahalides, $C_6H_6Cl_6$ and $C_6H_6Br_6$, respectively. The addition reaction proceed by the free radical mechanism.

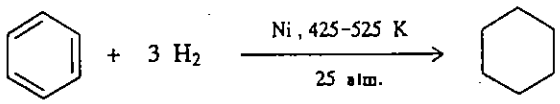


1,2,3,4,5,6-hexachlorocyclohexane

The 1, 2, 3, 4, 5, 6-hexachlorocyclohexane, theoretically can exist in eight stereoisomeric forms but only seven of these are known. One of the isomers, known as Gammexane, is a powerful insecticide. It is very stable and acts more quickly than D.D.T. All of the isomers have shown to exist in the chairform.

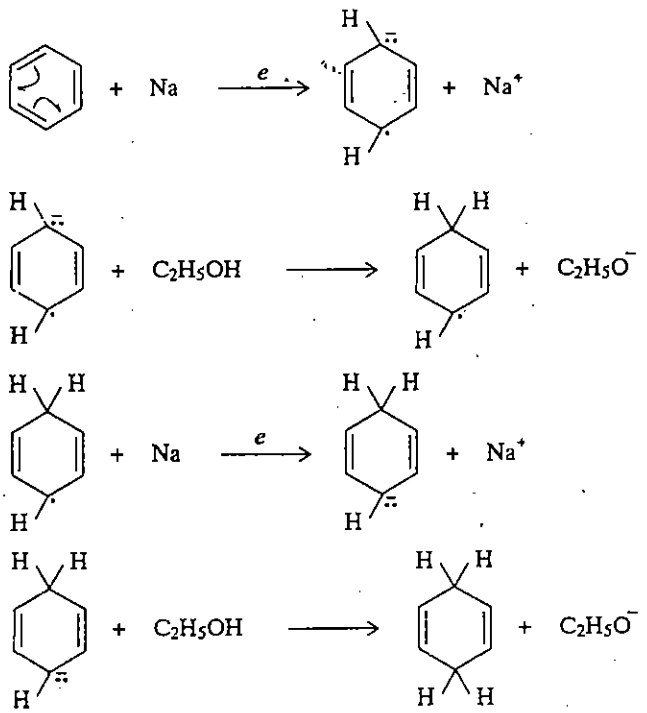
9.9 REDUCTION

Hydrogenation of benzene at higher temperature and under pressure yields cyclohexane.



benzene cyclohexane

Although benzene is not reduced by metal and acid, or by sodium in ethanol, it is reduced by sodium in liquid ammonia in the presence of ethanol (Birch reduction) to give 1, 4-dihydrobenzene (cyclohexa-1, 4-diene). This reaction has also been shown to have a fre radical mechanism.

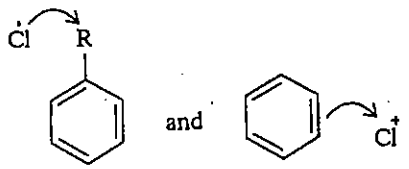


Lithium in anhydrous ethylamine, however, reduces benzene to cyclohexene and cyclohexane.

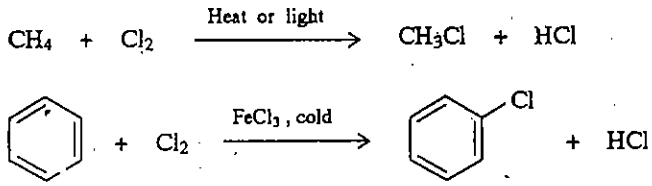
9.10 REACTIONS OF SIDE-CHAIN

9.10.1 Substitution in the Side-chain

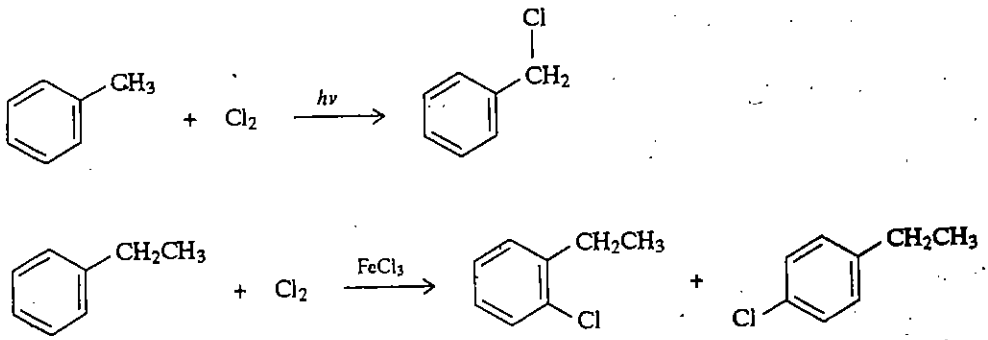
Alkylbenzene clearly offers two sites for attack by halogen: the ring and the side chain. One



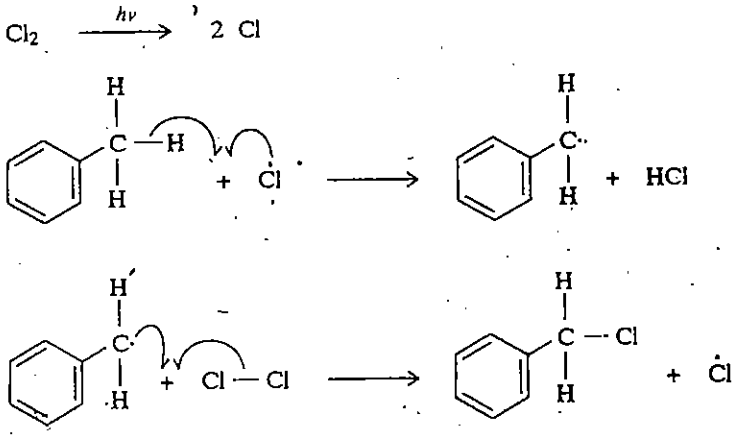
can control the position of attack by choosing the proper reaction conditions. Halogenation of alkanes requires condition under which halogen atoms are formed by homolyses of halogen molecules, that is, high temperature or light. Halogenation of benzene, on the other hand, involves transfer of positive halogen, which is promoted by Lewis acid catalyst like ferric chloride.



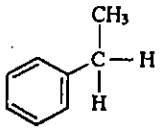
The position of attack in methylbenzene (toluene) would be decided by the nature of the attacking particle and by the condition employed. If the reaction is carried out in the presence of light, substitution occurs almost exclusively in the side chain. In the absence of light and in the presence of ferric chloride, substitution occurs mostly in the ring. For example:



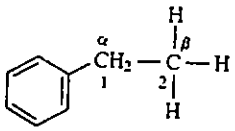
Chlorination of methylbenzene (toluene), in the presence of light, takes place via free radical chain mechanism as shown below:



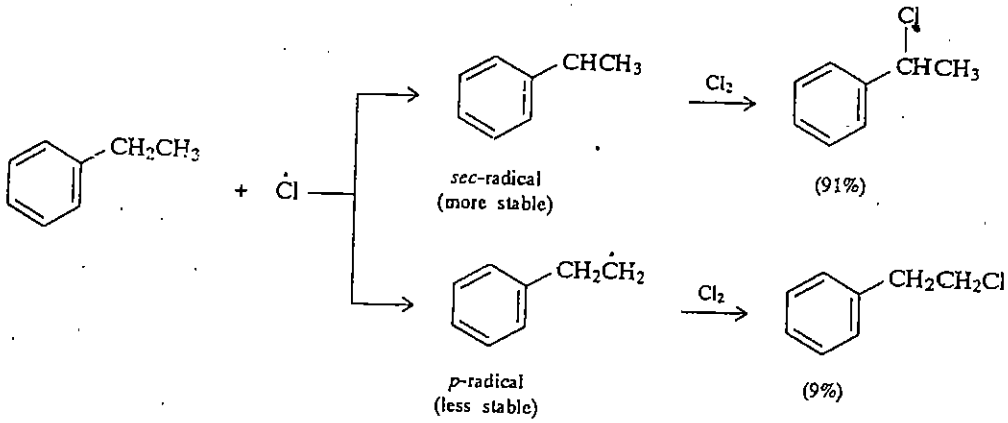
In alkyl benzenes with side chains larger than methyl, it is expected that the free radical substitution may take place on any of the side chain carbon atoms; so we must consider the likelihood of obtaining a mixture of isomers. For example, chlorination of ethylbenzene should give two isomeric products, 1-chloro-1-phenylethane and 2-chloro-1-phenylethane in equal amounts. But 1-chloro-1-phenylethane is the major (91%) product,



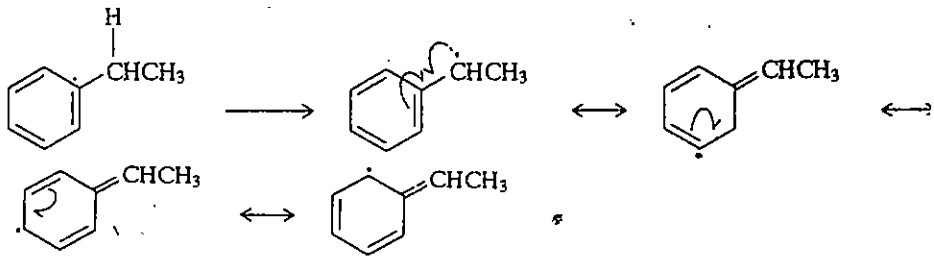
benzylic C — H bond



β-phenylethyl C — H bond



You can ask, why it is so. This is because the bond dissociation energy of benzylic C—H bond, $C_6H_5\overset{CH_3}{\overset{|}{C}}H—H$, (355 kJ mol^{-}) is less than β-phenyl ethyl C—H bond, $C_6H_5—CH_2CH_2—H$ (435 kJ mol^{-1}). That means, less energy is required for the homolylic fission of benzylic C—H bond. In other words, benzyl radical is more stable. The greater stability of benzyl radical is delocalisation of the odd electron over the ring as shown below :

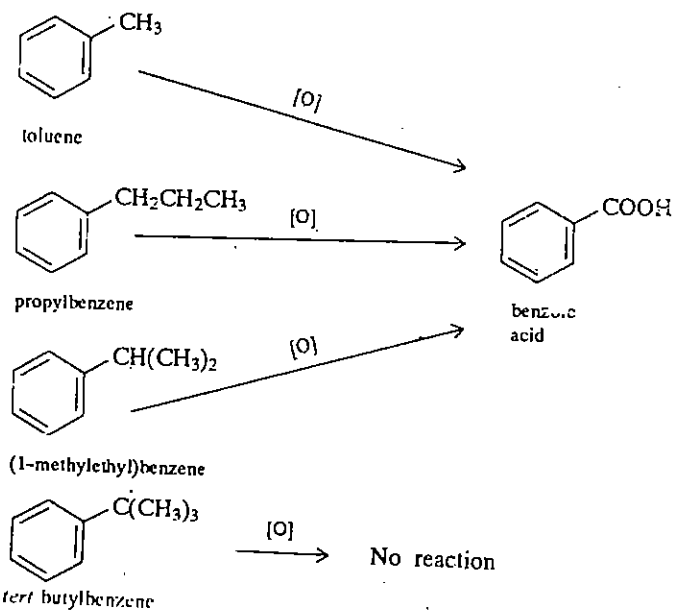


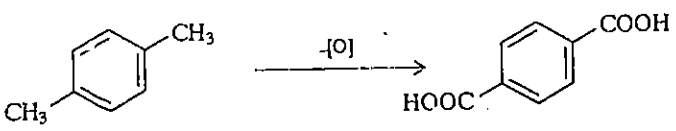
Since the benzylic radical formed is more stable, 1-chloro-1-phenylethane is the major product.

9.10.2 The Oxidation of Side-chain

Although benzene and alkanes are quite unreactive towards the usual oxidising agents ($KMnO_4$, $K_2Cr_2O_7$ etc.), the benzene ring renders an aliphatic side chain quite susceptible to oxidation. The side chain, irrespective of its length, is oxidised to a carboxyl group (-COOH). Tertiary alkyl substituted aromatic compounds do not follow this reaction. For example, toluene, propylbenzene, (1-methylethyl) benzene are oxidised to benzoic acid in higher yields. *p*-Methyltoluene on oxidation gives terephthalic (benzene-1, 4-dicarboxylic) acid but tertiary butylbenzene is not effected.

The number and the position of the carboxylic groups produced indicate the number and position of alkyl chain attached to the aromatic ring.





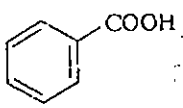
p-methyl toluene

This reaction is useful for two purposes:

- synthesis of carboxylic acids
- identification of alkylbenzenes

SAQ 7

Draw the structural formulas for the starting materials in the following reaction:

a) $C_8H_{10} \xrightarrow{KMnO_4, H_2O}$ 

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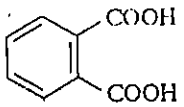
b) $C_8H_{10} \xrightarrow{KMnO_4, H_2O}$ 

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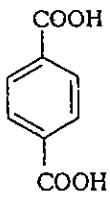
c) $C_8H_{10} \xrightarrow{KMnO_4, H_2O}$ 

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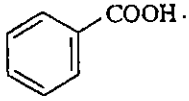
d) $C_9H_{10} \xrightarrow{KMnO_4, H_2O}$ 

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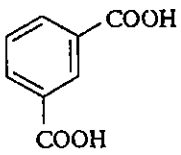
e) $C_9H_{10} \xrightarrow{KMnO_4, H_2O}$ 

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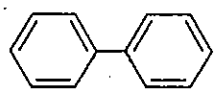
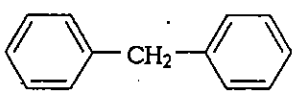
9.11 POLYNUCLEAR HYDROCARBONS

Polynuclear hydrocarbon is an assembly of more than one benzene ring in the molecule. Depending upon the mode of attachment of various rings, the polynuclear aromatic hydrocarbons may be classified into two broad classes: (i) isolated benzenoid hydrocarbon, and (ii) condensed or fused benzenoid hydrocarbons.

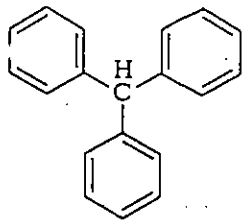
i) **Isolated benzenoid hydrocarbon:** In isolated systems, two or more rings are joined to each other either directly or through carbon chain. Some common examples are biphenyl, diphenylmethane and triphenylmethane.



biphenyl

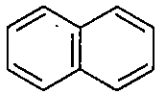


diphenylmethane

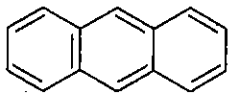


triphenylmethane

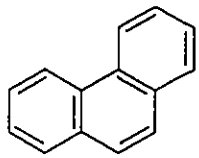
ii) **Condensed or fused benzenoid hydrocarbon:** The condensed or fused benzenoid hydrocarbons are those in which two or more benzene rings are fused together at the *ortho* position in such a way that each pair of rings shares two carbons. They include compounds like naphthalene, anthracene, phenanthrene etc.



naphthalene



antharacene



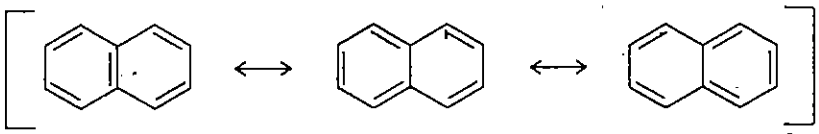
phenanthrene

The condensed polynuclear hydrocarbons is by far the larger and the more important group. A large number of them have been found to possess carcinogenic (cancer producing) activity. In this unit we will discuss the chemistry of naphthalene only.

9.11.1 Naphthalene

Naphthalene is the parent compound of polynuclear hydrocarbons. Naphthalene, m.p. 355 K, is a colourless volatile crystalline solid.

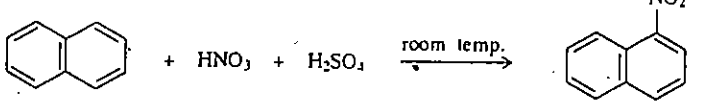
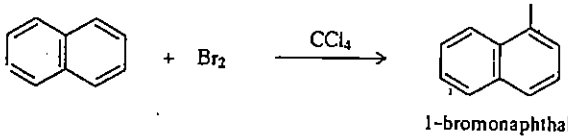
Naphthalene has three resonance hybrid structures. The bonds are not all of the same length, but are close to the benzene value of 139.7 pm.



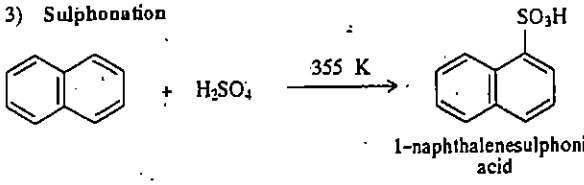
How can we explain the aromaticity of naphthalene? The above structure of naphthalene shows that it has 10 π electrons and 10 is the Huckel number which indicates that naphthalene should be an aromatic molecule.

Like benzene, naphthalene undergoes usual electrophilic substitution reactions. It also undergoes oxidation or reduction more readily than benzene. Some important reactions of naphthalene are given in Table 9.3.

Table 9.3 : Electrophilic substitution reactions of naphthalene

Reaction	Remarks
1) Nitration  1-nitronaphthalene	At higher temperatures, a mixture of 1, 5- and 1, 8-dinitronapthalene are formed
2) Halogenation  1-bromonaphthalene	1) 1-Chloronapthalene can form in presence of $FeCl_3$ 2) Only 1-substitution takes place

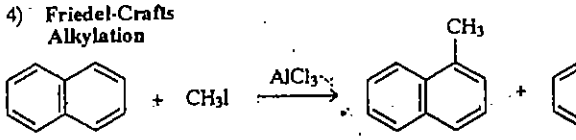
3) **Sulphonation**



1-naphthalenesulphonic acid

At 435 K, 2-naphalenesulphonic acid is the main product

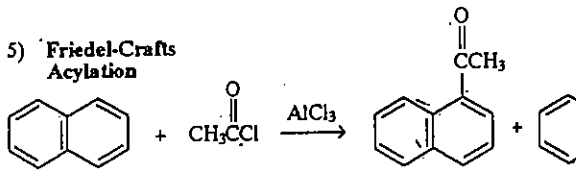
4) **Friedel-Crafts Alkylation**



1-methylnaphthalene 2-methylnaphthalene

The proportion of 1- and 2- substituted products depends on the size of the reagents

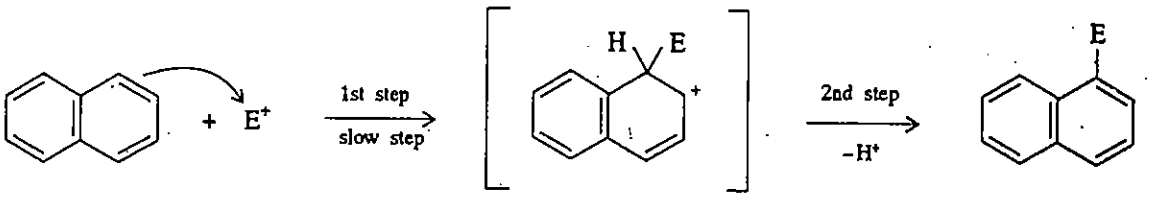
5) **Friedel-Crafts Acylation**



1-naphthyl methyl ketone 2-naphthyl methyl ketone

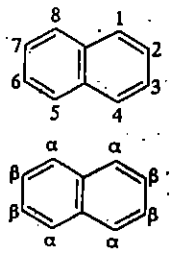
The proportion of 1- and 2- substituted products depends on the solvent used

Electrophilic substitution of naphthalene: Polynuclear hydrocarbons are more reactive towards electrophilic attack than benzene. Naphthalene undergoes a number of usual electrophilic substitution reactions, such as nitration, halogenation, sulphonation, Friedel-Crafts alkylation, Friedel-Crafts acylation, etc.



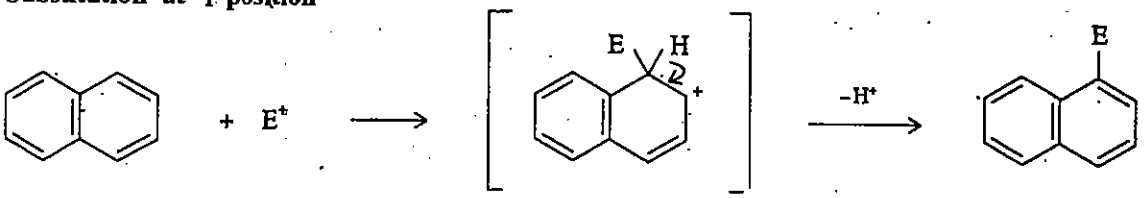
α-substituted product

The mechanism for napthalene substitution reaction is similar to that of benzene substitution.

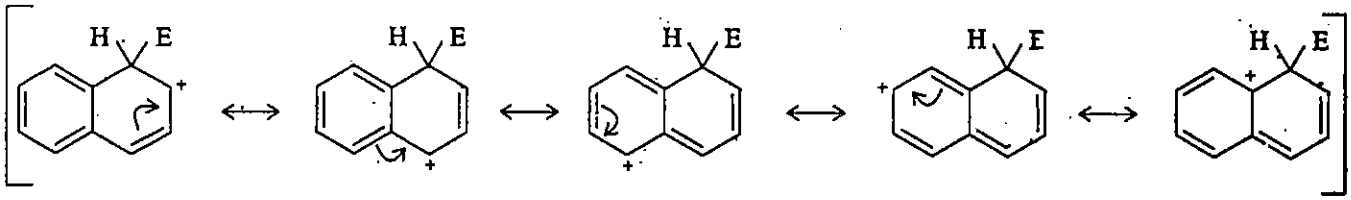


The first substituent goes to 1-position (α-position); that means, the 1-position is more reactive than the 2-position (β-position). You can ask why it is so. To understand this, let us examine the resonance structures of the two intermediate carbocations resulting from the respective attacks.

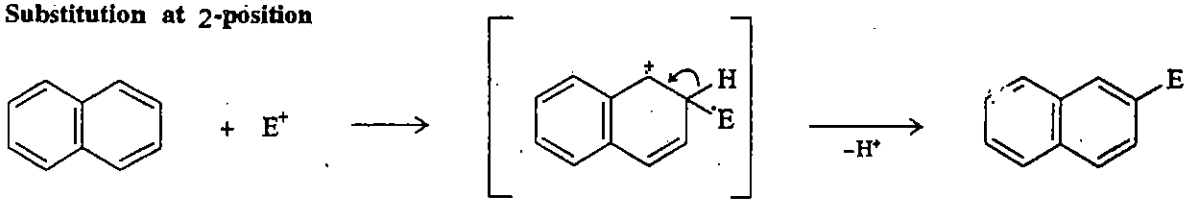
Substitution at 1-position



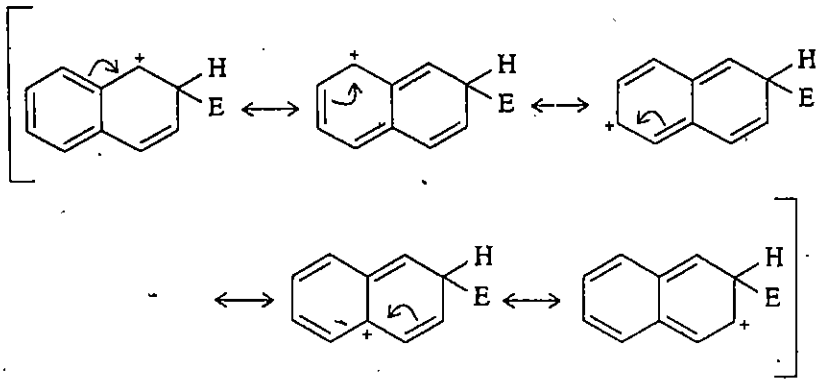
Resonance structure of carbocation



Substitution at 2-position

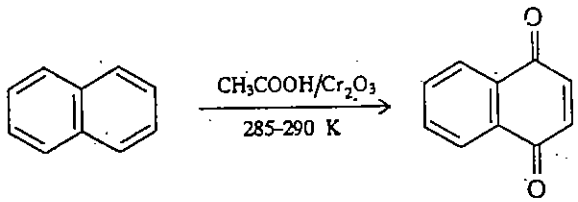


Resonance structure of carbocation



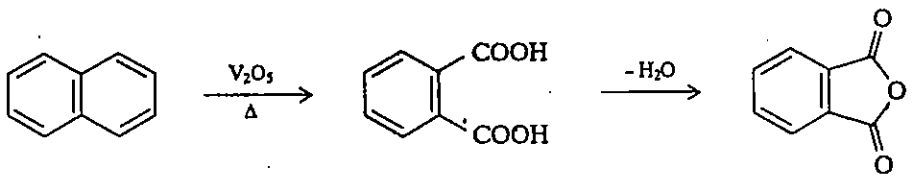
In both cases, the positive charge can be distributed to five different positions, but these carbocations are not equivalent in energy. In the first case, the first two structures have their benzene ring intact and are consequently more stable than the remaining three structures. In the second case, only one resonance structure has a benzenoid ring intact. The resulting resonance hybrid has higher energy in the second case than in the first case. The intermediate carbocation in the first case is more stabilised by resonance, and its transition state is of lower energy. For this reason the intermediate in the first case is formed faster and 1-position is more reactive.

Oxidation and reduction of nephthalene: Under controlled conditions, naphthalene is oxidised to 1, 4-naphthoquinone, but the yield is usually low.



1,4-naphthoquinone
(18-22%)

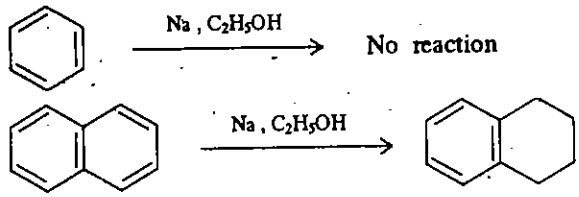
More vigorous oxidation results in the loss of one ring and yields phthalic anhydride. This reaction probably proceed through the formation of *ortho*-phthatic acid.



phthalic acid

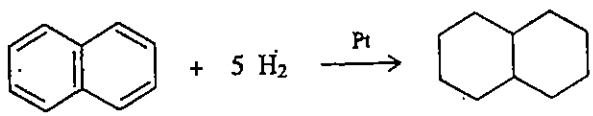
phthalic anhydride

Unlike benzene, naphthelene can be partially hydrogenated without heat and pressure, or which can be reduced with sodium and ethanol.



tetralin

For complete hydrogenation of napthelene, it requires heat and pressure just as in the case of benzene.



decalin

9.12 SUMMARY

- Coaltar is the chief source of aromatic hydrocarbons. Today, aromatic hydrocarbons are obtained by passing alkanes over platinum catalyst at 750-820 K. The process is called hydroforming or catalytic reforming.
- Unlike alkenes, benzene does not undergo electrophilic addition reactions, but it does undergo electrophilic substitution reactions, e.g., nitration, halogenation, sulphonation, Friedel-Crafts alkylation, Friedel-Crafts acylation, etc.
- In the presence of sunlight, benzene gives an additional product. For example, it gives benzenehexabromide and benzenehexachloride (gamaxene).
- Groups attached to the benzene ring affect the reactivity of the ring for further substitution and also determine the orientation of further substitution. Various substituents are classified into two groups. The electron-donating substituents, when attached to benzene, have *ortho* and *para* directing influence while electron-withdrawing substituents are *meta* directing.
- Alkylbenzenes offer two main areas for attack by halogen—the ring and the side chain. In the presence of light, halogen goes to side chain while, in the presence of acid catalyst, it goes to ring.
- In alkylbenzene, the entire side chain can be oxidised to carboxylic acid.
- Polynuclear hydrocarbons are made up of two or more benzene rings. There are two types of polynuclear hydrocarbons : isolated and condensed type.
- Polynuclear hydrocarbons undergo electrophilic substitution reaction. The 1-position of naphthalene is more reactive.
- Naphthalene also undergoes oxidation and reduction more readily than benzene.

9.13 TERMINAL QUESTIONS

1) Write equation to show how the following conversion takes place.
   a) Toluene to *m*-bromobenzonic acid
   b) Benzene to benzoic acid
   c) Benzene to *p*-nitrotoluene
   d) Benzene to *p*-nitroacetophenone

2) Write the chemical equation for the oxidation of the following compounds with hot $KMnO_4$.
   a) Butyl benzenes
   b) 1, 1-Dimethylethyl benzene
   c) 1, 3, 5-Trymethyl benzene

3) Rank the following compounds in the expected order of the reactivity towards Friedel-Crafts alkylation. Which of the following compound(s) are unreactive?
   a) Bromobenzene
   b) Toluene
   c) Phenol
   d) Aniline
   e) Nitrobenzene
   f) *p*-Bromotoluene

4) How do you convert benzene into the following compounds?
   a) Bromobenzene
   b) Benzenesulphonic acid
   c) Cyclohexane
   d) Ethylbenzene
   e) Hexachlorocyclohexane

5) Write the resonance structures of cation formed from $C_6H_5NH_2$ during :
   a) *ortho*-bromination
   b) *meta*-bromination
   c) *para*-bromination

6) Compound A, B and C are the three isomeric dibromobenzenes. Identify which is *ortho*, *para* and *meta* from the number of mononitration products.
   a) Compound A $\xrightarrow{HNO_3/H_2SO_4}$ two mononitration products

b) Compound B $\xrightarrow{HNO_3/H_2SO_4}$ three mononitration products

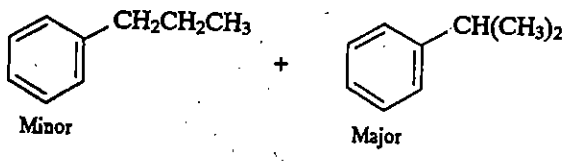
c) Compound C $\xrightarrow{HNO_3/H_2SO_4}$ one mononitration products

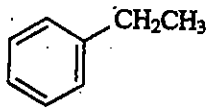
9.14 ANSWERS

Self Assessment Questions

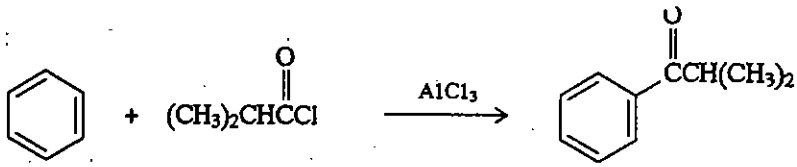
1) In compound a) one ring carbon in sp^3 hybridised and is not coplanar, hence it is not aromatic. Ion (b) contains sp^2 hybridised ring carbon atoms but does not follow Huckel's rule, hence it is not aromatic. Ion (c) is aromatic because it contains sp^2 hybridised ring atoms and follows Huckel's rule.

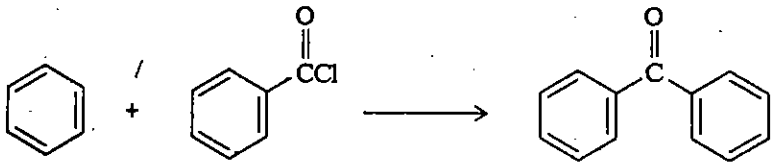
2) a) No reaction.

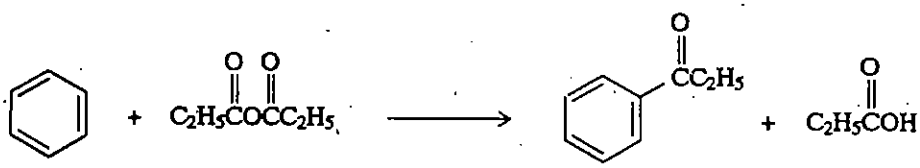
b) 

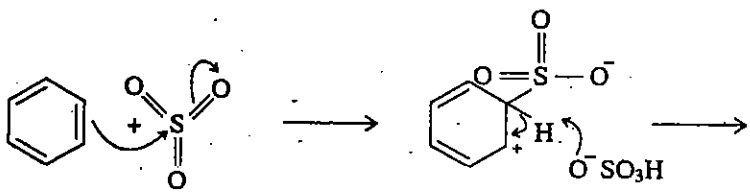
c) 

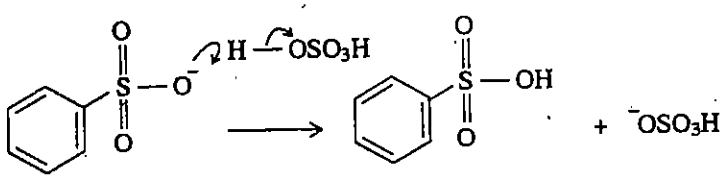
d) No reaction.

3) a) 

b) 

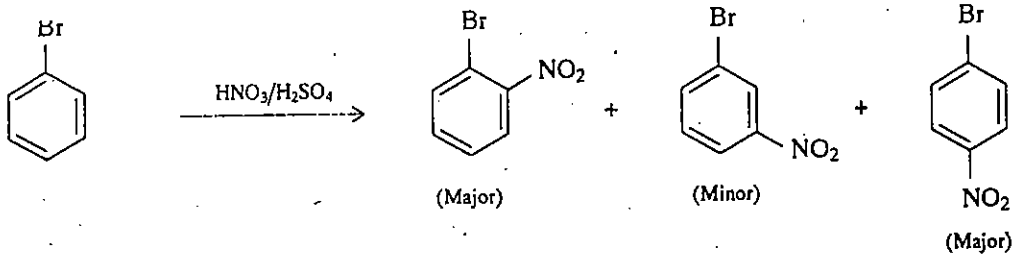
c) 

4) 

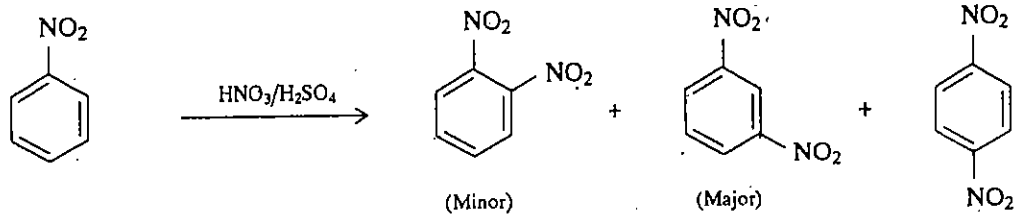


5) While the $-CH_3$ group is electron releasing and activates the ring, the CCl_3 group is strongly electron withdrawing because of the influence of the electronegative chlorine atoms and hence, deactivates the ring. Therefore, $C_6H_5CCl_3$ undergoes substitution more slowly.

6)

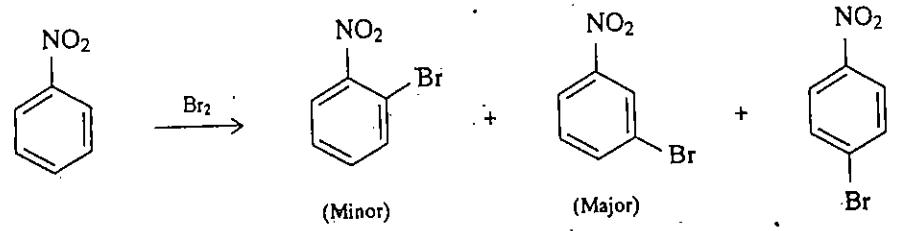


(Major) (Minor) (Major)



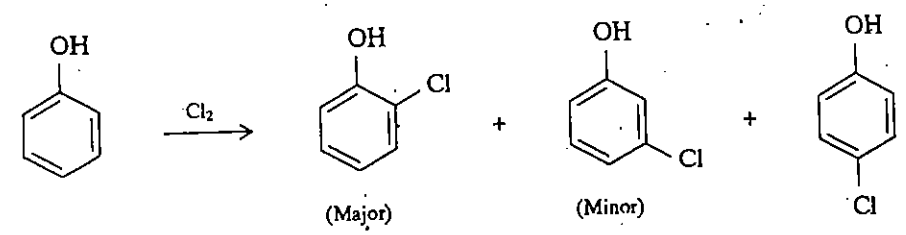
(Minor) (Major) (Minor)

c)



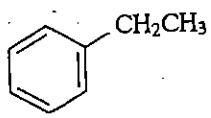
(Minor) (Major) (Minor)

d)



(Major) (Minor) (Major)

7) a)



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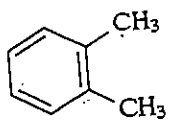

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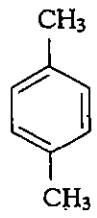

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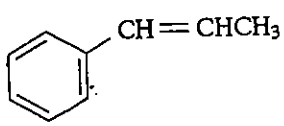

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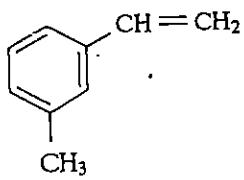
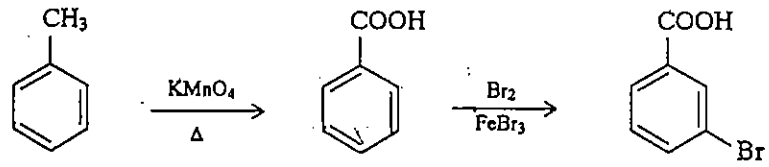


Terminal Questions

1) a)



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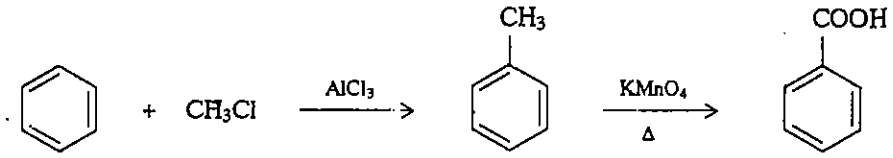

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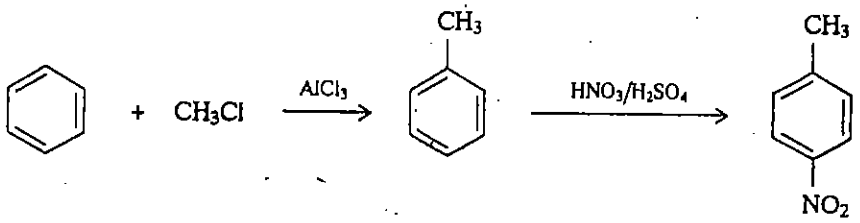

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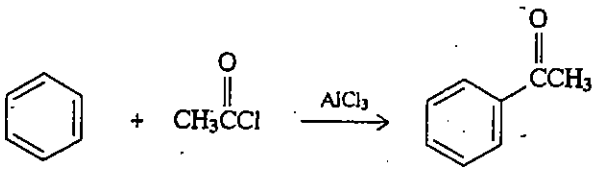

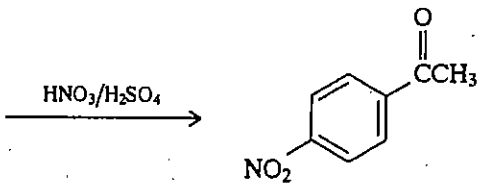

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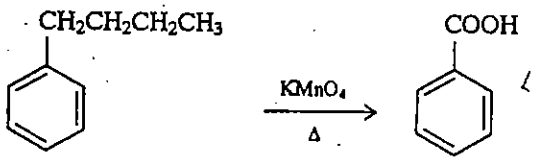

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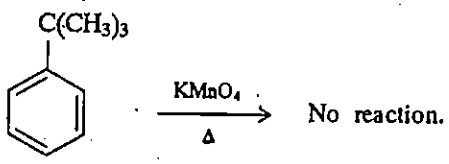
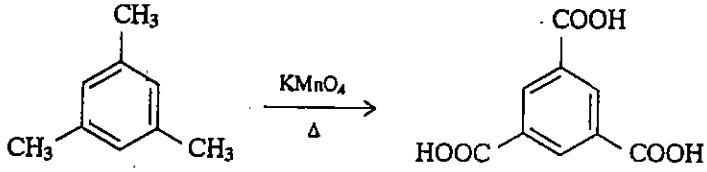


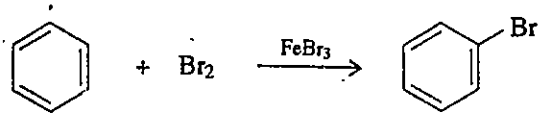
No reaction.

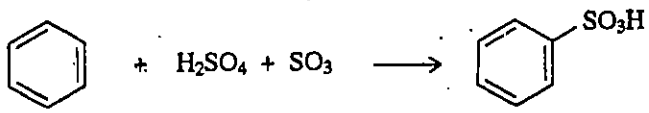
c)

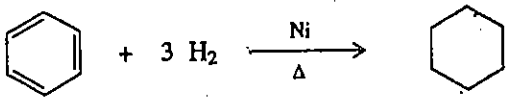


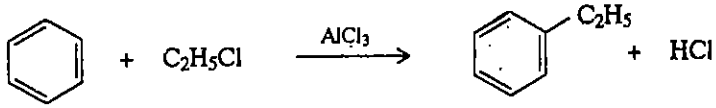
3) Order of reactivity of the given compounds towards Friedel-Crafts alkylation is : Phenol > Toluene > *p*-Bromotoluene > Bromobenzene. Nitrobenzene and Aniline are unreactive towards alkylation.

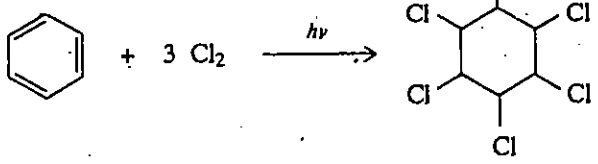
4) a)



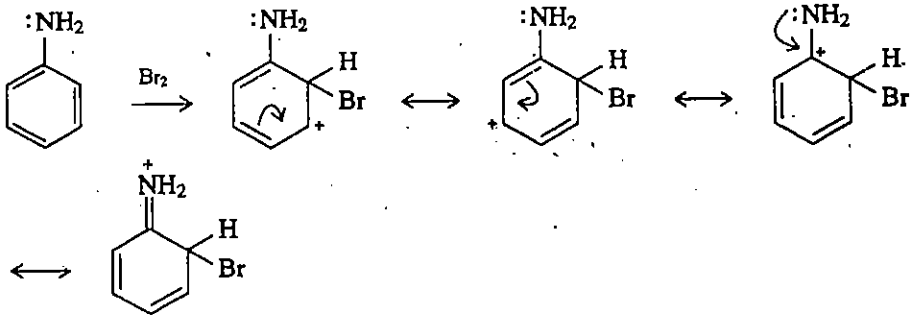
b) 

c) 

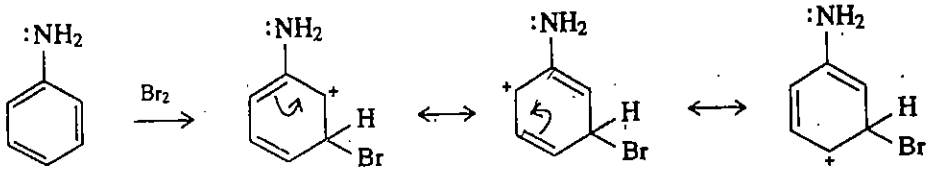
d) 

e) 

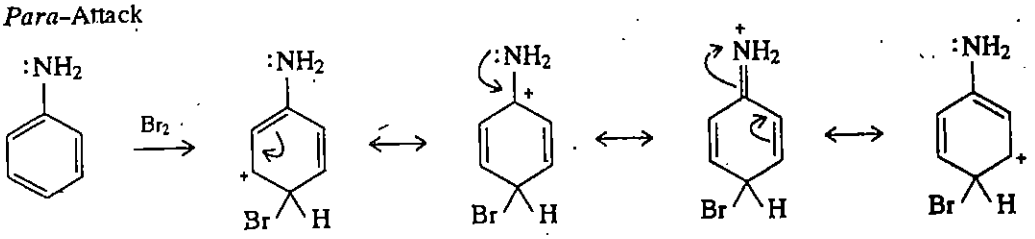
5) a) *Ortho*-Attack

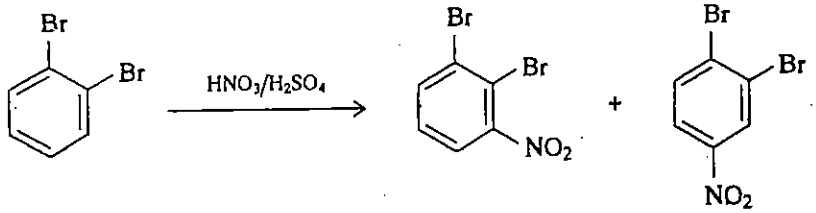


b) *Meta*-Attack

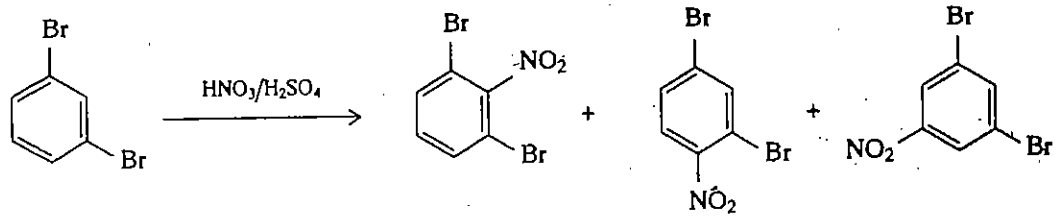


c) *Para*-Attack



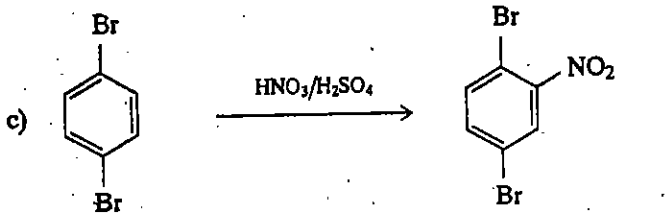
6) a) 

Only these two products are possible from *o*-dibromobenzene

b) 

Three products are possible from *m*-dibromobenzene

c)



Only one product is possible from *p*-dibromobenzene

On the basis of above reactions, we can say that :

Compound A is a *o*-dibromobenzene

Compound B is a *m*-dibromobenzene

Compound C is *p*-dibromobenzene.

UNIT 10 HETEROCYCLIC COMPOUNDS

Structure

10.1 Introduction
Objectives

10.2 Nomenclature

10.3 Five-Membered Heterocyclic Compounds
Source
Preparation
Basic Character of Pyrrole
Reactions of Five-Membered Heterocyclic Compounds

10.4 Six-Membered Heterocyclic Compounds : Pyridine
Source of Pyridine
Preparation of Pyridine
Basic Character of Pyridine
Reactions of Pyridine

10.5 Summary

10.6 Terminal Questions

10.7 Answers

10.1 INTRODUCTION

Our study of the cyclic systems upto this point was restricted to compounds in which the ring contains carbon atoms. Rings that contain, in addition to carbon, atoms of other elements in the ring are called heterocyclic. The hetero atoms that occur most frequently in heterocyclic rings are nitrogen, sulphur and oxygen. The rings in heterocyclic compounds may be saturated or unsaturated. Unsaturated heterocyclic systems may be aromatic or nonaromatic. Among aromatic heterocycles five and six-membered heterocyclic rings are most common.

In the biological world heterocyclic compounds are of wide occurrence and are often of critical physiological importance. Thus chlorophyll, the green pigment of leaves which catalyses photosynthesis is based on a heterocyclic framework. The same is true of haemin, which gives the red colour to our blood and functions as an oxygen carrier. Heterocyclic compounds form the sites of reaction in many enzymes and coenzymes. Heredity comes down, ultimately to the particular sequence of attachment of half a dozen heterocyclic rings to the long chains of nucleic acids.

The pyrrole ring is the basic unit of the porphyrin system which occurs, for example, in chlorophyll and in haemoglobin. From this unit, we can have some idea of the importance as well as the complexity of heterocyclic system.

Objectives

After studying this unit you should be able to :

- write down the name of some heterocyclic compounds,
- list the natural sources of furan, pyrrole, thiophene and pyridine,
- discuss the basic properties of heterocyclic compounds,
- list the different methods for the preparation of furan, pyrrole, thiophene and pyridene, and
- explain the chemical properties of these compounds.

10.2 NOMENCLATURE

In this section, we shall discuss some of the rules adopted by IUPAC for naming heterocyclic compounds. The size of the ring as well as the numbers, kind and position of the hetero atom

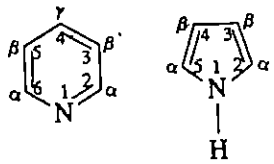
are specified by this system using a suitable prefix or suffix according to a set of rules given below:

i) The names of monocyclic compounds are derived by a prefix indicating the nature of the hetero-atom present, e.g. oxygen, oxa; sulphur, thia; nitrogen, aza. It may be noted that when the name contains two vowel a/e in a sequence then 'a' of the prefix is omitted.

ii) If the ring contains two or more identical hetero-atoms, the prefixes di, tri, etc. are used, e.g. dioxa, triaza. If the hetero atoms are different, oxygen takes precedence over sulphur and sulphur oyer nitrogen.

iii) The size of a five- and six-membered ring is indicated by the ending part, ole and ine, respectively.

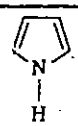
iv) In monocyclic compounds, containing only one hetero atom, numbering starts with the hetro atom and proceeds in such a way that substituent gets the lowest numbered position and the numbering proceeds counter clockwise around the ring. In common names, Greek letters may also be used to designate ring position. The carbon adiacent to the hetero atom is the α-carbon, the next atom is β-carbon and then γ-carbon For example



v) If the hetero atoms are different, then numbering starts at the atom cited first according to the rule in (ii) and proceeds round the ring in order of precedence.

Nomenclature of some five and six membered unsaturated heterocyclic compounds is summarised in Table 10.1.

Table 10.1 : Naming of the five- and six- membered heterocyclic compounds

Name of the Hetero atom	Ring Size	Beginning part of the name	Ending part of the name	Example.	
Nitrogen	5	aza	ole	aza + ole = azole,	
	6	aza	ine	aza + ine = azine,	
Oxygen	5	oxa	ole	oxa + ole = oxole,	
Sulphur	5	thia	ole	thia + ole = thiole,	

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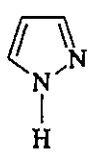
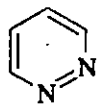
Give the IUPAC of the following compounds.

a)  , b)  , c)  d) 

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10.3 FIVE-MEMBERED HETEROCYCLIC COMPOUNDS

The three simplest five membered hetro cyclic compounds containing a hetero atom are furan (oxole), pyrrole (azole) and thiophene (thiole).

By looking at the structure of these compounds, you may say that they should have properties like those of conjugated dines. But these compounds do not show any such properties, rather these compounds are found to undergo electrophilic substitution reactions such as nitration, sulphonation, halogenation and the Friedel Crafts reaction with considerable ease. Thus, these compounds evidently have aromatic character. The heats of combustion of these compounds, are less than that of benzene 150.5 kJ mol^{-1}. The values are as follows: 66.8 kJ mol^{-1} for furan, 87.8 kJ mol^{-1} for pyrrole and 121.2 kJ mol^{-1} for thiophene.

In fact pyrrole, furan and thiophene are aromatic. These heterocycles are also planer pentagons consisting pf sp^2 hybridised carbon atoms (Fig. 10.1). Of the six π electrons required as per Huckel rule for aromaticity the double bonds account for four and the lone pair on the heteroatom for the remaining two.

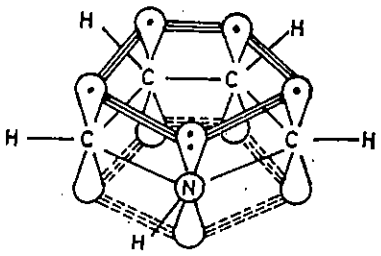


Fig. 10.1 : Orbital picture of Five-membered heterocycles.
X = N, O or S

10.3.1 Source

Pyrrole occurs in coal-tar and bone oil. It may be isolated from bone oil by washing the bone oil with dilute alkali to remove acidic substances, then with acid to remove strongly basic substances and finally by fractionating. Furan is extracted from coal tar and wood, especially pine-wood.

Bone Oil :
Product obtained by the destructive distillation of bones. It is a dark oily evil-smelling liquid.

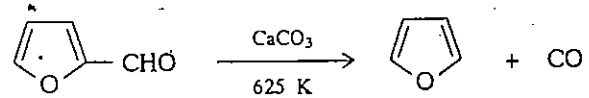
Thiophene occurs in coal tar and shale oil. Its boiling point (355 K) is close to that of benzene and hence it is difficult to separate from the benzene fraction, obtained from coal tar. Thiophene can be sulphonated more readily than benzene, and this property is used to separate the two compounds by repeatedly shaking benzene (from coal-tar) with cold concentrated sulphuric acid, so that water-soluble thiophenesulphonic acid is formed. When thiophenesulphonic acid is boiled with dilute hydrochloric acid or heated with steam. The $-SO_3H$ group is replaced by hydrogen to give thiophene.

Shale Oil :
Petroleum extracted from a kind of rock, known as shale. This rock is rich in hydrocarbons. Shale is subjected to destructive distillation where by the oil is reseased.

10.3.2 Preparation

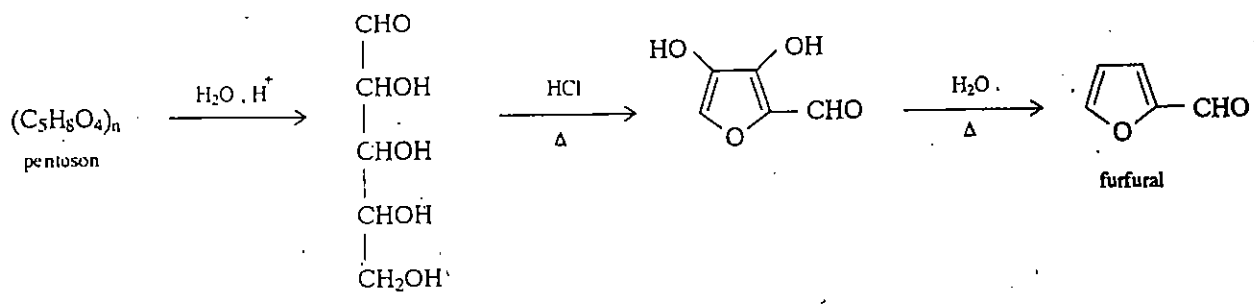
As mentioned above, although pyrrole, furan and thiophene can be obtained from natural sources, the quantities are too small to fulfill our demands. The following method for large scale preparation of these compounds are, therefore, important.

i) Furan is synthesised readily by decarbonylation (elimination of the CO group) of furfural.

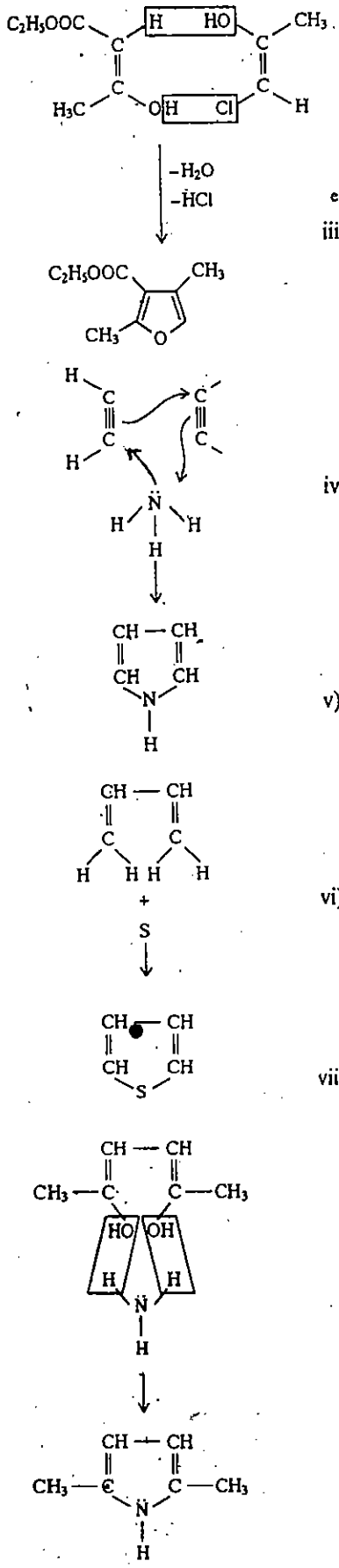


furfural furan

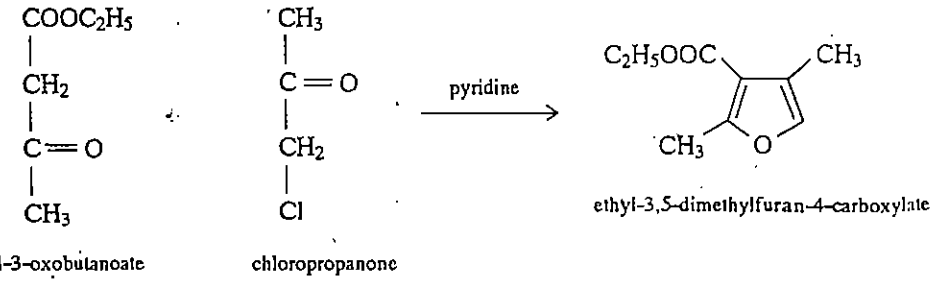
Furfural production is an interesting example of the use of industrial waste products. The hulls of rice and oats contain polymeric carbohydrates known as pentosans. Pentoses obtained from the polymeric material undergo subsequent dehydration and cyclisation to yield furfural.



You can see that in many of the synthesis procedures, it is probable that ketonic compounds react through enol form, e.g.

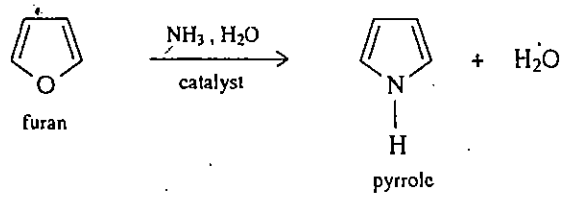


ii) An important method for laboratory preparation of substituted furans is the Fiest Benary synthesis in which a β-keto easter and an α haloketone are reacted in presence of pyridine. For example, the enol form of ethyl 3-oxobutanoate (ethyl acetoacetate) and chloropropanone (chloroacetone) react as shown below to give ethyl 3, 5-dimethylfuran-4-carboxylate.



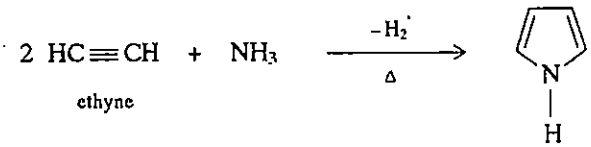
ethyl-3-oxobutanoate — chloropropanone — ethyl-3,5-dimethylfuran-4-carboxylate

iii) Pyrrole is commercially produced from furan, ammonia and steam using alumina as catalyst at 675 K.



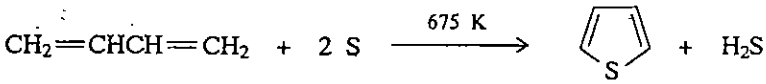
furan — pyrrole

iv) Pyrrole is also produced when a mixture of ethyne and ammonia is passed through a red hot tube.



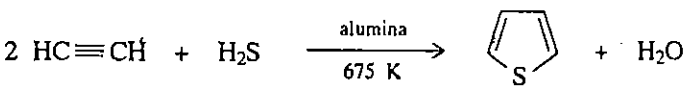
ethyne — pyrrole

v) Thiophene is produced from C_4 hydrocarbons such as butane, butene or butadiene. Butadiene, formed initially through dehydrogenation of butane or butene by sulphur at 875 K is the probable precursor of thiophene.



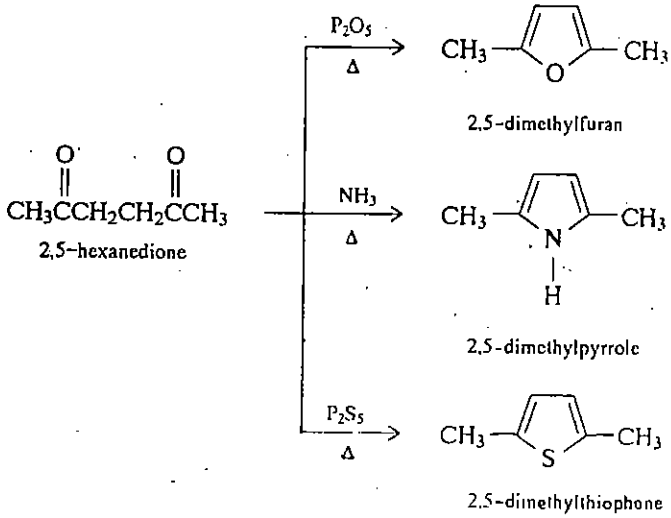
1,3-butadiene — thiophene

vi) Thiophene is also produced commercially by passing a mixture of ethyne and H_2S over heated alumina,



ethyne — thiophene

vii) 1, 4-dicarbonyl compounds are useful starting materials for the synthesis of these heterocycles. If the dicarbonyl compound is heated with a dihydrating agent, e.g., P_2O_5, $ZnCl_2$ a furan is formed. If heated with a source of nitrogen or sulphur, pyrrole or thiophene are formed. These reactions are also known as Paal-Knorr methods.



2,5-hexanedione — 2,5-dimethylfuran — 2,5-dimethylpyrrole — 2,5-dimethylthiophone

10.3.3 Basic Character of Pyrrole

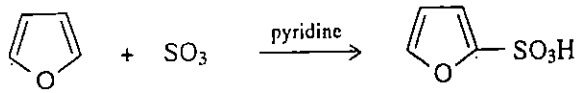
A lone pair of electrons on nitrogen is responsible for the basicity of nitrogen compounds. Pyrrole also has a lone pair of electrons on nitrogen and it, therefore, also acts as a base but it is a very weak base (K_b 2.5×10^{-14}). The reason for the weak basic character is that a lone pair of electrons on nitrogen is involved in the formation of the delocalised molecular orbital and is not available for the formation of a new bond with hydrogen. Furthermore, if a hydrogen is added to the nitrogen atom (through reaction with an acid), the resulting structure ceases to be aromatic. This makes the pyrrole cation extremely unstable. This is responsible for the absence of any significant basicity in pyrrole.

10.3.4 Reactions of Five-Membered Heterocyclic Compounds

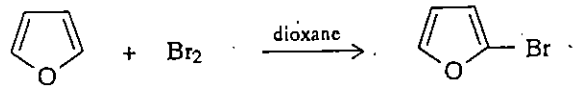
Five membered heterocyclic compounds undergo electrophilic substitution reduction, Diels-Alder and ring expansion reactions.

i) **Electrophilic Substitution Reaction**

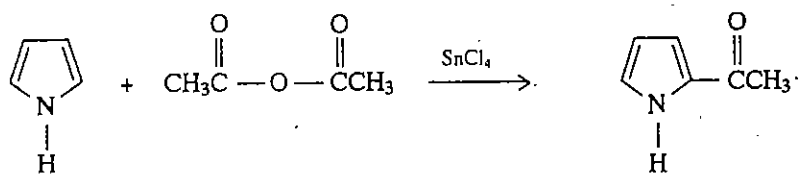
Like other aromatic compounds pyrrole, furan and thiophene commonly undergo electrophilic substitution reactions such as nitration, sulphonation, halogenation, Friedel Crafts acylation, e.g.,



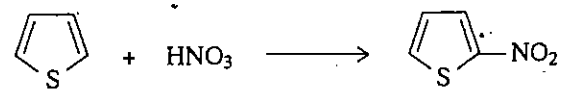
2-furansulphonic acid



2-bromofuran



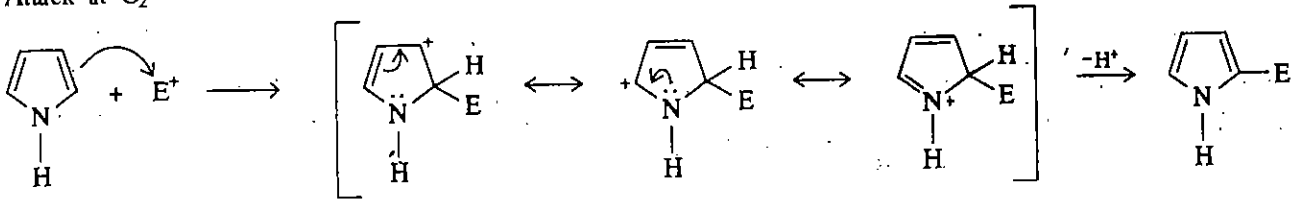
2-acetylpyrrole



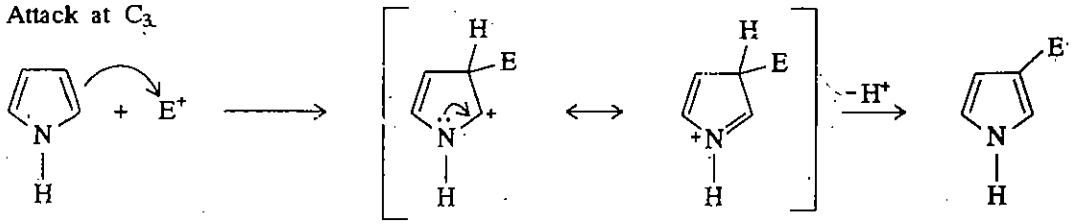
2-nitrothiophene

The attack of the electrophile in these heterocycles usually occurs at the C-2 (or β) position i.e., next to the hetero atom. In Unit 9 you have studied that you could account for orientation on the following basis : the controlling step is the attachment of electrophilic reagent to the aromatic ring, which takes place in such a way as to yield the most stable carbocation intermediate. Let us apply this approach to the reactions of pyrrole. Attack at position 2 of pyrrole yields a carbocation that is a hybrid of three structures, i.e., I, II and III whereas attack at position 3 yields carbocation which is a hybrid of only two structures, i.e., IV and V. The extra stabilisation of carbocation provided by structure III, in case of attack at position 2 makes positive charge at this position more stable. Thus, the attack at position 2 is favoured. Orientation of substitution in furan and thiophene can be accounted for in the same way.

Attack at C_2

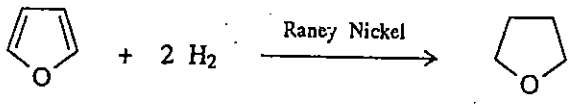


Attack at C_3



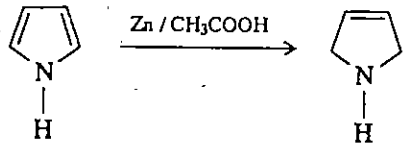
ii) Reduction

Tetrahydrofuran (THF) which is an industrially important solvent, results on catalytic reduction of furan over Raney Nickel catalyst.

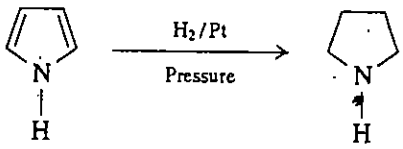


furan — tetrahydrofuran

Mild reduction of pyrrole with zinc and ethanoic acid yields 3-pyrroline (2, 5 dihydro pyrrole). Catalytic reduction completely hydrogenates the ring system yielding pyrrolidine.

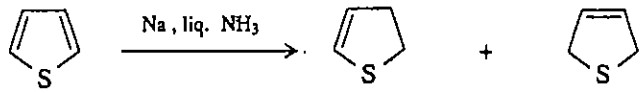


pyrrole — 3-pyrroline



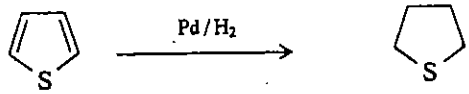
Pyrrole — pyrrolidine

Birch reduction (with sodium in liquid ammonia) is used to obtain 2, 3 dihydrothiophene and 2, 5 dihydrothiophene.



thiophene — 2,3-dihydrothiophene — 2,5-dihydrothiophene

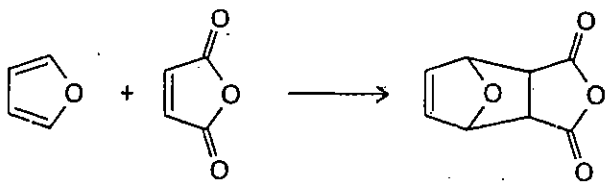
Tetrahydrothiophene is the product when a large amount of palladium is used as catalyst.



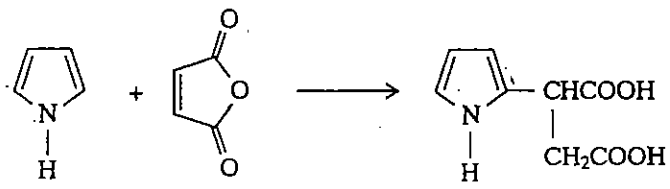
thiophene — tetrahydrothiophene

iii) Diels-Alder Reaction

Furan has sufficient diene character to undergo Diels-Alder reaction with maleic anhydride to form an addition product.



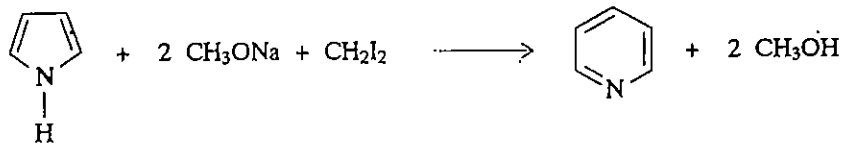
Pyrrole does not undergo Diels-Alder reaction on treatment with maleic anhydride. Rather a substitution product is obtained.



Thiophene does not undergo Diels-Alder reaction or substitution reaction with maleic anhydride.

iv) **Ring Expansion Reaction**

When treated with sodium methoxide and diiodomethane, pyrrole undergoes ring expansion forming pyridine.



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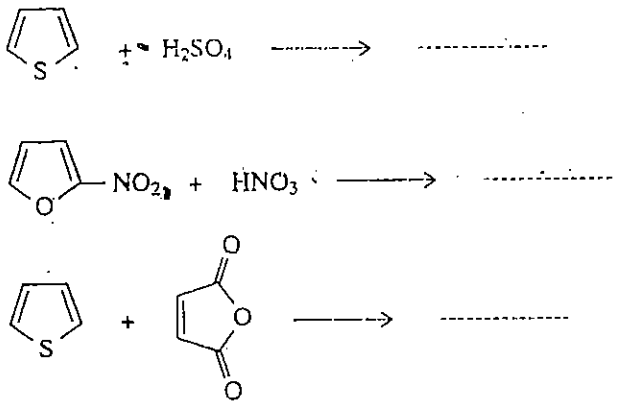
Predict the product of the following reactions:



10.4 SIX-MEMBERED HETEROCYCLIC COMPOUNDS : PYRIDINE

Of the six membered aromatic heterocyclic compounds only nitrogen heterocycles, pyridine, is a stable aromatic compound. So in this unit, we shall study only pyridine.

Pyridine contains a six membered ring consisting of five carbon atoms and one nitrogen atom. The structure of pyridine has close resemblance to that of benzene. The molecule is planar with bond angles of 120°. All the five carbon atoms and the nitrogen atom are sp^2 hybridised. Each of the five carbon atoms and the nitrogen atom use their sp^2 orbital in forming bonds. Note that the lone pair of electrons in nitrogen atom is responsible for the basic character of pyridine. The six electrons in the unhybridised orbitals of carbon and nitrogen atoms are responsible for the formation of three double bonds (Fig. 10.2).

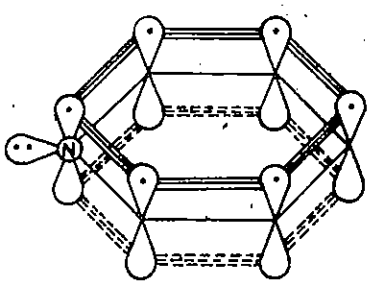


Fig. 10.2 : Orbital picture of pyridine.

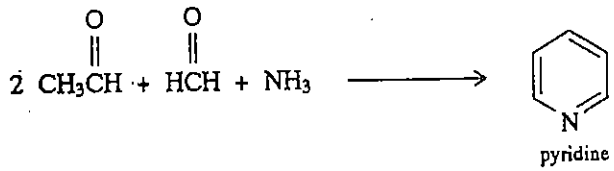
10.4.1 Source of Pyridine

Pyridine occurs in the light oil fraction of coal tar and in bone oil, and is a decomposition product of several alkaloids. Pyridine is obtained from light oil by treating it with dilute sulphuric acid. This dissolves pyridine and other basic substances. This solution is neutralised with sodium hydroxide and the liquid is repeatedly fractionated to get pyridine.

10.4.2 Preparation of Pyridine

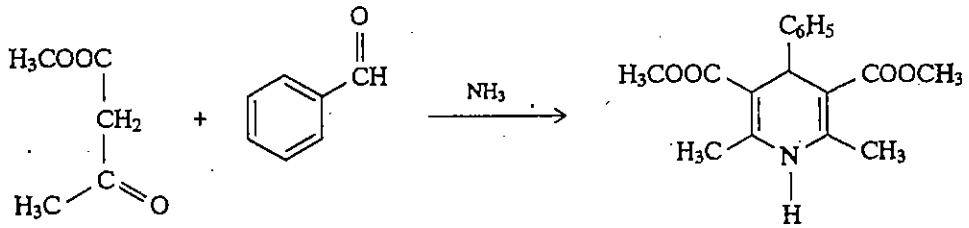
Pyridine can be prepared by the following methods:

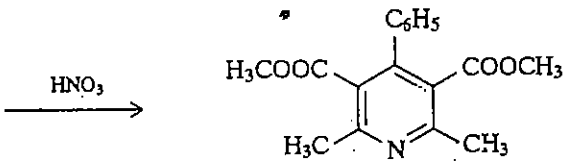
i) Pyridine is produced on a commercial scale by condensing methanal and ethanal in the presence of ammonia.



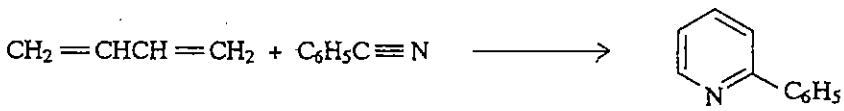
pyridine

ii) In the laboratory pyridine is usually produced by the Hantzsch synthesis in which two moles of a β keto easter combine with an aldehyde in presence of ammonia. The dihydropyridine produced initially is readily oxidised to aromatic product.





iii) Diels-Alder reaction is also used for the preparation of substituted pyridine using benzonitrile as the dienophile.



2-phenylpyridine

10.4.3 Basic Character of Pyridine

Pyridine is a base with $K_b = 2.3 \times 10^{-9}$. It has a pair of electrons in an sp^2 orbital which is available for sharing by a proton. In contrast to this, pyrrole ($K_b = 2.5 \times 10^{-14}$) can accept a proton only at the expense of its aromatic character. Hence, pyridine is much more basic than pyrrole.

Pyridine is, however, far less basic than the alkyl amines ($K_b = 10^{-14}$). This is so because the sp^2 hybridised nitrogen atom in pyridine is more electron attracting than the sp^3 hybridised nitrogen atom in aliphatic amines. Consequently, the lone pair is more tightly held in pyridine as compared to aliphatic amines and so is less available for protonation.

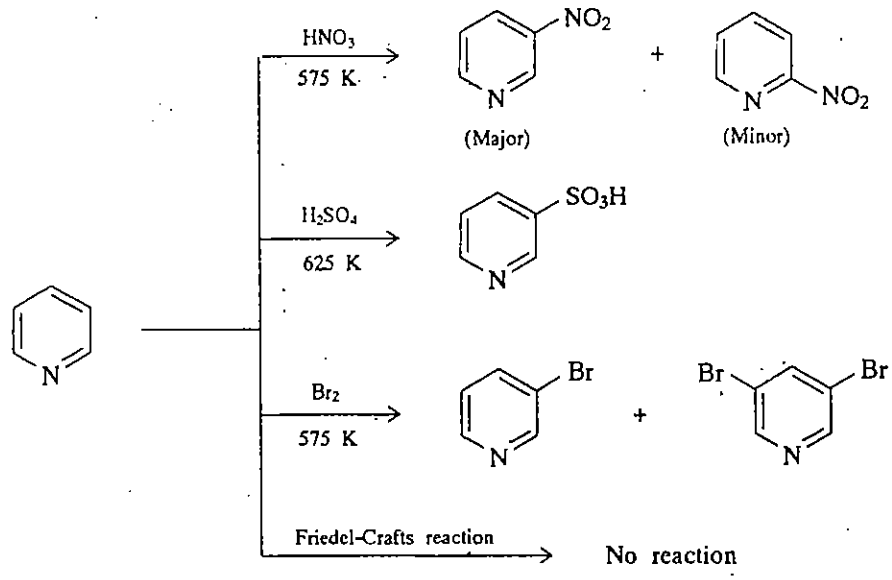
10.4.4 Reactions of Pyridine

Pyridine undergoes electrophilic and nucleophilic substitution reactions.

i) Electrophilic Substitution

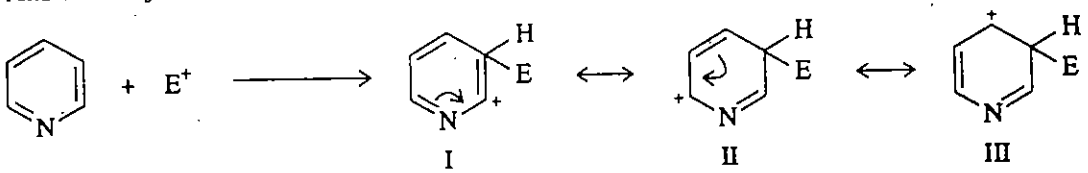
The pyridine ring is deactivated for electrophilic substitution as the electronegative nitrogen atom tends to attract the ring electrons towards itself. This effect is enhanced by protonation which occurs under the acidic reaction conditions.

It undergoes nitration, sulphonation and halogenation only under very vigorous condition these too in very poor yield. It does not undergo Friedel-Crafts reaction at all.

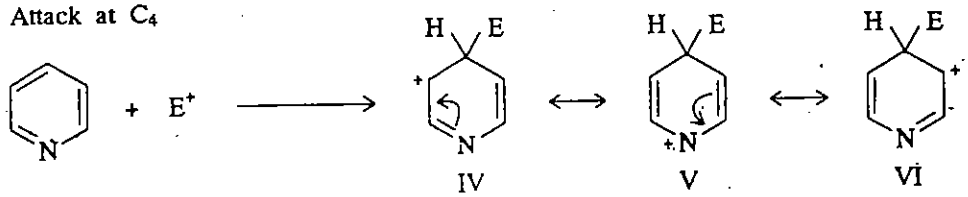


The substitution occurs chiefly at the 3-(or β) position as the transition state leading to substitution at this position is energetically more favourable; the intermediate positively charged species formed due to attack at 3-position is stabilised by three resonance structures, I to III.

Attack at C_3



Attack at C_4

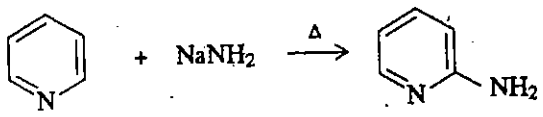


If the electrophile attacks at 4-position it results in a positive species which can be represented by three resonance structures, IV to VI. In one resonance structure (V) the positive charge is at the electronegative nitrogen atom. This greatly increases the energy of the transition state; hence, intermediate V is unstable. As a result, attack at 4-position is especially slow. No such structure is possible when the electrophile attacks 3-position, therefore substitution occurs predominantly at 3-position.

Attack at 2-position resembles attack at the 4-position just as *ortho* attack resembles *para* attack in the benzene series.

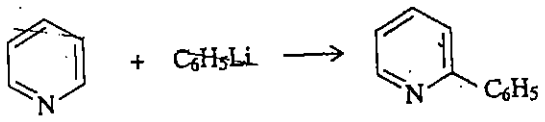
ii) **Nucleophilic Substitution**

Because of the presence of the electron withdrawing nitrogen atom, the reactivity of pyridine towards nucleophilic substitution is so great that even the powerfully basic hydride ion H^- can be displaced by the amide anion as in the following reaction.

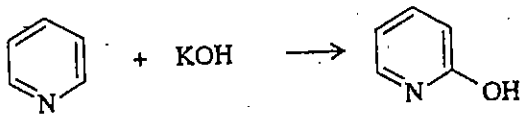


2-aminopyridine

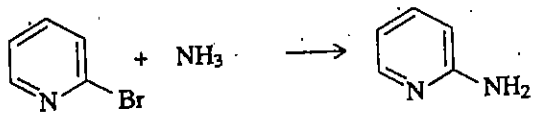
Other typical nucleophilic reactions of pyridine are :



2-phenylpyridine



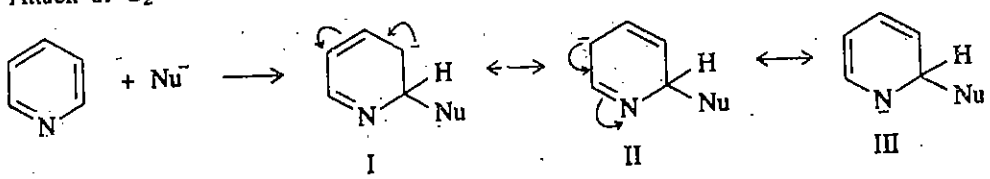
2-hydroxypyridine



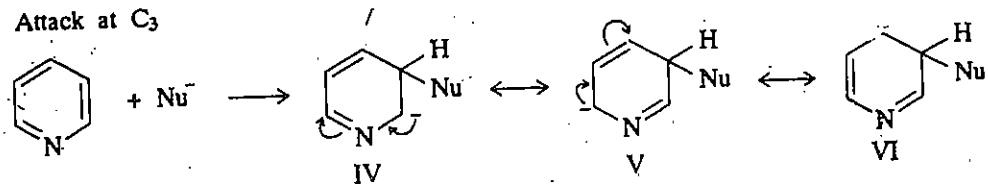
2-aminopyridine

We have illustrated nucleophilic substitution at 2-position only, although such substitutiuon takes place to a large extent at 2- and 4-positions and not at 3-position. This can be explained through the following structures.

Attack at C_2



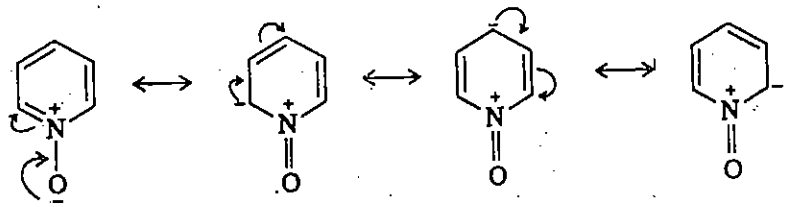
Attack at C_3

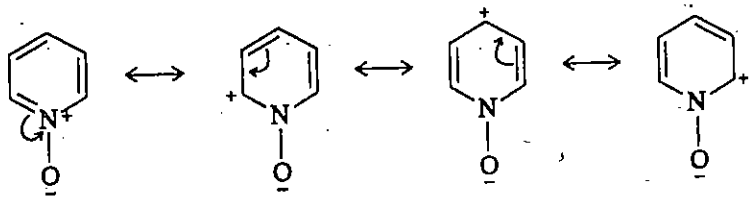


The attack of the nucleophile only at 2-position gives rise to resonance structures III where the negative charge resides on the electronegative nitrorgen atom; this is energetically favourable. We can apply similar arguments for the nucleophilic attack at 4-position. No such situation arises when nucleophile attacks 3-position. Thus the attack of the nucleophile occurs selectively on 2- and 4-positions of the pyridine ring.

iii) N-Oxides

Pyridine when treated with a peracid such as perethanoic acid or perbenzoic acid is converted into pyridine N-oxide. It can be depicted as a resonance hybrid of the following structures.





In some of the above structures, there is a decrease in electron density at various ring positions while in the others there is an increase in electron density. Thus pyridine N-oxide has been found to be more reactive towards both electrophilic and nucleophilic reagents than pyridine itself.

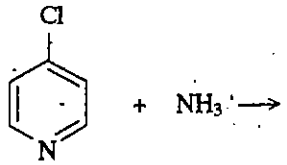
SAQ 3

Predict the product(s) of the following reactions :

a) $2CH_3CHO + CH_2O \longrightarrow$

b) $C_5H_5N \xrightarrow[\text{reactions}]{\text{Friedel Crafts}}$

c) $C_5H_5N + Br_2 \longrightarrow$

d) 

10.5 SUMMARY

- Furan, pyrrole and thiophen and pyridine are important heterocycles.
- Heterocyclic compound generally occur in coal tar and bone oils.
- Pyrole acts as a weak base, its K_b value being 2.5×10^{-14}. Pyridine is a stronger base ($K_b 2.3 \times 10^{-9}$) than pyrrole but much weaker than aliphatic amine.
- Five-membered heterocyclic compounds can be prepared by the Paal-Knorr method and some other methods.
- Five membered heterocyclic compounds undergo electrophilic substitution reduction and Ring expansion reactions.
- Pyridine can be prepared by Hantzsch synthesis, Diels-Alder reaction and by condensing methanal and ethanal.
- The electrophilic substitution occurs predominantly at the 2-position.
- Pyridine undergoes electrophilic substitution as well as nucleophilic substitution reaction.
- Electrophilic substitution occurs predominantly at 3-position and nucleophilic substitution occurs prominantly at 2- and 4-positions of the pyridine ring.

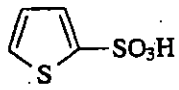
10.6 TERMINAL QUESTIONS

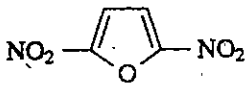
1) Arrange the following compounds in the increasing order of the basic strength.
   Pyridine, pyrrole and aliphatic amine
2) Write the structure for the product(s) obtained on treating furan with (a) maleic anhydride (b) catalytic reduction (c) $CH_3COONO_2^+$ (d) SO_3, pyridine.
3) Give the resonance structures for the intermediate in the reaction where electrophile E^+ attack on 2-position of pyridine.

10.7 ANSWERS

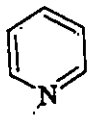
Self-Assessment Questions

1) a) 1, 2-Oxazole
   b) 1, 2-Diazole
   c) 1, 3-Thiazole
   d) 1, 2-Diazine

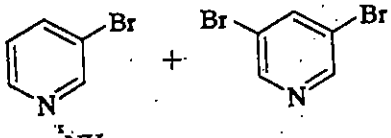
2) a) 

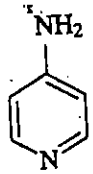
b) 

c) No reaction

3) a) 

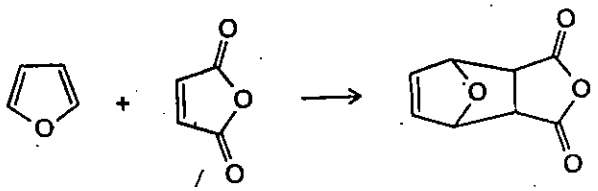
b) No reaction

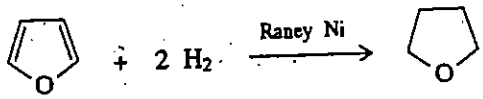
c) 

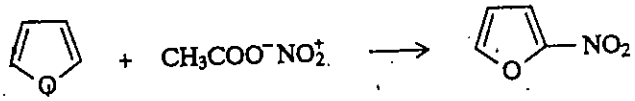
d) 

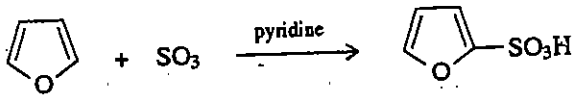
Terminal Questions

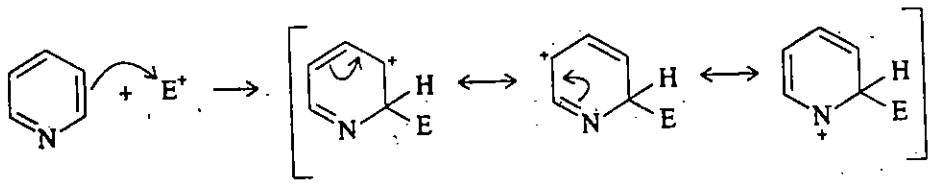
1) Aliphatic amine > pyridine > pyrrole

2) a) 

b) 

c) 

d) 

3) 

Further Reading

1) *Organic Chemistry*, 5th edition; by R.T. Morrison and R.N. Boyd; Prentice-Hall of India Pvt. Ltd.

2) *A Text Book of Organic Chemistry;* by B.S. Bahal and Arun Bahal; S. Chand & Company Ltd.

3) *Organic Chemistry,* Vol. I and II; by S.M. Mukherji, S.P. Singh and R.P. Kapoor; Wiley Eastern Ltd.

4) *Text Book of Organic Chemistry,* 24th edition; by P.L. Soni and H.M. Chawla; Sultan Chand & Sons.

5) *Text Book of Organic Chemistry,* 2nd edition; by Liyod N. Freguson; Affiliated East-West Press Pvt. Ltd.

NOTES

UTTAR PRADESH
RAJARSHI TANDON OPEN UNIVERSITY

UGCHE - 05
Organic Chemistry - I

Block

3

DERIVATIVES OF HYDROCARBONS-I

UNIT 11

Halogen Derivatives 5

UNIT 12

Alcohols and Phenols 32

UNIT 13

Ethers and Sulphur Analogues of Alcohols and Ethers 63

UNIT 14

Aldehydes and Ketones 76

BLOCK INTRODUCTION

In the first block of this course, we introduced you to the basic concepts of organic chemistry. In the second block, you learnt about the hydrocarbons and heterocyclic compounds. These compounds provide the basic skeleton for various types of organic compounds.

In this block, you will study organic compounds which have:

- carbon-halogen bonds: the halogen derivatives of hydrocarbons,
- carbon-oxygen single bonds: alcohols, phenols and ethers,
- carbon-sulphur single bonds: thiols and sulphides, and
- carbon-oxygen double bonds: aldehydes and ketones.

There are four units in this block. Unit 11 deals with the chemistry of the halogen derivatives. Here we focus our attention on some important reactions such as nucleophilic substitution and elimination.

Unit 12 is on alcohols and phenols. An alcohol has an $-OH$ group bonded to an aliphatic carbon atom. In a phenol, an $-OH$ group is bonded to an aromatic carbon atom. In this unit, we discuss laboratory and industrial preparation of alcohols and phenols. We also explain the behaviour of alcohols and phenols as weak acids and illustrate their chemical properties.

Unit 13 deals with the chemistry of ethers and sulphur analogues of alcohols and ethers. In this unit, first we shall discuss different types of ethers and their preparation. After that, we shall discuss their physical, spectral and chemical properties. We shall also introduce the thiols and sulphides briefly.

Chemistry of aldehydes and ketones is discussed in Unit 14. Here we will first take up the preparation of aldehydes and ketones and then the characteristic reactions of carbonyl group. Finally, you will study the industrial uses of aldehydes and ketones and their detection.

In this block, we have followed, the IUPAC nomenclature. However, the common names of important organic compounds are still widely used, therefore, here we are also giving common names of these compounds in brackets along with IUPAC names.

Objectives

After studying this block, you should be able to:

- classify and draw structures of simple halogen derivatives, alcohols, phenols, ethers, aldehydes and ketones and
  - outline their methods of preparation,
  - describe their physical and spectral properties,
  - describe their reactions,
  - list and describe their industrial uses,
  - describe their laboratory detection,
- explain the mechanism of nucleophilic substitution and elimination reactions of halogen derivatives and alcohols, and
- explain the mechanism of nucleophilic addition to the carbonyl group of aldehydes and ketones.

UNIT 11 HALOGEN DERIVATIVES

Structure

11.1 Introduction
Objectives

11.2 Classification of Halogen Derivatives

11.3 Preparation of Halogen Derivatives

Alkyl Halides
Aryl Halides
Alkenyl Halides

11.4 Structure and Properties of Halogen Derivatives

Structure of Halogen Derivatives
Physical Properties of Halogen Derivatives
Spectral Properties of Halogen Derivatives
Chemical Properties of Alkyl Halides
Chemical Properties of Aryl and Alkenyl Halides

11.5 Organometallic Compounds

11.6 Polyhalogen Derivatives

Dihalogen Derivatives
Trihalogen Derivatives

11.7 Uses of Halogen Derivatives

11.8 Lab Detection

11.9 Summary

11.10 Terminal Questions

11.11 Answers

11.1 INTRODUCTION

In Block 2, we have described the preparation and reactions of hydrocarbons and some heterocyclic compounds. In this unit and in the next units, we will study some derivatives of hydrocarbons.

Replacement of one or more hydrogen atoms in a hydrocarbon by halogen/atom(s) [F, Cl, Br, or I] gives the halogen derivatives. These compounds are important laboratory and industrial solvents and serve as intermediates in the synthesis of other organic compounds. Many chlorohydrocarbons have acquired importance as insecticides. Although there are not many naturally occurring halogen derivatives yet you might be familiar with one such compound, thyroxin—a thyroid hormone.

In this unit, we shall take up the chemistry of the halogen derivatives in detail beginning with classification of halogen derivatives and then going over to methods of their preparation. We shall also discuss the reactivity of halogen compounds and focus our attention specially, on some important reactions such as nucleophilic substitution (S_N) and elimination (E) reactions. Finally, we shall take up uses of halogen derivatives and the methods for their detection.

Objectives

After studying this unit, you should be able to:

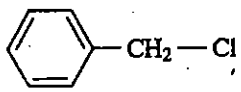
- classify the halogen derivatives,

- outline the methods of preparation of alkyl halides, chlorobenzene and chloroethene,
- list the physical and spectral properties of halogen derivatives,
- describe the reactions of halogen derivatives, specially nucleophilic substitution and elimination reactions,
- explain the difference in reactivity of alkyl, ethenyl, aryl and benzylhalides towards nucleophilic substitution reactions,
- describe the chemisty of organometallic compounds and polyhalogen derivatives,
- list and describe the industrial uses of halogen derivatives, and
- describe the laboratory detection of halogen derivatives.

11.2 CLASSIFICATION OF HALOGEN DERIVATIVES

The halogen derivatives are conveniently divided into three classes depending upon the nature of the hydrocarbon residue to which the halogen atom is attached: (i) Alkyl halides (ii) Aryl halides (iii) Alkenyl halides. Compounds in which the halogen atom is bonded to an alkyl or a substituted alkyl-group are called **alkyl halides.** Compounds in which one of the hydrogens of an aromatic ring is replaced by a halogen atom are called **aryl halides.** Finally a compound in which a halogen atom is attached to a carbon atom which is attached to another carbon atom by a double bond, are called **alkenyl (vinylic or vinyl) halides.** A few examples are given below:

Alkyl halides (R—X)

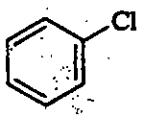
$CH_3—Br$ $CH_3CH_2—Cl$ 

bromomethane

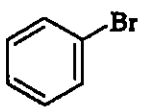
chloroethane
$CH_2=CHCH_2—Cl$
3-chloro-1-prepene or
3-chloropropene
(allyl chloride)

(chloromethyl) benzene
(benzyl chloride)

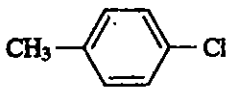
Aryl halides (Ar—X)



chlorobenzene



bromobenzene

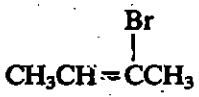


chloro-4-methyl benzene
(*p*-chlorotoluene)

Alkenyl halides (Vinyl halides)

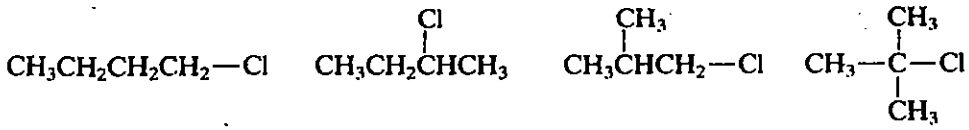
$CH_2=CH—Cl$

chloroethene
(vinyl chloride)



2-bromo-2-butene

Halogen derivatives may be mono−, di−, tri−, etc., substitution products according to the number of halogen atoms present in the molecule. The monohalogen derivatives of alkyl halides are subdivided into primary (1°), $RCH_2—X$; secondary (2°), $R_2CH—X$; and tertiary (3°), $R_3C—X$ types depending on the nature of the alkyl group or the position of the halogen atom in the molecule. For example, the molecular formula C_4H_9Cl can represent the following four isomeric mono-halogen derivatives:



1-chlorobutane | 2-chlorobutane | 1-chloro-2-methylpropane | 2-chloro-2-methylpropane

primary 1° | secondary 2° | primary 1° | tertiary 3°

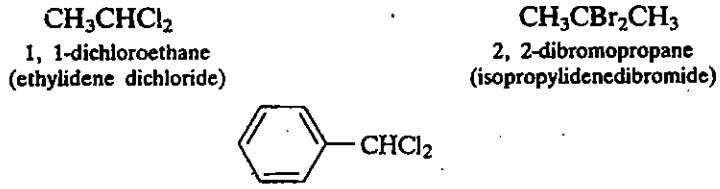
Di−, tri−, and tetrachloromethanes are examples of di−, tri−, and tetra halogen derivatives, respectively,

CH_2Cl_2	$CHCl_3$	CCl_4
dichloromethane (methylene chloride)	trichloromethane (chloroform)	tetrachloromethane (carbon tetrachloride)

These halogen derivatives are excellent solvents for nonpolar and slightly polar substances.

The dihalogen derivatives of alkyl halides can be subdivided into two types:

i) Geminal dihalides: In these both halogen atoms are attached to the same carbon atom i.e., they are in **geminal (gem-)** position. Geminal dihalides are also referred to as alkylidene halides.



1, 1-dichloroethane (ethylidene dichloride) | 2, 2-dibromopropane (isopropylidenedibromide)

(dichloromethyl) benzene (benzylidene chloride or benzal chloride)

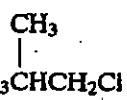
ii) Vicinal dihalides: When two halogen atoms are attached to adjacent carbon atoms, they are said to be in **vicinal (vic-)** position and such compounds are also named as the dihalides of the alkene from which they may be prepared by addition of the halogen, e.g.,

1, 2-dibromoethane (ethylene dibromide) | 1, 2-dichloropropane (propylene dichloride)

We have discussed above classification of halogen derivatives. In the next section we shall be discussing the preparation of mono halogen derivatives of aliphatic and aromatic hydrocarbons. We will take up polyhalogen derivatives separately in Sec. 11.6. Before that try the following SAQ to test your understanding of the classification of halogen derivatives.

SAQ 1

Classify each of the following alkyl halides as 1°, 2°, or 3°.

a) 

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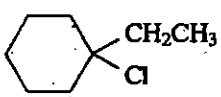
b) 

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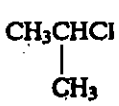
c) 

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11.3 PREPARATION OF HALOGEN DERIVATIVES

We have already looked at several methods of preparation of halogen derivatives in Units 6,7,8,9 and 10. In this section we shall briefly review these methods and also taking up some other methods for the preparation of halogen derivatives.

11.3.1 Alkyl Halides

Alkyl halides can be prepared from alcohols, alkenes, alkanes, Grignard reagents, carboxylic acids, other halides and from chloromethylation of benzene. General reactions of these methods of preparation are summarised below in Table 11.1.

Table 11.1: Preparations of alkyl halides

From Alcohols

$$-\overset{|}{\underset{|}{C}}-OH \xrightarrow[\text{or } SOCl_2 \text{ or } PCl_5]{HX \text{ or } PX_3} R-X$$

HX = HCl, HBr, HI
$PX_3 = PCl_3$, PBr_3

From Alkenes

$$-C=C- \xrightarrow{HX} -\overset{|}{C}-\overset{|}{C}-$$
(H, X)

HX = HCl, HBr, HI

From Alkanes

$$-\overset{|}{C}-H + X_2 \xrightarrow[\text{peroxide}]{\text{light or}} -\overset{|}{C}-X + HX$$

$X_2 = Cl_2, Br_2$

From Grignard Reagents

$$RMgX + X_2 \longrightarrow R-X + MgX_2$$
$X_2 = Cl_2, Br_2$

From Carboxylic Acids

$$RCOOAg + Br_2 \longrightarrow R-Br + AgBr + CO_2$$

Halide Exchange

$$R-X + KI \longrightarrow R-I + KX$$

From Chloromethylation of Benzene

$$Ar-H + CH_2O + HCl \longrightarrow ArCH_2-X + H_2O$$

Let us study these methods of preparation in a brief manner.

i) From alcohols: The most widely used method for the preparation of alkyl halides is from alcohols. The hydroxyl group of the alcohol (R—OH) can be replaced by a halogen atom by using either a hydrogen halide (HX), a phosphorus halide (PX_3 or PCl_5), or thionyl chloride ($SOCl_2$). These reactions will be discussed in more detail in Unit 12. The net reaction is represented by the equations,

$$R-OH + HX \longrightarrow R-X + H_2O$$
$$R-OH + PCl_3 \longrightarrow R-Cl + H_3PO_3$$
$$R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$$
$$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$$
$$C_6H_5CH_2-OH + SOCl_2 \longrightarrow C_6H_5CH_2-Cl + SO_2\uparrow + HCl$$

phenylmethanol (benzyl alcohol) → (chloromethyl) benzene (benzyl chloride)

ii) From alkenes: Hydrogen halides (HCl, HBr, HI) reacts with alkenes to form alkyl halides. The mode of addition follows Markownikoff's rule except for the addition of hydrogen bromide in the presence of peroxide. The mechanism for both modes of additions were shown in Unit 7.

Examples

$CH_3CH=CH_2 + HCl \longrightarrow CH_3CH(Cl)-CH_2(H)$
propene — 2-chloropropane

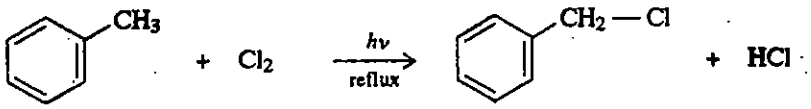
$CH_3CH=CH_2 + HBr \longrightarrow CH_3CH(Br)-CH_2(H)$
propene — 2-bromopropane

$CH_3CH=CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH(H)-CH_2(Br)$
propene — 1-bromopropane

iii) From Alkanes: Direct halogenation of alkanes is of limited application in most cases because of the formation of mixture of mono and polyhalogenated compounds. You have learned in Unit 6 that chloromethane, however, can be prepared directly by photochlorination if a large excess of methane is employed.

$$CH_4 + Cl_2 \xrightarrow{\text{sun light}} CH_3-Cl+HCl$$

(Chloromethyl) benzene can also be similarly prepared.



methylbenzene (toluene) — (chloromethyl) benzene (benzyl chloride)

iv) From Grignard reagents: Direct reaction of alkyl or aryl halides with metallic magnesium in a dry solvent (ether) gives the Grignard reagent, a valuable intermediate in synthetic organic chemistry. We will discuss this reagent in more detail in sec. 11.5. Grignard reagents react with halogens to give alkyl halides.

$$RMgX + X_2 \longrightarrow R-X + MgX_2$$

Grignard reagent — Alkyl halide

v) From carboxylic acids: The dry silver salt of a carboxylic acid upon refluxing with bromine in tetrachlomethane (carbon tetrachloride) afford the corresponding alkyl bromide. This reaction is known as **Hunsdiecker reaction.**

$$RCOOAg+Br_2 \longrightarrow R-Br+AgBr+CO_2\uparrow$$

Silver salt of carboxylic acid

vi) Halide exchange: This is a good procedure for preparing alkyl iodides and alkyl fluorides.

$$R-X+KI \xrightarrow{\text{propanone}} R-I+KX$$

Alkyl fluorides often are prepared by the reaction of mercurous or antimony fluorides with alkyl chlorides;

$$2R-Cl + Hg_2F_2 \longrightarrow 2R-F + Hg_2Cl_2$$

alkyl chloride — mercurous fluoride — alkyl fluoride — mercurous chloride

$$3CCl_4 + 2SbF_3 \longrightarrow 3CCl_2F_2 + 2SbCl_3$$

tetrachloromethane — antimony fluoride — dichlorodifluoromethane (Freon 12) a chlorofluorocarbon (CFC)

Chlorofluorocarbons (CFC) also called Freons are inert nontoxic gases used as refrigerants in air-conditioners and refrigerators. Freon 12 is the most commonly used refrigerant. Unfortunately Freons catalyse the decomposition of ozone and thus can destroy the protective layer that surrounds the earth. For this reason most of countries in the world have banned the use of Freons.

vii) Chloromethylation of benzene: This method is used to prepare benzylic halides.

$$\underset{\text{aromatic hydrocarbon}}{Ar-H} + \underset{\text{methanal (formaldehyde)}}{CH_2O} + \underset{\text{acid}}{HCl} \longrightarrow \underset{\text{benzylic halide}}{Ar-CH_2-Cl} + H_2O$$

11.3.2 Aryl Halides

Aryl halides may be prepared by one of the methods outlined below in Table 11.2

Table 11.2: Preparation of Aryl Halides

From Aromatic Hydrocarbons

$$Ar-H+X_2 \xrightarrow[X_2=Cl_2, Br_2]{\text{Lewis acid}} Ar-X+HX$$

Lewis acid = $FeCl_3$, $AlCl_3$ $TI(OAc)_3$, etc.

From Aromatic Amines

$$Ar-NH_2 \xrightarrow[273K]{HNO_2/HX} \underset{\text{diozonium salt}}{Ar-N_2^+} \xrightarrow{CuX} Ar-X+N_2$$

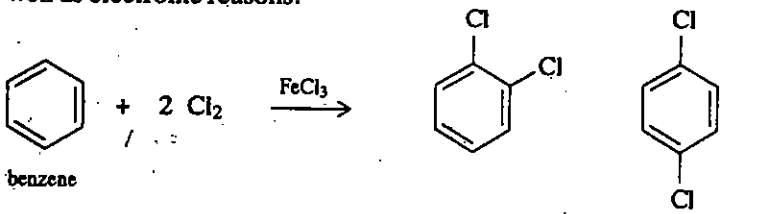
CuX = CuCl, CuBr

Let us briefly consider these methods of preparation.

i) From Aromatic Hydrocarbons: As discussed in Unit 10 the aromatic halogenation of aromatic hydrocarbon needs the assistance of a Lewis acid as a catalyst. Generally ferric chloride or aluminium chloride are used as catalysts.

$$\underset{\text{aromatic hydrocarbon}}{Ar-H} + X_2 \xrightarrow{\text{Lewis Acid}} \underset{\text{aryl halide}}{Ar-X} + HX$$

If two moles of chlorine (per mole of benzene) are used, a mixture of *ortho*- and *para*-dichlorobenzene is obtained in which the *para* compound predominates for steric as well as electronic reasons.



benzene

1,2-dichlorobenzene (*o*-dichlorobenzene) 1,4-dichlorobenzene (*p*-dichlorobenzene)

ii) From Aromatic Amines: In this process the amine is first converted to the diazonium salt ($ArN_2^+X^-$), which is then converted to aryl halide using the solution of cuprous halide dissolved in the concentrated halogen acid. This method is known as **Sandmeyer reaction.**

$$\underset{\text{aromatic amine}}{Ar-N^+} \xrightarrow[\text{cold}]{NaNO_2-HX} \underset{\text{(diazonium salt)}}{Ar-N_2^+X^-} \xrightarrow{CuX/HX} \underset{\text{aryl halide}}{Ar-X}$$

Replacement of the diazonium group by $-I$ does not require the use of a cuprous halide.

$$AR-N_2^+X^- \xrightarrow{KI} Ar-I+N_2+KX$$

Chlorobenzene is prepared commercially by the Rasching process in which a mixture of benzene vapour, air and hydrogen chloride is passed over copper chloride.

$$C_6H_6+HCl+1/2O_2 \xrightarrow{CuCl_2} C_6H_5Cl+H_2O$$

11.3.3 Alkenyl Halides

The most readily available Alkenyl halide is chloroethene (vinyl chloride) which can

be prepared by any of the following methods:

i) Chlorination of ethene: High temperature chlorination of ethene is a most economical commercial preparation:

$$\underset{\text{ethene}}{CH_2=CH_2} + Cl_2 \xrightarrow{673K} \underset{\text{chloroethene}}{CH_2=CH-Cl} + HCl$$

ii) From ethene and hydrogen chloride: Following steps are involved:

$$\underset{\text{ethene}}{CH_2=CH_2} + HCl + O_2 \xrightarrow[373-473\ K]{CuCl_2} \underset{\text{1,2-dichloroethene}}{CH_2(Cl)-CH_2(Cl)} \xrightarrow{-HCl} CH_2=CH-Cl$$

iii) Addition of hydrochloric acid to ethyne: This method is analogous to Hg^{2+} catalysed addition of water to ethyne, which gives ethanal (Unit 8).

$$\underset{\text{ethyne}}{CH\equiv CH} + HCl \xrightarrow[373-473K]{Hgcl_2} \underset{\text{chloroethene}}{CH_2=CH-Cl}$$

iv) Elimination of hydrogen chloride from dihalide: The final product of this reaction is ethyne but with a weaker base the reaction can be stopped with the elimination of only one mole of HCl. Following steps are involved in this process:

$$\underset{\text{1,2-dichloroethene}}{CH_2(Cl)-CH_2(Cl)} \xrightarrow[-HCl]{Base} \underset{\text{chloroethene}}{Ch_2=CH-Cl}$$

$$\underset{\text{1,1-dichloro ethene}}{CH_3-CHCl_2} \xrightarrow[-HCl]{Base} \underset{\text{chloroethene}}{CH_2=CH-Cl}$$

SAQ 2

Write equations showing the preparation of the following halides from the starting materials indicated.

a) $C_6H_5CHBrCH_3$ from $C_6H_5CH_2CH_3$

b) $CH_3CHBrCH_3$ from $CH_3CHOHCH_3$

c) 1-bromopropane from 1-propene

d) 2-chloropropane from 2-propanol

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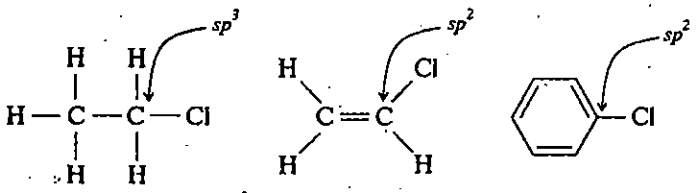
11.4 STRUCTURE AND PROPERTIES OF HALOGEN DERIVATIVES

In the previous section we have been concerned mainly with the preparation of halogen derivatives. Now we will discuss to the structure, spectral properties and chemical properties of these compounds.

11.4.1 Structure of halogen Derivatives

In a halogen derivative, halogen atom is the functional group, and the C—X bond is the site of chemical reactivity. As might be expected, the nature of the chemical bond between the halogen and carbon decides the reactivity of halogen derivatives.

In the alkyl halide, the carbon-halogen sigma bond results through overlap of the sp^3 hybrid orbital with the p orbital of the halogen atom. While the carbon-halogen sigma bond in alkenyal and aryl halides result from the overlap of sp^2 hybrid orbital of the carbon with a halogen p orbital.



As mentioned in unit 1, the bond formed with an sp^2 hybridised carbon is stronger than the bond formed with an sp^3 hybridised carbon. This difference in the nature of the C—X bond is mainly responsible for different bahaviour of aryl and alkenyl halides as compared to alkyl halides. To further explain the unique chemistry of aryl and alkenyl halides, we shall study the reactions of chlorobenzene and chloroethene in sub-section 11.4.5. Let us first examine the polar nature of the C—X bond here.

Electronegativity on the Pauling and Sanderson scales

Element	Pauling	Sanderson
F	4.0	4.000
Cl	3.0	3.475
Br	2.8	3.219
I	2.5	2.778
C	2.5	2.746

You will recall that halogens are more electronegative than carbon and thus the electron density along the C—X bond increases in the direction of X. The effect places a partial negative charge (δ^-) on the halogen atom and a partial positive charge (δ^+) on the carbon atom. The **resulting dipole moment is appreciable and governs a substantial part of the chemical and physical properties** of the halogen derivatives.

The magnitude of dipole moment for methyl halides is summarised in Table 11.3. In the subsequent sections we will see how the slight positive charge on the carbon is mainly responsible for the nucleophilic substitution (S_N) reactions of halogen derivatives.

Table 11.3 : Dipole Moments of Methyl Halides

Compound	μ, C m
CH_3F	6.07×10^{-30}
CH_3Cl	6.47×10^{-30}
CH_3Br	5.97×10^{-30}
CH_3I	5.47×10^{-30}

But before going into the detail of the reactions let us take a look at the physical properties of halogen derivatives.

11.4.2 Physical Properties of Halogen Derivatives

The physical properties such as boiling points and densities of some alkyl halides, aryl halides and alkenyl halides are summarised in Table 11.4. Common names of some of them are also given.

Table 11.4 : Physical properties of halogen derivatives

IUPAC Name	Common Name	Formula	Bp, K	Density, Kg dm^{-3} at 293 K
Alkyl halides				
Fluoromethane	methylfluoride	CH_3F	195	Gas
Chloromethane	methylchloride	CH_3Cl	249	Gas
Bromomethane	methylbromide	CH_3Br	277.5	Gas
Iodomethane	methyliodide	CH_3I	315.8	2.28
Dichloromethane	methylenelchloride	CH_2Cl_2	313	1.34
Trichloromethane	chloroform	$CHCl_3$	334	1.49
Tetrachloromethane	carbontetrachloride	CCl_4	350	1.60
Aryl halides				
Fluorobenzene	—	C_6H_5F	358	1.024
Chlorobenzene	—	C_6H_5Cl	405	1.107
Bromobenzene	—	C_6H_5Br	429	1.495
Iodobenzene	—	C_6H_5I	462	1.832
Alkenyl halides				
Chloroethene	vinyl chloride	$CH_2=CHCl$	259	Gas

Note the increase in boiling point and density with the increase in the atomic weight and atomic size of the halogens atom. The table emphasises also the increase in the boiling point with the progressive replacement of the hydrogen atoms with halogen atoms. These effects are related to the enhancement of van der Waal's attraction with the increase in molecular volume. Compare, for example, the boiling points of CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. The density would also increase in the same way.

In general, halogen compounds are insoluble in water but are readily soluble in organic solvents and with the exception of some fluro and mono-chloro compounds, they are more dense than water. Aryl halides are fairly pleasant smelling liquids, but benzylic halides having the structure $ArCH_2X$ are irritating to the eyes, skin and nasal passage. Toxicity varies. However, the polychlorinated hydrocarbons such as CCl_4 and $CHCl_2CHCl_2$ are quite toxic and should be used with care.

SAQ 3

Arrange the following molecules in order of increasing boiling points. Give reason for this trend.

$CHCl_3$, CH_2Cl_2, CCl_4, CH_3Cl

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11.4.3 Spectral Properties of Halogen Derivatives

The ultraviolet-visible spectra of alkyl halides show a weak absorption between 170-258 nm due to the presence of loosely held nonbonding electrons of halogen. These electrons undergo n-π^* transitions. Aryl halides exhibit additional absorption similar to those of the corresponding aromatic hydrocarbons.

The infrared (ir) spectra of alkyl halides show the C–X stretching frequency depending on the nature of halogen present. Generally the absorption region of C–F bond: 1100-1000 cm^{-1}; C–Cl bond: 750-700 cm^{-1}; C–Br bond: 600-500 cm^{-1} and C–I bond: 500 cm^{-1}. In all these cases carbon-halogen stretch is shown as a strong band in the spectrum. As illustration ir spectrum of trichloromethane (chloroform) is shown in Fig. 11.1. Aryl halides display (C–X) bands near 1100 cm^{-1}.

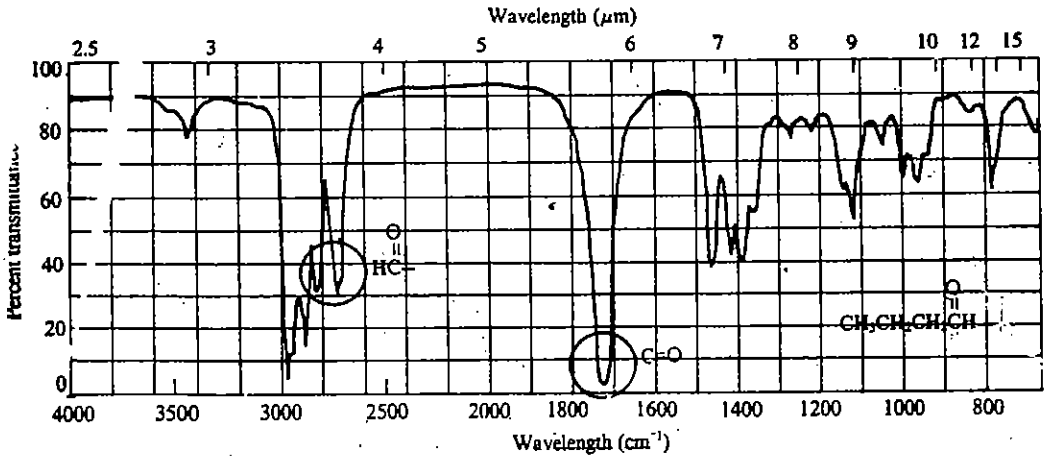


Fig. 11.1 : Infrared spectrum of trichloromethane (chloroform)

The nuclear magnetic resonance (nmr) spectra of alkyl halides exhibit a lower chemical shift (downfield) of the α- protons (dishielding) due to the marked electron-attracting (electro-negative) nature of the halogens. The order of deshielding, resulting in lowering of the chemical shift, is in the order of electronegatively i.e., I < Br < Cl < F. Thus the δ values of methyl protons are: CH_3I, 2.17 CH_3Br, 2.65; CH_3Cl, 3.02; and CH_3F, 4.30 ppm.

Since fluorine has a nuclear spin, with I= + 1/2 and −1/2 (similar to hydrogen), it can spin-spin couple with protons and thus give rise to splitting of the proton signal. In

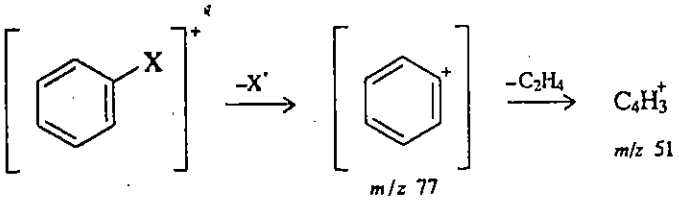
In common name, the Greek letters, α-, β-, γ-, δ-, ω-, etc., are used to indicate the point of attachment. The α- carbon is the one bearing the functional group and protons attached to this carbon are called α protons.

ω δ γ β α
C— C— C— C— C— X
H
β— proton

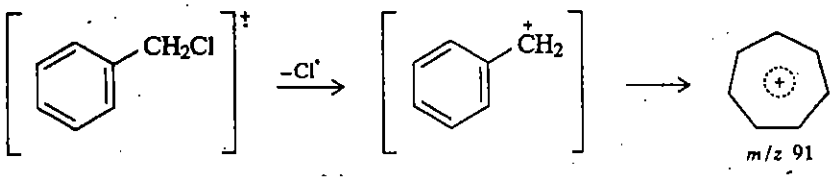
CH_3F, a doublet for the protons of the methyl group will be seen. The signal for fluorine is not observed under conditions of proton resonance, but on changing the conditions, the fluorine signal can be seen as a quartet in the nmr spectrum of CH_3F.

The mass spectrum of alkyl chlorides and bromides show molecular ion peaks at M and M+2 since chlorine and bromine exist as isotopes. In fluoro and iodo compounds the peak due to the molecular ion is strong. The intensity of the M^+ peak decreases with the increase in the size of the halogen atom and is in the order: I > Br > Cl > F.

The molecular ion peak is usually strong in the mass spectra of aromatic halides. The usual fragmentation observed is:



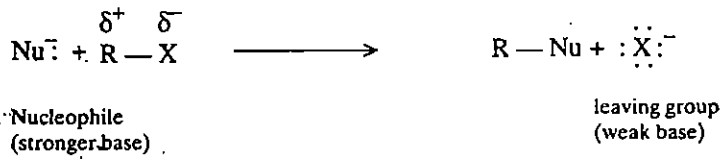
(Chloromethyl) benzene (benzylichalide) fragments as follows :



11.4.3 Chemical Properties of Alkyl Halides

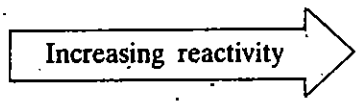
Most important reactions of alkyl halides are **nucleophilic substitution** (S_N) and **elimination (E).** In this section we shall take up a fairly detailed description of these reactions. We have already encountered the term nucleophilic reagent or nucleophile and have learned that it is applied to an electron rich atom or group such as, SH^-, $\ddot{N}H_3$, $R\ddot{O}H$, $H_2\ddot{O}$.

1) Substitution reactions: As explained earlier the C–X bond is polar, and the halogenated carbon of an alkyl halide carries a positive charge because of the higher electronegativity of halogens compared to carbon. The carbon atom is, therefore, susceptible to attack by a nucleophilic.



If we regard the reaction as a type of Lewis acid-base reaction, then we can understand that it tends to occur because of the formation of the halide ion which, as the conjugate base of a strong acid (HX), would be a weak base. Accordingly, a weak base like the halide ion is said to be a good **leaving group.** The order of reactivity of the alkyl halides increases from fluorides to iodides.

RF RCl RBr RI



The explanation of this order is that the iodide ion, being the weakest base as the conjugate base of the strongest acid, HI, is the best leaving group, the fluoride ion being a stronger base is the poor leaving group.

Now let us summarise some nucleophilic substitution reactions of alkyl halides in Table 11.5.

Table 11.5 Some Nucleophilic Substitution Reactions

R—X: + Nucleophile (name)	⟶	:X:⁻ + Product (name)
R—X: + :Y:⁻ (another halide)	⟶	:X:⁻ + R—Y: (another alkyl halide)
+ ⁻:C≡N: (cyanide)	⟶	+ R—C≡N: (nitrile)
+ ⁻:OH (hydroxide)	⟶	+ R—OH (alcohol)
+ ⁻:OR (alkoxide)	⟶	+ R—O—R (ether)
+ ⁻N₃ (azide = :N=N=N:)	⟶	+ R—N₃ (alkyl azide)
+ ⁻:SR′ (alkanethiolate)	⟶	+ R—S—R′ (thioether)
+ :NR′₃ (amine)	⟶	R—N⁺R′₃:X:⁻ (alkylammonium salt)
+ :OH₂ (water)	⟶	R—O⁺(H)—H:X:⁻ ⇌ R—O—H (alcohol) + HX:
+ :O(H)—R′ (alcohol)	⟶	R—O⁺(H)—R′:X:⁻ ⇌ R—O—R′ (ether) + HX:

On the basis of the mechanism of substitution reactions, nucleophilic substitution reaction can be divided into two types:

i) S_N2 reactions (S_N2 means 'substitution, nucleophilic bimolecular')

ii) S_N1 reactions (S_N1 means 'substitution, nucleophilic unimolecular')

The terms bimolecular and unimolecular are related to the number of molecules involved in the rate determining step in these reactions. Now, let us consider these reactions in detail.

The S_N2 reaction : The reaction of bromoethane with the hydroxide ion to yield ethanol and bromide ion is a typical example of S_N2 reaction.

$$\underset{\text{bromoethane}}{CH_3CH_2—Br} + OH^- \xrightarrow{H_2O} \underset{\text{ethanol}}{CH_3CH_2—OH} + Br^-$$

In general methyl or primary alkyl halides undergo S_N2 reaction with any relatively strong nucleophile : OH^-, OR^-, CN^- etc. Secondary alkyl halides can also undergo S_N2 reactions, but, tertiary alkyl halides do not. The above reaction has been found to follow of second order kinetics which means that the rate of the reaction is proportional to the concentrations to both the halide and the hydroxide ion. Thus for the above reaction,

$$\text{Rate} = k_2\,[C_2H_5Br]\,[OH^-]$$

where k_2, is the rate constant and $[C_2H_5Br]$ and $[OH^-]$ represent the concentrations in mole dm^{-3} of the alkyl halide and the hydroxide ion, respectively.

Mechanism : On the basis of reaction kinetics and the stereo chemistry of S_N2 reactions, a one step, concerted mechanism is proposed.

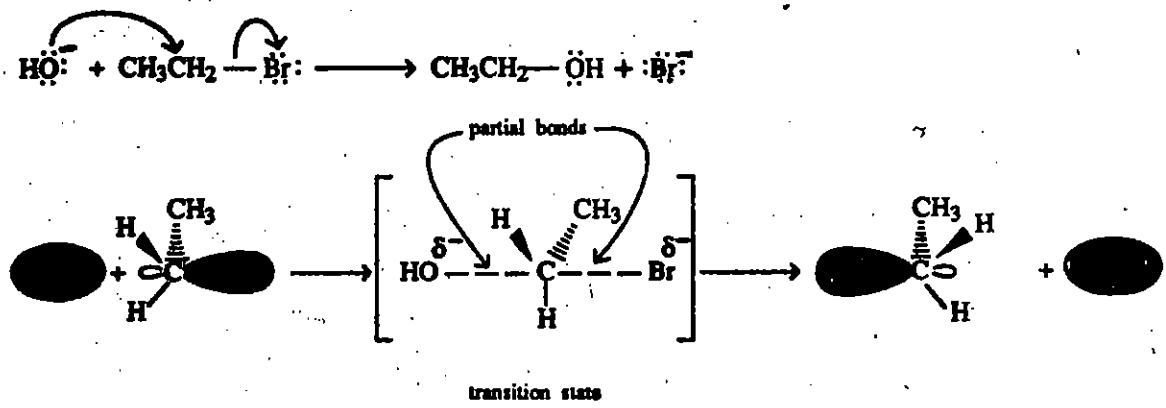


Fig. 11.2 : The mechanism for the S_N2 reaction

In an S_N2 reaction, the other three bonds, (which are not taking part in substitution change) to the central carbon progressively flatter out and flip to the other side of the carbon in a manner similar to the spokes of an umbrella inverting in a windstorm. The flipping is called inversion of configuration, or **Walden inversion**, which you have already studied in Unit 3.

Note how the hydroxide ion attacks from the rear, away from the negatively charged field of the bromide ion. As the hydroxide ion begins to bond to the carbon atom from the rear, the bromine begins to leave as the bromide ion from the front. Groups larger than hydrogen tend to block the approach of the nuclephile, so methyl halides are more reactive than other primary halides. Table 11.6 shows the effect of the structure of alkyl halides over the reaction rate. In this table we have given average reaction rates (taking the reaction rate for ethyl halides are one) of S_N2 reaction of some alkyl halides.

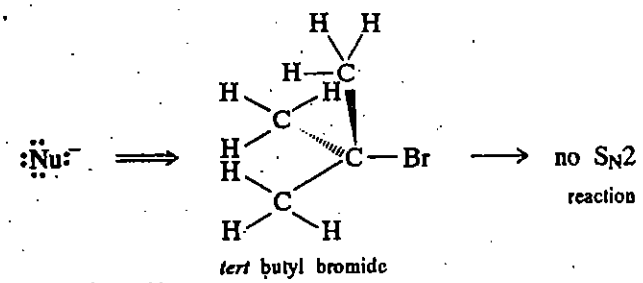
Table 11.6 : Effect of branching in the alkyl halide on the rate of S_N2 reaction

Alkyl halide	Reaction rate
$CH_3—X$	30
$CH_3CH_2—X$	1
$(CH_3)_2CH—X$	0.02
$(CH_3)_3C—X$	0

Therefore, among alkyl halides, order of relative rate is

$$CH_3 > p\ RX > sec\ RX > tert\ RX$$

This order of reactivity is interpreted to be due to steric hindrance, which means obstruction of space. The more alkyl groups there are clusters around the carbon holding the halogen, the more they hindered a nucleophile approaching at backside of that carbon.



tert butyl bromide

Fig. 11.3 : Steric hindrance in S_N2 reaction.

Nucleophiles such as H_2O or CH_3CH_2OH are also used as the solvents. Substitution reactions of such nucleophiles are sometime called a solvolysis reactions (from solvent and by "breaking down" or "loosing").

In most stepwise reactions, the slowest step in the entire sequence is the rate-determining step as a reaction cannot proceed faster than its slowest step does.

The S_N1 reaction

You can see from Table 11.6, that the tertiary alkyl halides do not undergo S_N2 reaction. And yet when tertiary butyl bromide is treated even with a very weak base (such as H_2O or CH_3CH_2OH) substitution takes place. Now, the question arises, if tertiary alkyl halides cannot undergo S_N2 reaction, how are the substitution products formed ? The answer is that tertiary alkyl halides undergo substitution by a different mechanism, called the **S_N1 reaction** (substitution, nucleophilic, unimolecular). An example of such a reaction is the hydrolysis of 2-chloro-2-methylpropane with water. This reaction is found to be of **first order** (S_N1). That means the rate of the reaction is

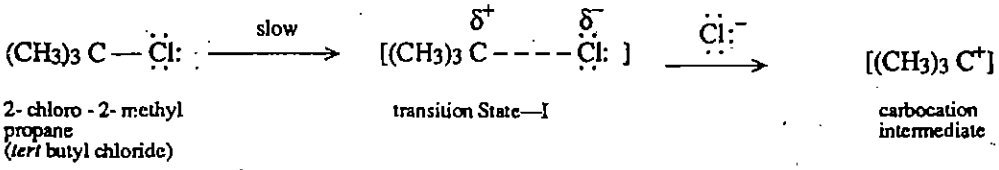
proportional to the concentration of the one reacting species i.e. alkyl halide and independent of the concentration of the nucleophile.

$$\text{Rate} = k_1 [(CH_3)_3CCl]$$

In this equation, k_1 represents the first order rate constant and $[(CH_3)_3CCl]$ represents the concentration in mole dm^{-3} of the alkyl halide.

Mechanism : On the basis of reaction kinetics and stereo chemistry of S_N1 reaction, a two step mechanism has been proposed for this reaction.

Step 1

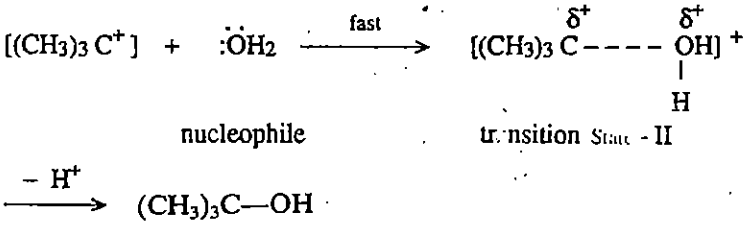


2- chloro - 2- methyl propane (*tert* butyl chloride)

transition State—I

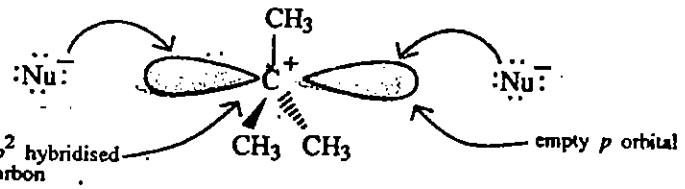
carbocation intermediate

Step 2



2-methyl-2-pro panol (*tert* butyl alcohol)

From the above it is clear that the first step in this mechanism is ionisation of alkyl halide to a carbocation intermediate. This ionisation is a simple heterolytic bond cleavage. In the second step, a nucleophile may approach the central carbon atom from either side with equal probability (unlike the S_N2 reaction where the nucleophile approaches only from the back side). As already discussed in unit 3 the carbocation has a planar geometry and, therefore, the nucleophile may engage the empty *p* orbital from either side of the molecule.



Thus as mentioned in unit 3, S_N1 reaction of an optically active alkyl halide should give recemic substitution products.

As in the case of S_N2 reaction the structure of the alkyl halide also effect the rate of the reaction. We are giving the relative rates of reaction of some alkyl bromides under typical S_N1 conditions in Table 11.7.

Table 11.7: Relative reaction rates of hydrolysis of some alkyl bromides under typical S_N1 conditions

Alkyl bromide	Relative rate
$CH_3—Br$	1.00[a]
$CH_3CH_2—Br$	1.00[a]
$(CH_3)_2CH—Br$	11.6
$(CH_3)_3C—Br$	1.2×10^6

[a] The observed reactions of the methyl or other primary bromides probably occur by different routes (S_N2, not S_N1).

Therefore, among alkyl halides, the order of relative rates is

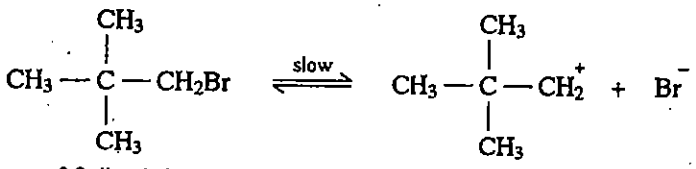
$$\textit{tert}\ RX > \textit{sec}\ RX > \textit{p}\ RX > CH_3X$$

This order is reasonable, since the order of stability of the intermediate carbocation formed in the slow rate determining step is also the same.

$$\underset{tert}{(CH_3)_3C^+} > \underset{sec}{(CH_3)_2CH^+} > \underset{p}{CH_3CH_2^+} > CH_3^+$$

The S_N1 reaction have been found to be subject to rearrangements when the intermediate carbocation can rearrange to a more stable carbocation. The following is an example of one such rearrangement:

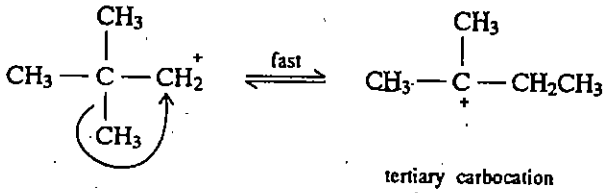
Step 1



1-bromo-2,2-dimethyl propane (neopentyl bromide)

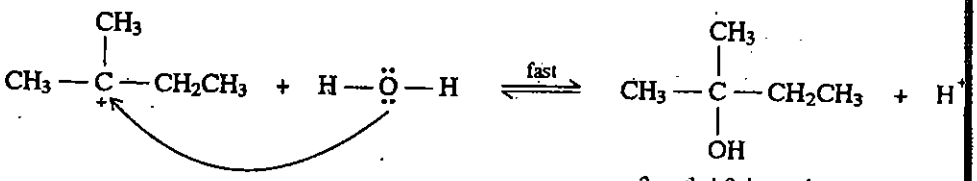
primary carbocation (less stable)

Step 2



tertiary carbocation (more stable)

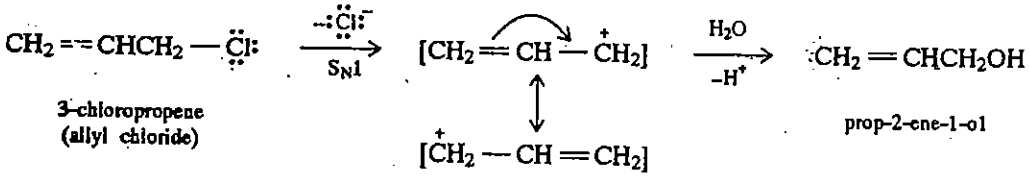
Step 3



2-methyl-2-butanol (*tert* amyl alcohol)

You can notice how that the primary carbocation ion rearranges, through the shift of a $-CH_3$ group, to produce the more stable tertiary carbocation.

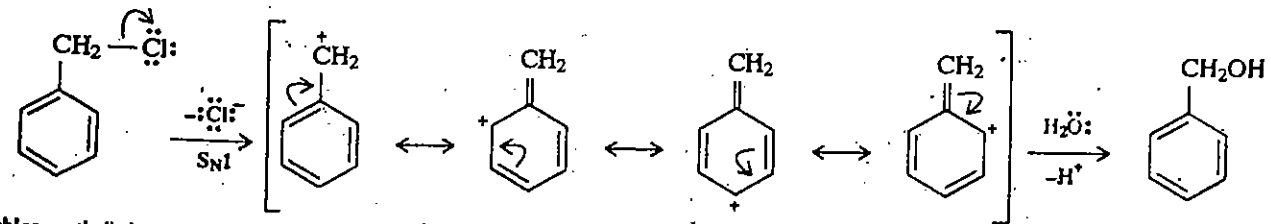
Substitution reactions of allylic and benzylic Halides : The behaviour of substituted alkyl halides such as allylic and benzylic halides in S_N1 and S_N2 reactions deserves to be considered separately. Both these halides are very reactive under both S_N1 and S_N2 conditions. They undergo S_N1 reaction at faster rate than tertiary alkyl halides. The reason for the enhanced reactivity under S_N1 conditions lies in the **resonance stabilisation** of the carbocation intermediate and for S_N2 reaction in the resonance stabilisation of the S_N2 transition state. To illustrate this, further let us consider S_N1 reaction of allyl chloride and benzyl chloride with H_2O.



3-chloropropene (allyl chloride)

prop-2-ene-1-ol

(Resonance structures of allyl cation)

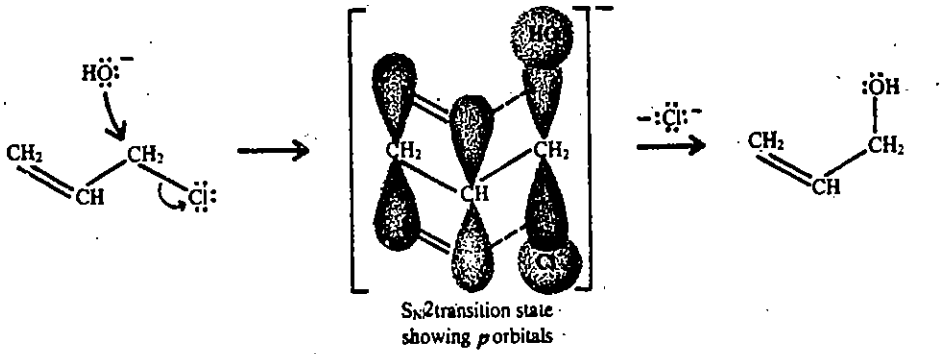


(chloromethyl) benzene (benzyl chloride)

(resonace structure for benzyl cation)

phenylmethanol (benzyl alcohol)

Now, consider the S_N2 reactions. Allylic halides and benzylic halides also undergo S_N2 reaction at a faster rate than primary alkyl halides or even methyl halides. The reason for the greater S_N2 reactivity of allylic and benzylic halides is stability of the transition state. In the case of allylic and benzylic halides partial overlap of the π bond orbitals helps in delocalisation of the negative charge on the transition structure thus increasing the rate of the reaction (see Fig. 11.4).



S_N2 transition state showing p orbitals

Fig. 11.4 : Stabilisation of the transition state in an S_N2 reaction of 3-chloropropene (allyl chloride), the case of (chloromethyl) benzene (benzyl chloride) is similar

SAQ 4

Which member of each of the following pairs would undergo the faster S_N2 reaction? Explain your aswer.

a) CH_2Cl or Cl

b) CH_2Cl or Cl

c) $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Cl$ or $(CH_3)_2CHCH_2Cl$

d) $CH_2=CHCH_2Cl$ or $CH_3CH_2CH_2Cl$

2) Elimination reactions: A side reaction that occurs during substitution reactions of alkyl halides is the elimination of HX (dehydrohalogenation) to produce an alkene.

Alkyl halide —(S_N1/S_N2)→ Substitution product

Alkyl halide —(E1/E2)→ Alkene (s)

Under appropriate conditions such as the use of a strong base (OH^- or OR^-), and high temperature, elimination can be the principal reaction and thus become a method for preparing alkenes. We have already introduced such reactions in unit 7.

Like the nucleophilic substitution reactions, elimination reactions of alkyl halides can proceed by either a first or a second order mechanism. The first order elimination reaction is symbolised as E1 and the second order elimination reaction as E2.

E1 reaction : In the absence of a strong base, tertiary alkyl halides, and to some extent secondary alkyl halides, dehydrohalogenate via the E1 mechanism. The mechanism has two steps.

The first step, as in S_N1 reactions is ionisation of the alkyl halide. Since, this is the slow i.e., rate determining step the E1 reaction follows first order kinetics.

Step 1 (slow)

$$(CH_3)_3C-Br \longrightarrow \underset{\text{transition state-I}}{[(CH_3)_3C^{\delta+} \cdots Br^{\delta-}]} \longrightarrow \underset{\text{carbocation intermediate}}{(CH_3)_3C^+} + :\ddot{Br}:^-$$

Step 2 (fast)

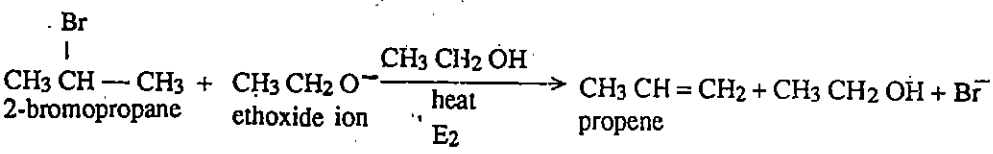
$$(CH_3)_2\overset{+}{C}-\underset{H}{CH_2} + \underset{\text{base}}{:\ddot{O}H_2} \longrightarrow \underset{\text{transition state-II}}{\left[(CH_3)_2C^{\delta+} \cdots \underset{H}{CH_2} \cdots H-O\overset{\delta+}{H_2}\right]^+} \longrightarrow (CH_3)_2C=CH_2 + H_3\overset{+}{O}:$$

Note that the base here attacks the hydrogen atom and not the carbon carrying the positive charge.

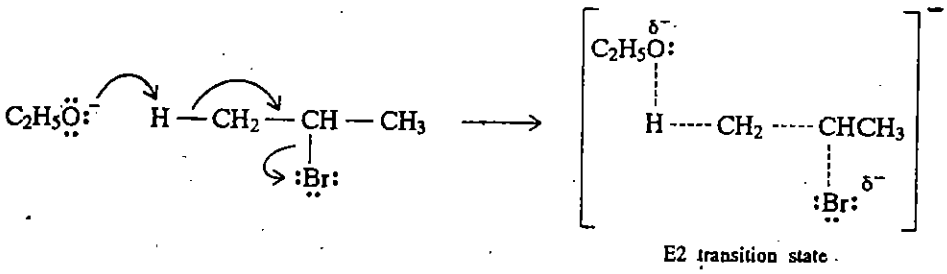
El reactions of alkyl halides occur under the same conditions as S_N1 reaction (polor solvent, very weak base etc.) Therefore the El reaction is a strong competitor of the S_N1 reaction. The order of reactivity of different halides types is the same in both reactions, that is *tert>sec>p*. The El reaction is favoured by the higher temperature and is most common in tertiary halides.

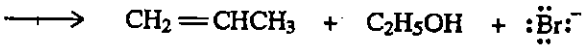
E2 elimination reaction is an example of β-elimination. In a β-elimination reaction two groups are eliminated from adjacent atoms. It is by far the most common type of elimination reaction in organic chemistry.

E2 reaction: The most useful elimination reaction of alkyl halides is the E2 reaction (bimolecular elimination). The E2 reactions of alkyl halides are favoured by the use of strong bases, such as OH^- or OR^- and high temperature. Typically the E2 reaction is carried out by heating the alkyl halide with KOH or $Na^+{}^-OCH_2CH_3$ in ethanol.



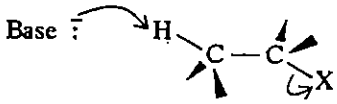
A mechanism consistent with the rate-law is tl e following one, in which the proton and the halide ion are removed simultaneously to give the alkene :





Stereochemical studies reveal that E2 elimination reactions are stereoselective *anti*-eliminations. The *anti*-elimination involves all backside electronic displacements.

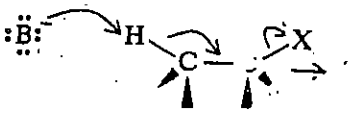
Backside attack of the base on the C—X bond



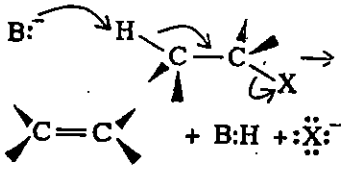
anti elimination

In a *syn*-elimination, H and X^- leave the alkyl halide molecule from the same side, in an *anti*-elimination, H and X^- leave from opposite sides.
An elimination reaction can occur in two stereodiamically different ways, illustrated as follows for the elimination of H—X from an alkyl halide.

Syn



anti



We have said earlier that substitution and elimination are competitive reactions; one reaction occurs at the expense of the other. Now, we consider the important variables which determine the direction of the reaction.

i) The structure of the alkyl halide
ii) The nature of the base.

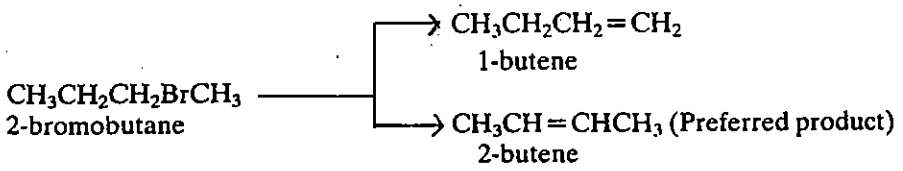
From the mechanism of S_N2 & E2 reaction, it is clear that branching in alkyl halides increases the ratio of elimination to substitution :

p RX *sec* RX *tert* RX →
Increasing rate of E2

←
Increasing ratio of S_N2

Thus the order of the reactivity with reference to the type of halides is *tert* > *sec* > *p*, which is also the order of stability of the resulting alkenes according to the Saytzeff rule. Now, let us discuss this rule.

Saytzeff rule : In the alkyl halides, where the halogen is not attached to the terminal carbon atom, elimination is possible in two directions, giving two isomeric alkenes. An illustrative example is the dehydrobromination of 2-bromobutane to give 1-and 2-butenes:

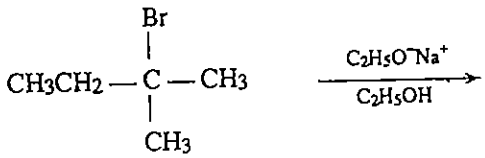


In the above reaction, the major product is 2-butene. This follows the rule formulated in 1875 by Alexander Saytzeff. Saytzeff rule states that in a dehydrohalogenation reaction of alkyl halides **the major product will be the one that has the more alkyl groups attached to the resultant carbon-carbon double bond.** The rule parallels the order of thermodynamic stability of the alkenes; that is, the alkene with more alkyl groups attached to the carbon-carbon double bond is more stable.

Because of the relative stability of the resultant alkenes, tertiary halides undergo dehydrohalogenation more readily than secondary halides, which dehydrohalogenate more readily than primary halides (as we have already concluded).

SAQ 5

Write the equation for the formation of alkenes from the following starting materials. If you expect more than one product, indicate which alkene is the major product.



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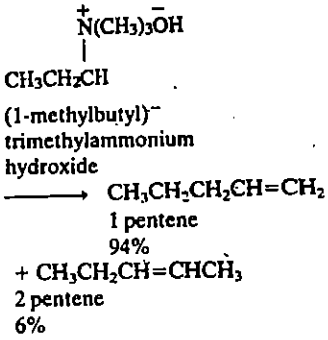
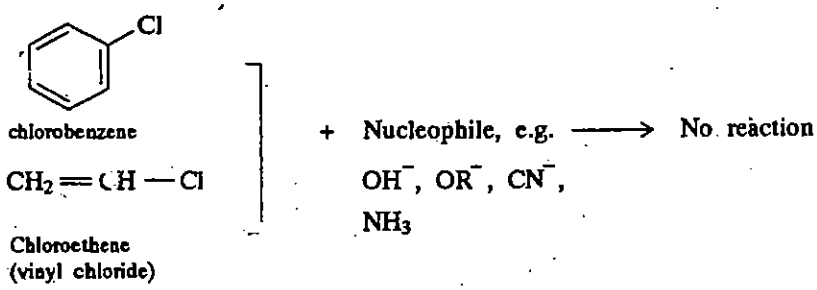
Elimination reaction in quaternary ammonium hydroxides ($R_4N^+OH^-$) does not follow Saytzeff rule, but they undergo elimination reactions and yield the Hofmann product, the alkene with fewer alkyl groups on the pi-bonded carbons. Such reactions are known as **Hofmann eliminations** and follow E2 mechanism. The formation of the less substituted less stable alkene can be attributed to steric hindrance in the transition state due to the group, e.g., butyl R_4N^+

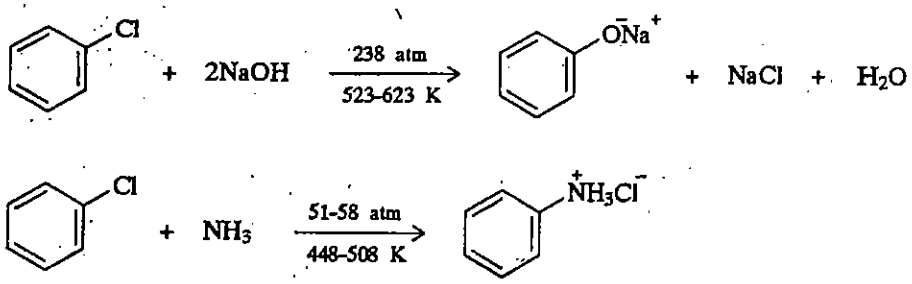


11.4.5 Chemical Properties of Aryl and Alkenyl Halides

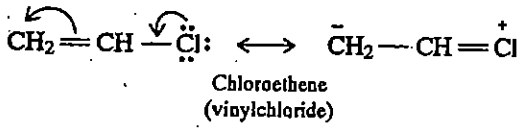
The aryl and alkenyl halides are relatively unreactive, they do not react under ordinary conditions with NaOH, $NaOC_2H_5$, NaCN, NaSH, H_2O, or NH_3.



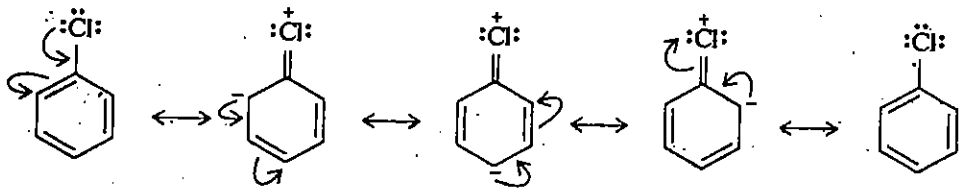
Aryl halides may be forced to react with nucleophiles under drastic conditions such as high temperature and pressure.



The reason for the low reactivity of the halogen atom in aryl and alkenyl halides is not quite clear. We have already encountered the one possible explanation of the low reactivity of aryl and alkenyl halides in subsection 11.4.1. The Cl atom in the C–Cl group is more tightly bound in Ar–Cl and C=C–Cl than in C–C–Cl because of the higher *s* character of sp^2 carbons. Another explanation is that due to resonance, the carbon-halogen bond in aryl and alkenyl halides acquires some double-bond character and hence the halogen atom is more strongly bound to carbon as compared to alkyl halides in which no resonance of this type exists:

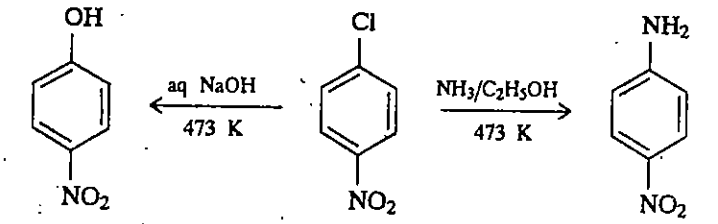


Chloroethene
(vinylchloride)



Chlorobenzene

On the other hand, when a strong electron withdrawing group is present at *ortho* and/or *para* to the halogen atom in aryl halides, the replacement of halogen by nucleophilic reagents is facilitated, e.g.

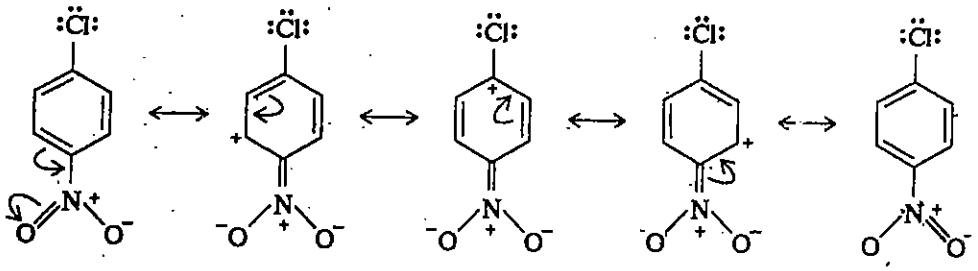


4-nitrophenol
(*p*-nitrophenol)

chloro-4-nitrobenzene
(*p*-chloronitrobenzene).

4-nitroaniline
p-nitroaniline

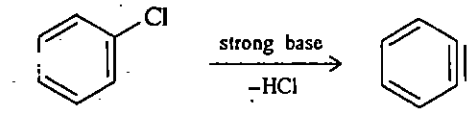
The resonance forms for the starting material (*p*-chloronitrobenzene) indicate a low electron density at the halogen-bearing carbon. Similar forms can be written for the *o*-chloronitrobenzene.



Resonance structure of chloro-nitrobenzene (*p*-chloronitrobenzene)

This facilitates attack by the hydroxide ion or other nucleophile.

Nucleophilic aromatic substitutions do not follow S_N1 and S_N2 pathways. They occur by two very different mechanism: The addition elimination mechanism and the benzyne intermediate mechanism, which involve the highly reactive elimination - reaction intermediate.



chlorobenzene benzyne

Mechanism of the nucleophilic aromatic substitutions will be described in the course of Organic Reaction Mechanism.

The aromatic ring to which halogen is attached can undergo typical electrophilic aromatic substitution reactions, which we have already discussed in Unit 9. As you would recall halogen is deactivating and *ortho*, *para* directing.

Elimination reactions of chloroethene (vinyl chloride) are less difficult, it is converted to ethyne by heating with base

$$CH_2=CH-Br+NaOH \xrightarrow{\text{heat}} HC\equiv CH+NaBr+H_2O$$

Chloroethene (vinyl chloride) undergoes polymerisation in the presence of radical initiators like peroxides to give polyvinyl chloride (PVC):

$$n CH_2=CHCl \longrightarrow -CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-$$

or $$(CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}})_n$$

So far we have been concerned with the nucleophilic substitution and elimination reactions of halogen derivatives. Now let us look at the reactions of these compounds with metals. But, before that try the following SAQ.

SAQ 6

How do you account for the fact that aryl and alkenyl halides are less reactive towards nucleophiles under ordinary conditions.

.....

.....

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11.5 ORGANOMETALLIC COMPOUNDS

Alkyl, aryl and alkenyl halides, when treated with metallic alloys, from organometallic compounds, in which carbon is bonded directly to a metal atom (R–M). For example, the reaction of chloroethane with a sodium lead alloy under pressure gives tetraethyl-lead.

$$4C_2H_5-Cl+4Na/Pb \longrightarrow (C_2H_5)_4Pb+4NaCl$$

chloroethane tetraethyl-lead

As stated earlier, tetramethyl and tetraethyl-lead are used as anti-knock additives to petrol.

Halogen derivatives of hydrocarbons are widely used to prepare **Grignard reagents** (organomagnesium halides), RMgX. These reagents are among the most useful classes of a compound in organic synthesis. A Grignard reagent is generally prepared by the reaction between magnesium and alkyl or aryl or ethenyl halide in dry aprotic solvent such as alcohol free ether.

$$R{-}X,\ Ar{-}X \xrightarrow[\text{dry ether}]{\text{Mg in}} \underset{\text{Grignard reagent}}{RMgX,\ ArMgX,\ CH_2{=}CHMgX}$$

or $CH_2{=}CHX$

Where R=alkyl, Ar=aryl, and X=Cl, Br or I.

Grignard reagents are highly reactive compounds because the carbon-magnesium bond is strongly polarised, making the carbon atom both nucleophilic and strongly basic. Grignard reagents, therefore, participate nucleophilic addition reaction. The mechanism of the nucleophilic addition of Grignard reagents to carbonyl group will be discussed in detail in unit 14. Grignard reagents are used to prepare a large variety of organic compounds. Some of the important reactions are:

i) Preparation of alkanes: Alkanes are prepared by the reaction of Grignard reagents with water, alcohols, ammonia, amines etc.:

$$RMgX + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{alkane}}{RH} + Mg(OH)X$$

$$RMgX + \underset{\text{alcohol}}{R'OH} \longrightarrow RH + Mg(OR')X$$

$$RMgX + \underset{\text{ammonia}}{NH_3} \longrightarrow RH + Mg(NH_2)X$$

$$RMgX + \underset{\text{amine}}{R'NH_2} \longrightarrow RH + Mg(NHR')X$$

ii) Preparation of alcohols: Primary alcohols are obtained either by the reaction of methanal and Grignard reagent followed by treatment with dilute acid:

$$\underset{\substack{\text{methanal}\\\text{(formaldehyde)}}}{HCHO} + RMgX \longrightarrow RCH_2OMgX \xrightarrow{H^+/H_2O} \underset{\text{primary alcohol}}{RCH_2OH} + Mg(OH)X$$

or by treatment of Grignard reagent with dry oxygen and subsequent decomposition by acid:

$$RMgX + \underset{\text{oxygen}}{O_2} \longrightarrow RO_2MgX \xrightarrow{RMgX} 2ROMgX \xrightarrow{H^+/H_2O} \underset{\substack{\text{primary}\\\text{alcohol}}}{2ROH} + 2Mg(OH)X$$

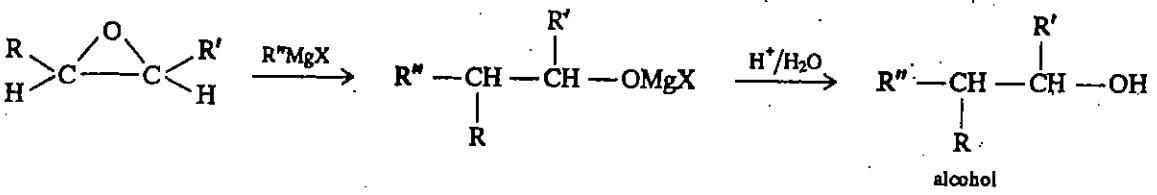
Secondary alcohols are obtained when a Grignard reagent is treated with any aldehyde (other than methanal) followed by decomposition of the addition product with a dilute acid:

$$\underset{\text{aldehyde}}{R'CHO} + RMgX \longrightarrow R'CH(OMgX){-}R \xrightarrow{H^+/H_2O} \underset{\text{secondary alcohol}}{R'CH(OH)R} + Mg(OH)X$$

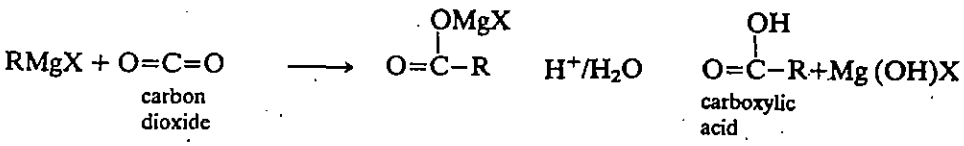
Tertiary alcohols are obtained on treatment of a ketone with Grignard reagent and subsequent addition of dilute acid:

$$\underset{\text{ketone}}{RC(=O)R'} + R''MgX \longrightarrow R{-}C(OMgX)(R'){-}R'' \xrightarrow{H^+/H_2O} \underset{\textit{tert}\text{-alcohol}}{R{-}C(OH)(R'){-}R''} + Mg(OH)X$$

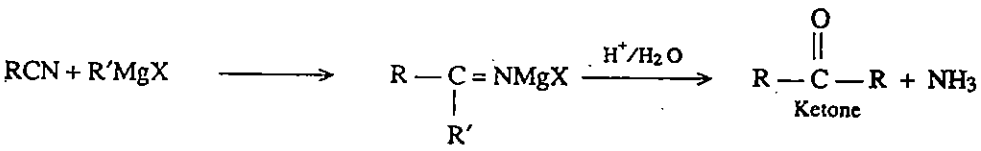
Alcohols are also obtained when epoxides are reacted with Grignard reagent and the addition product is hydrolysed with dilute acid:



iii) Preparation of carboxylic acids: The reaction of a Grignard reagent with carbon dioxide followed by decomposition of the addition product by dilute acid gives a carboxylic acid:



iv) Preparation of Ketones: Ketone can be prepared by the reaction of an alkyl nitrile with a Grignard reagent:



Using the reactions discussed above, attempt the following SAQ.

SAQ 7

How would you prepare primary, secondary and tertiary alcohols? Give one reaction for each case.

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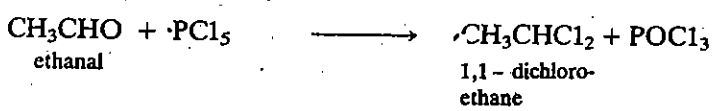
11.6 POLYHALOGEN DERIVATIVES

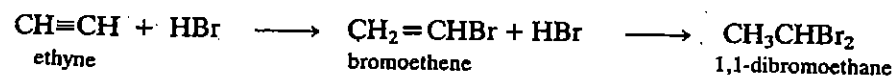
In this section we will briefly discuss some important di and tri halogen derivatives.

11.6.1 Dihalogen Derivatives

Gem or 1,1-dihalides are obtained either by the action of phosphorus pentahalides on aldehydes or ketones, e.g.,

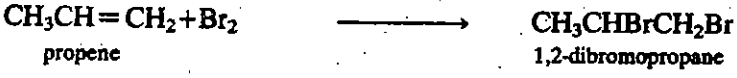


or by addition of halogen acids to alkynes, e.g.,



We have already discussed this reaction in unit 8.

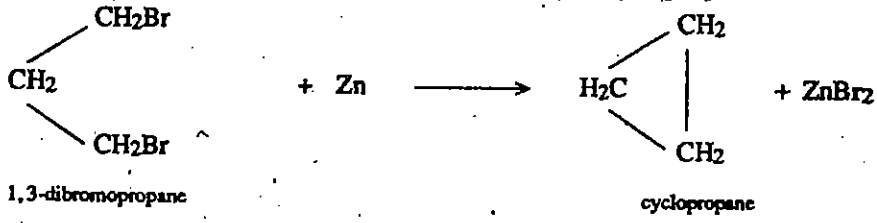
As mentioned in unit 7, vic or 1, 2-dihalides are prepared by the addition of halogens to alkenes, e.g.,



Let us discuss a few important reactions of dihalogen derivatives. Dehalogenation of 1,2-dihalides by zinc dust and methanol gives alkenes:

$$\underset{\text{1,2-dibromopropane}}{CH_3CHBrCH_2Br} + Zn/CH_3OH \longrightarrow \underset{\text{propene}}{CH_3CH{=}CH_2} + ZnBr_2$$

This reaction can also be used to prepare (3-6 membered) cyclic compounds. For example, trimethylene dibromide reacts with zinc to give cyclopropane:



1,3-dibromopropane — cyclopropane

In section 11.2 we mentioned some polyhalogen compounds derived from methane, i.e. dichloromethane (methylene chloride), trichloromethane (chloroform) and tetrachloromethane (carbon tetrachloride). These compounds are commercially important substances as they are widely used as solvents in laboratory and industry. In the following section we will discuss the chemistry of trichloromethane, a trihalogen derivative of methane.

11.6.2 Trihalogen Derivatives

One of the familiar examples of trihalogen derivatives is trichloromethane (chloroform). Trichloromethane was used as an anaesthetic till recently. Trichloromethane is prepared in the laboratory or industry by heating ethanol or propanone (acetone) with bleaching powder. The steps are:

$$\underset{\text{ethanol}}{CH_3CH_2OH} + \underset{\text{from bleaching powder}}{Cl_2} \longrightarrow \underset{\text{ethanal (acetaldehyde)}}{CH_3CHO} + 2HCl$$

$$\underset{\text{ethanal}}{CH_3CHO} + 3Cl_2 \longrightarrow \underset{\text{trichloroethanal}}{CCl_3CHO} + 3HCl$$

$$2CCl_3CHO + Ca(OH)_2 \longrightarrow \underset{\text{trichloromethane}}{2CHCl_3} + \underset{\text{calcium methanoate (calciumformate)}}{(HCO_2)_2Ca}$$

Bleaching powder provides chlorine which oxidises ethanol to ethanal in the first step and chlorinates the latter to trichloroethanal or trichloroacetaldehyde (chloral) in the second step. The reaction of tichloroethanal and calcium hydroxide (present in the bleaching powder) gives trichloromethane and calcium methanoate in the third step. When propanone (acetone) is used in place of ethanol, trichloropropane is formed in the first step which on reaction with calcium hydroxide gives trichloromethane and calcium ethanoate in the final step:

$$\underset{\text{propanone}}{CH_3COCH_3} + 3Cl_2 \longrightarrow \underset{\text{trichloropropanone}}{CCl_3COCH_3} + 3HCl$$

$$2CCl_3COCH_3 + Ca(OH)_2 \longrightarrow \underset{\text{trichloromethane}}{2CHCl_3} + \underset{\text{calcium ethanoate}}{(CH_3CO_2)_2Ca}$$

Trichloromethane is also prepared industrially by the chlorination of methane in the presence of nitrogen. Partially reduced cupric chloride is used as a catalyst. The amount of chlorine is suitably adjusted so as to give trichloromethane as the major product:

$$CH_4 + 3Cl_2 \longrightarrow CHCl_3 + 3HCl$$

Now, let us consider the properties of trichloromethane. It is sweet-smelling, colourless liquid. On boiling with alkali, it gives methanoate ion:

$$\underset{\text{trichloromethane}}{CHCl_3} + 4OH^- \longrightarrow 3Cl^- + \underset{\text{methanoate ion}}{HCOO^-} + 2H_2O$$

On warming trichloromethane with silver powder, ethyne is obtained:

$$\underset{\text{trichloro methane}}{2CHCl_3} + 6Ag \longrightarrow \underset{\text{ethyne}}{HC{\equiv}CH} + 6AgCl$$

When treated with concentrated nitric acid, trichloromethane gives trichloronitromethane (chloropicrin):

$$\underset{\text{trichloro-methane}}{CHCl_3} + HNO_3 \longrightarrow \underset{\text{trichloro-nitromethane}}{CCl_3NO_2} + H_2O$$

Trichloromethane is kept in well-stoppered dark coloured bottles, filled up to the brim, to avoid its oxidation to carbonyl chloride (phosgene), which is a poisonous gas. About 1% ethanol is added to convert any phosgene formed to harmless ethyl carbonate.

$$\underset{\text{trichloro methane}}{CHCl_3} + 1/2O_2 \longrightarrow \underset{\text{Carbonyl chloride (phosgene)}}{COCl_2} + HCl$$

$$COCl_2 + 2C_2H_5OH \longrightarrow \underset{\text{ethyl carbonate}}{(C_2H_5)_2CO_3} + 2HCl$$

On heating trichloromethane with a primary amine and ethanolic potassium hydroxide, isocyanide is formed which has a bad smell. This reaction is called **carbylamine reaction**, a delicate test for trichloromethane and also for primary amines.

$$\underset{\text{trichloro methane}}{CHCl_3} + \underset{\text{amine}}{RNH_2} + 3KOH \longrightarrow \underset{\text{(isocyanide)}}{RNC} + 3KCl + 3H_2O$$

Tribromomethane (bromoform) is obtained by methods similar to those used for trichloromethane. Industrially it is prepared by the electrolysis of an aqueous solution of propanone or ethanol containing sodium carbonate and potassium bromide.

Triiodomethane (iodoform) is prepared on a commercial scale by a similar method described above for tribromomethane. In place of potassium bromide, potassium iodide is used. Triiodomethane is a yellow crystalline solid, insoluble in water but soluble in ethanol or ether. It is used as an antiseptic.

11.7 USES OF HALOGEN DERIVATIVES

Many chloro compounds are used as insecticides, e.g., DDT. [2, 2-bis (*p*-chlorophenyl) 1,1,1-trichloroethane or *p, p*-dichlorodiphenyl trichloroethane, BHC (benzene hexachloride). DDT is manufactured by heating chlorobenzene and trichloroethanal with concentrated sulphuric acid.

$$\underset{\text{chlorobenzene}}{2\ C_6H_5Cl} + \underset{\text{trichloro-ethanal}}{CCl_3CHO} \xrightarrow{H_2SO_4} \underset{\text{DDT}}{Cl{-}C_6H_4{-}CH(CCl_3){-}C_6H_4{-}Cl}$$

Commercial DDT is a mixture of 75% *p,p'*-compound, 20% *o,p'* compound and 5% of other impurities. Most countries have banned the use of DDT, it is poisonous to human and it tends to concentrate in the environment owing to its slow degradation, the half life being 10 years. Similarly the insecticide-benzene hexachloride (BHC) also causes environmental pollution. We have mentioned the preparation of BHC in unit 9. Hexachloroethane is used as a moth repellant.

Chlorofluorocarbons (CFCs) are derivatives of methane and ethane which used as refrigerants and as aerosol propellants under the name of Freons. Freon-12, CF_2Cl_2, is the most commonly used refrigerant. The extensive use of CFCs is believed to have led to depletion of ozone layer in the atmosphere. CFCs are prepared by the action of hydrogen fluoride on tetrachloromethane (carbon tetrachloride), trichloromethane and hexachloroethane. Tetrafluoroethene ($CF_2{=}CF_2$) on polymerisation gives a

plastic **Teflon.** It is unaffected by chemical reagents, even by boiling aqua regia. It is widely used as a liner in frying pans and on other utensils and tools to provide nonsticking surfaces. Polychlorofluoroethenes are used as oils and greases. Perfluoroheptane is used in the separation of uranium isotopes. Poly (chloroethene) or polyvinyl chloride (PVC) is a plastic material of commercial importance.

11.8 LAB DETECTION

The presence of halogen in an organic compound is readily detected by the **Beilstein test.** In this test a small amount of the compound is placed on a small loop of copper wire, and the loop heated in a flame. A green flame is evidence of the presence of halogen. To ascertain which halogen is present, the covalently bonded halogen has to be converted to the halide ion which can then be identified by the usual methods of inorganic qualitative analysis. This is done by two methods; through sodium fusion (treatment with hot molten sodium metal):

$$\underset{\text{organic compound}}{Na + RX} \xrightarrow{\text{heat}} Na^+X^-$$

or through Schoniger oxidation by oxygen gas under alkaline condition

$$\underset{\text{organic compound}}{RX + O_2} \xrightarrow{NaOH} Na^+X^- + H_2O$$

In alkyl halides, benzyl halides and allyl halides the presence of halogen can be detected by warming the organic compound with alcoholic silver nitrate. The silver halide formed can be analysed further.

$$RX + AgNO_3 \longrightarrow AgX(s)\downarrow + RONO_2$$

However, aryl halides and alkenyl halides will not react with alcoholic silver nitrate.

The reaction helps in distinguishing alkyl halides from aryl and alkenyl halides.

11.9 SUMMARY

In this unit we have described the chemistry of halogen derivatives of hydrocarbons. We are summarising below what we have studied:

- Substitution of one or more hydrogen atoms in hydrocarbons by a halogen atom(s) gives rise to halogen derivatives: alkyl halides, aryl halides and alkenyl halides. Monohalogen derivatives of alkyl halide can be further classified as primary, secondary and tertiary halides depending on the alkyl group to which halogen is attached.
- Alkyl halides can be prepared from alcohols, from alkanes, from Grignard reagents and through halogenation of hydrocarbon in the presence of light or heat and/or catalysts.
- The halogen in alkyl halides can be replaced by various nucleophiles. Reaction occur by two different pathways, S_N1 and S_N2. Benzyl and allyl halides are more reactive than alkyl halides. Aryl and vinyl halides are least reactive and they do not follow S_N2 and S_N1 paths. The reactivity order of halides is allyl>benzyl > alkyl > aryl or vinyl. However, when a strong electron-withdrawing group is present in *ortho*-or/and *para*-position to the halogen atom in the benzene ring, the reactivity of the aryl halide is enhanced.
- Alkyl halides undergo elimination reaction (dehydrohalogenation) to give alkenes. These reactions occur by the E1 or E2 pathway. If the halides are such that the loss

of a hydrogen on adjacent carbon (β hydrogen) can occur from either side, isomeric alkenes are formed. Usually, the most stable i.e. more highly substituted alkene is formed as the major product (Saytzeff rule).

- Alkyl or aryl halides react with magnesium to form alkyl or aryl magnesium halides called the Grignard reagents. They are very reactive compounds and take part in many reactions to give alkanes, alcohols (primary, secondary and tertiary), ketones and carboxylic acids, etc.
- The di- and tri-halogen derivatives of alkanes are also reactive compounds.
- The halogen derivatives are very useful in industry. The chloro compounds are powerful insecticides and moth repellants. The chlorofluoro compounds (Freons) are refrigerants and aerosol propellants. Polymerisation of vinyl chloride and tetrafluoroethylene gives plastic in the name PVC and teflon, respectively.
- The halogen can be detected as halide ion. Infrared spectroscopy can be used to infer the presence of halogen in organic compounds.

11.10 TERMINAL QUESTIONS

1) Write the equations for the following reactions:

a) $CH_3CH_2CH_2CH_2Br + NaOH\ (aq) \longrightarrow$

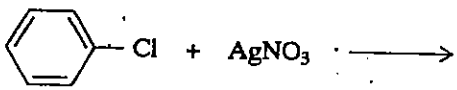
b) $C_6H_5CH_2Cl + H_2O \longrightarrow$

c) $CH_3CH_2CH_2Br + NaSH \longrightarrow$

2) Complete the equations given below:

a) $CH_3CH_2CH_2Br + Na^{+-}OCH_2CH_3 \longrightarrow$

b) $C_6H_5CH_2Cl + AgNO_3 + H_2O \longrightarrow$

c)  $+ AgNO_3 \longrightarrow$

3) Write the equation for each of the following reactions:

a) 2, 4-dinitrochlorobenzene and sodium hydroxide

b) 2, 4-dinitrochlorobenzene and sodium phenoxide ($C_6H_5O^-Na^+$)

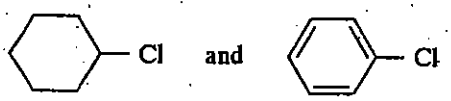
c) 2, 4-dinitrochlorobenzene and ammonia

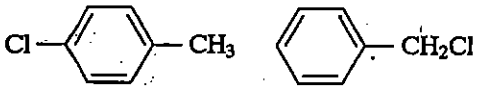
4) Complete the equation for each of the following reactions and if more than one product is formed, indicate which one is major.

a) $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 + KOH \xrightarrow{\text{alcohol}}$

b) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-Br + Na^{+-}OC_2H_5 \xrightarrow{\Delta}$

5) Name a simple chemical test or reagent which will readily distinguish between each of the following pair of compounds.

a)  and

b) 

c) $CH_2{=}CHCH_2{-}Cl$ and $CH_3CH{=}CHCl$

11.11 ANSWERS

Self Assessment Questions

1) a) Primary alkyl halide

b) tertiary alkyl halide

c) secondary alkyl halide

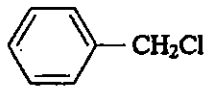
2) a) $C_6H_5—CH_2CH_3 + Br_2 \longrightarrow C_6H_5CHBrCH_3 + HBr$
ethylbenzene → 1-bromo-1-phenylethane

b) $CH_3CHOHCH_3 \xrightarrow{HBr} CH_3CHBrCH_3$

c) $CH_3CH=CH_2 \xrightarrow[\text{peroxide}]{HBr} CH_3CH_2CH_2Br$

d) $CH_3CHOHCH_3 \xrightarrow[\text{Heat}]{HCl} CH_3CHClCH_3$

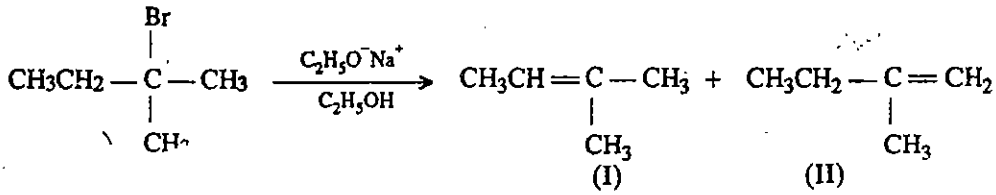
3) Increasing order of boiling point of following alkyl halides:
$CH_3Cl<CH_2Cl_2<CHCl_3<CCl_4$
Since molecular weight of compounds is also increasing in the same order

4) a) 

b) (Chloromethyl) benzene (benzyl chloride) undergoes S_N2 reaction at a faster rate than chlorobenzene. The reason for greater S_N2 reactivity of (chloromethyl) benzene is the stability of transition state. Further, the low reactivity of chlorobenzene is attributed to the stronger Ar—Cl bond.

c) $(CH_3)_2CHCH_2Cl$ d) $CH_2=CHCH_2Cl$

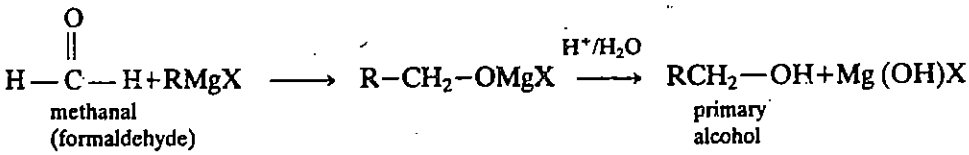
5) Over all reaction can be written as



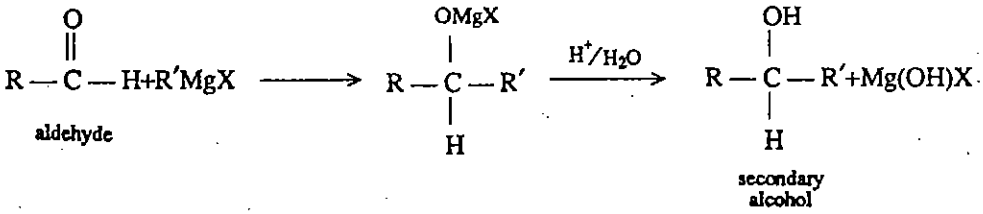
Two products are formed in this case, one (I) is three R substituted alkene and the other (II) is two R substituted, therefore, according to Saytzeff rule I alkene is the major product.

6) There are two reasons (1) the Cl atom in C—Cl group is more tightly bond in Ar—Cl and C=C—Cl than C—C—Cl because of higher *s* character of sp^2 carbon (ii) as shown in section 11.4, due to the resonance Ar—Cl and C=C—Cl acquire some double bond character.

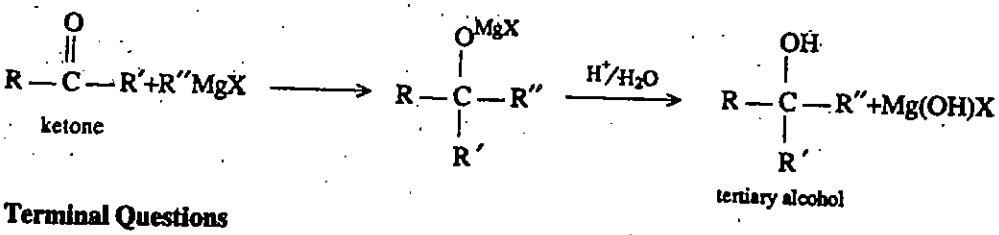
7) Primary alcohols are prepared by the reaction of Grignards reagents with methanal and followed by hydrolysis.



Secondary alcohols are obtained when a Grignard reagent reacts with an aldehydes (other than methanal) followed by hydrolysis.



Tertiary alcohols are prepared by the action of a ketone with Grignard reagent and subsequent addition of dilute acid



Terminal Questions

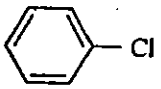
1) a) $CH_3CH_2CH_2Br + NaOH(aq) \longrightarrow CH_3CH_2CH_2OH + NaBr$

b) $C_6H_5CH_2Cl + H_2O \longrightarrow C_6H_5CH_2OH + HCl$

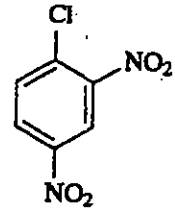
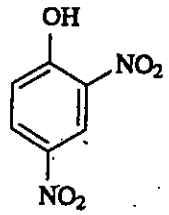
c) $CH_3CH_2CH_2Br + NaSH \longrightarrow CH_3CH_2CH_2SH + NaBr$

2) a) $CH_3CH_2CH_2Br + Na^+{}^-OCH_2CH_3 \longrightarrow CH_3CH{=}CH_2 + CH_3CH_2OH + NaBr$

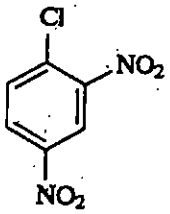
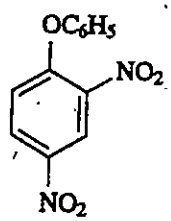
b) $C_6H_5CH_2Cl + AgNO_3 + H_2O \longrightarrow C_6H_5CH_2OH + AgCl$

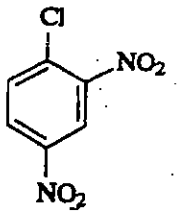
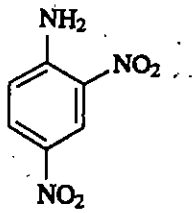
c)  + $AgNO_3$ + H_2O ⟶ no reaction.

3)

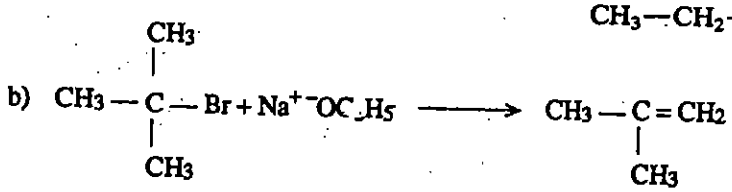
a)  + NaOH $\xrightarrow{-NaCl}$ 

2,4-dinitrohlorobenzene — 2,4-dinitrophenol

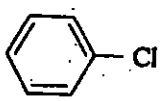
b)  + $NaOC_6H_5$ $\xrightarrow{-NaCl}$ 

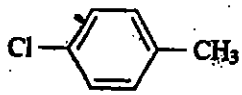
c)  + NH_3 $\xrightarrow{-HCl}$ 

4) a) $CH_3CH_2-\underset{Br}{CH}-CH_3 + KOH \xrightarrow{\text{alcohol}} CH_2-CH=CH-CH_3 +$ (major product, More substituted) $CH_3-CH_2-CH=CH_2$

b) 

5) Following pairs can be distinguished by the action of alcoholic $AgNO_3$ reagent with the halides.

a) With alcoholic $AgNO_3$  will not react

b)  also will not react with alcoholic $AgNO_3$

c) $CH_3CH{=}CHCl$ also will not react with $AgNO_3$.

UNIT 12 ALCOHOLS AND PHENOLS

Structure

12.1 Introduction
Objectives

12.2 Classification

12.3 Preparation of Alcohols and Phenols
General Methods of the Preparation of Alcohols
General Methods of the Preparation of Phenols
Commercial Preparations of Alcohols and Phenols

12.4 Physical Properties

12.5 Spectral Properties

12.6 Chemical Properties
Basicity and Acidity of Alcohols and Phenols
Reaction of Alcohols
Reaction of Phenols

12.7 Polyhydric Alcohols
Dihydric Alcohols
Trihydric Alcohols

12.8 Industrial Uses of Alcohols and Phenols

12.9 Lab Detection

12.10 Summary

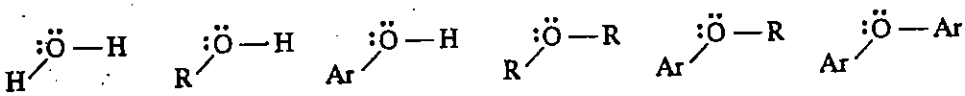
12.11 Terminal Questions

12.12 Answers

12.1 INTRODUCTION

In the previous Unit, we described the halogen derivatives of hydrocarbons. In this Unit and in subsequent Units we will discuss oxygen-containing organic compounds.

Alcohols and phenols can be regarded as monoalkyl and monoaryl substitution products of water, respectively. Similarly ether can also be considered a derivative of water in which both the hydrogen atoms of the water molecule have been replaced by alkyl or aryl groups or by both. We shall study the chemistry of ethers in Unit 13.



In this unit we shall take up alcohols and phenols. They may also be defined as hydroxy derivatives of hydrocarbons. Alcohols and phenols provide us with a great number of useful products, which include germicides, antifreeze agents, pharmaceuticals, explosives, solvents and plastics.

Here, first we will discuss the classification of alcohols and phenols, and then give you an outline of the different methods available for the preparation of alcohols and phenols. We will then review the physical properties of alcohols and phenols. The chemical properties of alcohols and phenols will be considered separately as the two types of compounds differ widely in their chemical behaviour. We will also take up the industrial uses of alcohols and phenols and the precautions to be taken in their handling. Finally, we will consider the methods employed for their detection.

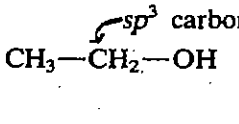
Objectives

After studying this unit, you should be able to:

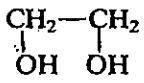
- classify alcohols and phenols,
- outline the preparation of alcohols and phenols,
- decribe the commercial methods for manufacture of alcohols and phenols,
- define the physical and spectral properties of alcohols and phenols,
- explain the comparative reactivity of primary, secondary and tertiary alcohols, and phenols,
- describe the reactions of alcohols and phenols,
- list and describe the industrial uses of alcohols and phenols, and
- describe the laboratory detection of alcohols and phenols.

12.2 CLASSIFICATION

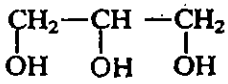
Hydrocarbons in which an sp^3 carbon carries a hydroxyl (–OH) group are called alcohols. Depending on the number of hydroxyl groups present in the molecule, alcohols are called monohydric (1 –OH group), dihydrics (2 –OH groups), trihydric (3 –OH groups) or polyhydric (more than 3 –OH groups).



ethanol
(ethyl alcohol)
monohydric alcohol

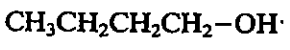


1,2-ethanediol
or ethane-1,2 diol
(glyc
dihydric alcohol

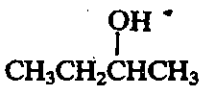


1,2,3-propanetriol
or propane-1,2,3, triol
(glycerol)
trihydric alcohol

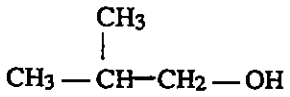
Monohydric alcohols, like the alkyl halides, may be subdivided into primary, secondary and tertiary alcohols. Primary alcohols contain a $-CH_2-OH$ group, secondary alcohols contain the $R_2CH—OH$ group and tertiary alcohols contain the $R_3C—OH$ group. For example, the molecular formula C_4H_9OH can represent the following four monohydric alcohols:



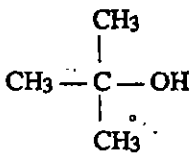
1-butanol
(butyl alcohol)
primary alcohol



2-butanol
(secondary butyl alcohol)
secondary alcohol

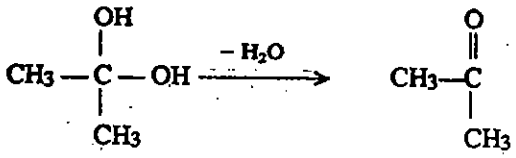


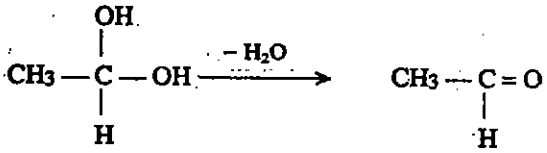
2-methyl-1-propanol
(isobutyl alcohol)
primary alcohol



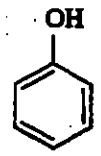
2-methyl-2-propanol
(*tert* butyl alcohol)
tertiary alcohol

Unlike gem dihalides gem diols are unstable as they undergo dehydration to the corresponding aldehyde or ketone.

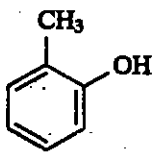




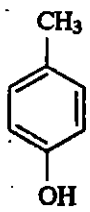
Phenols are aromatic compounds in which hydroxyl groups are attached to the benzene nucleus so they have the hydroxyl group on an aryl sp^2-hybridised carbon. Phenols are classified as mono, di or tri hydric on the basis of the number of —OH groups present in the ring. Some examples of phenols are given below.



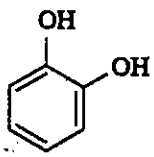
benzenol (phenol)



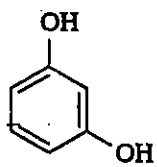
2-methylbenzenol (*o*-cresol)



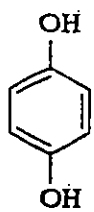
4-methylbenzenol (*p*-cresol)



1,2-benzenediol (catechol)

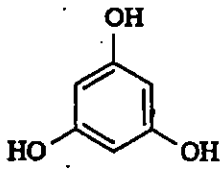


1,3-benzenediol (resorcinol)

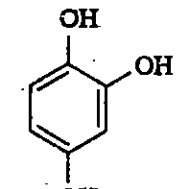


1,4-benzenediol (quinol or hydroquinone)

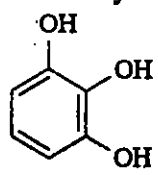
Monohydric phenols **Dihydric phenols**



1,3,5-benzenetriol (phloroglucinol)



1,2,4-benzenetriol (hydroxyquinol)



1,2,3-benzenetriol (pyrogallol)

Trihydric phenols

Common names of important phenols are still widely used, therefore, in this text we use both common names and IUPAC names.

Replacement of oxygen in alcohols and phenols by sulphur gives thioalcohols and thiophenol, respectively. We will consider the chemistry of thioalcohol and thiophenols in Unit 14. Let us now turn to the preparation of alcohols and phenols.

12.3 PREPARATION OF ALCOHOLS AND PHENOLS

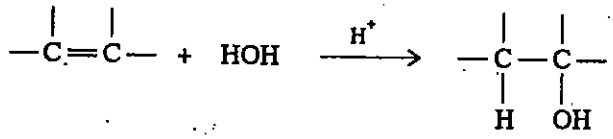
In this section, we will first consider the general methods for the laboratory preparation of alcohols and phenols and then take up the industrial preparation of a few important members of the two classes of compounds.

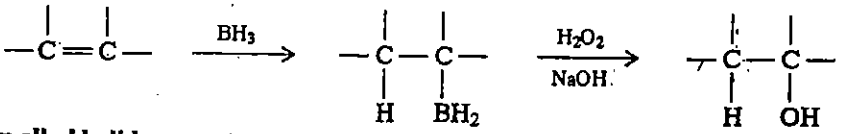
12.3.1 General Methods of the Preparations of Alcohols

Alcohols can be prepared from alkenes, alkyl halides, esters, ethers, aldehydes, ketones and from the Grignard reagents. General reactions of these methods of preparation are summarised below in Table 12.1.

Table 12.1: Preparation of Alcohols

From alkenes





From alkyl halides

$R—X + OH^-/H_2O \longrightarrow ROH + X^-$

From esters

$$RCOOR' + OH^- + H_2O \longrightarrow RCOOH + R'OH$$

or H^+/H_2O

From ethers

$$R{-}O{-}R + H_2O \xrightarrow{H_2SO_4} 2ROH$$

From aldehydes and ketones

$$-C{=}O \xrightarrow{2\,[H]} -\underset{\displaystyle H}{\overset{\displaystyle |}{C}}-OH$$

From Grignard reagents

$$-C{=}O + RMgX \xrightarrow[2.\ H^+/H_2O]{1.\ \text{dry ether}} -\underset{\displaystyle R}{\overset{\displaystyle |}{C}}-OH$$

Let us study these methods of preparation in a brief manner.

i) **From Alkenes:** We have already described the acid catalysed hydration of alkenes in Unit 7. In this reaction the direction of addition is governed by the Markownikoff's rule. The general reaction is,

$$-C{=}C- + HOH \xrightarrow{H^+} -\underset{\displaystyle H}{\overset{\displaystyle |}{C}}-\underset{\displaystyle OH}{\overset{\displaystyle |}{C}}-$$

This method is employed for the preparation of several alcohols:

$$\underset{\text{ethene}}{CH_2{=}CH_2} + HOH \xrightarrow{H^+} \underset{\text{ethanol}}{CH_3CH_2{-}OH}$$

$$\underset{\text{propene}}{CH_3CH{=}CH_2} + HOH \xrightarrow{H^+} \underset{\substack{\text{2-propanol}\\ \text{(isopropyl alcohol)}}}{CH_3\overset{\displaystyle OH}{\overset{|}{C}}HCH_3}$$

If sulphuric acid is used as the acid catalyst the reaction proceeds as follows:

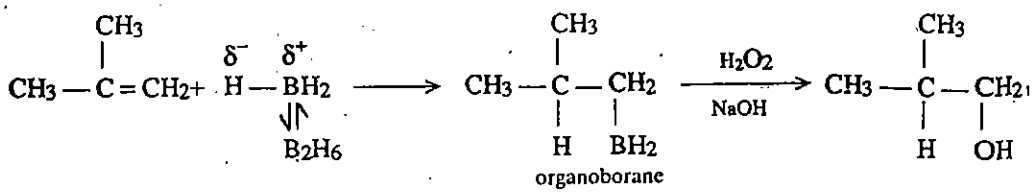
$$\underset{\text{ethene}}{CH_2{=}CH_2} + \underset{\text{sulfuric acid}}{HOSO_2OH} \longrightarrow \underset{\text{ethyl hydrogensulphate}}{CH_3CH_2OSO_2OH}$$

$$CH_3CH_2OSO_2OH \xrightarrow{H_2O} \underset{\text{ethanol}}{CH_3CH_2OH} + H_2SO_4$$

$$RCH{=}CH_2 + HOSO_2H \longrightarrow RCH(OSO_2H)CH_3 \xrightarrow{H_2O} \underset{\text{secondary alcohol}}{RCH(OH)CH_3}$$

These reactions are useful for laboratory synthesis as well as industrial preparation of alcohols.

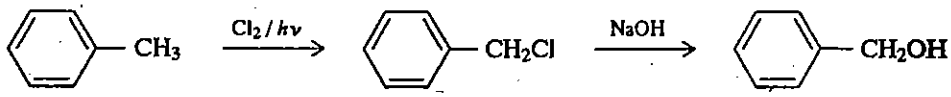
Hydroboration-oxidation method is also important because it leads to overall, effective anti-Markownikeft addition of water. We have already described this method in Unit 7. In this method diborane, B_2H_6, is allowed to react with alkene in an inert solvent such as ether. Diborane is in ready equilibrium with the Lewis acid borane, BH_3, which adds to the alkene. Here the electron seeking (acidic) part of reagent is boron, and addition of BH_3 proceeds according to Markowni Koff's rule to give an intermediate organoborane compound. Oxidation of this intermediate with basic hydrogen peroxide convert it to an alcohol.



ii) From Alkyl Halides: Hydrolysis of alkyl halides with an aqueous solution of an alkali is a common and convenient method for the synthesis of alcohols, e.g.,

$$\underset{\text{alkyl halide}}{R{-}X} + \underset{\text{aqueous alkali solution}}{OH^-/H_2O} \longrightarrow \underset{\text{alcohol}}{R{-}OH} + X^-$$

These reactions can proceed via S_N1 or S_N2 mechanism which we have described in Unit 11. A useful application of this method is in the synthesis of phenylmethanol (benzyl alcohol) from (chloromethyl) benzene (benzyl chloride) which is itself obtained from methylbenzene (toluene) as shown below:



methylbenzene (chloromethyl) benzene phenylmethanol

iii) From Esters: Alcohols may be prepared by base or acid catalysed hydrolysis of esters.

$$\underset{\text{esters}}{RCOOR'} + \underset{\text{or } H^+/H_2O}{OH^-/H_2O} \longrightarrow \underset{\text{carboxylic acid}}{RCOOH} + \underset{\text{alcohol}}{R'{-}OH}$$

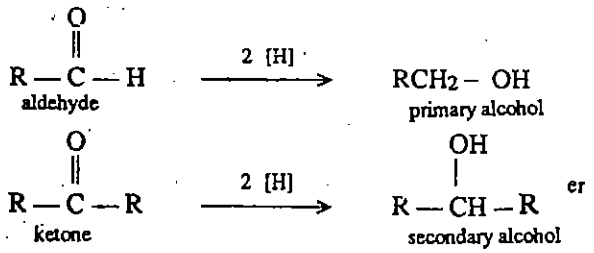
This method is used industrially as certain alcohols occur in nature as esters.

iv) From Ethers: Alcohols are also obtained by heating ethers with dilute sulphuric acid under pressure:

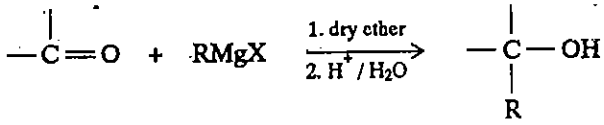
$$C_2H_5{-}O{-}C_2H_5 + H_2O \xrightarrow{H_2SO_4} \underset{\text{ethanol}}{2C_2H_5{-}OH}$$

This method is important industrially as ethers are formed as by-products in the preparation of some alcohols. We will discuss this reaction further in detail in Unit 13.

v) From Aldehydes and Ketones: Alcohols are also obtained by the reduction of aldehydes and ketones with sodium and ethanol or H_2/Ni or by metal hydrides, such as lithium aluminium hydride. Aldehydes give primary alcohols, ketones secondary alcohols.



vi) From Grignard Reagents: Primary, secondary and tertiary alcohols are also prepared by the reaction of suitable carbonyl compound with the Grignard reagent. We have already studied this method in Unit 11.



SAQ 1

Write chemical equation, showing all necessary reagents, for the preparation of 2-butanol by each of the following methods:

a) hydration of an alkene

.....

b) hydrolysis of an alkyl halide

.....

c) use of a Grignard reagent

.....

d) reduction of a ketone

.....

12.3.2 General Methods of the Preparation of Phenols

Phenols can be prepared from arylsulphonic acid, phenolic acids, diazonium salts and from Grignard reagents. General reactions of these methods of preparation are summarised below in Table 12.2.

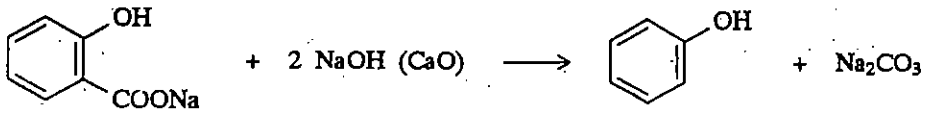
Table 12.2: Preparation of Phenol

Fusion of arylsulphonates with sodium hydroxide

$$ArSO_3Na \xrightarrow[2.\ H^+]{1.\ 573\ K/NaOH} Ar{-}OH$$

Phenol

Heating phenolic acid with soda-lime



Boiling diazonium salt with water

$$ArN_2^+X^- + H_2O \longrightarrow Ar{-}OH + HX + N_2$$

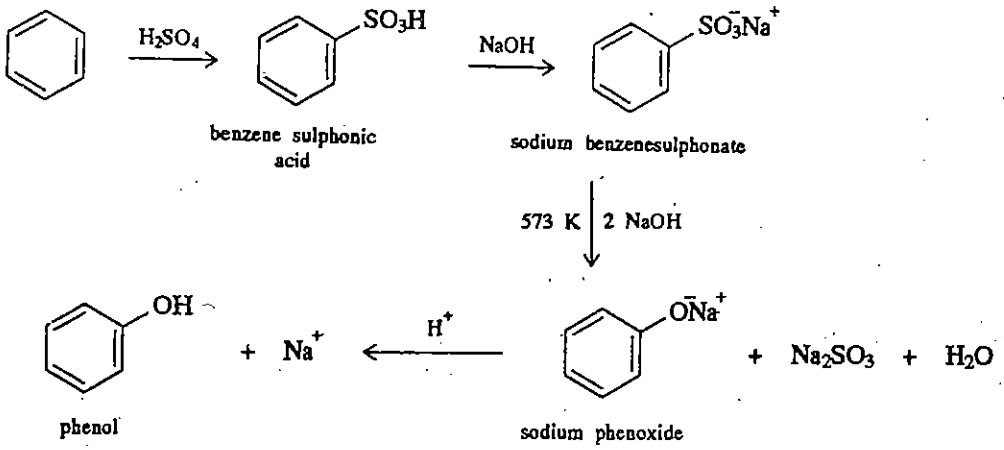
Action of oxygen on Grignard reagent followed by hydrolysis

$$2ArMgX + O_2 \longrightarrow 2ArOMgX \xrightarrow{H^+/H_2O} 2Ar{-}OH$$

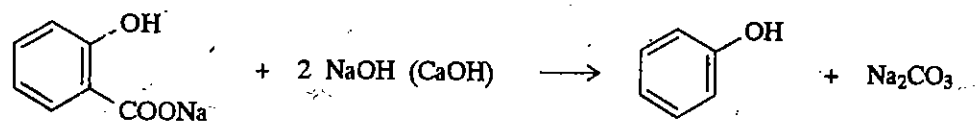
Let us study these reactions one by one.

i) Fusion of arylsulphonates with sodium hydroxide:

Phenol may be prepared by the fusion of sodium benzenesulphonate obtained through sulphonation of benzene (Unit 9), with sodium hydroxide. The sodium phenoxide produced in the reaction is converted into the free phenol by treatment with acid.

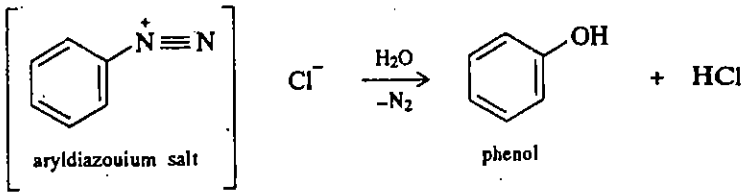


ii) Decarboxylation phenolic acids with soda-lime:



iii) Boiling diazonium salt with water:

Aromatic amines react with nitrous acid to give diazonium salts which, unlike their aliphatic analogues, are stable at low temperature and can be isolated. The aqueous solution of the salt decomposes to phenol on boiling with evolution of N_2.



iv) Action of oxygen on Grignard reagent followed by hydrolysis:

Just as Grignard reagent adds to CO_2, aryl Grignard reagents add to molecular oxygen.

The intermediate reacts with another molecule of the Grignard reagent and hydrolysis of the product gives phenol.

$$ArMgBr + O_2 \longrightarrow Ar{-}O{-}O{-}MgBr \xrightarrow{ArMgBr}$$

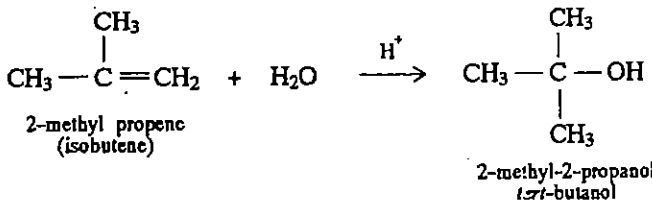
$$2\ Ar{-}O{-}MgBr \xrightarrow{H^+/H_2O} 2Ar{-}OH + 2\,Mg(OH)Br$$

12.3.3. Commercial Preparation of Alcohols and Phenols

Alcohols and phenols are of great commercial importance. In this section you will learn how large quantities of these compounds are prepared from different abundant natural sources.

i) Commercial preparation of alcohols

a) **By the catalytic hydration of alkenes in dilute acid solution:** We have already come across the conversion of alkenes to alcohol in connection with the general methods for small scale preparation of alcohols. The method has been extended to commercial preparations of some alcohols, such as ethanol and 2-propanol. The reactions for the preparation of ethanol and 2-propanol have been already shown. Similarly, hydration of 2-methylpropene (isobutene) in aqueous acidic medium gives *tert*-butanol.



In a recent modification ethene is hydrated directly by passing a mixture of the alkene and steam over a solid acid catalyst (phosphoric acid or silica at 573 K at a pressure of about 70 atmospheres:

$$\underset{\text{ethene}}{CH_2{=}CH_2} + H_2O \xrightarrow[70\ \text{atm}]{573\ \text{K}} \underset{\text{ethanol}}{CH_3CH_2OH}$$

b) **By heating a mixture of carbon monoxide and hydrogen under pressure in the presence of a catalyst:** This method is used for the preparation of methanol.

$$CO + 2H_2 \xrightarrow[533\ \text{K},\ 150\ \text{atm}]{\text{Cu Catalyst}} CH_3OH$$

c) **By the oxidation of natural gas:** A mixture of methanol, ethanol, propanols and butanols is obtained. Catalytic oxidation of methane gives methanol:

$$CH_4 + \frac{1}{2}O_2 \xrightarrow[473\ \text{K}]{\text{Cu tube}} CH_3OH$$

d) **Fermentation of starch:** This method has been the source of ethanol, the constituent of alcoholic beverages responsible for their intoxicating action, since times immemorial. Common sources of starch are wheat, barley, potato, etc. These are mashed with hot water and heated with malt (germinated barley) which contains the enzyme 'diastase'. Enzymatic hydrolysis of starch at 323 K gives the sugar maltose:

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + \frac{n}{2}H_2O \xrightarrow{\text{diastase}} \frac{n}{2}\underset{\text{maltose}}{C_{12}H_{22}O_{11}}$$

The product is cooled to 303 K and fermented with yeast, which contains various enzymes. One of these, 'maltase', converts maltose to glucose and the other 'zymase' decomposes glucose to ethanol:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{maltase}} \underset{\text{glucose}}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} \underset{\text{ethanol}}{2C_2H_5OH + 2CO_2}$$

Enzymes are a particularly important group of proteins. They are the catalysts which enable living organism to bring about necessary reactions.

Fermentation of molasses (a by-product of sugar industry) also gives ethanol.

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} \underset{\text{ethanol}}{2C_2H_5OH + 2CO_2}$$

Ethanol may also be prepared from glucose directly. Grape juice, a rich source of glucose, ferments to produce wine with a maximum alcoholic content of approximately 12% by volume. The alcoholic content of liquors is usually designated in terms of **proof spirit**, 100 proof indicating an alcoholic content of about 50% by volume. The term "proof spirit" supposedly has its origin in an early and rather crude analytical procedure for determining the alcoholic content of whisky. Whisky of high alcoholic content, when poured onto the gunpowder would ignite and burn with a flame sufficiently hot to ignite the powder also. This was 'proof' of spirit content. If the gunpowder failed to ignite, the presence of too much water was indicated, as the powder would have become too wet to burn.

Absolute ethanol: Regardless of the methods of manufacture, all aqueous solutions of ethanol yield, on fractional distillation, a 'constant boiling mixture' of 95 per cent ethanol and 5 per cent water, known as **rectified spirit.** A constant boiling mixture of two or more liquids, called an **azeotrope,** cannot be separated by fractional distillation. In order to obtain **absolute,** or 100% pure ethanol, water has to be removed by methods other than fractionation. In the laboratory, rectified spirit is refluxed over quicklime for about 6 hours, and then allowed to stand overnight. On distillation this gives 99.5 or lime distilled alcohol. The remaining water is removed by reaction with magnesium metal, by which water is converted into insoluble $Mg(OH)_2$.

In industry, calculated amount of benzene is added to the rectified spirit. Distillation of the mixture yield three fractions:

At 338 K, a constant boiling mixture of ethanol, benzene and water (a 'ternary azeotrope').

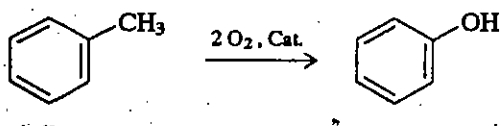
At 341 K, a constant boiling mixture of ethanol and benzene (a 'binary azeotrope').

At 351 K, pure ethanol or absolute alcohol.

ii) **Commercial preparation of phenols: From natural sources:** On a commercial scale, phenols are obtained from coal tar. Coal tar is fractionated and the middle oil is cooled when napthalene crystallises out. The liquid is treated with aqueous sodium hydroxide which dissolves phenols. Carbon dioxide is passed into the liquid and the aqueous layer is separated. Fractionation gives phenol (20%), cresols (43%), xylenols (26%) and the residue is pitch. A similar treatment of the heavy oil also gives di- and trihydroxy phenols.

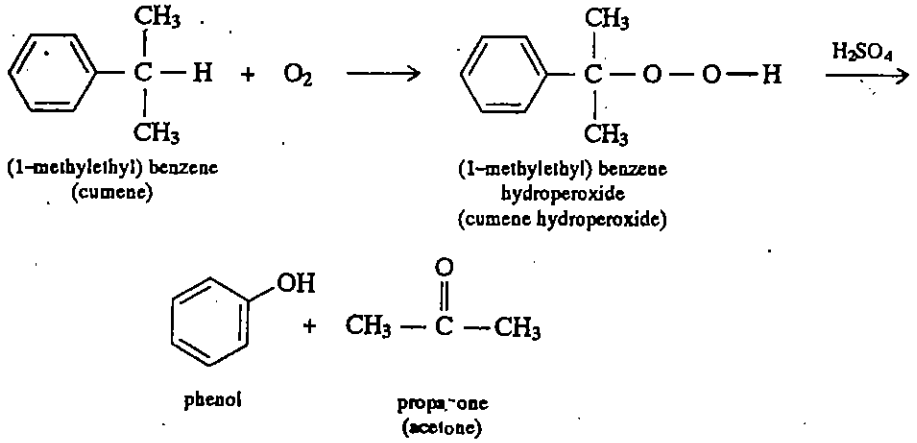
From other aromatic hydrocarbons:

a) Phenol can be obtained by the catalytic oxidation of methylbenzene by air in the presence of manganous and cupric salts.

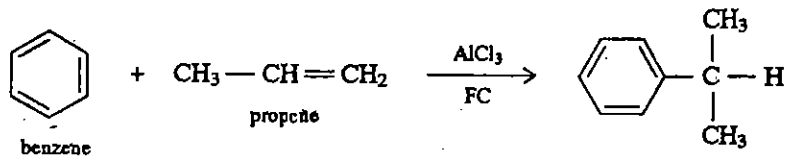


methylbenzene phenol

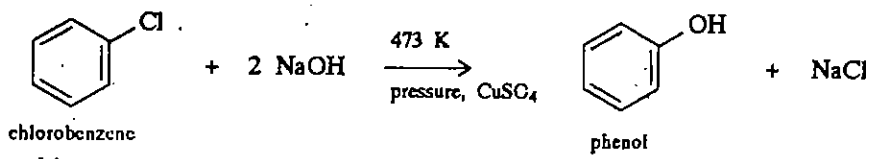
b) **The cumene process: Oxidation of (1-methylethyl) benzene (cumene or isopropylbenzene) to hydroperoxide followed by decomposition by acid gives phenol and an important by product propanone (acetone):**



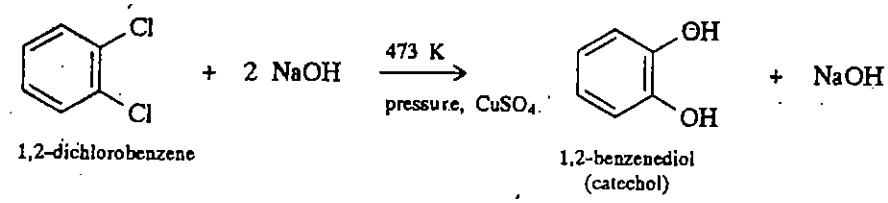
(1-Methylethyl) benzene is made almost exclusively from benzene and propene via a Friedel-Crafts reaction.



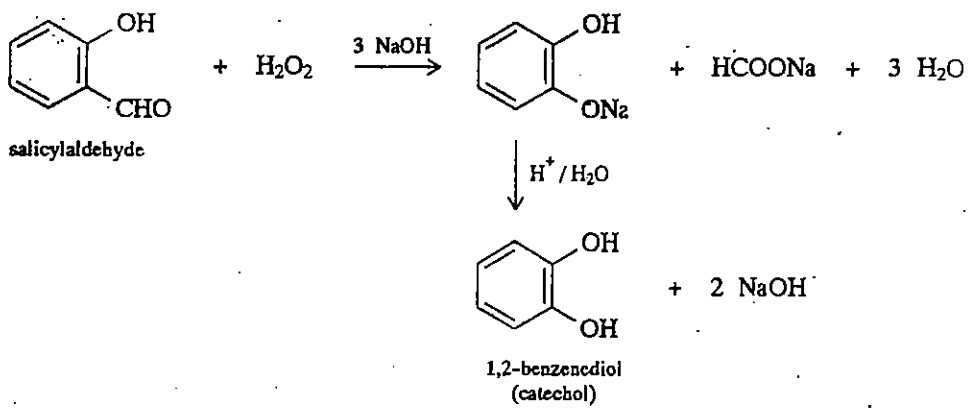
c) **The Dow process:** Chlorobenzene and sodium hydroxide react high temperature and under pressure in the presence of a catalyst (copper salts) to give phenols.



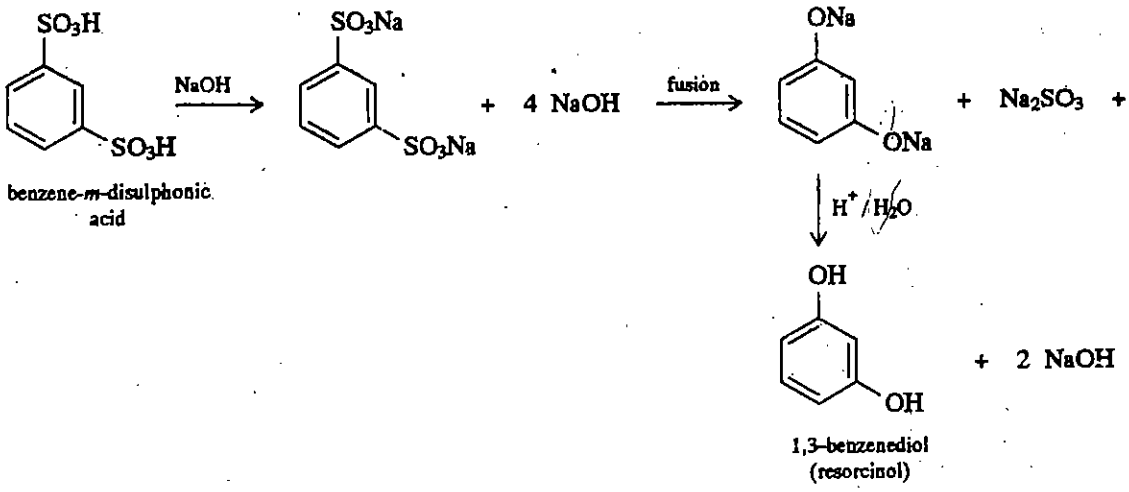
when this process is applied to 1,2-dichlorobenzenes catechol is obtained,



d) Catechol can be conveniently prepared by the action of alkaline hydrogen peroxide on salicylaldehyde. The reaction is an example of Baeyer, Villiger rearrangement which you will study in Unit 11 of the course 'Organic Reaction Mechanism'.



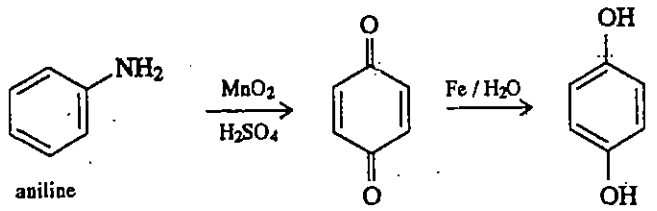
e) Resorcionol is prepared industrially by the alkaline fusion of benzene *m*-disulphonic acid:



benzene-*m*-disulphonic acid

1,3-benzenediol (resorcinol)

f) Quinol is made commercially by the oxidation of aniline with manganese dioxide and sulphuric acid. The product *p*-benzoquinone is reduced to quinol with iron and hot water.

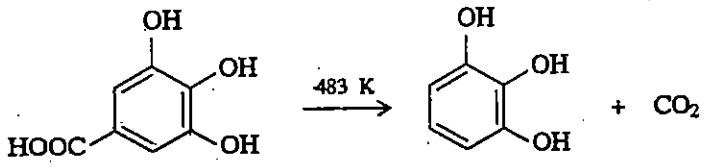


aniline

p-benzoquinone

1,4-benzenediol (quinol)

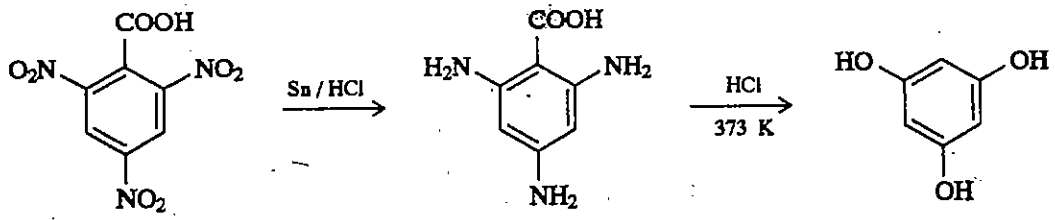
g) Pyrogallol is prepared by heating gallic acid (3,4,5-trihydroxybenzoic acid) in a stream of carbon dioxide or by heating an aqueous solution of gallic acid at 483 K under pressure:



(3,4,5-trihydroxybenzoic acid) gallic acid)

1,2,3-benzenetriol (pyrogallol)

h) Phloroglucinol is obtained by the fusion of many plant resins with alkali. It is also prepared by the reduction of 2,4,6-trinitrobenzoic acid to the amino derivative followed by reaction of hot hydrochloric acid.

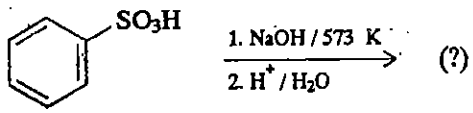


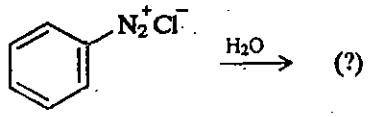
2,4,6-trinitrobenzoic

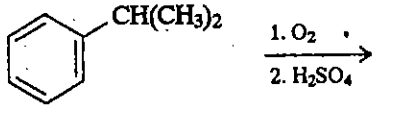
1,3,5-benzenetriol (phloroglucinol)

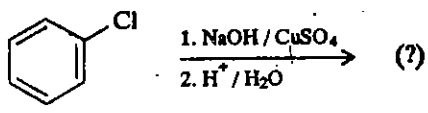
SAQ 2

Complate the following reactions

a) 

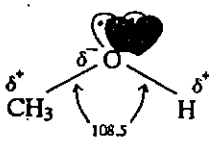
b) 

c) 

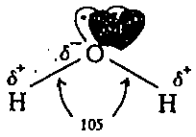
d) 

12.4 PHYSICAL PROPERTIES

Physical properties of alcohols can be understood if we consider again the fact that alcohols are similar in structure to water. Oxygen in alcohol molecule is in the sp^3 hybridised state and has two unshared pairs of valence electrons. Like the hydroxyl groups in water, the hydroxyl group in alcohols is polar.

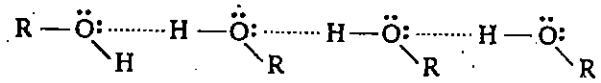


methanol



water

As might be expected, alcohols like water are strongly hydrogen bonded. The formation of hydrogen bonds leads to association of a large number of alcohol molecules. These molecular association have to be broken up before boiling occurs. Hence, the high boiling point of alcohol is observed when compared to other molecules of the same size.



hydrogen bonding in alcohol molecules

Table 12.3 compares the boiling points of some alcohols and chloro compounds with the same carbon skeletons.

Table 12.3: Comparison of the boiling points of some alcohols and chloroalkanes

Alcohols	Bp, K	Chloroalkane	Bp, K
$CH_3—OH$	337	$CH_3—Cl$	249
$CH_3CH_2—OH$	351	$CH_3CH_2—Cl$	286
$CH_3CH_2CH_2—OH$	370	$CH_3CH_2CH_2—Cl$	319

Further in a group of isomeric alcohols, the primary alcohol has the highest boiling point and the tertiary, the lowest, with the secondary having an intermediate value. In the straight chain compounds, the van der Waal's attractive forces are relatively large due to the large surface area. In the branched chain structures, the molecule tends to become spherical and hence with the decrease in surface area the attractive forces are small. Physical properties of some alcohols are summarised in Table 12.4.

Table 12.4: Physical properties of some alcohols

IUPAC Name	Common name	Formula	Bp. K	Density Kg dm^{-3}	Solubility in H_2O
Methanol	methyl alcohol	CH_3-OH	337	0.79	infinite
Ethanol	ethyl alcohol	CH_3CH_2-OH	351	0.79	infinite
1-Propanol	propyl alcohol	$CH_3CH_2CH_2-OH$	370	0.80	infinite
2-Propanol	isopropyl alcohol	$(CH_3)_2CH-OH$	355	0.79	infinite
1-Butanol	butyl alcohol	$CH_3(CH_2)_3-OH$	380	0.81	8.3 g/100cm^3

The water solubility of lower alcohols can also be explained by their ability to form hydrogen bonds with water molecule.

hydrogen bonding in water molecules

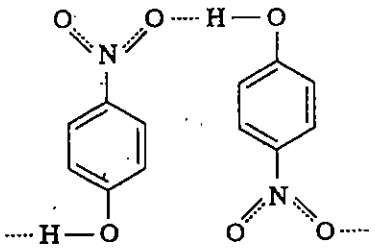
Solubility of alcohols in water decreases as the length of the hydrocarbon chain of the alcohol molecule increases. As discussed in Unit 4, the hydrocarbon character of the molecule, i.e., hydrophobic character increases in higher alcohols.

Like alcohols, phenols also have high boiling points and moderate solubility in water because of hydrogen bonding. On exposure to air and light they turn pink due to auto-oxidation. Physical properties of some phenols are summarised in Table 12.5.

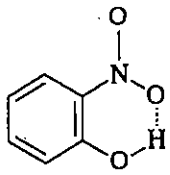
Table 12.5: Physical properties of some phenols

Name	Mp, K	Bp, K	Solubility g/100g H_2O
Phenol	314	455	9.3
Catechol	377	—	45.0
Resorcinol	383	—	123.0
Hydroquinone	446	—	8.0
o-Nitrophenol (volatile in steam)	318	—	0.2
p-Nitrophenol (nonvolatile in steam)	387	—	1.7

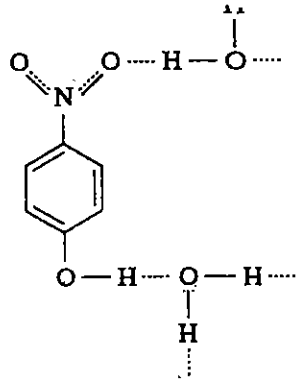
In Table 12.5, we notice that *ortho* and *para* isomers of nitrophenol differ considerably in their physical constants. How are we to account for these differences? Let us see how these isomers undergo hydrogen bonding:



Intermolecular hydrogen bonding *p*-nitrophenol



Intramolecular hydrogen bonding *o*-nitrophenol



hydrogen bonding with water molecules

From the above we can expect that the *p*-isomer should have a higher melting point and solubility in water due to the **intermolecular hydrogen bonding** and its association with water molecules. On the other hand, *o*-nitrophenol which has **intramolecular hydrogen bonding** or hydrogen bonding within a single molecule. It does not associate with other alcohol molecules or with water and, therefore, has lower melting point and lower solubility.

12.5 SPECTRAL PROPERTIES

In this section we will consider the spectral properties of alcohols and phenols. Let us first take the ultraviolet spectra. For alcohols, uv spectra are not of much use because they show absorption only in the 180-188 nm region which is not normally covered in uv spectroscopy.

The infrared spectra of alcohols show O—H stretching in the 3650–3590 cm^{-1} region. Intermolecular hydrogen bonding shifts this to the 3520-3200 cm^{-1} region and the band becomes broadened. Intramolecular hydrogen bonding shifts O–H stretching to the 3590-3420 cm^{-1} region. The C—O stretching is characteristic of the type of alcohol: primary near 1050 cm^{1}, secondary near 110 cm^{-1} and tertiary near 1150 cm^{-1}. As an illustration, infrared spectrum of 1-butanol is given in Fig. 12.1.

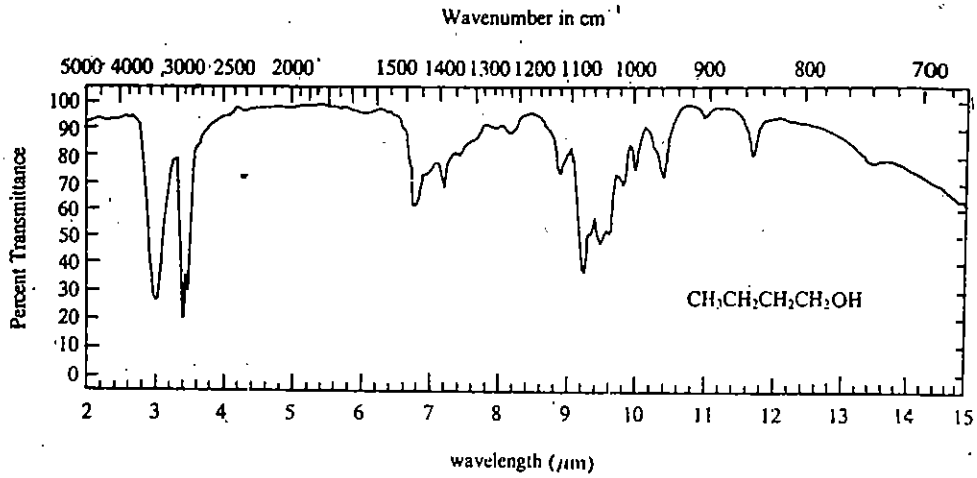


Fig. 12.1: Infrared spectra of 1-butanol

The broad band of 3400 cm^{-1} indicates the presence of the O—H stretching in the molecule. Broadening of the band suggests intermolecular hydrogen bonding. The C—O stretching at 1050 cm^{-1} is characteristic of the primary hydroxyl group ($-CH_2-OH$).

The infrared spectra of phenols combine the features of alcohols and aromatic compounds. Phenolic-O—H groups show a strong broad bond in the region 3600-3200 cm^{-1} due to O—H stretching and another strong broad bond at around 1200 to 1250 cm^{-1} due to C—O stretching. You can see these featrues in the infrared spectra of 4-methyl benzenol (*p*-cresol) in Fig. 12.2.

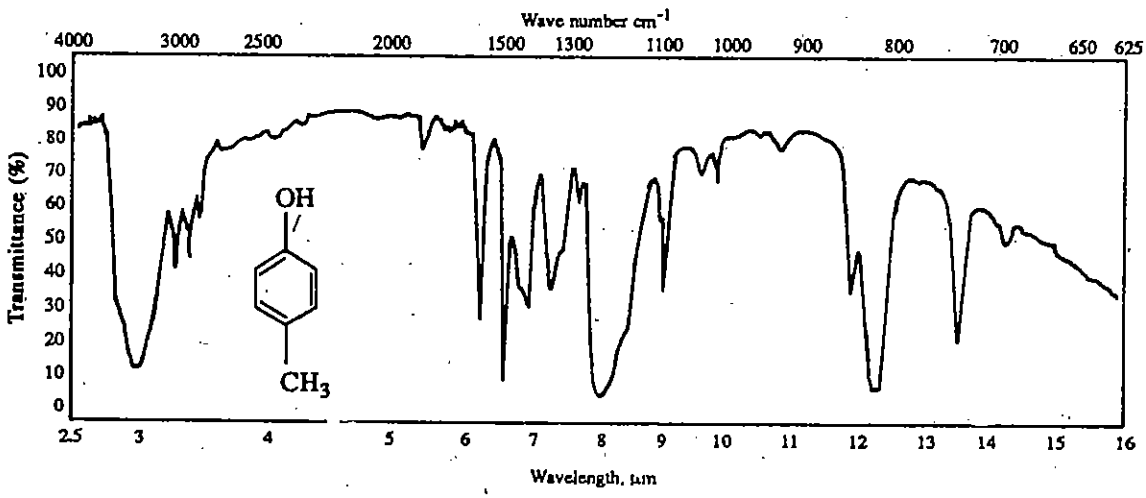


Fig. 12.2 : Infrared spectra of *p*-cresol.

The characteristic features of the nmr spectra of alcohols are the presence of the —O—H signal and the chemical shift of the proton of an H—C—O—unit when the alcohol is primary or secondary

—C—O—H	H—C—O—
$\delta = 0.5 = 5$ ppm	$\delta = 3.3 = 4.0$ ppm

Fig. 12.3 shows the nmr spectrum of 2-phenylethanol, in which the hydroxyl proton signal appears as a singlet at δ 1.6 ppm and the proton of the $-CH_2O-$ unit as a triplet at $\delta = 3.8$ ppm. The other triplet at $\delta = 2.8$ ppm and a singlet at $\delta = 7.2$ ppm is for benzylic and aromatic protons, respectively.

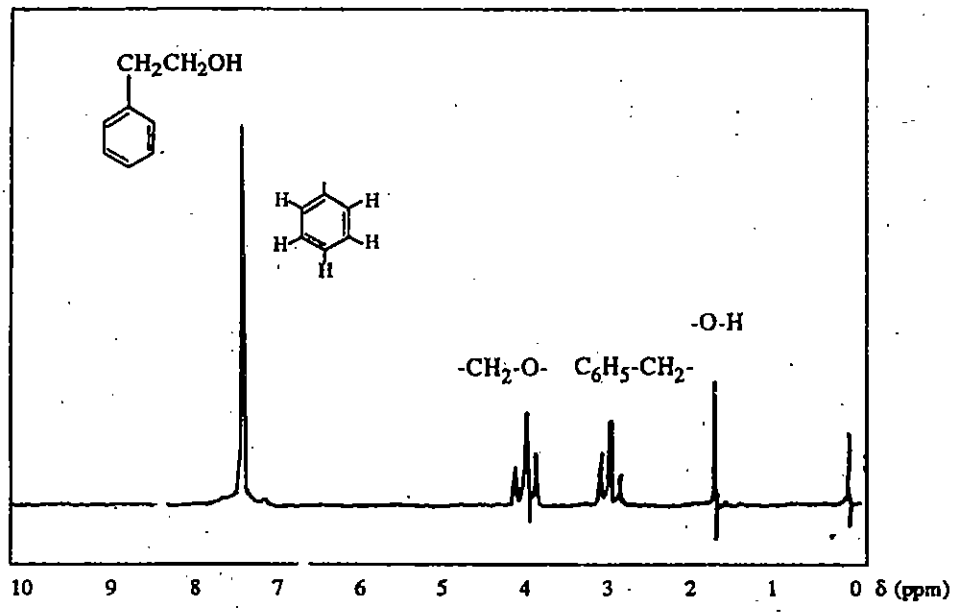
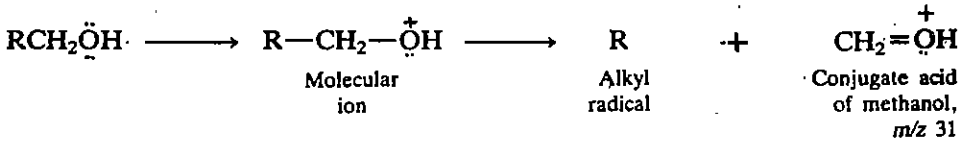


Fig. 12.3 : NMR spectrum of 2-phenylethanol.

On the other hand in the nmr spectra of phenols, the hydroxyl proton appears at much lower field (δ 4 to 12 ppm) than those of alcohols and aromatic proton appears around $\delta = 7$ ppm.

The mass spectra of primary and secondary alcohols show a weak peak due to the nolecular ion. The peak due to the molecule ion is very weak or absent in the spectra of tertiary alcohols. Phenols show a very intense peak due to the molecular ion. Further, alcohols also fragment readily by a pathway in which the molecular ion loses an alkyl group from the hydroxyl-bearing carbon to form a stable cation. Thus, the mass spectra of most primary alcohols exhibit a prominent peak at *m/z* 31.



12.6 CHEMICAL PROPERTIES

As stated earlier phenols have very different chemical properties than those of alcohols and, therefore, in this section, we will consider their chemical properties separately. However, it is worth comparing the acidity of alcohols and phenols and the effect alkyl/aryl group has on it.

12.6.1 Basicity and Acidity of Alcohols and Phenols

Alcohols are neutral towards litmus. But in their reactions they behave both as an acid and as a base depending upon the reaction conditions. For example, in acidic solution, alcohols are protonated and thus the acid-base equilibrium with alcohol acting as a base is established. It is the same type of reaction that occurs between water and an acid. A protonated alcohol molecule is called an oxonium ion.

The lone electron pairs of oxygen make alcohols act basic.

Molecules that act both as acids and as bases are called amphoteric (*ampho*, Greek, both). Examples are water, alcohol, etc.:

An alcohol can also lose a proton to a strong base yielding an alkoxide ion, RO^-. In this reaction the alcohol behaves as an acid.

Alkoxides are strong bases, generally stronger than hydroxides. To prepare an alkoxide from an alcohol, we need a base stronger than the alkoxide itself, such as, alkali metal hydrides, NaH, KH, etc.

$$ROH + Na^+H^- \longrightarrow RO^-Na^+ + H_2\uparrow$$

alcohol — sodium hydride — sodium alkoxide

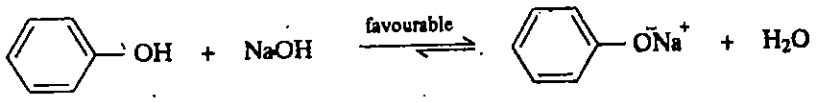
In dilute aqueous solutions alcohol has approximately the same pK_a values as water. For example, the pK_a ofmethanol in water is 15.5, while that of pure water is 15.74. Therefore it is as acidic as water.

$$CH_3OH + H_2O \text{ —— } CH_3O^- + H_3O^+$$

On the other hand, phenols are distinctly acidic in character. Phenol, with a pK_a of 10.00 is a stronger acid than an alcohol or water. Unlike alkoxide ion of alcohols, the phenoxide ion (ArO^-) is a weaker base than OH^-, therefore, a phenoxide can be prepared by treatment of the phenol with aqueous sodium hydroxide.

$$CH_3CH_2{-}OH + NaOH \underset{\text{unfavourable}}{\rightleftharpoons} CH_3CH_2\bar{O}Na^+ + H_2O$$

ethanol, $PK_a = 15.9$ — sodium ethoxide

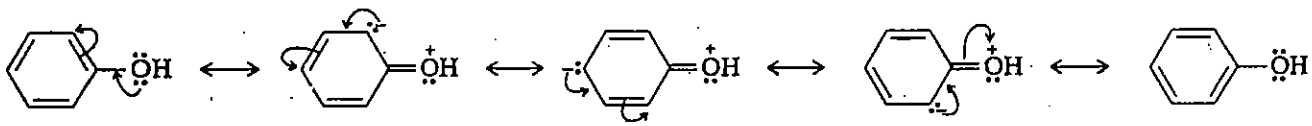


phenol, $pKa = 10$ — sodium phenoxide

We can explain the acidic character of phenol if we recall the fact that the degree of ionisation of a weak acid is determined by the relative stabilities of the unionised compound and the anion:

$$HA \text{ ——— } H^+ + A^-$$ (if A is stabilised relative to HA, acidity is increased)

The reason for the greater acidity of phenol compared to that of alcohol is that the ionised product is reasonance stabilised, with the negative charge delocalised by the aromatic ring.



$H\ddot{O}:^-$ pK_a 15.74 — $CH_3 \rightarrow \ddot{O}:^-$ 15.5

$CH_3 \rightarrow CH_2 \rightarrow \ddot{O}:^-$ 15.9 — $CH_3 \rightarrow \underset{CH_3}{CH} \rightarrow \ddot{O}:^-$ pK_a 17.1

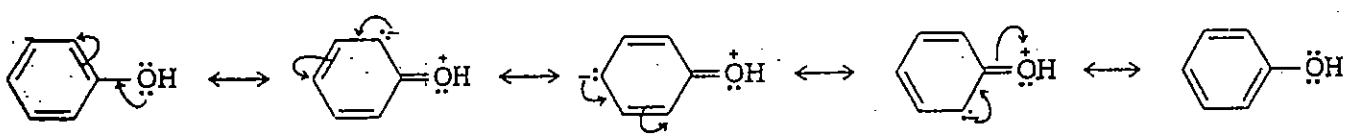
$CH_3 \rightarrow \underset{CH_3}{\overset{CH_3}{C}} \rightarrow \ddot{O}:^-$ 18.0

+ I effect of alkyl group which further intensity the negative charge on oxyzen

The negative charge in an alkoxide ion (RO^-) cannot be delocalised. Therefore, as alkoxide ion is of higher energy relative to the alcohol, and as a result, alcohols are not as strong acids as phenols. Further the alkyl group in the alkoxide ion has a destabilising effect because of positive inductive ($+I$) effect of the alkyl group. Therefore, addition of alkyl groups to the α-carbon decreases the acidity of alcohols. We can now write the order of decreasing acid strength

$H_2O > p > sec > tert$ alcohols.

Furthermore phenols, like alcohols can be protonated by strong acids to give the corresponding oxonium ions. Thus, as with the alcohols, the hydroxy group has amphoteric character. However, the basicity of phenols is even less than that of the alcohols,because the lone electron pairs on the oxgyen are delocalised into benzene ring.



Delocalisation of lone pair of oxygen

12.6.2 Reactions of Alcohols

Reactions of alcohols involve breaking either the O—H bond or the C—O bond. In this section first we shall take up the reactions of O—H bond and C—O bond. Then we shall look at the oxidation reactions of alcohol.

i) Reactions of the O—H Bond

Reaction with active metals:

Strongly electropositive metals like K, Na, Mg, Al and Zn liberate hydrogen from alcohols and form alkoxides, e.g.,

$$\underset{\text{ethanol}}{2C_2H_5OH} + 2Na \longrightarrow \underset{\substack{\text{sodium}\\ \text{ethoxide}}}{2C_2H_5O{-}Na^+} + H_2\uparrow$$

In the above reaction the oxygen-hydrogen bond of the alcohol is broken and the alcohol thus behaves as an acid. We have mentioned in the previous subsection that alcohols are, however, weaker acids than water. Therefore, the conjugate base of alcohols, the alkoxide ion, is a stronger base than the hydroxide ion, the conjugate base of water. The order of reactivity for different types of alcohols in this reaction is **$CH_3OH > p > sec > tert$.** This order is the same as given earlier for the acidity of alcohols.

The alkoxides of the alkali metals are strong bases (nucleophiles) that enter into S_N2 substitution of halogen from alkyl halides. This reaction, referred to as the Williamson ether synthesis, is best used to prepare ethers.

$$\underset{\substack{\text{sodium}\\ \text{methoxide}}}{CH_3O^-Na^+} + \underset{\text{iodoethane}}{C_2H_5{-}I} \xrightarrow{S_N2} \underset{\substack{\text{ethylmethyl}\\ \text{ether}}}{CH_3{-}O{-}C_2H_5} + NaI$$

Esterification: Another interesting reaction of alcohols is with acids to form esters and water. In this reaction the oxygen-hydrogen bond in the alcohol is broken.

$$RCOOH + R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} RCOOR' + H_2O$$

This reaction is known as esterification. These types of reactions will be discussed again in greater detail in Unit 15.

Any inorganic acid can be used in place of carboxylic acid to produce inorganic ester. Inorganic esters are valuable commercial products. For instance, nitroglycerin is readily prepared by the esterification of nitric acid with glycerol.

$$\underset{\substack{\text{1,2,3-propanetriol}\\ \text{(Glycerol)}}}{\begin{array}{l}CH_2{-}OH\\ |\\ CH{-}OH\\ |\\ CH_2{-}OH\end{array}} + 3HONO_2 \xrightarrow{H_2SO_4} \underset{\substack{\text{1,2,3-propane trinitrate}\\ \text{(nitroglycerin)}}}{\begin{array}{l}CH_2{-}ONO_2\\ |\\ CH{-}ONO_2\\ |\\ CH_2{-}ONO_2\end{array}} + 3H_2O$$

Nitroglycerin is an explosive used to make dynamite. Similarly, sodium lauryl sulphate, a synthetic detergent, can be obtained by esterification of lauryl alcohol,

$$\underset{\substack{\text{1-dodecanol}\\ \text{(lauryl alcohol)}}}{CH_3(CH_2)_{10}CH_2OH} + HOSO_2OH \longrightarrow \underset{\substack{\text{1-dodecanyl hydrogen sulphate}\\ \text{(lauryl hydrogen sulphate)}}}{CH_3(CH_2)_{10}CH_2OSO_2OH} + H_2O$$

$$\xrightarrow{NaOH} \underset{\substack{\text{sodium-1-dodecanyl sulphate}\\ \text{(sodium lauryl sulphate)}\\ \text{synthetic detergent}}}{CH_3(CH_2)_{10}CH_2OSO_2O^-Na^+}$$

Another important ester is **cellulose trinitrate** (gun cotton). It is a product obtained when cellulose (a polysacharide) is almost completely nitrated under conditions carefully controlled to prevent degradation of the cellulose molecule.

$$\underset{\text{cellulose}}{[C_6H_7O_2(OH)_3]_n} \xrightarrow{3n\ HNO_3/H_2SO_4} \underset{\text{gun cotton}}{[C_6H_7O_2(ONO_2)_3]_n}$$

Gun cotton contains about 12-13% of nitrogen, is explosive and is used in the manufacture of smokeless powder.

Esterification of cellulose with acetic anhydride gives **cellulose acetate,** it is an ester but is not explosive. Cellulose acetate is used to produce thin fibres. From such fibre

the acetate fabrics are woven. Photographic film is also produced from cellulose acetate.

Similarly, the alkyl halides described earlier in Unit 11 can be regarded as esters of halogen acids.

ii) Reactions of the C—O bond

Substitution reactions of alcohols: The reactions of alcohols with HX, PX_3, $SOCl_2$, PCl_5 to prepare alkyl halides have already been briefly discussed in Unit 11.

$$\underset{\text{alcohol}}{R{-}OH} + HX \longrightarrow \underset{\substack{\text{alkyl}\\\text{halide}}}{R{=}X} + H_2O$$

$$\underset{\text{alcohol}}{3R{-}OH} + PX_3 \longrightarrow \underset{\substack{\text{alkyl}\\\text{halide}}}{3R{-}X} + H_3PO_3$$

$$\underset{\text{alcohol}}{R{-}OH} + \underset{\substack{\text{sulphur-dichloride oxide (thionyl-chloride)}}}{SOCl_2} \longrightarrow \underset{\substack{\text{alkyl}\\\text{chloride}}}{R{-}Cl} + SO_2 + HCl$$

$$\underset{\text{alcohol}}{R{-}OH} + \underset{\substack{\text{phosphorous}\\\text{pentachloride}}}{PCl_5} \longrightarrow \underset{\substack{\text{alkyl-}\\\text{chloride}}}{R{-}Cl} + POCl_3 + HCl$$

Let us look more closely at substitution reaction of alcohol with hydrogen halides (HX). Alcohols can undergo substitution reactions with HX under acidic conditions or in the presence of Lewis acid like anhydrous zinc chloride ($ZnCl_2$). General reaction can be represented as,

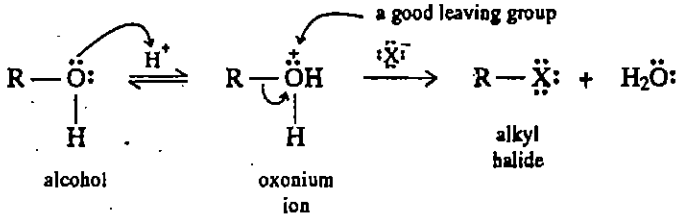
$$R{-}OH + HX \underset{\text{or } ZnCl_2}{\overset{H^+}{\rightleftharpoons}} R{-}X + H_2O$$

Example:

$$\underset{\text{1-butanol}}{CH_3CH_2CH_2CH_2{-}OH} + HBr \xrightarrow[\text{heat}]{ZnCl_2} \underset{\text{1-bromobutane}}{CH_3CH_2CH_2CH_2{-}Br} + H_2O$$

$$(CH_3)_3C{-}OH + HCl \longrightarrow (CH_3)_3C{-}Cl + H_2O$$

If we compare substitution reactions of alcohol and alkyl halide we can notice that unlike alkyl halides, alcohols do not undergo substitution under neutral or alkaline solution. The reaction requires acidic conditions (H^+) or catalysts like $ZnCl_2$. In Unit 11, we have seen that Cl^-, Br^- and I^- are good leaving-groups and weak bases. But, OH^-, is a strong base and thus a very poor leaving group. In acidic solution, alcohols get protonated,



Here, —OH is a poor leaving group, but $-OH_2^+$ is a good leaving group because it is lost as water, a weak base. A weak nucleophile, such as a halide ion can displace the water molecule to yield an alkyl halide. The function of zinc chloride is similar to that of H^+. Anhydrous zinc chloride is a powerful Lewis-acid with empty orbitals that can accept electrons from the oxygen atom of alcohol. The formation of a complex of $ZnCl_2$ with the alcohol oxygen weakens the C—O bond and thus enhances the leaving ability of the hydroxyl group.

In alcohol substitution reactions, the reactivity of the hydrogen halides is as follows:

$$HF < HCl < HBr < HI$$

Thus, the higher the acid strength and nucleophilicity of the anion, the higher the reactivity towards ROH.

The order of reactivity of alcohols towards hydrogen halides is as follows:

methyl < *p* < *sec* < *tert* alcohols

Increasing reactivity of ROH towards HX

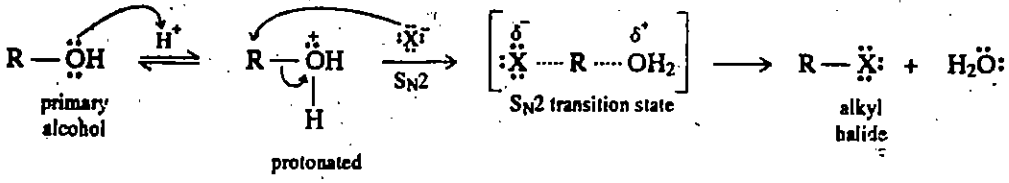
This order of reactivity forms the basis for the Lucas test which is used to differentiate primary, secondary and tertiary alcohols. The Lucas reagent is made up of concentrated HCl and $ZnCl_2$. Tertiary alcohols react immediately upon shaking with the Lucas reagent to produce an immiscible upper layer of alkyl chloride. Secondary alcohols react in 2-3 minutes, and primary alcohols do not react unless the mixture is heated.

Mechanism

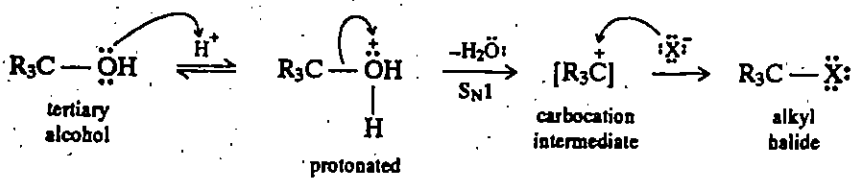
Like alkyl halides primary alcohols react by the S_N2 mechanism, tertiary alcohols by the S_N1 mechanism, and secondary alcohol by either an S_N1 or S_N2 mechanism.

A tertiary R_3C—OH most easily gives a carbocation and tends to react by the S_N1 mechanism. It is very difficult for a primary RCH_2—OH to form a carbocation, but the primary structure is open to backside attack, so an S_N2 reaction is possible. A secondary R_2CH—OH may react by either an S_N1 or S_N2 mechanism.

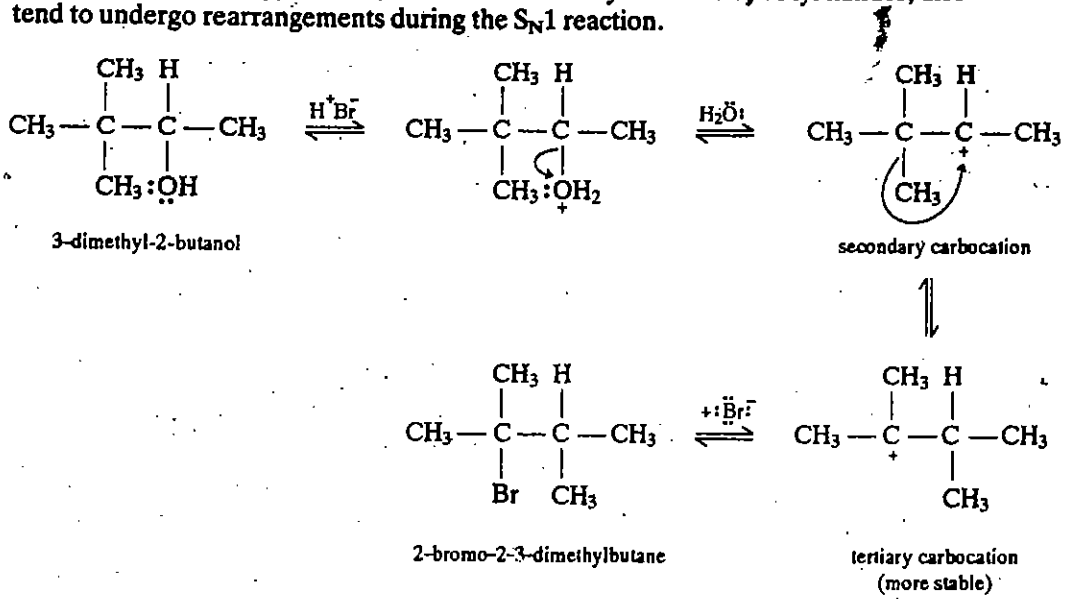
The mechanism for the reaction of HX with a primary alcohol is as follows :



The mechanism for the reaction of tertiary alcohols is as follows :



Secondary and tertiary alcohols, similar to secondary and tertiary alkyl halides, also tend to undergo rearrangements during the S_N1 reaction.



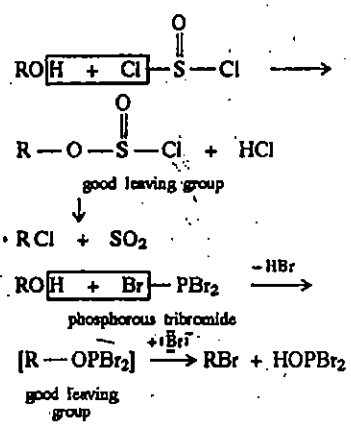
Primary, secondary and tertiary alcohols react with different reagents by different paths. In Table 12.6, we have summarised the substitution reaction of alcohols leading to alkyl halides.

Other halogenating reagent such as thionyl chloride ($SOCl_2$) and phosphorus trihalide (PX_3) undergo reaction with alcohol to form intermediate inorganic esters, discussed earlier. The resulting inorganic ester groups are good leaving groups that can be displaced by halide ions.

Table 12.6 . Summary of substitution reactions of alcohols leading to alkyl halides

Alcohol	Reagents	Product	Nature of reaction
p : RCH_2OH	$HCl+ZnCl_2$ or HBr or HI	RCH_2X	S_N2
	PBr_3	RCH_2Br	S_N2
sec : R_2CHOH	$HCl+ZnCl_2$ or HBr or HI	R_2CHX	S_N1
	PBr_3	R_2CH_2Br	S_N2
tert : R_3COH	HCl, HBr or HI	R_3CX	S_N1

The reaction of alcohol with thionyl chloride to give alkyl halides usually proceeds in the S_Ni mechanism (Substitution nucleophilic internal)

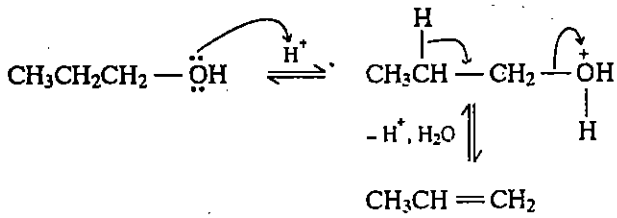


Dehydration of alcohol to alkenes : Another reaction of alcohols is the dehydration. This involves cleavage of C—O bond along with loss of a proton from the β position. It may be effected by heating alcohols to 673–1073 K or heating to a lower temperature in the presence of a catalyst such as alumina or a mineral acid, e.g., sulphuric acid. The product of dehydration of an alcohol is an alkene or a mixture of alkenes. The order of the ease of dehydration of alcohols is: *tert* > *sec* > *p*
Dehydration of primary alcohols gives only one product, e.g.,

$$\underset{\text{propanol}}{CH_3CH_2CH_2OH} \xrightarrow{H^+/\text{heat}} \underset{\text{1-propene}}{CH_3CH=CH_2} + H_2O$$

Primary alcohols undergo dehydration reaction by an E2 path similar to the dehydrohalogenation mechanism discussed in Unit 11.

For the above reaction the E2 mechanism can be written as,

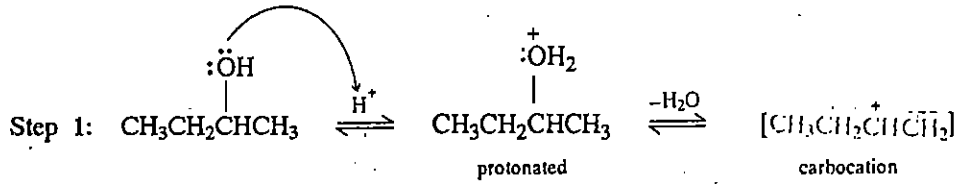


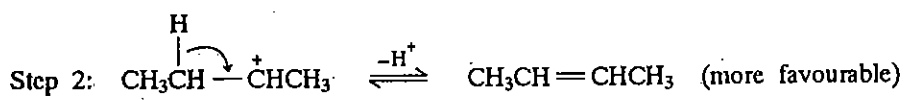
In the case of secondary or tertiary alcohols, a mixture of two alkenes is formed, e.g.,

$$\underset{\text{2-butanol}}{CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_3} \xrightarrow[-H_2O]{H^+/\text{heat}} \underset{\text{2-butene}}{CH_3CH=CHCH_3} + \underset{\text{1-butene}}{CH_3CH_2CH=CH_2}$$

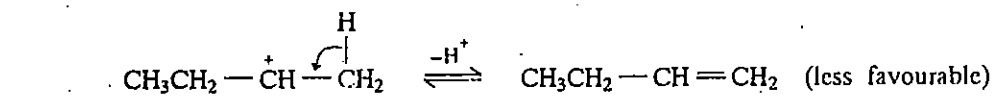
Like the dehydrohalogenation reaction of alkyl halides, the major product in the above reaction is 2-butene, the more substituted alkene (according to Saytzeff's rule which was given earlier in Unit 11).

In secondary and tertiary alcohols, dehydration follows the E 1 pathway. A detailed discussion of the E 1 mechanism has already been given in Unit 11. Now let us write down the mechanism for dehydration of 2-butanol.





or



iii) Oxidation of Alcohols

Alcohols undergo oxidation, the nature of the product depending on whether the alcohol is primary, secondary or tertiary. The common oxidising agents are acidic dichromate, acidic or alkaline potassium permanganate or hot concentrated nitric acid or chromic acid (H_2CrO_4) or the chromium trioxide (CrO_3) complex with pyridine.

A primary alcohol on oxidation gives an aldehyde, which on further oxidation gives a carboxylic acid. The oxidation products have the same number of carbon atoms as the alcohol, e.g.,

$$CH_3CH_2{-}OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$$

Chromium trioxide-pyridine complex is a better reagent for oxidising a primary alcohol into an aldehyde. Yields of aldehyde with the other reagents is very poor because the oxidation with these reagents usually continues until the carboxylic acid is formed.

A secondary alcohol on oxidation gives a ketone with the same number of carbon atoms as the alcohol. Ketones are not easily oxidised. However, drastic oxidations give a mixture of carboxylic acids containing a fewer carbon atoms than the alcohol :

$$CH_3CHOHCH_2CH_3 \xrightarrow{[O]} CH_3COCH_2CH_3 \xrightarrow{[O]} 2CH_3COOH$$

Acidic conditions are usually used to get ketones from secondary alcohols. Ketones can be oxidised further in alkaline condition with standard oxidising reagents.

Tertiary alcohols are not easily oxidised in neutral or alkaline conditions. Acidic oxidising agents convert a tertiary alcohol to the alkene then it is oxidised to a mixture of ketones and carboxylic acids, each having a lesser number of carbon atoms than the alcohol. Alkene oxidation was discussed in Unit 8.

$$R_3COH \xrightarrow[OH^-]{[O]} \text{no reaction}$$

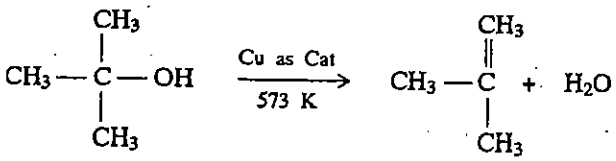
$$R_3COH \xrightarrow[H^+]{[O]} \text{alkene} \xrightarrow{[O]} \text{ketone} + \text{carboxylic acid}$$

Oxidation in alcohol can also be brought about by catalytic dehydrogenation. In this process vapour of the alcohol is healed over copper, for example,

$$\underset{\text{ethanol}}{CH_3CH_2{-}OH} \xrightarrow[573\ K]{\text{Cu as cat.}} \underset{\text{ethanal}}{CH_3CHO} + H_2$$

$$\underset{\text{propanol}}{(CH_3)_2CH{-}OH} \xrightarrow[573\ K]{\text{Cu as cat.}} \underset{\text{propanone}}{(CH_3)_2CO} + H_2O$$

As mentioned above tertiary alcohols are resistant to oxidation. When vapour of tertiary alcohols is passed over copper heated at 573 K, they undergo dehydration to give alkenes, for example,



2-methyl-2-propanol 2-methyl propene

Catalyst e.g., silver is also employed. For example,

$$\underset{\text{methanol}}{CH_3{-}OH} + 1/2O_2 \xrightarrow{\text{Ag as Cat.}} HCHO + H_2O$$

Dehydrogenation is more often used for industrial preparation of aldehydes and ketones.

SAQ 3

Show all the alkenes that could possibly be formed by dehydration of each alcohol

below. Tell which alkene would be produced in largest amount and which is smallest amount.

a) 2-methylbutanol
b) 2-pentanol
c) 2-methylcyclohexanol
d) 1, 2-dimethylcyclohexanol

.....

.....

.....

.....

SAQ 4

What product, if any would be obtained by passing each of these alcohol over copper metal at 573 K ?

a) 1-propanol
b) 2-butanol
c) 2-propanol
d) 2-methylbutanol

12.6.3 Reactions of Phenols

In phenols, as mentioned earlier, the hydroxyl group is attached to an sp^2 hybridised carbon of aromatic ring. In it the carbon oxygen bond has considerable double bond character as evident from the resonance structures shown for the delocalisation of lone pair of oxygen (sub-section 12.6.1). Due to these factors the bond is shorter and stronger than a carbon oxygen single bond. As hydroxyl group bonded to a aromatic ring is held tightly, therefore breaking up of the C—O bond is very difficult. Consequently, the substitution and elimination reactions so typical of an alcohol are not possible for a phenol.

$$\underset{\text{alcohol}}{R{-}OH} + HBr \xrightarrow{S_N1 \text{ or } S_N2} \underset{\substack{\text{alkyl}\\\text{bromide}}}{R{-}Br} + H_2O$$

$$\underset{\text{phenol}}{Ar{-}OH} + HBr \longrightarrow \text{no reaction}$$

With this background, now let us study the reactions of phenols.

i) Formation of phenoxides : We have already mentioned that phenols are weak acids. They react with strong alkalis forming phenoxides and water. This reactivity is in direct contrast to that of alcohols. We have seen that alcohols form alkoxide only with a strong base like NaH and metals like Na, K, Mg, etc.

$$\underset{\substack{\text{ethanol,}\\ pK_a\ 15.9}}{C_2H_5{-}OH} + NaOH \rightleftharpoons \underset{\text{sodium ethoxide}}{C_2H_5{-}O^-\,Na^+} + H_2 \quad \text{(not favoured)}$$

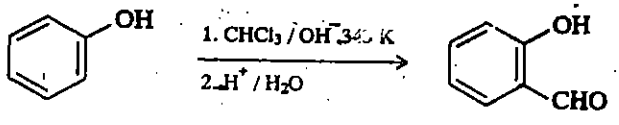
$$\underset{\substack{\text{phenol,}\\ pK_a\ 10.0}}{\text{C}_6\text{H}_5{-}OH} + NaOH \rightleftharpoons \underset{\text{sodium phenoxide}}{\text{C}_6\text{H}_5{-}O^-Na^+} + H_2O \quad \text{(favoured)}$$

Phenol is about 1 million times more acidic than alcohols.

Phenols is not as strong an acid as carbonic acid or a carboxylic acid. This afford a method for distinguishing phenol from a carboxylic acid. Phenol does not react with an aqueous solution of sodium carbonate, whereas carboxylic acid react to liberate carbon dioxide. The separation of a mixture of phenol and a carboxylic acid is based on the same principle.

Again recall from sub-section 12.6.1 that phenols are stronger acids than alcohols as the phenoxide ion is stabilised by resonance. No such stabilisation is possible in the case of alkoxide ions.

ii) Reimer-Tiemann reaction: Phenols undergo the Reimer-Tiemann reaction. In it an alkaline solution of phenol is heated with trichloromethane (chloroform) and the product is acidified to give 2-hydroxybenzaldehyde (salicylaldehyde).

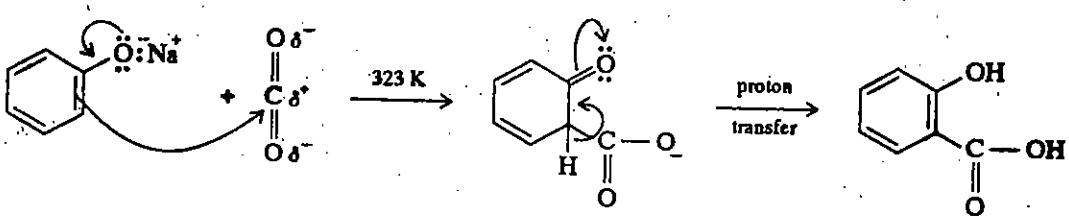


phenol

2-hydroxybenzaldehyde
(salicylaldehyde)

You will study the mechanism of this reaction in the course on Organic Reaction Mechanism.

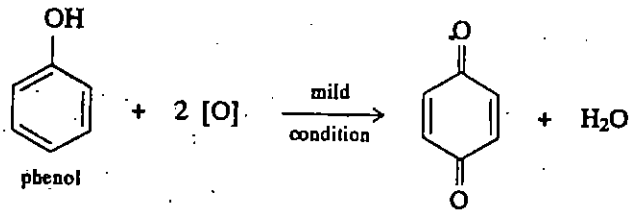
iii) Kolbe reaction: On heating sodium or potassium phenoxide with carbon dioxide and subsequent acidification, 2-hydroxybenzoic acid (salicyclic acid) is formed. This is known as **Kolbe reaction.** In this reaction carbon of CO_2 acts as an electrophile in aromatic substitution.



2-hydroxybenzoic acid
(salicylic acid)

iv) Oxidation of phenols: Phenols are easily oxidised, but their products are often complex. This oxidation may occur with air alone (**autoxidation**) or with other oxidising agents. The reaction of phenols with oxygen in the air is exploited industrially by the use of phenol as antioxidants in gasolin, rubber and other products. The phenols react with oxygen more readily than most other organic compounds and protect them form oxidation.

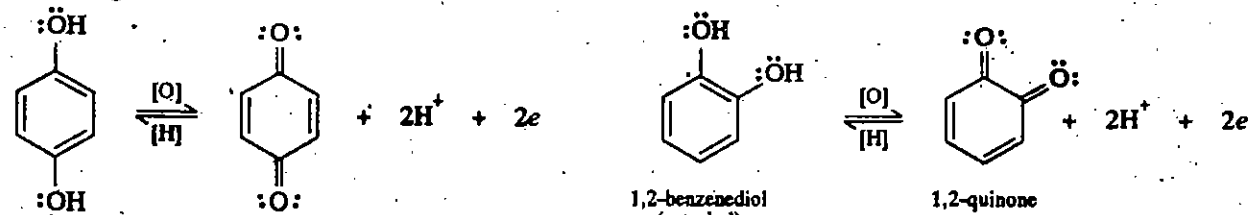
The ability of hydroquinone to reduce silver ions to silver metal is the Chemical basis of photography. Hydroquinone is the developer fluid which reduces the light-activated silver ions at a faster rate than the nonexposed silver ions. In the fixing process unreacted silver halide is converted into a water soluble silver complex of sodium thiosulphate, and washed from film. The result is the familiar photographic negative.



phenol

1,4-quinone
(1,4-benzoquinone)

Hydroquinone and catechol are easily oxidised to quinones by mild oxidising agents such as Ag^+ of Fe^{3+}.



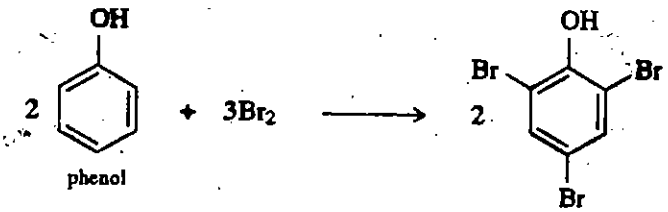
1,4-benzenediol
(hydroquinone)

1,4-quinone
(1,4-benzoquinone)

1,2-benzenediol
(catechol)

1,2-quinone

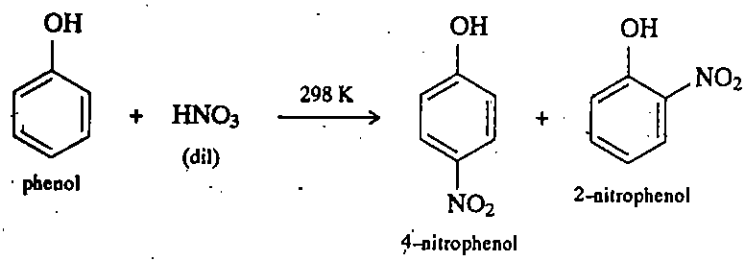
v) Electrophilic aromatic substitution reaction: As we mentioned in Unit 9, the —OH group is a powerful activator in electrophilic aromatic substitution reactions. Therefore, phenol undergoes electrophilic substitution quite readily. On shaking phenol with bromine water at room temperature, 2,4,6-tribromophenol is formed:



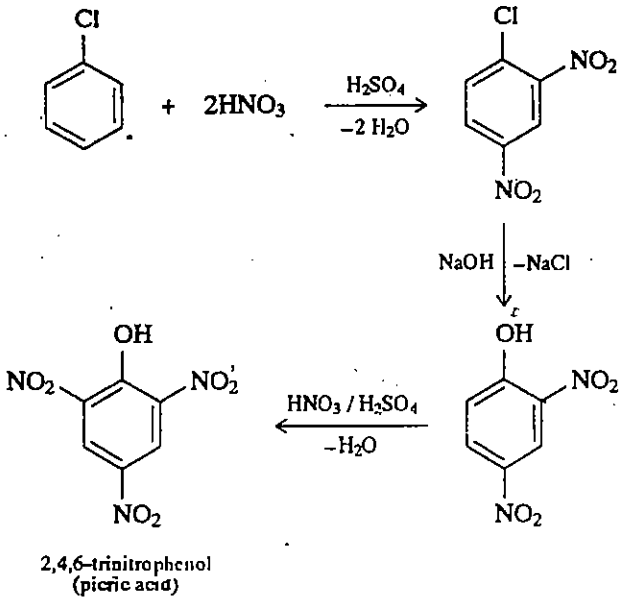
phenol

2,4,6-tribromophenol

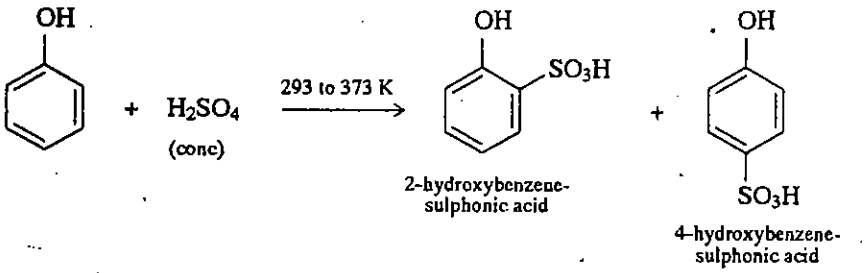
Treatment with dilute nitric acid gives *o* and *p* nitrophenols:



Phenol, when nitrated directly with concentrated nitric acid, undergoes oxidation. For this reason the highly explosive 2,4,6-trinitrophenol, or picric acid, is obtained through a synthesis that begins with chlorobenzene. The first product, 2,4-dinitrochlorobenzene, is then easily hydrolysed to, 2,4-dinitrophenol and the nitration continued to give picric acid in good yield.

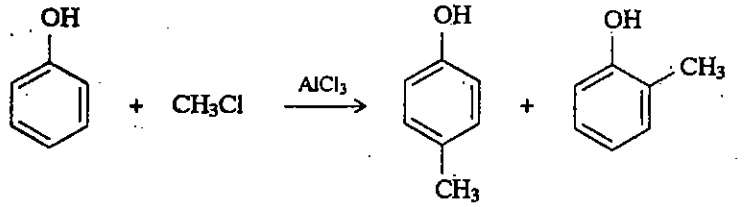


Phenol, when treated with sulphuric acid, yields both *ortho* and *para* products,

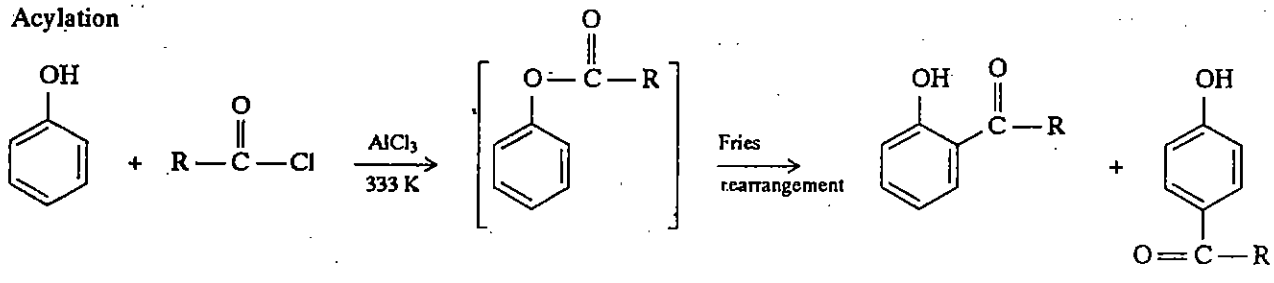


Phenol can easily undergo Friedel-Crafts alkylation or acylation.

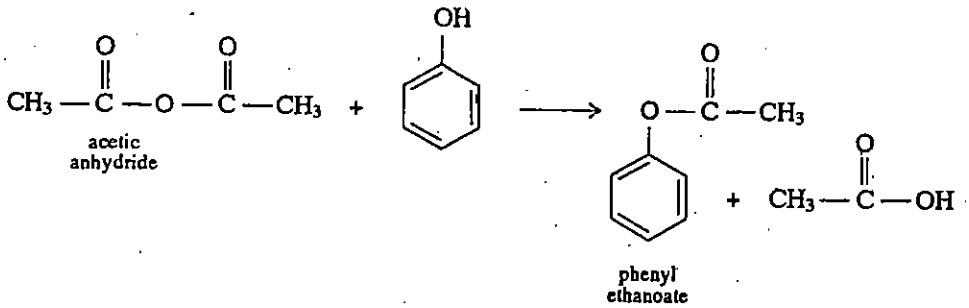
Alkylation



Acylation

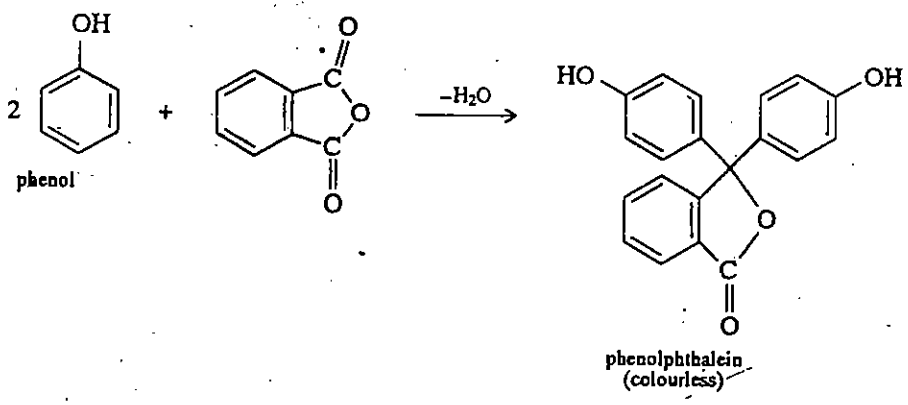


vi) Esterification of Phenols: Unlike alcohols, esterification of phenols does not involve cleavage of the strong C—O bond of the phenol; but depends on the cleavage of the O—H bond. We will discuss the mechanism of esterification of phenols in the course on reaction mechanism.



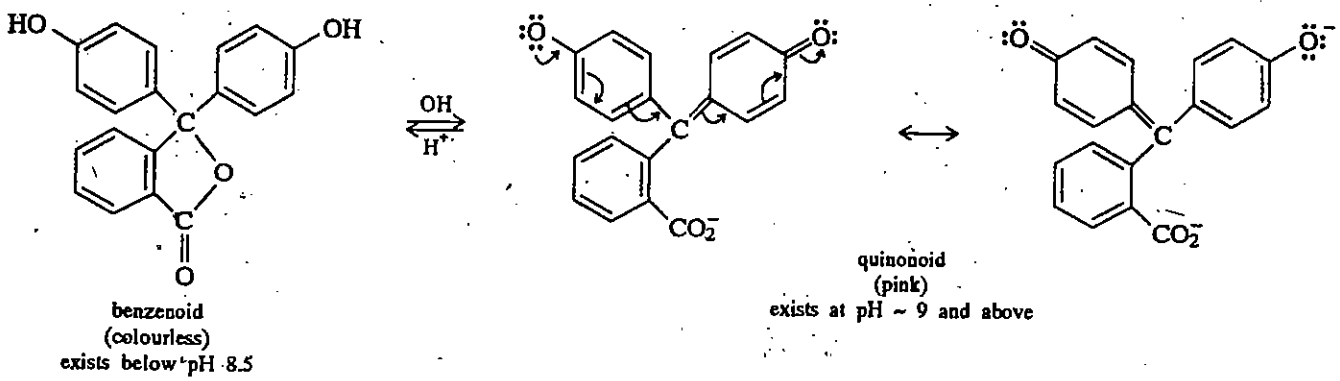
vii) Condensation reactions of phenols: Condensation of phenols with phthalic anhydride in the presence of a dehydrating agent gives a class of compounds known as **phthaleins.** These are dyes.

By heating a mixture of phenol and phthalic anhydride in the presence of concentrated sulphuric acid, phenolphthalein is formed:

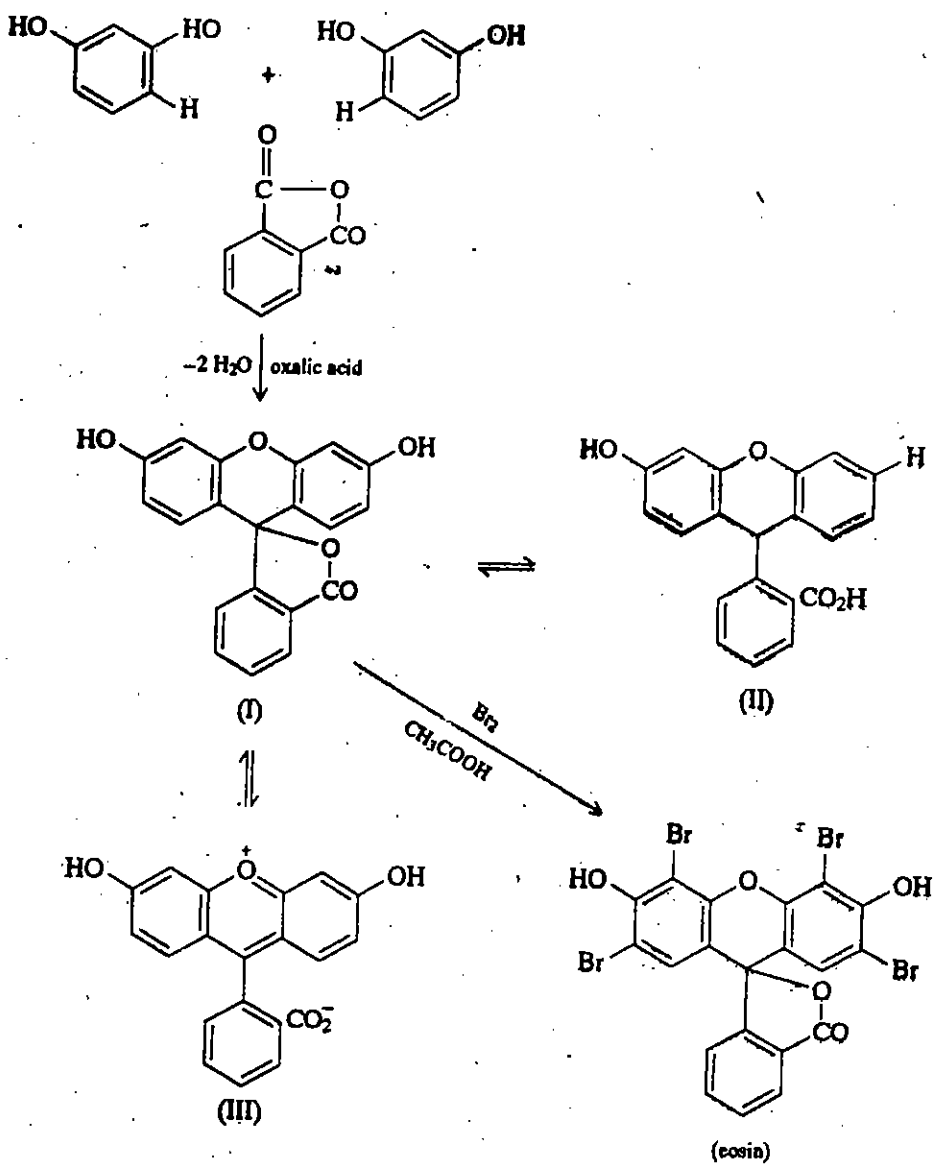


Phenolphthalein is colourless in acidic medium. On addition of alkali, a pink coloration develops due to the quinonoid form. Addition of excess alkali regenerates the benzenoid structure which is colourless. Phenolphthalein is commonly used in the laboratory as a pH indicator. At pH below 8.5 the molecule exists in colourless form and at pH~9 and above, in pink form.

Phenolphthalein as a pH indicator



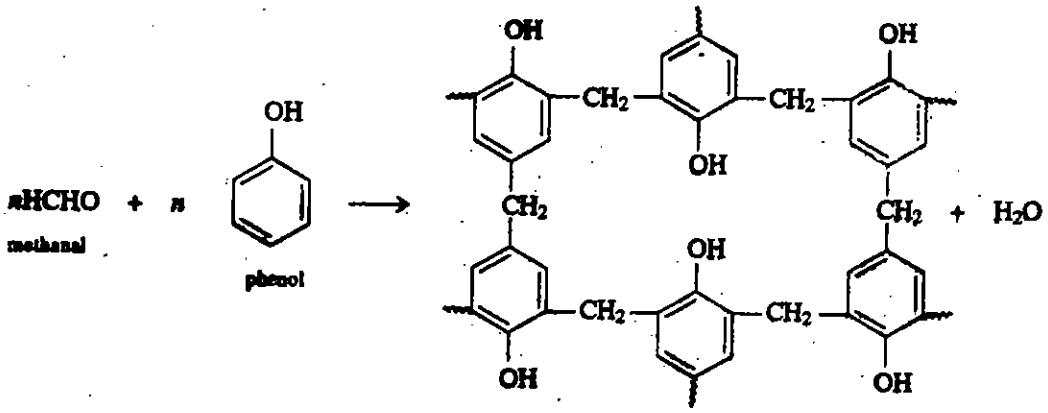
Heating a mixture of phthalic anhydride and resorcinol with anhydrous oxalic acid gives fluorescein:



Although two quinonoid structures II and III can be written for fluorescein, spectral evidence supports structure I. Fluorescein is a red powder which is insoluble in water. It dissolves in alkalis to give a reddish-brown solution which on dilution shows a yellow-green fluorescent. Action of bromine on fluorescein in glacial acetic acid solution gives tetrabromofluorescein which is commonly known as eosin.

The electric resistance of Bakelite makes it especially useful for electric plugs, switches and tools.

The condensation of phenol with excess of methanal (formaldehyde) in the presence of dilute sodium hydroxide gives polymers which are known as Bakelite. These are phenol methanal resins which are three-dimensional polymer of the following possible structure:



segment of Bakelite polymer

SAQ 5

Treatment of phenol with trichloromethane (chloroform) and aqueous sodium hydroxide gives:

a) 2-chlorophenol

b) 2-hydroxybenzaldehyde

c) 3-hydroxybenzaldehyde

d) 3-chlorophenol

12.7 POLYHYDRIC ALCOHOLS

So far we have studied monohydric alcohols. Now let us briefly consider polyhydric alcohols.

12.7.1 Dihydric Alcohols

The dihydric alcohols are known as glycols or diols (in IUPAC nomenclature). 1,2 ethanediol (ethylene glycol or simply glycol) can be prepared by the hydroxylation oxidation of ethene with cold dilute alkaline potassium permanganate:

$$CH_2{=}CH_2 + H_2O + [O] \longrightarrow \underset{\displaystyle OH}{\overset{\displaystyle CH_2-OH}{|}}\ \underset{\displaystyle OH}{\overset{\displaystyle CH_2}{|}}$$

Hydrolysis of ethene chlorohydrin or dihalide with mild alkali, such as aq. $NaHCO_3$ or Na_2CO_3 gives 1,2-ethenediol

$$\begin{array}{l} CH_2-Cl \\ | \\ CH_2-OH \end{array} + NaHCO_3 \longrightarrow \begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} + NaCl + CO_2$$

$$\begin{array}{l} CH_2-Br \\ | \\ CH_2-Br \end{array} + Na_2CO_3 + H_2O \longrightarrow \begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} + 2NaBr + CO_2$$

1,2-Ethanediol is manufactured by the hydration of oxirane (ethylene oxide)

$$\begin{array}{l} O \\ / \quad \backslash \\ H_2C-CH_2 \end{array} + H_2O \longrightarrow \underset{\displaystyle OH}{\overset{\displaystyle H_2C-OH}{|}}\ \underset{\displaystyle OH}{\overset{\displaystyle CH_2}{|}}$$

This is carried out in acid solution at about 333 K or with water at 473 K under pressure.

1, 2-Ethanediol is taken as a typical example. It shows the chemical reactions of monohydric alcohols except that more vigorous conditions are sometimes needed for reaction of the second of the two hydroxyl groups. For example:

i) It reacts with sodium to form a monoalkoxide and at higher temperature, dialkoxide:

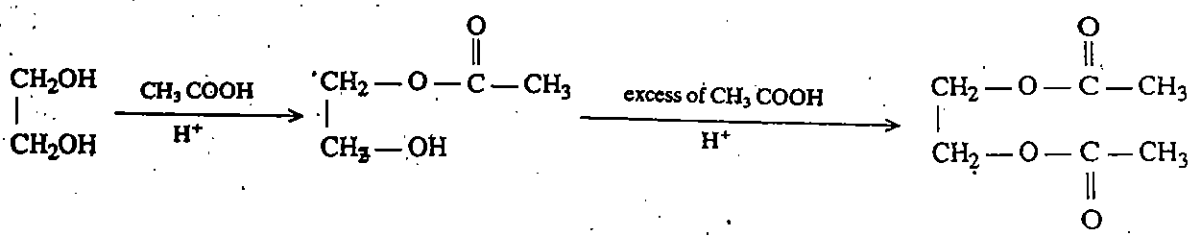
$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow[327\ K]{Na} \begin{array}{l} CH_2O^-Na^+ \\ | \\ CH_2OH \end{array} + \tfrac{1}{2}H_2$$

$$\begin{array}{l} CH_2O^-Na^+ \\ | \\ CH_2OH \end{array} \xrightarrow[423\ K]{Na} \begin{array}{l} CH_2O^-Na^+ \\ | \\ CH_2O^-Na^+ \end{array} + \tfrac{1}{2}H_2$$

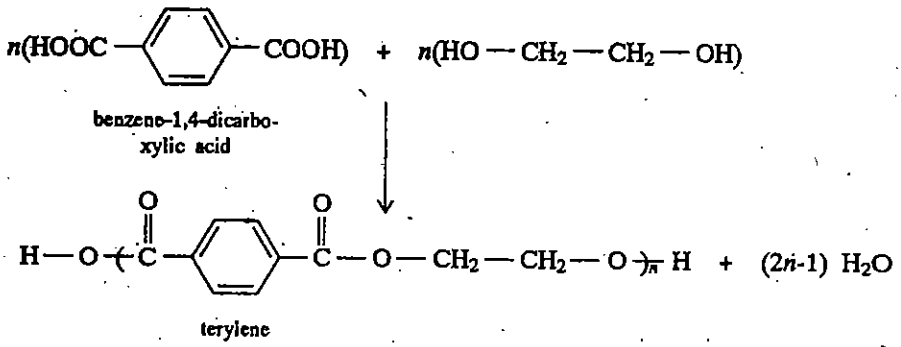
ii) It reacts with phosphorus halides to yield dihalide:

$$3\ \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2PBr_3 \longrightarrow 3\ \begin{array}{l} CH_2-Br \\ | \\ CH_2-Br \end{array} + 2H_3PO_3$$

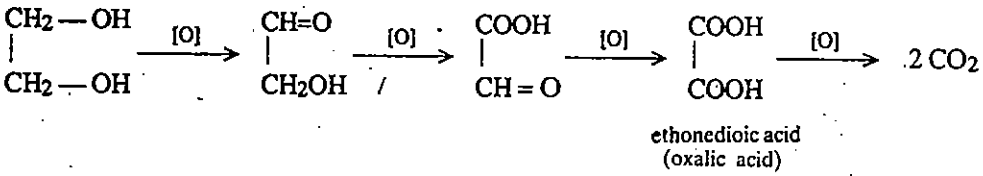
iii) It reacts with carboxylic acid to form esters:



When esterified with a dibasic acid, it forms polymers, for example,



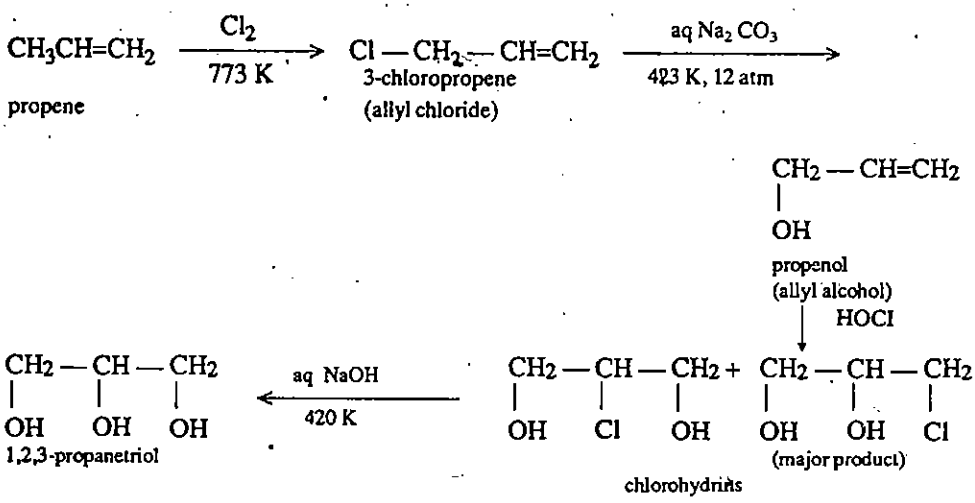
iv) On oxidation with nitric acid, both the primary alcohol groups are oxidised, first to aldehyde and then to carboxyl groups. Ethanedioic acid is finally oxidised to carbon dioxide and water,



1-2 Ethanediol is widely used as a solvent, antifreezeagent and in the manufacture of terylene.

12.7.2 Trihydric Alcohols

1,2,3-Propanetriol (glycerol or glycerin) is an important trihydric alcohol (triol). It occurs in nature as glyceryl ester or glycerides of higher aliphatic acids, for example, hexadecanoic acid, $CH_3—(CH_2)_{14}—COOH$ (palmiticacid) and octadecanoic acid, $CH_3—(CH_2)_{16}—COOH$ (steric acid) in oils and fats. It is obtained commercially as a by-product in the manufacture of soap. It can be prepared from propene by (i) chlorination, (ii) alkaline hydrolysis, (iii) addition of hypochlorous acid and (iv) alkaline hydrolysis of the chlorohydrin:



1,2,3-Propanetriol contains one secondary and two primary alcoholic groups. It undergoes many typical reactions of alcohols. It is also used as an antifreeze, for making explosives and as a moistening agent in soaps and tobacco.

i) As mentioned earlier, with a mixture of cold concentrated nitric and sulphuric acids, 1,2,3-propanetriol forms nitroglycerine—a powerful explosive.

ii) When 1,2,3-propanetriol is heated with a limited amount of hydrogen iodide, 3-iodopropene (allyl iodide) is formed:

$$HOCH_2CHOHCH_2OH + 3HI \longrightarrow [ICH_2CHICH_2I] \longrightarrow I_2 + CH_2{=}CHCH_2I$$

With excess of hydrogen iodide, 2-iodopropane is formed:

$$CH_2{=}CHCH_2I \xrightarrow{HI} CH_3CHICH_2I \xrightarrow{-I_2} CH_3CH{=}CH_2 \xrightarrow{+HI} CH_3CHICH_3$$

iii) When heated with potassium hydrogen sulphate, 1,2,3-propanetriol is dehydrated to propenal (acrolein):

$$HOCH_2CHOHCH_2OH \xrightarrow{KHSO_4} CH_2{=}CHCHO + H_2O$$

propenal (acrolein)

By heating ethanedioic acid (oxalic acid) or methanoic acid with 1,2,3-propanetriol at 533 K propenol (allyl alcohol) is obtained:

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} COOH \\ | \\ COOH \end{array} \dashrightarrow \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array} + 2CO_2 + 2H_2O$$

propenol (allyl alcohol)

Oxidation of 1,2,3-propanetriol gives a large number of products. Their nature depends on the type of oxidising agent used. The primary alcoholic groups are oxidised to aldehyde or carboxylic acid and the secondary alcoholic group to the ketonic group. The oxidation products of 1,2,3-propanetriol are:

$\begin{array}{l} CHO \\ \vert \\ CHOH \\ \vert \\ CH_2OH \end{array}$	$\begin{array}{l} COOH \\ \vert \\ CHOH \\ \vert \\ CH_2OH \end{array}$	$\begin{array}{l} COOH \\ \vert \\ CHOH \\ \vert \\ COOH \end{array}$	$\begin{array}{l} COOH \\ \vert \\ CO \\ \vert \\ COOH \end{array}$	$\begin{array}{l} CH_2OH \\ \vert \\ CO \\ \vert \\ CH_2OH \end{array}$
2,3-dihydroxy-propanal (glyceral-dehyde)	2,3-dihydroxy-propanole acid (glyceric acid)	2-hydroxy-propendioic acid (tartronic acid)	2-oxopropandioic acid (mesooxalic acid)	1,3-dihydroxypropanone (dihydroxy acetone)

Glyceryl esters or glycerides of higher fatty acids are known as **oil** and **fats.** They are simple **lipids** and can be simple glycerides or mixed glycerides. The mixed glycerides commonly occur in nature. Some of the examples are:

$\begin{array}{l} CH_2OCOC_{17}H_{35} \\ \vert \\ CHOCOC_{17}H_{35} \\ \vert \\ CH_2OCOC_{17}H_{35} \end{array}$

stearyolglycerol (tristearin)

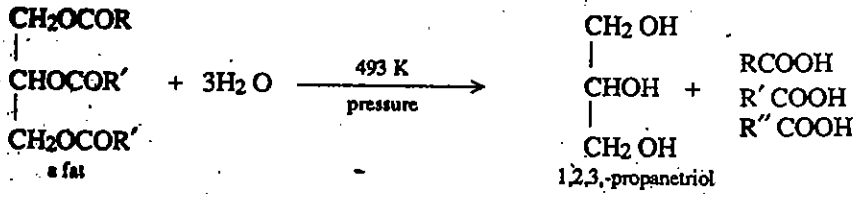
simple glyceride

$\begin{array}{l} CH_2OCOC_{15}H_{31} \\ \vert \\ CHOCOC_{17}H_{33} \\ \vert \\ CH_2OCOC_{17}H_{35} \end{array}$

1-stearyol-2-oleoyl 1-3--palmitoylglycerol

mixed glyceride

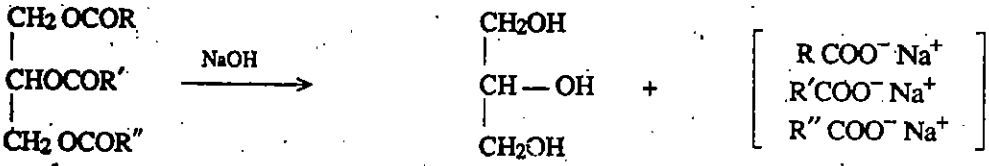
As said earlier, 1,2,3-propanetriol is obtained by the hydrolysis of oils and fats with water and high pressure at 493 K.



a fat

1,2,3,-propanetriol

The fatty acids so obtained, are used in the manufacture of candles. If the hydrolysis of oils and fats is done by alkali, sodium salts of fatty acids (soaps) are obtained. This process is known as saponification. We will consider soaps in more detail in Unit 15.

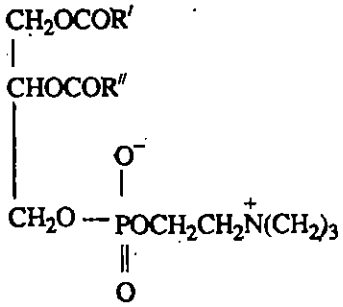


a fat

1,2,3-proponetriol

soap

Phospholipids are also glycerides in which two of the hydroxyl groups are esterified with fatty acid residues and the third with a phosphoric acid moiety. The latter contains phosphorus and nitrogen. One example is:

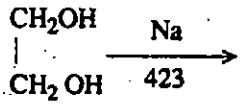


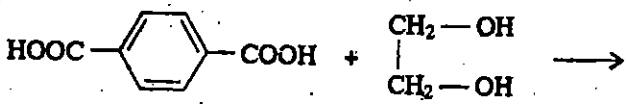
phosphatidylcholin

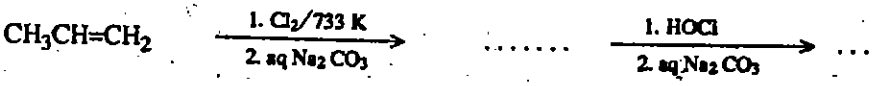
Phospholipids occur in the brain and the spinal chord.

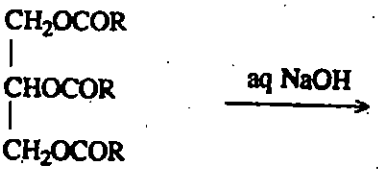
SAQ 6

Complete the following equations:

a) 

b) 

c) 



12.8 INDUSTRIAL USES OF ALCOHOLS AND PHENOLS

Methanol is poisonous. It is miscible with water and other organic solvents. It causes blindness. It is widely used as a solvent for paints, varnishes, etc., in the manufacture of dyes, perfumes, methanal (formaldehyde), and for making methylated spirit and antifreeze mixtures for automobiles.

Industrial alcohol is the ordinary rectified spirit, which contains 95% of ethanol, the rest being water. Ethanol is used for preparation of esters, ethers, trichloroethanal (chloral), trichloromethane (chloroform), as a solvent for gums, resins, paints, varnishes, etc., and as a fuel. It is also the main constituent of alcoholic drinks like whisky, rum, wine, beer, etc.

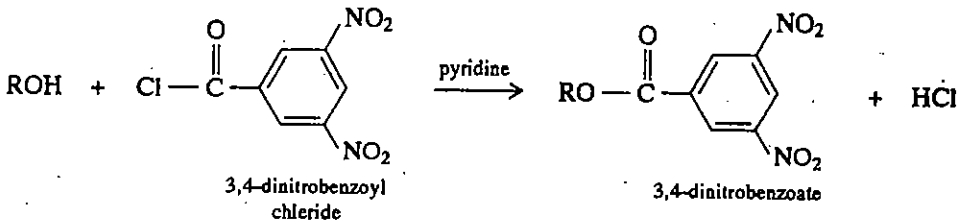
Phenols are used as antiseptic and disinfectant, in the preparation of dyes, drugs and plastics, and as developers in photography.

Some nitro derivatives of polyhydric alcohols (e.g., nitroglycerine) are used as explosives. Alfred Nobel discovered the powerful explosive, dynamite, which is nitroglycerine absorbed in kieselguhr. Another explosive, cellulose nitrate, is known as gun cotton. Cordite is a mixture of nitroglycerine, gun cotton and vaseline. Cellulose acetate is used for making artificial silk.

Polyhydric aldehydes and ketones constitute an important class of compounds which occur widely in nature, as carbohydrates. Amongst these, glucose is the main energy source in plants and animals.

12.9 LAB DETECTION

The reaction with sodium metal to evolve hydrogen gas is of some use for the detection of alcohols. The presence of traces of moisture, however, affects the characterisation. The presence of an hydroxyl group in a molecule is often indicated by the formation of an ester upon treatment with an acid chloride or an anhydride. Compounds like alcohols, phenols, primary and secondary amines (those containing an active hydrogen atom) on treatment with benzoyl chloride in the presence of dilute aqueous sodium hydroxide give benzoyl derivatives (**Schotten-Baumann reaction**). Sometimes 4-nitrobenzoyl or 3,5-dinitrobenzoyl chlorides are used to prepare derivatives of alcohols and phenols and thus for the characterisation of these compounds.



3,4-dinitrobenzoyl chleride

3,4-dinitrobenzoate

Phenols give violet or blue or green colouration with ferric chloride. The appearance of colour is a sensitive test used to characterise phenols.

As mentioned earlier, alcohols of different classes can be differentiated on the basis of their reaction rates with $HCl/ZnCl_2$. If we take alcohol in a test tube and add mixture of $HCl/ZnCl_2$ the following results are obtained:

primary alcohols $\xrightarrow{HCl/ZnCl_2}$ No reaction at room temperature.

secondary alcohol $\xrightarrow{HCl/ZnCl_2}$ Reaction mixture gets cloudy in 5-10 minutes.

Tertiary, alkyl, benzyl alcohols	$\xrightarrow{HCl/ZnCl_2}$	Reaction mixture gets cloudy immediately.
Phenols	$\xrightarrow{HCl/ZnCl_2}$	No reaction (even at high temperature).

12.10 SUMMARY

In this unit we have described the chemistry of alcohols and phenols. We are summarising below what we have studied:

- Alcohols are obtained by the hydrolysis of alkyl halides and reduction of aldehydes and ketones. They are prepared on a large scale by hydration of alkenes, catalytic treatment of water gas, catalytic oxidation of natural gas and fermentation of starch or sugars.
- Alcohols are very weak acids. The molecules tend to associate themselves by forming hydrogen bonds. Oxidation or dehydrogenation of alcohols give mainly carbonyl compounds. They react with carboxylic acids to form esters. Dehydration of alcohols leads to alkenes.
- Phenols are obtained by the decarboxylation of phenolic acid, action of water on diazonium salts and from Grignard reagent. They are prepared on a commercial scale by catalytic oxidation of methylbenzene (toluene) or decomposition of cumene pereoxide or from chlorobenzene by Dow process. Phenols are also obtained from coal tar.
- On heating phenol with trichloromethane (chloroform) and potassium hydroxide, 2-hydroxy benzaldehyde is obtained. On passing carbon dioxide in a mixture of phenol and aq. sodium hydroxide 2-hydroxy benzoic acid is formed.
- Phenol undergoes electrophilic substitution (nitration, halogenation, Friedel-Crafts reaction, sulphonation, etc.) quite readily giving a mixture a ortho- and para-derivatives.
- On condensation with phthalic anhydride in the presence of a dehydrating agent, phenol gives phthalein dyes. With methanal, phenol gives Bakelite—a polymer.
- The polyhydric alcohols have properties similar to those as described above for alcohols.
- Alcohols are commonly used as solvents in synthesis and industry (varnish, paints, etc.). They are also used for manufacture of various chemicals such as dyes, drugs, explosives, perfumes, scents, essences etc.
- Phenols are used as antiseptic and disinfectants and in the manufacture of dyes, drugs and plastics and as photographic developers.

12.11 TERMINAL QUESTIONS

1) Show a structural formula for each name and tell whether it is a primary, secondary or tertiary.
   a) 3-pentanol
   b) 2,2-dimethyl-1-propanol
   c) 2-methyl-1-butanol
   d) 3-methyl-2-pentanol
   e) 1-methylcyclopentanol
2) Which compound from each pair has a higher boiling point and more soluble in water.

a) 1-chloropropane or propanol

b) 1-butanol or 2-methyl-2-propanol

c) 2-butanol or 2-propanol

d) *o*-nitrophenol or *p*-nitrophenol

3) Which is the stronger acid and stronger base, ethanol or phenol? Explain.

4) Write a mechanism for the reaction of

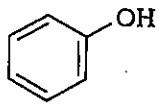
a) ethyl alcohol with HBr

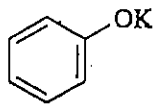
b) 3-dimethyl-2-butanol with HBr

5) Complete the following reactions;

a) $(CH_3)_3COH + HCl \longrightarrow$

b) $C_2H_5OH \xrightarrow[H_2O]{Na}$

c)  $+ \ 3Br_2 \xrightarrow{H_2O}$

d)  $+ \ CO_2 \xrightarrow[2.\ H^+ / H_2O]{1.\ heat}$

6) Give a simple chemical test that would distinguish primary alcohol from secondary and secondary alcohol from tertiary alcohols.

12.12 ANSWERS

Self Assessment Questions

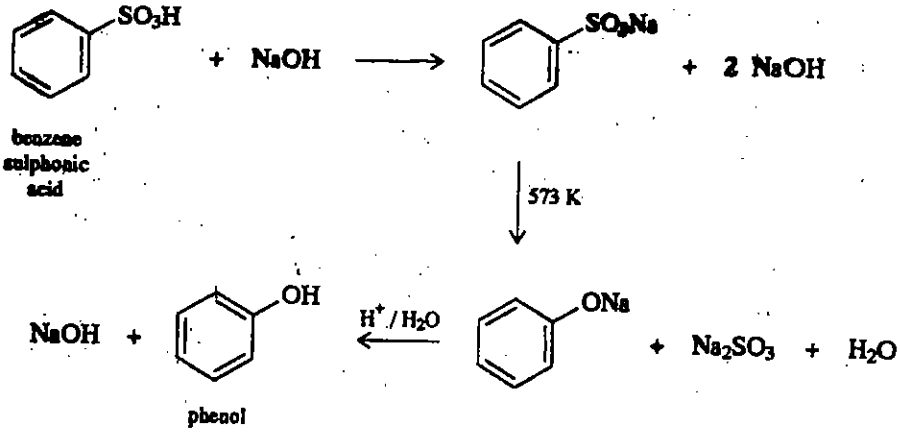
1) a) $CH_3CH_2{-}CH{=}CH_2 \xrightarrow[H^+]{HOH} CH_3{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$

b) $CH_3CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_3 \xrightarrow{OH^- / H_2O} CH_3{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$

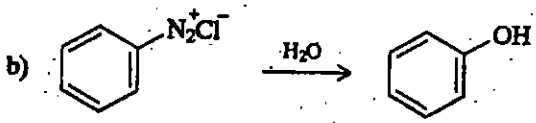
c) $CH_3CH_2{-}\underset{\displaystyle CH_3}{\overset{}{C}}{=}O \xrightarrow{RMgX} CH_3{-}CH_2{-}\underset{\displaystyle MgX}{\underset{|}{C}}RCH_3 \xrightarrow{H^+/H_2O} CH_3{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{C}}RCH_3 + Mg(OH)X$

d) $CH_3CH_2{-}\underset{\displaystyle CH_3}{\overset{}{C}}{=}O \xrightarrow[2.\ H_2O]{1.\ LiAlH_4,\ diethylether} CH_3{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$

2) a)

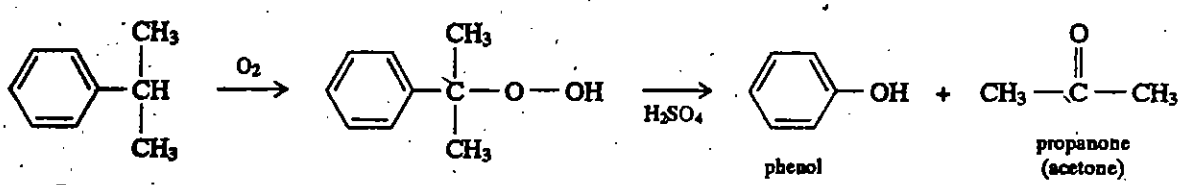


b)



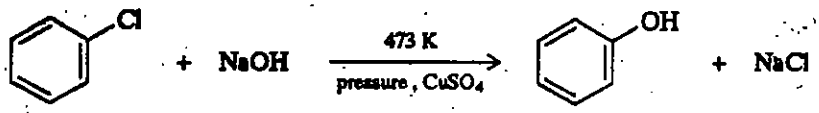
benzyldiazonium salt

c)



Cumene — Cumene hydro-peroxide — phenol — propanone (acetone)

d)

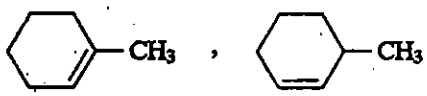


chloro-benzene — phenol

3) a) $CH_2{=}C(CH_3)CH_2CH_3$, less ; $CH_3C(CH_3){=}CHCH_3$, more

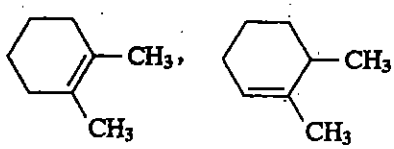
b) $CH_3CH_2CH_2CH{=}CH_2$, less ; $CH_3CH_2CH{=}CHCH_3$; more

c)



more — less

d)



more — less

4) a) 1-propanal; b) 2-butanone;
c) 2-propanone; d) 2-methyl-butene

5) b.

6) a) $HOCH_2CH_2OH \xrightarrow[433\ K]{Na} NaOCH_2CH_2ONa$

b) n(HOOC—C$_6$H$_3$(COOH)—) + nHO—CH$_2$CH$_2$—OH → H—O—(—C(=O)—C$_6$H$_3$(COOH)—C(=O)—OCH$_2$CH$_2$—O—)$_n$H

benzene 2,4-dicarboxylic acid

Terylene

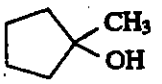
c) $CH_3CH{=}CH_2 \xrightarrow[2.\ aqNa_2CO_3]{1.\ Cl_2/773\ K} CH_2(OH)CH{=}CH_2 \xrightarrow[2.\ aqNa_2CO_3]{1.\ HOCl} CH_2(OH)CH(OH)CH_2OH$

$$\begin{array}{l}CH_2OCOR\\|\\CHOCOR\\|\\CH_2OCOR\end{array} \xrightarrow{3NaOH} \begin{array}{l}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + 3RCOONa$$

Terminal Questions

1) a) $CH_3CH_2CH(OH)CH_2CH_3$, secondary; b) $CH_3C(CH_3)_2CH_2OH$, primary;

c) $CH_3CH_2CH(CH_3)CH_2OH$, primary; d) $CH_3CH_2CH(CH_3)CH(OH)CH_3$, secondary;

e)  , tertiary

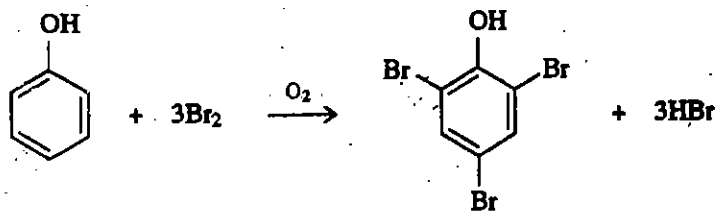
2)		a)	b)	c)	d)
	b.p.	propanol	1-butanol	2-butanol	*p*-nitrophanol
	Solubility in water	propanol	1-butanol	2-propanol	*p*-nitrophenol

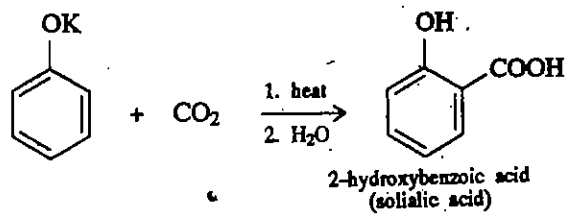
3) See subsection 12.6.1

4) See subsection 12.6.2

5) a) $(CH_3)_3COH + HCl \longrightarrow (CH_3)_3CCl + H_2O$

b) $C_2H_5OH \xrightarrow{Na} C_2H_5ONa + \frac{1}{2}H_2$

c) 

d) 

2-hydroxybenzoic acid (solilic acid)

6) Lucas reagent ($HCl/ZnCl_2$) is used to differentiate primary, secondary and tertiary alcohols. Tertiary alcohols react immediately upon shaking with lucas reagent in a test tube. Secondary alcohols react in 2, 3 minutes and primary alcohols do not react with reagent unless the mixture is heated.

UNIT 13 ETHERS AND SULPHUR ANALOGUES OF ALCOHOLS AND ETHERS

Structure

13.1 Introduction
Objectives

13.2 Classification

13.3 Preparation of Ethers
Preparation of Open Chain Ethers
Preparation of Epoxides

13.4 Properties of Ethers
Physical Properties
Spectral Properties
Chemical Properties of Open Chain Ethers
Chemical Properties of Epoxides

13.5 Crown Ethers

13.6 Industrial Uses

13.7 Sulphur Analogues of Alcohols and Ethers
Preparation of Thiols and Sulphides
Properties of Thiols and Sulphides

13.8 Summary

13.9 Terminal Questions

13.10 Answers

13.1 INTRODUCTION

In the previous unit, while discussing the chemistry of alcohol, it was pointed out that dialkyl derivatives of water are called ethers. In this unit we shall take up the chemistry of ethers.

In this unit we shall first take a look at the different types of ethers and give you their preparation. We shall then consider their structure, physical, spectral and chemical properties and industrial uses. We shall also touch briefly on a special type of macrocyclic (i.e. large ring) compounds, the crown ethers. Finally, we shall take up the chemistry of sulphur analogues of alcohols and ethers.

Objectives

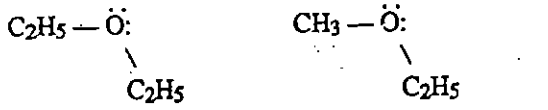
After studying this unit, you should be able to:

- list different types of ethers such as open chain ethers, epoxides and crown ethers,
- outline the preparation of open chain ethers and epoxides,
- explain the physical and spectral properties of ethers,
- describe the chemical properties of open chain ethers and epoxides,
- describe the crown ethers,
- state the different industrial uses of ethers, and
- describe the preparation and properties of thiols and sulphides.

UGCHE-05-20B

3.2 CLASSIFICATION

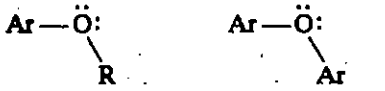
Ethers can be considered as derivatives of water. They can also be considered as alkyl derivatives of alcohols. Like water and alcohols, ethers contains an sp^3 hybridised oxygen atom. But, in an ether the oxygen is bonded to two carbon atoms. The groups bonded to the ether oxygen can be alkyl, aryl, ethenyl, or any other carbon containing groups. Aliphatic ethers may be simple or symmetrical in which both the alkyl groups are the same or mixed i.e. unsymmetrical in which case the two alkyl groups are different, e.g.,



diethyl ether (ether) — simple ether

methyl ethyl ether (methoxy ethane) — mixed ether

Aromatic ethers may be regarded as derivatives of phenol and are also divided into two groups, the alkyl aryl ethers and diaryl ethers:



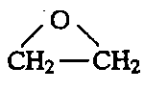
alkyl aryl ethers or phenolic ethers

diaryl ethers

where, R = alkyl group

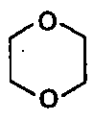
Ar = aryl group

Ethers can be either open chain or cyclic. When the ring size (including the oxygen atom) is five or greater, the chemistry of the cyclic ether is similar to that of an open chain ethers. Three membered cyclic ethers are called oxiranes (IUPAC name), which are often known as epoxides. Because of Baeyer strain associated with small ring, epoxides are more reactive than other ethers.



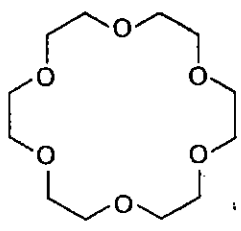
oxirane (ethylene oxide) epoxide

tetrahydrofuran (THF)



1,4-dioxane

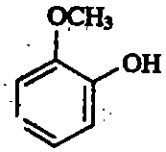
Large ring systems with repeating $-OCH_2CH_2-$ units are called **crown ethers.** These compounds are valuable reagents which can be used to help dissolve inorganic salts in organic solvents. Crown ethers are named as *X* crown *Y*, where *X*=the total number of atoms in the ring and *Y*=the total number of oxygen atoms in the ring. For example,



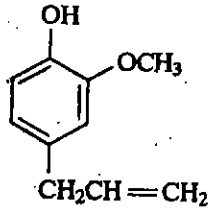
18-Crown-6

A crown ether with a total number of atoms 18 and 6 oxygen atoms in the ring

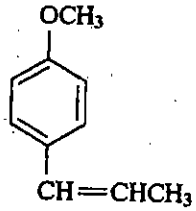
Ethers occur widely in nature, some examples of naturally occurring ethers are:



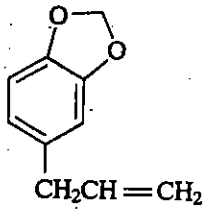
Guaicol (beech-wood tar)



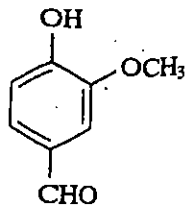
eugenol (oil of cloves)



anethol (aniseed oil)



safrole (camphol oil)



Vanillin (vanilla been)

13.3 PREPARATION OF ETHERS

In this sections, we will discuss first the preparation of open chain ethers and then the eparation of epoxides.

.3.3.1 Preparation of Open Chain Ethers

Ethers are commonly prepared from alcohols. There are two methods.

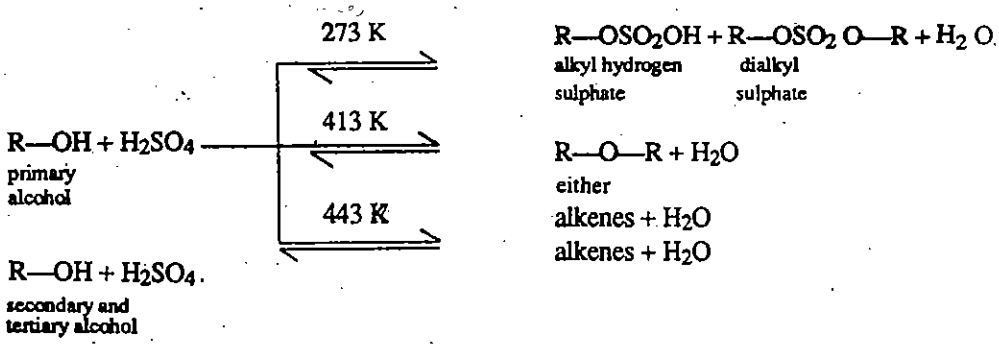
i) Acid catalysed dehydration

ii) Nucleophilic displacement (Williamson ether synthesis)

Let us discuss these preparative method briefly.

i) Acid catalysed dehydration

In Unit 7 we described the conversion of alcohols to alkenes in the presence of sulphuric acid. When an alcohol is reacted with H_2SO_4, a series of reversible reactions occur under different experimental conditions. Which reaction product predominates depends on the structure of the alcohol, the relative concentration of reactants, and the temperature of the reaction mixture. For example.

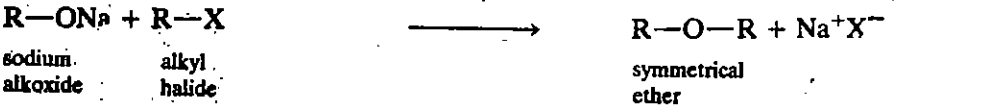


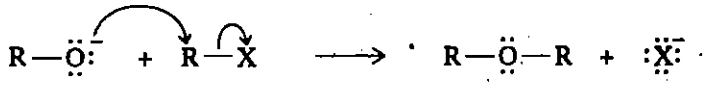
As shown above primary alcohols give alkyl hydrogen sulphate and dialkyl sulphate at low temperatures, symmetrical ethers at moderate temperature and alkenes at high temperature. Tertiary alcohols and to a large extent, secondary alcohols yield alkenes.

Industrially, diethyl ether is prepared by this method from ethanol in the presence of sulphuric acid. But in the laboratory, as might be expected, we get a large number of possible products, and this method is, therefore, seldom used for the synthesis of ethers.

ii) Williamson ether synthesis

Ethers are also prepared by Williamson's synthesis in which alcohols are employed as starting materials. One alcohol is converted to alkyl halide (R—X), another alcohol is converted to sodium or potassium alkoxide or then two products are heated together.





The mechanics of the reaction is S_N2, which we have discussed in detail in Unit 11.

As already mentioned the tendency for alkyl halides to undergo this reaction is *p* > *sec* > *tert*.

Secondary and tertiary alkyl halides lead to alkenes, while aryl and ethenyl halies do not undergo S_N2 reactions, therefore, they do not give ethers with alkoxides or phenoxides.

This method can also be used to prepare phenolic ethers:

$$Ar{-}O^-Na^+ + R{-}X \longrightarrow Ar{-}O{-}R + Na^+X^-$$

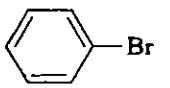
sodium phenoxide; alkyl halide; phenolic ethers or alkyl aryl ether

Before considering the properties of ethers, try the following SAQ.

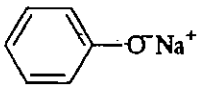
SAQ 1

Predict the major products of these reactions?

a) $CH_3CH_2OH + H_2SO_4 \xrightarrow[413]{\text{warm}}$

b) $CH_3CH_2O^-Na^+ +$  $\xrightarrow{\text{heat}}$

c) $CH_3O^-Na^+ + (CH_3)_3CCl \xrightarrow{\text{heat}}$

d)  $+ CH_3Br \xrightarrow{\text{heat}}$

13.3.2 Preparation of Epoxides

Epoxides are obtained by the reaction of alkenes with peracid, e.g.,

$$RCH{=}CHR + R'COOOH \xrightarrow{\text{in ether or trichloro methane}} \underset{\text{epoxide}}{RCH{-}CHR\ (O)} + R{-}COOH$$

alkene; peracid

They are also prepared by the reaction of chlorohydrin with alkali, e.g.,

$$HOCH_2CH_2Cl + KOH \longrightarrow \underset{\text{oxirane (ethylene oxide)}}{CH_2{-}CH_2\ (O)} + KCl + H_2O$$

2-chloro 1-ethanol chlorohydrin

Ethylene oxide is manufactured by the silver-catalysed oxidation of ethenes with oxygen.

$$\underset{\text{ethene}}{2CH_2{=}CH_2} + O_2 \xrightarrow[523\ K]{Ag} \underset{\text{oxirane (ethylene oxide)}}{CH_2{-}CH_2\ (O)}$$

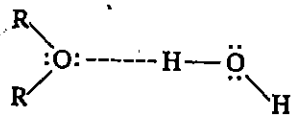
13.4 PROPERTIES OF ETHERS

Before studying the reactions of open chain ethers and epoxides in detail, let us first take up their physical and spectral proposition.

13.4.1 Physical Properties

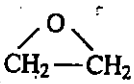
Ethers are polar compounds with dipole moment 3.9×10^{-30}C m (for diethyl ether). But they are not as polar as water, 6.0×10^{-30}C m and alcohols, 5.7×10^{-30}C m (for methanol). Ethers have lower boiling points as compared to those of alcohols containing the same number of carbon atoms. This is due to the fact that, unlike

alcohols, ethers cannot associate through hydrogen bonds in the pure state because they have no hydrogen attached to the oxygen. However, ethers can form hydrogen bonds with water, alcohols and phenols. Because of hydrogen bonding with water, ethers show a considerable solubility in water.



We are summarising the physical properties of some ethers in Table 13,1.

Table 13.1: Physical properties of some ethers

Name	Formula	Bp,K	Density kg dm^{-3} at 293 K	Solubility in H_2O
Dimethyl ether	CH_3OCH_3	249	gas	miscible
Diethyl ether	$C_2H_5OC_2H_5$	307.6	0.71	8 g/100 cm^3
Methyl phenyl ether (anisol)	C_6H_5—OCH_3	427	—	—
Tetrahydrofuran (THF)		339	0.89	miscible
Oxirane (ethylene oxide)		286.5	8.88 (at 283 K)	miscible

Before studying the spectral properties of ethers try the following SAQ.

SAQ 2

To what effect can you attribute water solubility of ethers?

.....

.....

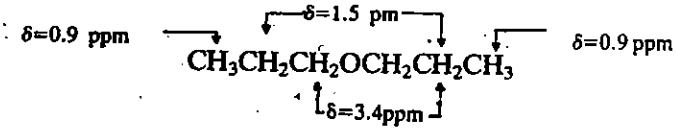
.....

.....

13.4.2 Spectral Properties

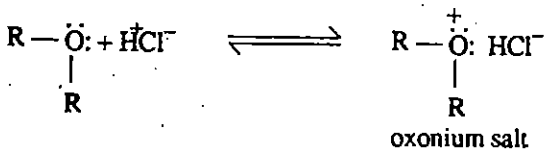
Like alcohols, ethers show the C—O, stretching vibration at 1060-1300 cm^{-1} range in ir spectra. The O—H band characteristic of alcohol is, of course, absent.

In the nmr spectra, as in the case of alcohols, the oxygen atoms cause deshielding of the protons on adjacent carbon (α protons) and shifts their absorption downfield.



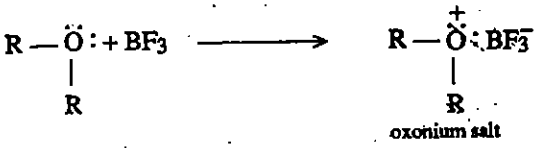
13.4.3 Chemical Properties of Open Chain Ethers

Ethers are quite unreactive and behave more like alkanes than like organic compounds containing functional groups. The bond between carbon and oxygen in a ether is called the **ether linkage.** This ether linkage is not affected by bases, oxidising agents and reducing agents. The oxygen atom in ethers can readily accept protons (base in Bronsted concept) and it also can be electron-pair donor (Lewis base). On treatment with acids, ethers give oxonium salts:



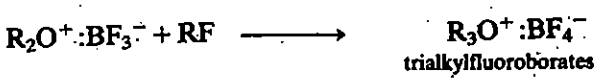
oxonium salt

The solubility in sulphuric acid is thus a convenient method for distinguishing between ethers and hydrocarbons and alkyl halides. Similarly, ethers react with Lewis acids,



oxonium salt

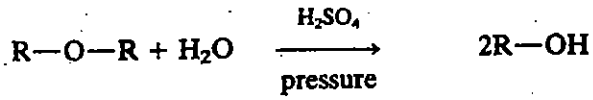
Further treatment with an alkyl fluoride gives a tertiary oxonium salt, trialkyl fluoroborate.



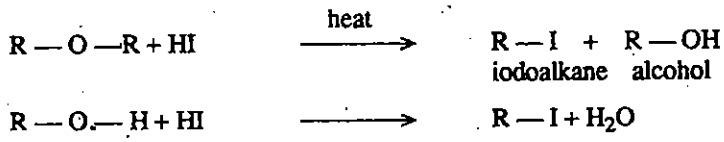
trialkylfluoroborates

The products of the above reaction, i.e. the trialkyl fluoborates are powerful alkylating agents in many reactions.

On heating ethers with dilute sulphuric acid under pressure alcohols are obtained:



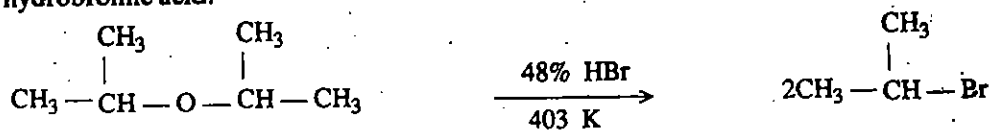
When they are heated with a strong acid (usually HI or HBr), ethers do undergo **substitution reactions.** This is the most important reaction of ethers. In this reaction, cleavage of the ether linkage (C—O) takes place. For example, when heated with HI an ether yields an alcohol and an iodoalkane. Under the reaction conditions, the alcohol formed in turn reacts with HI to give iodoalkane and water.



iodoalkane alcohol

We can write the net reaction as

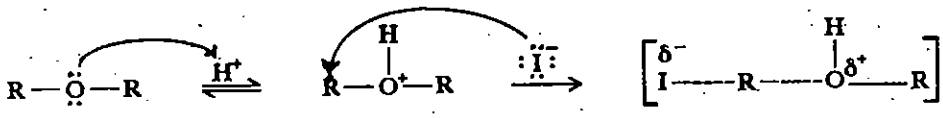
Cleavage of ethers may also be accomplished by the use of concentrated (48%) hydrobromic acid.



2-(1-methyl ethoxy) propane (isopropyl ether)

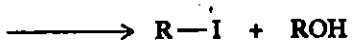
(2-bromopropane) (isopropyl bromide)

Ether cleavage with HI or HBr proceeds by almost the same path as the reaction of alcohol with HX: protonation of the oxygen, followed by S_N1 or S_N2 reaction.



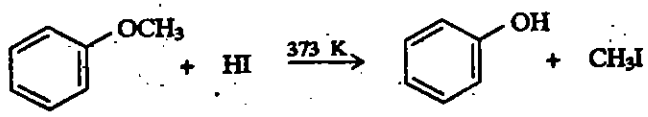
protonated

S_N2 transition state

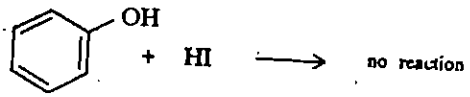


These reactions have great importance in synthesis. The hydroxul group in a poly- functional compound can be protected by converting it into an ether and later, after affecting a chemical transformation at another site in the molecule regenerating through treatment with concentrated hydriodic acid.

Aromatic ethers, such as anisol, yield the alkyl iodide and phenol, not iodobenzene and methanol, because sp^2-hybridise carbon does not under go reaction by an S_N1 or SN^2 path.



anisol



The Zeisel procedure for estimation of the number of methoxyl (CH_3O-) or ethoxyl (CH_3CH_2O-) groups in alkyl aryl ethers consists of ether cleavage with excess HI, followed by distillation of volatile iodomethane or iodoethane from the reaction mixture. Then, the iodoalkanes are treated with an ethanolic solution of silver nitrate and the silver iodide so formed is weighed.

SAQ 3

In Section 13.2, we mentioned the structures of vanillin, a naturally occurring ether. Now, write the equation for the reactions that would occur in the determination of the number of methoxyl groups.

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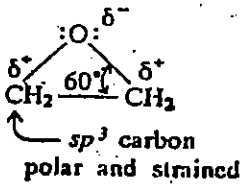
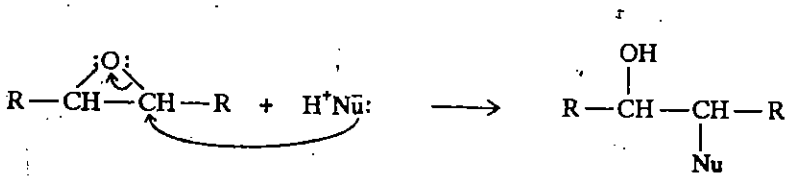
.....

13.4.4 Chemical Properties of Epoxides

An epoxide ring cannot have normal sp^3 bond angles of 109°; instead, the inter nuclear angles are 60°, a geometric requirement of the three-membered ring. The orbitals forming the ring bonds are incapable of maximum overlap. Therefore, epoxide ring are strained. The polarity of the C—O bond, along with the ring strain, contributes to the high reactivity of epoxides compared to the reactivity of other ethers

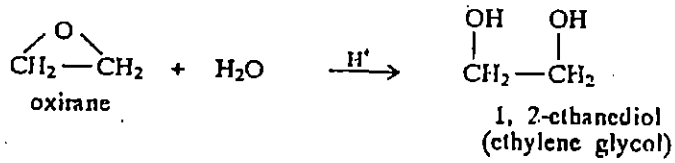


As stated earlier epoxides are highly reactive compounds. The characteristic reaction of epoxides is nucleophilic substitution reactions. In this reaction, ring opening takes place which can occur either under alkaline or acidic reaction conditions. General reaction can be written as

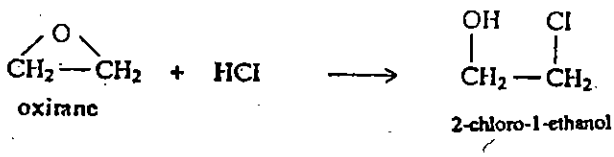


In Acid

Like other ethers, epoxides undergo carbon-oxygen bond cleavage when treated with an acid. However, because of their high reactivity much milder acidic conditions are employed than for cleavage of open chain others.

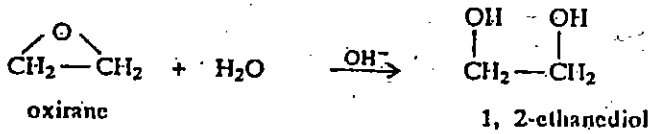


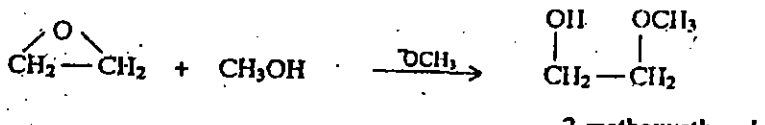
With concentrated acid, e.g., HCl, chlorohydrins are obtained:



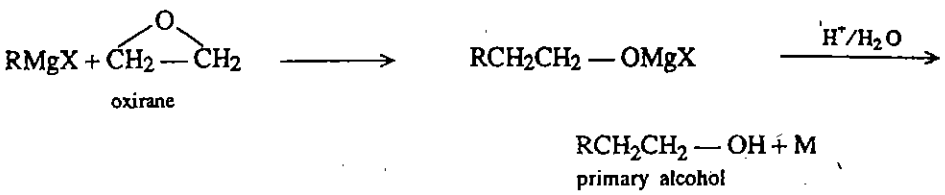
In Base

Unlike open chain or 5- or higher membered cyclic ethers epoxides react with bases, e.g., NaOH, $NaOCH_3$ to give 1,2-ethanediol (ethylene glycol) and 2-methoxyethanol, respectively.

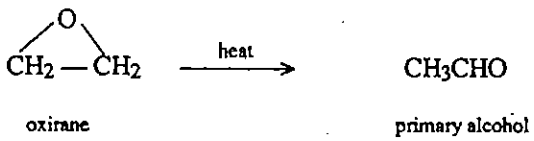




Epoxides are used as intermediates in synthesis. The reaction of epoxides with Grignard reagent has already been mentioned in Unit 11. Oxirane with Grignard reagent gives primary alcohol:



On heating oxirane ethanal is formed:



Reduction with lithium aluminium hydride converts epoxides into alcohols, e.g.,

SAQ 4

How would you prepare 1-butanol from the Grignard reagent C_2H_5MgBr? Show the steps involved in this synthesis.

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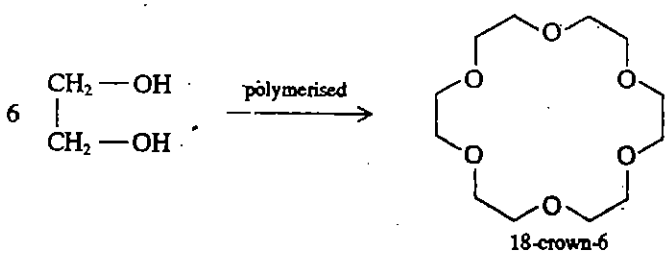
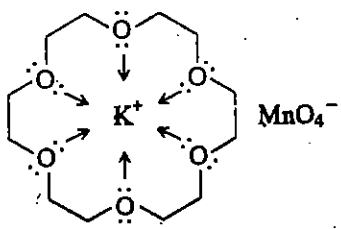
13.5 CROWN ETHERS

As mentioned earlier, crown ethers are cyclic ethers with structure consisting of repeating $-OCH_2CH_2-$ units. They are polymers of 1, 2 ethanediol (glycol).



The unique feature of crown ether is that they can chelate metal ions and give metal complexes which are soluble in nonpolar organic solvents. In this form the crown ether is referred to as the host, while the metal ion is called the guest. For example, purple benzene is a reagent in which $KMnO_4$, complexed by 18-crown-6, is dissolved in benzene.



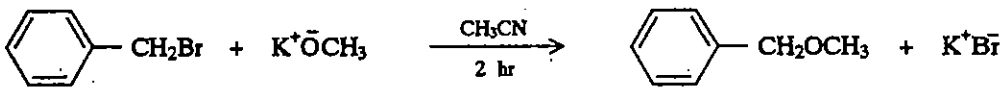
Some of the crown ethers are involved in the transport of ions across biological membranes.

13.6 INDUSTRIAL USES

Ethers are widely used as solvents for oils, fats, gums, resins, etc. Diethyl ether is used as a refrigerant. It is used as an solvent for extraction of organic matter, as an anaesthetic in surgery and in the laboratory for preparation of Grignard reagents. It is known that the Grignard reagents coordinate with ether and in the ether solution it exist as: $RMgX(OR'_2)_2$ (as dietherates). Methy *tert*-butyl ether and diisopropyl ether are used as an anti-knocking agent instead of the highly toxic tetraethyl lead. These compounds increase the octane number when mixed with petrol.

In the presence of air and light, ether forms peroxide, $CH_3CH(OOH)OC_2H_5$, which is highly explosive. To prevent the formation of peroxide either, some ethanol or a small amount of cuprous compound, e.g., cuprous oxide is added.

Crown ethers have great advantages in synthetic organic chemistry. One is that an ionic reagent can be dissolved in an organic phase where it can react with a water-insoluble organic compound. A second advantage is that the nucleophilicity of an anion such as CN^- or CH_3COO^- is greatly enhanced in nonpolar solvents, where the anion is poorly solvated, or naked. An example of how a crown ether increases the rate of a substitution reaction is preparation of the benzyl methyl ether shown in acetonitrite which does not dissolve ionic compounds.

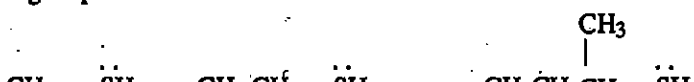


5% yield with no crown ether.
100% yield with 18-crown-6.

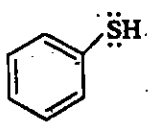
13.7 SULPHUR ANALOGUES OF ALCOHOLS AND ETHERS

In Unit 12 and in this unit we have described the chemistry of alcohols and ethers. In this section we shall take a look at the chemistry of sulphur analogues of alcohols and ethers.

The divalent sulphur compounds can be regarded as the sulphur analogues of the corresponding oxygen compounds. The sulphur analogue of an alcohol is called an **alkane thiol** or simply **thiol**, or by its older name **mercaptan**. Similarly sulphur analogue of a phenol is called an aromatic thiol or thiophenol. The –SH group is called a thiol group.



methanethiol ethanethiol 2-butanethiol



Thiophenol

The sulphur analogue of an ether is called a sulphides or thioether (R—S—R).

$CH_3—S—CH_3$ $CH_3CH_2CH_2—S—CH_2CH_3$

dimethyl sulphide ethyl propyl sulphide

Let us study the preparation of thiols and sulphides.

13.7.1 Preparation of Thiols and Sulphides

Thiols can be prepared from alkyl halides by displacement with hydrosulphide ion, HS^- in ethanol solution.

$$CH_3I + Na^+{}^-SH \xrightarrow{C_2H_5OH} CH_3{-}SH + Na^+I^-$$

methanethiol

Good yields are obtained only if an excess of hydrosulphide is used because of the equilibrium:

$$HS^- + CH_3{-}SH \longrightarrow H_2S + CH_3{-}S^-$$

The thiol anion produced by this equilibrium is itself a good nucleophile and can react with the alkyl halide to give the corresponding sulphide.

$$CH_3{-}S + CH_3{-}I \longrightarrow CH_3{-}S{-}CH_3 + I^-$$

dimethyl sulphide

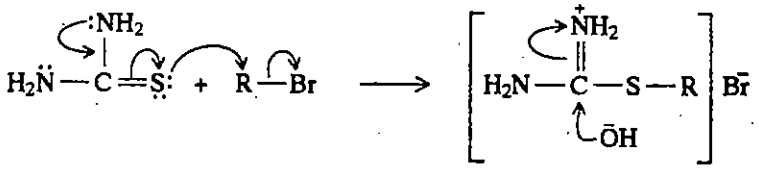
The use of a large excess of hydrosulphide makes its reaction with the alkly halide more probable and maximises the yield of a thiol.

Thiols can also be prepared by the reaction of Grignard reagent with sulphur.

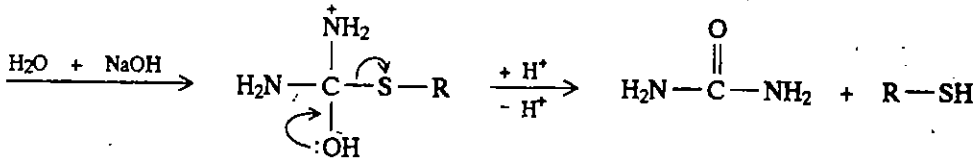
$$(CH_3)_3CMgBr + S_8 \longrightarrow (CH_3)_3CSMgBr \xrightarrow{HCl} (CH_3)_3C{-}SH + MgBrCl$$

2-methyl-2-propane thiol

Thiols may be prepared in good yield by alkylation of the highly nucleophilic thiourea followed by basic hydrolysis:



S-alkylisothiouronium bromide



Sulphides are prepared by a variation of the Williamson synthesis.

$$CH_3CH_2{-}SH + NaOH \longrightarrow CH_3CH_2{-}S^-Na^+ + H_2O$$

ethanethiol

$$CH_3CH_2{-}S^-Na^+ + CH_3Br \longrightarrow CH_3CH_2{-}S{-}CH_3 + NaBr$$

ethyl methyl sulphide

13.7.2 Properties of Thiols and Sulphides

The most characteristic property of the thiols and sulphides is their disagreeable odour. The human nose is very sensitive to these compounds and can detect their presence at levels of about 0.02 parts thiol to one billion parts air. For this reason, methyl sulphide is added to natural or L.P. gas as an odourant for safety precaution. Natural or L.P. gas is itself odourless.

Sulphur is less electronegative than oxygen and its outer electrons are more diffuse, therefore, sulphur atoms form weaker hydrogen bonds then oxygen atoms. For this reason, H_2S has a lower boiling point (b.p. 212 K) than water (b.p. 373 K) and thiols have lower boiling points than their analogous alcohols (see Table 13.2).

Table 13.2: Comparison of the boiling points of thiols and alcohols

Compound	Boiling point K
$CH_3—SH$	279.2
$CH_3—OH$	338.0
$CH_3CH_2—SH$	310.0
$CH_3CH_2—OH$	351.5

Because of the relatively weaker hydrogen sulphur bond, thiols are more acidic than water, with pK_a values ranging from 9 to 12. Unlike alcohols which can in deprotonated only by strong base such as sodium metal or $N\bar{H}_2$, thiols can be ionised by the hydroxide ion.

$$\underset{\text{stronger acid than } H_2O}{CH_3CH_2—SH} + \underset{\text{stronger base than } RS^-}{OH^-} \longrightarrow CH_3CH_2—S^- + H_2O$$

Chemical Reactivity of Thiols and Sulphides

Thiols and sulphides can react in ways that are very similar to those of the corresponding oxygen analogues. Thiols and sulphides react more rapidly than their oxygen analogues because the sulphur atom in thiols and sulphides is more nucleophilic than the oxygen atom in alcohols. The possible explanation for greater nucleophilicity of sulphur analogues is that the outer electrons on sulphur atom is more diffused because of the larger size of sulphur atom as compared to the smaller oxygen atom nucleophiles. Therefore, the electrons of sulphur readily available for substrate (electrophile) in a reaction.

Thiols react with alkyl halides by the normal S_N2 mechanism in the presence of a base to give sulphides.

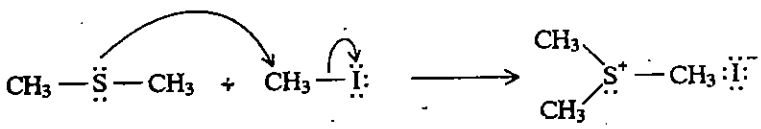
$$R—SH + R'—Br \xrightarrow{NaOH} \underset{\text{sulphide}}{R—S—R'} + NaBr + H_2O$$

Mechanism

$$R—SH + OH^- \longrightarrow R—S^- + H_2O$$

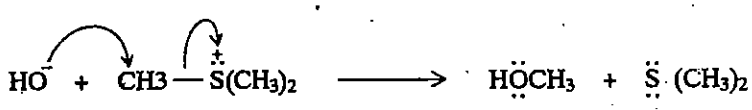
$$R—S^- + R'—Br \xrightarrow{S_N2} R—S—R' + Br^-$$

Similarly, sulphides react readily with alkyl halides by the S_N2 mechanism to produce trialkylsulphonium salts.



trimethylsulphonium iodide

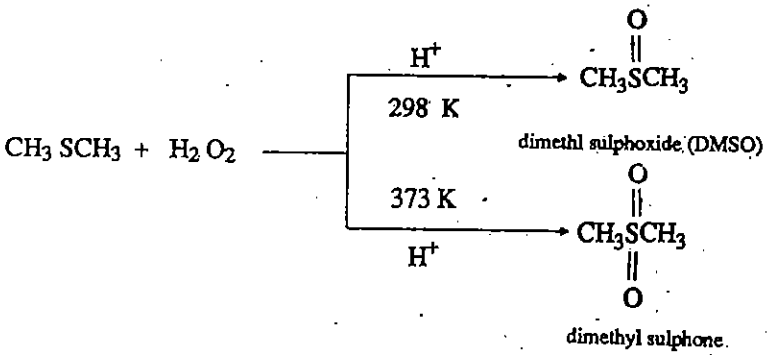
Like their oxonium analogues, sulphonium salts are subject to nucleophilic attack at carbon, sulphide functioning as the leaving group:



Thiols are readily oxidised by mild oxidising agents such as I_2 to disulphides. The disulphide bond is weak is easily reduced by either tin or zinc in dilute acid to give thiol.

$$2R—SH \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} \underset{\text{a disulphide}}{R—S—S—R}$$

The disulphide can be oxidised to a sulphoxide or a sulphone depending on the reaction conditions. For example, 30% hydrogen peroxide in the presence of an acidic catalyst oxidises a sulphides to sulphoxides at 298 K or to sulphones at 373 K.

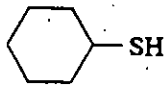


The unique behaviour of sulphoxide is due to the presence of the empty *d* orbital in the sulphur atom.

SAQ 5

Complete the following equations:

a) $CH_3—S—CH_3 \xrightarrow[298\ K]{H_2O_2}$

b)  $\xrightarrow[2.\ CH_3CH_2I]{1.\ NaOH}$

c) $C_2H_5SH \xrightarrow{I_2}$

13.8 SUMMARY

What we have studied in this unit can be summarised as follows:

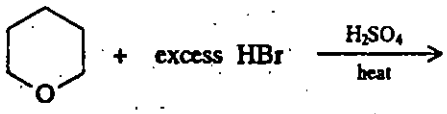
- Ethers can be prepared by the reaction of alcohols with sulphuric acid at moderate temperatures or by the reaction of an alkoxide (RO^-) or phenoxide (ArO^-), with an alkyl halide (Williamson ether synthesis).
- Epoxides can be prepared by the reaction of a per acid (RCOOOH) with an alkene or by the reaction of chlorohydrin with alkali.
- Ethers are less reactive than alcohols and they undergo only ether cleavage reaction when heated with HBr or HI.
- Epoxides are more reactive than other ethers and undergo ring opening with acids or with bases or with Grignard reagents.
- Crown ethers are cyclic ethers that are used to chelate metal ions.
- Cyclic ethers are intermediates in many synthetic reactions. Most ethers are used as solvents.
- Thiols and sulphides are similar to their oxygen analogues in many of their reactions, through they are stronger nucleophiles.

13.9 TERMINAL QUESTIONS

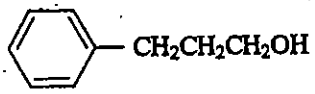
1) Complete the following equations:

a) $ROH + H_2SO_4 \xrightarrow{273\ K}$

b) $C_6H_5O^-Na + C_2H_5Br \longrightarrow$
sodium phenoxide

c) 

2) Write equation to show how you would prepare the following compound.



3) How are the methoxy and ethoxy groups estimated in a compound?

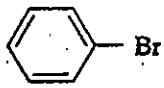
4) Give two important features of the crown ethers.

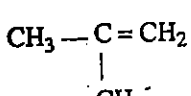
5) Why one sulphur analogues of alcohol and ethers more nucleophilic? Give two examples of their nucleophilic reactions.

13.10 ANSWERS

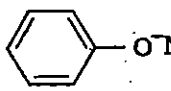
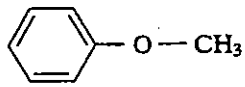
Self Assessment Questions

1) a) $CH_3CH_2OH + H_2SO_4 \xrightarrow[\text{excess of alcohol}]{\text{warm}} CH_3CH_2-O-CH_2CH_3 + H_2O$ (diethyl ether)

b) $CH_3CH_2O^-N^+a$ +  $\xrightarrow{\text{heat}}$ no reaction

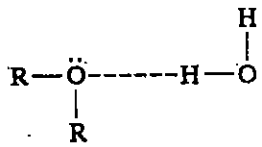
c) $CH_3O^-Na^+ + (CH_3)_3CCl \xrightarrow{\text{heat}}$ 

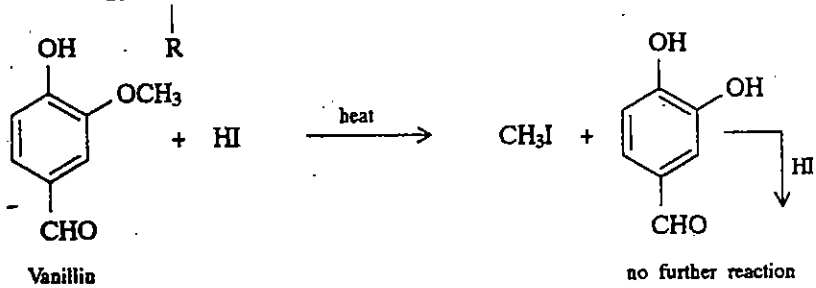
2-methyl propene

d)  + $CH_3Br \xrightarrow{\text{heat}}$ 

methyl phenyl ether (anisole)

2) Water solubility of ether can be attributed to hydrogen bonding between oxygen of ether with water.

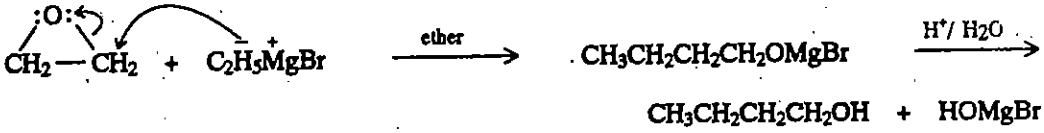


3) 

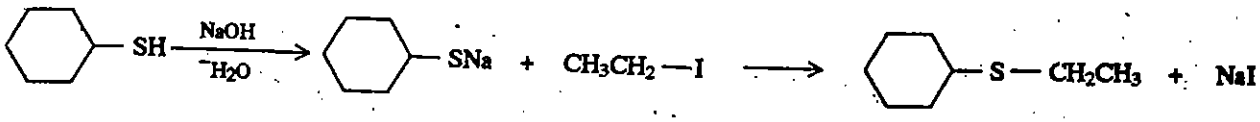
Vanillin

no further reaction

4) 1-Butanol can be obtained by the reaction of Grignard reagent C_2H_5MgBr with oxirane and followed by hydrolysis with water.



5) a) $CH_3—S—CH_3 \xrightarrow[298\ K]{H_2O_2} CH_3—\overset{\overset{O}{\|}}{S}—CH_3$ dimethyl sulphoxide

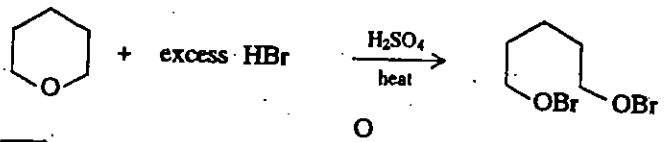
b) 

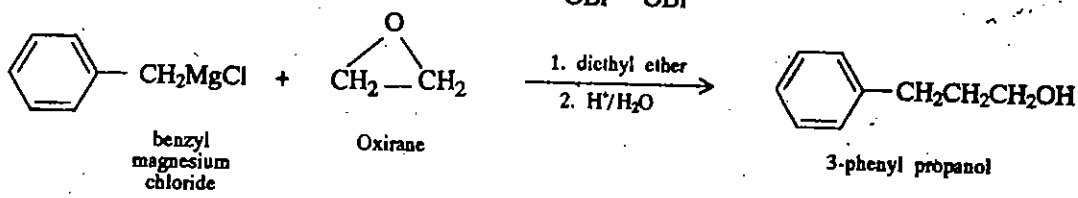
c) $C_2H_5—SH + I_2 \longrightarrow R—S—S—R$ a disulphide

Terminal Questions

1) a) $R—OH + H_2SO_4 \xrightarrow{273\ K} R—OSO_2OH + R—OSO_2O—R + H_2O$
alkyl hydrogen sulphate; dialkyl sulphate

b) $C_6H_5—ON_a + C_2H_5—Br \longrightarrow C_6H_5—C—C_2H_5 + NaBr$
sodium phenoxide; ethylphenyl ether

c) 

2) 

benzyl magnesium chloride; Oxirane; 3-phenyl propanol

3) Methoxy or ethoxyl groups in an organic compounds are estimated by the Zeisel method. In this method the organic compound is first heated with excess of HI followed by distillation of volatile iodomethane or iodoethane from the reaction mixture. Then the iodomethane or iodoethane is treated with ethanolic solution of silver nitrate, and silver iodide so formed is weighed.

4) i) Crown ethers can chelate metal ions and give metal complexes, which are soluble in non-polar organic solvents.

ii) Nucleophilicity of certain anions is also increased by the crown ether and hence increased the rate of reaction of such anions.

5) See section 13.10.2.

UNIT 14 ALDEHYDES AND KETONES

Structure

14.1 Introduction
Objectives

14.2 Preparation
General Methods of Preparation of Aldehydes and Ketones
Specific Methods of Benzaldehyde
Industrial Preparations of Aldehydes and Ketones

14.3 Physical and Spectral Properties
Nature of the Carbonyl Group
Physical Properties
Spectral Properties

14.4 Reactions of Aldehydes and Ketones
Addition Reactions
Reactions of α Hydrogen
Oxidation
Reduction
Specific Reactions of Methanal
Specific Reactions of Aldehydes
Specific Reactions of Ketones

14.5 Reactions of Aromatic Aldehydes and Ketones
Benzaldehyde
Phenylethanone

14.6 Industrial Uses

14.7 Lab Detection

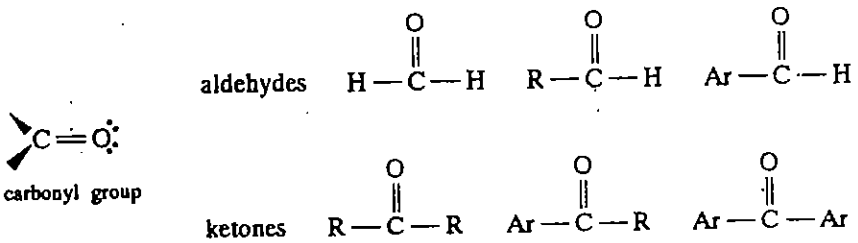
14.8 Summary

14.9 Terminal Questions

14.10 Answers

14.1 INTRODUCTION

In previous units you have studied the chemistry of alcohols and ethers. In this unit we take up aldehydes and ketones. Both these classes of organic compounds have a carbonyl group, >C=O. A ketone has two alkyl (or aryl) groups attached to the carbonyl carbon, while an aldehyde has at least one hydrogen atom attached to the carbonyl carbon. The other group in an aldehyde can be alkyl, or aryl



carbonyl group

The remarkable reactivity of the carbonyl group makes the chemistry of aldehydes and ketones the backbone of synthetic organic chemistry. The double bond between the carbon and oxygen atoms in these compounds serves as a model for the reaction of many other functional groups containing π bonds between dissimilar atoms. Although the reactions of carbonyl compounds are quite simple their synthetic utility is enormous. Additions and substitution reactions are of major interest. In this unit you

will learn the basic principles which are responsible for the extreme reactivity of these compounds and on the basis of which reliable predictions can be made.

Here we will first consider the preparation of aldehydes and ketones and then the characteristic reactions of the carbonyl-group. Finally, we will study industrial uses of aldehydes and ketones and methods used for their detection.

Objectives

After studying this unit, you should be able to:

- list and describe the preparation of aldehydes and ketones,
- describe the commercial methods of preparation of methanal, ethanal, propanone, benzaldehyde and phenylethanone,
- describe the physical properties and spectral characteristics of carbonyl compounds,
- explain the reactivity of aldehydes and ketones,
- describe the lab detection of carbonyl compounds and the test which distinguish aldehydes from ketones, and
- state the industrial uses of aldehyde and ketones.

14.2 PREPARATION

We have already learned several reactions that can be used for the preparation of aldehydes and ketones. Recall the oxidation of alkenes with ozone, hydration of alkynes and oxidation or dehydrogenation of alcohols.

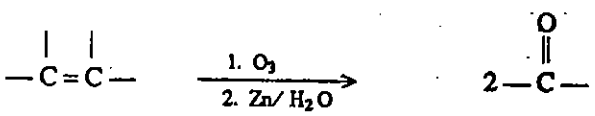
In this section we will first consider the general methods for the preparation of aldehyde and ketones and then follow them up with specific methods for benzaldehyde and industrial methods for the production of methanal, ethanal, propanone, benzaldehyde and phenylethanone (acetophenone).

14.2.1 General Methods of Preparation of Aldehydes and Ketones

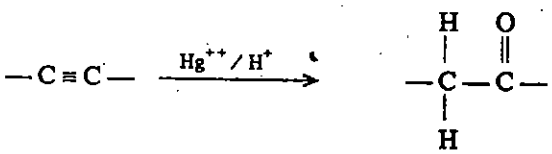
Aldehydes and ketones can be prepared from alkenes, alkynes, alcohols, carboxylic acids and their derivatives. We are summarising the general reactions of these methods of preparation in Table 14.1.

Table 14.1: Preparation of Aldehydes and Ketones

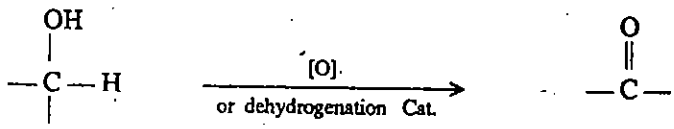
From alkenes



From Alkynes



From Alcohol



From Carboxylic Acids and their Derivatives

From Calcium Salts of Carboxylic Acids

$$(RCOO)_2Ca \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-R + CaCO_3$$

From the reaction of Carboxylic Acids with Manganous oxide

$$RCOOH \xrightarrow[573\ K]{MnO} R-\overset{O}{\overset{\|}{C}}-R + CO_2 + H_2O$$

From acid chlorides by the Rosenmund's Method

$$RCOCl + H_2 \xrightarrow{H_2/Pd/BaSO_4} RCHO + HCl$$

From the Stephen's Method

$$2\ RCN \xrightarrow[HCl]{SnCl_2} 2\ RCHO + (NH_4)_2SnCl_6$$

From the Friedel-Crafts Reaction

$$Ar-H + R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{AlCl_3} Ar-\overset{O}{\overset{\|}{C}}-R$$

Preparation of aldehydes and ketones from alkenes and alkynes has been discussed in Unit 7 and Unit 8, respectively. Here, we will consider preparation of these compounds from alcohols, and carboxylic acids and their derivatives.

i) From Alcohols

As mentioned in Unit 12, primary alcohols give aldehydes and secondary alcohols give ketones on dehydrogenation and oxidation. This is the most common way of synthesising an aldehydes and ketones in the laboratory.

$$RCH_2-OH \xrightarrow[\text{or Cu, 573 K}]{[O]} R-\overset{O}{\overset{\|}{C}}-H$$

primary alcohol — aldehyde

$$R-\overset{OH}{\overset{|}{C}}-R' \xrightarrow[\text{or Cu, 573 K}]{[O]} R-\overset{O}{\overset{\|}{C}}-R'$$

secondary alcohol — ketone

We generally use the following oxidising agents for the oxidation of alcohols:

i) alkaline potassium permanganate solution

ii) hot, concentrated HNO_3

iii) chromic acid (H_2CrO_4)

iv) chromium trioxide (CrO_3) complex with pyridine or with pyridine and HCl

For oxidation of secondary alcohols aluminium tertiary-butoxide is used in the **Oppenauer oxidation.** In this method, the reaction mixture is first heated and then propanone is added:

Oppenauer oxidation is reversible and the reverse reaction is known as the Meerwein-Ponndorf -Verley reduction

$$R-\overset{O}{\overset{\|}{C}}-R + CH_3-\overset{OH}{\overset{|}{C}}H-CH_3 \underset{Al(tert\text{-}BuO)_3}{\rightleftharpoons} R-\overset{OH}{\overset{|}{C}}H-R + CH_3\overset{O}{\overset{\|}{C}}CH_3$$

$$3\ R-\overset{OH}{\overset{|}{C}}H-R + Al(tert\text{—}BuO)_3 \longrightarrow R-\overset{R}{\overset{|}{C}}HO)_3Al + 3\ tert\text{—}BuOH$$

secondary alcohol — aluminium *tert*-butoxide — aluminium alkoxide

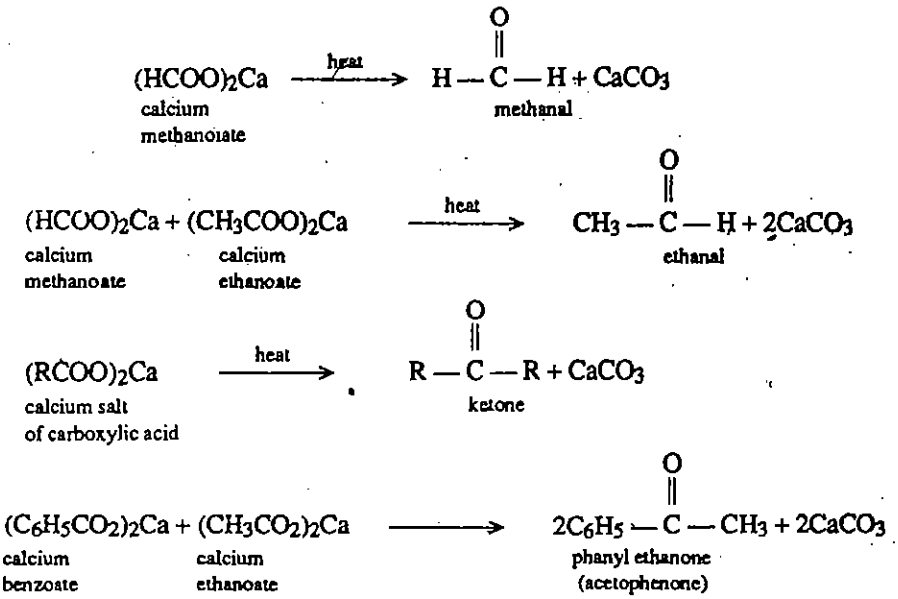
$$(R-\overset{R}{\overset{|}{C}}HO)_3Al + 3CH_3COCH_3 \longrightarrow (CH_3-\overset{CH_3}{\overset{|}{C}}HO)_3Al + R-\overset{O}{\overset{\|}{C}}-R$$

propanone (acetone) — aluminium isopropoxide — ketone

) From Carboxylic Acids and their Derivatives

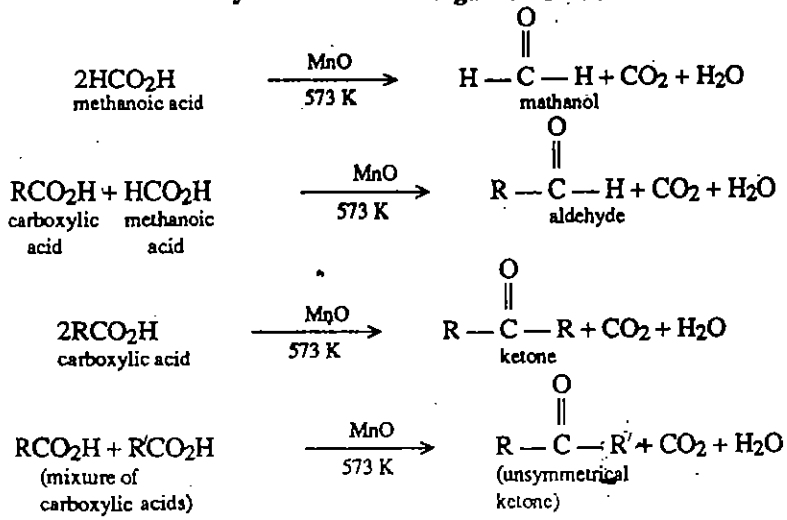
Carboxylic acids can be converted into aldehydes and ketones either by heating their alcium salts or by passing vapours of the acid over heated manganous oxide or by eduction of acid chlorides with hydrogen in the presence of palladium over barium ulphate (**Rosenmund's method**). We will consider these reactions in more detail in Units 15 and 17. General equations for these reactions are given below:

rom Calcium Salts of Carboxylic Acids



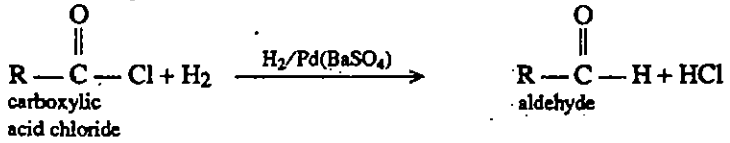
(mixture of calcium salt of carboxylic acid) (unsymmetrical ketone)

rom the Reaction of Carboxylic Acids with Manganous Oxide



lease note that for aldehydes other than methanal and for unsymmetrical ketones, a ixture of acids and their calcium salts in molar proportion is taken.

rom Acid Chlorides by the Rosanmund's Method



here R = CH_3 or C_6H_5

aSO_4 helps to stop the reduction at the aldehyde stage.

) From the Stephen's Method

eduction of an alkyl cyanide with stannous chloride and hydrochloric acid followed y hydrolysis with steam gives aldehydes (**Stephen's method**):

$$\underset{\text{alkyl cyanide}}{2R-CN} \xrightarrow[HCl]{SnCl_2} [RCH=NH_2]_2SnCl_6 \xrightarrow{H_2O} \underset{\text{aldehyde}}{2R-\overset{\overset{O}{\|}}{C}-H} + (NH_4)_2SnCl_6$$

where R = CH_3 or C_6H_5

iv) From the Friedel-Crafts Acylation Reaction

Aryl ketones can be prepared by Friedel-Crafts acylation reaction. For example, phenylethanone (acetophenone) is prepared as follows:

$$\underset{\text{benzene}}{C_6H_6} + CH_3-\overset{\overset{O}{\|}}{C}-\underset{\text{ethanoyl chloride}}{Cl} \xrightarrow{AlCl_3} \underset{\text{phenylethanone (acetophenone)}}{C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3} + HCl$$

SAQ 1

An organic compound A (molecular formula C_3H_7Cl) was treated with aqueous sodium hydroxide and the vapours of the product obtained were passed over heated copper to give propanone (acetone). A is

a) 1-chloropropane **b) 2-chloropropane**
c) cyclopropane hydrochloride

14.2.2 Specific Methods for Benzaldehyde

Benzaldehyde can be obtained by the following methods:

i) On boiling (chloromethyle) benzene (benzyl chloride) with aqueous copper or lead nitrate:

$$2C_6H_5CH_2-Cl + Pb(NO_3) \xrightarrow{[O]} 2C_6H_5-\overset{\overset{O}{\|}}{C}-H + PbCl_2 + 2HNO_2$$

ii) Oxidation of methylbenzene with chromium trioxide in ethanoic anhydride (acetic anhydride) or with chromyl chloride (**Etard' reaction**) gives benzaldehyde:

$$\underset{\substack{\text{methylbenzene}\\\text{(toluene)}}}{C_6H_5CH_3} \xrightarrow[\text{or } CrOCl_2]{CrO_3/(CH_3CO)_2O} \underset{\text{benzaldehyde}}{C_6H_5-\overset{\overset{O}{\|}}{C}-H} + HCl$$

iii) By passing a mixture of carbon monoxide and hydrochloric acid gas through benzene in the presence aluminium chloride and cuprous chloride (**Gattermann-Koch synthesis**):

$$C_6H_6 + CO + HCl \xrightarrow{AlCl_3, Cu_2Cl_2} \underset{\text{benzaldehyde}}{C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3} + HCl$$

iv) The reaction of hydrogen cyanide and hydrogen chloride with benzene in the presence of aluminium chloride (**Gattermann synthesis**) followed by treatment with water gives benzaldehyde:

$$C_6H_6 + HCN + HCl \xrightarrow{AlCl_3} C_6H_5CH=NH \xrightarrow{H_2O} \underset{\text{benzaldehyde}}{C_6H_5-\overset{\overset{O}{\|}}{C}-H} + NH_3 + HCl$$

v) Benzaldehyde occurs in nature as the glucoside amygdalin, present in bitter almonds. It is known as oil of bitter almonds. Hydrolysis of amygdalin by dilute acids or enzymes gives benzaldehyde, glucose and hydrogen cyanide:

$$\underset{\text{amygdalin}}{C_{20}H_{27}O_{11}N} + 2H_2O \xrightarrow[\text{or enzyme}]{H^+} \underset{\text{benzaldehyde}}{C_6H_5-\overset{\overset{O}{\|}}{C}-H} + 2C_6H_{12}O_6 + HCN$$

14.2.3 Industrial Preparations of Aldehydes and Ketones

Industrial preparation of some common carbonyl compounds are described below:

Methanal

It is manufactured from methanol by two processes:

i) Oxidation of methanol using silver or copper catalyst.

$$\underset{\text{methanal}}{H-\overset{\overset{O}{\|}}{C}-H} + H_2O \xleftarrow[773\ K]{Ag/air} \underset{\text{methanol}}{CH_3-OH} \xrightarrow[573\ K]{Cu} \underset{\text{methanal}}{H-\overset{\overset{O}{\|}}{C}-H} + H_2$$

Although the silver catalyst is expensive no silver is lost and catalyst is easily regenerated and can be recycled.

ii) Oxidation using zinc-chromium or iron-molybdenum oxide catalyst.

$$CH_3-OH \xrightarrow[\substack{\text{zinc-chromium or}\\ \text{iron-molybdenum}\\ \text{oxide catalyst}}]{[O]} H-\overset{\overset{O}{\|}}{C}-H$$

Methanol it salf is made from enriched water gas,

$$CO + 4H_2 \xrightarrow[523\ K,\ 70\ atm]{Cu\ as\ cat} CH_3-OH$$

Ethanal

The following methods can be used for the manufacture of ethanal:

i) By passing a mixture of ethene and oxygen under pressure over palladium (II)/cupric chloride catalyst in water at 323 K, ethanal is produced:

$$H_2C=CH_2 + 1/2O_2 \xrightarrow{PdCl_2,\ CuCl_2/H_2O} CH_3-\overset{\overset{O}{\|}}{C}-CH$$

This process is called **Wacker process.** Since ethene is cheaper than ethyne, this process has superseded the two older routes outlined below:

ii) By passing ethyne through dilute sulphuric acid, with mercury (II) sulphate as catalyst at 336 K.

$$\underset{\text{ethyne}}{HC\equiv CH} + H_2O \xrightarrow{H_2SO_4/Hg^{2+}} \underset{\text{ethanal}}{CH_3-\overset{\overset{O}{\|}}{C}-H}$$

iii) By the oxidation of ethanol (which is manufactured from ethene) in the gas phase over a silver or copper catalyst:

$$\underset{\text{ethanol}}{CH_3CH_2-OH} + {}^{1}/_{2}\,O_2 \xrightarrow[773\ K]{Ag} CH_3-\overset{\overset{O}{\|}}{C}-H + H_2O$$

$$\underset{\text{ethanol}}{CH_3CH_2-OH} \xrightarrow[773\ K]{Cu} \underset{\text{ethanal}}{CH_3-\overset{\overset{O}{\|}}{C}-H} + H_2$$

Propanone

Dehydrogenation of 2-propanol over heated copper or zinc oxide or air oxidation over heated silver gives propanone. 2-propanol is obtained from propene.

$$H_2 + \underset{\text{propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xleftarrow[heat]{Cu\ or\ ZnO} (CH_3)_2CH-OH \xrightarrow[heat]{air/Ag} \underset{\text{propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + H_2O$$

Propanone can also be manufactured by the direct oxidation of propene from natural gas with oxygen or air, catalysed by a mixture of palladium and cuprous chlorides (**The Wacker Process**).

$$CH_3CH{=}CH_2 + {}^1/_2O_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

propanone

We have already seen in Unit 12 that propanone is obtained as a by-product in the oxidation of cumene to phenol.

Benzaldehyde

It is prepared commercially by the oxidation of methylbenzene. This is done either in the vapour phase or in the liquid phase. In the vapour phase oxidation, methylbenzene vapours mixed with air is passed over a catalyst, a mixture of oxides of manganese, molybdenum, zirconium etc., heated to 773 K:

$$\underset{\text{methylbenzene (toluene)}}{C_6H_5CH_3} \xrightarrow[773\text{ K}]{O_2(N_2)} \underset{\text{catalyst}}{} \quad C_6H_5-\overset{\overset{O}{\|}}{C}-H + H_2O$$

benzaldehyde

Liquid phase oxidation uses manganese dioxide and 65% sulphuric acid at 313 K.

When (dichloromethyl) benzene (benzylidene chloride) is hydrolysed with aqueous acid, benzaldehyde is formed:

$$C_6H_5CHCl_2 + H_2O \xrightarrow{H^+} C_6H_5-\overset{\overset{O}{\|}}{C}-H + 2HCl$$

Phenylethanone

It is manufactured by the oxidation of ethylbenzene with air in the presence of manganous ethanoate (catalyst) at 399 K:

$$C_6H_5C_2H_5 \xrightarrow[Mn(CH_3COO)_2/399\text{ K}]{\text{air}} C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3 + H_2O$$

phenylethanone (acetophenone)

SAQ 2

Benzaldehyde is obtained by the hydrolysis of:

a) methylbenzoate
b) (chloromethyl) benzene
c) (dichloromethyl)benzene

14.3 PHYSICAL AND SPECTRAL PROPERTIES

Before going into details of the physical, spectral and chemical properties of aldehydes and ketones; we would like to discuss first the nature of the carbonyl group.

14.3.1 Nature of the Carbonyl Group

The carbonyl group consists of an sp^2 hybridised carbon atom joined to an oxygen atom by a sigma bond an a π bond (see Fig. 14.1).

Like alkenes, carbonyl compounds are planar about the double bond and have bond angles of approximately 120°.

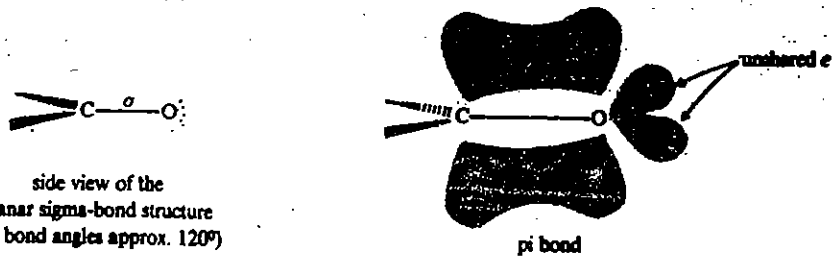
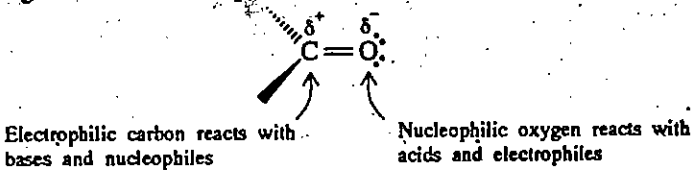


Fig. 14.1: Bonding in the carbonyl group

The carbon-oxygen, like the carbon-carbon, double bond results from a combination of σ and π bonds. But the carbonyl group has a dipole moment, with the oxygen slightly negative, the carbon slightly positive. As a result when carbonyl groups undergo addition reactions, the positive groups (electrophiles) attack the more negative carbonyl oxygen atom and negative group (nucleophiles) attack the more positive carbonyl carbon atom.

As we would expect, the carbon-oxygen double bond is polarised C=O because of the high electronegativity of oxygen relative to carbon. Therefore, **the carbonyl group is polar with the carbon carrying partial positive charge.** It is thus an electrophilic site and is attacked by nucleophiles. Conversely, the carbonyl oxygen is negatively charged and is a nucleophilic site.

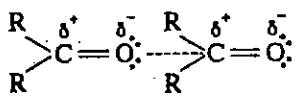


We will see in the next sections that all these structural features—the planari , the π bond, the polarity and the unshared electrons on oxygen—contribute to the properties and the reactivity of the carbonyl group.

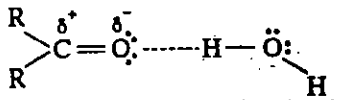
14.3.2 Physical Properties

As we have mentioned above the aldehydes and ketones are polar compounds an these compounds, therefore, posses intermolecular dipole-dipole attraction. Due to these interactions molecules have higher boiling points than nonpolar compounds of similar molecular weight. The boiling points of aldehydes and ketones are however, much lower than the boiling points of the corresponding alcohols. This is due to the fact that whereas alcohols molecules are held together by strong hydrogen bonds. The molecules of aldehydes and ketones are held together by the much weak electrostatic interaction between dipoles.

The partial solubility and also the formation of hydrates can be explained by the formation of hydrogen bonds between carbonyl compounds and water. The unshared electron pairs on oxygen are responsible for such hydrogen bonding. The carbonyl-carbonyl and carbonyl-water interactions are illustrated in the following structures:



dipole-dipole interaction between the molecules of cobonyl compound



hydrogen bonding between carbonyl compound and water

Physical properties of some aldehydes and ketones are summarised in Table 14.2.

Table 14.2: Physical properties of some aldehydes and ketones

IUAPC	Trivial Name	Structure	Bp, K	Solubility in H_2O
Aldehydes: methanal	formaldehyde	HCHO	252	miscible
ethanal	acetaldehyde	CH_3CHO	293	miscible
propanal	propionaldehyde	CH_3CH_2CHO	322	16 g/100 cm^3
butanal	butyraldehyde	$CH_3CH_2CH_2CHO$	349	7 g/100 cm^3
benzaldehyde	benzaldehyde	C_6H_5CHO	451	slightly
Ketones:				
propanone	acetone	CH_3COCH_3	329	miscible
2 butanone	methyl ethyl ketone	$CH_3COCH_2CH_3$	353	26 g/100 cm^3

phenylethanone (acetophenone)	acetophenone	$C_6H_5CCH_3$ (O)		475	insoluble
benzophenone		$C_6H_5CC_6H_5$ (O)	O	579	insoluble

SAQ 3

Without consulting Tables given for physical properties of organic compounds, tell which compound in each pair would have the higher boiling point.

a) 1-pentanal or 1-pentanol

b) methylbutane or methylpropanal

c) 2-pentanone or 2-pentanol

d) benzaldehyde or phenylmethanal

e) pentane or 1-pentanal

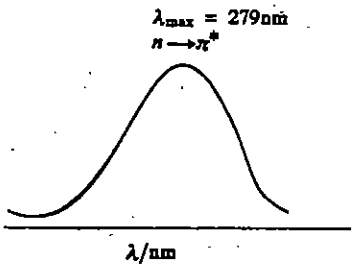


Fig 14.2: Ultraviolet spectrum of propanone.

14.3.3 Spectral Properties

The ultraviolet spectra of aldehydes and ketones show two absorption bands for the carbonyl group; in aldehydes, at 180 and 295 nm for and $n \rightarrow \pi^*$, $\pi^* \rightarrow \pi^*$ transitions, and in ketones at 190 and 270-280 nm for and $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ transitions. The spectrum of propanone is shown in Fig. 14.2.

The infrared spectrum is useful in the detection of the carbonyl group in a compound. In aldehydes and ketones their spectrum exhibits strong bands for C=O stretch at 1700-1740 cm^{-1} in aldehydes and at 1660-1750 cm^{-1} for ketones. We are giving some characteristic absorption bands in Table 14.3.

Table 14.3: Characteristic infrared absorption of aldehydes and ketones

Type of Vibration	Position of Absorption* cm^{-1}
Aldehydes:	
C—H stretching of —CHO	2700-2900
C=O stretching	1700-1740
Ketones:	
C=O stretching	1660-1750

* Other substituents or ring strain cause the carbonyl absorption to fall outside the listed ranges.

As an illustration the ir spectrum of 1-butanal is given in Fig. 14.3. Note the intense band around 1710 cm^{-1} which is characteristic of C=O stretching. In this spectrum, the C—H stretching of the aldehyde group is also visible as two peaks around 2700 cm^{-1}.

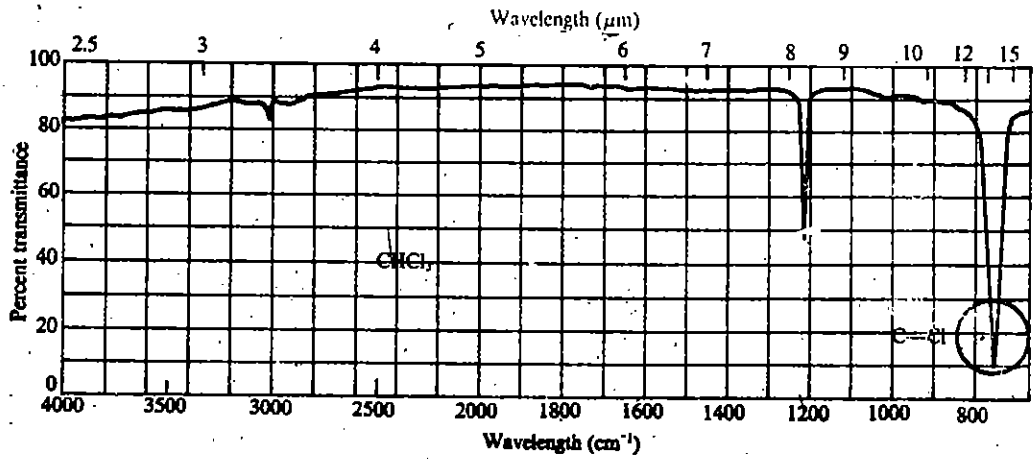


Fig. 14.3: Infrared spectrum of 1-butanal.

The NMR spectra display the aldehydic proton at $\delta = 9.0$-10 ppm, which is greatly deshielded. The large shift arises from the additive effects of both anisotropic deshielding by the π electrons and inductive deshielding by the electropositive carbon of the carbonyl group. Both in aldehydes and ketones the proton attached to adjacent carbon (α-carbon) appear at δ 2.0-2.5 ppm slightly downfield from that of the other C—H absorption (about $\delta \approx 1.5$) because of electron withdrawal by the electronegative oxygen atom. For example, the nmr spectrum of 1-butanal (Fig. 14.4), exhibits a signal near $\delta = 9.5$ ppm for the hydrogen in the –CHO group and a signal near $\delta = 2.4$ ppm for the α protons.

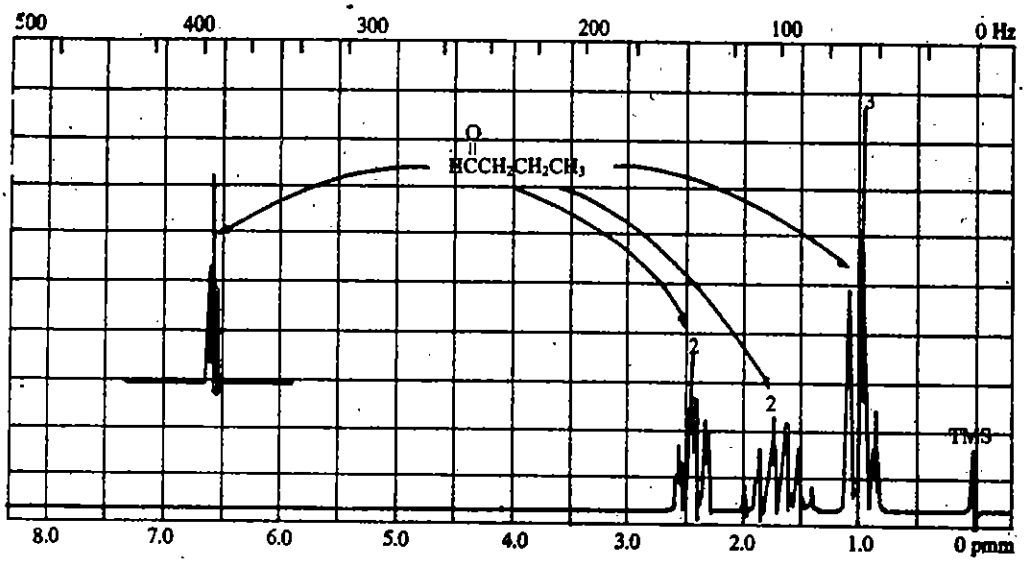


Fig. 14.4: NMR spectrum of 1-butanal

In the mass spectra of aldehydes, the molecular ion peak is observed with a low intensity and α cleavage occurs readily:

$$H^{\cdot} + RC^{+}=O \longleftarrow R-\underset{\displaystyle H}{\overset{\displaystyle |}{C}}=O^{+} \longrightarrow \underset{m/z\ 29}{R + HC^{+}=O}$$

The presence of $RC^{+}=O$ and m/e 29 peaks in the mass spectrum are characteristic of aldehydes.

A β-cleavage may also occur:

$$[RCH_2CH_2CHO]^{+\cdot} \longrightarrow RCH_2 + \underset{m/z\ 43}{[CH_2CHO]^{+}}$$

In the mass spectra of ketones, the molecular ion peak is strong and α-cleavage takes place quite readily. The $[RCO].^{+}$ peak is very often the base peak, e.g.,

$$RCOR'^{+\cdot} \longrightarrow [RCO]^{+} + R'^{\cdot}$$

SAQ 4

Propanone and propanal are isomers. What feature would distinguish between the two if we examine;

a) their ir spectra

b) their nmr spectra

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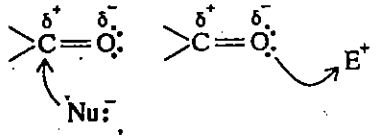
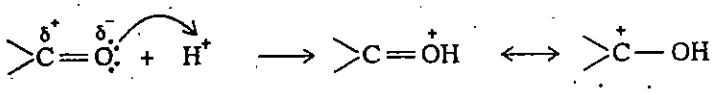
14.4 REACTIONS OF ALDEHYDES AND KETONES

We can group together the reactions of aldehyde and ketones into four categories (a) reactions of the carbonyl group (b) reactions of the α hydrogen (c) oxidation reactions and (d) reduction reactions.

As stated earlier, the carbon-oxygen double bond is polar. A carbonyl compound may be attacked either by a nucleophile or by an electrophile. Therefore, with most reagents carbonyl additions show the same overall course: addition of the negative, nucleophilic part, of the reagent to the carbon atom and addition of the positive electrophilic part to the oxygen atom.



In acidic medium the proton adds to the carbonyl oxygen. This increases further the electrophilic nature of the carbonyl carbon.

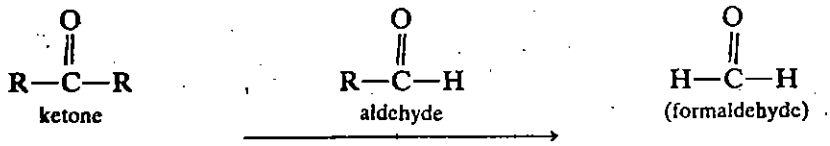


resonance structure for a protonated carbonyl group

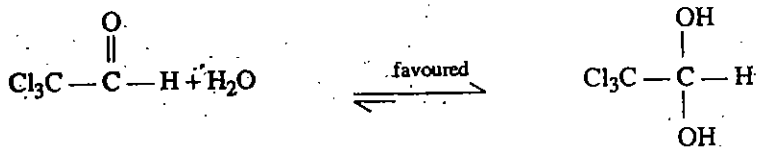
Hence nucleophilic additions to a carbonyl compounds are very often catalysed by acids. Before going into details of the reactions of carbonyl compounds, let us study the relative reactivities of aldehydes and ketones.

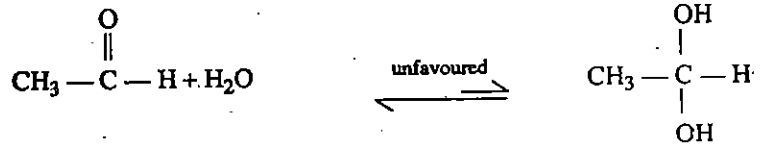
The relative reactivities of aldehydes and ketones in addition reactions may be attributed partly to the extent of polarisation on the carbonyl carbon. The more polarised the carbonyl group the greater the positive charge on the carbonyl carbon. A greater positive charge means higher reactivity. If this partial positive charge is dispersed throughout the molecule, then the carbonyl compound is less reactive.

As you already know the alkyl group is electron releasing (+I effect). Therefore, in ketones, due to the presence of two alkyl groups, the carbon of the carbonyl group will be less electron deficient than in aldehydes. Hence, ketones will be less reactive than aldehydes. Further, methanal with no alkyl groups attached to the carbonyl carbon is more reactive than ethanal and other unsubstituted aldehydes.



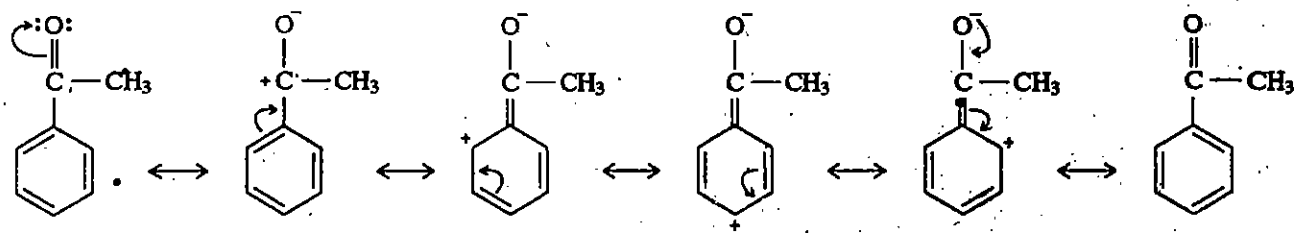
The most reactive aldehydes is trichloroethanal (chloral), Cl_3C-C-H, in which electron withdrawal by the three chlorine atoms depletes the electrons density on the carbonyl carbon so much that it forms stable hydrates.





Steric factors also play a role in the relative reactivities of aldehydes and ketones. Since hybridisation of the carbonyl carbon changes from sp^2 in the starting material to sp^3 in the addition product, ketones are less reactive than aldehyde because of the un-favourable steric interaction between the two alkyl groups and the other two groups in the product. Lack of such steric hindrance in the product is another reason for the higher reactivity of methanal.

A carbonyl group attached to an aromatic ring is less reactive in addition reactions than it is in aliphatic aldehydes and ketones. This can be attributed to resonance interaction between the carbonyl group and the aromatic ring:



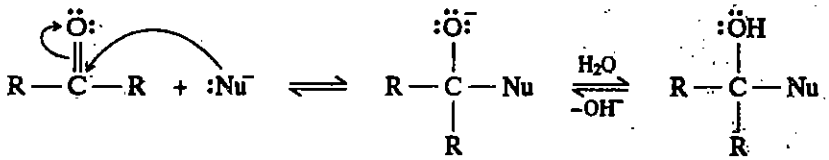
Resonance structure of phenylethanone (acetophenone)

The result of this interaction is a weakening of the positive charge on the carbonyl carbon atom through dispersal of the charge into the ring. From the above resonance structures it is also clear that a carbonyl group attached to an aromatic ring behaves as an electron withdrawing group and so it deactivates the ring towards electrophilic substitution. Further, since the electron density at the *meta* position is not much affected by the carbonyl group, the electrophil, when substituted does occur, goes to the *meta* position. We, therefore, say that the carbonyl group in, e.g., bezaldehyde, is *meta* directing.

With the above general ideas, it will be easier to study the reactions of aldehydes and ketones. Many of the reactions which follow are shown by all aldehydes and ketones, but some members show exceptional behaviours which we will take up separately.

14.4.1 Addition Reactions

The chief reaction of aldehydes and ketones is **nucleophilic addition** to the partially positive carbon of the carbonyl group. The mechanism for the general reactions is as follows:



The nucleophile, Nu:$^-$, can be OH^-, OR^-, CN^-, $\ddot{N}H_3$, $H_2\ddot{O}$:, $R\ddot{O}H$, $NH_2\ddot{O}$, $C_6H_5\ddot{N}H\ddot{N}H_2$, RMgX, etc.

As said above acid catalysis facilitates the reaction of the weaker nucleophiles, such as water, alcohol and ammonia by protonating and thereby increasing the positive nature of the carbon atom of carbonyl group:

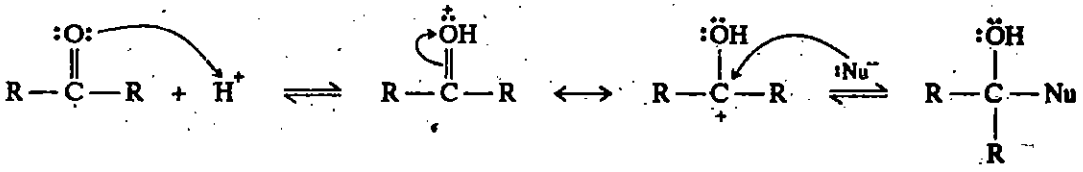
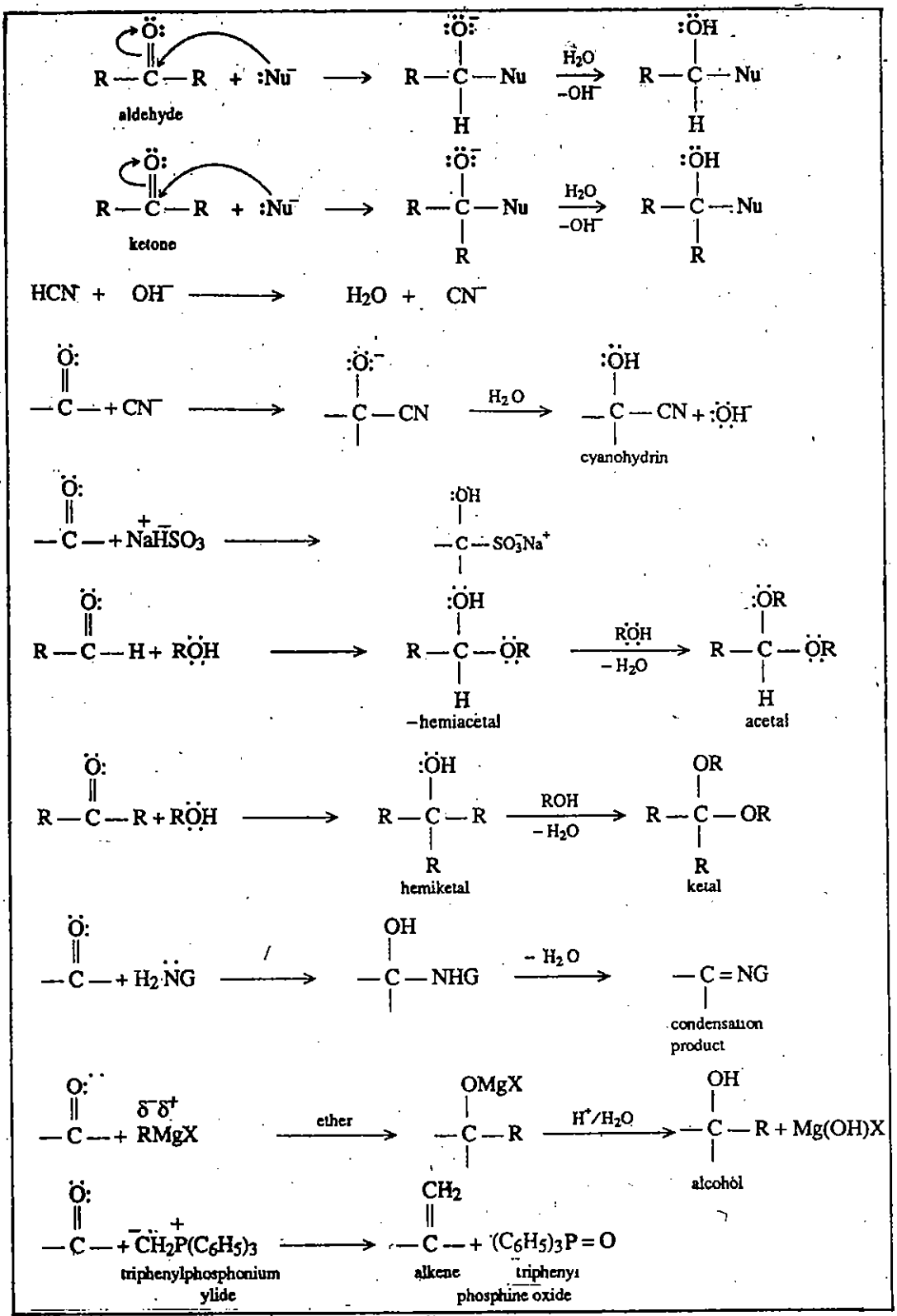


Table 4.4 gives the general equations for different types of nucleophilic addition reactions.

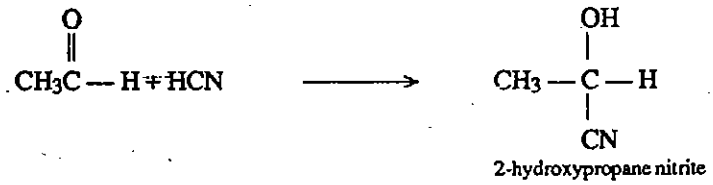
Table 14.4: Some nucleophilic addition reactions of aldehydes and ketones



Let us study these reactions in more detail.

Addition of hydrogen cyanide

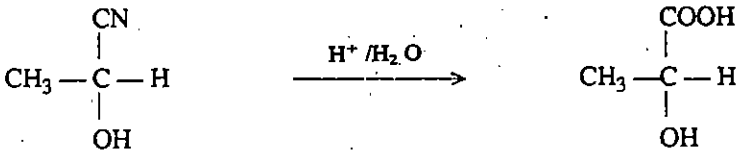
Aldehydes and ketones react with hydrogen cyanide to form cyanohydrins, for example,



These reactions occur very slowly, but their rates are greatly increased by the addition of alkali. This is because, alkali increases the concentration of the cyanide ion,

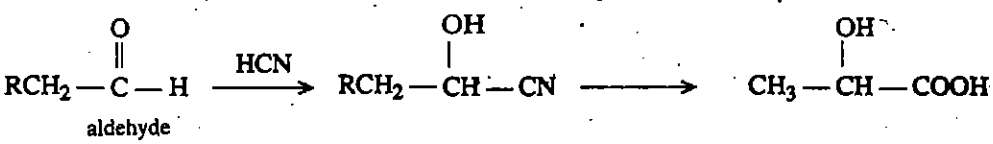
$$HCN + OH^- \rightleftharpoons CN^- + H_2O$$

Hydrolysis of cyanohydrins gives α-hydroxyacids:

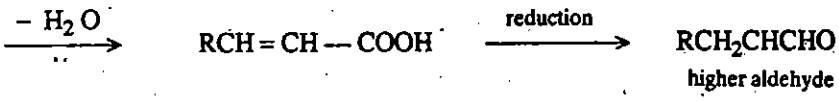


2-hydroxypropanoic acid

An important consequence of the hydrogen cyanide addition reaction is that one more carbon atom is added to the carbon chain. For example,



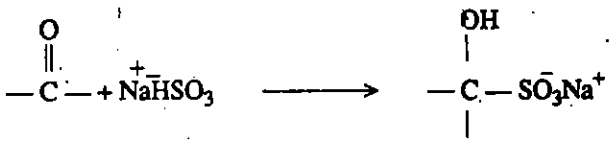
aldehyde



higher aldehyde

Addition of sodium hydrogen sulphite

The reaction with sodium hydrogen sulphite gives the hydrogen sulphite adduct.



The hydrogen sulphite adducts are crystalline solids. On heating with dilute acid or aqueous sodium carbonate, they regenerate the carbonyl compound. This reaction is often used for separation and purification of aldehydes and ketones.

Addition of Alcohols

Lewis bases, such as water, alcohols, ammonia and its derivatives can serve as nucleophiles in addition reactions to aldehydes and ketones. Fig14.5 summarises the net reactions of these nucleophiles.

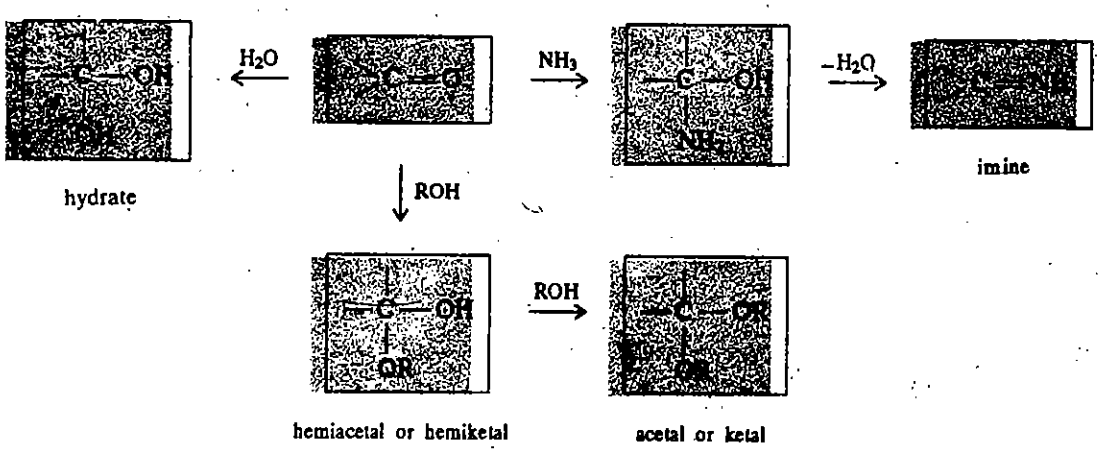
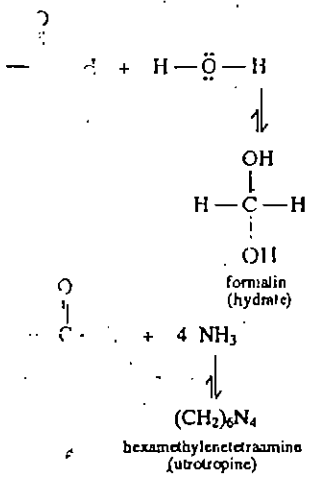


Fig 14.5 : Nucleophilic addition reactions of water, alcohol and ammonia

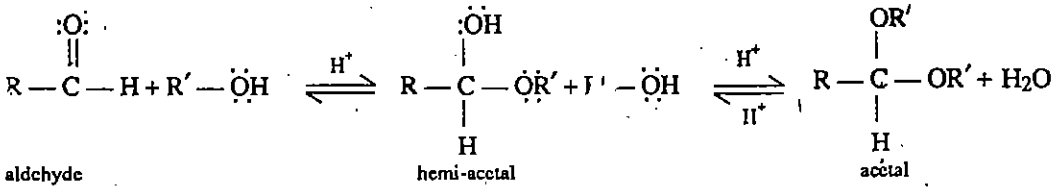
These reactions are reversible and the equilibrium is unfavourable for the addition of water and ammonia. Therefore, the addition of water and ammonia to aldehydes and ketones is generally not of much significance.

fer anal is one of the few rbonyl compounds that forms table products with water and mm nia.

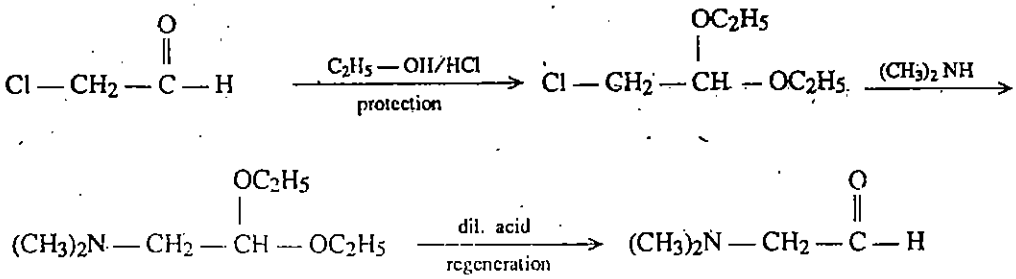


should note that equilibriums t that favour the stable drate, formalin and hexamethy- nate traa ne, respectively.

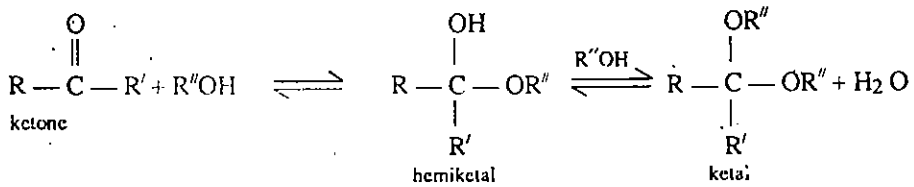
On the other hand, alcohols undergo appreciable nucleophilic addition reactions to aldehyde and ketones. Let us study these reactions in some more detail. Aldehydes give first hemi-acetals and on reaction with an additional equivalent of alcohol, give acetals. All these reactions are catalysed by a trace of strong acid.



Like other ethers, acetals are good solvents. They are stable to bases and oxidising agents, but are cleaved even by dilute acids. The mechanism is just the reverse of that for the formation of the acetal. This property of acetals is used in synthesis to protect the carbonyl function from reacting while a substitution or addition reaction is carried out elsewhere in the molecule. After the reaction the acetal is then hydrolysed back to the aldehyde. The example illustrates the utility of such protection in synthetic reactions,



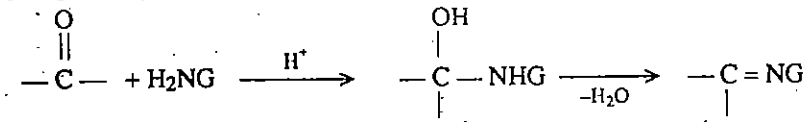
Similarly, ketones give hemiketals on t. atment with alcohols. Further reaction leading to ketals is much more difficult.



Ketals are also used to protect carbonyl groups.

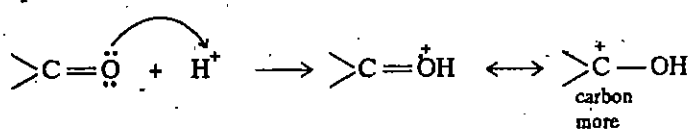
eactions in which two reactants ombine with the loss of a olecule of water or some other eutral molecule are called onde ations.

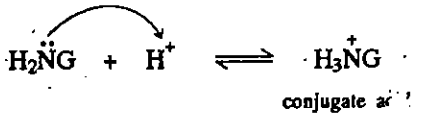
Addition of Ammonia derivatives: We mentioned above that the addition of ammonia is a reversible reaction with an unfavourable equilibrium. However, certain ammonia derivatives are added to carbonyl compounds to give another type of reactions **condensation** in which the initial addition is followed by dehydration to form a carbon-nitrogen double bond. The net result is substitution of oxygen by another group. The general reaction can be summed up as follows.



G=various groups (Table 14.5)

These reactions are catalysed by acids. While protonation of carbonyl compounds increases their reactivity towards nucleophiles. Protonation of the reagent, H_2NG will lower its nucleophilic character:

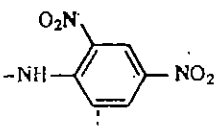
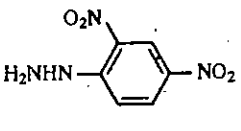
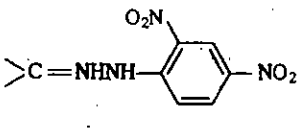




The optimum pH for the reaction depends on the nature of G in H_2NG. It is to be adjusted such that all of H_2NG is not converted to H_3^+NG and at the same time there is sufficient concentration of the conjugate acid of the carbonyl compound to activate it.

The names of reactants with different G, general condensation products and their class is given in Table 14.5. Many of these condensation products are crystalline solids with sharp melting points. For this reason they are frequently employed for the preparation of aldehyde and ketone derivatives needed for identification.

Table 14.5: Addition of ammonia derivatives

G	Ammonia derivative	General condensation	Class of product
—R/—Ar alkyl/aryl	$RNH_2/ArNH_2$ amine/aromatic amine	$>C=NR/>C=NAr$ N substituted imine	imine (Schiff base)
—OH	NH_2OH hydroxylamine	$>C=NOH$ Oxime	Oxime
$—NH_2$	H_2NNH_2 hydrazine	$>C=NNH_2$ hydrazone	hydrazone
$—NHC_6H_5$	$H_2NNHC_6H_5$ phenyl hydrazine	$>C=NNHC_6H_5$ phenyl hydrazone	substituted hydrazone
			
		2,4-dinitro-phenyl hydrazone	substituted hydrazone
$—NHCONH_2$	$H_2NNHCONH_2$		
	semicarbazide	$>C=NNHCONH_2$	semicarbazone

Some times the hydrazone formed above reacts with a second molecule of the carbonyl compound to give azines:

$$\underset{\text{benzaldehyde hydrazone}}{C_6H_5CH=NNH_2} + C_6H_5CHO \longrightarrow \underset{\text{benzaldehyde azine}}{C_6H_5CH=N—N=CHC_6H_5} + H_2O$$

When the hydrazones are heated with potassium hydroxide or sodium ethoxide, alkanes are formed with the loss of nitrogen:

$$—\overset{|}{C}=NNH_2 \xrightarrow[1,2-\text{ethanediol}]{KOH,\ 423\ K} —\overset{|}{C}H_2 + N_2$$

Thus the carbonyl group is converted into a methylene group via a hydrazone. This reaction is known as the **Wolff Kishner** reaction. Like hydrazones, semicarbozones can also be used in the above reaction.

Addition of Grignard Reagent

The general reaction of the addition of Grignard reagent to aldehydes or ketone is

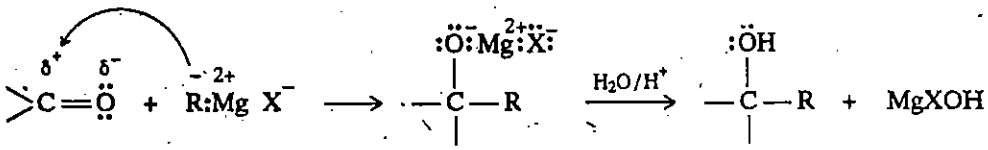
$$RMgX + —\overset{|}{C}=O \xrightarrow{\text{ether}} R—\overset{|}{C}—OMgX \xrightarrow{H^+/H_2O} R—\overset{|}{C}—OH$$

This reaction was discussed in Unit 11. We also mentioned that methanal (formaldehyde) gave primary alcohol, other aldehydes gave secondary alcohols and ketones gave tertiary alcohols. Let us study the mechanism of the reaction of Grignard reagent with carbonyl compounds.

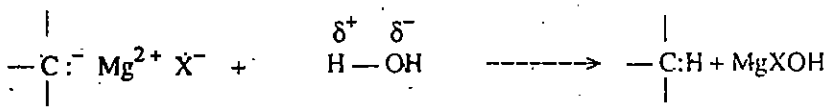
Mechanism: Analysing the charge distribution in the Grignard reagent, we find that since the magnesium is positive the hydrocarbon portion of the reagent must be negative and, therefore, a very powerful nucleophile.

$$R^{-}:Mg^{2+}:\ddot{X}:^{-}$$

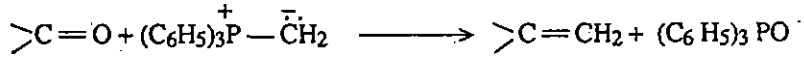
When a Grignard reagent is mixed with a aldehyde or ketone, the negative hydrocarbon group quickly attacks the positive carbonyl carbon and provides the two electrons needed for the new carbon-carbon bond. The π electrons are displaced to the oxygen, forming the alcohol salt that is then neutralised to an alcohol with water and acid.



Note that the hydrocarbon portion of a Grignard reagent essentially acts as a carbanion. It is for this reason that Grignard reactions must be performed in dry ether. Even traces of moisture can neutralise the reagent.



Wittig Reaction: A very important and useful synthesis of alkenes known as the witting reaction involves the reaction between an aldehyde or ketone and a phosphorus ylide.

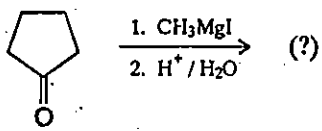


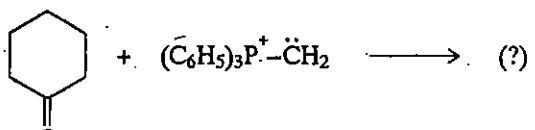
aldehyde or ketone — triphenyl phosphonium ylide — alkene — triphenylphos phine oxide

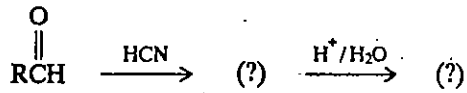
In this reaction, the oxygen of the carbonyl group is substituted by a methylene group, triphenyl phosphine oxide being the other product. Witting reaction is of considerable importance in industrial synthesis, much of the synthetic vitamin A is manufactured by a reaction sequence involving Witting reaction.

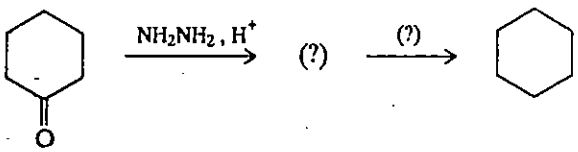
SAQ 5

Complete following reactions.

a) 

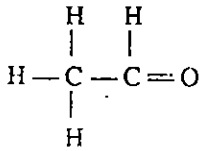
b) 

c) 

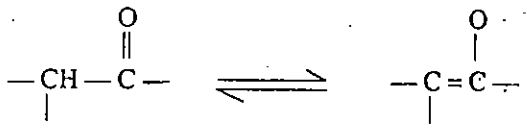
d) 

14.4.2 Reactions of α Hydrogen

Another important characteristic of carbonyl compounds is the acidity of hydrogen atoms on carbon atom alpha to the carbonyl group, called α-hydrogens. We have already encountered C—H acidity in the alkynes in Unit 8. Propanone is about 100,000 times as strong as an acid as ethyne. Because of the reactivity of the α hydrogens, aldehydes and ketones may exist as an equilibrium mixtures of the two isomeric forms, a keto form and an enol form.



ethanal (acetaldehyde)
three α hydrogen

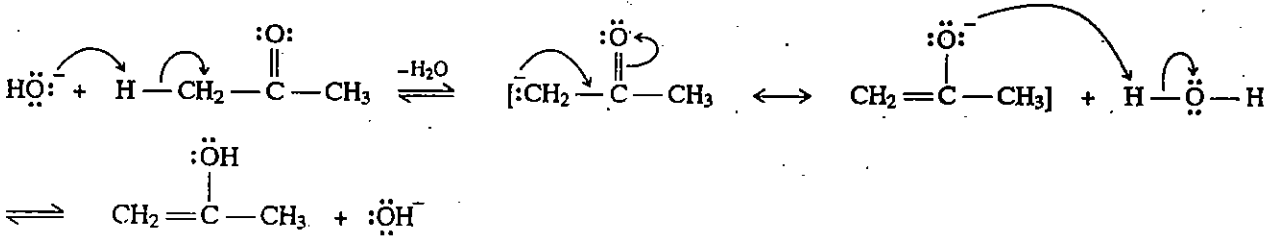


keto form enol form

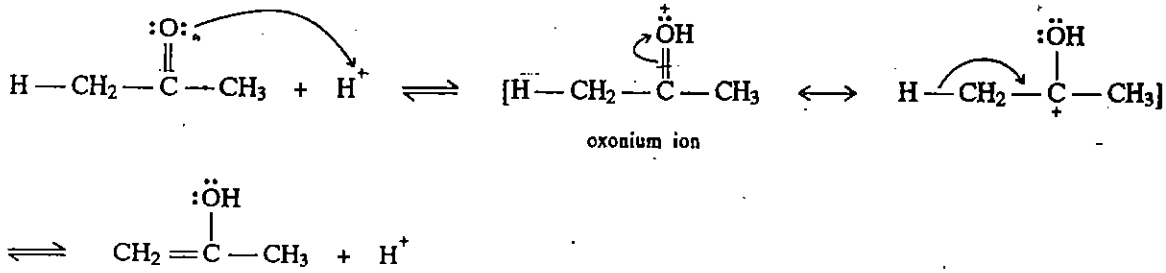
As we have mentioned in Unit 5 this type of isomerism in which there is dynamic equilibrium between the two forms is called tautomerism, and the isomers are called tautomers. In the pure liquid state or in neutral solutions only traces of the enol form are present. Since the enol form is less stable than the keto form.

Enolisation is catalysed by both acids and bases as shown in the following equation.

Base-catalysed enolisation



Acid-catalysed enolisation



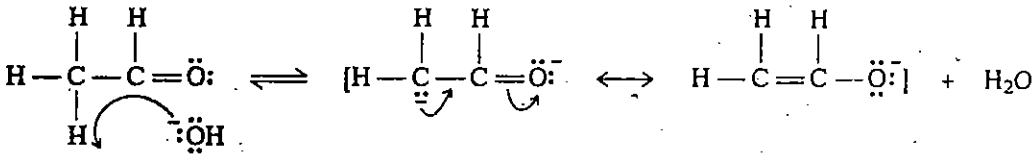
oxonium ion

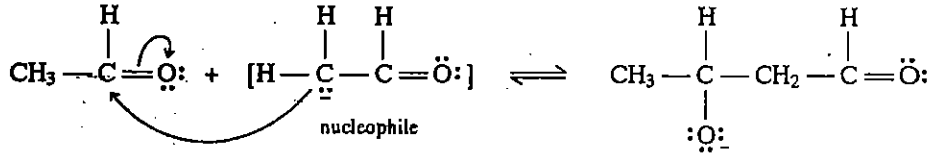
Strong acids give rise to weak conjugated bases on ionisation. The ionisation of propanone produces $^{-}CH_2COCH_3$ in which the negative change is delocalised and hence it as a weak base. On the other hand ionisation of CH_4 produces $^{-}CH_3$ which is a very strong base and, therefore, CH_4 is a very weak acid. The stabilisation of the anion by resonance is responsible for the greater acidity of propanone relative to methane and ethyne. We will now discuss those reactions of the carbonyl compounds in which α hydrogens are involved.

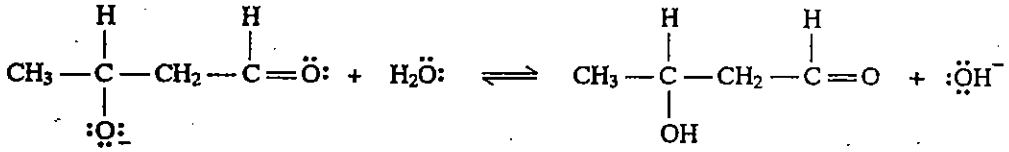
Aldol condensation

When an enolate ion adds to another molecule of the aldehyde or the ketone, the reaction is called the **aldol condensation.** This reaction is either base- or acid-catalysed. The aldol condensation involving self-condensation of two molecules of ethanal in presence of a basic catalyst is shown as an example:

Aldol, a composite word for aldehyde + alcohol.

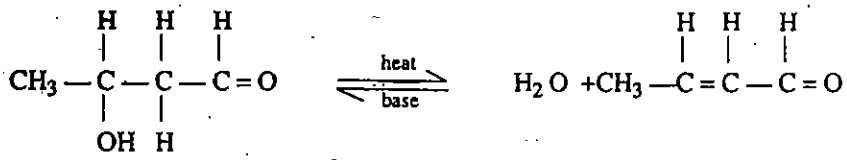






aldol
(3-hydroxybutanal)

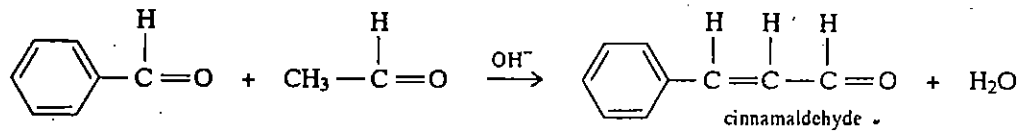
Under more vigorous conditions aldol lose water to give an α, β-unsaturated carbonyl compound.



2-butenal
(crotonaldehyde)

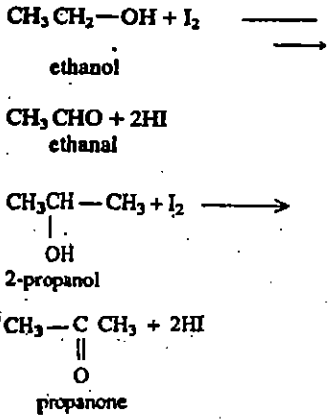
Ketones containing α hydrogens are also capable of aldol-type of condensations.

Aldehydes lacking α hydrogens enter into a mixed aldol condensation with other aldehydes having a hydrogens. They do this by acting as the carbanion acceptors. For example, benzaldehyde reacts with acetaldehyde to produce cinnamaldehyde, an α, β unsaturated aromatic aldehyde used as a flavouring agent:



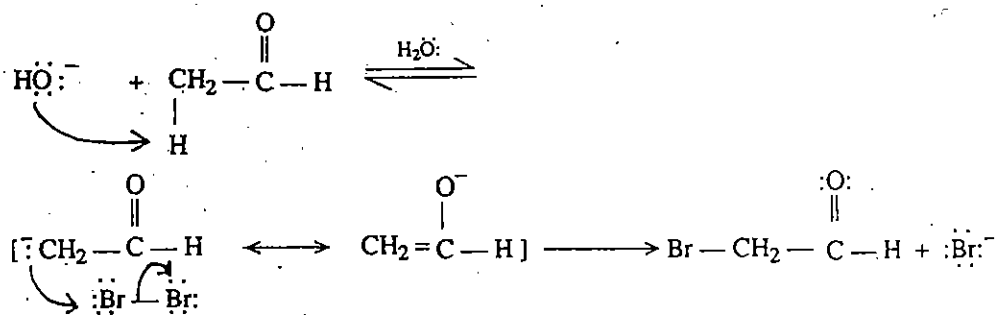
cinnamaldehyde

Haloform test is given by any compound containing $CH_3—C=O$ group or a group capable of giving $CH_3—C=O$ group under conditions of dehydrogenation. In the case of ethanol, dehydrogenation will give ethanal, and in the case of 2-propanol, propanone, both of which can give haloform reaction.



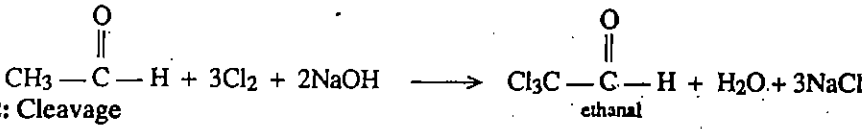
Haloform Reaction

The treatment of carbonyl compounds (having α-hydrogens) with halogens: chlorine, bromine or iodine in the presence of an alkali leads to halogenation, e.g.,

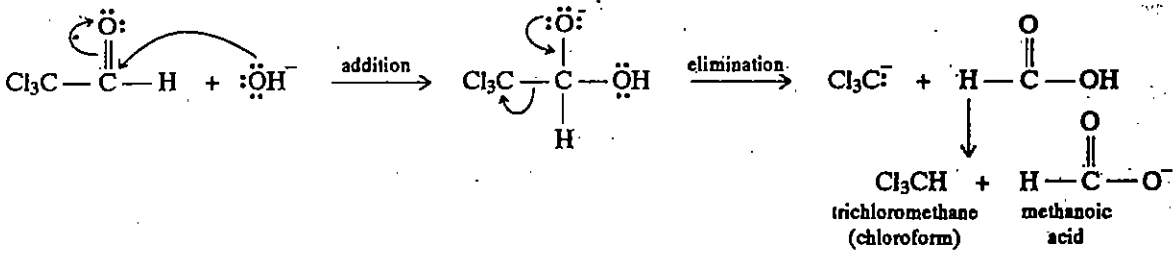


This type of halogenation tends to give polyhalogenation products. Further more, when ethanal or a methyl ketone is warmed with an alkaline solution of chlorine, bromine, or iodine, the product is trichloromethane (chloroform), tribromomethane (bromoform), or tri-iodomethane (iodoform), respectively. This reaction is called the haloform reaction and appears to take place in two stages:

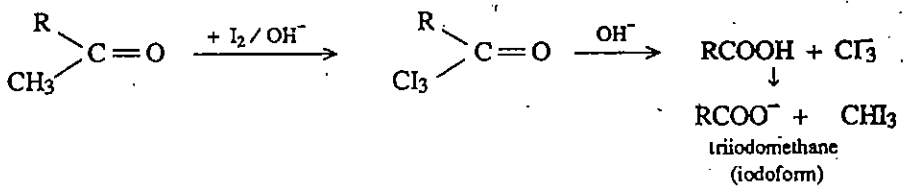
Stage 1: Halogenation



Stage 2: Cleavage



The first step is polyhalogenation via the enlolate ion. The second step is cleavage of the polarised $Cl_3C—C$ bond by base through an addition elimination mechanism. The haloform reaction is useful not only as a preparative method for the haloforms but also as a diagnostic test for the presence of the groupings indicated. In practice, a solution of iodine is added to the aqueous alkaline solution of the compound to be tested. A positive reaction will yield tri-iodomethane (iodoform), CHI_3, a bright yellow solid which may be identified by its sharp pungent odour and its melting point. Trichloromethane and tribromomethane are liquids.



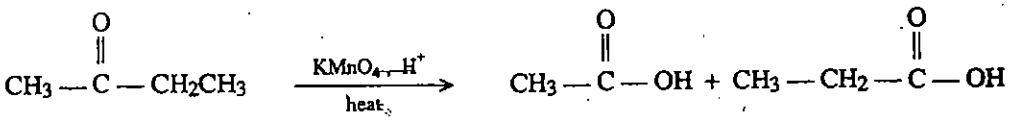
SAQ 6

A carbonyl compound does not form iodoform on being heated with iodine and sodium carbonate. It is:

a) ethanal
b) propanone
c) benzaldehyde
d) phenylethanone

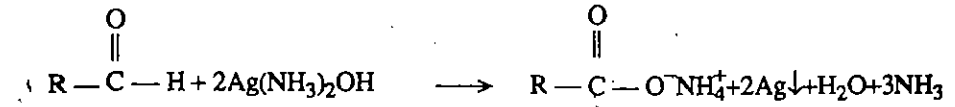
14.4.3 Oxidation

Aldehydes are so easily oxidised that even the mildest oxidising reagents will serve to bring about their conversion to acids. Ketones, on the other hand, are fairly resistant to oxidation. The oxidation of ketones, when forced by the use of strong oxidising reagents and heat, results in the rupture of carbon-carbon bonds to produce acids.



The ease with which oxidation of aldehydes takes place provides a simple method for distinguishing between aldehydes and ketones. Mild oxidising agents may be used for this purpose. **Tollen's reagent,** an ammonical solution of silver oxide, AG $(NH_3)_2OH$; **Fehling's solutiom;** an alkaline solution of cupric ion complexed with sodium potassium tartrate and **Benedicts solution,** an alkaline solution of cupric ion complexed with sodium citrate, are the three reagents commonly used to detect the presence of an aldehyde group.

When Tollen's reagent is used to oxidise an aldehyde, the silver ion is reduced to the metallic form and, if the reaction is carried out in a clean test tube, a silver mirror is formed.



Sodium borohydride is a milder reducing agent than $LiAlH_4$. $NaBH_4$, reduces aldehydes and ketones rapidly, but esters very slowly. Therefore carbonyl groups can be reduced selectively with $NaBH_4$. For example,

$$H-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow[2.\ H_3O/H^+]{1.\ NaBH_4} \overset{OH}{|}\ \ \overset{O}{\|}\ CH_2CH_2COC_2H_5$$

When Fehling's and Benedict's solution are used to oxidise an aldehyde, the complexed deep blue cupric ion is reduced to red cuprous oxide.

$$R-\overset{\overset{O}{\|}}{C}-H + 2Cu(OH)_2 + NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-O^-Na^+ + Cu_2O + 3H_2O$$

Aromatic aldehydes react with the Tollen's reagent but do not react with either Fehling's or Bendict's solution. A means of distinguishing aliphatic from aromatic aldehydes is thus provided by this difference in reactivity between the two types of reagents.

14.4.4 Reduction

Both aldehydes and ketones undergo reduction, the nature of the product depending on the reagent used for the purpose. Catalytic hydrogenation or reduction with dissolving metals (e.g., sodium and alcohol) or metallic hydrides (lithium aluminium hydride or sodium borohydride) gives alcohols. Aldehydes form primary alcohols and ketones give secondary alcohols:

$$R-\overset{\overset{H}{|}}{C}=O + H_2 \xrightarrow[\text{pressure}]{\text{Pt or Ni}} R-CH_2-OH$$

$$R-\overset{\overset{R}{|}}{C}=O \xrightarrow[2.\ \text{ether}]{1.\ LiAlH_4} (R-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-O)_4AlLi \xrightarrow{H^+} R-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-OH$$

$$R-\overset{\overset{R}{|}}{C}=O \xrightarrow[2.\ H_2O/H^+]{1.\ NaBH_4} R-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-OH$$

In lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$), the hydrogen is negatively charged (H^-) and, like other bases, is capable of adding to the carbon of a carbonyl group.

$$Li^+H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{Al^-}}-H$$

Lithium aluminum hydride

$$Na^+H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{B^-}}-H$$

Sodium borohydride

Alkanes are formed when carbonyl compounds are reduced with zinc amalgam and hydrochloric acid. This reaction is known as the **Clemmensen reduction.**

$$>C=O \xrightarrow{Zn(Hg)\ HCl} \underset{\text{alkane}}{>CH_2} + H_2O$$

An alternative to the Clemmensen reduction for an acid sensitive ketone is the Wolff Kishner reduction. As mentioned earlier which employs hydrazine (NH_2NH_2) and potassium hydroxide. The solvent is 1,2-ethanediol (glycol).

$$R-\overset{\overset{O}{\|}}{C}-R + NH_2NH_2 \xrightarrow[1,2,-\text{ethanediol}]{KOH,\ 423\ K} R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-R$$

14.4.5 Specific Reactions of Methanal

Methanal (formaldehyde) gives many of the general reactions of carbonyl compounds above but as it does not have α hydrogens it does not undergo those reactions in which hydrogens α to the carbonyl group are involved. Thus, for example, it does not undergo base-catalysed self condensation. On treatment with aqueous sodium or potassium hydroxide it forms methanol and methanoate ion. This reaction is known as the **Cannizzaro reaction.**

$$\underset{\text{methanal}}{2HCHO} + OH^- \longrightarrow \underset{\text{methanoate ion}}{HCOO^-} + \underset{\text{methanol}}{CH_3OH}$$

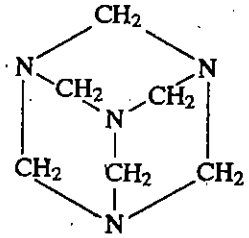
Benzaldehyde which also does not have any α-hydrogen undergoes the Cannizzaro reaction as well, e.g.,

$$\underset{\text{benzaldehyde}}{C_6H_5CHO} + OH^- \longrightarrow \underset{\text{benzoate ion}}{C_6H_5COO^-} + \underset{\text{benzyl alcohol}}{C_6H_5CH_2OH}$$

Treatment of methanol with ammonia gives hexamethylenetetramine:

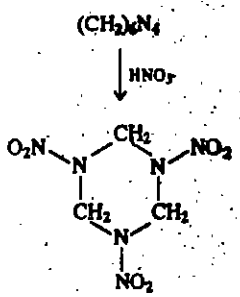
$$6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + H_2O$$

Hexamethylenetetramine is also called utropin has following cyclic structure.



hexamethylenetetramine

Hexamethylenetetramine is medicinally useful as a urinary antiseptic (urotropin) and is also oxidised by nitric acid to the important military explosive cyclonite (RDX).



cyclonite (RDX)

Methanol is also used as a methylating agent:

$$C_2H_5NH_2 + HCHO + HCOOH \longrightarrow C_2H_5NHCH_3 + CO_2 + H_2O$$

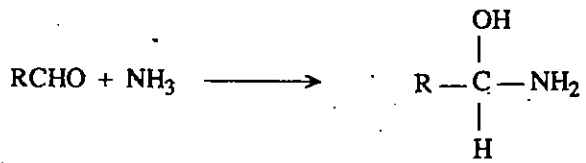
14.4.6 Specific Reactions of Aldehydes

In this subsection we will consider reactions which are given by aldehydes only and not those by ketones. Aldehydes restore the magenta colour of Schiff's reagent (aqueous rosaniline hydrochloride solution whose magneta colour has been discharged by sulphur dioxide).

As mentioned earlier, aldehydes are very easily oxidised. Hence they reduce Tollens' reagent to metallic silver, and Fehling's and Benedict's solutions to cuprous oxide.

Aldehydes (except methanal) on being warmed with concentrated sodium hydroxide solution, undergo repeated aldol condensations accompanied by dehydration. This leads to formation of polymeric products of uncertain structure which have a viscous or resinous appearance.

Aldehydes (except methanal) react with ammonia to give aldehyde-ammonia:



Methanal and ethanal polymerise readily, propanone does not. The polymer of formaldehyde is known as **paraformaldehyde**, $HO(CH_2O)_nH$, with n having an average value of 30. Paraformaldehyde is an amorphous white solid which is prepared by slowly evaporating **formalin** (a 37-40% aqueous solution of methanal) under reduced pressure.

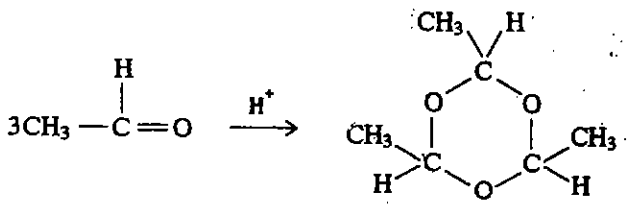
$$CH_2{=}O + H_2O \rightleftharpoons HOCH_2OH$$

$$[HOCHOH] + n HCHO \longrightarrow HO[-CH_2-O]_n-H$$

paraformaldehyde

Depolymerisation of paraformaldehyde is brought about by heating. This facile change of state from solid to gaseous allows methanal to be easily stored and used.

When treated with acid at a low temperature ethanal undergoes addition to give a cyclic trimer, paraldehyde (b.p. 398 K). Paraldehyde, when warmed, is depolymarised to regenerate ethanal. Like methanal, ethanal can also be easily stored and is used in the form of paraldehyde.



ethanal paraldehyde

Finally in the following subsection, we will see the reactions which are given by ketones only and not by aldehydes.

14.4.7 Specific Reactions of Ketones

Ketones react with ammonia to give complex condensation products. Treatment with nitrous acid converts ketones to oximino derivatives, e.g.,

$$CH_3COCH_3 + HNO_2 \longrightarrow CH_3COCH{=}NOH + H_2O$$

When reduced with magnesium amalgam and water, ketones give dimers, that from propanone being called pinacol.

$$CH_3COCH_3 \xrightarrow{Mg\text{–}\ Hg/H_2O} (CH_3)_2C(OH)\text{–}C(OH)(CH_3)_2$$

propanone

pinacol

Treatment of ketones with a peracids gives esters. This reaction is known as **Baeyer-Villiger oxidation:**

$$RCOR + R'COOOH \longrightarrow RCOOR + R'COOH$$

14.5 REACTIONS OF AROMATIC ALDEHYDES AND KETONES

In Section 14.4, we have mentioned that aromatic carbonyl compounds are less reactive in nucleophilic addition reactions than the aliphatic carbonyl complunds. We have also discussed the reasons for this lack of reactivity. Now, we will consider in some detail the chemistry of benzaldehyde and phenylethanone (acetophenone), two important members of this class of compounds.

14.5.1 Benzaldehyde

Benzaldehyde gives many general reactions of aldehydes described above. However, it does not reduce Fehling's solution. With zinc and hydrochloric acid or with sodium amalgam it undergoes reductive dimerisation to give hydrobenzoin:

$$2C_6H_5CHO \xrightarrow{2[H]} C_6H_5CH(OH)\text{–}CH(OH)C_6H_5$$

ethane
1,2-diphenyl-
1,2-dihydroxy
(hydrobenzoin)

We have seen earlier that benzaldehyde undergoes mixed aldol condensation with aldehydes or ketones having α-hydrogen in the presence of alkali to form α, β–unsaturated carbonyl compounds. This reaction is also known as **Claisen reaction.**

$$C_6H_5CHO + CH_3CHO \xrightarrow{CH^-} C_6H_5CH{=}CHCHO$$

3-phenylpropenal
(cinnamaldehyde)

$$C_6H_5CHO + CH_3COCH_3 \xrightarrow{OH^-} C_6H_5CH{=}CHCOCH_3$$

benzylidene propanone

On treatment with ethanoic anhydride and sodium ethanoate, benzaldehyde gives 3-phenylpropenoic acid (cinnamic acid). This condensation is known as **Perkin reaction.**

$$C_6H_5CHO + (CH_3CO)_2O + CH_3COONa \longrightarrow \underset{\text{3-phenylpropenoic acid (cinnamic acid)}}{C_6H_5CH{=}CHCOOH}$$

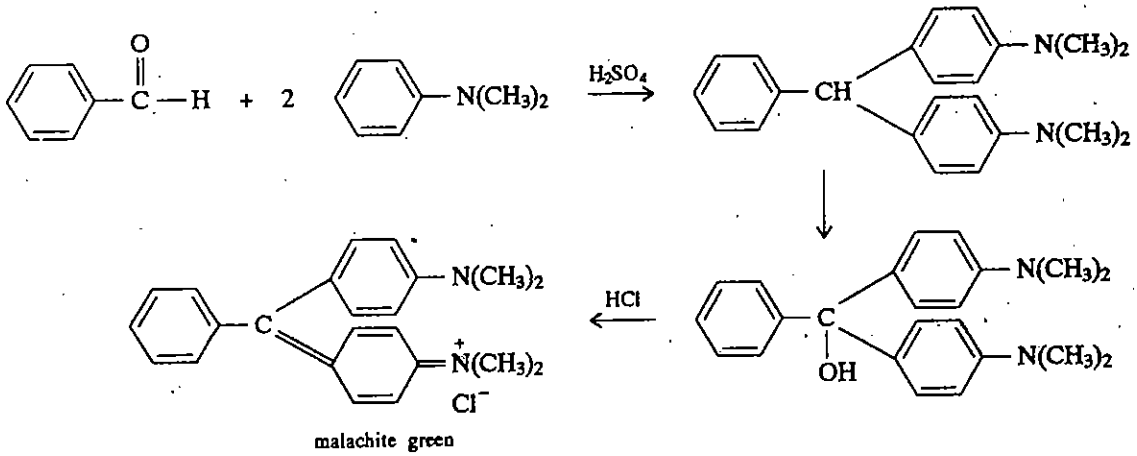
Benzoldehyde gives 3-phenylpropenoic acid with propanedioic acid (malonic acid) in the presence of pyridine. This reaction is known as **Knoevenagel reaction.**

$$C_6H_5CHO + CH_2(COOH)_2 \xrightarrow{\text{Pyridine}} \underset{\text{3-phenylpropenoic acid (cinnamic acid)}}{C_6H_5CH{=}CHCOOH}$$

On refluxing with aqueous ethanolic potassium cyanide, benzaldehyde forms benzoin. This condensation is known as **benzoin condensation.**

$$2C_6H_5CHO \xrightarrow{KCN} \underset{\text{benzoin}}{C_6H_5CHOHCOC_6H_5}$$

Condensation of benzaldehyde with phenols or tertiary aromatic amines in the presence of a dehydrating agents, H_2SO_4 or $ZnCl_2$, gives triphenyl derivatives. Oxidation with lead dioxide followed by treatment with hydrochloric acid gives a dye, e.g.,



malachite green

14.5.2 Phenylethanone

Phenylethanone (acetophenone) undergoes typical reactions of ketones, e.g., reduction with sodium and ethanol gives phenylethanol, Clemensen's reduction gives ethyl benzene.

It is oxidised by cold potassium permanganate to give phenyl-2-oxoethanoic acid (phenyl glyoxolic) acid which gets further oxidised to benzoic acid:

$$\underset{}{C_6H_5COCH_3} \xrightarrow{[O]} \underset{\text{phenyl-2-oxoethanoic acid (phenyl glyoxalic acid)}}{C_6H_5COCOOH} \xrightarrow{[O]} \underset{\text{benzoic acid}}{C_6H_5COOH}$$

Oxidation with selenium dioxide gives phenyl-oxoethanal:

$$C_6H_5COCH_3 + SeO_2 \longrightarrow \underset{\text{phenyl-2-oxoethanal (phenylglyoxal)}}{C_6H_5COCHO} + Se + H_2O$$

On treatment with bromine in ether at 273 K in the presence of aluminium chloride it gives phanyl-1-bromo-2-ethanone (phenacyl bromide):

$$C_6H_5COCH_3 + Br_2 \xrightarrow{AlCl_3} C_6H_5COCH_2Br + HBr$$

phenyl-1-bromo-2-ethanone (phenacyl bromide)

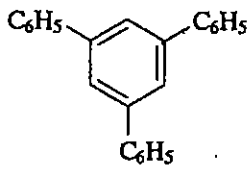
Two molecules of phenylethanone condense together in the presence of aluminium *tert* butoxide to give dyprone:

$$2C_6H_5COCH_3 \xrightarrow{(tert\text{—}BuO)_3Al} C_6H_5COCH=\overset{CH_3}{\overset{|}{C}}C_6H_5$$

dyprone

Condensation in the presence of hydrochloric acid forms 1,3,5-triphenylbenzene:

$$3C_6H_5COCH_3 \xrightarrow[-3H_2O]{}$$



With methanal and ammonia or a primary or secondary amine (as hydrochloride) phenylethanone reacts to give ketoamines called Mannich bases. This reaction is called the **Mannich reaction**, e.g.,

$$C_6H_5COCH_3+HCHO+(CH_3)_2NH{:}HCl \longrightarrow \underset{\text{Mannic base}}{C_6H_5COCH_2CH_2N(CH_3)_2HCl}+H_2O$$

1,3-Diketones are formed from phanyl ethanone by condensation either with ethyl ethanoate in the presence of sodium ethoxide or with ethanoic anhydride in the presence of boron trifluoride:

$$C_6H_5COCH_3+CH_3COOC_2H_5 \xrightarrow{C_2H_5O^-NA^+} \underset{\text{1,3-diketone}}{C_6H_5COCH_2COCH_3}$$

$$C_6H_5COCH_3+(CH_3CO)_2O \xrightarrow{BF_3} C_6H_5COCH_2COCH_3+CH_3COOH$$

By heating phenylethanone with aqueous yellow ammonium polysulphide, phenylethanamide and ammonium phenylethanoate are obtained (**Willgerodt reaction**):

$$C_6H_5COCH_3+(NH_4)_2S_x \longrightarrow C_6H_5CH_2CONH_2+C_6H_5CH_2COONH_4$$

14.6 INDUSTRIAL USES

Methanal is perhaps the most important member of the aldehyde family. Its industrial importance lies principally in its ability to copolymerise with phenol and with urea to produce bakelite and urea methanal resins, respectively. Methanal is also an antiseptic and disinfectant. As formalin it is used to preserve anatomical specimens, in the manufacture of dyes, for gelatin and casein.

Ethanal is used for preparing ethanol, ethanoic acid, phenolic resins, synthetic drugs and rubber accelerators. Its trimer, paraldehyde $(CH_3CHO)_3$, is used in medicine as an hypnotic.

Propanone is used as a solvent for celluloid, lacquers, cellulose acetate and nitrate and in the preparation of sulphonal and ketene ($CH_2=C=O$) for synthesis of organic compounds. Other ketones are used as solvents for resins and synthetic rubber.

Copolymerisation: a reaction in which two or more unlike monomers polymerise with together.

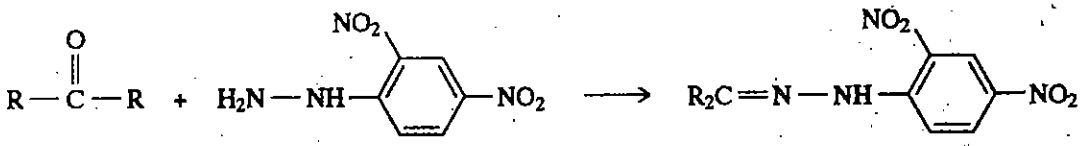
Benzaldehyde is used in perfumery, for preparation of dyes for flavouring purposes and for the preparation of α,β-unsaturated derivatives.

Phenylethanone (acetophenone) is used in perfumery and as hypnotic (hypnone). It is also used in the preparation of many organic compounds which are used in synthesis such as, phenacyl halides 1,3-diketones, etc.

Some insecticides are prepared from the condensation of carbonyl compound, e.g., DDT (Unit 11) is obtained by heating trichloroethanal (chloral) with chlorobenzene in the presence of concentrated sulphuric acid.

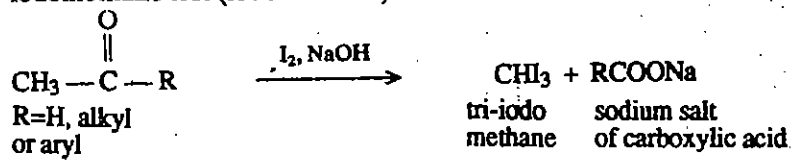
14.7 LAB DETECTION

Both aldehydes and ketones on heating with an alcoholic solution of 2,4-dinitrophenyl hydrazine (DNP) in acidic medium give orange red crystalline hydrazone derivatives which are identified by their characteristic melting points.



aldehyde or ketone — 2,4-dinitrophenyl hydrazine — 2,4-dinitrophenyl-hydrazone

Aldehydes reduce Tollens' reagent and Fehling or Benedict solutions, while ketones do not. These tests provide methods for distinguishing between aldehydes and ketones. Glucose (an aldehyde) when heated with Fehling solution gives red precipitate. This test is both qualitative as well as quantitative. It is used to estimate the amount of glucose in a sample of urine of diabetic patients. As mentioned in Section 14.4.3 ethanal and methyl ketones are characterised through the tri-iodomethane test (iodoform test).



R=H, alkyl or aryl

tri-iodo methane — sodium salt of carboxylic acid

SAQ 7

How might you use simple test tube reactions to distinguish between:

a) benzaldehyde
b) ethanal
c) propanone

14.8 SUMMARY

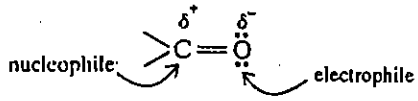
In this unit we have described the chemistry of aldehydes and ketones. We summarise below what we have studied so far:

- Aldehydes and ketones have carbonyl (>C=O) group which is quite reactive. Ketones can be regarded as alkyl or aryl derivatives of aldehydes.

- Aldehyde and ketones are prepared by oxidation or dehydrogenation of alcohols, decomposition of calcium salt of carboxylic acids or catalytic decomposition of carboxylic acids, Rosenmund's method and Stephen's method. Phenylethanone is prepared by acylation of benzene (Friedel-Crafts reaction).

- Methanal is commercially obtained by the catalytic oxidation of methanol. Ethanal and propanone are prepared industrially either by hydration of alkynes or catalytic oxidation of alkenes. Propanone is also obtained from oxidation of natural gas and as a by-product in the oxidation of cumene. Benzaldehyde is commercially prepared by the oxidation of methylbenzene and hydroly is of benzal chloride and phenylethanone by catalytic oxidation of ehtyl benzene.

- The >C=O function in aldehydes and ketones undergoes addition reaction. As it has a dipole moment, nucleophiles add to the carbonyl carbon atom and electrophiles add to the carbonyl oxygen atom.



Carbonyl group is attached by a variety of reagents such as HCN, $NaHSO_3$, ROH, ammonia derivatives, RMgX etc. to give addition products.

- The reaction with phosphorus yield gives alkenes from carbonyl compounds (Wittig reaction). In certain aldehydes and ketones, where α-hydrogens are present, acid or base catalysed enolisation, base-catalysed halogenation, haloform reaction and aldol condensation, etc., are observed.
- Aldehydes can be oxidised to carboxylic acid; ketones cannot be oxidised without breaking carbon-carbon bonds. The carbonyl group of an aldehyde or ketone can be reduced to alcohol by either catalytic hydrogenation or metallic hydrides. They can also be reduced to alkanes by either the Wolff-Kishner or Clemmensen reduction.
- Methanal and benzaldehyde react with aq. NaOH to give a mixture of alcohol and carboxylate ion (cannizzaro reaction). Methanal reacts with ammonia to form hexamethylenetetramine. Methanal and ethanal readily polymerise.
- Ketones form oximino derivatives with HNO_2, are oxidised to esters with peracids and form pinacols with magnesium amalgam and water.
- Benzaldehyde undergoes reductive dimerisation to give hydrobenzoin, forms α-β-unsaturated derivatives on condensation with other aldehydes and ketones, ethanoic anhydride and malonic acid. Condensation in the presence of CN^- gives benzoin and triphenylmethane derivatives are formed when benzaldehyde is condensed with aromatic amines.
- Phenylethanone gives phenyl-2-oxoethanoic acid and phenyl-2-oxoethanal on oxidation by $KMnO_4$ or SeO_2, respectively. Mannich bases are obtained from phenylethanone, methanal and ammonia or amines.
- Detection of carbonyl group in organic compounds is achieved by the formation of crystalline 2,4-dinitrophenyl hydrazones. Aldehydes are detected by the reduction of ammoniacal silver nitrate or Fehling solution and by Schiff's reagent.

14.9 TERMINAL QUESTIONS

1) Predict the products in the following reaction sequences?

a) $RCH_2OH \xrightarrow[\text{pyridine}]{CrO_3} ?$

b) $RC \equiv CR \xrightarrow[Hg^{2+}]{H_2O,\ H^+} ?$

c) $R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{H_2/Pd\ (BaSO_4)} ?$

d) $R-C \equiv N \xrightarrow[2.\ H_2O]{1.\ SnCl_2/HCl} ?$

2) Write a mechanism for the reaction of:
   a) addition of methanol to propanal
   b) addition of hydrazine to benzaldehyde

3) Predict the products:

a) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H_2NOH \xrightarrow{H^+} ?$

b) $CH_3CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CH_2P(C_6H_5)_3 \xrightarrow{DMSO}$

c) $CH_3CHO + Ag(NH_3)_2OH \longrightarrow$

d) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + Br_2 \xrightarrow{OH^-}$

e) $CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[1,2\text{-ethanediol}]{H_+,\ NNH_2,\ NaOH} ?$

f) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{Zn\ (Hg),\ HCl} ?$

4) An infrared spectrum of an aqueous solution of methanal does not have a C=O stretching band in the 1700 cm^{-1} region. Can you suggest an explanation.

5) Write equations for the following named reactions.
   a) Oppenaur oxidation
   b) Cannizzaro reaction
   c) Aldol condensation
   d) Gattermann-Koch synthesis
   e) Knoevenagel reaction
   f) Perkin reaction
   g) Benzoin condensation
   h) Mannich reaction.

6) How do you obtain
   a) benzaldehyde
   b) phenylethanone starting with benzene.

14.10 ANSWERS

Self-Assessment Questions

1) b); $CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3 + \text{aq NaOH} \longrightarrow CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{heat}]{Cu} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

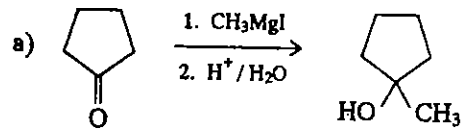
2) c); $C_6H_5CHCl_2 + H_2O \xrightarrow{H^+} C_6H_5-\overset{O}{\overset{\|}{C}}-H + 2HCl$

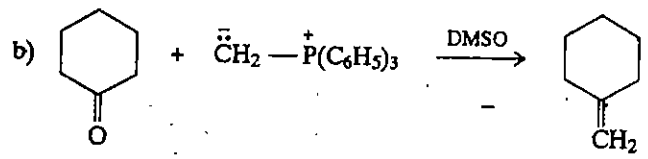
3) a) 1-pentanol; b) methylbutanone; c) 2-butanol; d) phenylmethanol; e) 1-pentanal

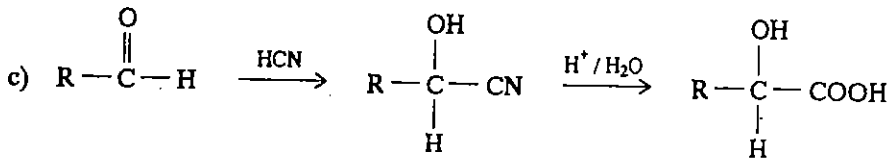
4) a) Ir spectra of propanal and propanone have the C=O band at about 1720 cm^{-1}, but strong band at 2720 and 2820 cm^{-1} due to the C–H band is only exhibited by propanal.

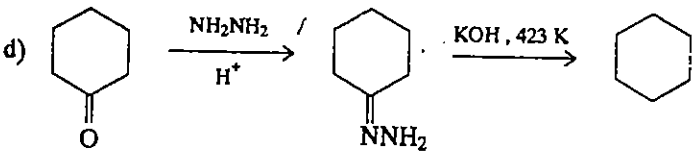
b) Nmr spectrum of propanal exhibits a characteristic signal near 10 ppm for the hydrogen in the –CHO group and this signal is, of course, absent in nmr spectrum of propanone.

5)

a) 

b) 

c) 

d) 

6) c; as it is not having α hydrogens.

7) Ethanal reduces both Tollen's reagents and Fehling's solution. Benzaldehyde can reduces Tollen's reagent but it does not reduce Fehling's solution. Propanone on the other hand does not react both with tollen's reagent and Fehling's solution.

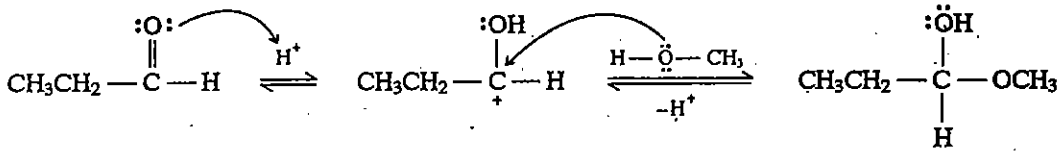
Terminal Questions

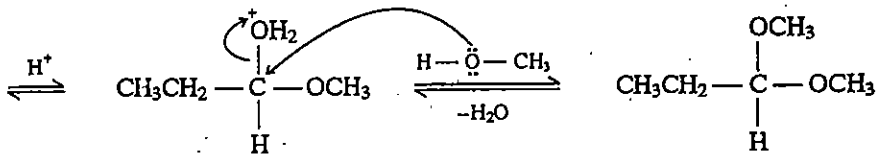
1) a) $RCH_2OH \xrightarrow[\text{pyridine}]{CrO_3} \overset{O}{\overset{\|}{R}}CH$

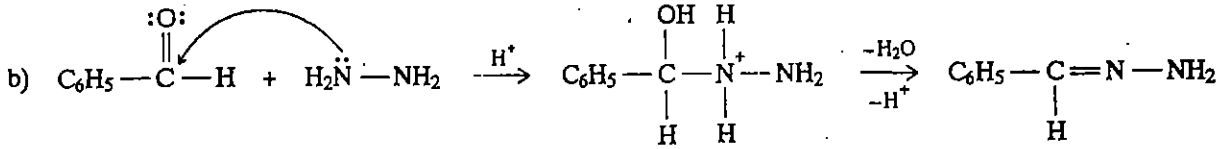
b) $RC\equiv CR \xrightarrow[Hg^{2+}]{H_2O,\ H^+} RCH_2\overset{O}{\overset{\|}{C}}R$

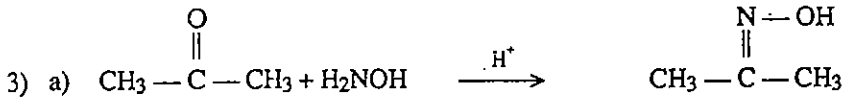
c) $R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{1.\ H_2/Pd/(BaSO_4)} R-\overset{O}{\overset{\|}{C}}-H$

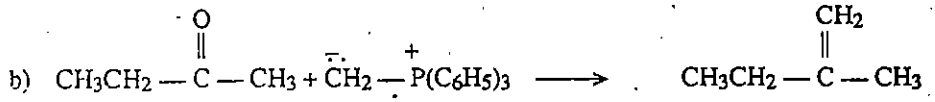
d) $RCN \xrightarrow[2.\ H_2O]{1.\ SnCl_2/HCl} R-\overset{O}{\overset{\|}{C}}-H$

2) a) 

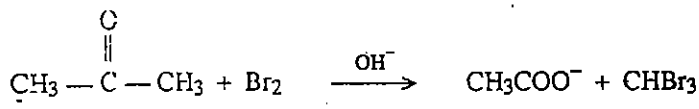


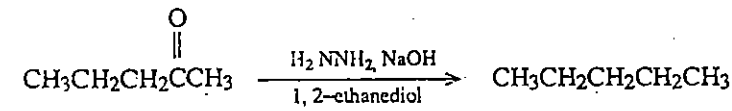
b) 

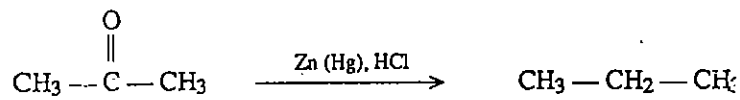
3) a) 

b) 

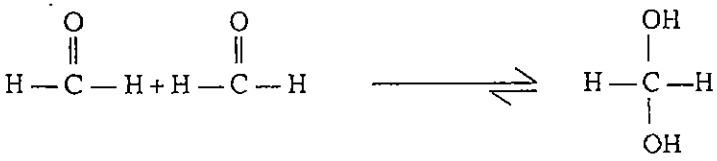
c) $CH_3CHO + Ag(NH_3)_2OH \longrightarrow CH_3-C(=O)-O^-NH_4^+ + 2Ag\downarrow + H_2O + 3NH_3$

d) 

e) 

f) 

4) In water, methanal is converted to stable hydrate, formalin.



formalin (a hydrate)

Formalin does not have carbonyl group, therefore it does not give a C=O stretching in ir spectra.

5) a) $R-\underset{\underset{OH}{|}}{CH}-R + CH_3\overset{\overset{O}{\|}}{C}CH_3 \underset{}{\overset{Al(tert-BuO)_3}{\rightleftharpoons}} R-\overset{\overset{O}{\|}}{C}-R + CH_3\underset{\underset{OH}{|}}{CH}-CH_3$

b) $2HCHO + OH^- \longrightarrow HCOO^- + CH_3OH$

c) $2CH_3CHO \longrightarrow CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO$ Or $CH_3-CH=CH-CHO$

d) $C_6H_6 + CO + HCl \xrightarrow{AlCl_3, Cu_2Cl_2} C_6H_5-\overset{\overset{O}{\|}}{C}-H + HCl$

e) $C_6H_5CHO + CH_2(COOH)_2 \xrightarrow{pyridine} C_6H_5CH=CHCOOH$

f) $C_6H_5CHO + (CH_3CO)_2O + CH_3COONa \longrightarrow C_6H_5CH=CHCOOH$

g) $2C_6H_5CHO \xrightarrow{KCN} C_6H_5CHOHCOC_6H_5$

h) $C_6H_5COCH_3 + HCHO + (CH_3)_2NH{:}HCl \longrightarrow C_6H_5COCH_2CH_2N(CH_3)_2{:}HCl$

6) a) $C_6H_5 + CO + HCl \xrightarrow{AlCl_3, CuCl_2} C_6H_5-\overset{\overset{O}{\|}}{C}-H + HCl$

b) $C_6H_6 + CH_3\overset{\overset{O}{\|}}{C}-Cl \xrightarrow{AlCl_3} C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3 + HCl$

Further Reading

1) *Organic Chemistry*, 6th Ed., by R.T. Morrison and R.N. Boyd, Prentice-Hall of India Pvt. Ltd.
2) *Text Book of Organic Chemistry*, 2nd Ed., by Lloyd N. Ferguson, Affiliated East-West Press Pvt. Ltd.
3) *Organic Chemistry*, Vol. I and II, by S.M. Mukherji, S.P. Singh and R.P. Kapoor, Wiley Eastern Ltd.
4) *Text Book of Organic Chemistry*, 24th Ed., by P.L. Soni and H.M. Chawla, Sultan Chand and Sons.
5) *The Chemistry of Carbonyl Compounds*; Gutsche, C. David, Prentice-Hall of India Pvt. Ltd.

UTTAR PRADESH
RAJARSHI TANDON OPEN UNIVERSITY

UGCHE - 05
Organic Chemistry - I

Block

4

DERIVATIVES OF HYDROCARBONS — II

UNIT 15

Monocarboxylic and Sulphonic Acids 5

UNIT 16

Substituted Carboxylic Acids 27

UNIT 17

Functional Derivatives of Monocarboxylic Acids 58

UNIT 18

Nitro Compounds 84

UNIT 19

Amino Compounds and Diazonium Salts 91

UNIT 20

Natural Products 116

DERIVATIVES OF HYDROCARBONS-II

In Block 3, you have studied the chemistry of some derivatives of hydrocarbons such as halogen derivatives, alcohols, phenols, ethers, sulphur analogues of alcohols and ethers, and carbonyl compounds such as aldehydes and ketones. In this block, we shall discuss more complex derivatives of hydrocarbons.

This is the last block of this course and it contains six units.

Unit 15, which is the first unit of this block, deals with carboxylic and sulphonic acids. In this unit, you will study the methods of preparation, physical and chemical properties, industrial uses and laboratory detection of these acids.

In Unit 16, we will discuss the chemistry of substituted carboxylic acids such as halo acids, hydroxy acids, amino acids, dicarboxylic acids, keto acids and unsaturated acids. In addition to their methods of preparation and the reactions of individual functional groups, you will also study the characteristic behaviour and reactions resulting from the interaction of the two functional groups.

Unit 17 describes the functional derivatives of carboxylic acids obtained by the substitution of the $-OH$ of the carboxy ($-\overset{\overset{O}{\|}}{C}-OH$) functional group. The functional derivatives such as carboxylic acid halides, anhydrides, esters and amides will be dealt with here. In addition to their method of preparation, physical properties and reactions, we will also compare their relative reactivities.

A large number of organic compounds contain nitrogen. This also leads to the possibility of a number of functional groups. Since it is not possible to discuss all of them in this course, we will confine our discussion to nitro compounds and amines. Unit 18 deals with the chemistry of nitro compounds. The study of nitro compounds is important because they provide a route to other organic compounds. The chemistry of amines is discussed in Unit 19. Amines constitute a large class of organic compounds. The discussion on amines will include their natural occurrence, physical and chemical properties, uses and laboratory detection. We will also deal with the synthetic importance of diazonium salts.

The last unit, Unit 20 is a window to the wide variety of naturally occurring organic compounds. It gives you an insight to the vast range of naturally occurring organic compounds, their structures and importance.

Objectives

After studying this block, you should be able to :

- describe the importance of carboxylic and sulphonic acids, nitro compounds and amines.
- discuss the methods of preparation, physical and chemical properties of various classes of compounds such as carboxylic and sulphonic acids, substituted carboxylic acids, functional derivatives of carboxylic acids, nitro compounds and amines,
- explain the relative reactivity of functional derivatives of carboxylic acids such as carboxylic acid halides, anhydrides, esters and amides, and
- give some examples of naturally occurring organic compounds, write their structures and explain their importance.

NIT 15 MONOCARBOXYLIC AND SULPHONIC ACIDS

ucture

1 Introduction
Objectives
2 Carboxylic Acids
3 Preparation of Monocarboxylic Acids
4 Physical Properties of Monocarboxylic Acids
5 Spectral Properties of Carboxylic Acids
6 Reactions of Carboxylic Acids
7 Sulphonic Acids
Preparation of Benzenesulphonic acid
Reactions of Benzenesulphonic acid
8 Industrial Uses of Carboxylic and Sulphonic Acids
9 Laboratory Detection of Carboxylic and Sulphonic Acids
10 Summary
11 Terminal Questions
12 Answers

.1 INTRODUCTION

rboxylic acids are the compounds which contain the **carboxy** (–COH) functional

up and can be represented either as RCOH or as RCOOH. The carboxylic acids
only form an important class of organic compounds but are also the parent
npounds of a large group of compounds called the functional derivatives of
boxylic acids which can be further classified as acid halides, acid anhydrides, aci
ides and esters. These classes of compounds will be discussed in Unit 17.
rboxylic acids also play an important role in various biological processes. In Unit
you will study about some such acids.

sides carboxylic acids, there is another important class of organic acids, called
phonic acids. The sulphonic acids are the compounds which contain a $-SO_3H$
up, called the **sulphonic acid group.** Sulphonic acids are organic acids related to
phuric acid. Sulphonic acids and carboxylic acids are closely related in their
emistry. Therefore, in this unit, we will first study the chemistry of carboxylic acids
l then that of the sulphonic acids.

bjectives

ter studying this unit, you should be able to:

list various methods of preparation of carboxylic acids,

outline the synthesis of various carboxylic acids using the above methods starting from appropriate starting materials,

predict and correlate the physical properties such as melting point, boiling point, solubility and spectral characteristics of carboxylic acids with their structures,

describe the reactions of carboxylic acids,

explain the preparation and reactions of sulphonic acids.

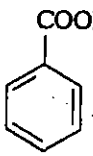
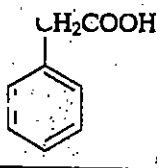
describe the importance and uses of carboxylic and sulphonic acids, and

explain how carboxylic and sulphonic acids can be identified in laboratory.

15.2 CARBOXYLIC ACIDS

You have already come across carboxylic acids in Unit 1. There you studied the nomenclature of monocarboxylic and dicarboxylic acids. Before studying the chemistry of monocarboxylic acids you can refresh your memory by going through the list of carboxylic acids given in Table 15.1.

Table 15.1 : Some Carboxylic Acids

Structure	IUPAC Name	Common Name
$HCOOH$	Methanoic acid	Formic acid
CH_3COOH	Ethanoic acid	Acetic acid
CH_3CH_2COOH	Propanoic acid	Propionic acid
$CH_3(CH_2)_2COOH$	Butanoic acid	Butyric acid
$CH_3(CH_2)_3COOH$	Pentanoic acid	Valeric acid
$CH_3(CH_2)_4COOH$	Hexanoic acid	Caproic acid
$CH_3(CH_2)_5COOH$	Heptanoic acid	Enanthic acid
$CH_3(CH_2)_6COOH$	Octanoic acid	Caprylic acid
$CH_3(CH_2)_7COOH$	Nonanoic acid	Pelargonic acid
$CH_3(CH_2)_8COOH$	Decanoic acid	Capric acid
$CH_3(CH_2)_{10}COOH$	Dodecanoic acid	Lauric acid
$CH_3(CH_2)_{12}COOH$	Tetradecanoic acid	Myristic acid
$CH_3(CH_2)_{14}COOH$	Hexadecanoic acid	Palmitic acid
$CH_3(CH_2)_{16}COOH$	Octadecanoic acid	Stearic acid
	Benzenecarboxylic acid	Benzoic acid
	Phenylethanoic acid	Phenylacetic acid

Aliphatic acids are also referred to as **fatty acids** because many of them were first obtained by the hydrolysis of fats and oils of vegetable or animal origin. Let us now study how monocarboxylic acids can be prepared.

15.3 PREPARATION OF MONOCARBOXYLIC ACIDS

Let us first have a look at Table 15.2 where various methods which can be used to prepare monocarboxylic acids have been listed. We will then discuss each one of them in more detail.

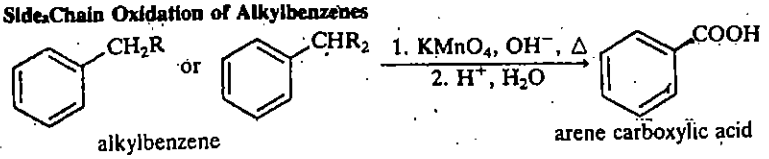
Table 15.2 : Some Methods of Preparation for Carboxylic Acids

1. **Oxidation of Alkenes**

$$RCH=CHR' \xrightarrow[2.\ H^+,\ H_2O]{1.\ KMnO_4,\ OH^-,\ \Delta} RCOOH + R'COOH$$

$$RCH=CR'_2 \xrightarrow[2.\ H^+,\ H_2O]{1.\ KMnO_4,\ OH^-,\ \Delta} RCOOH + R'_2C=O$$

2. **Side-Chain Oxidation of Alkylbenzenes**



alkylbenzene — arene carboxylic acid

Other oxidising agents used are $Na_2Cr_2O_7$ and CrO_3, etc.

3. **Oxidation of Primary Alcohols**

$$R-CH_2OH \xrightarrow[K_2Cr_2O_7,\ H_2SO_4]{KMnO_4 \text{ or}} RCOOH$$

primary alcohol — carboxylic acid

4. **Oxidation of Aldehydes**

$$RCHO \xrightarrow[2.\ H^+,\ \text{heat}]{1.\ Ag_2O \text{ or } Ag(NH_3)_2^+\ OH^-} RCOOH$$

Other oxidising agents like $KMnO_4$ and chromic acid can be used.

5. **Oxidation of Methyl Ketones (Haloform reaction)**

$$RCCH_3 \xrightarrow[OH^-]{X_2} [RCOCX_3] \xrightarrow[2.\ H^+,\ H_2O]{1.\ OH^-} RCOOH + CHX_3$$

(O)

6. **Carbonation of Organometallic Reagents**

$$RMgX \xrightarrow{CO_2} RCO_2MgX \xrightarrow{H_2O,H^+} RCOOH + Mg(OH)X$$

$$RLi \xrightarrow{CO_2} RCO_2Li \xrightarrow{H_2O,H^+} RCOOH$$

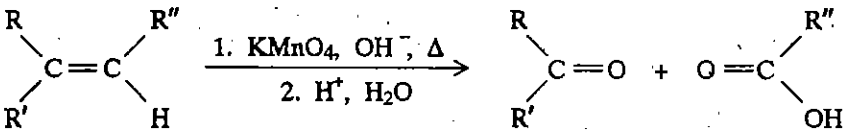
7. **Hydrolysis of Nitriles**

$$R-C\equiv N \xrightarrow[H^+ \text{ or } OH^-]{H_2O} RCONH_2 \xrightarrow[H^+ \text{ or } OH^-]{H_2O} RCOOH$$

nitrile — amide

1. Oxidation of Alkenes

Basic potassium permanganate cleaves alkenes to two carbonyl compounds. If one of the substituents at the double bond is hydrogen, the cleavage product is an aldehyde which is rapidly oxidised to a carboxylic acid under the reaction conditions, i.e.



alkene — ketone — carboxylic acid

In this oxidation, each carbon of the double bond becomes the carbon atom of the carbonyl group and a hydrogen substituent on the double bond is replaced by a hydroxyl group.

Since the carboxylic acids are formed in these reactions as their potassium carboxylate salts, the acidification step is necessary in order to isolate the product as free acid.

The intermediate in this reaction may be a diol which is oxidised further with the cleavage of carbon-carbon bond.

The terminal CH_2 group of 1-alkene is completely oxidised to carbon dioxide and water. For example,

$$CH_3(CH_2)_{10}CH=CH_2 \xrightarrow[2.\ H^+,\ H_2O]{1.\ KMnO_4,\ OH^-,\ \Delta} CH_3(CH_2)_{10}COOH + CO_2 + H_2O$$

1-tridecene — dodecanoic acid (84%)

Potassium permanganate is a dark purple crystalline solid which dissolves in water to give intense purple coloured solution. In permanganate anion, MnO_4^-, manganese has an oxidation state of +7. When used as an oxidising agent in basic solution, manganese reduces to MnO_2 which is obtained as brown precipitate. The oxidation state of Mn in MnO_2 is +4.

You may recall that alkenes can be oxidised to diols using cold dilute $KMnO_4$ (sub-Sec. 7.6.6, Unit 7, Block 2).

The terminal carbon of 1-alkenes contains two hydrogens on it, so it is oxidised to carbonic acid which is present as its potassium salt, i.e. potassium carbonate. This on acidification yields carbonic acid which decomposes into carbon dioxide and water.

$$KOCOK \xrightarrow{H^+} HOCOH \longrightarrow$$

potassium carbonate — Carbonic acid

$$CO_2 + H_2O$$

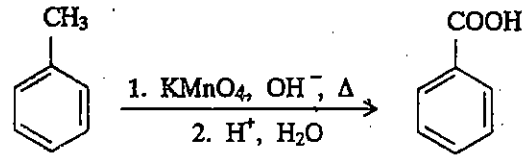
Carbon dioxide — water

Note that the acid produced from the terminal alkene contains one carbon less than the alkene.

2. Side Chain Oxidation of Alkylbenzenes

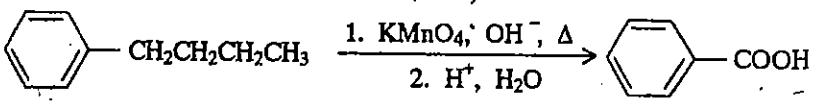
Aromatic carboxylic acids can be obtained by the oxidation of alkylbenzenes. The oxidation can be carried out by using potassium permanganate, Cr^{6+} derivatives such as sodium dichromate or aqueous nitric acid.

Note that the alkyl chain, regardless of length, is oxidised to a COOH group. However, *tert*-alkyl substituents do not undergo oxidation under these conditions.



methylbenzene (toluene)

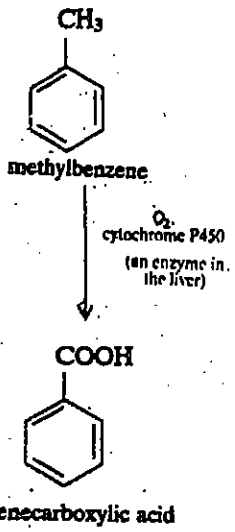
benzenecarboxylic acid (benzoic acid) (100%)

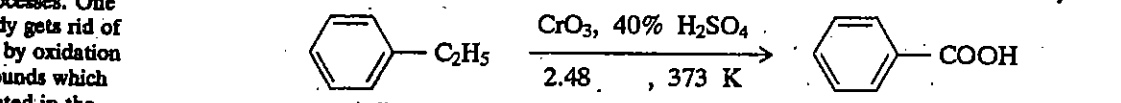


butylbenzene

benzenecarboxylic acid

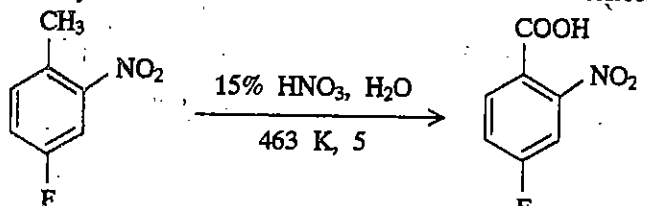
Side-chain oxidation of alkylbenzenes is important in certain metabolic processes. One way in which the body gets rid of foreign substances is by oxidation in the liver to compounds which are more easily excreted in the urine. Methylbenzene, for example, is oxidised to benzenecarboxylic acid which is easily eliminated.





ethylbenzene

benzenecarboxylic acid

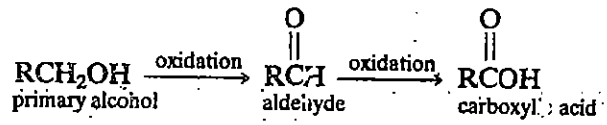


4-fluoro-1-methyl-2-nitrobenzene

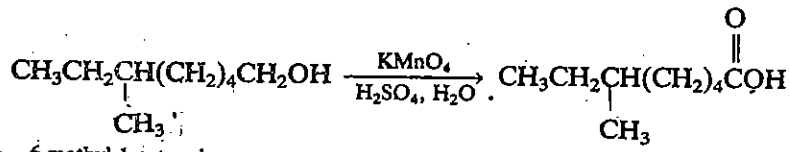
4-fluoro-2-nitro-benzenecarboxylic acid (69%)

3. Oxidation of Primary Alcohols

You have studied in Block 3, Unit 12, sub-Sec. 12.6.2 that primary alcohols can be oxidised to carboxylic acids using $KMnO_4$, CrO_3, nitric acid etc. The carboxylic acid obtained contains the same number of carbon atoms as present in the starting alcohol. The initial product of oxidation is an aldehyde. However, when aqueous $KMnO_4$ is used, the aldehyde is rapidly oxidised and the carboxylic acid is obtained as the product.



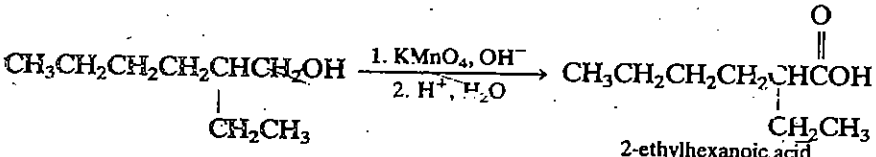
primary alcohol — aldehyde — carboxylic acid



6-methyl-1-octanol

6-methyloctanoic acid (66%)

When oxidation is carried out under basic conditions, the carboxylic acid is obtained as the carboxylate salt which on acidification yields carboxylic acid.

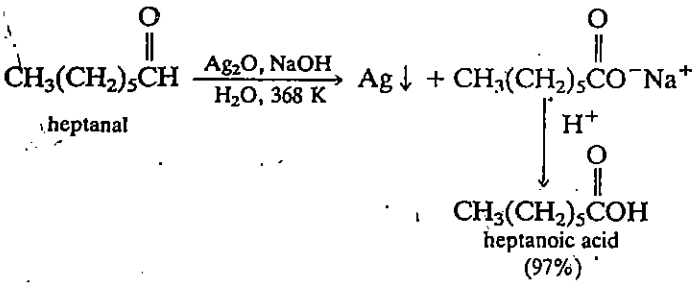


2-ethyl-1-hexanol

2-ethylhexanoic acid (74%)

4. Oxidation of Aldehydes

Aldehydes are readily oxidised to carboxylic acids by strong oxidising agents such as $KMnO_4$, CrO_3 and HNO_3 as discussed above. A mild oxidising agent used for this oxidation is moist silver oxide suspended in an aqueous base.



heptanal

heptanoic acid
(97%)

Silver oxide is usually prepared by mixing a solution of silver nitrate with sodium hydroxide. The precipitate obtained is filtered, washed with water and used as an aqueous suspension.

In this reaction, Ag(I) is reduced to metallic silver. When the reaction is carried out in a clean test-tube, a mirror is deposited on the walls of the tube. This reaction forms the basis of the *Tollens' test.*

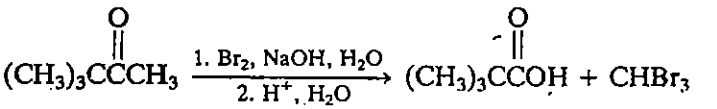
Tollens' test is a qualitative test for aldehydes. The compound is treated with ammoniacal silver nitrate in a clean test tube. Formation of a shiny mirror of silver on the walls of the test tube is taken as a positive indication of the presence of an aldehyde or other easily oxidisable group.

Silver oxide selectively oxidises the aldehyde functional group and the other sensitive groups such as double bonds and triple bonds are not affected.

Although this method gives the desired acid in good yields, its use is limited to small scale reactions because silver oxide is expensive.

5. Oxidation of Methylketones

The haloform reaction which you studied in sub-Sec. 14.4.2, Unit 14, Block 3, is occasionally used to prepare carboxylic acids from readily available methylketones.



3, 3-dimethyl-2-butanone

2, 2-dimethylpro-panoic acid
(71-74%)

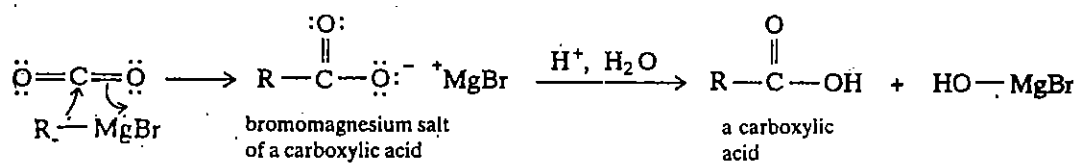
bromoform

Grignard reagents, RMgX, are named after the French Chemist Victor Grignard who discovered them in 1900 and for which he was awarded the Nobel prize in 1912.

6. Carbonation of Ogranometallic Reagents

Organometallic compounds such as Grignard reagents and organolithium compounds can be used for the synthesis of carboxylic acids.

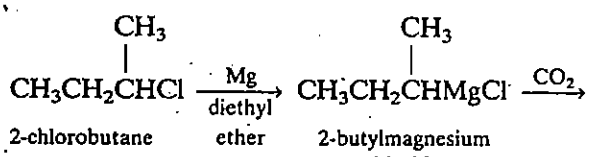
Organometallic reagents react with carbon dioxide to give salts of carboxylic acids. The salt is treated with a strong mineral acid to yield the carboxylic acid.



bromomagnesium salt of a carboxylic acid

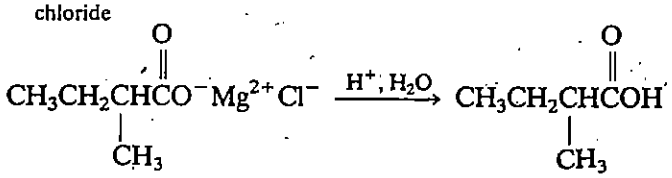
a carboxylic acid

Grignard reagents are usually prepared by the reaction of an alkyl or aryl halide with magnesium metal in an ether or hydrocarbon solvent.

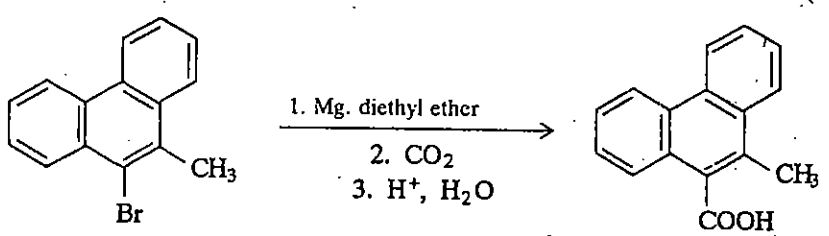


2-chlorobutane

2-butylmagnesium chloride



2-methylbutanoic acid
(~77%)

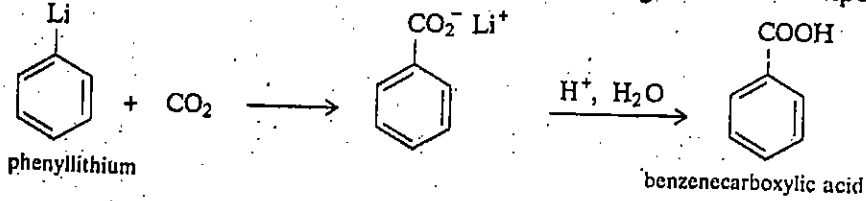


9-bromo-10-methylphenanthrene

10-methylphenanthrene-9-carboxylic acid (82%)

Note that the acid obtained contains one carbon atom more than the alkyl or aryl halide used to prepare the Grignard reagent.

A similar reaction occurs between carbon dioxide and organolithium compounds.



phenyllithium — benzenecarboxylic acid

7. Hydrolysis of nitriles

The reaction is of S_N2 type and is most effective with primary alkyl halides. It is slow with secondary alkyl halides. With tertiary alkyl halides, elimination occurs. Aryl and vinyl halides do not react.

DMSO, Dimethylsulphoxide, is the preferred solvent for this reaction, but alcohols and water-alcohol mixtures have also been used.

Primary and secondary alkyl halides may be converted to carboxylic acids containing one more carbon atom using a two step process. The first step involves the preparation of nitriles or alkyl cyanide. The nitrile on hydrolysis in acidic or basic conditions yields the carboxylic acid.

$$CH_3CH_2CH_2CH_2Br + NaCN \xrightarrow{DMSO} CH_3CH_2CH_2CH_2CN$$

1-bromobutane — pentanenitrile

$$CH_3CH_2CH_2CH_2CN \xrightarrow{KOH,\ H_2O,\ \Delta} CH_3CH_2CH_2CH_2COO^-K^+$$

$$CH_3CH_2CH_2CH_2COO^-K^+ \xrightarrow{H^+,\ H_2O} CH_3CH_2CH_2CH_2COOH$$

pentanoic acid (90%)

This method is complementary to carbonation of organometallic reagents as the hydroxy and carboxy groups present in the molecule do not need protection in this method.

SAQ 1

How will you prepare the following carboxylic acids using Grignard reagents?

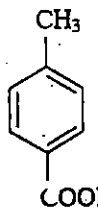
a) 2, 2-dimethylpentanoic acid

.....

b) Hexanoic acid

.....

c) 4-methylbenzenecarboxylic acid,



.....

15.4 PHYSICAL PROPERTIES OF MONO-CARBOXYLIC ACIDS

Physical properties such as melting point, boiling point and water solubility of some straight chain carboxylic acids are listed in Table 15.3.

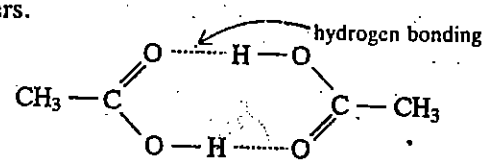
Table 15.3 : Physical Properties of Carboxylic Acids

Acid	Melting point/K	Boiling point/K	Solubility in $H_2O \times 10^2$ at 293K/kg dm^{-3}
Methanoic acid	281	374	∝
Ethanoic acid	289	391	∝
Propanoic acid	252	414	∝

Acid	Melting point/K	Boiling point/K	Solubility in $H_2O \times 10^2$ at 293K/kg dm^{-3}
Butanoic acid	268	437	∝
Pentanoic acid	239	459	4.97
Hexanoic acid	270	478	0.968
Heptanoic acid	265	496	0.244
Octanoic acid	290	512	0.068
Nonanoic acid	288	528	0.026
Decanoic acid	305	543	0.015
Benzenecarboxylic acid	395	522	0.21

You can see from Table 15.3 that the lower members are liquids at room temperature. Table 15.3 also shows that the carboxylic acids having an even number of carbon atoms have higher melting points as compared to the carboxylic acids having an odd number of carbon atoms. Thus, it illustrates the "saw-tooth" pattern which you studied in Block 1, Unit 4, Fig. 4.2. The higher members and aromatic acids are solid at room temperature.

Carboxylic acids are polar in nature. They can form hydrogen bonds in the solid as well as in the liquid state. As a result, they generally have high boiling points. In the solid state and under some conditions in gas and solution phase, carboxylic acids exist as hydrogen-bonded dimers.



dimer of ethanoic acid in vapour phase

Due to the hydrogen bonding lower members of this class show appreciable solubility in water. The first four monocarboxylic acids are miscible with water in all proportions. But, as the chain length increases, the water solubility decreases.

15.5 SPECTRAL PROPERTIES OF CARBOXYLIC ACIDS

Infrared spectra of carboxylic acids

The carboxy group consists of a carbonyl group and an attached hydroxy group. Characteristic stretching frequencies corresponding to both these groups are observed in the infrared spectra of carboxylic acids. This is illustrated in the infrared spectrum of propanoic acid as shown in Fig. 15.1.

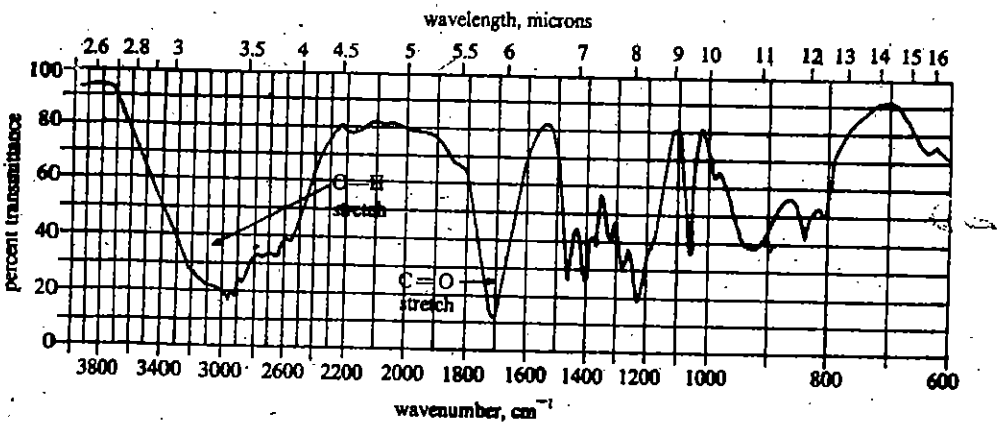


Fig. 15.1 : Infrared spectrum of propanoic acid.

The bands due to O–H stretching and C=O stretching are both broad due to hydrogen bonding.

The O–H stretching in carboxylic acids is observed as a broad band at wave numbers 2400 to 3600 cm^{-1} as shown in Fig. 15.1. The O–H stretching frequencies usually overlap with the C–H stretching frequencies of the molecules. The C=O stretching in carboxylic acids is observed near 1710 cm^{-1} (see Fig. 15.1). For acids in which the carbonyl group is conjugated with a double bond or with an aromatic ring, the C=O stretching appears between 1710–1680 cm^{-1}. For example, C=O stretching in benzenecarboxylic acid is observed at 1680 cm^{-1}.

NMR spectra of carboxylic acids

The hydroxyl proton (–O–H) of a carboxy group is normally the least shielded of all the hydrogens bonded to oxygen. It is observed downfield between δ 9–13 ppm depending upon the concentration, solvent and temperature which affect the extent of hydrogen bonding. As with other acidic protons (e.g. –OH protons of alcohols and phenols), the carboxy proton can be identified by adding D_2O to the sample. Hydrogen-deuterium exchange converts –COOH to –COOD and hence the signal corresponding to the –COOH proton disappears in the spectrum. The NMR spectrum of propanoic acid is shown in Fig. 15.2.

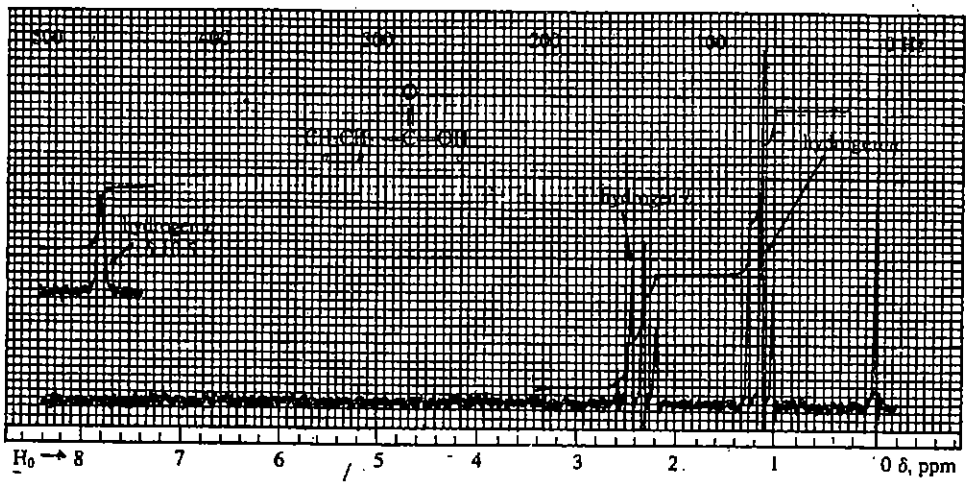


Fig. 15.2 : NMR spectrum of propanoic acid.

15.6 REACTIONS OF CARBOXYLIC ACIDS

The reactions of carboxylic acids are given below in Table 15.4 followed by their detailed discussion.

Table 15.4 : Reactions of Carboxylic acids

1. **As Acids**

$$RCOOH + NaOH \longrightarrow RCOO^- Na^+ + H_2O$$

$$RCOOH + NaHCO_3 \longrightarrow RCOO^- Na^+ + H_2O + CO_2$$

2. **As Bases**

$$R-\overset{\overset{:O:}{\|}}{C}-\ddot{O}H + H^+ \rightleftharpoons R-\overset{\overset{+\ddot{O}-H}{\|}}{C}-\ddot{O}H$$

(resonance stabilised)

3. **Esterification**

$$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} R\overset{\overset{O}{\|}}{C}OR' + H_2O \text{ (Fischer Esterification)}$$

$$RCOOH + CH_2N_2 \longrightarrow R\overset{\overset{O}{\|}}{C}OCH_3 + N_2 \text{ (by diazomethane)}$$

4. **Conversion to amides**

$$RCOOH + NH_3 \rightleftharpoons RCOO^-\overset{+}{N}H_4 \xrightarrow{\text{heat}} RCONH_2 + H_2O$$

$$RCOOH + R'NH_2 \rightleftharpoons RCOO^-\overset{+}{N}H_3R' \xrightarrow{\text{heat}} RCONHR' + H_2O$$

$$RCOOH + R_2'NH \rightleftharpoons RCOO^-\overset{+}{N}H_2R_2' \xrightarrow{\text{heat}} RCONR_2' + H_2O$$

5. **Conversion to 2-halo acids**

$$R{-}CH_2COOH + X_2 \xrightarrow{\text{Red P}} R{-}\underset{\displaystyle X}{\underset{|}{CH}}COOH$$

$X_2 = Cl_2$ or Br_2

6. **Reduction**

$$RCOOH \xrightarrow[2.\ H^+,\ H_2O]{1.\ LiAlH_4} RCH_2OH$$

7. **Decarboxylation**

i) $$2\,R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O^- \xrightarrow{\text{electrolysis}} R - R + 2\,CO_2$$

ii) $$\overset{\displaystyle O}{\overset{\|}{R}}COAg + Br_2 \xrightarrow[\Delta]{CCl_4} RBr + CO_2 + AgBr$$

8. **Conversion to alkanoyl halides**

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$
$$RCOOH + PCl_3 \longrightarrow 3\,RCOCl + H_3PO_3$$
$$RCOOH + PCl_5 \longrightarrow 3\,RCOCl + POCl_3 + HCl$$

1. Acidity

As the name indicates, carboxylic acids are acidic. The acidity of carboxylic acids and various factors affecting it were discussed in Unit 5, Block 1. It was explained in Unit 5 that the carboxylate ion so produced is resonance stabilised.

Another aspect related to the acidity of carboxylic acids is salt formation. Carboxylic acids on treatment with bases such as NaOH yield salts.

$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\ddot{O}H + NaOH \longrightarrow R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\underset{\text{(salt)}}{\ddot{O}:^-}\ Na^+ + H_2O$$

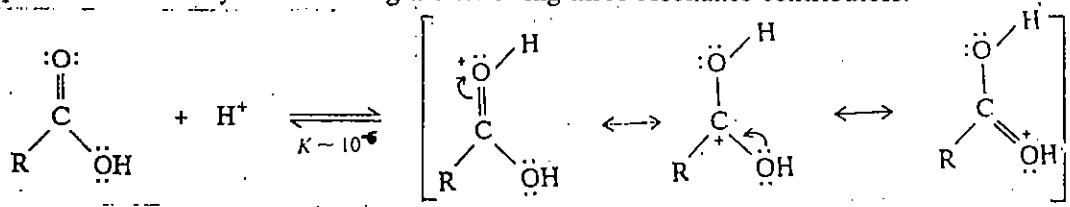
These salts are named by specifying the metal and replacing the **–ic acid** in the name of the acid by **–ate** ending.

Even a 5% sodium bicarbonate ($NaHCO_3$) solution is basic enough (pH = 8.5) to yield the sodium salt of a carboxylic acid. Thus, carboxylic acids react readily with aqueous solutions of sodium hydroxide and sodium bicarbonate to form soluble sodium salts.

Thus, water insoluble carboxylic acids can be differentiated from other water insoluble nonacidic substances. Water insoluble carboxylic acids will dissolve in either aqueous sodium hydroxide or sodium bicarbonate but the nonacidic compounds will not. After separating the basic aqueous solution, it can be acidified with mineral acid to yield the carboxylic acid.

2. Basicity of carboxylic acids

The carbonyl group of a carboxylic acid is weakly basic and its protonation yields the protonated carboxylic acid having the following three resonance contributors.



Such a protonation or basicity plays an important role in many reactions of the carboxylic acids and their derivatives about which you will study in the following units of this block.

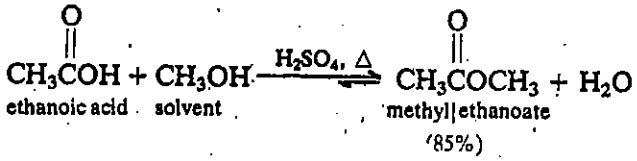
3. Esterification

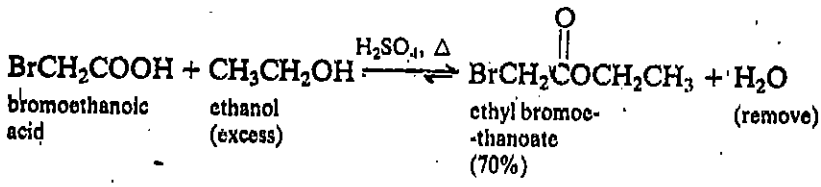
Carboxylic acids react with alcohols in the presence of an acid catalyst to yield esters. The reaction is known as **Fischer esterification.**

$$\underset{\text{carboxylic acid}}{RCOOH} + \underset{\text{alcohol}}{R'OH} \overset{H^+}{\rightleftharpoons} \underset{\text{ester}}{\overset{\displaystyle O}{\overset{\|}{R}}COR'} + \underset{\text{water}}{H_2O}$$

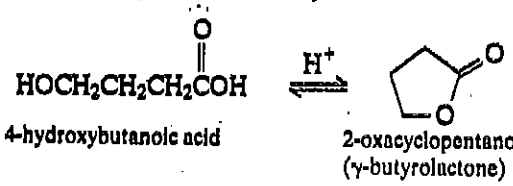
This reaction is an equilibrium process and can be driven in favour of the ester by removing the water formed. The second way of increasing the yield of an ester is by using one of the reactants in excess (Le Chatelier's principle). Generally, the cheaper of the two reactants is taken in excess. Thus, esterifications are often carried out by using the alcohol as the solvent.

A wide variety of esters can be prepared using this method. The common acid catalysts used are conc. sulphuric acid, hydrogen chloride or *p*-toluenesulphonic acid. Some examples of ester formation are given below.



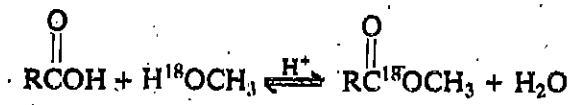


When the carboxy and hydroxy groups are present in the same molecule, a lactone (cyclic ester) is obtained by intramolecular esterification. For example,

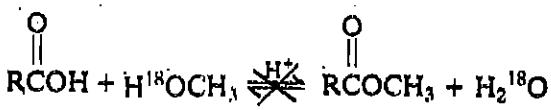


You will study more about lactones in sub-Sec. 16.3.2 of Unit 16.

Before studying the mechanism of acid-catalysed esterification, it is interesting to know whether the oxygen of the water formed in the reaction comes from the alcohol or from the acid. In an experiment using isotopically labelled alcohol (having ^{18}O isotope) it was observed that oxygen in the water produced comes exclusively from the carboxylic acid. Thus, it was observed that,



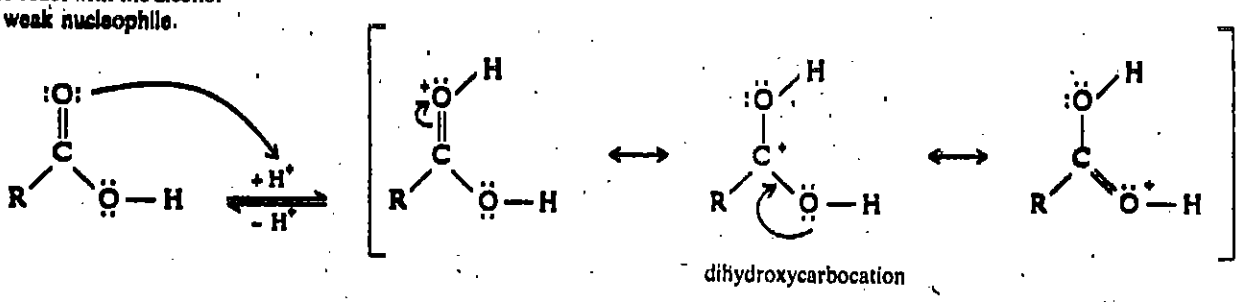
and not,



A carboxylic acid does not react with an alcohol unless a strong acid is used as a catalyst. Protonation of the carboxy group makes the carbonyl (>C=O) group more electrophilic and enables it to react with the alcohol which is a weak nucleophile.

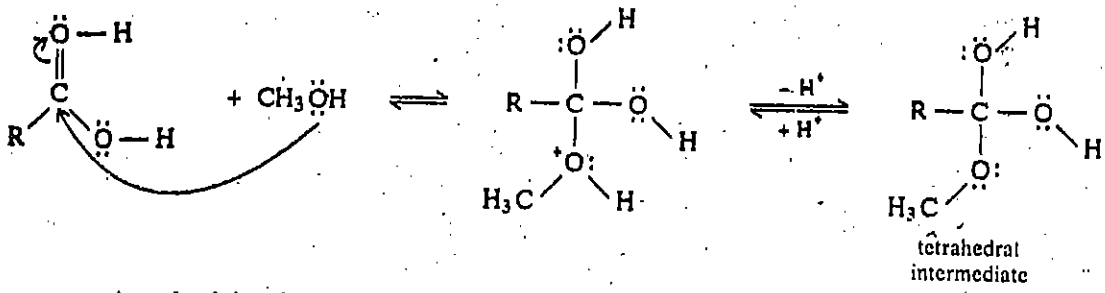
In other words, the alcohol oxygen is incorporated into the ester. This and other observations led to the following mechanism of esterification:

Step 1 : Protonation of the carboxy group



The protonated carboxylic acid is susceptible to attack by nucleophiles such as alcohol, as shown in step 2.

Step 2 : Attack by alcohol

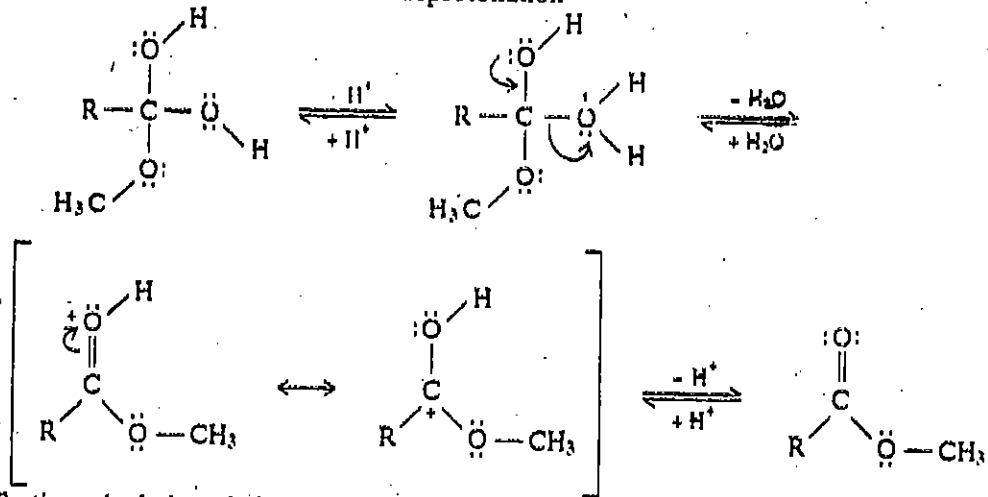


Addition of alcohol to carboxylic acid to form the tetrahedral intermediate is analogous to the addition of an alcohol to an aldehyde or ketone to form a hamiacetal which you have studied in, Block 3, Unit 14, sub-Sec. 14.4.1.

Step 2 is the rate-determining step in esterification reactions.

Attack of the alcohol on the protonated carboxylic acid yields an initial adduct which on loss of a proton yields the **tetrahedral intermediate.** The tetrahedral intermediate eliminates water and yields the ester as shown in step 3.

Step 3 : Elimination of water and deprotonation



Tertiary alcohols and phenols cannot be used in acid catalysed esterification. Due to steric factors, tertiary alcohols react very slowly in the esterification reaction and they usually undergo elimination instead of esterification. For phenols also, the equilibrium constants of esterification are very low.

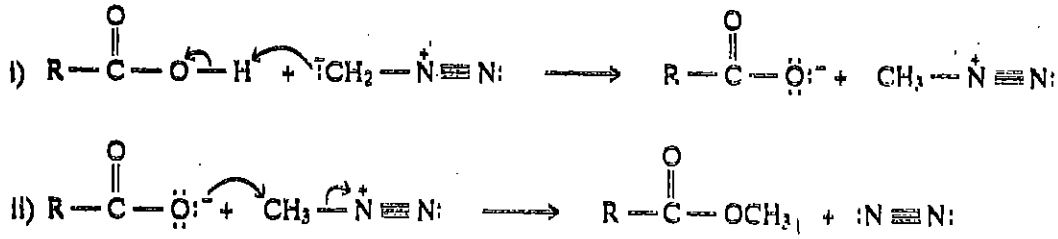
There are other ways of obtaining esters from tertiary alcohols and phenols about which you will study in Unit 17, sub-Sec. 17.5.2.

Another method of obtaining methyl esters from carboxylic acids involves the use of diazomethane, CH_2N_2. When a carboxylic acid is treated with diazomethane in ether solution, it is rapidly converted into a methyl ester.

Diazomethane is a toxic yellow gas. It is both explosive and allergenic. Therefore, this method can be used only for small scale preparations. But the esterification is so mild and free of side reactions that in many cases it is the method of choice for the synthesis of methyl esters.

$$RCOH + CH_2N_2 \longrightarrow RCOOCH_3 + N_2$$

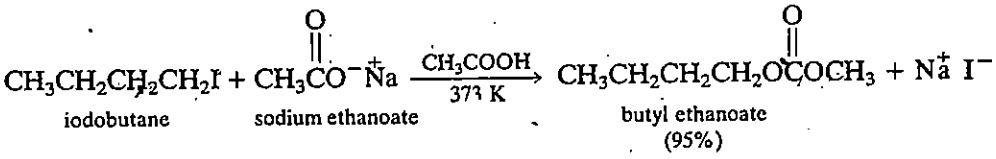
The following mechanism can be written for this esterification.



Step (i) is an acid-base reaction about which you studied in Unit 5, Block 1.

The first step involves the protonation of diazomethane. Therefore, you can understand that acidity of carboxylic acid is important in this reaction. The resulting methyl diazonium ion has one of the best leaving groups, i.e., molecular nitrogen. Thus, an S_N2 reaction of the carboxylate ion with the methyldiazonium ion results in the displacement of N_2 and formation of an ester. **Note that here the oxygen of the carboxylate group acts as a nucleophile whereas in acid-catalysed esterification, the carbonyl group of the protonated carboxyl group behaves as an electrophile.** This illustrates two of the general ways in which carboxylic acids react.

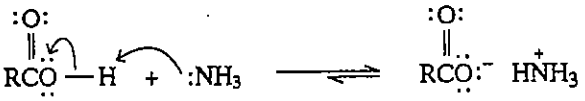
The nucleophilic nature of the carboxylate ion is also illustrated by the reaction of certain alkyl halides, particularly primary haloalkanes, with carboxylate ions. For example,



iodobutane — sodium ethanoate — butyl ethanoate (95%)

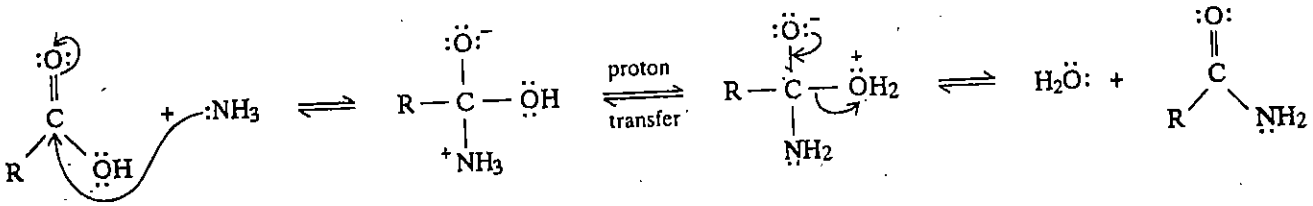
4. Amide formation

Carboxylic acids on reaction with ammonia or amines (primary or secondary) can lead to amides via the initial formation of ammonium salts.

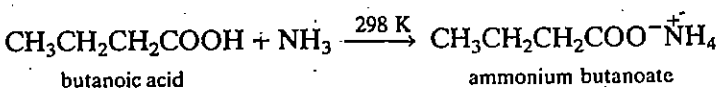


ammonia — an ammonium alkanoate

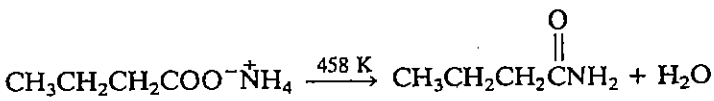
On heating salt formation is reversed and nucleophilic attack by nitrogen on the carbonyl carbon takes place. The elimination of water then leads to the formation of an amide as shown below:



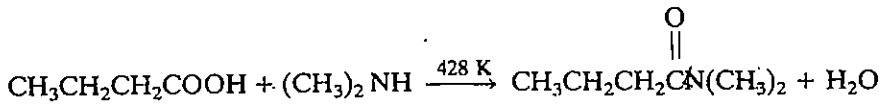
Some examples are given below:



butanoic acid — ammonium butanoate



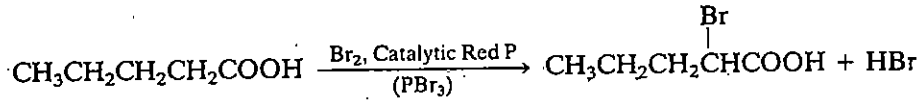
ammonium butanoate — butanamide



butanoic acid — *N, N*-dimethylamine — *N, N*-dimethylbutanamide (84%)

5. Formation of 2-halo acids

Aliphatic carboxylic acids react with bromine or chlorine in the presence of phosphorus (or a phosphorus halide) to give 2-halo acids. This reaction is known as **Hell-Vollhard-Zelinski** reaction after its discoverers.

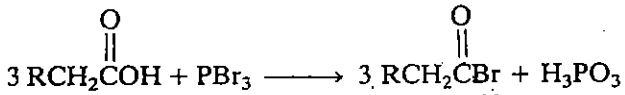


pentanoic acid — 2-bromopentanoic acid

Phosphorus reacts with Br_2 to give PBr_3.

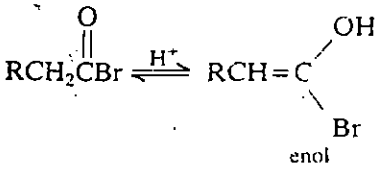
If more than one equivalent of halogen is used in the reaction, then 2,2-dihalo acids or 2,2,2-trihalo acids are obtained. The mechanism of this reaction is given below:

Step 1 : Alkanoyl bromide formation

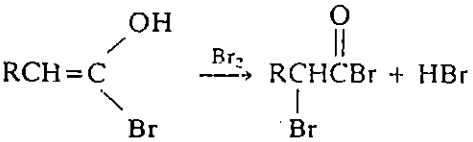


alkanoyl bromide

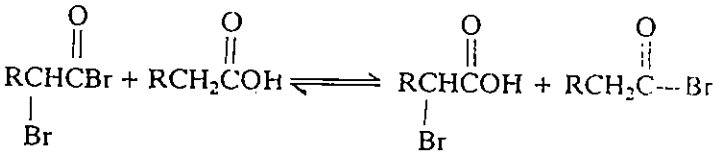
Step 2 : Enolisation



Step 3 : Bromination



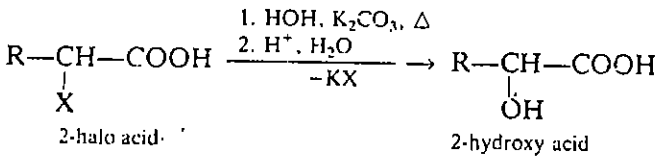
Step 4 : Exchange



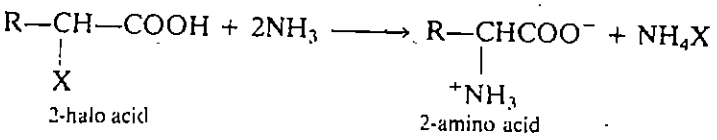
This can reenter the sequence at step 2.

The Hell-Volhard-Zelinsky reaction is of synthetic importance as the 2-halo acids obtained can further react with a variety of nucleophiles as shown below:

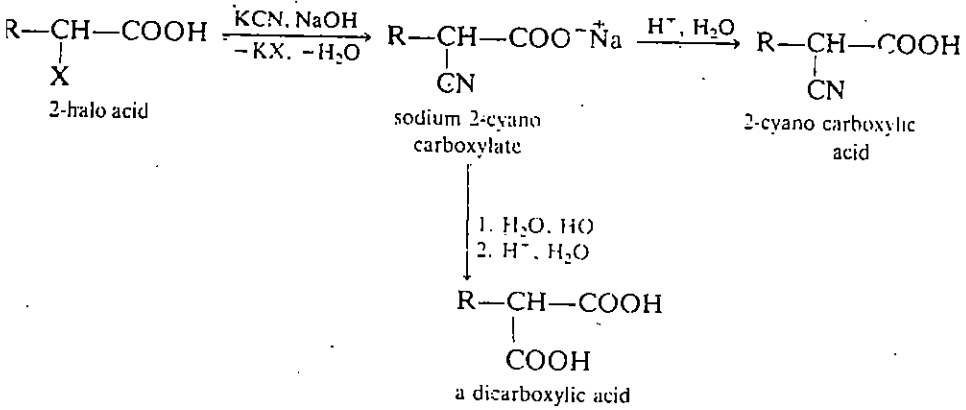
Conversion to 2–hydroxy acids:



Conversion to 2-amino acids:



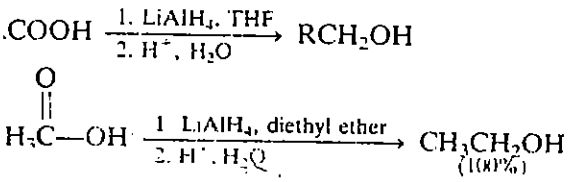
Conversion to 2–cyano carboxylic acid:

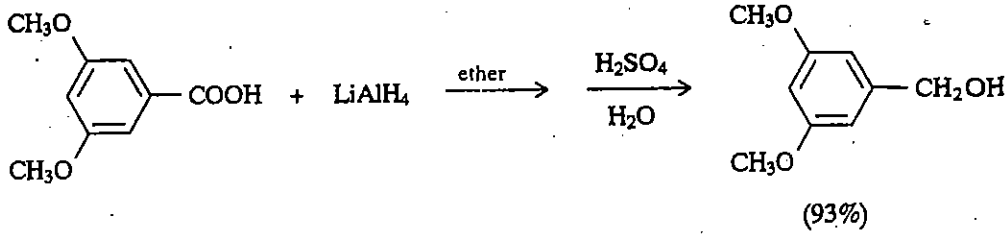


The cyano carboxylic acid can be subsequently hydrolysed to the dicarboxylic acid as shown above.

. Reduction of Carboxylic acids

Carboxylic acids can be reduced by powerful reducing agents such as lithium luminium hydride, $LiAlH_4$, to the primary alcohols.





(93%)

7. Decarboxylation

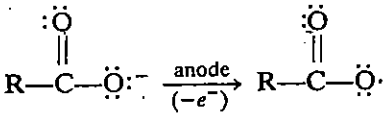
The loss of a molecule of carbon dioxide from a carboxylic acid is known as **decarboxylation.**

The simple aliphatic carboxylic acids do not decarboxylate easily and some structural features are required for it. For example, carboxylic acids having strongly electron-attracting groups at the 2-position, decarboxylate readily on heating at 373 to 423 K.

Among other carboxylic acids which decarboxylate readily are: i) 3-keto acids; ii) propanedioic acid (malonic acid) and its derivatives; and iii) carbonic acid derivatives. About these acids you will study in Unit 16, sub-Sec. 16.5.3 and Sec. 16.6.

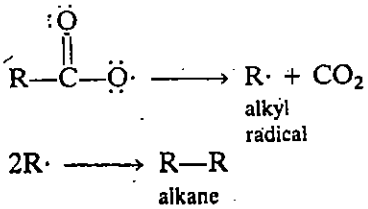
Decarboxylation reactions involving carboxyl radicals include **Kolbe electrolysis** and **Hunsdiecker reaction.**

In Kolbe electrolysis an aqueous solution of the sodium or potassium salt of a carboxylic acid is subjected to electrolysis. The carboxylate ion loses an electron at the anode to yield a carboxyl radical.



carboxylate ion — carboxyl radical

The carboxyl radical then decarboxylates and the alkyl radicals so produced combine to yield an alkane



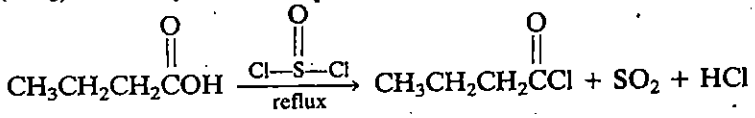
In the Hunsdiecker reaction, the silver salt of a carboxylic acid is heated with a halogen, usually bromine in CCl_4.

$$RCOO^-Ag^+ + Br_2 \longrightarrow RBr + CO_2 + AgBr$$

The reaction yields a bromoalkane having one carbon less than the starting acid.

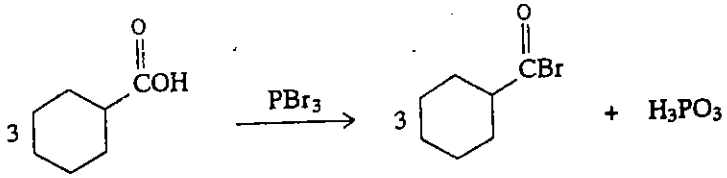
8. Formation of alkanoyl (acyl) halides

Carboxylic acids react with phosphorus trichloride (PCl_3), phosphorus pentachloride (PCl_5) or thionyl chloride ($SOCl_2$) to yield an alkanoyl chloride.



butanoic acid — butanoyl chloride (85%)

An alkanoyl bromide can be obtained by the reaction of a carboxylic acid with PBr_3.



(90%)

SAQ 2

Write the product obtained when 2-methylpropanoic acid reacts with:

a) diazomethane in ether

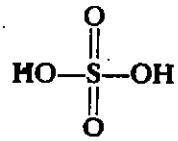
.....

b) butanol (as solvent), H_2SO_4

.....

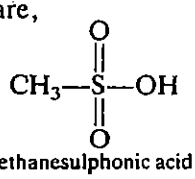
15.7 SULPHONIC ACIDS

It was stated earlier that sulphonic acids are organic acids related to sulphuric acid. Sulphuric acid can be written as shown below:

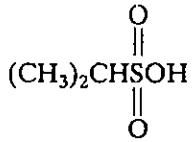


sulphuric acid

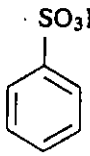
Replacement of one of the hydroxyl groups of sulphuric acid by an alkyl or aryl group leads to alkanesulphonic acid (RSO_3H) or arenesulphonic acid ($ArSO_3H$). Some examples are,



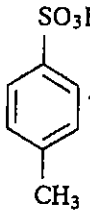
methanesulphonic acid



2-propanesulphonic acid



benzenesulphonic acid

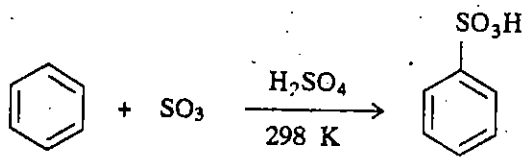


4-methylbenzenesulphonic acid
(*p*-toluenesulphonic acid)

You will now study about the representative arenesulphonic acid, i.e. benzenesulphonic acid.

15.7.1 Preparation of Benzenesulphonic Acid

Benzenesulphonic acid can be prepared by the **sulphonation** of benzene. You have already studied about the sulphonation of aromatic compounds in sub-Sec. 9.6.3 of Unit 9, Block 2. Sulphonation involves electrophilic substitution by sulphur trioxide. The source of sulphur trioxide is usually fuming sulphuric acid or oleum which contains 10–30% SO_3 dissolved in concentrated H_2SO_4.

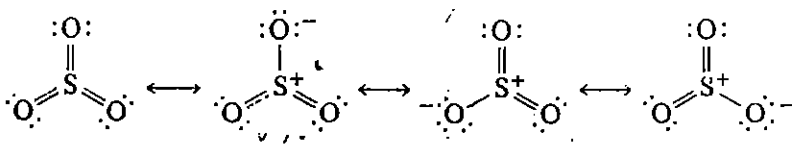


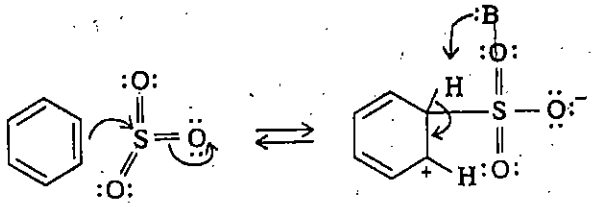
benzene

benzenesulphonic acid

The mechanism of sulphonation involves the following steps:

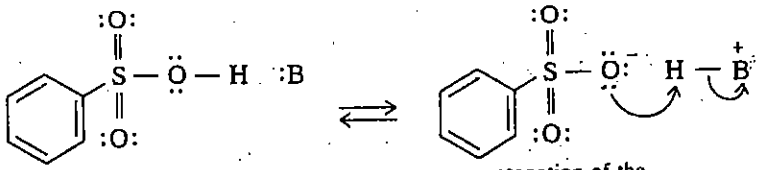
THE SULPHONATION REACTION





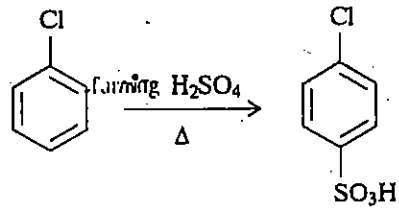
reaction of electrophile with the π electrons

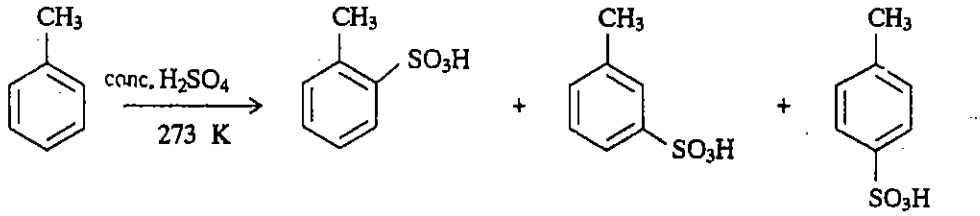
deprotonation of the cationic intermediate



protonation of the benzenesulphonate anion

Sulphonation is a general reaction and occurs with other substituted benzenes also. Examples are,





(43%) (4%) (53%)

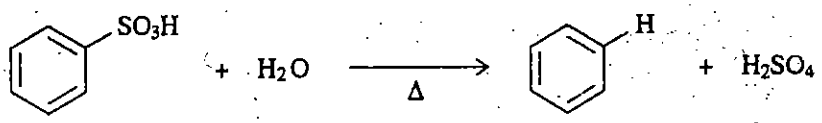
Sulphonation is a reversible reaction; therefore, to **sulphonate,** a high concentration of fuming sulphuric acid is employed. To **desulphonate,** dilute acid is used and superheated steam is passed through the mixture when the more volatile benzene is removed by steam distillation.

15.7.2 Reactions of Benzenesulphonic Acid

1. Desulphonation

The sulphonation reaction which you have studied above and also in Unit 9, is a reversible reaction. Thus, reversal of sulphonation or desulphonation can be achieved by heating the sulphonic acid with dilute sulphuric acid. Usually steam is also passed to carry out desulphonation.

Sulphonation and desulphonation reactions are useful in synthesis of organic compounds. For example, sulphonic acid group can be used as a protecting group to aromatic ring in substitution. This can thus influence the course of further reaction. Later it can be easily removed by desulphonation.

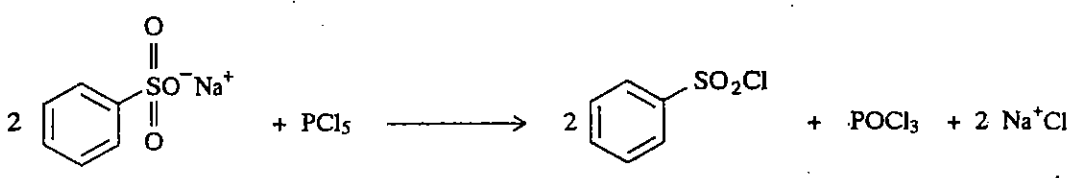


benzenesulphonic acid — water — benzene — sulphuric acid

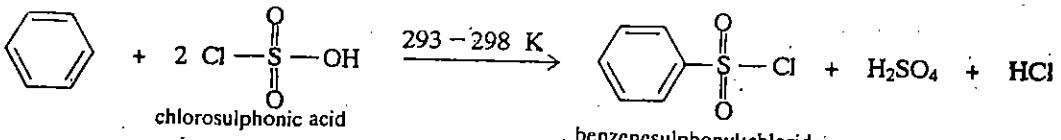
2. Formation of acid chloride

Similar to carboxylic acids, the acid chlorides of sulphonic acids, i.e., sulphonyl chlorides, can be prepared by heating the sulphonic acid with thionyl chloride or phosphorus pentachloride. Aromatic sulphonyl chlorides can also be prepared directly from aromatic compounds using chlorosulphonic acid.

4–Methylbenzenesulphonyl-chloride (*p*–toluene-sulphonyl chloride) is an important reagent in the laboratory.



sodium benzenesulphonate — benzenesulphonylchloride (80%)

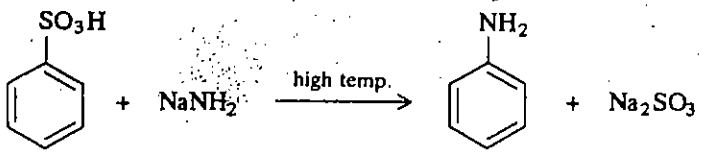


chlorosulphonic acid

benzenesulphonylchloride (73-77%)

3 Fusion with sodamide

When sodium salt of benzenesulphonic acid is treated with sodamide, $NaNH_2$, benzenamine (aniline) is obtained as the product.

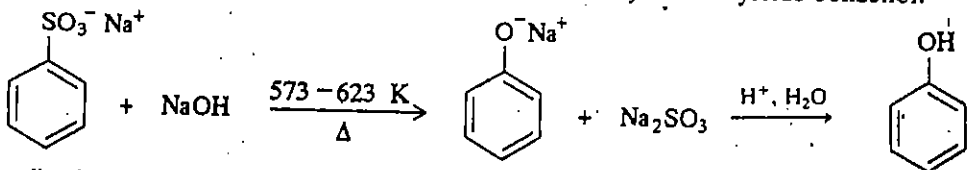


benzenesulphonic acid — benzenamine

4. Fusion with alkali hydroxide

This is the oldest method for the preparation of benzenol.

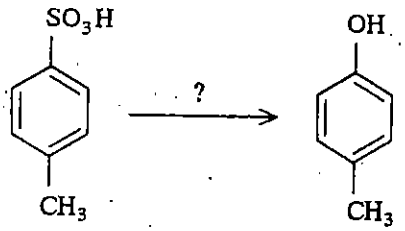
Fusion of sodium salt of sulphonic acid with alkali hydroxide yields benzenol.



sodium benzenesulphonate — benzenol (phenol)

SAQ 3

How will you carry out the following conversion:



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15.8 INDUSTRIAL USES OF CARBOXYLIC AND SULPHONIC ACIDS

1. Soaps and detergents

The sodium and potassium salts of long chain carboxylic acids were used as **soaps** until the 19th century. These molecules have an ionic **hydrophilic** *(water-loving)* carboxylate group and a nonpolar **lipophilic** *(fat-loving)* hydrocarbon chain. In aqueous solution, they form spherical aggregates known as **micelles**, as shown in Fig. 15.3

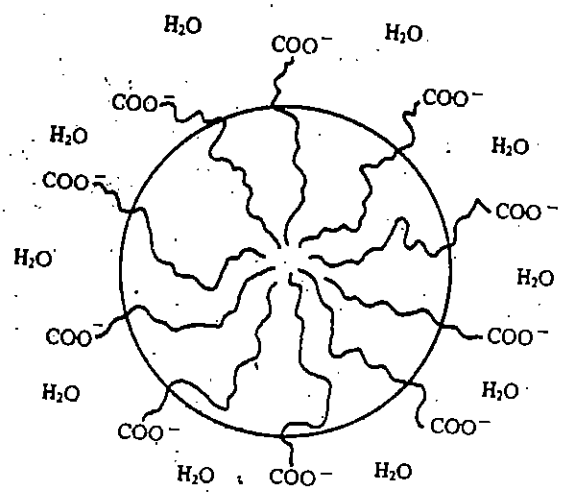


Fig. 15.3 : Schematic representation of a micelle.

The cleansing action of soap involves attracting nonpolar molecules as grease, oil etc. to the nonpolar centre of the micelle. The outer polar part of the micelle is attracted to water and the **solubilised** grease is washed away. This is shown in Fig. 15.4.

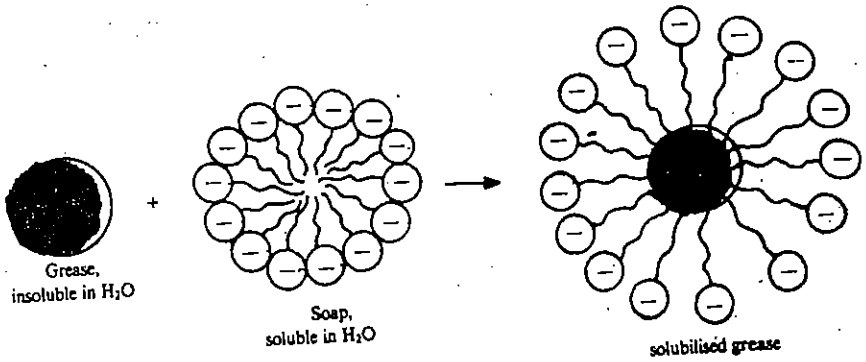
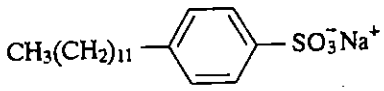


Fig. 15.4 : Cleansing action of soap.

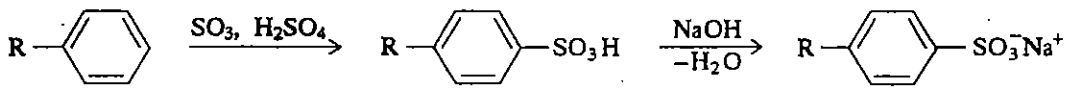
A major disadvantage of the carboxylate soaps is that they combine with calcium and magnesium ions often present in the water to form **insoluble scums.**

This problem was taken care of when synthetic detergents were marketed in 1933. The first detergents were alkylbenzenesulphonates. The advantages of these detergents is that they do not form insoluble scum with hard water. An example of a synthetic detergent is given below.



sodium 4–dodecylbenzenesulphonate

Until recently, long–chain branched alkylbenzenes were sulphonated to the corresponding sulphonic acids which were converted into sodium salts to be used as detergents.

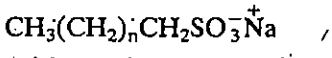


R = branched alkyl chain

Synthesis of alkylbenzenesulphonates

Biodegradable means degradation or breaking up into simple molecules by living organisms such as bacteria.

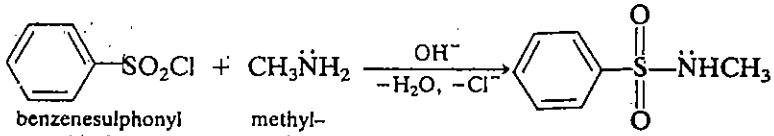
But these detergents are not readily biodegradable. After intensive research linear alkanesulphonate detergents were introduced which are biodegradable. The general structure of linear alkanesulphonates is given below:



alkanesulphonate detergent, n = 12 – 15

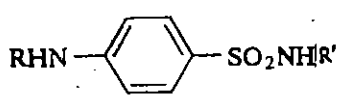
2. Sulphonamides as chemotherapeutic agents

Sulphonyl chlorides, which you studied in sub-Sec. 15.7.2, on treatment with ammonia or amines give the corresponding **sulphonamides**. For example,

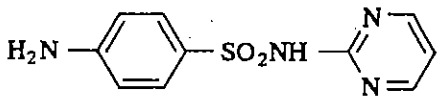


benzenesulphonyl chloride | methyl–amine | *N*–methylbenzenesulphonamide

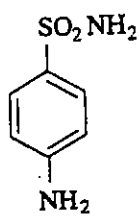
Many sulphonamides have important medicinal use as antibacterial agents. Some examples of such **sulpha drugs** are:



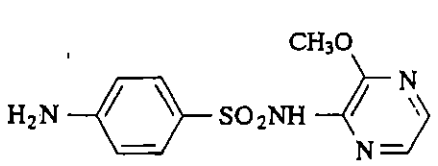
general structure



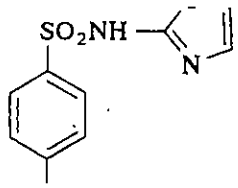
sulphadiazine
(antibacterial)



4–aminobenzenesulphonamide
or *p*–aminobenzenesulphonamide
(sulphanilamide)



sulphalene
(antilepral)

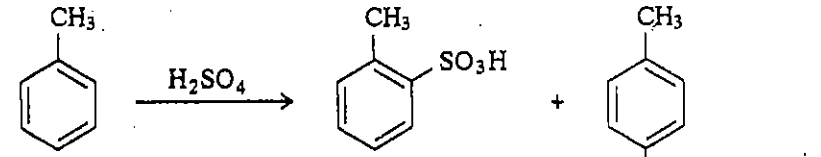


sulphathiazole

Sulpha drugs were used for treating human beings during 1930s and 1940s but now more effective antibiotics such as penicillins and tetracyclines have replaced them. These antibiotics will be dealt with in Unit 20.

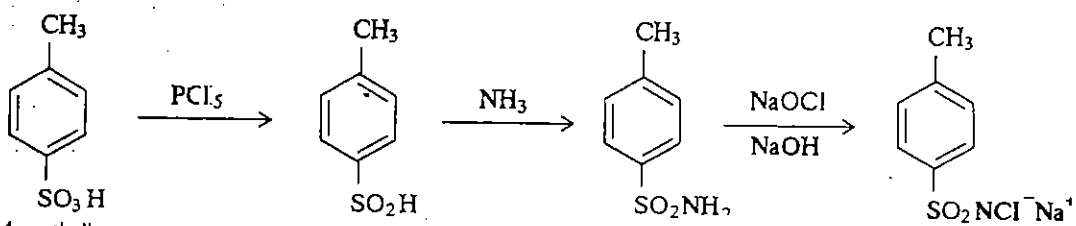
3. Chloramine T

When methylbenzene is treated with concentrated sulphuric acid, a mixture of 2–methylbenzenesulphonic and 4–methylbenzenesulphonic acids is formed. Low temperatures (below 373 K) favour the formation of 2–methylbenzenesulphonic acid and high temperatures (above 373 K) favour the 4–methylbenzenesulphonic acid.



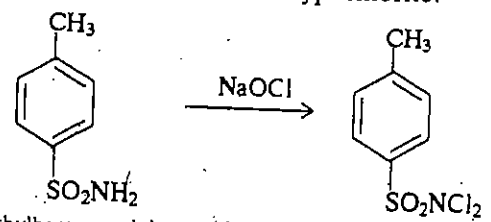
methylbenzene — 2–methylbenzenesulphonic acid — 4–methylbenzenesulphonic acid

4–Methylbenzenesulphonic acid is used in the preparation of the antiseptics **Chloramine–T** and **Dichloramine–T**. Chloramine–T is the sodium salt of *N*–chloro–4–methylbenzenesulphonamide and is prepared as follows:



4–methylbenzene–sulphonic acid — 4–methylbenzene–sulphonyl chloride — 4–methylbenzene–sulphonamide — chloramine–T

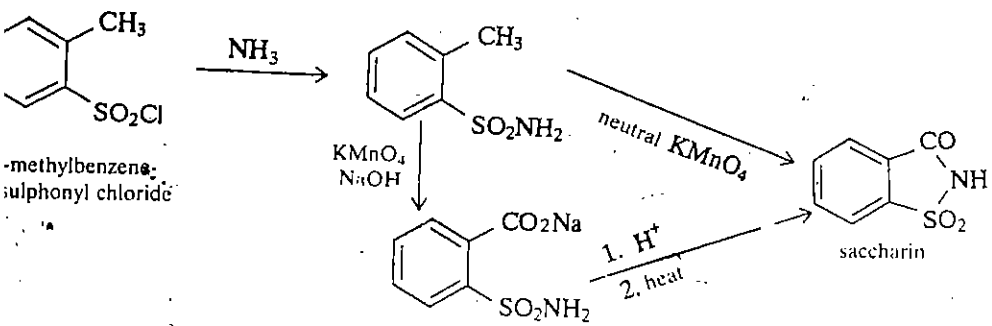
In addition to being used as an antiseptic, chloramine–T is also used as a laboratory reagent instead of hypochlorite salts, since it is stable and liberates hypochlorous acid when acidified. Dichloramine–T is obtained when 4– methylbenzenesulphonamide is treated with a large excess of sodium hypochlorite.



4–methylbenzenesulphonamide — dichloramine–T

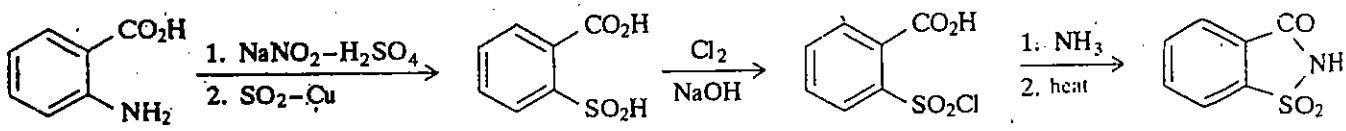
. Saccharin

–Methylbenzenesulphonyl chloride on treatment with ammonia, followed by xidation of the amide by potassium permanganate, gives the corresponding benzoic cid. This, on heating, forms saccharin.



-methylbenzene-sulphonyl chloride — saccharin

Although the above method was one of the first to be used industrially, other methods are now employed (e.g., from 2–aminobenzenecarboxylic acid (anthranilic acid).



2-aminobenzene--carboxylic acid

Saccharin is a crystalline solid, m.p. 497 K. It is about 550 times as sweet as sugar. It is used in place of sugar for many purposes, e.g., sweetening preserves, drinks, etc. It is also used as a substitute for sugar by diabetics and obese persons. In view of suspected carcinogenic properties, the use of saccharin has been discontinued in many countries.

SAQ 4

What is the difference between soaps and detergents?

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15.9 LABORATORY DETECTION OF CARBOXYLIC AND SULPHONIC ACIDS

The solubility in sodium bicarbonate helps to distinguish carboxylic acids from most phenols. Except for di–and trinitrophenols, phenols do not dissolve in sodium bicarbonate.

Carboxylic acids and sulphonic acids are recognised by their acidic nature. They dissolve in aqueous sodium hydroxide and sodium bicarbonate. The reaction with sodium bicarbonate is accompanied by the evolution of bubbles of carbon dioxide. Further, the elemental analysis in case of sulphonic acids shows presence of sulphur.

Determination of the physical constants and formation of derivatives leads to final identification. The commonly prepared derivatives of carboxylic acid include amides and esters. Similarly, sulphonic acids can be converted into sulphonamides.

15.10 SUMMARY

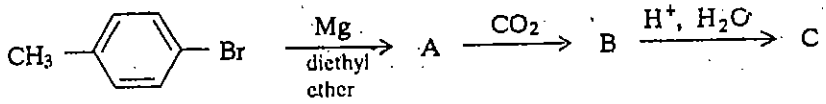
In this Unit, you have studied that

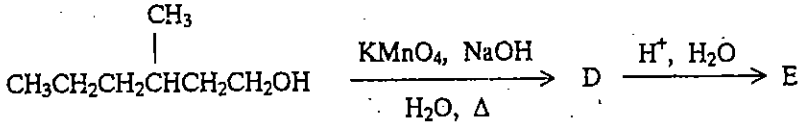
- carboxy group is the functional group of carboxylic acids and sulphonic acid group is the functional group of sulphonic acids.
- carboxylic acids with long unbranched carbon chains are called fatty acids.
- carboxylic acids can be prepared by the following methods:
  - i) Oxidation of alkenes.
  - ii) Side chain oxidation of alkylbenzenes.
  - iii) Oxidation of primary alcohols.
  - iv) Oxidation of aldehydes.
  - v) Oxidation of methylketones.
  - vi) Carbonation of organometallic reagents.
  - vii) Hydrolysis of nitriles.
- because of their acidity, carboxylic acids dissolve not only in aqueous sodium hydroxide but also in aqueous solutions of weaker bases such as sodium bicarbonate.
- carboxylic acids can be esterified using Fischer esterification or diazomethane.
- using appropriate reagents and conditions, carboxylic acids can be converted to:
  - i) amides.
  - ii) 2–halo acids.
  - iii) alcohols.
  - iv) alkanes.
  - v) alkanoyl halides.
- sulphonic acids can be obtained by the sulphonation reaction.
- sulphonation is a reversible reaction.

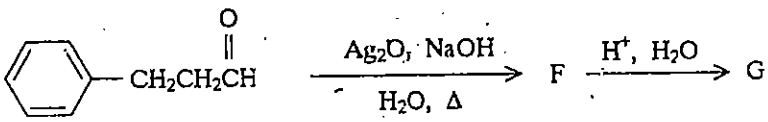
- benzenesulphonic acid can undergo:
  i) desulphonation
  ii) fusion with sodamide to give benzenamine and potassium hydroxide to yield benzenol.
- salts of carboxylic acids and sulphonic acids are used as soaps and detergents.
- sulphonic acids are also used in the preparation of chemotherapeutic agents such as sulphonamides and chloramine-T and also in the preparation of artificial sweetener, saccharin.

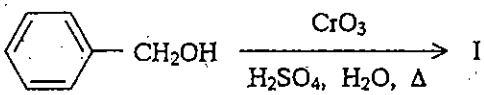
15.11 TERMINAL QUESTIONS

1) Assign structures to the compounds given in the following reactions:

a) 

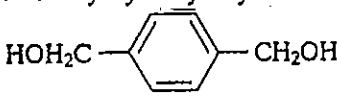
b) 

c) 

d) 

2) From a reaction mixture containing 4-bromomethylbenzene and 4-bromobenzenecarboxylic acid, how will you isolate pure acid?

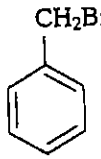
3) A carboxylic acid having molecular formula $C_8H_6O_3$ on reduction with $LiAlH_4$ followed by hydrolysis yielded the following product.



What is the structure of the acid?

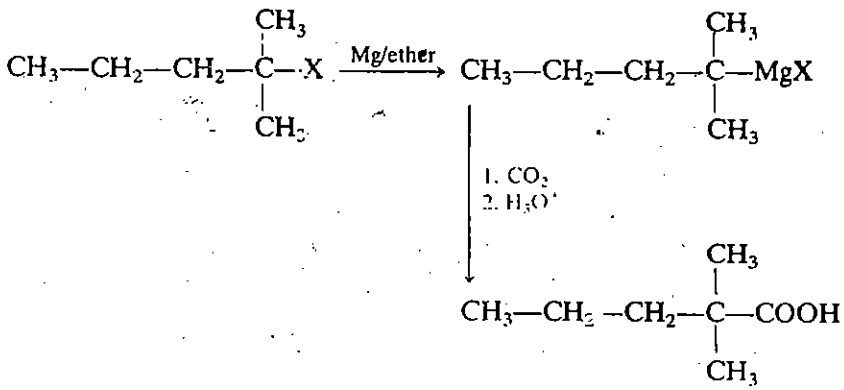
4) Using decarboxylation reactions, how will you obtain the following, using appropriate starting materials.

a) decane

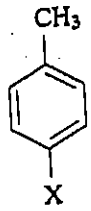
b) phenylmethyl (benzyl) bromide, 

15.12 ANSWERS

Self-Assessment Questions

1) a) 

b) Similar to (a) using $CH_3(CH_2)_4X$.

c) Similar to (a) starting with 

2) a) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH + CH_2N_2 \longrightarrow \underset{\displaystyle CH_3}{\underset{|}{CH}}CHCOOCH_3$

b) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH + CH_3CH_2CH_2CH_2OH \longrightarrow$

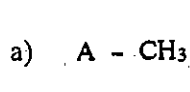
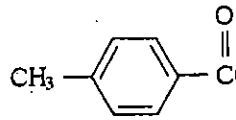
$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-OCH_2CH_2CH_2CH_3$$

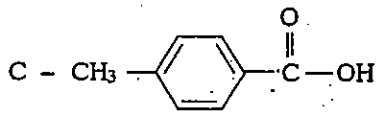
3) Fusing with NaOH / KOH at 500-600 K.

4) i) Soaps form insoluble scums with hard water whereas detergents do not,

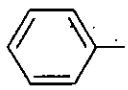
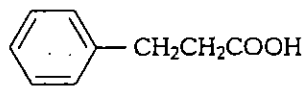
ii) Soaps are sodium or potassium salts of long chain carboxylic acids whereas detergents are sodium salts of sulphonic acids.

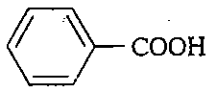
Terminal Questions

1) a) A -  B - 

C - 

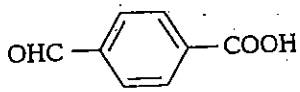
b) D – $CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2COO^-Na^+$, E – $CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2COOH$

c) F –  , G – 

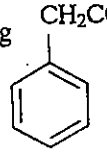
d) I – 

2) Dissolve the mixture in aqueous alkali, separate aqueous layer and acidify to get 4–bromobenzenecarboxylic acid.

3) Molecular formula, $C_8H_6O_3$



4) a) Kolbe Electrolysis of sodium or potassium salt of pentanoic acid.

b) heating  with Br_2 ; using Hunsdiecker reaction.

UNIT 16 SUBSTITUTED CARBOXYLIC ACIDS

Structure

16.1 Introduction
Objectives
16.2 Halo Acids
Reactions of the Halo Acids
16.3 Hydroxy Acids
Preparation of Hydroxy Acids
Reactions of Hydroxy Acids
16.4 Amino Acids
Synthesis of 2–Amino Acids
Physical Properties of Amino Acids
Reactions of Amino Acids
16.5 Dicarboxylic Acids
Preparation of Dicarboxylic Acids
Physical Properties of Dicarboxylic Acids
Reactions of Dicarboxylic Acids
16.6 Keto Acids
16.7 Ethyl 3–Oxobutanoate and Diethyl Propanedioate
16.8 Unsaturated Carboxylic Acids
Preparation of Unsaturated Carboxylic Acids
Reactions of Unsaturated Acids
16.9 Summary
16.10 Terminal Questions
16.11 Answers

16.1 INTRODUCTION

In Unit 15, you studied the chemistry of monocarboxylic acids in detail. In this unit, you will study the change in their properties caused by the introduction of a second functional group. The second functional group may be a halogen, a hydroxyl group, an amino group, a second carboxyl group, a carbonyl group or a double or triple bond. Corresponding to the above functional groups, we get haloacids, hydroxyacids, amino acids, dicarboxylic acids, keto acids and unsaturated acids, respectively. In this unit, we will study the chemistry of each of these classes.

Objectives

After studying this Unit, you should be able to:

- give the methods of preparation and reactions of halo acids,
- list a few naturally occurring hydroxy acids, write their structures and give their IUPAC names,
- outline the synthesis of hydroxy acids and write the products obtained from various hydroxy acids on treatment with aqueous acids,
- write structures of various amino acids and give their methods of preparation,
- explain the zwitterionic nature of amino acids,
- discuss the reactions of amino acids,
- outline the synthesis of a given dicarboxylic acid,
- explain the behaviour of various dicarboxylic acids on heating and discuss the other reactions shown by them,
- give examples of some keto acids,
- discuss the synthetic utility of ethyl 3–oxobutanoate and diethyl propanedioate, and
- describe the methods of preparation and reactions of unsaturated carboxylic acids.

16.2 HALO ACIDS

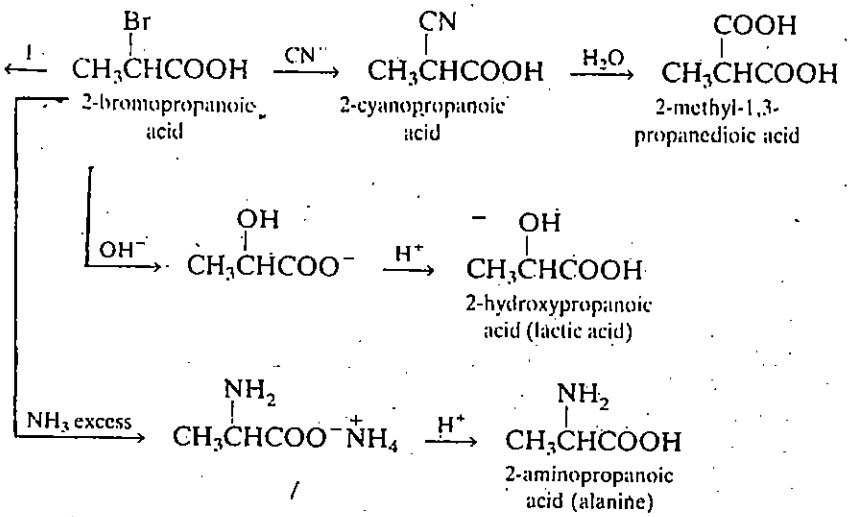
You have already studied about halo acids in Unit 5, Block 1 and Unit 15. In Unit 5, sub-Sec. 5.4.1, we discussed the inductive effect of halogen atoms on the acidity of the carboxylic acids. In Unit 15, Sec. 15.6, the preparation of 2-halo acids using the Hell-Volhard-Zelinsky reaction was discussed. However, 3-halo acids can be obtained by the addition of hydrogen halide to 2 , 3-unsaturated acid. For example,

$$\underset{\text{propenoic acid}}{CH_2=CHCOOH} \xrightarrow{HBr} \underset{\text{3-bromopropanoic acid}}{BrCH_2CH_2COOH}$$

16.2.1 Reactions of the Halo Acids

The halogen atom of 2-halo acids is readily replaced by nucleophilic reagents such as CN^-, OH^-, I^- and NH_3. This yields a variety of 2-substituted acids as shown below:

$CH_3CHCOOH$
2-iodopropanoic acid



3-Halo acids, however, undergo elimination of a molecule of HX when warmed with alcoholic KOH to give unsaturated acids.

$$\underset{\text{3-chlorobutanoic acid}}{CH_3CHCH_2COOH} \xrightarrow[KOH]{\text{alcoholic}} \underset{\text{but-2-enoic acid (crotonic acid)}}{CH_3CH=CH-COOH}$$

16.3 HYDROXY ACIDS

Many important hydroxy acids occur naturally. As stated earlier in case of saturated monocarboxylic acids in Unit 5, Block 1, the common names of hydroxy acids are also derived from the sources from which they were originally obtained. A few important hydroxy acids along with their natural source, common names and IUPAC names are listed in Table 16.1.

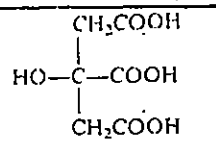
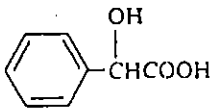
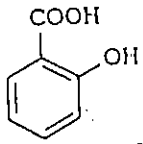
Table 16.1 : Hydroxy Acids

Structure	Source	Common Name	IUPAC Name
$HOCH_2COOH$	cane sugar juice	glycolic acid	hydroxyethanoic acid
$CH_3CHOHCOOH$	sour milk	lactic acid	2-hydroxypropanoic acid
$HOOCCH_2\underset{OH}{C}HCOOH$	fruit juices	malic acid	2-hydroxybutane-dioic acid
$HOOC\underset{OH}{\underset{\vert}{C}}H-\underset{OH}{\underset{\vert}{C}}HCOOH$	*dextro*-isomer found in fruits	tartaric acid	2 , 3-dihydroxy-butanedioic acid

Usually the hydroxy acids are named as derivatives of the parent acid. The position of the hydroxy group in the molecule is indicated by the Greek letters, i.e., α, β, γ, δ, ... The positions α β, γ, δ ... are as shown below:

$\ldots CH_2-CH_2-CH_2-CH_2-COOH$

$\ldots \delta \quad \gamma \quad \beta \quad \alpha$

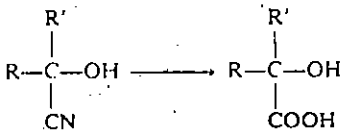
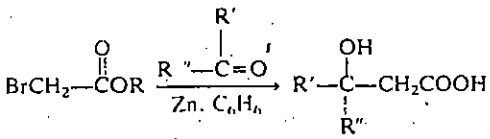
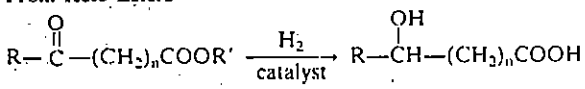
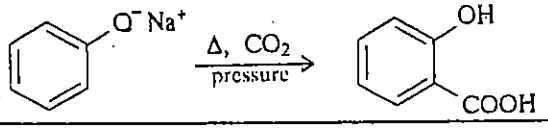
Structure	Source	Common Name	IUPAC Name
	*citrus* fruits	citric acid	2-hydroxy-1, 2, 3-propanetricarb-oxylic acid
	plums, peaches and other fruits	mandelic acid	2-hydroxy-2-phenylethanoic acid
	willow bark	salicylic acid	2-hydroxybenzene-carboxylic acid

Let us now study how hydroxy acids can be prepared in the laboratory.

16.3.1 Preparation of Hydroxy Acids

Table 16.2 gives briefly the methods of preparation of Hydroxy acids.

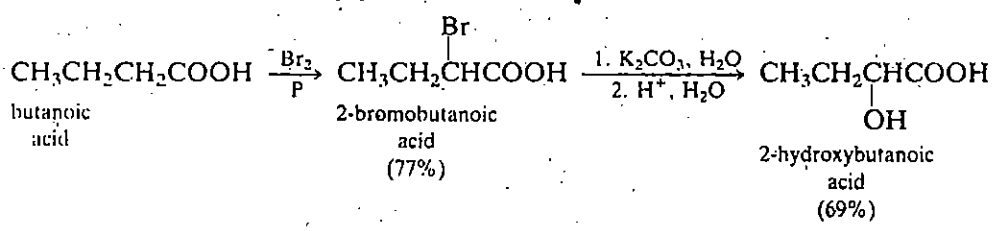
Table 16.2 : Methods of Preparation of Hydroxy Acids

	Comments
1. From Halo acids 	Can be used for 2-hydroxy acids but not for 3-hydroxy acids
2. From Cyanohydrins 	Works in acidic conditions only.
3. From 2-Bromoesters and Carbonyl Compounds 	Reformatsky reaction
4. From Keto Esters 	
5. Kolbe Schmidt Reaction 	Industrial method

Let us now study each of these methods in detail.

1. From Halo acids

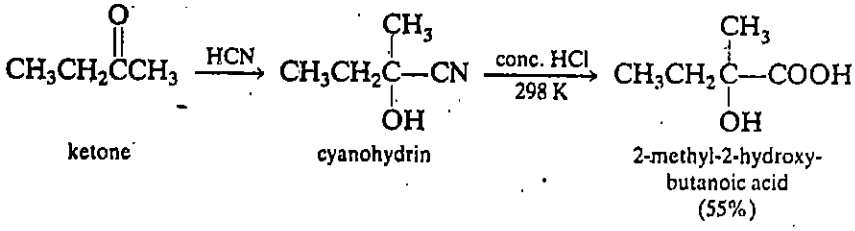
2-hydroxy (α-hydroxy) acids can be obtained by the hydrolysis of 2-halo acids. You may recall that 2-halo acids can in turn be obtained from the Hell-Volhard-Zelinsky reaction, (Sec. 15.6, Unit 15). Thus, a hydroxyl group can be introduced in the carboxylic acid in a two step process as shown below:



It was pointed out in the last section that 3-halo acids undergo elimination in base and yield unsaturated acids, therefore, a similar sequence cannot be used for the synthesis of 3-hydroxy acids.

2. By hydrolysis of cyanohydrins

Cynohydrins obtained from the reaction of HCN with aldehydes and ketones (sub-Sec. 14.4.1, Unit 14, Block 3) on hydrolysis yield hydroxy acids.

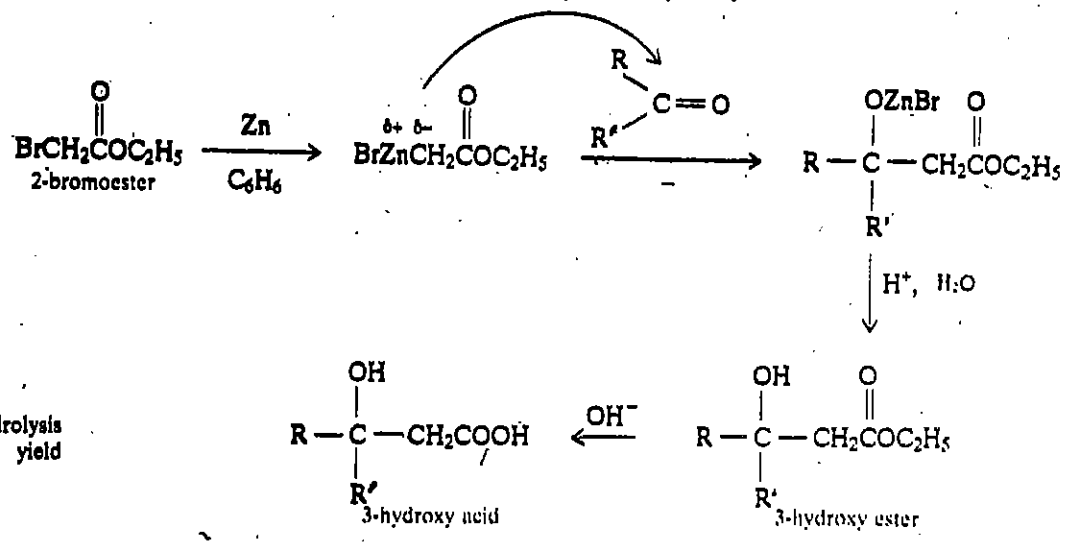


ketone — cyanohydrin — 2-methyl-2-hydroxy-butanoic acid (55%)

In the second step, it is necessary to hydrolyse the cyanohydrin under acidic conditions since under basic conditions, the first step of the reaction is reversed and the cyanohydrin intermediate returns the starting carbonyl compound.

3. Using 2-bromoesters and carbonyl compounds: Reformatsky reaction

2-Bromoesters react with aldehydes or ketones in the presence of zinc metal in nonhydroxylic solvents like benzene to yield 3-hydroxy esters.

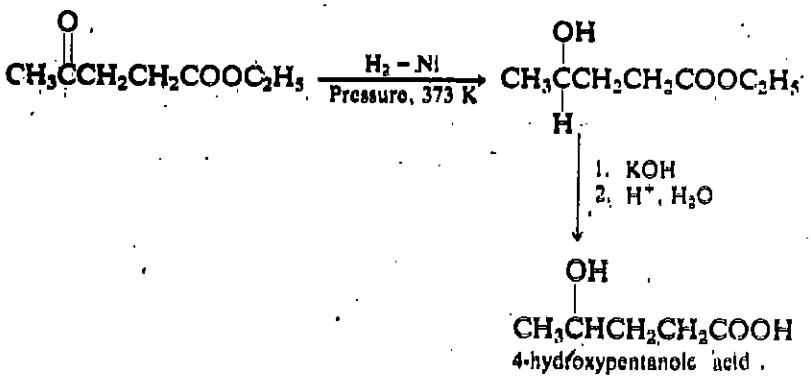


3-Hydroxy esters on hydrolysis under acidic conditions yield unsaturated esters.

The 3-hydroxy ester on alkaline hydrolysis finally yields 3-hydroxy acid.

4. By Catalytic reduction of keto esters

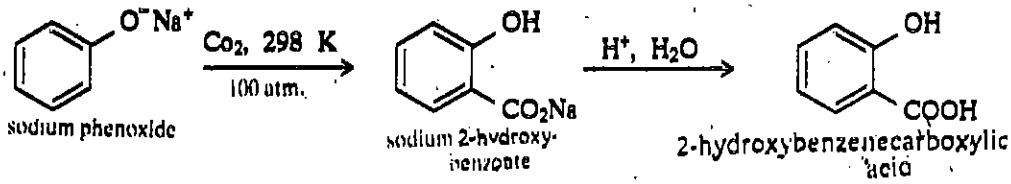
Hydroxy acids may also be prepared by catalytic reduction of the corresponding keto esters, e.g.,



5. Industrial preparation of 2-hydroxybenzenecarboxylic acid: Kolbe Schmidt reaction

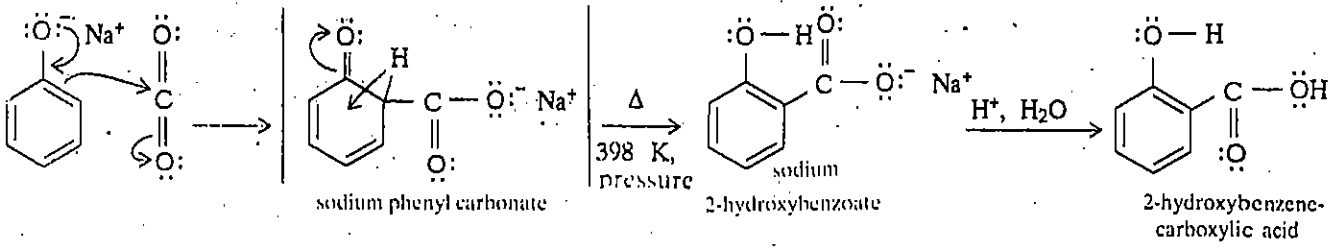
This reaction was also discussed in sub-Sec. 12.6.3, Unit 12, Block 3.

It involves heating the sodium salt of benzenol (phenol) with CO_2 under pressure.



sodium phenoxide — sodium 2-hydroxy-benzoate — 2-hydroxybenzenecarboxylic acid

It involves the initial absorption of CO_2 at room temperature to yield sodium phenyl carbonate as shown below:



sodium phenyl carbonate — sodium 2-hydroxybenzoate — 2-hydroxybenzenecarboxylic acid

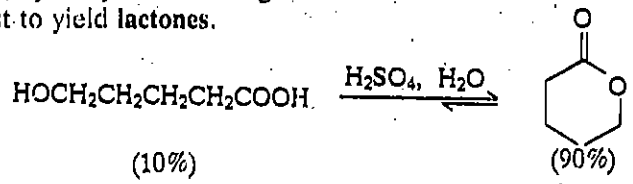
Sodium phenyl carbonate on heating to 398 K under pressure rearranges to sodium 2-hydroxybenzoate. Subsequent acidification yields 2-hydroxybenzenecarboxylic acid.

16.3.2 Reactions of Hydroxy Acids

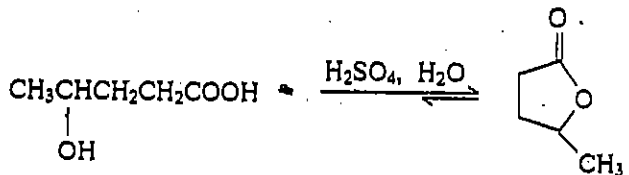
Since the hydroxy acids contain a **hydroxy** and a **carboxy** functional group, they exhibit the reactions of these functional groups particularly when these groups are far apart. For example, the carboxy group can be converted into the ester, amide, nitrile or alkanoyl halide and the hydroxyl group can be transformed into an ester or an ether.

In addition to the above reactions which are characteristic of individual functional groups, hydroxy acids undergo intramolecular esterification in the presence of acid catalyst to yield **lactones**.

Lactones are cyclic esters.



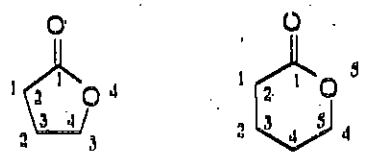
a lactone



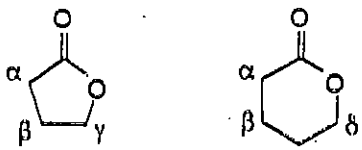
Lactone formation is favoured when the lactone formed is five or six-membered. Lactones containing five-membered rings are referred to as γ-lactones whereas the six-membered lactones are referred to as δ-lactones.

Reactions that are expected to produce hydroxy acids often yield lactones if a five or six membered lactone ring is possible.

A lactone can be named by replacing the *-oic acid* ending of the parent carboxylic acid by- *olide* and identifying its oxygenated atom by a number. This is illustrated below

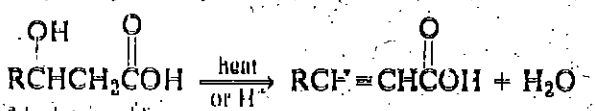


4-butanolide — 5-pentanolide



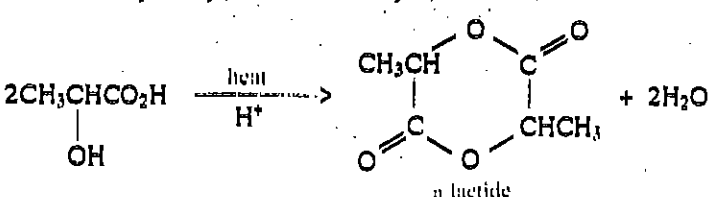
γ-lactone — δ-lactone

Lactones with four-membered rings (i.e., β-lactones) have been detected as highly reactive intermediates in some reactions. But, attempts to synthesise them from 3-hydroxy acids yield 2,3-unsaturated acids, i.e.,



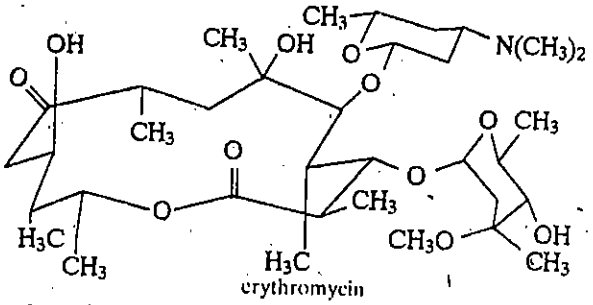
3-hydroxy acid

On the other hand, 2-hydroxy acids form a cyclic diester, called **lactide** as shown below:



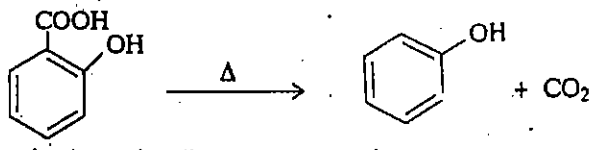
2- hydroxypropanoic acid (lactic acid) — a lactide

Synthesis of large ring lactones called **macrocylic lactones** is of special synthetic interest because substituted macrocyclic lactones form the basic framework of many antibiotics of which erythromycin is one example. Erythromycin has a 14-membered lactone ring.



erythromycin

However, 2-hydroxybenzenecarboxylic acid on slow heating undergoes decarboxylation to yield benzenol.

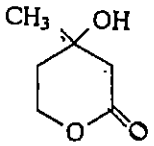


2-hydroxybenzenecarboxylic acid — benzenol

SAQ 1

Write the structure of the hydroxy acid from which the following lactones can be synthesised.

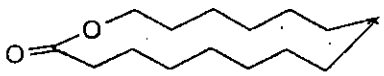
a)



mevalonolactone

(an intermediate in the biosynthesis of terpenes and steroids)

b)



1,5-pentadecanolide
(used in perfumes)

Proteins will be dealt in detail in Unit 20.

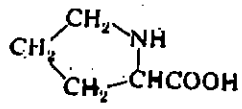
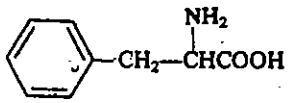
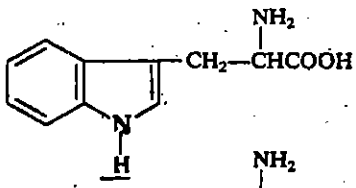
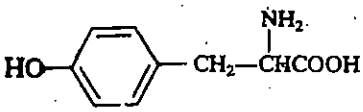
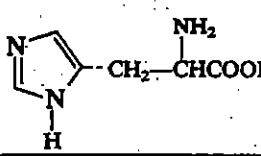
16.4 AMINO ACIDS

Amino acids are the compounds which contain both an amino group and a carboxy group in their molecules. They constitute a particularly important class of difunctional compounds as they are the building blocks of proteins.

While several hundred different amino acids are known to occur naturally, 20 of them deserve special mention as they are present in proteins. These amino acids are listed in Table 16.3. As given in this Table, for amino acids trivial names are common. The convention to use a three letter code, as an abbreviation, for each amino acid is also given in the table. These abbreviations are particularly useful in designating the sequence of amino acids in peptides and proteins which you will study in Unit 20.

Table 16.3 : Common Amino Acids found in Proteins

$R-CH(NH_2)COOH$	Name	Abbreviation
$H-CH(NH_2)COOH$	glycine	Gly
$CH_3-CH(NH_2)COOH$	alanine	Ala
$CH_3CH(CH_3)-CH(NH_2)COOH$	valine	Val

$R-\underset{\displaystyle NH_2}{\underset{\vert}{C}}HCOOH$	Name	abbreviation
$CH_3CHCH_2-\underset{\displaystyle NH_2}{\underset{\vert}{C}}HCOOH$	leucine	Leu
$CH_3CH_2\underset{\displaystyle CH_3}{\underset{\vert}{C}}H-\underset{\displaystyle NH_2}{\underset{\vert}{C}}HCOOH$	isoleucine	Ile
$CH_3SCH_2CH_2-\underset{\displaystyle NH_2}{\underset{\vert}{C}}HCOOH$	methionine	Met
	proline	Pro
	phenylalanine	Phe
	tryptophan	Trp
$HOCH_2-\underset{\displaystyle NH_2}{\underset{\vert}{C}}HCOOH$	serine	Ser
$CH_3\underset{\displaystyle OH}{\underset{\vert}{C}}H-\underset{\displaystyle NH_2}{\underset{\vert}{C}}HCOOH$	threonine	Thr
$HSCH_2-\underset{\displaystyle NH_2}{\underset{\vert}{C}}HCOOH$	cysteine	Cys
	tyrosine	Tyr
$H_2NC(=O)CH_2-\underset{\displaystyle NH_2}{\underset{\vert}{C}}HCOOH$	asparagine	Asn
$H_2NC(=O)CH_2CH_2-\underset{\displaystyle NH_2}{\underset{\vert}{C}}HCOOH$	glutamine	Gln
$HOC(=O)CH_2-\underset{\displaystyle NH_2}{\underset{\vert}{C}}HCOOH$	aspartic acid	Asp
$HOC(=O)CH_2CH_2-\underset{\displaystyle NH_2}{\underset{\vert}{C}}HCOOH$	glutamic acid	Glu
$H_2NCH_2CH_2CH_2CH_2-\underset{\displaystyle NH_2}{\underset{\vert}{C}}HCOOH$	lysine	Lys
$H_2NC(=NH)NHCH_2CH_2CH_2-\underset{\displaystyle NH_2}{\underset{\vert}{C}}HCOOH$	arginin	Arg
	histidine	His

Amino acids can be classified as α, β, γ, etc., depending upon the location of the amino group on the carbon chain containing the carboxy function. Some examples are illustrated below:

$H_2N\underset{\alpha}{-}CH_2COOH$
2-aminoethanoic acid
(α-amino acid)

$H_2N\underset{\gamma}{C}H_2\underset{\beta}{C}H_2\underset{\alpha}{C}H_2COOH$
4-aminobutanoic acid
(γ-amino acid)

$H_2N\underset{\beta}{C}H_2\underset{\alpha}{C}H_2COOH$
3-aminopropanoic acid
(β-amino acid)

Thus, the amino acids listed in Table 16.3 are α-amino acids or 2-amino acids.

Having learnt about some general aspects of the structure of amino acids, let us now focus our attention on the synthesis of 2-amino acids.

16.4.1 Synthesis of 2-amino Acids

2-Amino acids can be synthesised by using the methods given in Table 16.4.

Table 16.4 : Methods of preparation of 2-amino acids

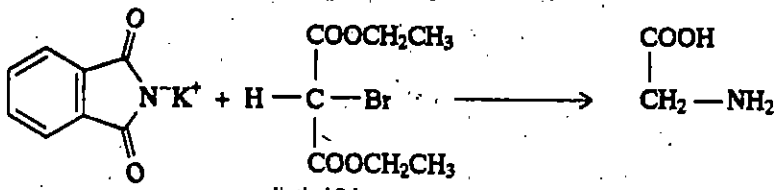
1. From 2-halo acids

$$R-\underset{X}{\underset{|}{C}}HCOOH + NH_3 \longrightarrow R-\underset{NH_2}{\underset{|}{C}}HCOOH$$

2. From aldehydes : Strecker Synthesis

$$R-CHO + NH_3 + HCN \longrightarrow R-\underset{NH_2}{\underset{|}{C}}H-COOH$$

3. By *N*-alkylation of 1,2-benzenedicarboxylic imide (phthalimide) anion.



diethyl 2-bromopropanedioate

2-substituted amino acids can also be prepared.

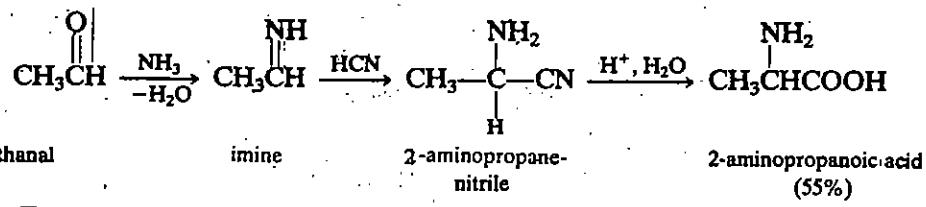
1. From 2-halo acids

In Unit 15, Sec. 15.6, you studied that 2-halo acids can be obtained from carboxylic acids using the Hell-Volhard-Zelinsky reaction. These 2-halo acids on nucleophilic substitution by NH_3 yield 2-amino acids as shown below:

$$\underset{\text{2-bromopropanoic acid}}{\underset{Br}{\underset{|}{CH_3CHCOOH}}} + 2NH_3 \xrightarrow{H_2O} \underset{\text{2-aminopropanoic acid (65-70%)}}{\underset{NH_2}{\underset{|}{CH_3CHCOH}}} + NH_4Br$$

2. From aldehydes : Strecker synthesis

It was pointed out in sub-Sec. 14.4.1, Unit 14, Block 3 that aldehydes on reaction with hydrogen cyanide yield a cyanohydrin. But, when the same reaction is carried out in the presence of ammonia, the first step is probably the initial formation of an imine from the reaction of the aldehyde with ammonia. The addition of hydrogen cyanide to the imine furnishes the corresponding 2-amino nitrile which on acidic or basic hydrolysis yields the 2-amino acid. This is also known as **Strecker synthesis**. The sequence of reactions involved in this synthesis is given below.



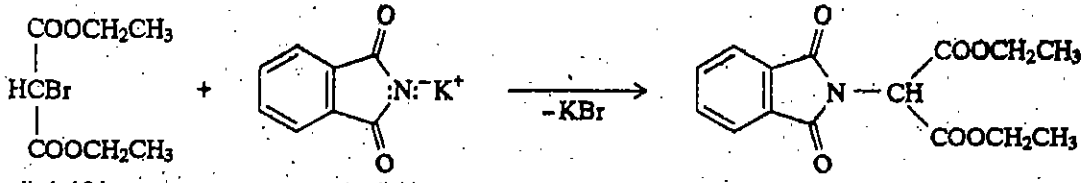
ethanal — imine — 2-aminopropane-nitrile — 2-aminopropanoic acid (55%)

3. From potassium phthalimide

This method is a modification of the Gabriel synthesis of amines which will be discussed in Unit 19, Sec. 19.6.

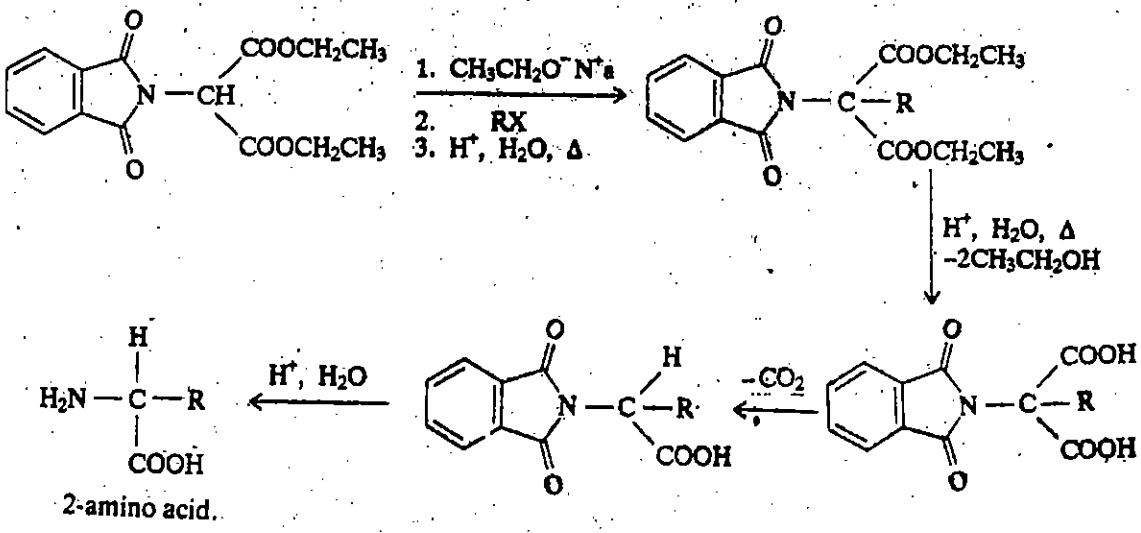
It involves the *N*-alkylation of 1,2-benzenedicarboxylic imide (phthalimide) anion with diethyl 2-bromopropanedioate as shown below:

Diethyl 2-bromopropanedioate can be prepared by the bromination of diethyl propanedioate.



diethyl 2-bromopropanedioate (diethyl 2-bromomalonate) + potassium 1,2-benzenedicarboxylic imide (potassium phthalimide) $\xrightarrow{-KBr}$ *N*-alkylated product (85%)

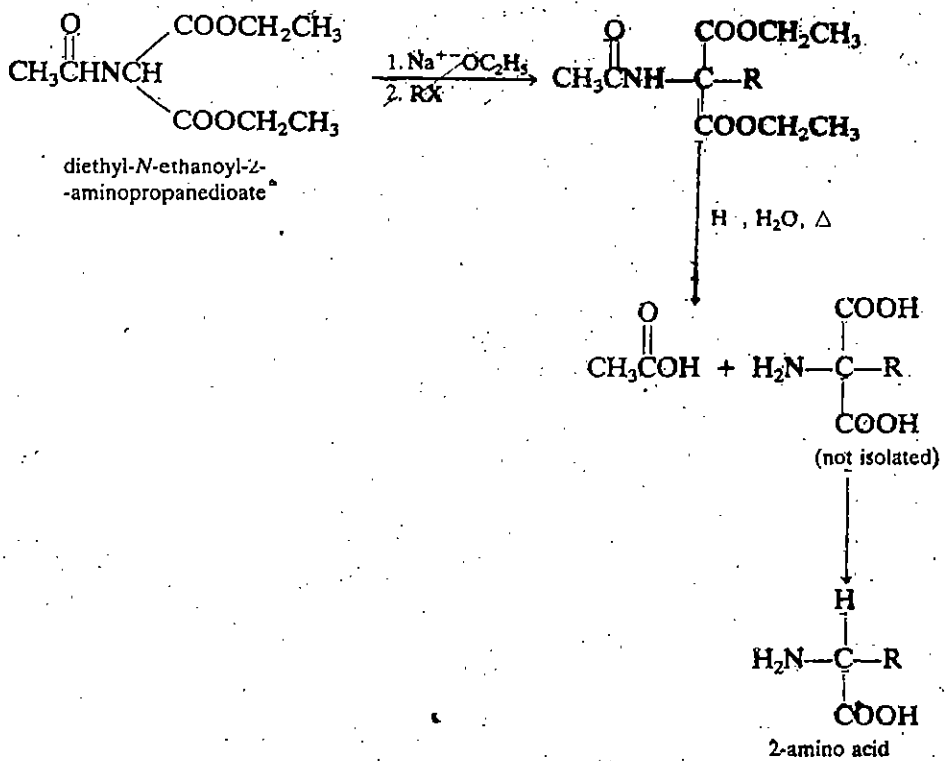
The advantage of this method is that the alkylated product obtained in the above reaction can be further alkylated to yield a variety of substituted amino acids by the following sequence of reactions.



2-amino acid.

Thus, we can get a variety of amino acids depending upon the nature of R.

A variation of the above method utilises diethyl *N*-ethanoyl-2-aminopropanedioate instead of the imide derivative. The sequence of reactions involved is shown below:



diethyl-*N*-ethanoyl-2-aminopropanedioate

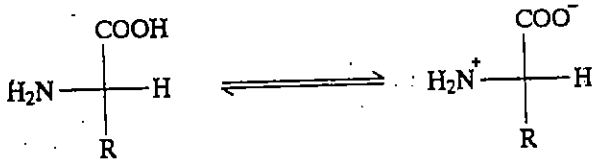
2-amino acid

16.4.2 Physical Properties of Amino Acids

1. Acid-base properties

Because amino acids contain both carboxy and amino groups in their molecules, they are *amphoteric* in nature, i.e. they behave both as acids and bases. Amino acids

actually exist as *inner salts*, called **zwitterions**. A zwitterionic structure is possible for amino acids because the amino group is basic in nature and can accept a proton from the acidic carboxy group. A zwitterion can be represented as shown below.

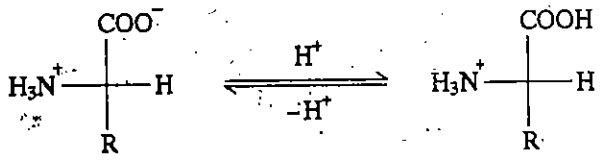


a zwitterion

The highly polar nature of zwitterion allows the formation of strong crystal lattices similar to the ionic compounds. Amino acids, therefore, resist conversion from solid to liquid state and *do not melt* but decompose on heating.

The zwitterionic nature is also reflected in their higher solubility in water and low solubility in nonpolar solvents. In addition to the above observations, large dipole moments also indicate the zwitterionic nature of amino acids.

Let us now study the zwitterionic form of amino acids in more detail. You can see in the zwitterion shown above that the amino group is protonated and the carboxy group exists as carboxylate anion. Thus, the acidic group is a substituted ammonium ion and the basic group is the carboxylate anion. As a result in strongly acidic medium i.e., at low pH, the carboxylate group will be protonated to yield the following species.

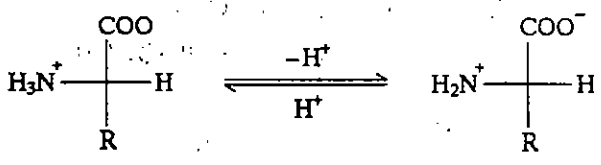


zwitterion

I

species present in strongly acidic medium

Let us next consider the species present in strongly basic medium, i.e. at higher pH of the solution. Under these conditions, the proton will be removed from the $\overset{+}{N}H_3$ group to yield the following species.

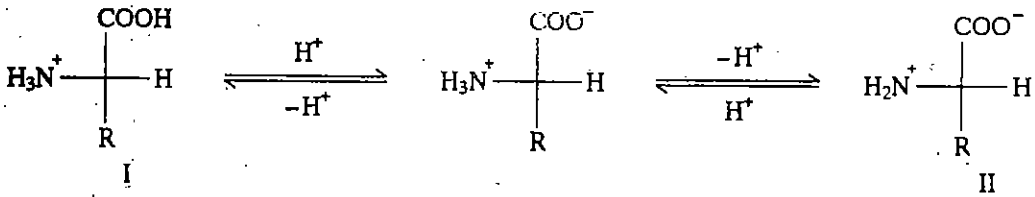


zwitterion

II

species present in strongly basic conditions

Thus, we can write a combined equation for the acid-base behaviour of the amino acids as shown below.



I

low pH (acidic conditions)

zwitterion

II

high pH (basic conditions)

You can see that a low pH, species I has a net positive charge and has two acidic sites ($\overset{+}{N}H_3$ and COOH). On the other hand, at high pH, species II has a net negative charge and has two basic sites (NH_2 and COO^-). It is clear from the above equation that the amino group will be first protonated and then the carboxylate anion. Also, at some intermediate pH, the amino acid exists as a zwitterion *with no net charge*. The pH at which this occurs is known as **isoelectric point**, pH_i of the amino acid. At this pH, the amino acid is stationary in an electric field, i.e., it migrates neither to the negative pole nor to the positive pole because the charges on it are balanced.

Since there are two acidic sites in an amino acid, it has two pK_a values. The pK_a value corresponding to the more acidic site is referred to as pKa_1 and that corresponding to the less acidic site as pKa_2. Thus, for the simplest amino acid, glycine, we can write the two equilibria as follows:

$$H_3\overset{+}{N}CH_2COOH + H_2O \underset{pKa_1 = 2.4}{\rightleftharpoons} H_3\overset{+}{N}CH_2COO^- + H_3O^+$$

and

$$H_3\overset{+}{N}CH_2COO^- + H_2O \underset{pKa_2 = 9.8}{\rightleftharpoons} H_2NCH_2COO^- + H_3O^+$$

At this stage you can compare the pKa_1, with the pK_a of ethanoic acid which is equal to 4.76. This leads to the conclusion that due to the electron withdrawing nature of the protonated amino group, the acidity of amino acid is increased as compared to ethanoic acid. Table 16.5 lists the pK_a values and pH_i of some amino acids.

Table 16.5 : pK_a and pH_i values of some amino acids

Amino acid	pKa_1	pKa_2	pH_i
Glycine	2.34	9.60	5.97
Alanine	2.34	9.69	6.00
Valine	2.32	9.62	5.96
Leucine	2.36	9.60	5.98
Isoleucine	2.36	9.60	6.02
Methionine	2.28	9.21	5.74
Proline	1.99	10.60	6.30
Phenylalanine	1.83	9.13	5.48
Tryptophan	2.83	9.39	5.89
Asparagine	2.02	8.80	5.41
Glutamine	2.17	9.13	5.65
Serine	2.21	9.15	5.68
Threonine	2.09	9.10	5.60

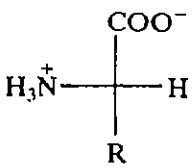
You can verify from Table 16.5 that $pH_i = \frac{pKa_1 + pKa_2}{2}$

The amino acids having acidic and basic side chains are characterised by three pK_a values. The third pK_a value, i.e., pKa_3 reflects the nature of the functional group present in the side chain.

Stereochemistry of amino acids

With the exception of 2-aminoethanoic acid (glycine), the 2-amino acids have at least one chiral centre.

According to the older D, L system of specifying the configuration (discussed in Sec. 3.3, Unit 3, Block 1), the 2-amino acids derived from animals or higher plants were found to have L configuration, i.e., they have the same relative configuration as L-glyceraldehyde. Thus, we can write the following Fischer projection formula of an L amino acid.

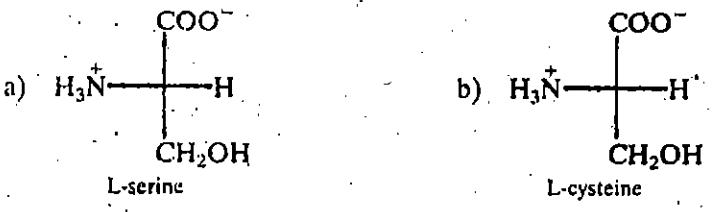


an L amino acid

On the basis of your knowledge about assigning the absolute configuration, can you attempt the following SAQ?

SAQ 2

What is the absolute configuration (*R* or *S*) of the following amino acids?



L-serine L-cysteine

.....

.....

It is also worthwhile to mention here that the amino acids obtained by synthesis using the methods discussed before are racemic mixtures. Enantiomerically pure amino acids can be obtained by resolution of the racemic mixtures or by biological methods using enzymes.

Enzymes use up one enantiomer preferentially.

3. Spectral properties of amino acids

Amino acids do not give any very useful absorptions in the ultraviolet spectra unless they possess aromatic groups such as those present in phenylalanine, tryptophan and tyrosine in which case they show λmax between 260 to 280 nm. However, these absorptions are more useful in monitoring the chemical and conformational changes in the proteins than in simple amino acids.

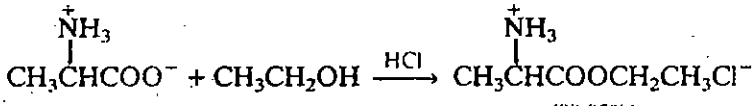
The infrared spectra of 2-amino acids show a strong absorption band near 1600 cm^{-1} due to the carboxylate anion. The N-H stretching (in $\overset{+}{N}H_3$) appears between 2600-3100 cm^{-1} as a strong broad band.

16.4.3 Reactions of Amino Acids

Amino acids undergo many of the reactions characteristic of the amino and carboxylic acid groups. For example, a typical reaction of the carboxy group is esterification and that of the amino functional group is alkanoylation. Let us now study these reactions in detail.

1. Esterification

The carboxy gruop of an amino acid can be esterified in the normal way using excess of an alcohol under acidic conditions.

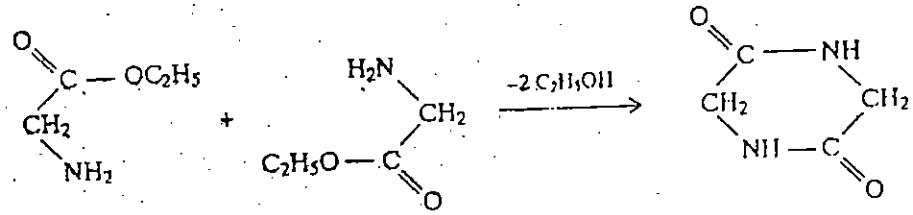


(90-95%)
hydrochloride salt
of amino acid ester

Methyl, ethyl and benzyl esters are used as intermediates in the synthesis of peptides.

Neutralisation of the hydrochloride with alkali yields the ester.

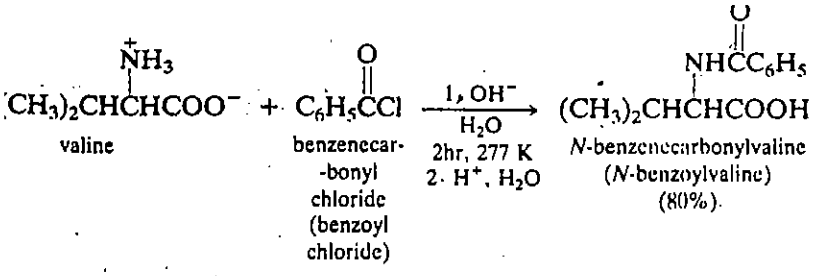
Esters of amino acids undergo intermolecular cyclisation to yield cyclic amides as shown below:

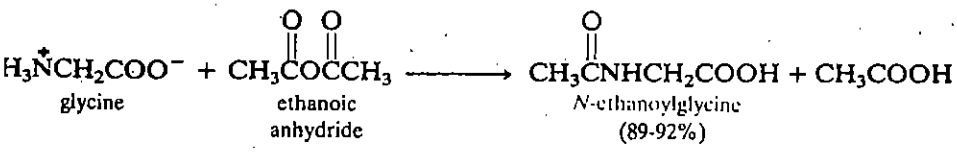


2,5-diazacyclohexane-1,4-dione (diketopiperazine)

2. Alkanoylation of amino acids

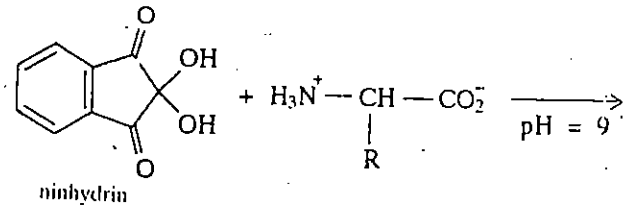
Alkanoylation of the amino group of an amino acid is carried out under basic conditions so that the free amino form is present in substantital concentration. Alkanoylation can be carried out by alkanoyl halides (acids chlorides) or carboxylic anhydrides. The product is finally obtained by acidifying the reaction mixture.



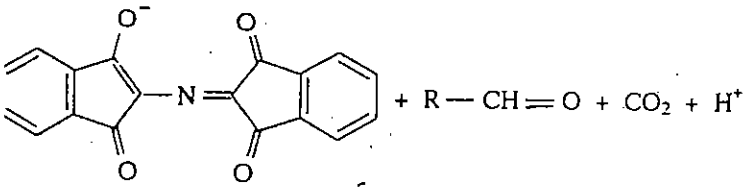


3. Reaction with Ninhydrin

When the aqueous solution of a 2-amino acid is treated with triketohydrindene hydrate (ninhydrin), a blue-violet colour is obtained.



ninhydrin



Ruhemann's purple λ_{max} = 570 nm

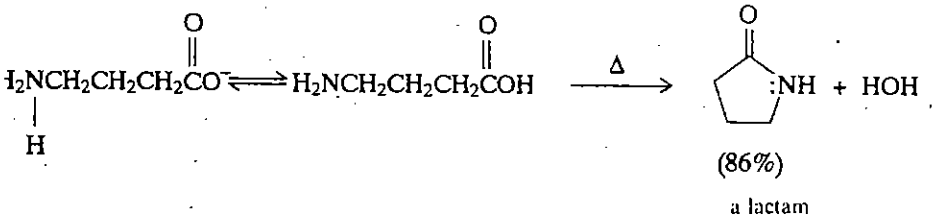
Ninhydrin test is given by amino acids containing primary amino group.

The blue-violet coloured compound formed is also known as *Ruhemann's purple.*

This is an important reaction used in the detection of small amounts of amino acids.

4. Formation of lactones

Some amino acids undergo cyclisation to yield cyclic amides, called **lactams.**
See Sec. 17.8, Unit 17 for nomenclature of lactams.



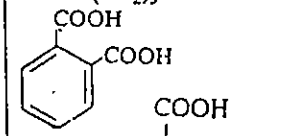
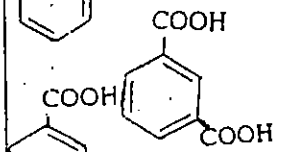
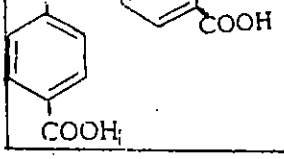
5. Formation of peptides

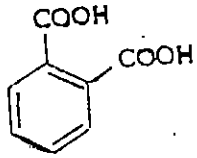
In addition to the above reactions, amino acids constitute the structural units of peptides and proteins about which you will study in Unit, 20, Section 20.3.

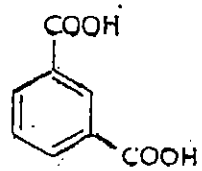
16.5 DICARBOXYLIC ACIDS

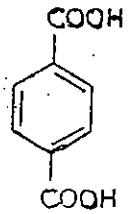
As the name indicates dicarboxylic acids are the acids which contain two carboxy groups in their molecules. You may recall from Block 1, Unit 1, Sec. 1.6 that dicarboxylic acids are called alkanedioic acids in the IUPAC system of nomenclature. Table 16.6 lists the common as well as IUPAC names for some saturated aliphatic and aromatic dicarboxylic acids.

Table 16.6 : Some Dicarboxylic acids

Structure	Common name	IUPAC name
HOOCCOOH	oxalic acid	ethanedioic acid
$HOOCCH_2COOH$	malonic acid	propanedioic acid
$HOOC(CH_2)_2COOH$	succinic acid	butanedioic acid
$HOOC(CH_2)_3COOH$	glutaric acid	pentanedioic acid
$HOOC(CH_2)_4COOH$	adipic acid	hexanedioic acid
$HOOC(CH_2)_5COOH$	pimelic acid	heptanedioic acid
	phthalic acid	1,2-benzenedicarboxylic acid
	isophthalic acid	1,3-benzenedicarboxylic acid
	terephthalic acid	1,4-benzenedicarboxylic acid







Let us now study how dicarboxylic acids can be obtained.

16.5.1 Preparation of Dicarboxylic Acids

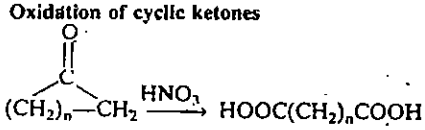
Table 16.7 : Methods of preparation of Dicarboxylic Acids

1. **By hydrolysis of nitriles**

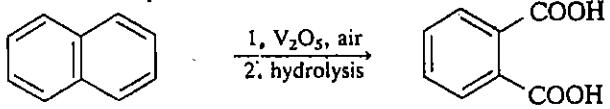
$$NC—CH_2—(CH_2)_n—COOH \xrightarrow{H^+/H_2O} HOOC—CH_2—(CH_2)_n—COOH$$

$$NC(CH_2)_nCN \xrightarrow{H^+/H_2O} HOOC(CH_2)_nCOOH$$

2. **Oxidation of cyclic ketones**



3. **Oxidation of naphthalene**



naphthalene — 1,2-benzenedicarboxylic acid

4. **Oxidation of dimethylbenzenes.**

Let us now study these methods in detail.

1. By hydrolysis of nitriles

You have earlier studied this method for the preparation of monocarboxylic acids in Sec. 15.3, Unit 15. It can also be applied to synthesise dicarboxylic acids. The starting material can be either a halo acid or a dibromoalkane. For example, chloroethanoic acid can be converted into cyanoethanoic acid which on hydrolysis yields the propanedioic acid.

$$\underset{\text{chloroethanoic acid}}{ClCH_2COOH} \xrightarrow{KCN} \underset{\text{cyanoethanoic acid}}{NCCH_2COOH} \xrightarrow[\text{hydrolysis}]{H_2O/H^+} \underset{\text{propanedioic acid}}{HOOCCH_2COOH}$$

The substitution by cyano group and hydrolysis can also be carried in a single step using NaOH and NaCN as shown below:

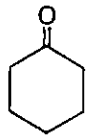
$$ClCH_2COOH + NaOH + NaCN \xrightarrow{H_2O} [NCCH_2COO^-Na^+] \xrightarrow[NaOH]{H_2O} Na^+\bar{O}OCCH_2COO^-Na^+ \xrightarrow[(77-82\%)]{HCl} HOOCCH_2COOH$$

Similarly, 1,3-dibromopropane can be converted into 1,3-dicyanopropane which on acid hydrolysis yields pentanedioic acid as shown below:

$$\underset{\text{1,3-dibromopropane}}{BrCH_2CH_2CH_2Br} \xrightarrow[H_2O]{NaCN} \underset{\text{1,3-dicyanopropane (82\%)}}{NCCH_2CH_2CH_2CN} \xrightarrow{H^+,\ H_2O} \underset{\text{pentanedioic acid (84\%)}}{HOOCCH_2CH_2CH_2COOH}$$

2. By oxidation of cyclic ketones

Cyclic ketones on oxidation with nitric acid yield dicarboxylic acids. This is illustrated by the synthesis of hexanedioic acid from cyclohexanone.

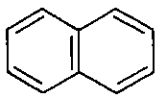


cyclohexanone

$$\xrightarrow{HNO_3} \underset{\text{hexanedioic acid}}{HOOCCH_2CH_2CH_2CH_2COOH}$$

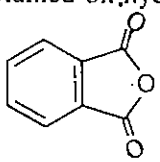
3. Oxidation of naphthalene

Vigorous oxidation of naphthalene yields the anhydride of 1,2-benzenedicarboxylic acid from which the acid can be obtained on hydrolysis.



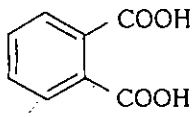
naphthalene

$\xrightarrow[\Delta]{V_2O_5,\ air}$



1,2-benzenedicarboxylic anhydride

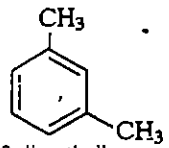
$\xrightarrow{hydrolysis}$



1,2-benzenedicarboxylic acid

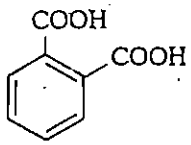
4. Oxidation of dimethylbenzenes

Alternatively, isomeric dimethylbenzenes can be oxidised to yield the corresponding benzenedicarboxylic acids.

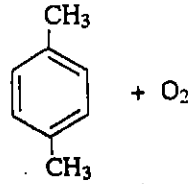


1,2-dimethylbenzene

$\xrightarrow{O_2,\ Co^{3+}}$

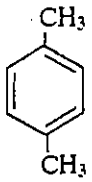


1,2-benzenedicarboxylic acid

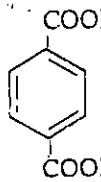


1,4-dimethylbenzene

$+ O_2 \xrightarrow[Co^{3+}]{CH_3COOH}$



$\xrightarrow[O_2,\ Co^{3+}]{CH_3COOH}$



1,4-benzenedicarboxylic

16.5.2 Physical Properties of Dicarboxylic Acids

Physical properties such as melting point and dissociation contants for some dicarboxylic acids are listed in Table 16.8.

Table 16.8 : Physical properties of some dicarboxylic acids

Acid	m.p./K	$k_1 \times 10^5$ at 298 K	$k_2 \times 10^5$ at 298 K
ethanedioic acid	462	5400.0	5.4
propanedioic acid	409 (decomposition)	140.0	0.20
butanedioic acid	458	6.2	0.23
pentanedioic acid	371	4.6	0.39
hexanedioic acid	425	3.7	0.24
1,2-benzene-dicarboxylic acid	504	130.0	0.39
1,3-benzene-dicarboxylic acid	618	29.0	2.5
1,4-benzene-dicarboxylic acid	sublimes	38.0	1.5

Where k_1 and k_2 refer to the following equilibria, respectively.

$$HOOC(CH_2)_nCOOH \overset{k_1}{\rightleftharpoons} HOOC(CH_2)_nCOO^- + H^+$$

$$HOOC(CH_2)_nCOO^- \overset{k_2}{\rightleftharpoons} {}^-OOC(CH_2)_nCOO^- + H^+$$

You can refer back to sub-Sec 5.4.1 of Unit 5, Block 1 where we explained why k_2 of a dicarboxylic is less than k_1.

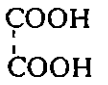
16.5.3 Reactions of Dicarboxylic Acids

1. Action of heat on dicarboxylic acids

The dicarboxylic acids undergo a variety of thermal reactions depending upon the length of the carbon chain separating the two carboxy groups. Let us study the effect of heat on some simple dicarboxylic acids.

i) Ethanedioic acid

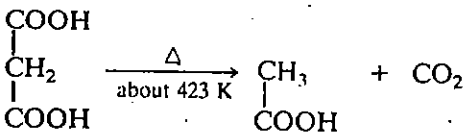
It decomposes on heating to yield carbon dioxide, carbon monoxide and water.



ethanedioic acid

ii) Propanedioic acid

It also decarboxylates on heating at 423 K to yield ethanoic acid.

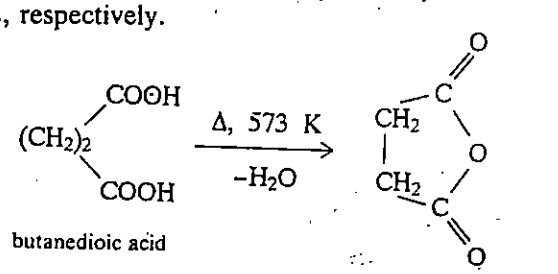


propanedioic acid — ethanoic acid

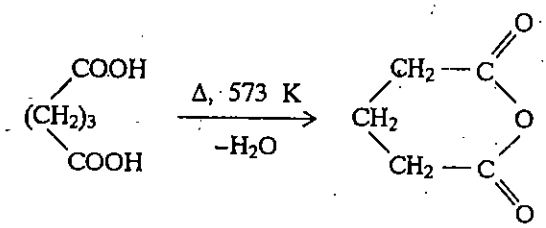
Decarboxylation is the characteristic feature of all those acids which have two carboxy groups on the same carbon atom as also of monocarboxylic acids having a strong electronegative group on the carbon atom next to the carboxy group.

iii) Butanedioic and pentanedioic acids

These dicarboxylic acids form cyclic anhydrides containing five and six membered rings, respectively.



butanedioic acid — butanedioic anhydride

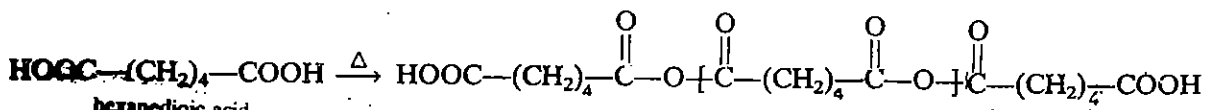


pentanedioic acid — pentanedioic anhydride

The formation of cyclic anhydrides is greatly aided by the use of dehydrating agents such as PCl_3, P_2O_5, $POCl_3$ and $SOCl_2$.

iv) Hexanedioic and higher dicarboxylic acids

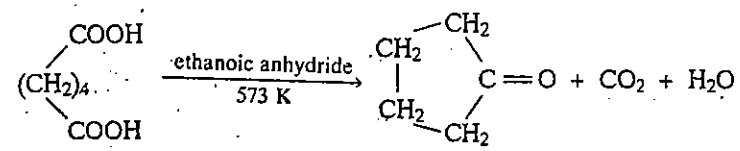
Only traces of a seven-membered ring compound, i.e., the corresponding anhydride is formed when hexanedioic acid is heated. Instead, the reaction yields a polymeric anhydride of relatively high molecular weight.



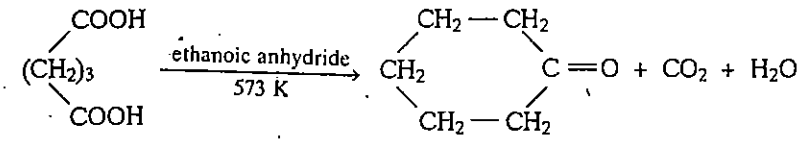
hexanedioic acid — polymeric anhydride

Dicarboxylic acids containing more than six carbon atoms behave in a similar fashion.

However, when hexanedioic and heptanedioic acids are heated with ethanoic anhydride and the product is distilled at 573 K, a cyclic ketone is obtained in each case.



hexanedioic acid — cyclopentanone

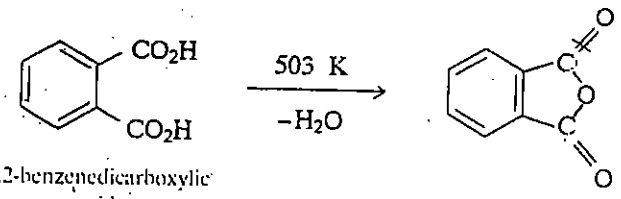


heptanedioic acid — cyclohexanone

Hexanedioic acid is used for the preparation of polyesters and is an intermediate in the manufacture of nylon 6.6 — a polyamide formed from hexanedioic acid and hexamethylene diamine, $NH_2(CH_2)_6NH_2$.

v) Benzenedicarboxylic acids

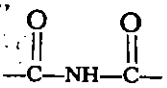
1,2-Benzenedicarboxylic acid forms a cyclic anhydride at its melting point. The two isomeric acids, 1,3-benzenedicarboxylic acid and 1,4-benzenedicarboxylic acid, evidently cannot form the anhydrides.

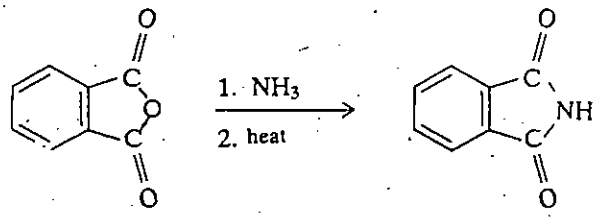


1,2-benzenedicarboxylic acid — cyclic anhydride

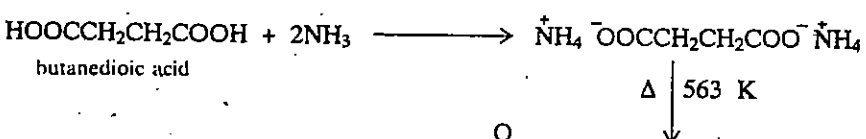
2. Formation of imides

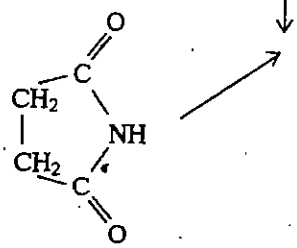
Imides are the nitrogen analogs of anhydrides. They can be prepared by the reaction of ammonia or amines with anhydrides or by heating the ammonium salt of the dicarboxylic acid. The formation of cyclic imides from 1,2-benzenedicarboxylic anhydride and butanedioic acid is shown below:

Imides contain two alkanoyl (acyl) groups attached to a nitrogen, i.e., they contain  linkage.



1,2-benzenedicarboxylic anhydride — 1,2-benzenedicarboxylicimide (phthalimide) (97%)





butanimide (82-83%)

$CH_3CH_2O\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$

diethyl propanedioate
(diethyl malonate)

3. An important derivative of propanedioic acid is its diethyl ester, called as diethyl propanedioate. It is a highly versatile reagent in organic synthesis about which you will study in Sec. 16.7 where we will also discuss the synthetic utility of ethyl-3-oxobutanoate which is a keto ester. But before that let us first study about keto acids.

16.6 KETO ACIDS

Keto acids are the compounds containing both the keto and the carboxy groups in their molecules. Depending upon the position of the keto group, keto acids are named as 2-oxo or 3-oxo alkanoic acids, etc.

$CH_3\overset{O}{\overset{\|}{C}}COOH$

2-oxopropanoic acid
(pyruvic acid)

$CH_3\overset{O}{\overset{\|}{C}}CH_2COOH$

3-oxobutanoic acid

2-Oxopropanoic acid is a physiologically important natural keto acid as the two molecules, 2-oxopropanoic acid and 2-hydroxypropanoic acid (lactic acid), are interconverted in the body by an enzyme present in the muscles called *lactic acid dehydrogenase*.

Lactic acid dehydrogenase reduces 2-oxopropanoic acid to 2-hydroxypropanoic acid during physical exercise. The enzyme reverses this process when the muscles rest.

$CH_3\overset{O}{\overset{\|}{C}}COOH \underset{}{\overset{\text{Lactic acid dehydrogenase}}{\rightleftharpoons}} HO\overset{H}{\underset{H_3C}{\overset{|}{\overset{|}{C}}}}-COOH$

2-oxopropanoic acid

(*S*)-(+)-2-hydroxypropanoic acid
(lactic acid)

3-Oxobutanoic acid undergoes decarboxylation on mild heating.

$CH_3\overset{O}{\overset{\|}{C}}CH_2COOH \xrightarrow[-CO_2]{\text{heat}} CH_3\overset{O}{\overset{\|}{C}}CH_3$

3-oxobutanoic acid — propanone

Thus, 3-oxobutanoic acid due to its instability, is not of much importance whereas its esters, particularly ethyl 3-oxobutanoate, are of great synthetic utility about which you will study in the next section. You can see that there is a similarity in the structures of ethyl 3-oxobutanoate and diethyl propanedioate. Therefore, both undergo similar kinds of reactions to yield a large variety of new compounds about which you will now study.

$CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$

ethyl 3-oxobutanoate

16.7 ETHYL 3-OXOBUTANOATE AND DIETHYL PROPANEDIOATE

Claisen condensation is the ester analog of the aldol condensation which you studied in sub-Sec. 14.4.2, Unit 14, Block 3.

3-Oxo esters are generally prepared by a condensation reaction, called **Claisen condensation**. Esters undergo self condensation on treatment with alkoxide bases to yield 3-oxo ester and an alcohol.

$2\,RCH_2\overset{O}{\overset{\|}{C}}OR' \xrightarrow[2.\ H^+,\ H_2O]{1.\ NaOR''} RCH_2\overset{O}{\overset{\|}{C}}\underset{R}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}OR' + R'OH$

ester — 3-oxo ester

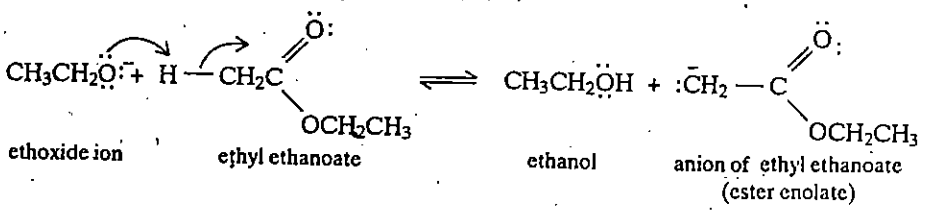
Thus, ethyl ethanoate reacts with sodium ethoxide to yield ethyl 3-oxobutanoate and ethanol.

$2\,CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3 \xrightarrow[2.\ H^+,\ H_2O]{1.\ \overset{+}{N}a\bar{O}CH_2CH_3} CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3 + CH_3CH_2OH$

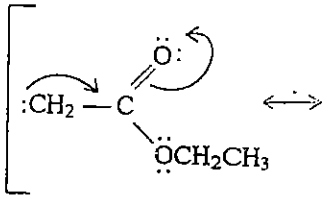
ethyl ethanoate — ethyl 3-oxobutanoate — **ethanol**

Ethyl 3-oxobutanoate is commonly known as ethyl acetoacetate or simply acetoacetic ester. The Claisen condensation, in general is also known as **acetoacetic ester condensation.**

The reaction involves a series of equilibrium reactions. The first step is the abstraction of a proton from the ester by the base, i.e.,

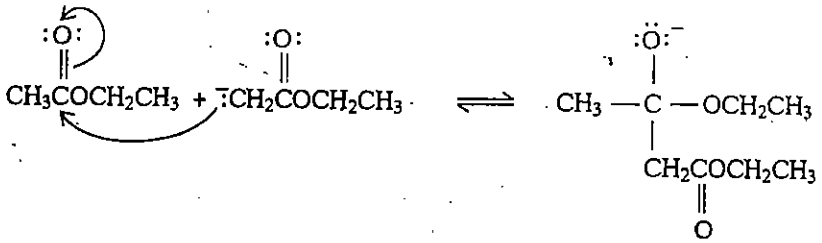


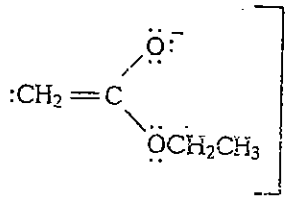
The resonance structures of ester enolate



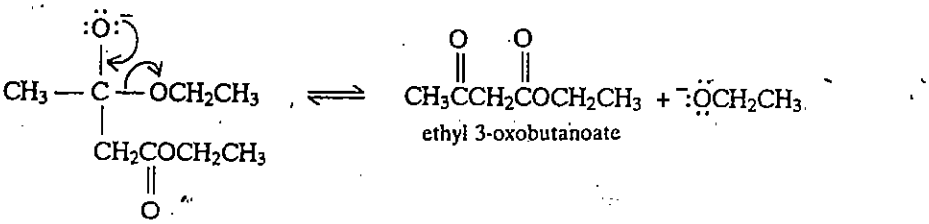
The ester enolate being a powerful nucleophile attacks the carbonyl carbon of the second ester molecule as shown below:

Nucleophilic addition



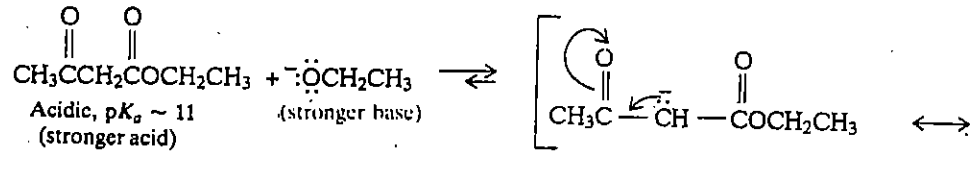


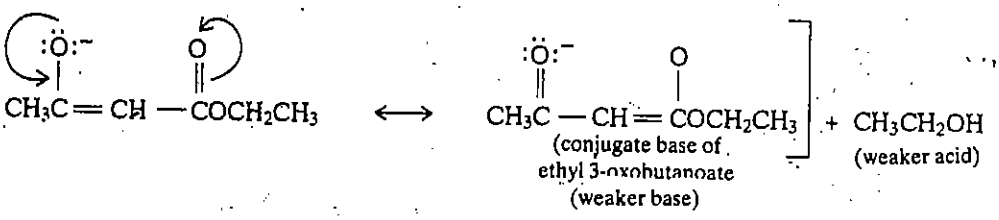
This is followed by the elimination of ethoxide ion to yield ethyl 3-oxobutanoate.



The acidic nature of hydrogen can be accounted on the basis of its position between two carbonyl groups.

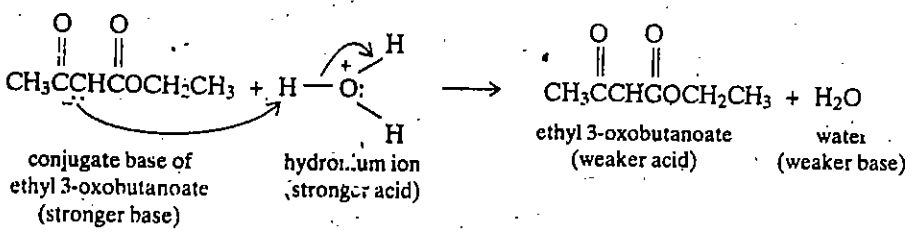
Ethyl 3-oxobutanoate so obtained is a stronger acid and hence, reacts with ethoxide ion to produce ethanol and the conjugate base of ethyl 3-oxobutanoate, as shown below:





The equilibrium for this reaction lies towards the right hand side and provides the driving force for the reaction.

Subsequent acidification converts the above anion to its neutral form which is then isolated.



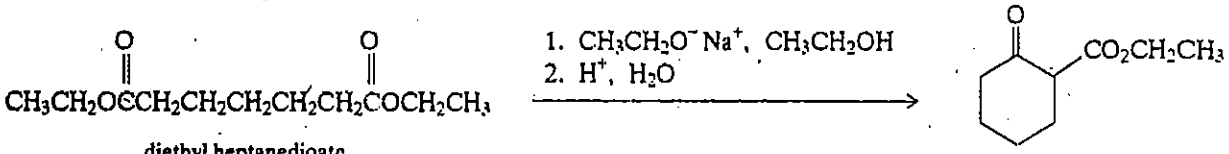
The formation of the final enolate ion is crucial for the Claisen condensation to occur. If a stable anion is not formed by deprotonation, the product is obtained only in trace amounts at equilibrium. For example, if you write the similar steps starting from ethyl

2-methylpropanoate, $(CH_3)_2CHCOCH_2CH_3$, you will see that the product has no acidic hydrogen and formation of the final enolate is not possible. Hence, the esters having only one hydrogen adjacent to the carbonyl group of the ester do not undergo Claisen condensation.

A variety of 3-oxo esters can be synthesised using mixed Claisen condensations. Mixed Claisen condensation involves the reaction between two different esters. Can you predict how many 3-oxo esters will be obtained using mixed Claisen condensation? The answer is *four*. Thus, the resulting product is a mixture of four oxo esters. However, a selective mixed condensation is possible when one of the esters has no hydrogen adjacent to the carbonyl group of the ester and is thus incapable of forming the enolate. Some such esters are given below.

methanoate ester | carbonate ester | ethanedioate ester | benzoate ester

Intramolecular Claisen condensation is called **Dieckmann condensation** and yields cyclic 3-oxo esters.



diethyl heptanedioate

ethyl 3-oxocyclo-hexanecarboxylate (60%)

SAQ 3

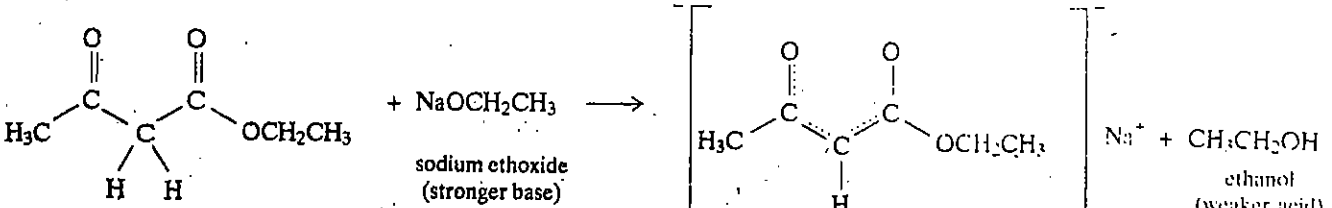
Write the possible series of reactions when ethyl 2-methylpropanoate is subjected to Claisen condensation and comment.

.....

.....

Having studied the preparation of 3-oxo esters in detail, let us study the synthetic applications of these compounds. We will study the representative example of ethyl 3-oxobutanoate.

You have studied above that ethyl 3-oxobutanoate on treatment with sodium ethoxide yields the ester enolate.



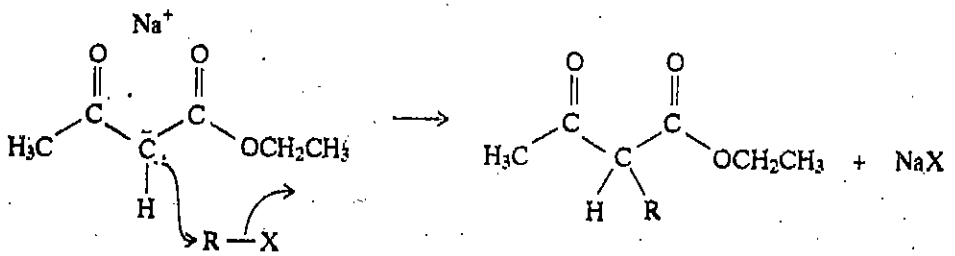
ethyl 3-oxobutanoate (Stronger acid) K_a 10^{-11} (pK_a 11)

sodium ethoxide (stronger base)

sodium salt of ethyl ethanoate (weaker base) ester enolate

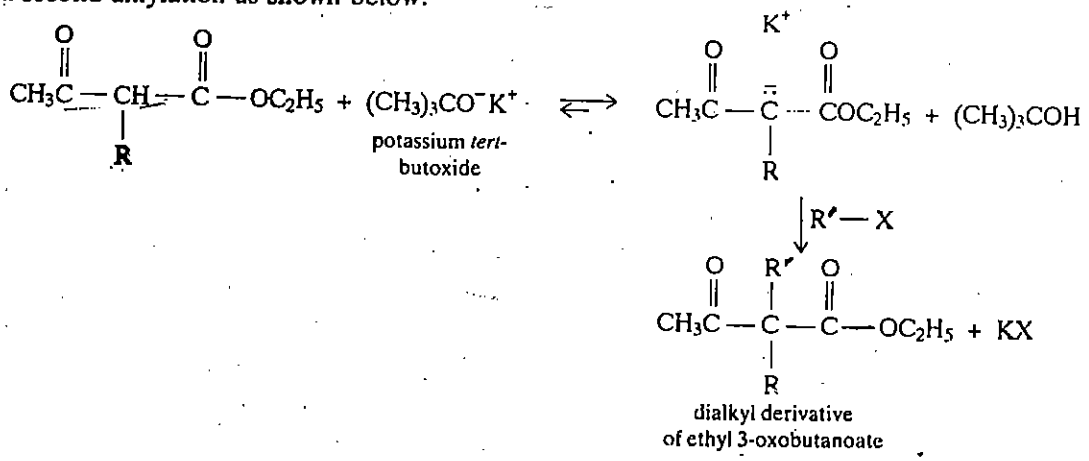
ethanol (weaker acid) K_a 10^{-16} (pk_a 16)

The ester enolate is nucleophilic and can be alkylated on treatment with alkyl halide.

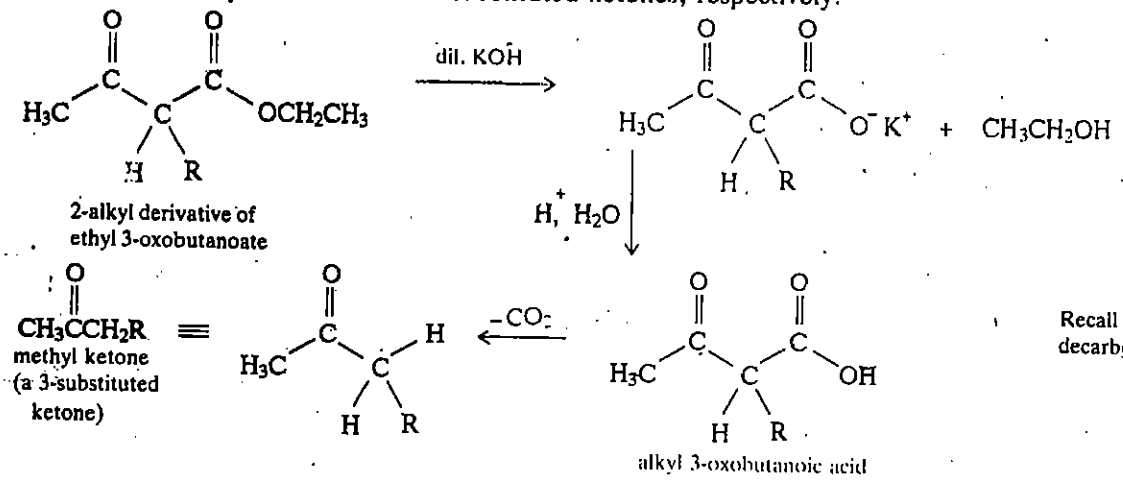


ethyl 2-alkyl-3-oxobutanoate

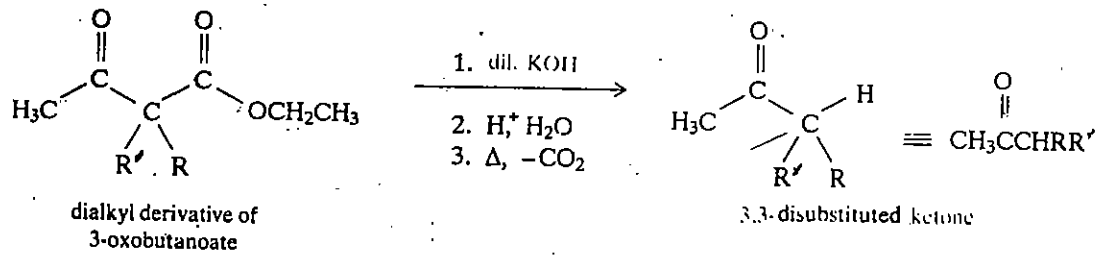
The 2-alkyl derivative still has one appreciably acidic hydrogen and we can carry out a second alkylation as shown below:



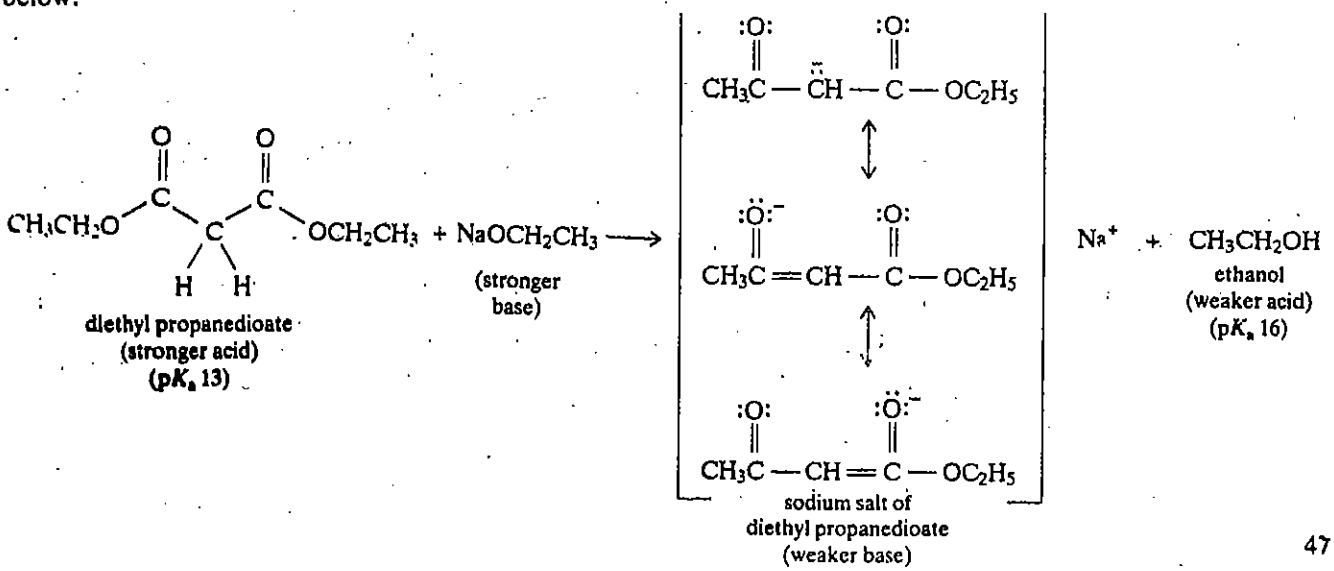
Sponification of mono- and dialkyl derivatives as obtained above, followed by acidification will yield mono- and disubstituted ketones, respectively.



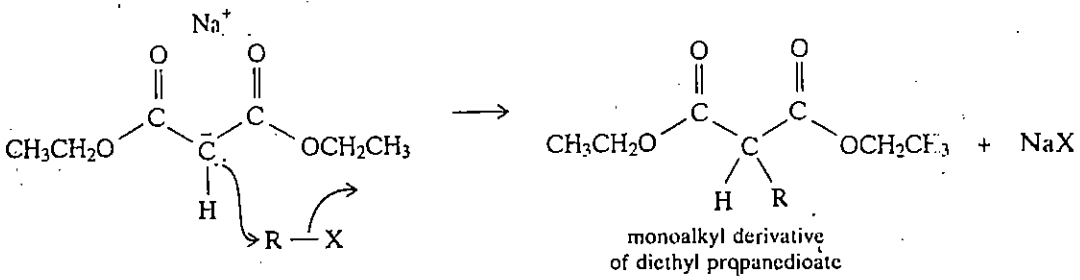
Recall that 3-oxo acids easily decarboxylate as stated earlier.



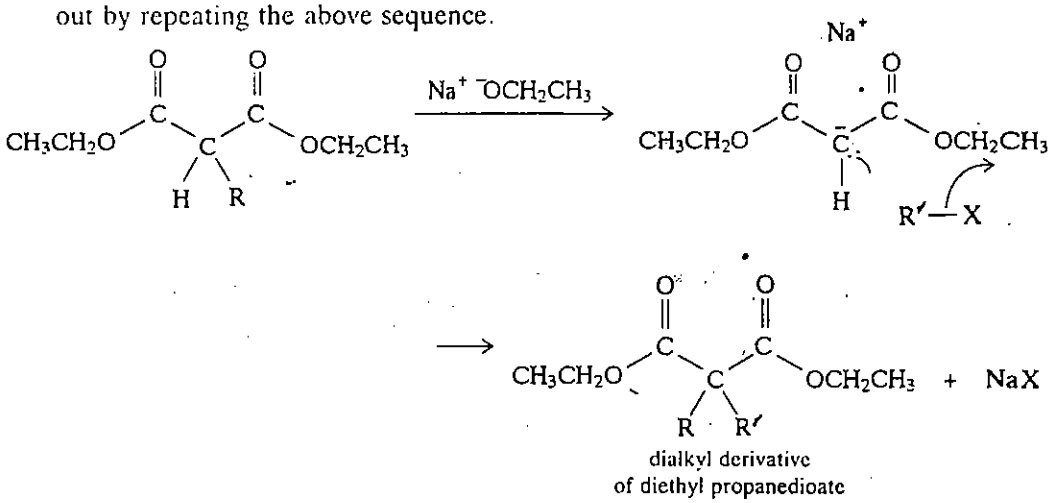
Let us now consider the structure of diethyl propanedioate. You will find that it also has two acidic hydrogens flanked by the two carbonyl groups. When treated with a strong base, $Na^+ \bar{O}CH_2CH_3$, it yields an anion which is resonance stabilised as shown below:



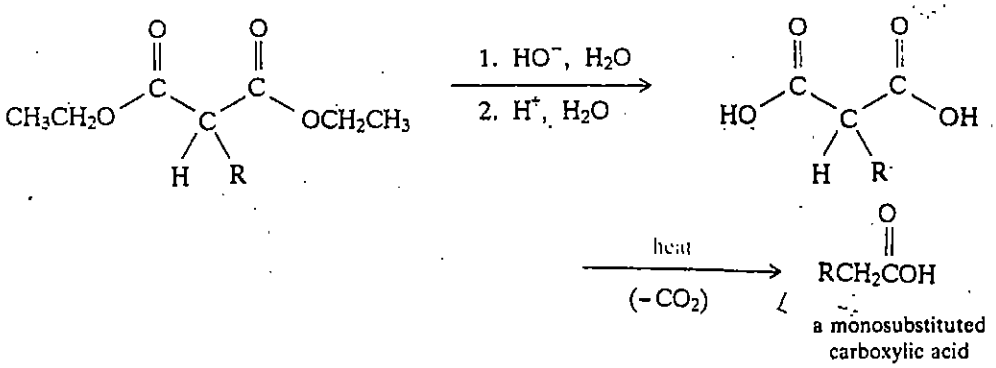
Treatment of the above anion with an alkyl halide leads to the alkylation at the carbon atom present between the two carbonyl carbons.

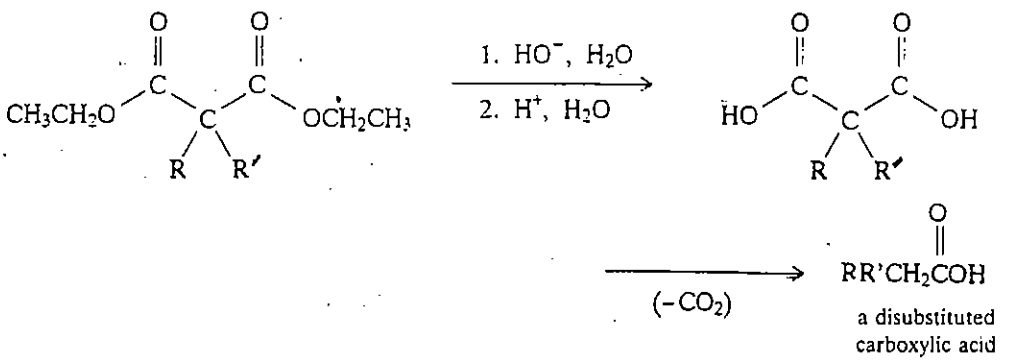


As in the case of ethyl 3-oxobutanoate, here also a second alkylation can be carried out by repeating the above sequence.



When monoalkyl and dialkyl derivatives of diethyl propanedioate are hydrolysed by alkali and heated to 453 K they undergo decarboxylation to yield substituted carboxylic acids as shown below:



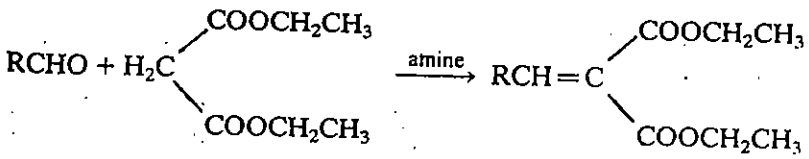


Thus, by suitably selecting the alkyl halides, we can synthesise a large variety of substituted carboxylic acids.

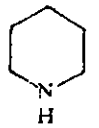
The synthesis of alkylated derivatives of diethyl propanedioate (malonic ester) is called **malonic ester synthesis.**

Reaction with aldehydes and ketones

Diethyl propanedioate readily reacts with aldehydes and ketones under basic conditions to give α, β-unsaturated diesters.

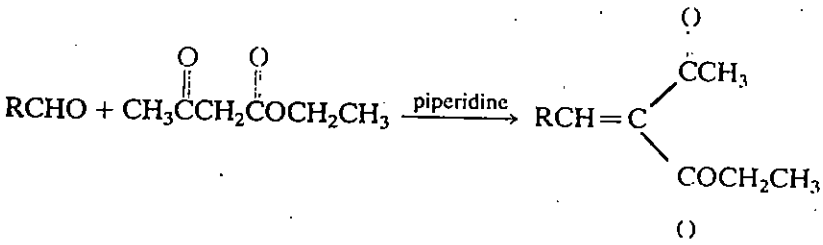


Amines such as piperidine are effective catalysts for this reaction which is called **Knoevenagel reaction**.



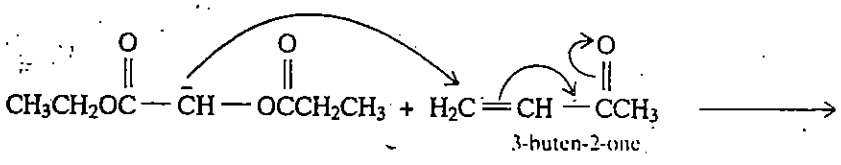
piperidine

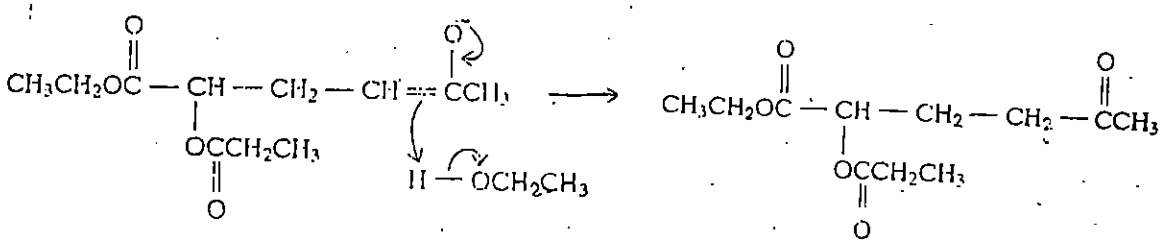
A similar reaction is observed with ethyl 3-oxobutanoate also. This is as shown below:



Reaction with α, β-unsaturated carbonyl compounds

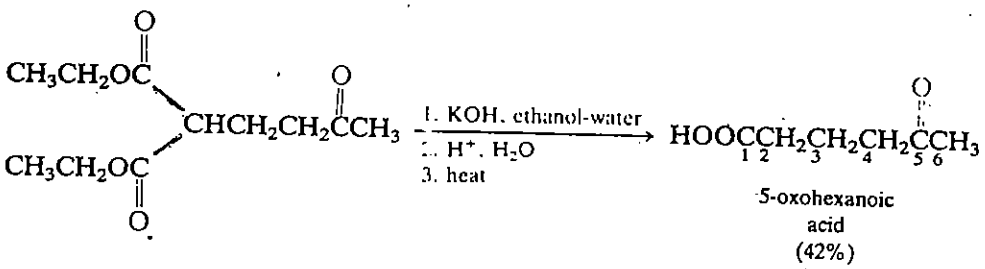
Anions of ethyl 3-oxobutanoate and diethyl propanedioate react with α, β-unsaturated carbonyl compounds in the presence of catalytic amounts of a base by adding on to the β carbon atom. The reaction works with saturated aldehydes, ketones, nitriles, carboxylic acid derivatives such as esters, amides, etc., and is called **Michael addition**.





diethyl 2-(3-oxobutyl) propanedioate (Michael adduct) (71%)

The Michael adduct so obtained on ester hydrolysis and decarboxylation yields a 5-keto acid.



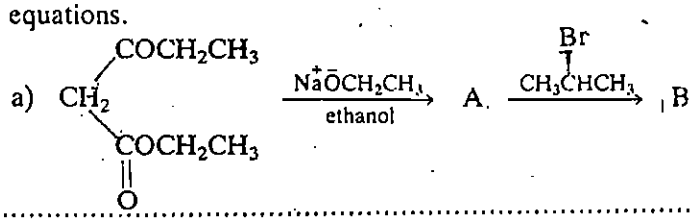
5-oxohexanoic acid (42%)

Thus, you can see that we can synthesise a wide variety of compounds using diethyl propanedioate and ethyl 3-oxobutanoate.

Using the knowledge acquired in the above section, answer the following SAQ.

SAQ 4

Write the structural formulas for the products indicated by letters in the following equations.

a) 

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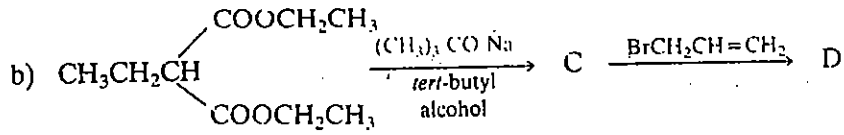
b) 

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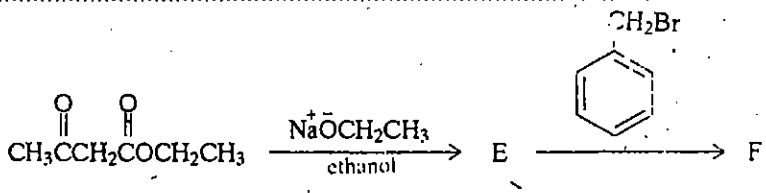

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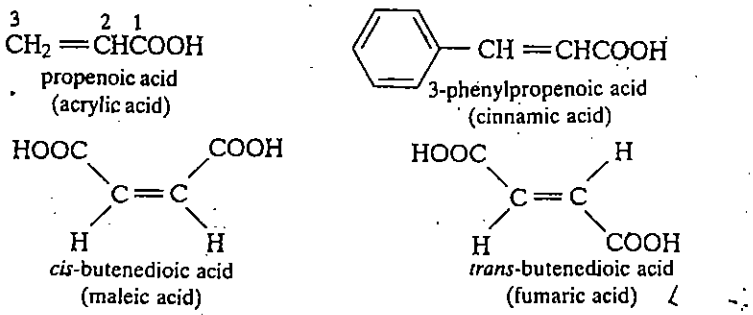
16.8 UNSATURATED CARBOXYLIC ACIDS

Unsaturated carboxylic acids contain a carboxy group and a double or/and a triple bond in their molecules. Some examples of unsaturated carboxylic acids are given below:



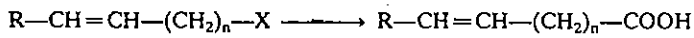
The geometric isomerism of butenedioic acid was discussed in Unit 2, Block 1.

16.8.1 Preparation of Unsaturated Carboxylic Acids

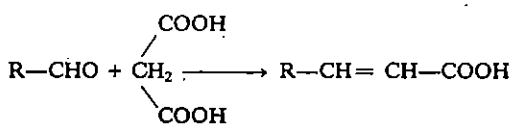
You can first have a look at the methods of preparation given in Table 16.9 before studying their details given below.

Table 16.9 : Methods of preparation of Unsaturated Carboxylic Acids

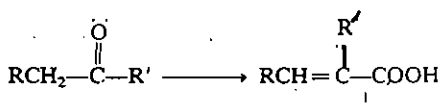
1. **From Alkenyl halides**



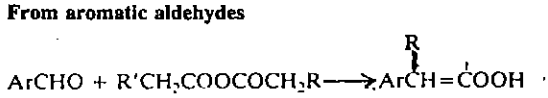
2. **Using Knoevenagel Condensation**



3. **From Ketones**



4. **From aromatic aldehydes**



5. **By oxidation of unsaturated aldehydes**

Some of the methods which were discussed for the preparation of saturated carboxylic acids can be used for the synthesis of unsaturated carboxylic acids also. For example, starting from appropriate halide.

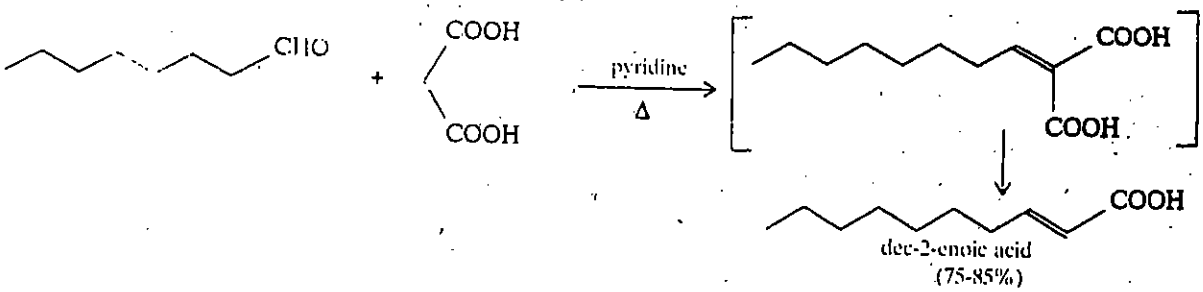
1. From alkenyl halides

Alkenyl halides containing the double bond at appropriate position can be converted into the nitrile which on hydrolysis yields the required unsaturated carboxylic acid.

$$CH_2{=}CHCH_2Cl \xrightarrow{CuCN} CH_2{=}CHCH_2CN \xrightarrow{aq.\ HCl} \underset{\text{but-3-enoic acid (52-62\%)}}{CH_2{=}CHCH_2COOH}$$

2. By Knoevenagel condensation

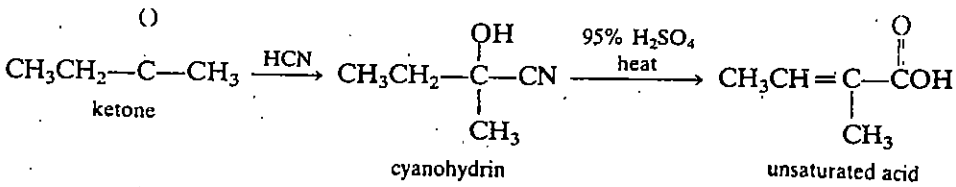
Knoevenagel condensation which you studied in the last section can also be used to prepare unsaturated carboxylic acids. A variation of this reaction involves the use of propanedioic acid which on condensation with a suitable aldehyde in the presence of catalytic amounts of a base followed by heating yields the unsaturated acid.



This reaction works best with aldehydes but the yields are generally low when ketones are used

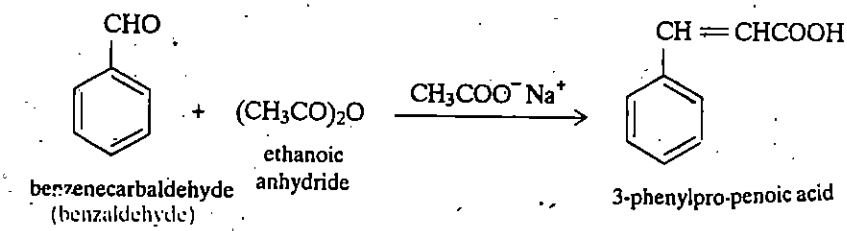
3. From ketones

The cyanohydrins obtained from ketones on acidic hydrolysis yield unsaturated carboxylic acids.



4. From aromatic aldehydes

Aromatic aldehydes on heating with anhydride of an aliphatic acid and the corresponding carboxylate salt are converted into 2,3-unsaturated carboxylic acids.



This reaction is also known as **Perkin Condensation.**

5. By oxidation of unsaturated aldehydes

Unsaturated aldehydes obtained from aldol condensation of aldehydes can be oxidised to unsaturated acids. Ammoniacal silver nitrate which is a mild oxidising agent is used in this oxidation.

$$\underset{\text{unsaturated aldehyde}}{CH_3CH{=}CHCHO} + 2Ag(NH_3)OH \rightarrow CH_3CH{=}CHCOO^-NH_4^+ + 2\,Ag + 3\,NH_3 + H_2O$$

$$\downarrow H^+$$

$$\underset{\text{unsaturated}}{CH_3CH{=}CHCOOH}$$

16.8.2 Reactions of Unsaturated Acids

Unsaturated carboxylic acids in which the two functional groups are isolated, show the characteristic properties associated with these functional groups. But, when these groups are sufficiently close, their interaction affects the reactivity and they exhibit some characteristic reactions which are given below:

1. Addition of halogen acids

2,3- and 3,4- unsaturated acids add on the halogen acid in such a way that the halogen atom is attached to the carbon atom which is farther away from the carboxy group, i.e., in anti-Markownikoff mode.

$$\underset{\text{propenoic acid}}{CH_2=CHCOOH} \xrightarrow{HBr} \underset{\text{3-bromopropanoic acid}}{BrCH_2CH_2COOH}$$

$$\underset{\text{3-pentenoic acid}}{CH_3CH=CHCH_2COOH} \xrightarrow{HBr} \underset{\text{4-bromopentanoic acid}}{CH_3CHBrCH_2CH_2COOH}$$

This can be attributed to the inductive effect of the carboxy group. But as you know, the inductive effect decreases with distance, therefore, in 4,5-unsaturated acids the addition of halogen acids is in accordance with the Markownikoff's rule.

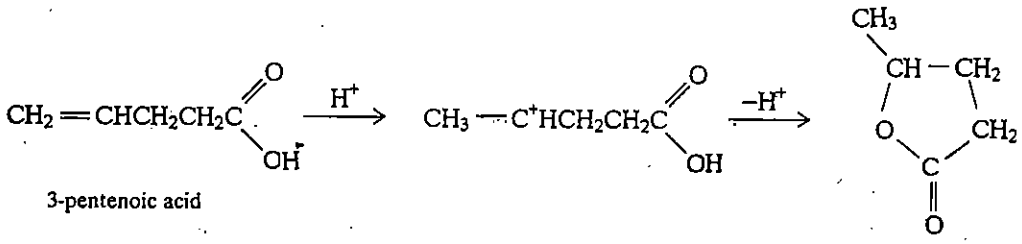
2. Migration of the double bond

2,3- and 3,4- unsaturated acids tend to interconvert by migration of the double bond.

$$RCH=CH-CH_2COO^- \underset{}{\overset{NaOH}{\rightleftharpoons}} RCH_2CH=CHCOO^-$$

3. Formation of lactones

The double bond and the carboxy group interact in the presence of acid catalysts to yield a lactone. Lactone formation occurs readily when a five-or six-membered ring can be formed.



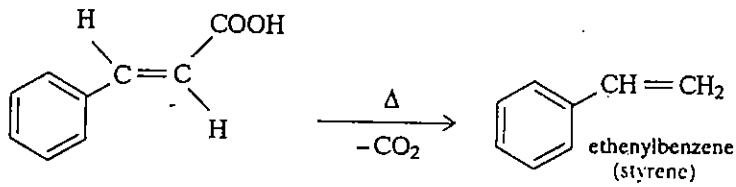
3-pentenoic acid

a lactone

4. Some reactions of 3-phenylpropenoic acid

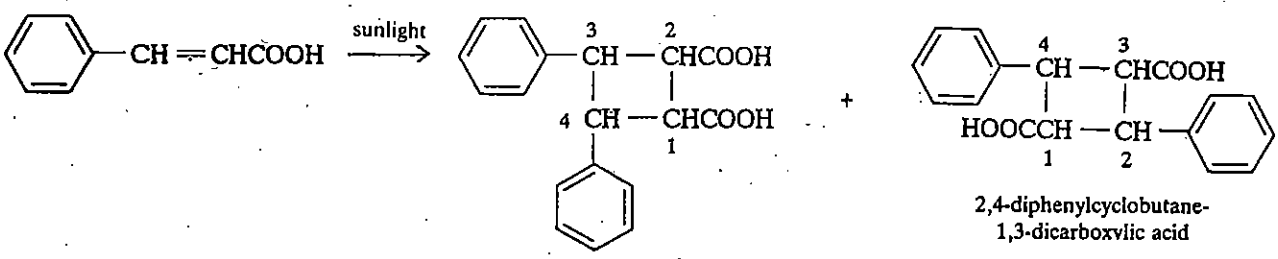
Cis- and *trans-* isomers of 3-phenylpropenoic acid exhibit some typical reactions which are discussed below:

a) The *trans-* isomer on dry distillation undergoes decarboxylation.



ethenylbenzene (styrene)

b) The *trans* isomer when exposed to sunlight dimerises.



3,4-diphenylcyclobutane-1,2-dicarboxylic acid

2,4-diphenylcyclobutane-1,3-dicarboxylic acid

c) The *cis*- isomer readily converts into the *trans*- isomer.

5. Reactions of *cis*- and *trans*- butenedioic acid

In addition to the other reactions like catalytic reduction to butanedioic acid and oxidation to 2,3-dihydroxybutanedioic acid, butenedioic acids yield acid anhydride. The formation of acid anhydrides was discussed in Unit 2, Block 1.

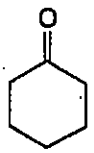
16.9 SUMMARY

In this unit, you studied that

- 2-halo acids undergo nucleophilic substitution reactions to yield 2-substituted acids whereas 3-halo acids undergo elimination to give unsaturated acids.
- hydroxy acids occur in nature and they can also be synthesised from halo acids, cyanohydrins, keto esters, from the reaction of bromoesters and carbonyl compounds, and by the Kolbe Schmidt reaction. In addition to the usual reactions of the hydroxy and the carboxy group, they can also be converted to lactones, unsaturated acids or lactides depending upon the position of the hydroxy group relative to the carboxy group.
- 20 amino acids occurring in proteins are L amino acids.
- 2-amino acids can be synthesised from 2-halo acids, aldehydes (Strecker synthesis) and potassium 1,2-benzenedicarboxylic imide.
- amino acids exist as inner salts called *zwitterions*.
- the reactions of amino acids include the usual reactions of the carboxy and the amino group. For example, they undergo esterification (characteristic of the carboxy group) and alkanoylation (characteristic of the amino group) reactions. They give a blue-violet colour with ninhydrin, and some amino acid can also be converted to lactams.
- dicarboxylic acids can be obtained by the hydrolysis of nitriles and oxidation of cyclic ketones, naphthalene and dimethylbenzenes. They can be converted into anhydrides by heating or by their reaction with ethanoic anhydride depending upon the starting acid. Lower members, for example, ethanedioic and propanedioic acids undergo decarboxylation on heating.
- ethyl 3-oxobutanoate and diethyl propanedioate are versatile reagents in synthesis. They can be used to prepare mono-and di-substituted ketones and substituted carboxylic acids. They yield unsaturated esters on reaction with aldehydes and ketones. They undergo Michael addition with unsaturated aldehydes, ketones, nitriles and carboxylic acid derivatives and hence can be used to synthesise a large variety of organic compounds.
- Finally, the synthetic methods and reactions of some unsaturated acids were also discussed.

16.10 TERMINAL QUESTIONS

1) Write the products obtained when the following hydroxy acids are heated with acid.
   a) 2-hydroxybutanoic acid
   b) 3-hydroxybutanoic acid
   c) 4-hydroxybutanoic acid
2) Outline the Strecker synthesis of tyrosine.
3) Write the products from the following Knoevenagel condensation reactions:

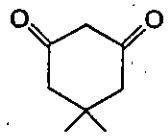
a)  + $N{\equiv}CCH_2C{\equiv}N \longrightarrow$

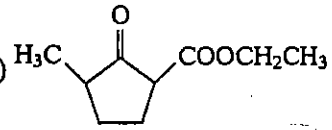
b) $CH_3CH_2CH_2CHO + N{\equiv}CCH_2COOCH_2CH_3 \longrightarrow$

c) $C_6H_5CHO + CH_3\overset{\overset{O}{\|}}{C}CH_2COOCH_2CH_3 \longrightarrow$

4) Give the products obtained from the following Michael additions :

a) $CH_3CH_2CH(COOCH_2CH_3)_2 + CH_2=CHC(=O)H \xrightarrow{Na^+O^-CH_2CH_3}$

b)  $+ CH_2=CHC\equiv N \xrightarrow{Na^+O^-CH_3}$

c)  $+ CH_3CH=CHCOOCH_2CH_3 \xrightarrow{K^+O^-CH_2CH_3}$

5) Which one of the following esters cannot undergo the Claisen condensation reaction? Write the Claisen condensation products of the other two.

a) $CH_3CH_2CH_2CH_2COOCH_2CH_3$
ethyl pentanoate

b) $C_6H_5COOCH_2CH_3$
ethyl benzoate

c) $C_6H_5CH_2COOCH_2CH_3$
ethyl phenylethanoate

6) Using ethyl 3-oxobutanoate, how will you prepare the following ketones? Write the other reagents used in the reaction.

a) 1-phenyl -1,4-pentanedione

b) 4-phenyl -2-butanone

c) 5-hexen-2-one

7) How will you synthesise 3-methylpentanoic acid from diethyl propanedioate?

16.11 ANSWERS

Self Assessment Questions

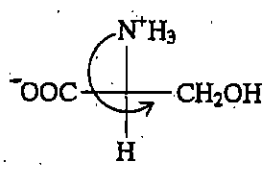
1) a) $HOCH_2CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2COOH$

b) $HOCH_2-(CH_2)_3-COOH$

2) a) The order of priority of substituents is

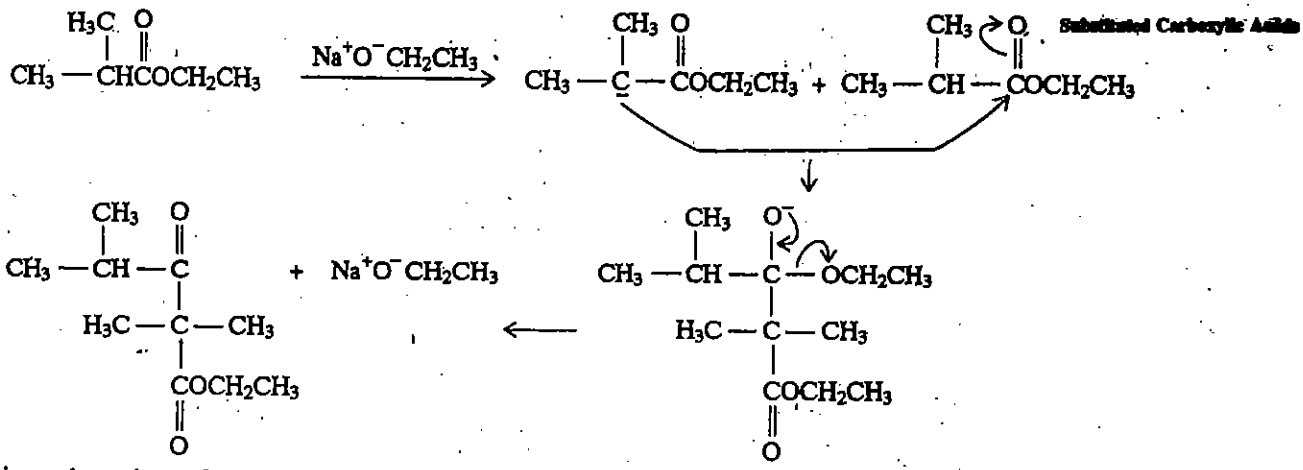
$-H_3\overset{+}{N} > -COO^- > -CH_2OH > -H$

The given Fischer projection can be converted to another Fischer projection given below by interchanging twice two substituents.

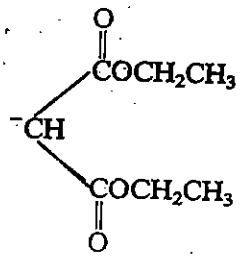


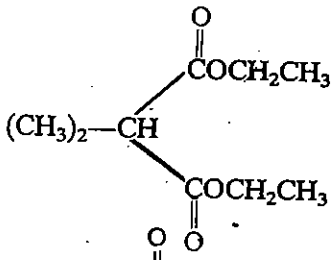
Overlooking H and moving from the substituents of highest priority to lower priority, the direction is anticlockwise, so the configuration is *S*.

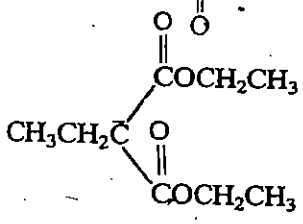
b) *R*

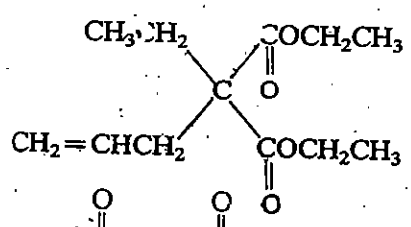
3) 

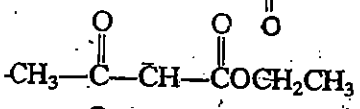
Since there is no hydrogen on the carbon atom adjacent to the ester carbonyl carbon, the equilibrium cannot shift towards the right hand side to yield the 3-oxo ester.

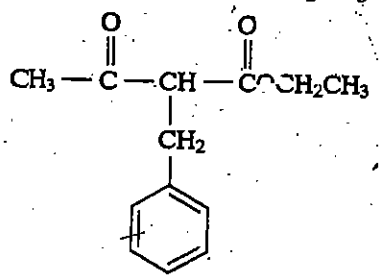
4) a) 

b) 

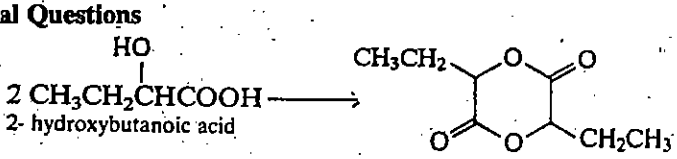
c) 

d) 

e) 

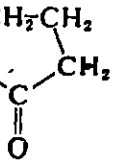
f) 

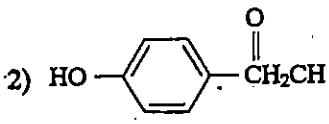
Terminal Questions

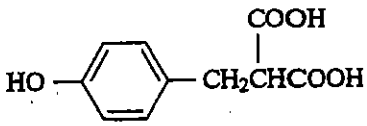
1) a) 
2- hydroxybutanoic acid

b) $CH_3\underset{\text{3-hydroxybutanoic acid}}{\underset{|}{\overset{OH}{C}}}HCH_2COOH \longrightarrow CH_3CH=CHCOH$ (=O)

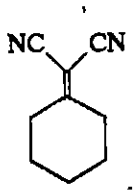
c) $HOH_2CCH_2CH_2COOH \longrightarrow$ oxacyclopentan-2-one (a lactone)

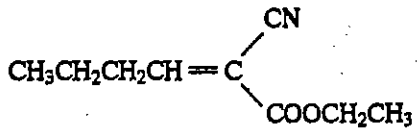


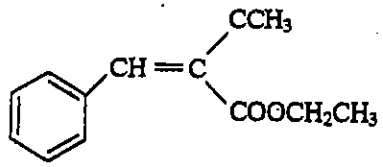
2) 

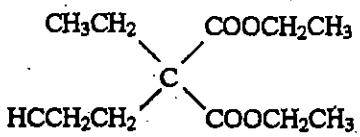


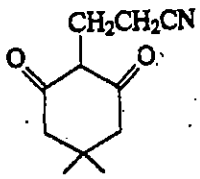
tyrosine

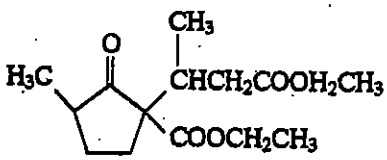
3) a) 

b) 

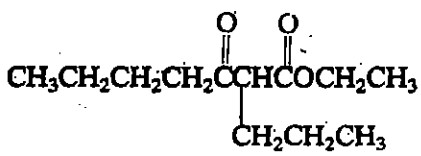
c) 

4) a) 

b) 

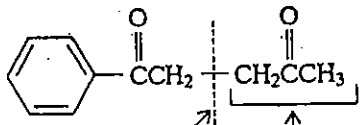
c) 

5) b) Ethyl benzoate cannot undergo the Claisen condensation. The Claisen condensation products of compounds given in (a) and (c) are given below

a) 

c) $C_6H_5CH_2\overset{\overset{O}{\|}}{C}\overset{\overset{C_6H_5}{|}}{C}H\overset{\overset{O}{\|}}{C}CH_2CH_3$

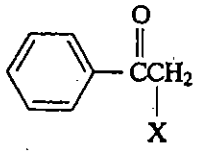
6) a)



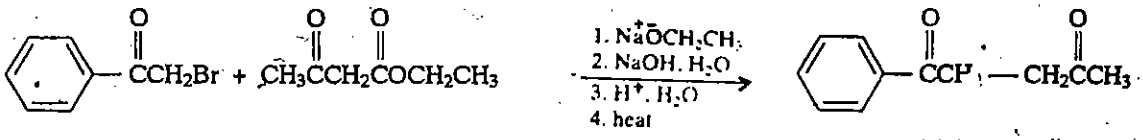
disconnect here
1-phenyl-
1,4-pentanedione

This part can be derived from ethyl 3-oxobutanoate

Therefore, the required halide is,

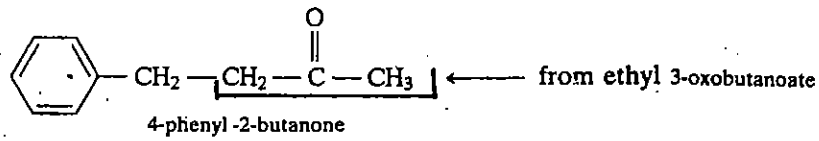


The reaction can be written as,



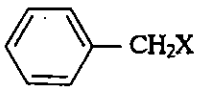
1-phenyl-1,4-pentanedione

b)



4-phenyl -2-butanone ← from ethyl 3-oxobutanoate

The required halide is



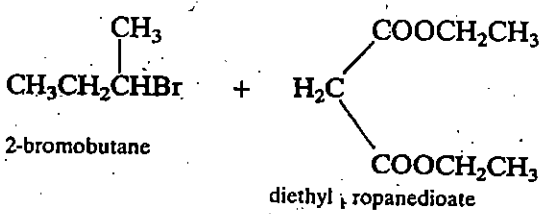
c) $H_2C{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_3$ ← from ethyl

5-hexen-2-one

The required halide is

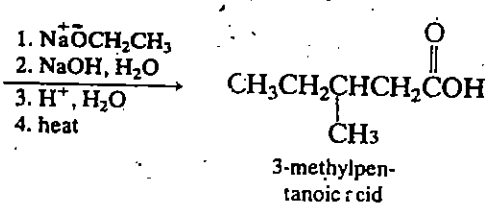
$H_2C{=}CH{-}CH_2X$

7)



2-bromobutane

diethyl propanedioate



3-methylpentanoic acid

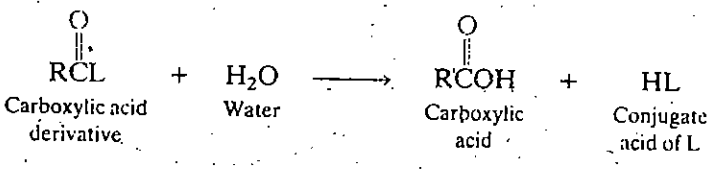
UNIT 17 FUNCTIONAL DERIVATIVES OF MONOCARBOXYLIC ACIDS

Structure

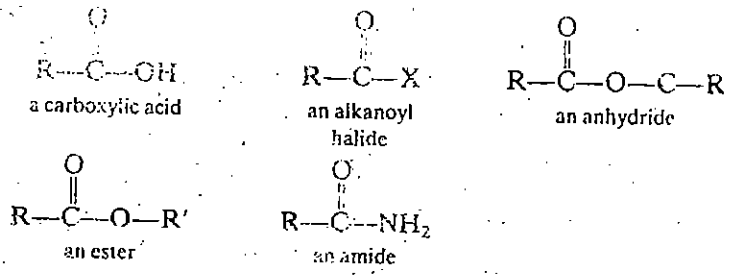
17.1 Introduction
Objective
17.2 Structure of Carboxylic Acid Derivatives
17.3 Physical Properties and Spectral Characteristics of Carboxylic Acid Derivatives
17.4 Basicity and Acidity of Carboxylic Acid Derivatives
17.5 Carboxylic Acid Halides.
Preparation of Carboxylic Acid Halides
Reactions of Carboxylic Acid Halides
17.6 Carboxylic Acid Anhydrides
Preparation of Carboxylic Acid Anhydrides
Reactions of Carboxylic Acid Anhydrides
17.7 Carboxylic Acid Esters.
Preparation of Carboxylic Acid Esters
Reactions of Carboxylic Acid Esters
17.8 Amides
Preparation of Amides
Reactions of Amides
17.9 Summary
17.10 Terminal Questions
17.11 Answers

17.1 INTRODUCTION

A **functional derivative** of a carboxylic acid is a compound which results on replacement of the hydroxyl group of the carboxylic acid by some other group, L. A characteristic feature of these derivatives is that they regenerate the carboxylic acid on hydrolysis, i.e.,



Various functional derivatives of carboxylic acids are possible depending upon the nature of L. The functional derivatives which you will study in this unit include carboxylic acid halides also called alkanoyl halides, anhydrides, ester and amides. These functional derivatives can be represented by the following structures.



You can see that all of these derivatives contain a R—C— or alkanoyl group in their structure. While studying this unit, you will realise that there is not only a structural similarity among carboxylic acids and their derivatives but also a close relationship in their chemistry.

Objectives

After studying this Unit, you should be able to :

- define carboxylic acid derivatives,
- give examples of various carboxylic acid derivatives,
- comment on the acidic and basic behaviour of various carboxylic acid derivatives,
- correlate the reactivities of carboxylic acid derivatives with their structures,
- outline the synthesis of various carboxylic acid derivatives,
- explain the reactions of various carboxylic acid derivatives,
- compare the behaviour of various carboxylic acid derivatives, reaction conditions required in various nucleophilic addition-elimination reactions like hydrolysis, formation of amides, etc., and the nature of products obtained,
- describe the reactions of various carboxylic acid derivatives with organometallic reagents, and
- explain the reduction reactions undergone by carboxylic acid derivatives.

17.2 STRUCTURE OF CARBOXYLIC ACID DERIVATIVES

Similar to the structure of carbonyl compounds and carboxylic acids, the derivatives of carboxylic acids have a trigonal geometry, i.e., all the bonds to the carbonyl carbon are in the same plane. This is shown in Fig. 17.1.

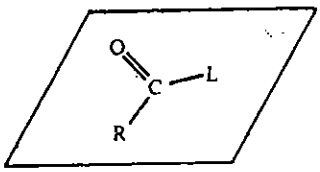


Fig. 17.1 : Planar arrangement of bonds to the carbonyl carbon in carboxylic acid derivatives

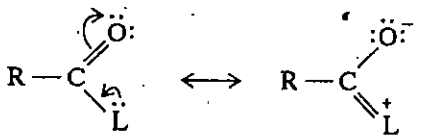
An important structural feature of carboxylic acid derivatives is that the atom attached to the $RC(=O)-$ group bears an unshared pair of electrons which is capable of interacting with the π electrons of the carbonyl group. This is shown in Fig. 17.2.

Individual p orbitals of a carboxylic acid derivative

Extended π system of a carboxylic acid derivative

Fig. 17.2 : The extended π electron system in carboxylic acid derivatives.

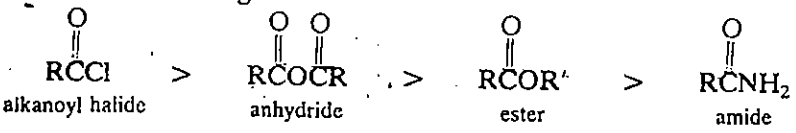
This electron delocalisation can be represented by the following resonance structures.



The extent of this electron delocalisation depends on the electron donating properties of L. Thus, a less electronegative L will donate the electrons more easily than a more electronegative L. The electron release from L reduces the polarisation of the carbonyl group, thereby, decreasing its electrophilic character. Thus, the greater the

electron release from L, the greater is its stabilising effect. Consequently, when L is more electronegative, the extent of resonance decreases and the reactivity increases. Thus, the reactivity of acid derivatives towards nucleophilic substitution reactions follows the following order:

A derivative higher in this order can be converted to the one lower but not vice-versa.



You will study the nucleophilic substitution reactions of acid derivatives in detail in the later sections of this unit.

The degree of resonance stabilisation is also reflected in the structural parameters and spectral characteristics of carboxylic acid derivatives about which you will study in the next section.

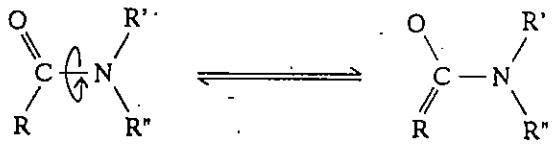
17.3 PHYSICAL PROPERTIES AND SPECTRAL CHARACTERISTICS OF CARBOXYLIC ACID DERIVATIVES

It was pointed out in the earlier section that the extent of resonance is reflected in the structural parameters. This can be understood when we compare the C-L bond lengths in various acid derivatives with the C-L bond lengths in the compounds of the type R-L. These bond lengths are listed in Table 17.1.

Table 17.1 : C-L Bond lengths of some carboxylic acid derivatives and of some compounds of R-L type

L	in R—C(=O)—L (pm)	in R—L (pm)
Cl	179	178
OCH_3	136	143
NH_2	136	147

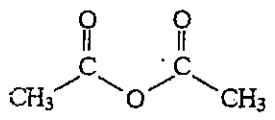
The bond lengths shown in Table 17.1 indicate that as we go from the most reactive alkanoyl halides to the much less reactive esters and amides, the C-L bond becomes shorter as compared to the normal C-L single bond. Thus, in amides the contribution of the dipolar structure II, is strong enough to impart a double bond character to the carbon-nitrogen bond. The double bond character is also indicated by a barrier of 75 to 84 kJ mol^{-1} to the rotation of the carbon-nitrogen bond.



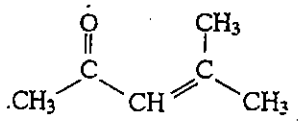
The other physical properties for various carboxylic acid derivatives are briefly stated below.

Alkanoyl halides and anhydrides

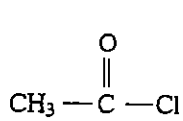
The lower members of these derivatives are dense, water-insoluble liquids with piercing odours. Their boiling points are not very different from those of other polar molecules of similar molecular weight and shape. Some examples are given below:



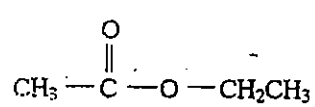
b.p. 413 K

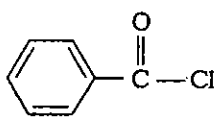


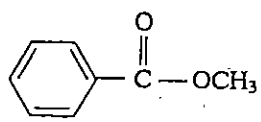
b.p. 403 K



b.p. 324 K





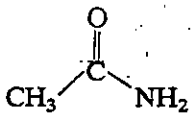


Esters

The lower members of this class are volatile, fragrant liquids having lower density than water. Most esters are not soluble in water.

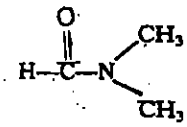
Amides

The lower members are water-soluble, polar in nature and have high boiling points. Primary and secondary amides associate to form hydrogen bonded dimers or higher aggregates in solid and liquid state.



ethanamide
m.p. 355 K
b.p. 494 K

A number of amides have high dielectric constants. *N, N*-dimethylmethanamide (commonly known as *N,N*-dimethylformamide, abbreviated as DMF) is widely used as polar aprotic solvent.



N,N-Dimethylmethanamide

Spectral Characteristics

The increased contribution of the dipolar resonance structure II, weakens the C=O bond resulting in a corresponding decrease in the carbonyl stretching frequency as shown in Table 17.2.

Table 17.2 : Carbonyl stretching frequencies of carboxylic acid derivatives, RCL

L	$\bar{\nu}_{c=o}$ (cm^{-1})	
Cl	1790-1815	
OCR	1740-1790 1800-1850	two bands are observed due to symmetric and asymmetric stretching.
OR	1735-1750	
NR_2	1650-1690	

Primary and secondary amides show the N-H stretching absorption in the region 3200-3400 cm^{-1} and a strong N-H bending absorption near 1640 cm^{-1}

The positions of signals in the NMR spectra of various carboxylic acid derivatives are given in Table 17.3.

Table 17.3 : The chemical shifts of the methyl protons in carboxylic acid derivatives

CH_3CL	δ (−CH_3 protons)
CH_3COR	2.1
CH_3CCl	2.67
CH_3CNR_2	2.0

The N-alkyl protons of amides show chemical shifts in the range δ 2.6-3 and the N-H protons of primary and secondary amides show chemical shifts in the δ 7.5-8.5 region. The N-H signals, similar to O-H signals are broad and are D_2O exchangeable.

SAQ 1

The amide, $CH_3\overset{\overset{O}{\|}}{C}NH—CH_3$ showed three signals in its NMR spectrum at the following δ values:

1.97(s), 2.74(d) and 8.18 (broad D_2O exchangeable).

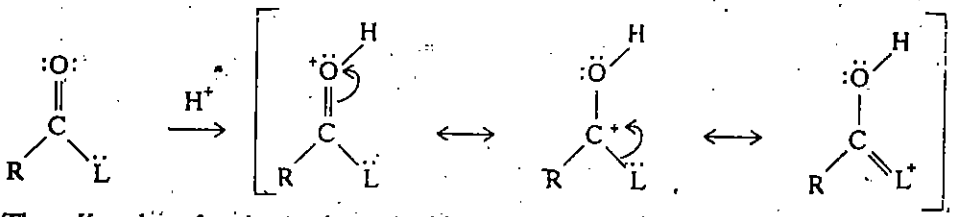
Assign these signals to the protons in the amide.

.....

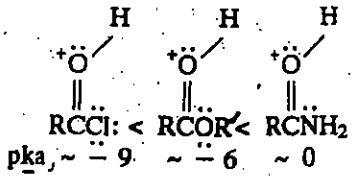
.....

17.4 BASICITY AND ACIDITY OF CARBOXYLIC ACID DERIVATIVES

Carboxylic acid derivatives are weakly basic at the carbonyl oxygen which can be protonated using strong acids. This property is particularly useful in some of the acid-catalysed reactions of esters and amides.

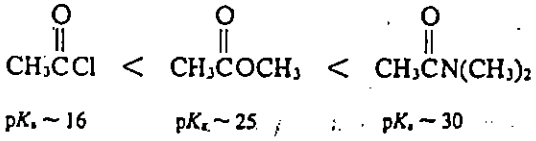


pK_a values of the conjugate acids of carboxylic acid derivatives.

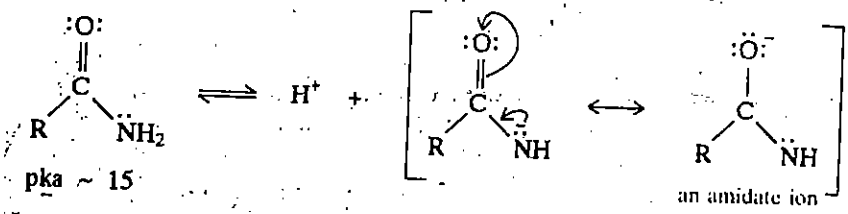


The pK_a values for the conjugate acids of carboxylic acid derivatives show that alkanoyl halides are the weakest bases as their conjugate acids have the lowest pK_a and are, therefore, strongest acids. Esters are about as basic as carboxylic acids whereas amides are the most basic.

The acidity of the hydrogens next to the carbonyl group shows the following order amongst carboxylic acid derivatives:



Primary and secondary amides are deprotonated at nitrogen to give an **amidate ion** which is resonance stabilised in the same way as the carboxylate ion.

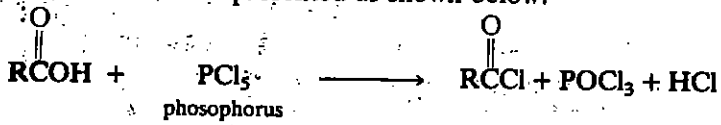


Let us now study about each of these derivatives in detail.

17.5 CARBOXYLIC ACID HALIDES

17.5.1 Preparation of Carboxylic Acid Halides

Carboxylic acid halides can be prepared from carboxylic acids using the acid chlorides of inorganic acids such as PCl_5 (acid chloride of phosphoric acid), PCl_3 (acid chloride of phosphorus acid) and $SOCl_2$ (acid chloride of sulphurous acid). The general reactions can be represented as shown below:



$$3\,RCOH + PCl_3 \longrightarrow 3\,RCCl + H_3PO_3$$

phosphorus trichloride

$$RCOH + SOCl_2 \longrightarrow RCCl + SO_2 + HCl$$

thionyl chloride

Carboxylic acid fluorides, bromides and iodides are prepared from carboxylic acid chlorides by reaction with HF, HBr and HI, respectively.

$$RCCl + HX \longrightarrow RCX + HCl$$

HX = HF, HBr or HI

17.5.2 Reactions of Carboxylic Acid Halides

The reactions of carboxylic acid halides are listed in Table 17.4.

Table 17.4 : Reactions of Carboxylic Acid Halides

A. Reactions with Nucleophiles

$$RCL + Nu^- \longrightarrow RCNu + L^-$$

where NuH = H_2O, RCOOH, ROH, $ArOH, NH_3$, NR_2 and organometallic reagents.

B. Reduction

$$RCl \xrightarrow[\text{or hydride reduction}]{H_2/\text{catalyst}} RCH$$

aldehydes

C. Friedal — Crafts reactions (discussed in Unit 9).

A. Reactions with nucleophiles

The reactions of carboxylic acid halides and other carboxylic acid derivatives with nucleophiles proceed via addition-elimination steps which leads to **nucleophilic substitution** at the carbonyl carbon. This is shown below.

$$RCL + :Nu^- \longrightarrow R-C(O^-)(Nu)-L \longrightarrow RCNu + L^-$$

Thus, the nucleophile $:Nu^-$ has substituted the group L in the carboxylic acid derivative.

Carboxylic acid halides react with a variety of nucleophilic reagents such as water, carboxylic acids, alcohols and phenols, amines and organometallic reagents. Let us study each of these reactions in detail using the examples of carboxylic acid chlorides as these are the most readily accessible among the halides.

1. Reaction with Water

It was pointed out earlier that carboxylic acid derivatives, on hydrolysis, yield carboxylic acids. Thus, carboxylic acid halides react with water to give carboxylic acids. For example,

$$CH_3CH_2CCl + HOH \longrightarrow CH_3CH_2COH + HCl$$

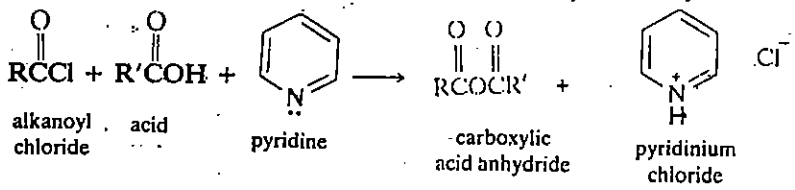
propanoyl chloride → propanoic acid (100%)

This reaction has little synthetic value because acid halides are themselves usually prepared from the acids.

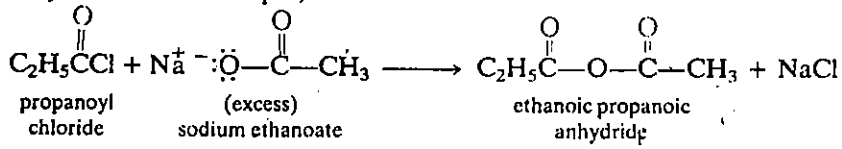
Pyridine acts both as a catalyst as well as a base and neutralises the hydrogen chloride formed in the reaction.

2. Reaction with Carboxylic Acids

Carboxylic acid halides on reaction with carboxylic acids yield acid anhydrides, i.e.,

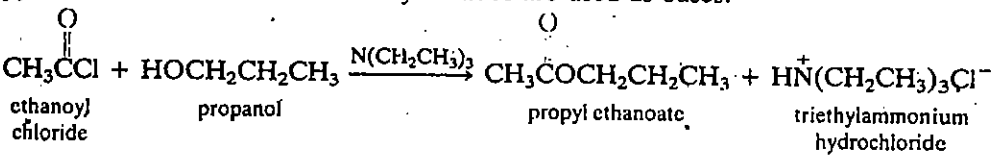


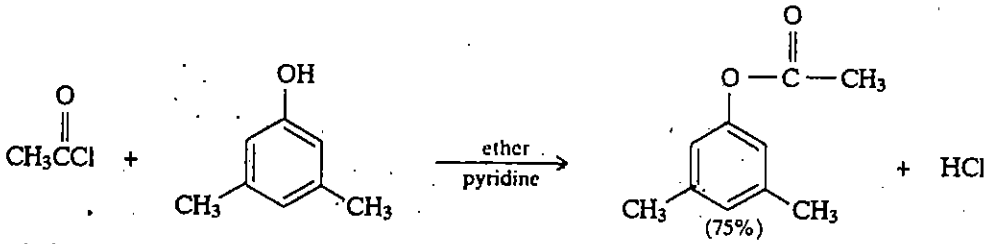
Salts of carboxylic acids also react with carboxylic acid halides to yield the acid anhydrides. For example,



3. Reaction with alcohols and phenols

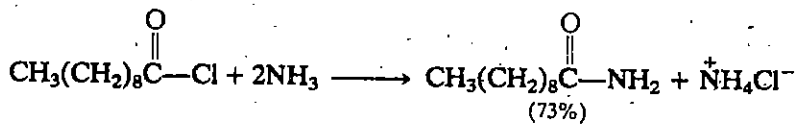
The reaction of carboxylic acid halides with alcohols and phenols yields esters. A base is usually added to neutralise the hydrogen chloride formed as a by-product. Usually pyridine, amines or alkali metal hydroxides are used as bases.



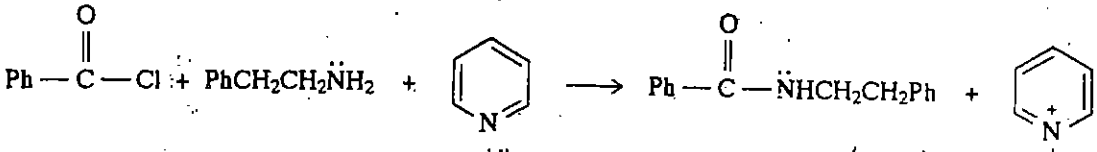


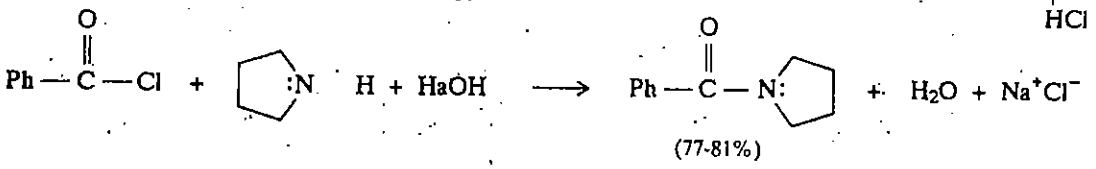
4. Reaction with ammonia and amines

Ammonia and primary and secondary amines react with carboxylic acid halides to yield amides. The reaction with ammonia yields a primary amide as shown below.

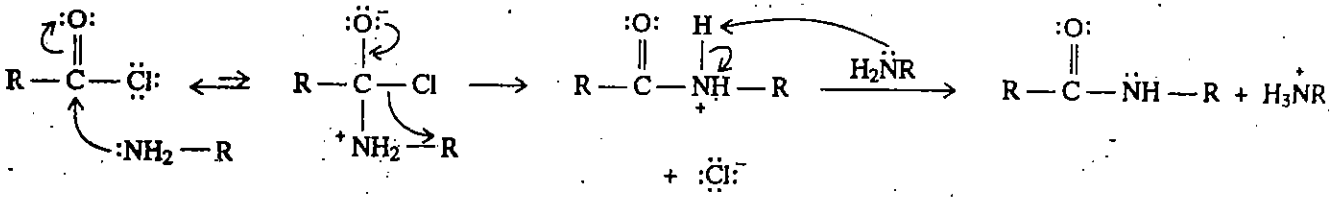


The reaction with primary amines yields a secondary amide whereas the reaction with secondary amines gives a tertiary amide.

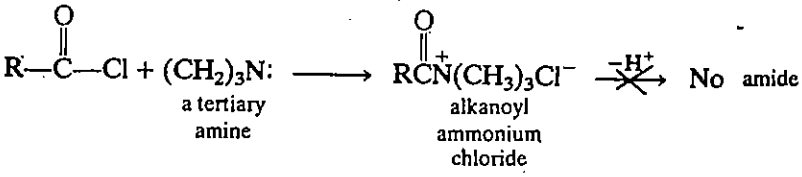




What about the tertiary amines? Do they react with carboxylic acid halides? Before finding an answer to these questions, let us first try to understand the mechanism of the amide formation which is given below:



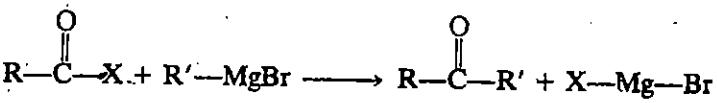
The last step in the mechanism involves loss of a proton from nitrogen which is not possible when the reaction is carried out with tertiary amines.



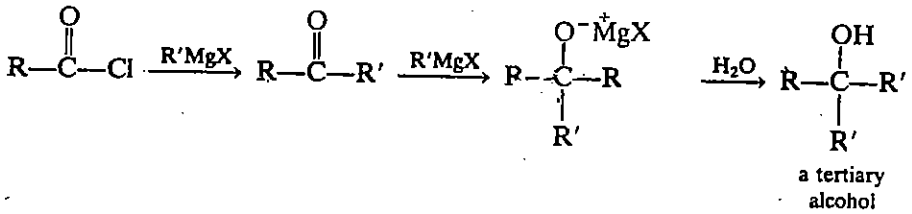
An important aspect of amide formation is that, for each equivalent of the amide formed, an additional equivalent of base is required to neutralise the hydrogen chloride formed. When the amine used in the reaction is cheap and readily available, it is used in excess to serve as a base also. When the amine used to form the amide is expensive and, hence, cannot be used in excess, a tertiary amine, which does not interfere with the reaction, can be used as a base.

5. Reaction with organometallic reagents

Carboxylic acid halides react with a number of organometallic compounds to yield ketones. When a Grignard reagent is used, the best results are obtained if the reaction is carried out at low temperature using *one* equivalent of the Grignard reagent.

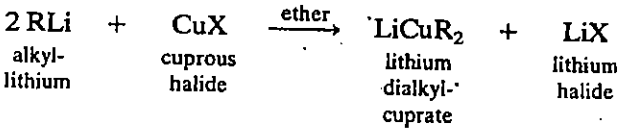


If an excess of the Grignard reagent is used, the ketone obtained reacts further to yield an alcohol as shown below:

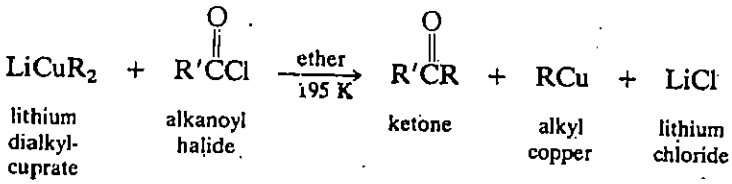


Thus, to synthesise a ketone from a carboxylic acid halide, the organometallic reagent used should be so chosen that it reacts much faster with the starting halide than it does with the product ketone. Two types of organometallic reagents which satisfy this requirement are organocuprate reagents and organocadmium reagents.

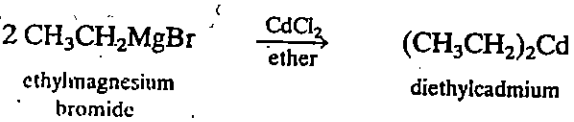
Organocuprate reagents such as dialkyl- and diaryl cuprates are prepared through the reaction of an alkyl- or aryllithium reagent with a cuprous salt.

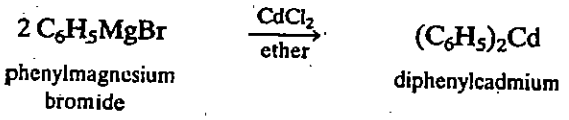


The reaction of a carboxylic acid halide with lithium diorganocuprate yields a ketone.

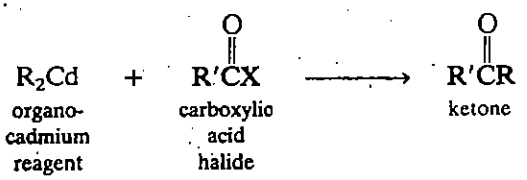


Organocadmium reagents such as dialkylcadmium and diarylcadmium are prepared by treating Grignard reagents with cadmium chloride.





The desired ketone can be prepared by the reaction of the suitable organocadmium reagent with a suitable carboxylic acid halide.

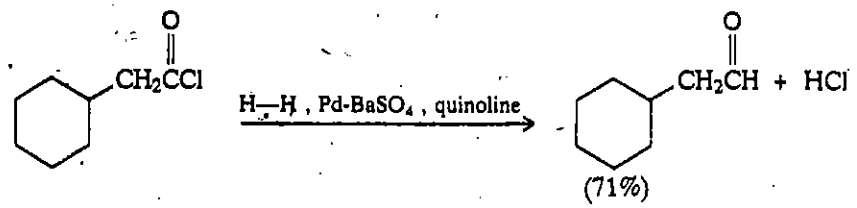


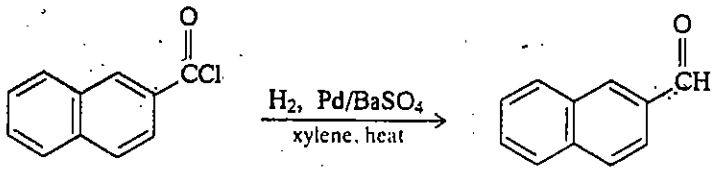
Secondary and tertiary alkylcuprates and also the secondary and tertiary alkylcadmium reagents are not stable and decompose readily and hence, cannot be employed for ketone synthesis. This then limits the synthetic utility of these reactions to primary alkyl and arylcuprates and to primary dialkyl or diarylcadmium reagents.

B. Reduction

Carboxylic acid halides can be reduced to aldehydes by either of two methods: the first method involves catalytic hydrogenation and the second involves hydride reduction.

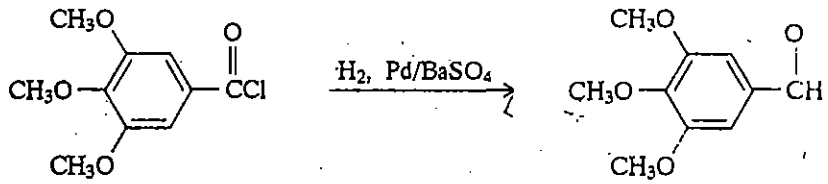
In **catalytic reduction**, the carboxylic acid halide is hydrogenated using a special catalyst such as palladium deposited on barium sulphate **poisoned** with an amine such as quinoline. The poisoning of the catalyst moderates its effectiveness and hence inhibits the subsequent reduction of the product aldehyde to alcohol. This reaction is called the **Rosenmund reduction.**





naphthalene-2-carbonyl chloride

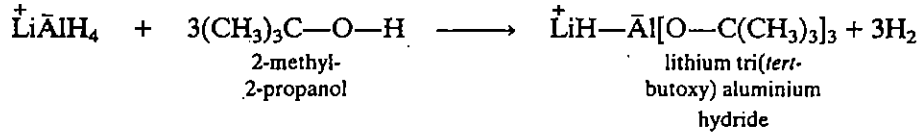
naphthalene-2-carbaldehyde (74-81%)



3,4,5-trimethoxybenzoylchloride

3,4,5-trimethoxybenzaldehyde (71%)

The **hydride reduction** using ordinary reducing hydrides, such as sodium borohydride or lithium aluminium hydride, converts the aldehydes obtained in the reaction to alcohols. This over-reduction can be prevented by using a modified lithium aluminium hydride namely, lithium tri(*tert*-butoxy) aluminium hydride which is obtained by the reaction of lithium aluminium hydride with three equivalents of 2-methyl-2-propanol.



In lithium tri(*tert*-butoxy) aluminium hydride, three of the reactive hydride atoms of lithium aluminium hydride are replaced with alkoxy groups and hence, the one remaining hydride reduces only the most reactive functional groups. Because acid halides are more reactive towards nucleophiles than aldehydes, the reagent preferentially reduces the carboxylic acid halide rather than the product aldehyde.

$$RCCl + LiAl[OC(CH_3)_3]_3H \xrightarrow[2.\ H^+,\ H_2O]{1.\ \text{ether}} RCH + LiCl + Al[OC(CH_3)_3]_3$$

C. Friedel-Crafts reactions

The Friedel-Crafts alkanoylation (acylation) of aromatic compounds using alkanoyl halides was dealt with in sub-Sec. 9.6.5 in Unit 9, Block 2.

SAQ 2

How will you convert butanoyl chloride into the following products.

a) $CH_3CH_2CH_2COH$

.....

b) $CH_3CH_2CH_2COCCH_3$

.....

c) $CH_3CH_2CH_2CO-C_6H_5$

.....

d) $CH_3CH_2CH_2CCN(CH_3)_2$

.....

e) $CH_3CH_2CH_2CCH_2CH_3$

.....

f) $CH_3CH_2CH_2CH$

.....

17.6 CARBOXYLIC ACID ANHYDRIDES

17.6.1 Preparation of Carboxylic Acid Anhydrides

Carboxylic acid anhydrides can be prepared using the methods listed in Table 17.5.

Table 17.5 : Methods of preparation of Carboxylic acid anhydrides

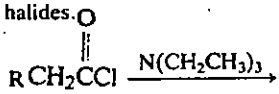
1. From carboxylic acid halides and carboxylic acids
$RCOOH + R'COCl \xrightarrow{\text{pyridine}} RCO{-}O{-}COR' + HCl$
2. From Ketene and carboxylic acids
$CH_2{=}C{=}O + RCOOH \longrightarrow RCO{-}O{-}COCH_3$
(used in commercial preparation of ethanoic anhydride)
3. Using other anhydrides
$2\,R{-}COOH \xrightarrow[\text{or ethanoic anhydride}]{P_2O_5} R{-}CO{-}O{-}CO{-}R$

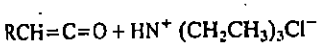
Let us now study these methods in detail.

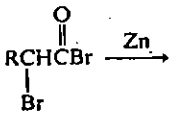
1. From carboxylic acid halides

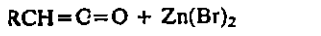
It was pointed out in the last section that carboxylic acid halides react with carboxylic acids or carboxylate salts to give carboxylic acid anhydrides. This reaction can be used to prepare both the simple and the mixed anhydrides.

A general method of preparation of substituted ketenes is based on the dehydrohalogenation of alkanoyl halides or the dehalogenation of 2-halo-alkanoyl halides.



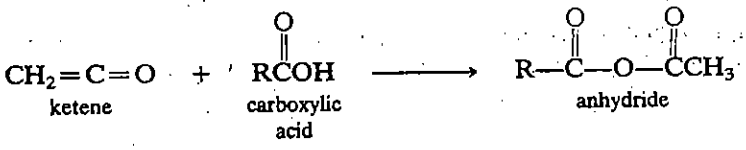






2. From ketene and carboxylic acids

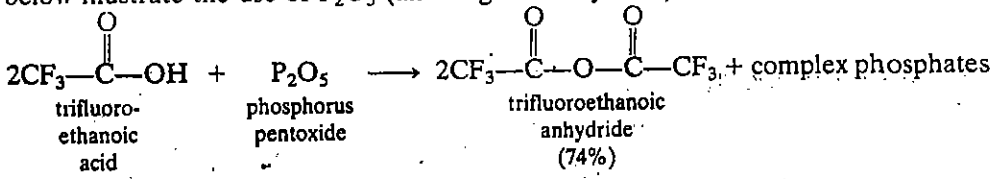
Carboxylic acid anhydrides can also be prepared by the reaction of ketene with carboxylic acids.

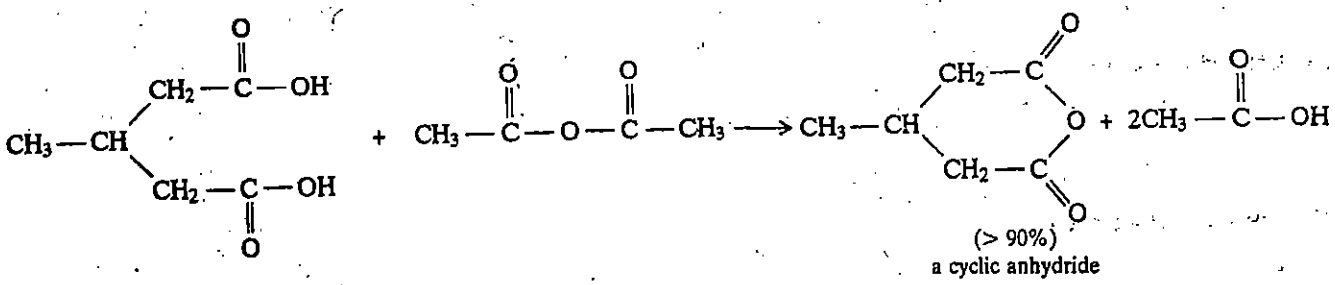


The commerical production of ethanoic anhydride, based on the above reaction, involves the use of ethanoic acid as the carboxylic acid.

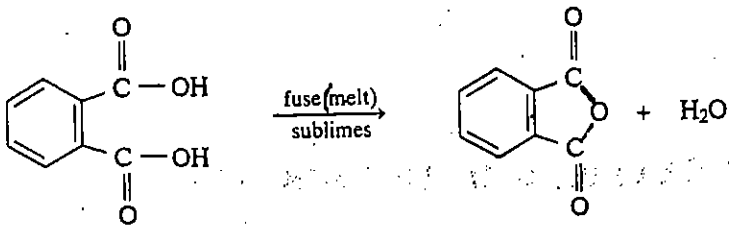
3. Using other anhydrides

Most anhydrides may themselves be used to form other anhydrides. Examples given below illustrate the use of P_2O_5 (an inorganic anhydride) and ethanoic anhydride.





Cyclic anhydrides containing five- and six-membered rings can also be readily prepared just by heating the dicarboxylic acid. For example, 1,2-benzenedicarboxylic acid gives 1,2-benzenedicarboxylic anhydride on heating.



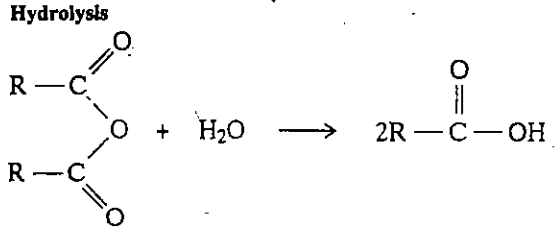
17.6.2 Reactions of Carboxylic Acid Anhydrides

Table 17.6 lists the reactions exhibited by carboxylic acid anhydrides.

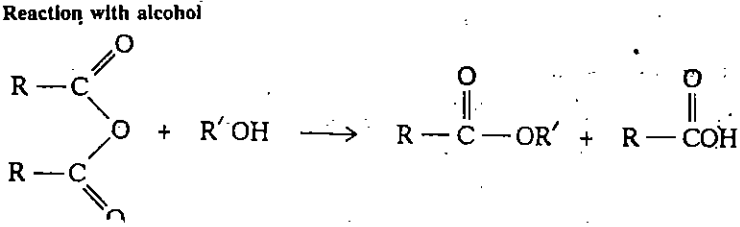
Table 17.6 : Reactions of Acid Anhydrides

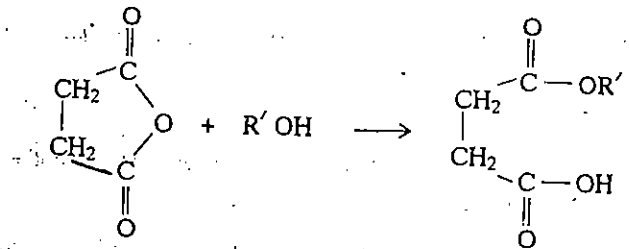
A. Reactions with nucleophiles

1. **Hydrolysis**

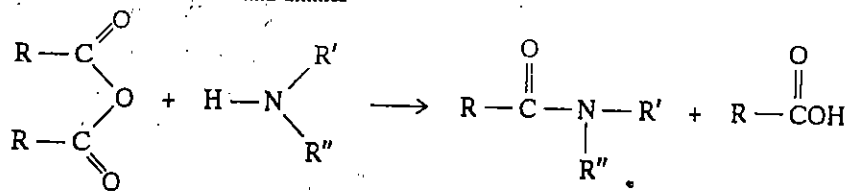


2. **Reaction with alcohol**

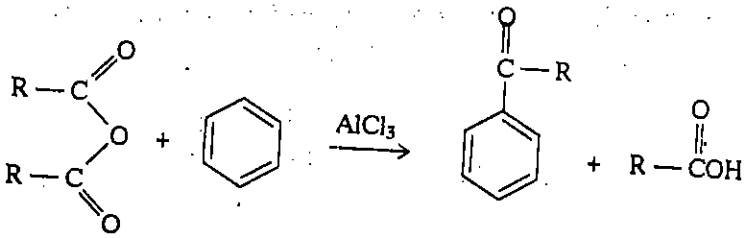




3. **Reaction with ammonia and amines**



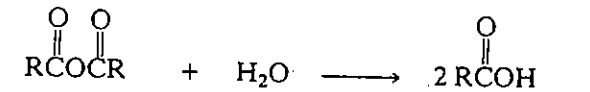
B. Friedel-Crafts alkanoylations



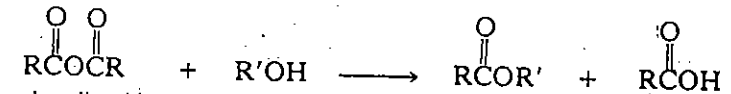
A. Reactions with nucleophiles

The reactions of carboxylic acid anhydrides with nucleophiles are analogous to those of the carboxylic acid halides with you have studied in the last section. The difference here is that the leaving group is a carboxylate ion instead of the halide ion in the case of carboxylic acid halides. The reactions of carboxylic acid anhydrides with water, alcohols and amines are given below:

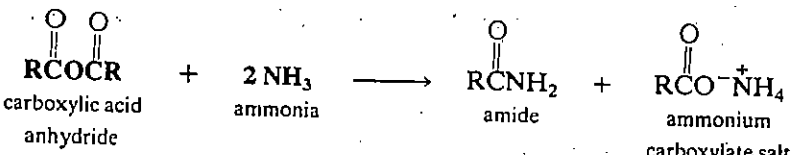
1. Hydrolysis

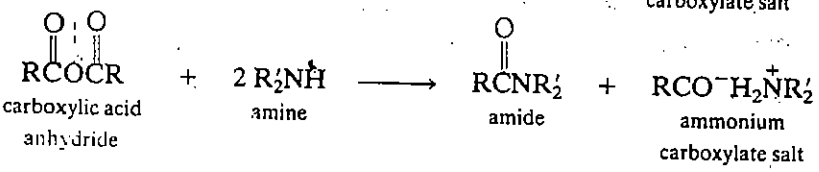


2. Reaction with alcohols



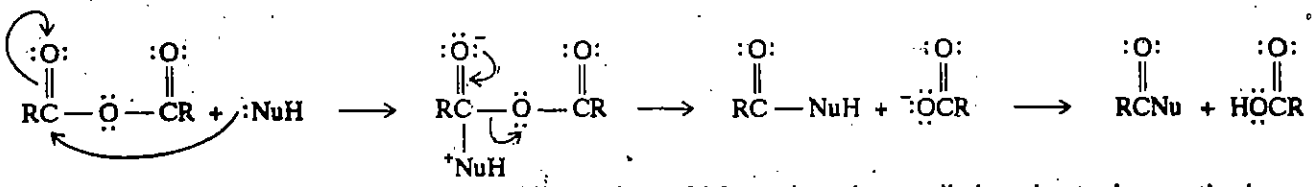
3. Reaction with ammonia and amines





The products in this reaction are amide and carboxylic acid. The carboxylic acid reacts with ammonia or amine to form a salt, therefore, two moles of ammonia or amines are required. Another alternative, as you have studied in the case of carboxylic acid halides is to use one equivalent of a tertiary amine.

The general nucleophilic addition-elimination of anhydrides is shown below:

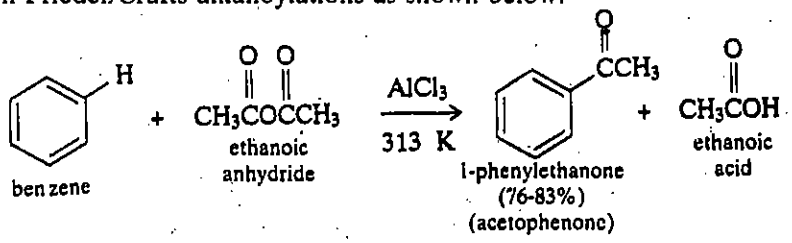


The nucleophilic reactions which you have just studied can be used to synthesise one carboxylic acid derivative from another, as you will study in the later sections.

If you recall the order of reactivities of various carboxylic acid derivatives given in Sec. 17.2 you will realise that the less reactive carboxylic acid derivatives can be synthesised from the more reactive ones but the reverse is usually difficult and requires special conditions or a catalyst.

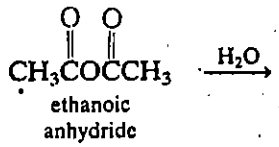
B. Friedel-Crafts alkanoylations

Carboxylic acid anhydrides also serve as sources of alkanoyl cations and can be used in Friedel-Crafts alkanoylations as shown below.



SAQ 3

Write the products of the following reactions:

a) 

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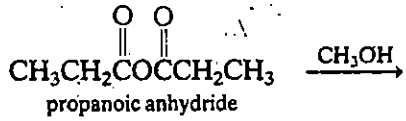
b) 

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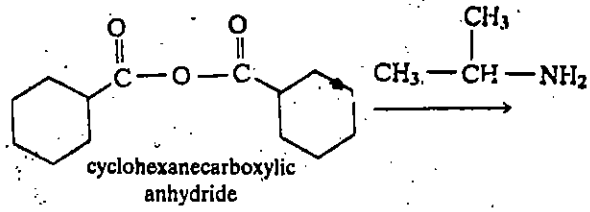
c) 

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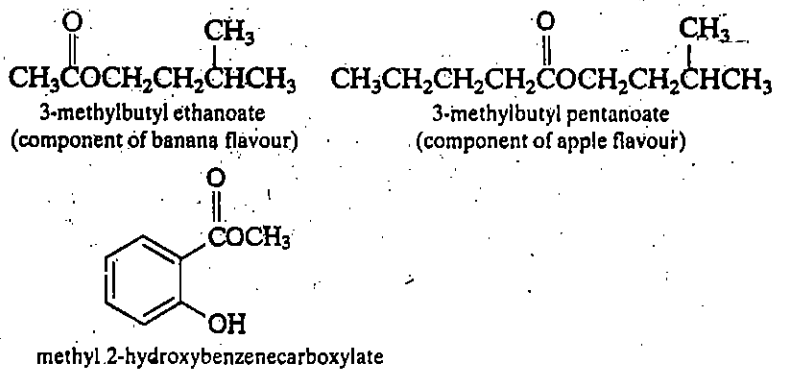
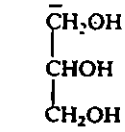
17.7 CARBOXYLIC ACID ESTERS

Carboxylic acid esters constitute a very important class of carboxylic acid derivatives. Some examples of naturally occurring esters are given below.

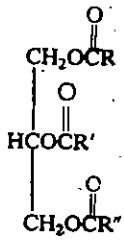
Esters have pleasing odors.



Triesters of 1,2,3-propanetriol (glycerol) constitute the oils and fats found in plants and animals.



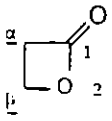
1,2,3-propanetriol (glycerol)



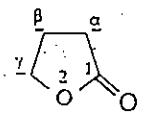
1,2,3-propanetriol triester (triglyceride)

The nomenclature of esters was discussed in Unit 1, Block 1, where you studied that esters are named as **alkyl alkanoates**.

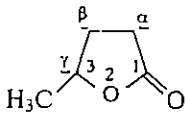
The systematic names of cyclic esters, i.e., lactones, which were not discussed there, are illustrated by the following examples.



oxacyclobutanone



2-oxacyclo-pentanone (γ-butyrolactone)



2-oxa-3-methylcyclo-pentanone (β-valerolactone)

Let us now study the methods of preparation of carboxylic acid esters.

17.7.1 Preparation of Carboxylic Acid Esters

Let us first list the methods of ester formation which you have already studied.

) **From the reaction of carboxylic acids and alcohols (Fischer esterification)** : It was lealt with in detail in sub-Sec. 17.5.2.

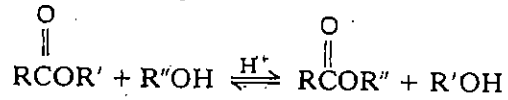
) **From carboxylic acids using diazomethane** : It was also dealt with in Sec. 15.6, Jnit 15.

) **From carboxylic acid halides** : The reaction of carboxylic acid halides with lcohols and phenols also yields esters. It involves the use of a weak base. It was iscussed in Sub-section 17.5.2.

) **From carboxylic acid anhydrides** : Carboxylic acid anhydrides react with alcohols ı the presence of acid catalysts to give esters. This reaction was discussed in ıb-Sec. 17.6.2.

ı addition to the above methods, esters can also be prepared by ester interchange hich is discussed below.

Ester interchange : Esters can also be obtained by ester interchange. When an ster reacts with an alcohol under acidic conditions or with an alkoxide ion under ısic conditions, a new ester is formed. This is called **transesterification**. The general action can be represented as shown below:



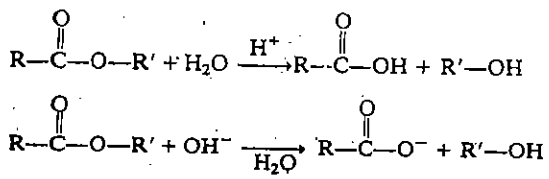
ransesterification will be discussed in detail under the reactions of esters in the next b-section.

7.7.2 Reactions of Carboxylic Acid Esters

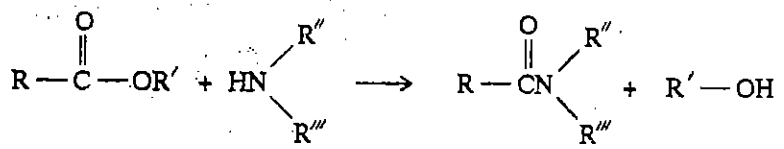
ıe reactions are listed in Table 17.7 followed by their detailed discussion.

Table 17.7 : Reactions of Esters

. Hydrolysis



. Conversion to amides



R′ and/or R‴ may be H

3. Conversion to other esters : transesterification

$$R{-}\overset{\overset{O}{\|}}{C}{-}O{-}R' + R''{-}OH \underset{}{\overset{H^+}{\rightleftharpoons}} R\overset{\overset{O}{\|}}{C}{-}O{-}R'' + R'{-}OH$$

4. Reaction with Grignard reagents

$$R{-}\overset{\overset{O}{\|}}{C}{-}OR'' + 2R'MgX \xrightarrow{\text{ether}} R{-}\overset{\overset{OMgX}{|}}{\underset{\underset{R''}{|}}{C}}{-}R'' + R'OMgX \xrightarrow{H^+} R{-}\overset{\overset{OH}{|}}{\underset{\underset{R''}{|}}{C}}{-}R''$$

5. Reduction

$$R{-}\overset{\overset{O}{\|}}{C}{-}O{-}R' + H_2 \xrightarrow{Ni} R{-}CH_2OH + R'{-}OH$$

$$R{-}\overset{\overset{O}{\|}}{C}{-}O{-}R' + LiAlH_4 \longrightarrow R{-}CH_2OH + R'{-}OH$$

$$R{-}\overset{\overset{O}{\|}}{C}{-}OR' + Na \xrightarrow{C_2H_5\ddot{O}H} R{-}CH_2OH + R'{-}OH$$

6. Formation of enolates

$$RCH_2\overset{\overset{O}{\|}}{C}OR' + :B^- \rightleftharpoons RCH{=}\underset{\underset{OR'}{}}{\overset{\overset{O^-}{}}{C}} + BH$$

ester — ester enolate

1. Hydrolysis

In contrast to the hydrolysis of carboxylic acid halides and anhydrides, esters do not react with water unless a catalyst is present. Both acid-catalysed and base-catalysed hydrolysis reactions are possible.

The acid-catalysed hydrolysis is just the reverse of acid-catalysed formation of esters which was discussed in detail in Sec. 15.6, Unit 15. You studied in Sec. 15.6 that esterification is an equilibrium reaction, i.e.

$$\underset{\text{acid}}{RCOH} + \underset{\text{alcohol}}{R'OH} \underset{}{\overset{H^+}{\rightleftharpoons}} \underset{\text{ester}}{RCOR'} + H_2O$$

In esterification, either excess of the starting alcohol is used or water produced is removed from the reaction mixture to shift the equilibrium in the forward direction. But when ester hydrolysis is the objective, the reaction is carried out using excess of water in the presence of a mineral acid. Remember that acid-catalysed hydrolysis is an equilibrium process.

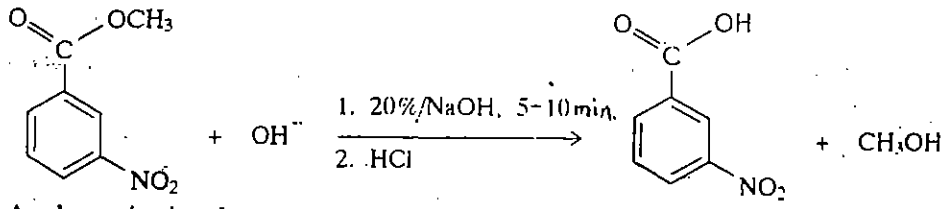
Base-catalysed hydrolysis of esters is called **saponification** because it was initially used in the manufacture of soaps from fats. This term is now sometimes used to refer to base-catalysed hydrolysis of any acid derivative.

Base-catalysed hydrolysis of esters is faster than acid-catalysed hydrolysis.

In contrast to acid-catalysed hydrolysis, base-catalysed hydrolysis of esters is not an equilibrium process but is *irreversible* because the carboxylic acid produced on hydrolysis is converted to its anion under the basic conditions.

$$\underset{\text{ester}}{RCOR'} + \underset{\text{hydroxide}}{HO^-} \longrightarrow \underset{\text{carboxylate ion}}{RCO^-} + \underset{\text{alcohol}}{R'OH}$$

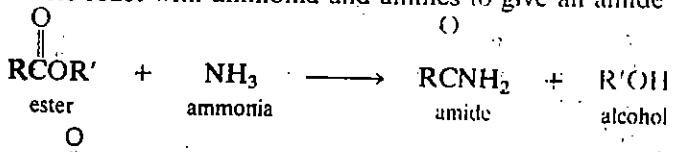
$$\underset{\text{ethyl 3-methylbutanoate}}{CH_3CHCH_2COCH_3} \xrightarrow[2.\ H^+,\ H_2O]{1.\ KOH,\ H_2O,\ CH_3OH,\ \Delta} \underset{\text{3-methylbutanoic acid}}{CH_3CHCH_2COH} + \underset{\text{methanol}}{CH_3OH}$$

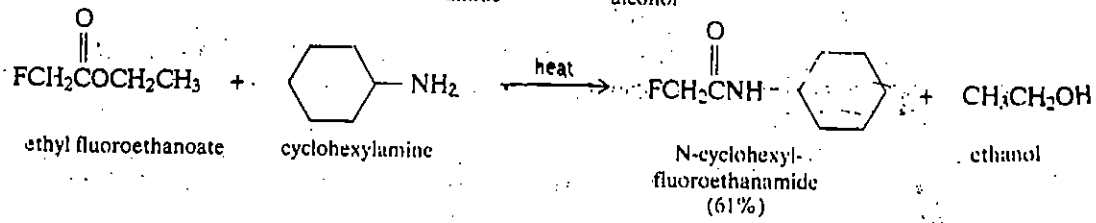


As shown in the above examples, a separate acidification step is required to get the free acid from the carboxylate ion.

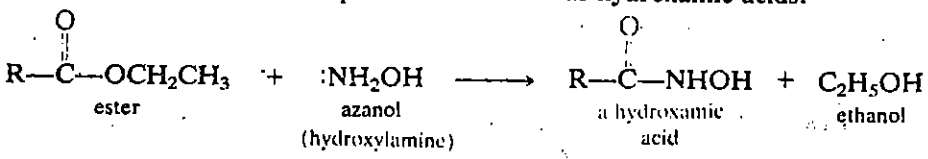
2. Reaction with ammonia and amines : Conversion to amides

Esters react with ammonia and amines to give an amide and an alcohol.





The reaction of esters with azanol (hydroxylamine), ($:NH_2OH$) gives N-hydroxyamides. These compounds are known as **hydroxamic acids.**

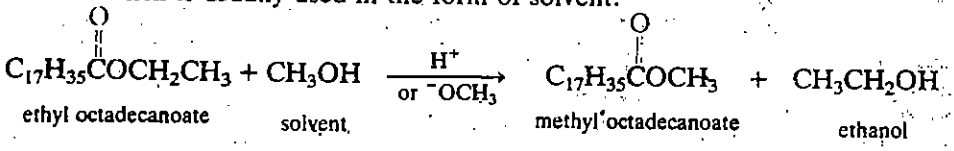


The hydroxamic acids form highly coloured complexes with ferric ion. This chemistry forms the basis of **hydroxamic test** used for the identification of esters.

3. Reaction with alcohols : Transesterification

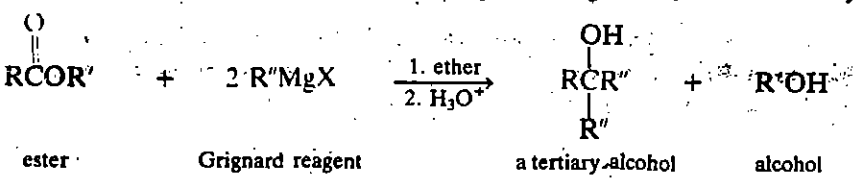
It was pointed out in the last sub-section that a new ester can be synthesised by the reaction of an ester with an alcohol by a process called *transesterification*.

Transesterification is an equilibrium reaction and requires a large excess of the alcohol which is usually used in the form of solvent.

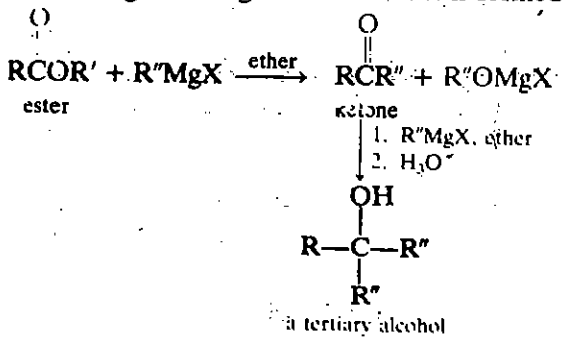


4. Reaction with Grignard reagents

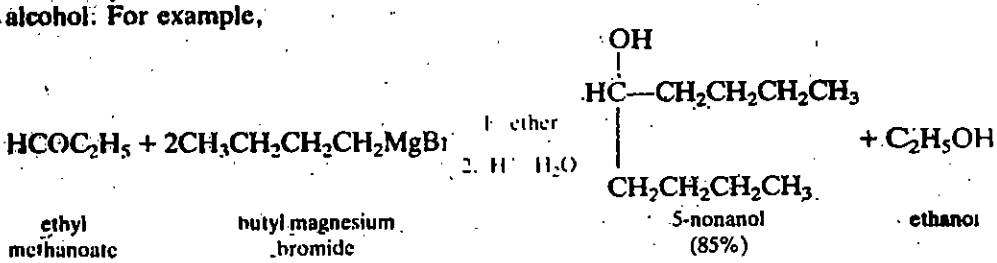
Esters react with two equivalents of a Grignard reagent to produce tertiary alcohols.



A ketone is an intermediate in the reaction but it reacts with the second equivalent of the Grignard reagent as soon as it is formed.



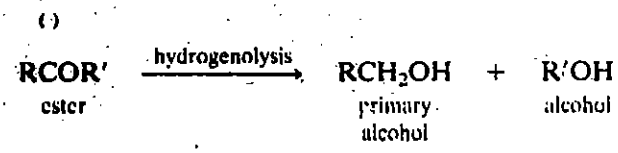
Obviously, methanoic esters on reaction with Grignard reagents yield a secondary alcohol. For example,



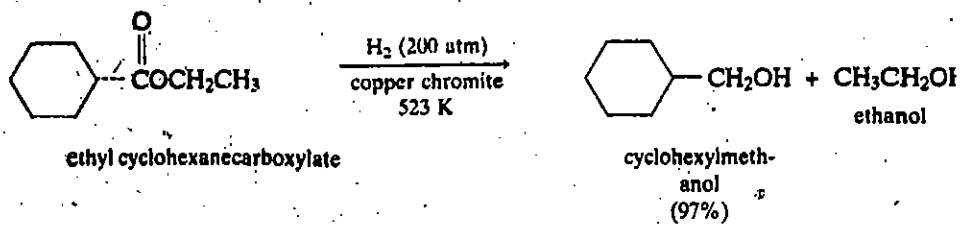
This reaction is a very important method for the synthesis of alcohols having two identical groups attached to carbon atom carrying the hydroxyl group.

5. Reduction

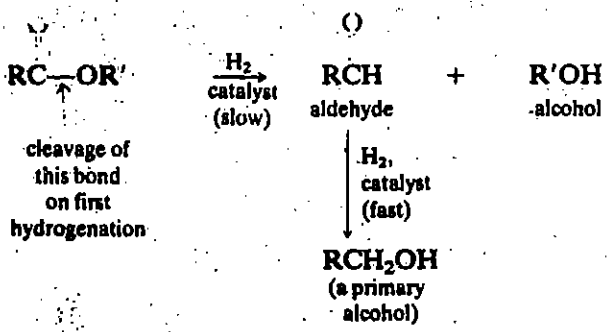
The hydrogenation of esters is accompanied by *cleavage* to yield two alcohols and is, therefore, referred to as **hydrogenolysis.**



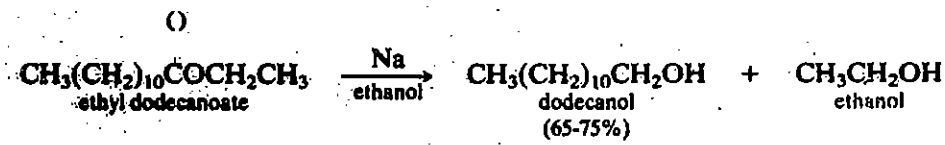
Hydrogenolysis is normally carried over a combination of copper-chromium oxides known as **copper chromite** at high temperature and pressure.



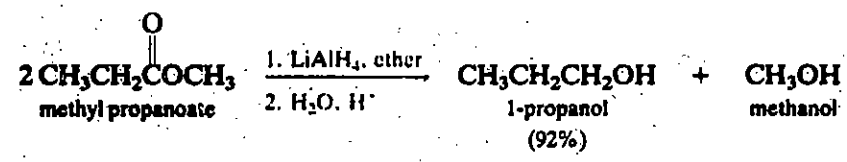
The reduction proceeds in two stages. The first stage involves the formation of an aldehyde which rapidly undergoes reduction to the primary alcohol.



Esters are also reduced by sodium in alcohol. This is a method of long standing and is known as Bouveault-Blanc reduction. It was the common laboratory method before the discovery of lithium aluminium hydride.



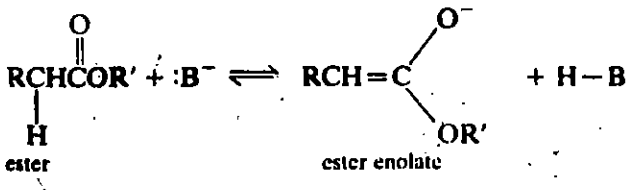
Reduction of esters using lithium aluminium hydride requires only 0.5 equivalent of $LiAlH_4$ because only two of the hydrogens are used per ester function.



This reduction proceeds via the formation of an aldehyde which reacts rapidly with $LiAlH_4$ and yields an alcohol after acidification.

6. Formation of enolates

When esters are treated with strong bases at low temperature, ester enolates are formed. This involves the abstraction of the acidic hydrogen from the carbon atom next to the ester function.



You have already studied the **Claisen condensation** involving ester enolates to yield 3-ketoesters such as ethyl 3-oxobutanoate in Sec. 16.7, Unit 16.

Having studied the reactions of esters, answer the following SAQ.

SAQ 4

Write the expected product(s) of the reaction between ethyl benzoate and the following reagents:

a) H^+, H_2O, heat

.....

b) NaOH, H_2O

.....

c) aqueous NH_3, heat

.....

d) i) $LiAlH_4$,
ii) H_3O^+

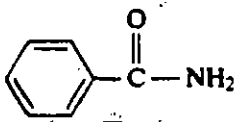
.....

e) i) excess $CH_3CH_2CH_2MgBr$
ii) H_2O, H^+

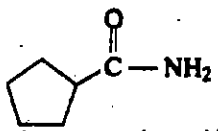
.....

17.8 AMIDES

You are aware from Sec. 1.6, Unit 1, Block 1, that amides can be named by replacing the *-ic* or *-oic acid* suffix of the carboxylic acid with the suffix *amide*. Thus, amides are named as **alkanamides**. Amides are also named as substituted **carboxamides**. The name of the group R in $R—\overset{O}{\overset{\|}{C}}—NH_2$ followed by the suffix carboxamide gives the name according to this system, examples being benzenecarboxamide and cyclopentanecarboxamide.



benzenecarboxamide

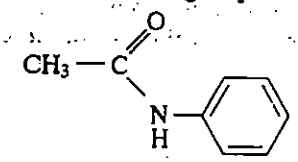


cyclopentanecarboxamide

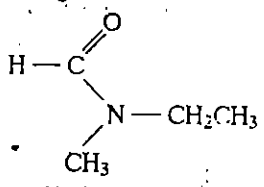
Amides can be classified as primary, secondary or tertiary according to the degree of substitution on the amide nitrogen.

$RCONH_2$	RCONHR'	RCONR'R"
a primary amide	a secondary amide	a tertiary amide

In the case of secondary and tertiary amides, the symbol *N* must precede the name of each different group attached to the nitrogen.

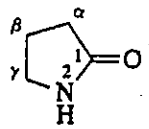


N-phenylethanamide

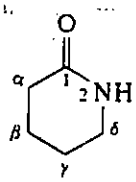


N-ethyl-*N*-methyl-methanamide

Cyclic amides are called **lactams**. The systematic names of some lactams are given below:



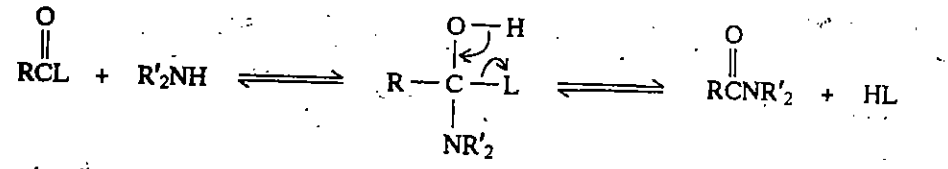
2-azacyclopentanone (γ-butyrolactam)



2-azacyclohexanone (δ-valerolactam)

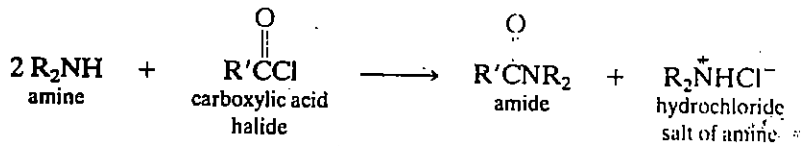
17.8.1 Preparation of Amides

The formation of amides from carboxylic acid halides, anhydrides and esters was discussed in Secs. 17.5.2, 17.6.2 and 17.7.2, respectively. General reactions of the above carboxylic acid derivatives with amines (or ammonia) can be represented as shown below:

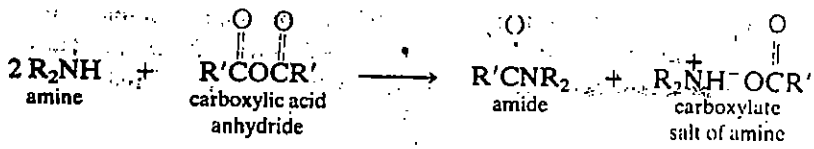


carboxylic acid derivative — amine — tetrahedral intermediate — amide — conjugate acid of the leaving group

You will recall that two molar equivalents of amine are required in case of carboxylic acid halide and anhydride.

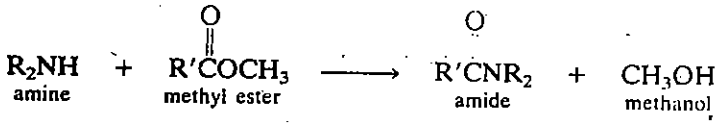


amine — carboxylic acid halide — amide — hydrochloride salt of amine



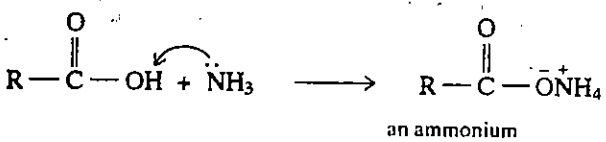
amine — carboxylic acid anhydride — amide — carboxylate salt of amine

But in the case of esters, no acid is formed, therefore, the reaction is carried out using the ester and the amine in 1:1 molar ratio to yield the amide.



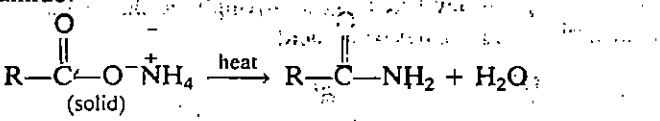
amine — methyl ester — amide — methanol

In addition to the above methods, amides can also be prepared from ammonium carboxylates. Ammonium carboxylates are prepared by the reaction of ammonia with carboxyic acids.



an ammonium carboxylate

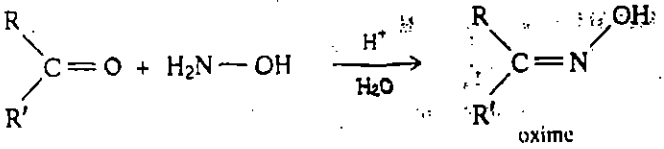
When dry ammonium carboxylates are heated, dehydration takes place to yield an amide.



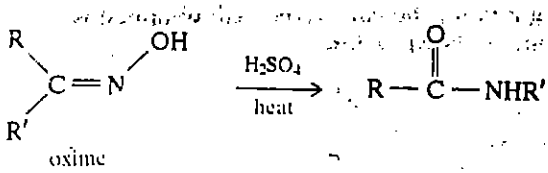
A similar sequence of reactions can be carried out using amines instead of ammonia.

This is a poor method of preparing amides. A much better method is to convert the acid into the acid halide which can yield the amide as discussed in Section 17.5.2, Unit 17.

You may recall from sub-Sec. 14.4.1, Unit 14, Block 3 that ketones react with RNH_2 compounds to yield condensation products. When azanol (hydroxylamine, $HO—NH_2$) reacts with ketones, an oxime is obtained as shown below.



Oximes on heating with a strong acid rearrange to give amides.



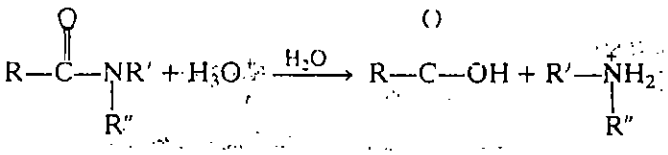
This reaction is known as **Beckmann rearrangement.**

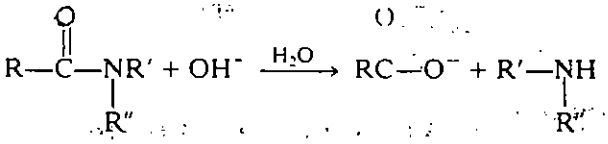
17.8.2 Reactions of amides

The reactions of amides are listed in Table 17.8.

Table 17.8 : Reactions of Amides

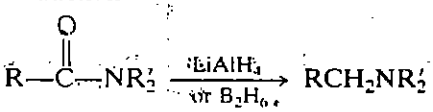
1. Hydrolysis



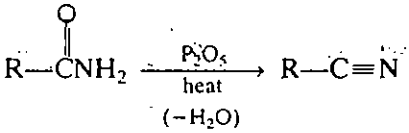


R, R′, and/or R″ may be H

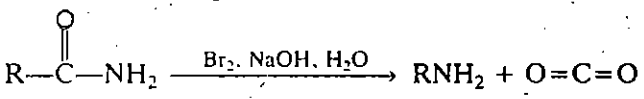
2. Reduction



3. Dehydration



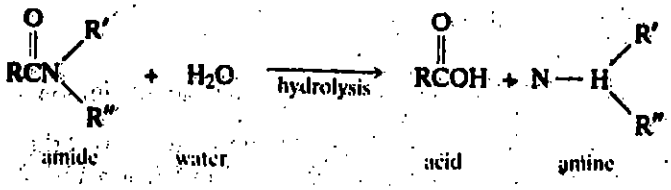
4. Hofmann rearrangement



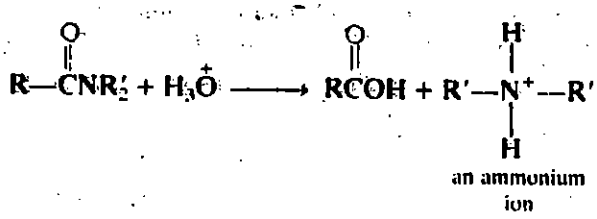
Amides are the least reactive among the carboxylic acid derivatives discussed so far. Therefore, their nucleophilic addition-elimination requires relatively vigrous reaction conditions. Let us understand this by taking the example of hydrolysis.

1. Hydrolysis of amides

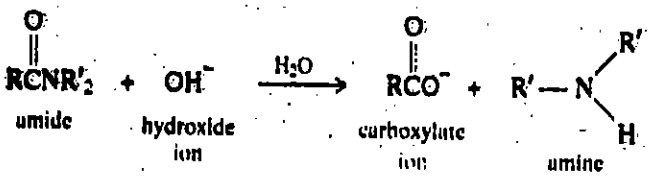
Hydrolysis of amides occurs only on prolonged heating in strongly acidic or basic aqueous conditions to yield an amine and a carboxylic acid.



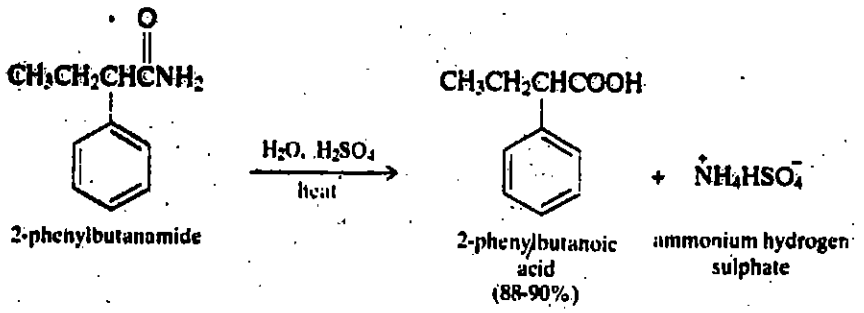
When the hydrolysis is carried out in acidic medium, the amine obtained is protonated to yield an ammonium ion, i.e.,

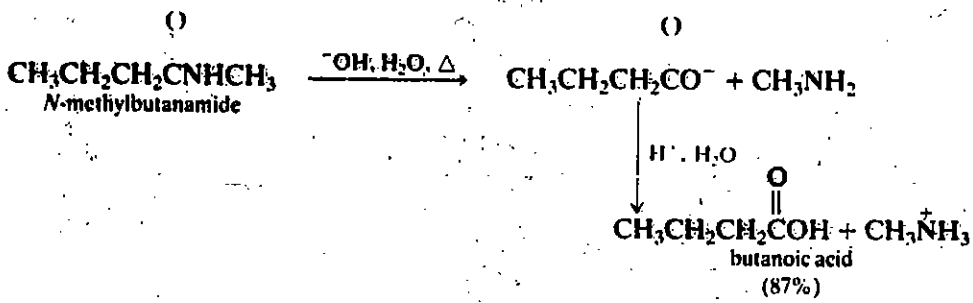


But when the hydrolysis is done using a base, the carboxylic acid obtained is deprotonated to give a carboxylate ion, as shown below:



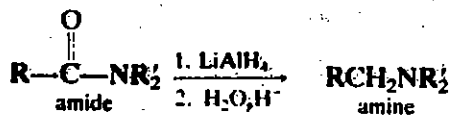
The following examples illustrate amide hydrolysis.

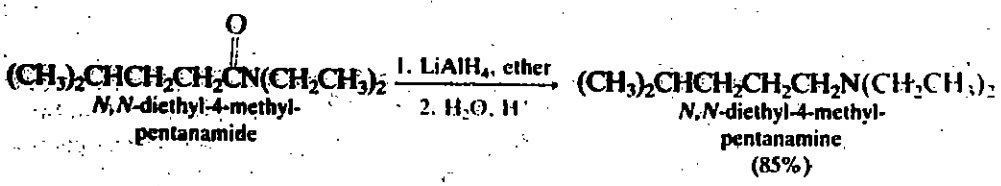




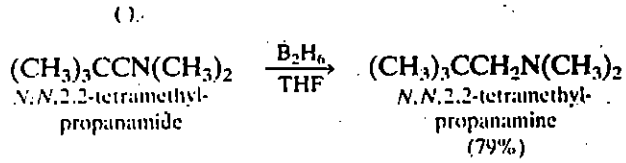
2. Reduction of amides

Amides can be converted into the corresponding amines on reduction with lithium aluminium hydride.





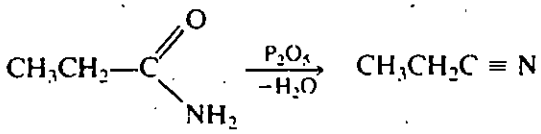
Diborane, B_2H_6, may also be used for the reduction of amides.



N,N,2,2-tetramethyl-propanamide — *N,N*,2,2-tetramethyl-propanamine (79%)

3. Dehydration of amides

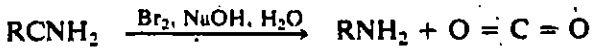
Amides can be dehydrated, using a number of dehydrating agents like P_2O_5 or ethanoic anhydride, to the corresponding nitriles. For example,



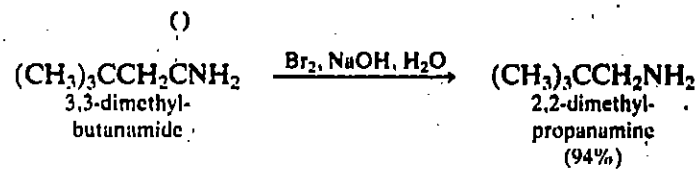
propanamide — propanenitrile (55-70%)

4. Hofmann rearrangement

Primary amides, $RCNH_2$, on treatment with bromine in basic solution undergo an interesting reaction to yield amines.



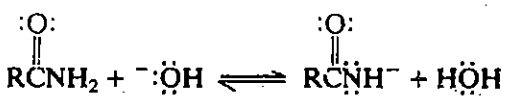
The overall reaction appears as if the carbonyl group is expelled from the amide to give an amine with one carbon atom less than the amide.



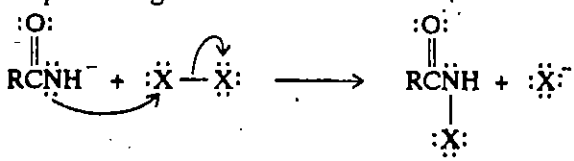
3,3-dimethyl-butanamide — 2,2-dimethyl-propanamine (94%)

The reaction proceeds via the following steps.

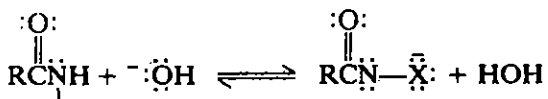
Step 1 Amidate formation



Step 2 Halogenation

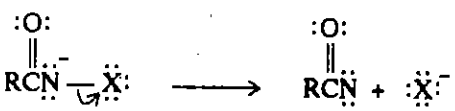


Step 3 *N*-Halo amidate formation

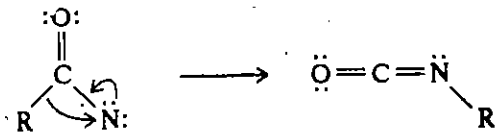


N-haloamidate

Step 4 Halide elimination

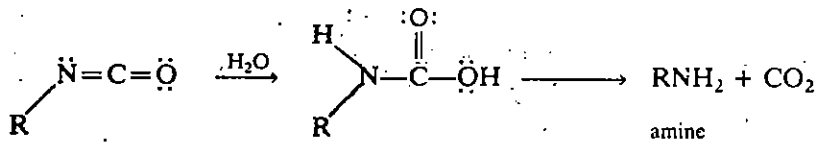


Step 5 Rearrangement



an isocyanate

Step 6 Hydrolysis to carbamic acid and decomposition



After studying the chemistry of amides, answer the following SAQ

SAQ 5

Outline the synthesis of propanamine, $CH_3CH_2CH_2NH_2$ from butanoic acid.

.....

.....

17.9 SUMMARY

In this unit, you have studied that

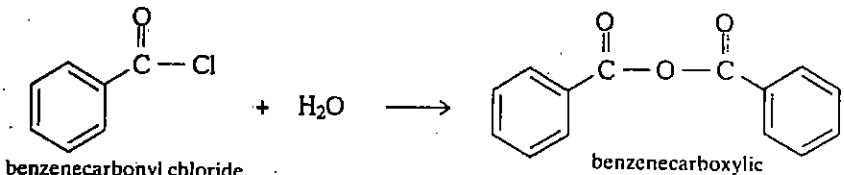
- the functional derivatives of carboxylic acids are those derivatives which are formed by substitution of OH of the carboxy group and can be hydrolysed to yield caboxylic acids.
- various carboxylic acid derivatives can be arranged according to their reactivity in the following order:

carboxylic acid halides > carboxylic acid anhydrides > esters > amides

- the electrophilic reactivity of the carbonyl carbon in carboxylic acid derivatives is weakened by good electron-donating substituents. This also explains the increasing basicity in the series: carboxylic acid halides < anhydrides < esters < amides.
- carboxylic acid derivatives undergo nucleophilic substitution reactions by addition-elimination mechanism.
- one carboxylic acid derivative can be converted into another by nucleophilic addition-elimination and the more reactive derivative can be converted to the less reactive derivative easily but the reverse requires special conditions and suitable catalysts.
- carboxylic acid halides undergo nucleophilic substitution reactions with water, carboxylic acids, alcohols, amines and organometallic reagents.
- reactions of carboxylic acid anhydrides with water, alcohol and amines are similar to carboxylic acid halides.
- esters can be obtained from carboxylic acids, carboxylic acid halides and carboxylic acid anhydrides by reaction with alcohols.
- esters can be hydrolysed both in acidic and basic conditions and they react with amines to yield amides and alcohols. Their catalytic hydrogenation, reaction with Grignard reagents and $LiAlH_4$, yield alcohols.
- amides can be prepared by the reaction of ammonia or amines with carboxylic acid halides, anhydrides and esters. Their important reactions include hydrolysis, reduction, dehydration and Hofmann rearrangement.

17.10 TERMINAL QUESTIONS

1) Benzenecarboxylic anhydride can be prepared by adding one molar equivalent of water to two molar equivalents of benzenecarbonyl chloride, i.e.,

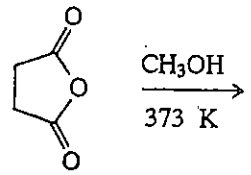


benzenecarbonyl chloride

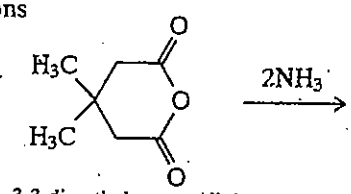
benzenecarboxylic anhydride

Explain how this reaction takes place.

2) Write products of the following reactions

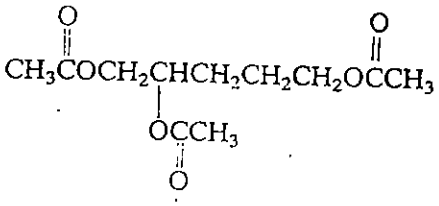
a) 

butanedioic anhydride

b) 

3,3-dimethylpentanedioic anhydride

3) The compound



on hydrolysis in acidic medium gave a compound of molecular formula $C_5H_{12}O_3$. Write the structure of this compound. What other compound is formed in this reaction?

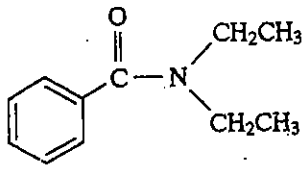
4) Suggest suitable starting materials for the following reactions.

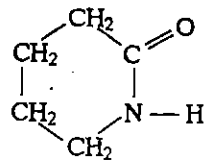
a) ? (an acid halide) + ? ⟶ $(CH_3)_2CHCNH_2$

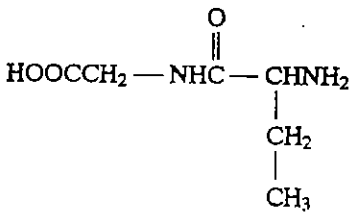
b) ? (an acid anhydride) + ? ⟶ CH_3CNHCH_3

c) ? (a methyl ester) + ? ⟶ $HCN(CH_3)_2$

5) Write the products of hydrolysis of the following compounds.

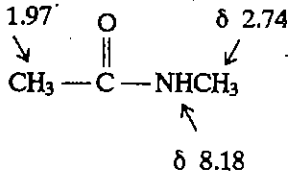
a) 

b) 

c) 

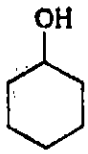
17.11 ANSWERS

Self Assessment Questions

1) 

2) a) H_2O

b) $CH_3\overset{\overset{O}{\|}}{C}O^- Na^+$

c) 

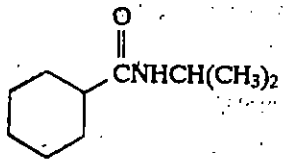
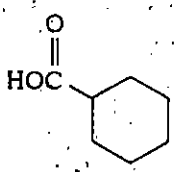
d) $(CH_3)_2NH$

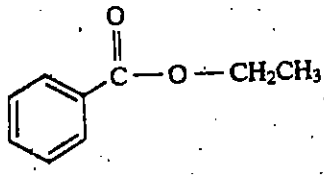
e) CH_3CH_2MgBr

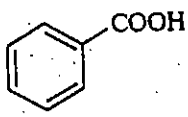
f) $LiAl[OC(CH_3)_3]_3H$

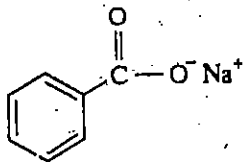
3) a) $2CH_3\overset{\overset{O}{\|}}{C}OH$
ethanoic acid

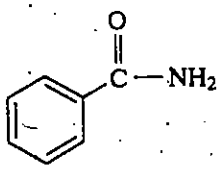
b) $CH_3CH_2\overset{\overset{O}{\|}}{C}OCH_3$ + $HO\overset{\overset{O}{\|}}{C}CH_2CH_3$
methyl propanoate — propanoic acid

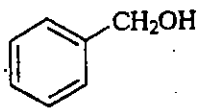
c)  + 
N-(1-methylethyl)-cyclohexanecarboxamide — cyclohexanecar-boxylic acid

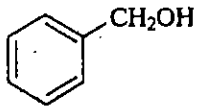
4) 
ethyl benzoate

a) $\xrightarrow{H^+,\ H_2O,\ heat}$  + CH_3CH_2OH

b) $\xrightarrow{NaOH,\ H_2O}$  + C_2H_5OH

c) $\xrightarrow{aq.\ NH_3,\ heat}$  + CH_3CH_2OH

d) $\xrightarrow[2.\ H_2O;\ H^+]{1.\ LiAlH_4}$  + CH_3CH_2OH

e) $\xrightarrow[2.\ H_2O,\ H^+]{1.\ excess\ CH_3CH_2CH_2MgBr,}$  + CH_3CH_2OH

5) $CH_3CH_2CH_2COOH \xrightarrow[2.\ NH_3]{1.\ SOCl_2} CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}NH_2 \xrightarrow[H_2O]{Br_2,\ NaOH} CH_3CH_2CH_2NH_2$

butanoic acid — butanamida — propanamine

Terminal Questions

1) Benzenecarbonyl chloride on reaction with water yields benzenecarboxylic acid which further reacts with second molar equivalent of benzenecarbonyl chloride to yield benzenecarboxylic anhydride.

2) a) $HO\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{O}{\|}}{C}OCH_3$

b) $^{+}NH_4^{-}O\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{CH_3}{|}}{C}CH_2\overset{\overset{O}{\|}}{C}NH_2$ (CH3 branch)

3) $HOH_2C\overset{\overset{OH}{|}}{C}HCH_2CH_2CH_2OH$

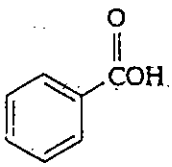
(molecular formula $C_5H_{12}O_3$)

The other product obtained is ethanoic acid.

4) a) $(CH_3)_2CH\overset{\overset{O}{\|}}{C}Cl$ and $2\ NH_3$

b) $CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}CH_3$ and $2\ CH_3NH_2$

c) $H\overset{\overset{O}{\|}}{C}OCH_3$ and $HN(CH_3)_2$

5) a)  + $NH(CH_2CH_3)_2$

b) $H_2NCH_2CH_2CH_2CH_2COOH$

c) $HOOCCH_2-NH_2 + HOOCCH(CH_2CH_3)-NH_2$

UNIT 18 NITRO COMPOUNDS

Structure

18.1 Introduction
Objectives
18.2 Structure and Properties of Nitro Compounds
18.3 Preparation of Nitro Compounds
18.4 Reactions of Nitro Compounds
18.5 Important Uses of Nitro Compounds
18.6 Summary
18.7 Terminal Questions
18.8 Answers

18.1 INTRODUCTION

In Unit 17, you studied the chemistry of carboxylic acid derivatives. In this unit, you will study a very important class of nitrogen containing organic compounds called nitro compounds. You may recall that the nomenclature of nitro compounds was discussed in Block 1, Unit 1, Sec. 1.6. The nitro group can be converted to many other functional groups which makes nitro compounds good starting materials for the synthesis of other organic compounds. Let us first study how nitro compounds can be prepared. Then, we will discuss various reactions of nitro compounds. Finally, the uses of nitro compounds will be explained.

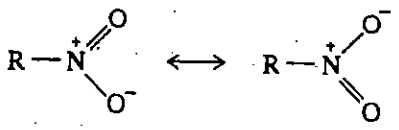
Objectives

After studying this unit, you should be able to:

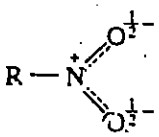
- outline the synthesis of a nitro compound,
- explain the acidic nature of nitro alkanes,
- write reduction products of nitro compounds in different reaction conditions, and
- list the uses of nitro compounds.

18.2 STRUCTURE AND PROPERTIES OF NITRO COMPOUNDS

The nitro group, $-NO_2$, which is the functional group of nitro compounds, is a resonance hybrid of two equivalent contributing structures as shown below.



Thus, it can be represented by the following hydrid structure:



Remember that a similar resonance hydrid was written in the case of carboxylate ion.

Nitro Compound	*b.p./K*
nitromethane	374
nitroethane	387
2-nitropropane	393
1-nitropropane	404
nitrobenzene	484

You can see in the hydrid structure that there is a positive charge on the nitrogen atom and the negative charge is distributed equally on the two oxygen atoms. This separation of charge is reflected in the high dipole moment values for nitro compounds which range between 11.67×10^{-30} C m and 13.35×10^{-30} C m, depending upon the nature of the hydrocarbon group. Their polar nature is also indicated by their high boiling points.

Spectral properties of nitro compounds

Aliphatic nitro compounds show an absorption near 270 nm in their ultraviolet spectrum due to $n \rightarrow \pi^*$ transitions. However, aromatic nitro compounds absorb at longer wavelengths, i.e., ~300 nm, due to the extended conjugation.

The infrared spectra of nitro alkanes show strong bands at about 1550 cm^{-1} and 1375 cm^{-1} whereas aromatic nitro compounds show these absorptions at slightly lower frequencies.

18.3 PREPARATION OF NITRO COMPOUNDS

The nitro compounds can be prepared by a number of methods. Let us now study these methods.

1. By direct nitration of hydrocarbons

Hydrocarbons can be nitrated using nitric acid. The reaction with aliphatic hydrocarbons requires high temperatures and is carried out in the vapour phase. For example,

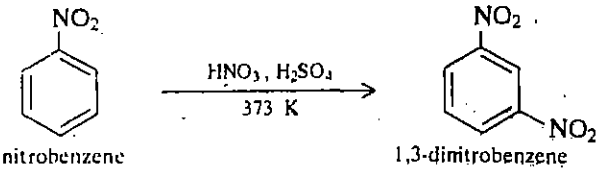
$$\underset{\text{methane}}{CH_4} + HNO_3 \xrightarrow{673\ K} \underset{\text{nitromethane}}{CH_3NO_2} + H_2O$$

Nitration is accompanied by oxidation.

You have studied, under the nitration of alkanes in sub-Sec. 6.6.2, Unit 6, Block 2, that nitration of higher alkanes yields a mixture of nitroalkanes which are separated using fractional distillation.

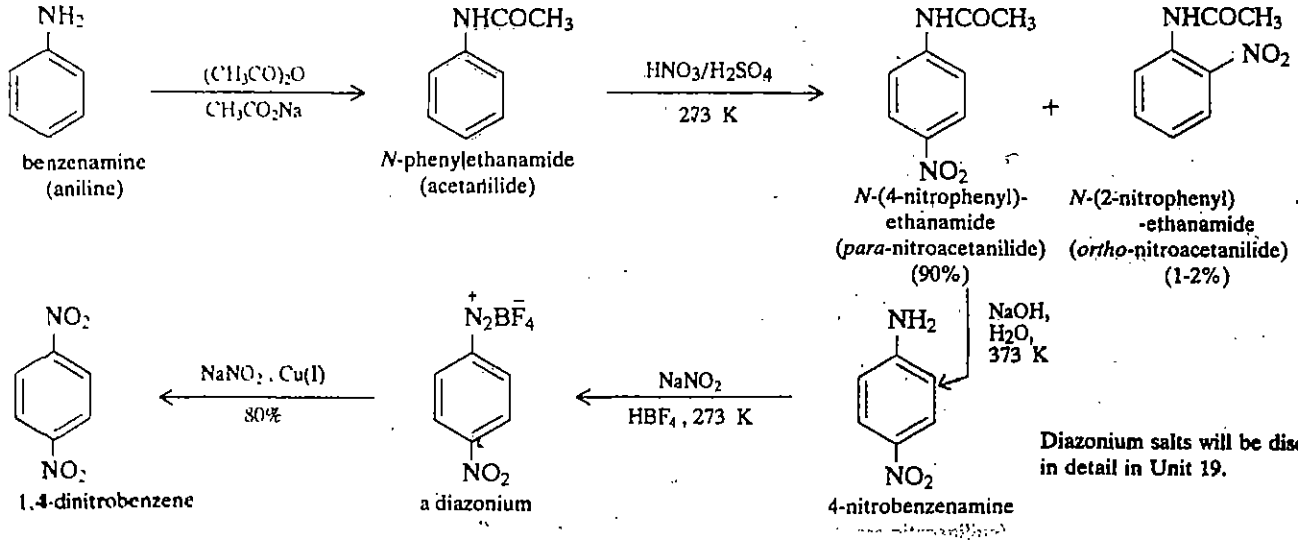
In contrast to this, nitration of aromatic compounds takes place readily in the liquid phase and can be carried out near room temperature or on a steam bath. You have already studied about the nitration of benzene in sub-Sec. 9.6.1, Unit 9, Block 2. You may recall that nitration of aromatic compounds is an electrophilic substitution reaction, the electrophile being the nitronium ion, NO_2^+.

The products of nitration of substituted benzenes depend upon the nature of the substituent groups already present in the molecule. The nitro group itself is *meta*-directing and, therefore, nitration of nitrobenzene yields 1,3-dinitrobenzene as the major product.



nitrobenzene — 1,3-dinitrobenzene

1,4-Dinitrobenzene can be prepared by starting with benzenamine. Since the amino group is *o*-, *p*- directing, nitration of benzenamine followed by the conversion of the amino group to nitro group, should give the desired compound. Benzenamine, however, is susceptible to oxidation, so the amino group is first protected by ethanoylation (acetylation). The sequence of reactions is outlined below:

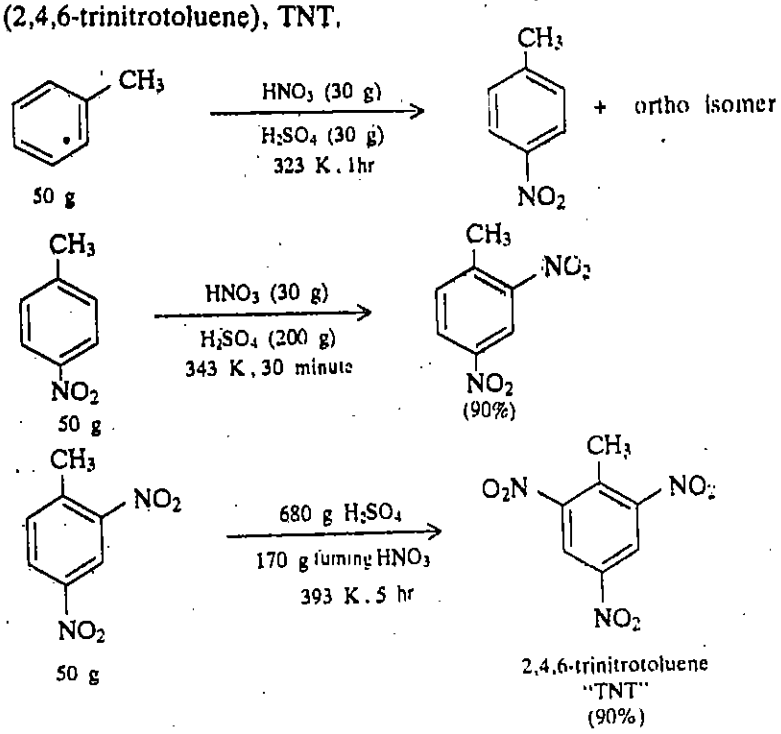


benzenamine (aniline) — *N*-phenylethanamide (acetanilide) — *N*-(4-nitrophenyl)-ethanamide (*para*-nitroacetanilide) (90%) — *N*-(2-nitrophenyl)-ethanamide (*ortho*-nitroacetanilide) (1-2%)

4-nitrobenzenamine — a diazonium — 1,4-dinitrobenzene

Diazonium salts will be discussed in detail in Unit 19.

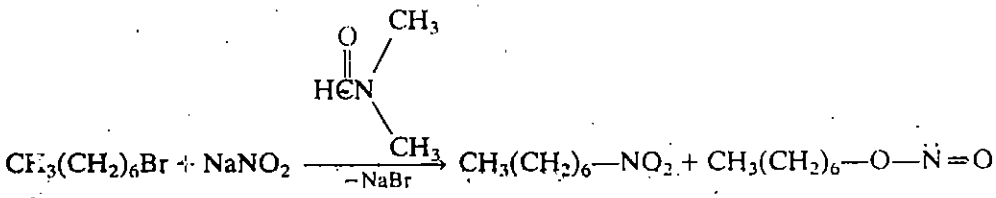
Nitration reactions to yield trinitro derivatives require very harsh reaction conditions, e.g. prolonged heating of the starting nitro compound with nitric acid in fuming sulphuric acid. But, by using activating groups further nitration is facilitated and methylbenzene can be converted more readily to 2-methyl-1,3,5-trinitrobenzene (2,4,6-trinitrotoluene), TNT.



TNT is an important explosive. It is relatively insensitive to shock and hence is used with a detonator. When mixed with ammonium nitrate it yields the explosive *amatol*.

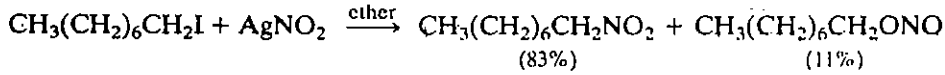
2. Substitution by nitrite ion

Some nitro compounds can be prepared by the reaction of alkyl halides with sodium nitrite using dimethylmethanamide as solvent.

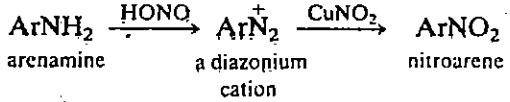


Some alkyl nitrite is usually obtained as by-product in this reaction.

Better yields of nitroalkanes are obtained when silver nitrite is used instead of sodium nitrite. But as you know, silver nitrite is expensive and is not economical for large scale production of nitro compounds.



Aryl nitro compounds or nitroarenes cannot be synthesised from aryl halide by a similar route. Instead, nitroarenes are prepared by displacement of the diazonium group. This will be dealt with in Unit 19. The reaction of arenamines to yield diazonium salts which can be used to prepare nitroarenes can be represented as shown below:



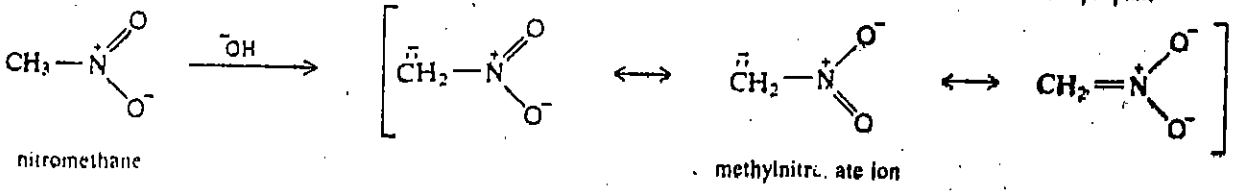
Let us now study the reactions of nitro compounds.

18.4 REACTIONS OF NITRO COMPOUNDS

1. As weak acids

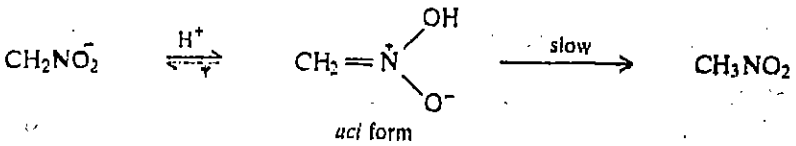
The hydrogen atoms bonded to the carbon atom carrying the nitro group are acidic in nature. Thus, nitro compounds dissolve in bases like sodium hydroxide. The anion so produced is resonance stabilised as shown below:

nitroalkane	pK_a
nitromethane	10.2
nitroethane	8.5
nitropropane	7.8



nitromethane — methylnitrate ion

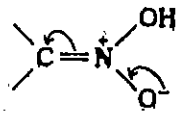
On acidification, the anion yields the acidic isomer of nitromethane known as the *aci* form which slowly changes to the more stable nitro form.



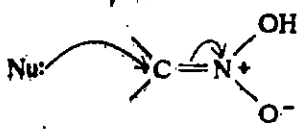
aci form

The aci form can behave both as a nucleophile as well as an electrophile.

as nucleophile:

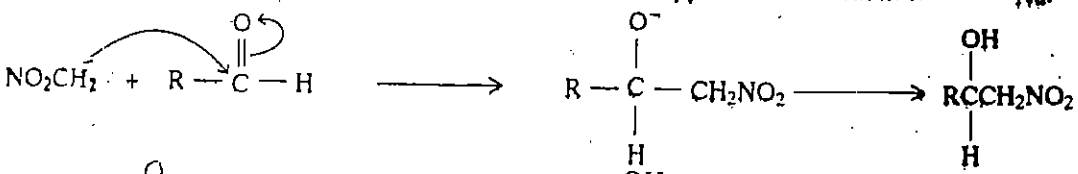


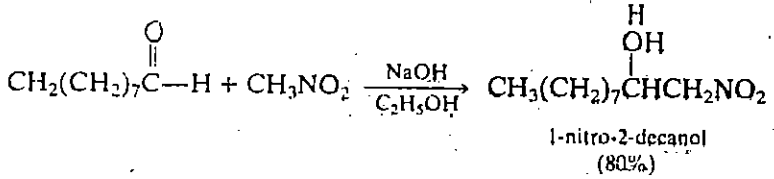
as electrophile:



2. Henry reaction

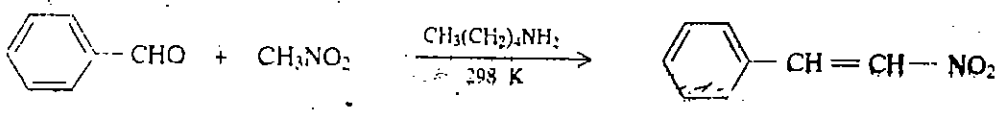
The anions obtained from nitroalkanes as explained above can undergo nucleophilic reactions with carbonyl compounds similar to the aldol type addition reaction.





1-nitro-2-decanol (80%)

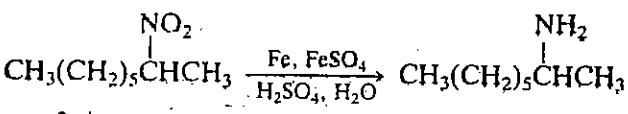
In case of aromatic aldehydes, the product obtained undergoes dehydration as shown below:



(75%)

3. Reduction

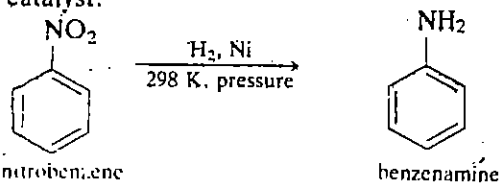
Nitro compounds can be reduced with a variety of reducing agents. Nitroalkanes can be converted to alkanamines as shown below:



2-nitrooctane — 2-octanamine (90%)

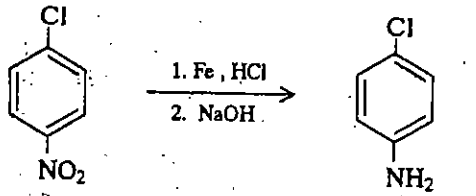
The product of reduction of aromatic nitro compounds depends on the reaction conditions employed. Catalytic reduction and reduction in acidic media yields aromatic amines.

Catalytic hydrogenation is carried out by using platinum, palladium or nickel as the catalyst.



nitrobenzene — benzenamine

For reduction in **acidic medium** a metal and an acid is used. Usually iron or zinc and hydrochloric acid are taken.



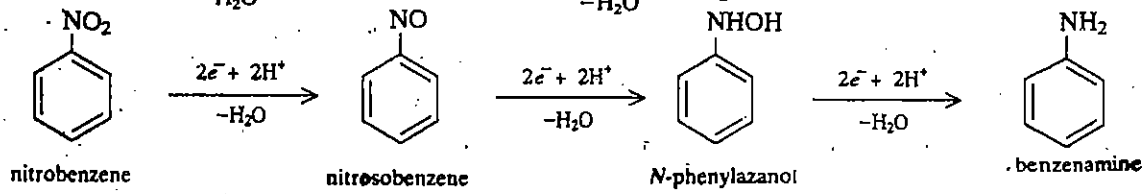
1-chloro-4-nitrobenzene 4-chlorobenzenamine

Reduction of a nitro compound to an amine requires six equivalents of the reducing agent, i.e.,

$$R{-}NO_2 + 6H^+ + 6e^- \longrightarrow RNH_2 + 2H_2O$$

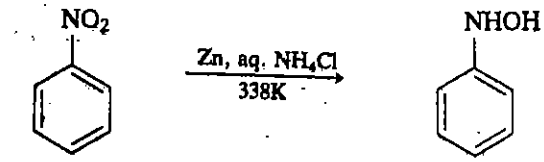
The reduction actually proceeds in a series of two-electron steps via the nitroso compounds (R—N=O) and *N*-substituted azanols (RNHOH) as successive intermediates.

$$RNO_2 \xrightarrow[-H_2O]{2[H]} RN{=}O \xrightarrow{2[H]} RNHOH \xrightarrow[-H_2O]{2[H]} RNH_2$$



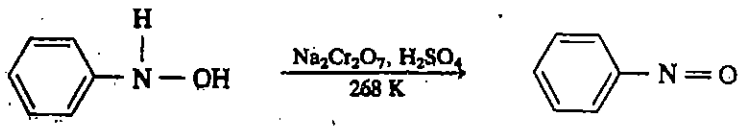
nitrobenzene nitrosobenzene *N*-phenylazanol benzenamine

Reduction can be stopped at the *N*-substituted azanol stage when reduction is carried out in **neutral conditions** using zinc and ammonium chloride.



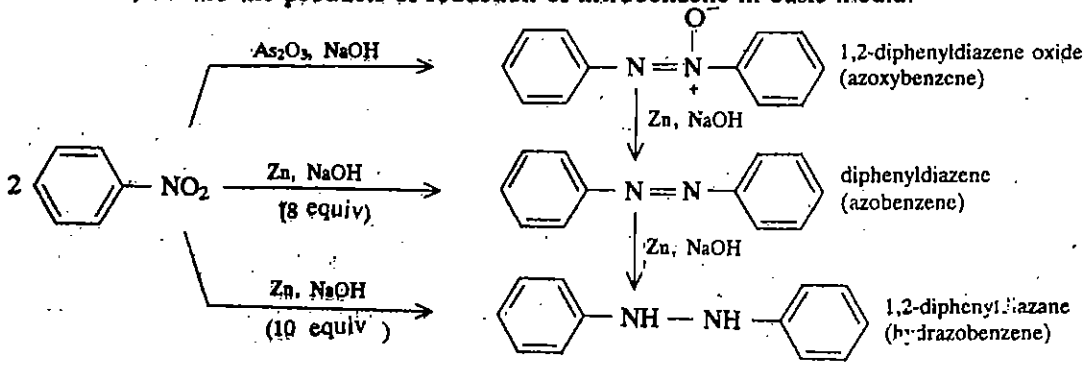
nitrobenzene *N*-phenylazanol (62-68%)

N-phenylazanol obtained above can be oxidised to nitrosobenzene.

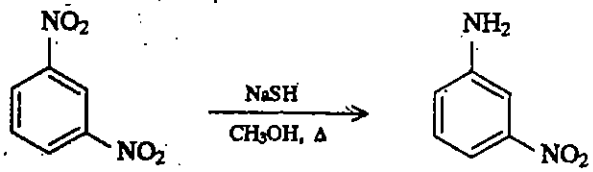


N-phenylazanol *N*-nitrosobenzene (65-70%)

Reduction of nitro compounds in **basic medium** gives binuclear compounds. Given below are the products of reduction of nitrobenzene in basic media.



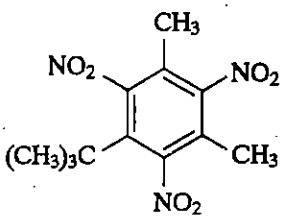
Selective reduction of the nitro group is also possible as shown below:



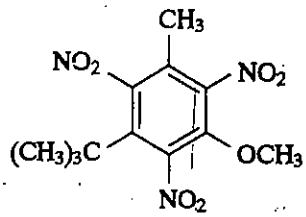
18.5 IMPORTANT USES OF NITRO COMPOUNDS

In addition to the synthetic utility of nitro compounds, you have studied that they are used in the preparation of explosives.

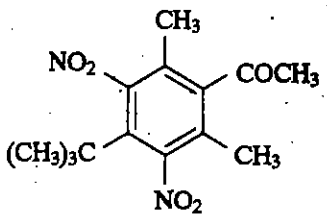
Several polynitro compounds possess an odour resembling musk and are used in perfumery. Some such examples are listed below:



musk xylol

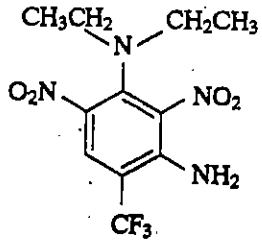


musk ambrette

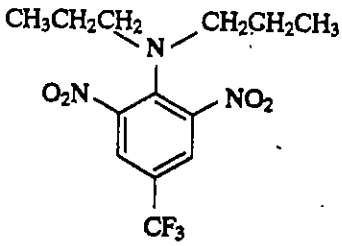


must ketone

Nitro compounds have important herbicidal uses. Some nitro compounds used as weedicides for the cotton, soyabean and peanut crops are shown below:



N^3,*N*^{3}-diethyl-5-trifluoromethyl-2,4-dinitro-1,3-benzenediamine (dinitramine)



N,*N*-dipropyl-4-trifluoromethyl-2,6-dinitrobenzenamine (trifluralin)

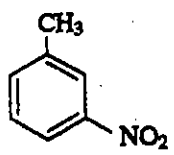
18.6 SUMMARY

In this unit, you have studied that :

- Drastic conditions are required for the preparation of nitroalkanes whereas aromatic nitro compounds are easier to synthesise.
- Primary and secondary nitro compounds behave as weak acids and they show nitro—acinitro tautomerism.
- Nitro compounds react with carbonyl compounds in alkaline medium to yield aldol type products.
- Nitroalkanes can be reduced to alkanamines.
- Aromatic nitro compounds on catalytic reduction and reduction in acidic conditions yield amines whereas in neutral media the product is N-substituted azanol. The reduction in basic media leads to a series of bimolecular reduction products, depending upon the nature of the reducing agent.

18.7 TERMINAL QUESTIONS

1) Write equations for the reactions of 3-nitropentane with
   a) H_2/Catalyst
   b) dil. NaOH, HCHO
2) Write the major product of reduction of



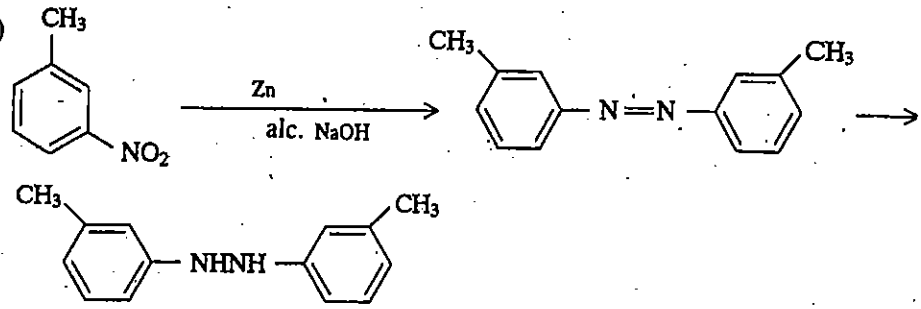
   a) with Zn/alc. NaOH
   b) Pt/H_2
   c) Zn/aq NH_4Cl
   d) $SnCl_2$/HCl

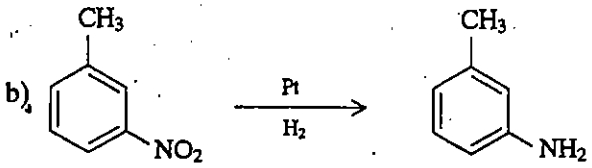
18.8 ANSWERS

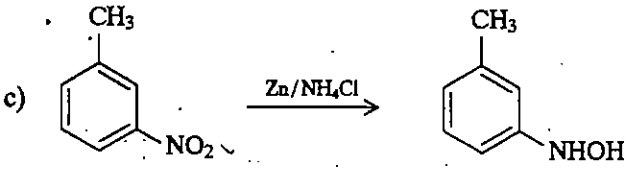
Terminal Questions

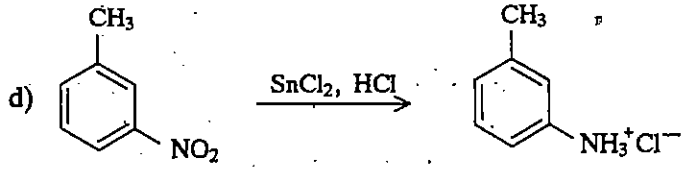
1) a) $CH_3CH_2\underset{\text{3-nitropentane}}{\underset{|}{\overset{NO_2}{C}}HCH_2CH_3} \xrightarrow{H_2 \,/\, \text{Catalyst}} \underset{\text{3-pentanamine}}{CH_3CH_2\underset{|}{\overset{NH_2}{C}}HCH_2CH_3}$

b) $CH_3CH_2\underset{\text{3-nitropentane}}{\underset{|}{\overset{NO_2}{C}}HCH_2CH_3} \xrightarrow[\text{dil. NaOH}]{\overset{O}{\overset{\|}{HCH}}} CH_3CH_2\underset{|}{\overset{NO_2}{C}}CH_2CH_3$ with CH_2OH

2) a) 

b) 

c) 

d) 

UNIT 19 AMINO COMPOUNDS AND DIAZONIUM SALTS

Structure

19.1 Introduction
Objectives
19.2 Natural Occurrence and Nomenclature of Amines
19.3 Structure of Amines
19.4 Physical Properties of Amines
19.5 Spectral Characteristics of Amines
19.6 Preparation of Amines
19.7 Reactions of Amines
19.8 Reactions of Diazonium Salts
19.9 Uses of Amines
19.10 Laboratory Detection of Amines
19.11 Summary
19.12 Terminal Questions
19.13 Answers

19.1 INTRODUCTION

Amines represent one of the largest classes of nitrogen containing organic compounds. You are aware that amines are compounds in which one or more alkyl or aryl groups are attached to nitrogen. You have studied in Unit 18 that nitro compounds can be reduced to amines. In this unit, you will study other methods of preparation of amines. Because of the pair of nonbonding electrons on the nitrogen atom, amines are important organic bases. They behave as nucleophiles as you studied in their reactions with carboxylic acid derivatives. They react with nitrous acid which is electrophilic in nature. The reaction of primary aromatic amines and nitrous acid gives diazonium salts which can lead to a large variety of organic compounds. The reactions of diazonium salts will also be dealt with in this unit. Finally, you will study about the uses of amines and the methods employed for their detection in the laboratory.

Objectives

After studying this unit, you should be able to:

- classify amines as primary, secondary or tertiary,
- give systematic names of amines,
- correlate the physical properties of amines with their structures,
- outline the synthesis of amines using various methods,
- describe the reactions of amines,
- explain the synthetic uses of diazonium salts,
- list some important amines and their uses, and
- give methods of detection of amines in the laboratory.

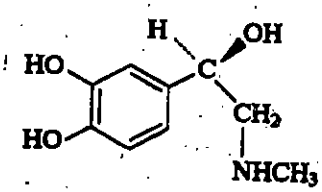
19.2 NATURAL OCCURRENCE AND NOMENCLATURE OF AMINES

Amines are widely distributed in nature. A large class of amines of plant origin is called **alkaloids.** *Strychnine* and *brucine* which you studied in Unit 3 with regard to the resolution of enantiomers are alkaloids. Some of the alkaloids have medicinal while others have poisonous properties. Examples of such alkaloids include *quinine*, which is antimalarial and antimicrobial, *caffeine* and *atropine* which are used as stimulants.

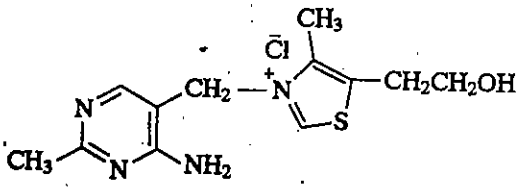
The term **alkaloid** was coined by F.W.A. Sertürner who in 1816, described morphine as basic and *alkali like.*

Alkaloids will also be discussed in Unit 20.

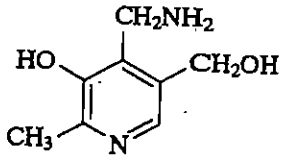
The alkaloids occurring in animals include many essential vitamins and hormones. Some examples are shown below.



adrenaline
(a hormone secreted by adrenal glands)

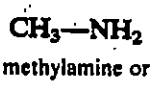


vitamin B_1
(thiamine chloride)



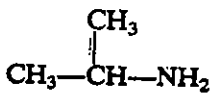
pyridoxamine
(one of the complex B_6 vitamins)

You may recall from Unit 1, Block 1, that amines can be classified as **primary, secondary** or **tertiary** depending on the number of alkyl or aryl groups attached to the nitrogen atom. When the substituents attached to the nitrogen are **alkyl** groups, the amine is called an **alkyl amine.** But the amines in which **at least one** of the substituents attached to the nitrogen atom is an **aryl** group, are called **aryl amines.** Examples of primary, secondary and tertiary, alkyl as well as aryl, amines are given below:



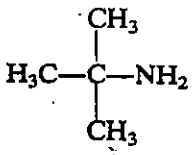
methylamine or methanamine

a primary alkyl amine



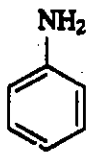
2-propanamine

a secondary alkyl amine



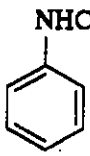
1,1-dimethylethanamine

a tertiary alkyl amine



benzenamine (aniline)

a primary aryl amine



N-methylbenzenamine (*N*-methylaniline)

a secondary aryl amine

N,N-dimethylbenzenamine (*N,N*-dimethylaniline)

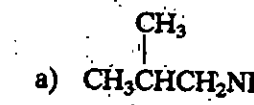
a tertiary aryl amine

The nomenclature of alkyl and aryl amines was discussed in Block 1, Unit 1, Sec 1.6, whereas the nomenclature of heterocyclic nitrogen compounds was discussed in Block 2, Unit 10, Sec. 10.2.

Why don't you check how much do you remember about the nomenclature of amines by answering the following SAQ.

SAQ 1

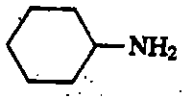
Write systematic names of the following amines:

a) 

.....

b) $(CH_3CH_2)_3N$

.....

c) 

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d) 

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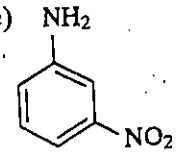
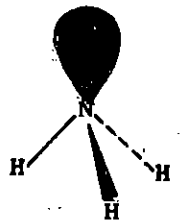
e) 

If you don't feel confident that you can correctly name the amines, go back to Block 1, Unit 1, Sec. 1.6 to refresh your knowledge about nomenclature.

19.3 STRUCTURE OF AMINES

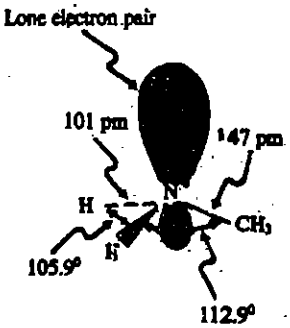
You may recall from your earlier studies that ammonia has a pyramidal shape. The HNH angle in ammonia, 107.3°, is very close to the angle of a tetrahedron, Hybridisation in ammonia can thus be described as nearly sp^3



ammonia

The structure of amines is similar to the structure of ammonia. Aliphatic amines have a pyramidal shape or if we regard the lone pair of electrons as a group, an approximately tetrahedral shape. The three vertices of the tetrahedron are occupied by three substituent groups and the fourth is occupied by the lone pair. If the three substituents are different then the nitrogen is *chiral*. This leads to the possibility of existence of enantiomers. The enantiomers of *N*-methylethanamine are shown in Fig. 19.1

The nearly tetrahedral structure of methanamine (methylamine)



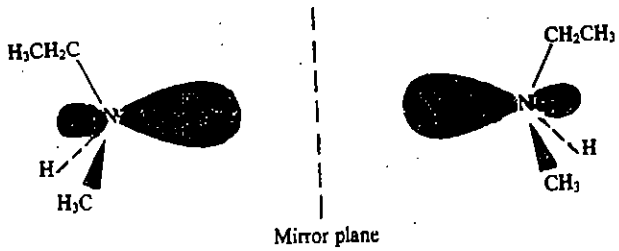


Fig. 19.1 : Enantiomers of *N*-methylethanamine.

But, in the absence of steric factors, amines undergo a *rapid inversion* at nitrogen via a planer transition state to yield their enantiomers, as is shown in Fig. 19.2. So it is not possible to isolate the enantiomers.

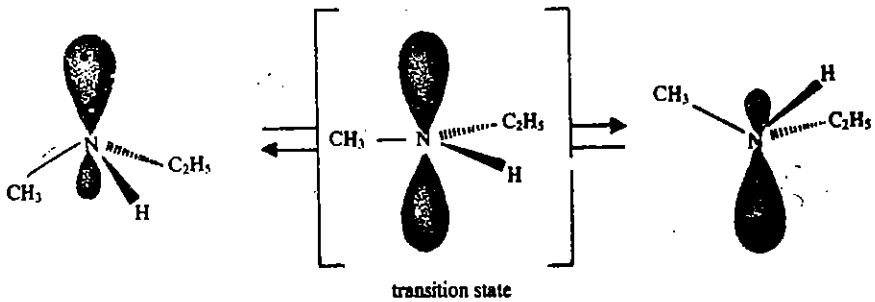
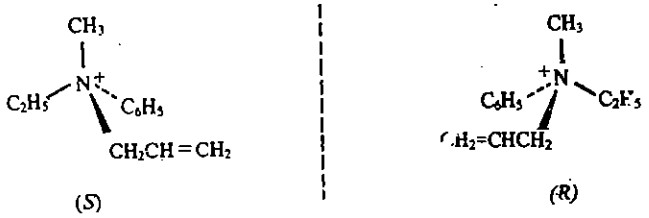
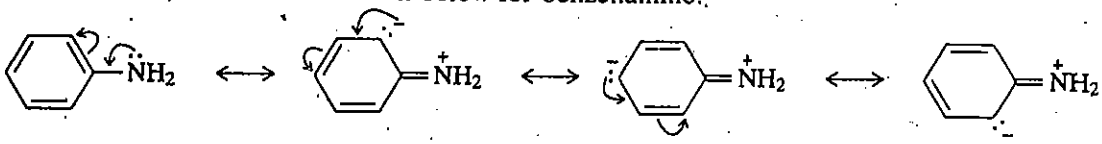


Fig. 19.2 : Inversion at nitrogen interconverts the enantiomers of *N*-methylethanamine.

Since such an inversion is not possible in quaternary ammonium compounds, they can be separated into enantiomers. The enantiomers of such a quaternary ammonium ion are shown below:

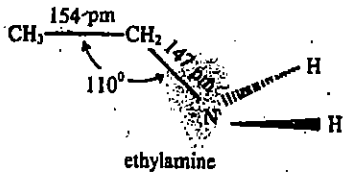


Aryl amines have larger HNH and HNC angles indicating that nitrogen in aryl amines is more nearly planer than in alkylamines. In aryl amines, the lone pair of electrons is delocalised with the π electrons of the aromatic ring. The resonance structures, thus, obtained are shown below for benzenamine.

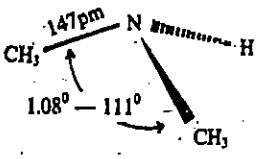


You can see the double bond character of C-N bond in some of these resonance structures. Thus, C—N bond in benzenamine is shorter (140 pm) as compared to that in aliphatic amines (147 pm).

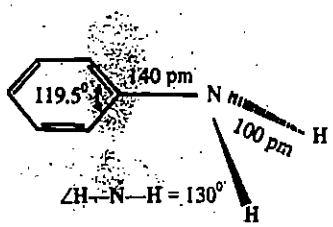
Let us now study the physical properties of amines and try to relate them to the structure of amines.



ethylamine



dimethylamine

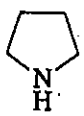


benzenamine
(aniline)

19.4 PHYSICAL PROPERTIES OF AMINES

The physical constants of some amines are given in Table 19.1.

Table 19.1: Physical constants of amines

Amine	Molecular weight	Melting point /K	Boiling point /K
Primary amines			
CH_3NH_2	31	179	277
$CH_3CH_2NH_2$	45	192	290
$CH_3CH_2CH_2NH_2$	59	190	321
$CH_3CH_2CH_2CH_2NH_2$	73	224	351
$(CH_3)_2CHCH_2NH_2$	73	188	341
$(CH_3)_3CNH_2$	73	206	318
aniline, $C_6H_5NH_2$	93	267	467
o-nitroaniline	138	345	557
m-nitroaniline	138	387	579
p-nitroaniline	138	421	605
Secondary amines			
$(CH_3)_2NH$	45	181	280
$(CH_3CH_2)_2NH$	73	223	329
	70	275	336
N-methylaniline	106	216	469
N-ethylaniline	120	210	478
diphenylamine	169	327	575
Tertiary amines			
trimethylamine, $(CH_3)_3N$	59	156	276
triethylamine, $(C_2H_5)_3N$	101	159	363
N,N-dimethylaniline	121	276	467
triphenylamine	245	400	638

The physical constants of the amines listed in Table 19.1 show that most amines are liquids. Amines generally have unpleasant fishlike odours.

You can clearly visualise certain trends in the physical constants of amines as listed in Table 19.1 which you studied in Unit 4, Block 1.

Primary and secondary amines can participate in intermolecular hydrogen bonding. The N—H...H hydrogen bonds are weaker than O—H...O hydrogen bonds because nitrogen is less electronegative than oxygen. Thus, the boiling points of primary amines are intermediate between those of alcohols and alkanes of comparable molecular weight. The hydrogen bonding is also a factor governing the water solubility of amines.

SAQ 2

The melting point and boiling point of 2-nitrobenzenamine (*o*-nitroaniline) are lower than its 3-nitro (*meta*-) or 4-nitro (*para*-) isomer. Why?

.....

.....

19.5 SPECTRAL CHARACTERISTICS OF AMINES

UV spectra

The absorptions due to $n \rightarrow \sigma^*$ transitions of saturated amines occur at short wavelengths (~ 220 nm) and, therefore, are not of much use for identification purposes.

IR spectra

The infrared spectra of primary and secondary amines show a characteristic broad bond due to N—H stretching absorption in the region between 3300 to 3500 cm^{-1}, see Fig. 19.3. Primary amines show two bands in this region whereas secondary amines show only one band. The N—H bending absorption of primary amines is observed near 1600 cm^{-1}

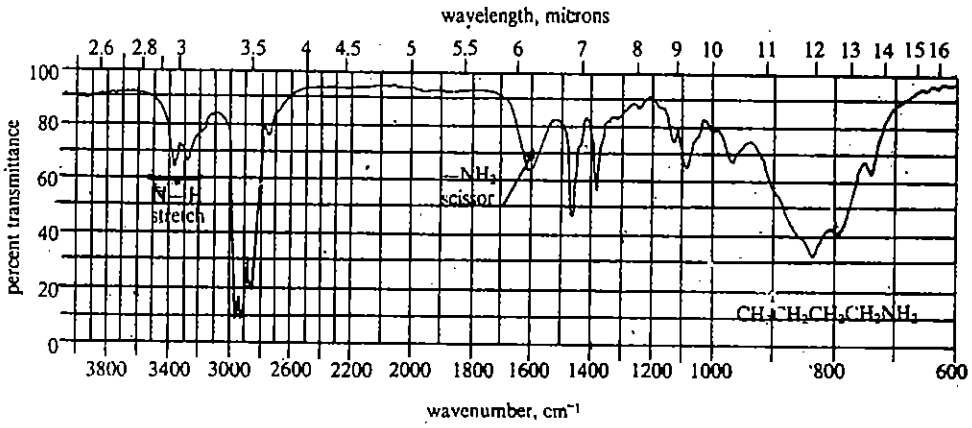
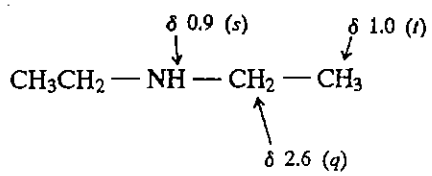


Fig. 19.3 : IR spectrum of butanamine.

NMR spectra

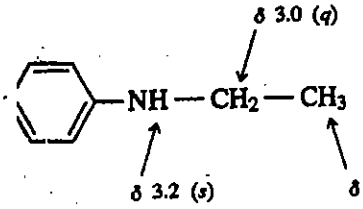
The H—C—N protons of alkylamines show absorption in the range δ 2.5-3.0. The absorption occurs further downfield in aromatic amines, i.e., near δ 3. The chemical shift of the N—H proton, like that of the O—H proton in alcohols, depends on the concentration of the amine and on other factors such as solvent and temperature. The N—H proton also undergoes chemical exchange as is observed in case of —OH protons of alcohols.

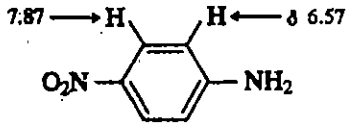


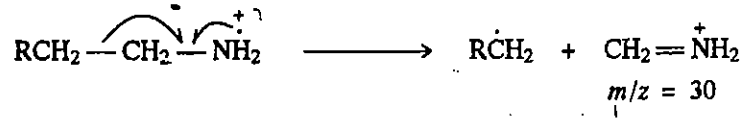
The absorption of protons of aromatic ring *ortho*- and *para*- to the amino nitrogen is shifted to higher field than that of the *meta*-protons indicating the increased electron density at the *ortho*-and *para*-positions.

Mass spectra

The mass spectra of aliphatic amines show a peak a $m/z = 30$ due to the following fragmentation from the M^+ ion:



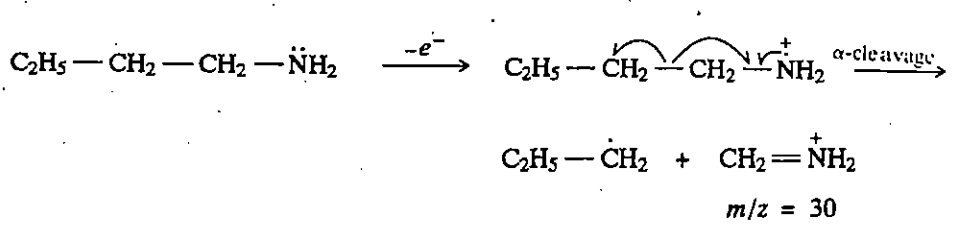




$$RCH_2 - \overset{\cdot}{C}H_2 - \overset{+}{\underset{\cdot}{N}}H_2 \longrightarrow R\dot{C}H_2 + CH_2 = \overset{+}{N}H_2$$

$m/z = 30$

For example,



$$C_2H_5 - CH_2 - CH_2 - \ddot{N}H_2 \xrightarrow{-e^-} C_2H_5 - \overset{\cdot}{C}H_2 - CH_2 - \overset{+}{N}H_2 \xrightarrow{\alpha\text{-cleavage}}$$

$$C_2H_5 - \dot{C}H_2 + CH_2 = \overset{+}{N}H_2$$

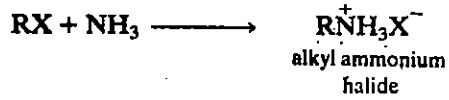
$m/z = 30$

19.6 PREPARATION OF AMINES

The various methods used for the preparation of amines are discussed below:

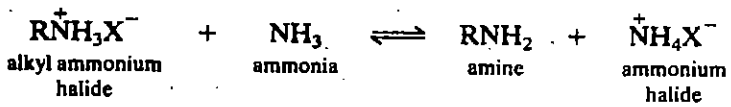
1) By direct alkylation of ammonia and other amines

Ammonia and amines react with alkyl halides to yield amines. Let us understand this reaction with the example of ammonia and a primary alkyl halide.



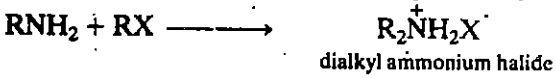
$$RX + NH_3 \longrightarrow \underset{\text{alkyl ammonium halide}}{R\overset{+}{N}H_3X^-}$$

This reaction follows the S_N2 path. If excess of ammonia is not used then the reaction stops at the stage of alkyl ammonium halide. In the presence of excess ammonia, another molecule of ammonia deprotonates the alkylammonium ion thereby liberating the free amine.

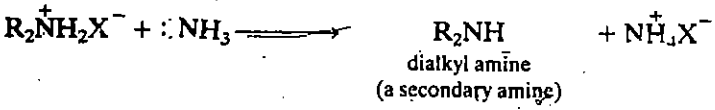


$$\underset{\substack{\text{alkyl ammonium}\\\text{halide}}}{R\overset{+}{N}H_3X^-} + \underset{\text{ammonia}}{NH_3} \rightleftharpoons \underset{\text{amine}}{RNH_2} + \underset{\substack{\text{ammonium}\\\text{halide}}}{\overset{+}{N}H_4X^-}$$

The resulting amine being a nucleophile reacts further with alkyl halide to yield dialkyl amine, trialkyl amine and quaternary ammonium salts as shown below.

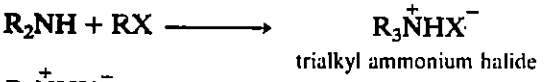


$$RNH_2 + RX \longrightarrow \underset{\text{dialkyl ammonium halide}}{R_2\overset{+}{N}H_2X^-}$$

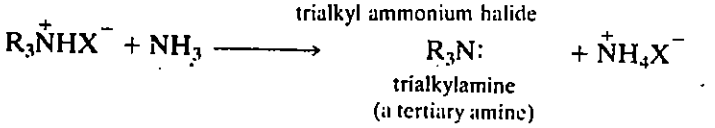


$$R_2\overset{+}{N}H_2X^- + :NH_3 \longrightarrow \underset{\substack{\text{dialkyl amine}\\\text{(a secondary amine)}}}{R_2NH} + \overset{+}{N}H_4X^-$$

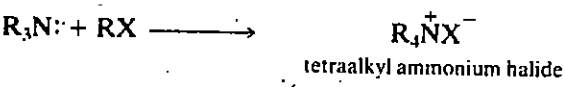
A secondary amine is a stronger nucleophile than a primary amine.



$$R_2NH + RX \longrightarrow \underset{\text{trialkyl ammonium halide}}{R_3\overset{+}{N}HX^-}$$

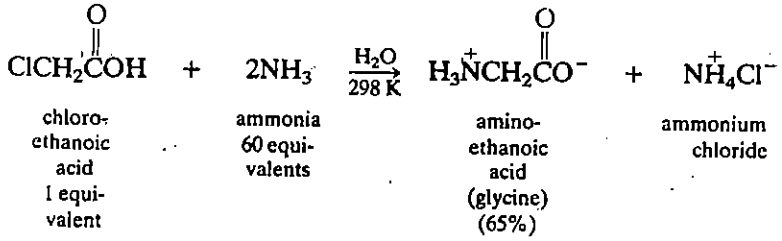


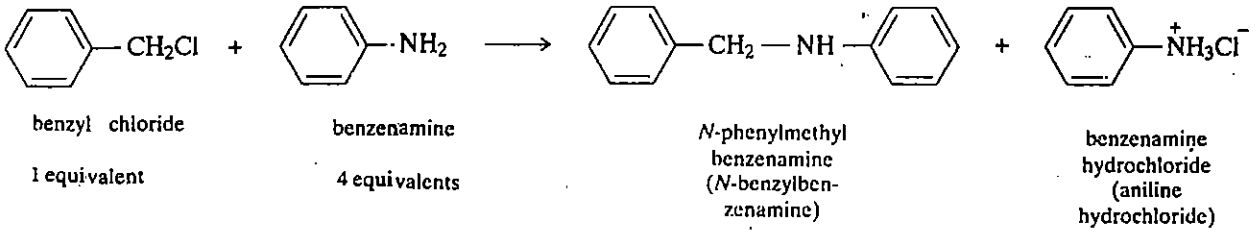
$$R_3\overset{+}{N}HX^- + NH_3 \longrightarrow \underset{\substack{\text{trialkylamine}\\\text{(a tertiary amine)}}}{R_3N:} + \overset{+}{N}H_4X^-$$



$$R_3N: + RX \longrightarrow \underset{\substack{\text{tetraalkyl ammonium halide}\\\text{(a quarternary ammonium salt)}}}{R_4\overset{+}{N}X^-}$$

Thus, a mixture of products is formed which limits the synthetic value of this reaction for the synthesis of primary amines. The overalkylation may be suppressed by using a large excess of ammonia or amine provided the amine is inexpensive and the desired product can be easily separated from the reaction mixture. Some examples follow:



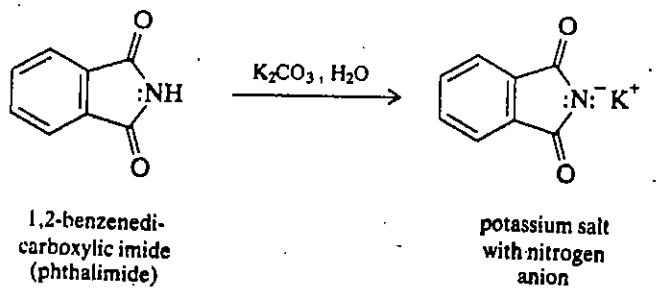


In many cases, even after using a large excess of the amine or ammonia, only moderate yields of desired amine are available. In such cases, indirect methods which give better yields are employed. One such method is the Gabriel synthesis which you will now study.

2. Indirect alkylation: The Gabriel synthesis

Pure primary amines can be prepared conveniently if the nitrogen atom is protected so that alkylation can take place only once.

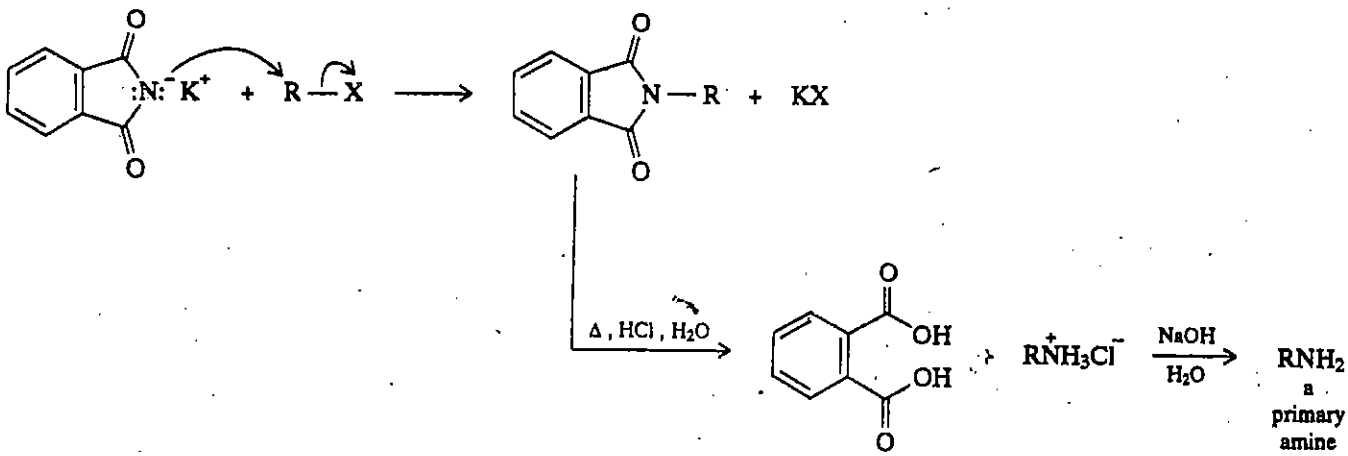
Such a protected nitrogen is present in 1,2-benzenedicarboxylic imide. Because the nitrogen atom has two adjacent carbonyl groups, the NH group is acidic enough (pK_a=8.3) to be deprotonated using a mild base to yield a nitrogen anion in a salt.



1,2-benzenedicarboxylic imide (phthalimide)

potassium salt with nitrogen anion

The nitrogen anion is a good nucleophile and can undergo a wide variety of nucleophilic substitution reactions. It reacts with alkyl halides to yield *N*-alkyl derivative in good yield. *N*-alkyl derivative on acidic hydrolysis yields the ammonium salt from which the free amine can be liberated by treatment with a base. Such a sequence of reactions can be used to prepare amines which are difficult to prepare by simple alkylation of ammonia and is known as Gabriel synthesis.



The use of the Gabriel synthesis is limited to primary and unbranched secondary alkyl halides. However, tertiary alkyl halides undergo eliminations under these conditions.

3. Reduction of nitro compounds

The reduction of nitro compounds to yield primary amines was discussed in Unit 18, Sec. 18.4.

4. Reduction of nitriles

Nitriles can be reduced to primary amines by catalytic hydrogenation or by the reaction with $LiAlH_4$.

$$R{-}C{\equiv}N \xrightarrow[\text{or } LiAlH_4]{H_2/Pd{-}C} RCH_2NH_2$$

$$CH_3CH_2CH_2CN \xrightarrow[\text{ether}]{1.\ LiAlH_4} \xrightarrow{2.\ H^+,\ H_2O} CH_3CH_2CH_2CH_2NH_2$$

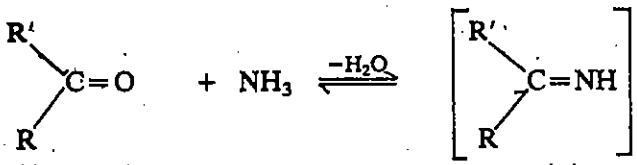
butanenitrile — butanamine (57%)

$$CH_3CH_2CH_2CH_2CN \xrightarrow{H_2\ /\ Ni} CH_3CH_2CH_2CH_2CH_2NH_2$$

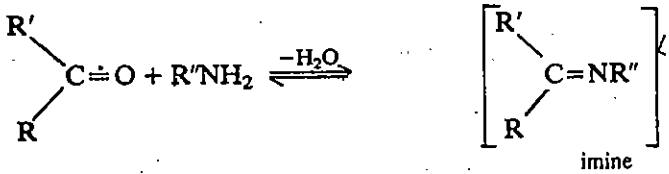
pentanenitrile — pentanamine (90%)

5. Reduction of imines

Ammonia and primary amines condense with aldehydes and ketones to yield imines as shown below:

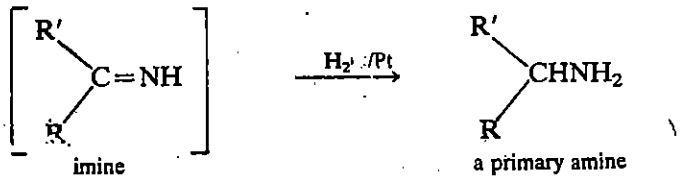


aldehyde or ketone — imine

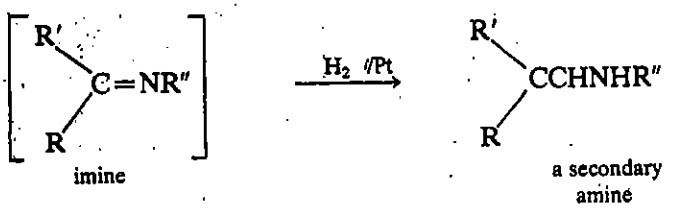


imine

The carbon nitrogen double bond of an imine can be reduced by catalytic hydrogenation to yield a primary or secondary amine.

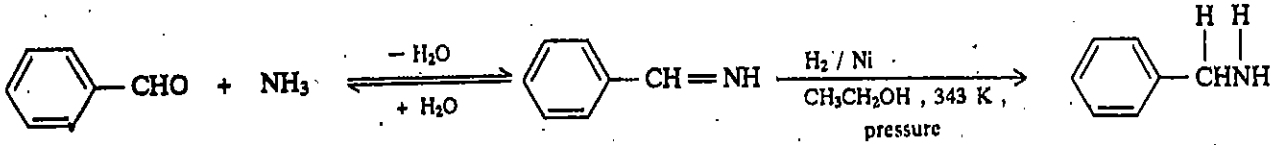


imine — a primary amine

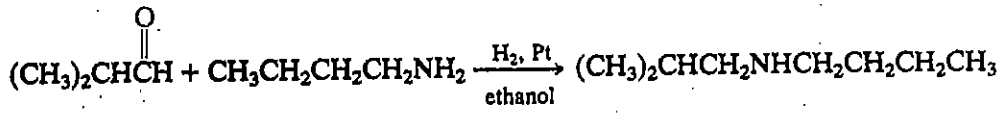


imine — a secondary amine

Some examples are given below:



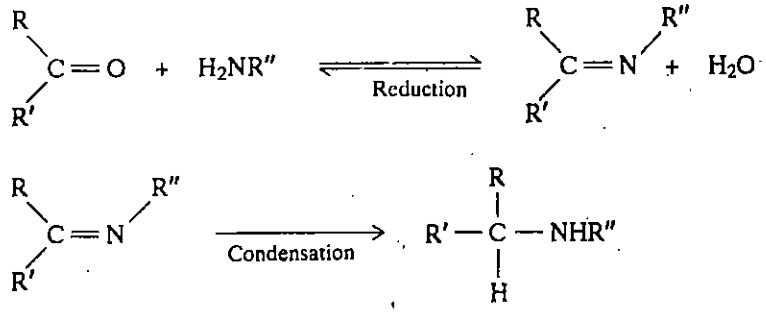
benzenecarboxaldehyde (benzaldehyde) — imine (not isolated) — phenylmethanamine (benzylamine) (89%)



2-methylpropanal — butanamine — *N*-2-methylpropylbutanamine

You can see that the carbonyl group is **reduced** in the above reaction and the amine is **alkylated**, hence, the reaction is also known as **reductive alkylation** or **reductive amination.**

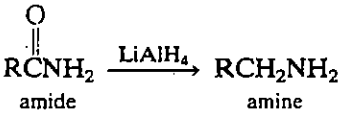
General Reductive Amination of a Ketone



What makes the reductive amination a useful synthetic procedure is that it can be carried out in a single operation involving the hydrogenation of a solution of the carbonyl compound and ammonia (or amine) in the presence of a catalyst without isolating the intermediate imine.

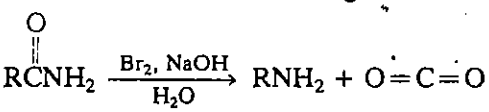
6. From amides

You are aware from Unit 17, Sec. 17.8, sub-Sec. 17.8.2 that amides can be reduced to amines, i.e.

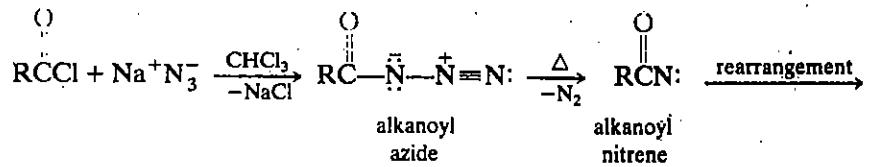


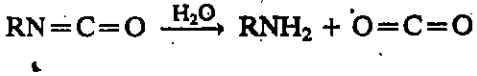
Depending upon the structure of the starting amide, primary, secondary or tertiary amines can be synthesised. Note that the same number of carbon atoms is present in the amine as in the starting amide.

Another method of preparing primary amines from amides is **Hofmann rearrangement.** The amine obtained contains one carbon atom less than the starting amide. Hofmann rearrangement was discussed in Unit 17, Sec. 17.8. The general reaction of Hofmann rearrangement is shown below :

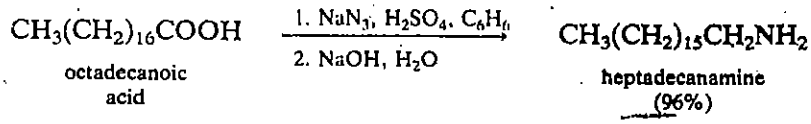


Similar transformation involving the reaction of an alkanoyl halide with sodium azide, NaN_3 to yield amines is known as **Curtius rearrangement.** This reaction proceeds via the following steps.



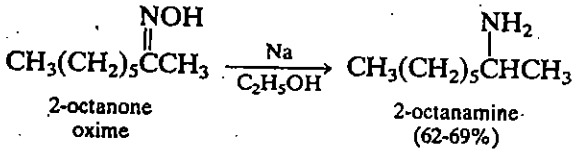


The same sequence of reactions is observed when the starting material is a carboxylic acid. A carboxylic acid when treated with sodium azide in acid catalyst yields an alkanoyl azide which finally yields the amine. This reaction is known as **Schmidt rearrangement.** An example of Schmidt rearrangement is shown below:



7. Reduction of oximes

It was pointed out in Block 3, Unit 14, Sec. 14.4 that aldehydes and ketones react with azanol (hydroxylamine) to yield oximes. Oximes so obtained can be reduced with $LiAlH_4$ or sodium in alcohol to yield primary amines.



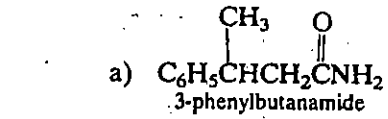
2-octanone oxime

2-octanamine (62-69%)

Using the knowledge gained so far, answer the following SAQ.

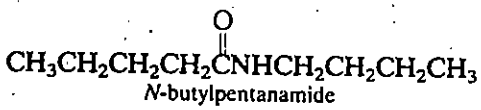
SAQ 3

Write the products of reduction of the following amides with $LiAlH_4$.

a) 

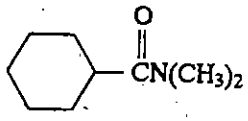
3-phenylbutanamide

.....

b) 

N-butylpentanamide

.....

c) 

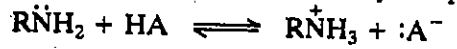
N,N-Dimethylcyclohexanecarboxamide

.....

19.7 REACTIONS OF AMINES

1. As bases

Amines behave as Lewis bases because of the nonbonding electron pair on nitrogen. They react with a variety of acids by accepting a proton.



$$R\ddot{N}H_2 + HA \rightleftharpoons R\overset{+}{N}H_3 + :A^-$$

The aqueous solutions of amines are basic in nature due to the following equilibrium.

$$R\ddot{N}H_2 + H_2O \overset{K_{eq}}{\rightleftharpoons} R\overset{+}{N}H_3 + OH^-$$

where K_{eq} is the equilibrium constant.

You may recall from Block 1, Unit 5, Sec. 5.3, Eq. 5.6 that K_{eq} is related to the basicity constant, K_b, by the following expression.

$$K_b = K_{eq}[H_2O] = \frac{[R\overset{+}{N}H_3][OH^-]}{[R\ddot{N}H_2]}$$

Also,

$$pK_b = -\log K_b$$

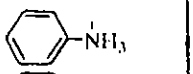
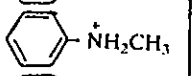
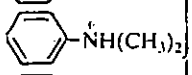
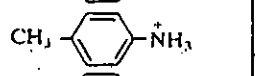
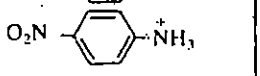
It was also pointed out in Unit 5, Block 1 that it is convenient to refer to the base strength also in terms of the dissociation constant, K_a, of the corresponding ammonium ion, i.e.,

$$R\overset{+}{N}H_3 + H_2O \overset{K_a}{\rightleftharpoons} R\ddot{N}H_2 + H_3O^+$$

where $K_a = \dfrac{[R\ddot{N}H_2][H_3\overset{+}{O}]}{[R\overset{+}{N}H_3]}$

The pK_a values of some typical ammonium ions are given in Table 19.2.

Table 19.2 : Basicities of some ammonium ions in terms of pK_a values.

Ammonium ion	pK_a	Ammonium ion	pK_a
$CH_3\overset{+}{N}H_3$	10.62		4.62
$(CH_3)_2\overset{+}{N}H_2$	10.64		4.85
$(CH_3)_3\overset{+}{N}H$	9.76		5.06
$C_2H_5\overset{+}{N}H_3$	10.63		5.07
$(C_2H_5)_2\overset{+}{N}H_2$	10.98		1.11
$(C_2H_5)_3\overset{+}{N}H$	10.65		

Using your knowledge about various factors affecting the basicity, you can observe the following trends in the pK_a values given in Table 19.2.

i) Increasing alkyl substitution at the nitrogen in the amine leads to an increase in the basicity.

ii) Lower pK_a values of tertiary amines in aqueous solution as compared to primary and secondary amines were explained as due to the effect of solvation of the ammonium ion in Unit 5, Block 1.

iii) The electron-donating substituents such as $-CH_3$, $-OCH_3$ etc. increase the basicity whereas electron-withdrawing substituents such as $-Cl$, $-CN$, $-NO_2$, etc. decrease the basicity.

iv) Since the electron pair on nitrogen is delocalised into the aromatic ring, benzenamine (aniline) is less basic than ammonia, (see Sec. 19.3 or Unit 5, Block 1 for resonance structures of aniline).

2. As nucleophiles

The amines act as nucleophiles in alkylation and alkanoylation reactions.

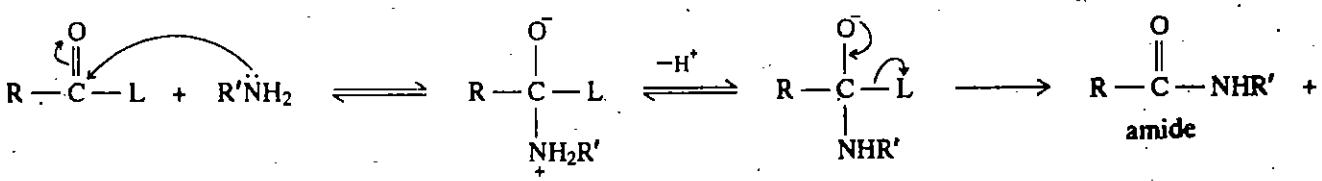
Alkylation Reactions

It was pointed out in Sec. 19.6 that alkyl halides react with primary amines to yield secondary amines, tertiary amines and quaternary ammonium salts. The mixture of amines thus obtained is then separated into individual amines. This reaction has practical value on an industrial scale.

Quaternary ammonium salts are useful in synthetic organic chemistry as phase transfer catalysts. Quaternary ammonium hydroxides are particularly used as substrates in elimination reactions to yield alkenes.

Alkanoylation Reactions

The alkanoylation reactions of amines with carboxylic acid derivatives to yield amides were discussed in Unit 17, Sections 17.5.2, 17.6.2 and 17.7.2. The general reaction can be represented as given below:



where L = halogen, $-O-\overset{O}{\overset{\|}{C}}-R$ or $-OR$.

3. Oxidation of amines

Amines are sensitive to oxidising agents such as hydrogen peroxide, (H_2O_2 and peroxy acids ($R\overset{O}{\overset{\|}{C}}OOH$).

Oxidation of primary and secondary aliphatic amines yields complex mixtures. Tertiary aliphatic amines, however, are oxidised to the corresponding **amine oxides**. Some examples are given below:

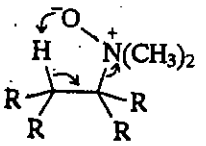
$$(CH_3)_3N: + 30\%\ H_2O_2 \xrightarrow{CH_3OH\ /\ H_2O} (CH_3)_3\overset{+}{N}—O^-$$

trimethylamine oxide (95%)

$$C_6H_5\underset{CH_3}{\underset{|}{C}}HNH(CH_3)_2 \xrightarrow[H_2O]{35\%\ H_2O_2} C_6H_5\underset{CH_3}{\underset{|}{C}}H\overset{O^-}{\overset{|}{\overset{+}{N}}}(CH_3)_2$$

(98%)

Amine oxides on heating above 373 K yield *N,N*-dialkylhydroxylamine and an alkene. This process is known as **Cope elimination** and is represented below:



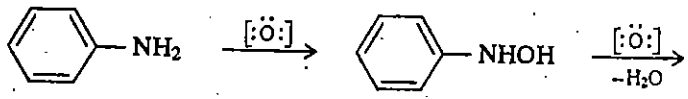
N,N-dimethylalkylamine *N*-oxide

$$\longrightarrow R_2C=CR_2 + (CH_3)_2\ddot{N}OH$$

alkene

N, N-dimethylazanol (*N, N*-dimethylhydroxyl amine)

Aromatic amines are easily oxidised by a variety of reagents including oxygen in the air. The product of oxidation depends upon the temperature, pH and amount of oxidising agent. Oxidation with hydrogen peroxide or peroxyacids yields various products as shown below:

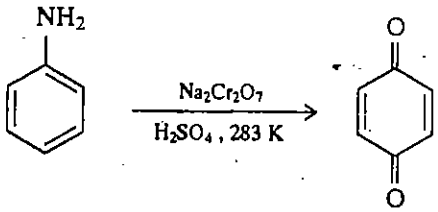


azanol

nitroso compound

nitro compound

Oxidation of benzenamine using sodium dichromate in aqueous sulphuric acid yields 1,4-cyclohexadienedione.



1,4-cyclohexadienedione (*para*-benzoquinone, 1,4-benzenedione)

4. With nitrous acid

Nitrous acid, HNO_2, is a weak unstable acid. It is usually prepared *in situ* by treating sodium nitrite with a strong mineral acid, usually hydrochloric acid at 273-278 K.

$$\overset{+}{N}a + NO_2^- + H_3O^+ + Cl^- \xrightarrow[273\ K]{H_2O} \underset{\text{nitrous acid}}{HO—N=O} + \overset{+}{N}a + Cl^-$$

In strongly acidic solutions, nitrous acid gets protonated and then loses water to give the **nitrosonium ion.**

$$\underset{\text{nitrous acid}}{HO—N=O} + H_3\overset{+}{O} \rightleftharpoons \underset{\text{conjugate acid of nitrous acid}}{\underset{H}{\overset{|}{HO}}\overset{+}{—}N=O} \longrightarrow H_2O + \underset{\text{nitrosonium ion}}{\overset{+}{N}=O}$$

The nitrosonium ion is electrophilic in nature and undergoes interesting reactions with amines, called **nitrosation reactions.** The products of nitrosation depend on whether the amine is primary, secondary or tertiary and whether it is aliphatic or aromatic. Let us now study each of them in detail.

Nitrosation of primary amines

Primary amines react with nitrous acid to yield **diazonium salts** via a number of intermediate species. This reaction is called **diazotisation.**

Diazotisation of primary aliphatic amines yields alkyl diazonium salts. Alkyl diazonium salts are unstable and decompose even at low temperatures to give nitrogen and various other products via the intermediate carbocations. This is explained in the following example.

$$CH_3CH_2CH_2CH_2NH_2 + NaNO_2 + HCl \xrightarrow{H_2O}$$

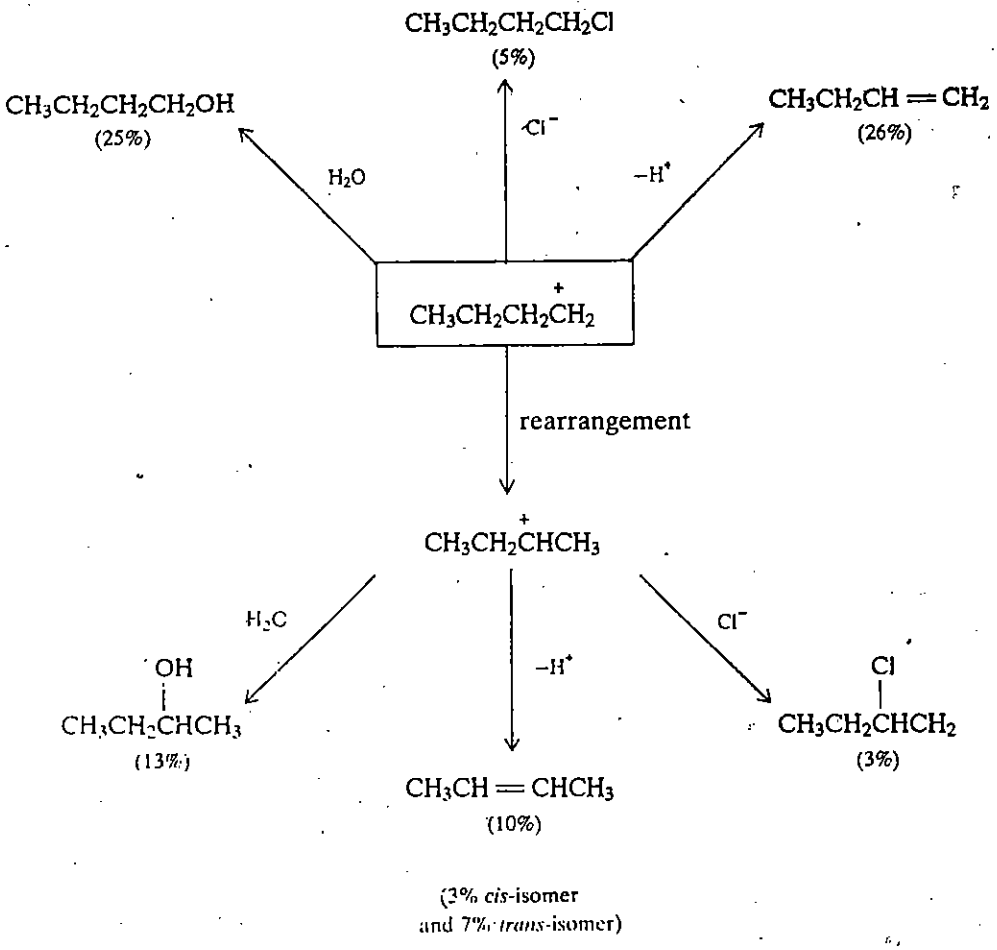
$$[CH_3CH_2CH_2CH_2{-}\overset{+}{N}{\equiv}N{:}Cl^-] \xrightarrow{-N_2} CH_3CH_2CH_2\overset{+}{C}H_2$$

1-butanediazonium chloride (a diazonium salt) (highly unstable)

(a carbocation)

The evolution of nitrogen during diazotisation is a good qualitative test for aliphatic primary amines.

This carbocation yields a complex mixture of various products as shown below:



Diazotisation of primary aromatic amines leads to **arenediazonium salts.** Arenediazonium salts are more stable than alkyldiazonium salts and can be stored at temperatures between 273 K to 278 K. Arenediazonium ions undergo a variety of reactions and are versatile intermediates in the synthesis of a variety of aromatic compounds about which you will study in detail in Sec. 19.8. However, the formation of an arenediazonium salt can be represented as shown below:

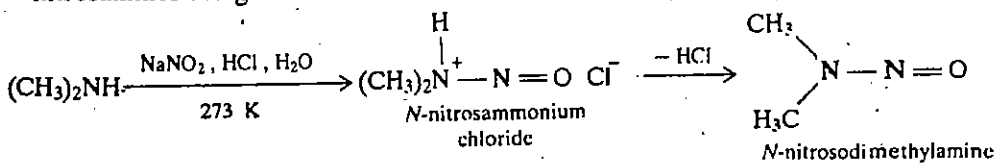
$$Ar{-}NH_2 + 2\,NaNO_2 + 2\,HX \longrightarrow Ar{-}\overset{+}{N} \equiv N{:}X^- + NaX + 2\,H_2O$$

primary aryl amine

arenediazonium salt (stable below 278 K)

Nitrosation of secondary amines

Aliphatic and aromatic secondary amines react with nitrous acid to yield *N*-nitroso compounds, also known as **nitrosamines**. Nitrosamines usually separate from the reaction mixture as yellow oily liquids. Some examples of the formation of nitrosamines are given below:

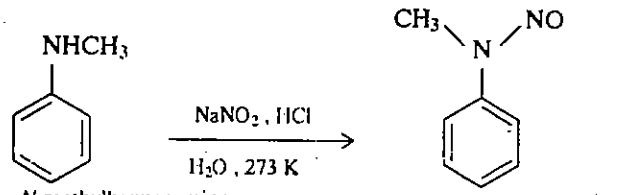


N-nitrosammonium chloride

N-nitrosodimethylamine (88-90%)

Nitrosamines are very powerful **carcinogens.** Sodium nitrite, used as a preservative in meats and also the nitrites produced by the reduction of nitrate fertilisers, react with natural amines in the presence of the acid found in stomach to yield nitrosamines.

Dimethylamine and methylethylamine are found in tobacco smoke also.



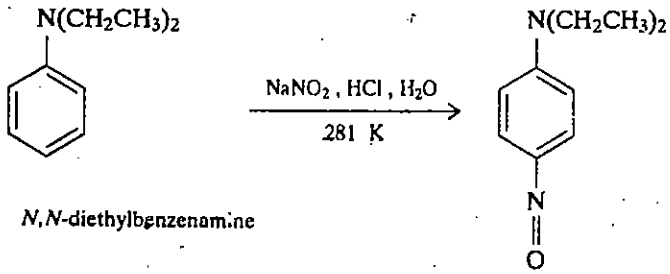
N-methylbenzenamine

N-nitroso-*N*-methylbenzenamine (87-93%)

Nitrosation of tertiary amines

Tertiary aliphatic amines react with nitrous acid without the evolution of nitrogen to yield complex mixtures.

Tertiary aromatic amines react with nitrous acid to give C-nitroso aromatic compounds. Nitrosation takes place almost exclusively at the *para* position of the aromatic ring.

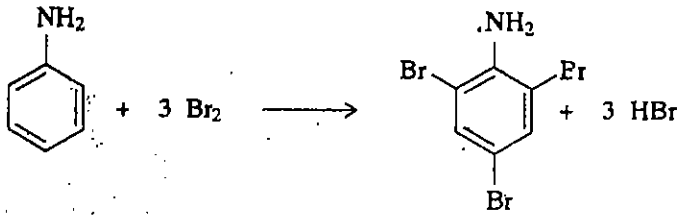


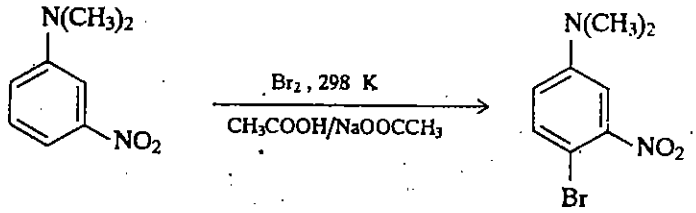
N,*N*-diethylbenzenamine

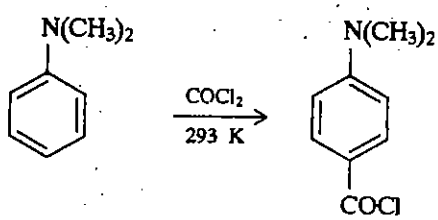
N,*N*-diethyl-*p*-nitrosobenzenamine (95%)

4. Electrophilic aromatic substitution

The amino group activates the aromatic ring towards substitution by electrophilic reagents and the reactions require mild conditions. The amino group is an *ortho*-, *para*-directing group, as is illustrated by the following examples:

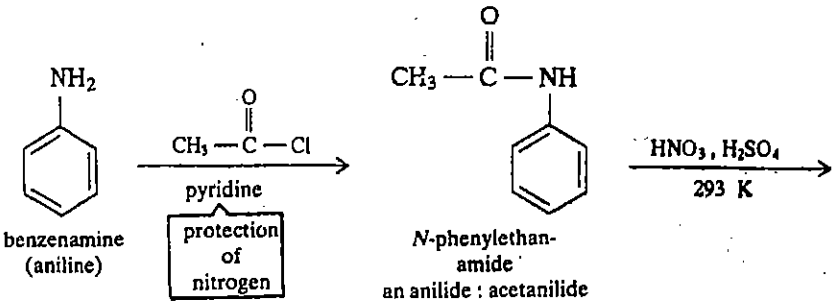






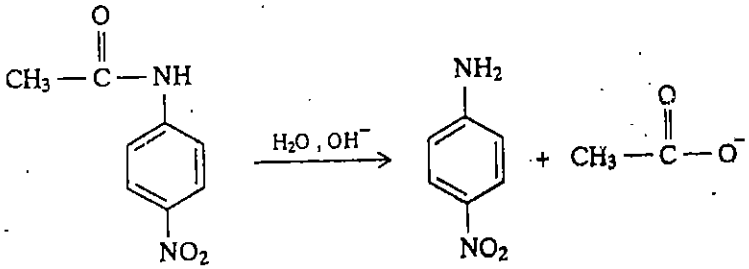
Since amino group is susceptible to attack by a wide variety of reagents such as oxidising agents, alkylating reagents and carbonyl compounds, it must be suitably protected.

The reactivity of the amino group is reduced when it is converted into an amide as is shown below:



benzenamine (aniline)

N-phenylethanamide
an anilide : acetanilide

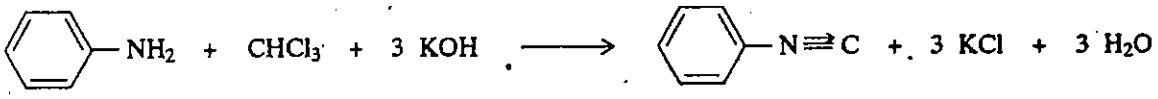


4-nitro-*N*-phenylethanamide
p-nitroacetanilide

4-nitrobenzenamine
(*p*-nitroaniline)

5. Isocyanide (carbylamine) reaction

Both aliphatic and aromatic primary amines react with chloroform in the presence of potassium hydroxide to produce an isocyanide that has a very nauseating odour. This reaction is so sensitive that it can be used as a test to detect the presence of very small amounts of primary amines as impurities in secondary and tertiary amines.



Caution : You should destroy the isocyanide by heating the reaction mixture with an acid before throwing the products into the laboratory sink.

SAQ 4

When 4-aminobenzenol reacts with one molar equivalent of ethanoic anhydride, a compound having molecular formula, $C_8H_9NO_2$ is formed which is soluble in alkali. Write its structure.

.....

.....

.....

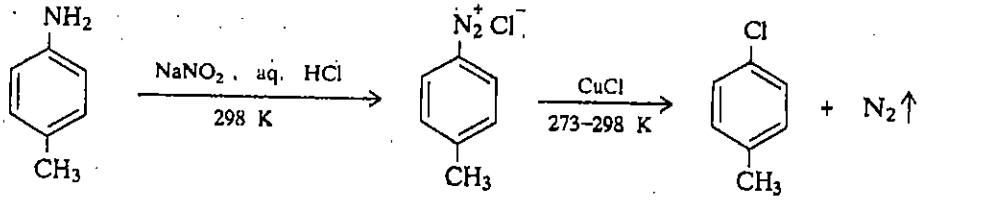
19.8 REACTIONS OF DIAZONIUM SALTS

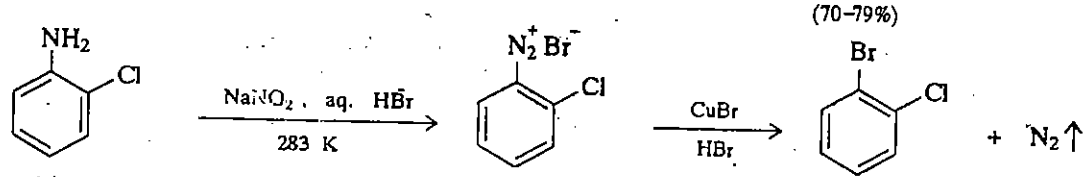
You have studied the formation of diazonium salts in the last section. It has been pointed out there that arenediazonium salts are stable at temperatures below 278 K and can be used in the synthesis of aromatic compounds. You will now study various reactions undergone by arenediazonium salts.

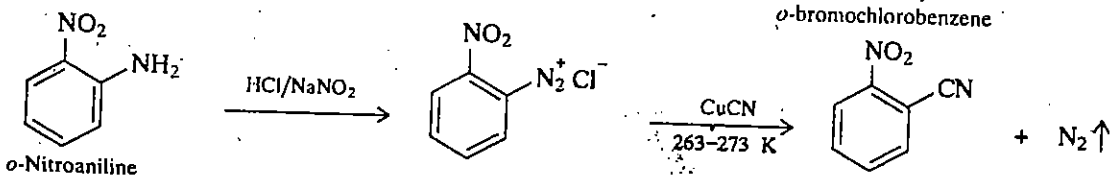
1. The Sandmeyer Reaction

The reactions of diazonium salts involving cuprous salts are called **Sandmeyer reactions.**

Arenediazonium salts react with cuprous chloride, cuprous bromide and cuprous cyanide to give products in which the diazonium group has been replaced by $-Cl$, $-Br$ and $-CN$ groups, respectively.







Reactions similar to the Sandmeyer reactions may be accomplished by the use of copper powder as a catalyst for decomposing the diazonium salt. This method is particularly useful in cases where the corresponding cuprous salt cannot be prepared. This variation is called the **Gattermann reaction.**

$$ArN_2^+X^- \xrightarrow{NaNO_2,\ Cu} ArNO_2$$

$$ArN_2^+X^- \xrightarrow[Cu]{SO_2,\ H_2O} ArSO_2H$$

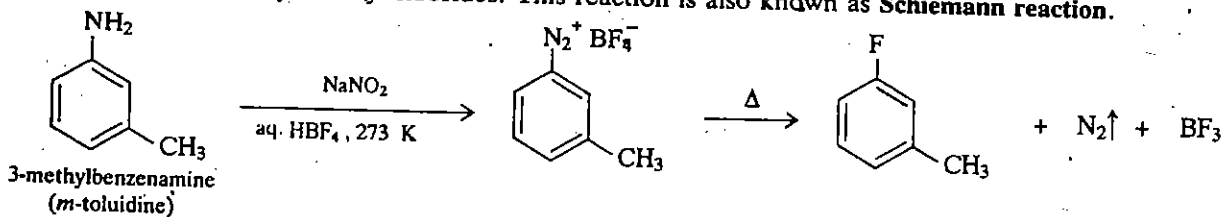
sulphinic acid

$$ArN_2^+X^- \xrightarrow{KOCN,\ Cu} Ar{-}N{=}C{=}O$$

aryl isocyanate

2. Formation of aryl fluorides

The diazotisation of an amine with sodium nitrite and fluoboric acid, HBF_4, yields fluoborate diazonium salt as a precipitate which is isolated and decomposed thermally to yield aryl fluorides. This reaction is also known as **Schiemann reaction.**



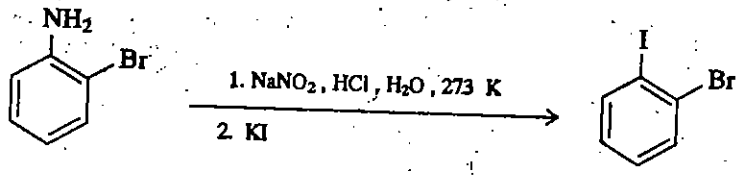
3-methylbenzenamine (*m*-toluidine)

3-methylbenzenediazonium fluoborate (*m*-methylbenzenediazonium fluoborate) (76-84%)

3-methylfluorobenzene (*m*-fluorotoluene)

3. With potassium iodide

Diazonium salts react with potassium iodide to yield **aryl iodides.** The diazonium salt is prepared in the usual way and a solution of potassium iodide is then added and the reaction mixture is heated to yield the aryl iodide.

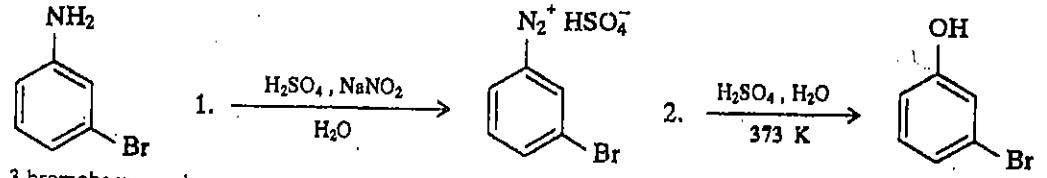


2-bromobenzenamine (*o*-bromoaniline)

2-bromoiodobenzene (*o*-bromoiodobenzene) (72-83%)

4. With water

The most general method for the preparation of phenols involves the heating of the diazonium salt in aqueous acid.

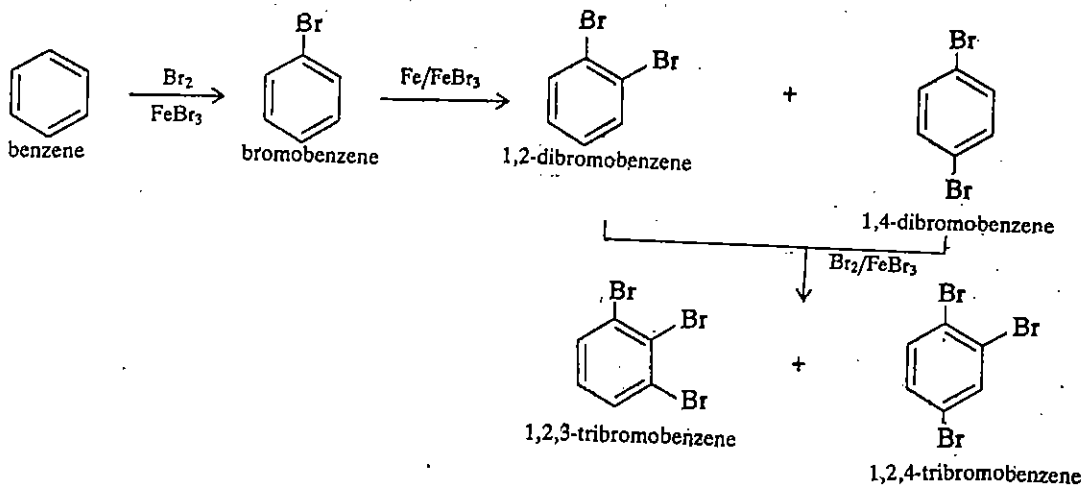


3-bromobenzenamine (*m*-bromoaniline)

3-bromobenzenol 3-bromophenol (*m*-bromophenol) (78%)

5. Replacement of diazonium group by hydrogen

When a diazonium salt is treated with hypophosphorous acid, H_3PO_2, the diazonium group is replaced by hydrogen. Reactions of this type are called **reductive deaminations**. This reaction is useful when we introduce an amino group into an aromatic ring to influence the orientation of a subsequent reaction. Later the amino group can be removed by converting it into the diazonium salt and then treating the diazonium salt with H_3PO_2. For example, direct bromination of benzene leads to 1,2,3- and 1,2,4-tribromobenzenes.



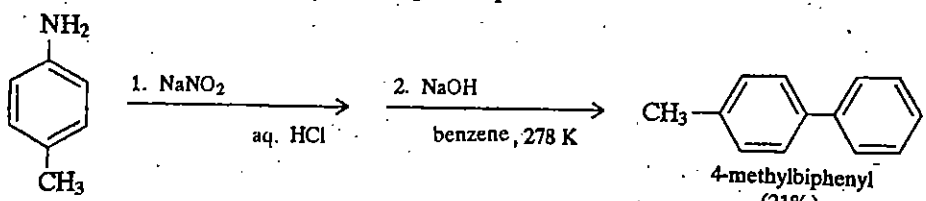
benzene — bromobenzene — 1,2-dibromobenzene + 1,4-dibromobenzene

1,2,3-tribromobenzene + 1,2,4-tribromobenzene

Thus, 1,3,5-tribromobenzene which cannot be prepared by direct bromination of benzene can be obtained by the reaction of the diazonium salt of tribromoaniline with H_3PO_2.

6. Arylation

Basic solutions of diazonium salts react with aromatic compounds in cold to yield biaryl compounds in which the diazonium group has been replaced by an aromatic ring. This is illustrated by the following example.



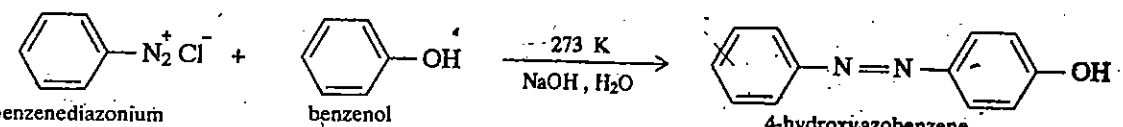
4-methylbenzenamine

4-methylbiphenyl (21%)

This reaction is called the **Gomberg-Bachmann reaction.**

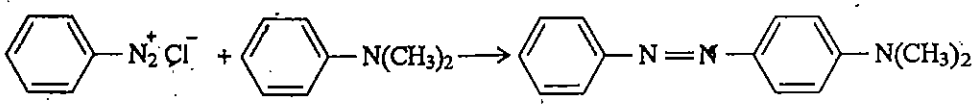
7. Coupling Reactions

Arenediazonium salts are weak electrophiles and attack aromatic ring of highly activated compounds such as amines and phenols to yield azo compounds. This electrophilic aromatic substitution reaction is called **diazo coupling** and is shown below:



benzenediazonium chloride + benzenol (phenol)

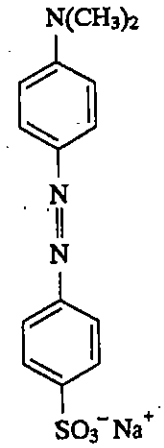
4-hydroxyazobenzene (orange)



benzenediazonium chloride + *N,N*-dimethylbenzenamine → 4-dimethylaminoazobenzene (butter yellow)

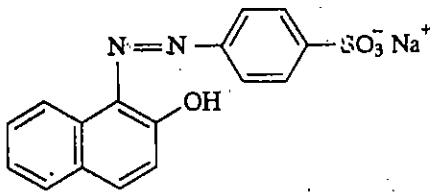
The azo compounds thus obtained are highly coloured and many of them are used as colouring agents and are called **azo dyes**. Butter yellow was once used as a food colouring agent. Azo dyes are also used as indicators and for textile dying. Some examples are given below:

Coupling takes place preferably at the *para* position, if it is free. If it is not, then, the coupling takes place at the *ortho* position.



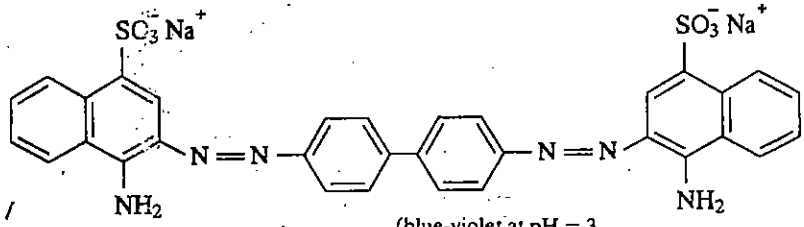
methyl orange (an indicator)

(red at pH = 3.1
yellow at pH = 4.4



Orange II

(an industrial dye for textiles)



Congo red

(blue-violet at pH = 3
red at pH = 5)

After studying the reactions of diazonium salts, answer the following SAQ.

SAQ 5

Write the starting materials required for the preparation of azo compounds methyl orange and congo red.

.....

.....

Before closing our discussion on amines, let us study the uses of amines and their detection in the laboratory.

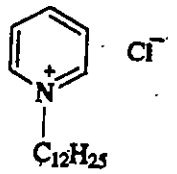
19.9 USES OF AMINES

Amines have diverse uses. You have already studied most of them in the discussion about amines in this unit. Let us now restate them.

1) Several amines are physiologically active and are used as drugs.
2) Some naturally occurring amines, particularly alkaloids are used as resolving agents for optically active compounds. You have studied them in Unit 3, Block 1 also.
3) It was also pointed out that quaternary ammonium salts also act as **phase transfe catalysts**. Quaternary ammonium salts are soluble in both water and organic solvents and thus act as mediators for reactions between species dissolved in immiscible liquids. Quaternary ammonium salts having long chain alkyl groups such as hexadecyl trimethylammonium chloride, $[C_{16}H_{33}N(CH_3)_3]^+ Cl^-$, have detergent properties. They are known as cationic surfactants or invert soaps

because the surface activity is found in a positive ion rather than in a negative ion as is the case with ordinary soaps. Most surface-active quaternary ammonium salts, such as dodecyl pyridinium chloride are potent germicides.

4) Diazonium salts available from amines can be used to synthesise a variety of aromatic compounds and azo dyes.



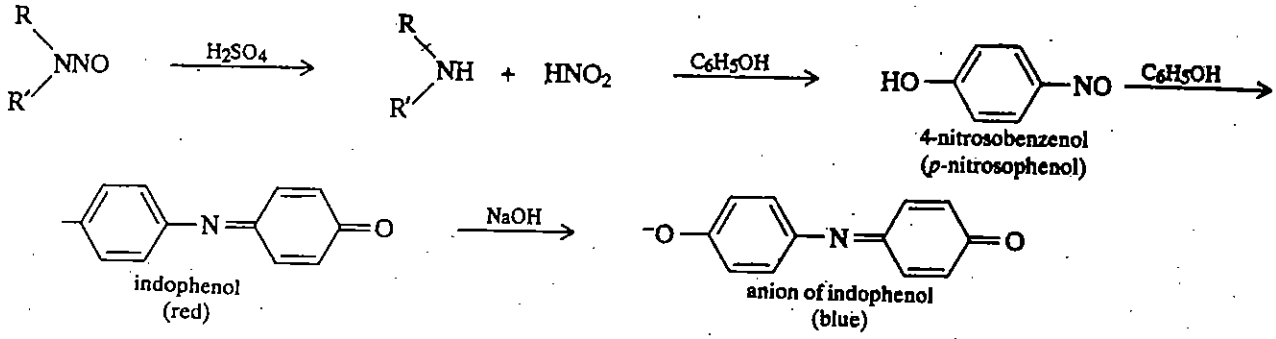
dodecyl pyridinium chloride

19.10 LABORATORY DETECTION OF AMINES

Amines are characterised by their basic nature. They dissolve in dilute aqueous acids. The elemental analysis of amines shows the presence of nitrogen.

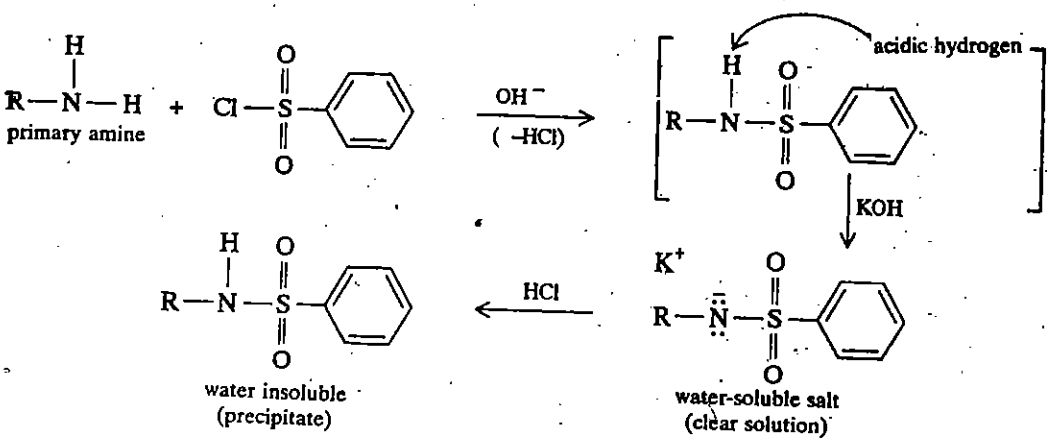
Amines can be characterised by their reaction with nitrous acid. The amine is dissolved in dilute HCl and an ice-cold solution of sodium nitrite is added to it. If a clear solution is obtained with the evolution of nitrogen, the amine is a **primary aliphatic** or **primary alkylaryl amine**. If no nitrogen is evolved, then a cold solution of 2-naphthol in sodium hydroxide solution is added to a portion of the above reaction mixture. If a coloured azo dye is formed, then the amine is a **primary aromatic amine.**

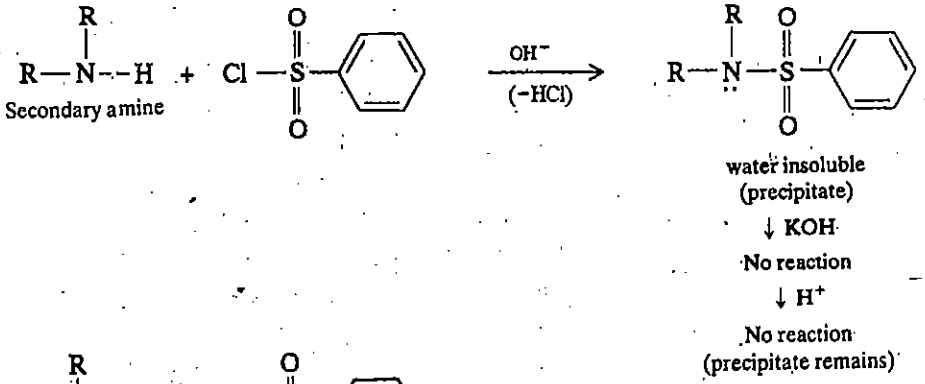
If a yellow oily substance separates out when cold sodium nitrite solution is added to the acidic solution of the amine, then the amine is a **secondary amine.** The formation of the oily nitrosamine is confirmed by the **Liebermann nitroso reaction.** The yellow oily substance is warmed with phenol and concentrated sulphuric acid. Sulphuric acid liberates nitrous acid from nitrosamine which reacts with phenol to yield *p*-nitrosophenol. The *p*-nitrosophenol reacts with another molecule of phenol to yield red coloured indophenol. In alkaline solution indophenol yields its anion which is blue in colour. The sequence of reactions which occur can be represented as shown below:

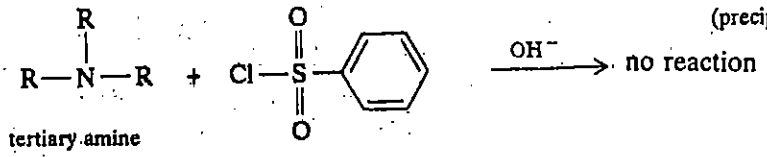


If a dark orange-red solution is obtained on treatment of the amine with nitrous acid and the colour changes to green on adding the alkali, then the amine is a **tertiary aromatic amine.**

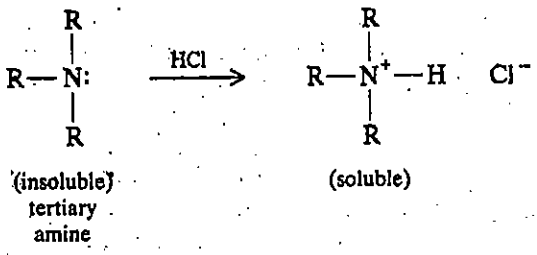
An efficient method to distinguish whether an amine is **primary, secondary** or **tertiary** is the **Hinsberg test**. This involves the reaction between an amine and benzenesulphonyl chloride in the presence of aqueous potassium hydroxide. Primary and secondary amines form substituted sulphonamides but tertiary amines do not. The sulphonamide from the primary amine may be further distinguished by the fact that it is soluble in potassium hydroxide, whereas the derivative from the secondary amine, having no acidic hydrogen, is insoluble in potassium hydroxide and, therefore, precipitates out. The reactions involved with each type of amine are shown below:







But amine will dissolve on acidification.



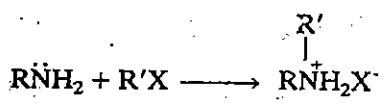
Let us now summarise what we have learnt in this unit.

19.11 SUMMARY

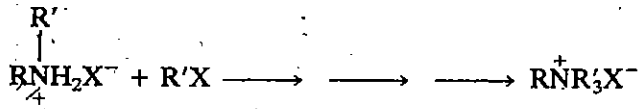
In this unit, you have studied that

- amines are nitrogen-containing organic bases.
- amines can be classified as primary, secondary and tertiary according to the degree of the substitution at the nitrogen atom.
- amines have tetrahedral structure in which the nitrogen is sp^3 hybridised. One of the sp^3 hybrid orbitals is occupied by the unshared pair of electrons.
- trends in the physical properties of amines such as melting and boiling point can be explained on the basis of various factors you studied in Unit 4, Block 1.
- primary and secondary amines can be differentiated with the help of the infrared spectra.
- amines can be prepared by the following methods:

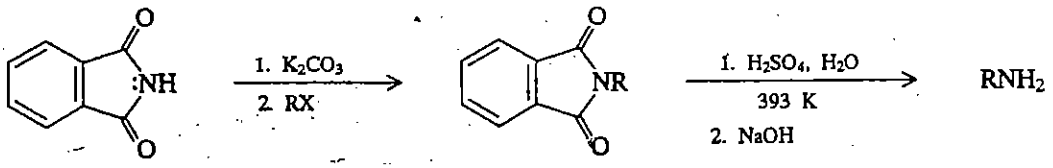
i) By alkylation



drawback: multiple alkylation.

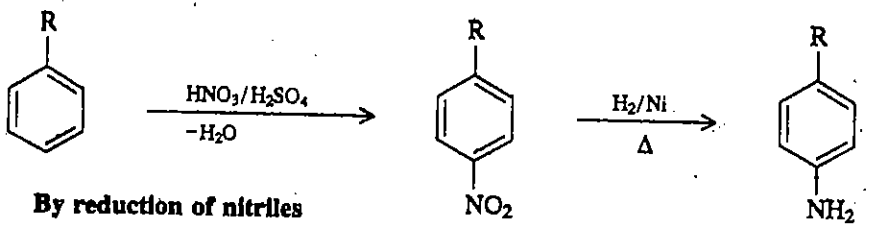


ii) Gabriel synthesis of primary amines



iii) Primary amines from nitro compounds

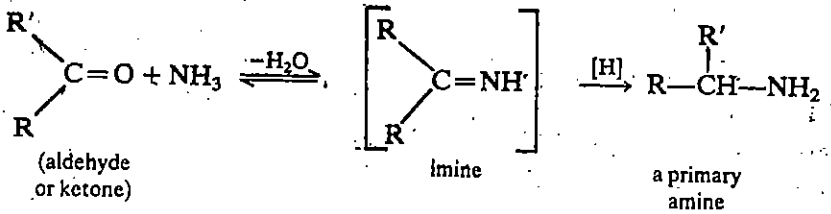
$$RX + NO_2^- \xrightarrow[-X^-]{S_N2} RNO_2 \xrightarrow[H^+]{Fe/FeSO_4} RNH_2$$

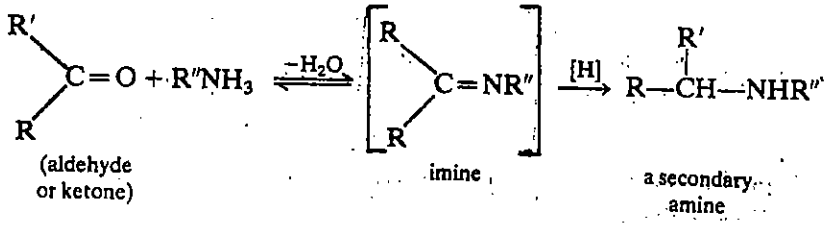


iv) By reduction of nitriles

$$RCN \xrightarrow[\text{or } H_2,\ \text{Catalyst}]{LiAlH_4} RNH_2$$

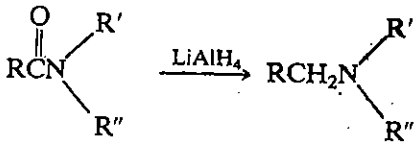
v) By reduction of imines



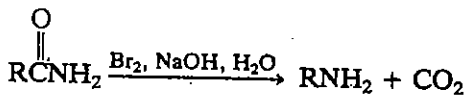


vi) From amides

a) By reduction

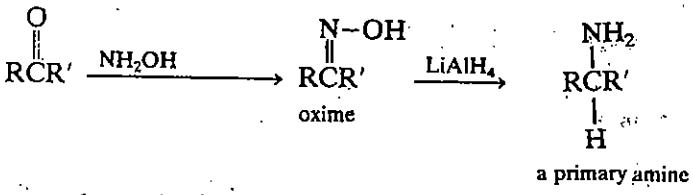


b) By Hofmann rearrangement



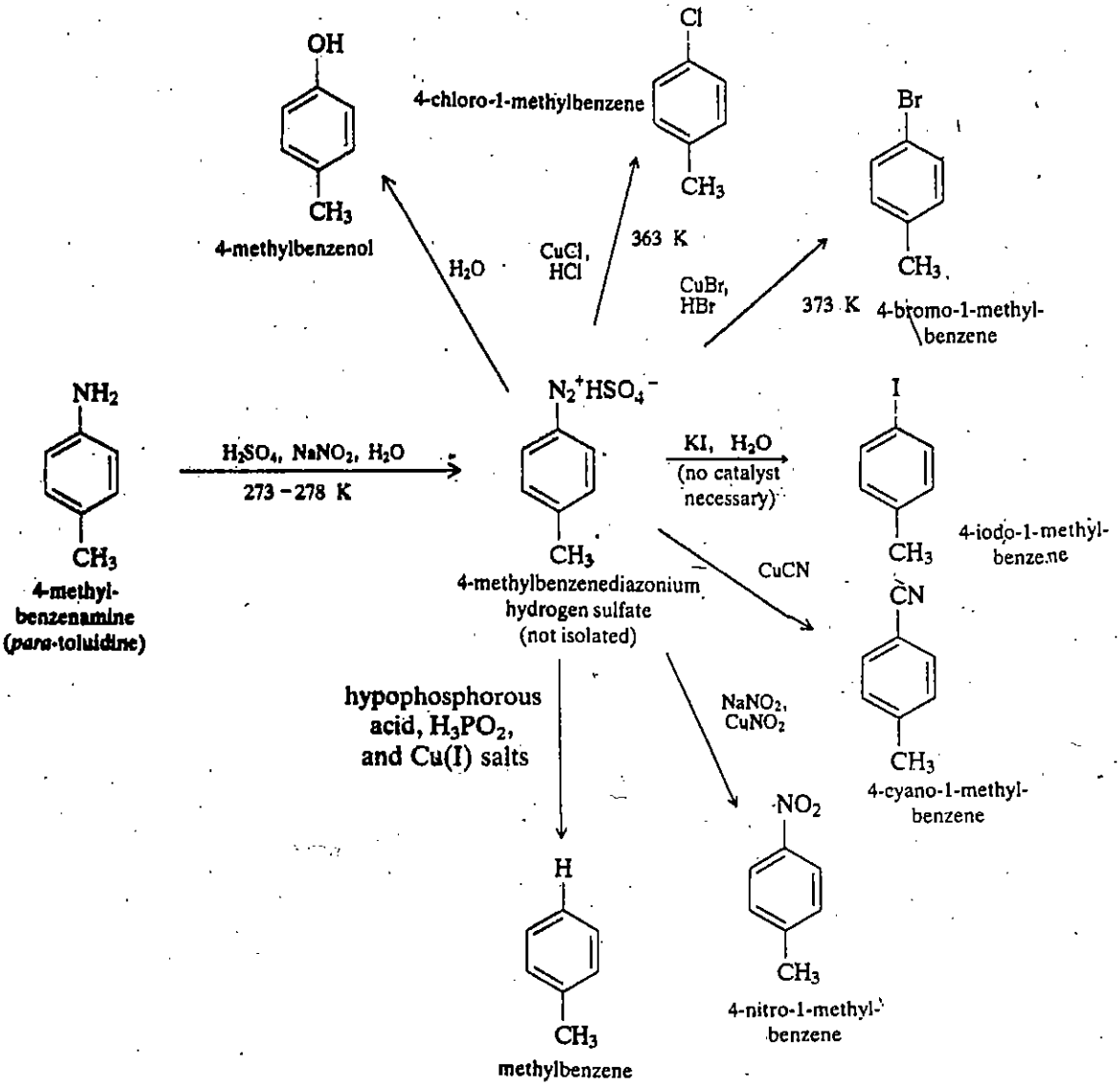
Similar transformations starting with alkanoyl halides (Curtius rearrangement) and carboxylic acids (Schmidt rearrangement) using sodium azide also yield amines.

vii) From Oximes



- Amines undergo the following reactions:
  - — they behave as bases in aqueous solutions and form salts with acids.
  - — they undergo alkylation with alkyl halides and alkanoylation with carboxylic acids and their derivatives.
  - — tertiary aliphatic amines can be oxidised to amine oxides which undergo Cope elimination on heating to yield an alkene and *N,N*-dialkylhydroxylamine.
  - — Oxidation of aromatic amines leads to a variety of oxidation products depending upon the oxidising agent and reaction conditions.
  - — **Amines** undergo **nitrosation reaction** with nitrous acid which gives various products depending upon whether the amine is primary, secondary or tertiary and is aliphatic or aromatic.

- amino group activates the aromatic ring towards electrophilic substitution reactions.
- Some of the reactions of diazonium salts can be summarised as follows:

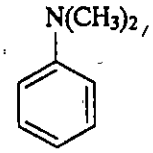


- Amines have various uses.
- Amines can be characterised in the laboratory by their reaction with nitrous acid and Hinsberg test.

19.12 TERMINAL QUESTIONS

1) Name the following amines:

a) $CH_3CH(NH_2)CH_2CH_3$

b) 

c) $BrCH_2CH_2CH_2CH_2CH(CH_3)NH_2$

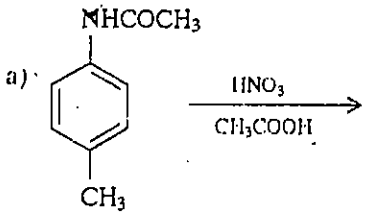
2) How will you carry out the following transformations?

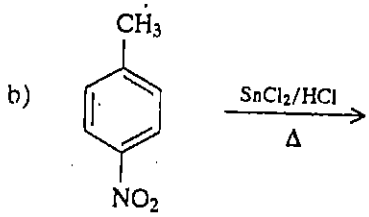
a) CH_3O–C$_6$H$_4$– $\rightarrow$ CH_3O–C$_6$H$_4$–NH_2

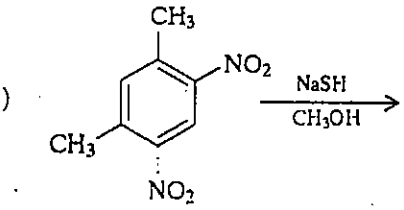
b) CH_3O–C$_6$H$_4$– $\rightarrow$ CH_3O–C$_6$H$_4$–$CH(CH_3)NH_2$

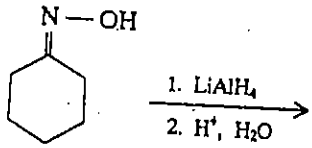
c) 

3) Complete the following reactions:

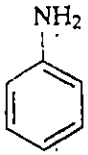
a) 

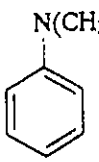
b) 

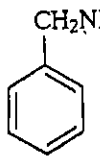
c) 

d) 

4) Write the products of nitrosation of the following compounds.

a) 

b) 

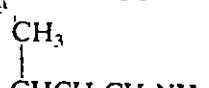
c) 

19.13 ANSWERS

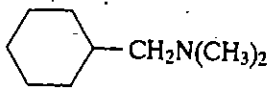
Self Assessment Questions

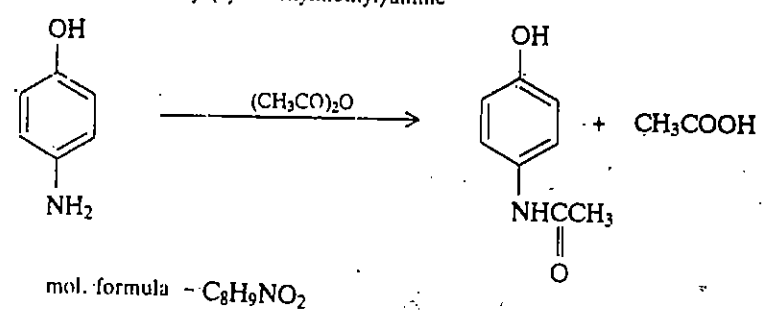
1) a) 2-methylpropanamine
   b) *N*,*N*-diethylethanamine or triethylamine
   c) cyclonexylamine
   d) 1,2-propanediamine
   e) 3-nitrobenzenamine or 3-nitroaniline

2) *o*-Nitroaniline can undergo **intramolecular** hydrogen bonding whereas its **meta-** and **para-** isomers show **intermolecular** hydrogen bonding. This leads to lower melting and boiling points for *o*-nitroaniline.

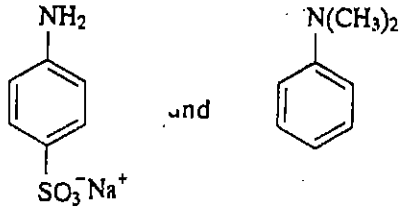
3) a) 
   3-phenyl-1-butanamine

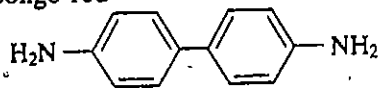
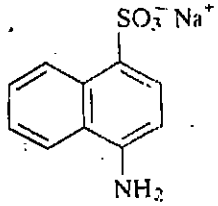
   b) $CH_3CH_2CH_2CH_2CH_2NHCH_2CH_2CH_2CH_3$
   N-butyl-1-pentanamine

   c) 
   N,*N*-dimethyl(cyclohexylmethyl)amine

4) 

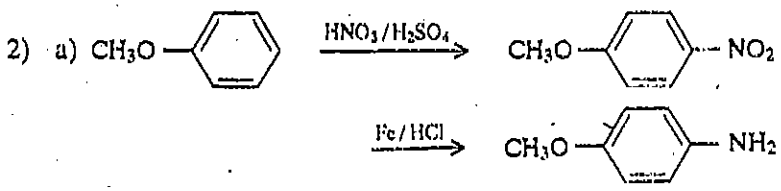
mol. formula – $C_8H_9NO_2$

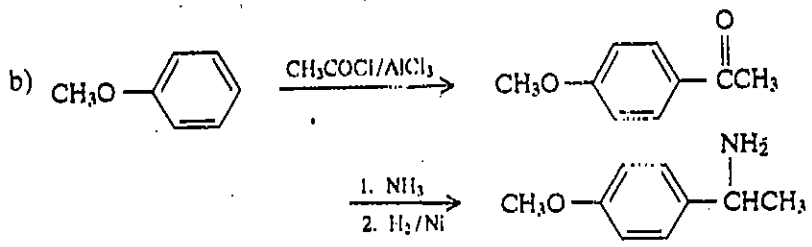
5) For methyl orange:  and

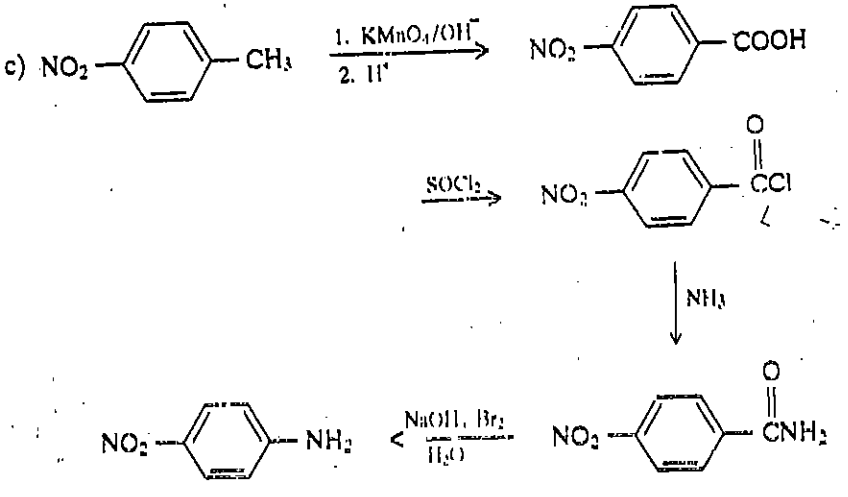
For congo red  and 2 equivalents of 

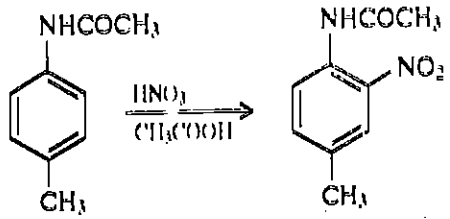
Terminal Questions

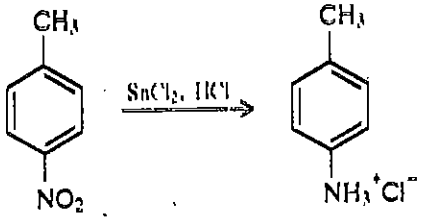
1) a) 2-butanamine
   b) *N,N*-dimethylbenzenamine
   c) 6-bromo-2-hexanamine

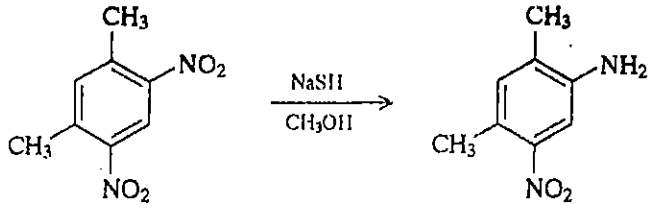
2) a) 

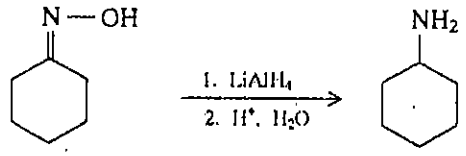
b) 

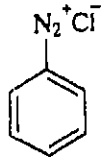
c) 

3) a) 

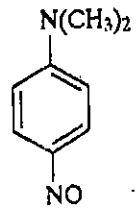
b) 

c) 

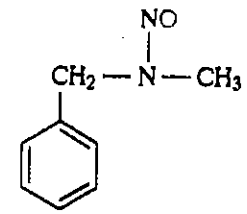
d) 

4) a) 

a diazonium salt

b) 

p-nitroso compound

c) 

N-nitroso compound

UNIT 20 NATURAL PRODUCTS

Structure

20.1 Introduction
Objectives
20.2 Carbohydrates
Classification and Structure of Carbohydrates
20.3 Peptides and Proteins
Structure of Peptides and Proteins
20.4 Nucleic Acids
Structure of Nucleic Acids
Nucleic Acids and the Genetic Code
20.5 Oils and Fats
Analysis of Oils and Fats
20.6 Terpenes
20.7 Steroids
20.8 Alkaloids
20.9 Antibiotics
20.10 Summary
20.11 Terminal Questions
20.12 Answers

20.1 INTRODUCTION

So far we have devoted much of our study of organic chemistry to describe the chemistry involved in the preparation and reactions of compounds containing different functional groups and correlating their behaviour with their structures. There is a unique and vast category of organic compounds produced by living organisms to which you have not yet been exposed. Such compounds are called **natural products**. There are many different classes of natural products. Natural products such as **carbohydrates, proteins, nucleic acids** and **fats** occur in almost all organisms and play an important and primary role in metabolic processes. These natural products are called **primary metabolites**. Another class of natural products, known as **secondary metabolites**, includes **terpenes, steroids** and **alkaloids.** The distribution of secondary metabolities is much more species-dependent. These compounds have been used as drugs, flavours, poisons, dyes and so on. This unit will be devoted to the basic concepts and genral chemistry associated with the natural products.

Objectives

After studying this unit, you should be able to:

- classify a carbohydrate as monosaccharide, oligosaccharide (disaccharide, trisaccharide and so on) or a polysaccharide,
- write the structures of various carbohydrates,
- write the structures of nucleic acids and discuss the role of DNA in protein synthesis,
- explain the primary, secondary, tertiary and quaternary structure of peptides and proteins,
- list the acids present in oils and fats,
- define acid value, sponification value and iodine value of oils and fats,
- give some examples of terpenes belonging to each category of this class of compounds,

- describe the physiological activities of some alkaloids, and
- give names, structures and uses of some antibiotics.

20.2 CARBOHYDRATES

Carbohydrates received their name because of their general formula $C_x(H_2O)y$, according to which they appear to be **hydrates of carbon.**

Carbohydrates are widespread in nature. In plants, they constitute upto 80% of the dry weight. Carbohydrates occurring in plants include **cellulose** (which gives structural support to plants), **starch** (which serves as the reserved energy source) and **sugars** (like sucrose and glucose). Glucose is an essential constituent of blood in higher animals and occurs in polymeric form as glycogen, in liver and in muscles. Carbohydrates also occur in adenosine triphosphate which is involved in biological energy storage and transport systems. They are also present in the nucleic acids which control the production of enzymes and the transfer of genetic information.

In nature, carbohydrates are synthesised by a process called **photosynthesis**. In this process, sunlight impinging on chlorophyll present in the green plants is absorbed and the photochemical energy thus obtained is used to convert carbon dioxide and water into carbohydrates and oxygen. The overall process can be represented as follows:

$$x\,CO_2 + y\,H_2O \xrightarrow{\text{Sunlight, chlorophyll}} \underset{\text{carbohydrate}}{C_x(H_2O)_y} + x\,O_2$$

20.2.1 Classification and Structure of Carbohydrates

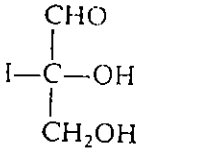
Carbohydrates are polyhydroxy aldehydes and ketones and substances which hydrolyse to polyhydroxy aldehydes and ketones.

The simplest carbohydrates are called **sugars** or **saccharides**, (Latin: *Saccharum*, sugar). Carbohydrates can be classified as **monosaccharides, oligosaccharides** and **polysaccharides**.

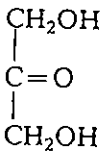
Sugars are crystalline substances having sweet taste and are soluble in water.

Monosaccharides

Monosaccharides are the simplest carbohydrates which cannot be hydrolysed into smaller and simpler carbohydrates. A monosaccharide may be further classified as an **aldose** or a **ketose** if it contains an *aldehyde* or a *keto* group, respectively. The simplest monosaccharides being 2,3-dihydroxypropanal (glyceraldehyde) and 1,3-dihydroxypropanone. Their structures are as shown below:



2,3-dihydroxylpropanal
(an aldose)



1,3-dihydroxypropanone
(a ketose)

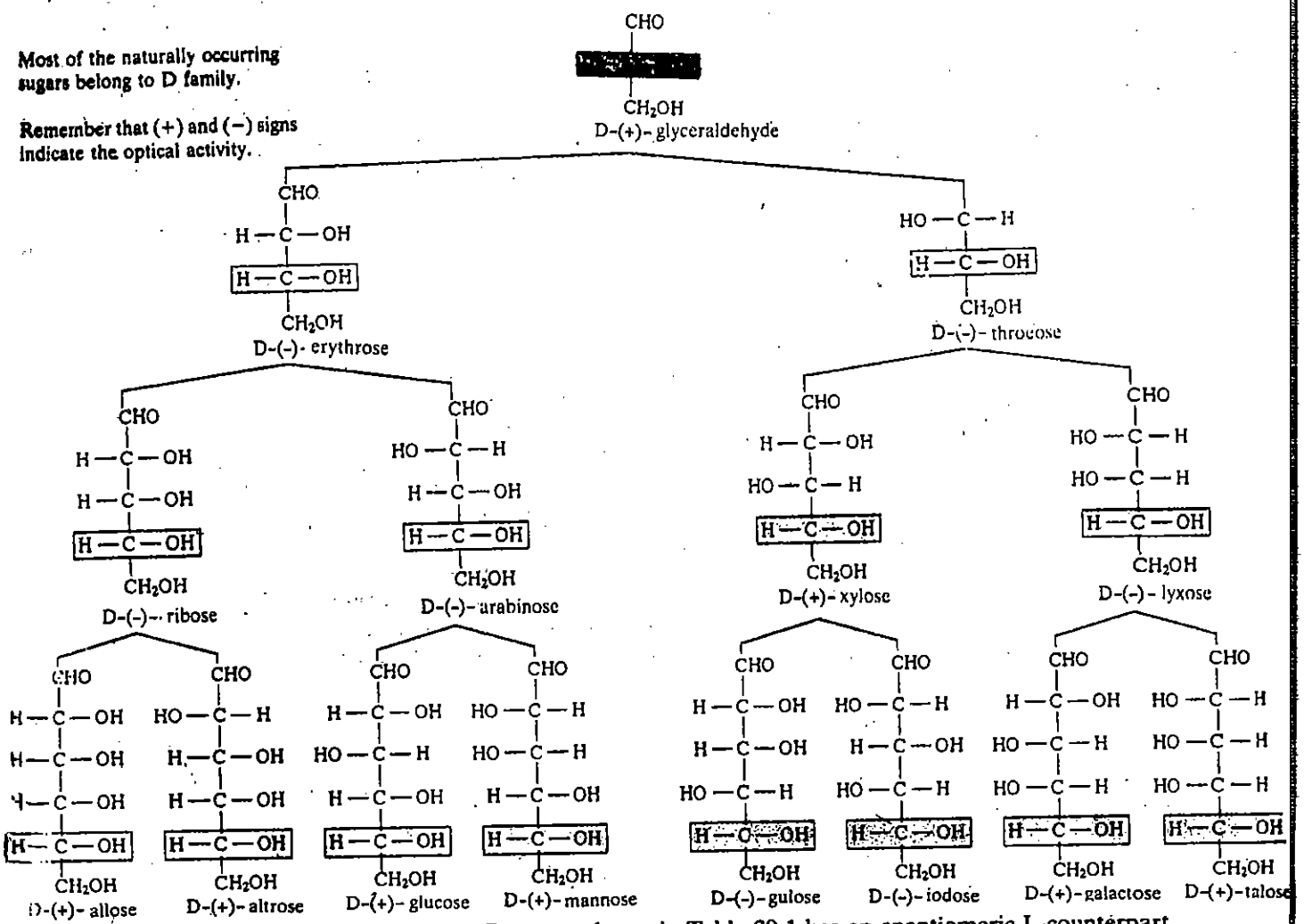
Depending upon the number of carbon atoms in the chain, sugars are called **trioses** (3 carbons), **tetroses** (4 carbons), **pentoses** (5 carbons), **hexoses** (6 carbons) and so on. Therefore, 2,3-dihydroxypropanal is an **aldotriose** and 1,3-dihydroxypropanone is a **ketotriose**.

It was pointed out in Unit 3 that monosaccharides can be classified as D or L depending upon whether the position of the hydroxyl group on carbon next to primary alcoholic group is right or left in the Fischer projection of the molecule projected vertically in such a way that the aldehyde function is on the top. The structures of aldoses belonging to D-family are given in Table 20.1.

Most of the naturally occurring sugars belong to D family.

Remember that (+) and (−) signs indicate the optical activity.

Table 20.1 : The D-family aldoses



Each of the D sugars shown in Table 20.1 has an enantiomeric L-counterpart.

You may recall that R, S system of assigning configurations was discussed in Unit 3, Block 1.

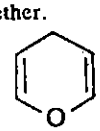
The absolute configurations are described by assigning the configuration to each stereocentre in the molecule. For example, D-(+)-glucose is (2*R*, 3*S*, 4*R*, 5*R*)—2, 3, 4, 5, 6-pentahydroxyhexanal.

As in the case of D-aldoses shown in Table 20.1, the Fischer projections of monosaccharides belonging to D-ketose series are shown in Table 20.2.

You are aware from seb-Sec. 14.4.1, Sec. 14.4, Unit 14, Block 3 that aldehydes and ketones form hemiacetals or hemiketals with alcohols. Since sugars are hydroxy carbonyl compunds, they are capable of forming intramolecular cyclic hemiacetals and hemiketals. While in principle, any one of the hydroxyl group could add to the carbonyl function; the formation of six-membered ring is preferred, although five-membered rings are also formed. This is shown below in case of glucose.

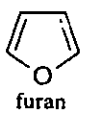
Cyclic Hemiacetal Formation by Glucose

The name **pyranose** is derived from pyran, a six-membered cyclic ether.

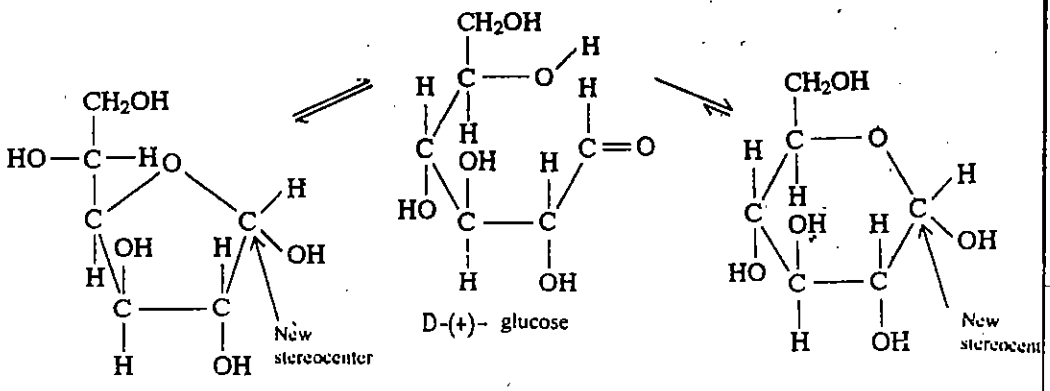


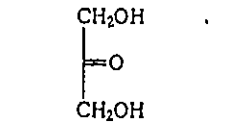
pyran

Similarly, **furanose** is derived from furan.

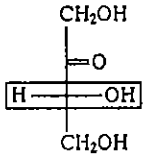


furan

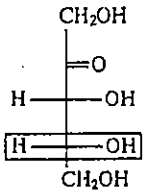




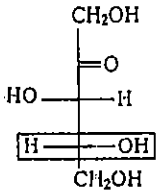
1,3-Dihydroxypropanone



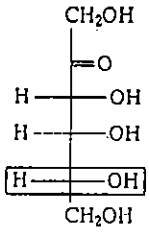
D-(−)-erythralose



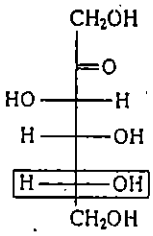
D-(+)-ribulose



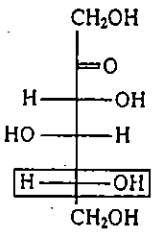
D-(+)-xylulose



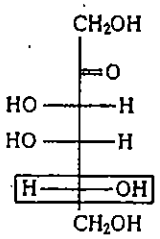
D-(+)-psicose



D-(−)-fructose

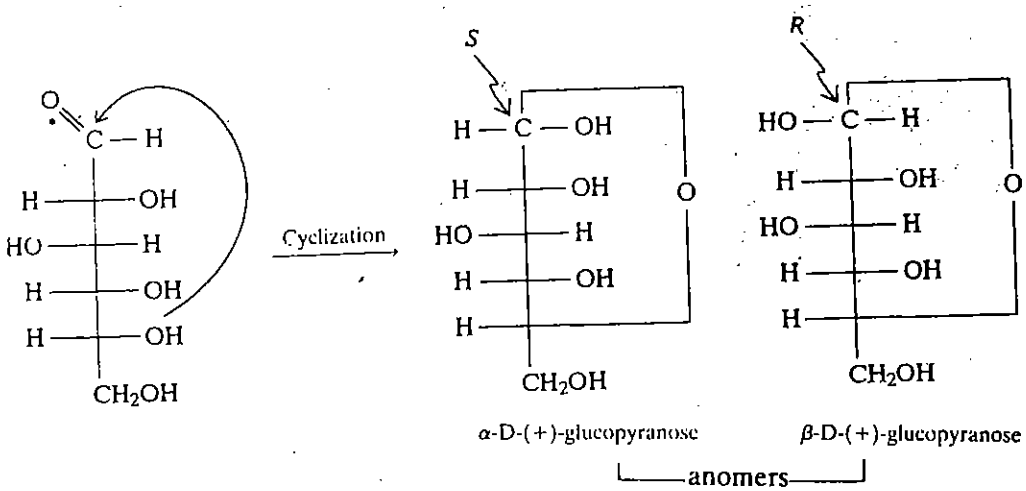


D-(+)-sorbose



D-(−)-tagatose

You can see that the formation of hemiacetal (or hemiketal) turns the carbonyl carbon into a new stereocentre. This leads to **two** new compounds which are diastereomers having different configurations at C-1. Such isomers are called **anomers** and the hemiacetal or hemiketal carbon (C-1) is called the **anomeric carbon.** The two anomers are differentiated by the Greek letters α and β. Thus, we can call the anomers of glucose as α-D-(+)-Glucopyranose and β−D−(+)−Glucopyranose. These anomers are represented below in the modified Fischer projections using elongated lines to indicate the new bonds formed.



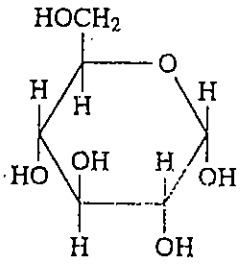
Note that in β-anomer the OH at C-1 is written to the left and that in the α-anomer is written to right.

Since these modified Fischer projections do not give the correct picture of the molecule in terms of bond lengths, Haworth introduced an alternate projection formula called **Haworth projections**. In Haworth projections, the cyclic ether is written as a planer pentagon or a hexagon having the anomeric carbon on the right and the ether oxygen at the top. The substituents located above and below the ring

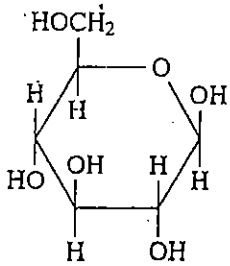
are joined by vertical lines to the ring carbons. The OH at the anomeric carbon (C–1) is shown up in the β-anomer and down in the α-anomer.

Haworth, the English Chemist, received the Nobel Prize in 1937 for his work in carbohydrate chemistry.

The Haworth projections of D-(+)-Glucose are shown below.



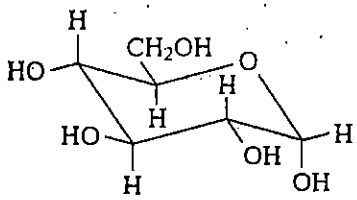
α-D-(+)-glucopyranose



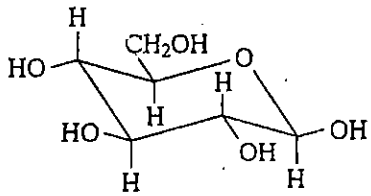
β-D-(+)-glucopyranose

Using our knowledge of conformations of cyclic systems gained in Unit 3, Block 1, we can write the chair conformations of the anomeric forms of D-(+)-glucose as given below.

Glucose exists mainly in the pyranose form whereas fructose forms an equilibrium mixture of pyranose and furanose forms in the ratio 70:30.

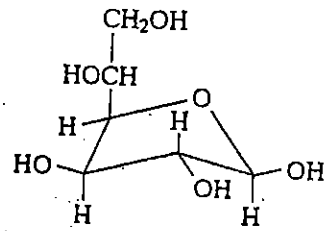


β-D-glucopyranose



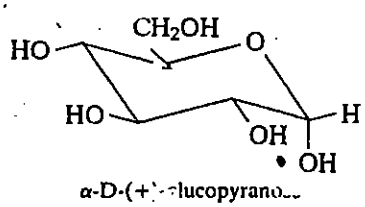
β-D-glucopyranose

The envelope conformation of the furanose form can be represented as shown below.



β-D-glucofuranose

Both α-D-(+)-glucopyranose and β-D-(+)-glucopyranose are optically active but differ widely in their optical rotations. The α-D-(+)-glucopyranose has the specific rotation of $[\alpha]_D^{298\,K} = +112°$ whereas β-D-(+)-glucopyranose has $[\alpha]_D^{298\,K} = +18.7°$. When dissolved in water, the optical rotation of the solution gradually changes with time until it reaches an equilibrium value of +52.7°. This is because α-D-(+)-glucopyranose rapidly establishes an equilibrium with a small amount of the open-chain aldehyde form which in turn undergoes renewed and reversible ring closure to the β-anomer.

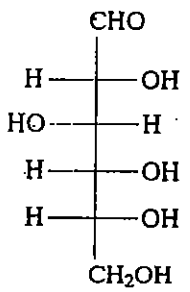


α-D-(+)-glucopyrano...

$[\alpha]_D^{298\,K} = +112°$

(36.4%)

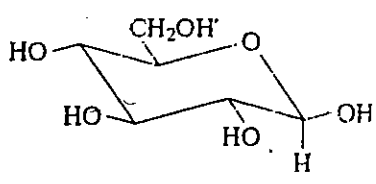
$\overset{H^+ \text{ or } HO^-}{\rightleftharpoons}$



aldehyde form

0.003%

$\overset{H^+ \text{ or } HO^-}{\rightleftharpoons}$



β-D-(+)-glucopyranose

$[\alpha]_D^{298\,K} = +18.7°$

(63.6%)

This interconversion is called **mutarotation** and was first observed in 1846. It involves change of configuration at one stereocentre in a compound having more than one such centres.

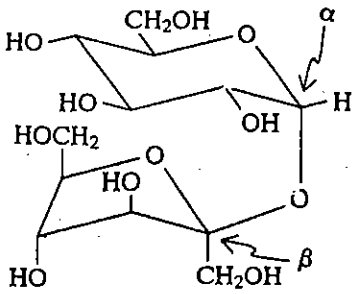
Mutarotation is catalysed by acid and bases.

In Latin, *mutare* means to change.

Oligosaccharides

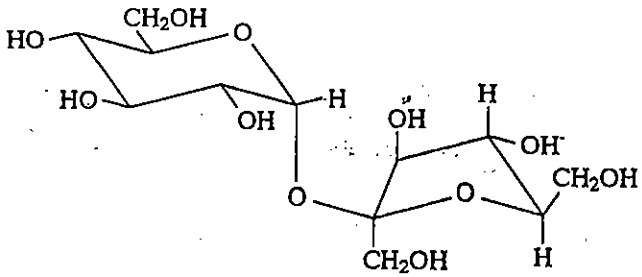
Oligosaccharides are the carbohydrates that yield two to eight monosaccharide units on hydrolysis. Carbohydrates which yield *two* monosaccharide units on hyrolysis are called **disaccharides** and those which yield *three* monosaccharide units are called **trisaccharides** and so on.

The most familiar disaccharide is the table sugar called **sucrose.** It contains one unit each of glucose and fructose joined by acetal linkage as shown below in its structure. Sucrose is abundant in cane sugar and sugar beets where it is present to the extent of 14-20% by weight.



(sugars represented in usual way)

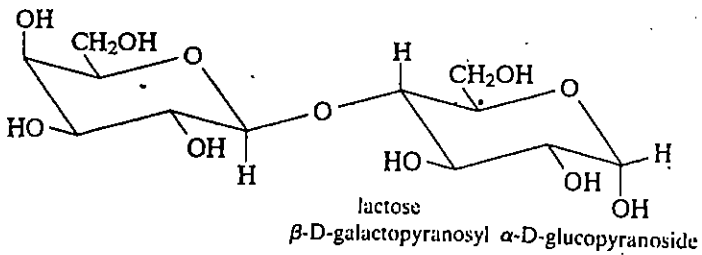
or



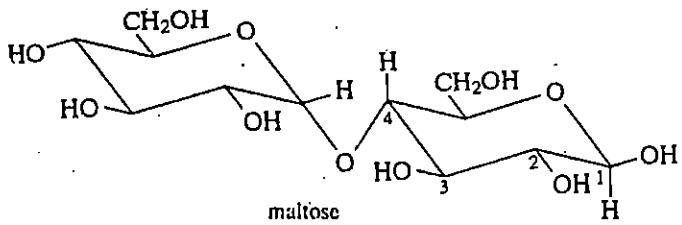
(sterically more favourable)

Sucrose an α-D-glucopyranosyl β-D-fructofuranoside

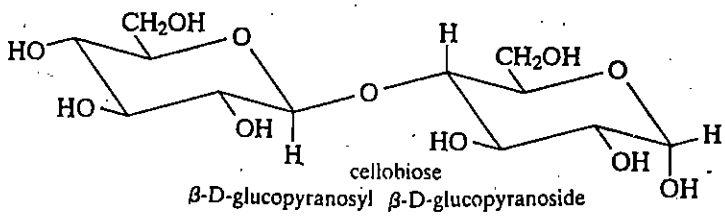
The other common disaccharides are **lactose, maltose** and **cellobiose** Their structures are given below:



lactose
β-D-galactopyranosyl α-D-glucopyranoside



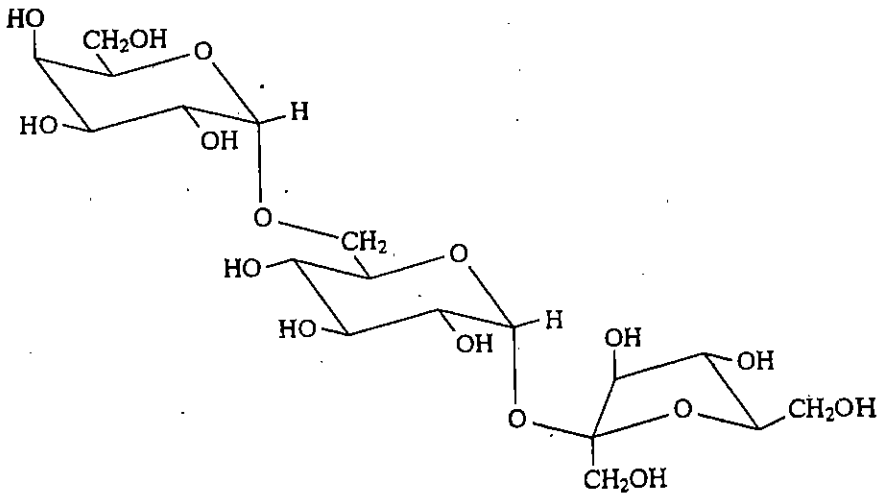
maltose
α-D-glucopyranosyl β-D-glucopyranoside



cellobiose
β-D-glucopyranosyl β-D-glucopyranoside

Lactose constitutes about 5% by weight of human and most animal milk. Maltose is obtained by enzymatic degradation of starch using the enzyme **amylase** whereas cellobiose is obtained by the hydrolysis of cellulose.

Raffinose is an example of a trisaccharide. It is found in sugar beets and also in cotton seeds. On hydrolysis, it yields one unit each of D-galacotose, D-glucose and D-fructose which are joined together as shown below.

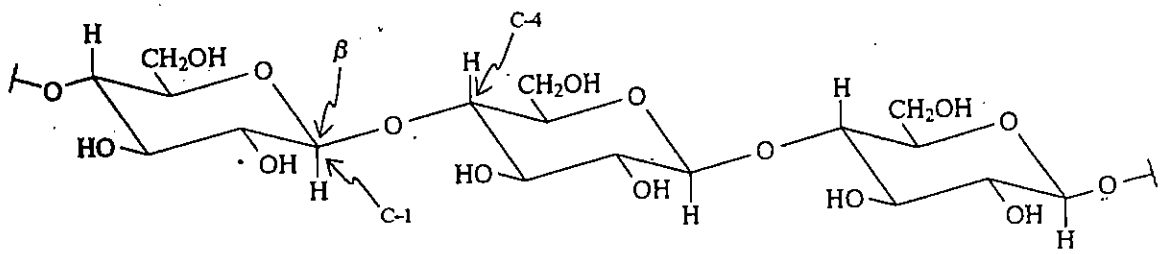


raffinose

Polysaccharides

Polysaccharides are the polymers of monosaccharides. The natural polysaccharides generally contain about 100-3000 monosaccharide units. The three most abundant natural polysaccharides-cellulose, starch and glycogen are derived from the same monomer, i.e., glucose.

Cellulose contains about 3000 monomeric units linked together and has a molecular weight of about 500,000. The individual units are linked by β-glycoside bonds which join the anomeric carbon of one unit to the C-4 hydroxyl of the next unit as shown below in the structure of cellulose.

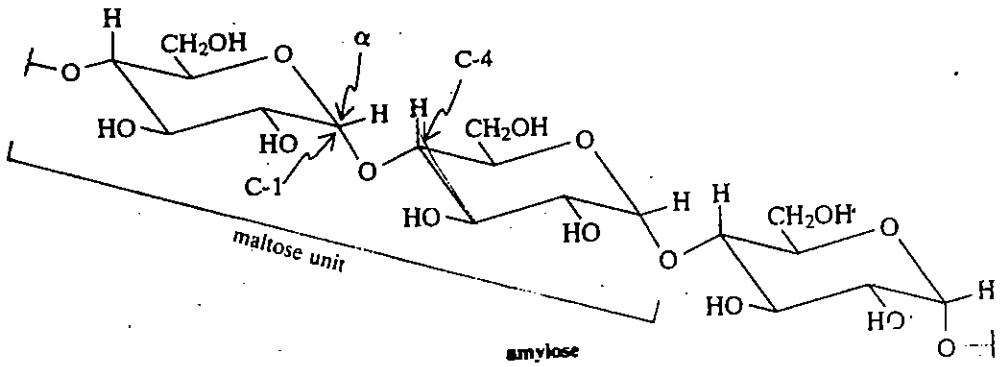


cellulose

Cellulose is abundant in trees and plants. Cotton fibre contains 90% cellulose by weight.

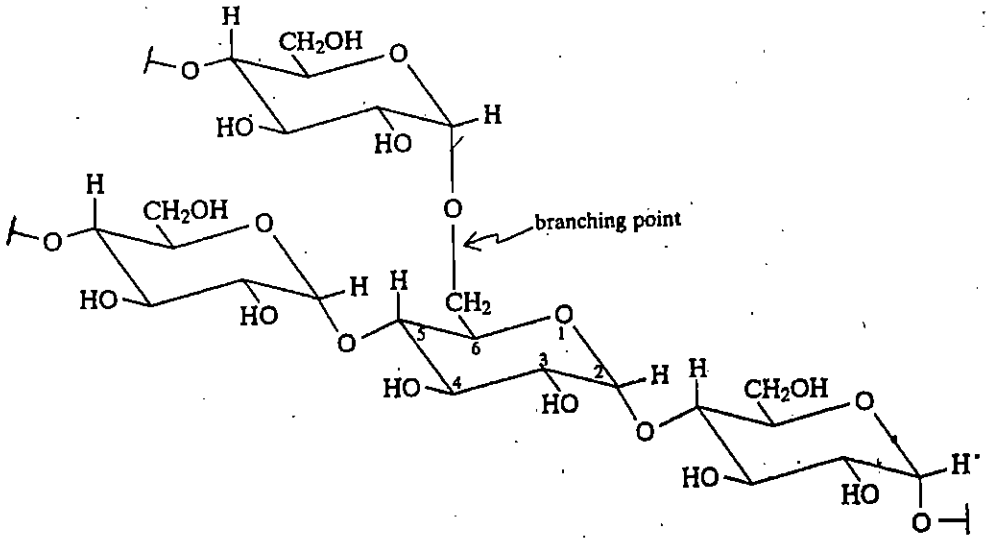
Unlike cellulose, **starch** contains glucose units linked by α-glucoside bonds. Major sources of starch are corn, potatoes, wheat and rice which constitute the chief carbohydrate sources for human beings. Starch is deposited in plants in the form of starch granules. The granules swell in hot water and can be separated into two major components: **amylose** (~ 20%) and **amylopectin** (~80%).

Amylose contains a few hundred units per molecule linked in an unbranched manner and has the molecular weight ranging between 1,50,000 – 6,00,000



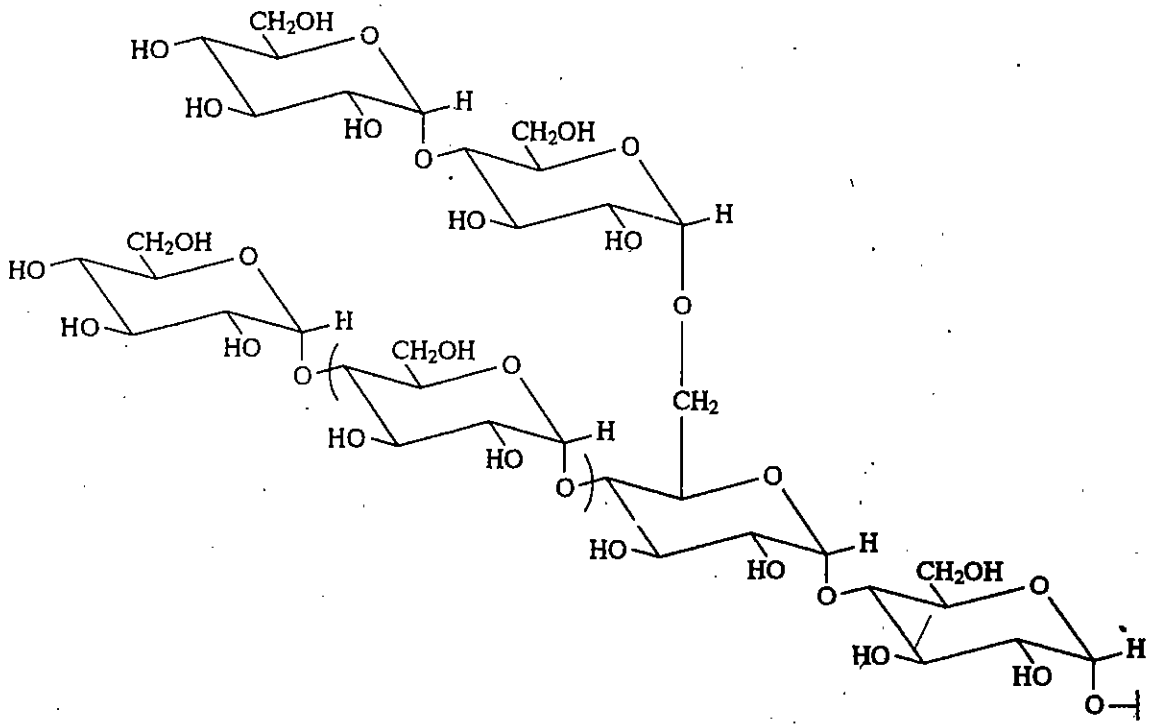
amylose

Amylopectin on the other hand is branched at the C-6 position. The branching occurs at about every twenty to twenty-five glucose units. Its molecular weight is in millions. A portion of the structure of amylopectin is shown below:



amylopectin

Glycogen is structurally similar to starch but has greater branching, i.e., one per ten glucose units. It is a source of stored energy in humans and accumulates in liver and muscles.



glycogen

SAQ 1

Write the hemiacetal formation for fructose.

.....

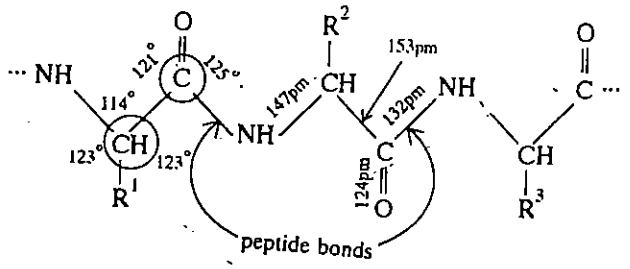
.....

.....

20.3 PEPTIDES AND PROTEINS

In the last section, you studied the polymers of monosaccharides which act as structural components in plants and serve as energy storage in animals. In this section, you will study another kind of natural polymers called **peptides** and **proteins.**

Peptides are biologically important polymers in which 2-amino acids are joined by the amide linkages, formed by the reaction of the carboxy group of one amino acid with the amino group of another amino acid. These amide linkages are also called **peptide bonds.** The general structure of a peptide is shown below:



general peptide structure

Remember that a three letter code to represent amino acids was given in Table 16.1, Sec. 16.4, Unit 16.

Peptides can be classified as **dipeptides, tripeptides** and **tetrapeptides**, depending on whether the number of amino acids is **two, three** or **four,** respectively. Peptides containing upto 50 amino acids are called **polypeptides.** *Bradykinin* is an important naturally occurring nonapeptide which is present in blood plasma and is involved in the regulation of blood pressure.

Arg-Pro-Pro-Gly-Phe-Ser-Pro-Phe-Arg
bradykinin

Proteins are large polypeptides containing from about 50 to more than 8,000 amino acids per molecule. Proteins have diverse biological functions. As enzymes and hormones, proteins catalyse and regulate various reactions occurring in our body. As skin and hair, they give outer covering to our body and as muscles they provide movement. In the form of antibodies, they protect us from diseases. The oxygen present in the air we breath, is transported by the protein **hemoglobin**. The nucleoproteins in the genes supply and transmit the genetic information in cell division. In addition, proteins also provide structural support in combination with other substances.

After having an idea about the importance of proteins, you must be curious to know about the structure of peptides and proteins.

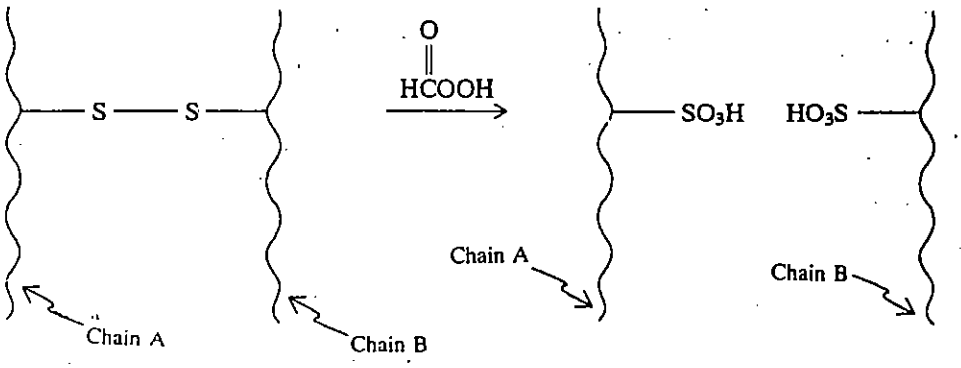
20.3.1 Structure of Peptides and Proteins

Since peptides and proteins contain a number of amino acids linked together, the first step in the determination of their structure requires a knowledge about which amino

acids are present and how they are linked together plus any *disulphide links* present in them. The order in which the amino acids are joined is called the **primary structure** of a peptide or protein.

Disulphide links hold peptide chains together in a protein molecule.

Determination of the primary structure involves oxidation of the disulphide bridges linking the chains in peptides or proteins to sulphonic acids using peroxymethanoic acid, as shown below:



Proteins can be degraded into peptides by **partial hydrolysis** using either dilute hydrochloric acid or enzymes. Peptides on **complete hydrolysis** by heating with 6 N HCl for 24 hours yield a mixture of all amino acids present. This mixture is then separated, taking advantage of the acid-base properties of amino acids, in an apparatus known as **amino acid analyser**. The separation involves ion-exchange chromatography. This analysis thus provides information about the amino acids present and their relative amounts.

The sequence of amino acids present in a peptide chain can be determined either by analysing the products of **partial hydrolysis** or by **end group analysis**. Let us understand these methods with the help of examples.

Partial Hydrolysis

In a particular case, partial hydrolysis of a tetrapeptide containing Ala, Gly, Phe and Val yielded a tripeptide Gly-Phe-Val and a dipeptide Ala-Gly.

$$\text{Tetrapeptide} \xrightarrow{\text{hydrolysis}} \text{Gly-Phe-Val} + \text{Ala-Gly}$$

Since the dipeptide shows that Ala is linked to Gly, the amino acids in the tetrapeptide are linked in the following sequence:

$$\text{Ala}\overset{b}{\text{—}}\text{Gly}\overset{a}{\text{—}}\text{Phy—Val}$$

Cleavage at *a* gives the tripeptide and that at *b* gives the dipeptide.

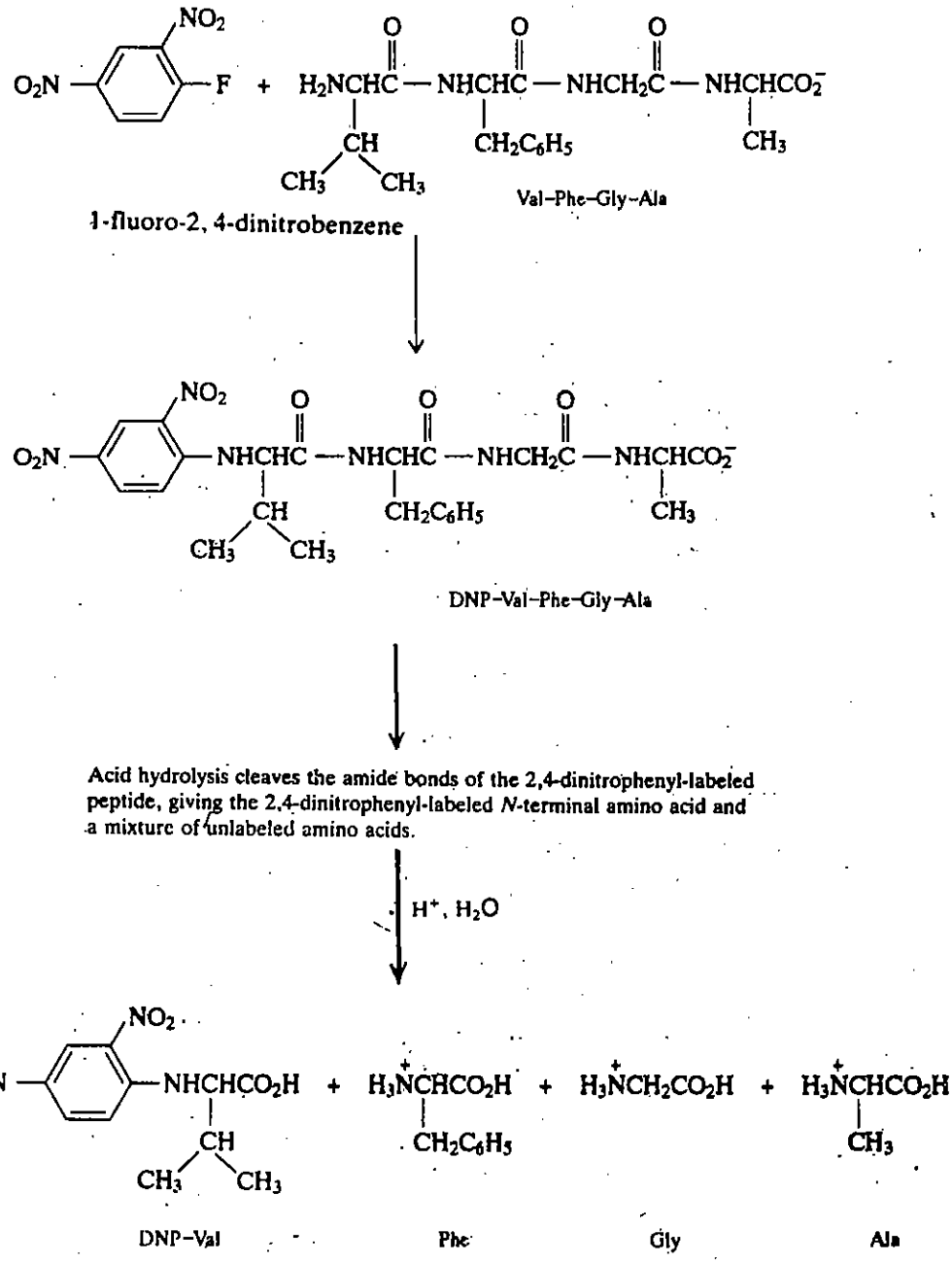
End Group Analysis

Let us first understand what is an end group? By convention, peptide structures are written in such a way that the amino group is at the left and the carboxy group is at the right. Thus, the amino end is called the **N-terminus** and the carboxy end is called the **C-terminus**, the end groups being amino and carboxy groups.

The amino groups of all the amino acids, except the N-terminal amino acid, are involved in the amide bond formation. Therefore, the amino group of the N-terminal

Sanger utilised this method in the determination of sequence of amino acids in insulin and was awarded Nobel Prize in 1958 for this pioneering work

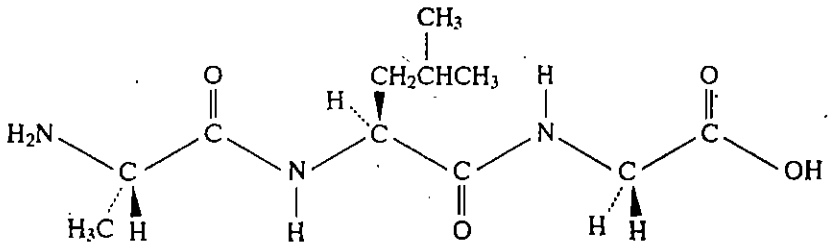
amino acid is free and can react as a nucleophile. The **Sanger method** of identifying N-terminal amino acid involves the reaction of the free amino group in the peptide with 1-fluoro-2, 4-dinitrobenzene to yield a peptide in which the N-terminal nitrogen is tagged with a 2,4-dinitrophenyl group. After complete hydrolysis of the peptide, the tagged amino acid is identified by chromotographic methods. This procedure is illustrated below.



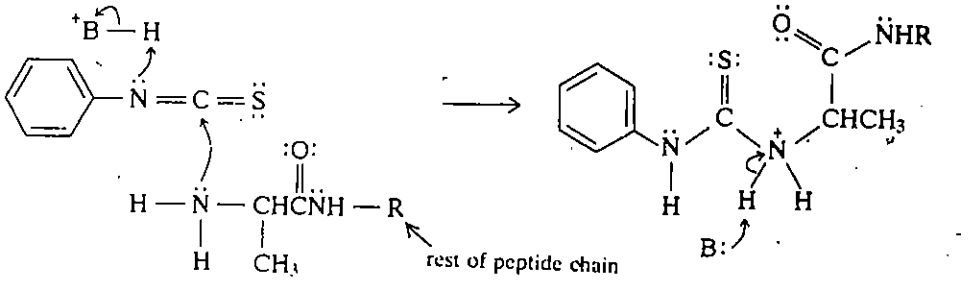
The drawback in this method is that complete degradation is required after the polypeptide is once tagged.

A more useful method is by the **selective removal** of the tagged terminal amino acid and leaving the remaining chain intact so that it can again be tagged with the reagent. One such method which enables identification of one amino acid in the sequence at a time is the **Edman degradation**.

In *Edman degradation*, the terminal amino group adds to phenyl isothiocyanate, $C_6H_5N{=}C{=}S$ to yield a thiourea derivative. Treatment with mild acid gives the tagged amino acid as a phenylthiohydantoin and the remainder of the peptide chain. The tagged amino acid is identified and the remaining peptide is again subjected to Edman degradation. This sequence is repeated till all the amino acids in the peptide are identified. An example using the peptide Ala-Leu-Gly is shown below:

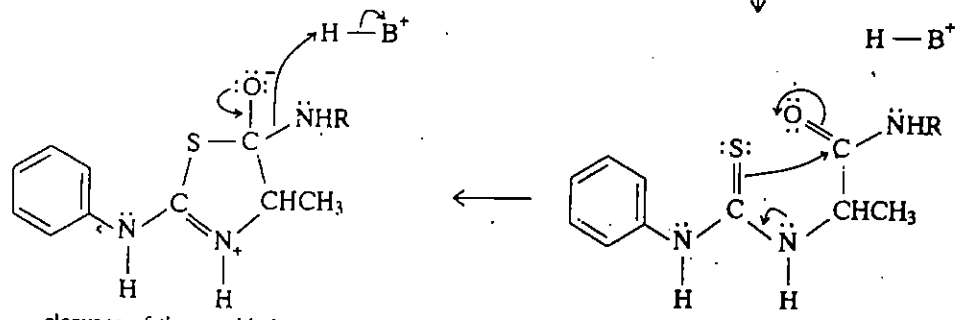


Ala-Leu-Gly
Peptide



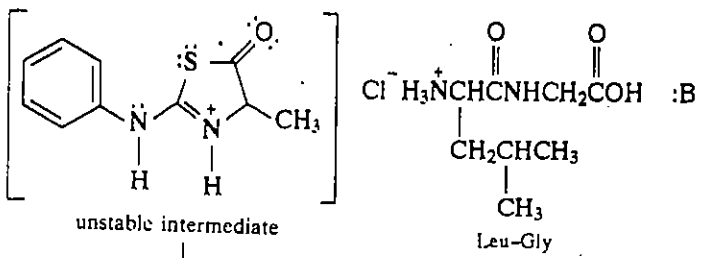
nucleophilic attack by amino group on isothiocyanate with subsequent protonation of nitrogen

deprotonation



cleavage of the peptide bond

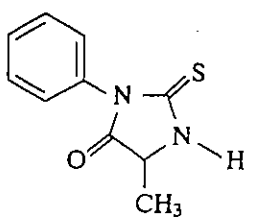
nucleophilic attack by sulphur on carbonyl group



unstable intermediate

Leu-Gly

△, rearrangment



phenylthiohydantoin derived from alanine

The amino acid at the C terminus is identified by **enzymatic hydrolysis**. The enzymes which are used are called **peptidases** or **proteases**. Thus, **carboxypeptidases** sequentially cleave the C-terminus amino acids and the amino acids so cleaved are monitored with time to know the sequence.

Certain peptidases which allow controlled hydrolysis by cleaving certain specific amide bonds, can also be used in sequence analysis. For example, **trypsin**, present in intestine, catalyses the hydrolysis of the peptide bonds involving carboxy groups of lysine or arginine. Similarly, **chymotrypsin** allows cleavage of the amide bonds of amino acids containing aromatic groups in their side chains, namely phenylalanine, tyrosine and tryptophan.

Till now you have learnt the primary structure of peptides and proteins. Let us now study their secondary structure, i.e., the spatial arrangement of the peptide chains.

Description of the conformational relationship of the nearest amino acids of a peptide is called its **secondary structure**. Two conformational arrangements called **α-helix** and **β-pleated sheet** are particularly stable.

The terms α and β refer to two characteristic X-ray diffraction patterns. The α-type pattern was associated with right handed helix and β-type with the pleated sheet.

In a right handed helix, the chain turns in clockwise direction.

The α-helix conformation is shown in Fig. 20.1. In this the polypeptide chain forms a right handed coil having 3.7 amino acids per turn. This allows hydrogen bonding between each carbonyl oxygen and an amide hydrogen which stabilises the conformation. α-Helix is important in structural proteins such as α-keratins which constitute proteins of skin, nails, hair and feathers.

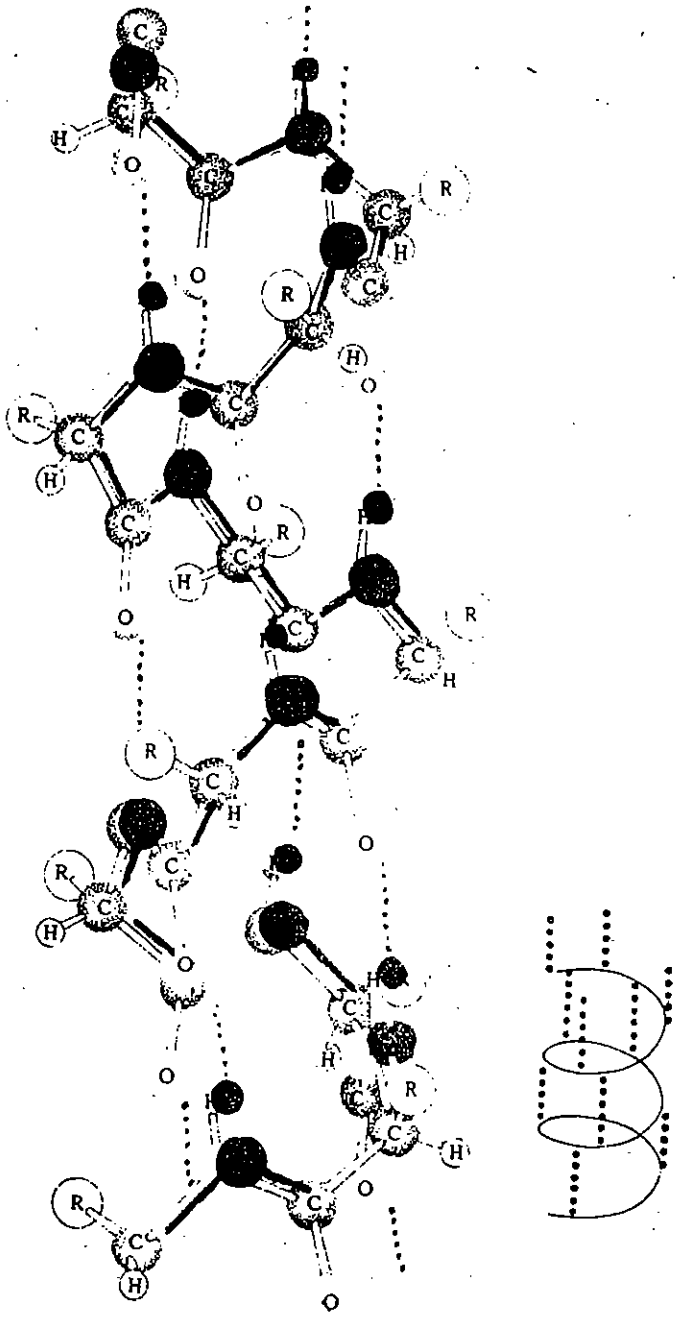


Fig. 20.1 α-helix.

The β-pleated sheet is shown in Fig. 20.2.

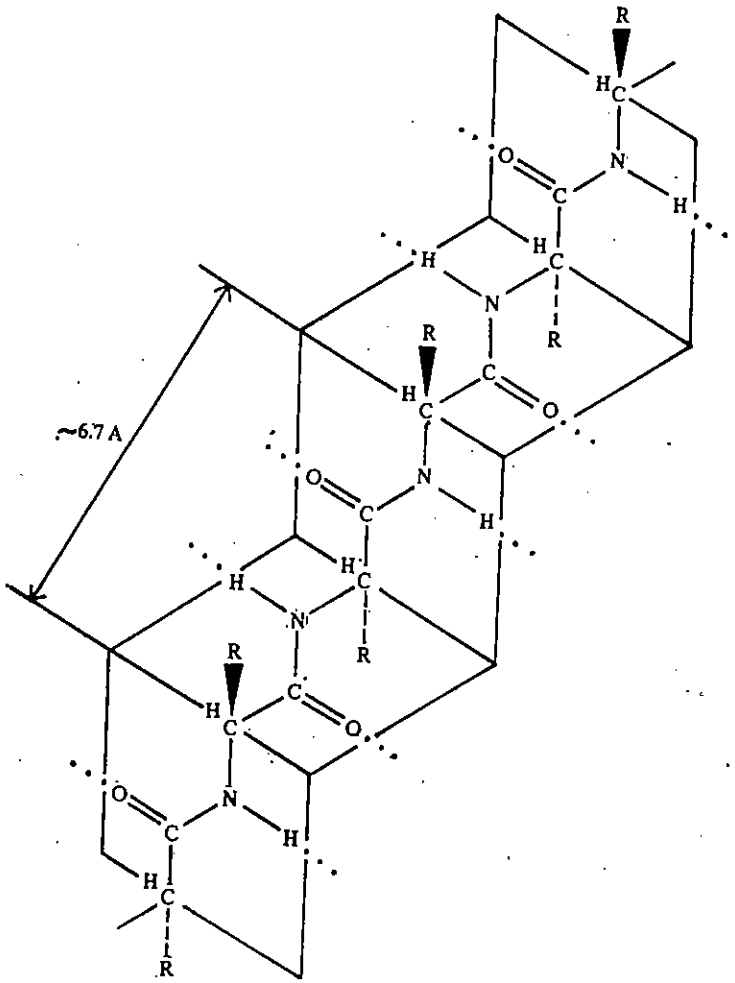


Fig. 20.2 : The β-pleated sheet in a polypeptide.

Note that the hydrogen bonds are formed between the carbonyl oxygen and the amide hydrogen of *two chains* in β-pleated sheet. You can see that the side chains alternate above and below the planes of the pleated sheets.

Tertiary structure refers to further folding of the peptide chain leading to its three-dimensional shape. Folding affects the physical and biological properties. Tertiary structure depends upon a variety of factors such as hydrogen bonding, van der Waal's forces and electrostatic forces. A protein adopts the tertiary structure in such a way that favourable interactions are maximised and the unfavourable ones are minimised. The tertiary structure of a protein is important in the sense that it defines an **active site** to fit in a substrate. This allows the specificity of enzyme action. The tertiary structure of **fibrous proteins** show a **superhelix** in which several α-helices are coiled, see Fig. 20.3.

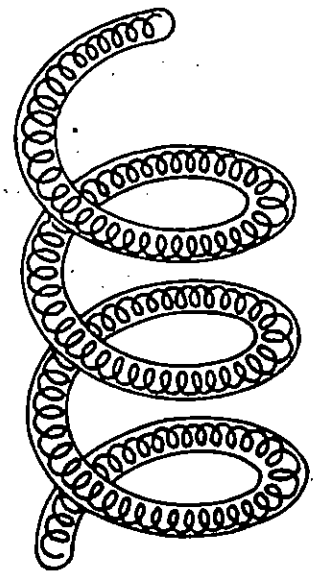


Fig. 20.3: A superhelix : helix within a helix.

Pronounced folding is observed in **globular proteins** in which the tertiary structure allows them to be spherical. The globular proteins perform a crucial part in chemical transport.

Some proteins such as hemoglobin have a **quaternary structure** in which two or more peptide chains combine to form an assembly. The manner in which these subunits are organised is referred to as the quaternary structure of the protein.

SAQ 2

Write the structure of the tripeptide Val-Phe-Ser.

.....

.....

.....

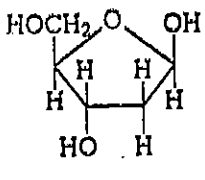
20.4 NUCLEIC ACIDS

Having studied the structure of peptides and proteins, let us now study the substances involved in the control of protein biosynthesis and transfer of genetic information. These are biological macromolecules present in the nuclei of the cells and are called **nucleic acids.** There are two major kinds of nucleic acids, **deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA).** Nucleic acids are the natural polymers which contain **nucleotide** repeating units and are, therefore, also known as **polynucleotides.**

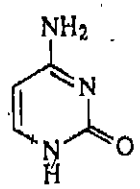
The prefix *deoxy* means without oxygen.

Nucleotides contain a **phosphate group** linked through a **sugar moiety** to a **nitrogen heterocycle.**

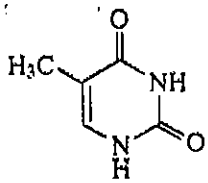
DNA contains the sugar *2-deoxyribose* and four nitrogen heterocyclic bases called *cytosine* (C), *thymine* (T), *adenine* (A) and *guanine* (G). Their structures are shown below:



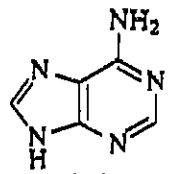
2-deoxyribose



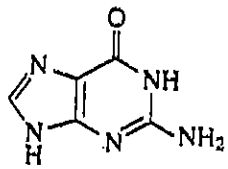
cytosine



thymine

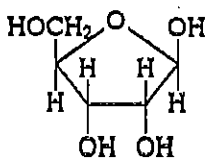


adenine

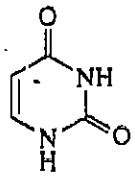


guanine

In kNA, the sugar moiety is ribose and the four bases present are cytosine, adenine, guanine and uracil. The structures of ribose and uracil are given below:

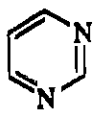


ribose

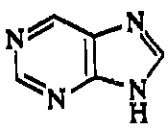


uracil

Note that the heterocyclic bases are derived from heterocyclic ring systems: pyrimidine and purine:



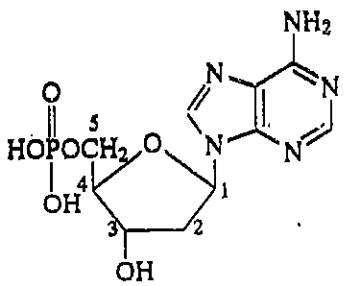
pyrimidine



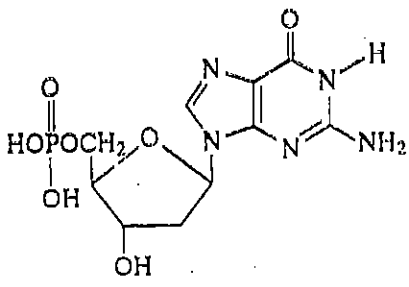
purine

Thus, the nucleotides present in DNA and RNA can be written as follows:

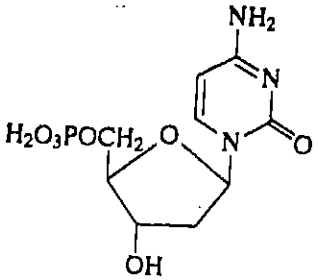
The Four Nucleotides of DNA



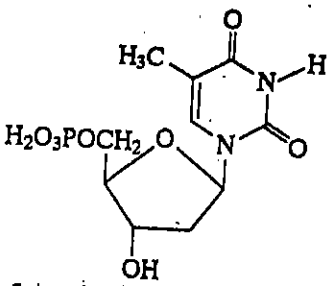
2-deoxyadenylic acid



2-deoxyguanidylic acid



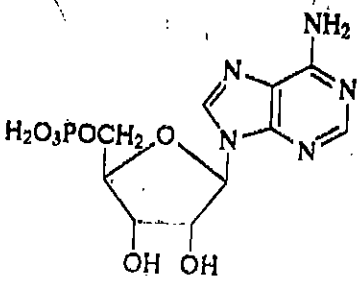
2-deoxycytidylic acid



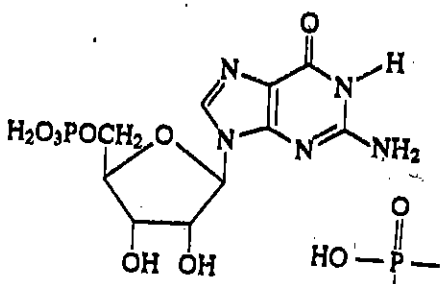
2-doxythymidylic acid

Other important 5'-nucleotides of adenosine include adenosine diphosphate (ADP) and adenosine triphosphate (ATP).

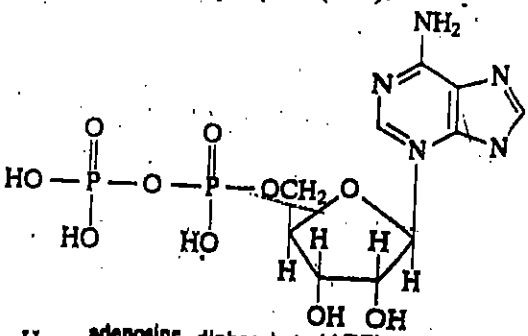
The Four Nucleotides of RNA



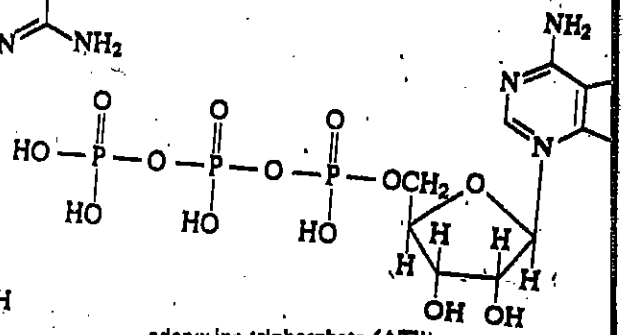
adenylic acid



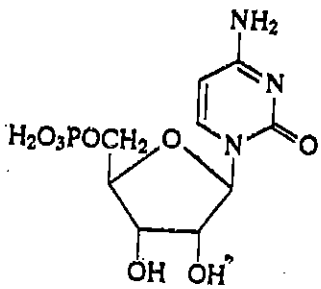
guanidylic acid



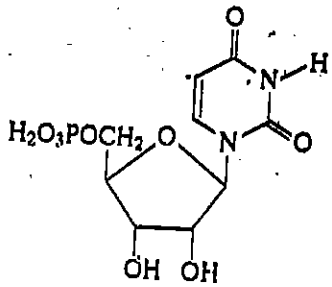
adenosine diphosphate (ADP)



adenosine triphosphate (ATP)

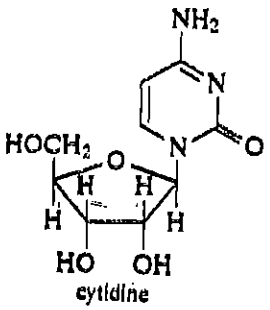


cytidylic acid

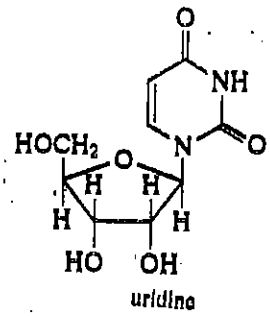


uridylic acid

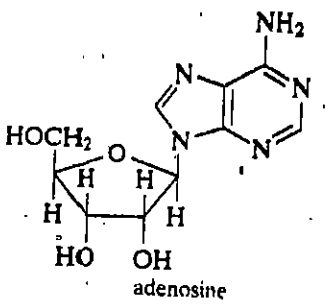
Base-catalysed hydrolysis of a nucleotide removes the phosphate group to yield a nucleoside. The nucleosides of RNA are shown below:



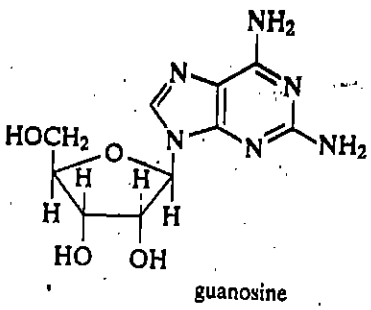
cytidine



uridine



adenosine



guanosine

20.4.1 Structure of Nucleic Acids

Nucleic acids are polynucleotides in which the phosphate esters link the 3′-hydroxyl of one sugar with 5′-hydroxyl of another, see Fig. 20.4 which shows a portion of a polynucleotide chain.

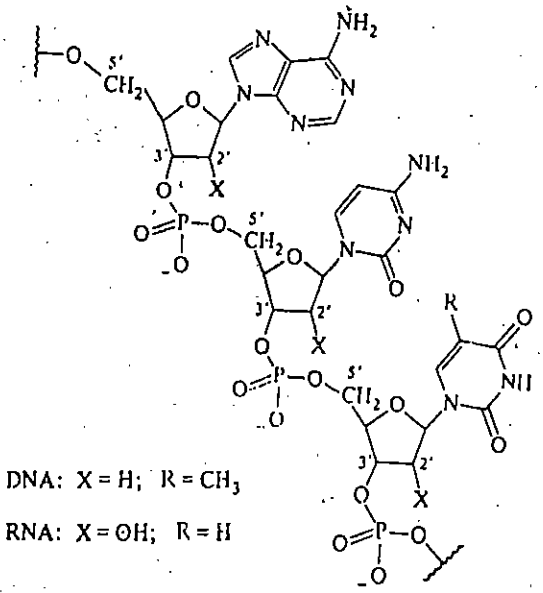


Fig. 20.4: A portion of a polynucleotide chain.

You can see in Fig. 20.4 that there is a **backbone** of alternating sugar and phosphate units with bases protruding from the chain at regular intervals.

In 1950, Chargaff observed that the ratios of adenine to thymine and guanine to cytosine in DNA was always one to one which indicated the association of adenine to thymine and guanine to cytosine by hydrogen bonds as shown below in Fig. 20.5.

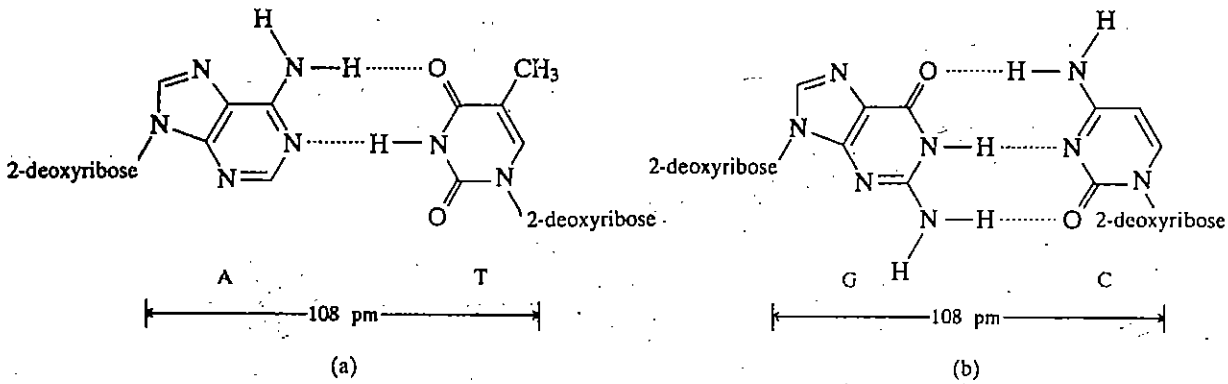


Fig. 20.5: Base pairing between (a) adenine and thymine and (b) guanine and cytosine.

J.D. Watson and F. Crick received Nobel Prize for medicine and physiology in 1962 for their work on structure of DNA.

This hydrogen bonding between the base pairs is a key element in the double helix structure of DNA proposed by Watson and Crick. Such a double helix is shown in Fig. 20.6.

20.4.2 Nucleic Acids and the Genetic Code

The sequence of nucleotides in DNA contains all the genetic information for cell duplication. At one stage of cell division, the double helix of DNA begins to unwind. Each of the separated chains function as a template upon which another chain, exactly complementary to itself, is constructed. This leads to two identical new double helices, each one of which passes the genetic information to the daughter cells. This is called **DNA replication** and is shown in Fig. 20.7.

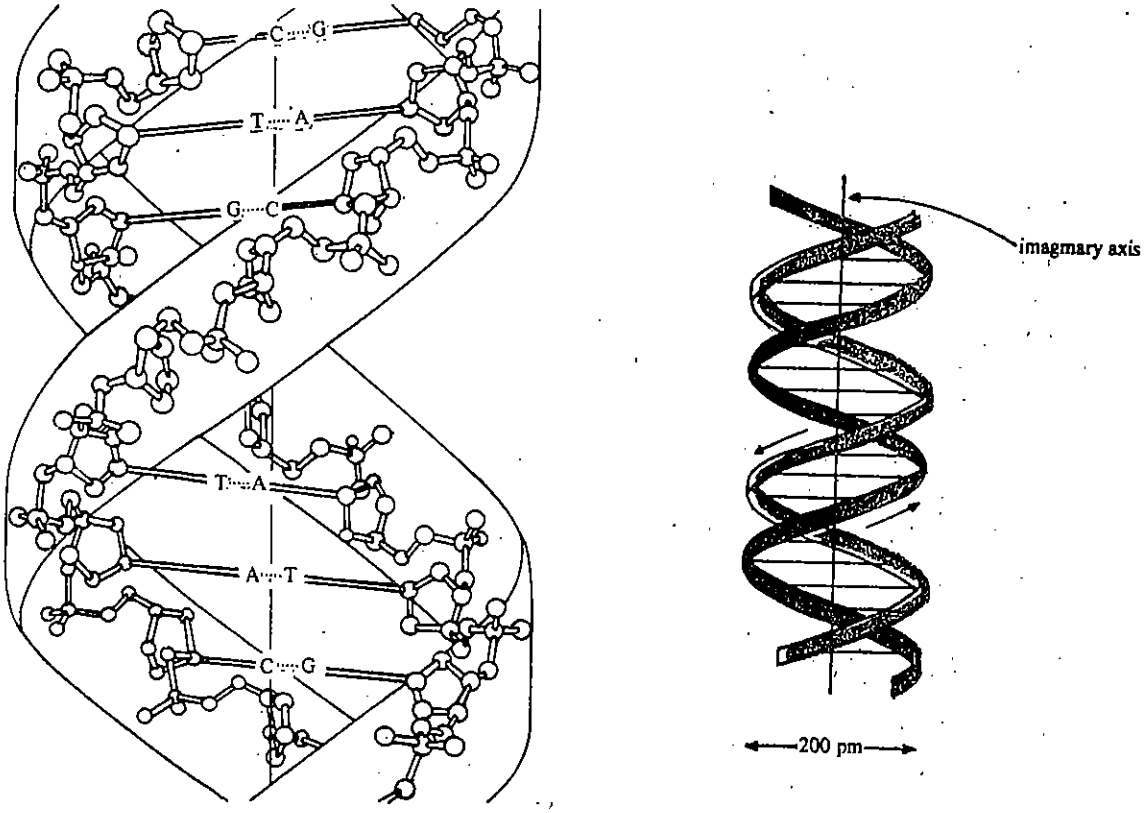


Fig. 20.6 : The double helix.

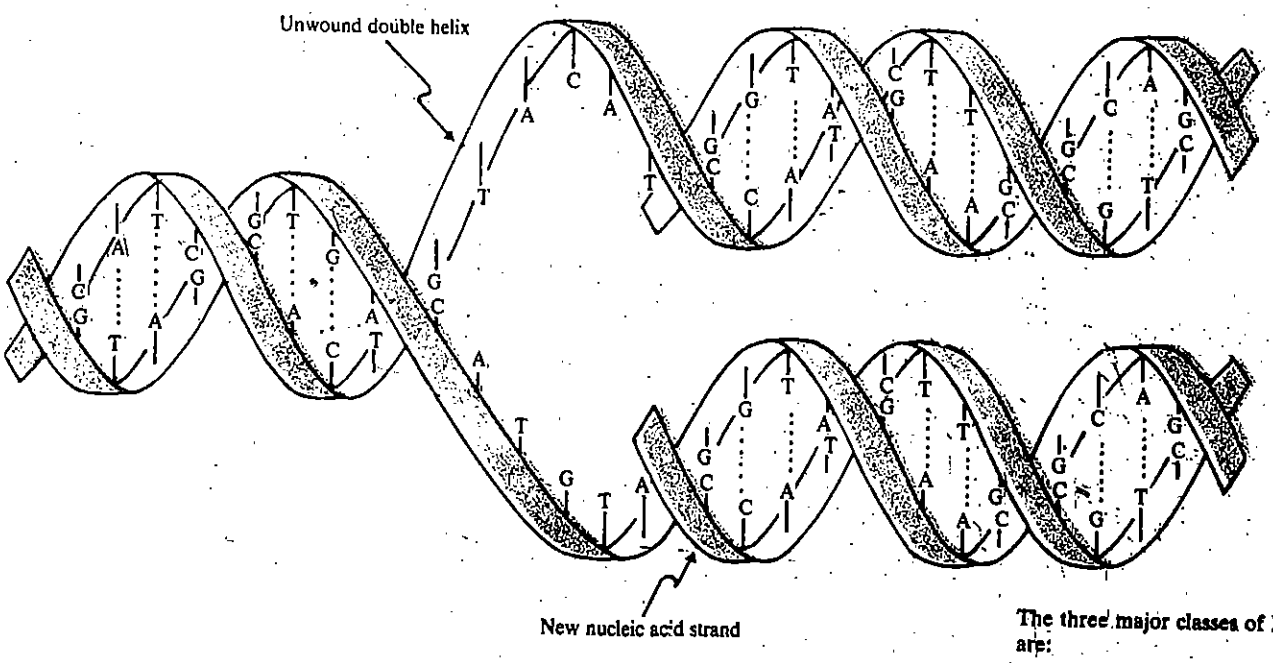


Fig. 20.7 : The DNA replication.

The synthesis of proteins involves the synthesis of a complementary strand of RNA, called **messenger RNA** by a process similar to replication of DNA. This process of formation of messenger RNA is called **transcription**. The messenger RNA sequence is used by the cell to direct the synthesis of a specific protein from the component amino acids by the process called **translation**. Each sequence of three bases, called a **codon**, specifies a particular amino acid. The 64 possible codons are listed in Table 20.3.

The three major classes of RNA are:

1) *Messenger RNA (m RNA):* It carries genetic information from DNA to the site of protein synthesis.
2) *Ribosomal RNA (r RNA):* It serves as structural material of ribosomes.
3) *Transfer RNA (t RNA):* It carries the amino acids to the ribosome for incorporation into the growing polypeptide chain.

Table 20.3 : The Codons for amino acids in protein synthesis

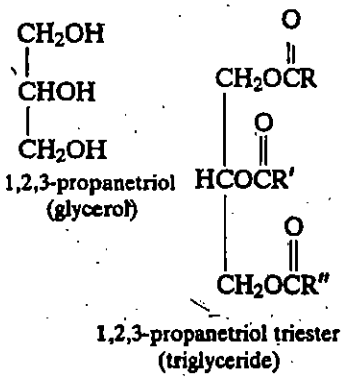
Amino acid	Base sequence	Amino acid	Base sequence	Amino acid	Base sequence
Ala	GCA	His	CAC	Ser	AGC
	GCC		CAU		AGU
	GCG	Ile	AUA		UCA
	GCU		AUC		UCG
Arg	AGA		AUU		UCC
	AGG	Leu	CUA		UCU
	CGA		CUC	Thr	ACA
	CGC		CUG		ACC
	CGG		CUU		ACG
	CGU		UUA		ACU
Asn	AAC		UUG	Trp	UGG
	AAU	Lys	AAA	Tyr	UAC
Asp	GAC		AAG		UAU
	GAU	Met	AUG	Val	GUA
Cys	UGC	Phe	UUU		GUG
	UGU		UUC		GUC
Gln	CAA	Pro	CCA		GUU
	CAG		CCC	Chain initiation	AUG
Glu	GAA		CCG	Chain termination	UGA
	GAG		CCU		UAA
Gly	GGA				UAG
	GGC				
	GGG				
	GGU				

The *codons* are recognised by transfer RNA (t RNA) for a particular amino acid, and that amino acid is added to the growing peptide chain in the protein synthesis. The complete base sequence of the DNA in a cell defines its **genetic code**.

20.5 OILS AND FATS

In addition to carbohydrates and proteins, oils and fats constitute the basic food substances. They are the most concentrated form of energy. While carbohydrates serve as a source of readily available energy, an equal amount of fat gives more than twice amount of the energy. They make foods more palatable, add flavour to it and make it more satisfying.

Fats can be obtained from animal sources, i.e., from the fatty tissues of hogs, cattle, sheep and poultry. Butter is obtained from milk. Vegetable oils include oils from various plant seeds, primarily from soybean, cottonseed, corn, peanut, sunflower, olive, rapeseed, coconut, saflower and oil palm.



Oils and fats belong to a broader class of compounds called **lipids**. Lipids are naturally occurring substances which are soluble in organic solvents but are insoluble in water.

Oils and fats are esters of 1,2,3-propanetriol (glycerol) and long chain carboxylic acids. They are also called **triglycerides** or **glyceryl trialkanoates**.

The difference between oils and fats is that *fats* are **solid** at room temperature whereas *oils* are **liquids**. The acids found in fats are predominantly saturated in nature whereas those present in oils such as peanut oil, corn oil, coconut and soybean are unsaturated. Table 20.4 lists the saturated and unsaturated carboxylic acids commonly occurring in oils and fats.

Table 20.4 : Some representative fatty acids

Structural formula	Systematic name	Common name	m.p./K
Saturated fatty acids			
$CH_3(CH_2)_{10}COOH$	Dodecanoic acid	Lauric acid	
$CH_3(CH_2)_{12}COOH$	Tetradecanoic acid	Myristic acid	327
$CH_3(CH_2)_{14}COOH$	Hexadecanoic acid	Palmitic acid	336
$CH_3(CH_2)_{16}COOH$	Octadecanoic acid	Stearic acid	343
Unsaturated fatty acids			
$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	(*Z*)-9-Octadecanoic acid	Oleic acid	286
$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	(9*Z*, 12*Z*)-9, 12-Octadecadienoic acid	Linoleic acid	268
$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$	(9*Z*, 12*Z*, 15*Z*)-9, 12, 15-Octadecatrienoic acid	Linolenic acid	257
$CH_3(CH_2)_4CH=CHCH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_3COOH$	(5*Z*, 8*Z*, 11*Z*, 14*Z*)-5, 8, 11, 14-Icosatetraenoic acid	Arachidonic acid	not accurately determined

You can see in Table 20.4 that melting points decrease with the increase in unsaturation. Thus, the melting points can be raised if the double bonds are hydrogenated. Industrially, this process is called **hardening**. The oil is heated to 423-473 K and hydrogen is passed under pressure in the presence of nickel catalyst to yield solid fats which are used in the manufacture of soap and as cooking medium for foods.

Certain unsaturated fatty acids are termed as *essential* because their absence in human diet may cause scaley skin, stunted growth and increased water loss from the skin.

Esters formed from cholesterol with saturated fatty acids are solids and, hence, deposit on the walls of blood vessels causing diseases of heart and arteries. Thus, for health considerations, the unsaturated vegetable oils are becoming increasingly popular over the animal fats and margarines which are rich in saturated fatty acids.

20.5.1 Analysis of Oils and Fats

In addition to their physical constants such as melting point, density and refractive index, oils and fats are characterised in terms of certain chemical tests which gives an idea about their nature. These tests involve the determination of **acid value, sponification value** and **iodine value**.

Acid value of an oil or a fat is the number of milligrams of potassium hydroxide required to neutralise one gram of an oil or a fat. This tells us about the amount of free acid present in the oil or fat.

Sponification value is the number of milligrams of potassium hydroxide required to neutralise the acids resulting from complete hydrolysis of one gram of the oil or fat. Since mineral oils which are hydrocarbons, do not react with alkali, this enables us to estimate the fat or oil present in a mixture of fatty oils and mineral oils.

The **iodine value** is the number of grams of iodine that combines with 100 grams of oil or fat. This indicates the degree of unsaturation of the acids present in oil or fat.

Till now you were studying about primary metabolites. We will now shift our focus to secondary metabolites such as terpenes, steroids and alkaloids. Finally, you will also study about *antibiotics* which are chemical substances produced by micro-organisms.

SAQ 3

What is the difference between an oil and a fat?

.....

.....

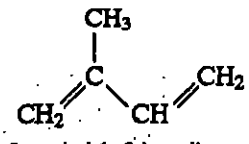
.....

20.6 TERPENES

The term *essential oil* has been applied in two different ways in the context of natural products. As used in the previous section with respect to fatty acids, **essential** meant

necessary. But it is also used as the adjective of the noun **essence**. Mixtures of **volatile, pleasant smelling** substances obtained by steam distillation of flowers, leaves or other parts of plants are called **essential oils**.

Essential oils have been used in perfumes and as flavours. Many of them also have medicinal uses. Very often, the principal volatile component of essential oils belongs to a class of compounds called **terpenes**.



2-methyl-1, 3-butadiene (isoprene)

Terpenes contain a characteristic structural unit called 2-methyl-1, 3-butadiene (**isoprene**) unit, therefore, they are also referred to as **isoprenoids**. Terpenes can be classified according to the number of carbon atoms present in their molecules as shown in Table 20.5.

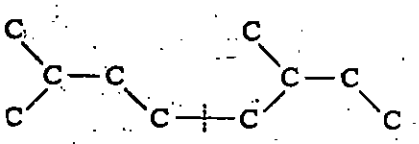
Table 20.5 : Classification of terpenes

Class	No. of carbon atoms
Monoterpene	10
Sesquiterpene	15
Diterpene	20
Sesterpene	25
Triterpene	30
Tetraterpene	40

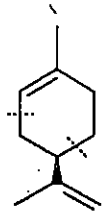
Structures of terpenes belonging to various classes are shown below.

Note the head to tail linkage of 2-methyl-1, 3-butadiene units in these structures.

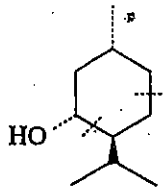
Monoterpenes



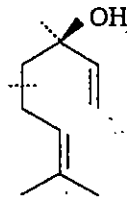
(head) (tail) (head) (tail)



R-(+)-limonene (from oil of oranges and lemon)

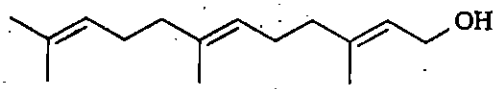


(−)-menthol (from peppermint oil)

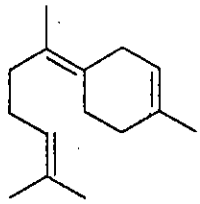


R-(−)-Linalool (from rose oil)

Sesquiterpenes

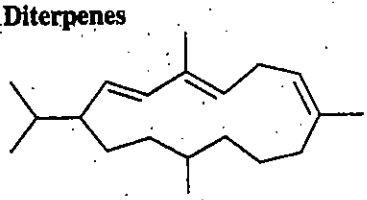


farnesol (from ambrette)

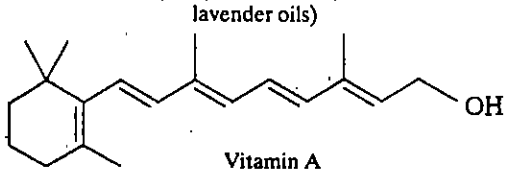


bisabolol (from chamomile and lavender oils)

Diterpenes

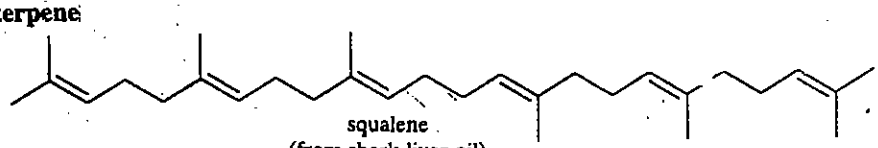


Cembrene (from pine).



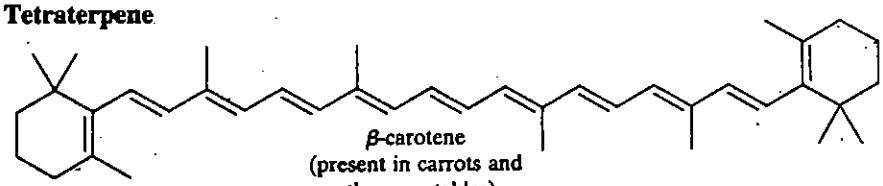
Vitamin A (present in mammalian tissue and fish oil)

Triterpene



squalene (from shark liver oil)

Tetraterpene



β-carotene (present in carrots and other vegetables)

SAQ 4

Mark 2-methyl-1, 3-butadiene units in β-carotene.

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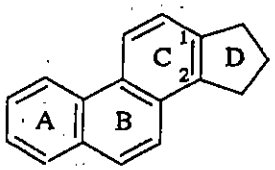
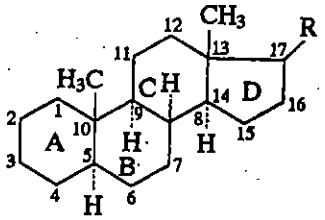
20.7 STEROIDS

Steroids are related to terpenes as they are bio-synthesised by a similar route.

The basic skeleton of steroids contains a hydrogenated 1,2-cyclopentenophenanthrene system.

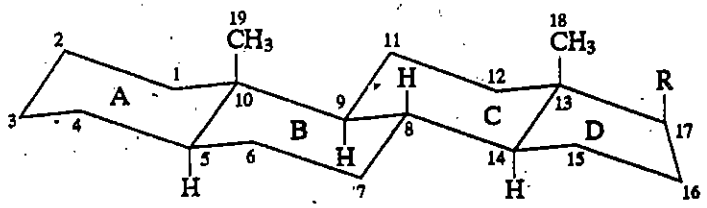


basic steroid ring structure

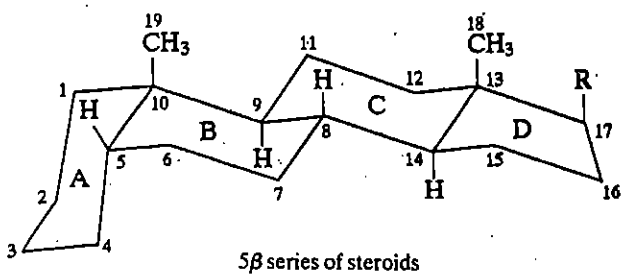


1,2-cyclopenteno-phenanthrene

In most steroids B, C and C, D ring junctions are *trans*. The A, B junction may be either *cis*- or *trans*-leading to two general groups of steroids having the three-dimensional structures as shown below.

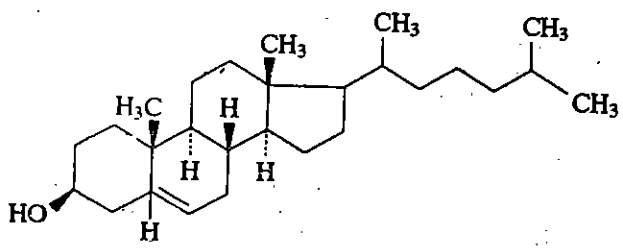


5α series of steroids
(all ring junctions are *trans*)



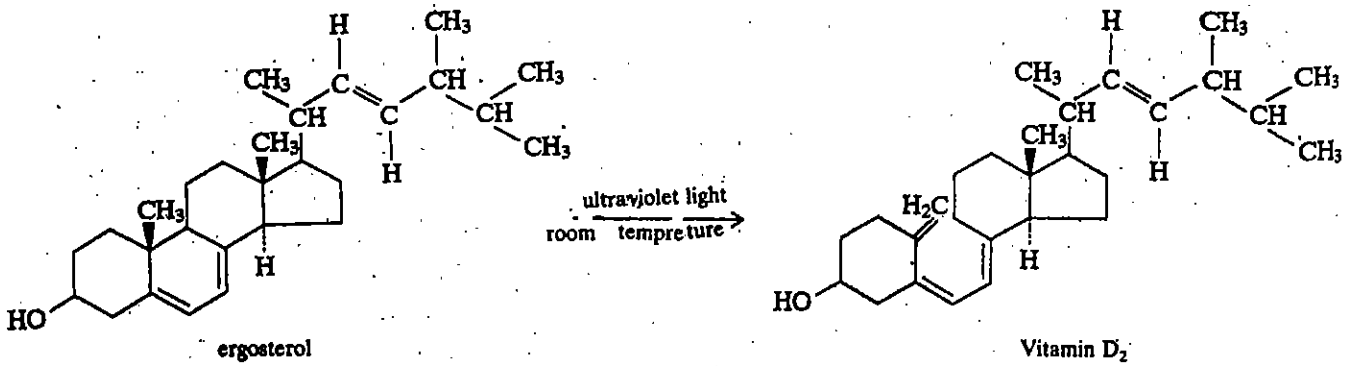
5β series of steroids
(A, B ring junction is *cis*)

Cholesterol is an important steroid. It is found in almost all animal tissues but is particularly abundant in the brain, spinal cord and gall stones. Its deposition in the arteries restricts the flow of blood causing high blood pressure and some forms of cardiovascular diseases.



Cholesterol

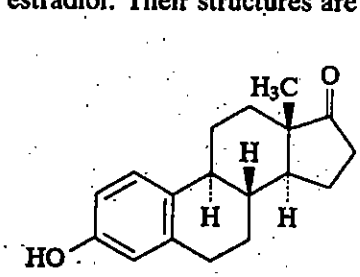
Although cholesterol is found only in animals, a large number of similar compounds are found in plants. These are called **phytosterols**. One such example is **ergosterol** which on irradiation yields calciferol, vitamin D_2.



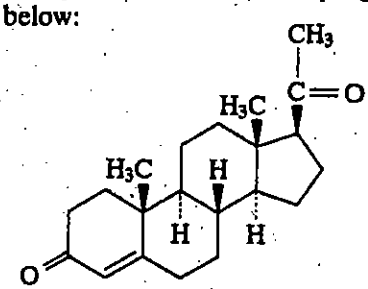
ergosterol

Vitamin D_2

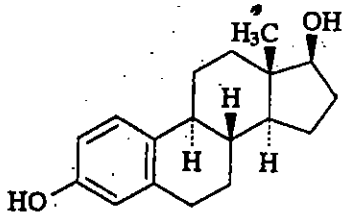
Among other important steroids are sex hormones and adrenocortical hormones. The examples of female sex hormones, called **estrogens**, include estrone, progesterone and estradiol. Their structures are shown below:



estrone

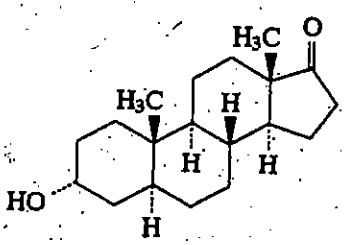


progesterone

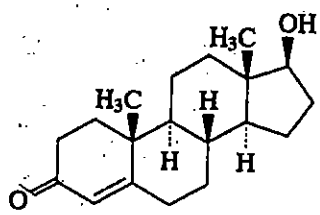


estradiol

The male sex hormones are called **androgens**. The examples are androsterone and testosterone.

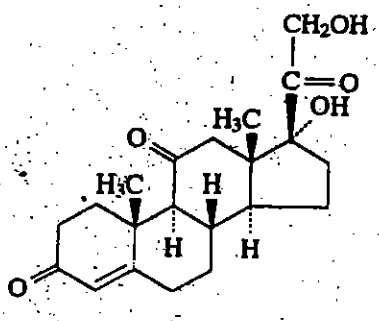


androsterone

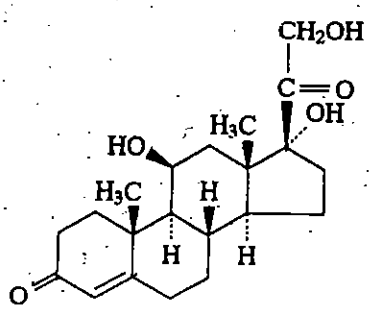


testosterone

The examples of adrenocortical hormones are cortisone and cortisol.



Cortisone



cortisol

They are involved in the regulation of a large number of biological activities such as metabolism of carbohydrates, proteins and lipids, water and electrolyte balance, and reactions to allergic and inflammatory phenomena. Cortisone has been used for the treatment of rheumatoid arthritis. Other steroids oxygenated at 11 position have also been used for treating asthama and the inflammations.

20.8 ALKALOIDS

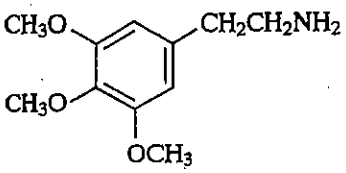
Alkaloids have been defined in Sec. 19.2, Unit 19, as amines of plant origin. They were called so because of their basic or **alkali like** properties.

Alkaloids are usually found in the seeds, roots, leaves or bark of the plants in the form of salts of acids. They can be extracted from dry, powdered plant material by extraction with methanol. After removal of the solvent, the residue is treated with inorganic acids which yield salts of the basic components.

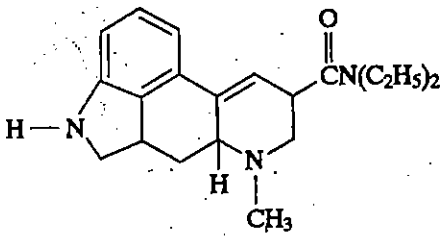
Free bases are liberated by treating the salts with sodium carbonate. Extraction of free bases using chloroform or ether yields a mixture which is separated into individual compounds by various methods including chromatographic methods.

Alkaloids can be classified, according to the nature of the basic structural moiety present in the molecule, into various groups. Representative alkaloids of some of these classes along with their physiological effects are given below:

1) Phenylethylamine alkaloids



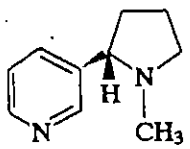
mescaline
(hellucinogen from various species of cactus)



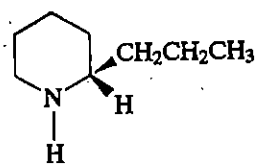
lysergic acid diethylamide
(LSD)
(hellucinogen)

Hallucinogens produce distortion of perception, vivid images or hallucinations.

2) Alkaloids containing a pyridine or piperidine ring

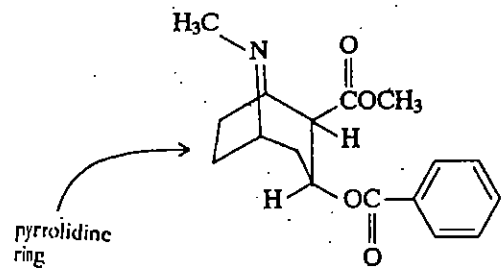


nicotine
(principal alkaloid of tobacco)



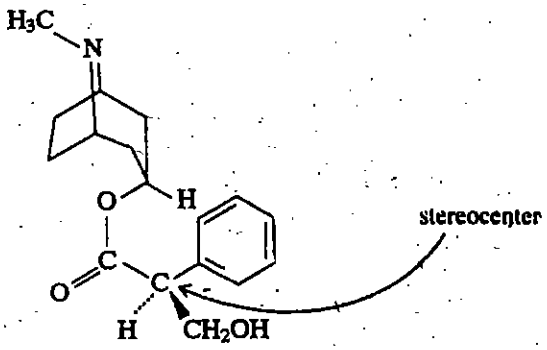
coniine
(from the posion hemlock)

3) Tropane alkaloids



pyrrolidine ring

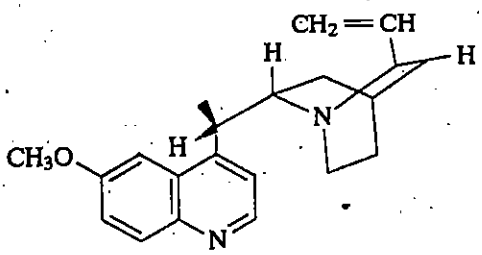
cocaine
(local anaesthetic, stimulant)
(from coca leaves)



stereocenter

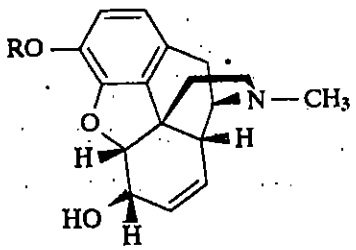
atropine
(a stimulant)

4) Quinoline alkaloids

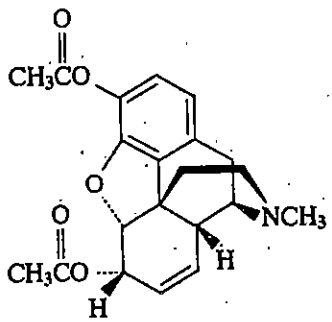


quinine
(antimicrobial, antimalarial)
(from cinchona bark)

5) Isoquinoline alkaloids

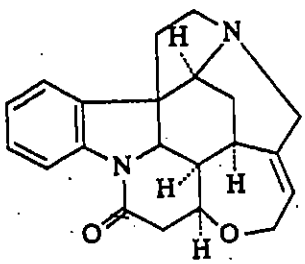


morphine (R=H)
codeine (R=CH_3)
(analgesic from opium)

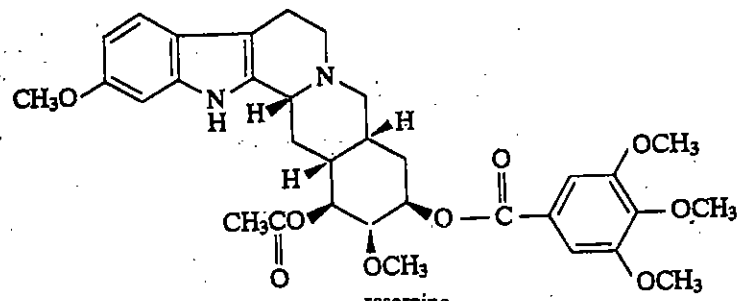


heroin
(diethanoyl derivative of morphine)

6) Indole alkaloids



strychnine
(rodent poison,
resolving agent)
(from seeds of
strychnos nuxvomica)



reserpine
(tranquiliser, reduces blood pressure)
(from Indian snake root
Rauwolfia serpentina)

SAQ 5

Write the structure of heterocyclic nucleus present in indole alkaloids and isoquinoline alkaloids.

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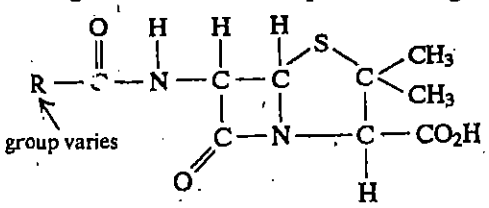
20.9 ANTIBIOTICS

In this section, you will study about the chemical substances produced by microorganisms which inhibit the growth or metabolism of other microorganisms, called *antibiotics*.

The first antibiotic, **penicillin**, was discovered by Fleming in 1929 from the mold *Penicillium notatum*. It inhibited the growth of certain bacterica.

In Unit 16, you studied about treatment of bacterial infections by sulpha drugs.

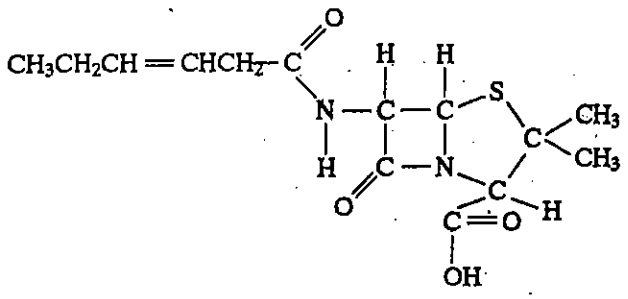
The general structure of penicillin is given below:



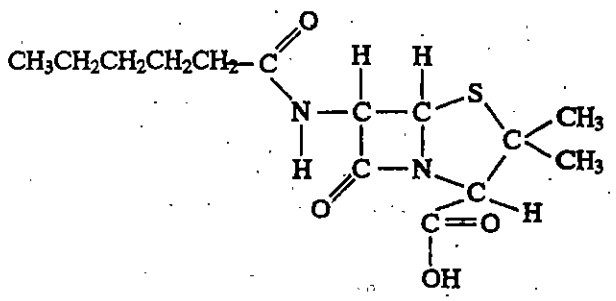
basic penicillin structure

Penicillin acts by inhibiting an enzyme which catalyses the synthesis of cell walls of reproducing bacteria. The new cells have defective cell walls and cell contents leak out, and the cell dies. Since the cell wall material of bacteria and of human beings is different, penicillin is used to treat bacterial infections in humans.

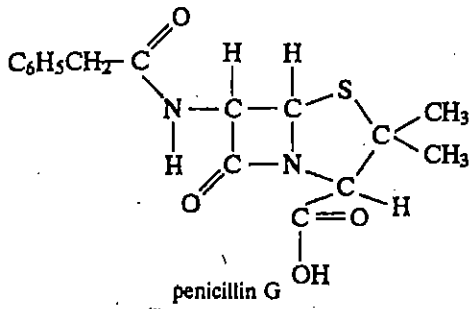
There are at least six natural penicillins depending upon the nature of group R. Their structures are shown below:



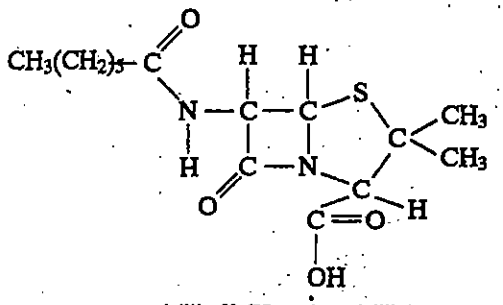
penicillin F (pent-2-enylpenicillin)



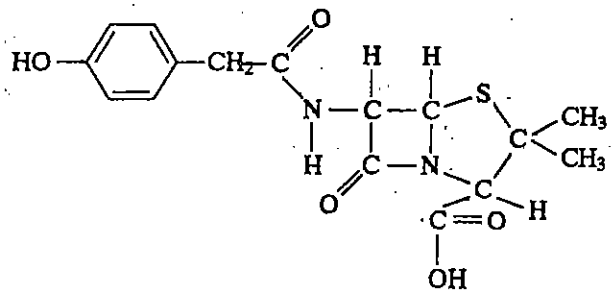
ditydro-F-penicillin



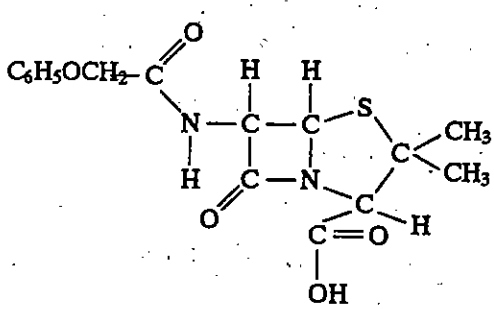
penicillin G
(Benzylpenicillin)



penicillin K (Heptyl penicillin)



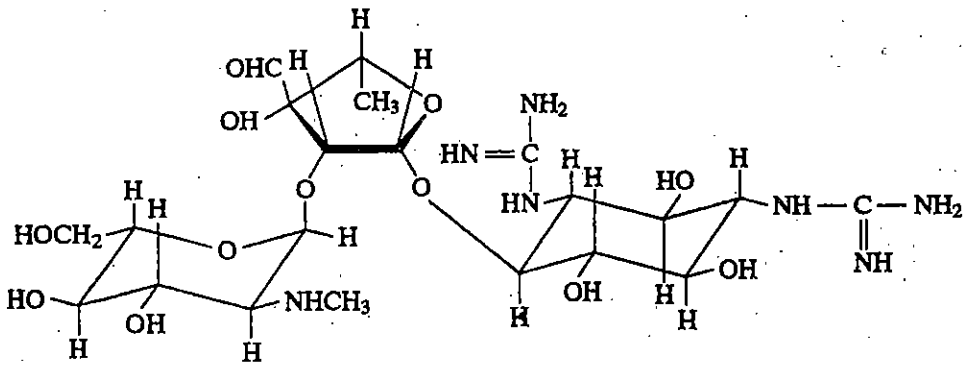
penicillin X (4-Hydroxybenzylpenicillin)



phenoxylmethylpenicillin

Antibiotics include compounds having a wide range of structures. Some examples are streptomycin, chloroamphenicol and tetracycline antibiotics.

Streptomycin

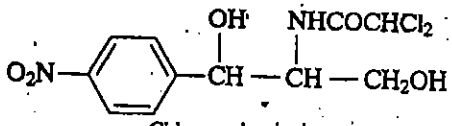


Streptomycin

Note that it contains two sugar units and a hexasubstituted cyclohexane unit.

It is used in the treatment of tuberculosis, meningitis and pnuemonia.

Chloramphenicol

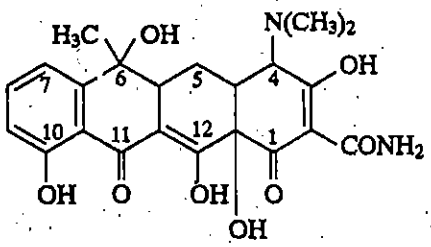


Chloramphenicol

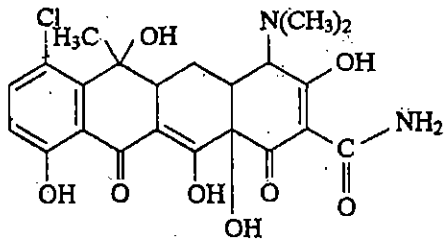
It is a broad spectrum anitbiotic isolated in 1947. It is used in the treatment of typhoid, dysentery, acute fever and certain urinary infections.

Tetracylines

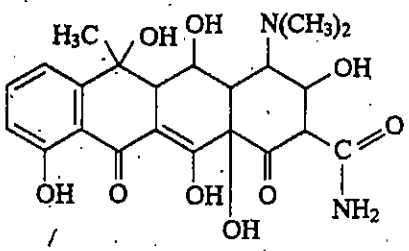
The basic nucleus of tetracycline antibiotics consists of four 6-membered rings fused to each other. Tetracycline, its 7-chloro derivative, aureomycin and its 5-hydroxy derivative, terramycin, are **broad spectrum** antibiotics which are used against a number of bacterial and viral diseases. Tetracyclines have also been used when the patient is allergic to penicillin.



Tetracycline



aureomycin



terramycin

20.10 SUMMARY

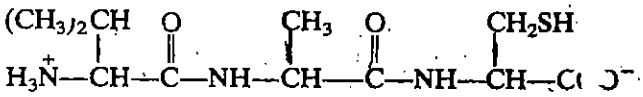
In this unit, you learnt that

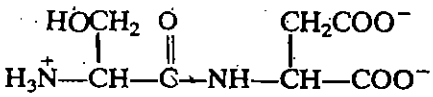
- Natural products such as carbohydrates, nucleic acids, proteins and fats have an important role in the functioning of organisms and are called **primary metabolites.** These are present in almost all organisms.
- Natural occurrence of **secondary metabolites** such as terpenes and alkaloids is species dependent and they also have a wide variety of characteristic uses.
- Carbohydrates are naturally occurring polyhydroxy carbonyl compounds and can be classified as monosaccharides, oligosaccharides (disaccharides, trisaccharides, etc.) and polysaccharides. The structures of carbohydrates belonging to each of the above classes were considered in detail.
- Two important nucleic acids are DNA and RNA.
- DNA has double helical structure and acts as a template during DNA replication and RNA Synthesis.
- DNA is indirectly involved in the protein synthesis. In protein synthesis, each amino acid is specified by a set of three consecutive RNA bases, called a codon. This base sequence or the genetic code in RNA is translated to a specific amino acid sequence in proteins.
- Oils and fats are esters of 1,2,3-propane-triol. They also constitute concentrated source of energy.

- Oils and fats are characterised by their acid values, sponification values and iodine values.
- 2-methyl-1, 3-butadiene is the characteristic structural unit in terpenes which are present in essential oils.
- Terpenes can be classified as mono-, sesqui-, di-, ses-, tri- and tetraterpenes. Various examples of these classes of terpenes were considered.
- Alkaloids are physiologically active basic compounds of plant origin. The examples of alkaloids illustrate that they can be classified into various categories depending upon the type of nucleus present in the molecule.
- Finally the natural products obtained from micro-organisms called antibiotics were discussed. Some examples were taken to show the wide variety of antibiotics and their uses.

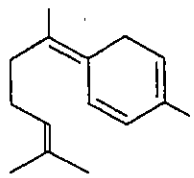
20.11 TERMINAL QUESTIONS

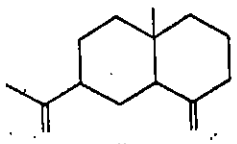
1) Write the structures and names of the D-aldoses which you have studied in Table 20.1.
2) What is the number of possible aldoheptoses?
3) Idenfity the peptide bonds in the following:

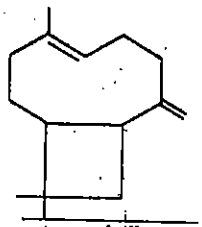
a) 

b) 

4) Define iodine value and give its significance.
5) Classify the following terpenes as monoterpenes, diterpenes and sc n.

a) 
zingiberine
(from oil of ginger)

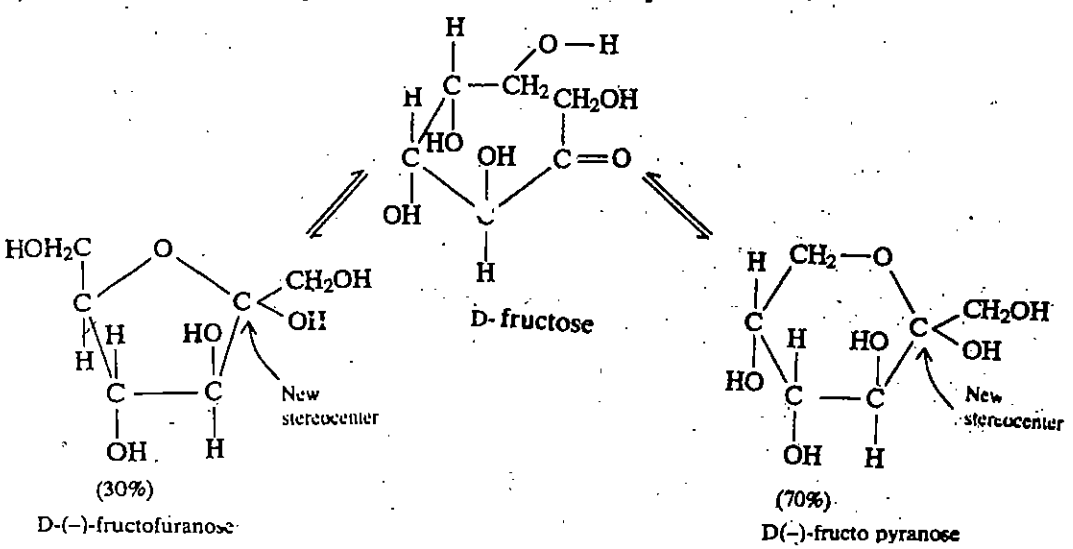
b) 
β-selinene
(from oil of celery)

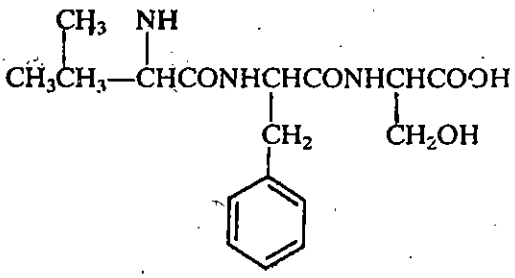
c) 
caryophyllene
(from oil of cloves)

20.12 ANSWERS

Self Assessment Questions

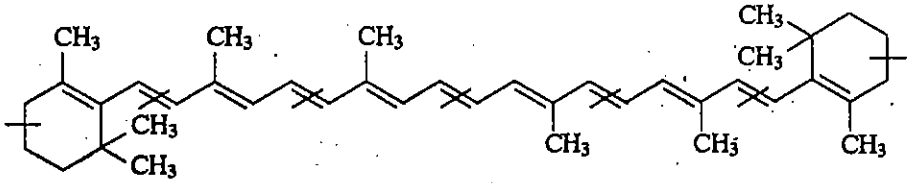
1) **Cyclic Hemiacetal Formation by Fructose**



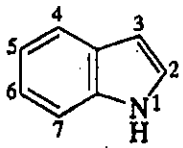
2) 

3) a) An oil is liquid at room temperature whereas a fat is solid.

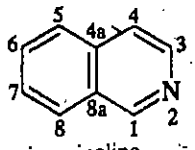
b) Oils are esters of unsaturated long chain carboxylic acids whereas fats are esters of saturated long chain carboxylic acids.

4) 

β-carotene

5) 

indole

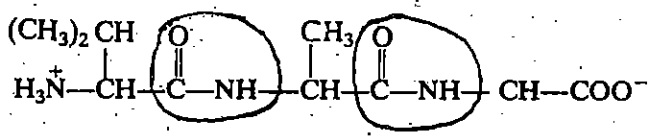


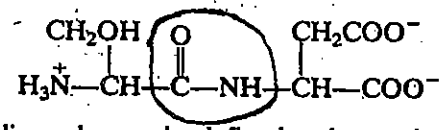
isoquinoline

Terminal Questions

1) See sub-Sec. 20.2.1.

2) 32, 16 D isomers and 16 L isomers.

3) a) 

b) 

4) Iodine value can be defined as the number of grams of iodine that combines with 100 gms of an oil or a fat. It indicates the amount of unsaturation in the carboxy part of the fat or oil.

5) a) Sesquiterpene b) Sesquiterpene
c) Sesquiterpene

Further Readings

1) *Organic Chemistry*, 6th Ed., By R.T. Morrison and R.N. Boyd, Prentice-Hall of India Pvt. Ltd.

2) *Text Book of Organic Chemistry*, 2nd Ed., by Lloyd N. Ferguson, Affiliated East-West Press Pvt. Ltd.

3) *Organic Chemistry*, Vol. I and II by S.M. Mukherji, S.P. Singh and R.P. Kapoor, Wiley Eastern Ltd.

4) *Text Book of Organic Chemistry*, 2nd Ed., by P.L. Soni and H.M. Chawla, Sultan Chand and Sons.