UNIT 1   EFFECT OF MOLECULAR ARCHITECTURE ON PHYSICAL PROPERTIES

CONTENTS

1.0   INTRODUCTION

In the proceeding 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

2.0   OBJECTIVES

After studying this unit, you would be able to:

- identify organic molecules using their physical properties such as melting and boiling points, solubility and refractive index.
- determine the relationship between molecular structure and physical properties of organic compounds.

3.0   MAIN CONTENT

3.1   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 structure of a compound is known, its physical properties can be predicated.

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.

3.1.1 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 molecule 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 interaction are depicted in Fig 1.1.
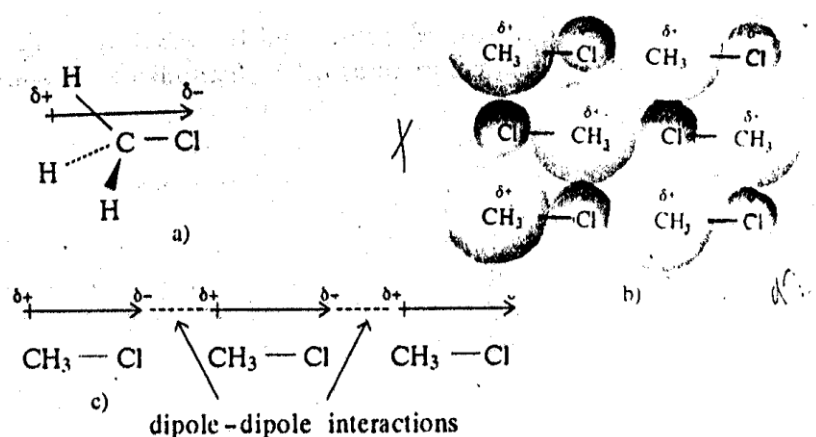

Fig.1.1: a) A polar chloromethane molecule showing positive and negative poles. b) Arrangement of chloromethane molecules and. c) Dipole-dipole interactions between chloromethane molecules.

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 no polar molecules also. Consider two non polar molecules A and B in which the centre of positive charge coincides with that of the negative charge.
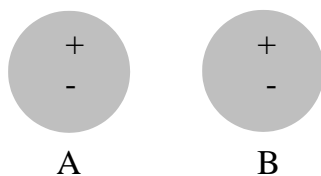
When the molecules A and B approach each other, there is a distortion in the distribution of the charge resulting in a small and momentary dipole in one molecule. This small dipole can then create another dipole in the second molecule which is called **induced dipole**. Thus, if
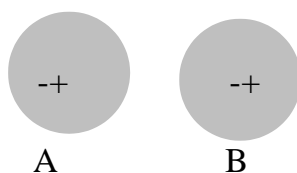

the momentary dipole of molecule A is as shown below;
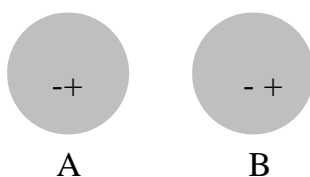
Such a distribution of charge leads to mutual attraction between the molecules.

These induced dipole – induced dipole interaction are also known as **London forces**. London forces are the only forces of attraction possible between non polar molecules. 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 $1/r^6$.

(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 non bonded 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 is a special type of dipole-dipole interactions. The hydrogen bonding in the case of ethanol is represented below:
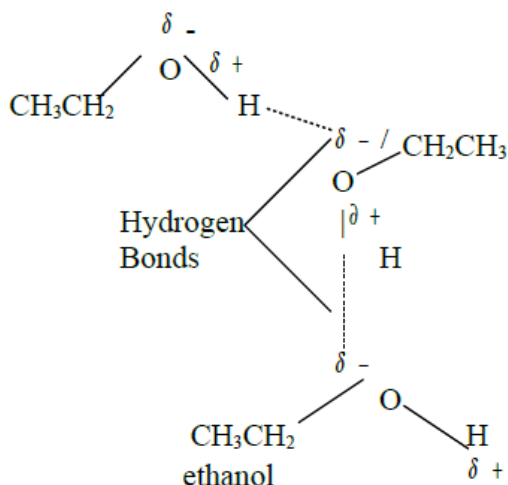
Note that the hydrogen bonds are indicated by the dash lines whereas the covalent bonds are represented by solid lines.

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**. Some authors prefer to give the name van der Waals forces only for London forces. Having understood the intermolecular forces, let us now study how the variation in molecular structure affects these intermolecular forces which in turn in reflected in the physical properties of the molecules.

SELF ASSESSMENT EXERCISE 1

How is a hydrogen bond different from a covalent bond?

3.1.2 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. 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. 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 temperatures. In a crystalline solid, the constituent ions or molecules are arranged in an orderly and rigid fashion. When such as 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. 1.2.
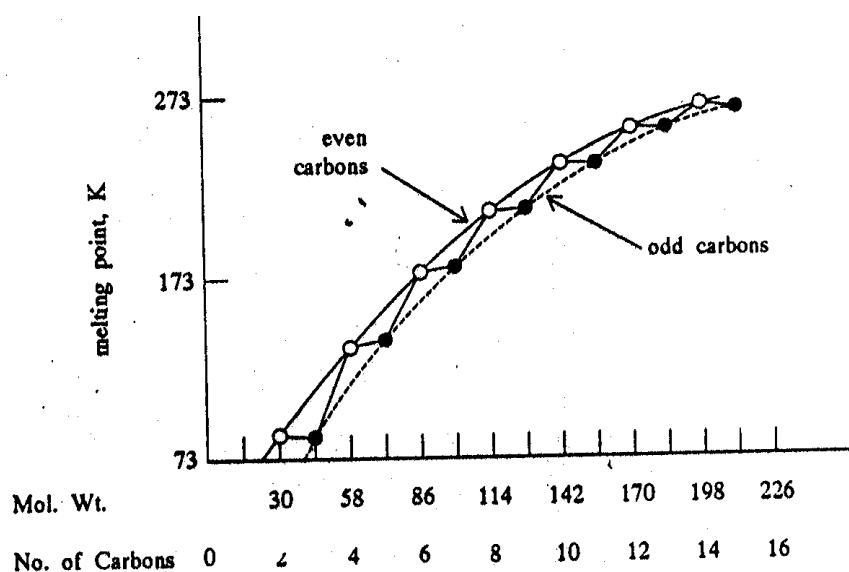

Fig. 1.2: Plot of melting points of straight chain alkanes against the molecular weight;   the number of carbon atoms present in alkane molecule are also indicated.
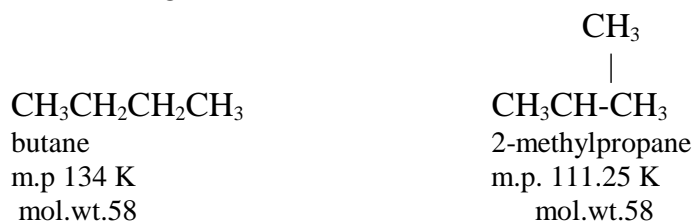
You can see in the figure that the melting point increases with the increase in the molecular weight. This can be explained due to increase in the London forces between the larger molecules of higher molecular weight. Thus, each additional methylene (-CH$_2$) unit contributes to the increase in melting point.

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 must have noticed in Fig. 1.2, 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
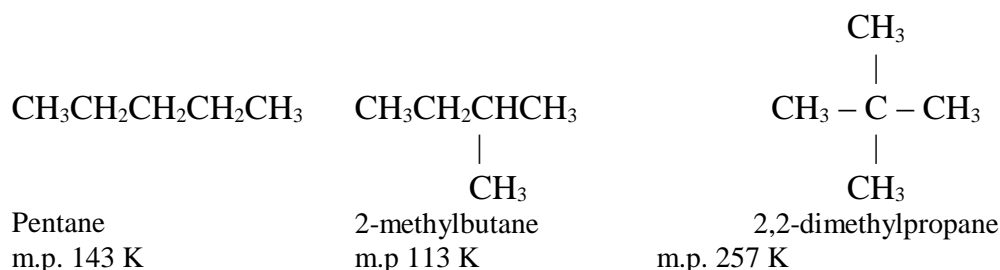
even number of carbon atoms. This is because the molecules of alkanes having odd number of carbon atoms do not fit well in the crystal lattice as compare to those of the alkanes having even number of carbon atoms.

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:

$$CH_3$$
$$|$$

$CH_3CH_2CH_2CH_3$ $CH_3CH\text{-}CH_3$
butane   2-methylpropane
m.p 134 K   m.p. 111.25 K
mol.wt.58   mol.wt.58

The branching of the carbon chain interferes with the regular packing of the molecules in the crystal; 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:

$$CH_3$$
$$|$$

$CH_3CH_2CH_2CH_2CH_3$ $CH_3CH_2CHCH_3$ $CH_3 - C - CH_3$
$$|$$ $$|$$
$$CH_3$$ $$CH_3$$
Pentane   2-methylbutane   2,2-dimethylpropane
m.p. 143 K   m.p 113 K   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.

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.

SELF ASSESSMENT EXERCISE 2

Why is butane (m.p 134K) having a higher melting point than 2-methylpropane (m.p. 111K) even though both compounds have the same molecular weight of 58?

3.1.3 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 vapor 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 characterization 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 increase 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. 1.3 for the isomers of butane.
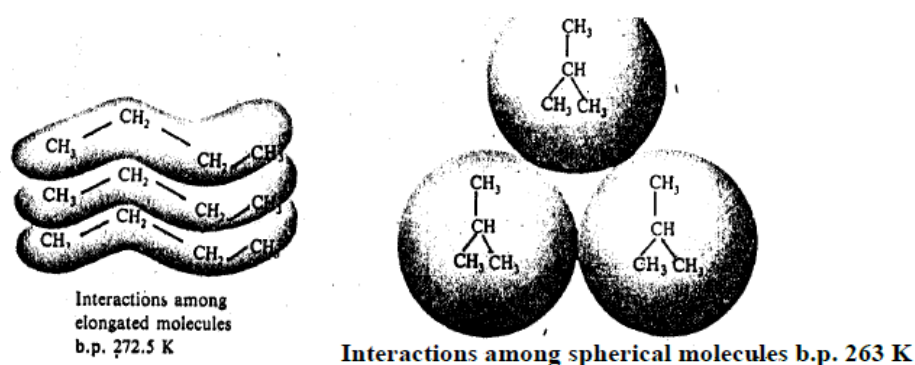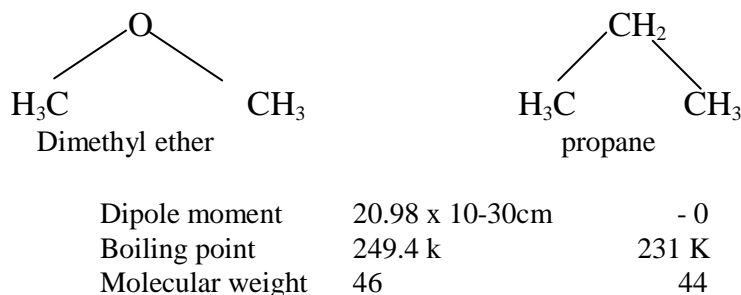
Fig.1.3: A comparison of intermolecular interactions for straight chain and branched chain isomers of butane

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 x 10-30cm	- 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 CH3CH2OH, 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 1.1.1. Thus, to vaporize such as 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-hydroxybenzaldehyde
b.p. 470 K

4-hydroxybenzaldehyde
b.p. 523 K
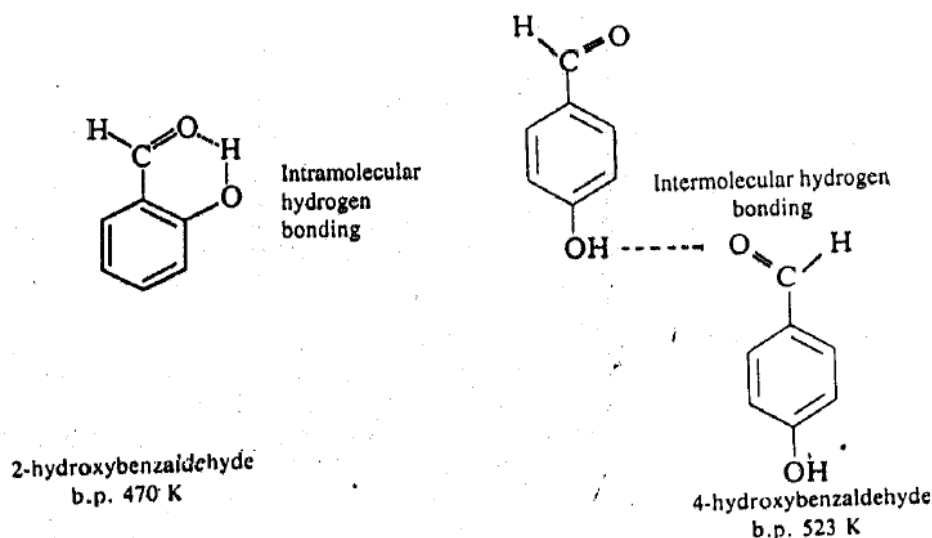
Hydrogen bonding can also occur within the same molecule in which case it   is called **intermolecular hydrogen bonding**. Thus, 2-hydroxybenzaldehyde can form only intermolecular hydrogen bonds.

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.

SELF ASSESSMENT EXERCISE (SAE 3)

Explain why diethylether has a high boiling point than propane.

3.1.4 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 a *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 compare 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 inter ionic 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 =1.2) 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 that it has a significant dipole momentμ. 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 dielectire 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 hezanol in water, as given below:
.
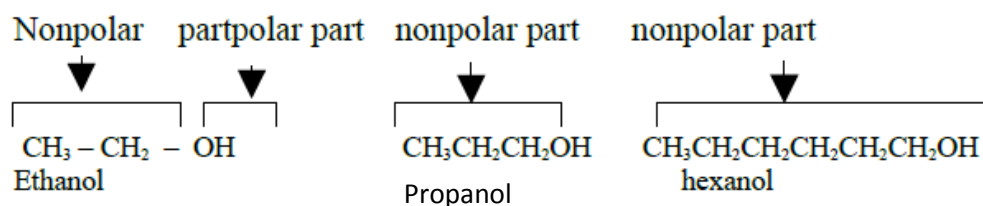
Solubility: Miscible with water   3.9 g in 1 dm^3 of water 5.9 g in 1 dm^3 of water in all proportions.

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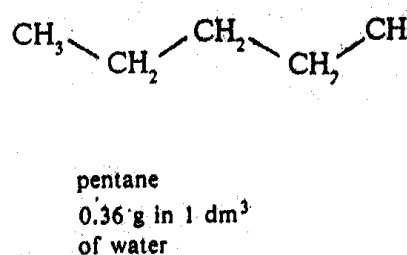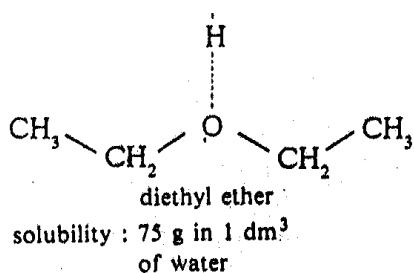
Since the olefinic, acetylenic or benzenoid character does not affect the polarity much, the solubility of unsaturated and aromatic hydrocarbons in water is similar to that of alkanes. In compounds like ethers, esters, aldehydes, ketones, alcohols, amides, acids and amines, solubility in water depends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

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 Polymers have high molecular weight. 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.

$$H_3O^+ + C_6H_5NH_2 \quad = \quad C_6H_5NH_3 \quad + H_2O$$
Aniline   anilinium
                            Ion
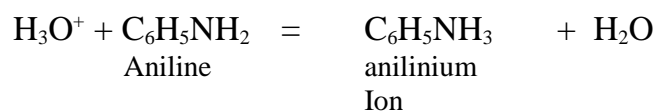
Although determination of the physical properties such as those discussed above helps in the identification of organic compounds, physical methods involving the use of spectroscopy allow determination of the molecular structure much more rapidly and nondestructively using small quantities of material.

SELF ASSESSMENT EXERCISE (SAE 4)

Why is diethylether more soluble in water than pentane?

4.0   CONCLUSION

We can safely conclude that a good knowledge of the physical and chemical properties of organic compounds is paramount in the identification of such compounds.

5.0   SUMMARY

During the course of this unit, we have learnt about the relationship between molecular architecture and physical properties of organic compounds. We have also learnt about the interrelationship between intermolecular forces, melting and boiling points and the solubility of organic compounds.

6.0   TUTOR-MARKED ASSIGNMENT

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

1.   London forces are the only forces operating between polar molecules.
2.   Within a homologous series, increase in molecular weight leads to decrease in the melting point.
3.   Highly symmetrical molecules have unusually high melting points.
4.   The shape of a molecule does not affect its boiling point.
5.   Polar compounds generally boil at higher temperatures as compared to the nonpolar compounds
6.   Hydrogen bonding increases the water solubility

7.0   REFERENCES/FURTHER READINGS

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UNIT 2   STRUCTURE – REACTIVITY RELATIONSHIP

CONTENTS

1.0   INTRODUCTION

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 make 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 familiarize 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 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.**
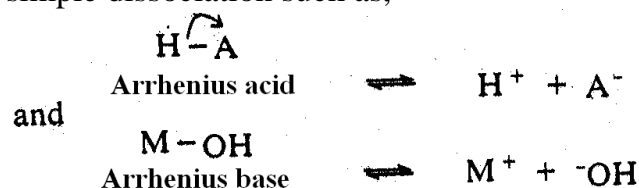
2.0   OBJECTIVES

After studying this unit, you should be able to:

1. define acids and bases
2. classify the given compounds as acids or bases according to
3. Bronsted – Lowry and Lewis definitions define pK_a of an acid
4. predict the relative acidities and basicities of compounds from them
5. list various factors affecting the strengths of acids and bases
6. explain the effect of structural changes on the acidic and basic behaviour of organic molecules
7. predict the relative reactivity of the molecules on the basis of inductive effect, resonance effect, steric effect, hydrogen bonding and, hyperconjugation, etc.
8. define tautomerism and give examples of various kinds of tautomerism.

3.0   MAIN CONTENT

3.1   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 ionizes in aqueous solution to produce hydrogen ions (H^+), also known as protons. And, a base is a substance which ionizes to produce hydroxide (OH) ions. Thus, Arrheniun theory assumes a simple dissociation such as,

$$H \overset{\frown}{-} A$$
Arrhenius acid $\rightleftharpoons$ $H^+ + A^-$

and

$$M - OH$$
Arrhenius base $\rightleftharpoons$ $M^+ + {}^-OH$

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.

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, Hl, 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 Bronsted and Lowry in 1922. According to the Bronstzed-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 Bronsted-Lowry sense is considered, a base must be present to accept the proton from the acid. The Bronsted acids are also called protic acids because they react by the transfer of a proton. Consider the following example,
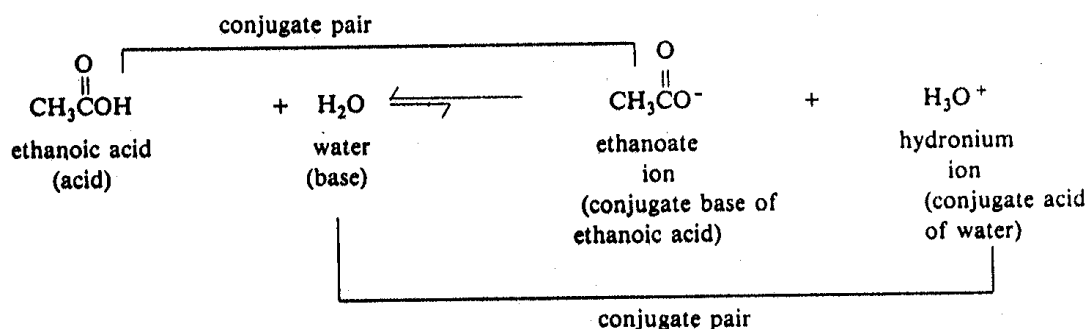
Here, the ethanoic acid is an acid because it donates a proton to water which is a base because it accepts the proton. Similarly, the ethanoate ion, which is formed by the loss of a proton from ethanoic acid, functions as a base because it can accept a proton to become ethanoci acid again. Thus, ethanoate 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 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:
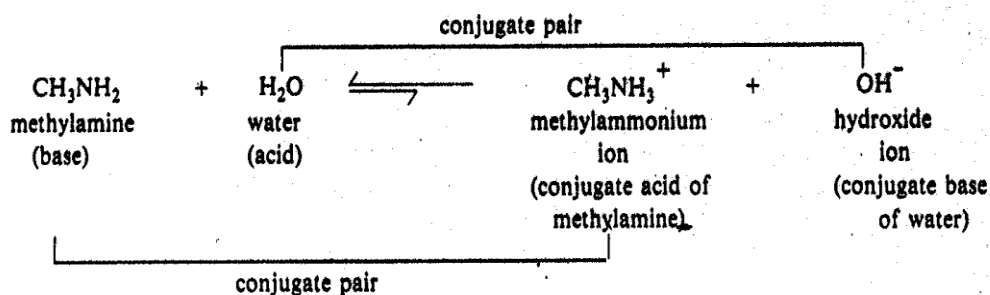
Note that water can act both as an acid as well as a base. It acts as an acid by donating a proton to yield the OH- ion which is its conjugate base. It can also act as a base by accepting a proton to yield a hydronium ion which is its conjugate acid.

Although, we have illustrated both the above examples using water as one of the components, the scope of Bronsted-Lowry definition of acids and bases is not limited to aqueous solutions as is the case in Arrhenius definition. The Bronsted-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;

A_1 + B_2 ⟶ B_1 + A_2
Acid   base   conjugate   conjugate
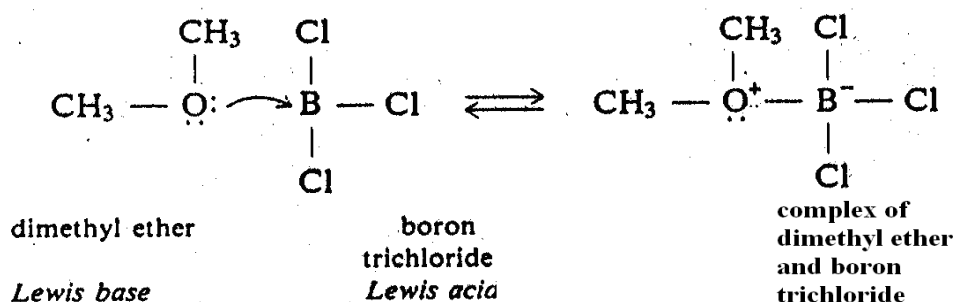   base of acid A_1 acid of base B_2
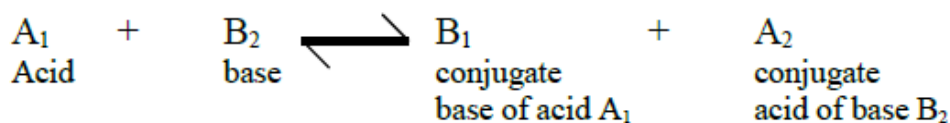
where $A_1 - B_1$ and $A_2 - B_2$ are conjugate acid-base pairs.

The acid-base theory was further broadened by Lewis in 1934. 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 carbonations 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 towards boron trichloride which acts as a Lewis acid. This acid-base reaction is represented below:

dimethyl ether   boron   complex of
                     trichloride   dimethyl ether
Lewis base   *Lewis acia*   and boron
                                   trichloride

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 Bronsted-Lowry definitions because a Bronsted-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.

SELF ASSESSMENT EXERCISE 1

Label the conjugate acid and the conjugate base in each of the following reactions.

$$(1) \quad CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + {}^-OH \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + H_2O$$

$$(2) \quad CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H_2SO_4 \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{+}{O}H_2 + HS\bar{O}_4$$

$$(3) \quad (CH_3)_3\overset{+}{N}H + CH_3O^- \longrightarrow (CH_3)_3N: + CH_3OH$$

$$(4) \quad \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\diagdown\diagup}}C=CH_2 + H_3O^+ \longrightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\displaystyle CH_3}{C^+}} + H_2O$$

.
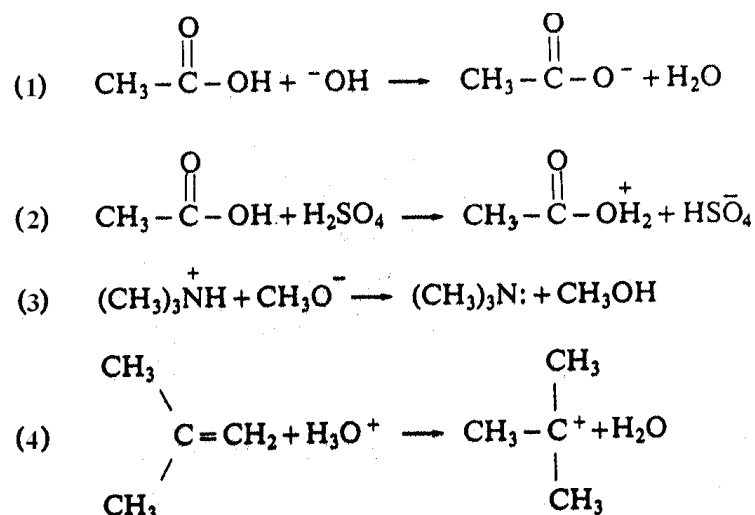
3.2   Strengths of Acids and Bases

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;

$$HA + H_2O \quad \rightleftharpoons \quad :A^- + H_3O^+$$

The equilibrium constant, K_{eq}, for the above equilibrium can be written as,

$$K_{eq} = \frac{[:A^-][H_3O]}{[HA][H_2O]} \quad\quad ....(2.1)$$

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, Ka, called the **acidity constant**, as given below:

$$K_{eq}[H_2O] = K_a = \frac{[:A^-][H_3O+]}{[HA]} \quad \text{..........................} \quad (2.2)$$

The dissociation of acid HA in solvents other than water can be generalized as,

$$HA + solvent \rightleftharpoons H^+ - solvent + :A^-$$

The expression for acidity constant can then be written as follows:

$$K_a = \frac{[H^+ - solvent][:A^-]}{[HA]} \quad \text{.....................} \quad (2.3)$$

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, Ka is generally expressed in terms of pKa, where

$$pK_a. = -\log_{10}K \quad \text{.................................} \quad (2.4$$

Taking – log of Eq. 1.2 and rearranging, we get

$$-\log K_a = -\log[H_3O^+] + \log \frac{[HA]}{[:A^-]}$$

By definition,

$$-\log K_a = ,pKa \text{ and } -\log[H_3O^+] = pH$$

Hence, $pKa = pH + \log \dfrac{[HA]}{[:A^-]}$

.

This expression relating the pK_a and pH is also known as **Henderson-Hasselbalch equation**.

Thus, when [HA] = [:A] then pK_a = pH. Table 2.1 shows the pKa values for a variety of acids along with their conjugate bases.
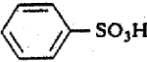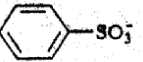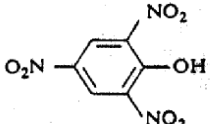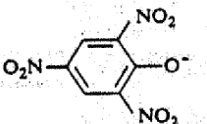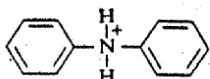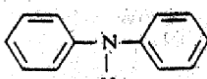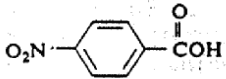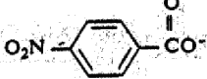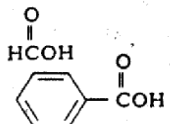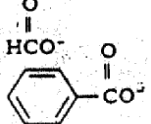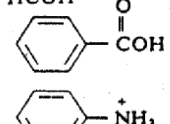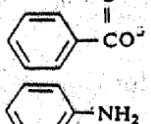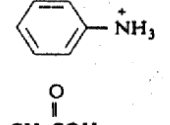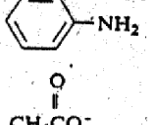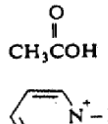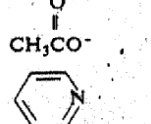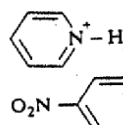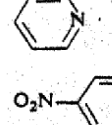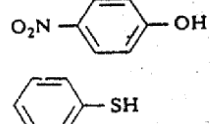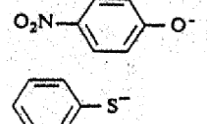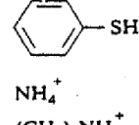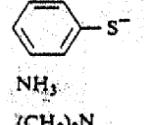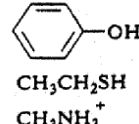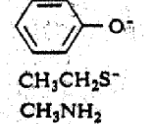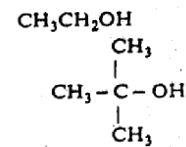
Acid	Base	pKa
H_2SO_4	HSO_4^-	~9
HCl	Cl^-	~7
H_3O^+	H_2O	~1.7
HNO_3	NO_3^-	~1.3
$C_6H_5\text{-}SO_3H$ (benzenesulfonic acid)	$C_6H_5\text{-}SO_3^-$	~0.6
2,4,6-trinitrophenol (O_2N, NO_2, NO_2 substituted phenol, -OH)	2,4,6-trinitrophenolate (-O^-)	0.25
diphenylammonium $(C_6H_5)_2NH_2^+$	diphenylamine $(C_6H_5)_2NH$	0.8
4-nitrobenzoic acid $O_2N\text{-}C_6H_4\text{-}COOH$	4-nitrobenzoate $O_2N\text{-}C_6H_4\text{-}CO_2^-$	3.4
$HCOOH$ (formic acid)	HCO_2^-	2.7
benzoic acid $C_6H_5\text{-}COOH$	benzoate $C_6H_5\text{-}CO_2^-$	4.2
anilinium $C_6H_5\text{-}NH_3^+$	aniline $C_6H_5\text{-}NH_2$	4.6
CH_3COOH	$CH_3CO_2^-$	4.8
pyridinium ($N^+\text{-}H$)	pyridine	5.2
4-nitrophenol $O_2N\text{-}C_6H_4\text{-}OH$	4-nitrophenolate $O_2N\text{-}C_6H_4\text{-}O^-$	7.2
thiophenol $C_6H_5\text{-}SH$	$C_6H_5\text{-}S^-$	7.8
NH_4^+	NH_3	9.4
$(CH_3)_3NH^+$	$(CH_3)_3N$	9.8
phenol $C_6H_5\text{-}OH$	phenolate $C_6H_5\text{-}O^-$	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
$CH_3\text{-}C(CH_3)_2\text{-}OH$	CH_3^-	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 2.1 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 Ka values. Therefore, it follows from Eq. 2.4 that the **stronger** the acid, the **smaller** the pKa value. Thus, as Table 2.1 shows, the sulponic acids and carboxylic acids are much more acidic as compared to phenol and alcohols.

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 generalize for conjugate acids. The **stronger** the acid, the **weaker** is its conjugate base and vice versa.

Note that Table 2.1 lists the pKa values for protic acids or Bronsted 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:

BF_3	>	$AlCl_3$	>	$FeCl_3$	>	$SbCl_3$	>	$ZnCl_2$	>	$HgCl_2$
Boron Trifluoride		Aluminium Chloride		Ferric Chloride		Antimony C hloride		Zinc Chloride		Mercuric Chloride
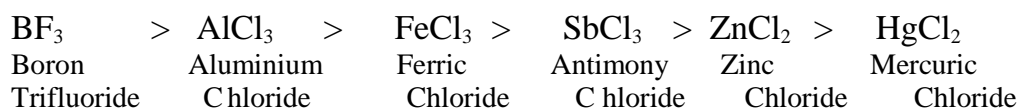
Lewis acids such as boron trifluoride and aluminium chloride are important acid catalysts for certain organic reactions.

The Table of pKa 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 pKa Table, Also, the larger the difference between the pKa 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 pKa 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 a,

$$:A^- + HOH \rightleftharpoons HA + OH^-$$

The equilibrium constant for such an equilibrium can be expressed as

$$K_{eq} = \frac{[HA][OH^-]}{[:A^-][HOH]} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.5)$$

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.2.5 in terms of the basicity constant, K_b, as

$$K_{eq} \ = \ [H_2O] = K_b = \frac{[HA][OH^-]}{[:A^-]} \quad \cdots\cdots\cdots\cdots \quad (2.6)$$

The two constants Ka and Ka 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,

$$pK_a + pK_b = 14$$

Where K_w is the self-ionization 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.

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}

The self-ionization 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^{-2}. Therefore, the self-ionization constant, K_w, of water is defined as,

$K_w = [H_3O^+] \ [OH^-] = 10^{-7} \ x \ 10^{-7}$ moles^2 dm^{-6} $= 10^{-14}$ moles^2 dm^{-6} 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 2.1 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 2.1).

A comparison of the pK_a values from Table 2.1 shows the following order of the basicities for some of the bases.

$$-CH_3 \quad > \quad NH_2 \quad > \quad RO \quad > \quad OH \quad > \quad RCOO$$

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_3N. The basic character of these compounds can be attributed to atoms such as nitrogen and oxygen which contain at least one lone pair of 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 Self Assessment Exercises.

SELF ASSESSEMENT EXERCISE 2

An acid HA₁ has pK_a = 20 and another acid HA₂ has pK_a = 10.

1. Which of these two acids is stronger?
2. If Na⁺ A₁ salt is added to acid HA₂, does any acid base reaction take place? Explain.

3.3   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 molecule. 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.

3.3.1 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 polarization of a bond can be felt by adjacent groups also. This phenomenon of the transmission of charge through a chain of atoms linked by bonds is called **inductive effect**.

$\overset{\delta+}{C} - \overset{\delta-}{X}$ (X is more
electronegative
than C)

a dipole

$C \rightarrow C \rightarrow C \rightarrow X$
3   2   1

Inductive effect of X
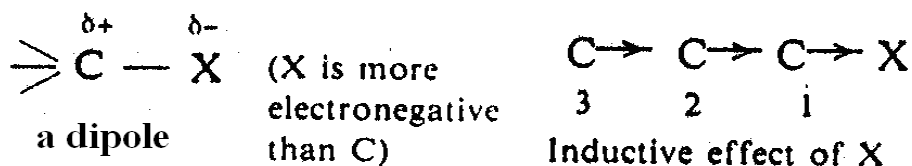
Note that the inductive effect is a permanent effect.

Let us now analyze 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
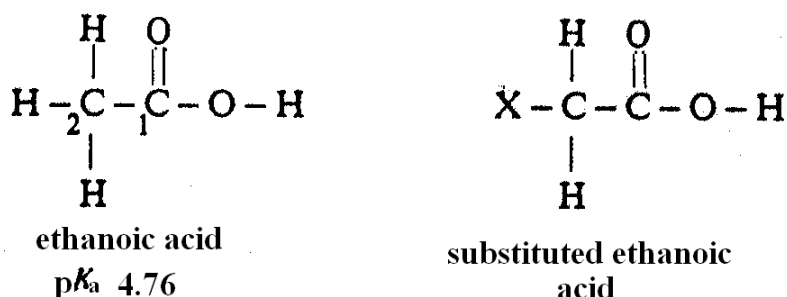
If we substitute one of the hydrogen atoms on the C – 2 carbon atom with a substituent X, then, the nature of the substituent group may affect the electron density of the O – H bond resulting in a change in the acidity of the molecule.

Depending upon whether the substituent X is electron-withdrawing of 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 election density at the bond between O and H atoms will make the proton release difficult, thereby, *decreasing* the acidity.

(i)   When the substitution X is electron withdrawing, it decreases the electron density at   H as shown below:
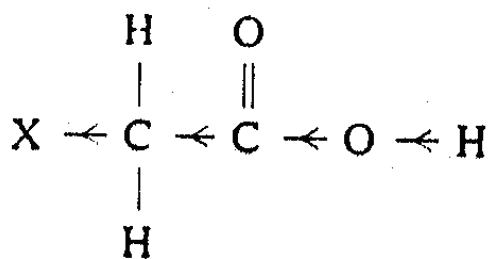
(ii)   When the substituent X is electron donating, it increases the electron density at H as represented below:

$$X \rightarrow \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} \rightarrow \underset{}{\overset{\overset{O}{\|}}{C}} \rightarrow O \rightarrow H$$
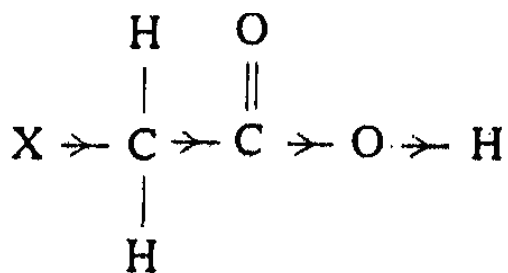
Table 2.2: Inductive effect of various functional groups

Electron-donating substituents (+I)	Electron-withdrawing substituents (-I)		
$-O^-$	$-F$	$-CO_2H$	⬡
$-CH_3$	$-Cl$	$-CO_2R$	$-\overset{+}{N}\langle$
$-CO_2-$	$-Br$	$-\overset{\overset{O}{\|}}{C}-$	$-\overset{+}{S}\langle$
	$-I$	$-C\equiv N$	
	$-OR$	$-NO_2$	
	$-OH$	$-SO_2-$	
	$-N\langle$ $-SR$	$-\overset{|}{C}=\overset{|}{C}-$	
	$-SH$	$-C\equiv C-$	

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 2.3

Table 2.3: pK_a values for some substituted acids determine in water at 298 K.

Name	Structure	pK_a
ethanoic acid	$\begin{array}{c} O \\ \parallel \\ CH_2COH \\ \mid \\ H \end{array}$	4.76
propanoic acid	$\begin{array}{c} O \\ \parallel \\ CH_2COH \\ \mid \\ CH_3 \end{array}$	4.87
fluoroethanoic acid	$\begin{array}{c} O \\ \parallel \\ CH_2COH \\ \mid \\ F \end{array}$	2.59
chloroethanoic acid	$\begin{array}{c} O \\ \parallel \\ CH_2COH \\ \mid \\ Cl \end{array}$	2.86
bromoethanoic acid	$\begin{array}{c} O \\ \parallel \\ CH_2COH \\ \mid \\ Br \end{array}$	2.90
iodoethanoic acid	$\begin{array}{c} O \\ \parallel \\ CH_2COH \\ \mid \\ I \end{array}$	3.17

Table 2.3 shows the decreased acidity for propanoic acid (larger pKa value) as compared to the ethanoic acid. Note that the propanoic acid has a methyl group in lace 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 1 are present. Note that the increase in acidity is in accordance with the electro negativity 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 2.4.

Table 2.4:   Effect of increase in the number of chlorine sustituents on acidity of ethanoic acid

Acid	Structure	pK_a
Ethanoic acid	$\begin{array}{c} \text{H} \quad \text{O} \\ | \quad \| \\ \text{H–C–C–O–H} \\ | \\ \text{H} \end{array}$	4.76
Monochloroethanoic acid	$\begin{array}{c} \text{Cl} \quad \text{O} \\ | \quad \| \\ \text{H–C–C–O–H} \\ | \\ \text{H} \end{array}$	2.86
Dichloroethanoic acid	$\begin{array}{c} \text{Cl} \quad \text{O} \\ | \quad \| \\ \text{Cl–C–C–O–H} \\ | \\ \text{H} \end{array}$	1.30
Trichloroethanoic acid	$\begin{array}{c} \text{Cl} \quad \text{O} \\ | \quad \| \\ \text{Cl–C–C–O–H} \\ | \\ \text{Cl} \end{array}$	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 δ bonds to the OH bond of the $\overset{\text{O}}{\overset{\|}{-\text{C–O–H}}}$

group. This results in a shift of the electrons constituting the O – H bond towards oxygen as shown below:

$$\text{Cl} \twoheadleftarrow \overset{\overset{\text{H}}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}} \twoheadleftarrow \overset{\overset{\text{O}}{\|}}{\text{C}} \twoheadleftarrow \text{O} \twoheadleftarrow \text{H}$$
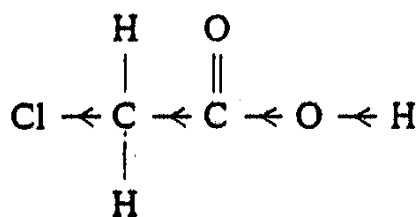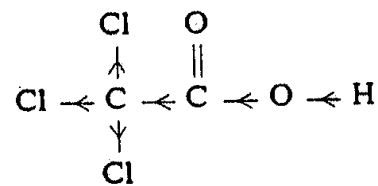
monochloroethanoic acid

Such an electron withdrawal by chlorine atom, thus, facilities the department of the proton and hence, increases the acidic character of monochloroethanoic acid as compared to ethanoic acids, the presence of second and third chlorine.

In the di – and trichloroethanoic acids, the presence of second and third chlorine
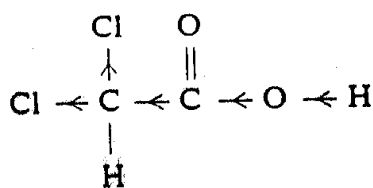
dichloroethanoic acid

trichloroethanoic acid

Atoms results in more electron withdrawal away from hydrogen of the $O - H$ bond and would, therefore, further increases 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.
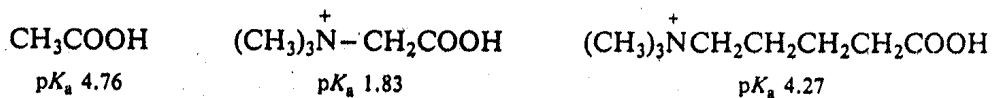
The position of electron-withdrawing substituents in a molecule also influences its acidic character. This is shown by the pka values of isomeric monochlorobutanoic acids given in Table 1.

Table 2.5: 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., $O - H$ 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 $(CH_3)_3 N^+$ - (trimethyl ammonium) or $^+NH_3$ (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:

$$CH_3COOH \qquad (CH_3)_3\overset{+}{N}-CH_2COOH \qquad (CH_3)_3\overset{+}{N}CH_2CH_2CH_2CH_2COOH$$

$$pK_a\ 4.76 \qquad\qquad pK_a\ 1.83 \qquad\qquad\qquad pK_a\ 4.27$$

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:

$$COOHCH_2COOH \overset{K_{a_1}}{\rightleftharpoons} HOOCCH_2COO^- + H^+$$

$$\text{propanedioic acid}$$
$$pK_{a_1} = 2.83$$
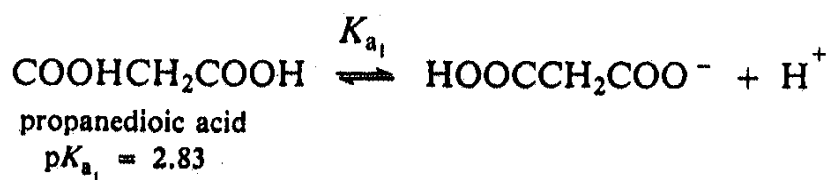
Where, K_{a1} is the dissociation constant.

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_{a1}. 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_{a2} because K_{a2} represents the second dissociation constant.

Always remember that Ka_1 is larger than Ka_2 for a dicarboxylic acid. Therefore, for these acids pK_{a1} is lower than pK_{a2}

From the above discussion, we can say that the substituents having − 1 effect increase the acidity while the substituednts having + effect decrease the acidity. On this basis, let us now analyze the stability of carbocations which are reactive intermediates formed during the chemical reactions. Look at the following examples of carbocations:
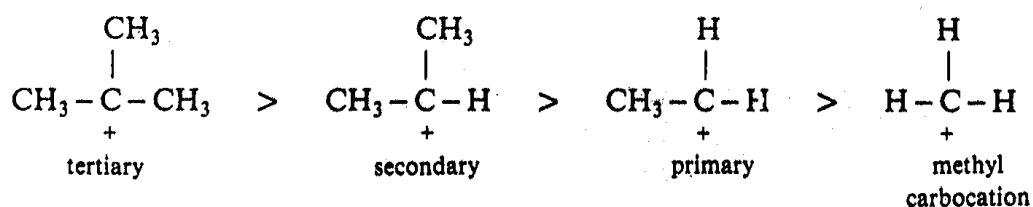
$$H \qquad\qquad H \qquad\qquad CH_3 \qquad\qquad CH_3$$
$$| \qquad\qquad\quad | \qquad\qquad\quad | \qquad\qquad\qquad |$$
$$H-\overset{+}{C}-H \quad CH_3-\overset{+}{C}-H \quad CH_3-\overset{+}{C}-H \quad CH_3-\overset{+}{C}-CH_3$$

| methyl | primary | secondary | tertiary |
| carbocation | carbocation | carbocation | carbocation |
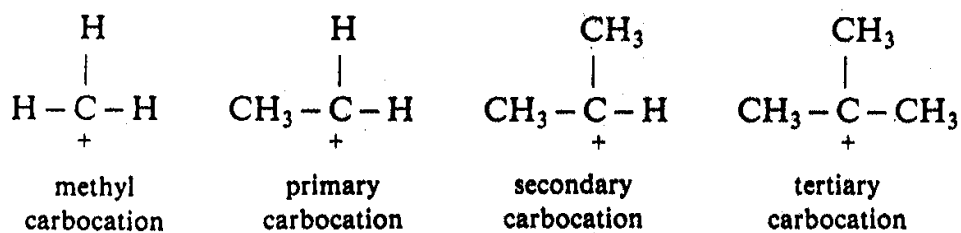
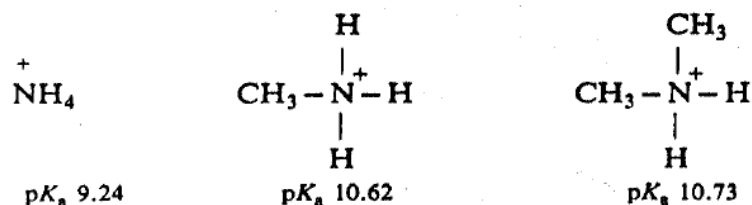The carbocations are classified by the degree of alkyl substitution at the positively charged carbon atom as primary, secondary or tertiary carbocation below.

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad R$$
$$\overset{+}{\quad}\qquad\qquad\qquad\qquad \overset{+}{\quad}\qquad\qquad\qquad\qquad |\,\overset{+}{\;}$$
$$R-CH_2 \qquad\qquad\quad R-CH-R \qquad\qquad\quad R-C-R$$

| a primary | a secondary | a tertiary |
| carbocation | carbocation | carbocation |
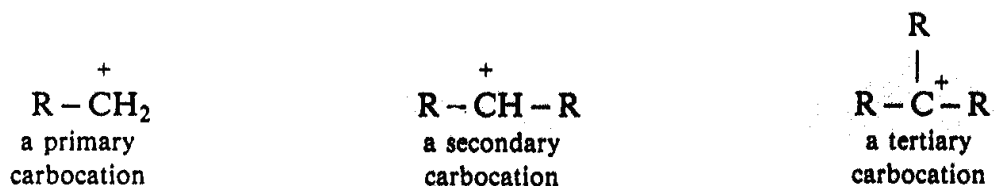
Where, R is the alkyl group

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;

$$CH_3 \qquad\qquad\quad CH_3 \qquad\qquad\quad H \qquad\qquad\quad H$$
$$| \qquad\qquad\qquad | \qquad\qquad\qquad | \qquad\qquad\qquad |$$
$$CH_3-\overset{+}{C}-CH_3 \; > \; CH_3-\overset{+}{C}-H \; > \; CH_3-\overset{+}{C}-H \; > \; H-\overset{+}{C}-H$$

| tertiary | secondary | primary | methyl |
| | | | carbocation |

Since the substitution having + 1, 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 pKa values of their conjugate acids.

$$\overset{+}{\quad}\qquad\qquad\qquad\qquad H \qquad\qquad\qquad\qquad CH_3$$
$$\qquad\qquad\qquad\qquad\quad |\,\overset{+}{\;} \qquad\qquad\qquad\qquad |\,\overset{+}{\;}$$
$$NH_4 \qquad\qquad CH_3-N-H \qquad\qquad CH_3-N-H$$
$$\qquad\qquad\qquad\qquad\quad | \qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\quad H \qquad\qquad\qquad\qquad\quad H$$

pK_a 9.24 $\qquad\qquad$ pK_a 10.62 $\qquad\qquad$ pK_a 10.73

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.

SELF ASSESSMENT EXERCISE 3

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, $HOOCCOOH$, $OOCCOOH$

2. 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

3.3.2 Resonance Effect

One of the factors which stabilize the A^- anion with respect to the acid HA, is resonance effect. Let us first revise the basic ideas about resonance.

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:

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:

$$CH_2 = CH - \ddot{O}: \longleftrightarrow \, ^-CH_2 - CH = \ddot{O}:$$

$$CH_2 = CH - \overset{+}{C}H_2 \longleftrightarrow \, ^+CH_2 - CH = CH_2$$
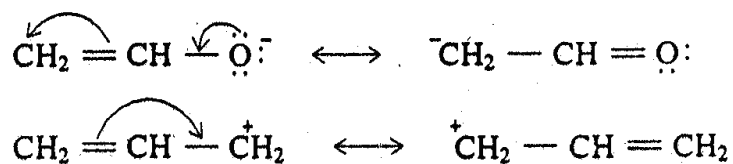
Not that a double headed arrow ($\longrightarrow$) is used to represent the resonance contributors. It should be clear to you that it does not mean that the resonance contributors are in rapid equilibrium but it implies that the actual molecule has one structure which has the contribution from various resonance contributors.

2. The nuclei of various atoms indifferent resonance contributors are in the same position. Hence, the structures which as shown below are not resonance structures because the location of the chlorine atom is different in them

$$CH_2 - CH = CH - CH_3 \overset{}{\longleftrightarrow} CH_2 = CH - CH - CH_3$$
$$\,\,\,\,\,\,\,\,\,| \qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\,\,\,\,\,\,\,\,Cl \qquad\qquad\qquad\qquad\qquad\qquad\qquad Cl$$
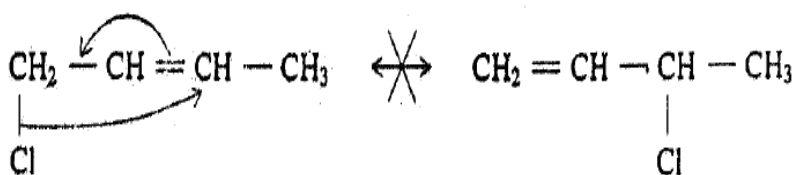
3. All reasonable contributors must have the same number of paired and unpaired electrons. This is illustrated below:

.
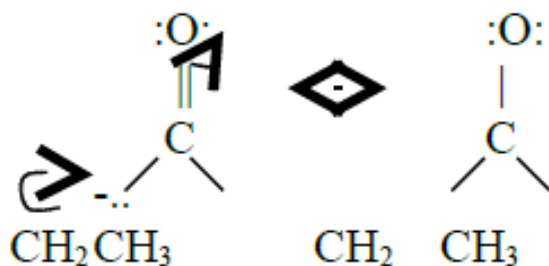
It is important to understand that the individual resonance structures have no reality and the actual compound is not a mixture of the various resonance

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 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 structure is the most important ones. Given below are some guidelines to enable you to assess the relative importance of resonance structures.

Table 2.6 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 hydroxyl (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=N), carbonyl (>C=O), and suphonic ($-SO_3H$) groups.

Table 2.6   Resonance effects of various groups

Electron donating + R groups	Electrons withdrawing - R groups
-F	-C=N
-Cl	
-Br	O
-1	$\parallel$
-O-	-C-
-OR	$-SO_2-$
-OH	$-NO_2$
O	
$\parallel$	
- 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:

```
    O
    ||
CH₃C – OH                CH₃CH₂OH
ethanoic                 ethanol
pKₐ 4.76                 pKₐ 17
```
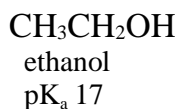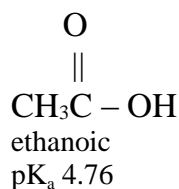
Consider the dissociation of these compounds as shown below:

```
    O                        O
    ||                       ||
CH₃C – OH + H₂O          CH₃ – C – O ⁻ + H₃O ⁺
                              ethanoate ion
```

$$CH_3CH_2OH + H_2O \qquad CH_3CH_2O^- + H_3O^+$$
<div align="center">ethoxide ion</div>
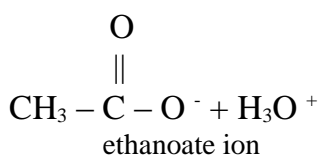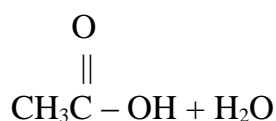
We find that the anion of ethanoic acid can be represented as a resonance hybrid of the following two resonance structures.

$$\underset{O:}{\overset{O}{CH_3C}} \qquad\qquad \underset{O:}{\overset{O:}{CH_3C}}$$
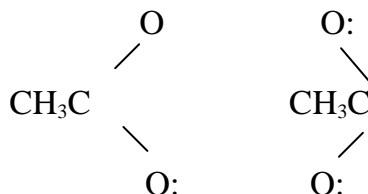
Since these two structures are equivalent, they contribute equally to the actual structure which can be represented as shown below:

$$\left. CH3 - C \underset{O:}{\overset{O:}{}} \right]$$
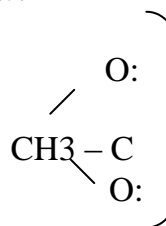
Thus, we can say that in the ethanoate anion the charge is not localized on any one of the oxygen atoms but is distributed equally, or is delocalized, over both the oxygen atoms. This dispersal of charge is resulting from the delocalization stabilities this anion. But, the delocalization of charge reduces the availability of lectrons, 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 stabilization is not possible for the ethoxide ion because such as stabilization is possible only if the system has electrons. Because of the absence of resonance stabilization of the ethoxide anion, ethanol is less acidic as compared to ethanoic acid.

Resonance structures discussed in this section involve electrons and in some cases nonbonded electrons. In the next section, you will study hyper conjugation which involves and electrons.

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 (-1 effect) of the aryl group, the following resonance structure are possible.

benzenamine (aniline)
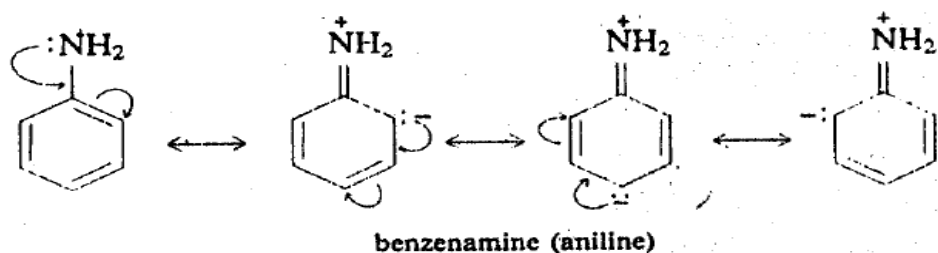
These resonance structures clearly show that the nonbonding electrons of the nitrogen atom are delocalized over the aromatic ring. Thus, the electron density at the nitrogen atom decreases which results in the lower basicity of aniline as compared to ammonia.

You can check your knowledge of resonance by answering the following **Self Assessment Exercise.**

SELF ASSESSMENT EXERCISE 4

Draw resonance structures for the following species to rationalize the facts given with them.

*1. $H_2C =: O^+–H$ is the conjugate acid of methanal (formaldehyde)
and has a substantial positive charge on carbon.*

2. In acetonitrile oxide. $H_3C – C = N – O:$ -, the inner carbon can act as a Lewis acid.

We will now study a special case of resonance which is known as hyperconjugation.

Hyperconjugation

Hyperconjugation involves the conjugation of sigma-electrons with adjacent *pi* electrons, as shown below:
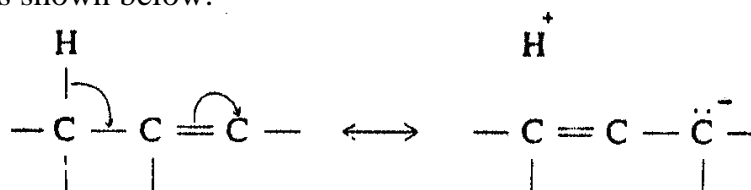
This is also known as conjugation.

This type of delocalization 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 hydrogen **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 delocalization of charge, as you will now study in case of carbocations. Hyperconjugation involving hydrogens is the most common.

The 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. 2.1.
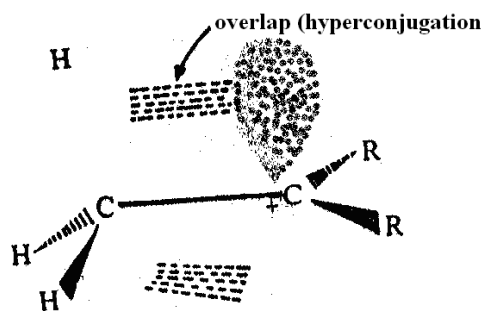
Fig 2.1: the hyperconjugation in a carbocation

Make a model of this carbonation and convince yourself about the overlap as shown here.

It is clear from the above structure that the electrons forming the - C– H bond can overlap, into the empty p orbital of the carbon atom carrying the positive charge. The C – H bond adjacent to the >C = C< or carbonation is referred here as -C-H bond. The resulting hyperconjugation can be represented as illustrated below:
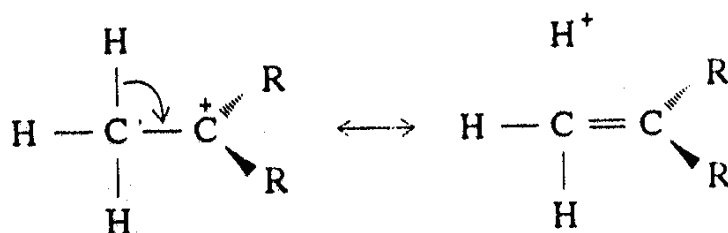
Note that hyperconjugation produces some additional bonding between the electron-deficient carbon and the adjacent carbon atom. Hence, hyperconjugation results in the stabilization of carbocation by delocalizing the positive charge. Obviously, the more the number -C – H bonds which can participate in hyperconjugation, the more stable will be the carbocation. You can see that in case of the primary carbocation shown above, there are three such - C – H bonds. Let us now examine the secondary and the tertiary carbocations.

For hyperconjugation to occur, the subsititunent next to the positively charged carbon must have a filled 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
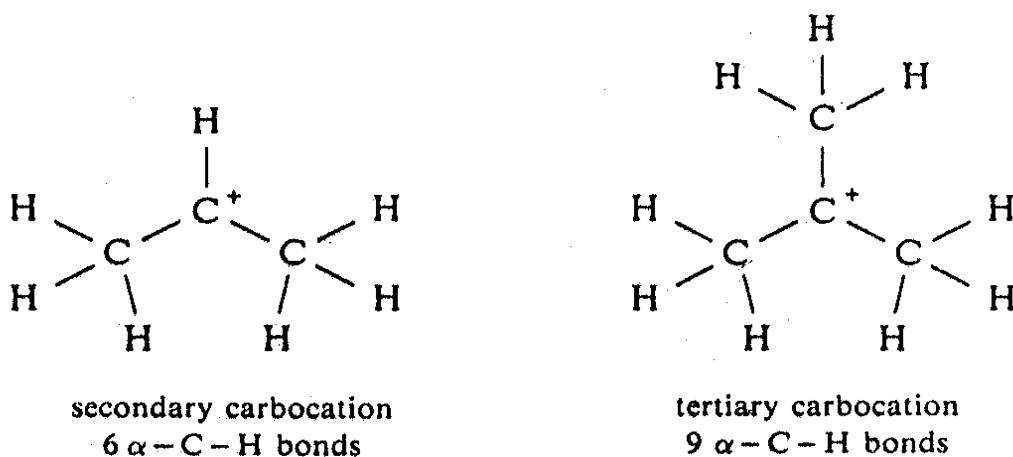
The secondary carbocation has 6 -C – H bonds which can participate in hyperconjugation whereas the tertiary carbocation has 9 - C – H bonds. Certainly, more delocalization of charge is possible in case of a tertiary carbocation than in a secondary carbocation which is in turn more than the possible in 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.
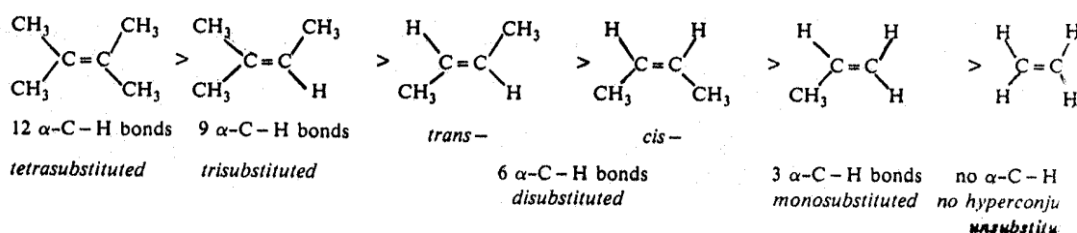
You can see that in an alkene, the more the number of   -C-H bonds which can participate in hyperconjugation, the higher is its stability.

In spite of the fact that hyperconjugation can be used to explain many otherwise unconnected phenomena, it is controversial as it involves the formation of 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, hydrogen bonding which you will now study.

3.3.4 Hydrogen Bonding

You are already familiar with the concept of hydrogen bonding from our earlier study. If you analyse the pKa values of benzenecarboxylic acid and 2-hydroxy-benzenecarboxylic acid, as given below, then you will conclude that 2-hydroxy benzenecarboxylic acid is much more acidic than benzenecarboxylic acid. This is because the anion formed from 2-hydroxy benzenecarboxylic acid is stabilized by

hydrogen bonding, as shown below:

benzenecarboxylic acid
pK_a 4.2

2-hydroxy benezenecarboxylic acid
pK_a 2.98
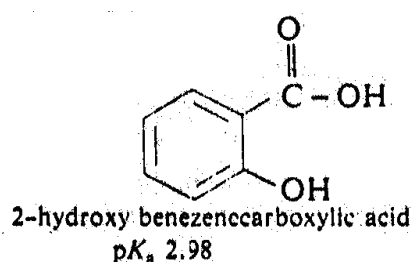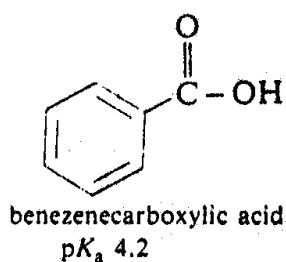
Hydrogen bonding stabilizes the anion by delocalizing the charge.
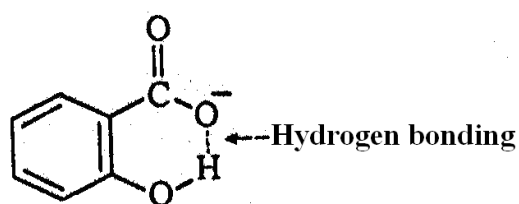
No similar stailisation is ossible for the benzenecarboxylate anion; therefore benzenecarboxylic acid is less acidie than 2-hydroxy benzenecarboxylic acid.

benzenecarboxylate anion
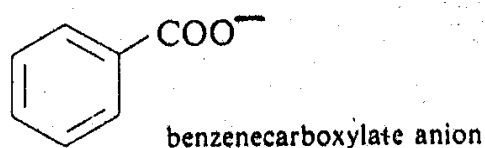
In the next section, you will study the steric effect on molecular reactivity.

3.3.5 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 (where you studied that the trans-isomer is more stable than the cis-isomers) and conformational isomers (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 delocalization of charge, as observed in case of N,N-dimethyl-o-toluidine. The delocalization of the nonbonded electron pair on nitrogen, as shown in the structure of N,N-dimethylaniline in Fig 2.2 (a).
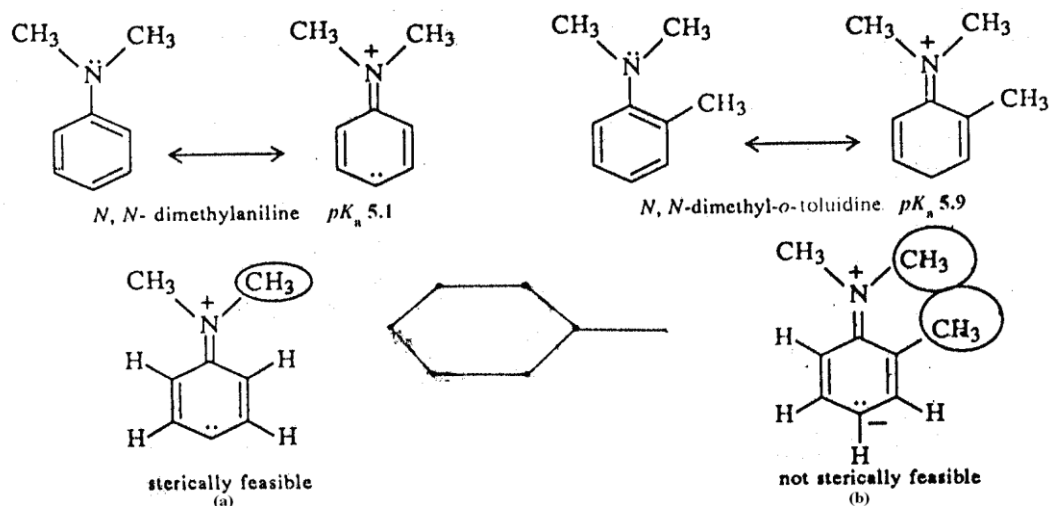
Fig 2.2: (a)   Delocalisation of nonbonded electrons on nitrogen into arom ring in N,N-dimethylaniline (b) Such a delocalization in not possible in N,N-denethy-o-toluidine requires that the p-orbital of nitrogen and those of the aromatic ring should be coplanar.

Such coplanarity is inhibited in the case N,N-dimethyl-o-toluidine due to the presence of the *ortho* methyl group, as shown in Gig. 1.2 (b). Therefore, in this molecule the electron pair is not delocalized 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.

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 atome 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. 2.3, the trimethylammonium cation, i.e. the conjugate acid of trimethylamin, is sterically the most hindered.

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.

methylammonium ion
hydrogen bonding with
three water molecules

trimethylammonium ion
hydrogen bonding with
only one water molecule
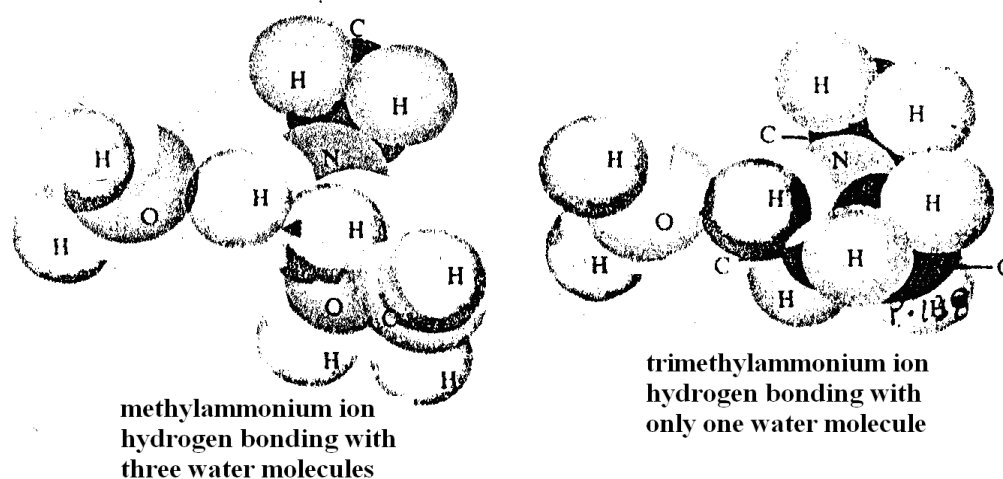
Activity 1

Make models of primary, secondary and tertiary amines and compare the steric hindrance observed in these molecules.

trimethylamine

trimethylammonium
cation
pK_a 9.8
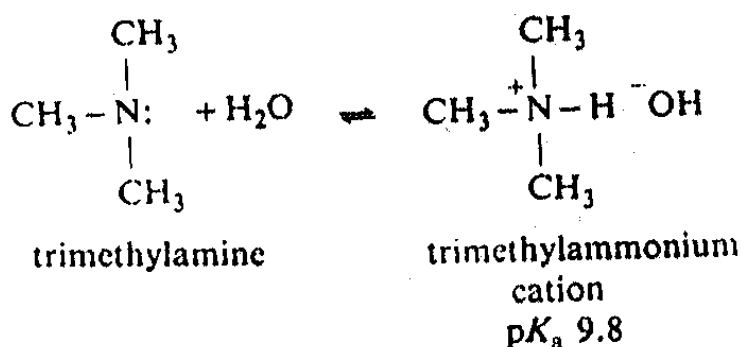
Fig 2.3: A comparison of the solvation of trimethylammonium and methylammonium ions

It is thus least stabilized by solvation, leading to the lower basicity of trimethylamine in water as compared to dimethylamine and methylamine. However, in the gas phase or nonaqueous media, the electron-donating inductive effect of a methyl group makes trimethylamine the most basic among the 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 ionized species which are the conjugate acid and the conjugate base when we are dealing with Bronsted acids and bases. Solvation refers to the interaction of the dissolved species and solvent molcules wherein several solvent molecules surround the dissolved species by forming a **solvent shell** or **solvent cage** around it, as shown below:
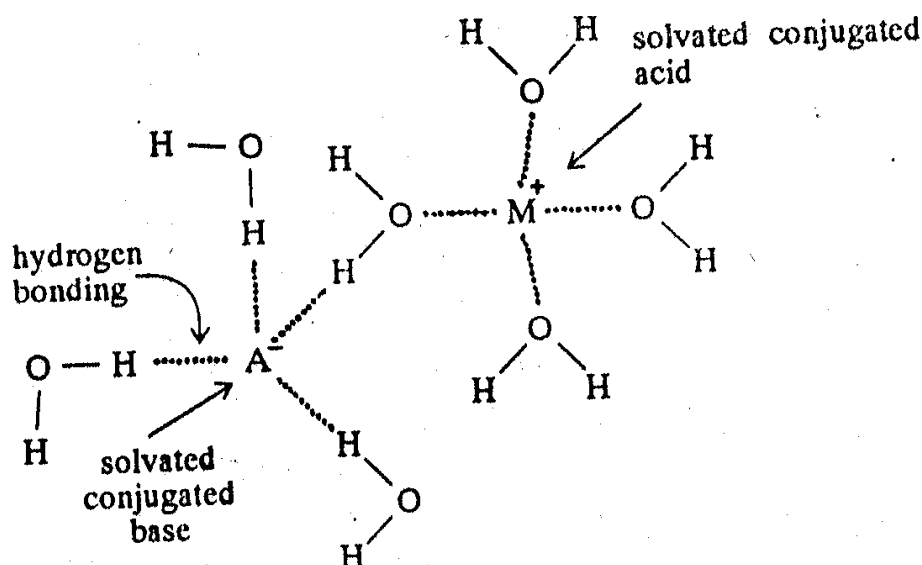
The greater the solvation, the greater is the delocalization of the charge on the species. Thus, increased solvation increases the dissociation of an acid or a base by increasing the stability of the ions.

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 ionization and the acidity of a substance increase with the increase in the dielectric constant of the solvent. This is illustrated in Table 2.3.

Table 2.7: Effect of solvent on pK_a of ethanoic acid at 298 K

Solvent	pK_a
Benzene	Almost unionized
82% Dioxane – 18% Water	10.14
70% Dioxane – 30% Water	4.32
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, pK_a value of the acid decreases.

Water is perculiar solvet 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.*

3.4   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 differe from each other only in the location of a hydrogen atom and a double bond are called **proton tautomers.** Table 2.8 shows some examples of proton tautomers.

In contrast to resonance structure, tautomers are real compounds and are capable of independent existence.
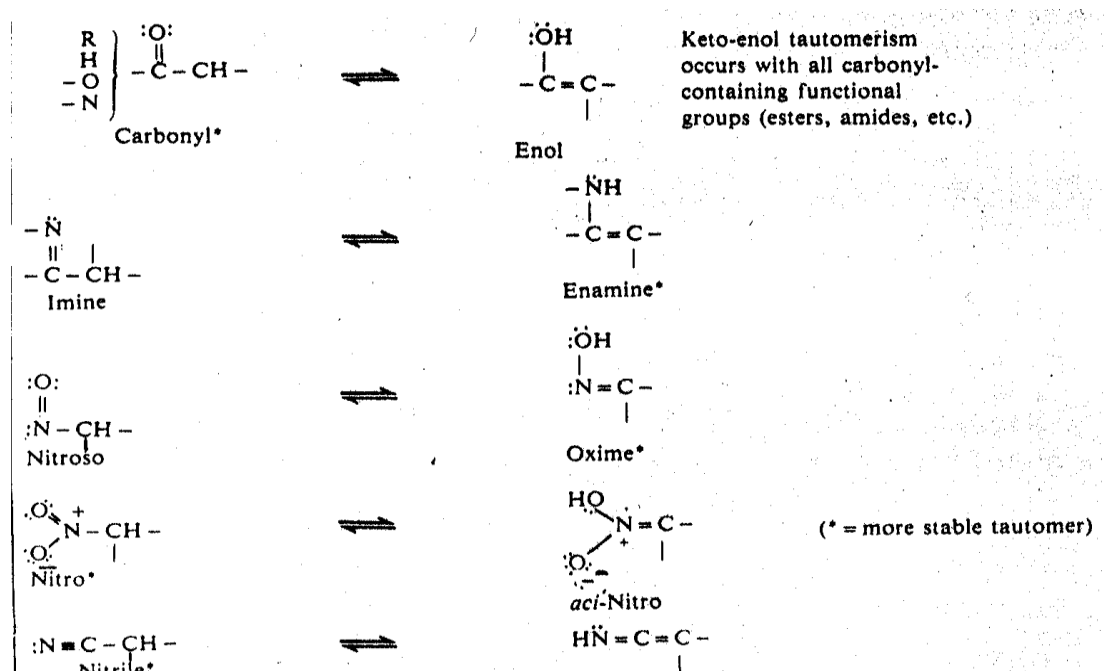
A particular example of tautomerism involving the ketones as carbonyl compounds is caled **keto-enol** tautomerism and is represented below:
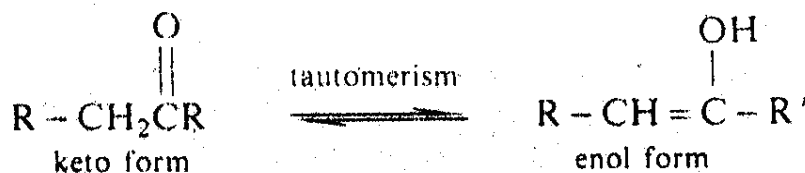
The keto-enol tautorism is enormous importance as you will study later in this course and also in the Organic Reactions Mechanism course. In keto-enol tautomers, the keto form is usually the more stable form and, therefore, it predominates at equilibrium.

The mechanism of enolisation involves solvent mediated proton transfer steps rather than a direct intramolecular jump of the proton from carbon to oxygen.

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:
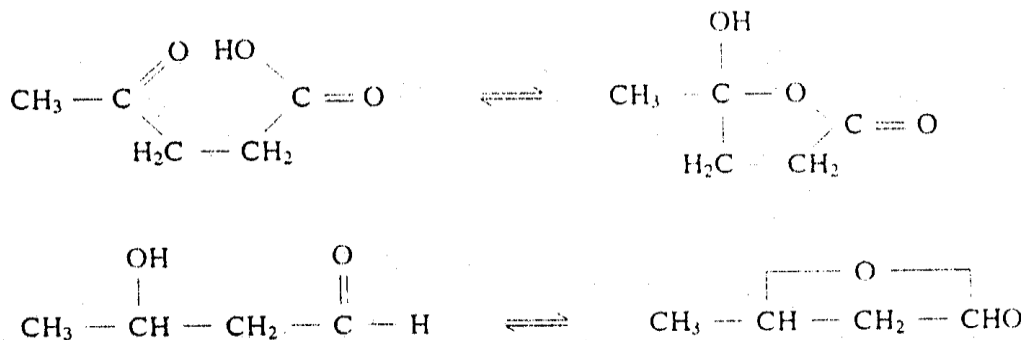
Another kind of tautomerism, known as **valence tautomerism** involves a shift in interatomic distance within a molecule, without the separation of any atom from the rest of the molecule, as an intermediate stage. This kind of tautomerism occurs as a result of movement of valence electrons of the molecule. 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 and electrons or the nonbonding electrons shift and the 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 hybridization of atoms which may result in a change in the shape of the molecule. While in resonance there is no such change in the hybridization and geometry of the molecule.

ii)   The tautomers have a physical reality while the resonance structures are imaginery.

iii)   Tautomerism involves equilibrium between two or more tautomers. On the other hand, the resonance implies that the actual structure of the molecule in the *weighted averaged* of various resonance contributors and not a mixture on them.

4.0   CONCLUSION

Bronsted-Lowry defined an acid as a proton donor and a base as proton acceptor. While Lewis definition classifies acids as electron pair acceptors and bases as electron pair donors. The acidities of Bronsted acids are 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.

5.0   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 Bronsted-Lowry definition, an acid is a proton donor and a base is proton acceptor.
- Lewis definition classifies acids as electron pair acceptors and bases as electric pair donors.
- The acidities of Bronsted 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 stabilization 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 Bronsted 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.

6.0   TUTOR-MARKED ASSIGNMENT
1. Explain the acidic nature of 2,2,2-trifluoroethanol as compared to ethanol.
2. Explain the difference between pK_{a1} (4.16) and pK_{a2} (5.61) of butanedioic acid.
3. Draw resonance structures for the following:

(i)   chlorobenzene   ii) acetonitrile   iii) pyrrole, ·
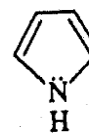
4. Ethylamine and aniline react with aq. HCl. Write the equation for these reactions.

5. Are the following pairs of compounds tautomers or resonance forms?
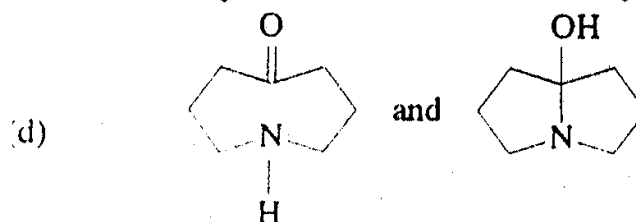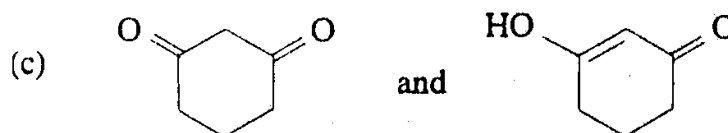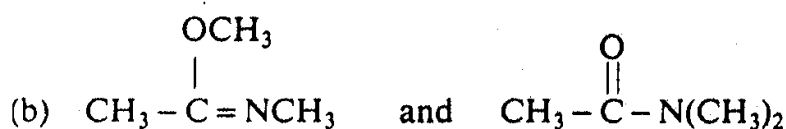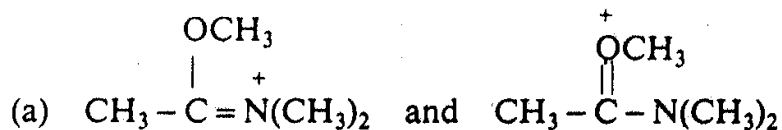
$$\text{(a)} \quad \underset{\underset{\displaystyle CH_3}{\overset{\displaystyle OCH_3}{|}}{CH_3-C=\overset{+}{N}(CH_3)_2}} \quad \text{and} \quad CH_3-\overset{\overset{\displaystyle \overset{+}{O}CH_3}{\|}}{C}-N(CH_3)_2$$

$$\text{(b)} \quad \underset{\underset{\displaystyle }{\overset{\displaystyle OCH_3}{|}}}{CH_3-C=NCH_3} \quad \text{and} \quad CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-N(CH_3)_2$$

(c)

and

(d)

and

7.0   REFERENCES/FURTHER READINGS

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UNIT 3   AROMATIC HYDROCARBONS AND OLYNUCLEAR AROMATICS

CONTENTS

1.0   INTRODUCTION

In CHM 132, 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 the 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 was 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 significance any longer.

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 benezene 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 transquiliser 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.

2.0   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 explains the resonance energy of aromatic compounds
- discuss the important reactions of aromatic compounds explain what the polynuclear hydrocarbons are
- list the important reactions of polynuclear hydrocarbons.

3.0   MAIN CONTENT

3.1   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:

$$CH_3(CH_2)_4CH_3 \xrightarrow{\Delta} C_6H_6 + 4H_2$$
hexane   benzene

$$CH_3(CH_2)_5CH_3 \xrightarrow{\Delta} C_6H_5CH_3 + 4H_2$$
heptane   toluene

$$CH_3(CH_2)_6CH_3 \xrightarrow{\Delta} C_6H_4(CH_3)_2 + C_6H_5C_2H_5$$
octane   xylenes   ethyl benzene
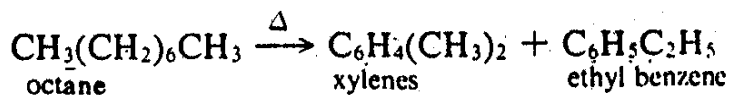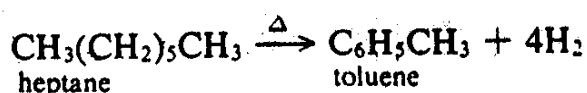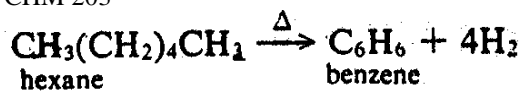
Note that a mixture o-, m- and p- xylenes is referred to as xylene

Various hydrocarbons are separated by a selective solvent process, but since, benzene is obtained in much smaller amount than toluence and the xyleness, these are converted into benzene by heating with hydrogen under pressure in the presence of a metal oxide catalyst. This process is called hydrodealkylation.

$$C_6H_5CH_3 + H_2 \xrightarrow{Catalyst} C_6H_6 + CH_4$$
toluene   benzene   methane
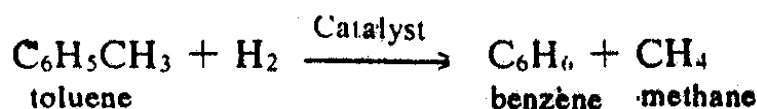
3.2   Spectral Properties

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 recognizing 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 1225-970cm^{-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 single at δ 3.27 ppm. Recall that olefinic protons appear at higher field values, generally at about δ5.0 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 ^{2}H 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 $(C_4H_3)^+$, 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.

3.3   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 120^0. Each carbon atom in the molecule is sp^2 hybridized. Two orbitals of the sp^2 hybridized 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 Is 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 nd because all p orbitals are equivalent, they overlap equally well with both the neighbouring p orbitals resulting in a delocalized doughnut shaped π orbital cloud above and below the ring. The picture that emerges out of this discussion is given below in Fig 3.1

σ Skeleton   π Skeleton
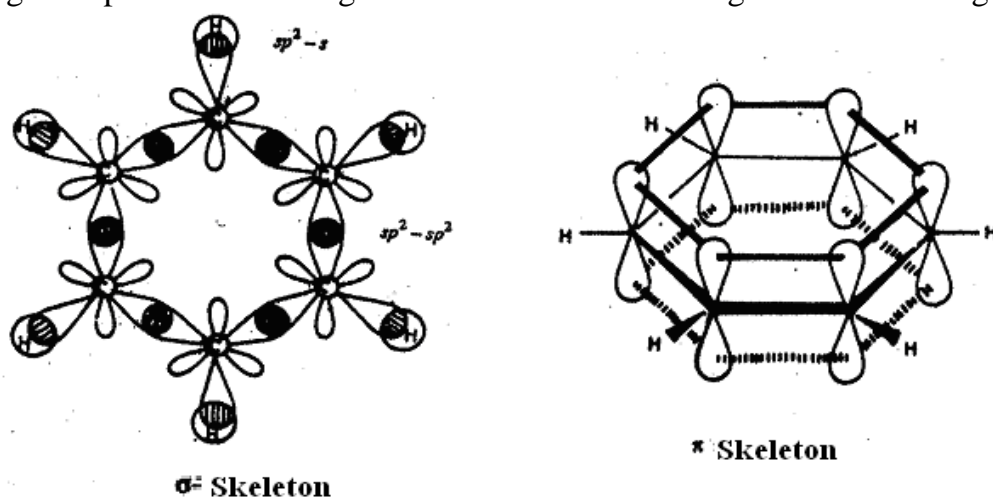
The benzene ring is a cyclic conjugated system and is usually represented as a regular hexagon with a circle inside the ring. This gives an idea of delocalization of π-electrons.

3.4   Resonance and Aromaticity

You have already studied the basic concept of resonance in Unit 7 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., ethane 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 moclecules, one of the examples being benzene. The structure of benzene (Fig 4.1) 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 woud 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 ethane). 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 cyclohexane and benzene determined experimentally are given below:
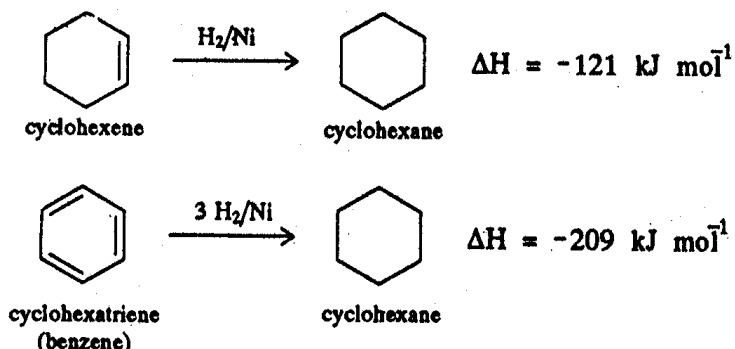
The heat eveoled when hydrogen is added to cyclohexene (having one C = C bond) is 121 kJ mol^{-1}. The expected value of the heat evoleved when hydrogen is added to benzene (having three C=C bonds) should be 3 x 121 kJ mol^{-1} = 363 kJ mol^{-1}, but the experimental value is 209 kJ mol^{-1}. We can infer that benzene is more stable (having lower energy content) than the hypothetical molecule containing three isolated C=C bonds 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.
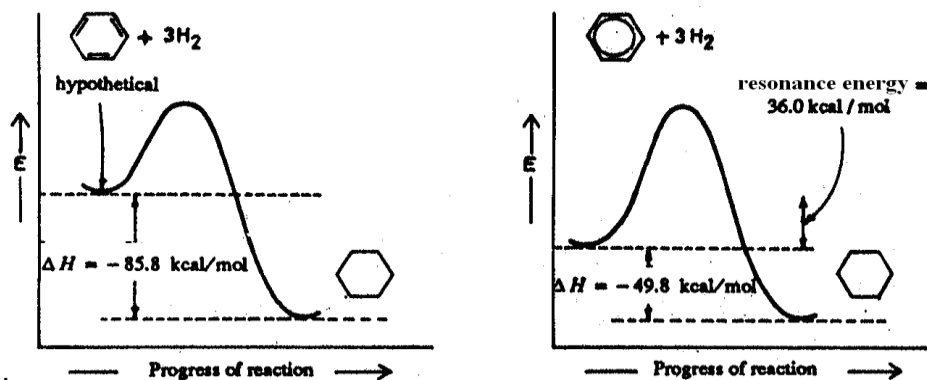
Fig 3.2: Energy diagram for the hydrogenation of cyclohexatriene (hypothetical) and benzene

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
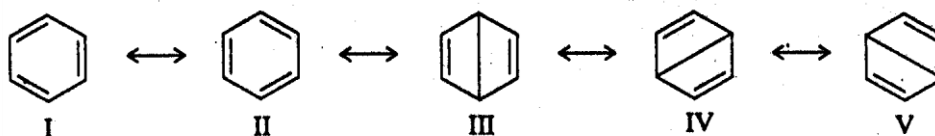
These structures are called resonance structures or contributors or canonical forms.

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 arise due to shift of π electrons within the molecule.

Aromaticity

Perhaps you have been wondering whether other cyclic compouns 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, Enrich Hűckel in 1931, proposed the Hűckels rule. According to this rule an aromatic molecule must be a cyclic conjugated species having ($4n + 2$) -electrons where n is an integral (n = 0, 1, 2, 3 …..). This means that only the ring with 2, 6, 10, and 14 … electrons may be aromatic but a ring with 4, 8, or 12 electrons may not be aromatic. Hűckel rule is also applicable to ionic species. Let us look at some of the evidence supporting the Hűckel rule.

1)   **Cyclobutadiene**
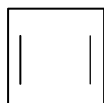
no. of π- electrons = 4

4 + 2 electrons are required for aromaticity. Cyclobutadiene has 4 -electrons, hence cyclobutadiene is not aromatic as it has 4   - electrons and is highly unstable.

2)   **Benzene**
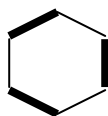
no. of π-electrons = 6

Here the 4n + 2 rule can be applied as it has 6 -electrons which are required for a single ring system. It is an excellent example of an aromatic system.

3)   **Cyclotatetraene**

no. of   -electrons = 8

It does not have $4n + 2\pi$ electrons and thus is not aromatic.

Another reason why cyclotatetraene 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.
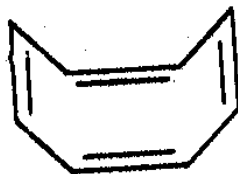
cyclooctatetrane

From the above example, it is clear that a flat planar geometry is required for proper overlap resulting in delocalization of π-electrons which is a necessary condition for aromaticity.

SELF ASSESSMENT EXERCISE 1

Which of the following compound is aromatic?
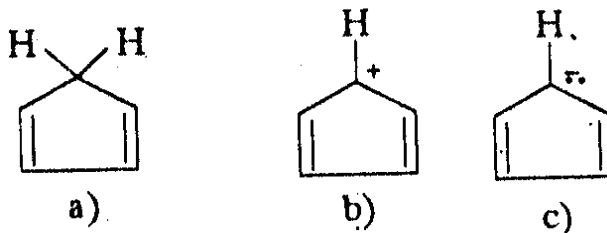
3.5 Reactions of Aromatic Compounds

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 πelectrons 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 3.1

Table 3.1: 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
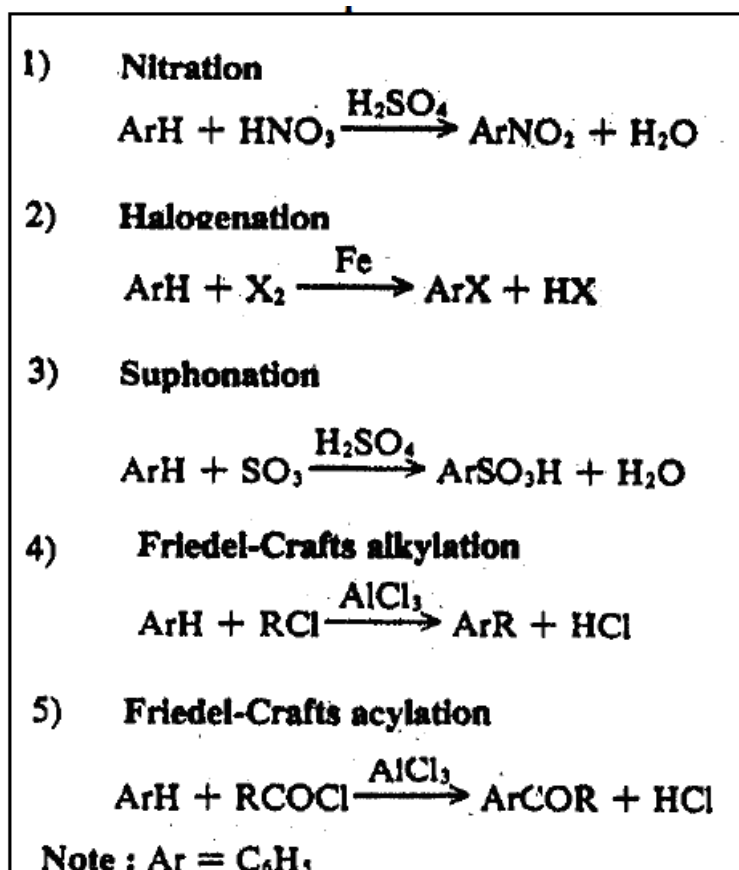
3.5.1 Nitration

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.
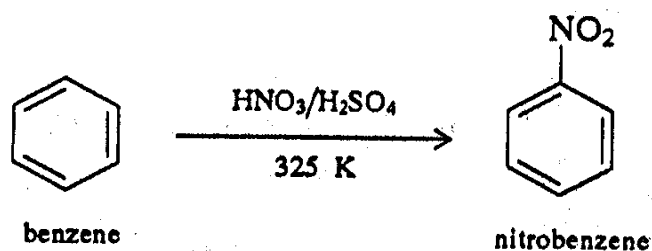
The electrophile in this reaction is the nitronium ion, NO_2^+. It is generated by the reaction of H_2SO_4 with HNO_2.

$$\overset{\overset{\displaystyle H}{\displaystyle |}}{H_2SO_4 + HONO_2 \rightleftharpoons HONO_2 + HSO_4}$$

$$\overset{\overset{\displaystyle H}{\displaystyle |}}{HONO_2} = H_2O + NO_2^+$$
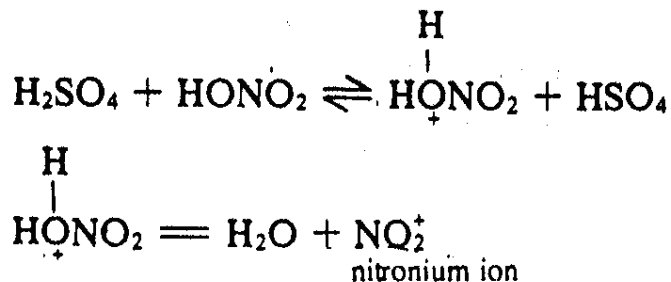
nitronium ion

Further evidence for the participation of the nitronium ion comes from the fact that other species capable of producing nitronium ion, such as $NO_2^+BF_4^-$, $NO_2^+NO_3^+$ and $NO_2^+NO_3^-$ and $NO_2^+ClO_4^-$ also nitrate benzenoid compounds.

Nitration of benzene is an important reaction because the nitro group can be converted into other functional groups.

3.5.2 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 polarize the halogen-halogen bond, e.g.
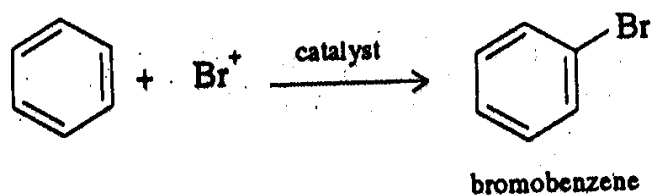
bromobenzene

A typical reaction of aromatic halogenation is the bromination of benzene. As a general rule, fluoride 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 oxidizing agent such as hydrogen peroxide, H_2O_2, or copper salt such as $CuCl_2$. This oxidizing agent oxidizes molecular iodine to an electrophile I^+.

$$I_2 + 2 Cu^{++} \longrightarrow 2 I^+ + 2 Cu^+$$

iodobenzene
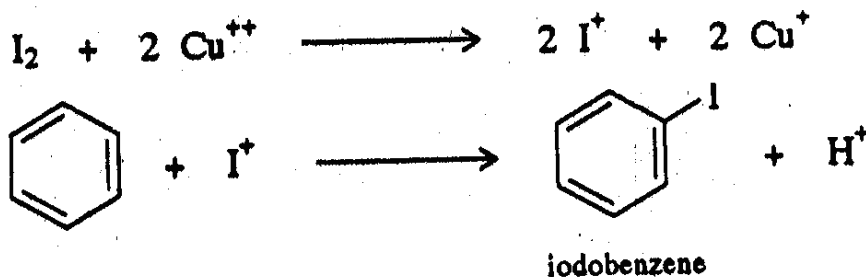
Halogenation can also be affected by other reagents, such as ypochlorous or hypobromous acids in presence of strong acids.

$$H-O-Cl + H^\cdot \longrightarrow H_2O-Cl$$

chlorobenzene
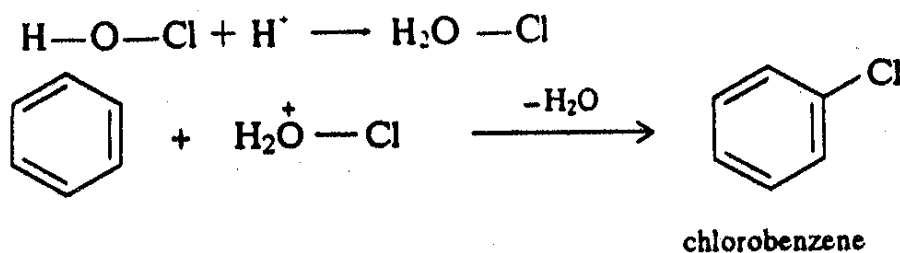
3.5.3 Sulphonation

Aromatic compounds in which the sulphonic group (-SO₃H) 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 usally accomplished using sulphuric acid or fuming sulphuric acid (H_2SO_4 + SO_3) containing varying proportions of sulphur trioxide.

sulphonic acid
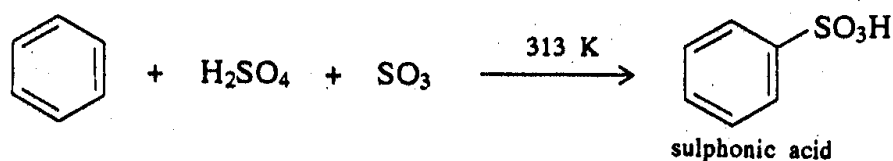
The reactive electrophile is neutral SO_3, as is evident from its structure given below:
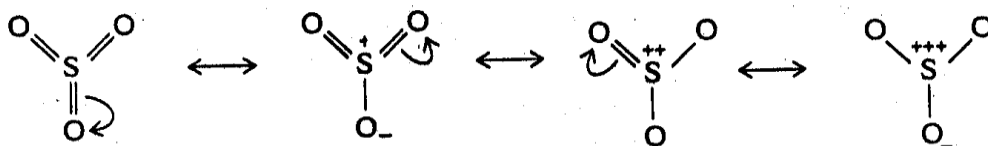
Unlike the other electrophilic substitution reaction reaction of benzene, sulphonation is a highly reversible reaction and the direction depends on the reaction conditions. Sulphonation is favoured in the presence of concentrated or fuming sulphuric acid, desulphonation in hot, dilute aqueous acids.

3.5.4 Friedel-Crafts Alkylation

Complex substituted aromatic compounds are 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.
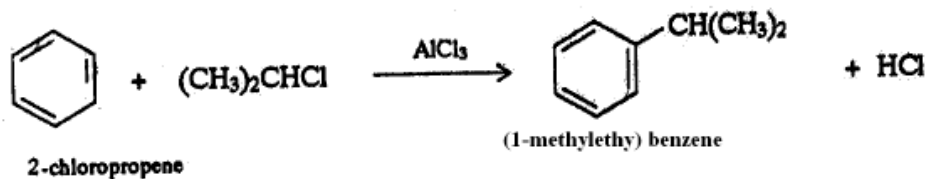
The electrophile in the Friedel-Crafts reaction is R^+. This ion is formed when an alkyl halide reacts with a Lewis acid. Lewis acids such as $AlCl_3$, $FeCl_3$, $ZnCl_2$, $AlBr_3$, BF_3 etc. are used in Friedel-Crafts alkylation. In case of alkylation with tertiary alkyl halides, the electrophilic species is a free carbonations, the electrophilic species is an alkyl halide-Lewis acid complex with positively polarized carbon.
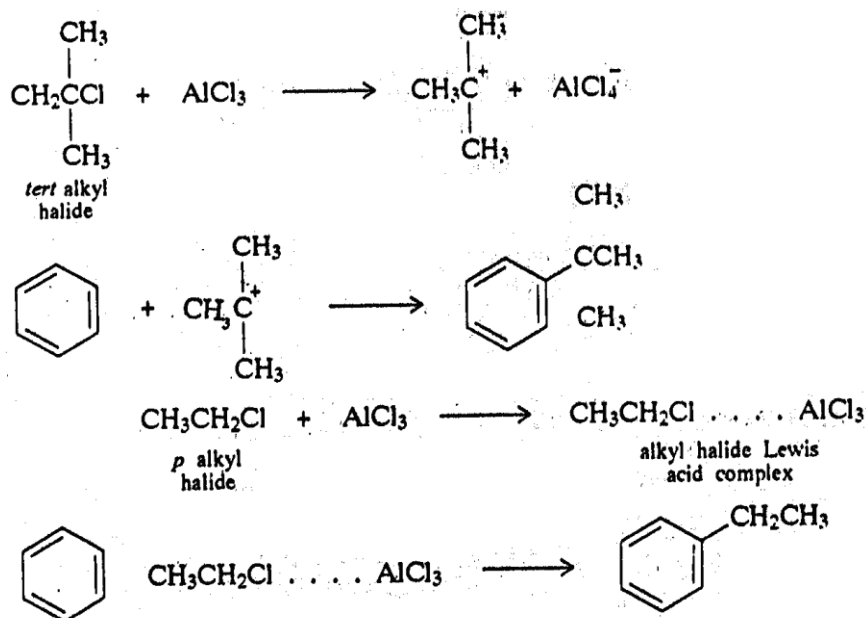
Though the Friedel-Crafts reaction is widely applicable in organic synthesis, it has some limitations as given below:

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 3.3.1.
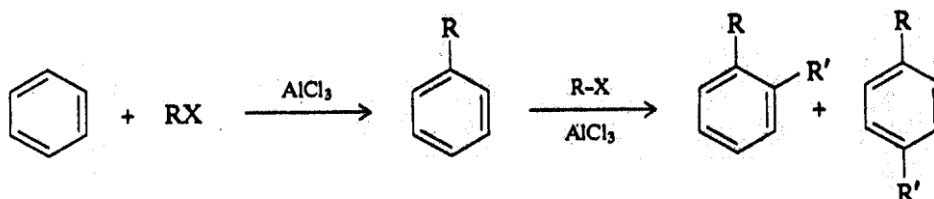
The best way of avoiding this second reaction is to use an excess of aromatic compound.

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
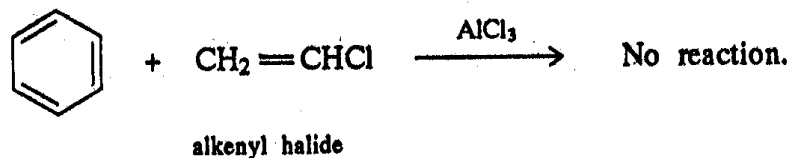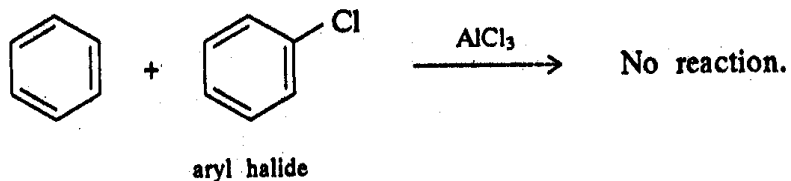
iii)   If the aromatic compound has an electron withdrawing substituent, it does not undergo Friedel-Crafts alkylation; the deactivated ring is not reactive to attack carbocations.

G = any electron-withdrawing group.
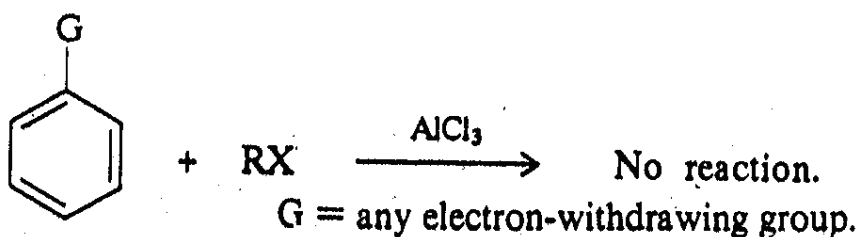
iv)   Aromatic amines fail to undergo alkylation, probably because amino group forms a complex with Lewis caid. Since this complex has a positive charge on nitrogen, it deactivates the aromatic ring for electrophilic substitution.
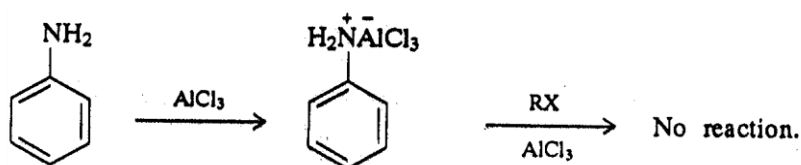
v)   Sometimes during alkylation, the attacking electrophile undergoes rearrangement by 1,2 shift of H or R. For example, the alkylation of benzene with chloropropane leads to a mixture of propylbenzene and (1-methylethyl) benzene.
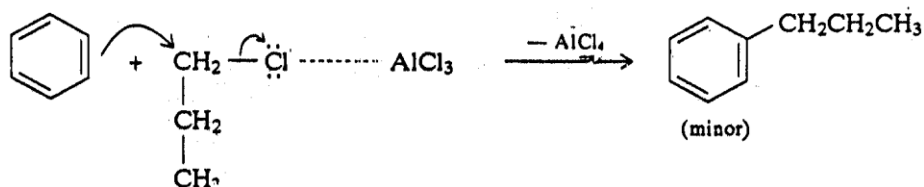
Rearrangement
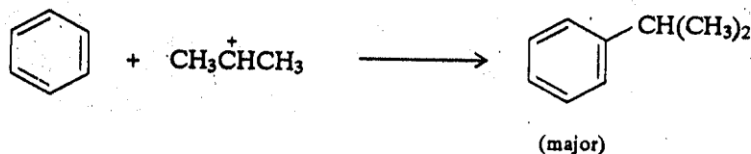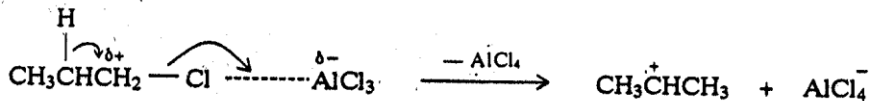
The mechanism is similar to alkylation with an alkyl halide and this reaction proceeds through the more stable carbocation intermediate.

SELF ASSESSMENT EXERCISE 2

*Give the product(s) of the following reactions:*
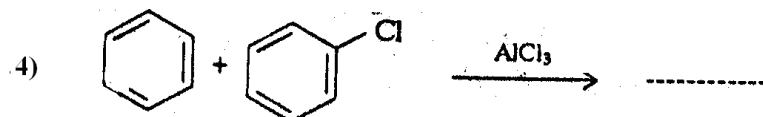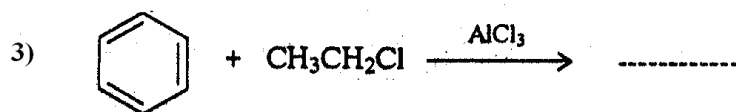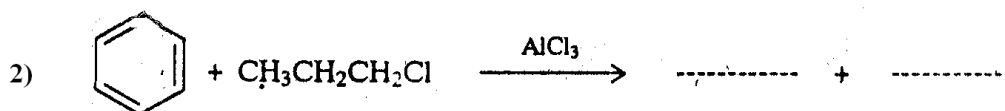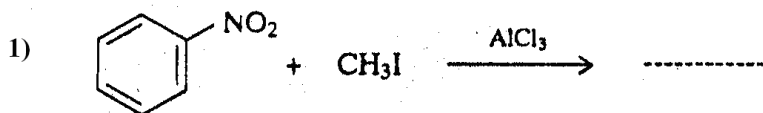
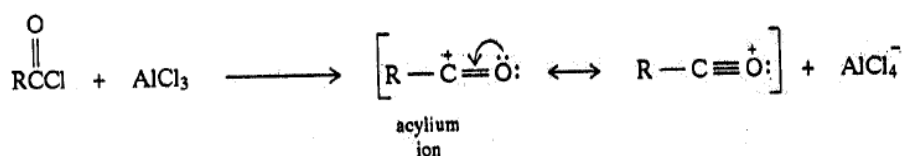## 3.5.5 Friedel-Crafts Acylation

$$\begin{matrix} O & & O \\ \| & & \| \end{matrix}$$
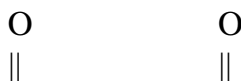
The RC-group or ArC-group is called an acyl group. Substitution of an acyl group into an aromatic ring by the reaction with an acid chloride in the presence of Lewis

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).
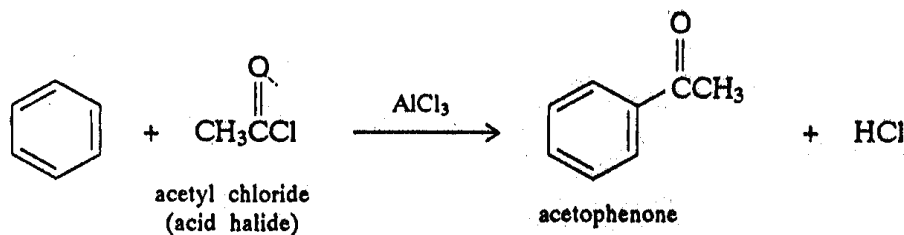

The mechanism of Friedel-Crafts acylation is similar to that of the other electrophilic aromatic substitution reactions. The electrophile in this reaction is the resonance – stabilised carbocation, acylium ion. This ion is formed when the acid chloride reacts with the Lewis acid, A1C1$_2$.

Carboxylic acid anhydride can be used as alternative to acid chloride for the Friedel-Crafts acylation reaction.
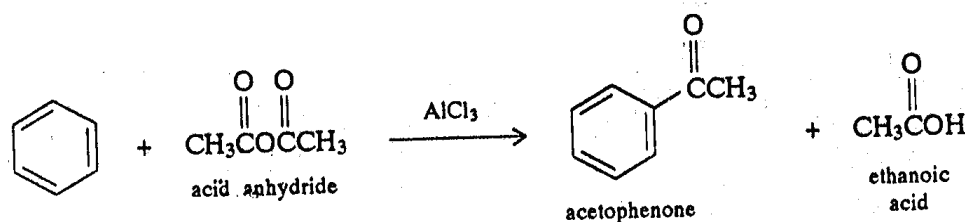
Friedel-Crafts acylation reaction is a synthetically useful reaction. For example, the carbonyl group of the ketone produced by Friedel-Crafts acylation can be reduced to > CH$_2$ group by using zinc amalgam and hydrochloric acid. This method of reduction is known as Clemmensen reduction. By the combination of Friedel-Crafts acylation and Clemmensen reduction, an alkylbenzene may be prepared.
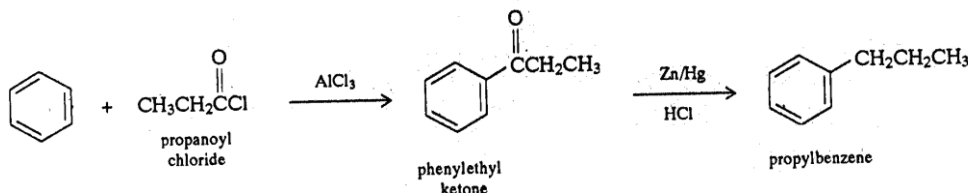

Unlike Friedel-Crafts alkylation, Friedel-Crafts acylations are not accompanied by rearrangements within the acyl group. Moreover, there is no polysubstitution as the aromatic ring is deactivated after the introduction of the first acyl group.

3.5.6 Mechanism of Electrophilic Substitution

There are reasons to believe that the electrophilic substitutions 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. Electrphilic attack on C=C gives carbocation intermediate which is then attacked by nucleophile to yield addition product.
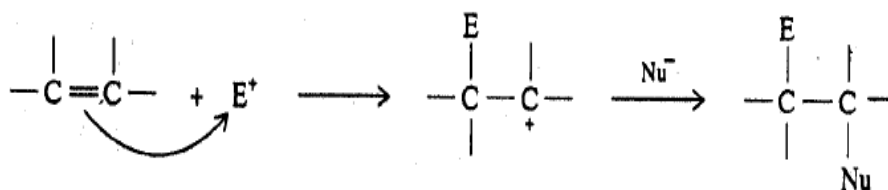
An electrophilic aromatic substitution reaction begins in a similar way. The electrons of the ring attack on electrophile E*, forming a σ bond with electrophile. In this process, the positive charge of the electrophile is to be transferred to the adjacent ring carbon atom which is called carbocation. This is a slow step and is, therefore, the rate determining step.
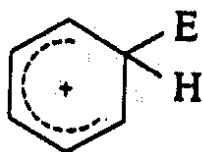
If a reaction takes place through a series of steps, the slowest step is called the rate-determining step (RDS).

This carbocation is stabilized by resonance as shown below:
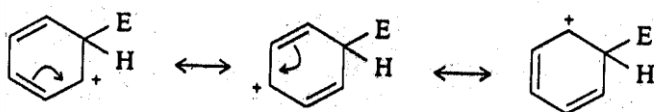
These three resonance structure of the intermediate are often combined and represented as follows:
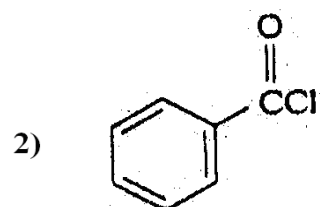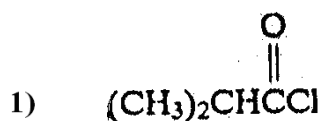
In the case of alkenes, you have seen that nucleophile attacks the carbocation to yield the addition product. Since, in the present case, the addition of the nucleophile would destroy the aromatic stabilisation of the benzene ring, this type of addition does not take place in aromatic carbocation. Instead, nucleophile acts as base and abstracts a ring proton yielding substituted aromatic product.
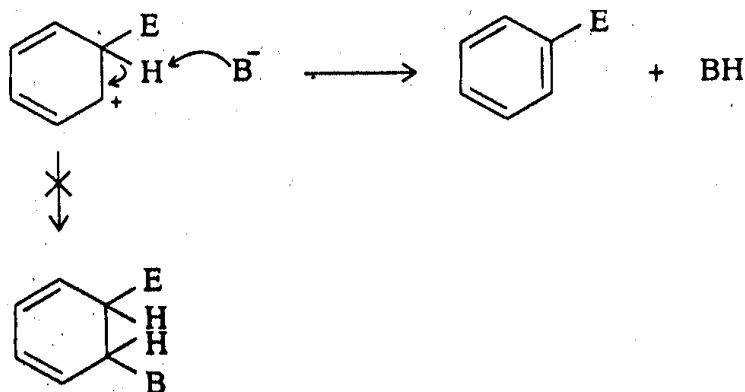
SELF ASSESSMENT EXERCISE 3

Give the structure of the product expected from the reaction of each of the following compounds with benzene in the presence of AlCl₂.

1) $(CH_3)_2CHCCl$ with O double bonded to the carbonyl carbon

2) benzene ring with CCl group, O double bonded to the carbonyl carbon

3) $C_2H_5COCC_2H_5$ with two O double bonded to the carbonyl carbons

SELF ASSESSMENT EXERCISE 4

Write the mechanism of sulphonation of benzene using SO₃ as electsrophile.

3.6 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 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 substitution 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.

$$\overset{O}{\underset{\parallel}{}} \quad \overset{O}{\underset{\parallel}{}} \quad \overset{O}{\underset{\parallel}{}}$$
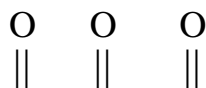
Halogens – CH, - CH, - COR, - CN, - NO_2, - NR_2. Now we will study the effect of substituents on reactivity and orientation.

3.6.1 Effect of Substituents on Reactivity

To compare the rates of electrophilic substitution in benezene, methyl substituted benzene (methyl benzene or totluene) 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 order 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.
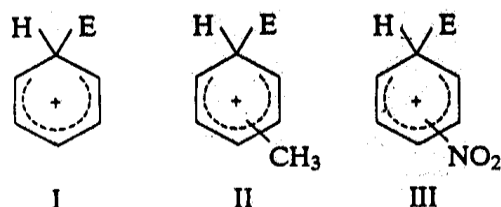
In the case of methylbenzene (II), the methyl group, which is an electron-donating group, tends to neutralize the echargeon, the carbocation, this dispersal of the charge stabilizes the carbocation thus leading to faster reaction than benzene.

In case of nitrobenzene (III), the NO_2 group which is an electron-withdrawing group, tends to intensify the positive charge and destabilize 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:
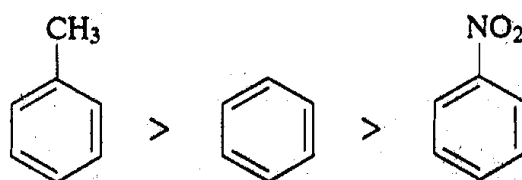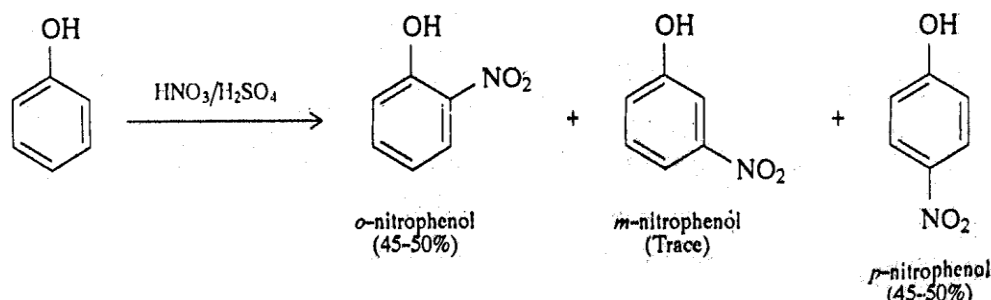
SELF ASSESSMENT EXERCISE 5

Which compound would you expect to undergo aromatic nitration more readily, C_6H_5-CH_3 or $C_6H_5 - CC_3$? and why?

3.6.2 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.
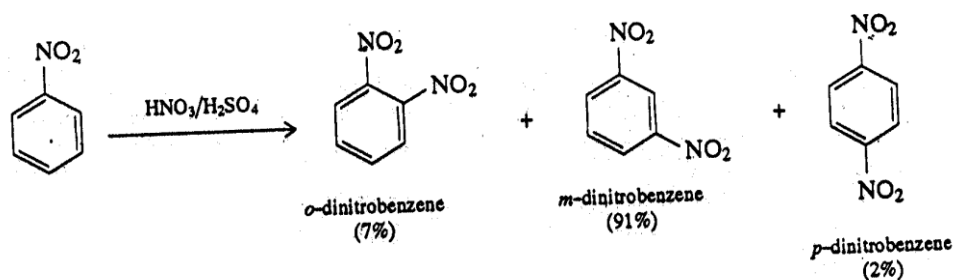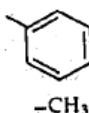

This shows that different substituents have different effect on substitution reaction. Thus substituents can be classified into three groups, i.e.

orho and para-directing activator

meta-directing deactivator   (No metadirecting activators are known.)

orho and para-directing deactivator.

Table 3.2   List some of the groups in each category

| *Ortho-*and *para-* directing activators	*Ortho-* and *para-* directing deactivators	*Meta-*directing deactivators
$-NH_2$	$-I$	$-N^+(CH_3)_3$
$-OH$	$-Br$	$-NO_2$
$-OCH_3$	$-Cl$	$-CN$
$-NHCOCH_3$	$-F$	$-\overset{\overset{\displaystyle O}{\|\|}}{C}CH_3$
$-CH_3$ (benzyl)		$-\overset{\overset{\displaystyle O}{\|\|}}{C}OCH_3$
		$-\overset{\overset{\displaystyle O}{\|\|}}{C}OH$
		$-\overset{\overset{\displaystyle O}{\|\|}}{C}H$

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 *otrho* and *para* position much more than they do the *meta* position. Similarly, deactivating groups deactivates all positions in the ring. They are *meta* directors because they deactivate the *orho* and *para* position more than they deactivie 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.
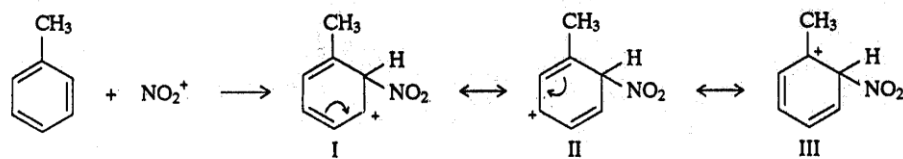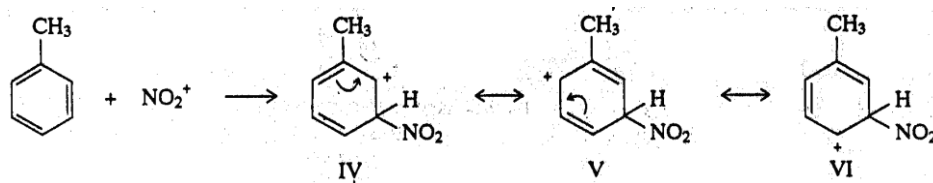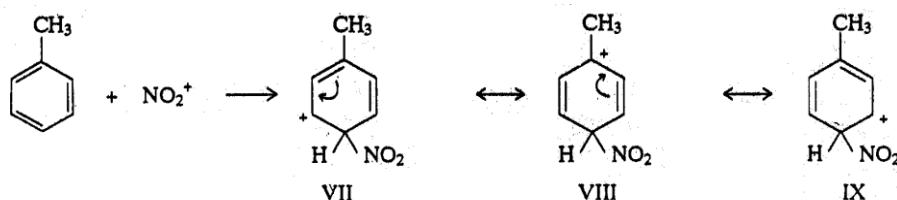
a)   *Ortho*-Attack

b)   *Meta*-Attack

c)   *Para*-Attack

VIII   IX   X   XI
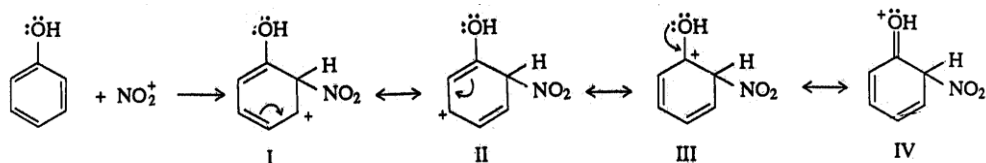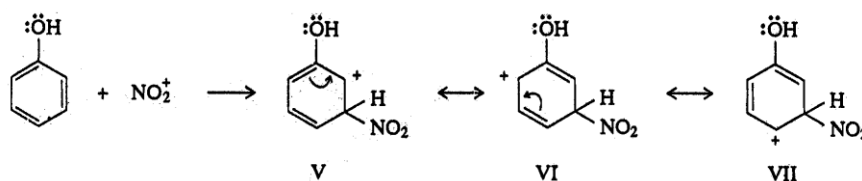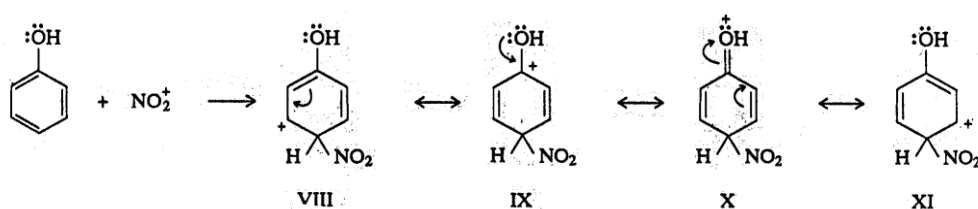
In case of ortho and para attacks, structures IV and X respectively show that the unshared electron pair of oxygen delocalize the positive charge on the carbocation and, hence, four resonance structures are possible. In the case of *meta* attack, since the charge and not be delocalised onto the – OH 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 ntrophenols 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, NO_2, on toluene.

1.   *Ortho*-Attack

I   II   III

2.   *Meta*-Attack

IV   V   VI

3.   *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 posive charge is at a secondary carbocation. On the other hand, *meta* attack produces an intermediate in which none of the resonance structure structures benefits from such tertiary carbocation stabilization. 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-substition.

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
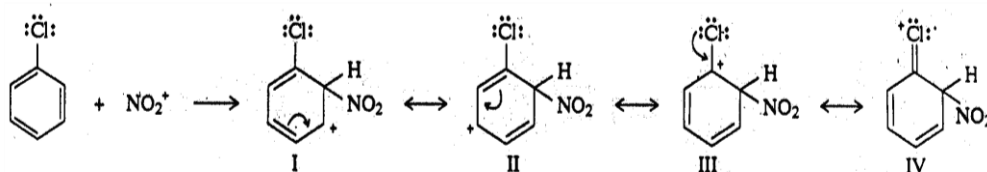

b) *Meta*-Attack

c) *Para*-Attack
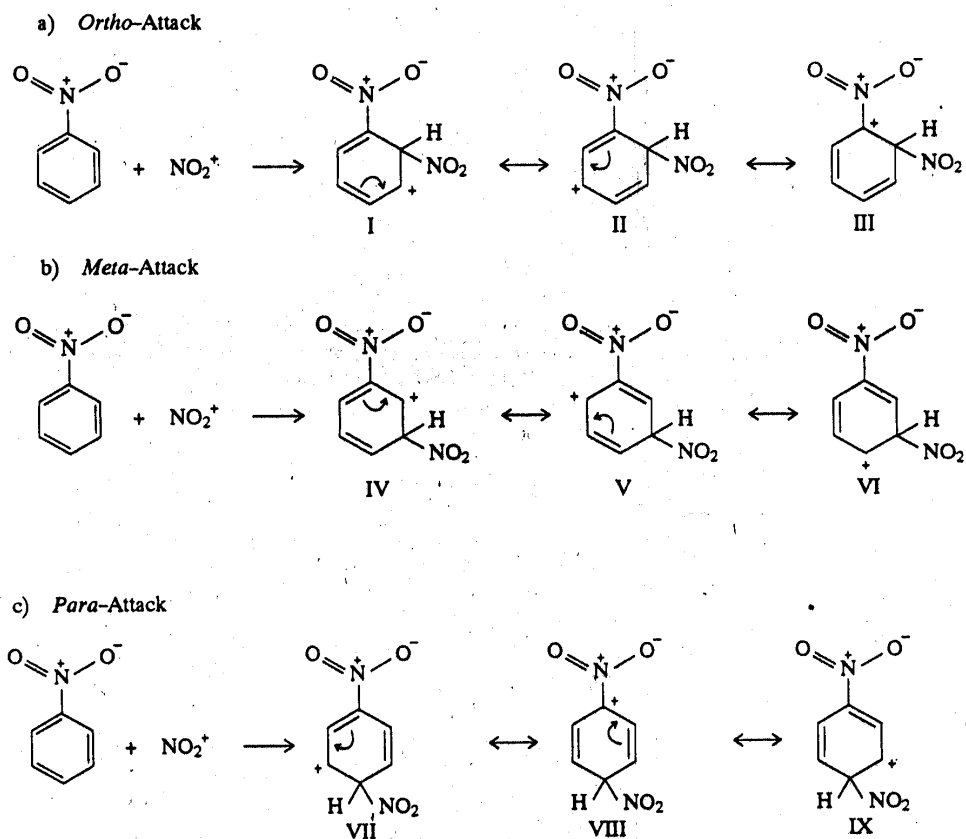
In all the three cases, carbocations formed have three resonance structures. But the structure III and VIII resulting from *ortho* and *para* respectively are very unfavourable because the positive charge is placed directly on the carbon carrying the electron withdrawing group. A severe electrostatic repulsive interaction between the carbocation and the positive end of the NO_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.
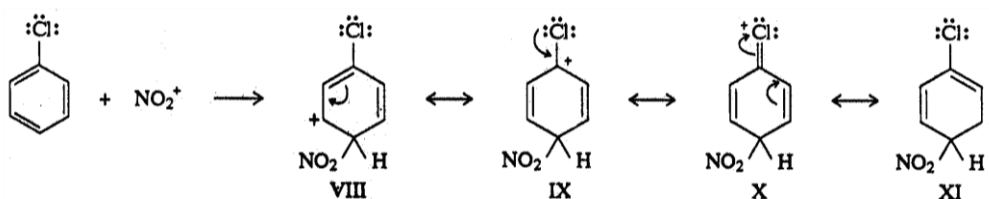
a) *Ortho* Attack.

b) *meta* Attack
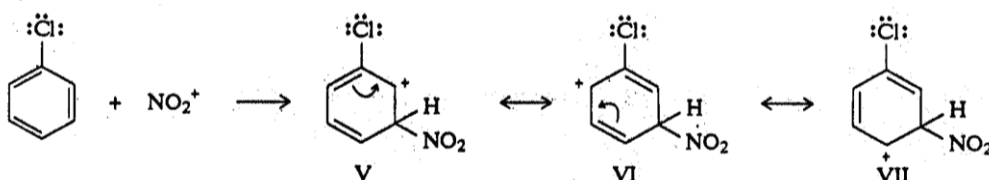
c) *para* Attack

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 attacks 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 prefered.
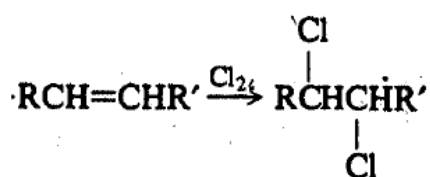
SELF ASSESSMENT EXERCISE 6

Predict the major and minor products of the following:

1.   *Nitration of bromobenzene*
2.   *Nitration of nitrobenzene*
3.   *Bromination of nitrobenzene*
4.   *Chlorination of phenol*

3.7   Addition Reactions of Benzene

You have already studied in Unit 5 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 exachlorocyclohexanes. 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 proceeds by the free radical mechanism.

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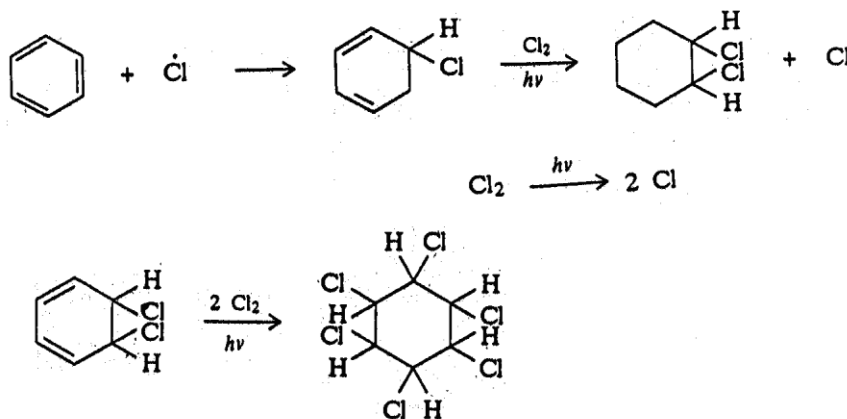
**1,2,3,4,5,6-hexachlorocyclohezane**

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.

3.8 Reduction

Hydrogenation of benzene at higher temperature and under pressure yields cyclohexane.
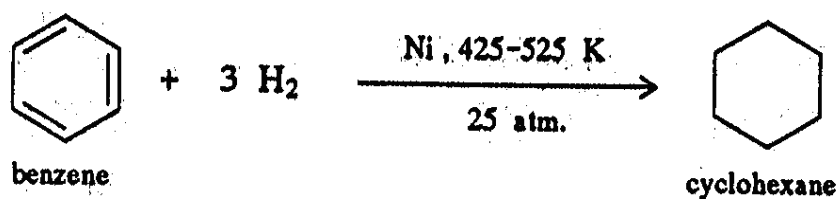
Although benzene is not reduced by metal and acid, or by sodium in ethanol, it is reduced by sodium in liquid ammonia in the presence of ethanol (Birch reduction) to give 1, 4-dihydrobenzene (cyclohexa-1,4-diene). This reaction has also been shown to have a free radical mechanism.
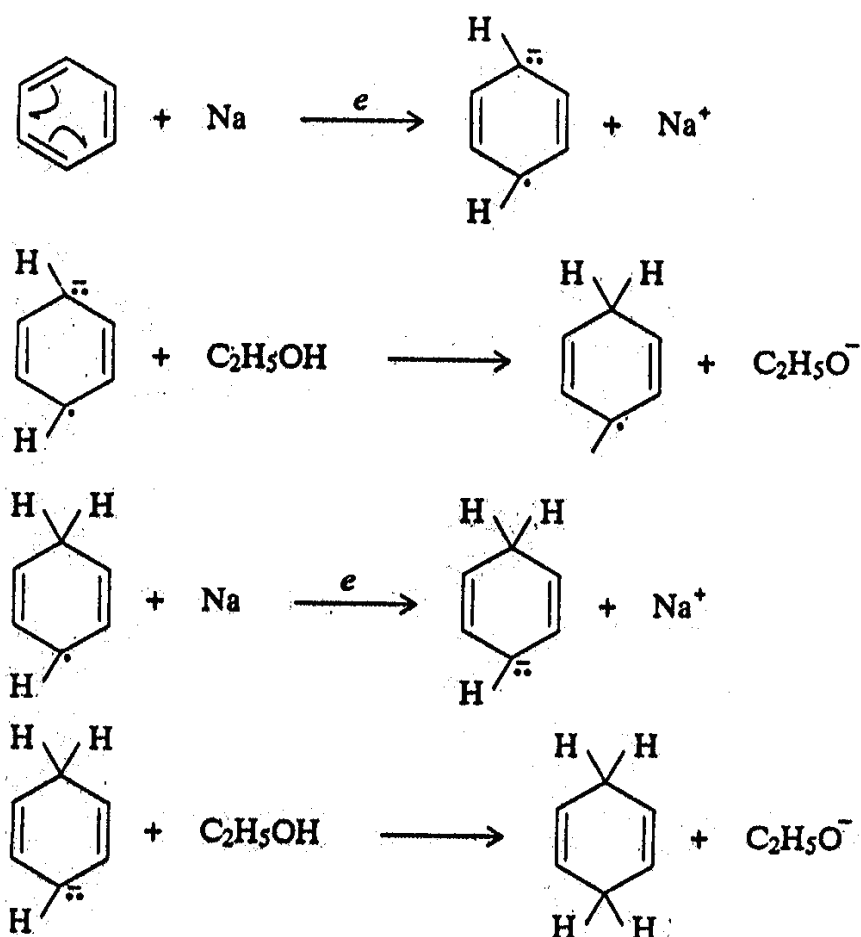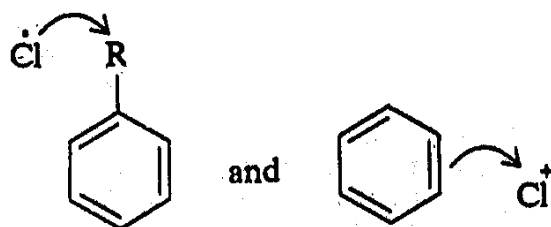

Lithium in anhydrous ethylamine, however, reduces benzene to cyclohexene and cyclohexane.

3.9   Reactions of Side-chain

3.9.1 Substitution in the Side-chain

Alkylbenzene clearly offers for attack by halogen: the ring and the side chain. We 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

$$CH_4 \ + \ Cl_2 \xrightarrow{\text{Heat or light}} CH_3Cl \ + \ HCl$$
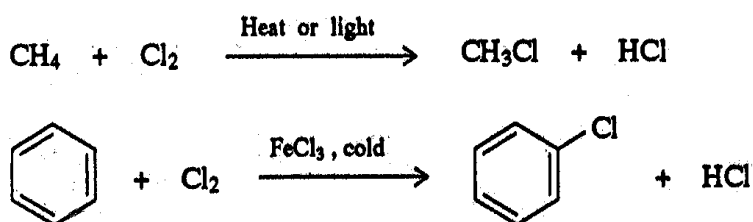
The position of attack in methylbenzene (toluene) would be decided by the nature of the attacking particle and by the condition employed. If the reaction is carried out in the presence of light, substitution occurs almost exclusively in the side chain. In the absence of light and in the presence of ferric chloride, substitution occurs mostly in the ring. For example;
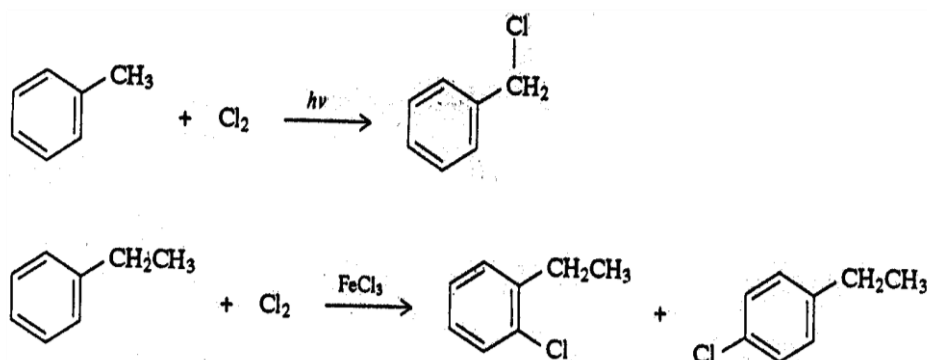
Chlorination of methylbenzene (toluene), in the presence of light, takes place via free radical chain mechanism as shown below:

$$Cl_2 \xrightarrow{\ h\nu\ } 2\ Cl$$
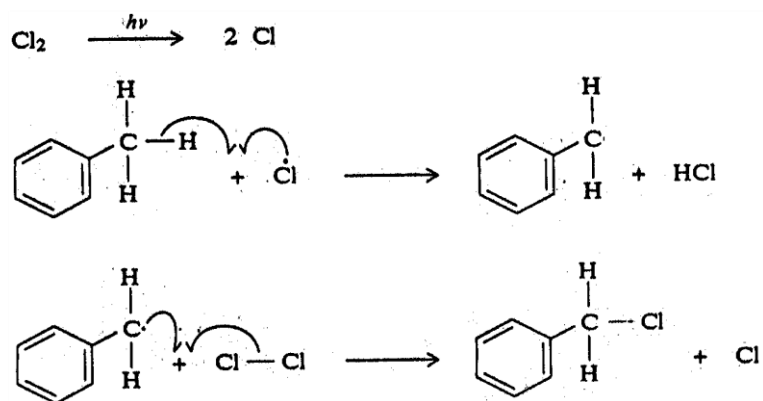
In alkyl benzenes with side chains larger than methyl, it is expected that the free radical substitution may take place on any of the side chain carbon atoms; so we must consider the likelihood of obtaining a mixture of isomers. For example, chlorination of ethylbenzene should give two isomeric products; 1-chloro-1-phenylethane is the major (91%) product,

benzylic C — H bond

-phenylethyl C – H bond
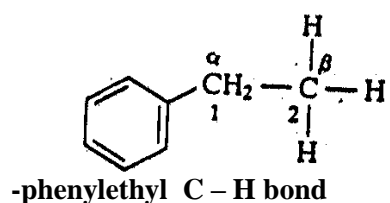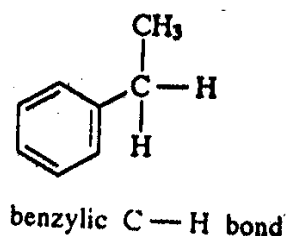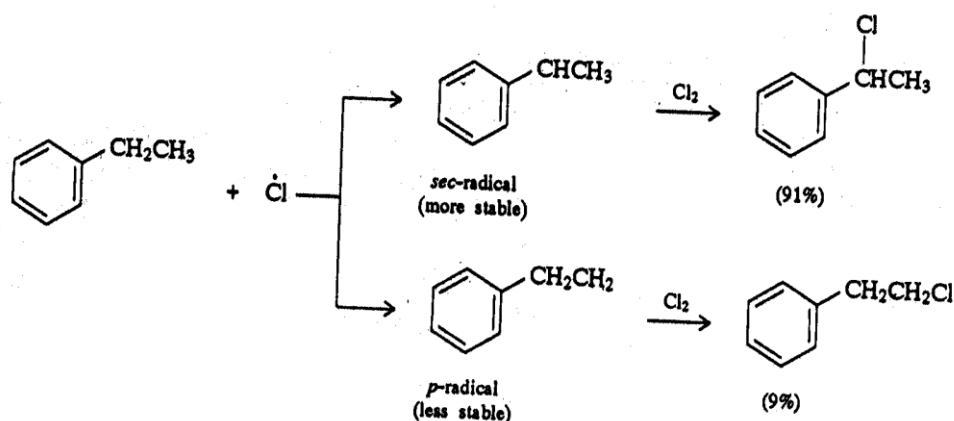
You can ask why it is so. This is because the bond dissociation energy of benzylic C – H.

        CH_3
        |

Bond, $C_6H_5CH - H$, (355 kJ mol) is less than β -phenyl ethyl C – H bond, C_6H_5 $-CH_2CH_2-H$ (435 K j 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 benxyl radical is, delocalisation of the odd electron over the ring as shown below:
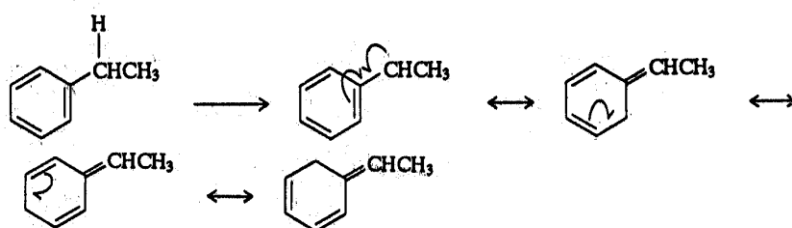
Since the benzylic radical formed is more stable, 1-chloro-1- phenylethane is the major product.

3.9.2 The Oxidation of Side-Chain

Although benzene and alkanes are quite unreactive towards the usual oxidizing 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 oxidized 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 affected.

The number and the position of the carboxylic groups produced indicate the number and position of alkyl chain attached to the aromatic ring.
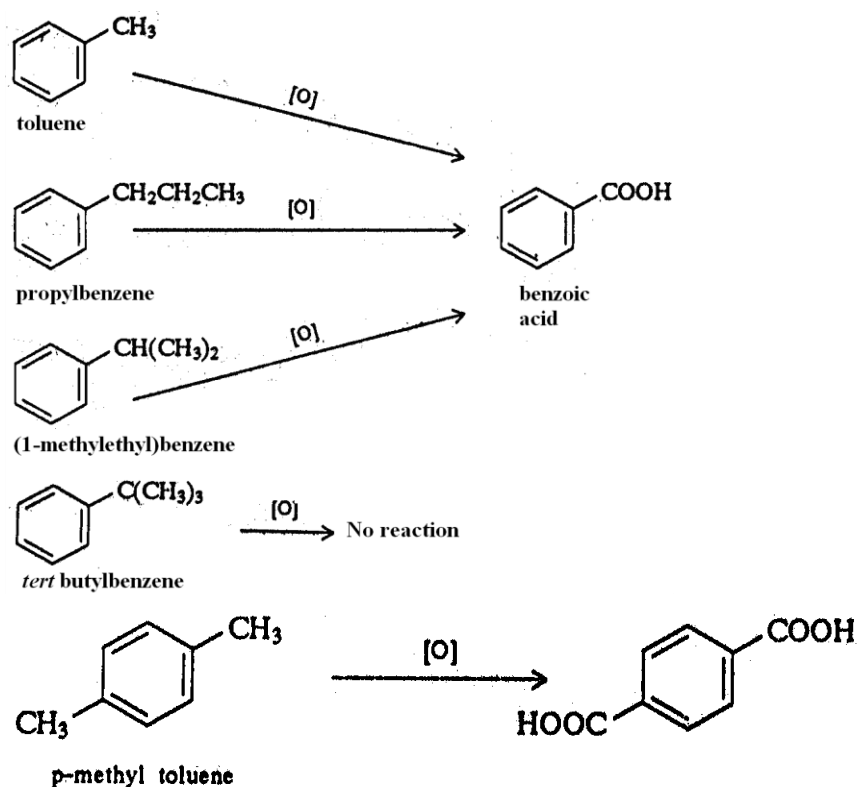
This reaction is useful for two purposes:

synthesis of carboxylic acids identification of alkylbenzenes

SELF ASSESSMENT EXERCISE 7

Draw the structural formulas for the starting materials in the following reaction.

1) C_8H_{10} $\xrightarrow{\text{KMnO}_4, \text{H}_2\text{O}}$ [benzene ring with COOH]

2) C_8H_{10} $\xrightarrow{\text{KMnO}_4, \text{H}_2\text{O}}$ [benzene ring with two ortho COOH groups]

3) C_8H_{10} $\xrightarrow{\text{KMnO}_4, \text{H}_2\text{O}}$ [benzene ring with two para COOH groups]

4) C_9H_{10} $\xrightarrow{\text{KMnO}_4, \text{H}_2\text{O}}$ [benzene ring with COOH]

5) C_9H_{10} $\xrightarrow{\text{KMnO}_4, \text{H}_2\text{O}}$ [benzene ring with two meta COOH groups]
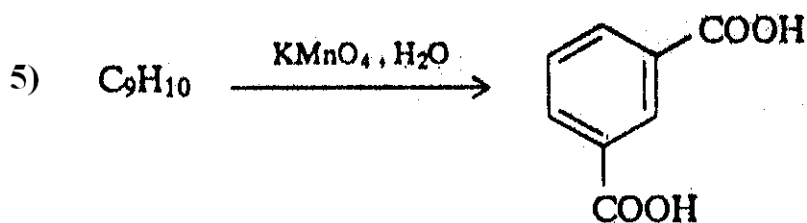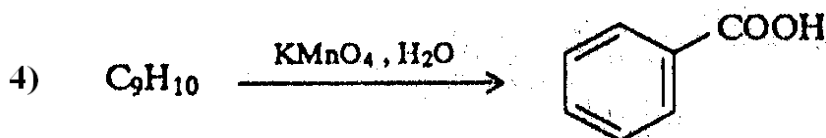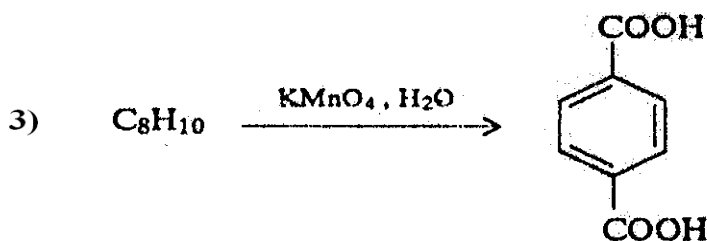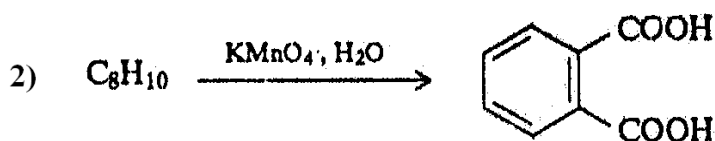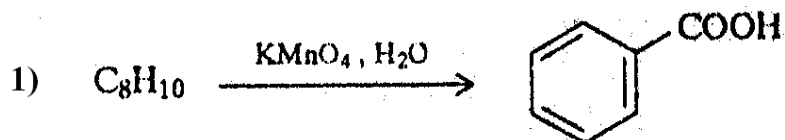
3.10 Polynuclear Hydrocarbons

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
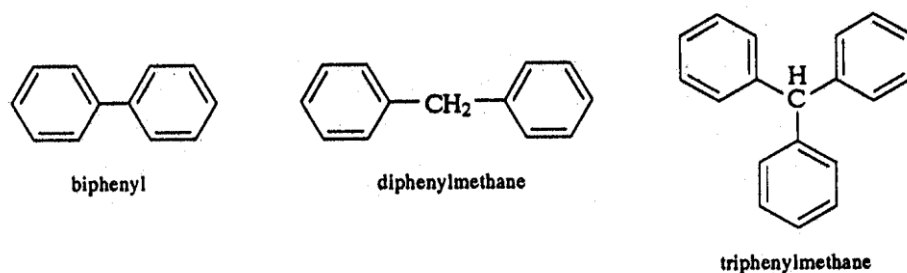
ii. **Condensed or Fused Benzenoid Hydrocarbon:** The condensed or fused benzenoid hydrocarbons are those in which two or more benzene rings are fused together at the ortho position in such a way that each pair of rings shares two carbons. They include compounds like naphthalene, anthracene; phenanthrene etc.

naphthalene   antharacene   phenanthrene
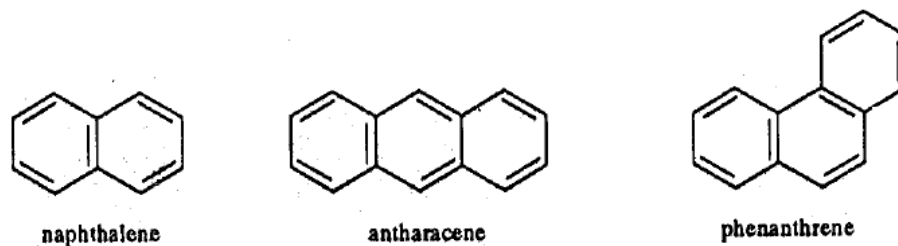
The condensed polynuclear is by far the larger and the more important group. A large number of them have been found to possess carcinogenic (cancer producing) activity. In this unit we will discuss the chemistry of naphthalene only.

3.10.1 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 p.m.
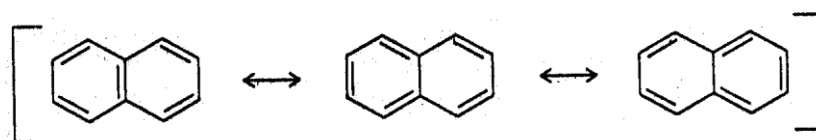
How can we explain the aromaticiity of naphthalene? The above structure of naphthalene shows that it has 10   electrons and 10 is the Huckel number which indicates that naphthalene should be an aromatic molecule.

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 3.3.

Table 3.3: Electrophilic substitution reactions of naphthalene

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.
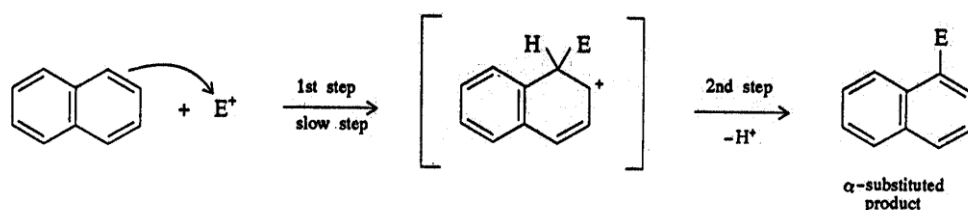
The mechanism for naphthalene substitution reaction is similar to that of benzene substitution.

The first subsitutuent 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.
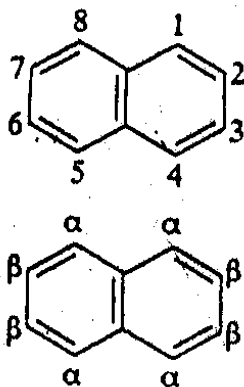
Substitution at 1-position
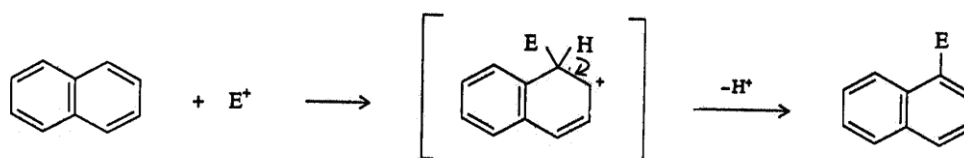
Resonance Structure of Carbocation
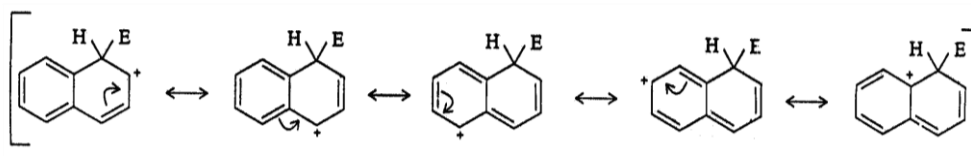
Substitution at 2-position
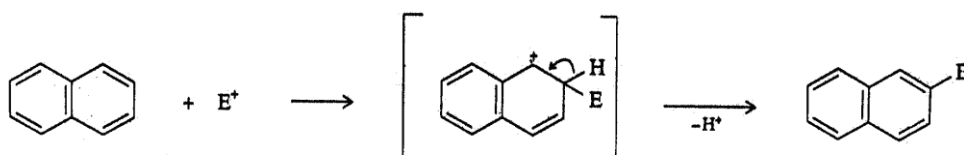
Resonance Structure of Carbocation
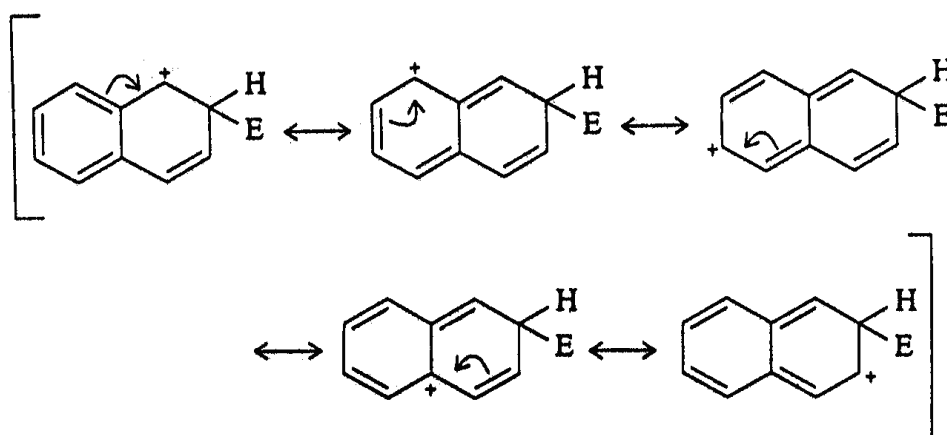
In both cases, the positive charge can be distributed to five different positions, but these carbocations are not equivalent in energy. In the first case, the first two structures have their benzene ring intact and are consequently more stable than the remaining three structures. In the second case, 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 Naphthalene: Under controlled conditions, naphthalene is oxidised to 1,4-naphthoquinone, but the yield is usually low.

1,4-naphthoquinone
(18-22%)
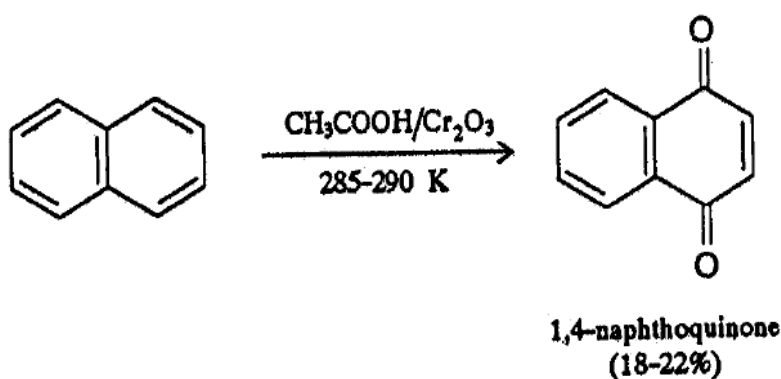
More vigorous oxidation results in the loss of one ring and yields phthalic anhydride. This reaction probably proceeds through the formation of ortho-phthatic acid.

phthalic acid

phthalic anhydride
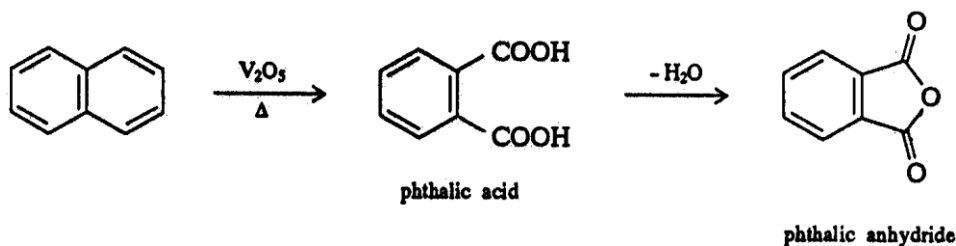
Unlike benzene, naphthalene can be partially hydrogenated without heat and pressure, or which can be reduced with sodium and ethanol.

tetralin
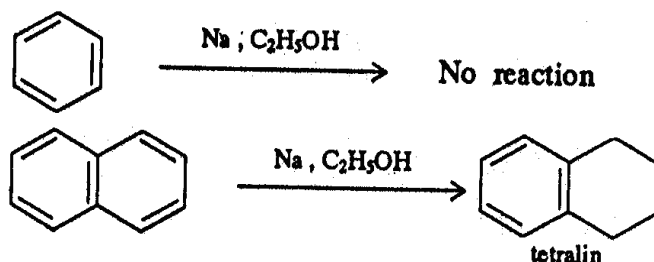
For complete hydrogenation of napthelene, it requires heat and pressure just as in the case of benzene.

decalin
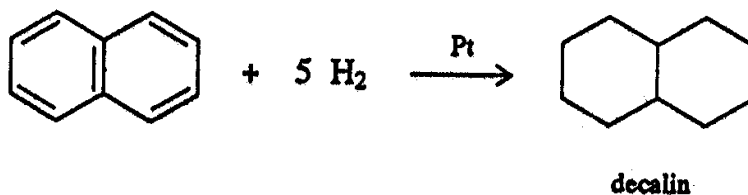
4.0   CONCLUSION

We have succeeded in explaining the isolation of benzene and some of its derivatives. We have also listed their importance. Also the importance and properties of polynuclear hydrocarbons have been described.

5.0   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.

6.0   TUTOR-MARKED ASSIGNMENT

(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 product

(a)   Compound A $\xrightarrow{\text{HNO}_3/\text{H}_2\text{SO}_4}$ two mononitration products

(b)   Compound B $\xrightarrow{\text{HNO}_3/\text{H}_2\text{SO}_4}$ three mononitration products

(c)   Compound .C $\xrightarrow{\text{HNO}_3/\text{H}_2\text{SO}_4}$ one mononitration products

7.0   REFERENCES/FURTHER READINGS

Morrison, R.T. and Boyd, R.N. (2011). *Organic Chemistry,* 6th Ed., India: Prentice-Hall, Ltd.

Ferguson, L. N. (   ).*Text book of Organic Chemistry,* 2nd Ed., Affiliated East-West Press Pvt. Ltd.

Mukherji, S.M., Singh, S.P. and Kapoor, R.P. ( ). *Organic Chemistry,* Vol. I and II WileyEastern Ltd.

Soni P.L.and Chawla, H.M. ().*Textbook of Organic Chemistry*, 24th Ed., Sultan Chand and Sons.

H. Hart, L. E. Craine and D. J. Hart (2003). *Organic Chemistry: A short course*. (11th Ed). Boston: Houghton Mifflin Company.

UNIT 4   HALOGEN DERIVATIVES OF AROMATIC
                 HYDROCARBONS

CONTENTS

1.0   INTRODUCTION

In this unit and in subsequent years, 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 chlorohydrocarbonds 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 details 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 reaction 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.

2.0   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 chemistry of organometallic compounds and polyhalogen derivatives
- list and describe the industrial uses of halogen derivatives, and describe the laboratory detection of halogen derivatives.

3.0   MAIN CONTENT

3.1   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 hydrogen 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)

$CH_3 — Br$ $CH_3CH_2 — Cl$
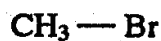
bromomethane

chloroethane
$CH_2 = CHCH_2 — Cl$
3-chloro-1-prepene or
3-chloropropene
(allyl chloride)
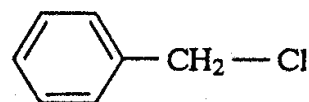
(chloromethyl) benzene
(benzyl chloride)

Aryl halides (Ar – X)
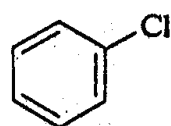
chlorobenzene
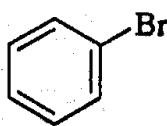
bromobenzene
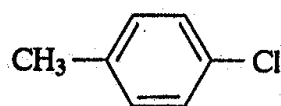
chloro-4-methyl benzene
(*p*-chlorotoluene)

Alkenyl halides (Vinyl halides)

$$CH_2 = CH - Cl$$

chloroethene
(vinyl chloride)

$$CH_3CH = CCH_3$$
with Br

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 (1^0), $RCH_2 - X$; secondary (2^0), $R_2CH - X$; and tertiary (3^0), $R_3C - X$ 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:

$CH_3CH_2CH_2CH_2 - Cl$ $CH_3CH_2CHCH_3$ $CH_3CHCH_2 - Cl$ $CH_3 - C - Cl$
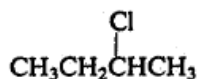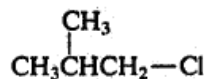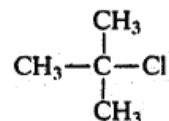
1-chlorobutane	2-chlorobutane	1-chloro-2-methylpropane	2-chloro-2-methylpropane
primary 1^0	secondary 2^0	primary 1^0	tertiary 3^0

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.

CH_3CHCl_2 $CH_3CBr_2CH_3$
1, 1-dichloroethene   2, 2-dibromopropane
(ethylidene dichloride)   (isopropyidenedibromide)
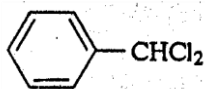
(dichloromethyl) benzene (benzylidene chloride or benzal chloride)

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.,

CH_2BrCH_2Br $CH_3CHClCH_2Cl$
1, 2-dibromoethane   1, 2-dichloropropane
(ethylene dibromide)   (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 4.6. Before that try the following SAE to test your understanding of the classification of halogen derivatives.

SELF ASSESSMENT EXERCISE 1

Classify each of the following alkyl halides as 1^0, 2^0, or 3^0

1)

2)

3)
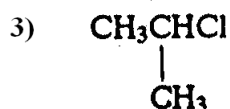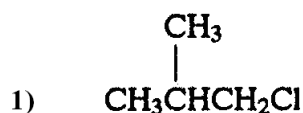
3.2   Preparation of Halogen Derivatives

We have already looked at several methods of preparation of halogen derivatives in previous Units. In this section we shall briefly review these methods and also take up some other methods for the preparation of halogen derivatives.

3.2.1 Alkyl Halides

Alkyl halides can be prepared from alcohol's, 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 4.1.

Table 4.1   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

$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow{HX} -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{X}{C}}-$$

$$HX = HCl, HBr, HI$$

From Alkanes

$$-\overset{|}{\underset{|}{C}}-H+X_2 \xrightarrow[\text{peroxide}]{\text{light or}} -\overset{|}{\underset{|}{C}}-X+HX$$

$$X_2 = Cl_2, Br_2$$

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

$$Ar-H + CH_2O + HCl \longrightarrow ArCH_2-X + H_2O$$
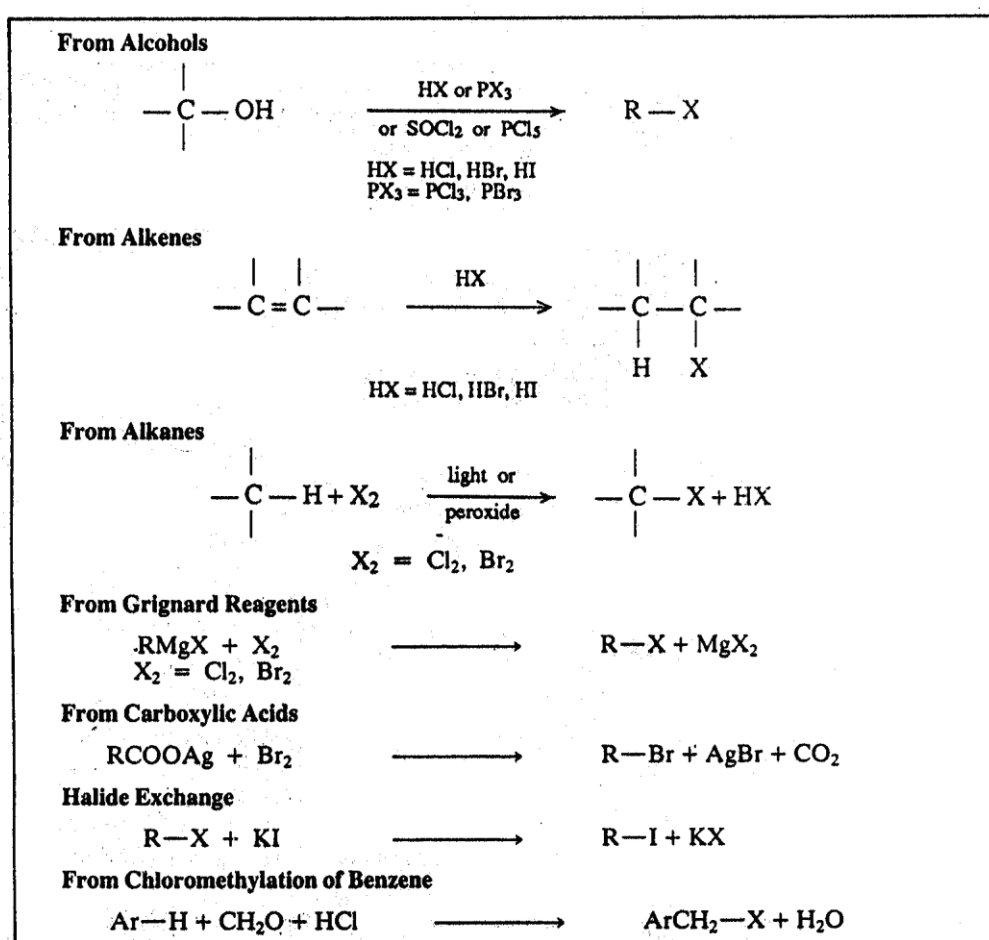
Let us study these methods of preparation in a brief manner.

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 either a hydrogen halide (HX), a phosporus halide (PX_3 or PCl_5), or thionyl chloride ($SOCl_2$). These reactions will be discussed in more detail in Unit 11. 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   (chloromethyl) benzene
(benzyl alcohol)   (benzyl chloride)
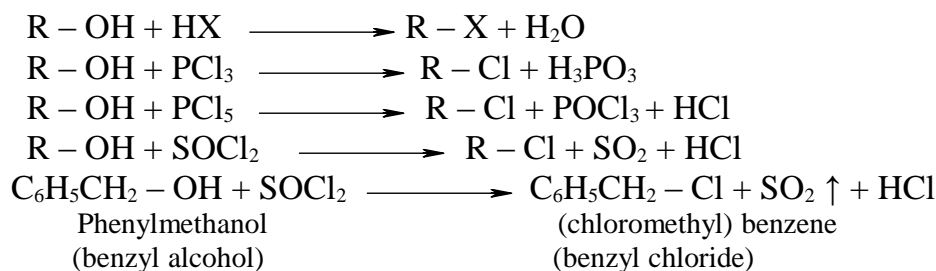
ii)   **From Alkenes:** Hydrogen halides (HCl, HBr, HI) react with alkenes to form alkyl halides. The mode of addition follows Markownikoff's rule except for the addition of hydrogen bromide in the presence of peroxide. The mechanisms for both modes of additions were shown in Unit 5.

Examples

$$CH_3CH = CH_2 + HCl \longrightarrow$$
propene

$$\begin{array}{cc} CH_3CH & \!\!\!\!- CH_2 \\ | & | \\ Cl & H \end{array}$$
2-chloropropane

$$CH_3CH = CH_2 + HBr \longrightarrow$$
propene

$$\begin{array}{cc} CH_3CH & \!\!\!\!- CH_2 \\ | & | \\ Br & H \end{array}$$
2-bromopropane

$$CH_3CH = CH_2 + HBr \xrightarrow{\text{peroxide}}$$
propene

$$\begin{array}{cc} CH_3CH & \!\!\!\!- CH_2 \\ | & | \\ H & Br \end{array}$$
1-bromopropane
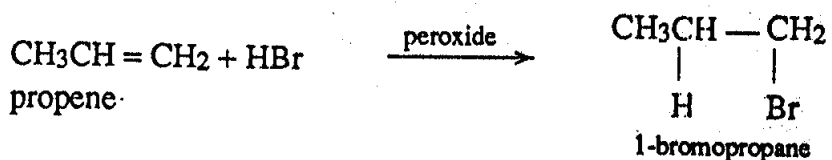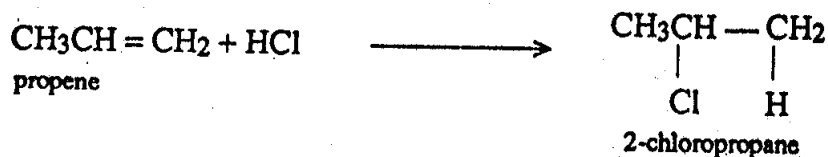
iii)From Alkanes: Direct halogenation of alkanes is of limited application in most cases because of the formation of mixture of mono and polyhalogenated compounds. You have learned in Unit 4 that chloromethane, however, can be prepared directly by photochlorination if a large excess of methane is employed.

$$CH_4 + Cl_2 \xrightarrow{\text{sunlight}} CH_3 - Cl + HCl$$
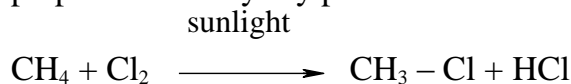
(Chloromethyl) benzene can also be similarly prepared.

methylbenzene   (chloromethyl) benzene
(toluene)   (benzyl chloride)
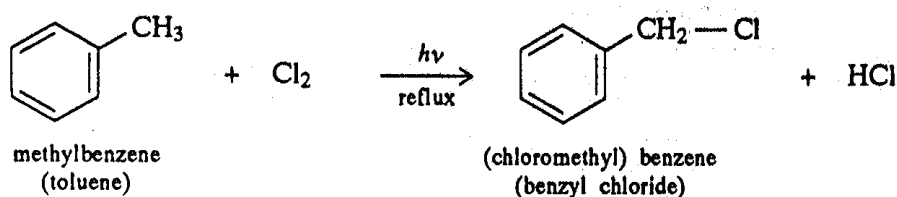
iv) From Grignard Reagent: Direct reaction of alkyl or aryl halides with metallic magnesium in a dry solvent (ether) gives the Grignard reagent, a valuable intermediate in synthetic organic chemistry. We shall discuss this reagent in more detail in sec 4.5. Grignard reagents react with halogens to give alkyl halides.

$$RMgX + X_2 \longrightarrow R - X + MgX_2$$

grignard   alkyl

reagent   halide
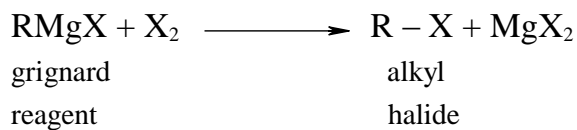
v)   **From Carboxylic Acids:** The dry silver salt of carboxylic acid upon refluxing with bromine in tetrachlomethane (carbon tetrachloride) affords the corresponding alkyl bromide. This reaction is known as **Hunsdiecker reaction.**

$$ROOAg + Br_2 \longrightarrow R - Br + AgBr + CO_2\uparrow$$

Silver salt of carboxylic acid
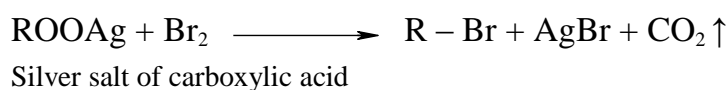
vi)   **Halide Exchange:** This is a good procedure for preparing alkyl iodides and alkyl fluorides.

              propanone

$$R - X + KI \longrightarrow R - I + KX$$
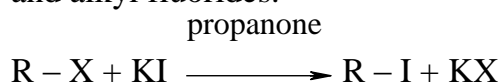
Alkyl fluorides often are prepared by the reaction of mercurous or antimony fluorides with alkyl chlorides;

$$2R - Cl + Hg_2F_2 \longrightarrow 2R - F + Hg_2Cl_2$$

Alkyl   mercurous   alkyl   mercurous

chloride   Fluoride   fluoride   chloride

$$3CCl_4 + 2SbF_3 \longrightarrow 3CCl_2F_2 + 2SbCl_3$$

tetrachlo   antimony   dichlorodi-

romethane   flouride   fluoromethane (Freon 12)

                     a chlorofluorocarbon (CFC)
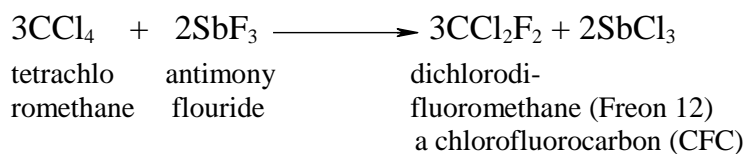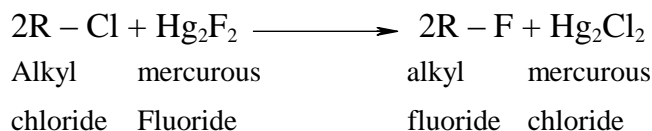
Chlorofluorocarbons (CFC) also called Freons are inert nontoxic gases used as refrigerants in air − conditioners and refrigerators. Freon 12 is the most commonly used refrigerant. Unfortunately Freons catalyse the decomposition of ozone and thus can destroy the protective layer that surrounds the earth. 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 benylic halides.

$$Ar - H \;+ CH_2O \;+\; HCl \longrightarrow Ar - CH_2 - Cl + H_2O$$

Aromatic acid methanol   benzylic halide
Hydrocarbon   (formaldehyde)
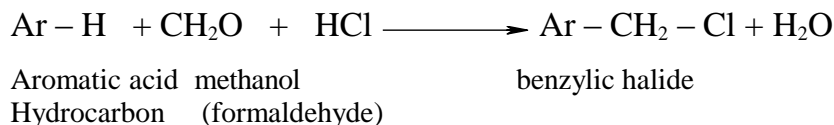
3.2.2 Aryl Halides

Aryl halides may be prepared by one of the methods outlined below in Table 4.2

Table 4.2:   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

$$Ar - NH_2 \xrightarrow[273K]{HNO_2/HX} \underset{\text{diozonium salt}}{Ar - N_2{}^+} \xrightarrow{CuX} Ar - X + N_2$$

$CuX = CuCl,\ CuBr$
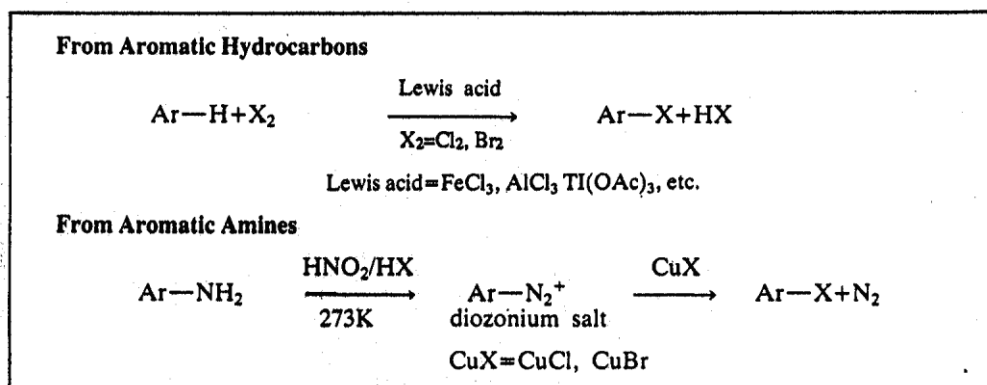
Let us briefly consider these methods of preparation.

i) From Aromatic Hydrocarbons: The aromatic halogenation of aromatic hydrocarbon needs the assistance of a Lewis acid as a cataylst. Generally ferric chloride or aluminum chloride are used as catalyst.

$$Ar - H + X_2 \quad \text{LewisAcid} \quad Ar - X + HX$$

aromatic   aryl
hydrocarbon   halide
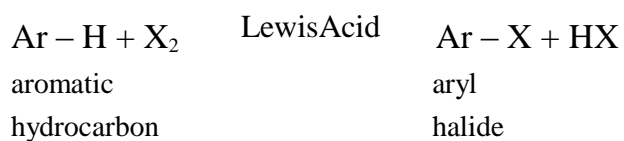
If two moles of chlorine (per mole of benzene) are used, a mixture of *ortho-* and *para-* dichlorobenzene is obtained in which the the *para* compound predominates for steric as well as electronic reasons.

$$\text{benzene} \quad + \quad 2\ Cl_2 \quad \xrightarrow{FeCl_3}$$

1,2-dichlorobenzene   1,4-dichlorobenzene
(o-dichlorobenzene)   (p-dichlorobenzene)
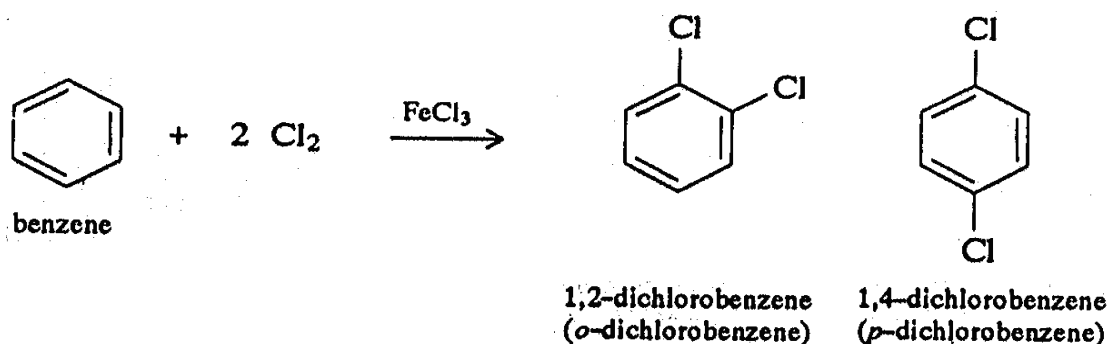
ii)From Aromatic Amines: In this process the amine is first converted to the diazonium salt $(ArN_2^+X^-)$, which is then converted to aryl halide using the solution of cuprous halide dissolved in the concentrated halogen acid. This method is known as **Sandmeyer reaction.**

$$Ar-NH_2 \xrightarrow{NaNO_2-HX} Ar-N_2^+X^- \xrightarrow{CuX/HXX} Ar-X$$

aromatic   cold   (diazonium   aryl halide
amine   salt)
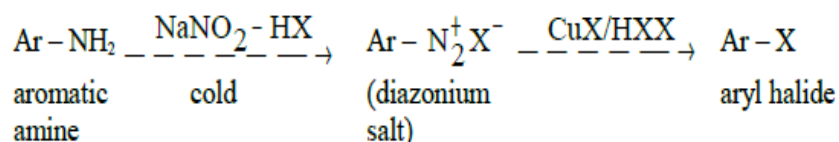
Replacement of the diazonium group by – I does not require the use of a cuprous halide.

$$Ar-N_2^{+}X^- \xrightarrow{KI} Ar-I+N_2+KX$$
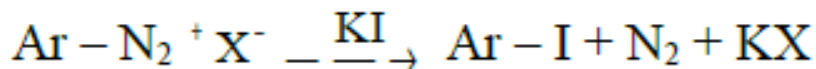
Chlorobenzene is prepared commercially by the **Rasching process** in which a mixture of benzene vapour, air and hydrogen chloride is passedover copper chloride.

$$C_6H_6 + HCl + 1/2O_2 \xrightarrow{CuCl_2} C_6H_5Cl + H_2O$$
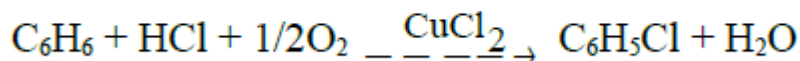
3.2.3 Alkenyl Halides

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:

$$CH_2=CH_2 + Cl_2 \xrightarrow{673K} CH_2=CH-Cl + HCl$$

ethene   chloroethene
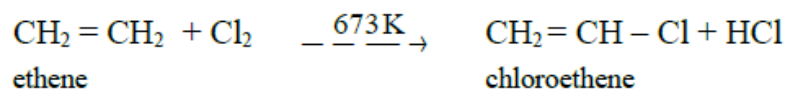
ii)   **From ethene and hydrogen chloride:** Following steps are involved

$$CH_2 = CH_2 + HCl + O_2 \xrightarrow[373-473\ K]{CuCl_2} \begin{matrix} CH_2 - CH_2 \\ | \quad\quad | \\ Cl \quad\quad Cl \end{matrix} \xrightarrow{-HCl} CH_2 = CH - Cl$$

ethene   1,2-dichloroethene
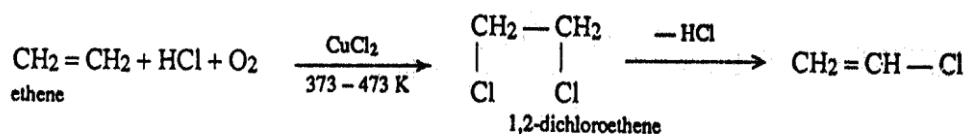
iii)   **Addition of Hydrochloric Acid to Ethyne:** This method is analogous to Hg^{2+} cataylzed addition of water to ethyne, which gives ethanal (Unit 6).

$$CH \equiv CH + HCl \xrightarrow[373-473K]{HgCl_2} CH_2 = CH - Cl$$

ethyne   chloroethene

.
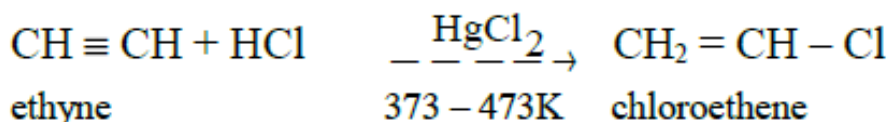
iv) Elimination of Hydrogen Chloride from Dihalide: The final product of this reaction is ethylene but with a weaker base the reaction can be stopped with the elimination of only one mole of HCl. Following steps are involved in this process:

$$\begin{matrix} CH_2 - CH_2 \\ | \quad\quad | \\ Cl \quad\quad Cl \end{matrix} \xrightarrow[-HCl]{Base} CH_2 = CH - Cl$$

1,2-dichloroethene   chloroethene

$$CH_3 - CHCl_2 \xrightarrow[-HCl]{Base} CH_2 = CH - Cl$$

1,1-dichloro   chloroethene
   ethene
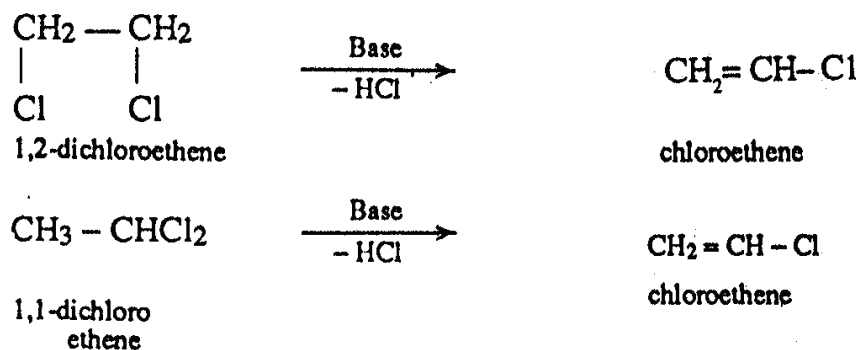
SELF ASSESSMENT EXERCISE 2

Write equations showing the preparation of the following halides from the starting materials indicated.

1. *$C_6H_5CHBrCH_3$ from $C_6H_5CH_2CH_3$*
2. *$CH_3CHBrCH_3$ from $CH_3CHOHCH_3$*
3   *1-bromopropane from 1-propene*
4. *2-chloropropane from 2-propanol*

3.3   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 the structure, spectral properties and chemical properties of these compounds.

3.3.1 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.
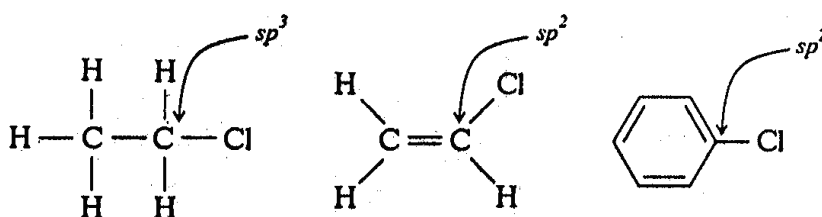
As mentioned in unit 1, the bond formed with an sp^2 hybridised carbon is stronger than the bond formed with an sp^3 hybridised carbon. This difference in the nature of the C – X bond is mainly responsible for different behaviour of aryl and alkenyl halides as compared to alkyl halides. To further explain the unique chemistry of aryl and alkenyl halides, we shall study the reactions of chlorobenzene and chloroethene in sub-section 4.4.5. Let us first examine the polar nature of the C – X bond here.

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.

Electronegativity on the Pauling and Sanderson Scales

Element	Pauling	Sanderson
F	4.0	4.000
Cl	2.0	2.475
Br	1.8	2.219
I	1.5	1.778
C	1.5	1.746

The magnitude of dipole moment for methyl halides is summarised in Table 4.2. 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 4.3:   Dipole Moment of Methyl Halides

Compound	μ, Cm
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.

3.3.2 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 4.4. Common names of some of them are also given.

Table 4.4:   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	273.5	Gas
Iodomethane	Methyliodide	CH_3I	315.8	1.28
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 emphasizes 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.

SELF ASSESSMENT EXERCISE

Arrange the following molecules in order of increasing boiling points. Give reason for this trend. $CHCl_3$, CH_2Cl_2, CCl_4, CH_3Cl

3.3.3 Spectral Properties of Halogen Derivatives

The ultraviolet-visible spectra of alkyl halides show a weak absorption between 170-258nm due to the presence of loosely held nonbonding electrons of halogen. The electrons undergo n -π^* transitions. Aryl halides   exhibit   additional absorption similar to those of   the corresponding aromatic hydrocarbons. The infra red (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 4.1 Aryl halides display (C – X) bands near 1100 cm^{-1}.
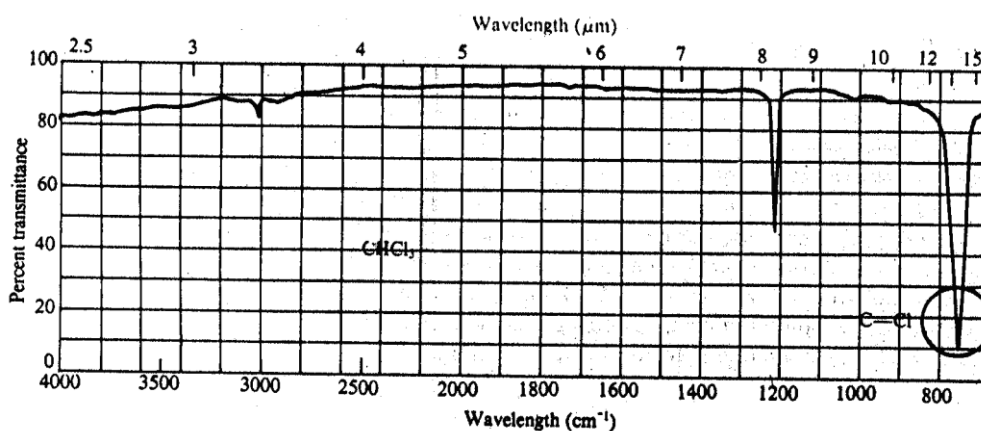
Fig 4.1: Infrared spectrum of trichloromethane (chloroform)

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, 1.17 CH_3Br, 1.65; CH_3Cl, 2.02; and CH_3F, 4.30ppm.

Note: In common name, the Greek letters, α-, β-, γ-, δ-, ω-, etc., are used to indicate the point of attachment. The   -carbon is the one bearing the functional group and proton attached to this carbon are called protons.

$$\overset{\omega}{C} - \overset{\delta}{C} - \overset{\gamma}{C} - \overset{\beta}{C} - \overset{\alpha}{C} - X$$
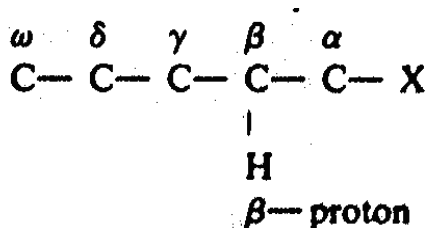
$$\underset{\beta - \text{proton}}{\overset{|}{H}}$$

Since fluorine has a nuclear spin, with I = + ½ and -½ (similar to hydrogen), it can spin – spin couple with protons and thus give rise to splitting of the proton of the proton signal. In CH_3F, a double for the protons of the methyl group will be seen. The signal for fluorine is not observed under conditions proton resonance, but on changing the conditions, the fluorine signal can be seen as 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.

3.3.4 Chemical Properties of Alkyl Halides

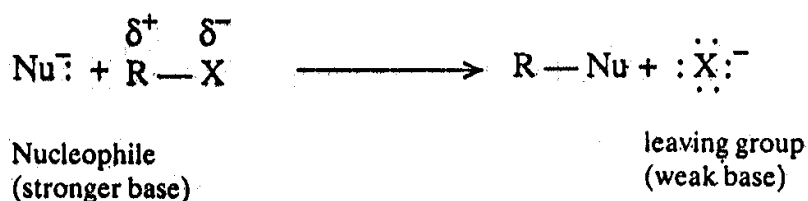Most important reactions of alkyl halides are nucleophilic substitution (S_N) and elimination (E). In this section we shall take up a fairly detailed description of these reactions. We have already encountered the term nucleophilic reagent or nucleophile and have learned that it is applied to an electron rich atom or group such as, SH^-, NH_3, ROH, H_2O.

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 nucleophile.

$$Nu^- + \overset{\delta^+}{R} - \overset{\delta^-}{X} \longrightarrow R - Nu + :\ddot{X}:^-$$

Nucleophile
(stronger base)

leaving group
(weak base)

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   RC1   RBr

RI Increasing reactivity →
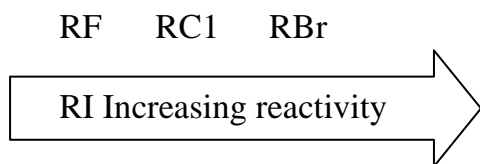
The explanation of this order is that the iodide ion, being the weakest base as the conjugate base of the strongest acid, HI, is the best leaving group, the fluoride ion being a stronger base is the poor leaving group.

Now let us summarise some nucleophilic substitution reactions of alkyl halides in Table 4.5.

Table 4.5: Some Nucleophillic Substitution Reactions

| $R-\ddot{X}:$ + Nucleophile (name)	$\longrightarrow$	$:\ddot{X}:^-$ + Product (name)
$R-\ddot{X}:$ + $:\ddot{Y}:^-$ (another halide)	$\longrightarrow$	$:\ddot{X}:^-$ + $R-\ddot{Y}:$ (another alkyl halide)
+ $^-:C\equiv N:$ (cyanide)	$\longrightarrow$	+ $R-C\equiv N:$ (nitrile)
+ $^-:\ddot{O}H$ (hydroxide)	$\longrightarrow$	+ $R-\ddot{O}H$ (alcohol)
+ $^-:\ddot{O}R$ (alkoxide)	$\longrightarrow$	+ $R-\ddot{O}-R$ (ether)
+ $^-N_3$ (azide = $:\ddot{N}=N=\ddot{N}:$)	$\longrightarrow$	+ $R-N_3$ (alkyl azide)
+ $^-:\ddot{S}R'$ (alkanethiolate)	$\longrightarrow$	+ $R-\ddot{S}-R'$ (thioether)
+ $:NR'_3$ (amine)	$\longrightarrow$	$R-\overset{+}{N}R'_3:\ddot{X}:^-$ (alkylammonium sah)
+ $:\ddot{O}H_2$ (water)	$\longrightarrow$	$R-\overset{+}{\underset{H}{\ddot{O}}}-H:\ddot{X}:^- \rightleftarrows R-\ddot{O}-H + H\ddot{X}:$ (alcohol)
+ $:\underset{H}{\ddot{O}}-R'$ (alcohol)	$\longrightarrow$	$R-\overset{+}{\underset{H}{\ddot{O}}}-R':\ddot{X}:^- \rightleftarrows R-\ddot{O}-R' + H\ddot{X}:$ (ether)

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 reactions.

$$CH_3CH_2 - Br + OH^- \xrightarrow{H_2O} CH_3CH_2 - OH + Br^-$$

bromoethane　　　　　　　　　　　　　　ethanol
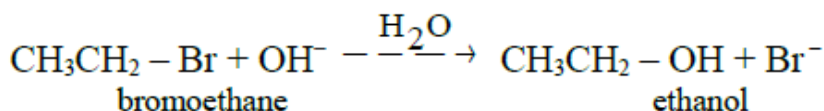
In general methyl or primary alkyl halides undergo S_N2 reaction with any relatively strong nucleophile; OH, OR, CN^- etc. Secondary alkyl halides can also undergo S_N2 reactions, but, tertiary alkyl halides do not. The above reaction has been found to follow second order kinetics which means that the rate of the reaction is proportional to the concentrations of both the halide and the hydroxide ion. Thus for the above reaction,

Rate $= k_2 [C_2H_5Br] \ [OH]$

where k_2 is the rate constant and $[C_2H_5Br]$ and $[OH]$ represent the concentration 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.
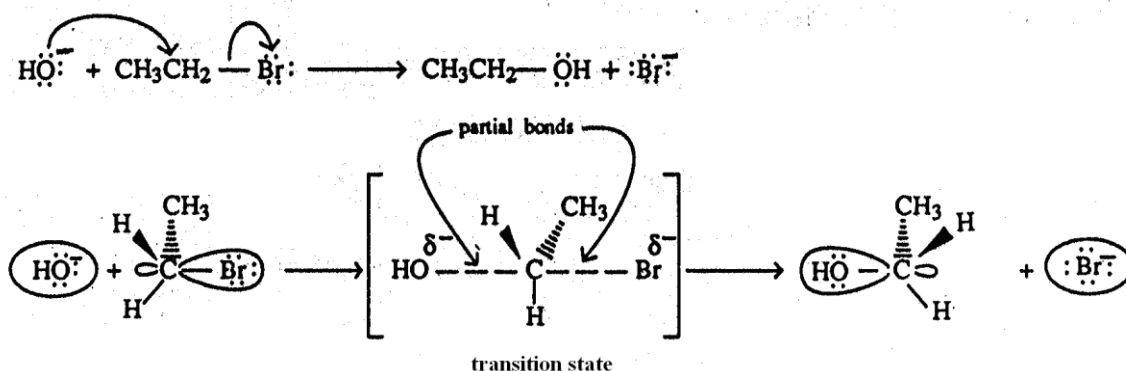
Fig 4.2: The mechanism for the S_N2 reaction

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 4.6 shows the effects 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 4.6: **Effects 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

In an S_N2 reaction, the other three bonds, (which are not taking part in substitution change) to the central carbon progressively flatten 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.

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 backside of that carbon.

tert butyl bromide
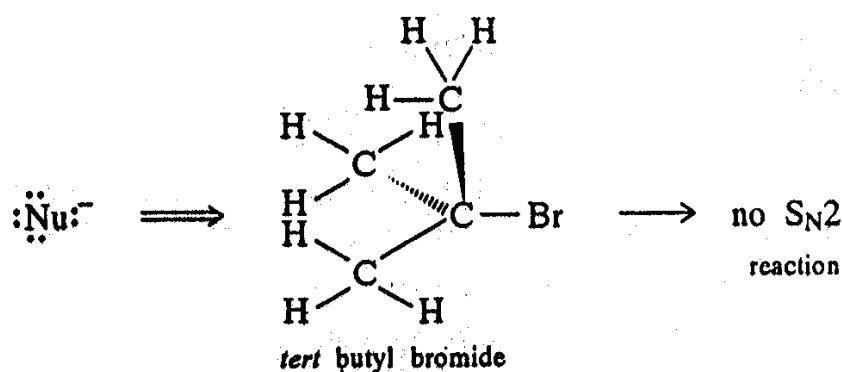
Fig. 4.3: Stearic hindrance in S_N2 reaction

Nucleophiles such as H_2O or CH_3CH_2OH are also used as the solvents. Substitution reactions of such nucleophiles are sometimes called solvolysis reactions (from solvent and by "breaking down" or "loosing

The S_N1 Reaction

You can see from Table 4.6, 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). In most stepwise reactions, the slowest step in the entire sequences is the rate determining step as a reaction cannot proceed faster than its lowest step does. 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
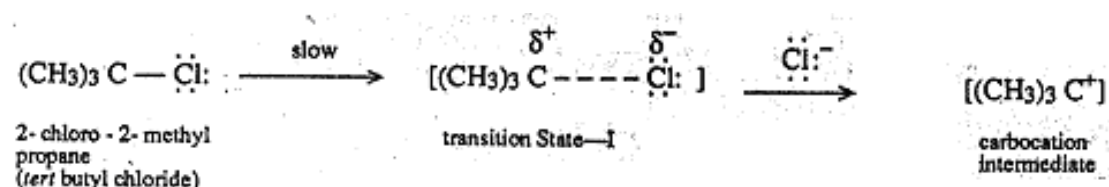
Step 2
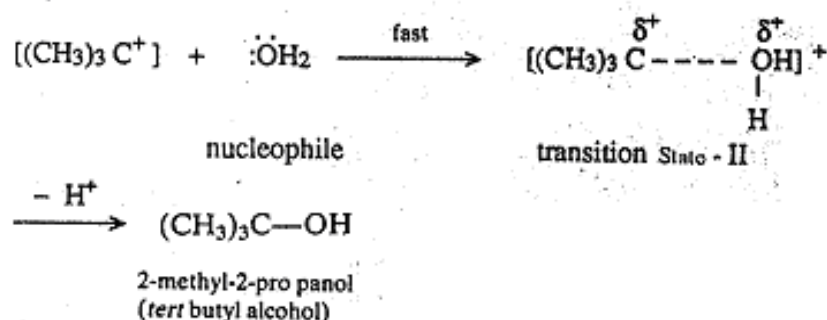
From the above it is clear that the first step in this mechanism is ionisation of alkyl halide to a carbocation intermediate. This ionisation is a simple heterolytic bond cleavage. In the second step, a nucleophile may approach the central carbon atom from either side with equal probability (unlike the S_N2 reaction where the nuclephile approaches only from the back side). As already discussed the carbocation has a planar geometry and, therefore, the nucleophile may engage the empty *p*-orbital from either side of the molecule.
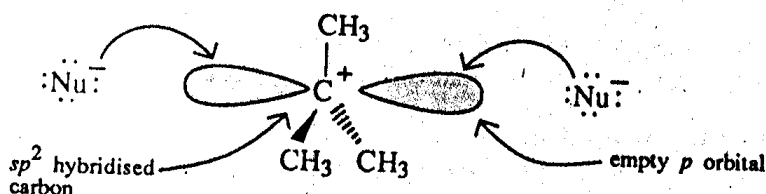
S_N1 reaction of an optically active alkyl halide should give recemic substitution products.

As in the case of S_N2 reaction the structure of the alkyl hande also affect the rate of the reaction. We are giving the relative rates of reaction of some alkyl bromides under typical S_N1 conditions in Table 4.3.

Table 4.7:   Relative reaction rates of hydrolysis of some alkyl bromides under typical S_N1 conditions.

Alkyl bromide	Relative rate
$CH_3 - Br$	1.00^9
$CH_3CH_2 - Br$	1.00^9
$(CH_3)_2CH - Br$	11.6
$(CH_3)_3 C - Br$	1.2×10^6

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

***tert* RX > *sec* RX > *p* RX > CH₃X**
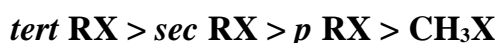
This order is reasonable, since the order of stability of the intermediate carbocation formed in the slow rate determining step is also the same.

$$(CH_3)_3C+ > (CH_3)_2CH^+ > CH_3CH_2{}^+ > CH_3{}^+$$
$$\quad\; tert \qquad\quad sec \qquad\qquad p$$
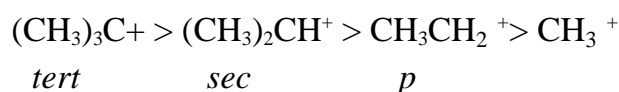
The S_N1 reactions have been found to be subject to rearrangements when the intermediate carbocation can rearrange to a more stable carbocation. The following is an example of one such rearrangement:

Step 1

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2Br \underset{}{\overset{slow}{\rightleftharpoons}} CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \overset{+}{CH_2} + Br^-$$

1-bromo-2,2-dimethyl propane   primary carbocation
(neopentyl bromide)   (less stable)

Step 2

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \overset{+}{CH_2} \underset{}{\overset{fast}{\rightleftharpoons}} CH_3 - \underset{+}{\overset{\overset{CH_3}{|}}{C}} - CH_2CH_3$$

tertiary carbocation
(more stable)

Step 3

$$CH_3 - \underset{+}{\overset{\overset{CH_3}{|}}{C}} - CH_2CH_3 + H - \ddot{\underset{}{O}} - H \overset{fast}{\rightleftharpoons} CH_3 - \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2CH_3 + H^+$$

2-methyl-2-butanol
(*tert* amyl alcohol)
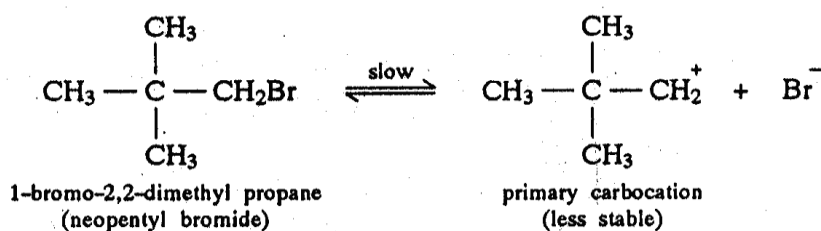
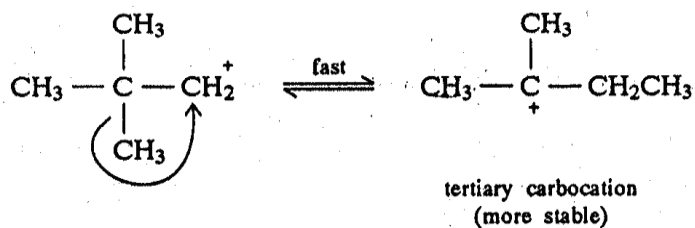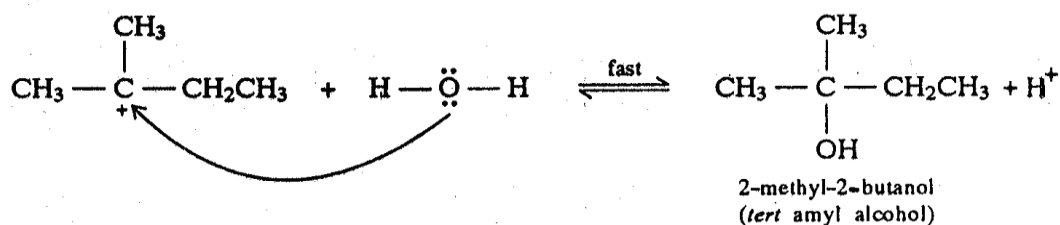You can notice now that the primary carbocation ion rearranges, through the shift of a - CH_3 group, to produce the more stable tertiary carbocation.

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 stabilization of the S_N2 transition state. To illustrate this, further let us consider S_N1 reacton of allyl chloride and benzyl chloride with H_2O.

$$CH_2 = CHCH_2 - \ddot{C}l: \xrightarrow[S_N1]{-:\ddot{C}l:^-} [CH_2 = CH - \overset{+}{C}H_2] \xrightarrow[-H^+]{H_2O} CH_2 = CHCH_2OH$$

3-chloropropene
(allyl chloride)

prop-2-ene-1-ol

$$[\overset{+}{C}H_2 - CH = CH_2]$$

(Resonance structures of allyl cation)

(chloromethyl) benzene
(benzyl chloride)

(resonace structure for benzyl cation)

phenylmethanol
(benzyl alcohol)
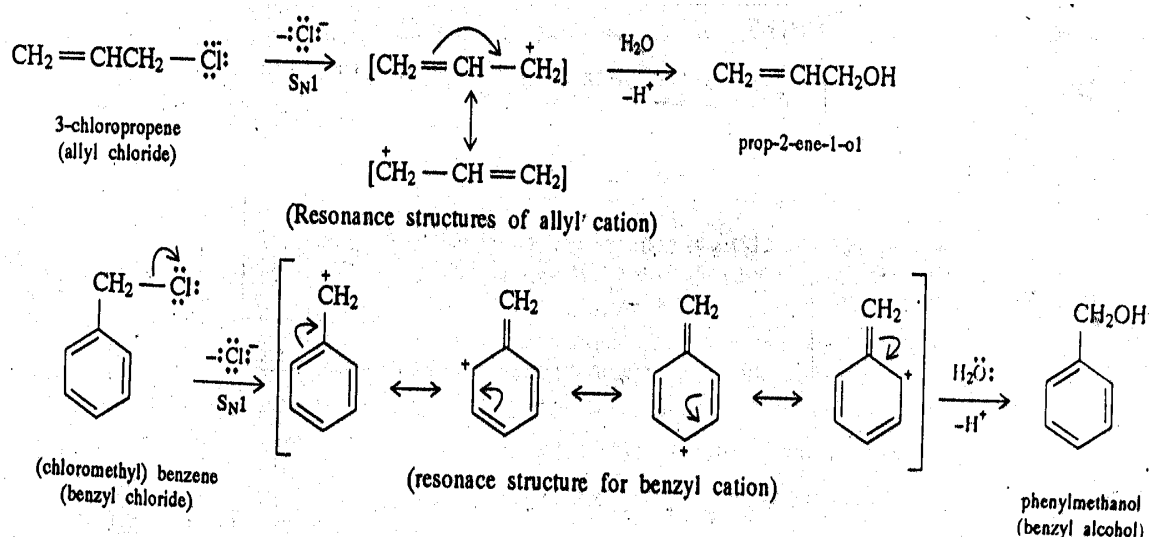
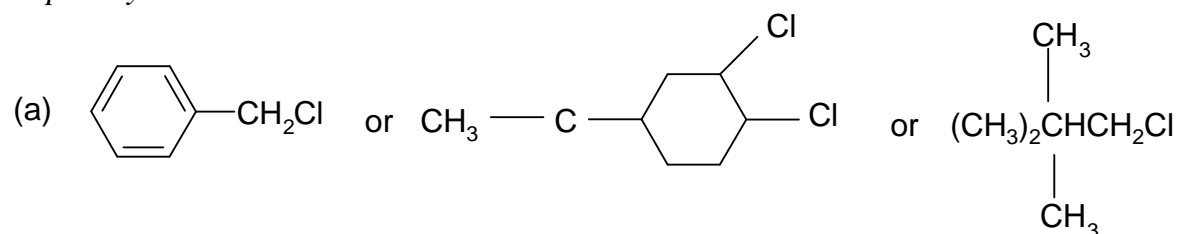Now, consider the S_N2 reactions. Allylic halides and benzylic halides also undergo S_N2 reaction at a faster rate than primary alkyl halides or even methyl halides. The reason for the greater S_N2 reactivity of allylic and benzylic halides is stability of the transition state. In the case of allylic and benzylic halides partial overlap of the   bond orbitals helps in delocalization of the negative charge on the transition structure thus increasing the rate of the reaction (see fig. 4.4).

SELF ASSESSMENT EXERCISE 4

Which member of each of the following   pairs would undergo the faster
$\hat{S}_N$ *reaction?*

Explain your answer.

(a) [benzene]—CH_2Cl or $CH_3 — C —$ [cyclohexane with Cl, Cl] or $(CH_3)_2CHCH_2Cl$ with CH_3

(b) CH_2Cl or [cyclohexane]— Cl (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.

.
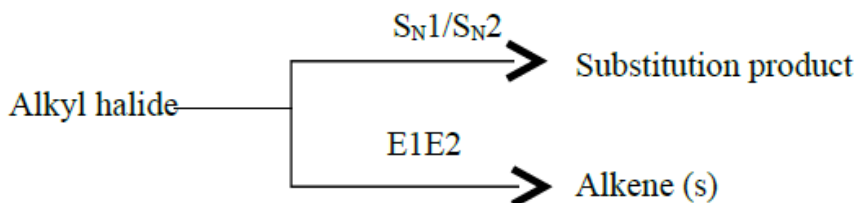
Under appropriate conditions such as the use of a strong base (OH- or OR-), and high temperature, elimination can be the principal reaction and thus become a method for preparing alkenes.

Like the nucleophilic substitutions, 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 E1.

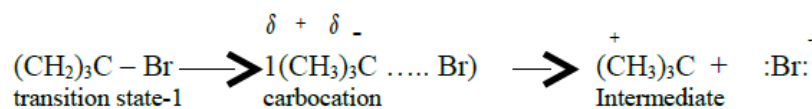**E1 Reaction:** In the absence of a strong base, tertiary alkyl halides, and to some extent secondary alkyl halides, dehydrohalogenate via the E1 mechanism. The mechanism has two steps.

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)

Step 2 (fast)

.
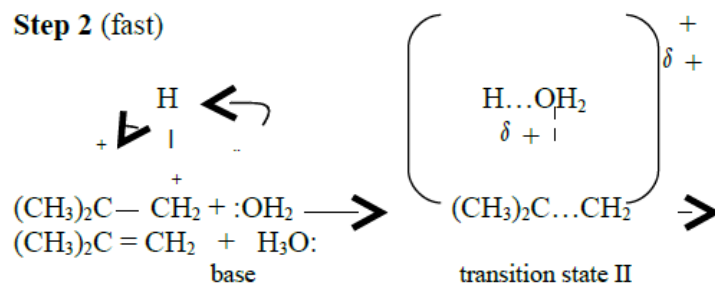
Note that the base here attacks the hydrogen atom and not the carbon carrying the positive charge.

E1 reactions of alkyl halides occur under the same conditions as S_N1 reaction (polar solvent, very weak base etc.) Therefore the E1 reaction is a strong competitor of the SNl 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 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. E2 elimination reaction is an example of elimination. In an elimination reaction two groups are eliminated from adjacent atoms. It is by far the most common type of elimination reaction in organic chemistry.

$$CH_3\ \overset{\overset{\displaystyle Br}{\displaystyle |}}{CH}\text{---}CH_3 + CH_3\ CH_2\ O^- \xrightarrow[\underset{E_2}{heat}]{CH_3\ CH_2\ OH} CH_3\ CH = CH_2 + CH_3\ CH_2\ OH + Br^-$$
$$\text{2-bromopropane} \qquad \text{ethoxide ion} \qquad\qquad\qquad\qquad \text{propene}$$
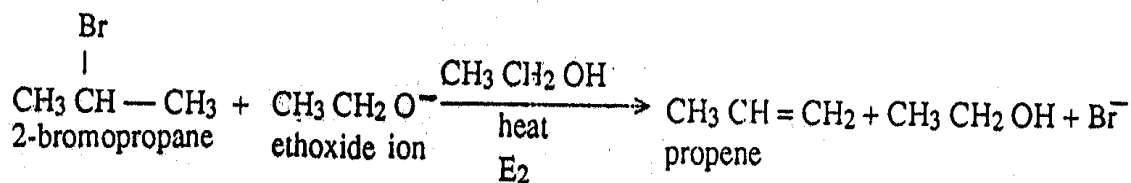
A mechanism consistent with the rate-law is the following one, in which the proton and the halide ions are removed simultaneously to give the alkene.

E2 transition state

$$\longrightarrow \quad CH_2 = CHCH_3 \quad + \quad C_2H_5OH \quad + \quad :\ddot{B}r:^-$$
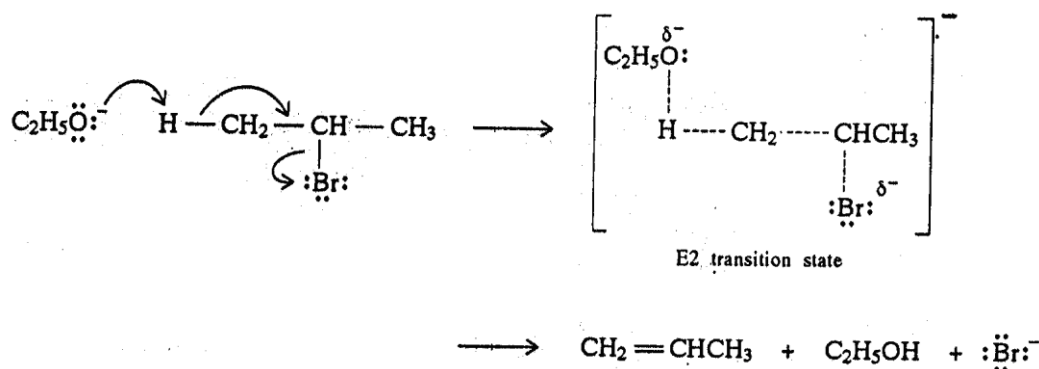
Stereochemical studies reveal that E2 elimination reactions are stereoselective *anti*-eliminations. The *anti*-elimination involves all backside electronic displacements.

Backside attack of the base on the C – X bond
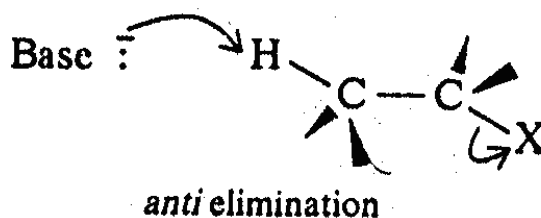
anti elimination

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

$$:\ddot{B}:^- \quad H \quad C - C \quad X$$

$$C = C \quad + \; B:H \; + :\ddot{X}:^-$$

anti

$$B:^- \quad H \quad C - C \quad X$$

$$C = C \quad + \; B:H \; + :\ddot{X}:^-$$
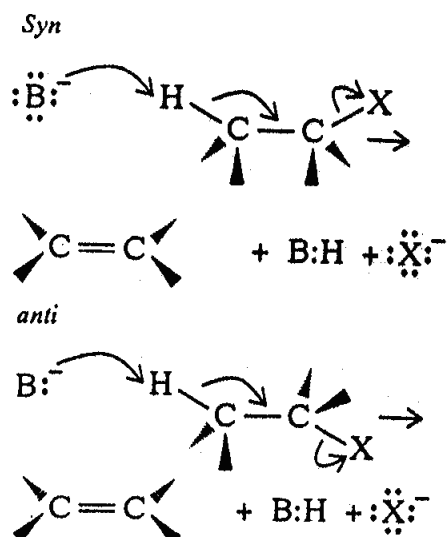
We have said earlier that substitution and elimination are competitive reactions; one reaction occurs at the expense of the other. Now, we consider the important variables which determine the direction of the reaction.

(i)   The structure of the alkyl halide

(ii)   The nature of the base.
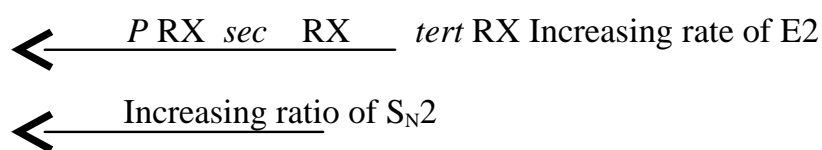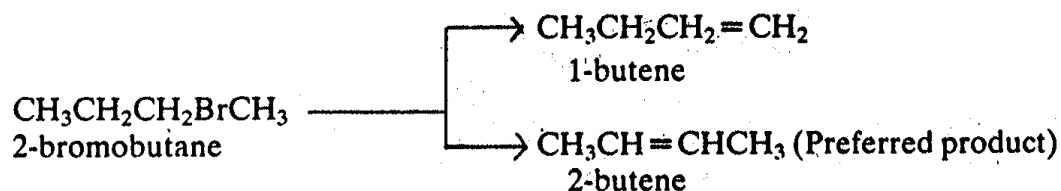
From the mechanism of S_N2 & E2 reaction, it is clear that branching in alkyl halides increases the ratio of elimination to substitution.

$\longleftarrow$ *P* RX *sec* RX *tert* RX Increasing rate of E2

$\longleftarrow$ 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:

$$CH_3CH_2CH_2BrCH_3 \quad \begin{cases} \longrightarrow CH_3CH_2CH_2 = CH_2 \quad \text{1-butene} \\ \longrightarrow CH_3CH = CHCH_3 \; \text{(Preferred product)} \quad \text{2-butene} \end{cases}$$

2-bromobutane

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.

Elimination reaction in quaternary ammonium hydroxides ($R_4N^+OH^-$) does not follow Saytzeff rule, but they undergo eliminiation 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

$$\overset{+}{N}(CH_3)_3\overset{-}{O}H$$
$$|$$
$$CH_3CH_2CH_2- CH\ CH_3$$

$$\xrightarrow[\Delta]{398K}\ CH_3CH_2CH_2CH=CH_2$$
1 pentene
94%
$$+\ CH_3CH_2CH=CHCH_3$$
2 pentene
6%
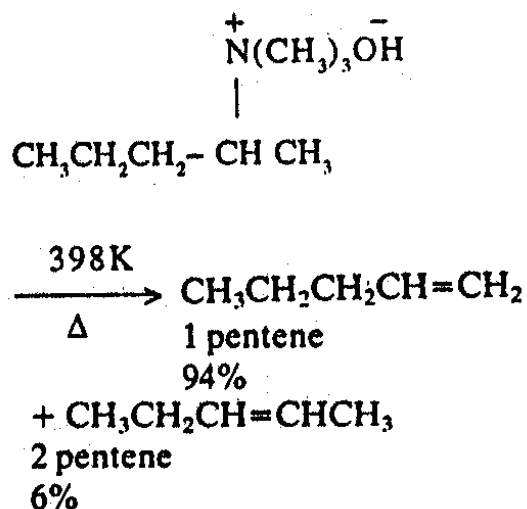
Because of the relative stability of the resultant alkenes, tertiary halides undergo dehydrohalogenation more readily than secondary halides, which dehydrohalogenate more readily than primary halides (as we have already concluded).

SELF ASSESSMENT EXERCISE 5

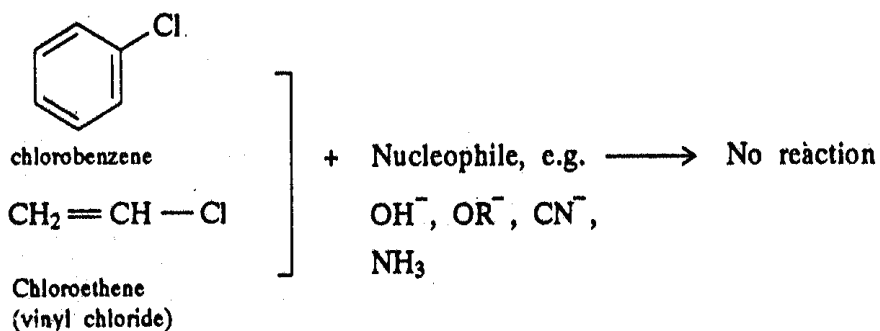Write the equation for the formation of alkenes from the following starting materials. If you expect than one product, indicate which alkene is the major product.

$$\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{CH_3CH_2 - C - CH_3}}\ \xrightarrow[C_2H_5OH]{C_2H_5O^-Na^+}$$
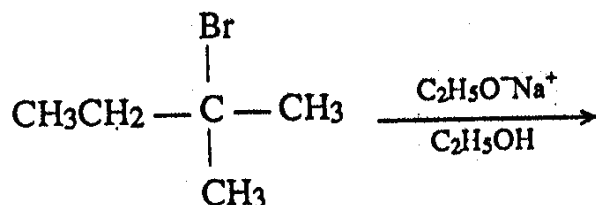
3.3.5 Chemical Properties of Aryl and Alkenyl Halides

*The aryl and alkenyl halides are relatively unreactive, they do not react under*

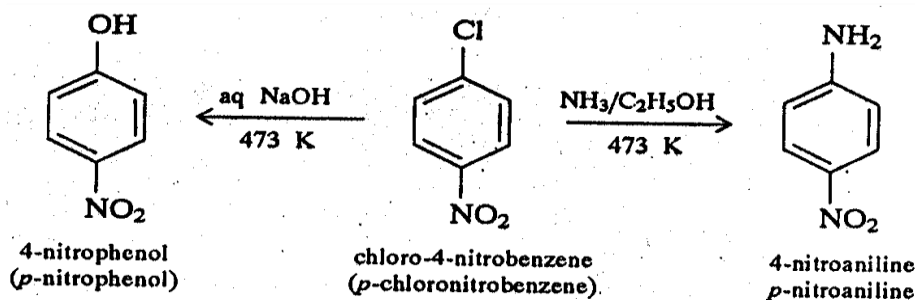*ordinary conditions with NaOH, NaOC$_2$H$_5$, NaCN, NaSH, H$_2$O, or NH$_2$.*

chlorobenzene

CH$_2$ = CH — Cl

Chloroethene
(vinyl chloride)

+ Nucleophile, e.g. ⟶ No reaction

OH⁻, OR⁻, CN⁻,

NH$_3$

Aryl halides may be forced to react with nucleophiles under drastic conditions such as high temperature and pressure.

+ 2NaOH $\xrightarrow[\text{523–623 K}]{\text{238 atm}}$ + NaCl + H$_2$O

+ NH$_3$ $\xrightarrow[\text{448–508 K}]{\text{51–58 atm}}$
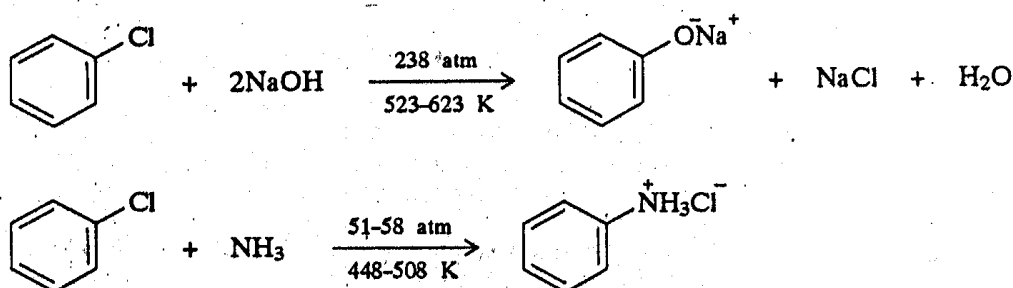
The reason of the low reactivity of the halogen atom in aryl and alkenyl halides is not quite clear. We have already encountered the one possible explanation of the low reactivity of aryl and alkenyl halides in subsection 3.4.1. The Cl atom in the C – Cl group is more tightly bound in Ar – Cl and C = 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;

CH$_2$ = CH — C̈l: ⟷ ⁻C̈H$_2$ — CH = C̈l⁺

Chloroethene
(vinylchloride)

Chlorobenzene
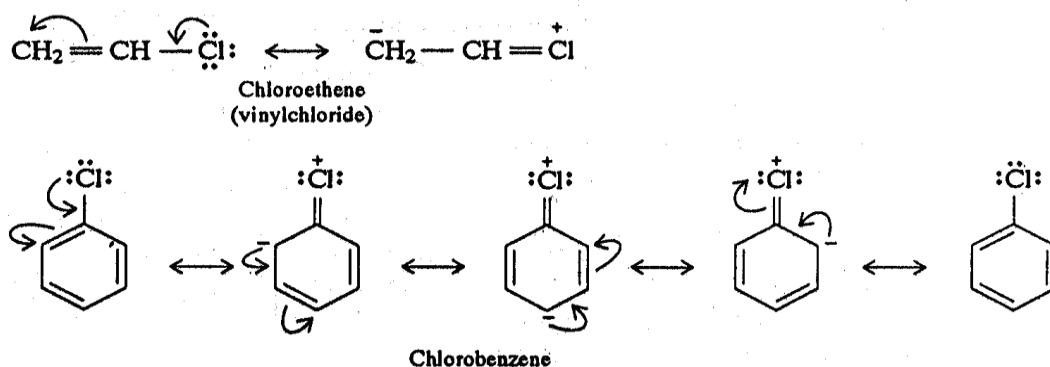
On the other hand, when a strong electron withdrawing group is present at *ortho* and/or *para* position to the halogen atom in aryl halides, the replacement of the halogen by nucleophilic reagents is facilitated, e.g.

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.
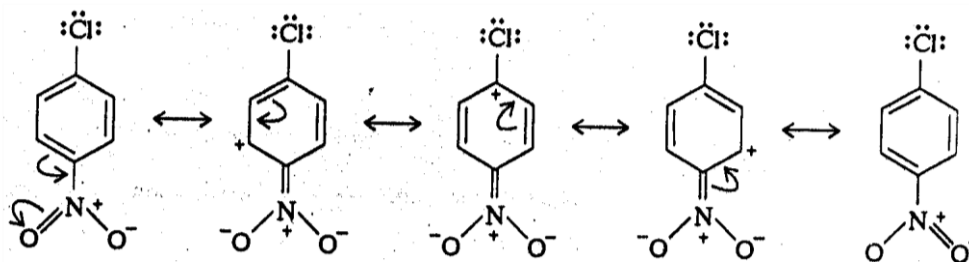
**Resonance structure of chloro-nitrobenzene (*p*-chloronitrobenzene)**

This facilitates attach 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 mechanisms: The addition elimination mechanism and the benzyne intermediate mechanism, which involve the highly reactive elimination reaction intermediate.

chlorobenzene

benzyne
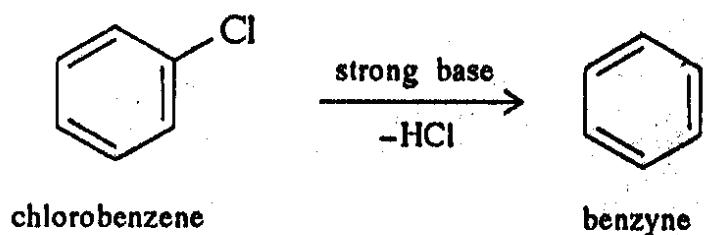
Mechanism of the nucleophilic aromatic substitutions will be described in the course of Organic Reaction Mechanism.

The aromatic ring to which halogen is attached can undergo typical electrophilic aromatic substitution reactions, which we have already discussed in Unit 3. 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.

$$CH_2= CH–Br + NaOH \xrightarrow{heat} HC = CH + NaBr + H_2O$$
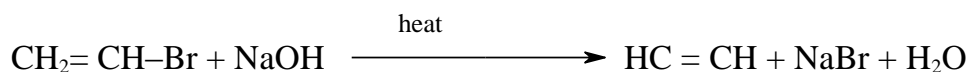
Chloroethene (vinyl chloride) undergoes polymerization in the presence of radical initiators like peroxides to give polyvinyl chloride (PVC):
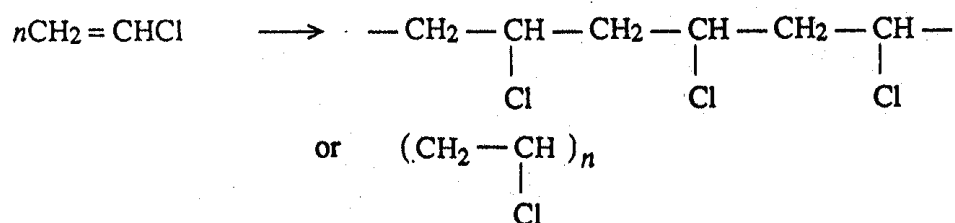
So far we have been concerned with the nucleophilic substitution and elimination reactions of halogen derivatives. Now let us look at the reactions of these compounds with metals. But, before this, try the following SAQ.

SELF ASSESSMENT EXERCISE 6

How do you account for the fact that aryl and alkenyl halides are less reactive towards nucleophiles under ordinary conditions?

3.4 Organometallic Compounds

Alkyl, aryl and alkenyl halides, when treated with metallic alloys, form 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
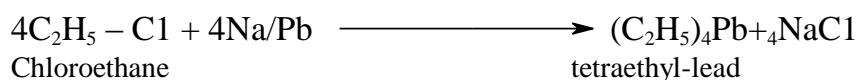
As stated earlier, tetramethyl and tetraethyl-lead are used as anti-knock additives to petrol.

Halogen derivatives of hydrocarbons are widely used to prepare Grignard reagents (organomagnesium halides). 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.
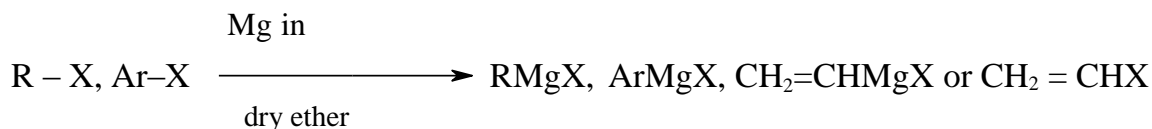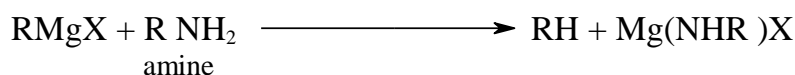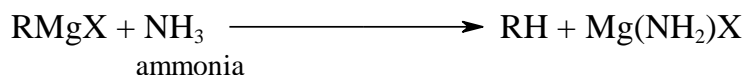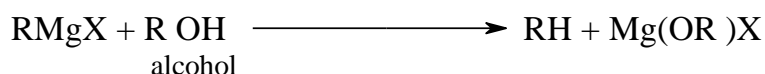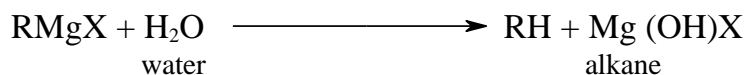
$$R – X, Ar–X \xrightarrow[dry\ ether]{Mg\ in} RMgX,\ ArMgX,\ CH_2=CHMgX\ or\ CH_2 = CHX$$
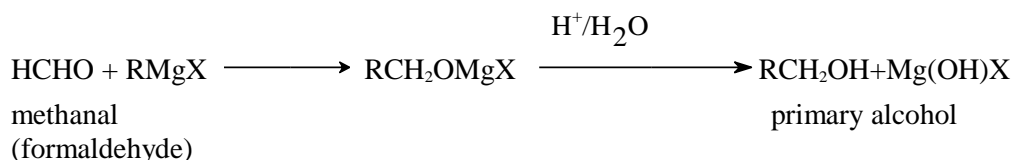Grignard reagent

Where R = alkyl, Ar = aryl, and X = Cl, Br or 1.

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 in nucleophic addition reaction. The mechanism of the nucleophilic addition of Grignard reagents to carbonyl group will be discussed in detail later Grignard reagents are used to prepare a large variety of organic compounds. Some of the important reactions are:
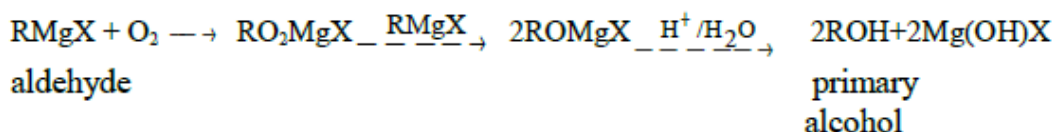
(i)   Preparation of alkanes: Alkanes are prepared by the reaction of Grignard reagents with water, alcohols, ammonia, amines etc:

$$RMgX + H_2O \longrightarrow RH + Mg(OH)X$$
$$\text{water} \text{alkane}$$

$$RMgX + R\,OH \longrightarrow RH + Mg(OR)X$$
$$\text{alcohol}$$

$$RMgX + NH_3 \longrightarrow RH + Mg(NH_2)X$$
$$\text{ammonia}$$

$$RMgX + R\,NH_2 \longrightarrow RH + Mg(NHR)X$$
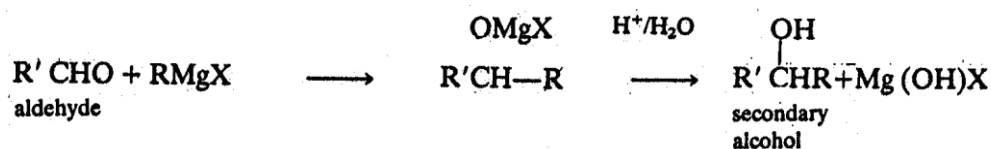$$\text{amine}$$

(ii)   Preparation of alcohols: Primary alcohols are obtained either by the reaction of methanal and Grignard reagent followed by treatment with dilute acid:

$$HCHO + RMgX \longrightarrow RCH_2OMgX \xrightarrow{H^+/H_2O} RCH_2OH + Mg(OH)X$$

methanal
(formaldehyde)
$$\phantom{HCHO + RMgX \longrightarrow RCH_2OMgX \xrightarrow{H^+/H_2O} }\text{primary alcohol}$$

or by treatment of Grignard reagent with dry oxygen and subsequent decomposition by acid:

$$RMgX + O_2 \longrightarrow RO_2MgX \xrightarrow{RMgX} 2ROMgX \xrightarrow{H^+/H_2O} 2ROH + 2Mg(OH)X$$

aldehyde
$$\phantom{RMgX + O_2 \longrightarrow RO_2MgX \xrightarrow{RMgX} 2ROMgX \xrightarrow{H^+/H_2O} }\text{primary alcohol}$$

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:

$$R'CHO + RMgX \longrightarrow \overset{OMgX}{R'CH-R} \xrightarrow{H^+/H_2O} \overset{OH}{R'CHR} + Mg(OH)X$$

aldehyde
$$\phantom{R'CHO + RMgX \longrightarrow R'CH-R \xrightarrow{H^+/H_2O} }\text{secondary}$$
$$\phantom{R'CHO + RMgX \longrightarrow R'CH-R \xrightarrow{H^+/H_2O} }\text{alcohol}$$

Tertiary alcohols are obtained on treatment of a ketone with Grignard reagent and subsequent addition of dilute acid:

$$RCR' + R''MgX \longrightarrow R-\underset{R''}{\overset{OMgX}{|}}C-R' \xrightarrow{H^+/H_2O} R-\underset{R''}{\overset{OH}{|}}C-R' + Mg(OH)X$$

ketone   tert-alcohol
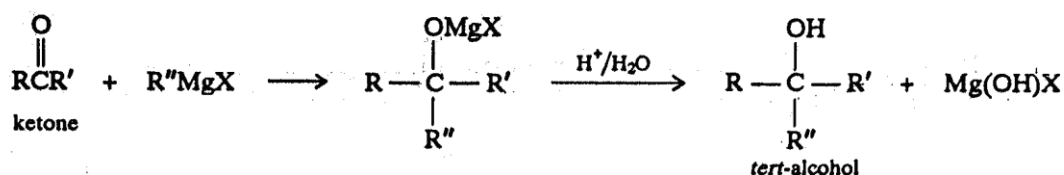
Alcohols are also obtained when epoxides are reacted with Grignard reagent and the addition product is hydrolysed with dilute acid:
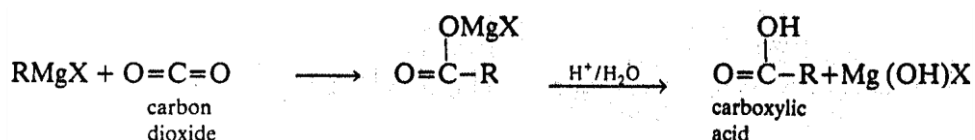
$$\underset{H}{\overset{R}{>}}C\overset{O}{\underset{}{\diagup\diagdown}}C\underset{H}{\overset{R'}{<}} \xrightarrow{R''MgX} R''-CH-\underset{R}{\overset{R'}{|}}CH-OMgX \xrightarrow{H^+/H_2O} R''-CH-\underset{R}{\overset{R'}{|}}CH-OH$$

alcohol
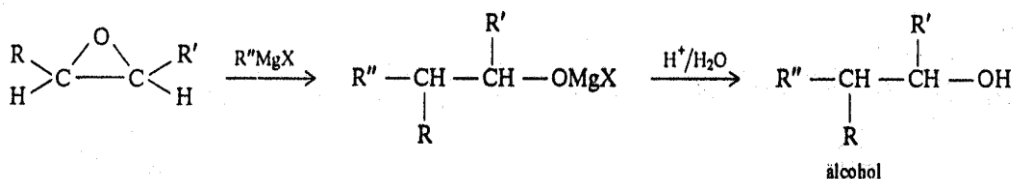
iii) Preparation of carboxylic acids: The reaction of a Grignard reagent with carbon dioxide followed by decomposition of the addition product by dilute acid gives a carboxylic acid:

$$RMgX + O=C=O \longrightarrow O=\overset{OMgX}{\underset{}{C}}-R \xrightarrow{H^+/H_2O} O=\overset{OH}{\underset{}{C}}-R+Mg(OH)X$$

carbon   carboxylic
dioxide   acid

iv) Preparation of Ketones: Ketone can be prepared by the reaction of an alkyl nitrile with a Grignard reagent:

$$RCN + R'MgX \longrightarrow R-\underset{R'}{\overset{}{C}}=NMgX \xrightarrow{H^+/H_2O} R-\overset{O}{\overset{||}{C}}-R + NH_3$$

Ketone
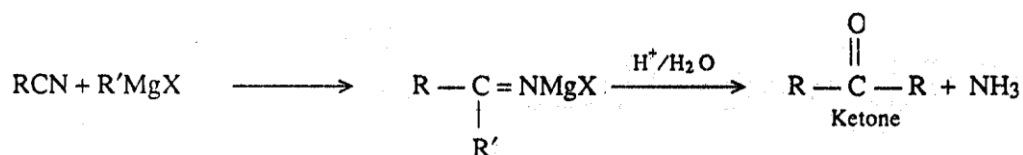
Using the reactions discussed above, attempt the following SAQ.

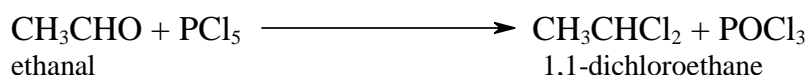**SELF ASSESSMENT EXERCISE 7**

How would you prepare primary, secondary and tertiary alcohols? Give one reaction for each case.
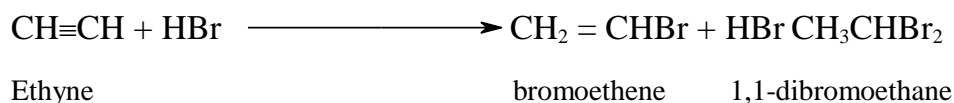
3.5   Polyhalogen Derivatives

In this section we will briefly discuss some important di and tri halogen derivatives.

3.5.1 Dihalogen Derivatives

Gem or 1,1-dihalides are obtained either by the action of phosphorus pentahalides on aldehydes or ketones, e.g.

$$CH_3CHO + PCl_5 \longrightarrow CH_3CHCl_2 + POCl_3$$
ethanal   1,1-dichloroethane

Or by addition of halogen acids to alkynes, e.g.

$$CH{\equiv}CH + HBr \longrightarrow CH_2 = CHBr + HBr\ CH_3CHBr_2$$

Ethyne   bromoethene   1,1-dibromoethane
We have already discussed this reaction in unit 6.

As mentioned in unit 5, vic or 1, 2-dihalides are prepared by the addition of halogens to alkenes, e.g.

$$CH_3CH = CH_2 + Br_2 \longrightarrow CH_3CHBrCH_2Br$$
propene   1, 2-dibromopropane
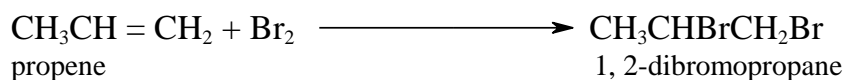
Let us discuss a few important reactions of dihalogen derivatives. Dehalogenation of 1, 2-dihalides by zinc dust and methanol gives alkenes:

$$CH_3CHBrCH_2Br + Zn/CH_3OH \longrightarrow CH_3CH = CH_2 + ZnBr_2$$
1, 2-dibromopropane   propene
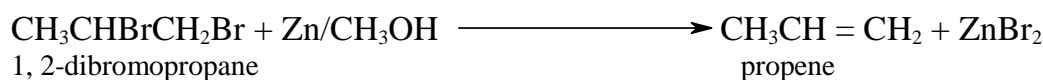
This reaction can also be used to prepare (3-6 membered) cyclic compounds. For example, 1, 3-dibromopropane reacts with zinc to give cyclopropane:
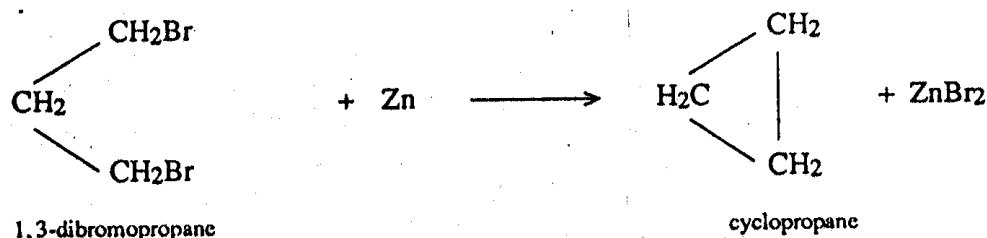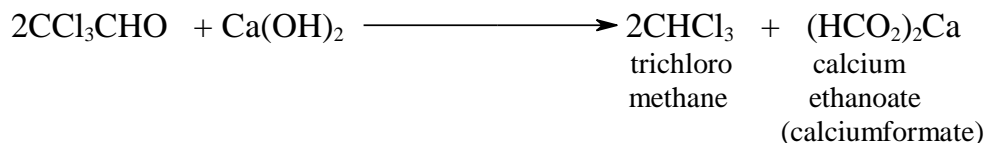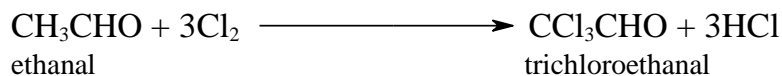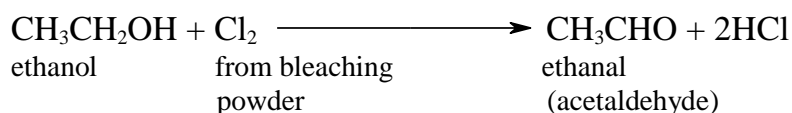

In section 4.2 we mentioned some polyhalogen compounds derived from methane i.e. dichloromethane (methylene chloride), trichloromethane (chloroform) and tetrachloromethane (carbon tetrachloride). These compounds are commercially important substances as they are widely used as solvents in laboratory and industry. In the following section we will discuss the chemistry of trichloromethane, a trihalogen derivative of methane.
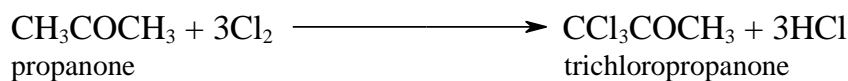
3.5.2 Trihalogen Derivatives

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:

$$CH_3CH_2OH + Cl_2 \longrightarrow CH_3CHO + 2HCl$$
ethanol   from bleaching   ethanal
               powder   (acetaldehyde)

$$CH_3CHO + 3Cl_2 \longrightarrow CCl_3CHO + 3HCl$$
ethanal   trichloroethanal

$$2CCl_3CHO + Ca(OH)_2 \longrightarrow 2CHCl_3 + (HCO_2)_2Ca$$
                                          trichloro   calcium
                                          methane   ethanoate
                                          (calciumformate)

Bleaching powder ($CaOCl_2$) can be obtained by the reaction of calcium hydroxide with chlorine. It acts as a source of chlorine.

Bleaching powder provides chlorine which oxidises ethanol to ethanal in the first step and chlorinates the latter to trichloroacetaldehyde (chloral) in the second step. The reaction of trichloroethanal 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:

$$CH_3COCH_3 + 3Cl_2 \longrightarrow CCl_3COCH_3 + 3HCl$$
propanone   trichloropropanone

$$2CCl_3COCH_3 + Ca(OH)_2 \longrightarrow 2CHCl_3 + (CH_3CO_2)_2Ca$$
                                         trichloro-   calcium
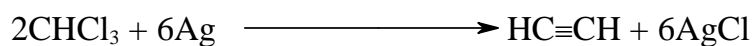   methane   ethanoate

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:

$$CH_4 + 3Cl_2 \longrightarrow CHCl_3 + 3HCl$$
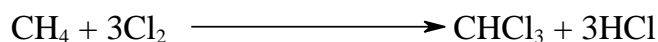
Now, let us consider the properties of trichloromethane. It is a sweet-smelling colourless liquid. On boiling with alkali, it gives methanoate ions:

$$CHCl_3 + 4OH \longrightarrow 3Cl + HCOO^- + 2H_2O$$
trichloro   methanoate
methane   ion
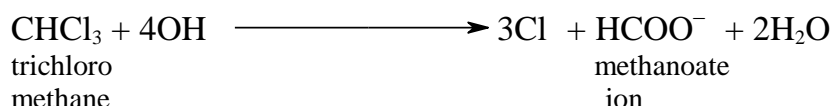
On warming trichloromethane with silver powder, ethyne is obtained:
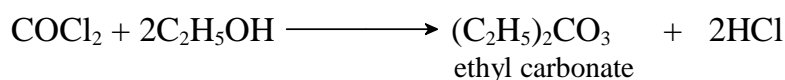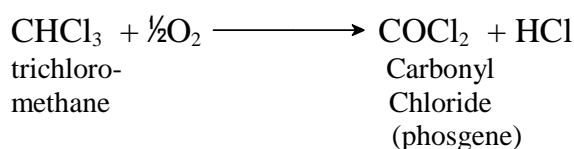
$$2CHCl_3 + 6Ag \longrightarrow HC\equiv CH + 6AgCl$$

trichloro
methane   ethyne

When treated with concentrated nitric acid, trichloromethane gives trichloronitromethane (chloropicrin):

$$CHCl_3 + HNO_3 \longrightarrow CCl_3NO_2 + H_2O$$

trichloro-   trichloro-
methane   nitromethane

Trichloromethane is kept in well-stopped 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.

$$CHCl_3 + \tfrac{1}{2}O_2 \longrightarrow COCl_2 + HCl$$

trichloro-   Carbonyl
methane   Chloride
               (phosgene)

$$COCl_2 + 2C_2H_5OH \longrightarrow (C_2H_5)_2CO_3 + 2HCl$$

               ethyl carbonate

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.

$$CHCl_3 + RNH_2 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$$

trichloro   amine   (isocyanide)
methane
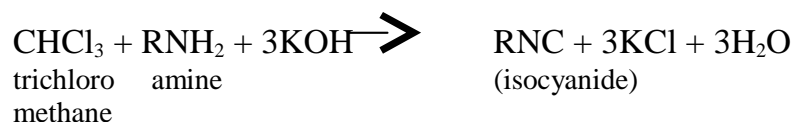
Tribromomethane (bromoform) is obtained by methods similar to those used for trichloromethane. Industrially it is prepared by the electrolysis of an aqueous solution of propanone or ethanol containing sodium carbonate and potassium bromide.

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.

3.6   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.

$$2 \ C_6H_5Cl \ + \ CCl_3CHO \xrightarrow{\text{H}_2\text{SO}_4}$$

chlorobenzene   trichloro-
ethanal
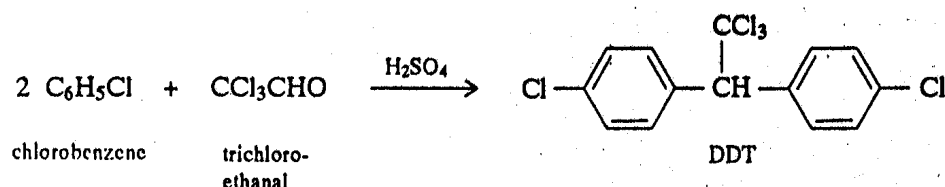
Commercial DDT is a mixture of 75% *p, p* – compound, 20% *o, p'* compound and 5% of other impurities. Most countries have banned the use of DDT, it is poisonous to human and it tends to concentrate in the environment owing to its slow degradation, the half life being 10 years. Similarly the insecticide-benzene hexachloride (BHC) also cause environmental pollution. We have mentioned the preparation of BHC in unit 3. Hexachloroethane is used as a moth repellant.

Chlorofluorocarbons (CFCs) are derivatives of methane and ethane which are used as refrigerants and as aerosol propellants under the name 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.

3.7 Laboratory 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):

$$\text{Na} \ + \ \text{RX} \longrightarrow \text{Na}^+\text{X}^-$$
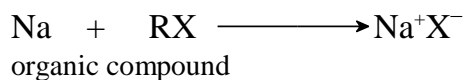
organic compound

or through Schoniger oxidation by oxygen gas under alkaline condition

$$\text{RX} \ + \ \text{O}_2 \xrightarrow{\text{NaOH}} \text{Na}^{+\ -}\text{X} + \text{H}_2\text{O}$$
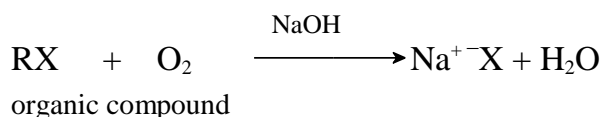
organic compound

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 analyzed further.

$$RX \quad + \quad AgNO_3 \quad \longrightarrow AgX(s) + RONO_2$$
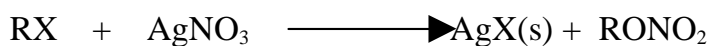
However, aryl halides and alkenyl halides will not react with alcoholic silver nitrate.

The reaction helps in distinguishing alkyl halides from aryl and alkenyl halides.

4.0   CONCLUSION

Halogen derivatives of benzene find extensive use in the industries as intermediates in the synthesis of organic compounds. Only few occur in nature. We have also, in this unit, described the preparation of some of these important chemicals while highlighting some of their important reactions involving Nucleophilic Substitution reaction S_N and Eliminiation reactions, E.

5.0   SUMMARY

In this unit we have described the chemistry of halogen derivatives of hydrocarbons.

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 occurs by two different pathways, S_N2 and S_N1. 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 hydrogen on adjacent carbon (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.
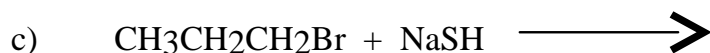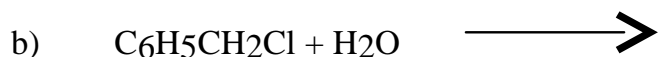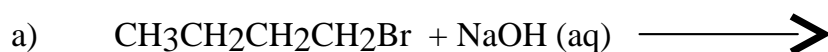
The di- and tri- halogen derivatives of alkanes are also reactive compounds.

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. Polymerization of vinyl chloride and tetrafluoroethylene gives plastic in the name PVC and Teflon, respectively.
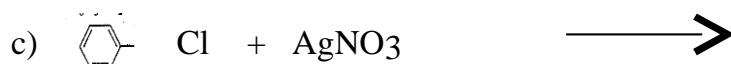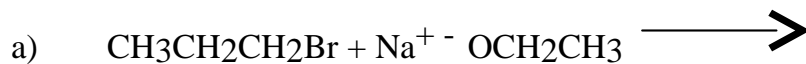
The halogen can be detected as halide ion. Infrared spectroscopy can be used to infer the presence of halogen in organic compounds.

6.0   TUTOR-MARKED ASSIGNMENT

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) $C_6H_5CH_2Cl + AgNO_3 + H_2O \longrightarrow$

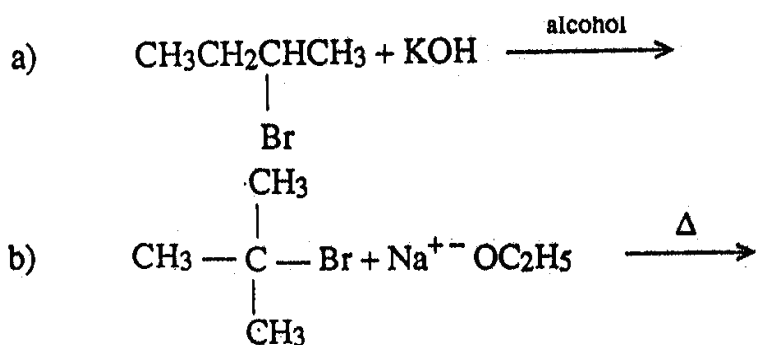c)   ⬡— Cl   + $AgNO_3$ $\longrightarrow$

3)   Write the equation for each of the following reactions:

a)   2, 4-dinitrochlorobenzene and sodium hydroxide
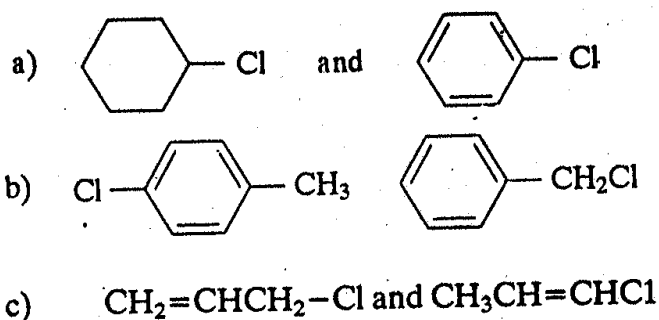b)   2, 4-dinitrochlorobenzene and sodium phenoxide ($C_6H_5O^-Na^+$)
c)   2, 4-nitrochlorobenzene and ammonia

4)   Complete the equation for each of the following reactions and if more than one product is formed, indicate which one is major.

a) $CH_3CH_2CHCH_3$ + KOH $\xrightarrow{\text{alcohol}}$
              |
              Br

b) $CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - Br + Na^+{}^-OC_2H_5 \xrightarrow{\Delta}$

5)   Name a simple chemical test or reagent which will readily distinguish between each of the following pair of compounds.

a)   [cyclohexyl]─Cl and [phenyl]─Cl

b)   Cl─[phenyl]─CH_3 [phenyl]─CH_2Cl

c) $CH_2=CHCH_2-Cl$ and $CH_3CH=CHCl$

7.0   REFERENCES/FURTHER READINGS

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APPENDIX 1

ANSWER TO SELF ASSESSMENT EXERCISE

UNIT 1: Effect of Molecular Architecture on Physical Properties

ANSWER TO SELF ASSESSMENT EXERCISE 1
Hydrogen bonding results when a hydrogen atom is covalently bonded to a strongly electronegative action such as oxygen, nitrogen or chlorine. Example of hydrogen bonding is in water (H_2O) molecule.

ANSWER TO SELF ASSESSMENT EXERCISE 2
Butane has a high melting point (M.P 134K) than 2-methyl propane (M.P. 111K) because the branching of the carbon chain in 2-methylpropane interferes with the regular packing of the molecules in the crystal, hence it tend to have lower melting point than straight chain butane.

ANSWER TO SELF ASSESSMENT EXERCISE 3
Dimethylether has high polarity than propane, hence, it has a higher boiling point than propane.

ANSWER TO SELF ASSESSMENT EXERCISE 4
The presence of hydrogen bonding in Dimethylether account for its high solubility in water than propane.

UNIT 2: Structure Reactivity Relationship

ANSWER TO SELF ASSESSMENT EXERCISE 1
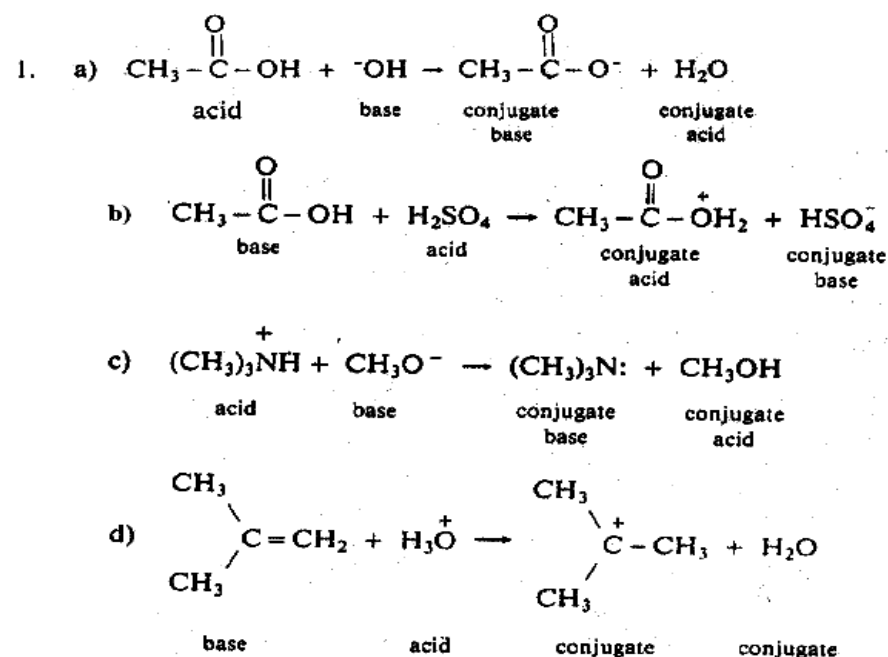
ANSWER TO SELF ASSESSMENT EXERCISE 2

a)   Acid HA_2 having the lower pK_a value is stronger than acid HA_1 having higher pK_a value.

Since HA_2 is stronger acid, therefore, A_2^- is the weaker base as compared to A^-. Thus, in an acid-base reaction between $Na^+ A_1^-$ and HA_2 which is shown below;

$$Na^+ A_1^- + HA_2 \rightleftharpoons \quad HA_1 + Na^+ A_2$$

the stronger base $^1A^-$ will abstract the proton from the acid HA_2 and the equilibrium will lie towards the right to yield HA_1 and $Na^+ A_2$.

ANSWER TO SELF ASSESSMENT EXERCISE 3

a)   The decreasing order of acidities is:

i) $NCCH_2COOH > NCCH_2 CH_2CH_2COOH > CH_3COOH$.
      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:

$$CH(NO_2)_3 > CH_2(NO_2)_2 > CH_3NO_2$$
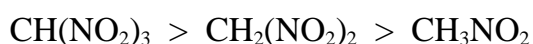
      As the $- NO_2$ group is strongly electron withdrawing, the acidity increases with the increase in the number of these substituents.

iii) $\underset{1}{HOOCCOOH} > \underset{2}{CH_3COOH} > \underset{3}{OOCCOOH}$

      The COOH group is $- 1$ 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 different 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
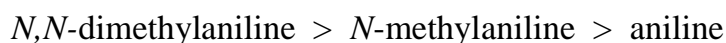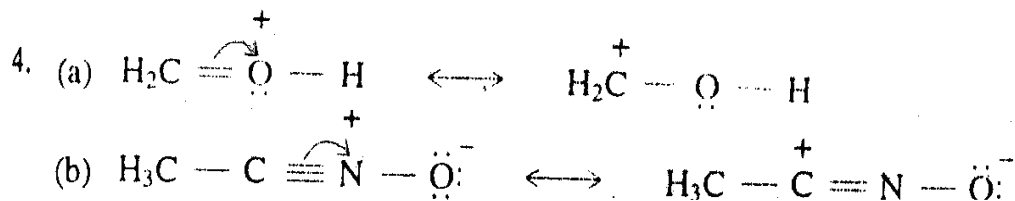
           As the methyl group is electron donating, it increases the basicity in case of N-methylaniline as compared to aniline. The basicity further increases in N, N-dimethylaniline due to the increase in the number of methyl groups.

ii) The decreasing order of basicities is as shown below:

$$CH_3NH_2 > NH_3 > NH_2OH$$

Since the methyl group has +1 effect, it increases the basicity of CH_3NH_2 as compared to NH_2. But, the substitution of an − OH group in NH_3 decreases its basicity because it has − 1 effect.
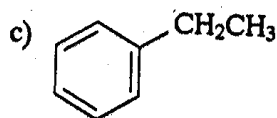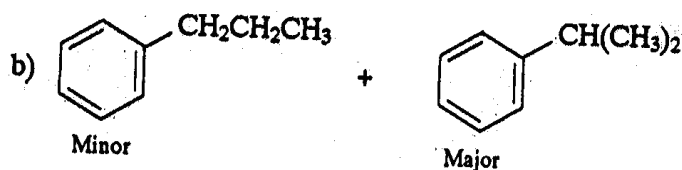
ANSWER TO SELF ASSESSMENT EXERCISE 4

4. (a) $H_2C = \overset{+}{O} — H$ ⟷ $H_2C — \overset{+}{O} — H$

(b) $H_3C — C \equiv \overset{+}{N} — \overset{-}{O}$ ⟷ $H_3C — \overset{+}{C} = N — \overset{-}{O}$

UNIT 3: Aromatic hydrocarbons and polynuclear aromatics

ANSWER TO SELF ASSESSMENT EXERCISE 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.
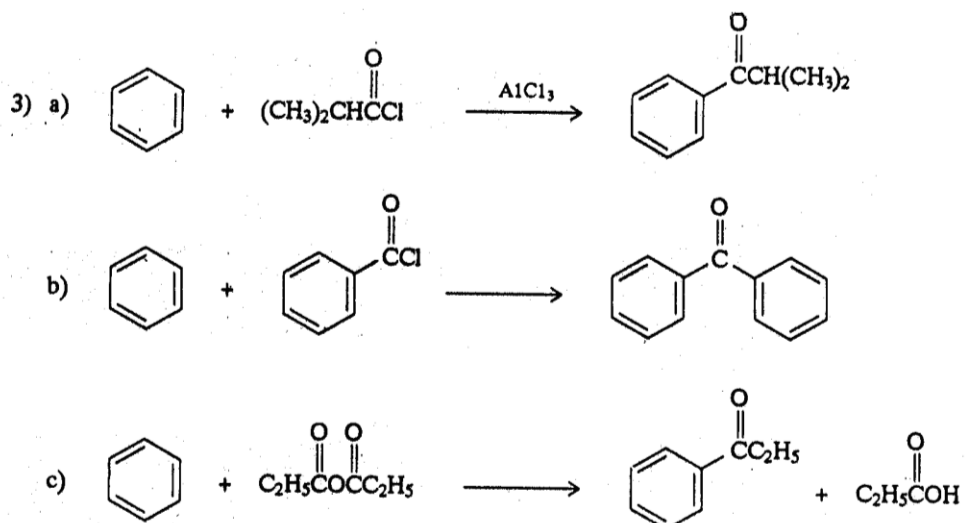
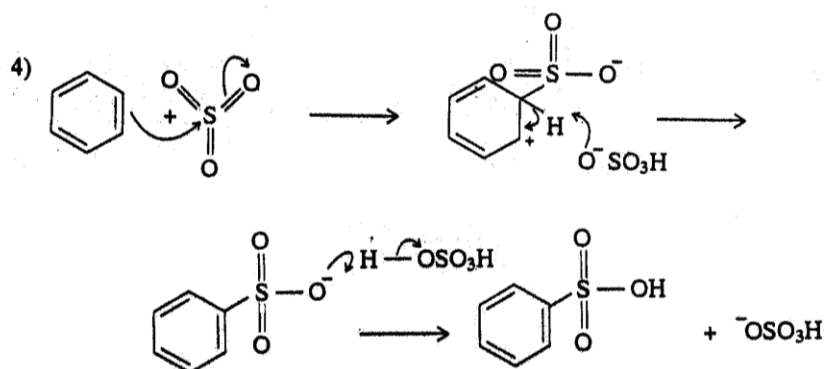### ANSWER TO SELF ASSESSMENT EXERCISE 2

2) a) No reaction

b) $CH_2CH_2CH_3$ + $CH(CH_3)_2$

Minor   Major

c) CH_2CH_3

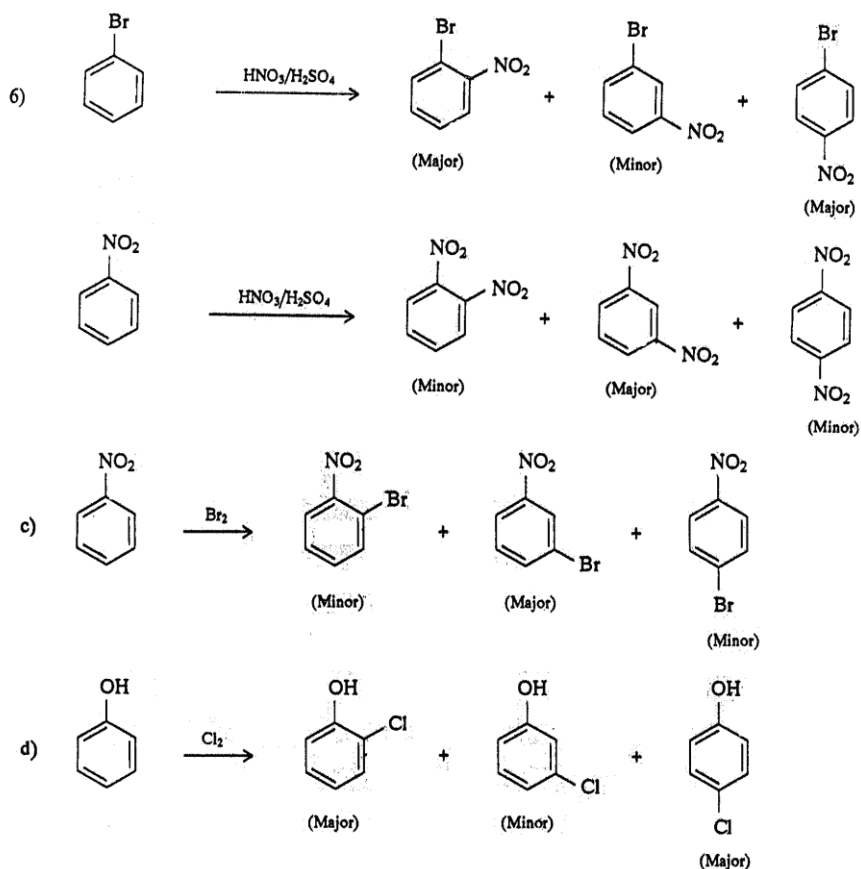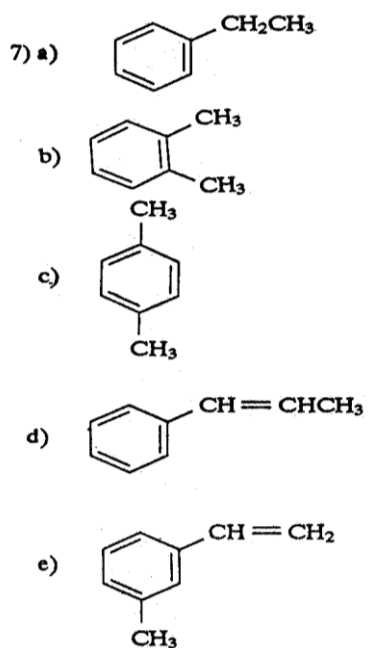d) No reaction.

ANSWER TO SELF ASSESSMENT EXERCISE 3

ANSWER TO SELF ASSESSMENT EXERCISE 4

ANSWER TO SELF ASSESSMENT EXERCISE 5

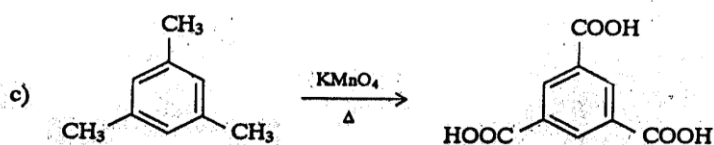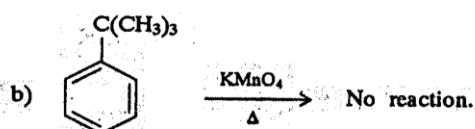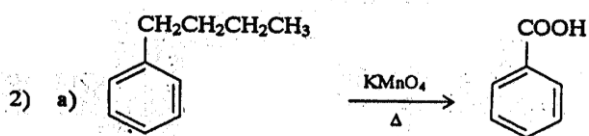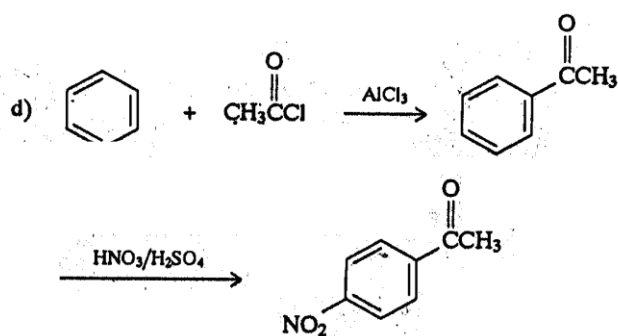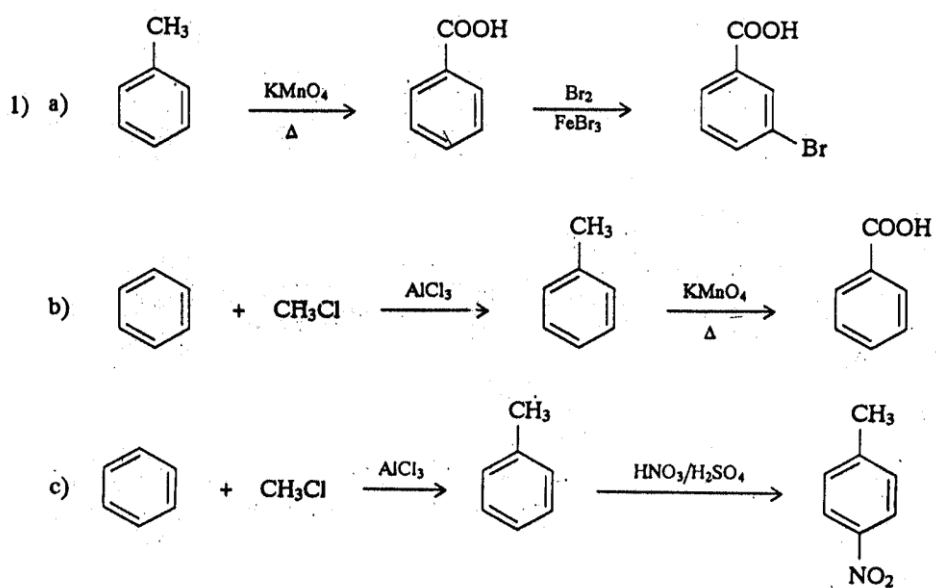While the $-CH_3$ group is electron releasing and activates the ring, the CCl_3 group is strongly electron withdrawing because of the influence of the electronegative chlorine atoms and hence, deactivates the ring. Therefore, $C_6H_5CCl_3$ undergoes substitution more slowly.

ANSWER TO SELF ASSESSMENT EXERCISE 6

6) $C_6H_5Br \xrightarrow{HNO_3/H_2SO_4}$ ortho-bromonitrobenzene (Major) + meta-bromonitrobenzene (Minor) + para-bromonitrobenzene (Major)

$C_6H_5NO_2 \xrightarrow{HNO_3/H_2SO_4}$ 1,2-dinitrobenzene (Minor) + 1,3-dinitrobenzene (Major) + 1,4-dinitrobenzene (Minor)

c) $C_6H_5NO_2 \xrightarrow{Br_2}$ ortho-bromonitrobenzene (Minor) + meta-bromonitrobenzene (Major) + para-bromonitrobenzene (Minor)

d) $C_6H_5OH \xrightarrow{Cl_2}$ ortho-chlorophenol (Major) + meta-chlorophenol (Minor) + para-chlorophenol (Major)

ANSWER TO SELF ASSESSMENT EXERCISE 7

7) a) $C_6H_5CH_2CH_3$

b) ortho-$C_6H_4(CH_3)_2$ (with two adjacent CH_3 groups)

c) para-$C_6H_4(CH_3)_2$

d) $C_6H_5CH=CHCH_3$

e) meta-$CH_3C_6H_4CH=CH_2$

1) a)

b)

c)

d)

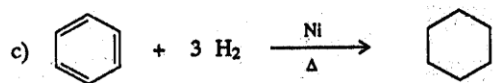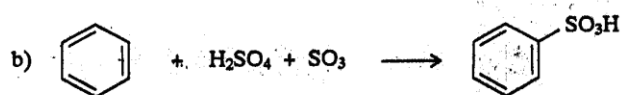2) a)

b)

c)

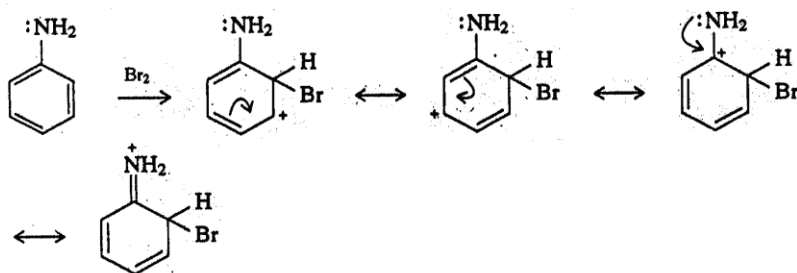3) Order of reactivity of the given compounds towards Friedel-Crafts alkylation is :
Phenol > Toluene > p-Bromotoluene > Bromobenzene. Nitrobenzene and
Aniline are unreactive towards alkylation.

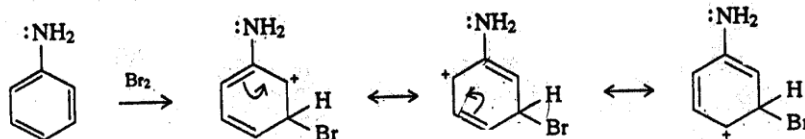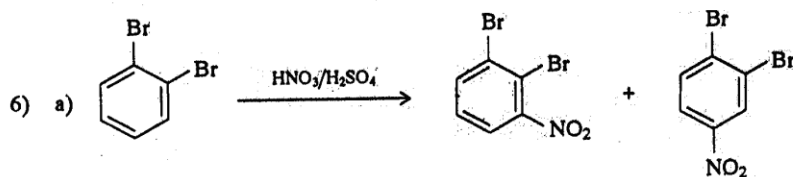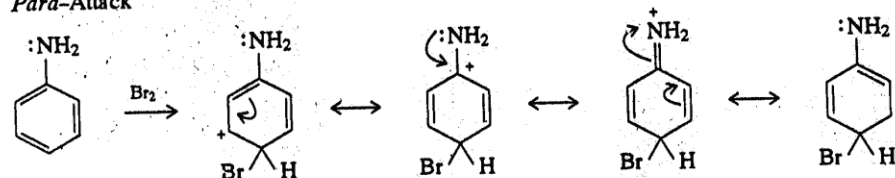4) a)

b)

c)

d)

e)
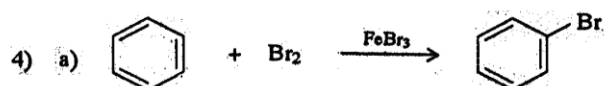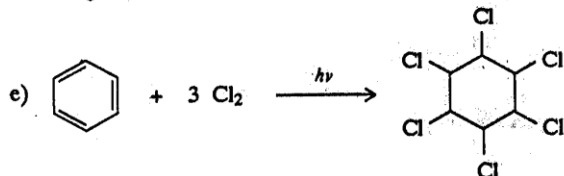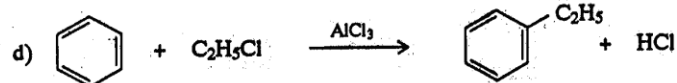
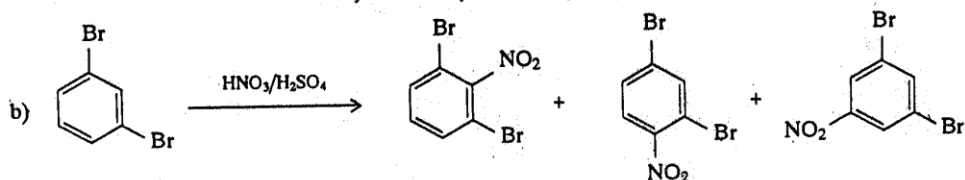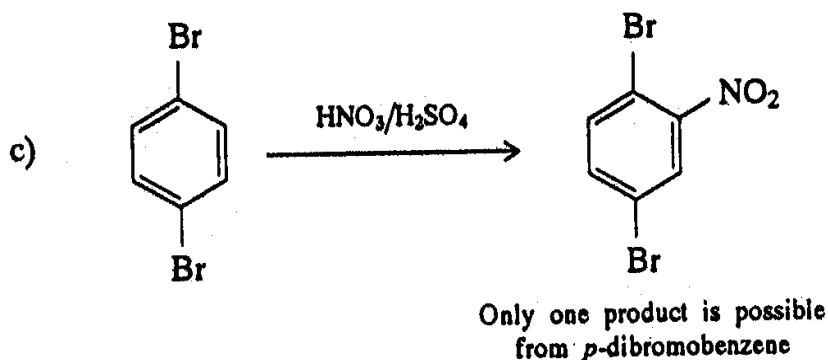5) a) *Ortho*-Attack

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

Only one product is possible
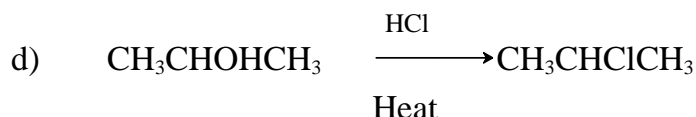from p-dibromobenzene

UNIT 4   Halogen Derivative of Aromatic Hydrocabon

ANSWER TO SELF ASSESSMENT EXERCISE 1

a)   Primary alkyl halide b)   tertiary alkyl halide secondary alkyl halide

ANSWER TO SELF ASSESSMENT EXERCISE 2

a) $C_6H_5 - CH_2CH_3 + Br_2 \longrightarrow C_6H_5CHBrCH_3 + HBr$
   Ethylbenzene   1-bromo-1-phenylethane

b) $CH_3CHOHCH_3 \xrightarrow{\text{HBr}} CH_3CHBrCH_3$

c) $CH_3CH = CH_2 \xrightarrow[\text{peroxide}]{\text{HBr}} CH_3CH_2CH_2Br$

d) $CH_3CHOHCH_3 \xrightarrow[\text{Heat}]{\text{HCl}} CH_3CHClCH_3$
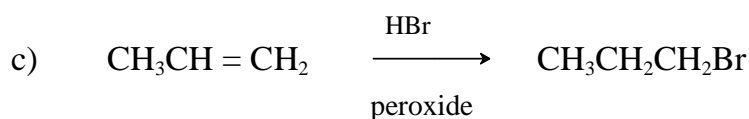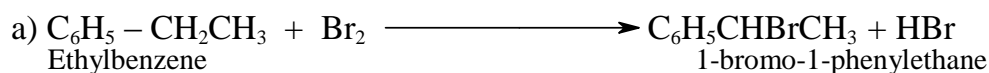
ANSWER TO SELF ASSESSMENT EXERCISE 3

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

ANSWER TO SELF ASSESSMENT EXERCISE 4

a) CH_2Cl

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 t the stronger Ar – Cl bonds.

c) $(CH_3)_2CHCH_2Cl$ d) $CH_2 = CHCH_2Cl$

ANSWER TO SELF ASSESSMENT EXERCISE 5

Overall reaction can be written as

$$CH_3CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}} - CH_3 \xrightarrow[C_2H_5OH]{C_2H_5O^-Na^+} CH_3CH = \underset{\underset{CH_3}{|}}{C} - CH_3 + CH_3CH_2 - \underset{\underset{CH_3}{|}}{C} = CH_2$$
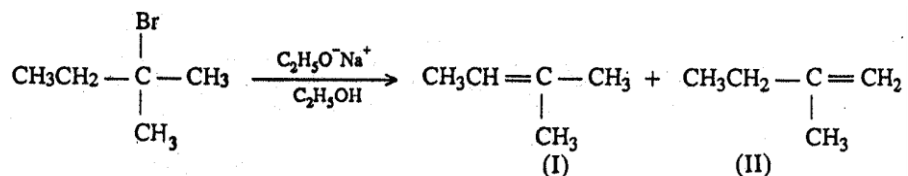$$\phantom{CH_3CH_2 - C - CH_3 \xrightarrow{C_2H_5O} CH_3CH = C - CH_3 aaaaaaa} \text{(I)} \text{(II)}$$
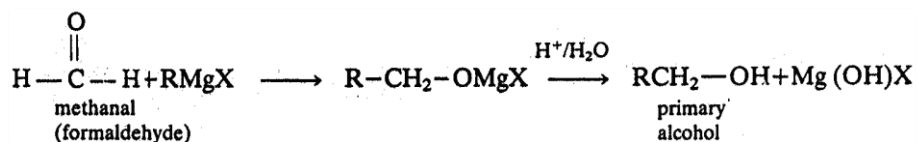
Two products are formed in this case, one (I) is three R substituted alkene and the other (II) is two R substituted, therefore, according to Saytzeff rule I alkene is the major product.

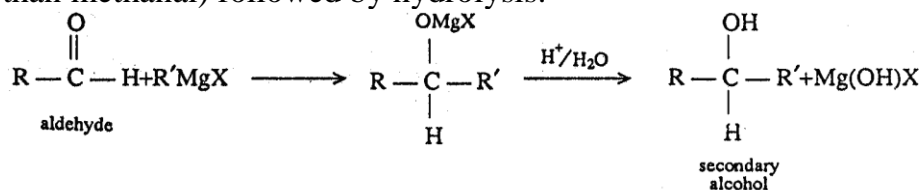## ANSWER TO SELF ASSESSMENT EXERCISE 6

There are two reasons (1) the Cl atom in C – Cl groups 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 4.4, due to the resonance Ar – Cl and C = C – Cl acquire some double bond character.

ANSWER TO SELF ASSESSMENT EXERCISE 7

Primary alcohols are prepared by the reaction of Grignards reagents with methanal and followed by hydrolysis.

$$\underset{\substack{\text{methanal} \\ \text{(formaldehyde)}}}{H - \overset{\overset{O}{\|}}{C} - H} + RMgX \longrightarrow R - CH_2 - OMgX \xrightarrow{H^+/H_2O} \underset{\substack{\text{primary} \\ \text{alcohol}}}{RCH_2 - OH} + Mg\,(OH)X$$

Secondary alcohols are obtained when a Grignard reagent reacts with an aldehyde (other than methanal) followed by hydrolysis.

$$\underset{\text{aldehyde}}{R - \overset{\overset{O}{\|}}{C} - H} + R'MgX \longrightarrow R - \underset{\underset{H}{|}}{\overset{\overset{OMgX}{|}}{C}} - R' \xrightarrow{H^+/H_2O} R - \underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}} - R' + Mg(OH)X$$
$$ \underset{\substack{\text{secondary} \\ \text{alcohol}}}{}$$

Tertiary alcohols are prepared by the action of a ketone with Grignard reagent and subsequent addition of dilute acid.

$$\underset{\text{ketone}}{R - \overset{\overset{O}{\|}}{C} - R'} + R''MgX \longrightarrow R - \underset{\underset{R}{|}}{\overset{\overset{O^{MgX}}{|}}{C}} - R'' \xrightarrow{H^+/H_2O} R - \underset{\underset{R'}{|}}{\overset{\overset{OH}{|}}{C}} - R'' + Mg(OH)X$$
$$ \underset{\text{tertiary alcohol}}{}$$