UNIT 11 HALOGEN DERIVATIVES

Structure

11.1 INTRODUCTION

In Block 2, we have described the preparation and reactions of hydrocarbons and some heterocyclic compounds. In this unit and in the next units, we will study some derivatives of hydrocarbons.

Replacement of one or more hydrogen atoms in a hydrocarbon by halogen atom(s) [F, Cl, Br, or I] gives the halogen derivatives. These compounds are important laboratory and industrial solvents and serve as intermediates in the synthesis of other organic compounds. Many chlorohydrocarbons have acquired importance as insecticides. Although there are not many naturally occurring halogen derivatives yet you might be familiar with one such compound, thyroxin—a thyroid hormone.

In this unit, we shall take up the chemistry of the halogen derivatives in detail beginning with classification of halogen derivatives and then going over to methods of their preparation. We shall also discuss the reactivity of halogen compounds and focus our attention specially, on some important reactions such as nucleophilic substitution (S_N) and elimination (E) reactions. Finally, we shall take up uses of halogen derivatives and the methods for their detection.

Objectives

After studying this unit, you should be able to:

- classify the halogen derivatives,

- outline the methods of preparation of alkyl halides, chlorobenzene and chloroethene,
- list the physical and spectral properties of halogen derivatives,
- describe the reactions of halogen derivatives, specially nucleophilic substitution and elimination reactions,
- explain the difference in reactivity of alkyl, ethenyl, aryl and benzylhalides towards nucleophilic substitution reactions,
- describe the chemisty of organometallic compounds and polyhalogen derivatives,
- list and describe the industrial uses of halogen derivatives, and
- describe the laboratory detection of halogen derivatives.

11.2 CLASSIFICATION OF HALOGEN DERIVATIVES

The halogen derivatives are conveniently divided into three classes depending upon the nature of the hydrocarbon residue to which the halogen atom is attached: (i) Alkyl halides (ii) Aryl halides (iii) Alkenyl halides. Compounds in which the halogen atom is bonded to an alkyl or a substituted alkyl-group are called **alkyl halides**. Compounds in which one of the hydrogens of an aromatic ring is replaced by a halogen atom are called **aryl halides.** Finally a compound in which a halogen atom is attached to a carbon atom which is attached to another carbon atom by a double bond, are called **alkenyl** (vinylic or vinyl) **halides.** A few examples are given below:

Alkyl halides (R—X)

$CH_3—Br$

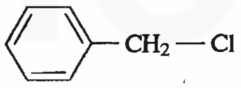
bromomethane

$CH_3CH_2—Cl$

chloroethane

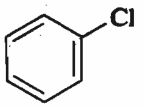
$CH_2=CHCH_2—Cl$

3-chloro-1-prepene or
3-chloropropene
(allyl chloride)

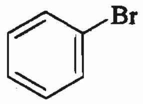


(chloromethyl) benzene
(benzyl chloride)

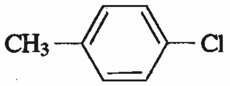
Aryl halides (Ar—X)



chlorobenzene



bromobenzene

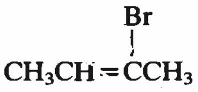


chloro-4-methyl benzene
(*p*-chlorotoluene)

Alkenyl halides (Vinyl halides)

$CH_2=CH—Cl$

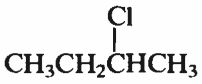
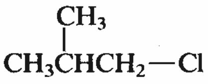
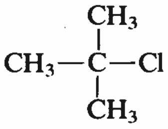
chloroethene
(vinyl chloride)



$$CH_3CH=\overset{\overset{\displaystyle Br}{|}}{C}CH_3$$

2-bromo-2-butene

Halogen derivatives may be mono−, di−, tri−, etc., substitution products according to the number of halogen atoms present in the molecule. The monohalogen derivatives of alkyl halides are subdivided into primary (1°), $RCH_2—X$; secondary (2°), $R_2CH—X$; and tertiary (3°), $R_3C—X$ types depending on the nature of the alkyl group or the position of the halogen atom in the molecule. For example, the molecular formula C_4H_9Cl can represent the following four isomeric mono-halogen derivatives:

$CH_3CH_2CH_2CH_2-Cl$	 $CH_3CH_2CH(Cl)CH_3$	 $CH_3CH(CH_3)CH_2-Cl$	 $CH_3-C(CH_3)_2-Cl$
1-chlorobutane	2-chlorobutane	1-chloro-2-methylpropane	2-chloro-2-methylpropane
primary	secondary	primary	tertiary
1°	2°	1°	3°

Di−, tri−, and tetrachloromethanes are examples of di−, tri−, and tetra halogen derivatives, respectively,

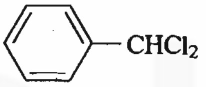
CH_2Cl_2	$CHCl_3$	CCl_4
dichloromethane (methylene chloride)	trichloromethane (chloroform)	tetrachloromethane (carbon tetrachloride)

These halogen derivatives are excellent solvents for nonpolar and slightly polar substances.

The dihalogen derivatives of alkyl halides can be subdivided into two types:

i) **Geminal dihalides:** In these both halogen atoms are attached to the same carbon atom i.e., they are in **geminal (gem-)** position. Geminal dihalides are also referred to as alkylidene halides.

CH_3CHCl_2	$CH_3CBr_2CH_3$
1, 1-dichloroethane (ethylidene dichloride)	2, 2-dibromopropane (isopropylidenedibromide)



(dichloromethyl) benzene (benzylidene chloride or benzal chloride)

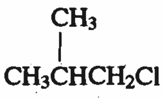
ii) **Vicinal dihalides:** When two halogen atoms are attached to adjacent carbon atoms, they are said to be in **vicinal (vic-)** position and such compounds are also named as the dihalides of the alkene from which they may be prepared by addition of the halogen, e.g.,

CH_2BrCH_2Br	$CH_3CHClCH_2Cl$
1, 2-dibromoethane (ethylene dibromide)	1, 2-dichloropropane (propylene dichloride)

We have discussed above classification of halogen derivatives. In the next section we shall be discussing the preparation of mono halogen derivatives of aliphatic and aromatic hydrocarbons. We will take up polyhalogen derivatives separately in Sec. 11.6. Before that try the following SAQ to test your understanding of the classification of halogen derivatives.

SAQ 1

Classify each of the following alkyl halides as 1°, 2°, or 3°.

a) 

$CH_3CH(CH_3)CH_2Cl$

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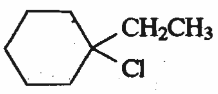
b) 

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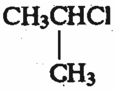
c) 

$CH_3CH(CH_3)Cl$

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11.3 PREPARATION OF HALOGEN DERIVATIVES

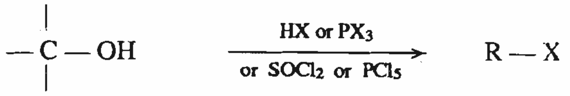
We have already looked at several methods of preparation of halogen derivatives in Units 6,7,8,9 and 10. In this section we shall briefly review these methods and also taking up some other methods for the preparation of halogen derivatives.

11.3.1 Alkyl Halides

Alkyl halides can be prepared from alcohols, alkenes, alkanes, Grignard reagents, carboxylic acids, other halides and from chloromethylation of benzene. General reactions of these methods of preparation are summarised below in Table 11.1.

Table 11.1: Preparations of alkyl halides

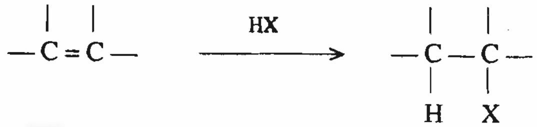
From Alcohols



$$-\overset{|}{\underset{|}{C}}-OH \xrightarrow[\text{or } SOCl_2 \text{ or } PCl_5]{HX \text{ or } PX_3} R-X$$

$HX = HCl, HBr, HI$
$PX_3 = PCl_3, PBr_3$

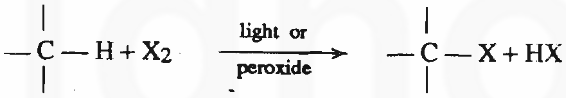
From Alkenes



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

$HX = HCl, HBr, HI$

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.

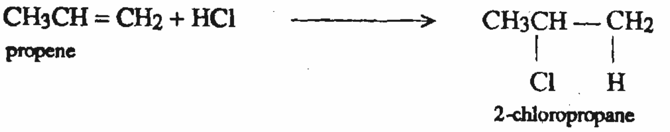
i) **From alcohols:** The most widely used method for the preparation of alkyl halides is from alcohols. The hydroxyl group of the alcohol (R—OH) can be replaced by a halogen atom by using either a hydrogen halide (HX), a phosphorus halide (PX_3 or PCl_5), or thionyl chloride ($SOCl_2$). These reactions will be discussed in more detail in Unit 12. The net reaction is represented by the equations,

$$R-OH + HX \longrightarrow R-X + H_2O$$
$$R-OH + PCl_3 \longrightarrow R-Cl + H_3PO_3$$
$$R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$$
$$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$$
$$C_6H_5CH_2-OH + SOCl_2 \longrightarrow C_6H_5CH_2-Cl + SO_2 \uparrow + HCl$$

phenylmethanol (benzyl alcohol) — (chloromethyl) benzene (benzyl chloride)

ii) **From alkenes:** Hydrogen halides (HCl, HBr, HI) reacts with alkenes to form alkyl halides. The mode of addition follows Markownikoff's rule except for the addition of hydrogen bromide in the presence of peroxide. The mechanism for both modes of additions were shown in Unit 7.

Examples

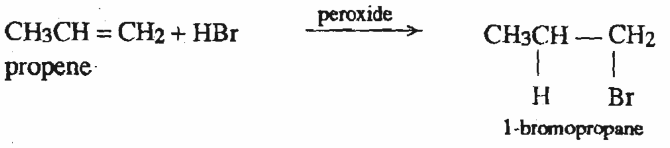


$$CH_3CH=CH_2 + HCl \longrightarrow CH_3\underset{Cl}{CH}-\underset{H}{CH_2}$$

propene → 2-chloropropane

$$CH_3CH=CH_2 + HBr \longrightarrow CH_3\underset{Br}{CH}-\underset{H}{CH_2}$$

propene → 2-bromopropane



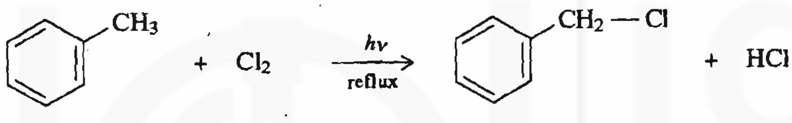
$$CH_3CH=CH_2 + HBr \xrightarrow{peroxide} CH_3\underset{H}{CH}-\underset{Br}{CH_2}$$

propene → 1-bromopropane

iii) From Alkanes: Direct halogenation of alkanes is of limited application in most cases because of the formation of mixture of mono and polyhalogenated compounds. You have learned in Unit 6 that chloromethane, however, can be prepared directly by photochlorination if a large excess of methane is employed.

$$CH_4 + Cl_2 \xrightarrow{\text{sun light}} CH_3{-}Cl + HCl$$

(Chloromethyl) benzene can also be similarly prepared.



methylbenzene (toluene) + Cl_2 $\xrightarrow[\text{reflux}]{h\nu}$ (chloromethyl) benzene (benzyl chloride) + HCl

iv) From Grignard reagents: Direct reaction of alkyl or aryl halides with metallic magnesium in a dry solvent (ether) gives the Grignard reagent, a valuable intermediate in synthetic organic chemistry. We will discuss this reagent in more detail in sec. 11.5. Grignard reagents react with halogens to give alkyl halides.

$$\underset{\text{Grignard reagent}}{RMgX} + X_2 \longrightarrow \underset{\text{Alkyl halide}}{R{-}X} + MgX_2$$

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

$$\underset{\text{Silver salt of carboxylic acid}}{RCOOAg} + Br_2 \longrightarrow R{-}Br + AgBr + CO_2 \uparrow$$

vi) Halide exchange: This is a good procedure for preparing alkyl iodides and alkyl fluorides.

$$R{-}X + KI \xrightarrow{\text{propanone}} R{-}I + KX$$

Alkyl fluorides often are prepared by the reaction of mercurous or antimony fluorides with alkyl chlorides;

$$\underset{\text{alkyl chloride}}{2R{-}Cl} + \underset{\text{mercurous fluoride}}{Hg_2F_2} \longrightarrow \underset{\text{alkyl fluoride}}{2R{-}F} + \underset{\text{mercurous chloride}}{Hg_2Cl_2}$$

$$\underset{\text{tetrachloromethane}}{3CCl_4} + \underset{\text{antimony fluoride}}{2SbF_3} \longrightarrow 3CCl_2F_2 + 2SbCl_3$$

dichlorodifluoromethane (Freon 12)
a chlorofluorocarbon (CFC)

Chlorofluorocarbons (CFC) also called Freons are inert nontoxic gases used as refrigerants in air—conditioners and refrigerators. Freon 12 is the most commonly used refrigerant. Unfortunately Freons catalyse the decomposition of ozone and thus can destroy the protective layer that surrounds the earth. For this reason most of countries in the world have banned the use of Freons.

vii) Chloromethylation of benzene: This method is used to prepare benzylic halides.

$$\underset{\text{aromatic hydrocarbon}}{Ar{-}H} + \underset{\text{methanal (formaldehyde)}}{CH_2O} + \underset{\text{acid}}{HCl} \longrightarrow \underset{\text{benzylic halide}}{Ar{-}CH_2{-}Cl} + H_2O$$

11.3.2 Aryl Halides

Aryl halides may be prepared by one of the methods outlined below in Table 11.2

Table 11.2: Preparation of Aryl Halides

From Aromatic Hydrocarbons

$$Ar{-}H+X_2 \xrightarrow[X_2=Cl_2,\ Br_2]{\text{Lewis acid}} Ar{-}X+HX$$

Lewis acid=$FeCl_3$, $AlCl_3$ $Tl(OAc)_3$, etc.

From Aromatic Amines

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

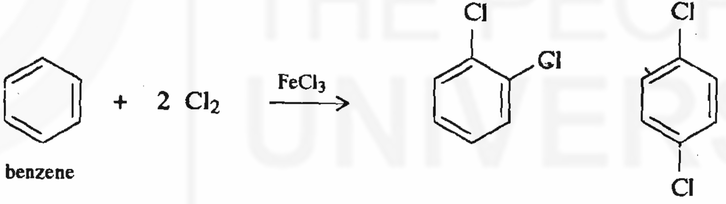
CuX=CuCl,. CuBr

Let us briefly consider these methods of preparation.

i) From Aromatic Hydrocarbons: As discussed in Unit 10 the aromatic halogenation of aromatic hydrocarbon needs the assistance of a Lewis acid as a catalyst. Generally ferric chloride or aluminium chloride are used as catalysts.

$$\underset{\text{aromatic hydrocarbon}}{Ar{-}H + X_2} \xrightarrow{\text{Lewis Acid}} \underset{\text{aryl halide}}{Ar{-}X} + HX$$

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



1,2-dichlorobenzene (*o*-dichlorobenzene) 1,4-dichlorobenzene (*p*-dichlorobenzene)

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

$$\underset{\text{aromatic amine}}{Ar{-}NH_2} \xrightarrow[\text{cold}]{NaNO_2{-}HX} \underset{\text{(diazonium salt)}}{Ar{-}N_2^+X^-} \xrightarrow{CuX/HX} \underset{\text{aryl halide}}{Ar{-}X}$$

Replacement of the diazonium group by —I does not require the use of a cuprous halide.

$$Ar{-}N_2^+X^- \xrightarrow{KI} Ar{-}I+N_2+KX$$

Chlorobenzene is prepared commercially by the **Rasching process** in which a mixture of benzene vapour, air and hydrogen chloride is passedover copper chloride.

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

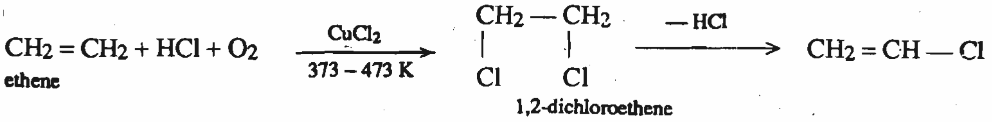
11.3.3 Alkenyl Halides

The most readily available Alkenyl halide is chloroethene (vinyl chloride) which can be prepared by any of the following methods:

i) Chlorination of ethene: High temperature chlorination of ethene is a most economical commercial preparation:

$$\underset{\text{ethene}}{CH_2=CH_2} + Cl_2 \xrightarrow{673K} \underset{\text{chloroethene}}{CH_2=CH-Cl} + HCl$$

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

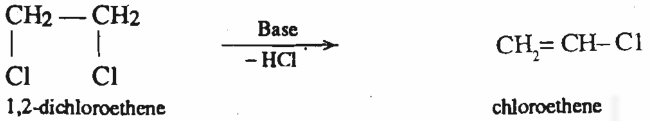


$$\underset{\text{ethene}}{CH_2=CH_2} + HCl + O_2 \xrightarrow[373-473\,K]{CuCl_2} \underset{\text{1,2-dichloroethene}}{\begin{array}{cc} CH_2 & -CH_2 \\ | & | \\ Cl & Cl \end{array}} \xrightarrow{-HCl} CH_2=CH-Cl$$

iii) Addition of hydrochloric acid to ethyne: This method is analogous to Hg^{2+} catalysed addition of water to ethyne, which gives ethanal (Unit 8).

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

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



$$\underset{\text{1,2-dichloroethene}}{\begin{array}{cc} CH_2 & -CH_2 \\ | & | \\ Cl & Cl \end{array}} \xrightarrow[-HCl]{Base} \underset{\text{chloroethene}}{CH_2=CH-Cl}$$

$$\underset{\text{1,1-dichloro ethene}}{CH_3-CHCl_2} \xrightarrow[-HCl]{Base} \underset{\text{chloroethene}}{CH_2=CH-Cl}$$

SAQ 2

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

a) $C_6H_5CHBrCH_3$ from $C_6H_5CH_2CH_3$

b) $CH_3CHBrCH_3$ from $CH_3CHOHCH_3$

c) 1-bromopropane from 1-propene

d) 2-chloropropane from 2-propanol

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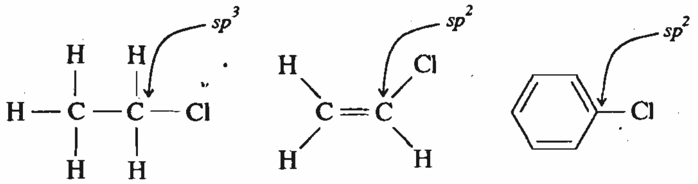
11.4 STRUCTURE AND PROPERTIES OF HALOGEN DERIVATIVES

In the previous section we have been concerned mainly with the preparation of halogen derivatives. Now we will discuss to the structure, spectral properties and chemical properties of these compounds.

11.4.1 Structure of halogen Derivatives

In a halogen derivative, halogen atom is the functional group, and the C—X bond is the site of chemical reactivity. As might be expected, the nature of the chemical bond between the halogen and carbon decides the reactivity of halogen derivatives.

In the alkyl halide, the carbon-halogen sigma bond results through overlap of the sp^3 hybrid orbital with the p orbital of the halogen atom. While the carbon-halogen sigma bond in alkenyal and aryl halides result from the overlap of sp^2 hybrid orbital of the carbon with a halogen p orbital.



As mentioned in unit 1, the bond formed with an sp^2 hybridised carbon is stronger than the bond formed with an sp^3 hybridised carbon. This difference in the nature of the C—X bond is mainly responsible for different bahaviour of aryl and alkenyl halides as compared to alkyl halides. To further explain the unique chemistry of aryl and alkenyl halides, we shall study the reactions of chlorobenzene and chloroethene in sub-section 11.4.5. Let us first examine the polar nature of the C—X bond here.

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	3.0	3.475
Br	2.8	3.219
I	2.5	2.778
C	2.5	2.746

The magnitude of dipole moment for methyl halides is summarised in Table 11.3. In the subsequent sections we will see how the slight positive charge on the carbon is mainly responsible for the nucleophilic substitution (S_N) reactions of halogen derivatives.

Table 11.3 : Dipole Moments of Methyl Halides

Compound	μ, C m
CH_3F	6.07×10^{-30}
CH_3Cl	6.47×10^{-30}
CH_3Br	5.97×10^{-30}
CH_3I	5.47×10^{-30}

But before going into the detail of the reactions let us take a look at the physical properties of halogen derivatives.

11.4.2 Physical Properties of Halogen Derivatives

The physical properties such as boiling points and densities of some alkyl halides, aryl halides and alkenyl halides are summarised in Table 11.4. Common names of some of them are also given.

Table 11.4 : Physical properties of halogen derivatives

IUPAC Name	Common Name	Formula	Bp, K	Density, Kg dm^{-3} at 293 K
Alkyl halides				
Fluoromethane	methylfluoride	CH_3F	195	Gas
Chloromethane	methylchloride	CH_3Cl	249	Gas
Bromomethane	methylbromide	CH_3Br	277.5	Gas
Iodomethane	methyliodide	CH_3I	315.8	2.28
Dichloromethane	methylenelchloride	CH_2Cl_2	313	1.34
Trichloromethane	chloroform	$CHCl_3$	334	1.49
Tetrachloromethane	carbontetrachloride	CCl_4	350	1.60
Aryl halides				
Fluorobenzene	—	C_6H_5F	358	1.024
Chlorobenzene	—	C_6H_5Cl	405	1.107
Bromobenzene	—	C_6H_5Br	429	1.495
Iodobenzene	—	C_6H_5I	462	1.832
Alkenyl halides				
Chloroethene	vinyl chloride	$CH_2{=}CHCl$	259	Gas

Note the increase in boiling point and density with the increase in the atomic weight and atomic size of the halogens atom. The table emphasises also the increase in the boiling point with the progressive replacement of the hydrogen atoms with halogen atoms. These effects are related to the enhancement of van der Waal's attraction with the increase in molecular volume. Compare, for example, the boiling points of CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. The density would also increase in the same way.

In general, halogen compounds are insoluble in water but are readily soluble in organic solvents and with the exception of some fluro and mono-chloro compounds, they are more dense than water. Aryl halides are fairly pleasant smelling liquids, but benzylic halides having the structure $ArCH_2X$ are irritating to the eyes, skin and nasal passage. Toxicity varies. However, the polychlorinated hydrocarbons such as CCl_4 and $CHCl_2CHCl_2$ are quite toxic and should be used with care.

SAQ 3

Arrange the following molecules in order of increasing boiling points. Give reason for this trend.

$CHCl_3$, CH_2Cl_2, CCl_4, CH_3Cl

....

....

....

....

11.4.3 Spectral Properties of Halogen Derivatives

The ultraviolet-visible spectra of alkyl halides show a weak absorption between 170-258 nm due to the presence of loosely held nonbonding electrons of halogen. These electrons undergo *n-π** transitions. Aryl halides exhibit additional absorption similar to those of the corresponding aromatic hydrocarbons.

The infrared (ir) spectra of alkyl halides show the C−X stretching frequency depending on the nature of halogen present. Generally the absorption region of C−F bond: 1100-1000 cm^{-1}; C−Cl bond: 750-700 cm^{-1}; C−Br bond: 600-500 cm^{-1} and C−I bond: 500 cm^{-1}. In all these cases carbon-halogen stretch is shown as a strong band in the spectrum. As illustration ir spectrum of trichloromethane (chloroform) is shown in Fig. 11.1. Aryl halides display (C−X) bands near 1100 cm^{-1}.

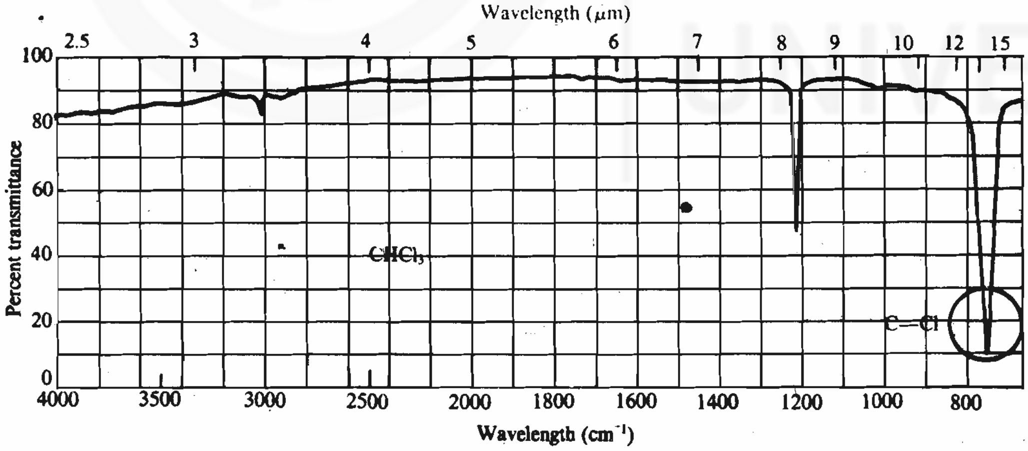
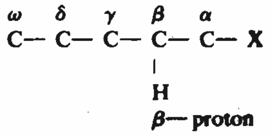


Fig. 11.1 : Infrared spectrum of trichloromethane (chloroform)

The nuclear magnetic resonance (nmr) spectra of alkyl halides exhibit a lower chemical shift (downfield) of the α- protons (dishielding) due to the marked electron-attracting (electro-negative) nature of the halogens. The order of deshielding, resulting in lowering of the chemical shift, is in the order of electronegatively i.e., I < Br < Cl < F. Thus the δ values of methyl protons are: CH_3I, 2.17 CH_3Br, 2.65; CH_3Cl, 3.02; and CH_3F, 4.30 ppm.

Since fluorine has a nuclear spin, with I = + 1/2 and − 1/2 (similar to hydrogen), it can spin-spin couple with protons and thus give rise to splitting of the proton signal. In

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

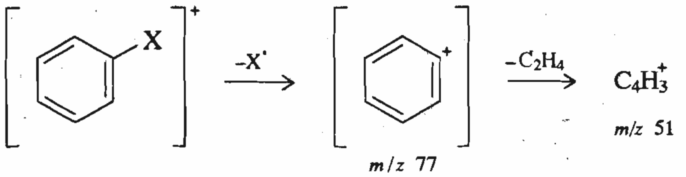

$$\overset{\omega}{C}-\overset{\delta}{C}-\overset{\gamma}{C}-\underset{\substack{|\\ H}}{\overset{\beta}{C}}-\overset{\alpha}{C}-X$$

β— proton

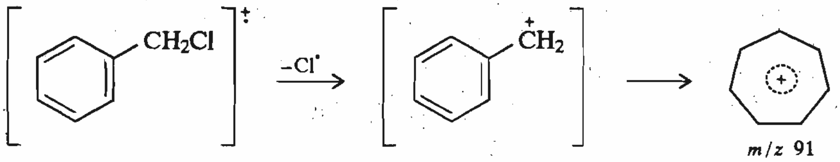
CH_3F, a doublet for the protons of the methyl group will be seen. The signal for fluorine is not observed under conditions of proton resonance, but on changing the conditions, the fluorine signal can be seen as a quartet in the nmr spectrum of CH_3F.

The mass spectrum of alkyl chlorides and bromides show molecular ion peaks at M and M+2 since chlorine and bromine exist as isotopes. In fluoro and iodo compounds the peak due to the molecular ion is strong. The intensity of the M^+ peak decreases with the increase in the size of the halogen atom and is in the order: $I > Br > Cl > F$.

The molecular ion peak is usually strong in the mass spectra of aromatic halides. The usual fragmentation observed is:



(Chloromethyl) benzene (benzylichalide) fragments as follows :



11.4.3 Chemical Properties of Alkyl Halides

Most important reactions of alkyl halides are **nucleophilic substitution (S_N)** and **elimination (E)**. In this section we shall take up a fairly detailed description of these reactions. We have already encountered the term nucleophilic reagent or nucleophile and have learned that it is applied to an electron rich atom or group such as, SH^-, $\dot{N}H_3$, $R\underset{\cdot\cdot}{\ddot{O}}H$, $H_2\underset{\cdot\cdot}{\ddot{O}}$.

1) Substitution reactions: As explained earlier the C–X bond is polar, and the halogenated carbon of an alkyl halide carries a positive charge because of the higher electronegativity of halogens compared to carbon. The carbon atom is, therefore, susceptible to attack by a nucleophilic.

$$Nu^{-}\!: + \overset{\delta^+}{R} — \overset{\delta^-}{X} \longrightarrow R — Nu + :\underset{\cdot\cdot}{\ddot{X}}:^{-}$$

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 11.5.

Table 11.5 Some Nucleophilic Substitution Reactions

$\mathrm{R}-\ddot{\underset{\cdot\cdot}{\mathrm{X}}}\!:$	+ Nucleophile (name)	$\longrightarrow$	$:\!\ddot{\underset{\cdot\cdot}{\mathrm{X}}}\!:^-$ +	Product (name)
$\mathrm{R}-\ddot{\underset{\cdot\cdot}{\mathrm{X}}}\!:$	+ $:\!\ddot{\underset{\cdot\cdot}{\mathrm{Y}}}\!:^-$ (another halide)	$\longrightarrow$	$:\!\ddot{\underset{\cdot\cdot}{\mathrm{X}}}\!:^-$ +	$\mathrm{R}-\ddot{\underset{\cdot\cdot}{\mathrm{Y}}}\!:$ (another alkyl halide)
	+ $^-\!:\mathrm{C}\equiv\mathrm{N}:$ (cyanide)	$\longrightarrow$	+	$\mathrm{R}-\mathrm{C}\equiv\mathrm{N}:$ (nitrile)
	+ $^-\!:\ddot{\underset{\cdot\cdot}{\mathrm{O}}}\mathrm{H}$ (hydroxide)	$\longrightarrow$	+	$\mathrm{R}-\ddot{\underset{\cdot\cdot}{\mathrm{O}}}\mathrm{H}$ (alcohol)
	+ $^-\!:\ddot{\underset{\cdot\cdot}{\mathrm{O}}}\mathrm{R}$ (alkoxide)	$\longrightarrow$	+	$\mathrm{R}-\ddot{\underset{\cdot\cdot}{\mathrm{O}}}-\mathrm{R}$ (ether)
	+ $^-\mathrm{N}_3$ (azide = $:\!\ddot{\mathrm{N}}=\mathrm{N}=\ddot{\mathrm{N}}\!:$)	$\longrightarrow$	+	$\mathrm{R}-\mathrm{N}_3$ (alkyl azide)
	+ $^-\!:\ddot{\underset{\cdot\cdot}{\mathrm{S}}}\mathrm{R}'$ (alkanethiolate)	$\longrightarrow$	+	$\mathrm{R}-\ddot{\underset{\cdot\cdot}{\mathrm{S}}}-\mathrm{R}'$ (thioether)
	+ $:\mathrm{NR}'_3$ (amine)	$\longrightarrow$		$\mathrm{R}-\overset{+}{\mathrm{N}}\mathrm{R}'_3\,:\!\ddot{\underset{\cdot\cdot}{\mathrm{X}}}\!:^-$ (alkylammonium salt)
	+ $:\ddot{\mathrm{O}}\mathrm{H}_2$ (water)	$\longrightarrow$		$\mathrm{R}-\underset{\substack{\mid\\ \mathrm{H}}}{\overset{+}{\ddot{\mathrm{O}}}}-\mathrm{H}\,:\!\ddot{\underset{\cdot\cdot}{\mathrm{X}}}\!:^- \rightleftarrows \underset{\text{(alcohol)}}{\mathrm{R}-\ddot{\underset{\cdot\cdot}{\mathrm{O}}}-\mathrm{H}} + \mathrm{H}\ddot{\underset{\cdot\cdot}{\mathrm{X}}}\!:$
	+ $:\underset{\substack{\mid\\ \mathrm{H}}}{\ddot{\mathrm{O}}}-\mathrm{R}'$ (alcohol)	$\longrightarrow$		$\mathrm{R}-\underset{\substack{\mid\\ \mathrm{H}}}{\overset{+}{\ddot{\mathrm{O}}}}-\mathrm{R}'\,:\!\ddot{\underset{\cdot\cdot}{\mathrm{X}}}\!:^- \rightleftarrows \underset{\text{(ether)}}{\mathrm{R}-\ddot{\underset{\cdot\cdot}{\mathrm{O}}}-\mathrm{R}'} + \mathrm{H}\ddot{\underset{\cdot\cdot}{\mathrm{X}}}\!:$

On the basis of the mechanism of substitution reactions, nucleophilic substitution reaction can be divided into two types:

i) S_N2 reactions (S_N2 means 'substitution, nucleophilic bimolecular')

ii) S_N1 reactions (S_N1 means 'substitution, nucleophilic unimolecular')

The terms bimolecular and unimolecular are related to the number of molecules involved in the rate determining step in these reactions. Now, let us consider these reactions in detail.

The S_N2 reaction : The reaction of bromoethane with the hydroxide ion to yield ethanol and bromide ion is a typical example of S_N2 reaction.

$$\underset{\text{bromoethane}}{CH_3CH_2-Br} + OH^- \xrightarrow{H_2O} \underset{\text{ethanol}}{CH_3CH_2-OH} + Br^-$$

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

$$\text{Rate} = k_2\,[C_2H_5Br]\,[OH^-]$$

where k_2, is the rate constant and $[C_2H_5Br]$ and $[OH^-]$ represent the concentrations in mole dm^{-3} of the alkyl halide and the hydroxide ion, respectively.

Mechanism : On the basis of reaction kinetics and the stereo chemistry of S_N2 reactions, a one step, concerted mechanism is proposed.

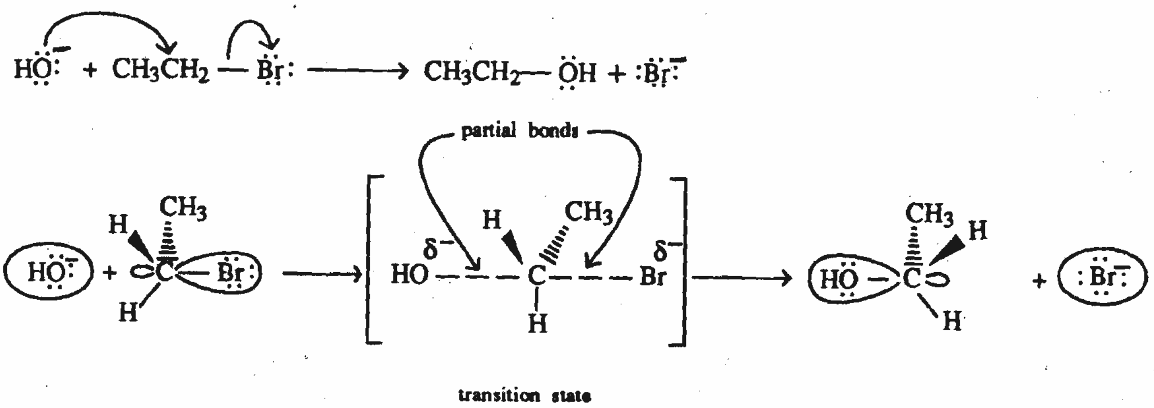


Fig. 11.2 : The mechanism for the S_N2 reaction

In an S_N2 reaction, the other three bonds, (which are not taking part in substitution change) to the central carbon progressively 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,** which you have already studied in Unit 3.

Note how the hydroxide ion attacks from the rear, away from the negatively charged field of the bromide ion. As the hydroxide ion begins to bond to the carbon atom from the rear, the bromine begins to leave as the bromide ion from the front. Groups larger than hydrogen tend to block the approach of the nuclephile, so methyl halides are more reactive than other primary halides. Table 11.6 shows the effect of the structure of alkyl halides over the reaction rate. In this table we have given average reaction rates (taking the reaction rate for ethyl halides are one) of S_N2 reaction of some alkyl halides.

Table 11.6 : Effect of branching in the alkyl halide on the rate of S_N2 reaction

Alkyl halide	Reaction rate
$CH_3{-}X$	30
$CH_3CH_2{-}X$	1
$(CH_3)_2CH{-}X$	0.02
$(CH_3)_3C{-}X$	0

Therefore, among alkyl halides, order of relative rate is

$$CH_3 > p\ RX > sec\ RX > tert\ RX$$

This order of reactivity is interpreted to be due to steric hindrance, which means obstruction of space. The more alkyl groups there are clusters around the carbon holding the halogen, the more they hindered a nucleophile approaching at backside of that carbon.

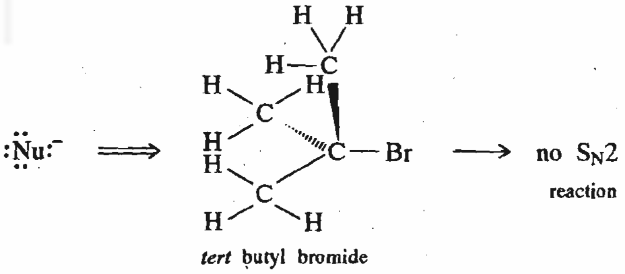


Fig. 11.3 : Steric hindrance in S_N2 reaction.

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

In most stepwise reactions, the slowest step in the entire sequence is the rate-determining step as a reaction cannot proceed faster than its slowest step does.

The S_N1 reaction

You can see from Table 11.6, that the tertiary alkyl halides do not undergo S_N2 reaction. And yet when tertiary butyl bromide is treated even with a very weak base (such as H_2O or CH_3CH_2OH) substitution takes place. Now, the question arises, if tertiary alkyl halides cannot undergo S_N2 reaction, how are the substitution products formed ? The answer is that tertiary alkyl halides undergo substitution by a different mechanism, called the **S_N1 reaction** (substitution, nucleophilic, unimolecular). An example of such a reaction is the hydrolysis of 2-chloro-2-methylpropane with water. This reaction is found to be of **first order** (S_N1). That means the rate of the reaction is proportional to the concentration of the one reacting species i.e. alkyl halide and independent of the concentration of the nucleophile.

$$\text{Rate} = k_1\,[(CH_3)_3CCl]$$

In this equation, k_1 represents the first order rate constant and $[(CH_3)_3CCl]$ represents the concentration in mole dm^{-3} of the alkyl halide.

Mechanism : On the basis of reaction kinetics and stereo chemistry of S_N1 reaction, a two step mechanism has been proposed for this reaction.

Step 1

$$(CH_3)_3\,C-\ddot{\underset{\cdot\cdot}{Cl}}: \xrightarrow{\text{slow}} [(CH_3)_3\,\overset{\delta^+}{C}----\overset{\delta^-}{\ddot{\underset{\cdot\cdot}{Cl}}}:\,] \xrightarrow{\ddot{Cl}:^-} [(CH_3)_3\,C^+]$$

2- chloro - 2- methyl propane (*tert* butyl chloride)

transition State—I

carbocation intermediate

Step 2

$$[(CH_3)_3\,C^+] + :\ddot{O}H_2 \xrightarrow{\text{fast}} [(CH_3)_3\,\overset{\delta^+}{C}----\underset{\underset{H}{|}}{\overset{\delta^+}{O}}H]^+$$

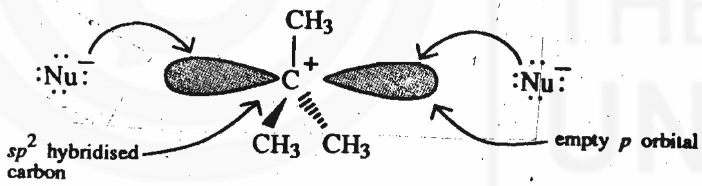
nucleophile

transition State - II

$$\xrightarrow{-\,H^+} (CH_3)_3C-OH$$

2-methyl-2-pro panol (*tert* butyl alcohol)

From the above it is clear that the first step in this mechanism is ionisation of alkyl halide to a carbocation intermediate. This ionisation is a simple heterolytic bond cleavage. In the second step, a nucleophile may approach the central carbon atom from either side with equal probability (unlike the S_N2 reaction where the nucleophile approaches only from the back side). As already discussed in unit 3 the carbocation has a planar geometry and, therefore, the nucleophile may engage the empty *p* orbital from either side of the molecule.



Thus as mentioned in unit 3, S_N1 reaction of an optically active alkyl halide should give recemic substitution products.

As in the case of S_N2 reaction the structure of the alkyl halide also effect the rate of the reaction. We are giving the relative rates of reaction of some alkyl bromides under typical S_N1 conditions in Table 11.7.

Table 11.7: Relative reaction rates of hydrolysis of some alkyl bromides under typical S_N1 conditions

Alkyl bromide	Relative rate
CH_3-Br	1.00[a]
CH_3CH_2-Br	1.00[a]
$(CH_3)_2CH-Br$	11.6
$(CH_3)_3C-Br$	1.2×10^6

[a] The observed reactions of the methyl or other primary bromides probably occur by different routes (S_N2, not S_N1).

Therefore, among alkyl halides, the order of relative rates is

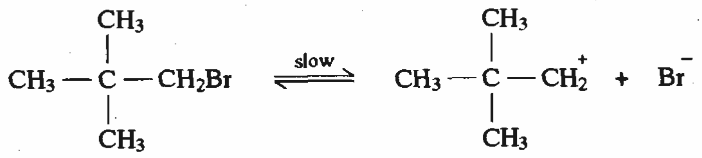
***tert* RX > *sec* RX > *p* RX > CH_3X**

This order is reasonable, since the order of stability of the intermediate carbocation formed in the slow rate determining step is also the same.

$$\underset{tert}{(CH_3)_3C^+} > \underset{sec}{(CH_3)_2CH^+} > \underset{p}{CH_3CH_2^+} > CH_3^+$$

The S_N1 reaction have been found to be subject to rearrangements when the intermediate carbocation can rearrange to a more stable carbocation. The following is an example of one such rearrangement:

Step 1

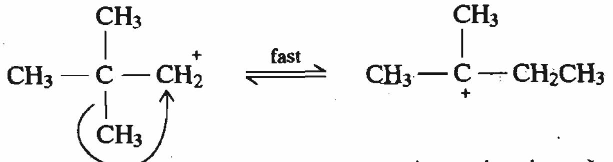


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2Br \xrightleftharpoons{\text{slow}} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{+}{C}H_2 + Br^-$$

1-bromo-2,2-dimethyl propane (neopentyl bromide)

primary carbocation (less stable)

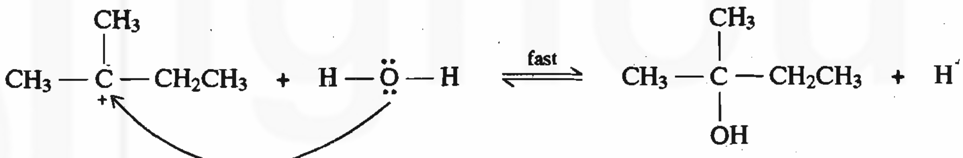
Step 2



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{+}{C}H_2 \xrightleftharpoons{\text{fast}} CH_3-\underset{+}{\overset{CH_3}{C}}-CH_2CH_3$$

tertiary carbocation (more stable)

Step 3

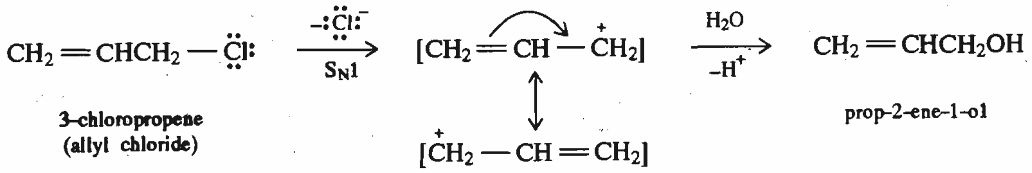


$$CH_3-\underset{+}{\overset{CH_3}{C}}-CH_2CH_3 + H-\ddot{O}-H \xrightleftharpoons{\text{fast}} CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2CH_3 + H$$

2-methyl-2-butanol (*tert* amyl alcohol)

You can notice how that the primary carbocation ion rearranges, through the shift of a $-CH_3$ group, to produce the more stable tertiary carbocation.

Substitution reactions of allylic and benzylic Halides : The behaviour of substituted alkyl halides such as allylic and benzylic halides in S_N1 and S_N2 reactions deserves to be considered separately. Both these halides are very reactive under both S_N1 and S_N2 conditions. They undergo S_N1 reaction at faster rate than tertiary alkyl halides. The reason for the enhanced reactivity under S_N1 conditions lies in the **resonance stabilisation** of the carbocation intermediate and for S_N2 reaction in the resonance stabilisation of the S_N2 transition state. To illustrate this, further let us consider S_N1 reaction of allyl chloride and benzyl chloride with H_2O.



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

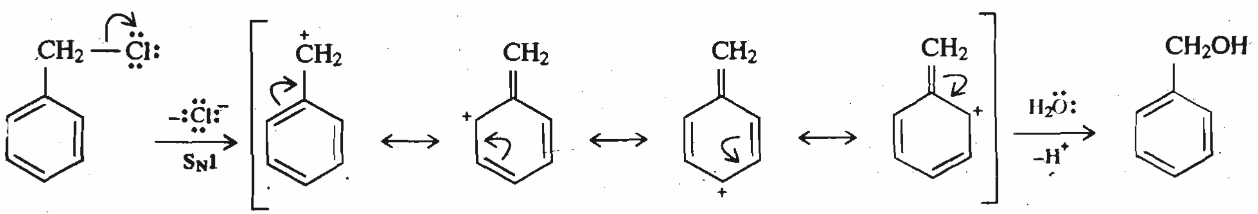
$$\updownarrow$$

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

3-chloropropene (allyl chloride)

prop-2-ene-1-ol

(Resonance structures of allyl cation)



(chloromethyl) benzene (benzyl chloride)

(resonance structure for benzyl cation)

phenylmethanol (benzyl alcohol)

Now, consider the S_N2 reactions. Allylic halides and benzylic halides also undergo S_N2 reaction at a faster rate than primary alkyl halides or even methyl halides. The reason for the greater S_N2 reactivity of allylic and benzylic halides is stability of the transition state. In the case of allylic and benzylic halides partial overlap of the π bond orbitals helps in delocalisation of the negative charge on the transition structure thus increasing the rate of the reaction (see Fig. 11.4).

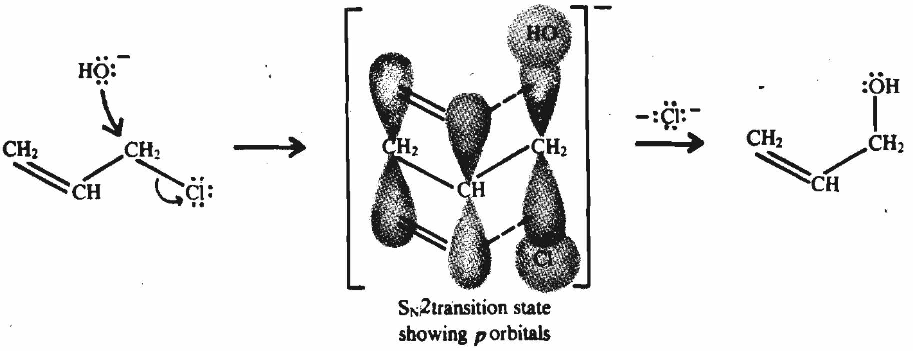
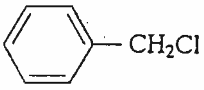
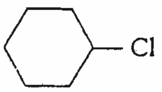
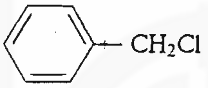
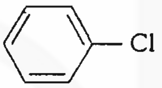


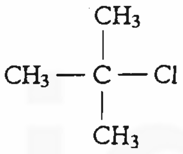
Fig. 11.4 : Stabilisation of the transition state in an S_N2 reaction of 3-chloropropene (allyl chloride), the case of (chloromethyl) benzene (benzyl chloride) is similar

SAQ 4

Which member of each of the following pairs would undergo the faster S_N2 reaction? Explain your aswer.

a)  or 

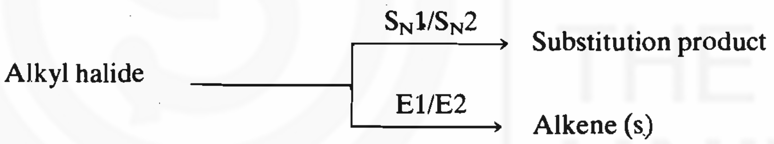
b)  or 

c)  or $(CH_3)_2CHCH_2Cl$

$CH_3-C(CH_3)_2-Cl$

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. We have already introduced such reactions in unit 7.

Like the nucleophilic substitution reactions, elimination reactions of alkyl halides can proceed by either a first or a second order mechanism. The first order elimination reaction is symbolised as E1 and the second order elimination reaction as E2.

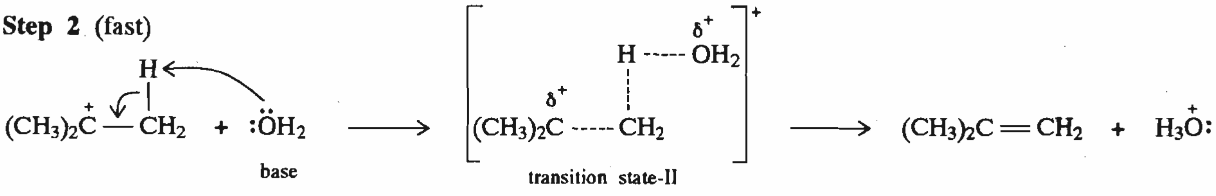
E1 reaction : In the absence of a strong base, tertiary alkyl halides, and to some extent secondary alkyl halides, dehydrohalogenate via the E1 mechanism. The mechanism has two steps.

The first step, as in S_N1 reactions is ionisation of the alkyl halide. Since, this is the slow i.e., rate determining step the E1 reaction follows first order kinetics.

Step 1 (slow)

$$(CH_3)_3C-Br \longrightarrow \underset{\text{transition state-I}}{[(CH_3)_3\overset{\delta^+}{C}\text{-----}\overset{\delta^-}{Br}]} \longrightarrow \underset{\text{carbocation intermediate}}{(CH_3)_3\overset{+}{C}} + :\ddot{B}r:^-$$

Step 2 (fast)



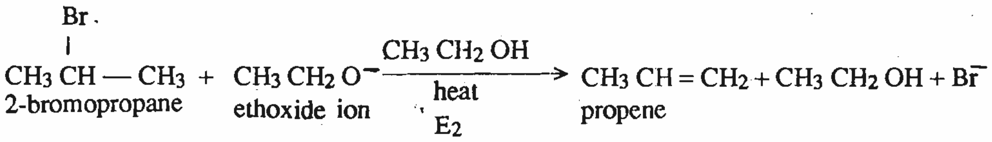
$$(CH_3)_2\overset{+}{C}-\overset{H}{\overset{|}{C}}H_2 + \underset{\text{base}}{:\ddot{O}H_2} \longrightarrow \underset{\text{transition state-II}}{\left[(CH_3)_2\overset{\delta^+}{C}\text{-----}\overset{H\text{-----}\overset{\delta^+}{O}H_2}{\overset{|}{C}}H_2\right]^+} \longrightarrow (CH_3)_2C=CH_2 + H_3\overset{+}{O}:$$

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

El reactions of alkyl halides occur under the same conditions as S_N1 reaction (polor solvent, very weak base etc.) Therefore the El reaction is a strong competitor of the S_N1 reaction. The order of reactivity of different halides types is the same in both reactions, that is *tert*>*sec*>*p*. The El reaction is favoured by the higher temperature and is most common in tertiary halides.

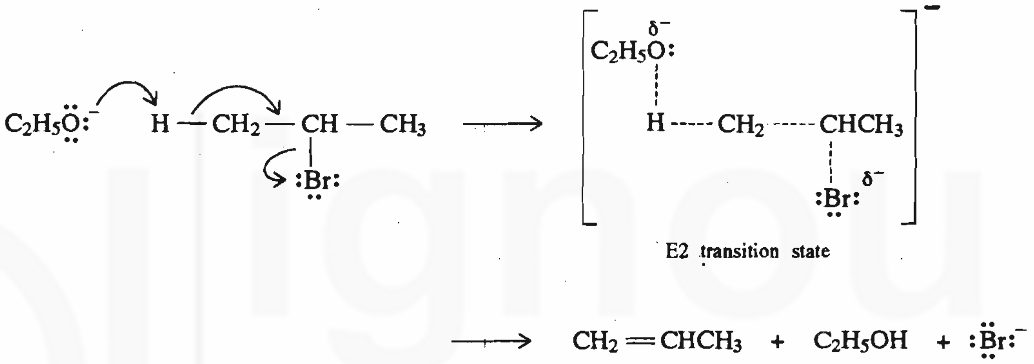
E2 elimination reaction is an example of β-elimination. In a β-elimination reaction two groups are eliminated from adjacent atoms. It is by far the most common type of elimination reaction in organic chemistry.

E2 reaction: The most useful elimination reaction of alkyl halides is the E2 reaction (bimolecular elimination). The E2 reactions of alkyl halides are favoured by the use of strong bases, such as OH^- or OR^- and high temperature. Typically the E2 reaction is carried out by heating the alkyl halide with KOH or $Na^{+-}OCH_2CH_3$ in ethanol.



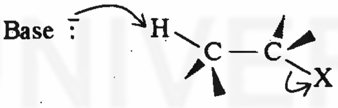
$$CH_3\overset{\overset{Br}{|}}{CH}-CH_3 + CH_3CH_2O^- \xrightarrow[\text{heat}\ E_2]{CH_3CH_2OH} CH_3CH=CH_2 + CH_3CH_2OH + Br^-$$

A mechanism consistent with the rate-law is the following one, in which the proton and the halide ion are removed simultaneously to give the alkene :



Stereochemical studies reveal that E2 elimination reactions are stereoselective *anti*-eliminations. The *anti*-elimination involves all backside electronic displacements.

Backside attack of the base on the C—X bond

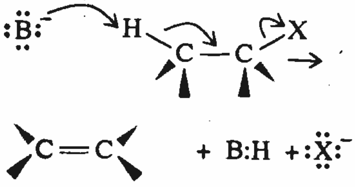


anti elimination

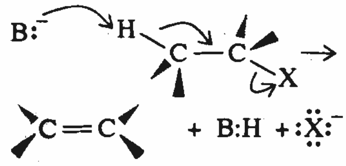
In a *syn*-elimination, H and X^- leave the alkyl halide molecule from the same side, in an *anti*-elimination, H and X^- leave from opposite sides.

An elimination reaction can occur in two stereodiamically different ways, illustrated as follows for the elimination of H—X from an alkyl halide.

Syn



anti



We have said earlier that substitution and elimination are competitive reactions; one reaction occurs at the expense of the other. Now, we consider the important variables which determine the direction of the reaction.

i) The structure of the alkyl halide
ii) The nature of the base.

From the mechanism of S_N2 & E2 reaction, it is clear that branching in alkyl halides increases the ratio of elimination to substitution :

p RX *sec* RX *tert* RX

$\longrightarrow$

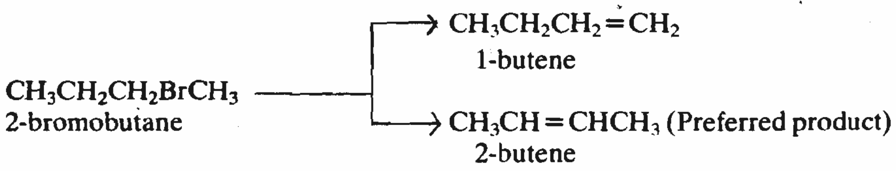
Increasing rate of E2

$\longleftarrow$

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.

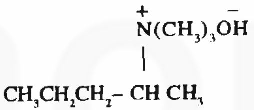
Saytzeff rule : In the alkyl halides, where the halogen is not attached to the terminal carbon atom, elimination is possible in two directions, giving two isomeric alkenes. An illustrative example is the dehydrobromination of 2-bromobutane to give 1-and 2-butenes:



In the above reaction, the major product is 2-butene. This follows the rule formulated in 1875 by Alexander Saytzeff. Saytzeff rule states that in a dehydrohalogenation reaction of alkyl halides **the major product will be the one that has the more alkyl groups attached to the resultant carbon-carbon double bond.** The rule parallels the order of thermodynamic stability of the alkenes; that is, the alkene with more alkyl groups attached to the carbon-carbon double bond is more stable.

Because of the relative stability of the resultant alkenes, tertiary halides undergo dehydrohalogenation more readily than secondary halides, which dehydrohalogenate more readily than primary halides (as we have already concluded).

Elimination reaction in quaternary ammonium hydroxides ($R_4N^+OH^-$) does not follow Saytzeff rule, but they undergo elimination reactions and yield the Hofmann product, the alkene with fewer alkyl groups on the pi-bonded carbons. Such reactions are known as **Hofmann eliminations** and follow E2 mechanism. The formation of the less substituted less stable alkene can be attributed to steric hindrance in the transition state due to the group, e.g., butyl

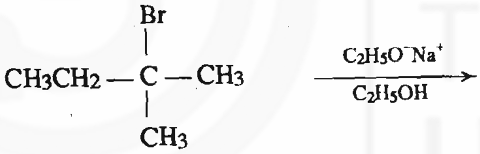


$CH_3CH_2CH_2-\underset{}{CH}(\overset{+}{N}(CH_3)_3\overset{-}{O}H)CH_3$

$\xrightarrow[\Delta]{398K}$ $CH_3CH_2CH_2CH=CH_2$
1 pentene
94%
+ $CH_3CH_2CH=CHCH_3$
2 pentene
6%

SAQ 5

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



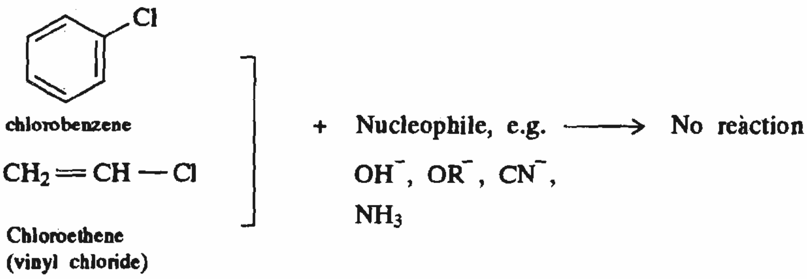
$CH_3CH_2-C(Br)(CH_3)-CH_3 \xrightarrow[C_2H_5OH]{C_2H_5O^-Na^+}$

....

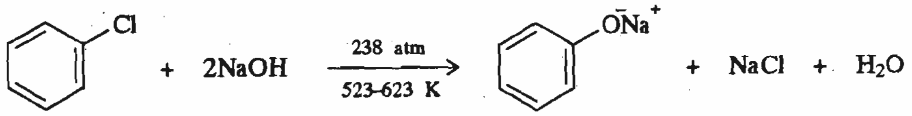
....

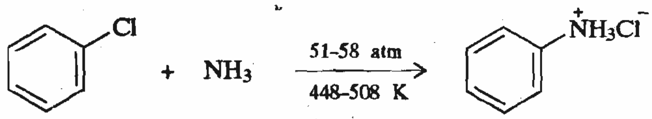
11.4.5 Chemical Properties of Aryl and Alkenyl Halides

The aryl and alkenyl halides are relatively unreactive, they do not react under ordinary conditions with NaOH, $NaOC_2H_5$, NaCN, NaSH, H_2O, or NH_3.



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

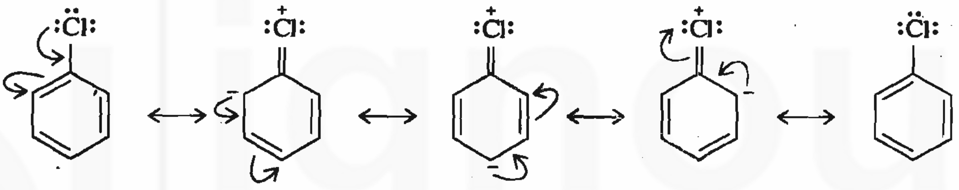




The reason for the low reactivity of the halogen atom in aryl and alkenyl halides is not quite clear. We have already encountered the one possible explanation of the low reactivity of aryl and alkenyl halides in subsection 11.4.1. The Cl atom in the C−Cl group is more tightly bound in Ar−Cl and C=C−Cl than in C−C−Cl because of the higher *s* character of sp^2 carbons. Another explanation is that due to resonance, the carbon-halogen bond in aryl and alkenyl halides acquires some double-bond character and hence the halogen atom is more strongly bound to carbon as compared to alkyl halides in which no resonance of this type exists:

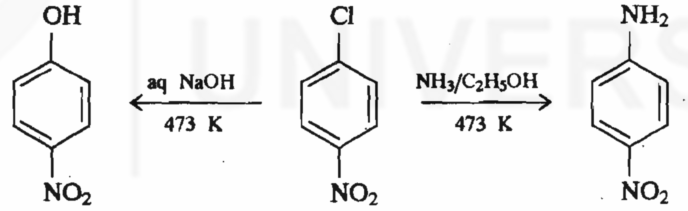
$$\mathrm{CH_2{=}CH{-}\ddot{\underset{\cdot\cdot}{Cl}}{:}} \longleftrightarrow \mathrm{\overset{-}{C}H_2{-}CH{=}\overset{+}{Cl}}$$

Chloroethene
(vinylchloride)



Chlorobenzene

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

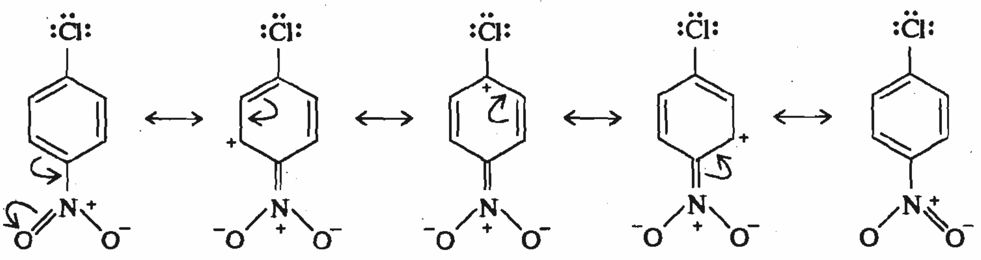


4-nitrophenol
(*p*-nitrophenol)

chloro-4-nitrobenzene
(*p*-chloronitrobenzene)

4-nitroaniline
p-nitroaniline

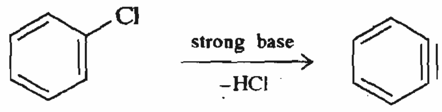
The resonance forms for the starting material (*p*-chloronitrobenzene) indicate a low electron density at the halogen-bearing carbon. Similar forms can be written for the *o*-chloronitrobenzene.



Resonance structures of chloro-nitrobenzene (*p*-chloronitrobenzene)

This facilitates attack by the hydroxide ion or other nucleophile.

Nucleophilic aromatic substitutions do not follow S_N1 and S_N2 pathways. They occur by two very different mechanism: The addition elimination mechanism and the benzyne intermediate mechanism, which involve the highly reactive elimination reaction intermediate.



chlorobenzene benzyne

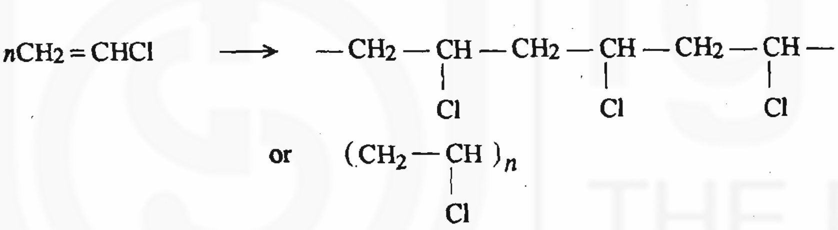
Mechanism of the nucleophilic aromatic substitutions will be described in the course of Organic Reaction Mechanism.

The aromatic ring to which halogen is attached can undergo typical electrophilic aromatic substitution reactions, which we have already discussed in Unit 9. As you would recall halogen is deactivating and *ortho*, *para* directing.

Elimination reactions of chloroethene (vinyl chloride) are less difficult, it is converted to ethyne by heating with base

$$CH_2{=}CH{-}Br+NaOH \xrightarrow{\text{heat}} HC{\equiv}CH+NaBr+H_2O$$

Chloroethene (vinyl chloride) undergoes polymerisation in the presence of radical initiators like peroxides to give polyvinyl chloride (PVC):



$$nCH_2=CHCl \longrightarrow -CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-$$

$$\text{or}\quad (CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}})_n$$

So far we have been concerned with the nucleophilic substitution and elimination reactions of halogen derivatives. Now let us look at the reactions of these compounds with metals. But, before that try the following SAQ.

SAQ 6

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

....

....

....

11.5 ORGANOMETALLIC COMPOUNDS

Alkyl, aryl and alkenyl halides, when treated with metallic alloys, from organometallic compounds, in which carbon is bonded directly to a metal atom (R–M). For example, the reaction of chloroethane with a sodium lead alloy under pressure gives tetraethyl-lead.

$$\underset{\text{chloroethane}}{4C_2H_5{-}Cl}+4Na/Pb \longrightarrow \underset{\text{tetraethyl-lead}}{(C_2H_5)_4Pb}+4NaCl$$

As stated earlier, tetramethyl and tetraethyl-lead are used as anti-knock additives to petrol.

Halogen derivatives of hydrocarbons are widely used to prepare **Grignard reagents** (organomagnesium halides), RMgX. These reagents are among the most useful classes of a compound in organic synthesis. A Grignard reagent is generally prepared by the reaction between magnesium and alkyl or aryl or ethenyl halide in dry aprotic solvent such as alcohol free ether.

$$\text{R—X, Ar—X or } CH_2{=}CHX \xrightarrow[\text{dry ether}]{\text{Mg in}} \underbrace{\text{RMgX, ArMgX, } CH_2{=}CHMgX}_{\text{Grignard reagent}}$$

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

Grignard reagents are highly reactive compounds because the carbon-magnesium bond is strongly polarised, making the carbon atom both nucleophilic and strongly basic. Grignard reagents, therefore, participate nucleophilic addition reaction. The mechanism of the nucleophilic addition of Grignard reagents to carbonyl group will be discussed in detail in unit 14. Grignard reagents are used to prepare a large variety of organic compounds. Some of the important reactions are:

i) Preparation of alkanes: Alkanes are prepared by the reaction of Grignard reagents with water, alcohols, ammonia, amines etc.:

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

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

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

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

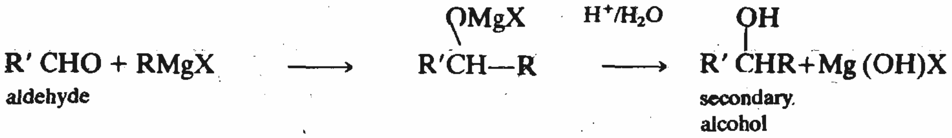
ii) Preparation of alcohols: Primary alcohols are obtained either by the reaction of methanal and Grignard reagent followed by treatment with dilute acid:

$$\underset{\substack{\text{methanal}\\\text{(formaldehyde)}}}{HCHO} + RMgX \longrightarrow RCH_2OMgX \xrightarrow{H^+/H_2O} \underset{\text{primary alcohol}}{RCH_2OH} + Mg(OH)X$$

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

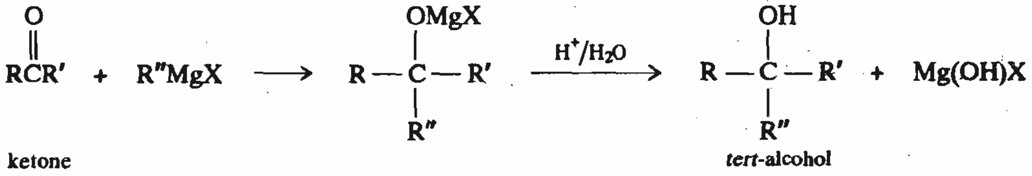
$$RMgX + \underset{\text{oxygen}}{O_2} \longrightarrow RO_2MgX \xrightarrow{RMgX} 2ROMgX \xrightarrow{H^+/H_2O} \underset{\substack{\text{primary}\\\text{alcohol}}}{2ROH} + 2Mg(OH)X$$

Secondary alcohols are obtained when a Grignard reagent is treated with any aldehyde (other than methanal) followed by decomposition of the addition product with a dilute acid:



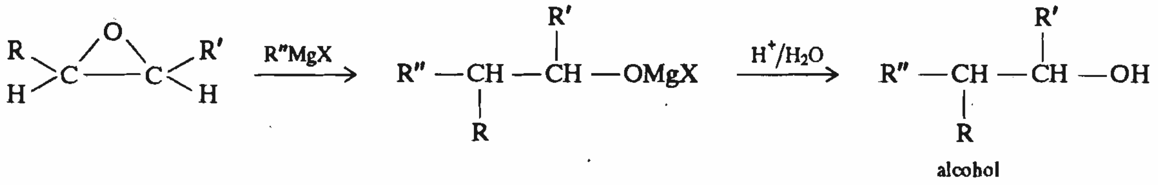
$$\underset{\text{aldehyde}}{R'CHO} + RMgX \longrightarrow R'\overset{OMgX}{CH}—R \xrightarrow{H^+/H_2O} \underset{\substack{\text{secondary}\\\text{alcohol}}}{R'\overset{OH}{C}HR} + Mg(OH)X$$

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

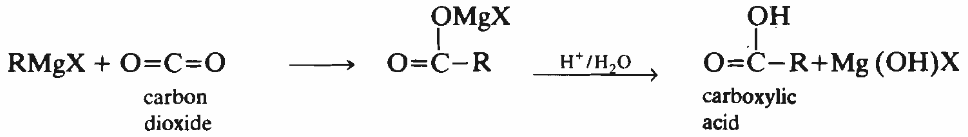


$$\underset{\text{ketone}}{R\overset{O}{\overset{\|}{C}}R'} + R''MgX \longrightarrow R—\underset{R''}{\overset{OMgX}{C}}—R' \xrightarrow{H^+/H_2O} \underset{\textit{tert}\text{-alcohol}}{R—\underset{R''}{\overset{OH}{C}}—R'} + Mg(OH)X$$

Alcohols are also obtained when epoxides are reacted with Grignard reagent and the addition product is hydrolysed with dilute acid:



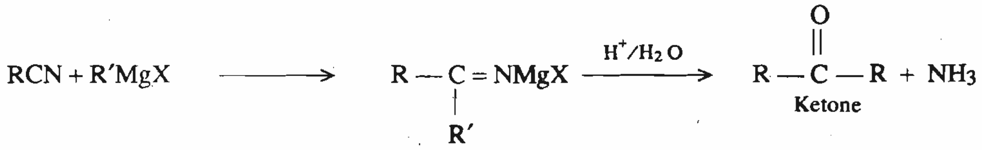
iii) Preparation of carboxylic acids: The reaction of a Grignard reagent with carbon dioxide followed by decomposition of the addition product by dilute acid gives a carboxylic acid:



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

carbon dioxide; carboxylic acid

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



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

Ketone

Using the reactions discussed above, attempt the following SAQ.

SAQ 7

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

....

....

....

....

11.6 POLYHALOGEN DERIVATIVES

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

11.6.1 Dihalogen Derivatives

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

$$\underset{\text{ethanal}}{CH_3CHO} + PCl_5 \longrightarrow \underset{\text{1,1-dichloroethane}}{CH_3CHCl_2} + POCl_3$$

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

$$\underset{\text{ethyne}}{CH{\equiv}CH} + HBr \longrightarrow \underset{\text{bromoethene}}{CH_2{=}CHBr} + HBr \longrightarrow \underset{\text{1,1-dibromoethane}}{CH_3CHBr_2}$$

We have already discussed this reaction in unit 8.

As mentioned in unit 7, vic or 1, 2-dihalides are prepared by the addition of halogens to alkenes, e.g.,

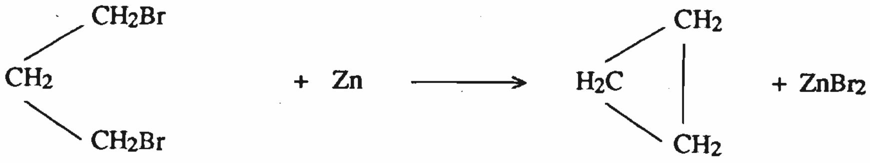
$$\underset{\text{propene}}{CH_3CH{=}CH_2+Br_2} \longrightarrow \underset{\text{1,2-dibromopropane}}{CH_3CHBrCH_2Br}$$

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:



1, 3-dibromopropane   cyclopropane

In section 11.2 we mentioned some polyhalogen compounds derived from methane, i.e. dichloromethane (methylene chloride), trichloromethane (chloroform) and tetrachloromethane (carbon tetrachloride). These compounds are commercially important substances as they are widely used as solvents in laboratory and industry. In the following section we will discuss the chemistry of trichloromethane, a trihalogen derivative of methane.

11.6.2 Trihalogen Derivatives

One of the familiar examples of trihalogen derivatives is trichloromethane (chloroform). Trichloromethane was used as an anaesthetic till recently. Trichloromethane is prepared in the laboratory or industry by heating ethanol or propanone (acetone) with bleaching powder. The steps are:

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

$$CH_3CH_2OH + Cl_2 \longrightarrow CH_3CHO + 2HCl$$

ethanol; from bleaching powder; ethanal (acetaldehyde)

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

ethanal; trichloroethanal

$$2CCl_3CHO + Ca(OH)_2 \longrightarrow 2CHCl_3 + (HCO_2)_2Ca$$

trichloromethane; calcium methanoate (calciumformate)

Bleaching powder provides chlorine which oxidises ethanol to ethanal in the first step and chlorinates the latter to trichloroethanal or trichloroacetaldehyde (chloral) in the second step. The reaction of tichloroethanal and calcium hydroxide (present in the bleaching powder) gives trichloromethane and calcium methanoate in the third step. When propanone (acetone) is used in place of ethanol, trichloropropane is formed in the first step which on reaction with calcium hydroxide gives trichloromethane and calcium ethanoate in the final step:

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

propanone; trichloropropanone

$$2CCl_3COCH_3 + Ca(OH)_2 \longrightarrow 2CHCl_3 + (CH_3CO_2)_2Ca$$

trichloromethane; calcium 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 sweet-smelling, colourless liquid. On boiling with alkali, it gives methanoate ion:

$$CHCl_3 + 4OH^- \longrightarrow 3Cl^- + HCOO^- + 2H_2O$$

trichloro methane; methanoate ion

On warming trichloromethane with silver powder, ethyne is obtained:

$$\underset{\text{trichloro methane}}{2CHCl_3} + 6Ag \longrightarrow \underset{\text{ethyne}}{HC{\equiv}CH} + 6AgCl$$

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

$$\underset{\text{trichloromethane}}{CHCl_3} + HNO_3 \longrightarrow \underset{\text{trichloronitromethane}}{CCl_3NO_2} + H_2O$$

Trichloromethane is kept in well-stoppered dark coloured bottles, filled up to the brim, to avoid its oxidation to carbonyl chloride (phosgene), which is a poisonous gas. About 1% ethanol is added to convert any phosgene formed to harmless ethyl carbonate.

$$\underset{\text{trichloro methane}}{CHCl_3} + 1/2O_2 \longrightarrow \underset{\text{Carbonyl chloride (phosgene)}}{COCl_2} + HCl$$

$$COCl_2 + 2C_2H_5OH \longrightarrow \underset{\text{ethyl carbonate}}{(C_2H_5)_2CO_3} + 2HCl$$

On heating trichloromethane with a primary amine and ethanolic potassium hydroxide, isocyanide is formed which has a bad smell. This reaction is called **carbylamine reaction,** a delicate test for trichloromethane and also for primary amines.

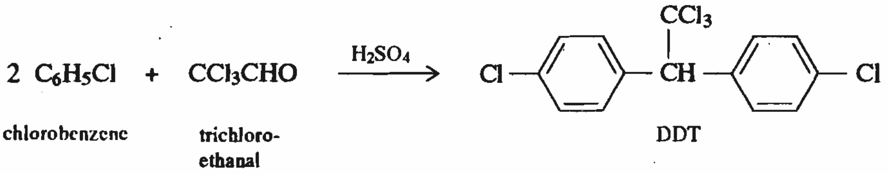
$$\underset{\text{trichloro methane}}{CHCl_3} + \underset{\text{amine}}{RNH_2} + 3KOH \longrightarrow \underset{\text{(isocyanide)}}{RNC} + 3KCl + 3H_2O$$

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

Triiodomethane (iodoform) is prepared on a commercial scale by a similar method described above for tribromomethane. In place of potassium bromide, potassium iodide is used. Triiodomethane is a yellow crystalline solid, insoluble in water but soluble in ethanol or ether. It is used as an antiseptic.

11.7 USES OF HALOGEN DERIVATIVES

Many chloro compounds are used as insecticides, e.g., DDT. [2, 2-bis (*p*-chlorophenyl) 1,1,1-trichloroethane or *p*, *p*-dichlorodiphenyl trichloroethane, BHC (benzene hexachloride). DDT is manufactured by heating chlorobenzene and trichloroethanal with concentrated sulphuric acid.



Commercial DDT is a mixture of 75% *p,p'*- compound, 20% *o,p'* compound and 5% of other impurities. Most countries have banned the use of DDT, it is poisonous to human and it tends to concentrate in the environment owing to its slow degradation, the half life being 10 years. Similarly the insecticide-benzene hexachloride (BHC) also causes environmental pollution. We have mentioned the preparation of BHC in unit 9. Hexachloroethane is used as a moth repellant.

Chlorofluorocarbons (CFCs) are derivatives of methane and ethane which used as refrigerants and as aerosol propellants under the name of Freons. Freon-12, CF_2Cl_2, is the most commonly used refrigerant. The extensive use of CFCs is believed to have led to depletion of ozone layer in the atmosphere. CFCs are prepared by the action of hydrogen fluoride on tetrachloromethane (carbon tetrachloride), trichloromethane and hexachloroethane. Tetrafluoroethene ($CF_2{=}CF_2$) on polymerisation gives a plastic **Teflon.** It is unaffected by chemical reagents, even by boiling aqua regia. It is widely used as a liner in frying pans and on other utensils and tools to provide nonsticking surfaces. Polychlorofluoroethenes are used as oils and greases. Perfluoroheptane is used in the separation of uranium isotopes. Poly (chloroethene) or polyvinyl chloride (PVC) is a plastic material of commercial importance.

11.8 LAB DETECTION

The presence of halogen in an organic compound is readily detected by the **Beilstein test.** In this test a small amount of the compound is placed on a small loop of copper wire, and the loop heated in a flame. A green flame is evidence of the presence of halogen. To ascertain which halogen is present, the covalently bonded halogen has to be converted to the halide ion which can then be identified by the usual methods of inorganic qualitative analysis. This is done by two methods; through sodium fusion (treatment with hot molten sodium metal):

$$\mathrm{Na} + \underset{\substack{\text{organic}\\ \text{compound}}}{\mathrm{RX}} \xrightarrow{\text{heat}} \mathrm{Na^+X^-}$$

or through Schoniger oxidation by oxygen gas under alkaline condition

$$\underset{\substack{\text{organic}\\ \text{compound}}}{\mathrm{RX}} + \mathrm{O_2} \xrightarrow{\text{NaOH}} \mathrm{Na^+X^-} + \mathrm{H_2O}$$

In alkyl halides, benzyl halides and allyl halides the presence of halogen can be detected by warming the organic compound with alcoholic silver nitrate. The silver halide formed can be analysed further.

$$\mathrm{RX} + \mathrm{AgNO_3} \longrightarrow \mathrm{AgX(s)}\downarrow + \mathrm{RONO_2}$$

However, aryl halides and alkenyl halides will not react with alcoholic silver nitrate.

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

11.9 SUMMARY

In this unit we have described the chemistry of halogen derivatives of hydrocarbons. We are summarising below what we have studied:

- Substitution of one or more hydrogen atoms in hydrocarbons by a halogen atom(s) gives rise to halogen derivatives: alkyl halides, aryl halides and alkenyl halides. Monohalogen derivatives of alkyl halide can be further classified as primary, secondary and tertiary halides depending on the alkyl group to which halogen is attached.

- Alkyl halides can be prepared from alcohols, from alkanes, from Grignard reagents and through halogenation of hydrocarbon in the presence of light or heat and/or catalysts.

- The halogen in alkyl halides can be replaced by various nucleophiles. Reaction occur by two different pathways, S_N1 and S_N2. Benzyl and allyl halides are more reactive than alkyl halides. Aryl and vinyl halides are least reactive and they do not follow S_N2 and S_N1 paths. The reactivity order of halides is allyl>benzyl > alkyl > aryl or vinyl. However, when a strong electron-withdrawing group is present in *ortho*-or/and *para*-position to the halogen atom in the benzene ring, the reactivity of the aryl halide is enhanced.

- Alkyl halides undergo elimination reaction (dehydrohalogenation) to give alkenes. These reactions occur by the El or E2 pathway. If the halides are such that the loss of a hydrogen on adjacent carbon (β hydrogen) can occur from either side, isomeric alkenes are formed. Usually, the most stable i.e. more highly substituted alkene is formed as the major product (Saytzeff rule).

- Alkyl or aryl halides react with magnesium to form alkyl or aryl magnesium halides called the Grignard reagents. They are very reactive compounds and take part in many reactions to give alkanes, alcohols (primary, secondary and tertiary), ketones and carboxylic acids, etc.
- The di- and tri-halogen derivatives of alkanes are also reactive compounds.
- The halogen derivatives are very useful in industry. The chloro compounds are powerful insecticides and moth repellants. The chlorofluoro compounds (Freons) are refrigerants and aerosol propellants. Polymerisation of vinyl chloride and tetrafluoroethylene gives plastic in the name PVC and teflon, respectively.
- The halogen can be detected as halide ion. Infrared spectroscopy can be used to infer the presence of halogen in organic compounds.

11.10 TERMINAL QUESTIONS

1) Write the equations for the following reactions:

   a) $CH_3CH_2CH_2CH_2Br + NaOH\,(aq) \longrightarrow$

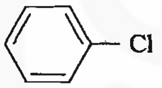
   b) $C_6H_5CH_2Cl + H_2O \longrightarrow$

   c) $CH_3CH_2CH_2Br + NaSH \longrightarrow$

2) Complete the equations given below:

   a) $CH_3CH_2CH_2Br + Na^{+-}OCH_2CH_3 \longrightarrow$

   b) $C_6H_5CH_2Cl + AgNO_3 + H_2O \longrightarrow$

   c)  + $AgNO_3 \longrightarrow$

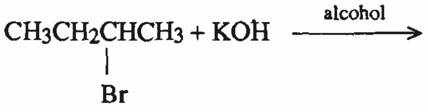
3) Write the equation for each of the following reactions:

   a) 2, 4-dinitrochlorobenzene and sodium hydroxide

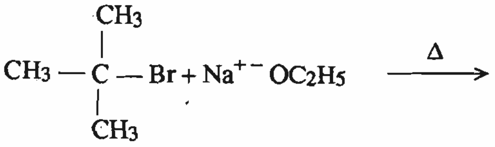
   b) 2, 4-dinitrochlorobenzene and sodium phenoxide ($C_6H_5O^-Na^+$)

   c) 2, 4-dinitrochlorobenzene and ammonia

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

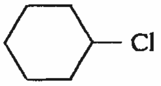
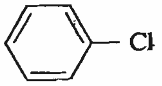
   a) 

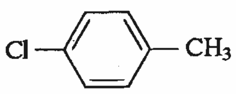
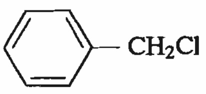
$$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 + KOH \xrightarrow{\text{alcohol}}$$

   b) 

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

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

   a)  and 

   b)  

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

11.11 ANSWERS

Self Assessment Questions

1) a) Primary alkyl halide

b) tertiary alkyl halide

c) secondary alkyl halide

2) a) $C_6H_5-CH_2CH_3 + Br_2 \longrightarrow C_6H_5CHBrCH_3 + HBr$

ethylbenzene 1-bromo-1-phenylethane

b) $CH_3CHOHCH_3 \xrightarrow{HBr} CH_3CHBrCH_3$

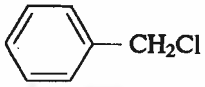
c) $CH_3CH=CH_2 \xrightarrow[peroxide]{HBr} CH_3CH_2CH_2Br$

d) $CH_3CHOHCH_3 \xrightarrow[Heat]{HCl} CH_3CHClCH_3$

3) Increasing order of boiling point of following alkyl halides:

$CH_3Cl<CH_2Cl_2<CHCl_3<CCl_4$

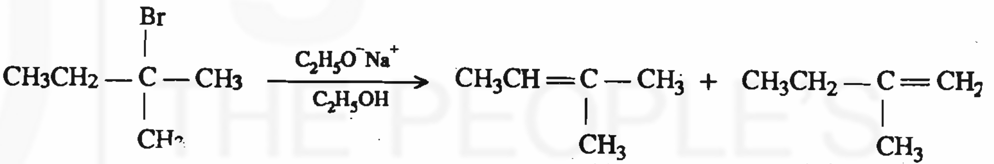
Since molecular weight of compounds is also increasing in the same order

4) a) 

b) (Chloromethyl) benzene (benzyl chloride) undergoes S_N2 reaction at a faster rate than chlorobenzene. The reason for greater S_N2 reactivity of (chloromethyl) benzene is the stability of transition state. Further, the low reactivity of chlorobenzene is attributed to the stronger Ar—Cl bond.

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

5) Over all reaction can be written as



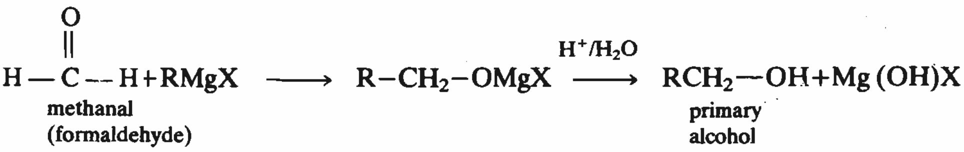
$$CH_3CH_2-\underset{CH_3}{\overset{Br}{C}}-CH_3 \xrightarrow[C_2H_5OH]{C_2H_5O^-Na^+} CH_3CH=\underset{CH_3}{C}-CH_3 + CH_3CH_2-\underset{CH_3}{C}=CH_2$$

(I) (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.

6) There are two reasons (1) the Cl atom in C—Cl group is more tightly bond in Ar—Cl and C=C—Cl than C—C—Cl because of higher *s* character of sp^2 carbon (ii) as shown in section 11.4, due to the resonance Ar—Cl and C=C—Cl acquire some double bond character.

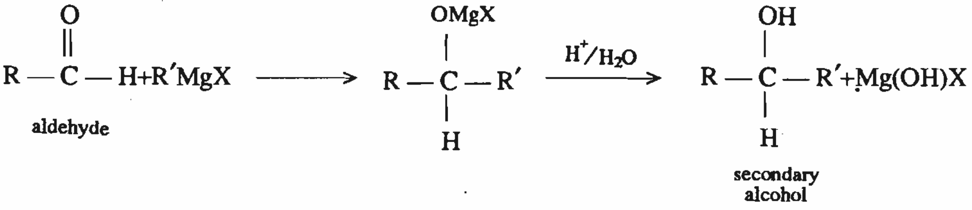
7) Primary alcohols are prepared by the reaction of Grignards reagents with methanal and followed by hydrolysis.



$$H-\overset{O}{\overset{\|}{C}}-H+RMgX \longrightarrow R-CH_2-OMgX \xrightarrow{H^+/H_2O} RCH_2-OH+Mg(OH)X$$

methanal (formaldehyde) primary alcohol

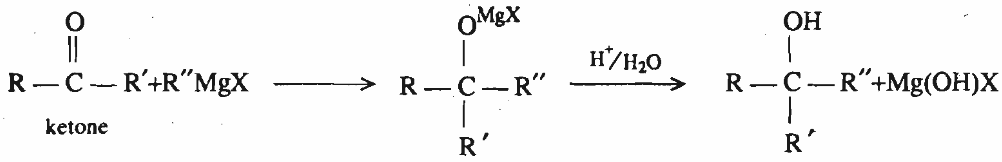
Secondary alcohols are obtained when a Grignard reagent reacts with an aldehydes (other than methanal) followed by hydrolysis.



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

aldehyde secondary alcohol

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



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

tertiary alcohol

Terminal Questions

1) a) $CH_3CH_2CH_2Br + NaOH(aq) \longrightarrow CH_3CH_2CH_2OH + NaBr$

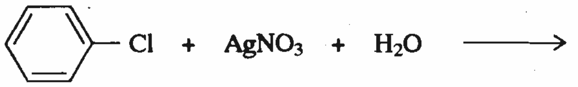
b) $C_6H_5CH_2Cl + H_2O \longrightarrow C_6H_5CH_2OH + HCl$

c) $CH_3CH_2CH_2Br + NaSH \longrightarrow CH_3CH_2CH_2SH + NaBr$

2) a) $CH_3CH_2CH_2Br + Na^{+-}OCH_2CH_3 \longrightarrow CH_3CH{=}CH_2 + CH_3CH_2OH + NaBr$

b) $C_6H_5CH_2Cl + AgNO_3 + H_2O \longrightarrow C_6H_5CH_2OH + AgCl$

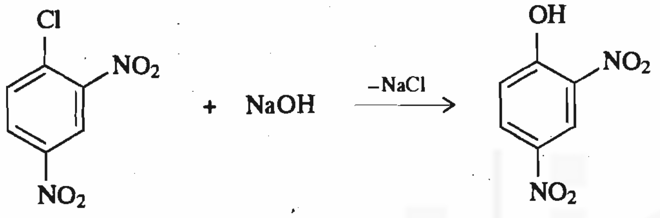
c)



$+ AgNO_3 + H_2O \longrightarrow$ no reaction.

3)

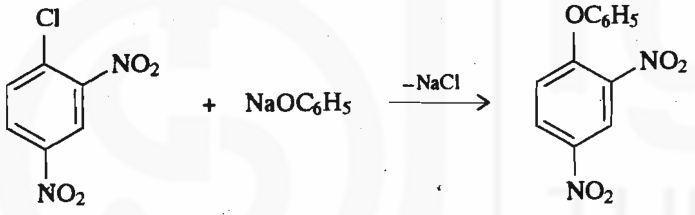
a)



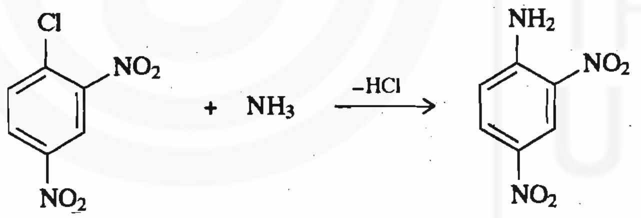
2,4-dinitrochlorobenzene

2,4-dinitrophenol

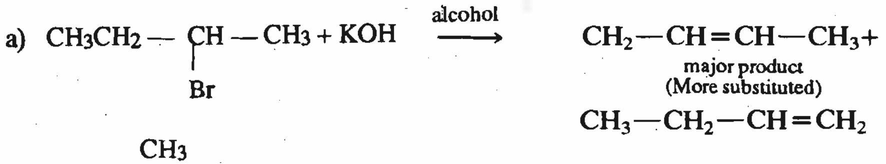
b)



c)

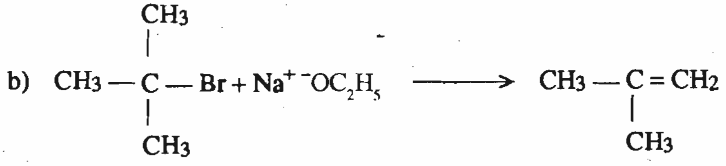


4) a)



$$CH_3CH_2-\underset{Br}{\underset{|}{CH}}-CH_3 + KOH \xrightarrow{\text{alcohol}} \underset{\substack{\text{major product}\\\text{(More substituted)}}}{CH_2-CH{=}CH-CH_3} + CH_3-CH_2-CH{=}CH_2$$

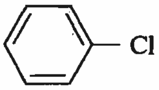
b)



$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-Br + Na^{+-}OC_2H_5 \longrightarrow CH_3-\underset{CH_3}{\underset{|}{C}}{=}CH_2$$

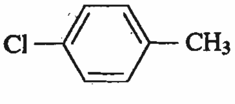
5) Following pairs can be distinguished by the action of alcoholic $AgNO_3$ reagent with the halides.

a) With alcoholic $AgNO_3$



will not react

b)



also will not react with alcoholic $AgNO_3$

c) $CH_3CH{=}CHCl$ also will not react with $AgNO_3$.

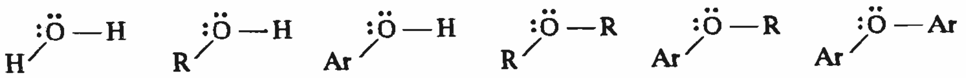
UNIT 12 ALCOHOLS AND PHENOLS

Structure

12.1 INTRODUCTION

In the previous Unit, we described the halogen derivatives of hydrocarbons.In this Unit and in subsequent Units we will discuss oxygen-containing organic compounds.

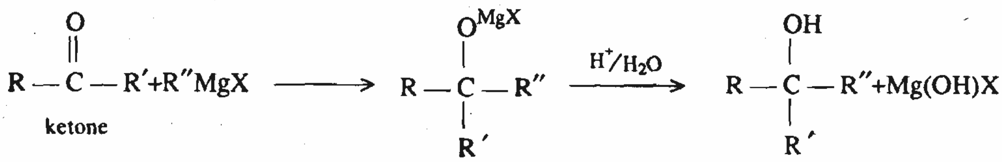
Alcohols and phenols can be regarded as monoalkyl and monoaryl substitution products of water, respectively. Similarly ether can also be considered a derivative of water in which both the hydrogen atoms of the water molecule have been replaced by alkyl or aryl groups or by both. We shall study the chemistry of ethers in Unit 13.



In this unit we shall take up alcohols and phenols. They may also be defined as hydroxy derivatives of hydrocarbons. Alcohols and phenols provide us with a great number of useful products, which include germicides, antifreeze agents, pharmaceuticals, explosives, solvents and plastics.

Here, first we will discuss the classification of alcohols and phenols, and then give you an outline of the different methods available for the preparation of alcohols and phenols. We will then review the physical properties of alcohols and phenols. The chemical properties of alcohols and phenols will be considered separately as the two types of compounds differ widely in their chemical behaviour. We will also take up the industrial uses of alcohols and phenols and the precautions to be taken in their handling. Finally, we will consider the methods employed for their detection.

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



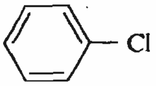
$$\underset{\text{ketone}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-R'} + R''MgX \longrightarrow R-\overset{\overset{\displaystyle OMgX}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-R'' \xrightarrow{H^+/H_2O} \underset{\text{tertiary alcohol}}{R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle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

Terminal Questions

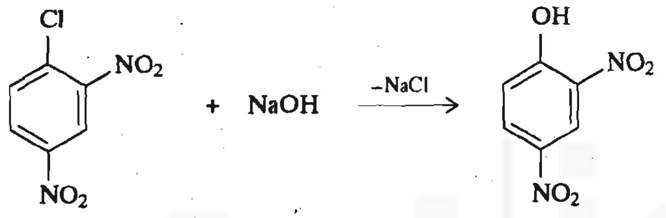
1) a) $CH_3CH_2CH_2Br + NaOH(aq) \longrightarrow CH_3CH_2CH_2OH + NaBr$
   b) $C_6H_5CH_2Cl + H_2O \longrightarrow C_6H_5CH_2OH + HCl$
   c) $CH_3CH_2CH_2Br + NaSH \longrightarrow CH_3CH_2CH_2SH + NaBr$

2) a) $CH_3CH_2CH_2Br + Na^{+-}OCH_2CH_3 \longrightarrow CH_3CH{=}CH_2 + CH_3CH_2OH + NaBr$

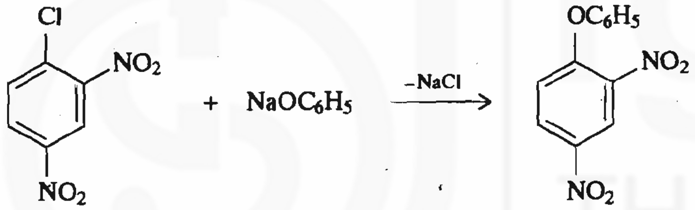
   b) $C_6H_5CH_2Cl + AgNO_3 + H_2O \longrightarrow C_6H_5CH_2OH + AgCl$

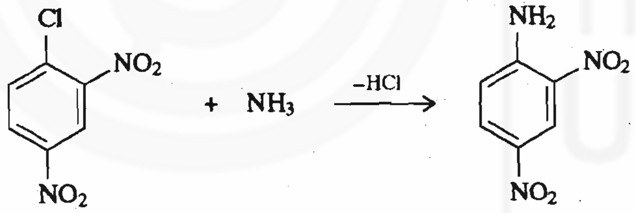
   c)  + $AgNO_3$ + H_2O $\longrightarrow$ no reaction.

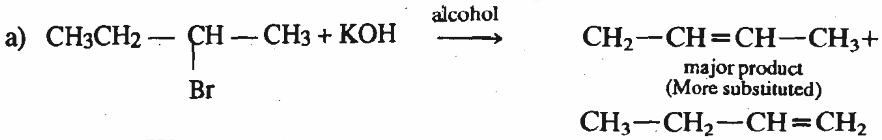
3)

a) 

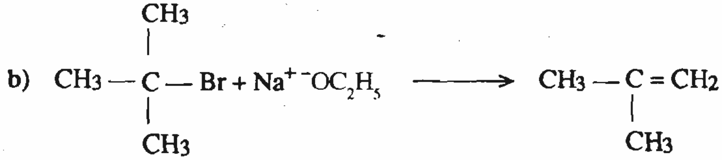
2,4-dinitrochlorobenzene   2,4-dinitrophenol

b) 

c) 

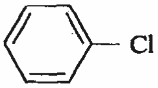
4) a) 

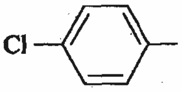
$$CH_3CH_2-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3 + KOH \xrightarrow{\text{alcohol}} \underset{\substack{\text{major product}\\\text{(More substituted)}}}{CH_2-CH{=}CH-CH_3} + CH_3-CH_2-CH{=}CH_2$$

b) 

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Br + Na^{+-}OC_2H_5 \longrightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH_2$$

5) Following pairs can be distinguished by the action of alcoholic $AgNO_3$ reagent with the halides.

   a) With alcoholic $AgNO_3$  will not react

   b)  also will not react with alcoholic $AgNO_3$

   c) $CH_3CH{=}CHCl$ also will not react with $AgNO_3$.

UNIT 12 ALCOHOLS AND PHENOLS

Structure

12.1 INTRODUCTION

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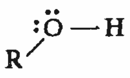

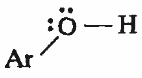

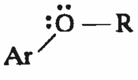

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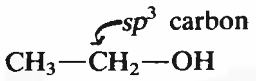
Objectives

After studying this unit, you should be able to:

- classify alcohols and phenols,
- outline the preparation of alcohols and phenols,
- decribe the commercial methods for manufacture of alcohols and phenols,
- define the physical and spectral properties of alcohols and phenols,
- explain the comparative reactivity of primary, secondary and tertiary alcohols, and phenols,
- describe the reactions of alcohols and phenols,
- list and describe the industrial uses of alcohols and phenols, and
- describe the laboratory detection of alcohols and phenols.

12.2 CLASSIFICATION

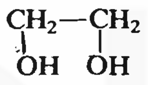
Hydrocarbons in which an sp^3 carbon carries a hydroxyl (−OH) group are called alcohols. Depending on the number of hydroxyl groups present in the molecule, alcohols are called monohydric (1 −OH group), dihydrics (2 −OH groups), trihydric (3 −OH groups) or polyhydric (more than 3 −OH groups).



$$CH_3—\overset{sp^3\ \text{carbon}}{CH_2}—OH$$

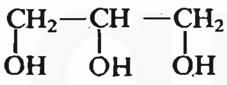
ethanol
(ethyl alcohol)

monohydric alcohol



$$\underset{OH}{CH_2}—\underset{OH}{CH_2}$$

1,2-ethanediol
or ethane-1,2 diol
(glyc
dihydric alcohol



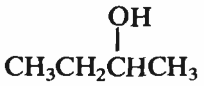
$$\underset{OH}{CH_2}—\underset{OH}{CH}—\underset{OH}{CH_2}$$

1,2,3-propanetriol
or propane-1,2,3, triol
(glycerol)
trihydric alcohol

Monohydric alcohols, like the alkyl halides, may be subdivided into primary, secondary and tertiary alcohols. Primary alcohols contain a $-CH_2-OH$ group, secondary alcohols contain the $R_2CH—OH$ group and tertiary alcohols contain the $R_3C—OH$ group. For example, the molecular formula C_4H_9OH can represent the following four monohydric alcohols:

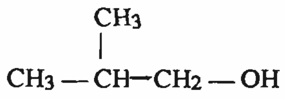
$$CH_3CH_2CH_2CH_2-OH$$

1-butanol
(butyl alcohol)
primary alcohol



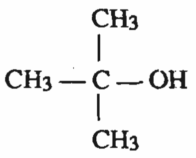
$$CH_3CH_2\overset{OH}{C}HCH_3$$

2-butanol
(secondary butyl alcohol)
secondary alcohol



$$CH_3—\overset{CH_3}{CH}—CH_2—OH$$

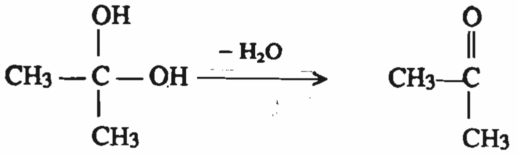
2-methyl-1-propanol
(isobutyl alcohol)
primary alcohol



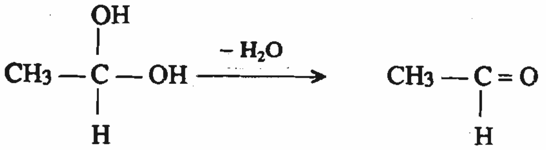
$$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—OH$$

2-methyl-2-propanol
(*tert* butyl alcohol)
tertiary alcohol

Unlike gem dihalides gem diols are unstable as they undergo dehydration to the corresponding aldehyde or ketone.

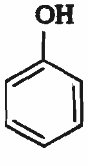


$$CH_3{-}\overset{OH}{\underset{CH_3}{C}}{-}OH \xrightarrow{-H_2O} CH_3{-}\overset{O}{\underset{CH_3}{C}}$$

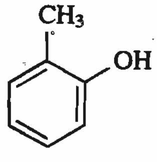


$$CH_3{-}\overset{OH}{\underset{H}{C}}{-}OH \xrightarrow{-H_2O} CH_3{-}\underset{H}{C}{=}O$$

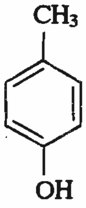
Phenols are aromatic compounds in which hydroxyl groups are attached to the benzene nucleus so they have the hydroxyl group on an aryl sp^2-hybridised carbon. Phenols are classified as mono, di or tri hydric on the basis of the number of $-OH$ groups present in the ring. Some examples of phenols are given below.



benzenol
(phenol)

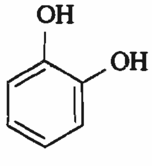


2-methylbenzenol
(*o*-cresol)

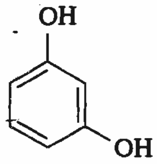


4-methylbenzenol
(*p*-cresol)

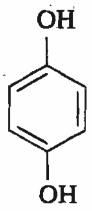
Monohydric phenols



1,2-benzenediol
(catechol)

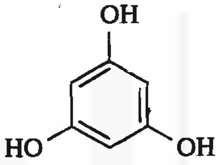


1,3-benzenediol
(resorcinol)

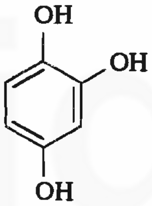


1,4-benzenediol
(quinol or hydroquinone)

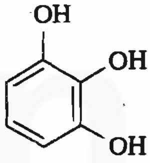
Dihydric phenols



1,3,5-benzenetriol
(phloroglucinol)



1,2,4-benzenetriol
(hydroxyquinol)



1,2,3-benzenetriol
(pyrogallol)

Trihydric phenols

Common names of important phenols are still widely used, therefore, in this text we use both common names and IUPAC names.

Replacement of oxygen in alcohols and phenols by sulphur gives thioalcohols and thiophenol, respectively. We will consider the chemistry of thioalcohol and thiophenols in Unit 14. Let us now turn to the preparation of alcohols and phenols.

12.3 PREPARATION OF ALCOHOLS AND PHENOLS

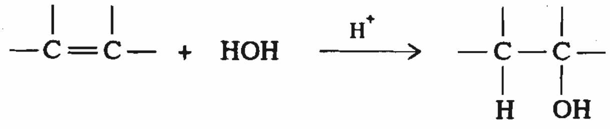
In this section, we will first consider the general methods for the laboratory preparation of alcohols and phenols and then take up the industrial preparation of a few important members of the two classes of compounds.

12.3.1 General Methods of the Preparations of Alcohols

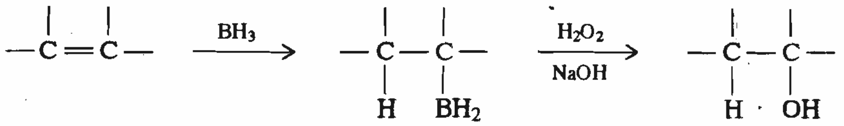
Alcohols can be prepared from alkenes, alkyl halides, esters, ethers, aldehydes, ketones and from the Grignard reagents. General reactions of these methods of preparation are summarised below in Table 12.1.

Table 12.1: Preparation of Alcohols

From alkenes



$$-\overset{|}{C}{=}\overset{|}{C}- + HOH \xrightarrow{H^+} -\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-$$



$$-\overset{|}{C}{=}\overset{|}{C}- \xrightarrow{BH_3} -\underset{H}{\overset{|}{C}}-\underset{BH_2}{\overset{|}{C}}- \xrightarrow[NaOH]{H_2O_2} -\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-$$

From alkyl halides

$R{-}X + OH^-/H_2O \longrightarrow ROH + X^-$

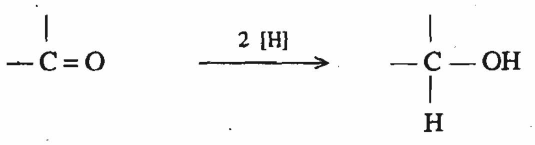
From esters

$$RCOOR' + OH^- + H_2O \longrightarrow RCOOH + R'OH$$
$$\text{or } H^+/H_2O$$

From ethers

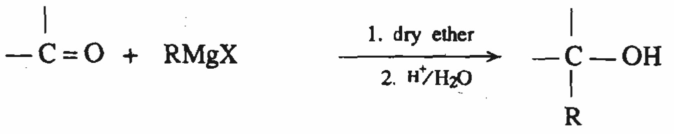
$$R{-}O{-}R + H_2O \xrightarrow{H_2SO_4} 2ROH$$

From aldehydes and ketones



$$-\overset{|}{C}=O \xrightarrow{2\,[H]} -\underset{H}{\overset{|}{\underset{|}{C}}}-OH$$

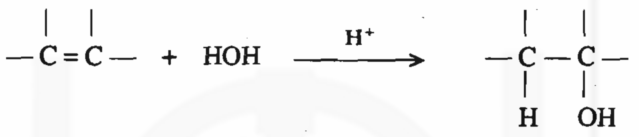
From Grignard reagents



$$-\overset{|}{C}=O + RMgX \xrightarrow[2.\ H^+/H_2O]{1.\ \text{dry ether}} -\underset{R}{\overset{|}{\underset{|}{C}}}-OH$$

Let us study these methods of preparation in a brief manner.

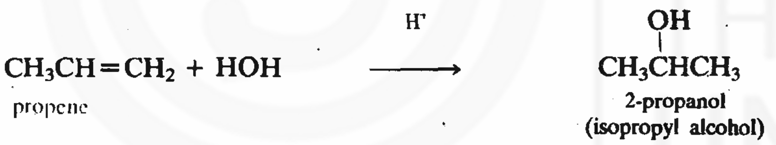
i) **From Alkenes:** We have already described the acid catalysed hydration of **alkenes** in Unit 7. In this reaction the direction of addition is governed by the Markownikoff's rule. The general reaction is,



$$-\overset{|}{C}=\overset{|}{C}- + HOH \xrightarrow{H^+} -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-$$

This method is employed for the preparation of several alcohols:

$$\underset{\text{ethene}}{CH_2{=}CH_2} + HOH \xrightarrow{H^+} \underset{\text{ethanol}}{CH_3CH_2{-}OH}$$

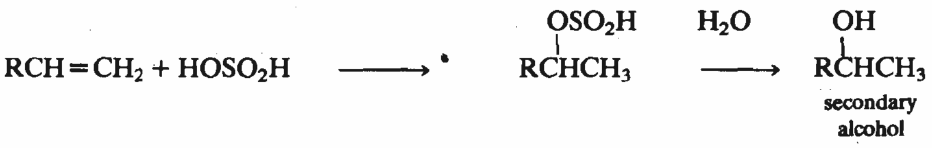


$$\underset{\text{propene}}{CH_3CH{=}CH_2} + HOH \xrightarrow{H^+} \underset{\substack{\text{2-propanol}\\ \text{(isopropyl alcohol)}}}{CH_3\overset{\overset{OH}{|}}{C}HCH_3}$$

If sulphuric acid is used as the acid catalyst the reaction proceeds as follows:

$$\underset{\text{ethene}}{CH_2{=}CH_2} + \underset{\text{sulfuric acid}}{HOSO_2OH} \longrightarrow \underset{\text{ethyl hydrogensulphate}}{CH_3CH_2OSO_2OH}$$

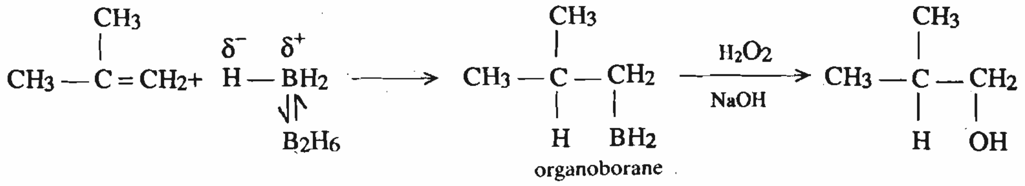
$$CH_3CH_2OSO_2OH \xrightarrow{H_2O} \underset{\text{ethanol}}{CH_3CH_2OH + H_2SO_4}$$



$$RCH{=}CH_2 + HOSO_2H \longrightarrow R\overset{\overset{OSO_2H}{|}}{C}HCH_3 \xrightarrow{H_2O} \underset{\substack{\text{secondary}\\ \text{alcohol}}}{R\overset{\overset{OH}{|}}{C}HCH_3}$$

These reactions are useful for laboratory synthesis as well as industrial preparation of alcohols.

Hydroboration-oxidation method is also important because it leads to overall, effective anti-Markownikeft addition of water. We have already described this method in Unit 7. In this method diborane, B_2H_6, is allowed to react with alkene in an inert solvent such as ether. Diborane is in ready equilibrium with the Lewis acid borane, BH_3, which adds to the alkene. Here the electron seeking (acidic) part of reagent is boron, and addition of BH_3 proceeds according to Markowni Koff's rule to give an intermediate organoborane compound. Oxidation of this intermediate with basic hydrogen peroxide convert it to an alcohol.

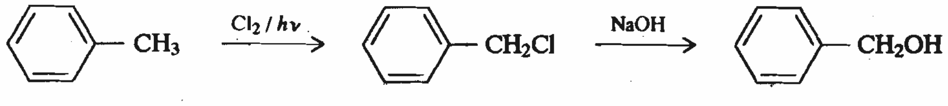


$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2+\underset{\underset{B_2H_6}{\rightleftharpoons}}{\overset{\delta^-}{H}-\overset{\delta^+}{BH_2}}\longrightarrow \underset{\text{organoborane}}{CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{BH_2}{|}}{CH_2}}\xrightarrow[NaOH]{H_2O_2}CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{CH_2}$$

ii) From Alkyl Halides: Hydrolysis of alkyl halides with an aqueous solution of an alkali is a common and convenient method for the synthesis of alcohols, e.g.,

$$\underset{\text{alkyl halide}}{R-X}\ +\ \underset{\text{aqueous alkali solution}}{OH^-/H_2O}\longrightarrow \underset{\text{alcohol}}{R-OH}+X^-$$

These reactions can proceed via S_N1 or S_N2 mechanism which we have described in Unit 11. A useful application of this method is in the synthesis of phenylmethanol (benzyl alcohol) from (chloromethyl) benzene (benzyl chloride) which is itself obtained from methylbenzene (toluene) as shown below:



methylbenzene (chloromethyl) benzene phenylmethanol

iii) From Esters: Alcohols may be prepared by base or acid catalysed hydrolysis of esters.

$$\underset{\text{esters}}{RCOOR'}\ +\ \underset{\text{or } H^+/H_2O}{OH^-/H_2O}\longrightarrow \underset{\text{carboxylic acid}}{RCOOH}+\underset{\text{alcohol}}{R'-OH}$$

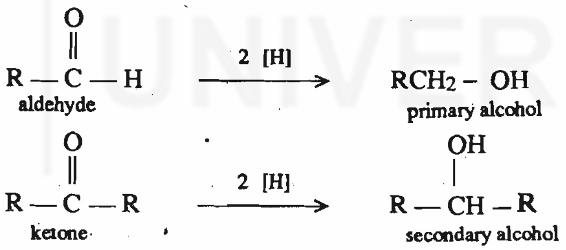
This method is used industrially as certain alcohols occur in nature as esters.

iv) From Ethers: Alcohols are also obtained by heating ethers with dilute sulphuric acid under pressure:

$$C_2H_5-O-C_2H_5+H_2O\xrightarrow{H_2SO_4}\underset{\text{ethanol}}{2C_2H_5-OH}$$

This method is important industrially as ethers are formed as by-products in the preparation of some alcohols. We will discuss this reaction further in detail in Unit 13.

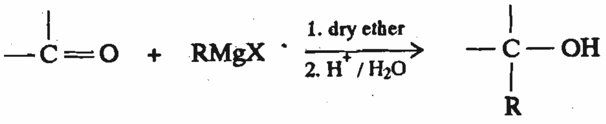
v) From Aldehydes and Ketones: Alcohols are also obtained by the reduction of aldehydes and ketones with sodium and ethanol or H_2/Ni or by metal hydrides, such as lithium aluminium hydride. Aldehydes give primary alcohols, ketones secondary alcohols.



$$\underset{\text{aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H}\xrightarrow{2\ [H]}\underset{\text{primary alcohol}}{RCH_2-OH}$$

$$\underset{\text{ketone}}{R-\overset{\overset{O}{\|}}{C}-R}\xrightarrow{2\ [H]}\underset{\text{secondary alcohol}}{R-\overset{\overset{OH}{|}}{CH}-R}$$

vi) From Grignard Reagents: Primary, secondary and tertiary alcohols are also prepared by the reaction of suitable carbonyl compound with the Grignard reagent. We have already studied this method in Unit 11.



$$-\overset{|}{C}=O\ +\ RMgX\xrightarrow[2.\ H^+/H_2O]{1.\ \text{dry ether}}-\underset{\underset{R}{|}}{\overset{|}{C}}-OH$$

SAQ 1

Write chemical equation, showing all necessary reagents, for the preparation of 2-butanol by each of the following methods:

a) hydration of an alkene ....

b) hydrolysis of an alkyl halide ....

c) use of a Grignard reagent ....

d) reduction of a ketone ....

12.3.2 General Methods of the Preparation of Phenols

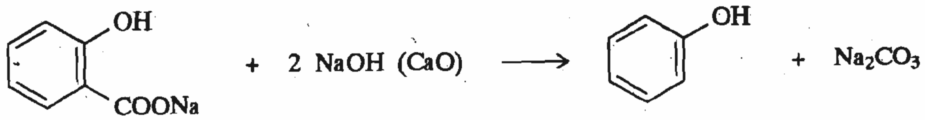
Phenols can be prepared from arylsulphonic acid, phenolic acids, diazonium salts and from Grignard reagents. General reactions of these methods of preparation are summarised below in Table 12.2.

Table 12.2: Preparation of Phenol

Fusion of arylsulphonates with sodium hydroxide

$$ArSO_3Na \xrightarrow[2.\ H^+]{1.\ 573\ K/NaOH} \underset{\text{Phenol}}{Ar{-}OH}$$

Heating phenolic acid with soda-lime



Boiling diazonium salt with water

$$ArN_2{}^+X^- + H_2O \longrightarrow Ar-OH + HX + N_2$$

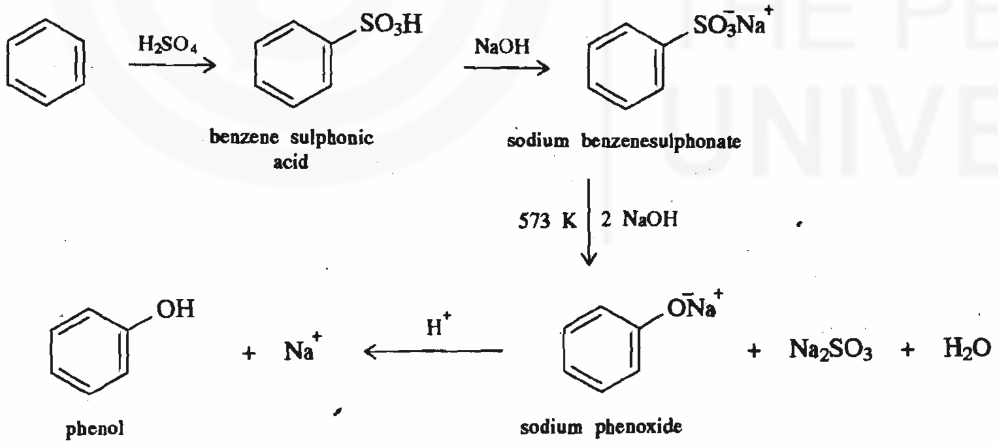
Action of oxygen on Grignard reagent followed by hydrolysis

$$2ArMgX + O_2 \longrightarrow 2ArOMgX \xrightarrow{H^+/H_2O} 2Ar-OH$$

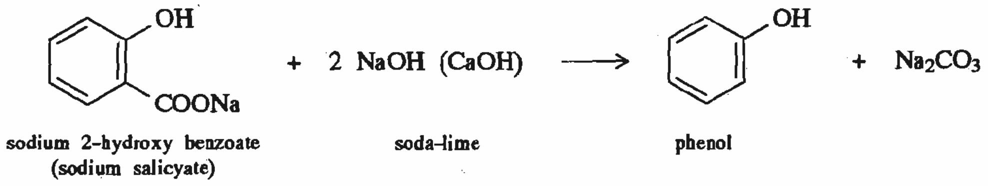
Let us study these reactions one by one.

i) Fusion of arylsulphonates with sodium hydroxide:

Phenol may be prepared by the fusion of sodium benzenesulphonate obtained through sulphonation of benzene (Unit 9), with sodium hydroxide. The sodium phenoxide produced in the reaction is converted into the free phenol by treatment with acid.

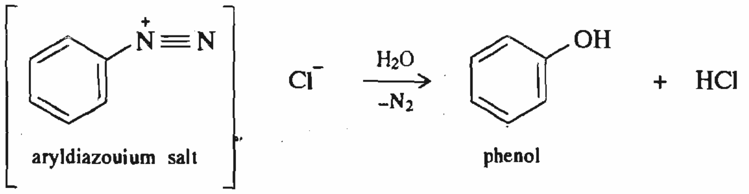


ii) Decarboxylation phenolic acids with soda-lime:



iii) Boiling diazonium salt with water:

Aromatic amines react with nitrous acid to give diazonium salts which, unlike their aliphatic analogues, are stable at low temperature and can be isolated. The aqueous solution of the salt decomposes to phenol on boiling with evolution of N_2.



iv) Action of oxygen on Grignard reagent followed by hydrolysis:

Just as Grignard reagent adds to CO_2, aryl Grignard reagents add to molecular oxygen.

The intermediate reacts with another molecule of the Grignard reagent and hydrolysis of the product gives phenol.

$$ArMgBr + O_2 \longrightarrow Ar{-}O{-}O{-}MgBr \xrightarrow{ArMgBr}$$

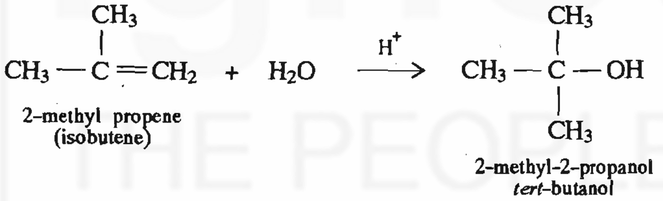
$$2\ Ar{-}O{-}MgBr \xrightarrow{H^+/H_2O} 2Ar{-}OH + 2\,Mg(OH)Br$$

12.3.3. Commercial Preparation of Alcohols and Phenols

Alcohols and phenols are of great commercial importance. In this section you will learn how large quantities of these compounds are prepared from different abundant natural sources.

i) Commercial preparation of alcohols

a) **By the catalytic hydration of alkenes in dilute acid solution:** We have already come across the conversion of alkenes to alcohol in connection with the general methods for small scale preparation of alcohols. The method has been extended to commercial preparations of some alcohols, such as ethanol and 2-propanol. The reactions for the preparation of ethanol and 2-propanol have been already shown. Similarly, hydration of 2-methylpropene (isobutene) in aqueous acidic medium gives *tert*-butanol.



$$CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2 + H_2O \xrightarrow{H^+} CH_3{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}OH$$

2-methyl propene (isobutene)

2-methyl-2-propanol *tert*-butanol

In a recent modification ethene is hydrated directly by passing a mixture of the alkene and steam over a solid acid catalyst (phosphoric acid or silica at 573 K at a pressure of about 70 atmospheres:

$$\underset{\text{ethene}}{CH_2{=}CH_2} + H_2O \xrightarrow[70\ \text{atm}]{573\ \text{K}} \underset{\text{ethanol}}{CH_3CH_2OH}$$

b) **By heating a mixture of carbon monoxide and hydrogen under pressure in the presence of a catalyst:** This method is used for the preparation of methanol.

$$CO + 2H_2 \xrightarrow[533\ \text{K},\ 150\ \text{atm}]{\text{Cu Catalyst}} CH_3OH$$

c) **By the oxidation of natural gas:** A mixture of methanol, ethanol, propanols and butanols is obtained. Catalytic oxidation of methane gives methanol:

$$CH_4 + \frac{1}{2}O_2 \xrightarrow[473\ \text{K}]{\text{Cu tube}} CH_3OH$$

d) **Fermentation of starch:** This method has been the source of ethanol, the constituent of alcoholic beverages responsible for their intoxicating action, since times immemorial. Common sources of starch are wheat, barley, potato, etc. These are mashed with hot water and heated with malt (germinated barley) which contains the enzyme 'diastase'. Enzymatic hydrolysis of starch at 323 K gives the sugar maltose:

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} + \frac{n}{2}H_2O \xrightarrow{\text{diastase}} \frac{n}{2}\underset{\text{maltose}}{C_{12}H_{22}O_{11}}$$

The product is cooled to 303 K and fermented with yeast, which contains various enzymes. One of these, 'maltase', converts maltose to glucose and the other 'zymase' decomposes glucose to ethanol:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{maltase}} \underset{\text{glucose}}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} \underset{\text{ethanol}}{2C_2H_5OH} + 2CO_2$$

Enzymes are a particularly important group of proteins. They are the catalysts which enable living organism to bring about necessary reactions.

Fermentation of molasses (a by-product of sugar industry) also gives ethanol.

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}+H_2O} \xrightarrow{\text{invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} \underset{\text{ethanol}}{2C_2H_5OH} + 2CO_2$$

Ethanol may also be prepared from glucose directly. Grape juice, a rich source of glucose, ferments to produce wine with a maximum alcoholic content of approximately 12% by volume. The alcoholic content of liquors is usually designated in terms of **proof spirit,** 100 proof indicating an alcoholic content of about 50% by volume. The term "proof spirit" supposedly has its origin in an early and rather crude analytical procedure for determining the alcoholic content of whisky. Whisky of high alcoholic content, when poured onto the gunpowder would ignite and burn with a flame sufficiently hot to ignite the powder also. This was 'proof' of spirit content. If the gunpowder failed to ignite, the presence of too much water was indicated, as the powder would have become too wet to burn.

Absolute ethanol: Regardless of the methods of manufacture, all aqueous solutions of ethanol yield, on fractional distillation, a 'constant boiling mixture' of 95 per cent ethanol and 5 per cent water, known as **rectified spirit.** A constant boiling mixture of two or more liquids, called an **azeotrope,** cannot be separated by fractional distillation. In order to obtain **absolute,** or 100% pure ethanol, water has to be removed by methods other than fractionation. In the laboratory, rectified spirit is refluxed over quicklime for about 6 hours, and then allowed to stand overnight. On distillation this gives 99.5 or lime distilled alcohol. The remaining water is removed by reaction with magnesium metal, by which water is converted into insoluble $Mg(OH)_2$.

In industry, calculated amount of benzene is added to the rectified spirit. Distillation of the mixture yield three fractions:

At 338 K, a constant boiling mixture of ethanol, benzene and water (a 'ternary azeotrope').

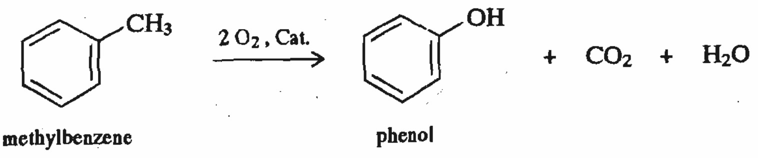
At 341 K, a constant boiling mixture of ethanol and benzene (a 'binary azeotrope').

At 351 K, pure ethanol or absolute alcohol.

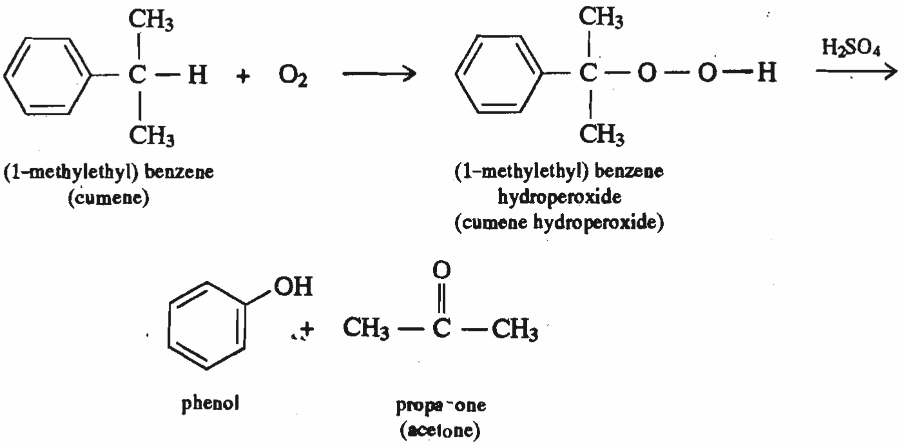
ii) **Commercial preparation of phenols: From natural sources:** On a commercial scale, phenols are obtained from coal tar. Coal tar is fractionated and the middle oil is cooled when napthalene crystallises out. The liquid is treated with aqueous sodium hydroxide which dissolves phenols. Carbon dioxide is passed into the liquid and the aqueous layer is separated. Fractionation gives phenol (20%), cresols (43%), xylenols (26%) and the residue is pitch. A similar treatment of the heavy oil also gives di- and trihydroxy phenols.

From other aromatic hydrocarbons:

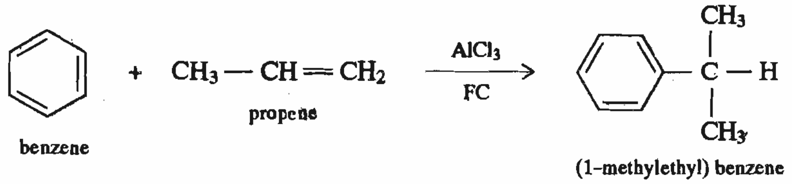
a) Phenol can be obtained by the catalytic oxidation of methylbenzene by air in the presence of manganous and cupric salts.



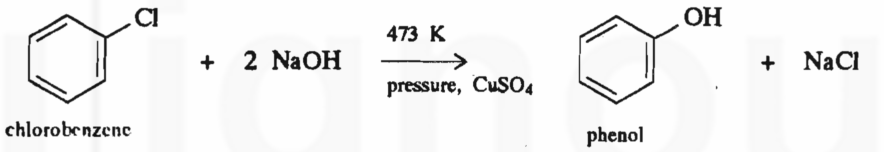
b) **The cumene process:** Oxidation of (1-methylethyl) benzene (cumene or isopropylbenzene) to hydroperoxide followed by decomposition by acid gives phenol and an important by product propanone (acetone):



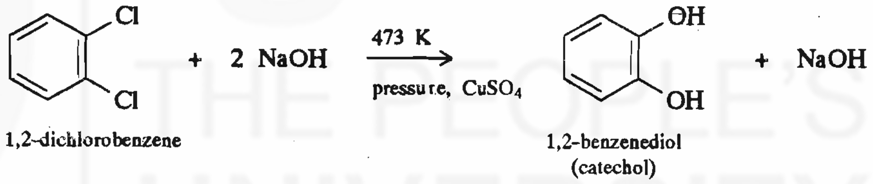
(1-Methylethyl) benzene is made almost exclusively from benzene and propene via a Friedel-Crafts reaction.



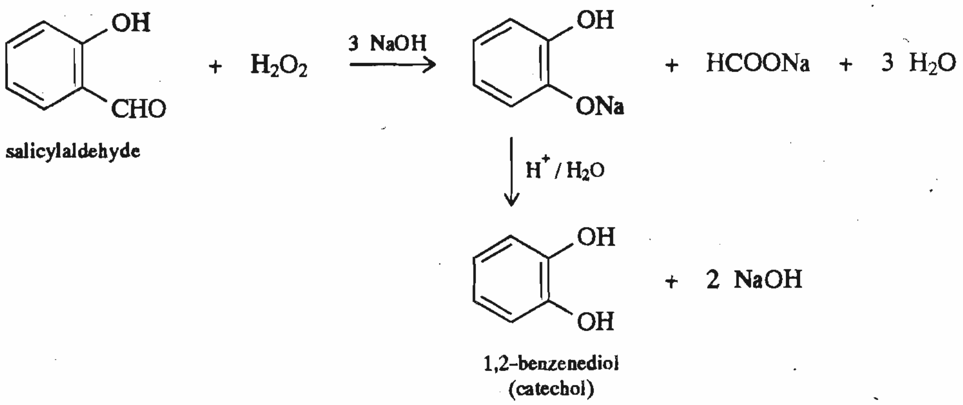
c) **The Dow process:** Chlorobenzene and sodium hydroxide react high temperature and under pressure in the presence of a catalyst (copper salts) to give phenols.



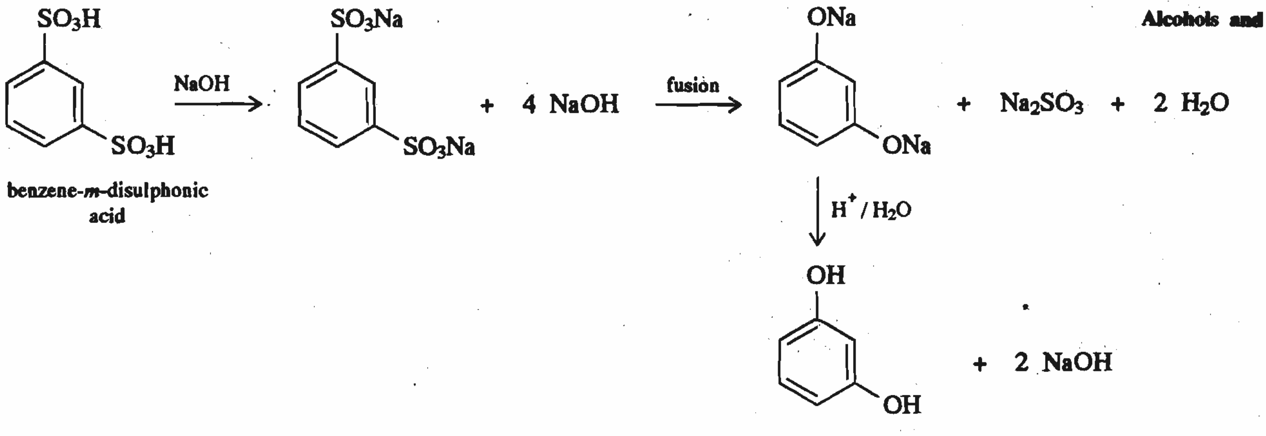
when this process is applied to 1,2-dichlorobenzenes catechol is obtained,



d) Catechol can be conveniently prepared by the action of alkaline hydrogen peroxide on salicylaldehyde. The reaction is an example of Baeyer, Villiger rearrangement which you will study in Unit 11 of the course 'Organic Reaction Mechanism'.



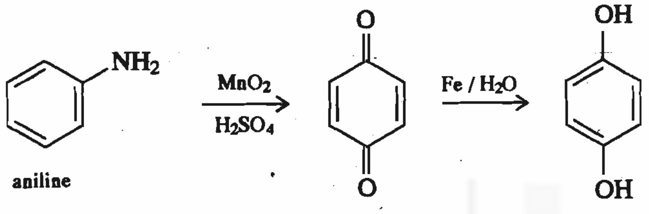
e) Resorcionol is prepared industrially by the alkaline fusion of benzene *m*-disulphonic acid:



benzene-*m*-disulphonic acid

1,3-benzenediol (resorcinol)

f) Quinol is made commercially by the oxidation of aniline with manganese dioxide and sulphuric acid. The product *p*-benzoquinone is reduced to quinol with iron and hot water.

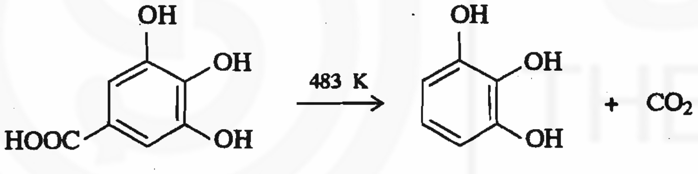


aniline

p-benzoquinone

1,4-benzenediol (quinol)

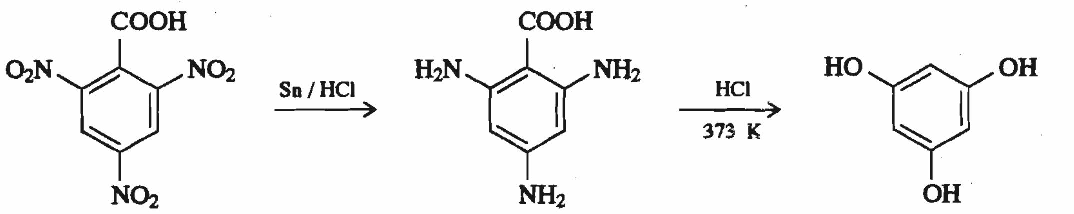
g) Pyrogallol is prepared by heating gallic acid (3,4,5-trihydroxybenzoic acid) in a stream of carbon dioxide or by heating an aqueous solution of gallic acid at 483 K under pressure:



(3,4,5-trihydroxybenzoic acid) (gallic acid)

1,2,3-benzenetriol (pyrogallol)

h) Phloroglucinol is obtained by the fusion of many plant resins with alkali. It is also prepared by the reduction of 2,4,6-trinitrobenzoic acid to the amino derivative followed by reaction of hot hydrochloric acid.



2,4,6-trinitrobenzoic acid

1,3,5-benzenetriol (phloroglucinol)

SAQ 2

Complate the following reactions

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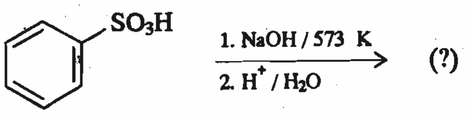

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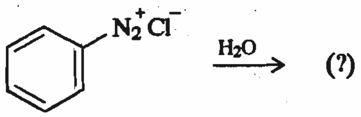

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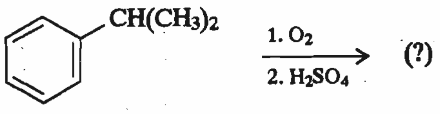
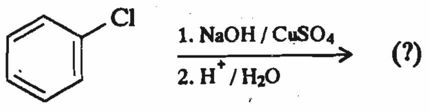
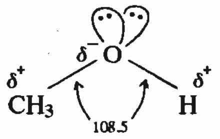


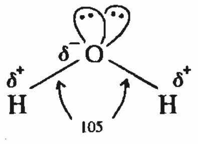
d)


12.4 PHYSICAL PROPERTIES

Physical properties of alcohols can be understood if we consider again the fact that alcohols are similar in structure to water. Oxygen in alcohol molecule is in the sp^3 hybridised state and has two unshared pairs of valence electrons. Like the hydroxyl groups in water, the hydroxyl group in alcohols is polar.

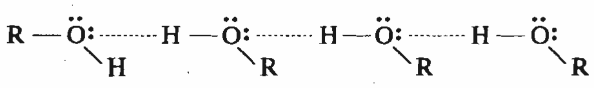


methanol



water

As might be expected, alcohols like water are strongly hydrogen bonded. The formation of hydrogen bonds leads to association of a large number of alcohol molecules. These molecular association have to be broken up before boiling occurs. Hence, the high boiling point of alcohol is observed when compared to other molecules of the same size.



hydrogen bonding in alcohol molecules

Table 12.3 compares the boiling points of some alcohols and chloro compounds with the same carbon skeletons.

Table 12.3: Comparison of the boiling points of some alcohols and chloroalkanes

Alcohols	Bp, K	Chloroalkane	Bp, K
CH_3-OH	337	CH_3-Cl	249
CH_3CH_2-OH	351	CH_3CH_2-Cl	286
$CH_3CH_2CH_2-OH$	370	$CH_3CH_2CH_2-Cl$	319

Further in a group of isomeric alcohols, the primary alcohol has the highest boiling point and the tertiary, the lowest, with the secondary having an intermediate value. In the straight chain compounds, the van der Waal's attractive forces are relatively large due to the large surface area. In the branched chain structures, the molecule tends to become spherical and hence with the decrease in surface area the attractive forces are small. Physical properties of some alcohols are summarised in Table 12.4.

Table 12.4: Physical properties of some alcohols

IUPAC Name	Common name	Formula	Bp. K	Density Kg dm^{-3}	Solubility in H_2O
Methanol	methyl alcohol	CH_3-OH	337	0.79	infinite
Ethanol	ethyl alcohol	CH_3CH_2-OH	351	0.79	infinite
1-Propanol	propyl alcohol	$CH_3CH_2CH_2-OH$	370	0.80	infinite
2-Propanol	isopropyl alcohol	$(CH_3)_2CH-OH$	355	0.79	infinite
1-Butanol	butyl alcohol	$CH_3(CH_2)_3-OH$	380	0.81	8.3 g/100cm^3

The water solubility of lower alcohols can also be explained by their ability to form hydrogen bonds with water molecule.

hydrogen bonding in water molecules

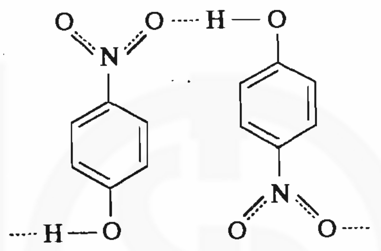
Solubility of alcohols in water decreases as the length of the hydrocarbon chain of the alcohol molecule increases. As discussed in Unit 4, the hydrocarbon character of the molecule, i.e., hydrophobic character increases in higher alcohols.

Like alcohols, phenols also have high boiling points and moderate solubility in water because of hydrogen bonding. On exposure to air and light they turn pink due to auto-oxidation. Physical properties of some phenols are summarised in Table 12.5.

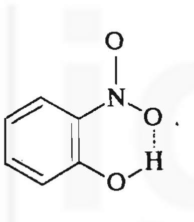
Table 12.5: Physical properties of some phenols

Name	Mp, K	Bp, K	Solubility g/100g H_2O
Phenol	314	455	9.3
Catechol	377	—	45.0
Resorcinol	383	—	123.0
Hydroquinone	446	—	8.0
o-Nitrophenol (volatile in steam)	318	—	0.2
p-Nitrophenol (nonvolatile in steam)	387	—	1.7

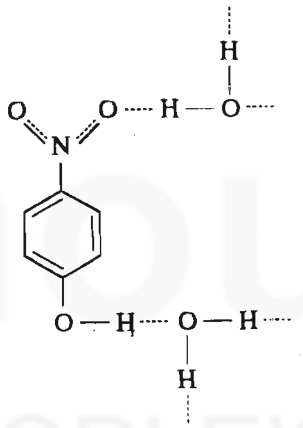
In Table 12.5, we notice that *ortho* and *para* isomers of nitrophenol differ considerably in their physical constants. How are we to account for these differences? Let us see how these isomers undergo hydrogen bonding:



Intermolecular hydrogen bonding *p*-nitrophenol



Intramolecular hydrogen bonding *o*-nitrophenol



hydrogen bonding with water molecules

From the above we can expect that the *p*-isomer should have a higher melting point and solubility in water due to the **intermolecular hydrogen bonding** and its association with water molecules. On the other hand, *o*-nitrophenol which has **intramolecular hydrogen bonding** or hydrogen bonding within a single molecule. It does not associate with other alcohol molecules or with water and, therefore, has lower melting point and lower solubility.

12.5 SPECTRAL PROPERTIES

In this section we will consider the spectral properties of alcohols and phenols. Let us first take the ultraviolet spectra. For alcohols, uv spectra are not of much use because they show absorption only in the 180-188 nm region which is not normally covered in uv spectroscopy.

The infrared spectra of alcohols show O—H stretching in the 3650–3590 cm^{-1} region. Intermolecular hydrogen bonding shifts this to the 3520-3200 cm^{-1} region and the band becomes broadened. Intramolecular hydrogen bonding shifts O–H stretching to the 3590-3420 cm^{-1} region. The C—O stretching is characteristic of the type of alcohol: primary near 1050 cm^{1}, secondary near 1100cm^{-1} and tertiary near 1150cm^{-1}. As an illustration, infrared spectrum of 1-butanol is given in Fig. 12.1.

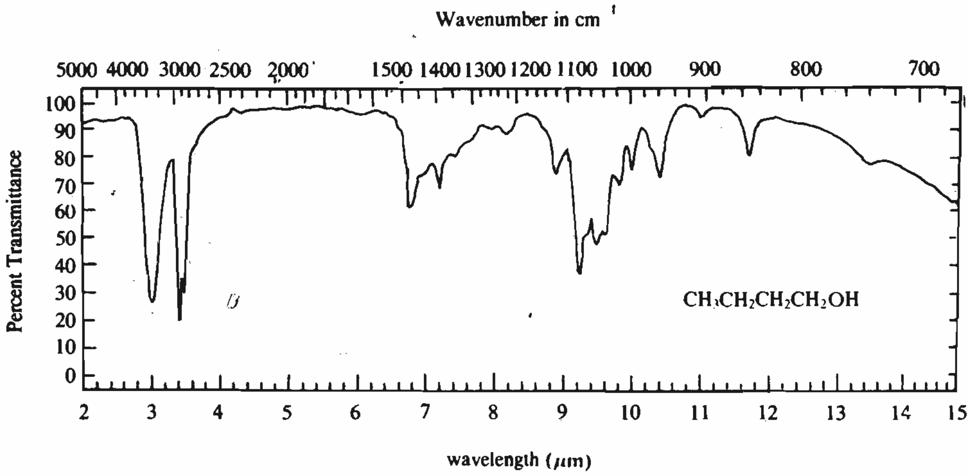


Fig. 12.1: Infrared spectra of 1-butanol

The broad band of 3400 cm^{-1} indicates the presence of the O—H stretching in the molecule. Broadening of the band suggests intermolecular hydrogen bonding. The C—O stretching at 1050 cm^{-1} is characteristic of the primary hydroxyl group (—CH_2—OH).

The infrared spectra of phenols combine the features of alcohols and aromatic compounds. Phenolic-O—H groups show a strong broad bond in the region 3600-3200 cm^{-1} due to O—H stretching and another strong broad bond at around 1200 to 1250 cm^{-1} due to C—O stretching. You can see these featrues in the infrared spectra of 4-methyl benzenol (*p*-cresol) in Fig. 12.2.

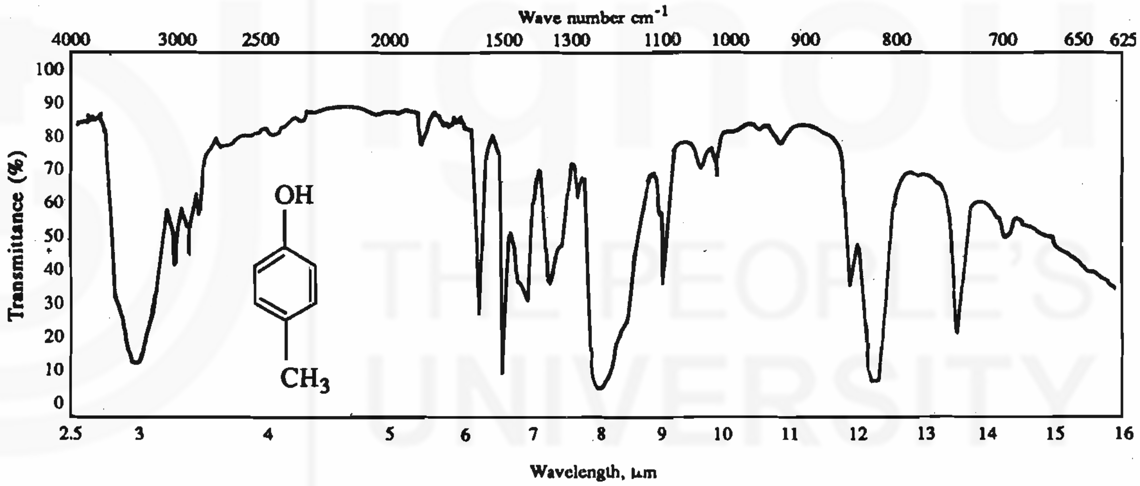


Fig. 12.2 : Infrared spectra of *p*-cresol.

The characteristic features of the nmr spectra of alcohols are the presence of the —O—H signal and the chemical shift of the proton of an H—C—O—unit when the alcohol is primary or secondary

—C—O—H H—C—O—

$\delta = 0.5 - 5$ ppm $\delta = 3.3 - 4.0$ ppm + · ....

Fig. 12.3 shows the nmr spectrum of 2-phenylethanol, in which the hydroxyl proton signal appears as a singlet at δ 1.6 ppm and the proton of the —CH_2O— unit as a triplet at $\delta = 3.8$ ppm. The other triplet at $\delta = 2.8$ ppm and a singlet at $\delta = 7.2$ ppm is for benzylic and aromatic protons, respectively.

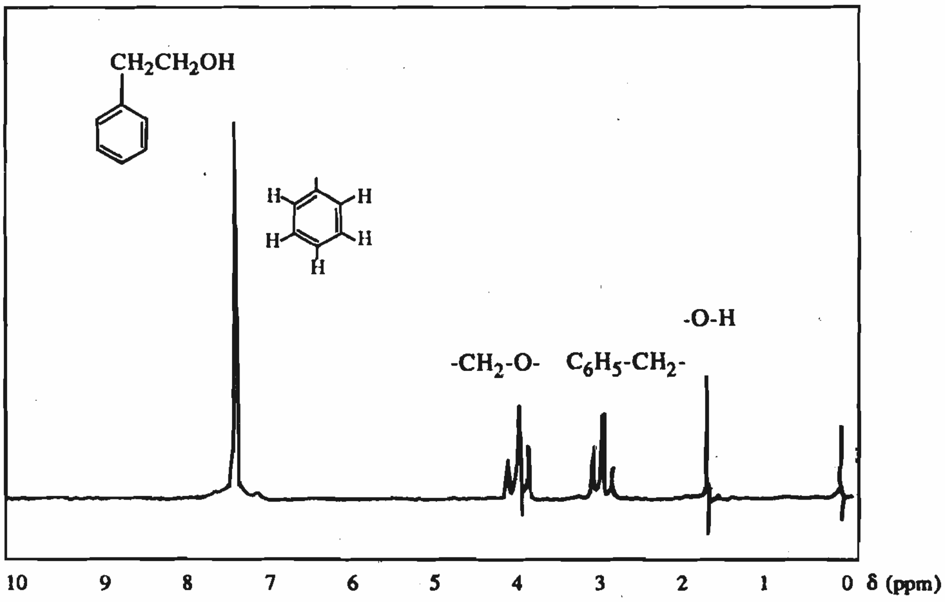
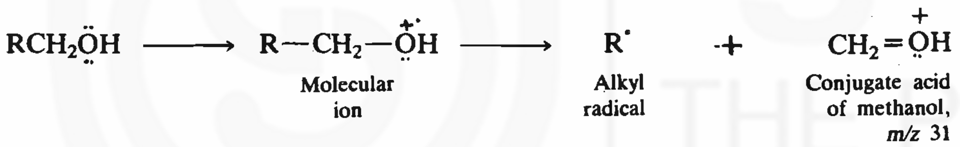


Fig. 12.3 : NMR spectrum of 2-phenylethanol.

On the other hand in the nmr spectra of phenols, the hydroxyl proton appears at much lower field (δ 4 to 12 ppm) than those of alcohols and aromatic proton appears around $\delta \approx 7$ ppm.

The mass spectra of primary and secondary alcohols show a weak peak due to the molecular ion. The peak due to the molecule ion is very weak or absent in the spectra of tertiary alcohols. Phenols show a very intense peak due to the molecular ion. Further, alcohols also fragment readily by a pathway in which the molecular ion loses an alkyl group from the hydroxyl-bearing carbon to form a stable cation. Thus, the mass spectra of most primary alcohols exhibit a prominent peak at *m/z* 31.



$$RCH_2\ddot{O}H \longrightarrow \underset{\text{Molecular ion}}{R-CH_2-\overset{+\cdot}{\ddot{O}}H} \longrightarrow \underset{\text{Alkyl radical}}{R^{\cdot}} + \underset{\text{Conjugate acid of methanol, } m/z\ 31}{CH_2=\overset{+}{\ddot{O}}H}$$

12.6 CHEMICAL PROPERTIES

As stated earlier phenols have very different chemical properties than those of alcohols and, therefore, in this section, we will consider their chemical properties separately. However, it is worth comparing the acidity of alcohols and phenols and the effect alkyl/aryl group has on it.

12.6.1 Basicity and Acidity of Alcohols and Phenols

Alcohols are neutral towards litmus. But in their reactions they behave both as an acid and as a base depending upon the reaction conditions. For example, in acidic solution, alcohols are protonated and thus the acid-base equilibrium with alcohol acting as a base is established. It is the same type of reaction that occurs between water and an acid. A protonated alcohol molecule is called an oxonium ion.

The lone electron pairs of oxygen make alcohols act basic.

Molecules that act both as acids and as bases are called amphoteric (*ampho*, Greek, both). Examples are water, alcohol, etc.:

$$R-\underset{\displaystyle H}{\underset{|}{\ddot{O}}}: + H^+Cl^- \longrightarrow R-\underset{\displaystyle H}{\underset{|}{\overset{+}{\ddot{O}}}}-H + :\ddot{Cl}:^-$$

An alcohol can also lose a proton to a strong base yielding an alkoxide ion, RO^-. In this reaction the alcohol behaves as an acid.

Alkoxides are strong bases, generally stronger than hydroxides. To prepare an alkoxide from an alcohol, we need a base stronger than the alkoxide itself, such as, alkali metal hydrides, NaH, KH, etc.

$$ROH + Na^+H^- \longrightarrow RO^-Na^+ + H_2\uparrow$$

alcohol — sodium hydride — sodium alkoxide

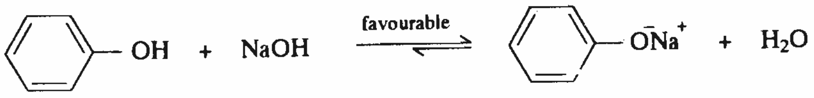
In dilute aqueous solutions alcohol has approximately the same pK_a values as water. For example, the pK_a of methanol in water is 15.5, while that of pure water is 15.74. Therefore it is as acidic as water.

$$CH_3OH + H_2O \longrightarrow CH_3O^- + H_3O^+$$

On the other hand, phenols are distinctly acidic in character. Phenol, with a pK_a of 10.00 is a stronger acid than an alcohol or water. Unlike alkoxide ion of alcohols, the phenoxide ion (ArO^-) is a weaker base than OH^-, therefore, a phenoxide can be prepared by treatment of the phenol with aqueous sodium hydroxide.

$$CH_3CH_2{-}OH + NaOH \underset{}{\overset{\text{unfavourable}}{\rightleftharpoons}} CH_3CH_2\bar{O}Na^+ + H_2O$$

ethanol, $PK_a = 15.9$ — sodium ethoxide



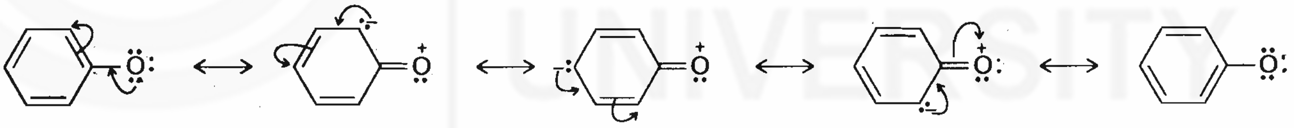
phenol
pKa = 10

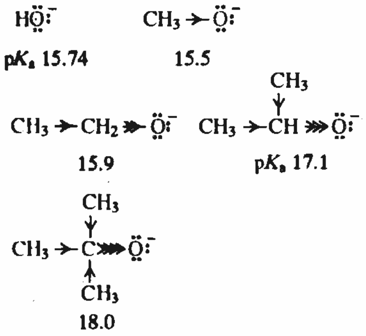
sodium phenoxide

We can explain the acidic character of phenol if we recall the fact that the degree of ionisation of a weak acid is determined by the relative stabilities of the unionised compound and the anion:

$$HA \longrightarrow H^+ + A^-$$ (if A^- is stabilised relative to HA, acidity is increased)

The reason for the greater acidity of phenol compared to that of alcohol is that the ionised product is reasonance stabilised, with the negative charge delocalised by the aromatic ring.

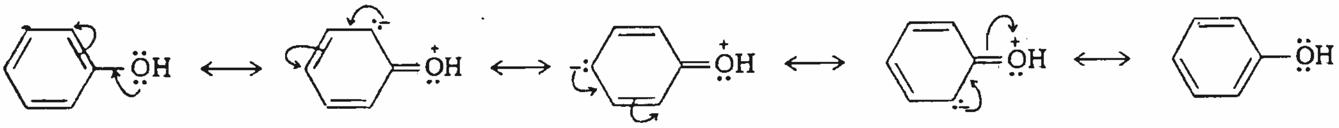




+ I effect of alkyl group which further intensity the neyative charge on oxyzen

The negative charge in an alkoxide ion (RO^-) cannot be delocalised. Therefore, as alkoxide ion is of higher energy relative to the alcohol, and as a result, alcohols are not as strong acids as phenols. Further the alkyl group in the alkoxide ion has a destabilising effect because of positive inductive (+I) effect of the alkyl group. Therefore, addition of alkyl groups to the α−carbon decreases the acidity of alcohols. We can now write the order of decreasing acid strength **H_2O>*p*>*sec*>*tert* alcohols.**

Furthermore phenols, like alcohols can be protonated by strong acids to give the corresponding oxonium ions. Thus, as with the alcohols, the hydroxy group has amphoteric character. However, the basicity of phenols is even less than that of the alcohols, because the lone electron pairs on the oxgyen are delocalised into benzene ring.



Delocalisation of lone pair of oxygen

12.6.2 Reactions of Alcohols

Reactions of alcohols involve breaking either the O—H bond or the C—O bond. In this section first we shall take up the reactions of O—H bond and C—O bond. Then we shall look at the oxidation reactions of alcohol.

i) Reactions of the O—H Bond

Reaction with active metals:

Strongly electropositive metals like K, Na, Mg, Al and Zn liberate hydrogen from alcohols and form alkoxides, e.g.,

$$\underset{\text{ethanol}}{2C_2H_5OH} + 2Na \longrightarrow \underset{\text{sodium ethoxide}}{2C_2H_5O{-}Na^+} + H_2\uparrow$$

In the above reaction the oxygen-hydrogen bond of the alcohol is broken and the alcohol thus behaves as an acid. We have mentioned in the previous subsection that alcohols are, however, weaker acids than water. Therefore, the conjugate base of alcohols, the alkoxide ion, is a stronger base than the hydroxide ion, the conjugate base of water. The order of reactivity for different types of alcohols in this reaction is **$CH_3OH > p > sec > tert$.** This order is the same as given earlier for the acidity of alcohols.

The alkoxides of the alkali metals are strong bases (nucleophiles) that enter into S_N2 substitution of halogen from alkyl halides. This reaction, referred to as the Williamson ether synthesis, is best used to prepare ethers.

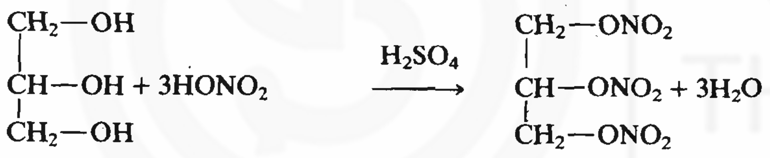
$$\underset{\text{sodium methoxide}}{CH_3O^-Na^+} + \underset{\text{iodoethane}}{C_2H_5{-}I} \xrightarrow{S_N2} \underset{\text{ethylmethyl ether}}{CH_3{-}O{-}C_2H_5} + NaI$$

Esterification: Another interesting reaction of alcohols is with acids to form esters and water. In this reaction the oxygen-hydrogen bond in the alcohol is broken.

$$RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$$

This reaction is known as esterification. These types of reactions will be discussed again in greater detail in Unit 15.

Any inorganic acid can be used in place of carboxylic acid to produce inorganic ester. Inorganic esters are valuable commercial products. For instance, nitroglycerin is readily prepared by the esterification of nitric acid with glycerol.



$$\begin{array}{l} CH_2{-}OH \\ | \\ CH{-}OH \\ | \\ CH_2{-}OH \end{array} + 3HONO_2 \xrightarrow{H_2SO_4} \begin{array}{l} CH_2{-}ONO_2 \\ | \\ CH{-}ONO_2 \\ | \\ CH_2{-}ONO_2 \end{array} + 3H_2O$$

1,2,3-propanetriol (Glycerol) — 1,2,3-propane trinitrate (nitroglycerin)

Nitroglycerin is an explosive used to make dynamite. Similarly, sodium lauryl sulphate, a synthetic detergent, can be obtained by esterification of lauryl alcohol,

$$\underset{\substack{\text{1-dodecanol}\\\text{(lauryl alcohol)}}}{CH_3(CH_2)_{10}CH_2OH} + HOSO_2OH \longrightarrow \underset{\substack{\text{1-dodecanyl hydrogen sulphate}\\\text{(lauryl hydrogen sulphate)}}}{CH_3(CH_2)_{10}CH_2OSO_2OH} + H_2O$$

$$\xrightarrow{NaOH} \underset{\substack{\text{sodium-1-dodecanyl sulphate}\\\text{(sodium lauryl sulphate)}\\\text{synthetic detergent}}}{CH_3(CH_2)_{10}CH_2OSO_2O^-Na^+}$$

Another important ester is **cellulose trinitrate** (gun cotton). It is a product obtained when cellulose (a polysacharide) is almost completely nitrated under conditions carefully controlled to prevent degradation of the cellulose molecule.

$$\underset{\text{cellulose}}{[C_6H_7O_2(OH)_3]_n} \xrightarrow{3n\ HNO_3/H_2SO_4} \underset{\text{gun cotton}}{[C_6H_7O_2(ONO_2)_3]_n}$$

Gun cotton contains about 12-13% of nitrogen, is explosive and is used in the manufacture of smokeless powder.

Esterification of cellulose with acetic anhydride gives **cellulose acetate,** it is an ester but is not explosive. Cellulose acetate is used to produce thin fibres. From such fibre the acetate fabrics are woven. Photographic film is also produced from cellulose acetate.

ii) Reactions of the C—O bond

Substitution reactions of alcohols: The reactions of alcohols with HX, PX_3; $SOCl_2$, PCl_5 to prepare alkyl halides have already been briefly discussed in Unit 11.

$$\underset{\text{alcohol}}{R{-}OH} + HX \longrightarrow \underset{\text{alkyl halide}}{R{-}X} + H_2O$$

$$\underset{\text{alcohol}}{3R{-}OH} + PX_3 \longrightarrow \underset{\text{alkyl halide}}{3R{-}X} + H_3PO_3$$

$$\underset{\text{alcohol}}{R{-}OH} + \underset{\text{sulphur-dichloride oxide (thionyl-chloride)}}{SOCl_2} \longrightarrow \underset{\text{alkyl chloride}}{R{-}Cl} + SO_2 + HCl$$

$$\underset{\text{alcohol}}{R{-}OH} + \underset{\text{phosphorous pentachloride}}{PCl_5} \longrightarrow \underset{\text{alkyl—chloride}}{R{-}Cl} + POCl_3 + HCl$$

Let us look more closely at substitution reaction of alcohol with hydrogen halides (HX). Alcohols can undergo substitution reactions with HX under acidic conditions or in the presence of Lewis acid like anhydrous zinc chloride ($ZnCl_2$). General reaction can be represented as,

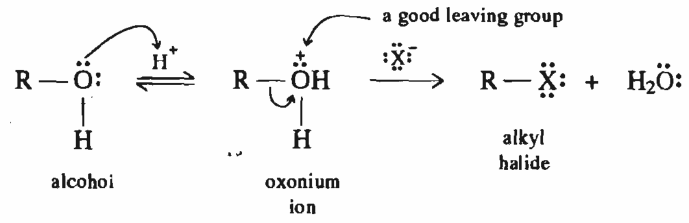
$$R{-}OH + HX \underset{\text{or } ZnCl_2}{\overset{H^+}{\rightleftharpoons}} R{-}X + H_2O$$

Example:

$$\underset{\text{1-butanol}}{CH_3CH_2CH_2CH_2{-}OH} + HBr \xrightarrow[\text{heat}]{ZnCl_2} \underset{\text{1-bromobutane}}{CH_3CH_2CH_2CH_2{-}Br} + H_2O$$

$$(CH_3)_3C{-}OH + HCl \longrightarrow (CH_3)_3C{-}Cl + H_2O$$

If we compare substitution reactions of alcohol and alkyl halide we can notice that unlike alkyl halides, alcohols do not undergo substitution under neutral or alkaline solution. The reaction requires acidic conditions (H^+) or catalysts like $ZnCl_2$. In Unit 11, we have seen that Cl^-, Br^- and I^- are good leaving-groups and weak bases. But, OH^-, is a strong base and thus a very poor leaving group. In acidic solution, alcohols get protonated,



Here, —OH is a poor leaving group, but $—OH_2^+$ is a good leaving group because it is lost as water, a weak base. A weak nucleophile, such as a halide ion can displace the water molecule to yield an alkyl halide. The function of zinc chloride is similar to that of H^+. Anhydrous zinc chloride is a powerful Lewis-acid with empty orbitals that can accept electrons from the oxygen atom of alcohol. The formation of a complex of $ZnCl_2$ with the alcohol oxygen weakens the C—O bond and thus enhances the leaving ability of the hydroxyl group.

In alcohol substitution reactions, the reactivity of the hydrogen halides is as follows:

$$HF < HCl < HBr < HI$$

Thus, the higher the acid strength and nucleophilicity of the anion, the higher the reactivity towards ROH.

The order of reactivity of alcohols towards hydrogen halides is as follows:

methyl < *p* < *sec* < *tert* alcohols

Increasing reactivity of ROH towards HX →

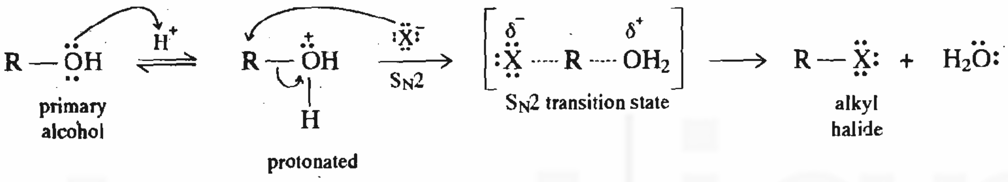
This order of reactivity forms the basis for the Lucas test which is used to differentiate primary, secondary and tertiary alcohols. The Lucas reagent is made up of concentrated HCl and $ZnCl_2$. Tertiary alcohols react immediately upon shaking with the Lucas reagent to produce an immiscible upper layer of alkyl chloride. Secondary alcohols react in 2-3 minutes, and primary alcohols do not react unless the mixture is heated.

Mechanism

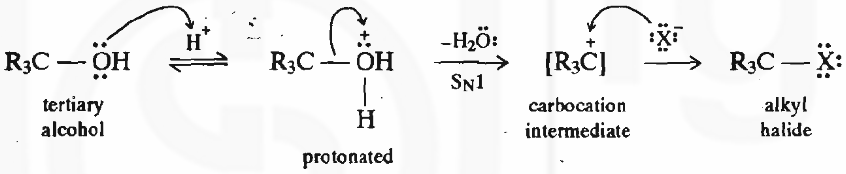
Like alkyl halides primary alcohols react by the S_N2 mechanism, tertiary alcohols by the S_N1 mechanism, and secondary alcohol by either an S_N1 or S_N2 mechanism.

A tertiary $R_3C—OH$ most easily gives a corbocation and tends to react by the S_N1 mechanism. It is very difficult for a primary $RCH_2—OH$ to form a carbocation, but the primary structure is open to backside attack, so an S_N2 reaction is possible. A secondary $R_2CH—OH$ may react by either an S_N1 or S_N2 mechanism.

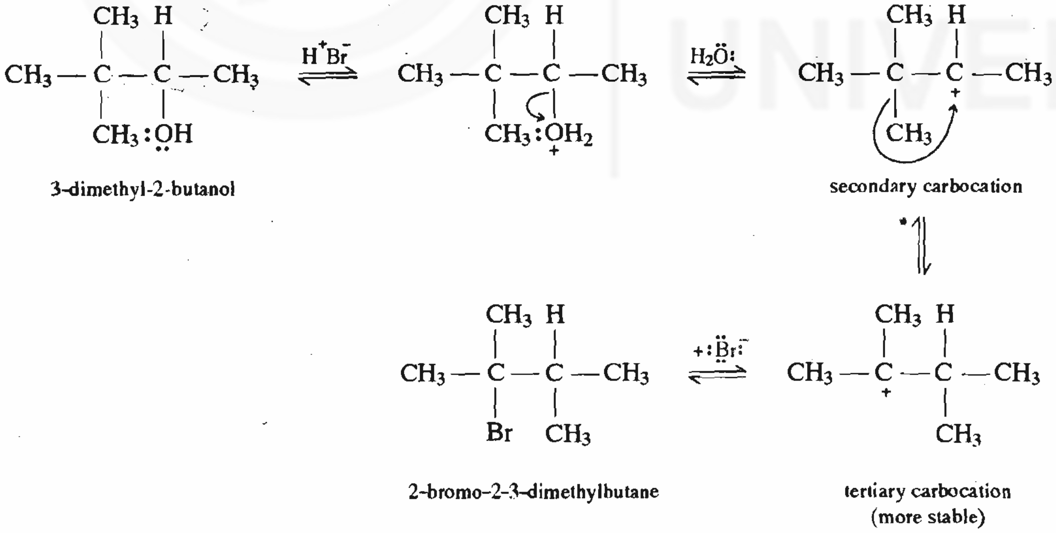
The mechanism for the reaction of HX with a primary alcohol is as follows :



The mechanism for the reaction of tertiary alcohols is as follows :



Secondary and tertiary alcohols, similar to secondary and tertiary alkyl halides, also tend to undergo rearrangements during the S_N1 reaction.



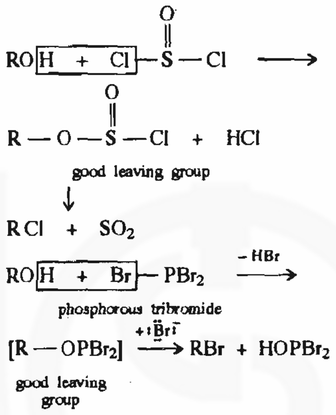
Primary, secondary and tertiary alcohols react with different reagents by different paths. In Table 12.6, we have summarised the substitution reaction of alcohols leading to alkyl halides.

Other halogenating reagent such as thionyl chloride ($SOCl_2$) and phosphorus trihalide (PX_3) undergo reaction with alcohol to form intermediate **inorganic esters**, discussed earlier. The resulting inorganic ester groups are good leaving groups that can be displaced by halide ions.

Table 12.6 . Summary of substitution reactions of alcohols leading to alkyl halides

Alcohol	Reagents	Product	Nature of reaction
p : RCH_2OH	$HCl+ZnCl_2$ or HBr or HI	RCH_2X	S_N2
	PBr_3	RCH_2Br	S_N2
sec : R_2CHOH	$HCl+ZnCl_2$ or HBr or HI	R_2CHX.	S_N1
	PBr_3	R_2CH_2Br	S_N^2
tert : R_3COH	HCl, HBr or HI	R_3CX	S_N1

The reaction of alcohol with thionyl chloride to give alkyl halides usually proceeds in the S_Ni mechanism (Substitution nucleophilic internal)

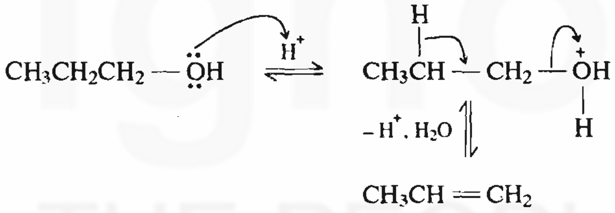


Dehydration of alcohol to alkenes : Another reaction of alcohols is the dehydration. This involves cleavage of C—O bond along with loss of a proton from the β position. It may be effected by heating alcohols to 673–1073 K or heating to a lower temperature in the presence of a catalyst such as alumina or a mineral acid, e.g., sulphuric acid. The product of dehydration of an alcohol is an alkene or a mixture of alkenes. The order of the ease of dehydration of alcohols is: ***tert*> *sec*> *p***
Dehydration of primary alcohols gives only one product, e.g.,

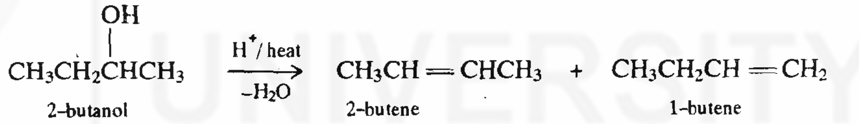
$$\underset{\text{propanol}}{CH_3CH_2CH_2OH} \xrightarrow{H^+/\text{heat}} \underset{\text{1-propene}}{CH_3CH{=}CH_2} + H_2O$$

Primary alcohols undergo dehydration reaction by an E2 path similar to the dehydrohalogenation mechanism discussed in Unit 11.

For the above reaction the E2 mechanism can be written as,



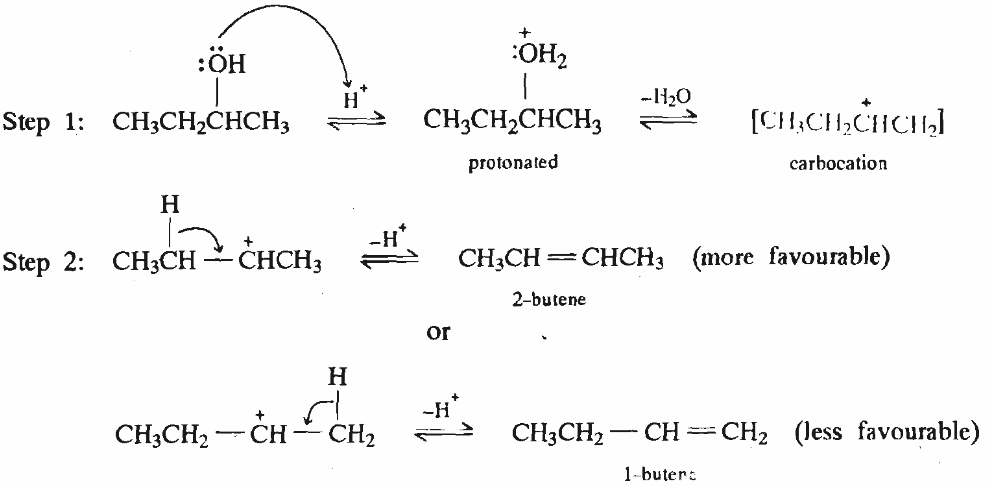
In the case of secondary or tertiary alcohols, a mixture of two alkenes is formed, e.g.,



$$\underset{\text{2-butanol}}{CH_3CH_2\overset{\overset{\displaystyle OH}{|}}{C}HCH_3} \xrightarrow[-H_2O]{H^+/\text{heat}} \underset{\text{2-butene}}{CH_3CH{=}CHCH_3} + \underset{\text{1-butene}}{CH_3CH_2CH{=}CH_2}$$

Like the dehydrohalogenation reaction of alkyl halides, the major product in the above reaction is 2-butene, the more substituted alkene (according to Saytzeff's rule which was given earlier in Unit 11).

In secondary and tertiary alcohols, dehydration follows the E 1 pathway. A detailed discussion of the E 1 mechanism has already been given in Unit 11. Now let us write down the mechanism for dehydration of 2-butanol.



iii) Oxidation of Alcohols

Alcohols undergo oxidation, the nature of the product depending on whether the alcohol is primary, secondary or tertiary. The common oxidising agents are acidic dichromate, acidic or alkaline potassium permanganate or hot concentrated nitric acid or chromic acid (H_2CrO_4) or the chromium trioxide (CrO_3) complex with pyridine.

A primary alcohol on oxidation gives an aldehyde, which on further oxidation gives a carboxylic acid. The oxidation products have the same number of carbon atoms as the alcohol, e.g.,

$$CH_3CH_2-OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$$

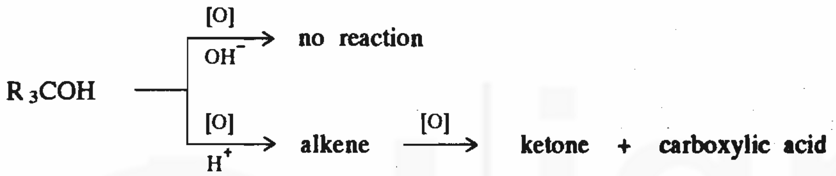
Chromium trioxide-pyridine complex is a better reagent for oxidising a primary alcohol into an aldehyde. Yields of aldehyde with the other reagents is very poor because the oxidation with these reagents usually continues until the carboxylic acid is formed.

A secondary alcohol on oxidation gives a ketone with the same number of carbon atoms as the alcohol. Ketones are not easily oxidised. However, drastic oxidations give a mixture of carboxylic acids containing a fewer carbon atoms than the alcohol :

$$CH_3CHOHCH_2CH_3 \xrightarrow{[O]} CH_3COCH_2CH_3 \xrightarrow{[O]} 2CH_3COOH$$

Acidic conditions are usually used to get ketones from secondary alcohols. Ketones can be oxidised further in alkaline condition with standard oxidising reagents.

Tertiary alcohols are not easily oxidised in neutral or alkaline conditions. Acidic oxidising agents convert a tertiary alcohol to the alkene then it is oxidised to a mixture of ketones and carboxylic acids, each having a lesser number of carbon atoms than the alcohol. Alkene oxidation was discussed in Unit 8.

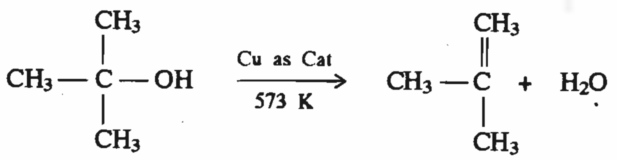


Oxidation in alcohol can also be brought about by catalytic dehydrogenation. In this process vapour of the alcohol is heated over copper, for example,

$$\underset{\text{ethanol}}{CH_3CH_2-OH} \xrightarrow[573\ K]{Cu\ as\ cat.} \underset{\text{ethanal}}{CH_3CHO} + H_2$$

$$\underset{\text{2-propanol}}{(CH_3)_2CH-OH} \xrightarrow[573\ K]{Cu\ as\ cat.} \underset{\text{propanone}}{(CH_3)_2CO} + H_2O$$

As mentioned above tertiary alcohols are resistant to oxidation. When vapour of tertiary alcohols is passed over copper heated at 573 K, they undergo dehydration to give alkenes, for example,



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH \xrightarrow[573\ K]{Cu\ as\ Cat} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{\|}{C}}}} + H_2O$$

2-methyl-2-propanol 2-methyl propene

Catalyst e.g., silver is also employed. For example,

$$\underset{\text{methanol}}{CH_3-OH+1/2O_2} \xrightarrow{Ag\ as\ Cat.} HCHO \quad +H_2O$$

Dehydrogenation is more often used for industrial preparation of aldehydes and ketones.

SAQ 3

Show all the alkenes that could possibly be formed by dehydration of each alcohol below. Tell which alkene would be produced in largest amount and which is smallest amount.

a) 2-methylbutanol
b) 2-pentanol
c) 2-methylcyclohexanol
d) 1, 2-dimethylcyclohexanol

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SAQ 4

What product, if any would be obtained by passing each of these alcohol over copper metal at 573 K ?

a) 1-propanol
b) 2-butanol
c) 2-propanol
d) 2-methylbutanol

12.6.3 Reactions of Phenols

In phenols, as mentioned earlier, the hydroxyl group is attached to an *sp*^{2} hybridised carbon of aromatic ring. In it the carbon oxygen bond has considerable double bond character as evident from the resonance structures shown for the delocalisation of lone pair of oxygen (sub-section 12.6.1). Due to these factors the bond is shorter and stronger than a carbon oxygen single bond. As hydroxyl group bonded to a aromatic ring is held tightly, therefore breaking up of the C—O bond is very difficult. Consequently, the substitution and elimination reactions so typical of an alcohol are not possible for a phenol.

$$\underset{\text{alcohol}}{R-OH} + HBr \xrightarrow{S_N1 \text{ or } S_N2} \underset{\text{alkyl bromide}}{R-Br} + H_2O$$

$$\underset{\text{phenol}}{Ar-OH} + HBr \longrightarrow \text{no reaction}$$

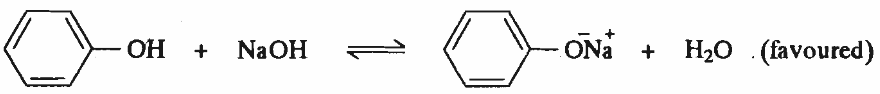
With this background, now let us study the reactions of phenols.

i) Formation of phenoxides : We have already mentioned that phenols are weak acids. They react with strong alkalis forming phenoxides and water. This reactivity is in direct contrast to that of alcohols. We have seen that alcohols form alkoxide only with a strong base like NaH and metals like Na, K, Mg, etc.

Phenol is about 1 million times more acidic than alcohols.

Phenols is not as strong an acid as carbonic acid or a carboxylic acid. This afford a method for distinguishing phenol from a carboxylic acid. Phenol does not react with an aqueous solution of sodium carbonate, whereas carboxylic acid react to liberate carbon dioxide. The separation of a mixture of phenol and a carboxylic acid is based on the same principle.

$$\underset{\substack{\text{ethanol,}\\ pK_a\ 15.9}}{C_2H_5-OH} + NaOH \rightleftharpoons \underset{\text{sodium ethoxide}}{C_2H_5-\bar{O}\,\overset{+}{Na}} + H_2 \quad \text{(not favoured)}$$

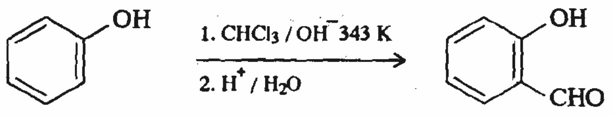


phenol, pK_a 10.0

sodium phenoxide

Again recall from sub-section 12.6.1 that phenols are stronger acids than alcohols as the phenoxide ion is stabilised by resonance. No such stabilisation is possible in the case of alkoxide ions.

ii) Reimer-Tiemann reaction: Phenols undergo the Reimer-Tiemann reaction. In it an alkaline solution of phenol is heated with trichloromethane (chloroform) and the product is acidified to give 2-hydroxybenzaldehyde (salicylaldehyde).

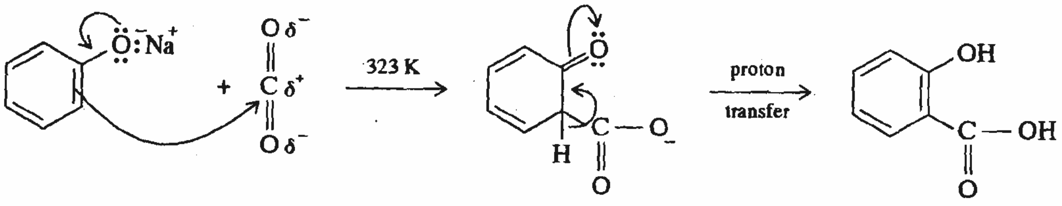


phenol

2-hydroxybenzaldehyde
(salicylaldehyde)

You will study the mechanism of this reaction in the course on Organic Reaction Mechanism.

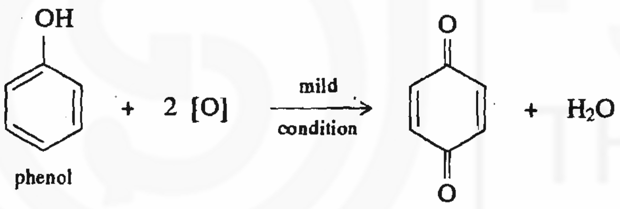
iii) Kolbe reaction: On heating sodium or potassium phenoxide with carbon dioxide and subsequent acidification, 2-hydroxybenzoic acid (salicyclic acid) is formed. This is known as **Kolbe reaction.** In this reaction carbon of CO_2 acts as an electrophile in aromatic substitution.



2-hydroxybenzoic acid
(salicylic acid)

iv) Oxidation of phenols: Phenols are easily oxidised, but their products are often complex. This oxidation may occur with air alone (**autoxidation**) or with other oxidising agents. The reaction of phenols with oxygen in the air is exploited industrially by the use of phenol as antioxidants in gasolin, rubber and other products. The phenols react with oxygen more readily than most other organic compounds and protect them form oxidation.

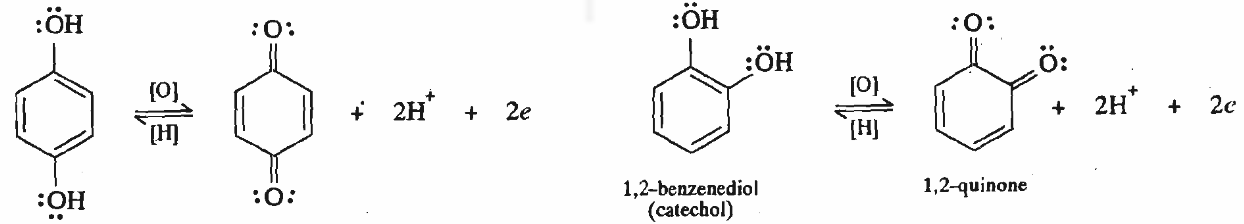
The ability of hydroquinone to reduce silver ions to silver metal is the Chemical basis of photography. Hydroquinone is the developer fluid which reduces the light activated silver ions at a faster rate than the nonexposed silver ions. In the fixing process unreacted silver halide is converted into a water soluble silver complex of sodium thiosulphate, and washed from film. The result is the familiar photographic negative.



phenol

1,4-quinone
(1,4-benzoquinone)

Hydroquinone and catechol are easily oxidised to quinones by mild oxidising agents such as Ag^+ of Fe^{3+}.



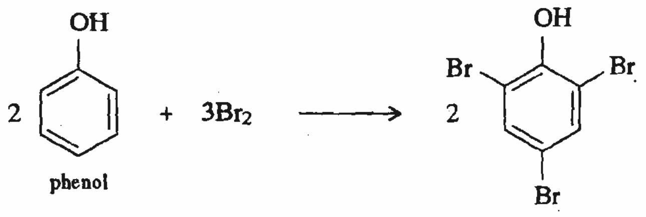
1,4-benzenediol
(hydroquinone)

1,4-quinone
(1,4-benzoquinone)

1,2-benzenediol
(catechol)

1,2-quinone

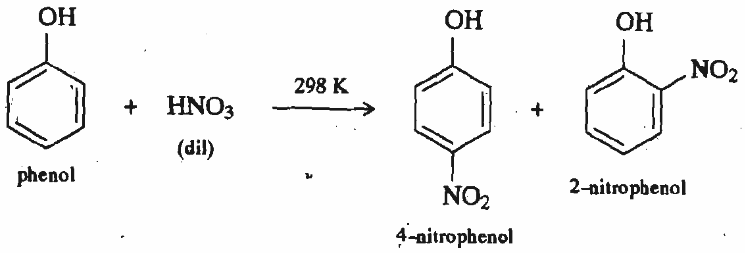
v) Electrophilic aromatic substitution reaction: As we mentioned in Unit 9, the —OH group is a powerful activator in electrophilic aromatic substitution reactions. Therefore, phenol undergoes electrophilic substitution quite readily. On shaking phenol with bromine water at room temperature, 2,4,6-tribromophenol is formed:



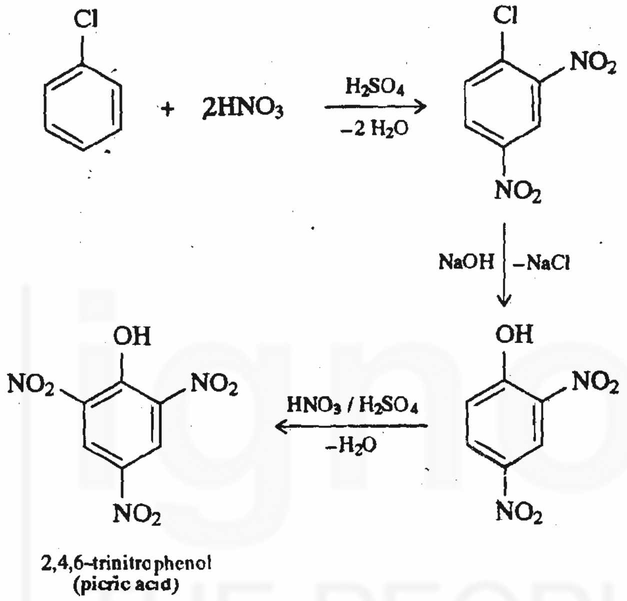
phenol

2,4,6-thibromophenol

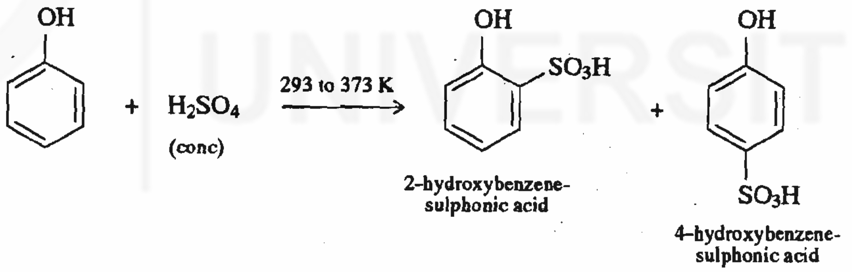
Treatment with dilute nitric acid gives *o* and *p* nitrophenols:



Phenol, when nitrated directly with concentrated nitric acid, undergoes oxidation. For this reason the highly explosive 2,4,6-trinitrophenol, or picric acid, is obtained through a synthesis that begins with chlorobenzene. The first product, 2,4-dinitrochlorobenzene, is then easily hydrolysed to, 2,4-dinitrophenol and the nitration continued to give picric acid in good yield.

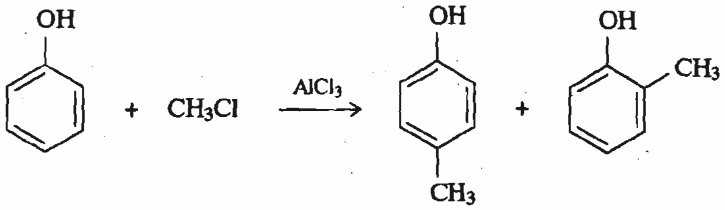


Phenol, when treated with sulphuric acid, yields both *ortho* and *para* products,

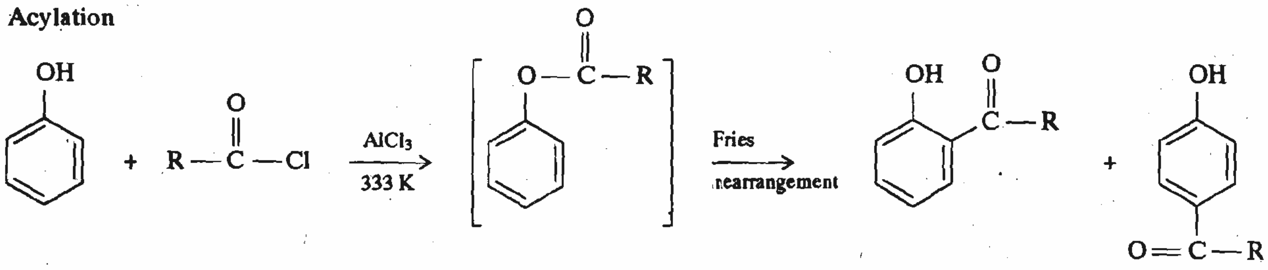


Phenol can easily undergo Friedel-Crafts alkylation or acylation.

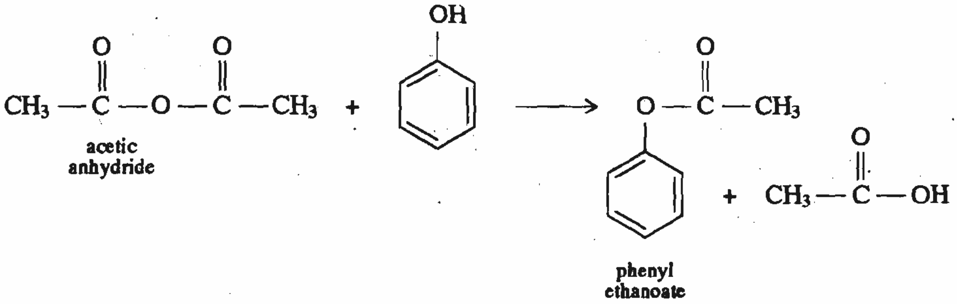
Alkylation



Acylation

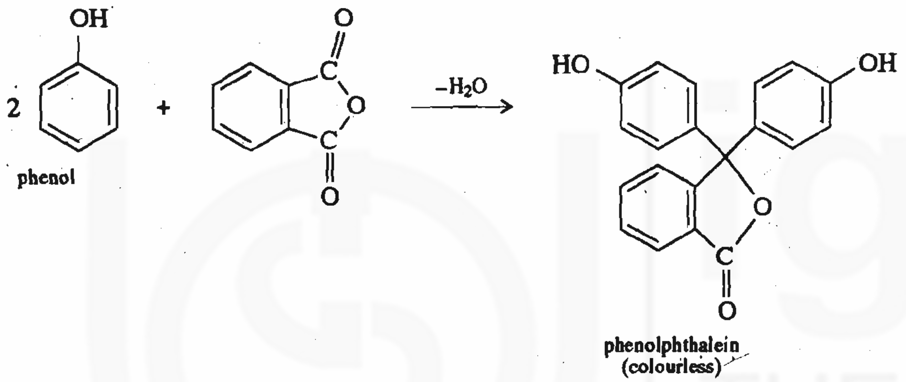


vi) Esterification of Phenols: Unlike alcohols, esterification of phenols does not involve cleavage of the strong C—O bond of the phenol; but depends on the cleavage of the O—H bond. We will discuss the mechanism of esterification of phenols in the course on reaction mechanism.



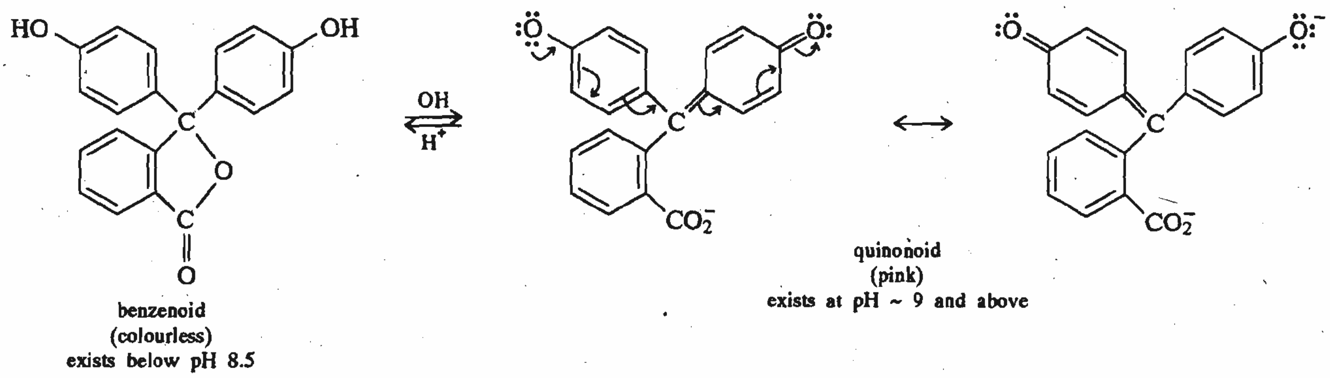
vii) Condensation reactions of phenols: Condensation of phenols with phthalic anhydride in the presence of a dehydrating agent gives a class of compounds known as **phthaleins.** These are dyes.

By heating a mixture of phenol and phthalic anhydride in the presence of concentrated sulphuric acid, phenolphthalein is formed:

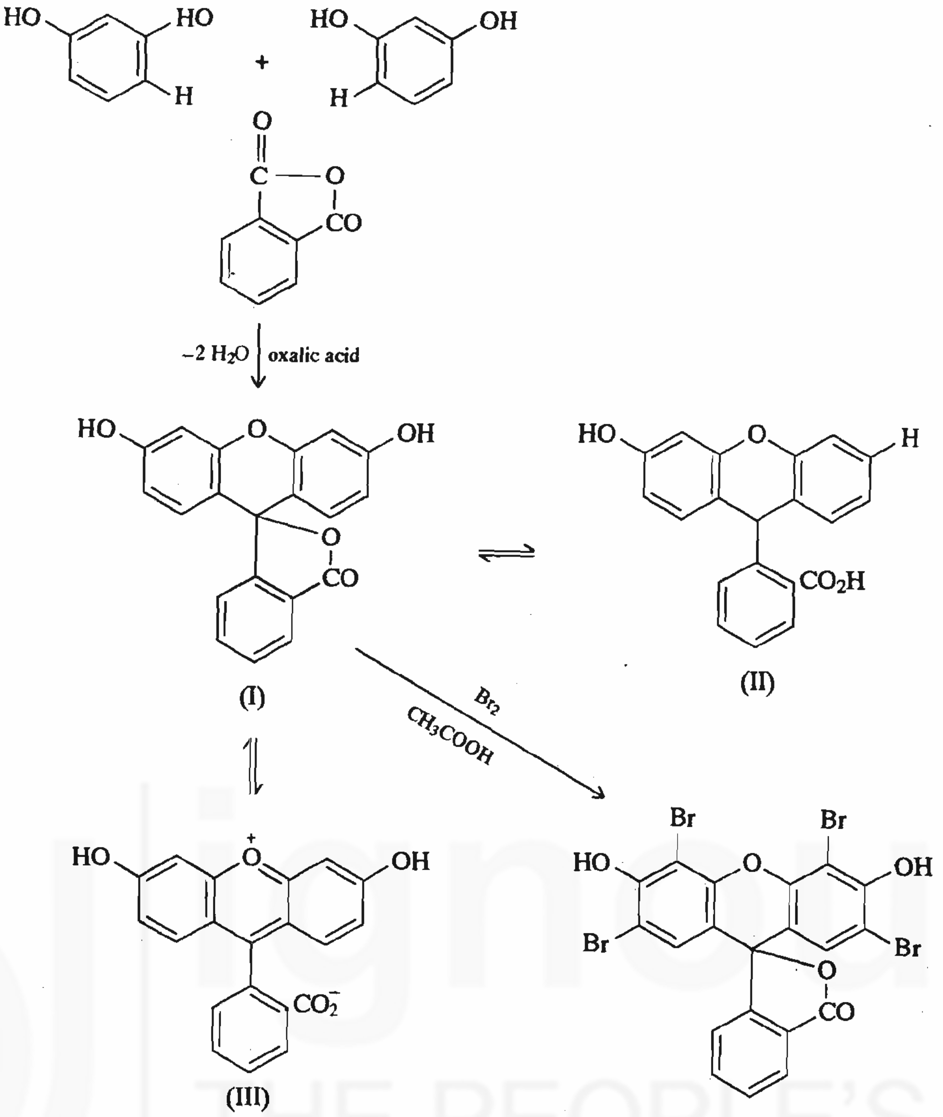


Phenolphthalein is colourless in acidic medium. On addition of alkali, a pink coloration develops due to the quinonoid form. Addition of excess alkali regenerates the benzenoid structure which is colourless. Phenolphthalein is commonly used in the laboratory as a pH indicator. At pH below 8.5 the molecule exists in colourless form and at pH~9 and above, in pink form.

Phenolphthalein as a pH indicator



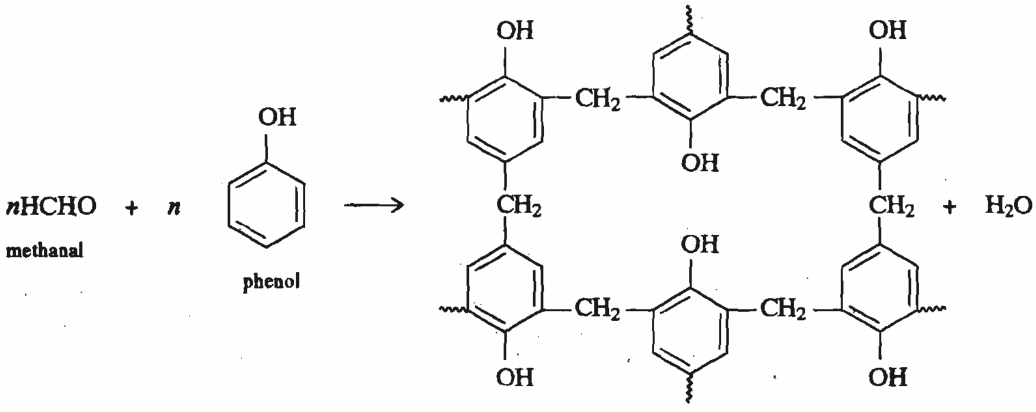
Heating a mixture of phthalic anhydride and resorcinol with anhydrous oxalic acid gives fluorescein:



Although two quinonoid structures II and III can be written for fluorescein, spectral evidence supports structure I. Fluorescein is a red powder which is insoluble in water. It dissolves in alkalis to give a reddish-brown solution which on dilution shows a yellow-green fluorescent. Action of bromine on fluorescein in glacial acetic acid solution gives tetrabromofluorescein which is commonly known as eosin.

The electric resistance of Bakelite makes it especially useful for electric plugs, switches and tools.

The condensation of phenol with excess of methanal (formaldehyde) in the presence of dilute sodium hydroxide gives polymers which are known as Bakelite. These are phenol methanal resins which are three-dimensional polymer of the following possible structure:



segment of Bakelite polymer

SAQ 5

Treatment of phenol with trichloromethane (chloroform) and aqueous sodium hydroxide gives:

a) 2-chlorophenol

b) 2-hydroxybenzaldehyde

c) 3-hydroxybenzaldehyde

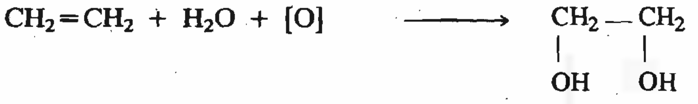
d) 3-chlorophenol

12.7 POLYHYDRIC ALCOHOLS

So far we have studied monohydric alcohols. Now let us briefly consider polyhydric alcohols.

12.7.1 Dihydric Alcohols

The dihydric alcohols are known as glycols or diols (in IUPAC nomenclature). 1,2 ethanediol (ethylene glycol or simply glycol) can be prepared by the hydroxylation oxidation of ethene with cold dilute alkaline potassium permanganate:



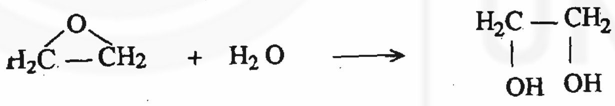
$$CH_2{=}CH_2 + H_2O + [O] \longrightarrow \begin{array}{cc} CH_2 - & CH_2 \\ | & | \\ OH & OH \end{array}$$

Hydrolysis of ethene chlorohydrin or dihalide with mild alkali, such as aq. $NaHCO_3$ or Na_2CO_3 gives 1,2-ethenediol

$$\begin{array}{l} CH_2 - Cl + NaHCO_3 \\ | \\ CH_2 - OH \end{array} \longrightarrow \begin{array}{l} CH_2 - OH + NaCl + CO_2 \\ | \\ CH_2 - OH \end{array}$$

$$\begin{array}{l} CH_2 - Br + Na_2CO_3 + H_2O \\ | \\ CH_2 - Br \end{array} \longrightarrow \begin{array}{l} CH_2 - OH + 2NaBr + CO_2 \\ | \\ CH_2 - OH \end{array}$$

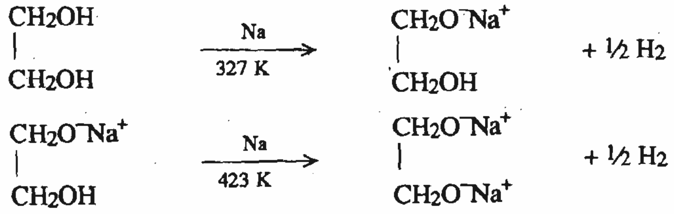
1,2-Ethanediol is manufactured by the hydration of oxirane (ethylene oxide)



This is carried out in acid solution at about 333 K or with water at 473 K under pressure.

1, 2-Ethanediol is taken as a typical example. It shows the chemical reactions of monohydric alcohols except that more vigorous conditions are sometimes needed for reaction of the second of the two hydroxyl groups. For example:

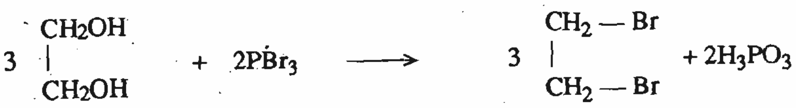
i) It reacts with sodium to form a monoalkoxide and at higher temperature, dialkoxide:



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow[327\ K]{Na} \begin{array}{l} CH_2O^-Na^+ \\ | \\ CH_2OH \end{array} + \tfrac{1}{2} H_2$$

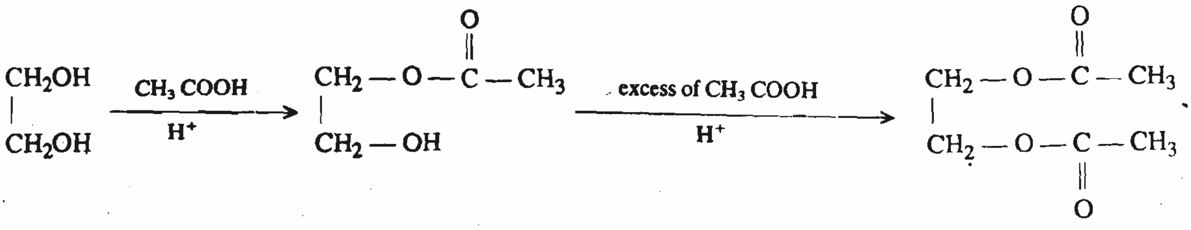
$$\begin{array}{l} CH_2O^-Na^+ \\ | \\ CH_2OH \end{array} \xrightarrow[423\ K]{Na} \begin{array}{l} CH_2O^-Na^+ \\ | \\ CH_2O^-Na^+ \end{array} + \tfrac{1}{2} H_2$$

ii) It reacts with phosphorus halides to yield dihalide:



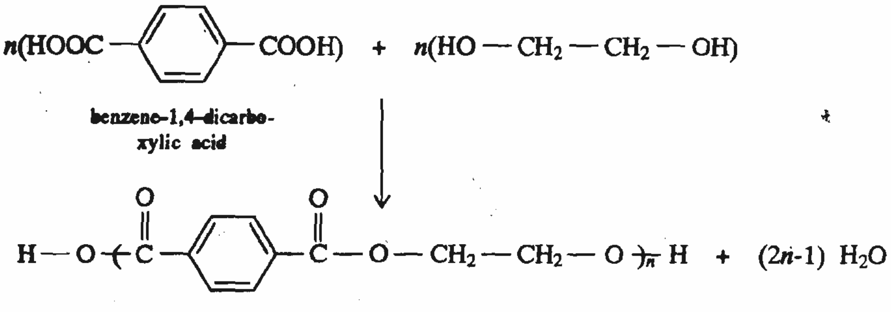
$$3 \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2PBr_3 \longrightarrow 3 \begin{array}{l} CH_2 - Br \\ | \\ CH_2 - Br \end{array} + 2H_3PO_3$$

iii) It reacts with carboxylic acid to form esters:



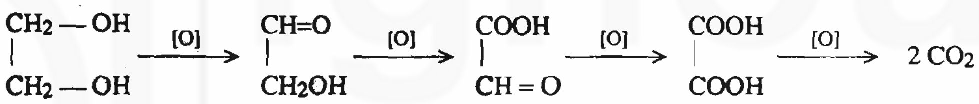
$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \xrightarrow[H^+]{CH_3COOH} \begin{matrix} CH_2-O-\overset{\overset{\large O}{\|}}{C}-CH_3 \\ | \\ CH_2-OH \end{matrix} \xrightarrow[H^+]{\text{excess of } CH_3COOH} \begin{matrix} CH_2-O-\overset{\overset{\large O}{\|}}{C}-CH_3 \\ | \\ CH_2-O-\underset{\underset{\large O}{\|}}{C}-CH_3 \end{matrix}$$

When esterified with a dibasic acid, it forms polymers, for example,



terylene

iv) On oxidation with nitric acid, both the primary alcohol groups are oxidised, first to aldehyde and then to carboxyl groups. Ethanedioic acid is finally oxidised to carbon dioxide and water,



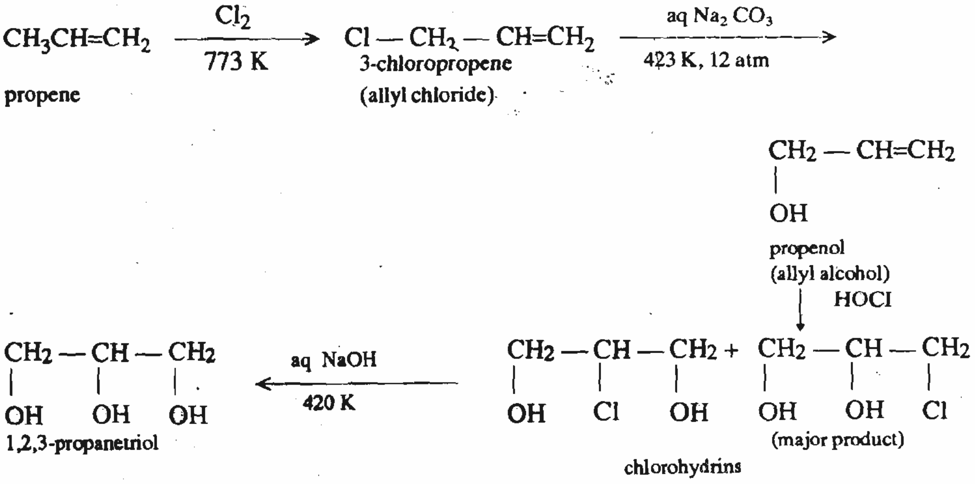
$$\begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix} \xrightarrow{[O]} \begin{matrix} CH{=}O \\ | \\ CH_2OH \end{matrix} \xrightarrow{[O]} \begin{matrix} COOH \\ | \\ CH=O \end{matrix} \xrightarrow{[O]} \begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{[O]} 2\,CO_2$$

ethanedioic acid
(oxalic acid)

1-2 Ethanediol is widely used as a solvent, antifreezeagent and in the manufacture of terylene.

12.7.2 Trihydric Alcohols

1,2,3-Propanetriol (glycerol or glycerin) is an important trihydric alcohol (triol). It occurs in nature as glyceryl ester or glycerides of higher aliphatic acids, for example, hexadecanoic acid, $CH_3-(CH_2)_{14}-COOH$ (palmitic acid) and octadecanoic acid, $CH_3-(CH_2)_{16}-COOH$ (steric acid) in oils and fats. It is obtained commercially as a by-product in the manufacture of soap. It can be prepared from propene by (i) chlorination, (ii) alkaline hydrolysis, (iii) addition of hypochlorous acid and (iv) alkaline hydrolysis of the chlorohydrin:



$$\underset{\text{propene}}{CH_3CH{=}CH_2} \xrightarrow[773\ K]{Cl_2} \underset{\substack{\text{3-chloropropene} \\ \text{(allyl chloride)}}}{Cl-CH_2-CH{=}CH_2} \xrightarrow[423\ K,\ 12\ atm]{aq\ Na_2CO_3} \underset{\substack{\text{propenol} \\ \text{(allyl alcohol)}}}{\begin{matrix} CH_2-CH{=}CH_2 \\ | \\ OH \end{matrix}}$$

$$\xrightarrow{HOCl} \underset{\text{chlorohydrins}}{\begin{matrix} CH_2-CH-CH_2 \\ |\qquad\ |\qquad\ | \\ OH\quad Cl\quad OH \end{matrix} + \underset{\text{(major product)}}{\begin{matrix} CH_2-CH-CH_2 \\ |\qquad\ |\qquad\ | \\ OH\quad OH\quad Cl \end{matrix}}} \xrightarrow[420\ K]{aq\ NaOH} \underset{\text{1,2,3-propanetriol}}{\begin{matrix} CH_2-CH-CH_2 \\ |\qquad\ |\qquad\ | \\ OH\quad OH\quad OH \end{matrix}}$$

1,2,3-Propanetriol contains one secondary and two primary alcoholic groups. It undergoes many typical reactions of alcohols. It is also used as an antifreeze, for making explosives and as a moistening agent in soaps and tobacco.

i) As mentioned earlier, with a mixture of cold concentrated nitric and sulphuric acids, 1,2,3-propanetriol forms nitroglycerine—a powerful explosive.

ii) When 1,2,3-propanetriol is heated with a limited amount of hydrogen iodide, 3-iodopropene (allyl iodide) is formed:

$$HOCH_2CHOHCH_2OH+3HI \longrightarrow [ICH_2CHICH_2I] \longrightarrow I_2+CH_2=CHCH_2I$$

With excess of hydrogen iodide, 2-iodopropane is formed:

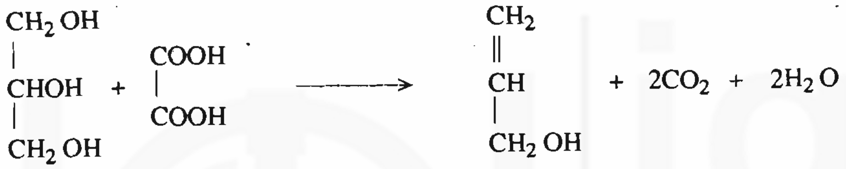
$$CH_2=CHCH_2I \xrightarrow{HI} CH_3CHICH_2I \xrightarrow{-I_2} CH_3CH=CH_2 \xrightarrow{+HI} CH_3CHICH_3$$

iii) When heated with potassium hydrogen sulphate, 1,2,3-propanetriol is dehydrated to propenal (acrolein):

$$HOCH_2CHOHCH_2OH \xrightarrow{KHSO_4} CH_2=CHCHO + H_2O$$

propenal
(acrolein)

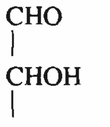
By heating ethanedioic acid (oxalic acid) or methanoic acid with 1,2,3-propanetriol at 533 K propenol (allyl alcohol) is obtained:



$$\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} + \begin{array}{l}COOH\\ |\\ COOH\end{array} \longrightarrow \begin{array}{l}CH_2\\ \|\\ CH\\ |\\ CH_2OH\end{array} + 2CO_2 + 2H_2O$$

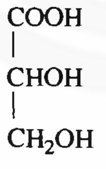
propenol
(allyl alcohol)

Oxidation of 1,2,3-propanetriol gives a large number of products. Their nature depends on the type of oxidising agent used. The primary alcoholic groups are oxidised to aldehyde or carboxylic acid and the secondary alcoholic group to the ketonic group. The oxidation products of 1,2,3-propanetriol are:



$$\begin{array}{l}CHO\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

2,3-dihydroxypropanal
(glyceraldehyde)

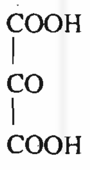


$$\begin{array}{l}COOH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$$

2,3-dihydroxypropanoic acid
(glyceric acid)

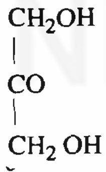
$$\begin{array}{l}COOH\\ |\\ CHOH\\ |\\ COOH\end{array}$$

2-hydroxypropenedioic acid
(tartronic acid)



$$\begin{array}{l}COOH\\ |\\ CO\\ |\\ COOH\end{array}$$

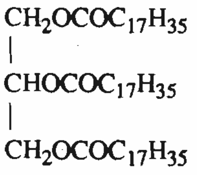
2-oxopropanedioic acid (mesooxalic acid)



$$\begin{array}{l}CH_2OH\\ |\\ CO\\ |\\ CH_2OH\end{array}$$

1,3-dihydroxypropanone
(dihydroxy acetone)

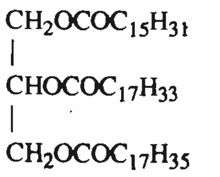
Glyceryl esters or glycerides of higher fatty acids are known as **oil** and **fats.** They are simple **lipids** and can be simple glycerides or mixed glycerides. The mixed glycerides commonly occur in nature. Some of the examples are:



$$\begin{array}{l}CH_2OCOC_{17}H_{35}\\ |\\ CHOCOC_{17}H_{35}\\ |\\ CH_2OCOC_{17}H_{35}\end{array}$$

stearyolglycerol
(tristearin)

simple glyceride

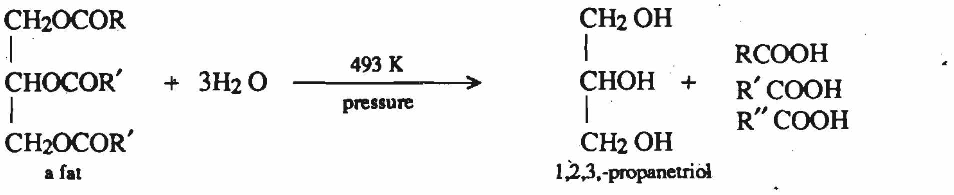


$$\begin{array}{l}CH_2OCOC_{15}H_{31}\\ |\\ CHOCOC_{17}H_{33}\\ |\\ CH_2OCOC_{17}H_{35}\end{array}$$

1-stearyol-2-oleoyl 1-3--palmitoylglycerol

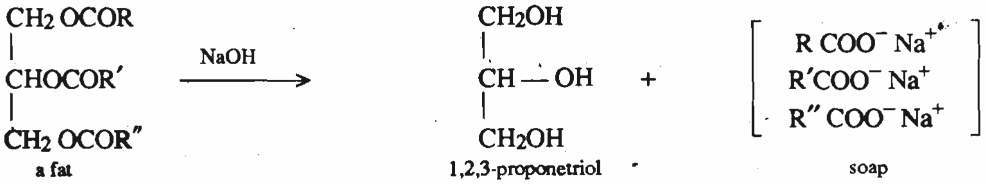
mixed glyceride

As said earlier, 1,2,3-propanetriol is obtained by the hydrolysis of oils and fats with water and high pressure at 493 K.



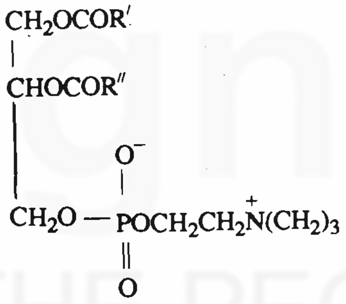
$$\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR' \\ | \\ CH_2OCOR' \\ \text{a fat} \end{array} + 3H_2O \xrightarrow[\text{pressure}]{493\text{ K}} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \\ \text{1,2,3,-propanetriol} \end{array} + \begin{array}{l} RCOOH \\ R'COOH \\ R''COOH \end{array}$$

The fatty acids so obtained, are used in the manufacture of candles. If the hydrolysis of oils and fats is done by alkali, sodium salts of fatty acids (soaps) are obtained. This process is known as saponification. We will consider soaps in more detail in Unit 15.



$$\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR' \\ | \\ CH_2OCOR'' \\ \text{a fat} \end{array} \xrightarrow{NaOH} \begin{array}{l} CH_2OH \\ | \\ CH-OH \\ | \\ CH_2OH \\ \text{1,2,3-proponetriol} \end{array} + \left[\begin{array}{c} RCOO^-Na^+ \\ R'COO^-Na^+ \\ R''COO^-Na^+ \end{array} \right] \atop \text{soap}$$

Phospholipids are also glycerides in which two of the hydroxyl groups are esterified with fatty acid residues and the third with a phosphoric acid moiety. The latter contains phosphorus and nitrogen. One example is:



$$\begin{array}{l} CH_2OCOR' \\ | \\ CHOCOR'' \\ | \\ CH_2O-\overset{\overset{O^-}{|}}{\underset{\underset{O}{\|}}{P}}OCH_2CH_2\overset{+}{N}(CH_2)_3 \end{array}$$

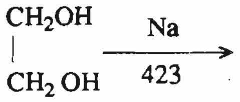
phosphatidylcholin

Phospholipids occur in the brain and the spinal chord.

SAQ 6

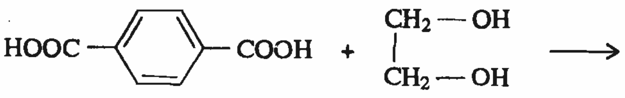
Complete the following equations:

a)



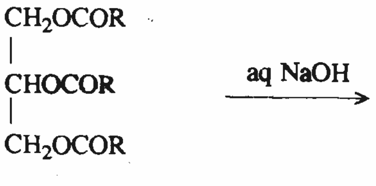
$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow[423]{Na}$$

b)



c) $CH_3CH{=}CH_2 \xrightarrow[\text{2. aq } Na_2CO_3]{\text{1. } Cl_2/733\text{ K}} \ldots\ldots\ldots \xrightarrow[\text{2. aq } Na_2CO_3]{\text{1. HOCl}} \ldots$

d)



$$\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array} \xrightarrow{\text{aq NaOH}}$$

12.8 INDUSTRIAL USES OF ALCOHOLS AND PHENOLS

Methanol is poisonous. It is miscible with water and other organic solvents. It causes blindness. It is widely used as a solvent for paints, varnishes, etc., in the manufacture of dyes, perfumes, methanal (formaldehyde), and for making methylated spirit and antifreeze mixtures for automobiles.

Industrial alcohol is the ordinary rectified spirit, which contains 95% of ethanol, the rest being water. Ethanol is used for preparation of esters, ethers, trichloroethanal (chloral), trichloromethane (chloroform), as a solvent for gums, resins, paints, varnishes, etc., and as a fuel. It is also the main constituent of alcoholic drinks like whisky, rum, wine, beer, etc.

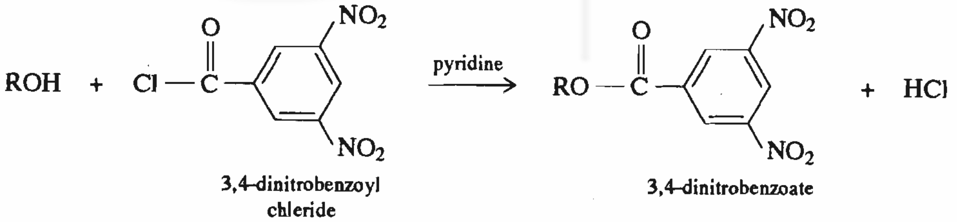
Phenols are used as antiseptic and disinfectant, in the preparation of dyes, drugs and plastics, and as developers in photography.

Some nitro derivatives of polyhydric alcohols (e.g., nitroglycerine) are used as explosives. Alfred Nobel discovered the powerful explosive, dynamite, which is nitroglycerine absorbed in kieselguhr. Another explosive, cellulose nitrate, is known as gun cotton. Cordite is a mixture of nitroglycerine, gun cotton and vaseline. Cellulose acetate is used for making artificial silk.

Polyhydric aldehydes and ketones constitute an important class of compounds which occur widely in nature, as carbohydrates. Amongst these, glucose is the main energy source in plants and animals.

12.9 LAB DETECTION

The reaction with sodium metal to evolve hydrogen gas is of some use for the detection of alcohols. The presence of traces of moisture, however, affects the characterisation. The presence of an hydroxyl group in a molecule is often indicated by the formation of an ester upon treatment with an acid chloride or an anhydride. Compounds like alcohols, phenols, primary and secondary amines (those containing an active hydrogen atom) on treatment with benzoyl chloride in the presence of dilute aqueous sodium hydroxide give benzoyl derivatives (**Schotten-Baumann reaction**). Sometimes 4-nitrobenzoyl or 3,5-dinitrobenzoyl chlorides are used to prepare derivatives of alcohols and phenols and thus for the characterisation of these compounds.



Phenols give violet or blue or green colouration with ferric chloride. The appearance of colour is a sensitive test used to characterise phenols.

As mentioned earlier, alcohols of different classes can be differentiated on the basis of their reaction rates with $HCl/ZnCl_2$. If we take alcohol in a test tube and add mixture of $HCl/ZnCl_2$ the following results are obtained:

primary alcohols $\xrightarrow{HCl/ZnCl_2}$ No reaction at room temperature.

secondary alcohol $\xrightarrow{HCl/ZnCl_2}$ Reaction mixture gets cloudy in 5-10 minutes.

Tertiary, alkyl, benzyl alcohols	$\xrightarrow{HCl/ZnCl_2}$	Reaction mixture gets cloudy immediately.
Phenols	$\xrightarrow{HCl/ZnCl_2}$	No reaction (even at high temperature).

12.10 SUMMARY

In this unit we have described the chemistry of alcohols and phenols. We are summarising below what we have studied:

- Alcohols are obtained by the hydrolysis of alkyl halides and reduction of aldehydes and ketones. They are prepared on a large scale by hydration of alkenes, catalytic treatment of water gas, catalytic oxidation of natural gas and fermentation of starch or sugars.
- Alcohols are very weak acids. The molecules tend to associate themselves by forming hydrogen bonds. Oxidation or dehydrogenation of alcohols give mainly carbonyl compounds. They react with carboxylic acids to form esters. Dehydration of alcohols leads to alkenes.
- Phenols are obtained by the decarboxylation of phenolic acid, action of water on diazonium salts and from Grignard reagent. They are prepared on a commercial scale by catalytic oxidation of methylbenzene (toluene) or decomposition of cumene pereoxide or from chlorobenzene by Dow process. Phenols are also obtained from coal tar.
- On heating phenol with trichloromethane (chloroform) and potassium hydroxide, 2-hydroxy benzaldehyde is obtained. On passing carbon dioxide in a mixture of phenol and aq. sodium hydroxide 2-hydroxy benzoic acid is formed.
- Phenol undergoes electrophilic substitution (nitration, halogenation, Friedel-Crafts reaction, sulphonation, etc.) quite readily giving a mixture a ortho- and para-derivatives.
- On condensation with phthalic anhydride in the presence of a dehydrating agent, phenol gives phthalein dyes. With methanal, phenol gives Bakelite—a polymer.
- The polyhydric alcohols have properties similar to those as described above for alcohols.
- Alcohols are commonly used as solvents in synthesis and industry (varnish, paints, etc.). They are also used for manufacture of various chemicals such as dyes, drugs, explosives, perfumes, scents, essences etc.
- Phenols are used as antiseptic and disinfectants and in the manufacture of dyes, drugs and plastics and as photographic developers.

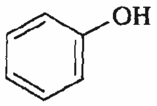
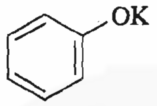
12.11 TERMINAL QUESTIONS

1) Show a structural formula for each name and tell whether it is a primary, secondary or tertiary.
   a) 3-pentanol
   b) 2,2-dimethyl-1-propanol
   c) 2-methyl-1-butanol
   d) 3-methyl-2-pentanol
   e) 1-methylcyclopentanol
2) Which compound from each pair has a higher boiling point and more soluble ir water.

- a) 1-chloropropane or propanol
- b) 1-butanol or 2-methyl-2-propanol
- c) 2-butanol or 2-propanol
- d) *o*-nitrophenol or *p*-nitrophenol

3) Which is the stronger acid and stronger base, ethanol or phenol? Explain.

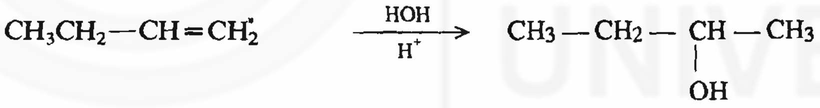
4) Write a mechanism for the reaction of
   - a) ethyl alcohol with HBr
   - b) 3-dimethyl-2-butanol with HBr

5) Complete the following reactions;
   - a) $(CH_3)_3COH + HCl \longrightarrow$
   - b) $C_2H_5OH \xrightarrow[H_2O]{Na}$
   - c)  + $3Br_2 \xrightarrow{H_2O}$
   - d)  + $CO_2 \xrightarrow[2.\ H^+/H_2O]{1.\ heat}$

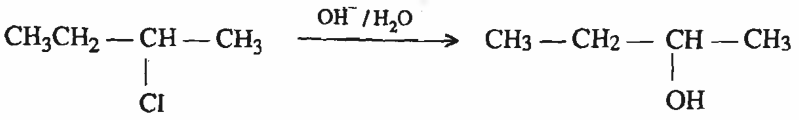
6) Give a simple chemical test that would distinguish primary alcohol from secondary and secondary alcohol from tertiary alcohols.

12.12 ANSWERS

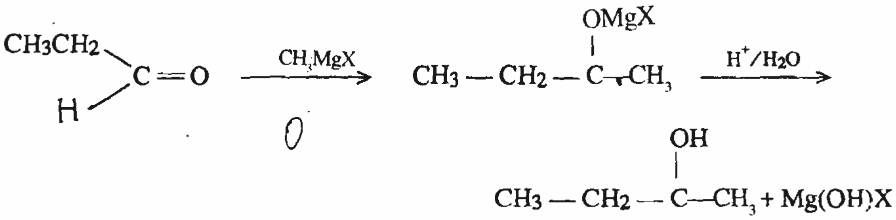
Self Assessment Questions

1) a) 

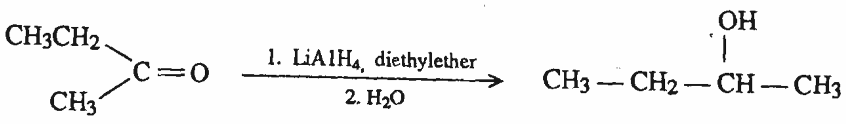
$$CH_3CH_2{-}CH{=}CH_2 \xrightarrow[H^+]{HOH} CH_3{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$$

b) 

$$CH_3CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_3 \xrightarrow{OH^-/H_2O} CH_3{-}CH_2{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$$

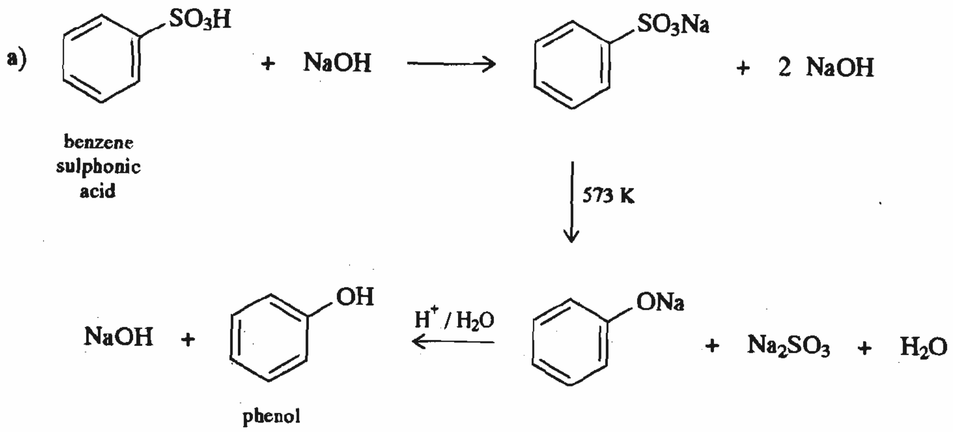
c) 

$$\begin{matrix}CH_3CH_2\\H\end{matrix}\!\!>C{=}O \xrightarrow{CH_3MgX} CH_3{-}CH_2{-}\overset{\displaystyle OMgX}{\overset{|}{C}}{-}CH_3 \xrightarrow{H^+/H_2O} CH_3{-}CH_2{-}\overset{\displaystyle OH}{\overset{|}{C}}{-}CH_3 + Mg(OH)X$$

d) 

$$\begin{matrix}CH_3CH_2\\CH_3\end{matrix}\!\!>C{=}O \xrightarrow[2.\ H_2O]{1.\ LiAlH_4,\ diethylether} CH_3{-}CH_2{-}\overset{\displaystyle OH}{\overset{|}{CH}}{-}CH_3$$

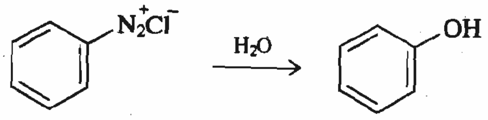
2) a)



benzene sulphonic acid

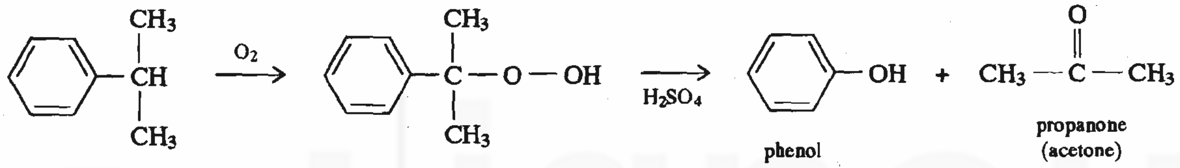
phenol

b)



benzyldiazonium salt

c)



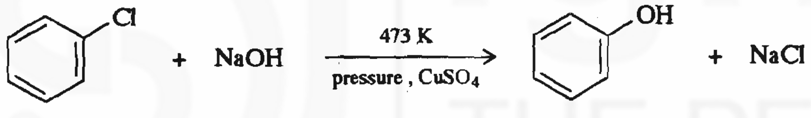
Cumene

Cumene hydroperoxide

phenol

propanone (acetone)

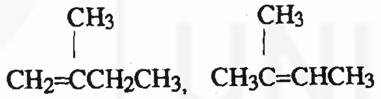
d)



chlorobenzene

phenol

3) a)



$CH_2{=}\overset{CH_3}{\overset{|}{C}}CH_2CH_3$, $CH_3\overset{CH_3}{\overset{|}{C}}{=}CHCH_3$

less more

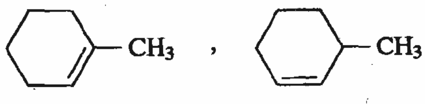
b) $CH_3CH_2CH_2CH{=}CH_2$,

less

$CH_3CH_2CH{=}CHCH_3$;

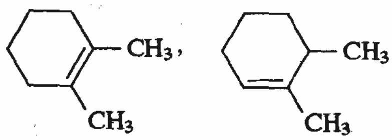
more

c)



more less

d)

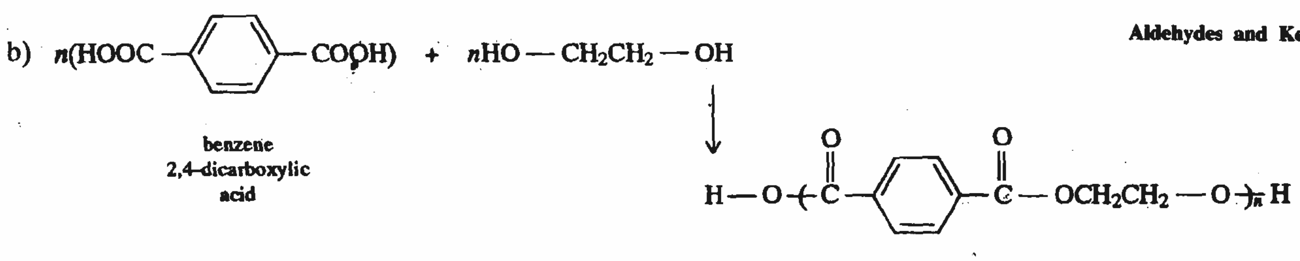


more less

4) a) 1-propanal; b) 2-butanone;
c) 2-propanone; d) 2-methyl-butene

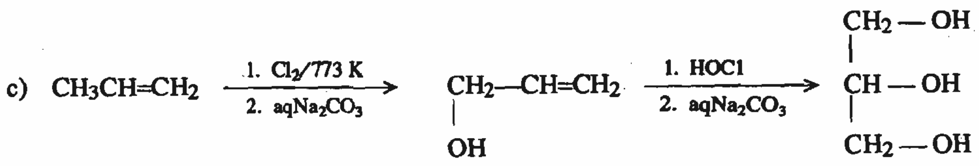
5) b.

6) a) $HOCH_2CH_2OH \xrightarrow[433\ K]{Na} N_aOCH_2CH_2ON_a$

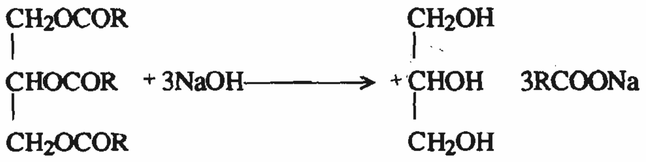
b) 

benzene 2,4-dicarboxylic acid

Terylene

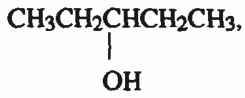
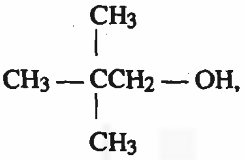
c) 

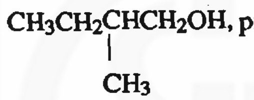
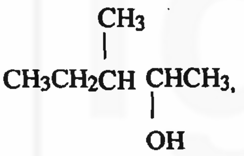
$$CH_3CH{=}CH_2 \xrightarrow[2.\ aqNa_2CO_3]{1.\ Cl_2/773\ K} \underset{\substack{|\\ OH}}{CH_2}{-}CH{=}CH_2 \xrightarrow[2.\ aqNa_2CO_3]{1.\ HOCl} \begin{matrix}CH_2-OH\\ |\\ CH-OH\\ |\\ CH_2-OH\end{matrix}$$

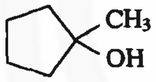


$$\begin{matrix}CH_2OCOR\\ |\\ CHOCOR\\ |\\ CH_2OCOR\end{matrix} + 3NaOH \longrightarrow + \begin{matrix}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix} \quad 3RCOONa$$

Terminal Questions

1) a)  $CH_3CH_2\underset{\substack{|\\ OH}}{C}HCH_2CH_3$, secondary; b)  $CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}CH_2-OH$, primary;

c)  $CH_3CH_2\underset{\substack{|\\ CH_3}}{C}HCH_2OH$, primary; d)  $CH_3CH_2\overset{\substack{CH_3\\ |}}{C}H\ \underset{\substack{|\\ OH}}{C}HCH_3$, secondary;

e)  , tertiary

2)

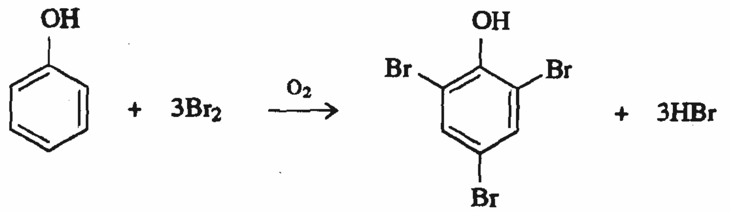
	a)	b)	c)	d)
b.p.	propanol	1-butanol	2-butanol	*p*-nitrophanol
Solubility in water	propanol	1-butanol	2-propanol	*p*-nitrophenol

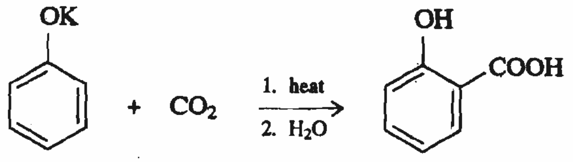
3) See subsection 12.6.1

4) See subsection 12.6.2

5) a) $(CH_3)_3COH + HCl \longrightarrow (CH_3)_3CCl + H_2O$

b) $C_2H_5OH \xrightarrow{Na} C_2H_5ONa + \frac{1}{2}H_2$

c) 

d) 

2-hydroxybenzoic acid (solialic acid)

6) Lucas reagent ($HCl/ZnCl_2$) is used to differentiate primary, secondary and tertiary alcohols. Tertiary alcohols react immediately upon shaking with lucas reagent in a test tube. Secondary alcohols react in 2, 3 minutes and primary alcohols do not react with reagent unless the mixture is heated.

UNIT 13 ETHERS AND SULPHUR ANALOGUES OF ALCOHOLS AND ETHERS

Structure

13.1 INTRODUCTION

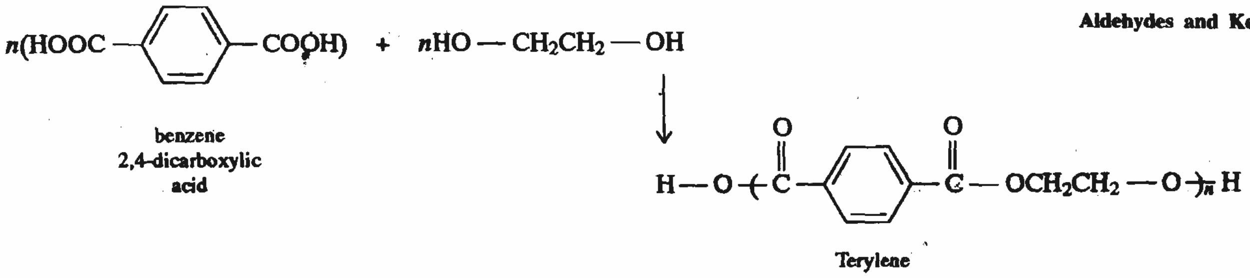
In the previous unit, while discussing the chemistry of alcohol, it was pointed out that dialkyl derivatives of water are called ethers. In this unit we shall take up the chemistry of ethers.

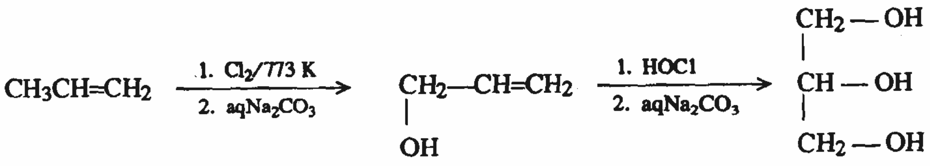
In this unit we shall first take a look at the different types of ethers and give you their preparation. We shall then consider their structure, physical, spectral and chemical properties and industrial uses. We shall also touch briefly on a special type of macrocyclic (i.e. large ring) compounds, the crown ethers. Finally, we shall take up the chemistry of sulphur analogues of alcohols and ethers.

Objectives

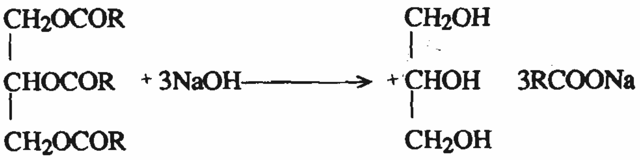
After studying this unit, you should be able to:

- list different types of ethers such as open chain ethers, epoxides and crown ethers,
- outline the preparation of open chain ethers and epoxides,
- explain the physical and spectral properties of ethers,
- describe the chemical properties of open chain ethers and epoxides,
- describe the crown ethers,
- state the different industrial uses of ethers, and
- describe the preparation and properties of thiols and sulphides.

b) 

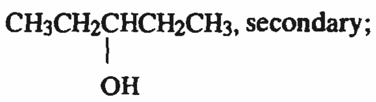
c) 

$$CH_3CH{=}CH_2 \xrightarrow[2.\ aqNa_2CO_3]{1.\ Cl_2/773\ K} \underset{\displaystyle OH}{CH_2}{-}CH{=}CH_2 \xrightarrow[2.\ aqNa_2CO_3]{1.\ HOCl} \begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

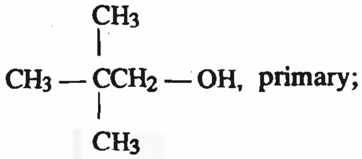


$$\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array} + 3NaOH \longrightarrow + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \quad 3RCOONa$$

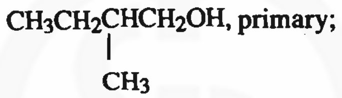
Terminal Questions

1) a) 

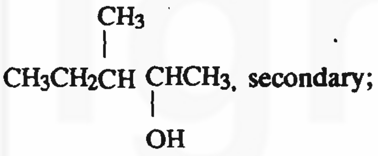
$CH_3CH_2\underset{\displaystyle OH}{C}HCH_2CH_3$, secondary;

b) 

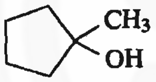
$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_2-OH$, primary;

c) 

$CH_3CH_2\underset{\displaystyle CH_3}{C}HCH_2OH$, primary;

d) 

$CH_3CH_2\overset{\displaystyle CH_3}{C}H\ \underset{\displaystyle OH}{C}HCH_3$, secondary;

e) 

, tertiary

2)		a)	b)	c)	d)
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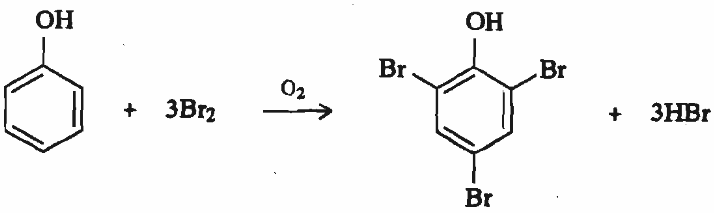
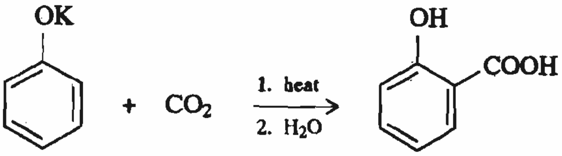
c) 

d) 

2-hydroxybenzoic acid
(solialic acid)

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UNIT 13 ETHERS AND SULPHUR ANALOGUES OF ALCOHOLS AND ETHERS

Structure

13.1 INTRODUCTION

In the previous unit, while discussing the chemistry of alcohol, it was pointed out that dialkyl derivatives of water are called ethers. In this unit we shall take up the chemistry of ethers.

In this unit we shall first take a look at the different types of ethers and give you their preparation. We shall then consider their structure, physical, spectral and chemical properties and industrial uses. We shall also touch briefly on a special type of macrocyclic (i.e. large ring) compounds, the crown ethers. Finally, we shall take up the chemistry of sulphur analogues of alcohols and ethers.

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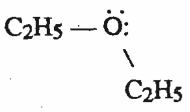
- describe the chemical properties of open chain ethers and epoxides,
- describe the crown ethers,
- state the different industrial uses of ethers, and
- describe the preparation and properties of thiols and sulphides.

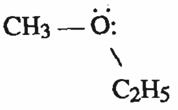
13.2 CLASSIFICATION

Ethers can be considered as derivatives of water. They can also be considered as alkyl derivatives of alcohols. Like water and alcohols, ethers contains an sp^3 hybridised oxygen atom. But, in an ether the oxygen is bonded to two carbon atoms. The groups bonded to the ether oxygen can be alkyl, aryl, ethenyl, or any other carbon containing groups. Aliphatic ethers may be simple or symmetrical in which both the alkyl groups are the same or mixed i.e. unsymmetrical in which case the two alkyl groups are different, e.g.,



diethyl ether
(ether)

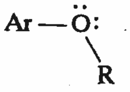
simple ether



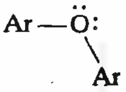
methyl ethyl ether
(methoxy ethane)

mixed ether

Aromatic ethers may be regarded as derivatives of phenol and are also divided into two groups, the alkyl aryl ethers and diaryl ethers:



alkyl aryl ethers
or phenolic ethers

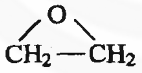


diaryl ethers

where, R = alkyl group

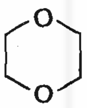
Ar = aryl group

Ethers can be either open chain or cyclic. When the ring size (including the oxygen atom) is five or greater, the chemistry of the cyclic ether is similar to that of an open chain ethers. Three membered cyclic ethers are called oxiranes (IUPAC name), which are often known as epoxides. Because of Baeyer strain associated with small rings, epoxides are more reactive than other ethers.



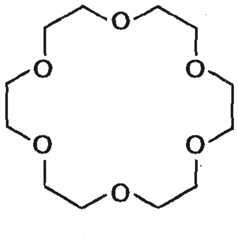
oxirane
(ethylene oxide)
epoxide

tetrahydrofuran
(THF)



1,4-dioxane

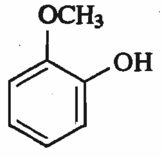
Large ring systems with repeating $-OCH_2CH_2-$ units are called **crown ethers.** These compounds are valuable reagents which can be used to help dissolve inorganic salts in organic solvents. Crown ethers are named as *X* crown *Y*, where *X*=the total number of atoms in the ring and *Y*=the total number of oxygen atoms in the ring. For example,

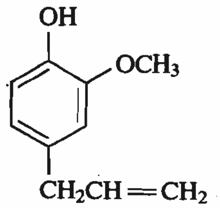


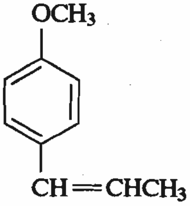
18-Crown-6

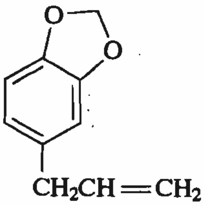
A crown ether with a total number of atoms 18 and 6 oxygen atoms in the ring

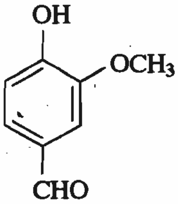
Ethers occur widely in nature, some examples of naturally occurring ethers are:


Guaicol
(beech-wood
tar)


eugenol
(oil of
cloves)


anethol
(aniseed
oil)


safrole
(camphol
oil)


Vanillin
(vanilla
been)

13.3 PREPARATION OF ETHERS

In this sections, we will discuss first the preparation of open chain ethers and then the preparation of epoxides.

13.3.1 Preparation of Open Chain Ethers

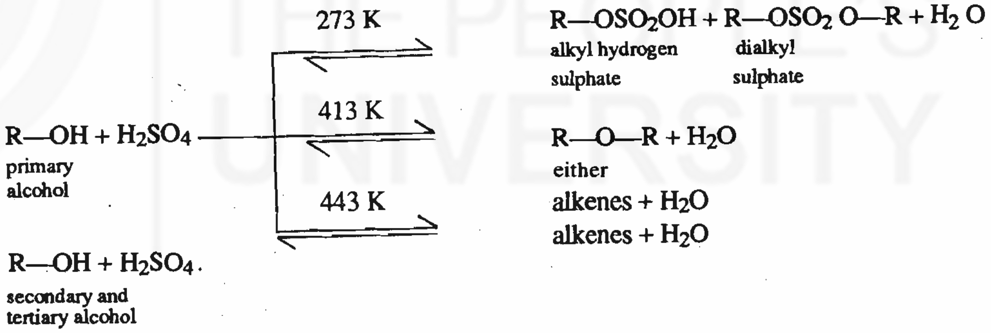
Ethers are commonly prepared from alcohols. There are two methods.

i) Acid catalysed dehydration
ii) Nucleophilic displacement (Williamson ether synthesis)

Let us discuss these preparative method briefly.

i) Acid catalysed dehydration

In Unit 7 we described the conversion of alcohols to alkenes in the presence of sulphuric acid. When an alcohol is reacted with H_2SO_4, a series of reversible reactions occur under different experimental conditions. Which reaction product predominates depends on the structure of the alcohol, the relative concentration of reactants, and the temperature of the reaction mixture. For example.



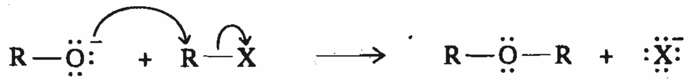
As shown above primary alcohols give alkyl hydrogen sulphate and dialkyl sulphate at low temperatures, symmetrical ethers at moderate temperature and alkenes at high temperature. Tertiary alcohols and to a large extent, secondary alcohols yield alkenes.

Industrially, diethyl ether is prepared by this method from ethanol in the presence of sulphuric acid. But in the laboratory, as might be expected, we get a large number of possible products, and this method is, therefore, seldom used for the synthesis of ethers.

ii) Williamson ether synthesis

Ethers are also prepared by Williamson's synthesis in which alcohols are employed as starting materials. One alcohol is converted to alkyl halide (R—X), another alcohol is converted to sodium or potassium alkoxide or then two products are heated together.

$$\underset{\text{sodium alkoxide}}{R\text{—}ONa} + \underset{\text{alkyl halide}}{R\text{—}X} \longrightarrow \underset{\text{symmetrical ether}}{R\text{—}O\text{—}R} + Na^+X^-$$



The mechanics of the reaction is S_N2, which we have discussed in detail in Unit 11.

As already mentioned the tendency for alkyl halides to undergo this reaction is *p > sec > tert*.

Secondary and tertiary alkyl halides lead to alkenes, while aryl and ethenyl halies do not undergo S_N2 reactions, therefore, they do not give ethers with alkoxides or phenoxides.

This method can also be used to prepare phenolic ethers:

$$Ar—O^-Na^+ + R—X \longrightarrow Ar—O—R + Na^+X^-$$

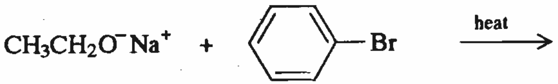
sodium phenoxide	alkyl halide	phenolic ethers or alkyl aryl ether

Before considering the properties of ethers, try the following SAQ.

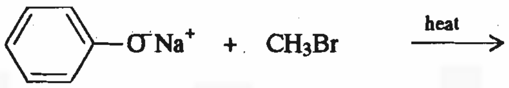
SAQ 1

Predict the major products of these reactions?

a) $CH_3CH_2OH + H_2SO_4 \xrightarrow[413]{warm}$

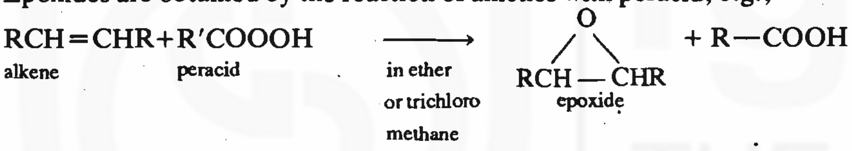
b) 

c) $CH_3O^-Na^+ + (CH_3)_3CCl \xrightarrow{heat}$

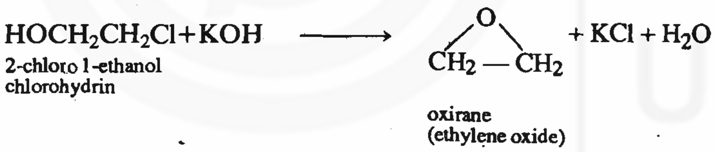
d) 

13.3.2 Preparation of Epoxides

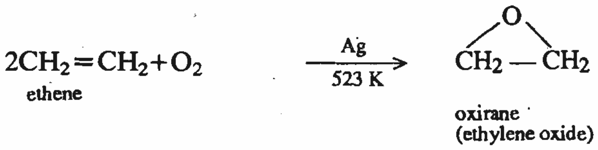
Epoxides are obtained by the reaction of alkenes with peracid, e.g.,



They are also prepared by the reaction of chlorohydrin with alkali, e.g.,



Ethylene oxide is manufactured by the silver-catalysed oxidation of ethenes with oxygen.

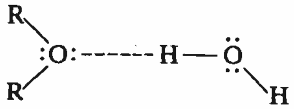


13.4 PROPERTIES OF ETHERS

Before studying the reactions of open chain ethers and epoxides in detail, let us first take up their physical and spectral proposition.

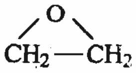
13.4.1 Physical Properties

Ethers are polar compounds with dipole moment 3.9×10^{-30}C m (for diethyl ether). But they are not as polar as water, 6.0×10^{-30}C m and alcohols, 5.7×10^{-30}C m (for methanol). Ethers have lower boiling points as compared to those of alcohols containing the same number of carbon atoms. This is due to the fact that, unlike alcohols, ethers cannot associate through hydrogen bonds in the pure state because they have no hydrogen attached to the oxygen. However, ethers can form hydrogen bonds with water, alcohols and phenols. Because of hydrogen bonding with water, ethers show a considerable solubility in water.



We are summarising the physical properties of some ethers in Table 13.1.

Table 13.1: Physical properties of some ethers

Name	Formula	Bp,K	Density kg dm^{-3} at 293 K	Solubility in H_2O
Dimethyl ether	CH_3OCH_3	249	gas	miscible
Diethyl ether	$C_2H_5OC_2H_5$	307.6	0.71	8 g/100 cm^3
Methyl phenyl ether (anisol)	$C_6H_5—OCH_3$	427	—	—
Tetrahydrofuran (THF)		339	0.89	miscible
Oxirane (ethylene oxide)		286.5	8.88 (at 283 K)	miscible

Before studying the spectral properties of ethers try the following SAQ.

SAQ 2

To what effect can you attribute water solubility of ethers?

....

....

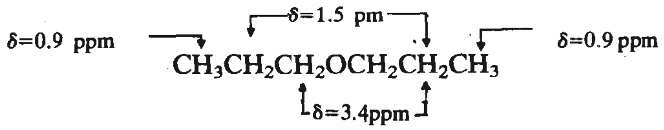
....

....

13.4.2 Spectral Properties

Like alcohols, ethers show the C—O, stretching vibration at 1060-1300 cm^{-1} range in ir spectra. The O—H band characteristic of alcohol is, of course, absent.

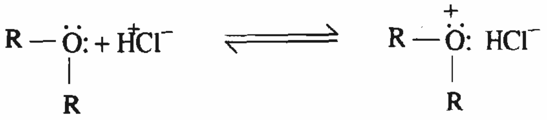
In the nmr spectra, as in the case of alcohols, the oxygen atoms cause deshielding of the protons on adjacent carbon (α protons) and shifts their absorption downfield.



$CH_3CH_2CH_2OCH_2CH_2CH_3$

13.4.3 Chemical Properties of Open Chain Ethers

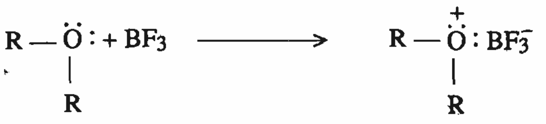
Ethers are quite unreactive and behave more like alkanes than like organic compounds containing functional groups. The bond between carbon and oxygen in a ether is called the **ether linkage.** This ether linkage is not affected by bases, oxidising agents and reducing agents. The oxygen atom in ethers can readily accept protons (base in Bronsted concept) and it also can be electron-pair donor (Lewis base). On treatment with acids, ethers give oxonium salts:



$$R—\ddot{O}{:}(—R) + \overset{+}{H}Cl^- \rightleftharpoons R—\overset{+}{\ddot{O}}{:}(—R)\ HCl^-$$

oxonium salt

The solubility in sulphuric acid is thus a convenient method for distinguishing between ethers and hydrocarbons and alkyl halides. Similarly, ethers react with Lewis acids,



$$R-\ddot{O}(R): + BF_3 \longrightarrow R-\overset{+}{\ddot{O}}(R):BF_3^-$$

oxonium salt

Further treatment with an alkyl fluoride gives a tertiary oxonium salt, trialkyl fluoroborate.

$$R_2O^+:BF_3^- + RF \longrightarrow \underset{\text{trialkylfluoroborates}}{R_3O^+:BF_4^-}$$

The products of the above reaction, i.e. the trialkyl fluoborates are powerful alkylating agents in many reactions.

On heating ethers with dilute sulphuric acid under pressure alcohols are obtained:

$$R—O—R + H_2O \xrightarrow[\text{pressure}]{H_2SO_4} 2R—OH$$

When they are heated with a strong acid (usually HI or HBr), ethers do undergo **substitution reactions.** This is the most important reaction of ethers. In this reaction, cleavage of the ether linkage (C—O) takes place. For example, when heated with HI an ether yields an alcohol and an iodoalkane. Under the reaction conditions, the alcohol formed in turn reacts with HI to give iodoalkane and water.

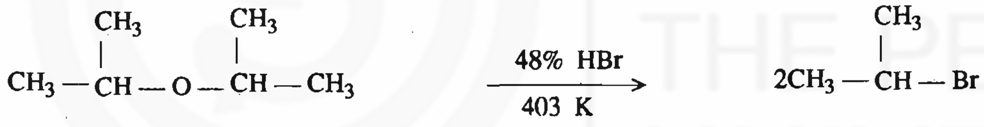
$$R—O—R + HI \xrightarrow{\text{heat}} \underset{\text{iodoalkane}}{R—I} + \underset{\text{alcohol}}{R—OH}$$

$$R—O—H + HI \longrightarrow R—I + H_2O$$

We can write the net reaction as

$$R—O—R + 2HI \xrightarrow[403\text{–}423\ K]{\text{heat}} 2RI + H_2O$$

Cleavage of ethers may also be accomplished by the use of concentrated (48%) hydrobromic acid.

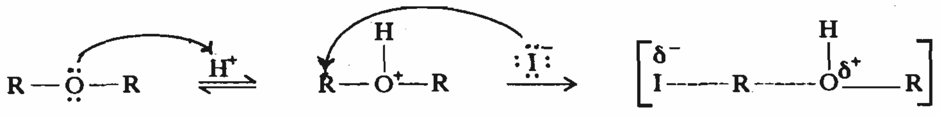


$$CH_3—\underset{}{\overset{CH_3}{CH}}—O—\overset{CH_3}{CH}—CH_3 \xrightarrow[403\ K]{48\%\ HBr} 2CH_3—\overset{CH_3}{CH}—Br$$

2-(1-methyl ethoxy) propane
(isopropyl ether)

(2-bromopropane)
(isopropyl bromide)

Ether cleavage with HI or HBr proceeds by almost the same path as the reaction of alcohol with HX: protonation of the oxygen, followed by S_N1 or S_N2 reaction.



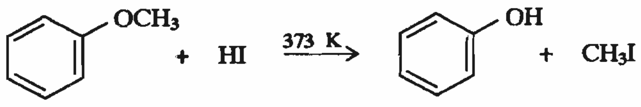
protonated

S_N2 transition state

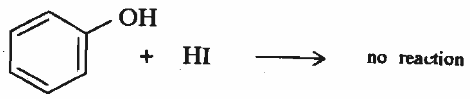
$$\longrightarrow R—I + ROH$$

These reactions have great importance in synthesis. The hydroxyl group in a poly- functional compound can be protected by converting it into an ether and later, after affecting a chemical transformation at another site in the molecule regenerating through treatment with concentrated hydriodic acid.

Aromatic ethers, such as anisol, yield the alkyl iodide and phenol, not iodobenzene and methanol, because sp^2-hybridise carbon does not under go reaction by an S_N1 or SN^2 path.



anisol



The Zeisel procedure for estimation of the number of methoxyl (CH_3O-) or ethoxyl (CH_3CH_2O-) groups in alkyl aryl ethers consists of ether cleavage with excess HI, followed by distillation of volatile iodomethane or iodoethane from the reaction mixture. Then, the iodoalkanes are treated with an ethanolic solution of silver nitrate, and the silver iodide so formed is weighed.

SAQ 3

In Section 13.2, we mentioned the structures of vanillin, a naturally occurring ether. Now, write the equation for the reactions that would occur in the determination of the number of methoxyl groups.

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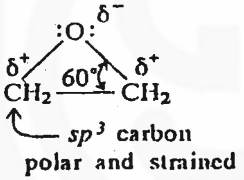
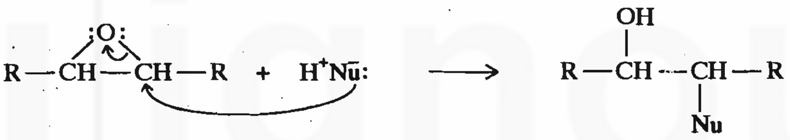
An epoxide ring cannot have normal *sp*^{3} bond angles of 109°; instead, the inter nuclear angles are 60°, a geometric requirement of the three-membered ring. The orbitals forming the ring bonds are incapable of maximum overlap. Therefore, epoxide ring are strained. The polarity of the C—O bond, along with the ring strain, contributes to the high reactivity of epoxides compared to the reactivity of other ethers



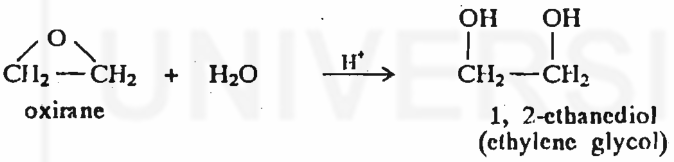
13.4.4 Chemical Properties of Epoxides

As stated earlier epoxides are highly reactive compounds. The characteristic reaction of epoxides is nucleophilic substitution reactions. In this reaction, ring opening takes place which can occur either under alkaline or acidic reaction conditions. General reaction can be written as

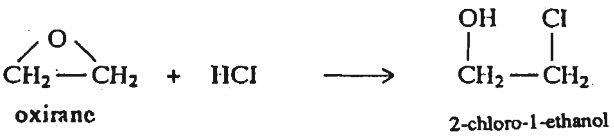


In Acid

Like other ethers, epoxides undergo carbon-oxygen bond cleavage when treated with an acid. However, because of their high reactivity much milder acidic conditions are employed than for cleavage of open chain others.

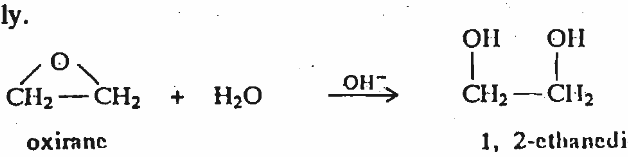


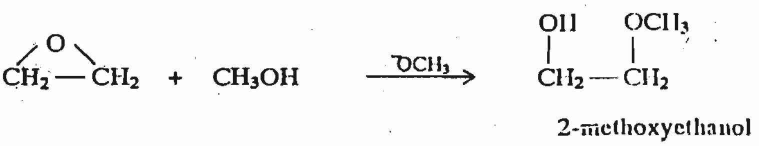
With concentrated acid, e.g., HCl, chlorohydrins are obtained:



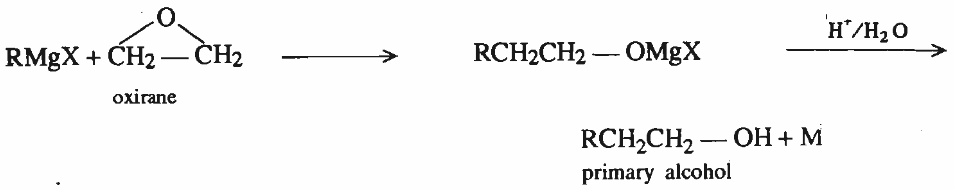
In Base

Unlike open chain or 5- or higher membered cyclic ethers epoxides react with bases, e.g., NaOH, $NaOCH_3$ to give 1,2-ethanediol (ethylene glycol) and 2-methoxyethanol, respectively.

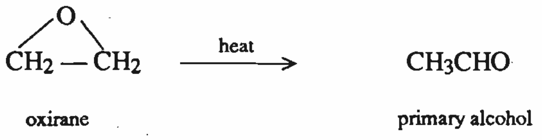




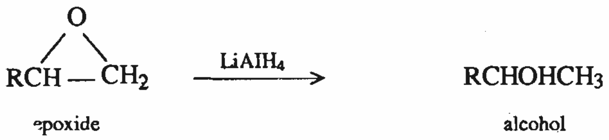
Epoxides are used as intermediates in synthesis. The reaction of epoxides with Grignard reagent has already been mentioned in Unit 11. Oxirane with Grignard reagent gives primary alcohol:



On heating oxirane ethanal is formed:



Reduction with lithium aluminium hydride converts epoxides into alcohols, e.g.,



SAQ 4

How would you prepare 1-butanol from the Grignard reagent C_2H_5MgBr? Show the steps involved in this synthesis.

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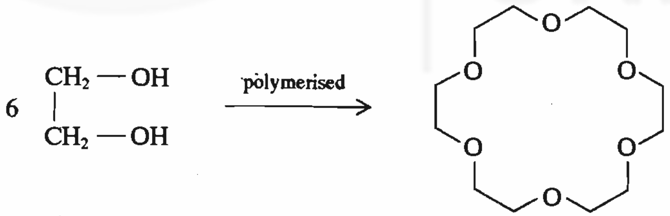
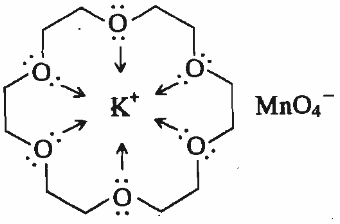
13.5 CROWN ETHERS

As mentioned earlier, crown ethers are cyclic ethers with structure consisting of repeating $-OCH_2CH_2-$ units. They are polymers of 1, 2 ethanediol (glycol).



18-crown-6

The unique feature of crown ether is that they can chelate metal ions and give metal complexes which are soluble in nonpolar organic solvents. In this form the crown ether is referred to as the host, while the metal ion is called the guest. For example, purple benzene is a reagent in which $KMnO_4$, complexed by 18-crown-6, is dissolved in benzene.



18-crown-6-complex

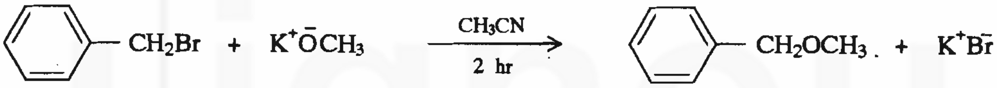
Some of the crown ethers are involved in the transport of ions across biological membranes.

13.6 INDUSTRIAL USES

Ethers are widely used as solvents for oils, fats, gums, resins, etc. Diethyl ether is used as a refrigerant. It is used as an solvent for extraction of organic matter, as an anaesthetic in surgery and in the laboratory for preparation of Grignard reagents. It is known that the Grignard reagents coordinate with ether and in the ether solution it exist as: $RMgX(OR'_2)_2$ (as dietherates). Methy *tert*-butyl ether and diisopropyl ether are used as an anti-knocking agent instead of the highly toxic tetraethyl lead. These compounds increase the octane number when mixed with petrol.

In the presence of air and light, ether forms peroxide, $CH_3CH(OOH)OC_2H_5$, which is highly explosive. To prevent the formation of peroxide either, some ethanol or a small amount of cuprous compound, e.g., cuprous oxide is added.

Crown ethers have great advantages in synthetic organic chemistry. One is that an ionic reagent can be dissolved in an organic phase where it can react with a water-insoluble organic compound. A second advantage is that the nucleophilicity of an anion such as CN^- or CH_3COO^- is greatly enhanced in nonpolar solvents, where the anion is poorly solvated, or naked. An example of how a crown ether increases the rate of a substitution reaction is preparation of the benzyl methyl ether shown in acetonitrite which does not dissolve ionic compounds.



5% yield with no crown ether.
100% yield with 18-crown-6.

13.7 SULPHUR ANALOGUES OF ALCOHOLS AND ETHERS

In Unit 12 and in this unit we have described the chemistry of alcohols and ethers. In this section we shall take a look at the chemistry of sulphur analogues of alcohols and ethers.

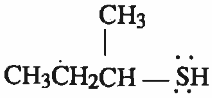
The divalent sulphur compounds can be regarded as the sulphur analogues of the corresponding oxygen compounds. The sulphur analogue of an alcohol is called an **alkane thiol** or simply **thiol**, or by its older name **mercaptan**. Similarly sulphur analogue of a phenol is called an aromatic thiol or thiophenol. The $-SH$ group is called a thiol group.

$CH_3 — \ddot{\underset{..}{S}}H$

methanethiol

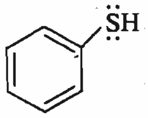
$CH_3\,CH_2 - \ddot{\underset{..}{S}}H$

ethanethiol



$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}H — \ddot{\underset{..}{S}}H$

2-butanethiol



Thiophenol

The sulphur analogue of an ether is called a sulphides or thioether (R—S—R).

$CH_3—S—CH_3$

dimethyl sulphide

$CH_3CH_2CH_2—S—CH_2CH_3$

ethyl propyl sulphide

Let us study the preparation of thiols and sulphides.

13.7.1 Preparation of Thiols and Sulphides

Thiols can be prepared from alkyl halides by displacement with hydrosulphide ion, HS^- in ethanol solution.

$$CH_3I + Na^{+-}SH \xrightarrow{C_2H_5OH} \underset{\text{methanethiol}}{CH_3{-}SH} + Na^+I^-$$

Good yields are obtained only if an excess of hydrosulphide is used because of the equilibrium:

$$HS^- + CH_3{-}SH \rightleftharpoons H_2S + CH_3{-}S^-$$

The thiol anion produced by this equilibrium is itself a good nucleophile and can react with the alkyl halide to give the corresponding sulphide.

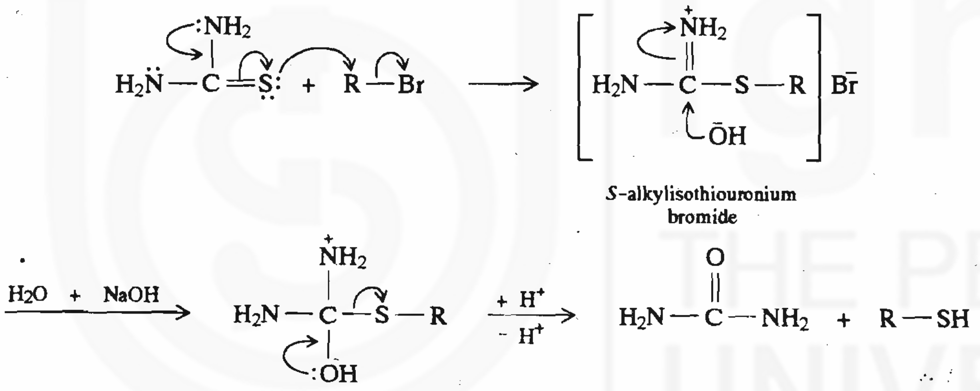
$$CH_3{-}S^- + CH_3{-}I \rightleftharpoons \underset{\text{dimethyl sulphide}}{CH_3{-}S{-}CH_3} + I^-$$

The use of a large excess of hydrosulphide makes its reaction with the alkly halide more probable and maximises the yield of a thiol.

Thiols can also be prepared by the reaction of Grignard reagent with sulphur.

$$(CH_3)_3CMgBr + S_8 \longrightarrow (CH_3)_3CSMgBr \xrightarrow{HCl} \underset{\text{2-methyl-2-propane thiol}}{(CH_3)_3C{-}SH} + MgBrCl$$

Thiols may be prepared in good yield by alkylation of the highly nucleophilic thiourea followed by basic hydrolysis:



Sulphides are prepared by a variation of the Williamson synthesis.

$$\underset{\text{ethanethiol}}{CH_3CH_2{-}SH} + NaOH \qquad CH_3CH_2{-}S^-Na^+ + H_2O$$

$$CH_3CH_2{-}S^-Na^+ + CH_3Br \longrightarrow \underset{\text{ethyl,methyl sulphide}}{CH_3CH_2{-}S{-}CH_3} + NaBr$$

13.7.2 Properties of Thiols and Sulphides

The most characteristic property of the thiols and sulphides is their disagreeable odour. The human nose is very sensitive to these compounds and can detect their presence at levels of about 0.02 parts thiol to one billion parts air. For this reason, methyl sulphide is added to natural or L.P. gas as an odourant for safety precaution. Natural or L.P. gas is itself odourless.

Sulphur is less electronegative than oxygen and its outer electrons are more diffuse, therefore, sulphur atoms form weaker hydrogen bonds then oxygen atoms. For this reason, H_2S has a lower boiling point (b.p. 212 K) than water (b.p. 373 K) and thiols have lower boiling points than their analogous alcohols (see Table 13.2).

Table 13.2: Comparison of the boiling points of thiols and alcohols

Compound	Boiling point K
$CH_3—SH$	279.2
$CH_3—OH$	338.0
$CH_3CH_2—SH$	310.0
$CH_3CH_2—OH$	351.5

Because of the relatively weaker hydrogen sulphur bond, thiols are more acidic than water, with pK_a values ranging from 9 to 12. Unlike alcohols which can in deprotonated only by strong base such as sodium metal or $N\bar{H}_2$, thiols can be ionised by the hydroxide ion.

$$CH_3CH_2—SH + OH^- \longrightarrow CH_3CH_2—S^- + H_2O$$

stronger acid than H_2O	stronger base than RS^-

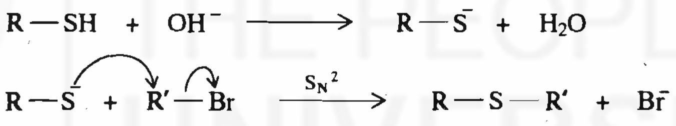
Chemical Reactivity of Thiols and Sulphides

Thiols and sulphides can react in ways that are very similar to those of the corresponding oxygen analogues. Thiols and sulphides react more rapidly than their oxygen analogues because the sulphur atom in thiols and sulphides is more nucleophilic than the oxygen atom in alcohols. The possible explanation for greater nucleophilicity of sulphur analogues is that the outer electrons on sulphur atom is more diffused because of the larger size of sulphur atom as compared to the smaller oxygen atom nucleophiles. Therefore, the electrons of sulphur readily available for substrate (electrophile) in a reaction.

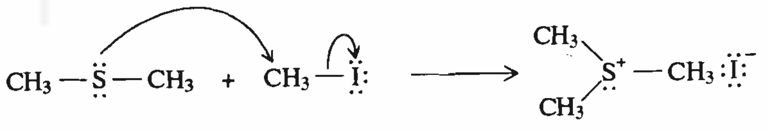
Thiols react with alkyl halides by the normal S_N2 mechanism in the presence of a base to give sulphides.

$$R—SH + R'—Br \xrightarrow{NaOH} \underset{\text{sulphide}}{R—S—R'} + NaBr + H_2O$$

Mechanism

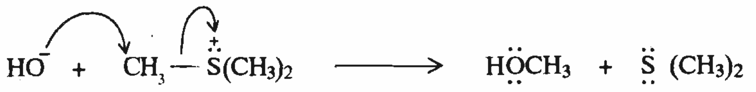


Similarly, sulphides react readily with alkyl halides by the S_N2 mechanism to produce trialkylsulphonium salts.



trimethylsulphonium iodide

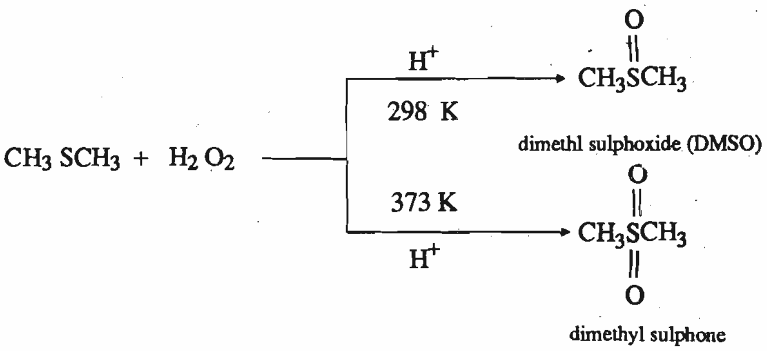
Like their oxonium analogues, sulphonium salts are subject to nucleophilic attack at carbon, sulphide functioning as the leaving group:



Thiols are readily oxidised by mild oxidising agents such as I_2 to disulphides. The disulphide bond is weak is easily reduced by either tin or zinc in dilute acid to give thiol.

$$2R—SH \underset{\text{reduction}}{\xrightarrow{\text{oxidation}}} \underset{\text{a disulphide}}{R—S—S—R}$$

The disulphide can be oxidised to a sulphoxide or a sulphone depending on the reaction conditions. For example, 30% hydrogen peroxide in the presence of an acidic catalyst oxidises a sulphides to sulphoxides at 298 K or to sulphones at 373 K.



The unique behaviour of sulphoxide is due to the presence of the empty *d* orbital in the sulphur atom.

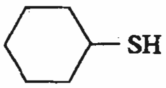
The disulphide link is an important structural feature of some proteins, like insulin. The disulphide bond helps hold protein chains together in their proper shapes.

Dimethyl sulfoxide (DMSO) is a unique and versatile solvent. It has a high dielectric constant. It is a powerful solvent for both inorganic ions and organic Compounds. Reactants often have enhanced reactivity in DMSO compared to that in alcoholic solvents. DMSO readily penetrates the skin and has been used to promote the dermal absorption of drugs.

SAQ 5.

Complete the following equations:

a) $CH_3-S-CH_3 \xrightarrow[298\ K]{H_2O_2}$

b)  $\xrightarrow[2.\ CH_3CH_2I]{1.\ NaOH}$

c) $C_2H_5SH \xrightarrow{I_2}$

13.8 SUMMARY

What we have studied in this unit can be summarised as follows:

- Ethers can be prepared by the reaction of alcohols with sulphuric acid at moderate temperatures or by the reaction of an alkoxide (RO^-) or phenoxide (ArO^-), with an alkyl halide (Williamson ether synthesis).
- Epoxides can be prepared by the reaction of a per acid (RCOOOH) with an alkene or by the reaction of chlorohydrin with alkali.
- Ethers are less reactive than alcohols and they undergo only ether cleavage reaction when heated with HBr or HI.
- Epoxides are more reactive than other ethers and undergo ring opening with acids or with bases or with Grignard reagents.
- Crown ethers are cyclic ethers that are used to chelate metal ions.
- Cyclic ethers are intermediates in many synthetic reactions. Most ethers are used as solvents.
- Thiols and sulphides are similar to their oxygen analogues in many of their reactions, through they are stronger nucleophiles.

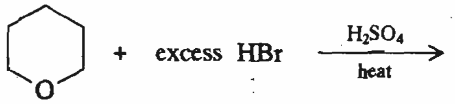
13.9 TERMINAL QUESTIONS

1) Complete the following equations:

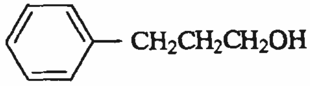
a) $ROH + H_2SO_4 \xrightarrow{273\ K}$

b) $\underset{\text{sodium phenoxide}}{C_6H_5O^-Na} + C_2H_5Br \longrightarrow$

c)



2) Write equation to show how you would prepare the following compound.



3) How are the methoxy and ethoxy groups estimated in a compound?

4) Give two important features of the crown ethers.

5) Why one sulphur analogues of alcohol and ethers more nucleophilic? Give two examples of their nucleophilic reactions.

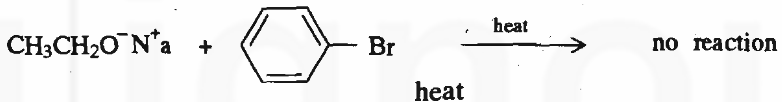
13.10 ANSWERS

Self Assessment Questions

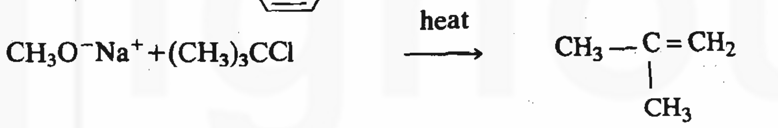
1) a) $CH_3CH_2OH + H_2SO_4 \xrightarrow[\text{excess of alcohol}]{\text{warm}} CH_3CH_2{-}O{-}CH_2CH_3 + H_2O$

diethyl ether

b)



c)



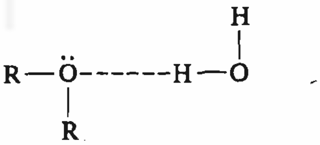
$$CH_3O^-Na^+ + (CH_3)_3CCl \xrightarrow{\text{heat}} CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$$

2-methyl propene

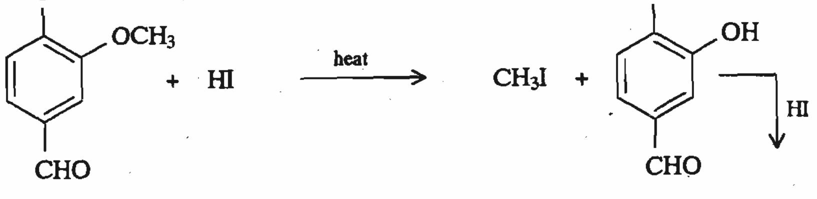
d)

methyl phenyl ether (anisole)

2) Water solubility of ether can be attributed to hydrogen bonding between oxygen of ether with water.



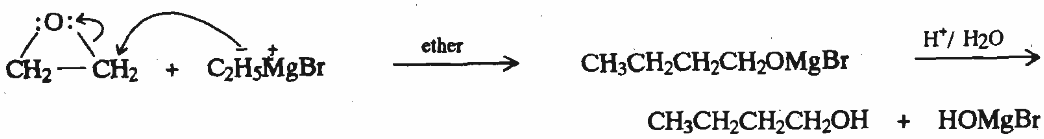
3)



Vanillin

no further reaction

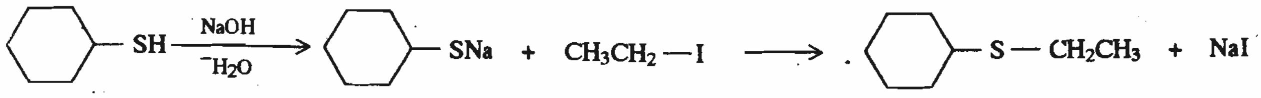
4) 1-Butanol can be obtained by the reaction of Grignard reagent C_2H_5MgBr with oxirane and followed by hydrolysis with water.



5) a) $CH_3-S-CH_3 \xrightarrow[298\ K]{H_2O_2} CH_3-S-CH_3$

dimethyl sulphoxide

b)



c) $C_2H_5-SH + I_2 \longrightarrow R-S-S-R + 2\,HI$

a disulphide

Terminal Questions

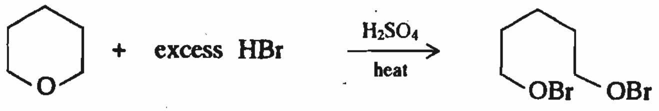
1) a) $R-OH + H_2SO_4 \xrightarrow{273\ K} R-OSO_2OH + R-OSO_2O-R + H_2O$

alkyl hydrogen sulphate; dialkyl sulphate

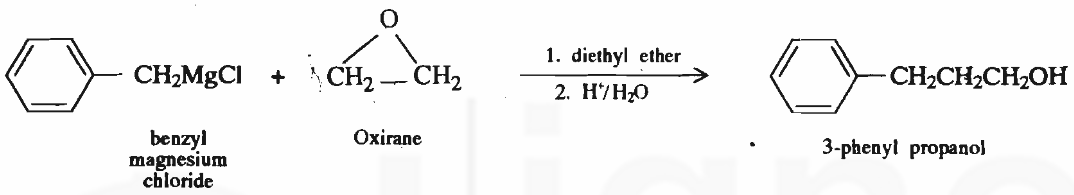
b) $C_6H_5-ON_a + C_2H_5-Br \longrightarrow C_6H_5-O-C_2H_5 + NaBr$

sodium phenoxide; ethylphenyl ether

c)



2)



3) Methoxy or ethoxyl groups in an organic compounds are estimated by the Zeisel method. In this method the organic compound is first heated with excess of HI followed by distillation of volatile iodomethane or iodoethane from the reaction mixture. Then the iodomethane or iodoethane is treated with ethanolic solution of silver nitrate, and silver iodide so formed is weighed.

4) i) Crown ethers can chelate metal ions and give metal complexes, which are soluble in non-polar organic solvents.

ii) Nucleophilicity of certain anions is also increased by the crown ether and hence increased the rate of reaction of such anions.

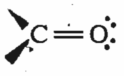
5) See section 13.10.2.

UNIT 14 ALDEHYDES AND KETONES

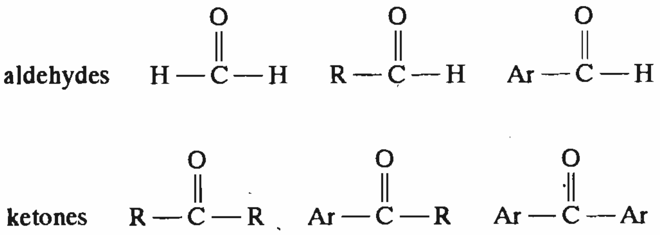
Structure

14.1 INTRODUCTION

In previous units you have studied the chemistry of alcohols and ethers. In this unit we take up aldehydes and ketones. Both these classes of organic compounds have a carbonyl group, >C=O. A ketone has two alkyl (or aryl) groups attached to the carbonyl carbon, while an aldehyde has at least one hydrogen atom attached to the carbonyl carbon. The other group in an aldehyde can be alkyl, or aryl



carbonyl group



aldehydes $H-\overset{\overset{O}{\|}}{C}-H$ $R-\overset{\overset{O}{\|}}{C}-H$ $Ar-\overset{\overset{O}{\|}}{C}-H$

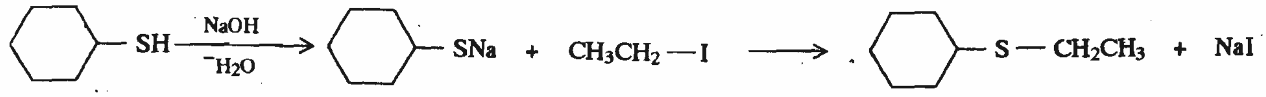
ketones $R-\overset{\overset{O}{\|}}{C}-R$ $Ar-\overset{\overset{O}{\|}}{C}-R$ $Ar-\overset{\overset{O}{\|}}{C}-Ar$

The remarkable reactivity of the carbonyl group makes the chemistry of aldehydes and ketones the backbone of synthetic organic chemistry. The double bond between the carbon and oxygen atoms in these compounds serves as a model for the reaction of many other functional groups containing π bonds between dissimilar atoms. Although the reactions of carbonyl compounds are quite simple their synthetic utility is enormous. Additions and substitution reactions are of major interest. In this unit you

5) a) $CH_3—S—CH_3 \xrightarrow[298\ K]{H_2O_2} CH_3—S—CH_3$

dimethyl sulphoxide

b)



c) $C_2H_5—SH + I_2 \longrightarrow R—S—S—R + 2\ HI$

a disulphide

Terminal Questions

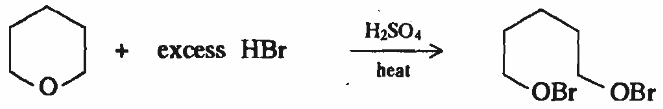
1) a) $R—OH + H_2SO_4 \xrightarrow{273\ K} R—OSO_2OH + R—OSO_2O—R + H_2O$

alkyl hydrogen sulphate; dialkyl sulphate

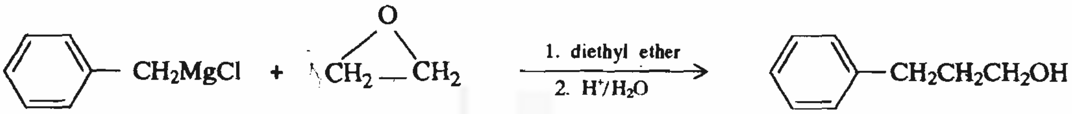
b) $C_6H_5—ON_a + C_2H_5—Br \longrightarrow C_6H_5—O—C_2H_5 + NaBr$

sodium phenoxide; ethylphenyl ether

c)



2)



benzyl magnesium chloride; Oxirane; 3-phenyl propanol

3) Methoxy or ethoxyl groups in an organic compounds are estimated by the Zeisel method. In this method the organic compound is first heated with excess of HI followed by distillation of volatile iodomethane or iodoethane from the reaction mixture. Then the iodomethane or iodoethane is treated with ethanolic solution of silver nitrate, and silver iodide so formed is weighed.

4) i) Crown ethers can chelate metal ions and give metal complexes, which are soluble in non-polar organic solvents.

ii) Nucleophilicity of certain anions is also increased by the crown ether and hence increased the rate of reaction of such anions.

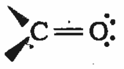
5) See section 13.10.2.

UNIT 14 ALDEHYDES AND KETONES

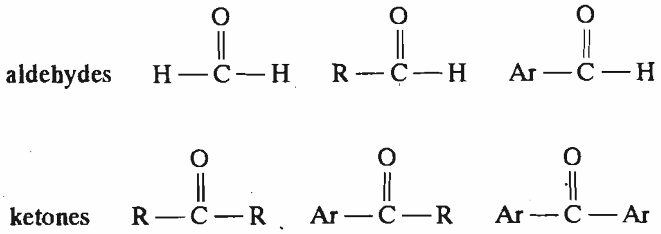
Structure

14.1 INTRODUCTION

In previous units you have studied the chemistry of alcohols and ethers. In this unit we take up aldehydes and ketones. Both these classes of organic compounds have a carbonyl group, $>C=O$. A ketone has two alkyl (or aryl) groups attached to the carbonyl carbon, while an aldehyde has at least one hydrogen atom attached to the carbonyl carbon. The other group in an aldehyde can be alkyl, or aryl



carbonyl group



aldehydes $H-\overset{\overset{O}{\|}}{C}-H$ $R-\overset{\overset{O}{\|}}{C}-H$ $Ar-\overset{\overset{O}{\|}}{C}-H$

ketones $R-\overset{\overset{O}{\|}}{C}-R$ $Ar-\overset{\overset{O}{\|}}{C}-R$ $Ar-\overset{\overset{O}{\|}}{C}-Ar$

The remarkable reactivity of the carbonyl group makes the chemistry of aldehydes and ketones the backbone of synthetic organic chemistry. The double bond between the carbon and oxygen atoms in these compounds serves as a model for the reaction of many other functional groups containing π bonds between dissimilar atoms. Although the reactions of carbonyl compounds are quite simple their synthetic utility is enormous. Additions and substitution reactions are of major interest. In this unit you will learn the basic principles which are responsible for the extreme reactivity of these compounds and on the basis of which reliable predictions can be made.

Here we will first consider the preparation of aldehydes and ketones and then the characteristic reactions of the carbonyl-group. Finally, we will study industrial uses of aldehydes and ketones and methods used for their detection.

Objectives

After studying this unit, you should be able to:

- list and describe the preparation of aldehydes and ketones,
- describe the commercial methods of preparation of methanal, ethanal, propanone, benzaldehyde and phenylethanone,
- describe the physical properties and spectral characteristics of carbonyl compounds,
- explain the reactivity of aldehydes and ketones,
- describe the lab detection of carbonyl compounds and the test which distinguish aldehydes from ketones, and
- state the industrial uses of aldehyde and ketones.

14.2 PREPARATION

We have already learned several reactions that can be used for the preparation of aldehydes and ketones. Recall the oxidation of alkenes with ozone, hydration of alkynes and oxidation or dehydrogenation of alcohols.

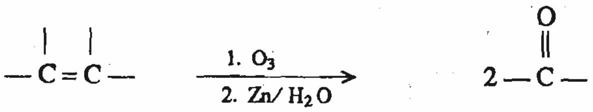
In this section we will first consider the general methods for the preparation of aldehyde and ketones and then follow them up with specific methods for benzaldehyde and industrial methods for the production of methanal, ethanal, propanone, benzaldehyde and phenylethanone (acetophenone).

14.2.1 General Methods of Preparation of Aldehydes and Ketones

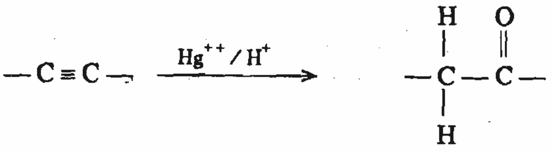
Aldehydes and ketones can be prepared from alkenes, alkynes, alcohols, carboxylic acids and their derivatives. We are summarising the general reactions of these methods of preparation in Table 14.1.

Table 14.1: Preparation of Aldehydes and Ketones

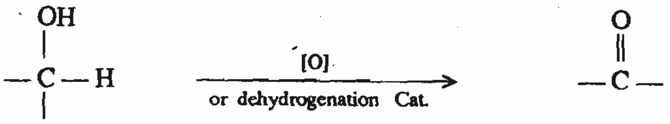
From alkenes



From Alkynes

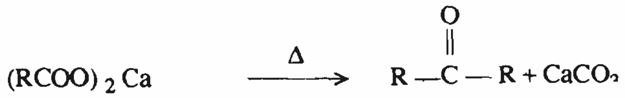


From Alcohol



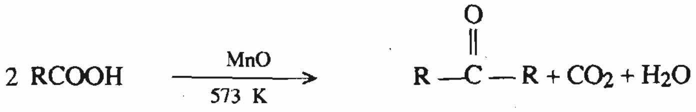
From Carboxylic Acids and their Derivatives

From Calcium Salts of Carboxylic Acids



$$(RCOO)_2Ca \xrightarrow{\Delta} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R + CaCO_3$$

From the reaction of Carboxylic Acids with Manganous oxide



$$2\ RCOOH \xrightarrow[573\ K]{MnO} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R + CO_2 + H_2O$$

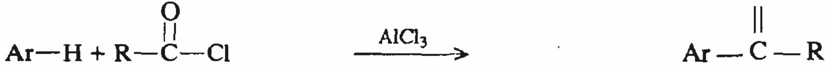
From acid chlorides by the Rosenmund's Method

$$RCOCl + H_2 \xrightarrow{H_2/Pd/BaSO_4} RCHO + HCl$$

From the Stephen's Method

$$2\ RCN \xrightarrow[HCl]{SnCl_2} 2\,RCHO + (NH_4)_2SnCl_6$$

From the Friedel-Crafts Reaction

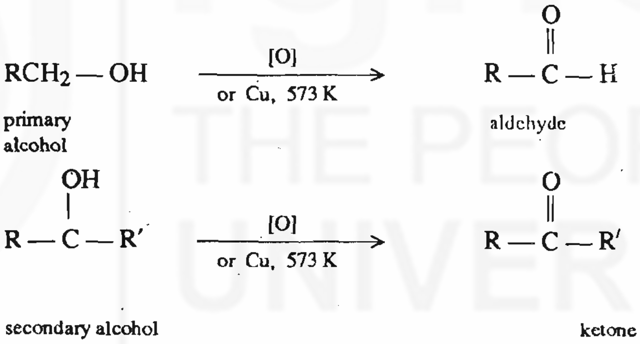


$$Ar{-}H + R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl \xrightarrow{AlCl_3} Ar{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R$$

Preparation of aldehydes and ketones from alkenes and alkynes has been discussed in Unit 7 and Unit 8, respectively. Here, we will consider preparation of these compounds from alcohols, and carboxylic acids and their derivatives.

i) From Alcohols

As mentioned in Unit 12, primary alcohols give aldehydes and secondary alcohols give ketones on dehydrogenation and oxidation. This is the most common way of synthesising an aldehydes and ketones in the laboratory.



$$\underset{\text{primary alcohol}}{RCH_2{-}OH} \xrightarrow[\text{or Cu, 573 K}]{[O]} \underset{\text{aldehyde}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H}$$

$$\underset{\text{secondary alcohol}}{R{-}\overset{\overset{\displaystyle OH}{|}}{C}{-}R'} \xrightarrow[\text{or Cu, 573 K}]{[O]} \underset{\text{ketone}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'}$$

We generally use the following oxidising agents for the oxidation of alcohols:

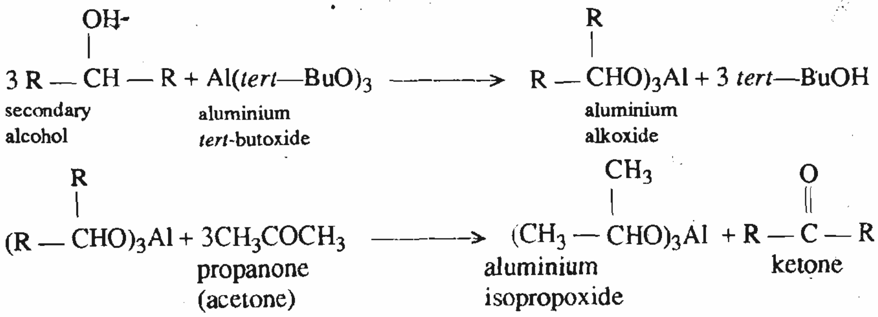
i) alkaline potassium permanganate solution

ii) hot, concentrated HNO_3

iii) chromic acid (H_2CrO_4)

iv) chromium trioxide (CrO_3) complex with pyridine or with pyridine and HC1

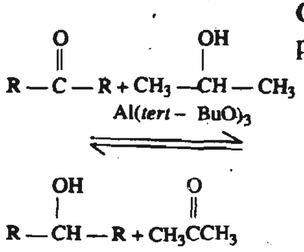
For oxidation of secondary alcohols aluminium tertiary-butoxide is used in the **Oppenauer oxidation.** In this method, the reaction mixture is first heated and then propanone is added:



$$3\,\underset{\text{secondary alcohol}}{R{-}\overset{\overset{\displaystyle OH}{|}}{CH}{-}R} + \underset{\text{aluminium } tert\text{-butoxide}}{Al(tert{-}BuO)_3} \longrightarrow \underset{\text{aluminium alkoxide}}{(R{-}\overset{\overset{\displaystyle R}{|}}{CH}O)_3Al} + 3\ tert{-}BuOH$$

$$(R{-}\overset{\overset{\displaystyle R}{|}}{CH}O)_3Al + \underset{\text{propanone (acetone)}}{3CH_3COCH_3} \longrightarrow \underset{\text{aluminium isopropoxide}}{(CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}O)_3Al} + \underset{\text{ketone}}{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R}$$

Oppenauer oxidation is reversible and the reverse reaction is known as the Meerwein-Ponndorf -Verley reduction

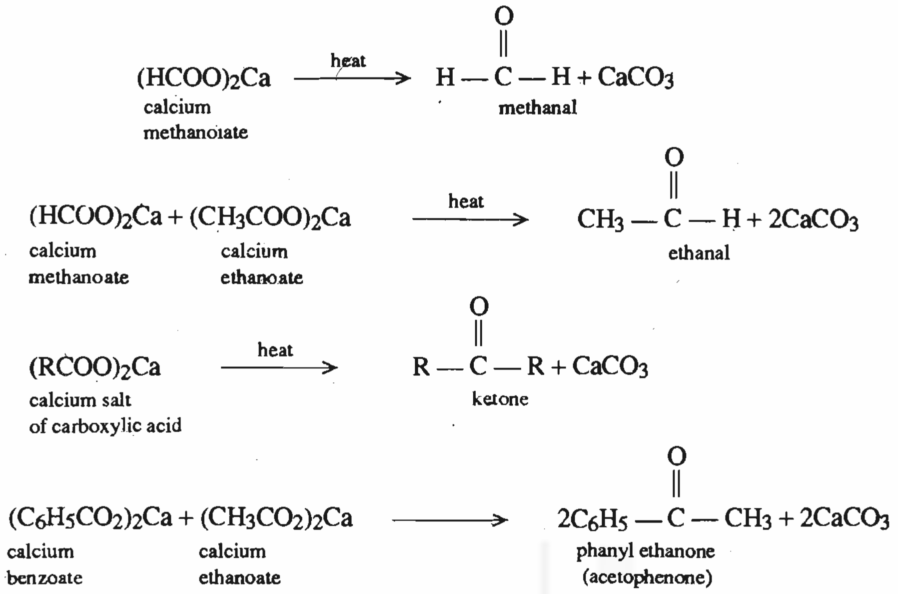


$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R + CH_3{-}\overset{\overset{\displaystyle OH}{|}}{CH}{-}CH_3 \xrightleftharpoons{Al(tert-BuO)_3} R{-}\overset{\overset{\displaystyle OH}{|}}{CH}{-}R + CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$

ii) From Carboxylic Acids and their Derivatives

Carboxylic acids can be converted into aldehydes and ketones either by heating their calcium salts or by passing vapours of the acid over heated manganous oxide or by reduction of acid chlorides with hydrogen in the presence of palladium over barium sulphate (**Rosenmund's method**). We will consider these reactions in more detail in Units 15 and 17. General equations for these reactions are given below:

From Calcium Salts of Carboxylic Acids



$$\underset{\text{calcium methanoate}}{(HCOO)_2Ca} \xrightarrow{\text{heat}} \underset{\text{methanal}}{H-\overset{\overset{O}{\|}}{C}-H} + CaCO_3$$

$$\underset{\text{calcium methanoate}}{(HCOO)_2Ca} + \underset{\text{calcium ethanoate}}{(CH_3COO)_2Ca} \xrightarrow{\text{heat}} \underset{\text{ethanal}}{CH_3-\overset{\overset{O}{\|}}{C}-H} + 2CaCO_3$$

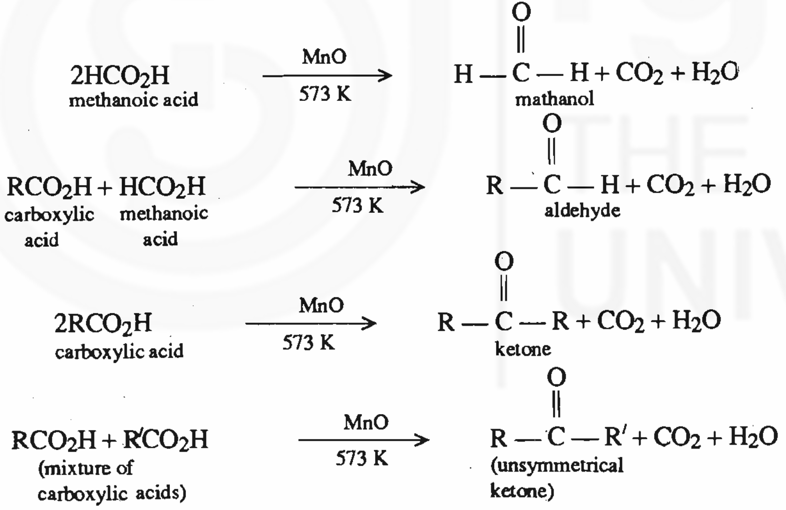
$$\underset{\text{calcium salt of carboxylic acid}}{(RCOO)_2Ca} \xrightarrow{\text{heat}} \underset{\text{ketone}}{R-\overset{\overset{O}{\|}}{C}-R} + CaCO_3$$

$$\underset{\text{calcium benzoate}}{(C_6H_5CO_2)_2Ca} + \underset{\text{calcium ethanoate}}{(CH_3CO_2)_2Ca} \longrightarrow \underset{\text{phanyl ethanone (acetophenone)}}{2C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3} + 2CaCO_3$$

(mixture of calcium salt of carboxylic acid)

(unsymmetrical ketone)

From the Reaction of Carboxylic Acids with Manganous Oxide



$$\underset{\text{methanoic acid}}{2HCO_2H} \xrightarrow[573\text{ K}]{MnO} \underset{\text{mathanol}}{H-\overset{\overset{O}{\|}}{C}-H} + CO_2 + H_2O$$

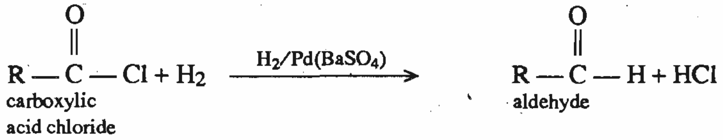
$$\underset{\text{carboxylic acid}}{RCO_2H} + \underset{\text{methanoic acid}}{HCO_2H} \xrightarrow[573\text{ K}]{MnO} \underset{\text{aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H} + CO_2 + H_2O$$

$$\underset{\text{carboxylic acid}}{2RCO_2H} \xrightarrow[573\text{ K}]{MnO} \underset{\text{ketone}}{R-\overset{\overset{O}{\|}}{C}-R} + CO_2 + H_2O$$

$$\underset{\text{(mixture of carboxylic acids)}}{RCO_2H + R'CO_2H} \xrightarrow[573\text{ K}]{MnO} \underset{\text{(unsymmetrical ketone)}}{R-\overset{\overset{O}{\|}}{C}-R'} + CO_2 + H_2O$$

Please note that for aldehydes other than methanal and for unsymmetrical ketones, a mixture of acids and their calcium salts in molar proportion is taken.

From Acid Chlorides by the Rosanmund's Method



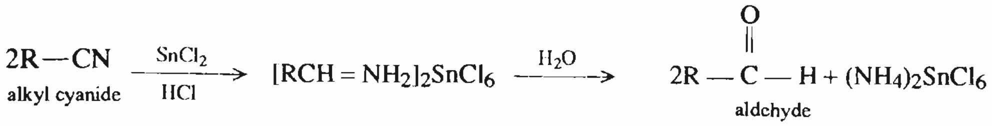
$$\underset{\text{carboxylic acid chloride}}{R-\overset{\overset{O}{\|}}{C}-Cl} + H_2 \xrightarrow{H_2/Pd(BaSO_4)} \underset{\text{aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H} + HCl$$

where R = CH_3 or C_6H_5

$BaSO_4$ helps to stop the reduction at the aldehyde stage.

iii) From the Stephen's Method

Reduction of an alkyl cyanide with stannous chloride and hydrochloric acid followed by hydrolysis with steam gives aldehydes (**Stephen's method**):

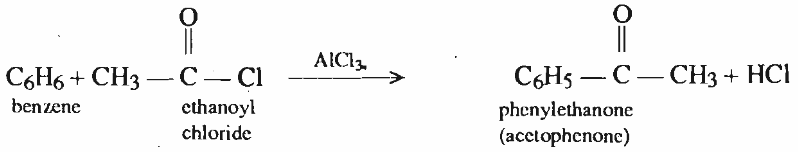


$$\underset{\text{alkyl cyanide}}{2R-CN} \xrightarrow[\text{HCl}]{\text{SnCl}_2} [RCH=NH_2]_2SnCl_6 \xrightarrow{H_2O} \underset{\text{aldehyde}}{2R-\overset{\overset{\displaystyle O}{\|}}{C}-H} + (NH_4)_2SnCl_6$$

where R = CH_3 or C_6H_5

iv) From the Friedel-Crafts Acylation Reaction

Aryl ketones can be prepared by Friedel-Crafts acylation reaction. For example, phenylethanone (acetophenone) is prepared as follows:



$$\underset{\text{benzene}}{C_6H_6} + \underset{\text{ethanoyl chloride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} \xrightarrow{AlCl_3} \underset{\text{phenylethanone (acetophenone)}}{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + HCl$$

SAQ 1

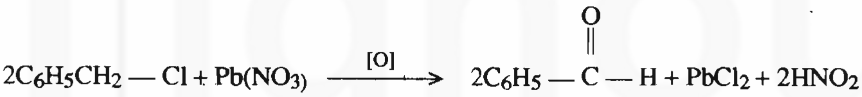
An organic compound A (molecular formula C_3H_7Cl) was treated with aqueous sodium hydroxide and the vapours of the product obtained were passed over heated copper to give propanone (acetone). A is

a) 1-chloropropane
b) 2-chloropropane
c) cyclopropane hydrochloride

14.2.2 Specific Methods for Benzaldehyde

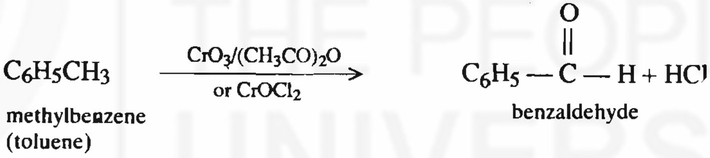
Benzaldehyde can be obtained by the following methods:

i) On boiling (chloromethyle) benzene (benzyl chloride) with aqueous copper or lead nitrate:



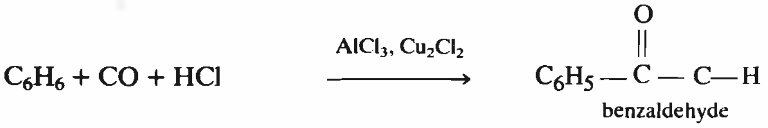
$$2C_6H_5CH_2-Cl + Pb(NO_3) \xrightarrow{[O]} 2C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H + PbCl_2 + 2HNO_2$$

ii) Oxidation of methylbenzene with chromium trioxide in ethanoic anhydride (acetic anhydride) or with chromyl chloride (**Etard' reaction**) gives benzaldehyde:



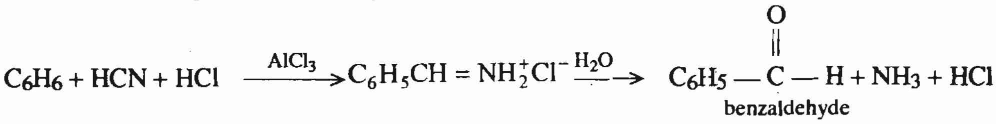
$$\underset{\text{methylbenzene (toluene)}}{C_6H_5CH_3} \xrightarrow[\text{or } CrOCl_2]{CrO_3/(CH_3CO)_2O} \underset{\text{benzaldehyde}}{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H} + HCl$$

iii) By passing a mixture of carbon monoxide and hydrochloric acid gas through benzene in the presence aluminium chloride and cuprous chloride (**Gattermann-Koch synthesis**):



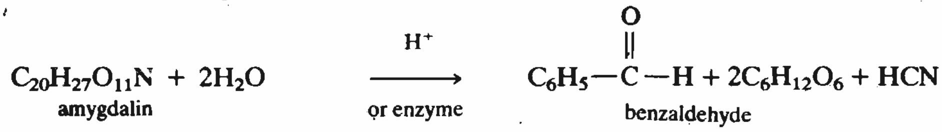
$$C_6H_6 + CO + HCl \xrightarrow{AlCl_3,\ Cu_2Cl_2} \underset{\text{benzaldehyde}}{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-C-H}$$

iv) The reaction of hydrogen cyanide and hydrogen chloride with benzene in the presence of aluminium chloride (**Gattermann synthesis**) followed by treatment with water gives benzaldehyde:



$$C_6H_6 + HCN + HCl \xrightarrow{AlCl_3} C_6H_5CH=NH_2^+Cl^- \xrightarrow{H_2O} \underset{\text{benzaldehyde}}{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H} + NH_3 + HCl$$

v) Benzaldehyde occurs in nature as the glucoside amygdalin, present in bitter almonds. It is known as oil of bitter almonds. Hydrolysis of amygdalin by dilute acids or enzymes gives benzaldehyde, glucose and hydrogen cyanide:



$$\underset{\text{amygdalin}}{C_{20}H_{27}O_{11}N} + 2H_2O \xrightarrow[\text{or enzyme}]{H^+} \underset{\text{benzaldehyde}}{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H} + 2C_6H_{12}O_6 + HCN$$

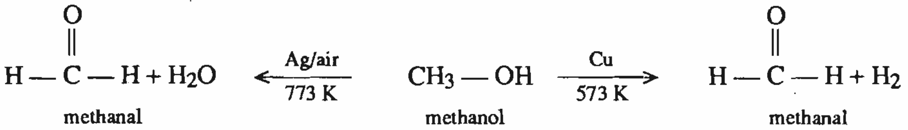
14.2.3 Industrial Preparations of Aldehydes and Ketones

Industrial preparation of some common carbonyl compounds are described below:

Methanal

It is manufactured from methanol by two processes:

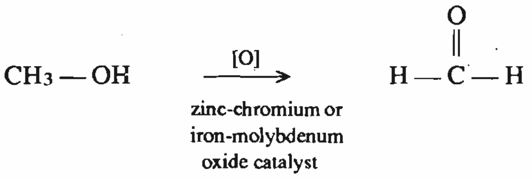
i) Oxidation of methanol using silver or copper catalyst.



$$\underset{\text{methanal}}{H-\overset{\overset{O}{\|}}{C}-H+H_2O} \xleftarrow[773\text{ K}]{\text{Ag/air}} \underset{\text{methanol}}{CH_3-OH} \xrightarrow[573\text{ K}]{\text{Cu}} \underset{\text{methanal}}{H-\overset{\overset{O}{\|}}{C}-H+H_2}$$

Although the silver catalyst is expensive no silver is lost and catalyst is easily regenerated and can be recycled.

ii) Oxidation using zinc-chromium or iron-molybdenum oxide catalyst.



$$CH_3-OH \xrightarrow[\substack{\text{zinc-chromium or}\\ \text{iron-molybdenum}\\ \text{oxide catalyst}}]{[O]} H-\overset{\overset{O}{\|}}{C}-H$$

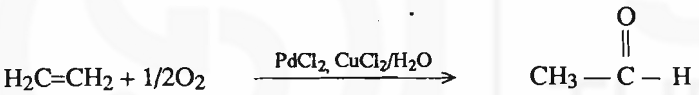
Methanol it salf is made from enriched water gas,

$$CO + 4H_2 \xrightarrow[523\text{ K, }70\text{ atm.}]{\text{Cu as cat}} CH_3-OH$$

Ethanal

The following methods can be used for the manufacture of ethanal:

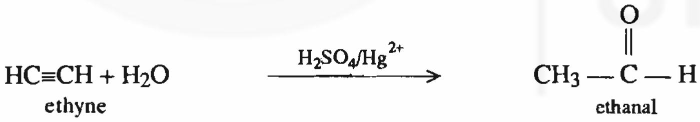
i) By passing a mixture of ethene and oxygen under pressure over palladium (II)/cupric chloride catalyst in water at 323 K, ethanal is produced:



$$H_2C{=}CH_2 + 1/2O_2 \xrightarrow{PdCl_2,\ CuCl_2/H_2O} CH_3-\overset{\overset{O}{\|}}{C}-H$$

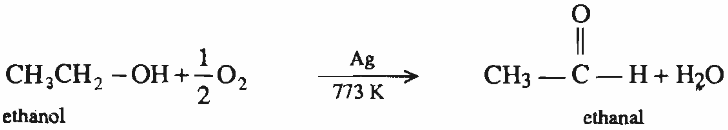
This process is called **Wacker process.** Since ethene is cheaper than ethyne, this process has superseded the two older routes outlined below:

ii) By passing ethyne through dilute sulphuric acid, with mercury (II) sulphate as catalyst at 336 K.

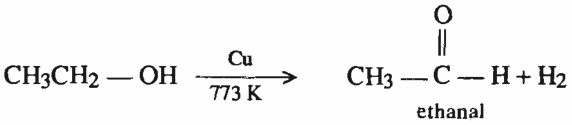


$$\underset{\text{ethyne}}{HC{\equiv}CH + H_2O} \xrightarrow{H_2SO_4/Hg^{2+}} \underset{\text{ethanal}}{CH_3-\overset{\overset{O}{\|}}{C}-H}$$

iii) By the oxidation of ethanol (which is manufactured from ethene) in the gas phase over a silver or copper catalyst:



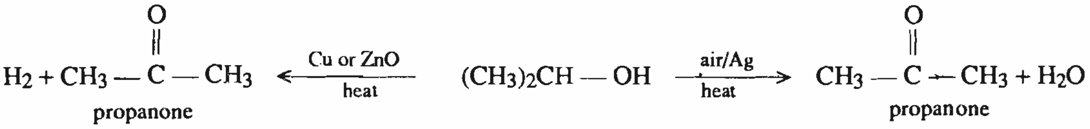
$$\underset{\text{ethanol}}{CH_3CH_2-OH+\frac{1}{2}O_2} \xrightarrow[773\text{ K}]{\text{Ag}} \underset{\text{ethanal}}{CH_3-\overset{\overset{O}{\|}}{C}-H+H_2O}$$



$$CH_3CH_2-OH \xrightarrow[773\text{ K}]{\text{Cu}} \underset{\text{ethanal}}{CH_3-\overset{\overset{O}{\|}}{C}-H+H_2}$$

Propanone

Dehydrogenation of 2-propanol over heated copper or zinc oxide or air oxidation over heated silver gives propanone. 2-Propanol is obtained from propene.



$$H_2 + \underset{\text{propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \xleftarrow[\text{heat}]{\text{Cu or ZnO}} (CH_3)_2CH-OH \xrightarrow[\text{heat}]{\text{air/Ag}} \underset{\text{propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + H_2O$$

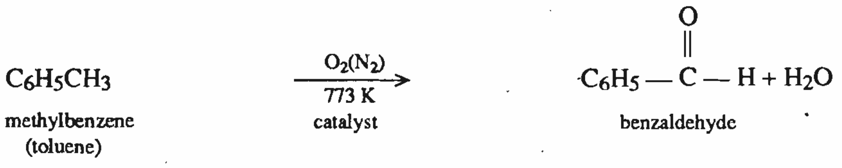
Propanone can also be manufactured by the direct oxidation of propene from natural gas with oxygen or air, catalysed by a mixture of palladium and cuprous chlorides (**The Wacker Process**).

$$CH_3CH{=}CH_2 + {}^1/_2O_2 \longrightarrow \underset{\text{propanone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

We have already seen in Unit 12 that propanone is obtained as a by-product in the oxidation of cumene to phenol.

Benzaldehyde

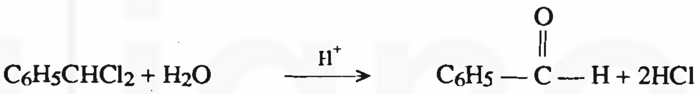
It is prepared commercially by the oxidation of methylbenzene. This is done either in the vapour phase or in the liquid phase. In the vapour phase oxidation, methylbenzene vapours mixed with air is passed over a catalyst, a mixture of oxides of manganese, molybdenum, zirconium etc., heated to 773 K:



$$\underset{\substack{\text{methylbenzene}\\\text{(toluene)}}}{C_6H_5CH_3} \xrightarrow[\substack{773\ K\\\text{catalyst}}]{O_2(N_2)} \underset{\text{benzaldehyde}}{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H} + H_2O$$

Liquid phase oxidation uses manganese dioxide and 65% sulphuric acid at 313 K.

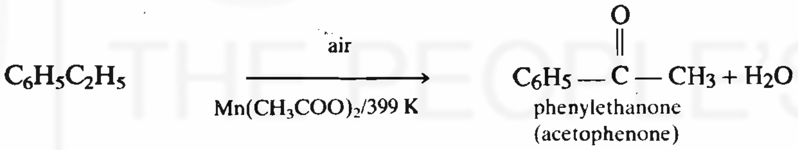
When (dichloromethyl) benzene (benzylidene chloride) is hydrolysed with aqueous acid, benzaldehyde is formed:



$$C_6H_5CHCl_2 + H_2O \xrightarrow{H^+} C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H + 2HCl$$

Phenylethanone

It is manufactured by the oxidation of ethylbenzene with air in the presence of manganous ethanoate (catalyst) at 399 K:



$$C_6H_5C_2H_5 \xrightarrow[Mn(CH_3COO)_2/399\ K]{\text{air}} \underset{\substack{\text{phenylethanone}\\\text{(acetophenone)}}}{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + H_2O$$

SAQ 2

Benzaldehyde is obtained by the hydrolysis of:

a) methylbenzoate
b) (chloromethyl) benzene
c) (dichloromethyl)benzene

14.3 PHYSICAL AND SPECTRAL PROPERTIES

Before going into details of the physical, spectral and chemical properties of aldehydes and ketones; we would like to discuss first the nature of the carbonyl group.

14.3.1 Nature of the Carbonyl Group

The carbonyl group consists of an sp^2 hybridised carbon atom joined to an oxygen atom by a sigma bond and a π bond (see Fig. 14.1).

Like alkenes, carbonyl compounds are planar about the double bond and have bond angles of approximately 120°.

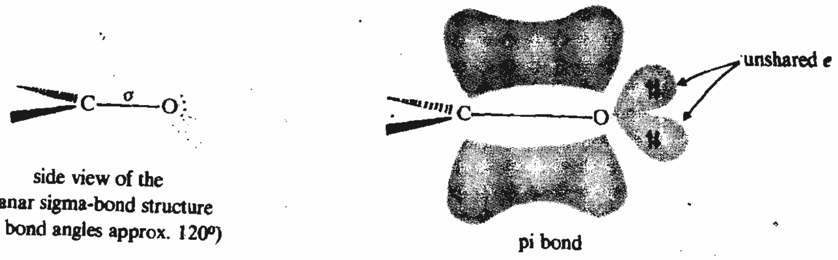
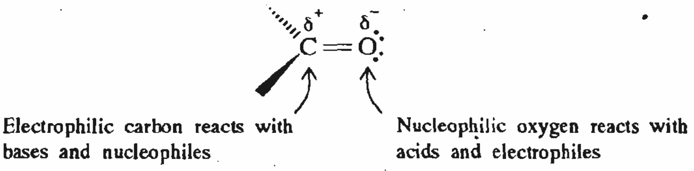


Fig. 14.1: Bonding in the carbonyl group

The carbon-oxygen, like the carbon-carbon, double bond results from a combination of σ and π bonds. But the carbonyl group has a dipole moment, with the oxygen slightly negative, the carbon slightly positive. As a result when carbonyl groups undergo addition reactions, the positive groups (electrophiles) attack the more negative carbonyl oxygen atom and negative group (nucleophiles) attack the more positive carbonyl carbon atom.

As we would expect, the carbon-oxygen double bond is polarised $C=O$ because of the high electronegativity of oxygen relative to carbon. Therefore, **the carbonyl group is polar with the carbon carrying partial positive charge.** It is thus an electrophilic site and is attacked by nucleophiles. Conversely, the carbonyl oxygen is negatively charged and is a nucleophilic site.

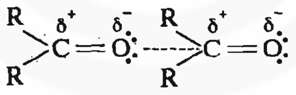


We will see in the next sections that all these structural features—the planarity, the π bond, the polarity and the unshared electrons on oxygen—contribute to the properties and the reactivity of the carbonyl group.

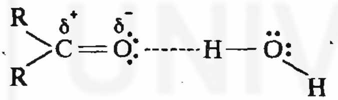
14.3.2 Physical Properties

As we have mentioned above the aldehydes and ketones are polar compounds and these compounds, therefore, posses intermolecular dipole-dipole attraction. Due to these interactions molecules have higher boiling points than nonpolar compounds of similar molecular weight. The boiling points of aldehydes and ketones are however, much lower than the boiling points of the corresponding alcohols. This is due to the fact that whereas alcohols molecules are held together by strong hydrogen bonds. The molecules of aldehydes and ketones are held together by the much weak electrostatic interaction between dipoles.

The partial solubility and also the formation of hydrates can be explained by the formation of hydrogen bonds between carbonyl compounds and water. The unshared electron pairs on oxygen are responsible for such hydrogen bonding. The carbonyl-carbonyl and carbonyl-water interactions are illustrated in the following structures:



dipole-dipole interaction between the molecules of cobonyl compound



hydrogen bonding between carbonyl compound and water

Physical properties of some aldehydes and ketones are summarised in Table 14.2.

Table 14.2: Physical properties of some aldehydes and ketones

IUAPC	Trivial Name	Structure	Bp, K	Solubility in H_2O
Aldehydes:				
methanal	formaldehyde	$\mathrm{H}\overset{\overset{O}{\|}}{\mathrm{C}}\mathrm{H}$	252	miscible
ethanal	acetaldehyde	$\mathrm{CH_3}\overset{\overset{O}{\|}}{\mathrm{C}}\mathrm{H}$	293	miscible
propanal	propionaldehyde	$\mathrm{CH_3CH_2}\overset{\overset{O}{\|}}{\mathrm{C}}\mathrm{H}$	322	16 g/100 cm^3
butanal	butyraldehyde	$\mathrm{CH_3CH_2CH_2CH}$	349	7 g/100 cm^3
benzaldehyde	benzaldehyde	$\mathrm{CH_6CH_5}\overset{\overset{O}{\|}}{\mathrm{C}}\mathrm{H}$	451	slightly
Ketones:				
propanone	acetone	$\mathrm{CH_3}\overset{\overset{O}{\|}}{\mathrm{C}}\mathrm{CH_3}$	329	miscible
2 butanone	methyl ethyl ketone	$\mathrm{CH_3}\overset{\overset{O}{\|}}{\mathrm{C}}\mathrm{CH_2CH_3}$	353	26 g/100 cm^3

phenylethanone (acetophenone)	acetophenone	$C_6H_5\overset{\overset{O}{\|}}{C}CH_3$	475	insoluble
benzophenone	–	$C_6H_5\overset{\overset{O}{\|}}{C}C_6H_5$	O 579	insoluble

SAQ 3

Without consulting Tables given for physical properties of organic compounds, tell which compound in each pair would have the higher boiling point.

a) 1-pentanal or 1-pentanol

b) methylbutane or methylpropanal

c) 2-pentanone or 2-pentanol

d) benzaldehyde or phenylmethanal

e) pentane or 1-pentanal

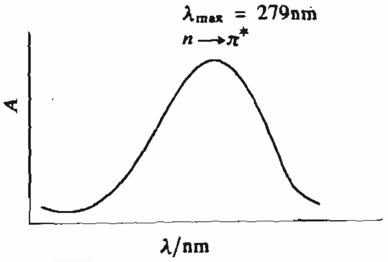


Fig 14.2: Ultraviolet spectrum of propanone.

14.3.3 Spectral Properties

The ultraviolet spectra of aldehydes and ketones show two absorption bands for the carbonyl group; in aldehydes, at 180 and 295 nm for and $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions. and in ketones at 190 and 270-280 nm for and $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions. The spectrum of propanone is shown in Fig. 14.2.

The infrared spectrum is useful in the detection of the carbonyl group in a compound. In aldehydes and ketones their spectrum exhibits strong bands for C=O stretch at 1700-1740 cm^{-1} in aldehydes and at 1660-1750 cm^{-1} for ketones. We are giving some characteristic absorption bands in Table 14.3.

Table 14.3: Characteristic infrared absorption of aldehydes and ketones

Type of Vibration	Position of Absorption[a] cm^{-1}
Aldehydes:	
C—H stretching of —CHO	2700-2900
C=O stretching	1700-1740
Ketones:	
C=O stretching	1660-1750

[a] Other substituents or ring strain cause the carbonyl absorption to fall outside the listed ranges.

As an illustration the ir spectrum of 1-butanal is given in Fig. 14.3. Note the intense band around 1710 cm^{-1} which is characteristic of C=O stretching. In this spectrum, the C—H stretching of the aldehyde group is also visible as two peaks around 2700 cm^{-1}.

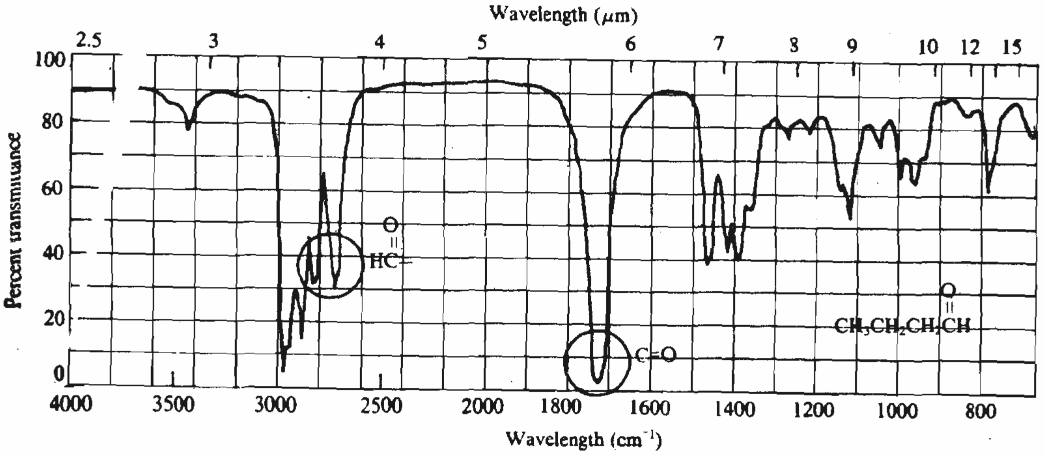


Fig. 14.3: Infrared spectrum of 1-butanal.

The NMR spectra display the aldehydic proton at $\delta = 9.0$-10 ppm, which is greatly deshielded. The large shift arises from the additive effects of both anisotropic deshielding by the π electrons and inductive deshielding by the electropositive carbon of the carbonyl group. Both in aldehydes and ketones the proton attached to adjacent carbon (α-carbon) appear at δ 2.0-2.5 ppm slightly downfield from that of the other C—H absorption (about $\delta = 1.5$) because of electron withdrawal by the electronegative oxygen atom. For example, the nmr spectrum of 1-butanal (Fig. 14.4), exhibits a signal near $\delta = 9.5$ ppm for the hydrogen in the –CHO group and a signal near $\delta = 2.4$ ppm for the α protons.

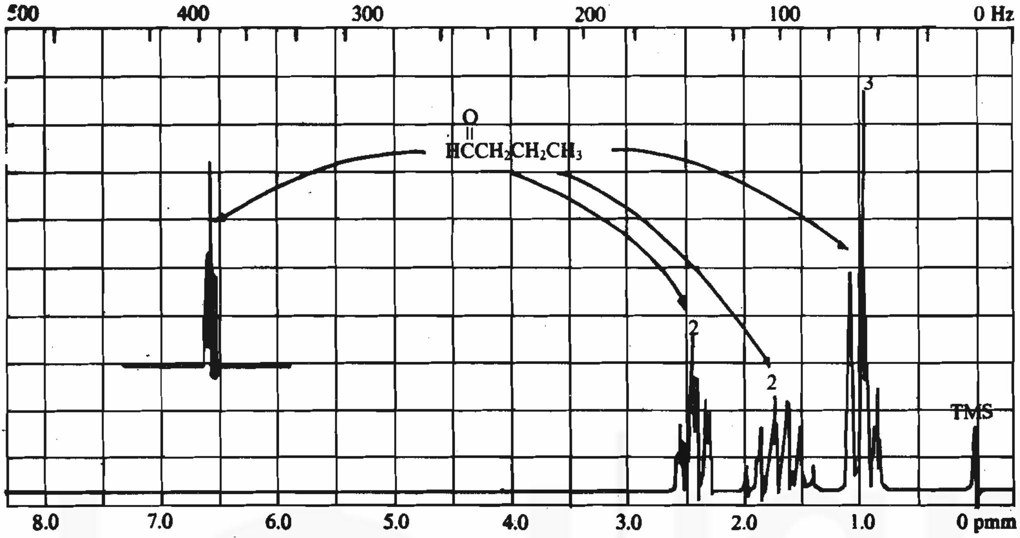


Fig. 14.4: NMR spectrum of 1-butanal

In the mass spectra of aldehydes, the molecular ion peak is observed with a low intensity and α cleavage occurs readily:

$$H^{\cdot} + RC^{+} = O \longleftarrow R - \underset{\displaystyle H}{\underset{|}{C}} = O^{+} \longrightarrow R + \underset{m/z\ 29}{HC^{+} = O}$$

The presence of $RC^{+} = O$ and m/e 29 peaks in the mass spectrum are characteristic of aldehydes.

A β-cleavage may also occur:

$$[RCH_2CH_2CHO]^{+\cdot} \longrightarrow RCH_2 + \underset{m/z\ 43}{[CH_2CHO]^{+}}$$

In the mass spectra of ketones, the molecular ion peak is strong and α-cleavage takes place quite readily. The $[RCO]^{\cdot +}$ peak is very often the base peak, e.g.,

$$RCOR'^{\dot{+}} \longrightarrow [RCO]^{+\cdot} + R'^{\cdot}$$

SAQ 4

Propanone and propanal are isomers. What feature would distinguish between the two if we examine;

a) their ir spectra

b) their nmr spectra

....

....

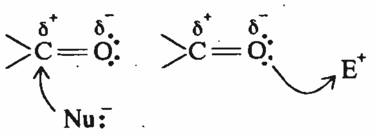
....

....

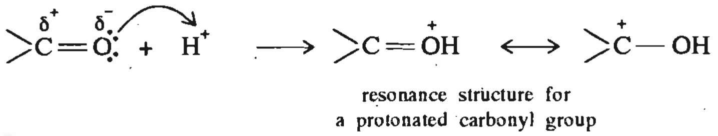
14.4 REACTIONS OF ALDEHYDES AND KETONES

We can group together the reactions of aldehyde and ketones into four categories (a) reactions of the carbonyl group (b) reactions of the α hydrogen (c) oxidation reactions and (d) reduction reactions.

As stated earlier, the carbon-oxygen double bond is polar. A carbonyl compound may be attacked either by a nucleophile or by an electrophile. Therefore, with most reagents carbonyl additions show the same overall course: addition of the negative, nucleophilic part, of the reagent to the carbon atom and addition of the positive electrophilic part to the oxygen atom.



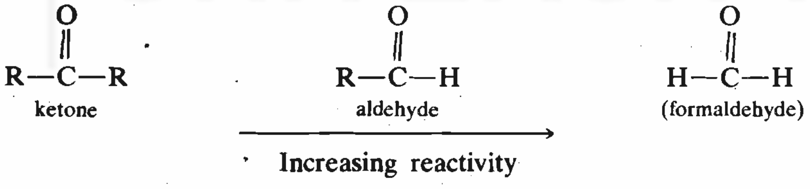
In acidic medium the proton adds to the carbonyl oxygen. This increases further the electrophilic nature of the carbonyl carbon.



Hence nucleophilic additions to a carbonyl compounds are very often catalysed by acids. Before going into details of the reactions of carbonyl compounds, let us study the relative reactivities of aldehydes and ketones.

The relative reactivities of aldehydes and ketones in addition reactions may be attributed partly to the extent of polarisation on the carbonyl carbon. The more polarised the carbonyl group the greater the positive charge on the carbonyl carbon. A greater positive charge means higher reactivity. If this partial positive charge is dispersed throughout the molecule, then the carbonyl compound is less reactive.

As you already know the alkyl group is electron releasing (+I effect). Therefore, in ketones, due to the presence of two alkyl groups, the carbon of the carbonyl group will be less electron deficient than in aldehydes. Hence, ketones will be less reactive than aldehydes. Further, methanal with no alkyl groups attached to the carbonyl carbon is more reactive than ethanal and other unsubstituted aldehydes.

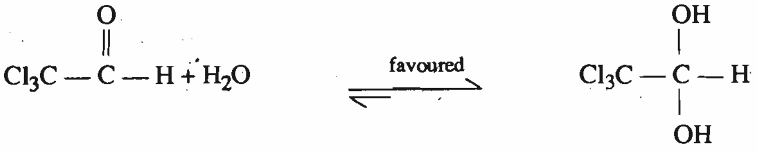


$$\underset{\text{ketone}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-R} \qquad \underset{\text{aldehyde}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-H} \qquad \underset{\text{(formaldehyde)}}{H-\overset{\overset{\displaystyle O}{\|}}{C}-H}$$

$$\xrightarrow{\hspace{4cm}}$$

Increasing reactivity

The most reactive aldehydes is trichloroethanal (chloral), $Cl_3C—C—H$, in which electron withdrawal by the three chlorine atoms depletes the electrons density on the carbonyl carbon so much that it forms stable hydrates.

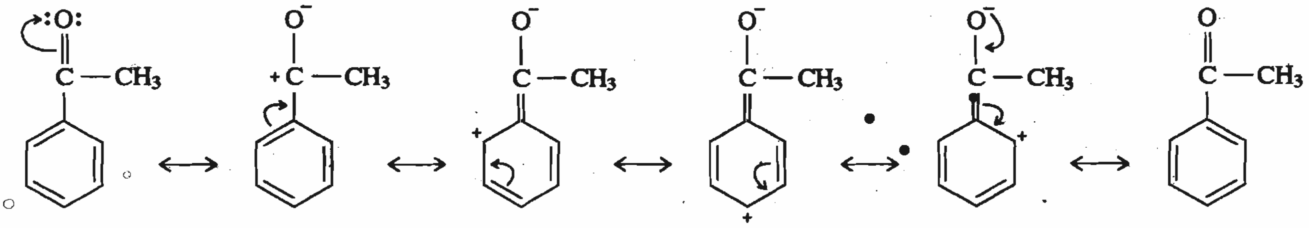


$$Cl_3C-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2O \xrightleftharpoons{\text{favoured}} Cl_3C-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-H$$

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2O \xrightleftharpoons{\text{unfavoured}} CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-H$$

Steric factors also play a role in the relative reactivities of aldehydes and ketones. Since hybridisation of the carbonyl carbon changes from sp^2 in the starting material to sp^3 in the addition product, ketones are less reactive than aldehyde because of the un-favourable steric interaction between the two alkyl groups and the other two groups in the product. Lack of such steric hindrance in the product is another reason for the higher reactivity of methanal.

A carbonyl group attached to an aromatic ring is less reactive in addition reactions than it is in aliphatic aldehydes and ketones. This can be attributed to resonance interaction between the carbonyl group and the aromatic ring:



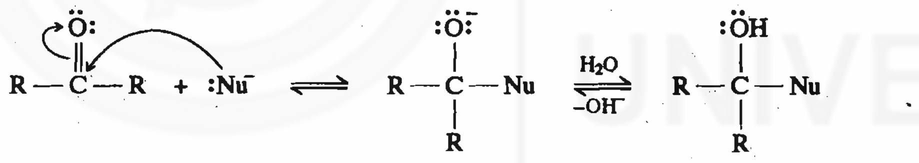
Resonance structure of phenylethanone (acetophenone)

The result of this interaction is a weakening of the positive charge on the carbonyl carbon atom through dispersal of the charge into the ring. From the above resonance structures it is also clear that a carbonyl group attached to an aromatic ring behaves as an electron withdrawing group and so it deactivates the ring towards electrophilic substitution. Further, since the electron density at the *meta* position is not much affected by the carbonyl group, the electrophil, when substituted does occur, goes to the *meta* position. We, therefore, say that the carbonyl group in, e.g., bezaldehyde, is *meta* directing.

With the above general ideas, it will be easier to study the reactions of aldehydes and ketones. Many of the reactions which follow are shown by all aldehydes and ketones, but some members show exceptional behaviours which we will take up separately.

14.4.1 Addition Reactions

The chief reaction of aldehydes and ketones is **nucleophilic addition** to the partially positive carbon of the carbonyl group. The mechanism for the general reactions is as follows:



The nucleophile, $Nu:^-$, can be OH^-, OR^-, CN^-, $\ddot{N}H_3$, $H_2\ddot{O}:$, $R\ddot{O}H$, $NH_2\ \ddot{O}$ $C_6H_5\ddot{N}H\ddot{N}H_2$, RMgX, etc.

As said above acid catalysis facilitates the reaction of the weaker nucleophiles, such as water, alcohol and ammonia by protonating and thereby increasing the positive nature of the carbon atom of carbonyl group:

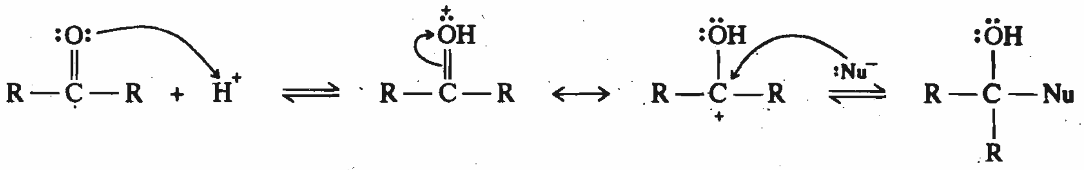
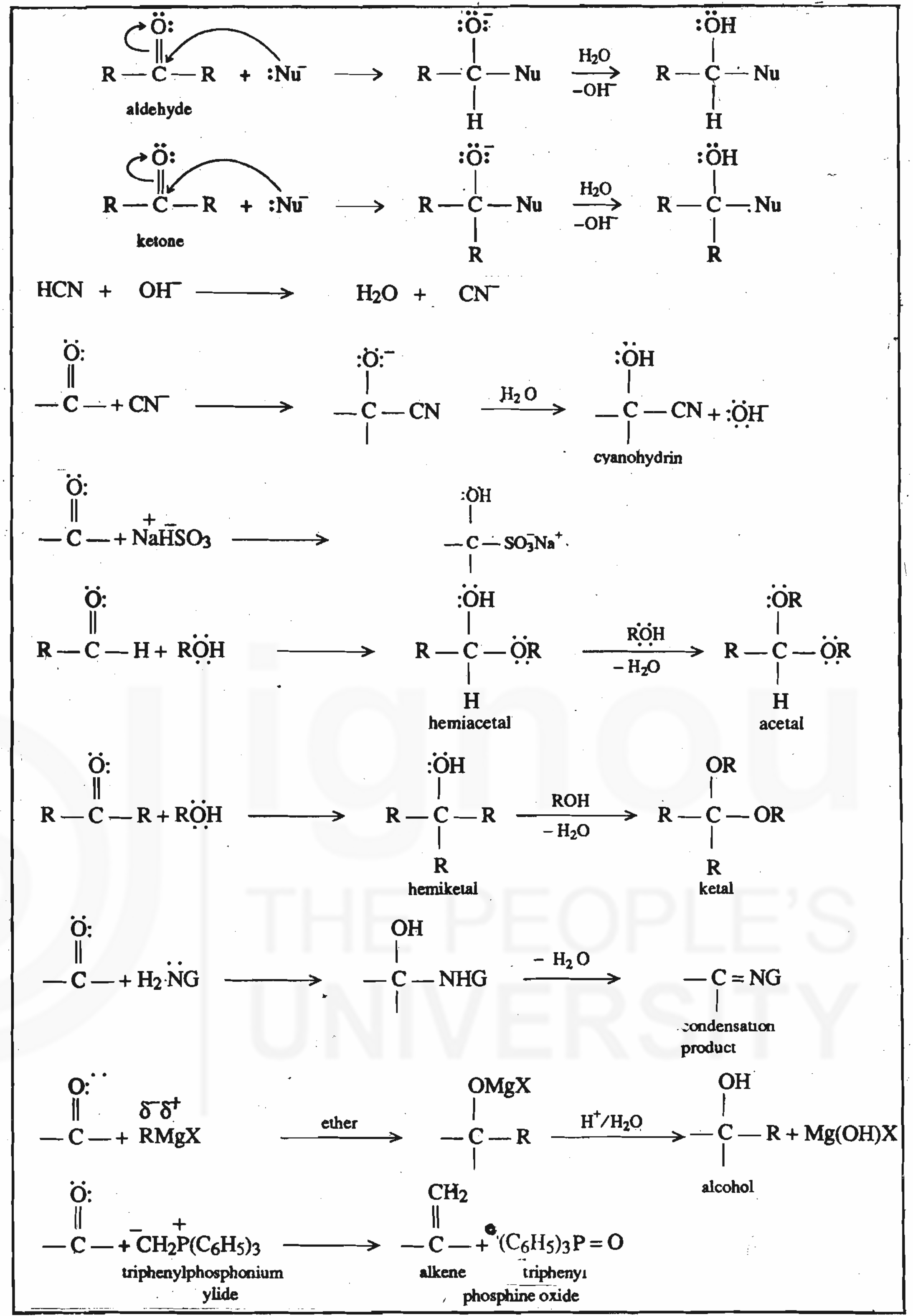


Table 4.4 gives the general equations for different types of nucleophilic addition reactions.

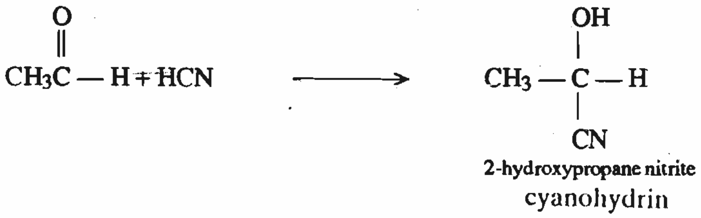
Table 14.4: Some nucleophilic addition reactions of aldehydes and ketones



Let us study these reactions in more detail.

Addition of hydrogen cyanide

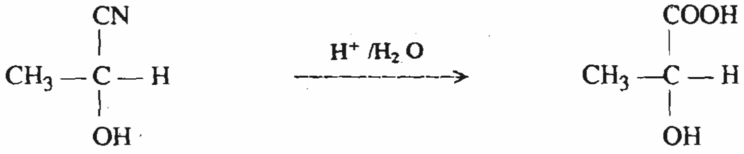
Aldehydes and ketones react with hydrogen cyanide to form cyanohydrins, for example,



These reactions occur very slowly, but their rates are greatly increased by the addition of alkali. This is because, alkali increases the concentration of the cyanide ion,

$$HCN + OH^- \rightleftharpoons CN^- + H_2O$$

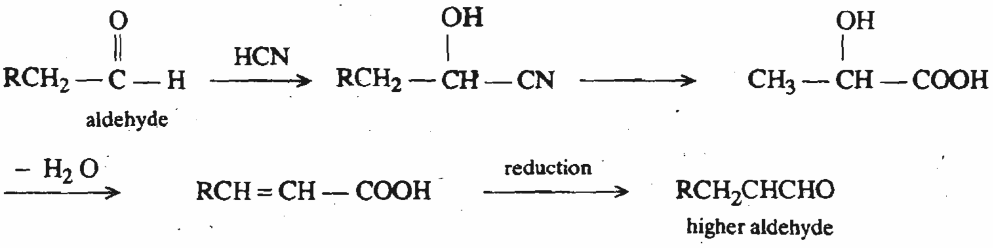
Hydrolysis of cyanohydrins gives α-hydroxyacids:



$$CH_3-\overset{\overset{CN}{|}}{\underset{\underset{OH}{|}}{C}}-H \xrightarrow{H^+/H_2O} CH_3-\overset{\overset{COOH}{|}}{\underset{\underset{OH}{|}}{C}}-H$$

2-hydroxypropanoic acid

An important consequence of the hydrogen cyanide addition reaction is that one more carbon atom is added to the carbon chain. For example,



$$\underset{\text{aldehyde}}{RCH_2-\overset{\overset{O}{\|}}{C}-H} \xrightarrow{HCN} RCH_2-\overset{\overset{OH}{|}}{CH}-CN \longrightarrow CH_3-\overset{\overset{OH}{|}}{CH}-COOH$$

$$\xrightarrow{-H_2O} RCH=CH-COOH \xrightarrow{\text{reduction}} \underset{\text{higher aldehyde}}{RCH_2CHCHO}$$

Addition of sodium hydrogen sulphite

The reaction with sodium hydrogen sulphite gives the hydrogen sulphite adduct.

$$-\overset{\overset{O}{\|}}{C}- + \overset{+}{Na}\overset{-}{H}SO_3 \longrightarrow -\overset{\overset{OH}{|}}{\underset{|}{C}}-S\bar{O}_3Na^+$$

The hydrogen sulphite adducts are crystalline solids. On heating with dilute acid or aqueous sodium carbonate, they regenerate the carbonyl compound. This reaction is often used for separation and purification of aldehydes and ketones.

Addition of Alcohols

Lewis bases, such as water, alcohols, ammonia and its derivatives can serve as nucleophiles in addition reactions to aldehydes and ketones. Fig14.5 summarises the net reactions of these nucleophiles.

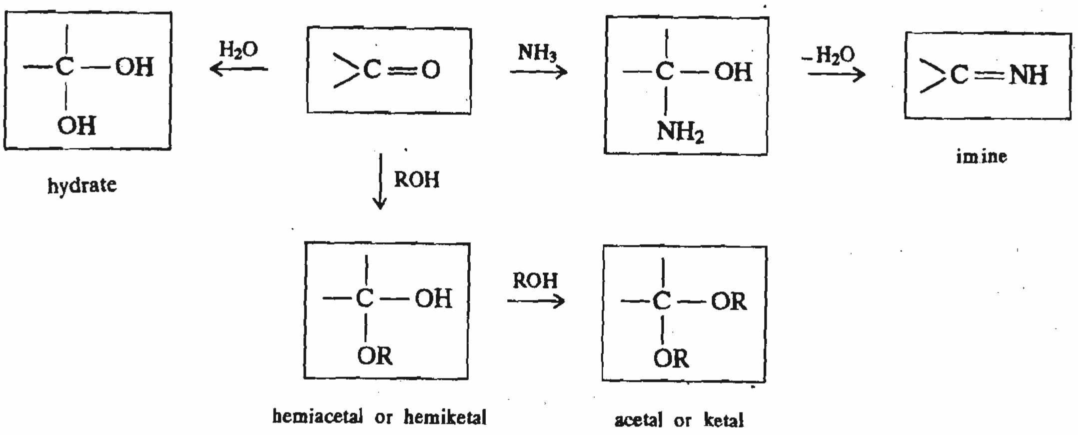
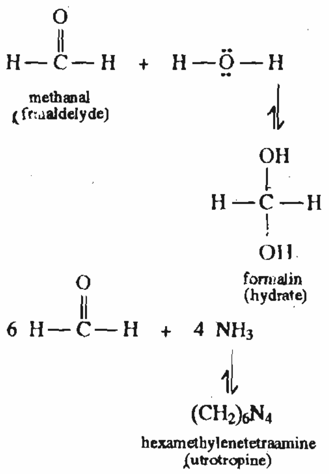


Fig 14.5 : Nucleophilic addition reactions of water, alcohol and ammonia

These reactions are reversible and the equilibrium is unfavourable for the addition of water and ammonia. Therefore, the addition of water and ammonia to aldehydes and ketones is generally not of much significance.

Methanal is one of the few carbonyl compounds that forms stable products with water and ammonia.

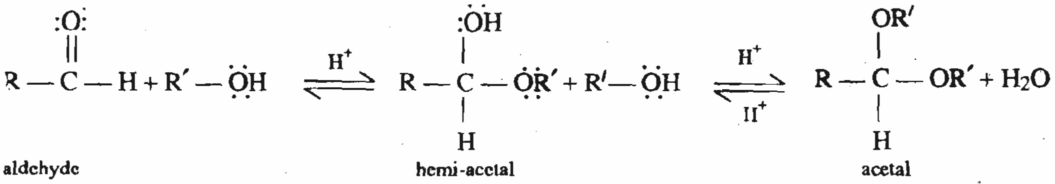


$$H-\overset{\overset{\displaystyle O}{\|}}{C}-H + H-\ddot{O}-H \rightleftharpoons H-\underset{\displaystyle OH}{\overset{\displaystyle OH}{C}}-H$$

$$6\ H-\overset{\overset{\displaystyle O}{\|}}{C}-H + 4\ NH_3 \rightleftharpoons (CH_2)_6N_4$$

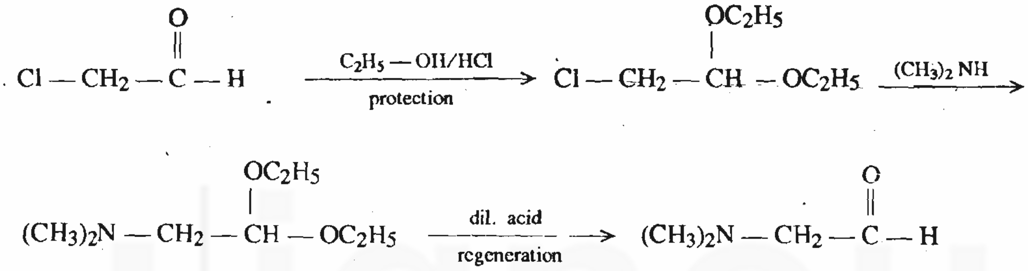
You should note that equilibriums exist that favour the stable hydrate, formalin and hexamethylenate traamine, respectively.

On the other hand, alcohols undergo appreciable nucleophilic addition reactions to aldehyde and ketones. Let us study these reactions in some more detail. Aldehydes give first hemi-acetals and on reaction with an additional equivalent of alcohol, give acetals. All these reactions are catalysed by a trace of strong acid.



$$R-\overset{\overset{\displaystyle :O:}{\|}}{C}-H + R'-\ddot{O}H \overset{H^+}{\rightleftharpoons} R-\underset{\displaystyle H}{\overset{\displaystyle :\ddot{O}H}{\overset{|}{C}}}-\ddot{O}R' + R'-\ddot{O}H \underset{H^+}{\overset{H^+}{\rightleftharpoons}} R-\underset{\displaystyle H}{\overset{\displaystyle OR'}{\overset{|}{C}}}-OR' + H_2O$$

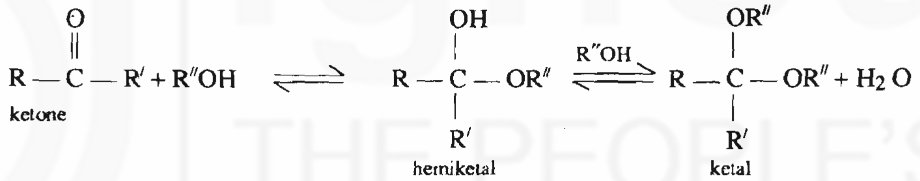
Like other ethers, acetals are good solvents. They are stable to bases and oxidising agents, but are cleaved even by dilute acids. The mechanism is just the reverse of that for the formation of the acetal. This property of acetals is used in synthesis to protect the carbonyl function from reacting while a substitution or addition reaction is carried out elsewhere in the molecule. After the reaction the acetal is then hydrolysed back to the aldehyde. The example illustrates the utility of such protection in synthetic reactions,



$$Cl-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow[\text{protection}]{C_2H_5-OH/HCl} Cl-CH_2-\overset{\overset{\displaystyle OC_2H_5}{|}}{CH}-OC_2H_5 \xrightarrow{(CH_3)_2NH}$$

$$(CH_3)_2N-CH_2-\overset{\overset{\displaystyle OC_2H_5}{|}}{CH}-OC_2H_5 \xrightarrow[\text{regeneration}]{\text{dil. acid}} (CH_3)_2N-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

Similarly, ketones give hemiketals on treatment with alcohols. Further reaction leading to ketals is much more difficult.

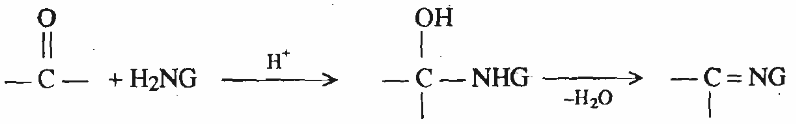


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R' + R''OH \rightleftharpoons R-\underset{\displaystyle R'}{\overset{\displaystyle OH}{\overset{|}{C}}}-OR'' \overset{R''OH}{\rightleftharpoons} R-\underset{\displaystyle R'}{\overset{\displaystyle OR''}{\overset{|}{C}}}-OR'' + H_2O$$

Ketals are also used to protect carbonyl groups.

Reactions in which two reactants combine with the loss of a molecule of water or some other neutral molecule are called condensations.

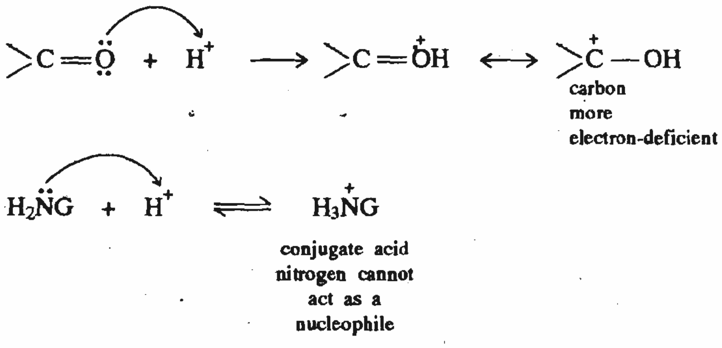
Addition of Ammonia derivatives: We mentioned above that the addition of ammonia is a reversible reaction with an unfavourable equilibrium. However, certain ammonia derivatives are added to carbonyl compounds to give another type of reactions **condensation** in which the initial addition is followed by dehydration to form a carbon-nitrogen double bond. The net result is substitution of oxygen by another group. The general reaction can be summed up as follows.



$$-\overset{\overset{\displaystyle O}{\|}}{C}- + H_2NG \xrightarrow{H^+} -\underset{|}{\overset{\overset{\displaystyle OH}{|}}{C}}-NHG \xrightarrow[-H_2O]{} -\underset{|}{C}=NG$$

G=various groups (Table 14.5)

These reactions are catalysed by acids. While protonation of carbonyl compounds increases their reactivity towards nucleophiles. Protonation of the reagent, H_2NG will lower its nucleophilic character:



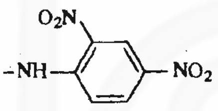
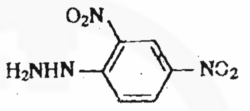
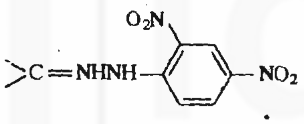
$$>C=\ddot{O} + H^+ \longrightarrow >C=\overset{+}{O}H \longleftrightarrow >\overset{+}{C}-OH$$

$$H_2\ddot{N}G + H^+ \rightleftharpoons H_3\overset{+}{N}G$$

The optimum pH for the reaction depends on the nature of G in H_2NG. It is to be adjusted such that all of H_2NG is not converted to H_3^+NG and at the same time there is sufficient concentration of the conjugate acid of the carbonyl compound to activate it.

The names of reactants with different G, general condensation products and their class is given in Table 14.5. Many of these condensation products are crystalline solids with sharp melting points. For this reason they are frequently employed for the preparation of aldehyde and ketone derivatives needed for identification..

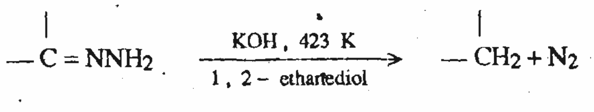
Table 14.5: Addition of ammonia derivatives

G	Ammonia derivative	General condensation	Class of product
—R/—Ar alkyl/aryl	$RNH_2/ArNH_2$ amine/aromatic amine	$>C=NR/>C=NAr$ N substituted imine	imine (Schiff base)
—OH	NH_2OH hydroxylamine	$>C=NOH$ Oxime	Oxime
$—NH_2$	H_2NNH_2 hydrazine	$>C=NNH_2$ hydrazone	hydrazone
$—NHC_6H_5$	$H_2NNHC_6H_5$ phenyl hydrazine	$>C=NNHC_6H_5$ phenyl hydrazone	substituted hydrazone
		 2,4-dinitro-phenyl hydrazone	substituted hydrazone
$—NHCONH_2$	$H_2NNHCONH_2$ semicarbazide	$>C=NNHCONH_2$	semicarbazone

Some times the hydrazone formed above reacts with a second molecule of the carbonyl compound to give azines:

$$\underset{\text{benzaldehyde hydrazone}}{C_6H_5CH{=}NNH_2} + C_6H_5CHO \longrightarrow \underset{\text{benzaldehyde azine}}{C_6H_5CH{=}N{-}N{=}CHC_6H_5} + H_2O$$

When the hydrazones are heated with potassium hydroxide or sodium ethoxide, alkanes are formed with the loss of nitrogen:

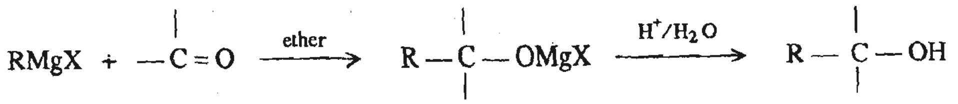


$$-\overset{|}{C}=NNH_2 \xrightarrow[1,2-\text{ethanediol}]{KOH,\ 423\ K} -\overset{|}{C}H_2 + N_2$$

Thus the carbonyl group is converted into a methylene group via a hydrazone. This reaction is known as the **Wolff Kishner** reaction. Like hydrazones, semicarbozones can also be used in the above reaction.

Addition of Grignard Reagent

The general reaction of the addition of Grignard reagent to aldehydes or ketone is



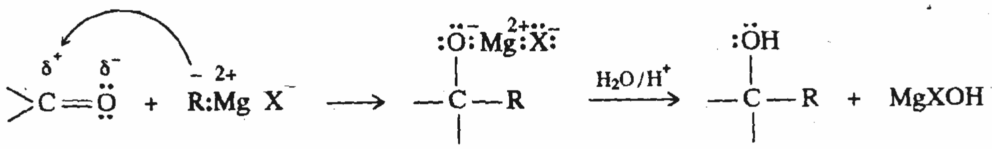
$$RMgX + -\overset{|}{C}=O \xrightarrow{\text{ether}} R-\underset{|}{\overset{|}{C}}-OMgX \xrightarrow{H^+/H_2O} R-\underset{|}{\overset{|}{C}}-OH$$

This reaction was discussed in Unit 11. We also mentioned that methanal (formaldehyde) gave primary alcohol, other aldehydes gave secondary alcohols and ketones gave tertiary alcohols. Let us study the mechanism of the reaction of Grignard reagent with carbonyl compounds.

Mechanism: Analysing the charge distribution in the Grignard reagent, we find that since the magnesium is positive the hydrocarbon portion of the reagent must be negative and, therefore, a very powerful nucleophile.

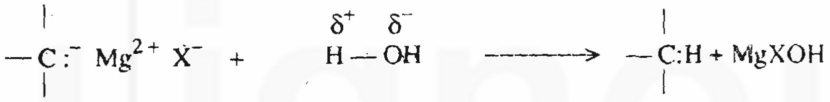
$$R^{-}:Mg^{2+}\ :\ddot{\underset{\cdot\cdot}{X}}:^{-}$$

When a Grignard reagent is mixed with a aldehyde or ketone, the negative hydrocarbon group quickly attacks the positive carbonyl carbon and provides the two electrons needed for the new carbon-carbon bond. The π electrons are displaced to the oxygen, forming the alcohol salt that is then neutralised to an alcohol with water and acid.



$$\overset{\delta^+}{>C}=\overset{\delta^-}{\ddot{\underset{\cdot\cdot}{O}}} + R:\overset{-\ \ 2+}{Mg}\ X^{-} \longrightarrow -\overset{:\ddot{O}:Mg^{2+}:\ddot{X}:^{-}}{\underset{|}{\overset{|}{C}}}-R \xrightarrow{H_2O/H^+} -\overset{:\ddot{O}H}{\underset{|}{\overset{|}{C}}}-R + MgXOH$$

Note that the hydrocarbon portion of a Grignard reagent essentially acts as a carbanion. It is for this reason that Grignard reactions must be performed in dry ether. Even traces of moisture can neutralise the reagent.



$$-\underset{|}{\overset{|}{C}}:^{-}\ Mg^{2+}\ X^{-} + \overset{\delta^+}{H}-\overset{\delta^-}{OH} \longrightarrow -\underset{|}{\overset{|}{C}}:H + MgXOH$$

Wittig Reaction: A very important and useful synthesis of alkenes known as the witting reaction involves the reaction between an aldehyde or ketone and a phosphorus ylide.

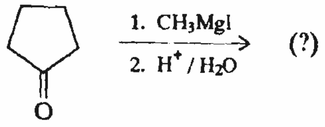
$$>C=O + (C_6H_5)_3\overset{+}{P}-\overset{-}{C}H_2 \longrightarrow >C=CH_2 + (C_6H_5)_3PO$$

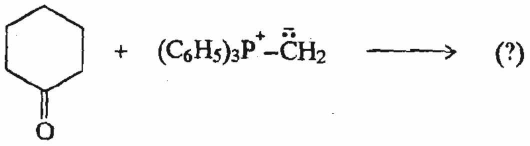
aldehyde or ketone	triphenyl phosphonium ylide	alkene	triphenylphosphine oxide

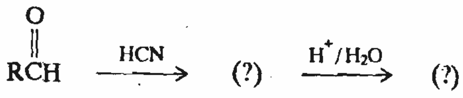
In this reaction, the oxygen of the carbonyl group is substituted by a methylene group, triphenyl phosphine oxide being the other product. Witting reaction is of considerable importance in industrial synthesis, much of the synthetic vitamin A is manufactured by a reaction sequence involving Witting reaction.

SAQ 5

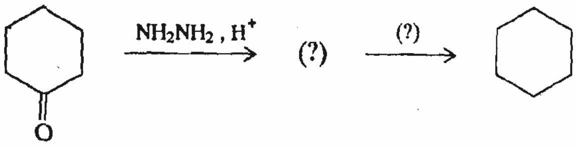
Complete following reactions.

a) 

b) 

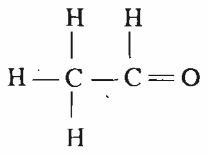
c) 

$$R\overset{O}{\overset{\|}{C}}H \xrightarrow{HCN} (?) \xrightarrow{H^+/H_2O} (?)$$

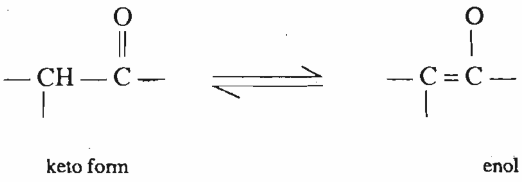
d) 

14.4.2 Reactions of α Hydrogen

Another important characteristic of carbonyl compounds is the acidity of hydrogen atoms on carbon atom alpha to the carbonyl group, called α hydrogens. We have already encountered C—H acidity in the alkynes in Unit 8. Propanone is about 100,000 times as strong as an acid as ethyne. Because of the reactivity of the α hydrogens, aldehydes and ketones may exist as an equilibrium mixtures of the two isomeric forms, a keto form and an enol form.



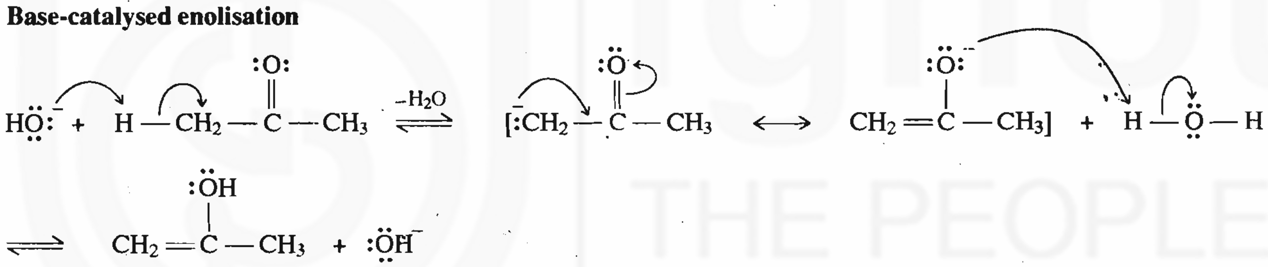
ethanal (acetaldehyde)
three α hydrogen



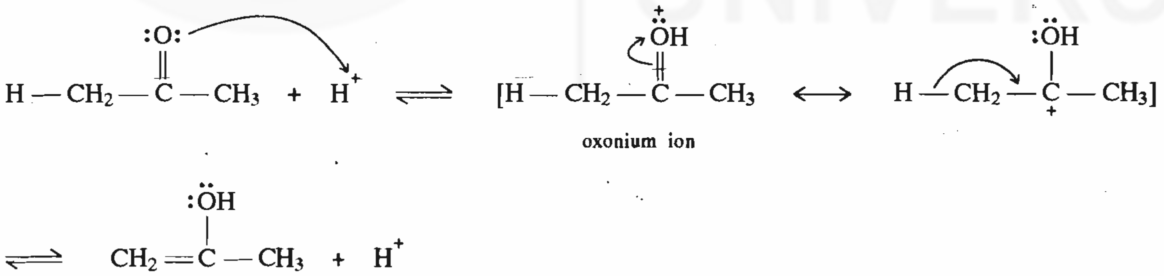
As we have mentioned in Unit 5 this type of isomerism in which there is dynamic equilibrium between the two forms is called tautomerism, and the isomers are called tautomers. In the pure liquid state or in neutral solutions only traces of the enol form are present. Since the enol form is less stable than the keto form.

Enolisation is catalysed by both acids and bases as shown in the following equation.

Base-catalysed enolisation



Acid-catalysed enolisation

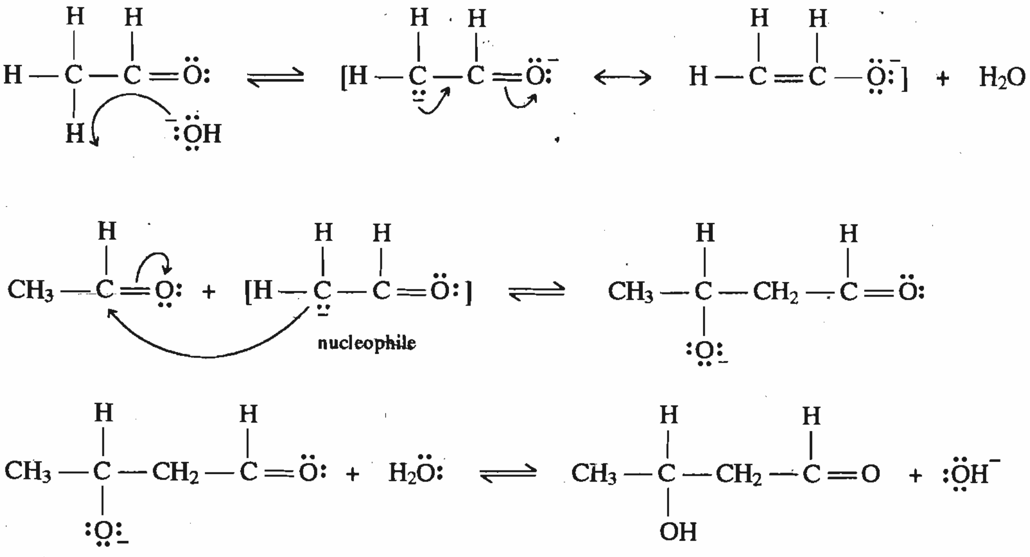


Strong acids give rise to weak conjugated bases on ionisation. The ionisation of propanone produces $^{-}CH_2COCH_3$ in which the negative change is delocalised and hence it as a weak base. On the other hand ionisation of CH_4 produces $^{-}CH_3$ which is a very strong base and, therefore, CH_4 is a very weak acid. The stabilisation of the anion by resonance is responsible for the greater acidity of propanone relative to methane and ethyne. We will now discuss those reactions of the carbonyl compounds in which α hydrogens are involved.

Aldol condensation

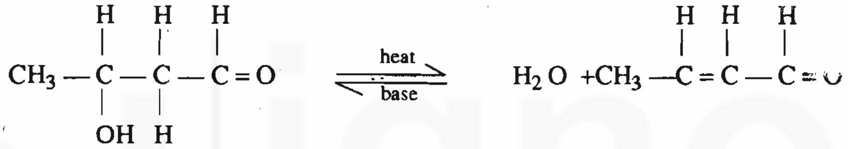
When an enolate ion adds to another molecule of the aldehyde or the ketone, the reaction is called the **aldol condensation.** This reaction is either base- or acid-catalysed. The aldol condensation involving self-condensation of two molecules of ethanal in presence of a basic catalyst is shown as an example:

Aldol, a composite word for **aldehyde + alcohol.**



aldol
(3-hydroxybutanal)

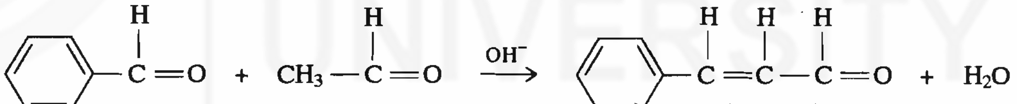
Under more vigorous conditions aldol lose water to give an α, β-unsaturated carbonyl compound.



2-butenal
(crotonaldehyde)

Ketones containing α hydrogens are also capable of aldol-type of condensations.

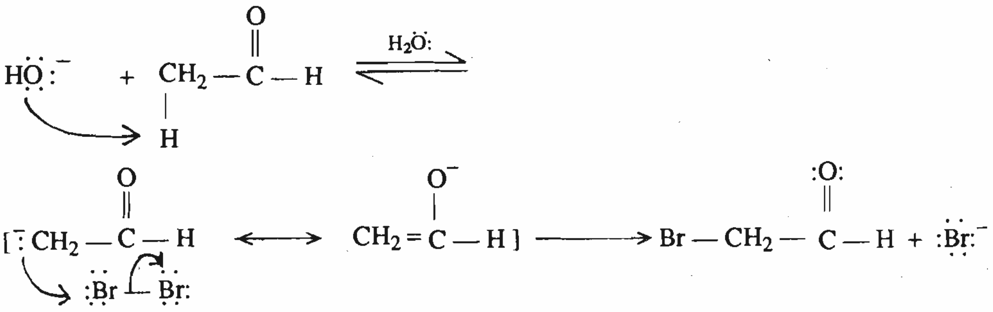
Aldehydes lacking α hydrogens enter into a mixed aldol condensation with other aldehydes having a hydrogens. They do this by acting as the carbanion acceptors. For example, benzaldehyde reacts with acetaldehyde to produce cinnamaldehyde, an α, β unsaturated aromatic aldehyde used as a flavouring agent:



cinnamaldehyde

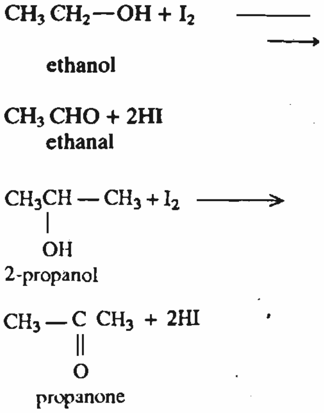
Haloform Reaction

The treatment of carbonyl compounds (having α-hydrogens) with halogens: chlorine, bromine or iodine in the presence of an alkali leads to halogenation, e.g.,



This type of halogenation tends to give polyhalogenation products. Further more, when ethanal or a methyl ketone is warmed with an alkaline solution of chlorine, bromine, or iodine, the product is trichloromethane (chloroform), tribromomethane (bromoform), or tri-iodomethane (iodoform), respectively. This reaction is called the haloform reaction and appears to take place in two stages:

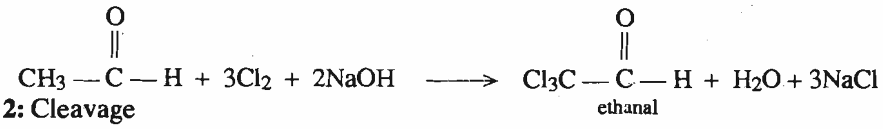
Haloform test is given by any compound containing $CH_3{-}C{=}O$ group or a group capable of giving $CH_3{-}C{=}O$ group under conditions of dehydrogenation. In the case of ethanol, dehydrogenation will give ethanal, and in the case of 2-propanol, propanone, both of which can give haloform reaction.



$CH_3CH_2{-}OH + I_2 \longrightarrow CH_3CHO + 2HI$
ethanol ethanal

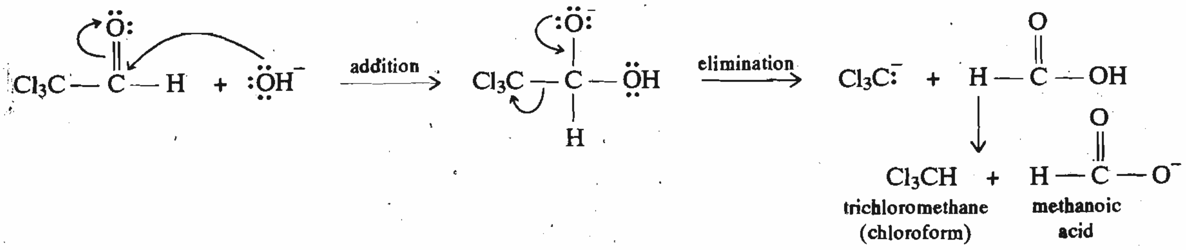
$CH_3CH(OH){-}CH_3 + I_2 \longrightarrow CH_3{-}C(=O){-}CH_3 + 2HI$
2-propanol propanone

Stage 1: Halogenation

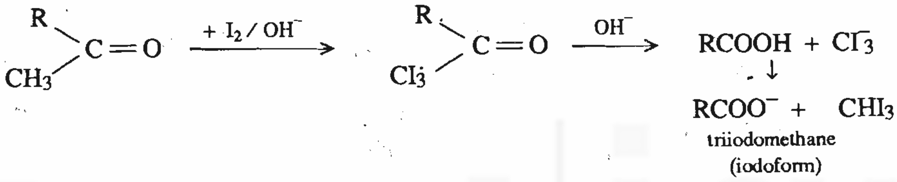


$$CH_3-\overset{\overset{\large O}{\|}}{C}-H + 3Cl_2 + 2NaOH \longrightarrow Cl_3C-\underset{\text{ethanal}}{\overset{\overset{\large O}{\|}}{C}}-H + H_2O + 3NaCl$$

Stage 2: Cleavage



The first step is polyhalogenation via the enlolate ion. The second step is cleavage of the polarised Cl_3C-C bond by base through an addition elimination mechanism. The haloform reaction is useful not only as a preparative method for the haloforms but also as a diagnostic test for the presence of the groupings indicated. In practice, a solution of iodine is added to the aqueous alkaline solution of the compound to be tested. A positive reaction will yield tri-iodomethane (iodoform), CHI_3, a bright yellow solid which may be identified by its sharp pungent odour and its melting point. Trichloromethane and tribromomethane are liquids.



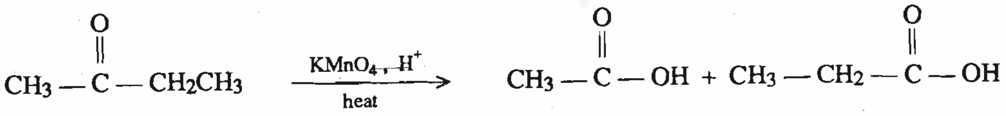
SAQ 6

A carbonyl compound does not form iodoform on being heated with iodine and sodium carbonate. It is:

a) ethanal
b) propanone
c) benzaldehyde
d) phenylethanone

14.4.3 Oxidation

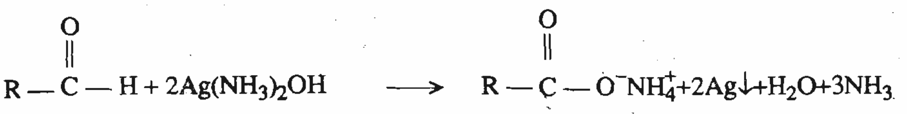
Aldehydes are so easily oxidised that even the mildest oxidising reagents will serve to bring about their conversion to acids. Ketones, on the other hand, are fairly resistant to oxidation. The oxidation of ketones, when forced by the use of strong oxidising reagents and heat, results in the rupture of carbon-carbon bonds to produce acids.



$$CH_3-\overset{\overset{\large O}{\|}}{C}-CH_2CH_3 \xrightarrow[\text{heat}]{KMnO_4,\ H^+} CH_3-\overset{\overset{\large O}{\|}}{C}-OH + CH_3-CH_2-\overset{\overset{\large O}{\|}}{C}-OH$$

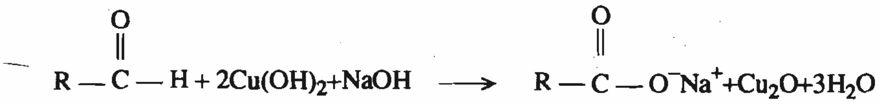
The ease with which oxidation of aldehydes takes place provides a simple method for distinguishing between aldehydes and ketones. Mild oxidising agents may be used for this purpose. **Tollen's reagent,** an ammonical solution of silver oxide, AG $(NH_3)_2OH$; **Fehling's solution;** an alkaline solution of cupric ion complexed with sodium potassium tartrate and **Benedicts solution,** an alkaline solution of cupric ion complexed with sodium citrate, are the three reagents commonly used to detect the presence of an aldehyde group.

When Tollen's reagent is used to oxidise an aldehyde, the silver ion is reduced to the metallic form and, if the reaction is carried out in a clean test tube, a silver mirror is formed.



$$R-\overset{\overset{\large O}{\|}}{C}-H + 2Ag(NH_3)_2OH \longrightarrow R-\overset{\overset{\large O}{\|}}{C}-O^-\overset{+}{N}H_4 + 2Ag\downarrow + H_2O + 3NH_3$$

When Fehling's and Benedict's solution are used to oxidise an aldehyde, the complexed deep blue cupric ion is reduced to red cuprous oxide.



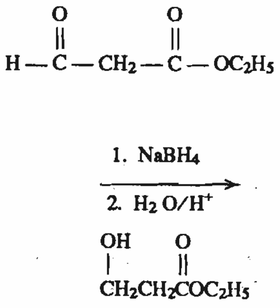
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H+2Cu(OH)_2+NaOH \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-O^-Na^++Cu_2O+3H_2O$$

Aromatic aldehydes react with the Tollen's reagent but do not react with either Fehling's or Bendict's solution. A means of distinguishing aliphatic from aromatic aldehydes is thus provided by this difference in reactivity between the two types of reagents.

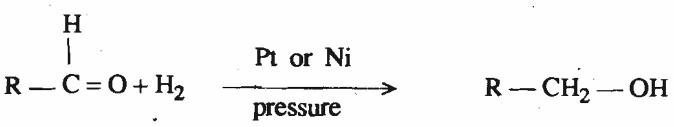
14.4.4 Reduction

Both aldehydes and ketones undergo reduction, the nature of the product depending on the reagent used for the purpose. Catalytic hydrogenation or reduction with dissolving metals (e.g., sodium and alcohol) or metallic hydrides (lithium aluminium hydride or sodium borohydride) gives alcohols. Aldehydes form primary alcohols and ketones give secondary alcohols:

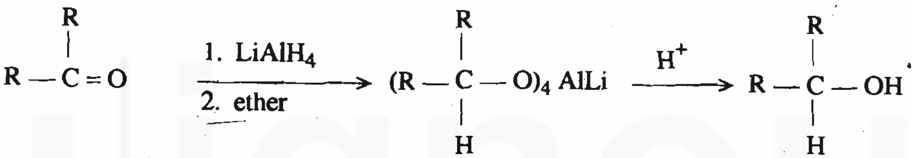
Sodium borohydride is a milder reducing agent than $LiAlH_4$. $NaBH_4$, reduces aldehydes and ketones rapidly, but esters very slowly, Therefore carbonyl groups can be reduced selectively with $NaBH_4$. For example,



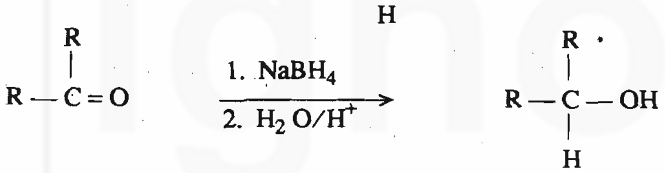
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OC_2H_5 \xrightarrow[2.\ H_2O/H^+]{1.\ NaBH_4} \overset{\overset{\displaystyle OH}{|}}{C}H_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OC_2H_5$$



$$R-\overset{\overset{\displaystyle H}{|}}{C}=O+H_2 \xrightarrow[\text{pressure}]{\text{Pt or Ni}} R-CH_2-OH$$

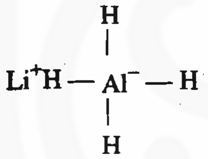


$$R-\overset{\overset{\displaystyle R}{|}}{C}=O \xrightarrow[2.\ \text{ether}]{1.\ LiAlH_4} (R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}-O)_4\,AlLi \xrightarrow{H^+} R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}-OH$$



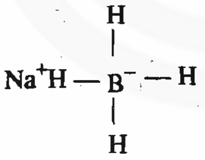
$$R-\overset{\overset{\displaystyle R}{|}}{C}=O \xrightarrow[2.\ H_2O/H^+]{1.\ NaBH_4} R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}-OH$$

In lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$), the hydrogen is negatively charged (H^-) and, like other bases, is capable of adding to the carbon of a carbonyl group.



$$Li^+H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{Al^-}}-H$$

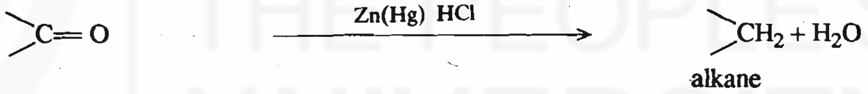
Lithium aluminum hydride



$$Na^+H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{B^-}}-H$$

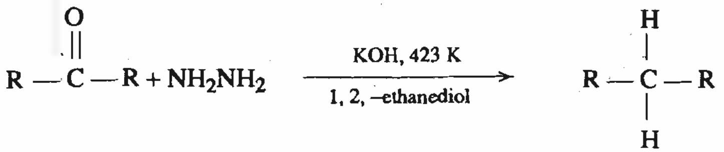
Sodium borohydride

Alkanes are formed when carbonyl compounds are reduced with zinc amalgam and hydrochloric acid. This reaction is known as the **Clemmensen reduction.**



$$>C=O \xrightarrow{Zn(Hg)\ HCl} \underset{\text{alkane}}{>CH_2} + H_2O$$

An alternative to the Clemmensen reduction for an acid sensitive ketone is the Wolff Kishner reduction. As mentioned earlier which employs hydrazine (NH_2NH_2) and potassium hydroxide. The solvent is 1,2-ethanediol (glycol).



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R+NH_2NH_2 \xrightarrow[1,\,2,\text{-ethanediol}]{KOH,\ 423\ K} R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-R$$

14.4.5 Specific Reactions of Methanal

Methanal (formaldehyde) gives many of the general reactions of carbonyl compounds above but as it does not have α hydrogens it does not undergo those reactions in which hydrogens α to the carbonyl group are involved. Thus, for example, it does not undergo base-catalysed self condensation. On treatment with aqueous sodium or potassium hydroxide it forms methanol and methanoate ion. This reaction is known as the **Cannizzaro reaction.**

$$\underset{\text{methanal}}{2HCHO} + OH^- \longrightarrow \underset{\text{methanoate ion}}{HCOO^-} + \underset{\text{methanol}}{CH_3OH}$$

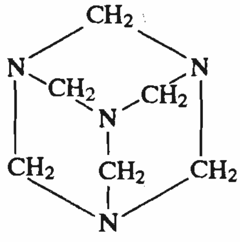
Benzaldehyde which also does not have any α-hydrogen undergoes the Cannizzaro reaction as well, e.g.,

$$\underset{\text{benzaldehyde}}{C_6H_5CHO} + OH^- \longrightarrow \underset{\text{benzoate ion}}{C_6H_5COO^-} + \underset{\text{benzyl alcohol}}{C_6H_5CH_2OH}$$

Treatment of methanol with ammonia gives hexamethylenetetramine:

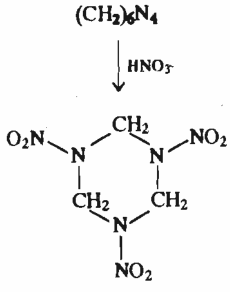
$$6HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + H_2O$$

Hexamethylenetetramine is also called utropin has following cyclic structure.



hexamethylenetetramine

Hexamethylenetertramine is medicinally useful as a urinary antiseptic (urotropin) and is also oxidised by nitric acid to the important military explosive cyclonite (RDX).



cyclonite (RDX)

Methanol is also used as a methylating agent:

$$C_2H_5NH_2+HCHO+HCOOH \longrightarrow C_2H_5NHCH_3+CO_2+H_2O$$

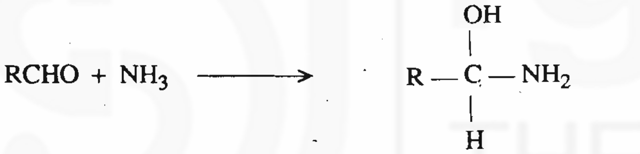
14.4.6 Specific Reactions of Aldehydes

In this subsection we will consider reactions which are given by aldehydes only and not those by ketones. Aldehydes restore the magenta colour of Schiff's reagent (aqueous rosaniline hydrochloride solution whose magneta colour has been discharged by sulphur dioxide).

As mentioned earlier, aldehydes are very easily oxidised. Hence they reduce Tollens' reagent to metallic silver, and Fehling's and Benedict's solutions to cuprous oxide.

Aldehydes (except methanal) on being warmed with concentrated sodium hydroxide solution, undergo repeated aldol condensations accompanied by dehydration. This leads to formation of polymeric products of uncertain structure which have a viscous or resinous appearance.

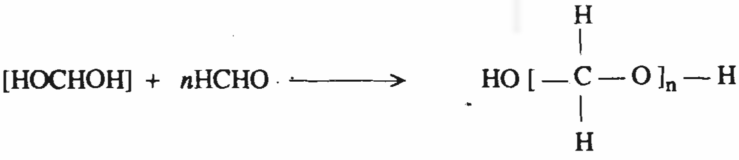
Aldehydes (except methanal) react with ammonia to give aldehyde-ammonia:



$$RCHO + NH_3 \longrightarrow R-\underset{H}{\overset{OH}{C}}-NH_2$$

Methanal and ethanal polymerise readily, propanone does not. The polymer of formaldehyde is known as **paraformaldehyde**, $HO(CH_2O)_nH$, with *n* having an average value of 30. Paraformaldehyde is an amorphous white solid which is prepared by slowly evaporating **formalin** (a 37-40% aqueous solution of methanal) under reduced pressure.

$$CH_2=O + H_2O \rightleftharpoons HOCH_2OH$$

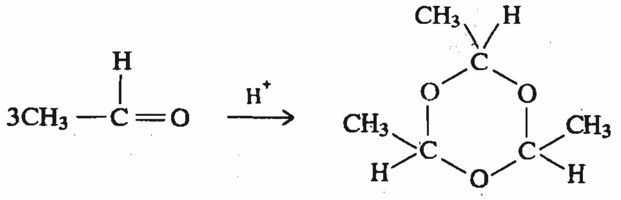


$$[HOCHOH] + nHCHO \longrightarrow HO[-\underset{H}{\overset{H}{C}}-O]_n-H$$

paraformaldehyde

Depolymerisation of paraformaldehyde is brought about by heating. This facile change of state from solid to gaseous allows methanal to be easily stored and used.

When treated with acid at a low temperature ethanal undergoes addition to give a cyclic trimer, paraldehyde (b.p. 398 K). Paraldehyde, when warmed, is depolymarised to regenerate ethanal. Like methanal, ethanal can also be easily stored and is used in the form of paraldehyde.



ethanal paraldehyde

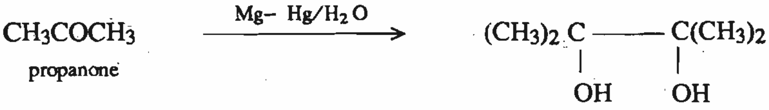
Finally in the following subsection, we will see the reactions which are given by ketones only and not by aldehydes.

14.4.7 Specific Reactions of Ketones

Ketones react with ammonia to give complex condensation products. Treatment with nitrous acid converts ketones to oximino derivatives, e.g.,

$$CH_3COCH_3 + HNO_2 \longrightarrow CH_3COCH{=}NOH + H_2O$$

When reduced with magnesium amalgam and water, ketones give dimers, that from propanone being called pinacol.



$$\underset{\text{propanone}}{CH_3COCH_3} \xrightarrow{Mg-\ Hg/H_2O} (CH_3)_2\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}(CH_3)_2$$

pinacol

Treatment of ketones with a peracids gives esters. This reaction is known as **Baeyer-Villiger oxidation:**

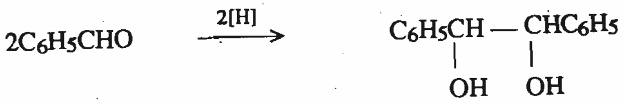
$$RCOR + R'COOOH \longrightarrow RCOOR + R'COOH$$

14.5 REACTIONS OF AROMATIC ALDEHYDES AND KETONES

In Section 14.4, we have mentioned that aromatic carbonyl compounds are less reactive in nucleophilic addition reactions than the aliphatic carbonyl complunds. We have also discussed the reasons for this lack of reactivity. Now, we will consider in some detail the chemistry of benzaldehyde and phenylethanone (acetophenone), two important members of this class of compounds.

14.5.1 Benzaldehyde

Benzaldehyde gives many general reactions of aldehydes described above. However, it does not reduce Fehling's solution. With zinc and hydrochloric acid or with sodium amalgam it undergoes reductive dimerisation to give hydrobenzoin:



$$2C_6H_5CHO \xrightarrow{2[H]} C_6H_5\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}C_6H_5$$

ethane
1,2-diphenyl-
1,2-dihydroxy
(hydrobenzoin)

We have seen earlier that benzaldehyde undergoes mixed aldol condensation with aldehydes or ketones having α-hydrogen in the presence of alkali to form $\alpha, \beta-$ unsaturated carbonyl compounds. This reaction is also known as **Claisen reaction.**

$$C_6H_5CHO + CH_3CHO \xrightarrow{OH^-} C_6H_5CH = CHCHO$$

3-phenylpropenal
(cinnamaldehyde)

$$C_6H_5CHO + CH_3COCH_3 \xrightarrow{OH^-} C_6H_5CH = CHCOCH_3$$

benzylidene propanone

On treatment with ethanoic anhydride and sodium ethanoate, benzaldehyde gives 3-phenylpropenoic acid (cinnamic acid). This condensation is known as **Perkin reaction.**

$$C_6H_5CHO + (CH_3CO)_2O + CH_3COONa \longrightarrow \underset{\substack{\text{3-phenylpropenoic acid}\\ \text{(cinnamic acid)}}}{C_6H_5CH{=}CHCOOH}$$

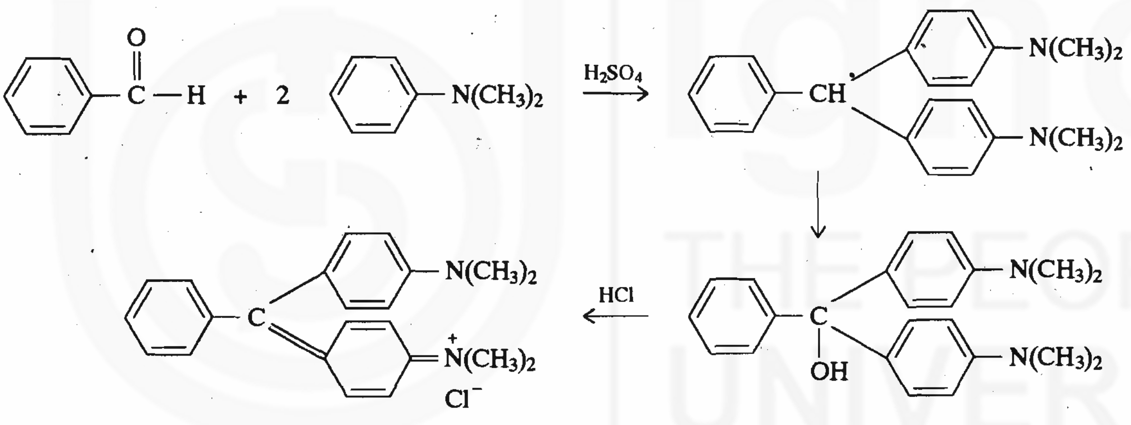
Benzoldehyde gives 3-phenylpropenoic acid with propanedioic acid (malonic acid) in the presence of pyridine. This reaction is known as **Knoevenagel reaction.**

$$C_6H_5CHO + CH_2(COOH)_2 \xrightarrow{\text{Pyridine}} \underset{\substack{\text{3-phenylpropenoic acid}\\ \text{(cinnamic acid)}}}{C_6H_5CH{=}CHCOOH}$$

On refluxing with aqueous ethanolic potassium cyanide, benzaldehyde forms benzoin. This condensation is known as **benzoin condensation.**

$$2C_6H_5CHO \xrightarrow{\text{KCN}} \underset{\text{benzoin}}{C_6H_5CHOHCOC_6H_5}$$

Condensation of benzaldehyde with phenols or tertiary aromatic amines in the presence of a dehydrating agents, H_2SO_4 or $ZnCl_2$, gives triphenyl derivatives. Oxidation with lead dioxide followed by treatment with hydrochloric acid gives a dye, e.g.,



malachite green

14.5.2 Phenylethanone

Phenylethanone (acetophenone) undergoes typical reactions of ketones, e.g., reduction with sodium and ethanol gives phenylethanol, Clemensen's reduction gives ethyl benzene.

It is oxidised by cold potassium permanganate to give phenyl-2-oxoethanoic acid (phenyl glyoxolic) acid which gets further oxidised to benzoic acid:

$$C_6H_5COCH_3 \xrightarrow{[O]} \underset{\substack{\text{phenyl-2-}\\ \text{oxoethanoic}\\ \text{acid}\\ \text{(phenyl glyoxalic}\\ \text{acid)}}}{C_6H_5COCOOH} \xrightarrow{[O]} \underset{\text{benzoic acid}}{C_6H_5COOH}$$

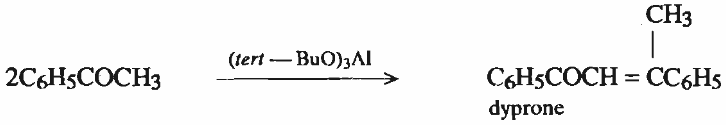
Oxidation with selenium dioxide gives phenyl-oxoethanal:

$$C_6H_5COCH_3 + SeO_2 \longrightarrow \underset{\substack{\text{phenyl-2-}\\ \text{oxoethanal}\\ \text{(phenylglyoxal)}}}{C_6H_5COCHO} + Se + H_2O$$

On treatment with bromine in ether at 273 K in the presence of aluminium chloride it gives phanyl-1-bromo-2-ethanone (phenacyl bromide):

$$C_6H_5COCH_3 + Br_2 \xrightarrow{AlCl_3} \underset{\text{phenyl-1-bromo-2-ethanone (phenacyl bromide)}}{C_6H_5COCH_2Br} + HBr$$

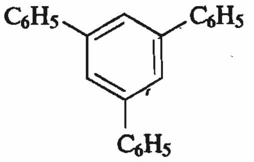
Two molecules of phenylethanone condense together in the presence of aluminium *tert* butoxide to give dyprone:



$$2C_6H_5COCH_3 \xrightarrow{(tert - BuO)_3Al} \underset{\text{dyprone}}{C_6H_5COCH = \overset{\overset{CH_3}{|}}{C}C_6H_5}$$

Condensation in the presence of hydrochloric acid forms 1,3,5-triphenylbenzene:

$$3C_6H_5COCH_3 \xrightarrow[-3H_2O]{}$$



With methanal and ammonia or a primary or secondary amine (as hydrochloride) phenylethanone reacts to give ketoamines called Mannich bases. This reaction is called the **Mannich reaction,** e.g.,

$$C_6H_5COCH_3 + HCHO + (CH_3)_2NH{:}HCl \longrightarrow \underset{\text{Mannic base}}{C_6H_5COCH_2CH_2N(CH_3)_2HCl} + H_2O$$

1,3-Diketones are formed from phanyl ethanone by condensation either with ethyl ethanoate in the presence of sodium ethoxide or with ethanoic anhydride in the presence of boron trifluoride:

$$C_6H_5COCH_3 + CH_3COOC_2H_5 \xrightarrow{C_2H_5O^-Na^+} \underset{\text{1,3-diketone}}{C_6H_5COCH_2COCH_3}$$

$$C_6H_5COCH_3 + (CH_3CO)_2O \xrightarrow{BF_3} C_6H_5COCH_2COCH_3 + CH_3COOH$$

By heating phenylethanone with aqueous yellow ammonium polysulphide, phenylethanamide and ammonium phenylethanoate are obtained (**Willgerodt reaction**):

$$C_6H_5COCH_3 + (NH_4)_2S_x \longrightarrow C_6H_5CH_2CONH_2 + C_6H_5CH_2COONH_4$$

14.6 INDUSTRIAL USES

Methanal is perhaps the most important member of the aldehyde family. Its industrial importance lies principally in its ability to copolymerise with phenol and with urea to produce bakelite and urea methanal resins, respectively. Methanal is also an antiseptic and disinfectant. As formalin it is used to preserve anatomical specimens, in the manufacture of dyes, for gelatin and casein.

Ethanal is used for preparing ethanol, ethanoic acid, phenolic resins, synthetic drugs and rubber acceleraters. Its trimer, paraldehyde $(CH_3CHO)_3$, is used in medicine as an hypnotic.

Propanone is used as a solvent for celluloid, lacquers, cellulose acetate and nitrate and in the preparation of sulphonal and ketene ($CH_2=C=O$) for synthesis of organic compounds. Other ketones are used as solvents for resins and synthetic rubber.

Copolymerisation: a reaction in which two or more unlike monomers polymerise with together.

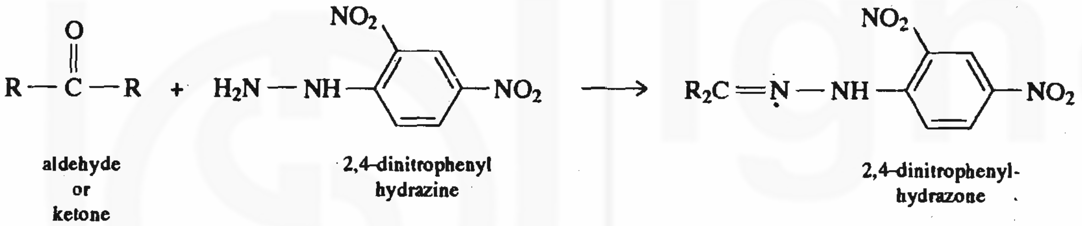
Benzaldehyde is used in perfumery, for preparation of dyes for flavouring purposes and for the preparation of α,β-unsaturated derivatives.

Phenylethanone (acetophenone) is used in perfumery and as hypnotic (hypnone). It is also used in the preparation of many organic compounds which are used in synthesis such as, phenacyl halides 1,3-diketones, etc.

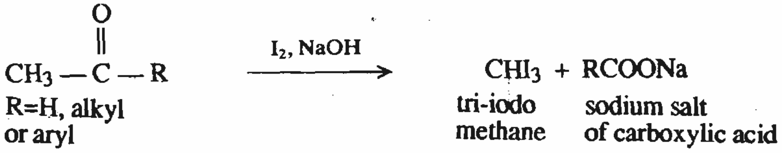
Some insecticides are prepared from the condensation of carbonyl compound, e.g., DDT (Unit 11) is obtained by heating trichloroethanal (chloral) with chlorobenzene in the presence of concentrated sulphuric acid.

14.7 LAB DETECTION

Both aldehydes and ketones on heating with an alcoholic solution of 2,4-dinitrophenyl hydrazine (DNP) in acidic medium give orange red crystalline hydrazone derivatives which are identified by their characteristic melting points.



Aldehydes reduce Tollens' reagent and Fehling or Benedict solutions, while ketones do not. These tests provide methods for distinguishing between aldehydes and ketones. Glucose (an aldehyde) when heated with Fehling solution gives red precipitate. This test is both qualitative as well as quantitative. It is used to estimate the amount of glucose in a sample of urine of diabetic patients. As mentioned in Section 14.4.3 ethanal and methyl ketones are characterised through the tri-iodomethane test (iodoform test).



$$CH_3-\overset{\overset{O}{\|}}{C}-R \xrightarrow{I_2,\ NaOH} CHI_3 + RCOONa$$

SAQ 7

How might you use simple test tube reactions to distinguish between:

a) benzaldehyde
b) ethanal
c) propanone

14.8 SUMMARY

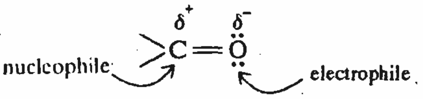
In this unit we have described the chemistry of aldehydes and ketones. We summarise below what we have studied so far:

- Aldehydes and ketones have carbonyl ($>C=O$) group which is quite reactive. Ketones can be regarded as alkyl or aryl derivatives of aldehydes.

- Aldehyde and ketones are prepared by oxidation or dehydrogenation of alcohols, decomposition of calcium salt of carboxylic acids or catalytic decomposition of carboxylic acids, Rosenmund's method and Stephen's method. Phenylethanone is prepared by acylation of benzene (Friedel-Crafts reaction).

- Methanal is commercially obtained by the catalytic oxidation of methanol. Ethanal and propanone are prepared industrially either by hydration of alkynes or catalytic oxidation of alkenes. Propanone is also obtained from oxidation of natural gas and as a by-product in the oxidation of cumene. Benzaldehyde is commercially prepared by the oxidation of methylbenzene and hydrolysis of benzal chloride and phenylethanone by catalytic oxidation of ehtyl benzene.

- The $>C=O$ function in aldehydes and ketones undergoes addition reaction. As it has a dipole moment, nucleophiles add to the carbonyl carbon atom and electrophiles add to the carbonyl oxygen atom.



Carbonyl group is attached by a variety of reagents such as HCN, $NaHSO_3$, ROH, ammonia derivatives, RMgX etc. to give addition products.

- The reaction with phosphorus yield gives alkenes from carbonyl compounds (Wittig reaction). In certain aldehydes and ketones, where α-hydrogens are present, acid or base catalysed enolisation, base-catalysed halogenation, haloform reaction and aldol condensation, etc., are observed.

- Aldehydes can be oxidised to carboxylic acid; ketones cannot be oxidised without breaking carbon-carbon bonds. The carbonyl group of an aldehyde or ketone can be reduced to alcohol by either catalytic hydrogenation or metallic hydrides. They can also be reduced to alkanes by either the Wolff-Kishner or Clemmensen reduction.

- Methanal and benzaldehyde react with aq. NaOH to give a mixture of alcohol and carboxylate ion (cannizzaro reaction). Methanal reacts with ammonia to form hexamethylenetetramine. Methanal and ethanal readily polymerise.

- Ketones form oximino derivatives with HNO_2, are oxidised to esters with peracids and form pinacols with magnesium amalgam and water.

- Benzaldehyde undergoes reductive dimerisation to give hydrobenzoin, forms α-β-unsaturated derivatives on condensation with other aldehydes and ketones, ethanoic anhydride and malonic acid. Condensation in the presence of CN^- gives benzoin and triphenylmethane derivatives are formed when benzaldehyde is condensed with aromatic amines.

- Phenylethanone gives phenyl-2-oxoethanoic acid and phenyl-2-oxoethanal on oxidation by $KMnO_4$ or SeO_2, respectively. Mannich bases are obtained from phenylethanone, methanal and ammonia or amines.

- Detection of carbonyl group in organic compounds is achieved by the formation of crystalline 2,4-dinitrophenyl hydrazones. Aldehydes are detected by the reduction of ammoniacal silver nitrate or Fehling solution and by Schiff's reagent.

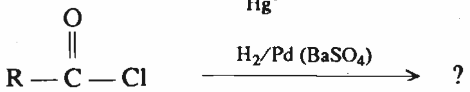
14.9 TERMINAL QUESTIONS

1) Predict the products in the following reaction sequences?

a) $RCH_2OH \xrightarrow[\text{pyridine}]{CrO_3} ?$

b) $RC \equiv CR \xrightarrow[Hg^{2+}]{H_2O,\ H^+} ?$

c)



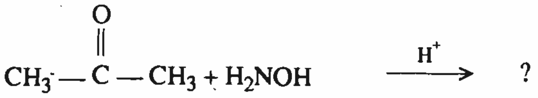
$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{H_2/Pd\ (BaSO_4)} ?$

d) $R-C\equiv N \xrightarrow[2.\ H_2O]{1.\ SnCl_2/HCl} ?$

2) Write a mechanism for the reaction of:
   a) addition of methanol to propanal
   b) addition of hydrazine to benzaldehyde

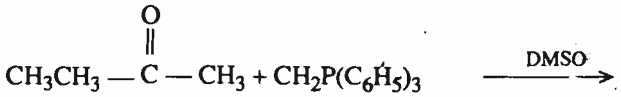
3) Predict the products:

a)



$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2NOH \xrightarrow{H^+} ?$

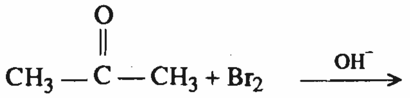
b)



$CH_3CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_2P(C_6H_5)_3 \xrightarrow{DMSO}$

c) $CH_3CHO + Ag(NH_3)_2OH \longrightarrow$

d)



$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + Br_2 \xrightarrow{OH^-}$

e)

$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[1,2\text{-ethanediol}]{H_2NNH_2,\ NaOH} ?$

f)

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{Zn\ (Hg),\ HCl} ?$

4) An infrared spectrum of an aqueous solution of methanal does not have a C=O stretching band in the 1700 cm^{-1} region. Can you suggest an explanation.

5) Write equations for the following named reactions:

   a) Oppenaur oxidation
   b) Cannizzaro reaction
   c) Aldol condensation
   d) Gattermann-Koch synthesis
   e) Knoevenagel reaction
   f) Perkin reaction
   g) Benzoin condensation
   h) Mannich reaction.

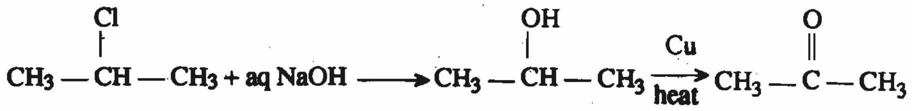
6) How do you obtain

   a) benzaldehyde
   b) phenylethanone starting with benzene.

14.10 ANSWERS

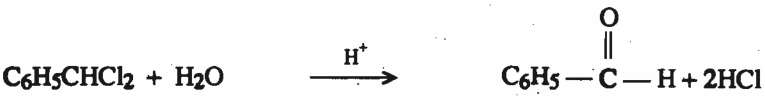
Self-Assessment Questions

1) b);



$$CH_3-\overset{Cl}{\overset{|}{C}}H-CH_3 + aq\ NaOH \longrightarrow CH_3-\overset{OH}{\overset{|}{C}}H-CH_3 \xrightarrow[heat]{Cu} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

2) c);



$$C_6H_5CHCl_2 + H_2O \xrightarrow{H^+} C_6H_5-\overset{O}{\overset{\|}{C}}-H + 2HCl$$

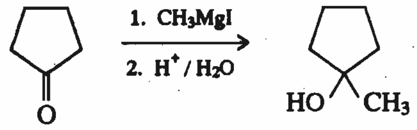
3) a) 1-pentanol; b) methylbutanone; c) 2-butanol; d) phenylmethanol;
e) 1-pentanal

4) a) Ir spectra of propanal and propanone have the C=O band at about 1720 cm^{-1}, but strong band at 2720 and 2820 cm^{-1} due to the C−H band is only exhibited by propanal.

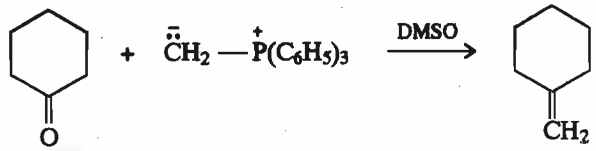
b) Nmr spectrum of propanal exhibits a characteristic signal near 10 ppm for the hydrogen in the −CHO group and this signal is, of course, absent in nmr spectrum of propanone.

5)

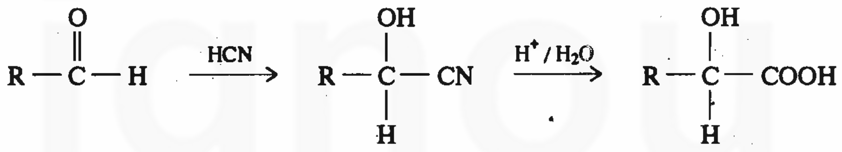
a)



b)

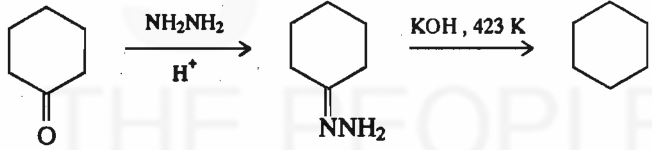


c)



$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{HCN} R-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CN \xrightarrow{H^+/H_2O} R-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-COOH$$

d)

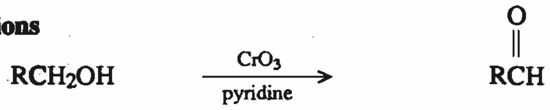


6) c; as it is not having α hydrogens.

7) Ethanal reduces both Tollen's reagents and Fehling's solution. Benzaldehyde can reduces Tollen's reagent but it does not reduce Fehling's solution. Propanone on the other hand does not react both with tollen's reagent and Fehling's solution.

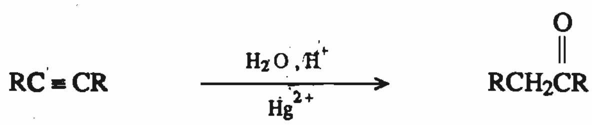
Terminal Questions

1) a)



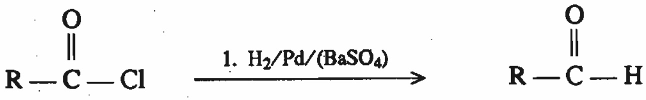
$$RCH_2OH \xrightarrow[pyridine]{CrO_3} \overset{O}{\overset{\|}{RCH}}$$

b)



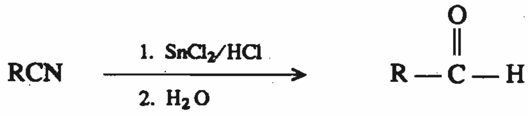
$$RC \equiv CR \xrightarrow[Hg^{2+}]{H_2O,\ H^+} RCH_2\overset{O}{\overset{\|}{C}}R$$

c)



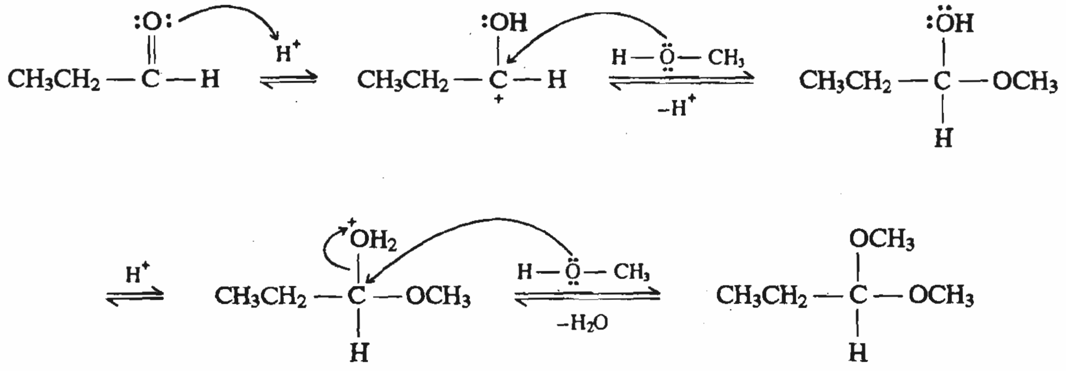
$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{1.\ H_2/Pd/(BaSO_4)} R-\overset{O}{\overset{\|}{C}}-H$$

d)



$$RCN \xrightarrow[2.\ H_2O]{1.\ SnCl_2/HCl} R-\overset{O}{\overset{\|}{C}}-H$$

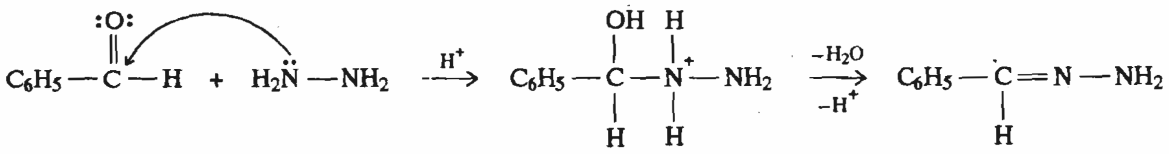
2) a)



$$CH_3CH_2-\overset{:O:}{\overset{\|}{C}}-H \overset{H^+}{\rightleftharpoons} CH_3CH_2-\overset{:OH}{\overset{|}{\underset{+}{C}}}-H \underset{-H^+}{\overset{H-\ddot{O}-CH_3}{\rightleftharpoons}} CH_3CH_2-\overset{:\ddot{O}H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-OCH_3$$

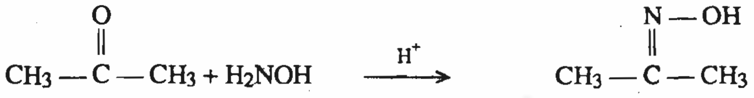
$$\overset{H^+}{\rightleftharpoons} CH_3CH_2-\overset{\overset{+}{O}H_2}{\overset{|}{\underset{H}{\underset{|}{C}}}}-OCH_3 \underset{-H_2O}{\overset{H-\ddot{O}-CH_3}{\rightleftharpoons}} CH_3CH_2-\overset{OCH_3}{\overset{|}{\underset{H}{\underset{|}{C}}}}-OCH_3$$

b)



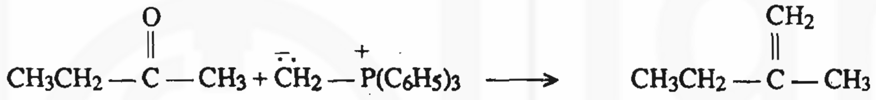
$$C_6H_5-\overset{:O:}{\overset{\|}{C}}-H + H_2\ddot{N}-NH_2 \xrightarrow{H^+} C_6H_5-\overset{OH}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{\overset{+}{N}}}}}-NH_2 \underset{-H^+}{\xrightarrow{-H_2O}} C_6H_5-\underset{H}{\underset{|}{C}}=N-NH_2$$

3) a)



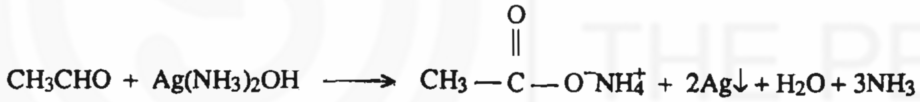
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2NOH \xrightarrow{H^+} CH_3-\overset{N-OH}{\overset{\|}{C}}-CH_3$$

b)



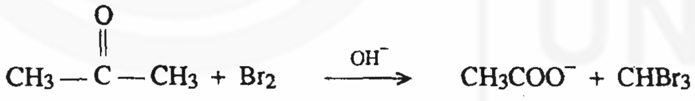
$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + \overset{-}{\ddot{C}}H_2-\overset{+}{P}(C_6H_5)_3 \longrightarrow CH_3CH_2-\overset{CH_2}{\overset{\|}{C}}-CH_3$$

c)



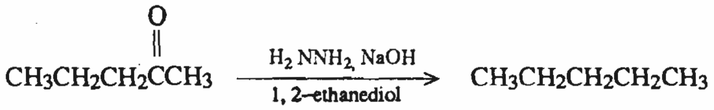
$$CH_3CHO + Ag(NH_3)_2OH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O^-NH_4^+ + 2Ag\downarrow + H_2O + 3NH_3$$

d)



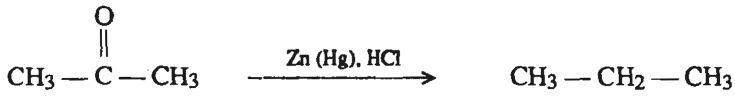
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + Br_2 \xrightarrow{OH^-} CH_3COO^- + CHBr_3$$

e)



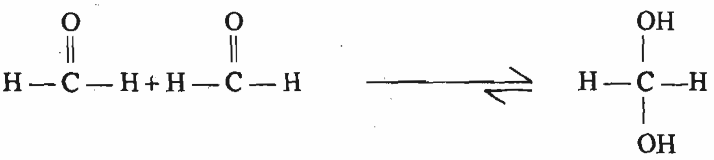
$$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[1,2\text{-ethanediol}]{H_2NNH_2,\ NaOH} CH_3CH_2CH_2CH_2CH_3$$

f)



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{Zn\ (Hg),\ HCl} CH_3-CH_2-CH_3$$

4) In water, methanal is converted to stable hydrate, formalin.

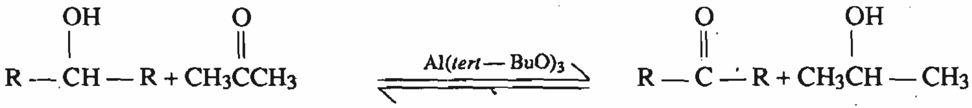


$$H-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons H-\overset{OH}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-H$$

formalin (a hydrate)

Formalin does not have carbonyl group, therefore it does not give a C=O stretching in ir spectra.

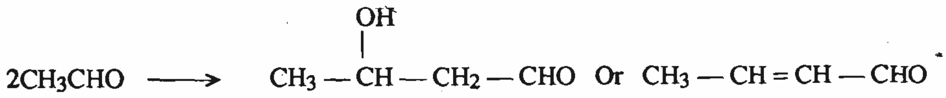
5) a)



$$R-\overset{OH}{\overset{|}{C}H}-R + CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightleftharpoons{Al(tert-BuO)_3} R-\overset{O}{\overset{\|}{C}}-R + CH_3\overset{OH}{\overset{|}{C}H}-CH_3$$

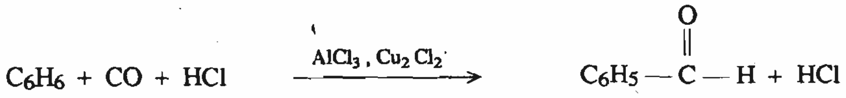
b) $2HCHO + OH^- \longrightarrow HCOO^- + CH_3OH$

c)



$$2CH_3CHO \longrightarrow CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CHO \text{ Or } CH_3-CH=CH-CHO$$

d)



$$C_6H_6 + CO + HCl \xrightarrow{AlCl_3,\ Cu_2Cl_2} C_6H_5-\overset{O}{\overset{\|}{C}}-H + HCl$$

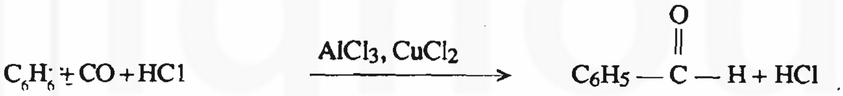
e) $C_6H_5CHO + CH_2(COOH)_2 \xrightarrow{pyridine} C_6H_5CH=CHCOOH$

f) $C_6H_5CHO + (CH_3CO)_2O + CH_3COONa \longrightarrow C_6H_5CH=CHCOOH$

g) $2C_6H_5CHO \xrightarrow{KCN} C_6H_5CHOHCOC_6H_5$

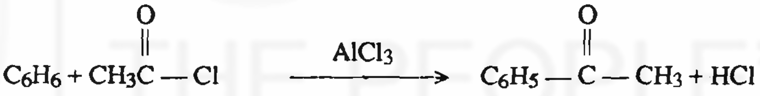
h) $C_6H_5COCH_3 + HCHO + (CH_3)_2NH{:}HCl \longrightarrow C_6H_5COCH_2CH_2N(CH_3)_2{:}HCl$

6) a)



$$C_6H_6 + CO + HCl \xrightarrow{AlCl_3,\ CuCl_2} C_6H_5-\overset{O}{\overset{\|}{C}}-H + HCl$$

b)



$$C_6H_6 + CH_3\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{AlCl_3} C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3 + HCl$$

Further Reading

1) *Organic Chemistry* 6th Ed., by R.T. Morrison and R.N. Boyd, Prentice-Hall of India Pvt. Ltd.
2) *Text Book of Organic Chemistry*, 2nd Ed., by Lloyd N. Ferguson, Affiliated East-West Press Pvt. Ltd.
3) *Organic Chemistry*, Vol. I and II, by S.M. Mukherji, S.P. Singh and R.P. Kapoor, Wiley Eastern Ltd.
4) *Text Book of Organic Chemistry*, 24th Ed., by P.L. Soni and H.M. Chawla, Sultan Chand and Sons.
5) *The Chemistry of Carbonyl Compounds*; Gutsche, C. David, Prentice-Hall of India Pvt. Ltd.