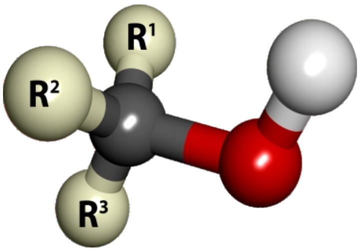
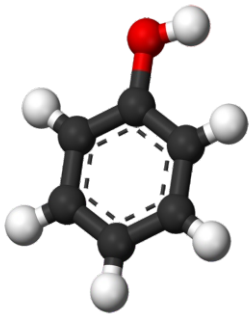
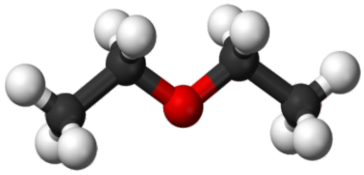
CHAPTER 7

Alcohols, Phenols and Ethers

Teaching Periods	09	Assessment	01	Weightage %	07







Students will be able to:

- ✓ Describe the physical properties and structure of alcohol. (Understanding)
- ✓ Explain the preparation of alcohols by reduction of aldehydes, ketones, carboxylic acids and esters. (Applying)
- ✓ Explain the preparation of alcohols by hydrolysis of alkyl halide and Grignard reagent with aldehyde and ketone. (Applying)
- ✓ Describe reactivity of alcohols (Understanding)
- ✓ Describe the preparation of ether and ester by alcohol and oxidative cleavage of 1, 2- diols. (Understanding)
- ✓ Discuss the physical properties and structure of phenols. (Applying)
- ✓ Explain the preparation of phenol from chlorobenzene and hydrolysis of diazonium salts. (Applying)
- ✓ Explain the reactions of phenol. (Applying)
- ✓ Differentiate between alcohol and phenol. (Understanding)
- ✓ Enlist the important compounds of Alcohols, Phenols and Ethers with their application (Applying)
- ✓ Explain identification test of alcohol and phenol. (Understanding)

INTRODUCTION

Alcohols, Phenols and Ethers are three classes of oxygen containing organic compounds. Alcohols and Phenols are derived by replacing one hydrogen atom of water with an alkyl and aryl group respectively but ethers are formed by replacing both hydrogen atoms of water with alkyl or aryl groups.

Alcohols, phenols and ethers have a wide range of industrial as well as pharmaceutical applications. Methanol and Ethanol are good car fuels with high octane rating, Isopropyl alcohol is a common sanitizer, Ethylene glycol is frequently used as automotive antifreeze, Phenol is the oldest mild antiseptic agent and ethers are known for their anaesthetic properties.

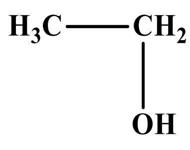
Ethanol has been used by humans since prehistory, however it was first prepared synthetically in early eighteenth century by Michael Faraday. Phenol was isolated from coaltar in the mid eighteenth century whereas ether was first synthesized by distillation of sulphuric acid with ethanol in the mid fifteenth century.

7.1 ALCOHOL

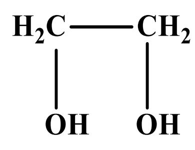
Alcohol is a class of organic compounds in which hydroxyl group (-OH) is attached to an aliphatic carbon atom. They are classified according to the number of hydroxyl groups present in the molecule. Monohydric alcohols contain one hydroxyl group. If two or more hydroxyl groups (-OH) are present in the molecule, these are identified as dihydric and polyhydric alcohols respectively.

DO YOU KNOW?

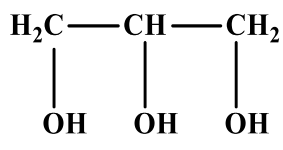
Wood sprit is a term used to refer to methanol, which was traditionally obtained by heating wood through a process known as destructive distillation.



Ethanol
(monohydric alcohol)

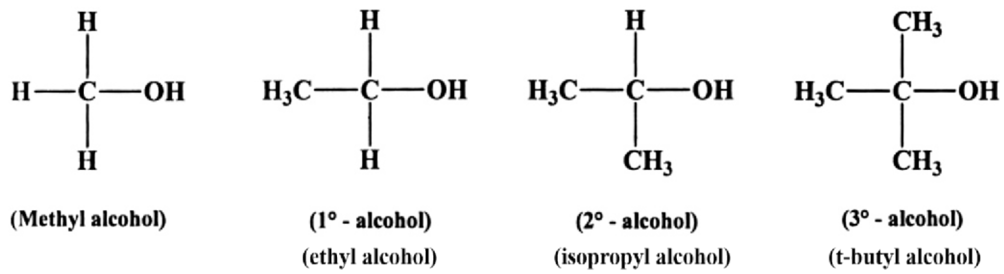


Ethylene glycol
(Dihydric alcohol)



Glycerol
(Trihydric alcohol)

Monohydric alcohols are represented by a general formula R-OH or $C_nH_{2n+1}OH$. Monohydric alcohols are further classified into primary (1°-alcohol), secondary (2°-alcohol) and tertiary (3°-alcohol) depending upon whether the hydroxyl group is attached to primary, secondary or tertiary carbon atom.



7.1.1 Structure of Alcohol

The structure of an alcohol molecule is similar to that of water molecule as shown in figure Fig.7.1. The carbon atom which is bonded to hydroxyl group is sp^3-hybridized. The oxygen atom of –OH group is also sp^3 hybridized. Oxygen atom utilizes its two sp^3 hybrid orbitals in the formation of sigma bond with carbon and hydrogen atoms while the remaining two sp^3 hybrid orbitals of oxygen contain lone pairs of electrons. The C-O-H bond angle is 108.9°, which is slightly higher than exists in water molecule (104.5°).

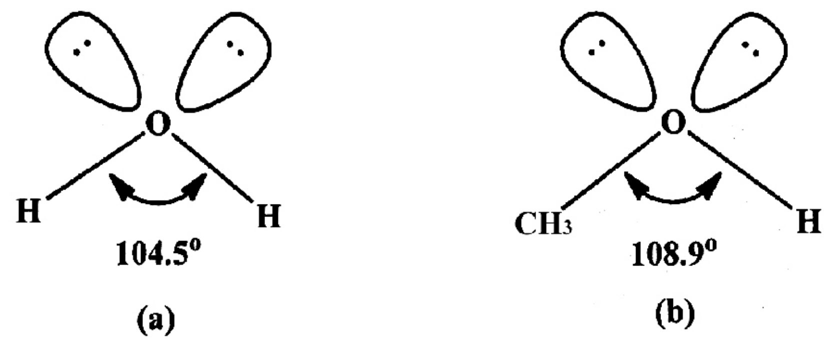


Fig 7.1: Structure of (a) water and (b) methanol molecule

7.1.2 Physical Properties

Physical State: Alcohols of lower molecular mass (up to butanol) are colorless liquids with characteristic sweet smell. Higher members are waxy solids.

Boiling Point: Boiling point of alcohol is much higher than that of alkanes and ethers of comparable molecular mass. This is because of the existence of inter molecular hydrogen bonding. The greater the number of carbons in the molecule, the higher the boiling point of alcohol. Further, the boiling point of straight chain alcohol is higher than branch chain (Fig.7.2).

Table 7.1 Boling points of straight chain and branch chain alcohols

Compound	Boiling Point (°C)
Ethanol	78.37
Propanol	97.2
Isopropanol	82.6
n-Butanol	117.7
Isobutanol	107.89

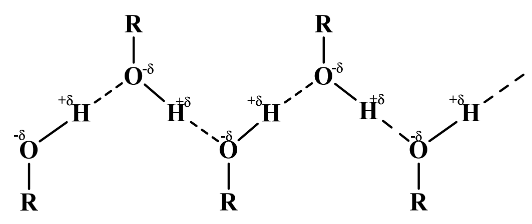


Fig 7.2: Intermolecular hydrogen bonding among alcohol molecules

Solubility: Alcohols are generally soluble in water since they form hydrogen bonds with water molecules. However, solubility decreases with increasing the number of alkyl groups in the molecule (Fig.7.3).

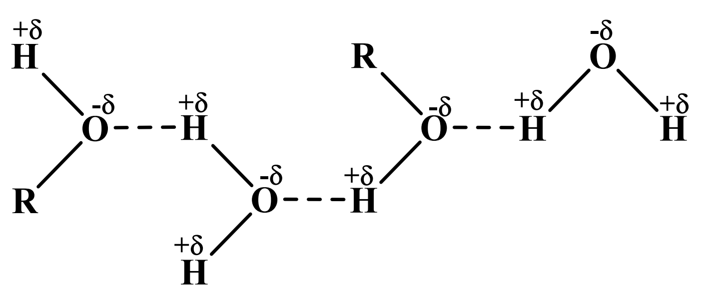


Fig 7.3: Intermolecular hydrogen bonding among alcohol molecules

Self Assessment

Arrange the following alcohol molecules in increasing order of their boiling point.

C_2H_5OH, $CH_3(CH_2)_3OH$, $CH_3CH(OH)CH_3$, $CH_3C(CH_3)_2OH$

Acidity of Alcohol

Alcohols are generally classified as weak acids due to their ability to donate a proton to a strong base. The acidity of alcohol is determined by the stability of resulting alkoxide ion after the alcohol donates a proton. Compared to tertiary and secondary alcohols, primary alcohols generate more stable alkoxide ions making them relatively more acidic (Table.7.2).

Table 7.2 pka values of comparative alcohol compounds

Types of Alcohols	Structural formula	pka
Methyl alcohol	CH_3OH	15.5
Ethyl alcohol	C_2H_5OH	15.9
Sec. Propyl alcohol	$CH_3CH(CH_3)OH$	16.3
Tert. Butyl Alcohol	$CH_3C(CH_3)_2OH$	17

Acidic behavior of alcohol can be observed by the evolution of hydrogen gas when a piece of active metal (Sodium or Potassium) is put into anhydrous alcohol.

$$\underset{\text{(Ethyl alcohol)}}{2\,C_2H_5OH} + 2Na \longrightarrow \underset{\text{(Sodium ethoxide)}}{2\,C_2H_5ONa} + H_2\uparrow$$

7.1.3 Preparations of Alcohols

There are several methods for the preparation of alcohols. Below are some commonly used methods.

7.1.3.1 Hydration of an Alkene

Alkene when boils with water in the presence of concentrated sulphuric acid to give corresponding alcohol.

$$\underset{\text{(Ethene)}}{H_2C{=}CH_2} + H_2O \xrightarrow[100^\circ C]{H_2SO_4\,(conc.)} \underset{\text{(Ethyl alcohol)}}{H_3C{-}CH_2{-}OH}$$

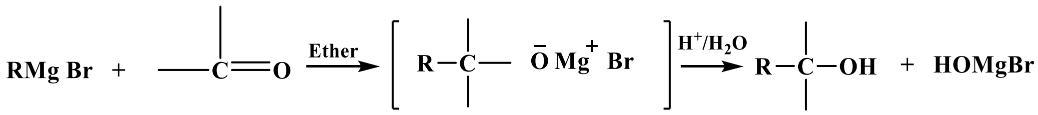
7.1.3.2 Hydrolysis of an Alkyl halide

When an alkyl halide is heated with aqueous alkali (NaOH, KOH), it gives corresponding alcohol.

$$\underset{\text{(Ethyl Chloride)}}{C_2H_5Cl} + NaOH \xrightarrow[Heat]{H_2O} \underset{\text{(Ethyl alcohol)}}{C_2H_5OH} + NaCl$$

7.1.3.3 Reaction of Grignard reagent with Aldehyde and Ketone

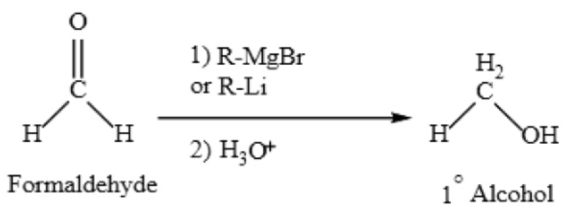
Grignard reagent when reacts with a formaldehyde, acetaldehyde and acetone molecule, it gives primary, secondary and tertiary alcohols respectively.



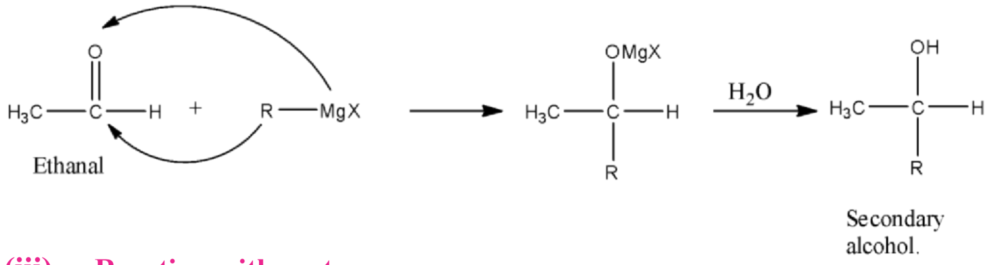
(Grignard regent) (Carbonyl Compond) (Addition Product) (Alcohol)

Preparation of primary, secondary and tertiary alcohol

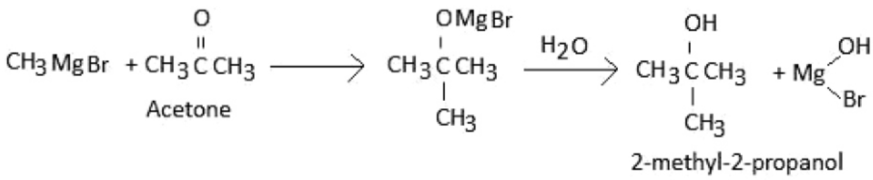
(i) Reaction with formaldehyde



(ii) Reaction with acetaldehyde (ethanal)



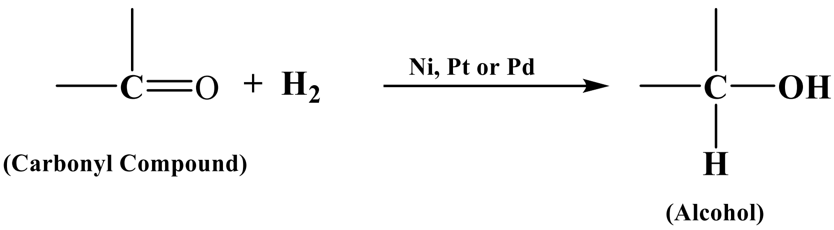
(iii) Reaction with acetone



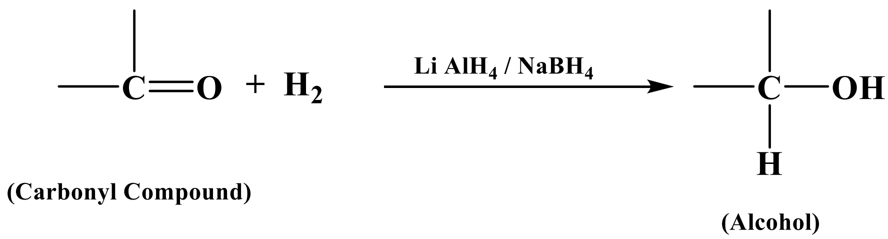
7.1.3.4 Reduction of Aldehydes and Ketones

Aldehydes and Ketones can be reduced to alcohols by using any one of the following two methods:

(a) Hydrogenation of aldehyde and ketone at high temperature and pressure in the presence of catalyst like nickel (Ni), platinum (Pt) or palladium (Pd).



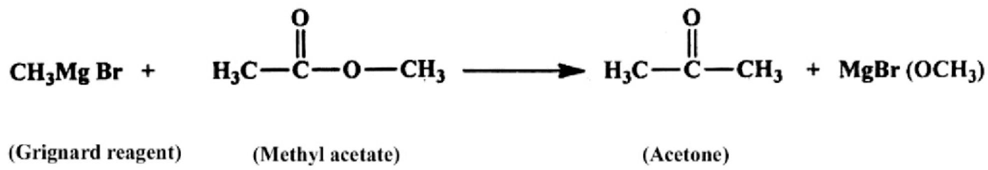
(b) Reaction of aldehyde and ketone with a reducing agent like lithium aluminum hydride (Li AlH_4) or sodium borohydride ($NaBH_4$).



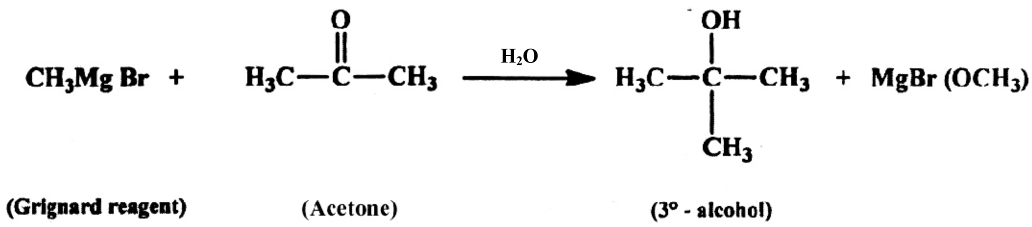
It is important to note that aldehydes on reduction give primary alcohols, and ketones on reduction give secondary alcohols.

7.1.3.5 Reaction of Grignard reagent with Esters

When a Grignard reagent is mixed with an ester, it chemically changes into carbonyl compound (aldehyde or ketone).

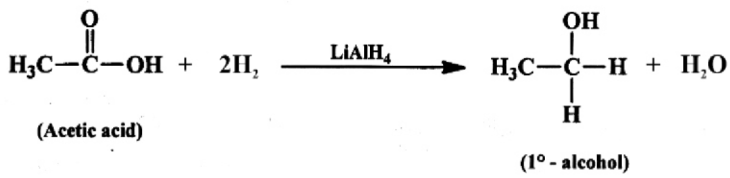


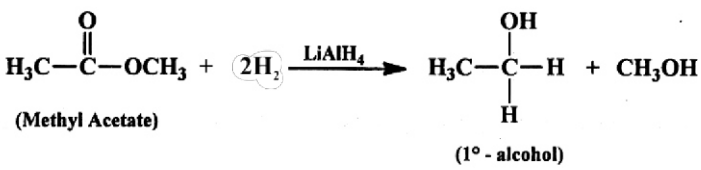
The carbonyl compound thus formed then reacts with another molecule of Grignard reagent and finally gives an alcohol (Discussed in Chap. 18).



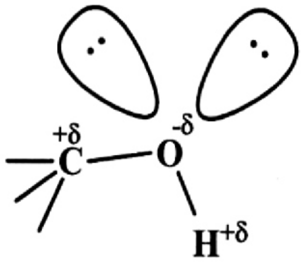
7.1.3.6 Reduction of Carboxylic acids and Esters

Carboxylic acids and esters can be reduced to the primary alcohols (1°-alcohols) in the presence of a very strong reducing agent such as lithium aluminum hydride.





7.1.4 Reactivity of Alcohol



The oxygen atom in the alcohol molecule (R-OH) is more electronegative than the carbon and hydrogen atoms that are bonded to it. This creates a polarity in C-O and O-H bonds. In addition, oxygen has two unshared electron pairs which cause it to act as an electron rich centre.

Thus, the reactivity of alcohol can be attributed to the breaking of either C – OH bond with the removal of –OH group or by the breaking O – H bond with the removal of hydrogen (H). The common reactions of alcohol are substitution, elimination and oxidation.

7.1.5 Reactions of Alcohols

A variety of reactions can occur with alcohols, including dehydration, oxidation, reduction, esterification, as well as reactions involving halogens and metals. During reactions with other reagents, alcohol can experience cleavage of either the C-O or O-H bonds (Table.7.3).

(i) The C-O bond in an alcohol molecule breaks when it is attacked by a nucleophile.

(ii) The H-O bond in an alcohol molecule breaks when it is attacked by an electrophile.

Table 7.3 Types of reactions of alcohols and their order of reactivity

Type of Bond Breaking	Type of Attacking Reagent	Order of reactivity of alcohols
O – H	Electrophile	1° > 2° > 3°
C – O	Nucleophile	3° > 2° > 1°

7.1.5.1 Reaction with Halogen acids (HX)

In the presence of a catalyst, zinc chloride ($ZnCl_2$), ethyl alcohol reacts with hydrochloric acid (HCl) to produce ethyl chloride.

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

(Ethyl alcohol) (Ethyl chloride)

The mixture of concentrated HCl and $ZnCl_2$is called "Lucas reagent" and used to distinguish between primary, secondary and tertiary alcohol.

DO YOU KNOW?

In the Lucas test, primary alcohols show no immediate reaction, secondary alcohols form turbidity within a few minutes, and tertiary alcohols produce an immediate and vigorous formation of a cloudy precipitate (alkyl chloride) with Lucas reagent (conc. HCl and $ZnCl_2$).

7.1.5.2 Reaction with $SOCl_2$ and PX_3

When alcohol is treated with Phosphorus tri halide (PX_3) or thionyl chloride ($SOCl_2$), it gives corresponding alkyl halide (Discussed in chap. 18).

$$3\,C_2H_5OH + PCl_3 \longrightarrow 3\,C_2H_5Cl + H_3PO_3$$

(Ethyl alcohol) (Ethyl chloride)

$$C_2H_5OH + SOCl_2 \xrightarrow{Pyridine} C_2H_5Cl + SO_2 + HCl$$

(Ethyl alcohol) (Ethyl chloride)

7.1.5.3 Acid Catalyzed Dehydration

When an alcohol is heated with concentrated sulphuric acid at 170°C, it undergoes a dehydration process, resulting in the formation of an alkene. In this process, a water molecule is eliminated.

$$C_2H_5OH \xrightarrow[170°C]{Conc.\ H_2SO_4} H_2C{=}CH_2 + H_2O$$

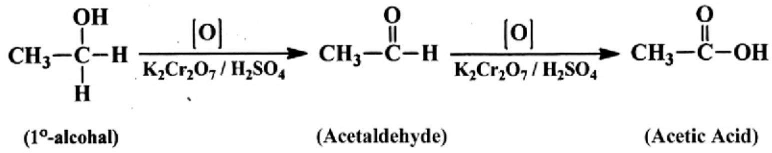
(Ethyl alcohol) (Ethene)

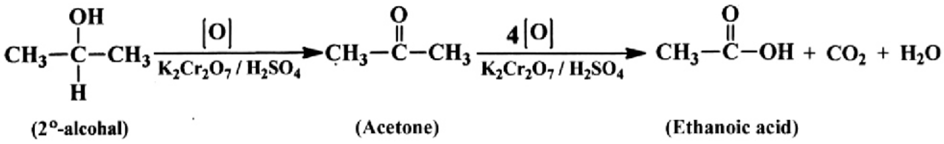
The ease of acid catalyzed dehydration of alcohol is given as

3°-alcohol > 2°-alcohol > 1°-alcohol

7.1.5.4 Oxidation Reaction

Primary and secondary alcohols oxidize in the presence of strong oxidizing agents such as acidified potassium dichromate ($K_2Cr_2O_7$) or potassium per manganate ($KMnO_4$) to give carboxylic acid through an aldehyde or ketone intermediate. Tertiary alcohol cannot be oxidized due to the unavailability of hydrogen on its hydroxyl-bearing carbon.





Since the oxidation of ketone involves the breaking of carbon-carbon sigma bond, it is a relatively slow process.

7.1.5.5 Cleavage of 1, 2-diols

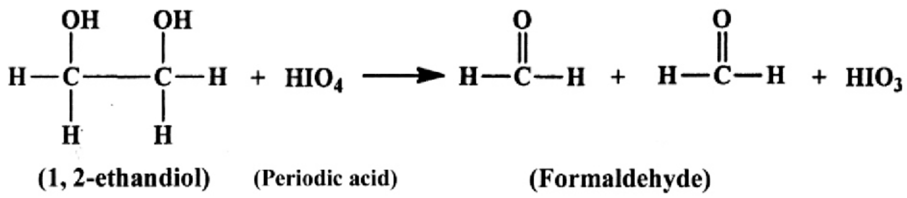
An alcohol molecule in which two hydroxyl groups (-OH) are attached on position 1 and 2 is called as 1, 2 –diol or vicinal diol.

When a 1, 2-diol molecule is treated with per iodic acid (HIO_4), an oxidative cleavage occurs between carbon 1 and carbon 2 atoms resulting in the formation of two carbonyl molecules. These carbonyl molecules may be aldehyde or Ketone depending upon the number of alkyl groups attached to the carbon atom bearing hydroxyl groups. In this reaction periodic acid (HIO_4) is reduced into iodic acid (HIO_3).

DO YOU KNOW?

Periodic acid is a white crystalline solid that dissolves in water and possesses high oxidizing potential owing to the presence of iodine in its composition. Apart from its use in organic chemistry as an oxidizing agent, it is also utilized for staining biological specimens.

For example, ethylene glycol (1, 2- ethanediol) is broken down into two formaldehydes molecules if treated with per iodic acid.



Self Assessment

Mention the reagents required for the following conversions.

(i)	Ethanol to Ethene	(ii)	Acetic acid to Ethanol
(iii)	Ethanol to Acetic acid	(iv)	Ethylene glycol to formaldehyde

Uses of Alcohol

(i) Methanol is used as antifreeze solution and also in the preparation of perfumes, dyes, drugs etc.

(ii) Ethanol is used as a raw material in the synthesis of a variety of organic compounds such as gums, resins, tinctures, chloroform, esters, acetone and acetic acid.

(iii) The mixture of isopropyl alcohol in water is used as rubbing alcohol (antiseptic).

7.2 PHENOLS

Organic compounds in which hydroxyl group (-OH) is directly attached to benzene ring are called Phenols. The parent compound of this family is monohydroxy benzene which is also known as carbolic acid or benzenol.

On the basis of number of hydroxyl groups (-OH) attached to aromatic ring, Phenols are classified into monohydric, dihydric and trihydric Phenols (Fig.7.4).

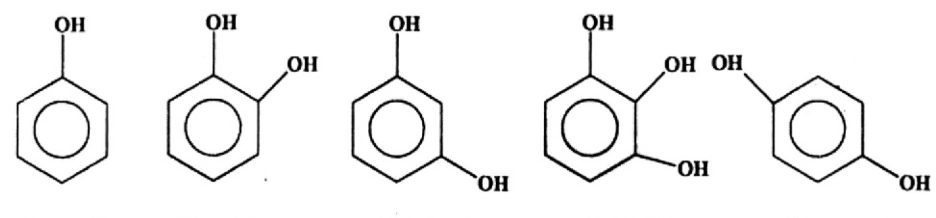
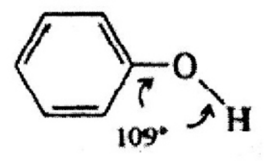


Fig 7.4: Structure of various monohydric, dihydric and trihydric phenols

7.2.1 Structure of Phenol

In the molecule of phenol the carbon atom of aromatic ring is attached to an –OH group. The oxygen atom in the –OH group is sp^3 hybridized, while the carbon atoms in the aromatic ring are sp^2 hybridized. An sp^3-sp^2 sigma bond is formed between oxygen atom of –OH group and carbon atom of aromatic ring.



Phenol

The C – O - H bond angle is set at 109° which is almost the same as the bond angle of tetrahedral geometry (109.5°) but due to two non-bonded electrons pairs of oxygen atom, the geometry is slightly distorted from a normal tetrahedron and exists in a bent shape.

7.2.2 Physical Properties

(i) **Physical State:** Pure phenol is a white crystalline solid at room temperature however it may appear in red colour due to the presence of some oxidized products as impurities.

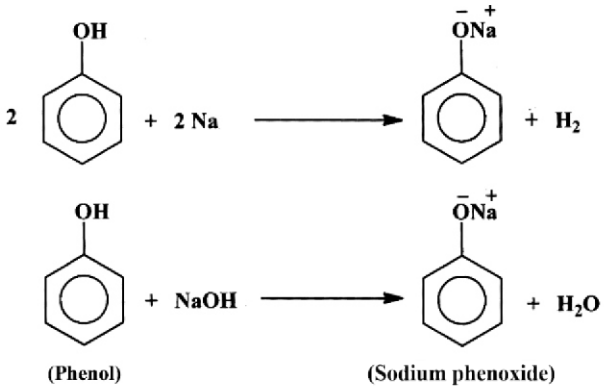
(ii) **Boiling Point:** The boiling point of phenol is higher than that of other compounds of comparable size because the presence of –OH group enables a phenol molecule to form hydrogen bond with other phenol molecules.

(iii) **Toxicity:** Phenol is toxic and corrosive in nature. When it comes into contact with skin it can lead to a severe burns and tissue damage.

(iv) **Solubility:** The hydroxyl group attached to the aromatic ring allows phenol to make hydrogen bond with water molecules that is why it is soluble in water.

7.2.3 Acidity of Phenol

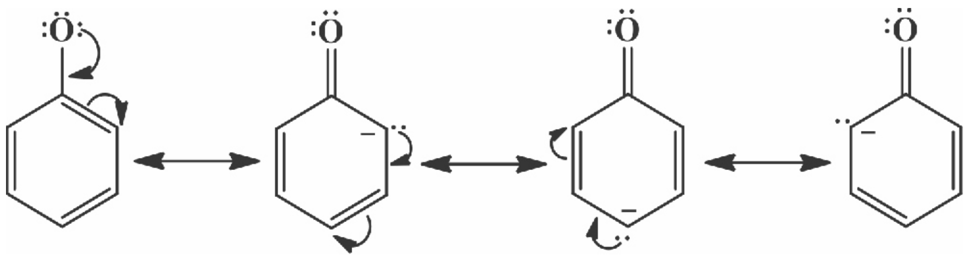
Phenol is fairly acidic since it reacts with an alkali or alkali metal to form salt.



The pka value of phenol is approximately 10, which is far less than carboxylic acid (pka ≈ 5) but much higher than alcohol (pka = 15 – 18) that is why phenol is much weaker acid than carboxylic acid but stronger than alcohol.

Comparing phenoxide ion with ethoxide ion, it is noted that the negative charge on oxygen atom of phenoxide ion is delocalized over the entire ring through a process called as resonance and make the phenoxide ion stable.

$$\underset{\text{(Phenol)}}{C_6H_5OH} + H_2O \rightleftharpoons \underset{\text{(Phenoxide ion)}}{C_6H_5\bar{O}} + H_3O^+$$



On the other hand, in ethoxide ion the negative charge is localized on the oxygen atom due to the absence of aromatic ring result in a less stable structure compared to phenoxide ion.

$$\underset{\text{(Ethanol)}}{C_2H_5OH} + H_2O \rightleftharpoons \underset{\text{(Ethoxide ion)}}{C_2H_5\bar{O}} + H_3O^+$$

Self Assessment

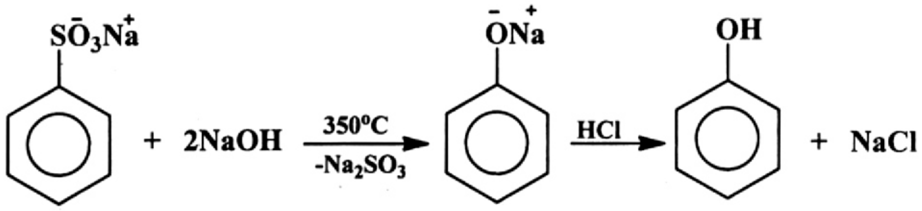
Compare the relative acid strength and water solubility of Phenol with Ethanol.

7.2.4 Preparation of Phenol

Phenol can be prepared by various methods. The two most common methods are described below.

7.2.4.1 From Sodium Benzene Sulphonate

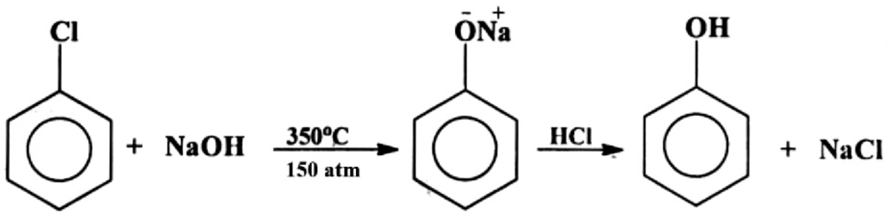
Sodium benzene sulphonate when fused with sodium hydroxide at 300 - 350°C, produces sodium phenoxide which on acidification yield phenol.



(Sodium benzene sulphonate) (Sodium phenoxide) (Phenol)

7.2.4.2 From Chlorobenzene (Dow's Process)

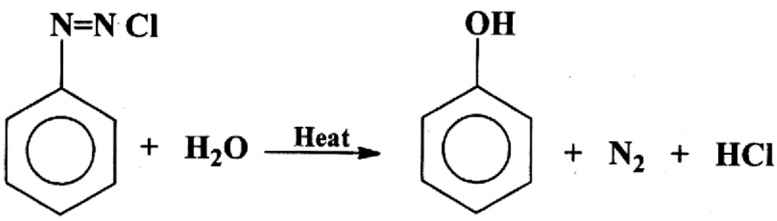
Chlorobenzene when fused with aqueous sodium hydroxide (NaOH) at 350°C and 150 atmospheric pressures, it gives sodium phenoxide which then acidified with dilute hydrochloric acid to yield phenol.



(Chloro benzene) (Sodium phenoxide) (Phenol)

7.2.4.3 Hydrolysis of Diazonium salt

It is a laboratory method for the preparation of phenol. Benzene diazonium chloride on heating with water, changes into phenol with the release of nitrogen gas.



(Diazonium salt) (Phenol)

Diazonium salt is a class of organic compounds that contain a functional group $-N_2Cl$ attached with alkyl or aryl carbon chain.

7.2.5 Reactivity of Phenol

The aromatic part of phenol is similar to benzene which favors the electrophilic substitution reactions. The hydroxyl group (-OH) attached to aromatic ring is ortho-para director and ring activator. Its presence orients the incoming electrophile toward ortho and para positions with a faster speed.

7.2.6 Reactions of Phenol

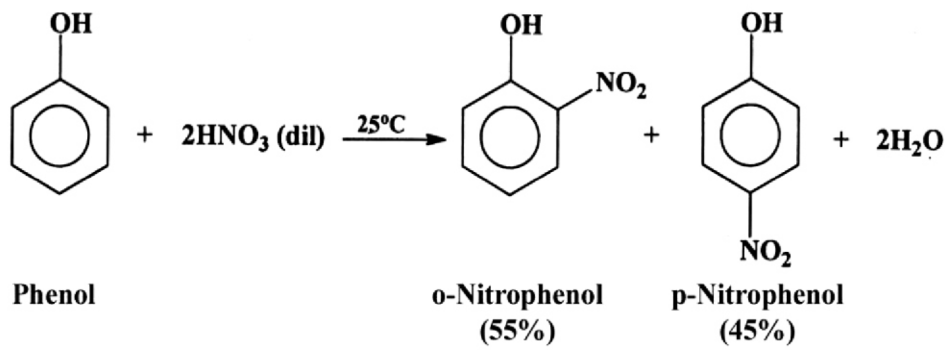
Phenol typically undergoes two types of reactions; those involving the hydroxyl group and those involving the aromatic ring. In the first type of reactions, the –OH part usually broken to form substances such as salts and esters, which are similar to those of alcohols. In the second type of reactions, the aromatic ring of phenol undergoes electrophillic substitution reactions.

7.2.6.1 Electrophilic Aromatic Substitutions

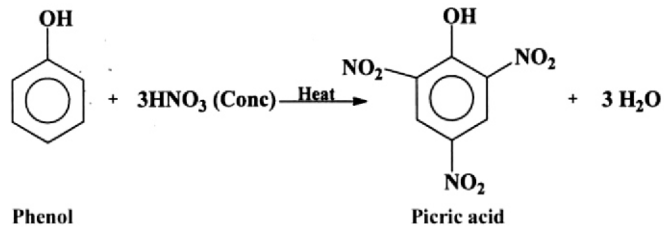
These reactions occur due to aromatic part of molecule. Most common electrophilic aromatic substitution reactions of phenol are nitration, sulphonation and halogenation.

Nitration

Phenol on treating with dilute nitric acid at 25°C gives a mixture of o-nitrophenol and p- nitrophenol.



When phenol heated with concentrated nitric acid, it gives 2, 4, 6–trinitrophenol (picric acid).



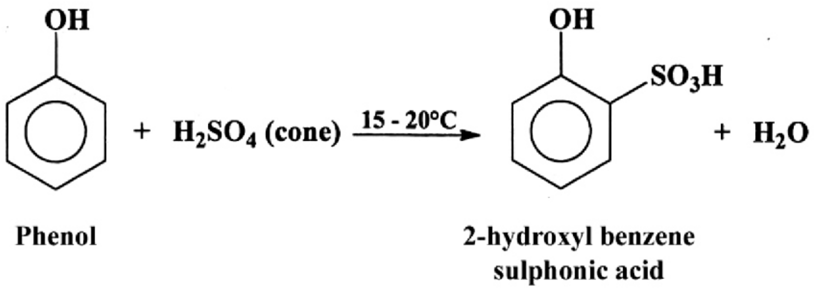
DO YOU KNOW?

Picric acid (2, 4, 6–trinitrophenol) is a yellow colored crystalline solid. It is explosive in dry form that is why it is stored in bottles under a layer of water to reduce the risk of explosion.

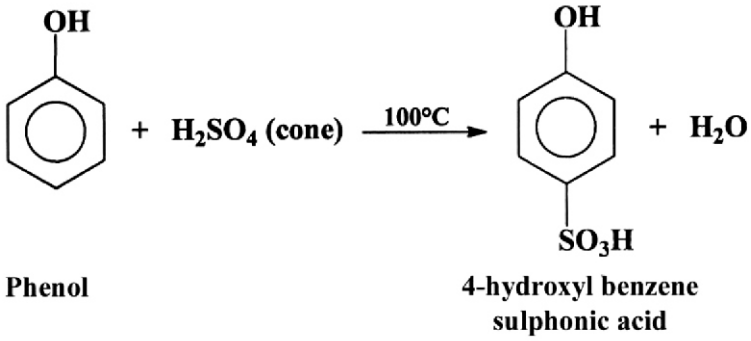
Sulphonation

When phenol is treated with sulphuric acid, it gives Phenol sulphonic acid, however the relative proportion of isomers depends upon temperature.

(a) On heating at 15° – 20°C, ortho phenol sulphonic acid is formed as major proportion.

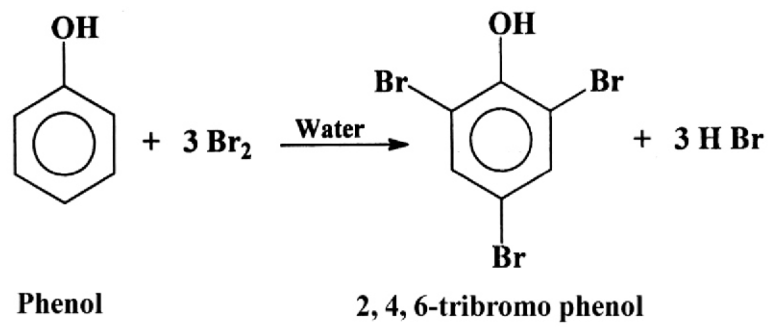


(b) On heating at 100°C it gives major product of para phenol sulphonic acid.

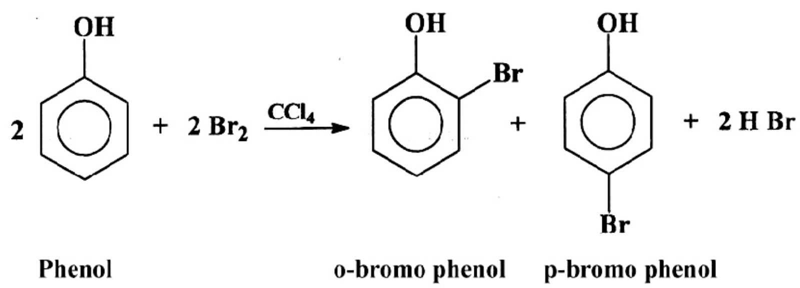


Halogenation

Phenol if reacts with aqueous bromine, it produces 2, 4, 6 – tribromophenol

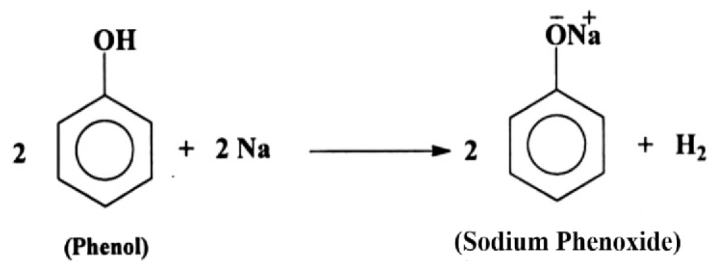


Phenol reacts with Bromine in carbon tetra chloride, it gives a mixture of ortho and para bromophenol.



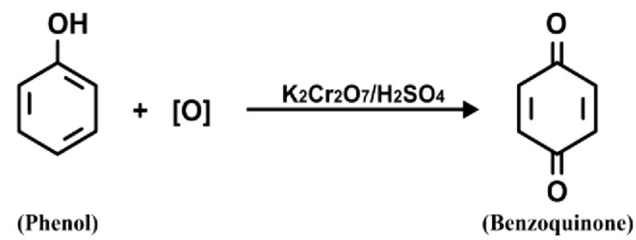
7.2.6.2 Reaction with Sodium Metal

Phenol is an acidic compound. The hydrogen atom of its hydroxyl part (-OH) is ionizable. Thus phenol when reacts with highly active metal such as sodium, the sodium donate an electron to the oxygen atom of the hydroxyl group in phenol forming sodium phenoxide which is an important intermediate in the synthesis of various organic compounds.



7.2.6.3 Oxidation of Phenol

In this reaction potassium dichromate acts as oxidizing agent and the sulphuric acid serves as catalyst. Phenol is oxidized to yellow coloured benzoquinone (conjugated diketone).



DO YOU KNOW?

Benzoquinone has a variety of applications, including its use as a raw material for the production of nylon and polyester polymers. It is also used as a photographic developing agent, and in the production of certain antibiotics.

7.2.7 Difference between Alcohol and Phenol

Table 7.4 Difference between Alcohol and Phenol

Property	Alcohol	Phenol
Functional Group	-OH attached to alkyl carbon (R-OH)	-OH attached to aryl carbon (Ar-OH)
Hydrogen Bonding	Can form intermolecular hydrogen bonding	Can form stronger hydrogen bonding
Boiling Point	Generally lower than phenol	Generally higher than alcohols
Acidity	Weaker acids (higher pKa values)	Stronger acids (lower pKa values)
Solubility in Water	Readily soluble in water	Lower solubility in water
Aromatic Properties	Lacks aromatic properties	Contains an aromatic ring

Uses of Phenol

(i) It is used as an antiseptic and disinfectant
(ii) It is used in the manufacturing of soap, Plastics, ointments and lozenges etc.
(iii) It is used in the preparation of picric acid and, phenolphthalein.
(iv) It is used as ink preservative.

7.2.8 Identification tests for Alcohols and Phenols

Tests of identification of Alcohol

(i) Sodium metal test

Alcohol readily reacts with sodium metal at room temperature to form sodium alkoxide with the liberation of hydrogen gas.

$$\underset{\text{(Phenol)}}{2\ C_6H_5OH} + 2\ Na \rightleftharpoons \underset{\text{(Sodium Phenoxide)}}{2\ C_6H_5ONa} + H_2\uparrow$$

Brisk effervescence in the solution indicates the presence of alcoholic group in the given organic molecule.

(ii) Ester test

Alcohol when heated with acetic acid in the presence of small amount of concentrated sulphuric acid, it forms an ester.

$$\underset{\text{(Ethyl alcohol)}}{C_2H_5OH} + \underset{\text{(Acetic acid)}}{CH_3COOH} \xrightleftharpoons[\text{Heat}]{H_2SO_4\ \text{Conc.}} \underset{\text{(Ethyl acetate)}}{CH_3COOC_2H_5} + H_2O$$

Fruity smell of ester indicates the presence of alcoholic group in the given organic compound.

Tests for identification of Phenol

(i) Ferric chloride test

When freshly prepared aqueous solution of ferric chloride ($FeCl_3$) is added to phenol, it forms a ferric phenoxide complex.

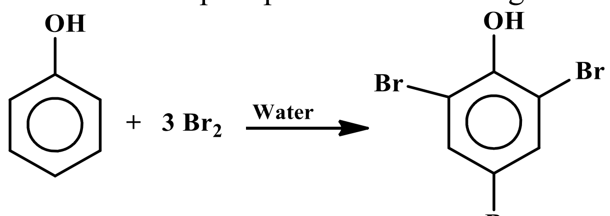
$$6\,C_6H_5OH + FeCl_3 \longrightarrow H_3[Fe(C_6H_5O)_6] + 3HCl$$

(Phenol) (Voilet or Purple Ferric Phenoxide Complex)

Appearance of violet, blue or purple coloration indicates the formation of complex and identifies the presence of phenol.

(ii) Bromine water test

When bromine water is added to phenol, an electrophilic substitution reaction occurs on orho and para positions of the ring.



(Phenol) (2,4,6-tribromo Phenol)

Disappearance of brown color of bromine and appearance of white precipitates of 2,4,6-tribromophenol identifies the presence of phenols

7.3 ETHERS

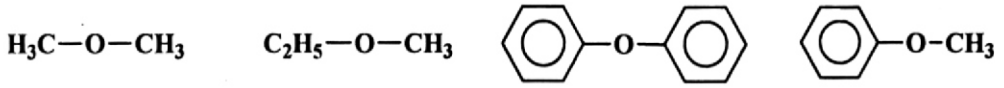
Ethers are an organic compounds having a general formula R-O-R', characterized by an oxygen atom bonded to two alkyl or aryl groups. It has low reactivity and is commonly used as a solvent in various chemical reactions.

A symmetrical or simple ether is that in which both groups are of same type whereas

DO YOU KNOW?

Diethyl ether has been used as anaesthetic in surgery since 1846. It suppresses response to sensory stimulation of brain and produces a temporary local or general anaesthesia.

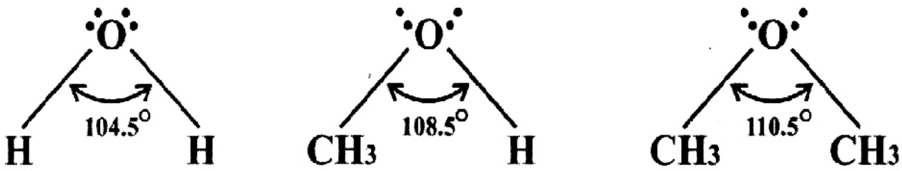
unsymmetrical or mixed ether consists of two different groups.



Dimethyl ether (symmetrical ehter)	**Ethyl methyl ether (unsymmetrical ether)**	**Diphenyl ether (symmetrical ether)**	**Phenyl methyl ether (unsymmetrical ether)**

7.3.1 Structure of Ether

The geometry of ether molecule is bent shaped similar to alcohol and water, however the bond angle of C-O-C in ether molecule is 110.5° which is larger than water (104.5°) and alcohol (108.5°). The hybridization of oxygen atom is sp^3 while the hybridization of carbon depends on the nature substituent group (alkyl or aryl) attached to the oxygen atom.



The greater (C-O-C) bond angle in ether is due to greater internal repulsion of hydrocarbon part than the external repulsion of lone pair on oxygen.

7.3.2 Preparation of Ether

(i) Dehydration of alcohol

Excess of alcohol when heated with concentrated H_2SO_4 at 140°C, an intermolecular dehydration occurs to give ether.

$$\underset{\text{(Ethyl alcohol)}}{C_2H_5OH} + \underset{\text{(Ethyl alcohol)}}{HOC_2H_5} \xrightarrow[140°C]{H_2SO_4} \underset{\text{(Diethyl ether)}}{C_2H_5—O—C_2H_5} + H_2O$$

(ii) Williamson synthesis

It is a well-known method for the preparation of ethers. In this method an alkoxide ion acts as a nucleophile and reacts with an alkyl halide to produce ether.

$$\underset{\text{(Sodium ethoxide)}}{C_2H_5\bar{O}\overset{+}{Na}} + \underset{\text{(Ethyl chloride)}}{C_2H_5Cl} \longrightarrow \underset{\text{(Diethyl ether)}}{C_2H_5-O-C_2H_5} + NaCl$$

The alkoxide is obtained by treating an alcohol with sodium metal.

$$\underset{\text{(Ethyl alcohol)}}{2\,C_2H_5OH} + 2\,Na \longrightarrow \underset{\text{(Sodium ethoxide)}}{2\,C_2H_5ONa} + H_2\uparrow$$

7.3.3 Physical Properties

(i) Dimethyl ether and ethyl methyl ether are gases, however other higher members of ether family exist in volatile liquid state at room temperature.

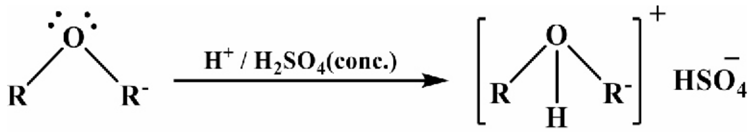
(ii) The boiling point of ether is lower than alcohol due to the absence of intermolecular hydrogen bond.

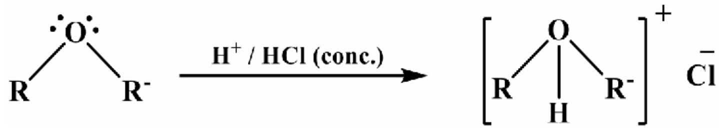
(iii) Ethers are moderately soluble in water since the presence of oxygen makes the molecule polar. However, solubility decreases with increasing the number of carbons of alkyl or aryl groups.

7.3.4 Chemical Reactivity

Ethers are relatively less reactive organic compounds compared to other functional group because the C-O bond of ether is stable and shows low reactivity towards nucleophile or electrophile. The relatively low reactivity of ethers makes them useful as solvents and anaesthetics.

Since oxygen atom of ether possess lone pairs of electrons, they serve as weak base and hence can react with strong acids to form oxonium salt.





The oxonium salt of ether remains stable if acid is concentrated but on dilution with water, it dissociates to reform ether and acid. The reason is that water is stronger Lewis acid than ether.

Self Assessment

- Provide an example of a symmetrical ether.
- Can ethers form hydrogen bonds with water? Why or why not?

Uses of Ethers

(i) Ether is used as solvent in the manufacturing of waxes, gums, resins, oils etc.

(ii) Diethyl ether is used as solvent in Wurtz reaction and in the preparation of Grignard reagent.

SOCIETY, TECHNOLOGY AND SCIENCE

Antiseptics and disinfectants are chemicals used to kill germs such as bacteria, viruses and fungi etc. They are frequently used in our society to reduce the risk of infection.

Although both antiseptic and disinfectant are infection control chemicals, however their applications are different. Antiseptics are substances that are applied on human skin to kill germs whereas disinfectants are used to kill the germs on animate surfaces such as furniture, floors, walls of hospitals, clinics, homes and shopping centres etc. The chemicals used in antiseptics and disinfectants are called 'Biocides'. The concentration of biocides in antiseptics is quite lower than disinfectants to avoid irritation and other toxic effects on the skin. Antiseptics are used for various reasons such as hand sanitizing, infection prevention of minor cut or burn etc.

SUMMARY

- Alcohols are organic compounds in which one or more hydroxyl groups are attached with aliphatic carbon chain. The formula of monohydric alcohol is R-OH.
- Monohydric alcohols are classified into primary alcohol, secondary alcohol and tertiary alcohol depending upon the number of alkyl groups attached to the alpha carbon atom
- Phenols are hydroxyl derivatives of benzene; the simplest phenol is carbolic acid, which has the formula C_6H_5OH
- Methyl alcohol, primary alcohol and secondary alcohol oxidize to carboxylic acids in the presence of hot acidified dichromate or permanganate. Tertiary alcohol does not oxidize due to the unavailability of alpha hydrogen.

- Acidic character of phenol (pKa = 10) is higher than alcohol (pKa ≈ 16) because phenoxide ion is more stable than alkoxide ion.
- Boiling points of alcohol and phenol are higher than alkanes and ethers of comparable molecular mass because they form intermolecular hydrogen bonds.
- Both alcohols and phenols are water soluble but solubility of alcohols is higher than phenols.
- The cleavage of ethylene glycol in the presence of periodic acid (HIO_4) gives two formaldehyde molecules.
- Phenols are commercially prepared by Dow's Process during which chlorobenzene is fused with aqueous sodium hydroxide at 350°C and 150 atmospheric Pressure.
- The aromatic part of phenol is similar to the benzene which favours electrophilic substitution reaction.
- Phenols are identified by bromine water test as well as ferric chloride test.
- Alcohols are identified by sodium metal test and ester test.
- Ethers are considered as the dialkyl or diaryl derivatives of water. They are represented by a general formula R-O-R.
- Boiling point of ethers are much lower than alcohol and phenol since they do not form intermolecular hydrogen bonds.
- Symmetrical ethers are those in which similar alkyl or aryl groups are attached with oxygen atom.
- Ethers are relatively less reactive because C-O-C bond of ether is susceptible for nucleophilic or electrophilic attack.

EXERCISE

Multiple Choice Questions

(i) In the molecule of phenol, the carbon atom which is attached to hydroxyl group is.

(a) sp-hybridized (b) sp^2-hybridized
(c) sp^3-hybridized (d) Unhybridized

(ii) Which of the following is a trihydric phenol?

(a) Resorcinol (b) Cresol
(c) Pyrogallol (d) Catechol

(iii) Ethanol reacts with PCl_3 to form.
(a) Diethyl ether (b) Ethene
(c) Ethyl chloride (d) Ethanoic acid

(iv) Which of the following alcohols has highest boiling Point
(a) Ethyl alcohol (b) n-pentyl alcohol
(c) iso-pentyl alcohol (d) neo-pentyl alcohol

(v) Which of the following Products is mainly formed if ethanol is dehydrated with concentrated sulphuric acid at 170°C?
(a) Ethene (b) Ethyne
(c) Ethanol (d) Diethyl ether

(vi) Lucas reagent is a mixture of
(a) Zn and Hg (b) Zn and HCl
(c) $ZnCl_2$ and HCl (d) NaOH and CaO

(vii) Oxidative cleavage of 1, 2 – diol occur in the presence of
(a) $K_2Cr_2O_7$ (b) $KMnO_4$
(c) HNO_3 (d) HIO_4

(viii) Which of the following molecule cannot form hydrogen bonding with water molecule?
(a) Phenol (b) Resorcinol
(c) Ethyl chloride (d) Ethyl alcohol

(ix) Secondary alcohols, undergo oxidation with potassium dichromate to produce carboxylic acid through an intermediate product known as:
(a) Aldehyde (b) Ketone
(c) Ether (d) Alkyl halide

(x) Which of the following is an anaesthetic agent
(a) Phenol (b) Ethyl alcohol
(c) Diethyl ether (d) Acetone

Short Questions

1. Define Phenol? Write the equations for the preparation of Phenol from.
   (i) Chlorobenzene
   (ii) Sodium benzene sulphonate
2. Write the equations for the following chemical Process
   (i) Reduction of acetic acid with $LiAlH_4$.

(ii) Hydration of ethene with hot concentrated H_2SO_4
(iii) Oxidation of ethanol with acidified dichromate.
(iv) Hydrolysis of diazonium salt

3. Explain the following with scientific reason
   (i) Boiling point of ether is less than alcohol?
   (ii) Alcohols are soluble in water?
   (iii) Ethanol is liquid but ethyl chloride is gas at room temperature?
4. Identify each of following with two laboratory tests.
   (i) Phenol
   (ii) Alcohol
5. What is Lucas reagent? Describe its use to distinguish between primary, secondary and tertiary alcohol.
6. What is oxonium ion? How can ether form oxonium ion?

Descriptive Questions

1. (a) What are alcohols? How alcohols are they classified?
   (b) Starting from Grignard reagent how is primary, secondary and tertiary alcohol prepared?
2. Write the equations for the following possible conversions.
   (i) Ethyl alcohol to diethyl ether
   (ii) Phenol to benzoquinone
   (iii) Ethyl bromide to ethanol
   (iv) 2°- alcohol to carboxylic acid

3 Differentiate between alcohol and phenol on the basis of
   (i) Solubility in water
   (ii) Boiling Point
   (iii) Acidic character
4. Write the equation and name the final product when phenol reacts with the following
   (i) Hot and concentrated nitric acid.
   (ii) Concentrated sulphuric acid at 100°C
   (iii) Bromine water
   (iv) Sodium metal
5. Enlist the commercial applications of Alcohol, Phenol and eth