Chapter
11

ALCOHOLS, PHENOLS AND ETHERS

INTRODUCTION

Alcohols, phenols and ethers are classes of organic compounds which are much closer to water in structure and hence considered as derivatives of water.



Water Alcohol Phenol Ether

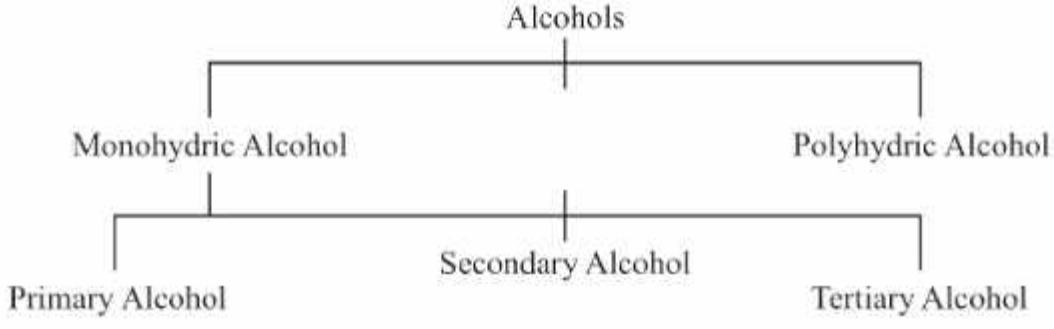
Alcohol and phenol both have — OH in them. Alcohol is called hydroxyl derivative of alkane while phenol is hydroxyl derivative of benzene. In ether both hydrogen of water are replaced by alkyl or aryl group.

ALCOHOLS

"The compound in which one or more hydrogen of alkanes are replaced by —OH groups are called alcohols." The general formula of monohydric alcohol is R —OH or $C_nH_{2n+1}OH$.

CLASSIFICATION OF ALCOHOL

Alcohols are classified as follows.



MONOHYDRIC ALCOHOL

"The alcohol in which one hydrogen of alkane is replaced by one —OH group is called monohydric alcohol." e.g.,

CH_3OH	C_2H_5OH	$CH_3—CH_2—CH_2—OH$
Methyl Alcohol	Ethylalcohol	n-propyl alcohol

Monohydric alcohols are further classified into primary, secondary and tertiary alcohols.

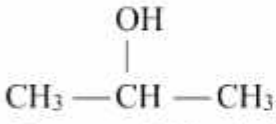
(i) Primary Alcohols:

"The alcohols in which hydroxyl group is attached with primary carbon, are called primary alcohols". e.g.,

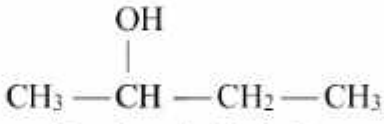
CH_3OH	C_2H_5OH	$CH_3—CH_2—CH_2—OH$
Methanol	Ethanol	1-Propanol

(ii) Secondary Alcohols:

"The alcohols in which hydroxyl group is attached with secondary carbon, are called secondary alcohols." e.g.,



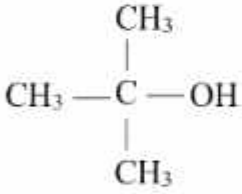
(Iso-propyl Alcohol)



(Sec-butyl Alcohol)

(iii) Tertiary Alcohols:

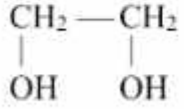
"The alcohols in which hydroxyl group is attached with tertiary carbon, are known as tertiary alcohols." e.g.,



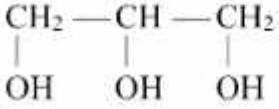
2-Methyl, 2-Propanol (Ter-butyl alcohol)

Polyhydric Alcohols:

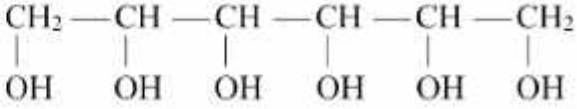
"If more than one hydroxyl group —OH are present in a compound, it is called polyhydric alcohol." If number of —OH groups are two, it is dihydric if it is three it is called trihydric etc. some examples of polyhydric alcohols are given below.



1,2 Ethanediol
(Ethylene glycol)



1,2,3, Propanetriol
(Glycerine or Glycerol)



(Mannitol)

There are two methods for naming alcohols.

(a) Common or Trivial Names:

In common method of naming word "alcohol" is added after the name of alkyl radical. Lowers alcohols or simpler alcohols are usually named by this method. e.g;

$CH_3—OH$ (Methyl Alcohols)

$C_2H_5—OH$ (Ethyl Alcohols)

$CH_3—CH_2—CH_2—OH$ (n-propyl alcohol)

$C_6H_5—CH_2—OH$ (Benzyl Alcohol)

(If one hydrogen from methyl group of toluene is removed, it is called benzyl radical)



Toluene Benzyl Radical

(b) IUPAC System:

Following rules are obeyed for the nomenclature of alcohol.

(1) Select longest possible chain of carbon atoms containing the hydroxyl group in it.

(2) Start numbering from that end which is near to —OH group.

(3) The suffix used for alcohol is "ol".

(4) The position of —OH group is indicated by a number placed before the name.

(5) If substituents of different nature are present, they are named in alphabetical order.

$CH_3—CH_2—CH_2—CH_2—OH$ 1-butanol

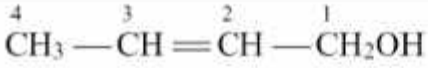
$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$ 4-Methyl-2-pentanol

(6) If more than one hydroxyl group are present on a molecule, they are indicated by an appropriate suffix diol, triol, etc. For example,

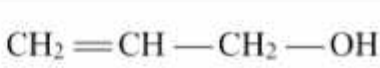
$\underset{\displaystyle OH}{\underset{|}{CH_2}}—\underset{\displaystyle OH}{\underset{|}{CH_2}}$ 1,2 Ethanediol

$\underset{\displaystyle OH}{\underset{|}{CH_2}}—\underset{\displaystyle OH}{\underset{|}{CH}}—\underset{\displaystyle OH}{\underset{|}{CH_2}}$ 1,2,3-Propanetriol

(7) The unsaturated alcohols are named in such a way that hydroxyl group rather than the point of un-saturation gets the lower number, e.g.,



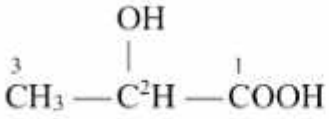
2-Buten-1-ol



2-Propen-1-ol

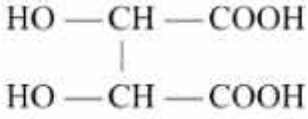
If both alkene and alcohol are present in same group, the suffix of alkene should be "en" rather than "ene".

(8) When hydroxyl group is not a preferred functional group as in hydroxyl acids, aldehydes and ketones, the substituent name hydroxyl is used as a prefix to indicate the position of OH group, e.g;



2-Hydroxy propanoic acid

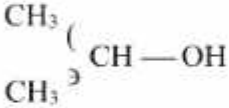
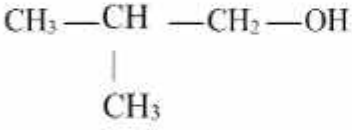
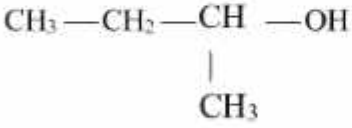
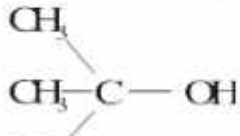
(Latic Acid)



2, 3-Dihydroxy butandioic acid

(Tartaric Acid)

The names of some alcohols in the two systems are given below:

Formula	Common Name	I.U.P.A Name
CH_3OH	Methyl alcohol	Methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	n-propyl alcohol	1-Propanol
	iso-propyl alcohol	2-Propanol
	n-Butyl alcohol	1-Butanol
	iso-butyl alcohol	2-Methyl-1-propanol
	sec-butyl alcohol	2-Butanol
	ter-butyl alcohol	2-Methyl-2-propanol
	Neo-pentyl alcohol	2,2-Dimethyl-1-propanol

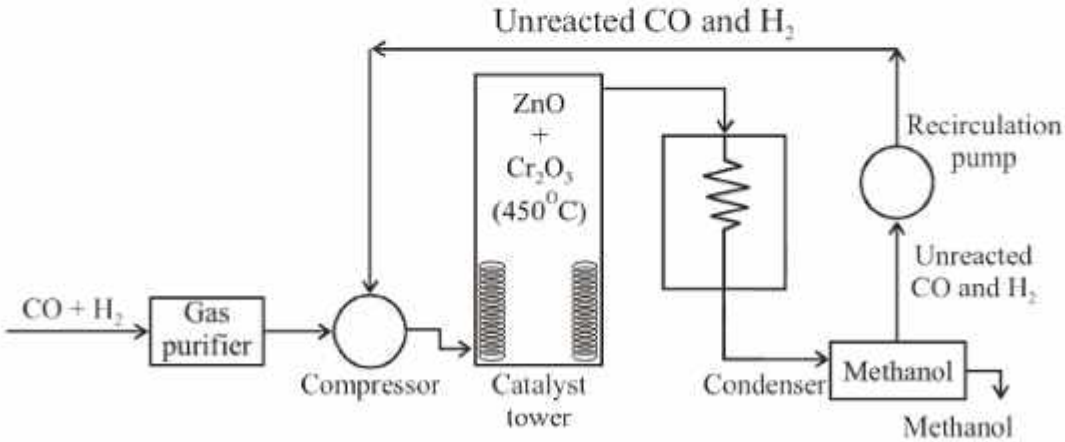
INDUSTRIAL PREPARATION OF ALCOHOLS

(1) Methanol or Methyl Alcohol or Wood Spirit (Wood Naphtha):

Methyl alcohol was obtained by the destructive distillation of wood logs and also called "wood spirit". Now a days, methanol is prepared from carbon monoxide and hydrogen or water gas.

CO reacts with H_2 at high temperature (450°C), 200 atmospheric pressure and in the presence of ZnO, + Cr_2O_3 catalyst following reaction take place.

$$CO + 2H_2 \xrightarrow[450^{\circ}C:\ 200atm]{ZnO + Cr_2O_3} CH_3OH$$



First of all, a mixture of carbon monoxide and hydrogen (water gas) is purified, compressed under a pressure of 200 atmospheres and taken into ' a reaction chamber by means of coiled pipe. Here the catalyst is heated upto 450-500°C. Gases react to form methanol vapours. These vapours are passed through a condenser to get methanol. Un-reacted gases are re-cycled through compressor into reaction chamber.

Properties of Methyl Alcohol:

(1) Its specific gravity is 0.793 g/cm^3.

(2) It boils at 64.5°C.

(3) It is solvent for oils and fats.

(4) It is poisonous.

(5) It causes blindness and even death.

(6) It is used for denaturing of alcohol.

(2) Ethanol or Ethyl Alcohol or Grain alcohol:

Ethanol is prepared on industrial scale by the process of fermentation.

"Fermentation is a chemical, change in which larger molecules are broken down to smaller molecules in the presence of enzymes (living catalyst) present in the bacteria or yeast."

Optimum Conditions:

The optimum conditions of temperature is 25 – 35°C, which is a optimum temperature for the growth of enzymes. Moreover, proper aeration, dilution of solution and the absence of any preservative are essential conditions for fermentation.

In Pakistan, ethanol is prepared by the fermentation of molasses, starch grains or fruit juices.

From Molasses:

The residue obtained after the crystallization of sugar from concentrated sugar cane juice is called molasses. It undergoes fermentation in the presence of enzymes present in yeast to give ethanol.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Yeast}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[\text{Yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

From Starch:

Starch is a natural polymer of glucose. It is mostly present in grains of wheat or barley or potatoes.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[\text{Yeast}]{\text{Diastase}} \underset{\text{Malt-sugar or maltose}}{nC_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Yeast}]{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[\text{Yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Rectified Spirit:

Alcohol obtained by fermentation is only upto 12% and never exceeds 14% because beyond this limit, enzymes become inactive. This alcohol is distilled again and again to obtain 95% alcohol which is called **rectified spirit.**

Absolute Alcohol:

"Ethyl alcohol which is 100% pure is called absolute alcohol." Absolute alcohol is obtained by re-distillation of rectified spirit in the presence of quick-lime. CaO, which absorb moisture.

Denaturing of Alcohol:

Sometimes, ethanol is denatured by the addition of 10% methanol to avoid its use for drinking purposes. Such alcohol is called "methylated spirit".

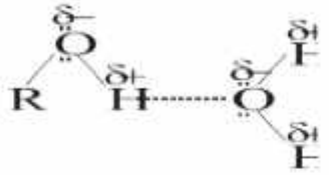
Methanol is toxic to humans, causing blindness in low dose (15 cm^3) and death in larger amount (100 – 250 cm^3).

A. Small quantity of pyridine or acetone may also be added for denaturing of alcohol.

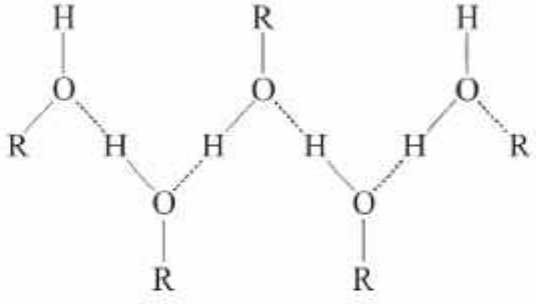
PHYSICAL PROPERTIES

(1) Lower alcohols are generally colourless liquids with characteristic sweet smell and burning taste.

(2) They are readily soluble in water but solubility decreases in higher alcohols. The solubility of alcohols is due to hydrogen bonding which is prominent in lower alcohols but diminish in higher alcohol.



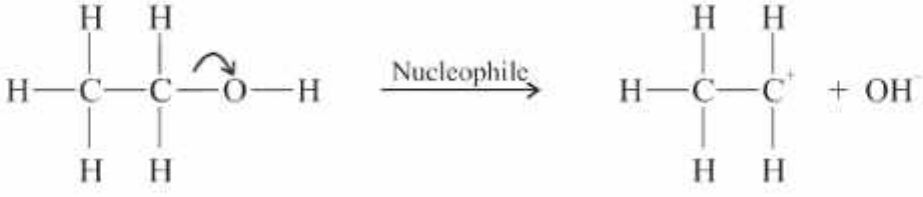
(3) Melting and boiling points of alcohols are higher than corresponding alkanes. Methyl alcohol and ethyl alcohol are liquids while methane and ethane are gases. This is also due to hydrogen bonding which is present in alcohols but absent in alkanes.



REACTIONS OF ALCOHOLS

Alcohols are reactive in two ways.

(1) Reactions in which C — O Bond Breaks:



(2) Reaction in which O — H Bond Breaks:



Which bond will break, depends upon the nature of the attacking reagent. If a nucleophile attacks, it is the C — O bond which breaks. On the other hand, if an electrophile attacks on alcohol, it is the O — H bond which breaks.

The order of reactivity of alcohols when C — O bond breaks.

Tertiary Alcohol > Secondary Alcohol > Primary Alcohol

The order of reactivity of alcohols when O — H bond breaks.

CH_3OH > Primary Alcohol > Secondary Alcohol > Tertiary Alcohol

(1) Reaction in which C — O Bond is Broken:

(i) $C_2H_5OH + SOCl_2 \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$

Ethanol Thionyl chloride

(ii) $C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$

(iii) $C_2H_5OH + HNH_2 \xrightarrow{ThO_2} C_2H_5NH_2 + H_2O$

(2) Reactions in which O — H bond is broken:

$2C_2H_5OH + 2Na \longrightarrow 2C_2H_5O^-Na^+ + H_2$

$C_2H_5OH + \overset{\delta-\ \delta+}{CH_3MgI} \longrightarrow CH_4 + Mg\begin{matrix} I \\ OC_2H_5 \end{matrix}$

(3) Oxidation of Alcohols:

Alcohol are oxidised in the presence of concentrated H_2SO_4 and potassium dichromate to aldehyde and then to carboxylic acid.

Primary alcohol $\xrightarrow{Oxi}$ Aldehyde $\xrightarrow{Oxi}$ Carboxylic Acid

Secondary Alcohol $\xrightarrow{Oxi}$ Ketone

(i) Oxidation of Primary Alcohol:

$$CH_3—CH_2OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3—CHO + H_2O$$

Ethanol Ethanal

$$CH_3—CHO + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3—COOH$$

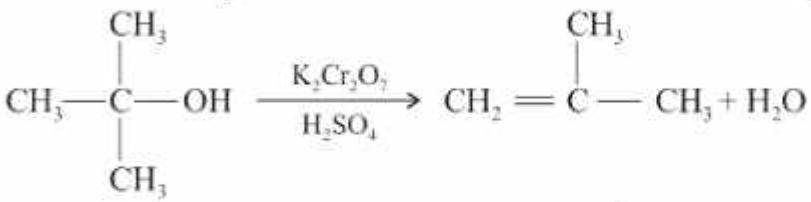
Ethanal Ethanoic Acid

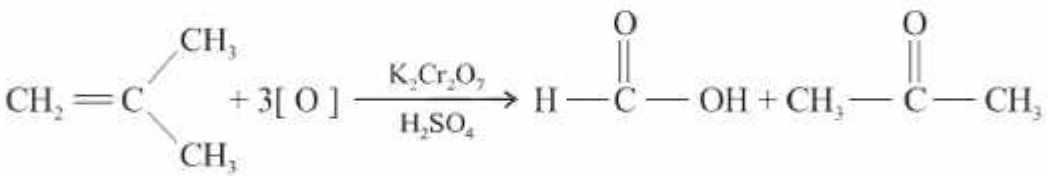
(ii) Oxidation of Secondary Alcohol:



Iso-Propylalochol Dimethyl Ketone

(iii) Tertiary alcohols do not oxidise. Tertiary alcohols, in the presence of mixture of H_2SO_4 and potassium dichromate undergo, dehydration or elimination reaction and alkenes are produced which on oxidation form carboxylic acid and ketones.





(4) Dehydration:

Alcohols reacts with concentrated H_2SO_4 and different products are formed. Formation of products, depend upon the temperature and the amount of H_2SO_4 taken.

(i) At 180°C and greater amount of H_2SO_4, alkene is formed.

$$CH_3—CH_2—OH \xrightarrow[180°C]{H_2SO_4} CH_2 = CH_2 + H_2O$$

(ii) At 140°C and greater amount of alcohol, ether is formed.

$$CH_3 - CH_2 - OH + HO - CH_2 - CH_3 \xrightarrow[H_2SO_4]{140°C} CH_3–CH_2–O–CH_2–CH_3 + H_2O$$

(5) Reactions with Phosphorus Halides, PX_3 and PX_5:

$$3C_2H_5—OH + PCl_3 \longrightarrow 3C_2H_5Cl + H_3PO_3$$

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + POCl_3 + HCl$$

DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

Lucas Test:

Primary, secondary and tertiary alcohols are identified and distinguished by reacting them with con. HCl in anhydrous $ZnCl_2$. An oily layer of alkyl halides separates out in these reactions.

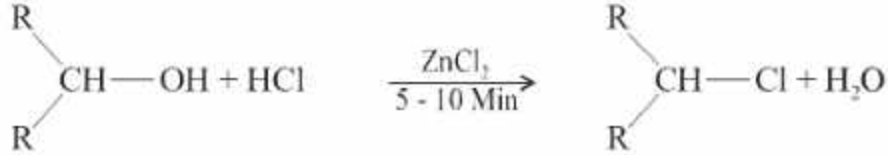
(i) Tertiary alcohols form an oily layer immediately.

(ii) Secondary alcohols form an oily layer in 5 – 10 minutes.

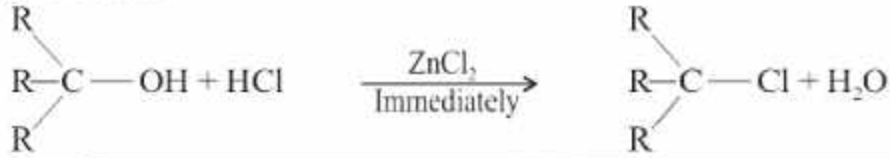
(iii) Primary alcohols form an oil layer only on heating only.

$$ROH + HCl \xrightarrow[Heat]{ZnCl_2} RCl + H_2O$$

Secondary Alcohol:



Tertiary Alcohol:



DISTINCTION BETWEEN METHANOL AND ETHANOL BY IODOFORM TEST

Ethanol reacts with iodine in the presence of NaOH to form yellow crystalline solid iodoform, CHI_3. Methanol does not give iodoform test.

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow \underset{\text{Iodoform (Yellow ppt.)}}{CHI_3} + HCOONa + 5NaI + 5H_2O$$

$$CH_3OH + I_2 + NaOH \longrightarrow \text{No yellow ppt.}$$

USES OF ALCOHOLS

(1) Methanol is used as a solvent for fats, oils, paints, varnishes.

(2) It is also used as antifreeze in the radiators of automobiles and for denaturing of alcohol.

(3) Ethanol is also used as a solvent for paints, oils, drugs, dyes, perfumes, gums and varnishes, as a drink and as a fuel in some countries.

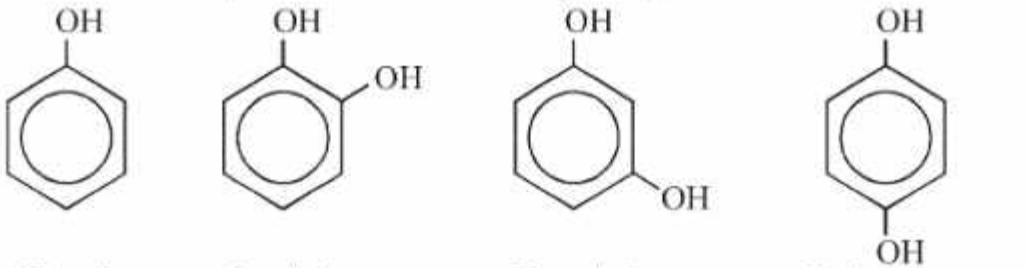
(4) It is used in pharmaceutical preparation and as a preservative for biological specimen.

(5) As preservative for biological specimens.

PHENOLS

The aromatic compounds which contain one or more — OH groups attached directly to benzene ring are called phenols. e.g., carbolic acid or phenol. C_6H_5 — OH is the simplest example of phenols.

Carbolic acid or phenol was discovered by Runge in 1834 from coal tar.

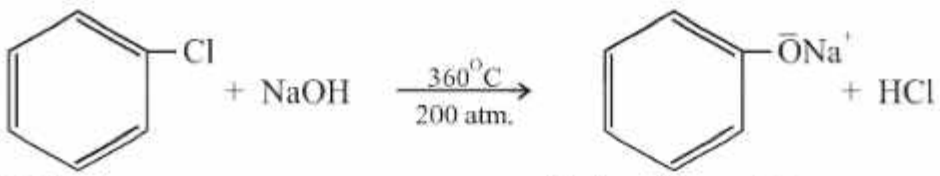


Phenol | Catechol (o-Dihydroxy benzene) | Resorcinol (m-Dihydroxy benzene) | Hydroquinone (m-Dihydroxy benzene)

PREPARATION OF PHENOL

(1) From Chlorobenzene (Dow's Process):

In this process, chlorobenzene is heated at 360°C with dilute solution (10%) of NaOH at 200 atmospheric pressure.



Chlorobenzene — Sodium Phenoxide

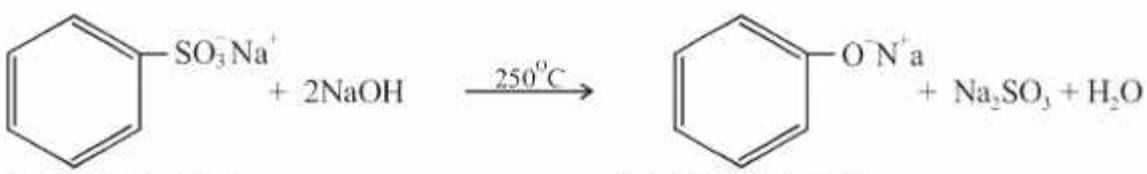
Sodium phenoxide is converted to phenol by treating it with hydrochloric acid.



Phenol

(2) Fusion of Sodium Benzenesulphonate with NaOH:

Phenol is obtained by fusing the mixture of sodium benzene sulphonate and solid sodium hydroxide at 250°C.



Sod. benzene sulphonate — Sodium Phenoxide

The resulting sodium phenoxide is treated with an acid stronger than phenol to regenerate the free product.



PHYSICAL PROPERTIES OF PHENOL

(1) Phenol is colourless, crystalline solid and is deliquescent. The deliquescence is the process in which a substance absorbs moisture and changes into a liquid form.

(2) Its melting point is 41°C and boiling point is 182°C.

(3) It is sparingly soluble in water forming pink solution at room temperature but completely soluble at 65.9°C which is the consulate temperature, for water-phenol system.

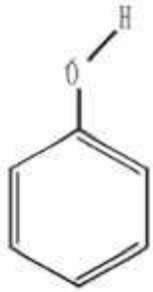
(4) It is poisonous and used as disinfectant in hospitals and washrooms.

Reactions of Phenol:

Phenol shows two types of reactions.

(i) Reactions due to — OH group.

(ii) Reactions due to benzene ring.



Following structure helps to understand the behaviour of phenol.

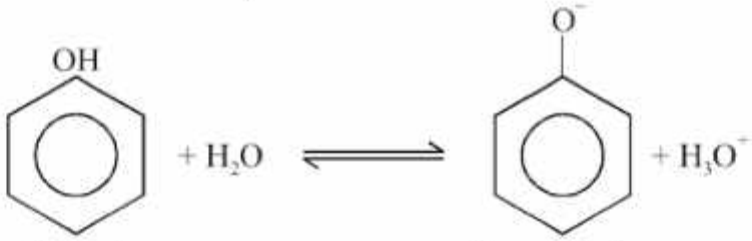
Phenols are less reactive to nucleophile so nucleophilic attack is less favoured i.e. OH is not easy to replace while electrophilic attack on the ring is easy.

ACIDITY OF PHENOL

(1) Phenol is less acidic than carboxylic acids and more acidic than alcohols. It is partially soluble in water but highly soluble in a alkali like NaOH.

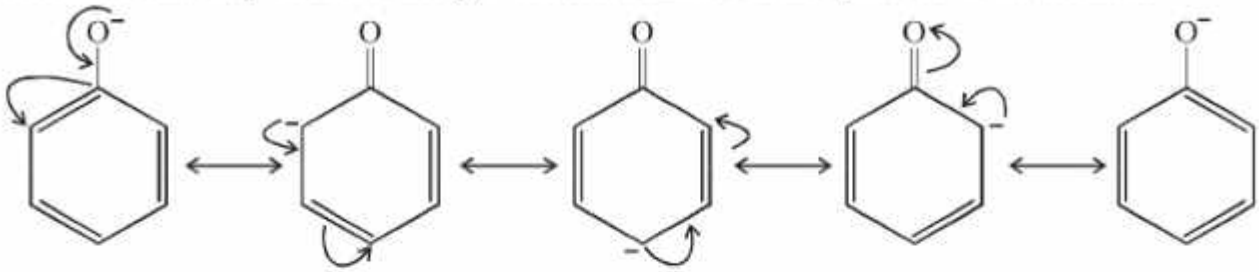
(2) Phenol does not reacts with $NaHCO_3$ and no CO_2 is evolved while carboxylic acids evolve CO_2 due to greater reactivity.

(3) When phenol is dissolved in water it, dissociate slightly. The dissociation constant of phenol is 1.3×10^{-10} and pH of solution is between 5 to 6. It dissociates as.



Phenol Phenoxide Ion

Acidity of phenol is due to the resonance stability in phenoxide ion. Strength of an acid, depends upon the stability of conjugate base or anion of an acid. Greater will be the stability of anion or conjugate base, stronger will be the acid. In phenoxide ion, the negative charge on oxygen atom can become involved with the π-electron cloud on the benzene ring. The negative charge is thus delocalized on the ring and the phenoxide ion becomes relatively stable. This type of delocalization is not possible with alcohols.



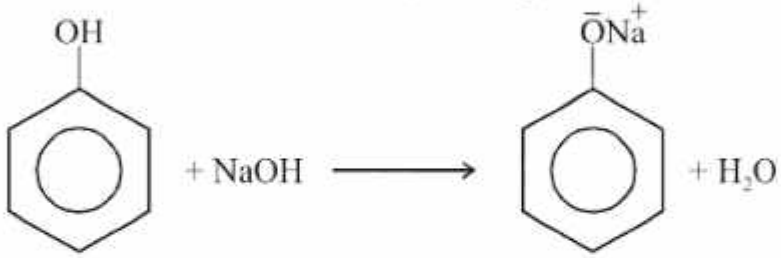
Relative acidic strength of alcohol, phenol, water and carboxylic acid is as follows:

Carboxylic acid > Phenol > Water > Alcohol

(a) Reaction of Phenol Due to OH Group:

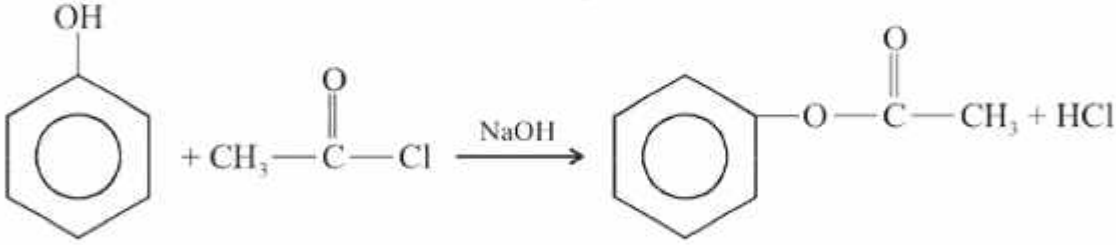
(1) Salt Formation:

Phenol reacts with alkalis to form salt (sodium phenoxide and water)



(2) Ester Formation:

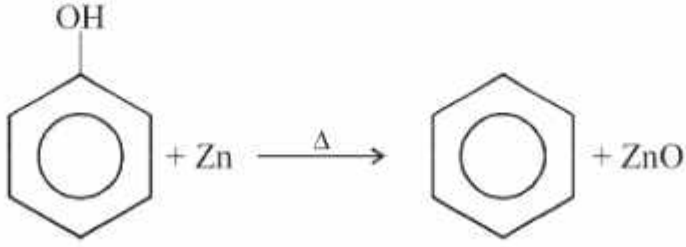
Phenol reacts with acetyl chloride in the presence of a base to form an ester.



(Acetyl chloride) Phenyl Acetate (Ester)

(3) Reaction with Zinc:

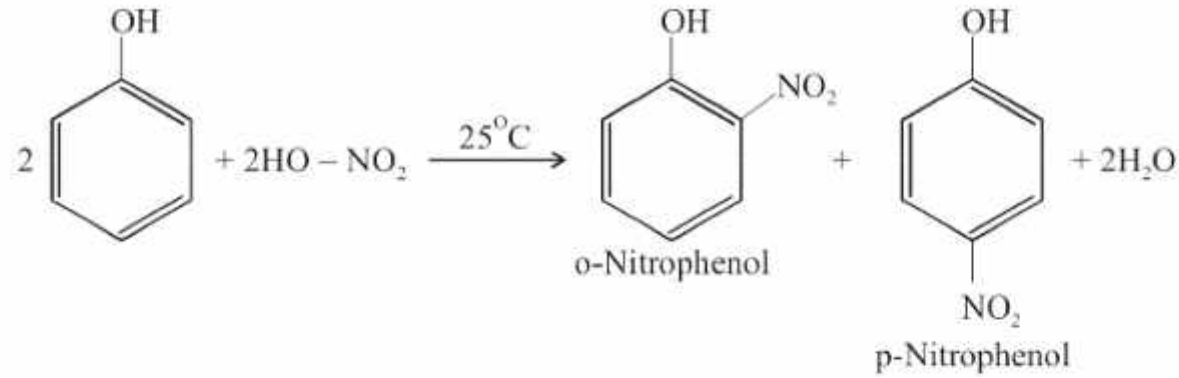
Phenol is reduced to benzene when reacts with Zinc dust.

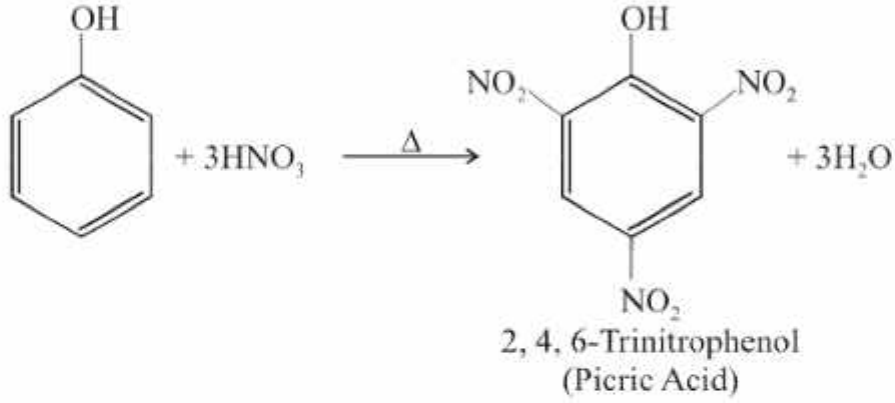


(b) Reaction Due to Benzene Ring:

(1) Nitration:

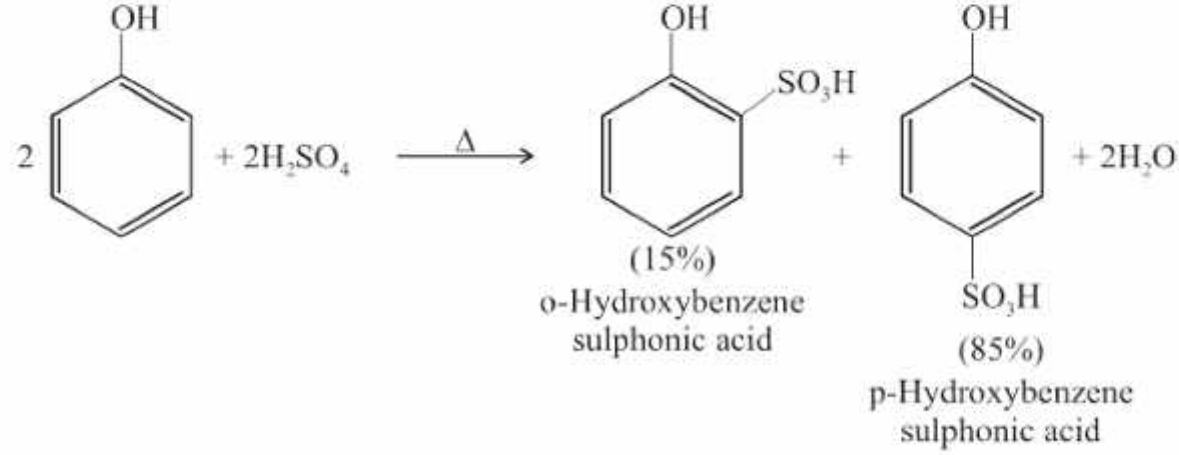
Phenol reacts with dil, and conc. HNO_3 at different temperature as follows.





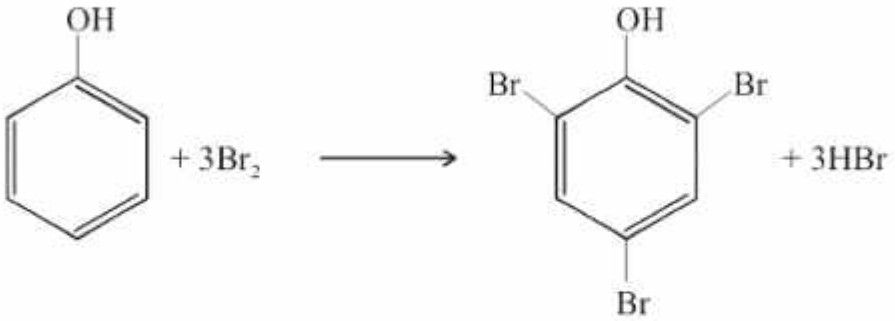
(2) Sulphonation:

Phenol reacts with conc. H_2SO_4 at room temperature giving ortho and para benzens sulphonic acids.



(3) Halogenation:

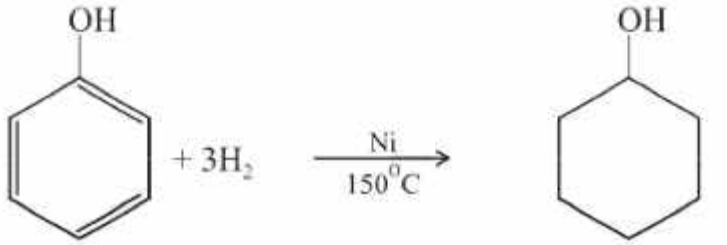
Aqueous solution of phenol reacts with bromine water to give white ppt. of 2, 4, 6 tribromophenol.



2, 4, 6-Tribromophenol

(4) Hydrogenation:

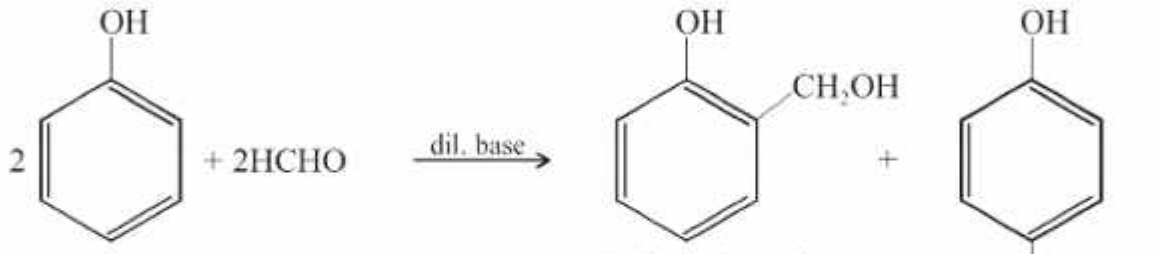
When hydrogen is passed through phenol at 150°C in the presence of Ni catalyst it gives cyclohexanol.



Cyclohexanol

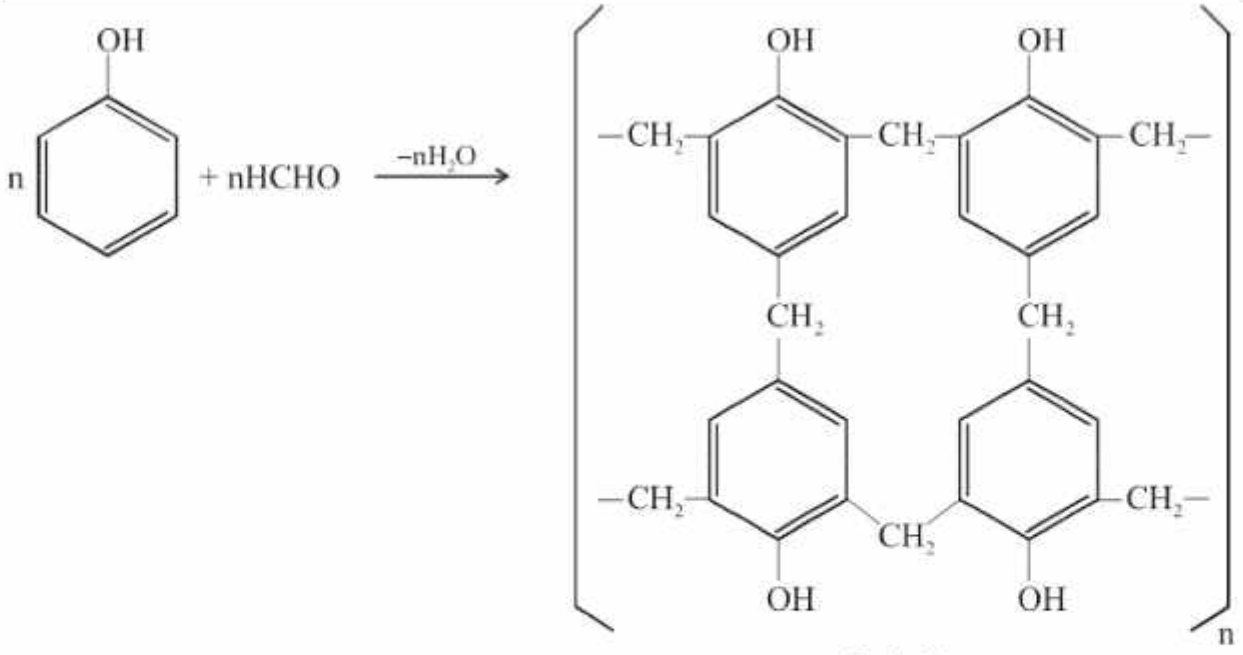
(5) Reaction with Formaldehyde:

Phenol react with formaldehyde (methanal) in the presence of acid or alkali to give hydroxy benzyl alcohol which on further reaction with other phenol molecules yield a polymer called bakelite.



o-Hydroxybenzyl Alcohol

p-Hydroxybenzyl Alcohol



Bakelite

USES OF PHENOL

(1) Phenol is used for the preparation of bakelite (plastic resin)

(2) Phenol is used to prepare picric acid. Picric acid and its salts are used as explosives.

(3) Phenol is used as antiseptic (dettol), herbicide and wood and ink preservatives. As antiseptic, it is used in soaps, lotions and ointments.

(4) Phenol is used as starting material for many pharmaceuticals like salicylic acid, aspirin, phenacetin, salol etc.

(5) It is used to prepare cyclohexanol which is a good organic solvent.

ETHERS

"The organic compounds in which different alkyl or aryl groups are attached on both side of oxygen atom are called ethers."

Ether are classified into two types.

(1) Simple or Symmetrical Ethers:

The ethers in which two similar alkyl or aryl are present on both side of oxygen atom e.g; CH_3 — OCH_3 dimethyl ether, $(C_2H_5)_2O$ diethyl ethyl, $(C_6H_5)_2O$ diphenyl ether.

(2) Mixed or Unsymmetrical Ethers:

The ethers in which two different groups (alkyl or aryl) are attached with oxygen atom are called mixed ethers. e.g; methyl ethyl ether $CH_3OC_2H_5$.

NOMENCLATURE

Ethers are named either by IUPAC system or by common names. In IUPAC system the large alkyl groups is taken as parent molecule and given the last name (suffix) while the smaller alkyl group along with oxygen is used as prefix and given the name alkoxy (e.g methoxy, ethoxy, propoxy etc).

IUPAC names are not common as they are difficult. Usually ethers are known by their general names, as given below:

Formula	Common Names	IUPAC
CH_3OCH_3	Dimethyl ether	Methoxy methane
$CH_3OC_2H_5$	Ethyl-methyl ether	Methoxy ethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxy ethane
$C_2H_5O\,CH_2 - CH_2 - CH_3$	Ethyl n-propylether	Ethoxy propane
$CH_3OC_6H_5$	Methyl phenyl ether	Methoxy benzene
$C_6H_5OC_6H_5$	Dipheyl ether	Phenoxy benzene

PREPARATION OF ETHER

Ethers are prepared from alcohols either directly or indirectly. Usually they are obtained by the following methods:

(1) Williamson's Synthesis:

Alcohols are reacted with metallic sodium to form alkoxides. This alkoxide is a strong nucleophile and readily reacts with alkyl halide to produce an ether.

$$2C_2H_5OH + 2Na \longrightarrow C_2H_5O^-Na^+ + H_2$$

$$C_2H_5O^-Na^+ + C_2H_5Br \longrightarrow C_2H_5OC_2H_5 + NaBr$$

(2) From Silver Oxide and Alkyl Halides:

When alkyl halides are heated with silver oxide, ethers are formed.

$$2CH_3Br + Ag_2O \longrightarrow CH_3OCH_3 + 2AgBr$$

$$2CH_3{-}CH_2{-}Br + Ag_2O \longrightarrow CH_3{-}CH_2{-}O{-}CH_2{-}CH_3 + 2AgBr$$

(3) Action of H_2SO_4 on Ethanol:

$$2CH_3 - CH_2OH \xrightarrow[140^\circ C]{H_2SO_4} CH_3 - CH_2 - O - CH_2 - CH_3 + H_2O$$

PHYSICAL PROPERTIES

(1) Usually ethers are volatile liquids, highly inflammable with low boiling points.

(2) They are slightly soluble in water but fairly soluble in organic solvent.

(3) Ether molecules do not show hydrogen bonding with one another but they show week hydrogen bonding with water molecules due to which they are slightly soluble in water.

CHEMICAL PROPERTIES

Ethers are less reactive than alcohols because no hydrogen atom is attached with oxygen atom directly. Ethers do not react with alkalies, NH_3, sodium metal dilute acids, oxidising agents or reducing agents. However ethers react with halogen acid HI. Ethers do not react with HF, HCI.

(i) Reaction of Ether with HBr:

$$C_2H_5 - O - C_2H_5 + \overset{+}{H}\overset{-}{Br} \longrightarrow C_2H_5 - \underset{\displaystyle H}{\overset{\displaystyle +}{O}} - C_2H_5 + \overset{-}{Br}$$

(Oxonium ion)

(ii) Reaction of Ether with HI:

Ethers react with HI to form alcohol. This alcohol further reacts with halogen acid to form alkyl halide only.

$$C_2H_5OC_2H_5 + HI \longrightarrow C_2H_5 - \underset{\displaystyle H}{O^{+}} - C_2H_5 + I^{-}$$

(Oxonium ion)

$$C_2H_5 - \underset{\displaystyle H}{O^{+}} - C_2H_5 + I^{-} \longrightarrow C_2H_5OH + C_2H_5I$$

$$C_2H_5OH + HI \longrightarrow C_2H_5I + H_2O$$

Note: In case of mixed either, smaller radical is attached to the halide and bigger radical is attached to the alcohol.

(ii) Ethers also react with hot phosphorous pentachloride to give alkyl chloride.

$$C_2H_5 - O - C_2H_5 + PCl_5 \longrightarrow 2C_2H_5Cl + POCl_3$$

Uses of Ethers:

(1) As anesthetic

(2) As refrigerant

(3) Solvent for extraction of organic compounds.

(4) For dissolving oils, fats, resins.

(5) For the manufacture of smokeless gunpowder.

EXERCISE

Q.1 Fill in the blanks:

(i) Primary, secondary and tertiary alcohols can be identified by ———— test.

(ii) Oxidation of ———— alcohols give ketones.

(iii) Alcohols on heating with ———— give alkenes at high temperature.

(iv) Alcohols have ———— boiling points than ethers due to stronger hydrogen bonding.

(v) Williamson's synthesis is used to prepare ————.

(vi) ———— is also called wood spirit.

(vii) Carbolic acid is the other name of ————.

(viii) Primary, secondary and tertiary alcohols can be prepared by reacting Grignard reagent with ————.

(ix) Alcohols and ———— react to produce esters.

(x) ———— is used as anti-freezing agent in automobile radiator.

(xi) The process of conversion of starch into alcohol with the help of microorganisms is called ————.

(xii) Ketones on reduction give ———— alcohols.

ANSWERS

(i)	Lucas	**(ii)**	secondary	**(iii)**	H_2SO_4
(iv)	high	**(v)**	ether	**(vi)**	methanol
(vii)	phenol	**(viii)**	carbonyl compound	**(ix)**	carboxylic acids
(x)	glycol	**(xi)**	fermentation	**(xii)**	secondary

Q.2 Indicate True or False:

(i) Methylated spirit contains 95% methyl alcohol and 5% ethyl alcohol.

(ii) Ethyl alcohol is a very good anti-freezing agent.

(iii) Methanol is also called wood spirit.

(iv) Only 14% ethyl alcohol can be prepared by fermentation.

(v) Ethers do not show hydrogen bonding.

(vi) Alcohols are more acidic than phenols.

(vii) Phenol is more soluble in water than lower alcohols.

(viii) Alcohols are more basic than ethers.

(ix) Ethers have higher boiling points than alcohols and phenols.

(x) Methanol and ethanol can be distinguished by iodoform test.

ANSWERS

(i)	False	**(ii)**	False	**(iii)**	True	**(iv)**	True	**(v)**	True
(vi)	False	**(vii)**	False	**(viii)**	False	**(ix)**	False	**(x)**	True

Q.3 Multiple choice questions. Encircle the correct answer:

(i) Which compound shows hydrogen bonding:

(a) C_2H_6 **(b)** C_2H_5Cl

(c) $CH_3–O–CH_3$ **(d)** C_2H_5OH

(ii) Which compound shows maximum hydrogen bonding with water:

(a) CH_3OH **(b)** C_2H_5OH

(c) $CH_3–O–CH_3$ **(d)** C_6H_5OH

(iii) Which compound is more soluble in water:

(a) C_2H_5OH **(b)** C_6H_5OH

(c) CH_3COCH_3 **(d)** n-Hexanol

(iv) Which compound will have the maximum repulsion with H_2O:

(a) C_6H_6 **(b)** C_2H_5OH

(c) $CH_3CH_2CH_2OH$ **(d)** $CH_3—O—CH_3$

(v) Ethanol can be converted into ethanoic acid by:

(a) Hydrogenation **(b)** Hydration

(c) Oxidation **(d)** Fermentation

(vi) Which enzyme is not involved in fermentation:

(a) Diastase **(b)** Zymase

(c) Urease **(d)** Invertase

(vii) Which compound is called a universal solvent:

(a) H_2O **(b)** CH_3OH

(c) C_2H_5OH **(d)** $CH_3—O—CH_3$

(viii) Methyl alcohol is not used:

(a) As a solvent **(b)** As an anti-freezing agent

(c) As a substitute for petrol **(d)** For denaturing of ethyl alcohol

(ix) Rectified spirit contains alcohol about:

(a) 80% **(b)** 85%

(c) 90% **(d)** 95%

(x) According to Lewis concept ethers behave as:

(a) Acid **(b)** Base

(c) Acid as well as a base **(d)** None of these

ANSWERS

(i)	(d)	**(ii)**	(a)	**(iii)**	(a)	**(iv)**	(a)	**(v)**	(c)
(vi)	(c)	**(vii)**	(a)	**(viii)**	(c)	**(ix)**	(d)	**(x)**	(b)

Q.4 What are alcohols? How are they classified? How will you distinguish between primary, secondary and tertiary alcohols?

Ans. The organic compounds having formula ROH are called alcohols. They are of three types:

(i) Primary alcohols (ii) Secondary alcohols (iii) Tertiary alcohols

They can be distinguished by the Lucas test.

(See Answer of Q.8)

Q.5 How is methyl alcohol obtained on large scale? How it may be distinguished from ethyl alcohol?

Ans. First part is detailed question. Consult text book for answer.

Ethanol gives iodoform test with iodine in the presence of NaOH. Formation of yellow crystals indicate the presence of ethanol or ethyl alcohol.

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$$

While methyl alcohol does not give this reaction.

$$CH_3–OH + I_2 + NaOH \longrightarrow \text{No yellow ppt.}$$

Q.6 What is fermentation? Which compound may be obtained on industrial scale by fermentation?

Ans. **Fermentation:** It is a biochemical process which occurs in the presence of certain enzymes secreted by microorganisms such as yeast.

More detail see in the text book.

Ethanol (C_2H_5OH) is obtained by fermentation at industrial scale.

Q.7 Explain the following terms:

(i) Absolute alcohol **(ii) Methylated spirit**

(iii) Rectified spirit **(iv) Denaturing of alcohols**

Ans.

(i) Absolute Alcohol: 100% ethyl alcohol is called absolute alcohol. It is obtained by redistilation of rectified spirit with CaO which absorbs moisture.

(ii) Methylated Spirit: Ethyl alcohol containing small amount of methyl alcohol is called methylated spirit.

(iii) Rectified Spirit: Alcohol obtained by fermentation is 12 – 14%. It is distilled again and again to obtain 95% alcohol which is called rectified spirit.

(iv) Denaturing of Alcohol: The addition of methanol (poisonous) into ethanol to render it unfit for the drinking purpose is called denaturing of alcohol.

Q.8 How does ethylalcohol react with the following reagents?

Ans.

(i) Conc. H_2SO_4:

$$CH_3CH_2 - OH \xrightarrow[180°C]{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$$

$$CH_3CH_2OH \xrightarrow[140°C]{\text{Conc. } H_2SO_4} CH_3 - CH_2 - O - CH_2 - CH_3 + H_2O$$

(ii) Na:

$$CH_3 - CH_2 - OH + Na \longrightarrow CH_3CH_2ONa + \frac{1}{2} H_2$$

(iii) PCl_5:

$$CH_3 - CH_2 - OH + PCl_5 \longrightarrow CH_3CH_2 - Cl + POCl_3 + HCl$$

(iv) CH_3COOH:

$$CH_3 - CH_2OH + CH_3COOH \xrightleftharpoons{\text{Conc. } H_2SO_4} CH_3 - \overset{\overset{O}{\|}}{C} - OC_2H_5 + H_2O$$

(v) $SOCl_2$:

$$CH_3 - CH_2 - OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3 - CH_2 - Cl + SO_2 + HCl$$

Q.10 How will you distinguish between:

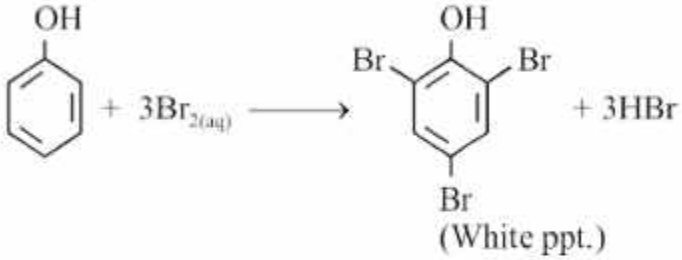
(i) An alcohol and a phenol **(ii) An alcohol and an ether**

(iii) Methanol and ethanol **(iv) A tertiary alcohol and a primary alcohol**

(v) 1-propanol and 2-propanol

Ans.

(i) Phenol gives white ppt. with bromine water.



(White ppt.)

While alcohols do not react with bromine water.

(ii) Alcohols give oily layer of alkyl halides while reacting with conc. HCl in anhydrous $ZnCl_2$.

$$R{-}CH_2{-}OH + HCl \xrightarrow[\text{Heat}]{ZnCl_2} R{-}CH_2{-}Cl + H_2O$$

While ethers do not give this reactions.

(iii) Ethanol gives iodoform with iodine in the presence of NaOH. Formation of yellow crystals indicate the presence of ethanol.

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$$

While methanol does not give yellow ppt. of CH_3I.

$$CH_3OH + I_2 + NaOH \longrightarrow \text{No yellow ppt.}$$

(iv) Tertiary alcohol form an oily layer immediately when react with conc. HCl in anhydrous $ZnCl_2$.

$$\begin{array}{l} R \\ | \\ R - C - OH \\ | \\ R \end{array} + HCl \xrightarrow[\text{Immediately}]{ZnCl_2} \begin{array}{l} R \\ | \\ R - C - Cl \\ | \\ R \end{array} + H_2O$$

While primary alcohol form an oily layer only on heating.

$$R{-}CH_2{-}OH + HCl \xrightarrow[\text{Heat}]{ZnCl_2} R{-}CH_2{-}Cl + H_2O$$

(v) 1-propanol is primary alcohol and 2-propanol is secondary alcohol. We can distinguish them by Lucas test as following:

$$CH_3–CH_2–CH_2–OH + HCl \xrightarrow[\text{Heat}]{ZnCl_2} CH_3–CH_2–CH_2–Cl + H_2O$$

$$CH_3–\underset{\underset{OH}{|}}{CH}–CH_3 + HCl \xrightarrow[5\text{-}10\ min]{ZnCl_2} H–\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}–Cl + H_2O$$

2-propanol

Q.11 Give reasons for the followings:

(i) Ethyl alcohol is a liquid which methyl chloride is a gas.

(ii) Ethanol has higher boiling point than diethyl ether.

(iii) Absolute alcohol cannot be prepared by fermentation process.

(iv) Ethanol gives different products with conc. H_2SO_4 under different conditions.

(v) Water has higher boiling point than ethanol.

Ans.

(i) Ethyl alcohol has strong hydrogen bonding between its molecule whereas methyl chloride does not have, rather its molecules experience weaker dipole-dipole forces. That is why ethyl alcohol is liquid while methyl chloride is gas.

(ii) Ethanol has higher boiling point than diethyl ether because strong hydrogen bonding is present in ethanol.

Whereas diethyl ether has dipole-dipole forces which are weaker than hydrogen bonding due to this ethanol has higher boiling point than diethyl ether.

(iii) Alcohol obtained by fermentation is only upto 12% and never exceeds 14% because beyond this limit enzymes become inactive and the process is ceased, that is why absolute (100%) alcohol cannot prepared from fermentation process.

(iv) High concentration of ethanol when treated with conc. H_2SO_4 at 140°C produce diethyl ether.

$$2C_2H_5OH \xrightarrow[140°C]{\text{Conc. } H_2SO_4} H_5C_2–O–C_2H_5 + H_2O$$

Whereas at lower concentration of ethanol when treated with conc. H_2SO_4 at 180°C then it produce ethene.

$$C_2H_5OH \xrightarrow[180°C]{\text{Conc. } H_2SO_4} H_2C = CH_2 + H_2O$$

(v) In case of water, there is strong three dimensional hydrogen bonding due to two hydrogen bonds per molecule.

Whereas, in case of ethanol, there is weak hydrogen bonding due to only one hydrogen bond per molecule. Hence, boiling point of water is higher than ethanol.

Q.12 How will you convert:

(i) Methanol into ethanol **(ii) Ethanol into methanol**

(iii) Ethanol into isopropyl alcohol **(iv) Formaldehyde into ethyl alcohol**

(v) Acetone into ethyl alcohol

Ans.

(i) $\mathbf{CH_3OH \longrightarrow C_2H_5OH}$

(a) $CH_3{-}OH + HCl \xrightarrow{ZnCl_2} CH_3Cl + H_2O$

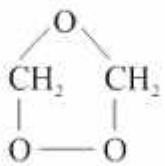
(b) $2CH_3{-}Cl + 2Na \xrightarrow{Ether} CH_3{-}CH_3 + 2NaCl$

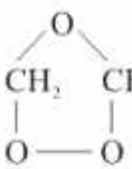
(c) $CH_3{-}CH_3 + Cl_2 \xrightarrow{hv} CH_3{-}CH_2{-}Cl + HCl$

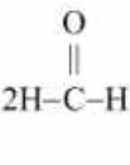
(d) $CH_3{-}CH_2{-}Cl + \underset{(aq)}{KOH} \longrightarrow \underset{\text{Ethanol}}{CH_3{-}CH_2{-}OH} + KCl$

(ii) $\mathbf{C_2H_5OH \longrightarrow CH_3OH}$

(a) $C_2H_5OH \xrightarrow[180°C]{H_2SO_4} CH_2 = CH_2 + H_2O$

(b) $CH_2 = CH_2 + O_3 \longrightarrow$ 

(c)  $+ Zn \longrightarrow$  $+ ZnO$

(d)  $+ H_2 \xrightarrow[Ni]{Pd/Pt} CH_3OH$

(iii) $C_2H_5OH \longrightarrow CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

(a) $C_2H_5-OH + [O] \xrightarrow{K_2Cr_2O_7,\ H_2SO_4} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H + H_2O$

(b) $CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H + \overset{\delta-}{CH_3}-\overset{\delta+}{Mg}-Br \xrightarrow{\text{Ether}} CH_3-\underset{\displaystyle O^-Mg^+Br}{\underset{|}{CH}}-CH_3$

$CH_3-\underset{\displaystyle O^-Mg^+Br}{\underset{|}{CH}}-CH_3 \xrightarrow{H_3O^+} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 + Mg\begin{matrix}Br^-\\Cl^-\end{matrix}$

(iv) $\mathbf{H-\overset{\displaystyle O}{\overset{\|}{C}}-H \longrightarrow C_2H_5OH}$

(a) $H-\overset{\displaystyle O}{\overset{\|}{C}}-H + \overset{\delta-}{CH_3}-\overset{\delta+}{Mg}-Br \longrightarrow CH_3-CH_2-\overset{-}{O}\overset{+}{M}gBr \xrightarrow{H_3O+} CH_3-CH_2OH + Mg\begin{matrix}Br^-\\Cl^-\end{matrix}$

(v) $\mathbf{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \longrightarrow C_2H_5-OH}$

(a) $CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 + 3[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OH + H-\overset{\displaystyle O}{\overset{\|}{C}}-OH$

(b) $CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OH + 4[H] \xrightarrow{LiAlH_4} C_2H_5-OH + H_2O$

Q.13 Explain the following terms using ethyl alcohol as an example.

Ans.

(i) **Oxidation:** Ethyl alcohol on oxidation changes to acetaldehyde and on further oxidation changes to acetic acid. Mixture of $K_2Cr_2O_7$ and conc. H_2SO_4 is good oxidizing agent.

$$CH_3 - CH_2 - OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3CHO + H_2O$$

$$CH_3CHO + [O] \longrightarrow CH_3COOH$$

(ii) **Dehydration:** Ethyl alcohol when reacted with conc. H_2SO_4 at 180°C, dehydration takes place. Removal of water from a substance in called dehydration.

$$CH_3 - CH_2 - OH \xrightarrow[180°C]{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$$

(iii) **Esterification:** The process in which alcohol and carboxylic acid reacts together to form ester.

$$CH_3 - CH_2 - OH + CH_3 - \overset{\overset{O}{\|}}{C} - OH \overset{H^+}{\rightleftharpoons} CH_3 - \overset{\overset{O}{\|}}{C} - OC_2H_5 + H_2O$$

(iv) **Ether Formation:** When excess amount of ethyl alcohol reacts with less amount of conc. H_2SO_4 at 140°C ether is formed.

$$CH_3CH_2OH + CH_3 - CH_2 - OH \xrightarrow[180°C]{\text{Conc. } H_2SO_4} CH_3 - CH_2 - O - CH_2 - CH_3 + H_2O$$

Q.14 Compare the reactions of phenol with that of ehtanol. Discuss the difference if any.

Ans.

Sr. No.	Properties	Phenol $C_6H_5 - OH$	Ethanol $C_2H_5 - OH$
1.	Solubility in H_2O	Partially miscible	Soluble in all proportions
2.	Acidity	Weakly acidic	Neutral
3.	Physical state	Solid at room temp	Liquid state
4.	Hydrogenation in the presence of Ni	Cyclohexanol is formed	No reaction
5.	Bromination	Ring is brominated	No reaction
6.	Reduction with hot Zn dust	Benzene is formed	No reaction
7.	Action of dilute nitric acid	Ring is nitrated	No reaction
8.	Action of ferric chloride	Purple colour is obtained	No purple colour

9.	Action of organic acids	No reaction	Formation of esters takes place
10.	Action of HX	No reaction	Formation of alkyl halides takes place
11.	Action of conc. H_2SO_4	Ring is sulphonated	Ethylene or ether is formed according to the conditions
12.	Iodoform reaction	No ppt.	Yellow ppt. of CHI_3

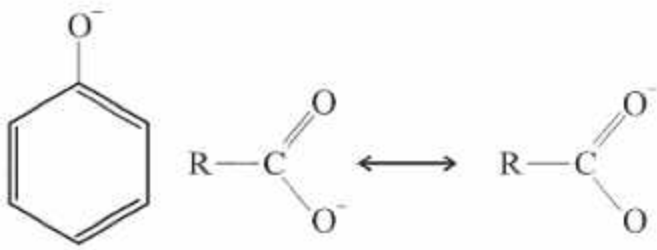
Q.15 Arrange the following compounds in order to their increasing acid strength and give reason. H_2O, C_2H_5OH, C_6H_5OH, C_6H_5COOH.

Ans. Increasing acid strength is the following order.

$$C_2H_5OH < H_2O < C_6H_5OH < C_6H_5COOH$$

Acid strength depend upon the dissociation of compound and stability of the anion conjugate base.

Carboxylate ions $RCOO^-$ are more stable than phenolate ion due to resonance stability.



Phenolate Ion Carboxylate Ion

Alcohol are less acidic than phenol because in phenoxide ion, charge of oxygen is delocalized while charge of oxygen in RO^- is localized.

Anion of water OH^- is least stable and most reactive.

Dissociation of compounds is as follows.

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$ROH \rightleftharpoons RO^- + H^+$$

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$$

$$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$$

Q.16 Write down two methods for preparing phenol. What is the action of following on phenol.

Ans. See articles "Preparation of Phenols" and "reaction of phenols".

Q.17 Give the uses of phenols. How bakelite is prepared from it.

Ans. See article "Uses of Phenol".

Q.18 (a) Write I.U.P.A.C. names of the following compounds:

(i) $(CH_3)_2CH–OH$, **(ii)** $(CH_3)_2CHCH_2OH$

(iii) $(CH_3)_3COH$, **(iv)** $C_2H_5–\underset{\displaystyle CH_3}{\underset{|}{CH}}–OH$

(b) Write structure formulas for the following compounds:

Glycol, Glycerol, Carbolic acid, Acetophenone, Picric acid

Ans. (a)

(i) $(CH_3)_2CH–OH$ 2-Propanol

(ii) $(CH_3)_2CHCH_2OH$ 2-Methyl-1-propanol

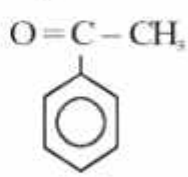
(iii) $(CH_3)_3COH$ 2-Methyl-2-propanol

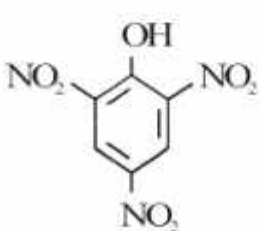
(iv) $C_2H_5–\underset{\displaystyle CH_3}{\underset{|}{CH}}–OH$ 2-Butanol

(b) Glycol $CH_2(OH)–CH_2(OH)$

Carbolic acid 

Glycerol $CH_2(OH)–CH(OH)–CH_2(OH)$

Acetophenone 

Picric acid 

Q.19 (a) Name the following compounds:

$CH_3—CH_2—CH_2—O—CH_3$, $C_6H_5—O—C_6H_5$

$(CH_3)_2CH—O—CH(CH_3)_2$, $CH_3—O—C_6H_5$

$CH_3—CH_2—CH_2—O—CH_2—CH_3$

(b) Write down structural formulas of the following compounds:

Methoxy ethane, Ethoxy benzene, Sodium ethoxide, Sodium phenoxide, Propoxy propane

Ans.

(a)

(i) $CH_3—CH_2—CH_2—O—CH_3$ Methoxy propane

(ii) $C_6H_5—O—C_6H_5$ Phenoxy benzene

(iii) $(CH_3)_2CH—O—CH(CH_3)_2$ Isopropoxy iso-propane

(iv) $CH_3—O—C_6H_5$ Methoxy benzene

(v) $CH_3—CH_2—CH_2—O—CH_2—CH_3$ Ethoxy propane

(b)

(i) Methoxy ethane $CH_3–O–C_2H_5$

(ii) Ethoxy benzene $C_2H_5–O–C_6H_5$

(iii) Sodium ethoxide $CH_3–CH_2–\overset{-}{O}\overset{+}{N}a$

(iv) Sodiumphenoxide



(v) Propoxy propane $CH_3–CH_2–CH_2–O–CH_2–CH_2–CH_3$

DO YOU KNOW?

(1) Methyl alcohol is called wood spirit or wood naphtha.

(2) Ethyl alcohol is called grain alcohol.

(3) CH_3OH is poisonous and causes blindness, madness and even death.

(4) 95% ethanol is called rectified spirit.

(5) The process of conversion of starch or sugars into alcohol in the presence of yeast is called fermentation.

(6) Lucas test is used to distinguish between primary, secondary and tertiary alcohols.

(7) Primary alcohols on oxidation form aldehydes and secondary alcohols on oxidation form ketones.

(8) Ethanol gives iodoform test but methanol does not.

(9) Phenol is also called carbolic acid.

(10) Williamson's synthesis is used for the preparation of ethers.

(11) Phenol was obtained by Runge in 1834 from coal tar.

(12) Phenol is partially miscible with water but becomes completely miscible at 65.9°C.

(13) K_a for phenol is in the order of 10^{-10}.

(14) Relative acidic strength of alcohol, phenol, water and carboxylic acids is:

$$\text{Carboxylic acid} > \text{Phenol} > H_2O > \text{Alcohol}$$

(15) Dimethyl ether is a gas.

(16) Phenol is deliquescent solid.

(17) Zymase is combination of 14 enzymes.

CHAPTER 11

ALCOHOLS, PHENOLS AND ETHERS

MULTIPLE CHOICE QUESTIONS

1. Williamsons synthesis is used for the synthesis of:

(a) Phenol **(b)** Alcohol

(c) Ether **(d)** Aldehyde

2. Aldehydes after catalytic reduction change to:

(a) P° alcohol **(b)** S° alcohol

(c) T° alcohol **(d)** P° and S° alcohol

3. When ether is protonated, the conjugate acid formed is called:

(a) An oxonium ion **(b)** Carbanion

(c) An oxide ion **(d)** A hydration ion

4. Which of the following alcohol is commonly used as anti-freeze:

(a) Methanol **(b)** Ethanol

(c) Ethylene glycol **(d)** All of the above

5. Which of the following will have the highest boiling point:

(a) Methanal **(b)** Ethanal

(c) Propanal **(d)** 2-hexanone

6. 95% ethanol is called:

(a) Absolute alcohol **(b)** Rectified spirit

(c) Methylated spirit **(d)** Wood spirit

7. Which of the following alcohol is used in the perfumes and for flavouring:

(a) Methanol **(b)** Ethanol

(c) 1-propanol **(d)** 1-butanol

8. According to Lewis concept ethers behaves as:

(a) Acid **(b)** Base

(c) Acid as well as base **(d)** None of above

9. Which enzyme is not involved in fermentation of starch:

(a) Diastase **(b)** Zymase

(c) Urease **(d)** Maltase

10. The hydrolysis of sugar is called:

(a) Condensation **(b)** Polymerization

(c) Inversion **(d)** Reduction

11. Which compound shows maximum hydrogen bonding with water:

(a) C_6H_5OH **(b)** C_2H_5OH

(c) $CH_3 - O - CH_3$ **(d)** n-hexanol

12. Which statement is incorrect about phenol:

(a) It is colourless, crystalline poisonous solid

(b) It does not turn blue litmus paper red

(c) It liberates CO_2 gas from carbonate

(d) Above 65.9°C it is miscible wither water

13. Which of the following is the weakest acid:

(a) Phenol **(b)** Alcohol

(c) Carboxylic acid **(d)** Water

14. Which inorganic reagent may be used to distinguish between phenol and methanol:

(a) Alkaline aqueous I_2 **(b)** Aqueous $NaHCO_3$

(c) $K_2Cr_2O_7$ in dil. H_2SO_4 **(d)** Na

15. Phenol is also called:

(a) Carbonic acid **(b)** Carbolic acid

(c) Carboxylic acid **(d)** Fatty acid

16. Which of the following give iodoform test:

(a) CH_3OH **(b)** C_2H_5OH

(c) Methanal **(d)** 1-propanol

17. Which of the following is more reactive where O – H bonds break:

(a) P° alcohol **(b)** S° alcohol

(c) T° alcohol **(d)** Cannot be predicted

18. Which of the following alcohol is least soluble in water:

(a) CH_3OH **(b)** C_2H_5OH

(c) C_3H_7OH **(d)** C_4H_9OH

19. 100% pure alcohol is called:

(a) Methylated spirit **(b)** Rectified spirit

(c) Power alcohol **(d)** Absolute alcohol

20. The correct name of $H_2C = CH - CH_2 - CH_2 - OH$ is:

(a) 1-butene-4-ol **(b)** 2-butene-1-ol

(c) 3-butene-1-ol **(d)** None of these

21. Which of the following is more reactive:

(a) Benzene **(b)** Phenol

(c) Nitrobenzene **(d)** Benzoic acid

22. Bakelite is thermosetting plastic, it is formed by the polymerization of:

(a) Ethanol and formaldehyde **(b)** Phenol and ethanol

(c) Phenol and formaldehyde **(d)** Phenol and acetaldehyde

23. Which of the following compound should have lowest boiling point:

(a) C_2H_6 **(b)** C_2H_5Cl

(c) $CH_3 - O - CH_3$ **(d)** C_2H_5OH

24. Ethanol can be converted into ethanoic acid by:

(a) Hydrogenation **(b)** Fermentation

(c) Oxidation **(d)** Hydration

25. When 2-pentanol undergoes oxidation the product is:

(a) Pentanol **(b)** 3-pentanone

(c) 2-pentanone **(d)** Pentanoic acid

26. When ethyl bromide (C_2H_5Br) is heated with Ag_2O in the abscence of moisture the product formed is:

(a) Ethanol **(b)** Diethyl ether

(c) Ethanal **(d)** Ethene

27. Which of the following compound has no unsaturation:

(a) Methanal **(b)** Methoxy methane

(c) Phenol **(d)** Benzoic acid

28. The conversion of ethanol to ethene is an example of:

(a) Dehydration **(b)** Hydration

(c) Hydrogenation **(d)** Fermentation

29. Ethanol reacts with sodium metal to liberate:

(a) CO_2 gas **(b)** H_2 gas

(c) CO gas **(d)** Steam

30. Diethyl ether can be decomposed by heating with:

(a) HI **(b)** NaOH

(c) Water **(d)** $KMnO_4$

answers

1.	(c)	**2.**	(a)	**3.**	(a)	**4.**	(c)	**5.**	(d)
6.	(b)	**7.**	(d)	**8.**	(b)	**9.**	(c)	**10.**	(c)
11.	(b)	**12.**	(c)	**13.**	(b)	**14.**	(c)	**15.**	(b)
16.	(b)	**17.**	(a)	**18.**	(d)	**19.**	(d)	**20.**	(c)
21.	(b)	**22.**	(c)	**23.**	(a)	**24.**	(c)	**25.**	(c)
26.	(b)	**27.**	(b)	**28.**	(a)	**29.**	(b)	**30.**	(a)

SOLVED EXERCISE

Q.1 Fill in the blanks:

(i) Primary, secondary and tertiary alcohols can be identified by ———— test.

(ii) Oxidation of ———— alcohols give ketones.

(iii) Alcohols on heating with ———— give alkenes at high temperature.

(iv) Alcohols have ———— boiling points than ethers due to stronger hydrogen bonding.

(v) Williamson's synthesis is used to prepare ————.

(vi) ———— is also called wood spirit.

(vii) Carbolic acid is the other name of ————.

(viii) Primary, secondary and tertiary alcohols can be prepared by reacting Grignard reagent with ————.

(ix) Alcohols and ———— react to produce esters.

(x) ———— is used as anti-freezing agent in automobile radiator.

(xi) The process of conversion of starch into alcohol with the help of microorganisms is called ————.

(xii) Ketones on reduction give ———— alcohols.

answers

(i)	Lucas	**(ii)**	secondary	**(iii)**	H_2SO_4
(iv)	high	**(v)**	ether	**(vi)**	methanol
(vii)	phenol	**(viii)**	carbonyl compound	**(ix)**	carboxylic acids
(x)	glycol	**(xi)**	fermentation	**(xii)**	secondary

Q.2 Indicate True or False:

(i) Methylated spirit contains 95% methyl alcohol and 5% ethyl alcohol.

(ii) Ethyl alcohol is a very good anti-freezing agent.

(iii) Methanol is also called wood spirit.

(iv) Only 14% ethyl alcohol can be prepared by fermentation.

(v) Ethers do not show hydrogen bonding.

(vi) Alcohols are more acidic than phenols.

(vii) Phenol is more soluble in water than lower alcohols.

(viii) Alcohols are more basic than ethers.

(ix) Ethers have higher boiling points than alcohols and phenols.

(x) Methanol and ethanol can be distinguished by iodoform test.

answers

(i)	False	**(ii)**	False	**(iii)**	True	**(iv)**	True	**(v)**	True
(vi)	False	**(vii)**	False	**(viii)**	False	**(ix)**	False	**(x)**	True

Q.3 Multiple choice questions. Encircle the correct answer:

(i) Which compound shows hydrogen bonding:

(a) C_2H_6 **(b)** C_2H_5Cl

(c) $CH_3–O–CH_3$ **(d)** C_2H_5OH

(ii) Which compound shows maximum hydrogen bonding with water:

(a) CH_3OH **(b)** C_2H_5OH

(c) $CH_3–O–CH_3$ **(d)** C_6H_5OH

(iii) Which compound is more soluble in water:

(a) C_2H_5OH **(b)** C_6H_5OH

(c) CH_3COCH_3 **(d)** n-Hexanol

(iv) Which compound will have the maximum repulsion with H_2O:

(a) C_6H_6 **(b)** C_2H_5OH

(c) $CH_3CH_2CH_2OH$ **(d)** $CH_3—O—CH_3$

(v) Ethanol can be converted into ethanoic acid by:

(a) Hydrogenation **(b)** Hydration

(c) Oxidation **(d)** Fermentation

(vi) Which enzyme is not involved in fermentation:

(a) Diastase **(b)** Zymase

(c) Urease **(d)** Invertase

(vii) Which compound is called a universal solvent:

(a) H_2O **(b)** CH_3OH

(c) C_2H_5OH **(d)** $CH_3—O—CH_3$

(viii) Methyl alcohol is not used:

(a) As a solvent **(b)** As an anti-freezing agent

(c) As a substitute for petrol **(d)** For denaturing of ethyl alcohol

(ix) Rectified spirit contains alcohol about:

(a) 80% **(b)** 85%

(c) 90% **(d)** 95%

(x) According to Lewis concept ethers behave as:

(a) Acid **(b)** Base

(c) Acid as well as a base **(d)** None of these

answers

(i)	(d)	**(ii)**	(a)	**(iii)**	(a)	**(iv)**	(a)	**(v)**	(c)
(vi)	(c)	**(vii)**	(a)	**(viii)**	(c)	**(ix)**	(d)	**(x)**	(b)

Q.4 What are alcohols? How are they classified? How will you distinguish between primary, secondary and tertiary alcohols?

Ans. The organic compounds having formula ROH are called alcohols. They are of three types:

(i) Primary alcohols (ii) Secondary alcohols (iii) Tertiary alcohols

They can be distinguished by the Lucas test.

(See Answer of Q.8)

Q.5 How is methyl alcohol obtained on large scale? How it may be distinguished from ethyl alcohol?

Ans. First part is detailed question. Consult text book for answer.

Ethanol gives iodoform with iodine in the presence of NaOH. Formation of yellow crystals indicate the presence of ethanol or ethyl alcohol.

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$$

While methyl alcohol does not give this reaction.

$CH_3–OH + I_2 + NaOH \longrightarrow$ No yellow ppt.

Q.6 What is fermentation? Which compound may be obtained on industrial scale by fermentation?

Ans. **Fermentation:** It is a biochemical process which occurs in the presence of certain enzymes secreted by microorganisms such as yeast.

More detail see in the text book.

Ethanol (C_2H_5OH) is obtained by fermentation at industrial scale.

Q.7 Explain the following terms:

(i) Absolute alcohol **(ii) Methylated spirit**

(iii) Rectified spirit **(iv) Denaturing of alcohols**

Ans.

(i) Absolute Alcohol: 100% ethyl alcohol is called absolute alcohol. It is obtained by redistilation of rectified spirit with CaO which absorbs moisture.

(ii) Methylated Spirit: Ethyl alcohol containing small amount of methyl alcohol is called methylated spirit.

(iii) Rectified Spirit: Alcohol obtained by fermentation is 12 – 14%. It is distilled again and again to obtain 95% alcohol which is called rectified spirit.

(iv) Denaturing of Alcohol: The addition of methanol (poisonous) into ethanol to render it unfit for the drinking purpose is called denaturing of alcohol.

Q.8 How does ethylalcohol react with the following reagents?

Ans.

(i) Conc. H_2SO_4:

$$CH_3CH_2 - OH \xrightarrow[180°C]{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$$

$$CH_3CH_2OH \xrightarrow[140°C]{\text{Conc. } H_2SO_4} CH_3 - CH_2 - O - CH_2 - CH_3 + H_2O$$

(ii) Na:

$$CH_3 - CH_2 - OH + Na \longrightarrow CH_3CH_2ONa + \frac{1}{2} H_2$$

(iii) PCl_5:

$$CH_3 - CH_2 - OH + PCl_5 \longrightarrow CH_3CH_2 - Cl + POCl_3 + HCl$$

(iv) CH_3COOH:

$$CH_3 - CH_2OH + CH_3COOH \underset{}{\overset{conc.\ H_2SO_4}{\rightleftharpoons}} CH_3 - \overset{O}{\overset{\|}{C}} - OC_2H_5 + H_2O$$

(v) $SOCl_2$:

$$CH_3 - CH_2 - OH + SOCl_2 \xrightarrow{Pyridine} CH_3 - CH_2 - Cl + SO_2 + HCl$$

Q.10 How will you distinguish between:

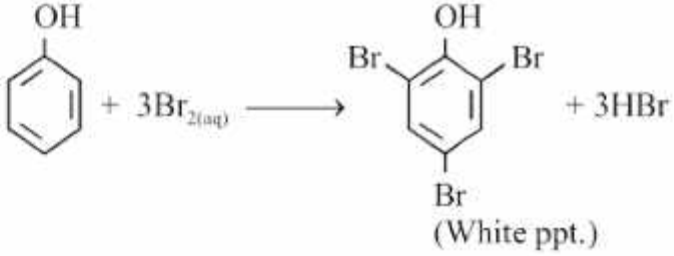
(i) An alcohol and a phenol **(ii) An alcohol and an ether**

(iii) Methanol and ethanol **(iv) A tertiary alcohol and a primary alcohol**

(v) 1-propanol and 2-propanol

Ans.

(i) Phenol gives white ppt. with bromine water.



(White ppt.)

While alcohols do not react with bromine water.

(ii) Alcohols give oily layer of alkyl halides while reacting with conc. HCl in anhydrous $ZnCl_2$.

$$R{-}CH_2{-}OH + HCl \xrightarrow[Heat]{ZnCl_2} R{-}CH_2{-}Cl + H_2O$$

While ethers do not give this reactions.

(iii) Ethanol gives iodoform with iodine in the presence of NaOH. Formation of yellow crystals indicate the presence of ethanol.

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$$

While methanol does not give yellow ppt. of CHI_3.

$$CH_3OH + I_2 + NaOH \longrightarrow \text{No yellow ppt.}$$

(iv) Tertiary alcohol form an oily layer immediately when react with conc. HCl in anhydrous $ZnCl_2$.

$$\begin{array}{l} R \\ | \\ R - C - OH \\ | \\ R \end{array} + HCl \xrightarrow[Immediately]{ZnCl_2} \begin{array}{l} R \\ | \\ R - C - Cl \\ | \\ R \end{array} + H_2O$$

While primary alcohol form an oily layer only on heating.

$$R{-}CH_2{-}OH + HCl \xrightarrow[Heat]{ZnCl_2} R{-}CH_2{-}Cl + H_2O$$

(v) 1-propanol is primary alcohol and 2-propanol is secondary alcohol. We can distinguish them by Lucas test as following:

$$CH_3{-}CH_2{-}CH_2{-}OH + HCl \xrightarrow[Heat]{ZnCl_2} CH_3{-}CH_2{-}CH_2{-}Cl + H_2O$$

$$CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3 + HCl \xrightarrow[5\text{-}10\ min]{ZnCl_2} H - \underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - Cl + H_2O$$

2-propanol

Q.11 Give reasons for the followings:

(i) Ethyl alcohol is a liquid which methyl chloride is a gas.

(ii) Ethanol has higher boiling point than diethyl ether.

(iii) Absolute alcohol cannot be prepared by fermentation process.

(iv) Ethanol gives different products with conc. H_2SO_4 under different conditions.

(v) Water has higher boiling point than ethanol.

Ans.

(i) Ethyl alcohol has strong hydrogen bonding between its molecule whereas methyl chloride does not have, rather its molecules experience weaker dipole-dipole forces. That is why ethyl alcohol is liquid while methyl chloride is gas.

(ii) Ethanol has higher boiling point than diethyl ether because strong hydrogen bonding is present in ethanol.

Whereas diethyl ether has dipole-dipole forces which are weaker than hydrogen bonding due to this ethanol has higher boiling point than diethyl ether.

(iii) Alcohol obtained by fermentation is only upto 12% and never exceeds 14% because beyond this limited enzymes become inactive and the process is ceased, that is why absolute (100%) alcohol cannot be prepared from fermentation process.

(iv) High concentration of ethanol when treated with conc. H_2SO_4 at 140°C produce diethyl ether.

$$2C_2H_5OH \xrightarrow[140°C]{Conc.\ H_2SO_4} H_5C_2{-}O{-}C_2H_5 + H_2O$$

Whereas at lower concentration of ethanol when treated with conc. H_2SO_4 at 180°C then it produce ethene.

$$C_2H_5OH \xrightarrow[180°C]{\text{Conc. } H_2SO_4} H_2C = CH_2 + H_2O$$

(v) In case of water, there is strong three dimensional hydrogen bonding due to two hydrogen bonds per molecule.

Whereas, in case of ethanol, there is weak hydrogen bonding due to only one hydrogen bond per molecule. Hence, boiling point of water is higher than ethanol.

Q.12 How will you convert:

(i) Methanol into ethanol **(ii) Ethanol into methanol**

(iii) Ethanol into isopropyl alcohol **(iv) Formaldehyde into ethyl alcohol**

(v) Acetone into ethyl alcohol

Ans.

(i) $\mathbf{CH_3OH \longrightarrow C_2H_5OH}$

(a) $CH_3{-}OH + HI \xrightarrow{ZnCl_2} CH_3I + H_2O$

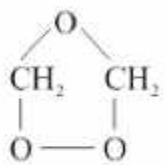
(b) $2CH_3{-}I + 2Na \xrightarrow{\text{Ether}} CH_3{-}CH_3 + 2NaI$

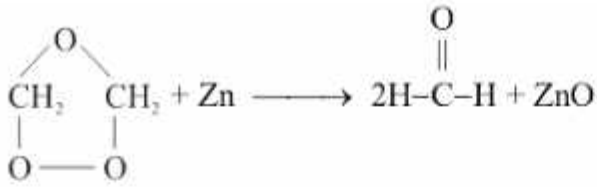
(c) $CH_3{-}CH_3 + Cl_2 \xrightarrow{h\nu} CH_3{-}CH_2{-}Cl + HCl$

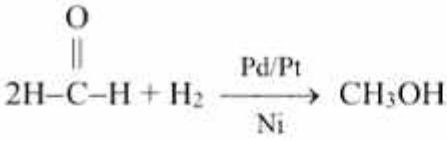
(d) $CH_3{-}CH_2{-}Cl + \underset{(aq)}{KOH} \longrightarrow \underset{\text{Ethanol}}{CH_3{-}CH_2{-}OH} + KCl$

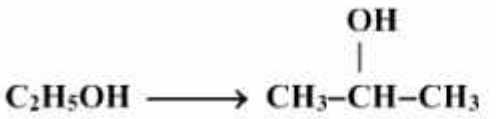
(ii) $\mathbf{C_2H_5OH \longrightarrow CH_3OH}$

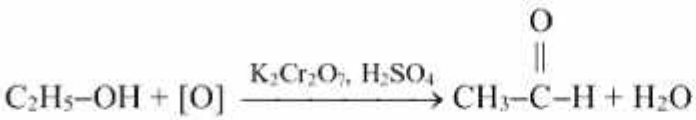
(a) $C_2H_5OH \xrightarrow[180°C]{H_2SO_4} CH_2 = CH_2 + H_2O$

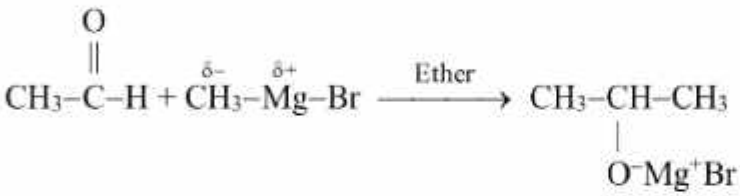
(b) $CH_2 = CH_2 + O_3 \longrightarrow$ 

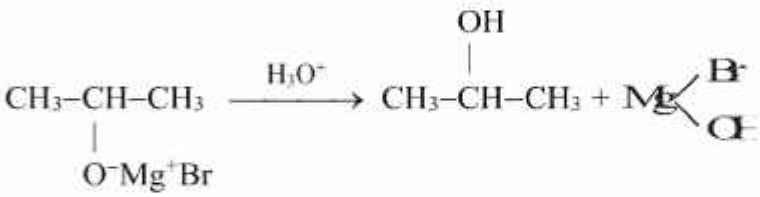
(c) 

(d) 

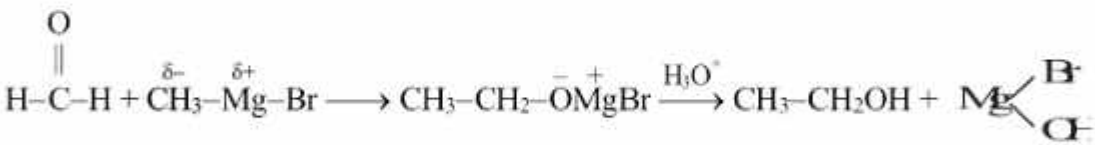
(iii) 

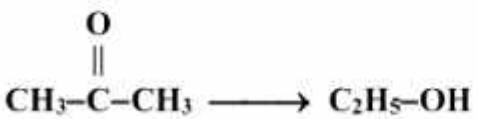
(a) 

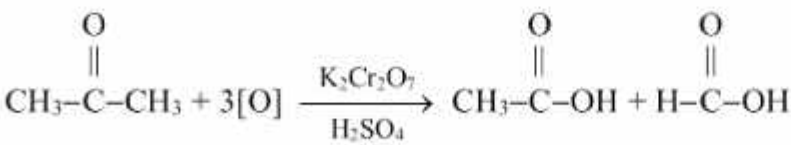
(b) 



(iv) 

(a) 

(v) 

(a) 

(b) $CH_3-\overset{\overset{O}{\|}}{C}-OH + 4[H] \xrightarrow{LiAlH_4} C_2H_5-OH + H_2O$

Q.13 Explain the following terms using ethyl alcohol as an example.

Ans.

(i) Oxidation: Ethyl alcohol on oxidation changes to acetaldehyde and on further oxidation changes to acetic acid. Mixture of $K_2Cr_2O_7$ and conc. H_2SO_4 is good oxidizing agent.

$$CH_3 - CH_2 - OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3CHO + H_2O$$

$$CH_3CHO + [O] \longrightarrow CH_3COOH$$

(ii) Dehydration: Ethyl alcohol when reacted with conc. H_2SO_4 at 180°C, dehydration takes place. Removal of water from a substance in called dehydration.

$$CH_3 - CH_2 - OH \xrightarrow[180°C]{Conc.\ H_2SO_4} CH_2 = CH_2 + H_2O$$

(iii) Esterification: The process in which alcohol and carboxylic acid reacts together to form ester.

$$CH_3 - CH_2 - OH + CH_3 - \overset{\overset{O}{\|}}{C} - OH \xrightarrow{H^+} CH_3 - \overset{\overset{O}{\|}}{C} - OC_2H_5 + H_2O$$

(iv) Ether Formation: When excess amount of ethyl alcohol reacts with less amount of conc. H_2SO_4 at 140°C ether is formed.

$$CH_3CH_2OH + CH_3-CH_2-OH \xrightarrow[180°C]{Conc.\ H_2SO_4} CH_3-CH_2-O-CH_2-CH_3 + H_2O$$

Q.18 (a) Write I.U.P.A.C. names of the following compounds:

(i) $(CH_3)_2CH-OH$, **(ii)** $(CH_3)_2CHCH_2OH$

(iii) $(CH_3)_3COH$, **(iv)** $C_2H_5-\underset{\underset{CH_3}{|}}{CH}-OH$

(b) Write structure formulas for the following compounds:

Glycol, Glycerol, Carbolic acid, Acetophenone, Picric acid

Ans. (a)

(i) $(CH_3)_2CH-OH$ 2-propanol

(ii) $(CH_3)_2CHCH_2OH$ 2-methyl-1-propanol

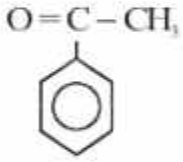
(iii) $(CH_3)_3COH$ 2-methyl-2-propanol

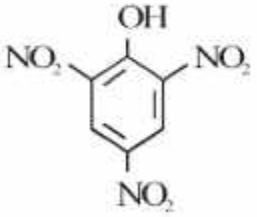
(iv) $C_2H_5-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH$ 2-butanol

(b) Glycol $CH_2(OH)-CH_2(OH)$

Carbolic acid 

Glycerol $CH_2(OH)-CH(OH)-CH_2(OH)$

Acetophenone 

Picric acid 

Q.19 (a) Name the following compounds:

$CH_3—CH_2—CH_2—O—CH_3$, $C_6H_5—O—C_6H_5$

$(CH_3)_2CH—O—CH(CH_3)_2$, $CH_3—O—C_6H_5$

$CH_3—CH_2—CH_2—O—CH_2—CH_3$

(b) Write down structural formulas of the following compounds:

Methoxy ethane, Ethoxy benzene, Sodium ethoxide, Sodium phenoxide, Propoxy propane

Ans.

(a) **(i)** $CH_3—CH_2—CH_2—O—CH_3$ Methoxy propane

(ii) $C_6H_5—O—C_6H_5$ Phenoxy benzene

(iii) $(CH_3)_2CH—O—CH(CH_3)_2$ Isopropoxy iso-propane

(iv) $CH_3—O—C_6H_5$ Methoxy benzene

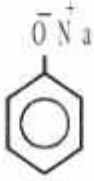
(v) $CH_3—CH_2—CH_2—O—CH_2—CH_3$ Ethoxy propane

(b) **(i)** Methoxy ethane $CH_3-O-C_2H_5$

(ii) Ethoxy benzene $C_2H_5–O–C_6H_5$

(iii) Sodium ethoxide $CH_3–CH_2–\overset{-}{O}\overset{+}{N}a$

(iv) Sodium phenoxide



(v) Propoxy propane $CH_3–CH_2–CH_2–O–CH_2–CH_2–CH_3$

DO YOU KNOW?

1. Methyl alcohol is called wood spirit or wood naphtha.
2. Ethyl alcohol is called grain alcohol.
3. CH_3OH is poisonous and causes blindness, madness and even death.
4. 95% ethanol is called rectified spirit.
5. The process of conversion of starch or sugars into alcohol in the presence of yeast is called fermentation.
6. Lucas test is used to distinguish between primary, secondary and tertiary alcohols.
7. Primary alcohols on oxidation form aldehydes and secondary alcohols on oxidation form ketones.
8. Ethanol gives iodoform test but methanol does not.
9. Phenol is also called carbolic acid.
10. Williamson's synthesis is used for the preparation of ethers.
11. Phenol was obtained by Runge in 1834.
12. Phenol is partially miscible with water but becomes completely miscible at 65.9°C.
13. K_a for phenol is in the order of 10^{-10}.
14. Relative acidic strength of alcohol, phenol, water and carboxylic acids is:

    Carboxylic acid > Phenol > H_2O > Alcohol
15. Dimethyl ether is a gas at ordinary temperature.
16. Phenol was discovered by Runge in 1834 from coal tar.
17. Phenol is deliquescent solid.
18. Ethyl-methyl ether is also a gas at ordinary temperature.

SHORT QUESTIONS

Q.1 Ethyl alcohol is a liquid while ethyl chloride is a gas?

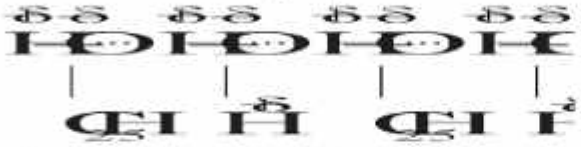
Ans. In ethyl alcohol due to the presence of –OH group, hydrogen bonding is present between the molecules. In case of ethylcholride only dipole-dipole forces are present. Due to greater intermolecular forces ethylalcohol exists in liquid state at room temperature.

Q.2 Ethanol has higher boiling point than diethyl ether?

Ans. The boiling point of ethylalcohol is high due to hydrogen bonding in it. In diethyl ether, no hydrogen atom is linked with highly electronegative element and hydrogen bonding does not exist.

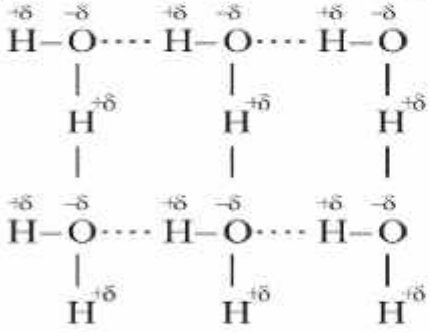
Q.3 Alcohols is soluble in water with any proportion, why?

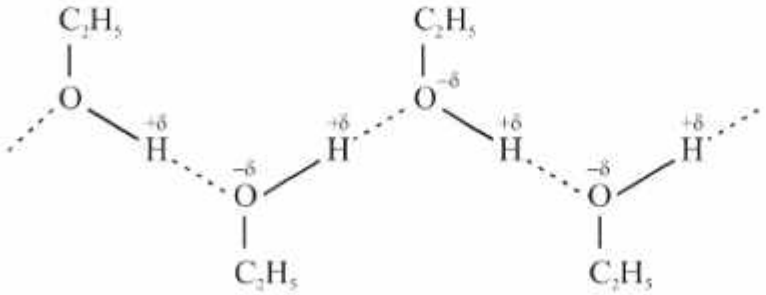
Ans. Both water and ethanol develops hydrogen bonding in them. Due to hydrogen bonding they can dissolve with any proportion.



Q.4 Water has higher boiling point than ethanol?

Ans. Water and ethanol both have hydrogen bonding in them separately. Water utilizes its two lone pair for hydrogen bonding while ethanol utilizes only one pair. Due to strong hydrogen bonding in water it has higher boiling point.





Q.5 Absolute alcohol cannot be prepared by fermentation process?

Ans. The optimum conditions for the activity of enzyme are based upon the pH, temperature, dilution of solution. In dilute solution, enzymes are more active. In fermentation process,

maximum 12 – 14% alcohol can be prepared. If concentration of alcohol increases activity of enzymes decreases.

Q.6 Ethanol gives different products with concentrated sulphuric acid under different conditions?

Ans. Ethanol gives different products under different conditions with conc. sulphuric acid:

(i) If concentration of acid is high and alcohol is low at 180°C on dehydration ethene is formed.

$$CH_3 - CH_2 - OH \xrightarrow[\text{Conc. } H_2SO_4]{180^\circ C} CH_2 = CH_2 + H_2O$$

(ii) If concentration of acid is less and alcohol is high at 140°C ether is formed on dehydration.

$$2CH_3CH_2OH \xrightarrow[\text{Conc. } H_2SO_4]{140^\circ C} CH_3 - CH_2OCH_2 - CH_3 + H_2O$$

(iii) At room temperature, ethyl bisulphate is formed.

$$CH_3 - CH_2OH + H.HSO_4 \longrightarrow CH_3 - CH_2.HSO_4 + H_2O$$

Q.7 When C – O bond of alcohol breaks the order of reactivity is ter alcohol > sec alcohol > primary alcohol, why?

Ans. When C – O bond of alcohol breaks, carbocation are formed. Tertiary carbocation is more stable than secondary and it is more stable than primary carbocations. The stability gives the estimation of bond breakage. The stability order is

$$R_3C^+ > R_2CH^+ > RCH_2^+ > CH_3^+$$

Q.8 How will you distinguish between primary, secondary and tertiary alcohols?

Ans. Primary, secondary and tertiary alcohols can be distinguished by Lucas test. In this test alcohol is treated with HCl and $ZnCl_2$. Tertiary alcohols react immediately, secondary alcohol react after 5 to 10 min while primary alcohol react only on heating.

$$R - OH + HCl \xrightarrow[\text{On heating}]{ZnCl_2} RCl + H_2O$$

$$R - \underset{\displaystyle OH}{\underset{|}{CH}} - R + HCl \xrightarrow[5\text{-}10 \text{ min}]{ZnCl_2} R - \underset{\displaystyle Cl}{\underset{|}{CH}} - R + H_2O$$

$$R - \underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R}{\overset{|}{C}}}} - OH + HCl \xrightarrow[\text{Immediately}]{ZnCl_2} R - \underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R}{\overset{|}{C}}}} - Cl + H_2O$$

Q.9 How will you distinguish between methanol and ethanol?

Ans. Methanol and ethanol can be distinguished by iodoform test. Ethanol reacts with NaOH and iodine to form the yellow precipitate of CHI_3 while methanol does not perform this test.

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$$

Q.10 Carboxylic acids are more acidic than phenol, why?

Ans. Strength of acid depends upon its dissociation Carboxylate ions is more stable than phenolate ion.

$$C_6H_5OH + H_2O \rightleftharpoons H_3O^+ + C_6H_5O^- \quad \text{(Phenolate ion)}$$

$$RCOOH + H_2O \rightleftharpoons H_3O^+ + RCOO^- \quad \text{(Carboxylate ion)}$$

Q.11 How will you distinguish between carboxylic acid and phenol?

Ans. Phenol and carboxylic acid can be distinguished by $NaHCO_3$ test. Add $NaHCO_3$ in both the solutions. Phenols do not react with $NaHCO_3$ while carboxylic acid evolves carbondioxide with effervescence.

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + CO_2 + H_2O$$

Q.12 Phenol is acidic while ethanol is not although both have –OH group in them, why?

Ans. The strength of an acid depends upon the stability of conjugate base of an acid. Phenolate ion is more stable due to resonance in it, while ethoxy ion is not stable and does not lose proton.

$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$$

Q.13 Ethers are less reactive than alcohols, why?

Ans. In case of alcohol one hydrogen atom is directly linked with highly electronegative atom oxygen and bond is polar in nature.

$$\overset{-\delta}{R-O}-\overset{-\delta}{H} \qquad\qquad R-O-R$$

In case of ether no hydrogen is linked with oxygen atom directly. Ethers do not react with alkalies, sodium metal, dilute acids, oxidizing or reducing agents.

Q.14 How will you distinguish between ethanol and diethyl ether?

Ans. Ethers do not react with sodium metal while all alcohols react with sodium metal and hydrogen gas is evolved.

$$C_2H_5OH + Na \longrightarrow C_2H_5O^-Na^+ + \frac{1}{2}H_2$$

$$C_2H_5OC_2H_5 + Na \longrightarrow \text{No reaction}$$

Both can also be distinguish by iodoform test.

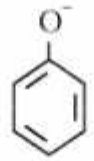
Q.15 Arrange the following compounds in order to their increasing acid strength and give reason. H_2O, C_2H_5OH, C_6H_5OH, C_6H_5COOH.

Ans. Increasing acid strength is the following order:

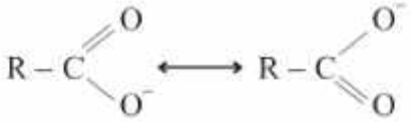
$$C_2H_5OH < H_2O < C_6H_5OH < C_6H_5COOH$$

Acid strength depends upon the dissociation of compound and stability of the anion conjugate base.

Carboxylate ions $RCOO^-$ are more stable than phenolate ion due to resonance stability.



Phenolate ion



Carboxylate ion

Alcohols are less acidic than phenol because in phenoxide ion, charge of oxygen is delocalized while change of oxygen in RO^- is localized.

Anion of water OH^- is least stable and most reactive.

Dissociation of compounds is as follows:

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$ROH \rightleftharpoons RO^- + H^+$$

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^-$$

$$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$$