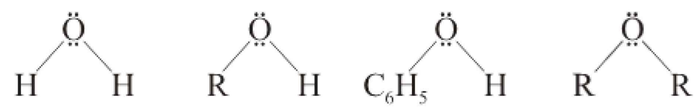
Chapter 11

# 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

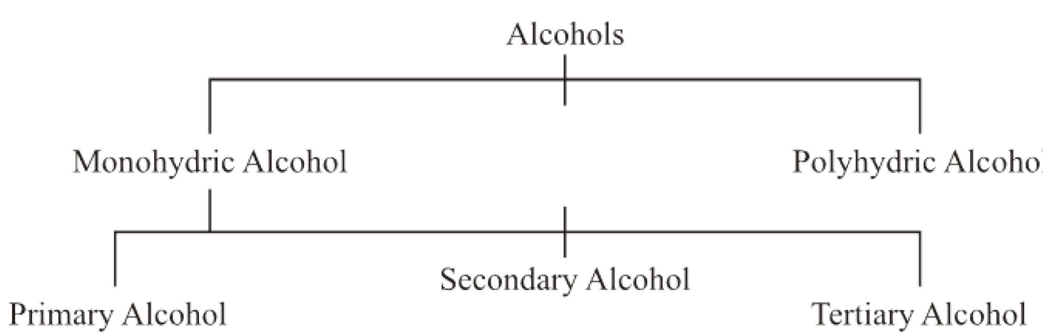
Alcohol and phenol both have — OH in them. Alcohol is called hydroxyl derivative of alkane while phenol is hydroxyl derivative of benzene. In ether both hydrogen of water are replaced by alkyl or aryl group.

## 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.,*

$$\begin{array}{c} \quad OH \\ \quad | \\ CH_3—CH—CH_3 \end{array} \qquad \begin{array}{c} OH \qquad\qquad \\ | \qquad\qquad \\ CH_3—CH—CH_2—CH_3 \end{array}$$

(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.,*

$$\begin{array}{c} CH_3 \\ | \\ CH_3—C—OH \\ | \\ CH_3 \end{array}$$

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.

$$\begin{array}{cc} CH_2 & —CH_2 \\ | & | \\ OH & OH \end{array} \qquad \begin{array}{ccc} CH_2 & —CH & —CH_2 \\ | & | & | \\ OH & OH & OH \end{array} \qquad \begin{array}{cccccc} CH_2 & —CH & —CH & —CH & —CH & —CH_2 \\ | & | & | & | & | & | \\ OH & OH & OH & OH & OH & OH \end{array}$$

1,2 Ethanediol (Ethylene glycol) 1,2,3, Propanetriol (Glycerine or Glycerol) (Mannitol)

There are two methods for naming alcohols.

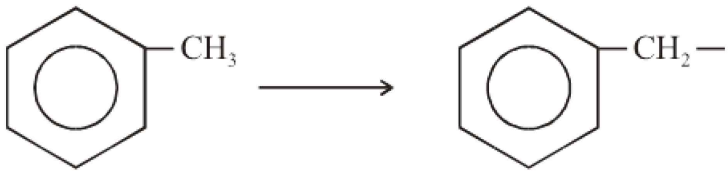
**(a) Common or Trivial Names:**

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;

| $CH_3 — OH$ | $C_2H_5 — OH$ | $CH_3 — CH_2 — CH_2 — OH$ |
|---|---|---|
| (Methyl Alcohols) | (Ethyl Alcohols) | (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

```
        CH3          OH
        |            |
CH3 — CH — CH2 — CH — CH3
```
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,

```
CH2 — CH2
|      |
OH     OH
```
1,2 Ethanediol

```
CH2 — CH — CH2
|      |     |
OH     OH    OH
```
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.,

$$\overset{4}{C}H_3-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_2OH \qquad\qquad CH_2=CH-CH_2-OH$$

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;

$$\overset{3}{C}H_3-\underset{}{\overset{OH}{\overset{|}{C^2H}}}-\overset{1}{C}OOH \qquad\qquad \begin{array}{c} HO-CH-COOH \\ | \\ HO-CH-COOH \end{array}$$

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 |
| $(CH_3)_2CH-OH$ | iso-propyl alcohol | 2-Propanol |
| $CH_3-CH_2-CH_2-CH_2-OH$ | n-Butyl alcohol | 1-Butanol |
| $CH_3-\underset{CH_3}{\underset{\mid}{CH}}-CH_2-OH$ | iso-butyl alcohol | 2-Methyl-1-propanol |
| $CH_3-CH_2-\underset{CH_3}{\underset{\mid}{CH}}-OH$ | sec-butyl alcohol | 2-Butanol |
| $(CH_3)_3C-OH$ | ter-butyl alcohol | 2-Methyl-2-propanol |
| $(CH_3)_3C-CH_2-OH$ | Neo-pentyl alcohol | 2,2-Dimethyl-1-propanol |

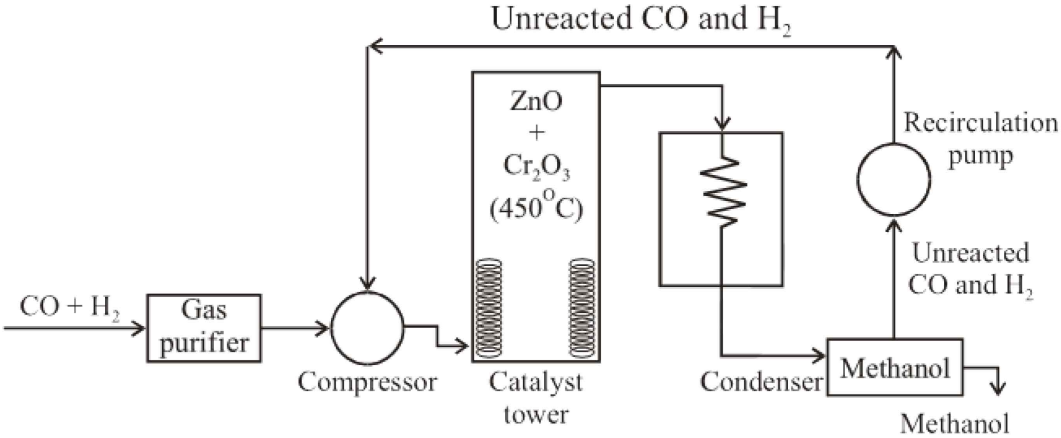
# INDUSTRIAL PREPARATION OF ALCOHOLS

**(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.

$$CO + 2H_2 \xrightarrow[450^{o}C:\ 200atm]{ZnO + Cr_2O_3} CH_3\ OH$$




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".

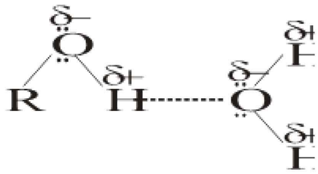
Methanol is toxic to humans, causing blindness in low dose (15 $cm^3$) and death in larger amount (100 – 250 $cm^3$).

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

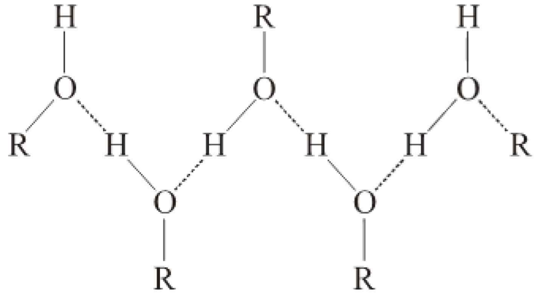
## PHYSICAL PROPERTIES

(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.



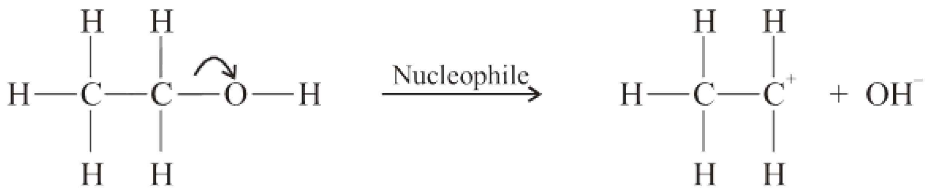
(3) Melting and boiling points of alcohols are higher than corresponding alkanes. Methyl alcohol and ethyl alcohol are liquids while methane and ethane are gases. This is also due to hydrogen bonding which is present in alcohols but absent in alkanes.



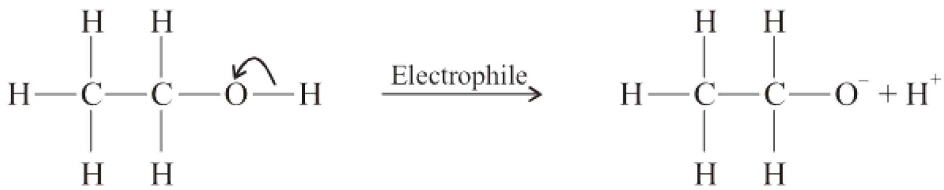
## REACTIONS OF ALCOHOLS

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:**

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

$C_2H_5OH + \overset{\delta-}{C}H_3\overset{\delta+}{Mg}I \longrightarrow CH_4 + Mg\begin{matrix} \diagup I \\ \diagdown OC_2H_5 \end{matrix}$

**(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 $\xrightarrow{\text{Oxi}}$ Aldehyde $\xrightarrow{\text{Oxi}}$ Carboxylic Acid

Secondary Alcohol $\xrightarrow{\text{Oxi}}$ Ketone

**(i) Oxidation of Primary Alcohol:**

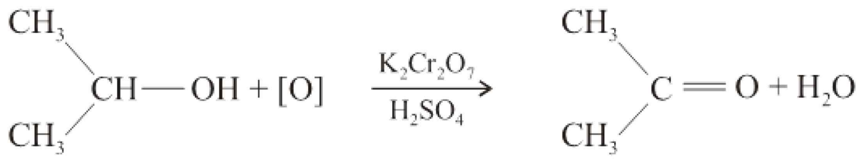
$$CH_3 - CH_2OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - CHO + H_2O$$

Ethanol Ethanal

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

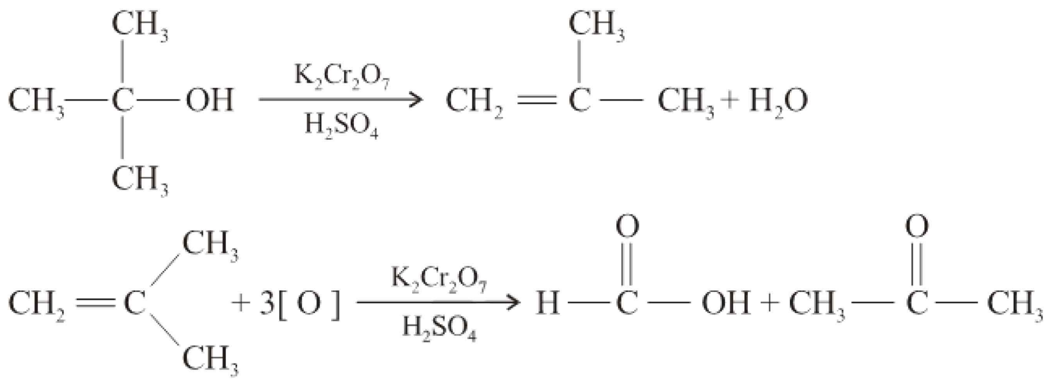
Ethanal Ethanoic Acid

**(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.

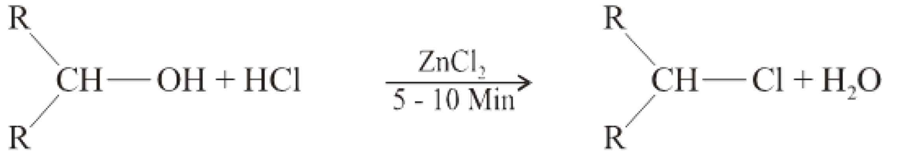
(i) Tertiary alcohols form an oily layer immediately.

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

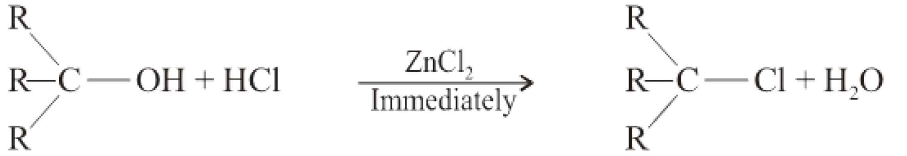
(iii) Primary alcohols form an oil layer only on heating only.

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

**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.

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

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

## 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.

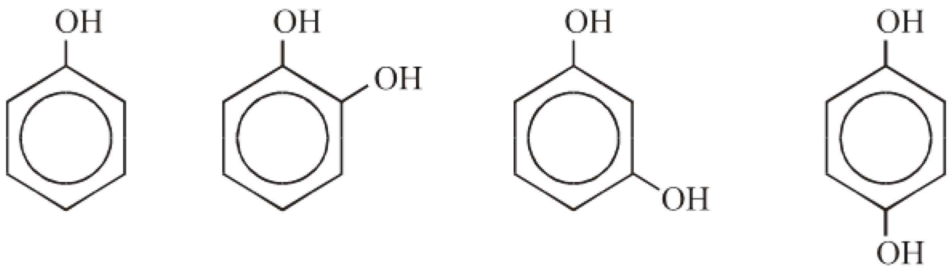
(4) It is used in pharmaceutical preparation and as a preservative for biological specimen.

(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.

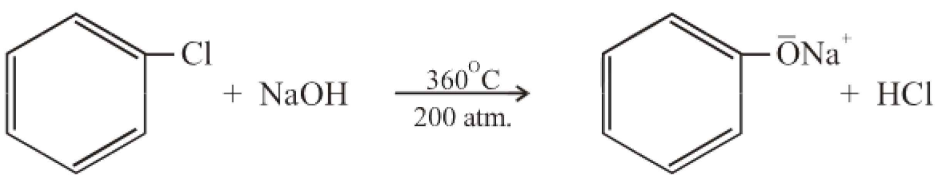



Phenol | Catechol (o-Dihydroxy benzene) | Resorcinol (m-Dihydroxy benzene) | Hydroquinone (m-Dihydroxy benzene)

# PREPARATION OF PHENOL

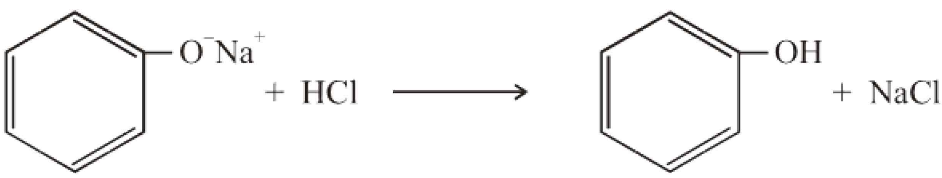
**(1) From Chlorobenzene (Dow's Process):**

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




Chlorobenzene    Sodium Phenoxide

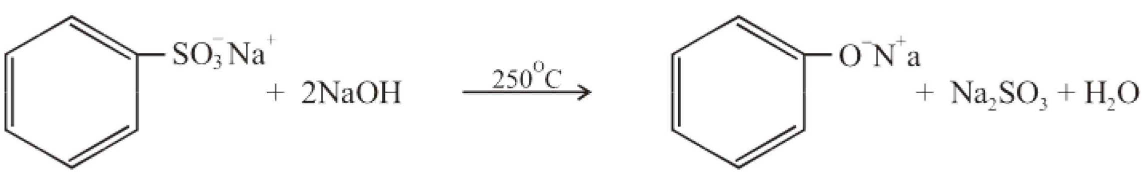
Sodium phenoxide is converted to phenol by treating it with hydrochloric acid.




Phenol

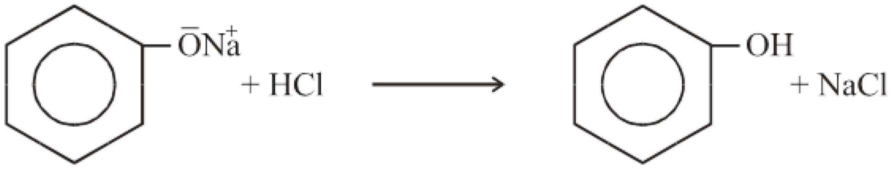
**(2) Fusion of Sodium Benzenesulphonate with NaOH:**

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.

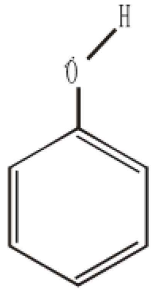
**Reactions of Phenol:**

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.



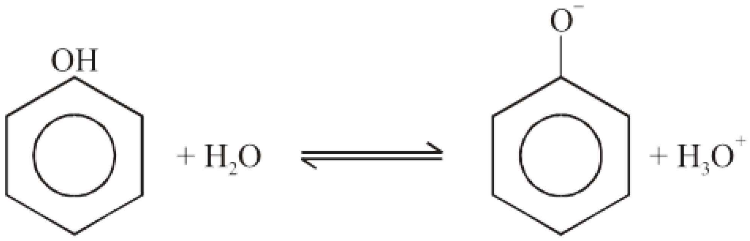
Phenols are less reactive to nucleophile so nucleophilic attack is less favoured i.e. OH is not easy to replace while electrophilic attack on the ring is easy.

## ACIDITY OF PHENOL

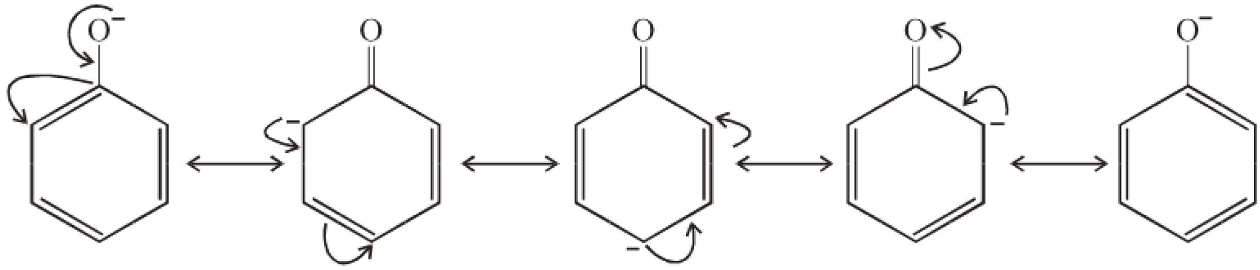
(1) Phenol is less acidic than carboxylic acids and more acidic than alcohols. It is partially soluble in water but highly soluble in a alkali like NaOH.

(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 $1.3 \times 10^{-10}$ and pH of solution is between 5 to 6. It dissociates as.



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.



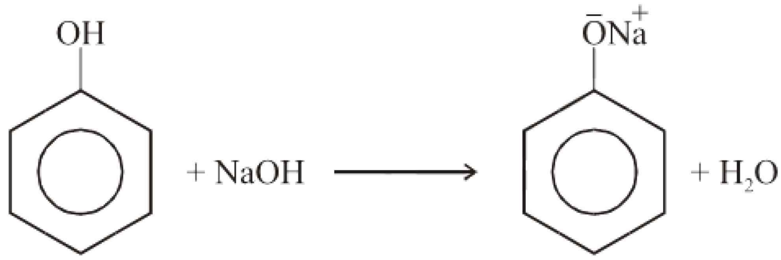
Relative acidic strength of alcohol, phenol, water and carboxylic acid is as follows:

Carboxylic acid > Phenol > Water > Alcohol

## (a) Reaction of Phenol Due to OH Group:

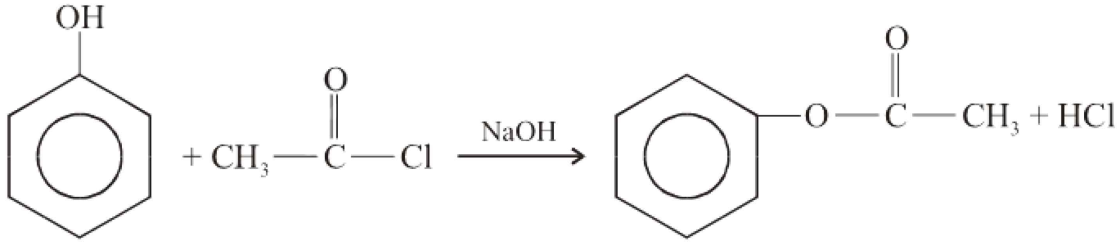
### (1) Salt Formation:

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



### (2) Ester Formation:

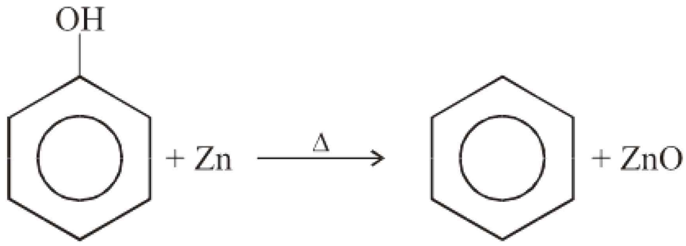
Phenol reacts with acetyl chloride in the presence of a base to form an ester.



(Acetyl chloride) Phenyl Acetate (Ester)

### (3) Reaction with Zinc:

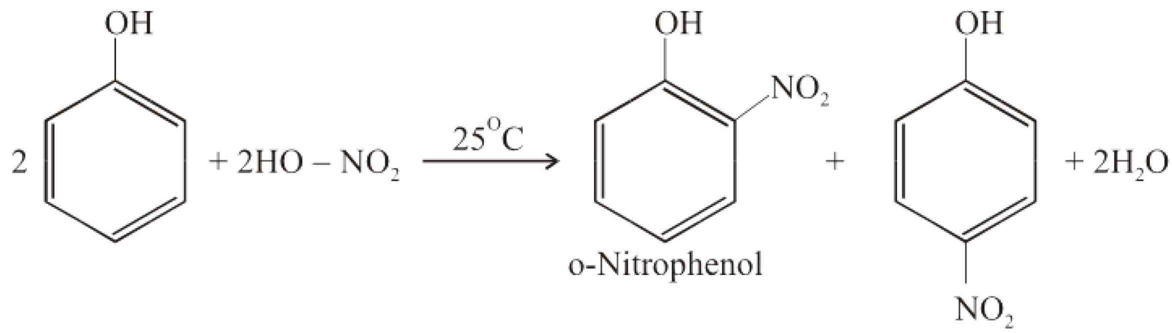
Phenol is reduced to benzene when reacts with Zinc dust.



## (b) Reaction Due to Benzene Ring:

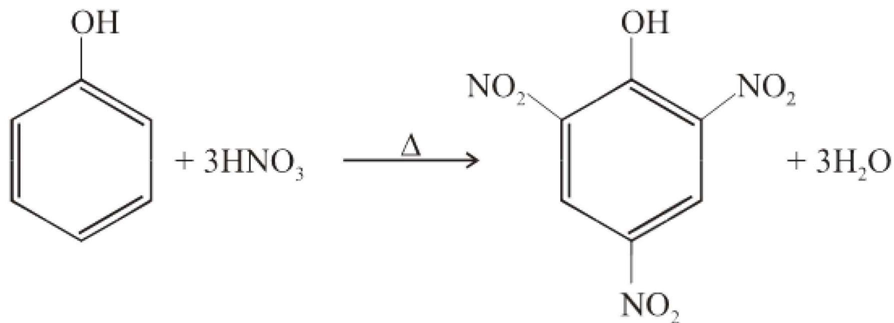
### (1) Nitration:

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




o-Nitrophenol

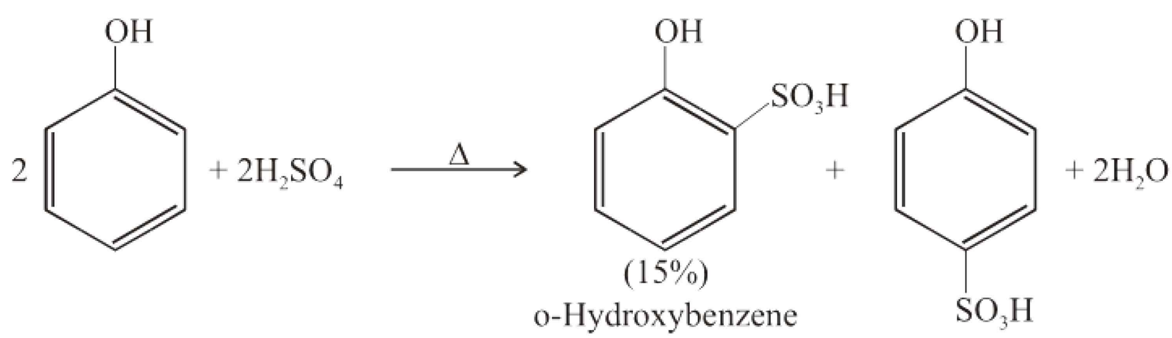
p-Nitrophenol




2, 4, 6-Trinitrophenol
(Picric Acid)

### (2) Sulphonation:

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

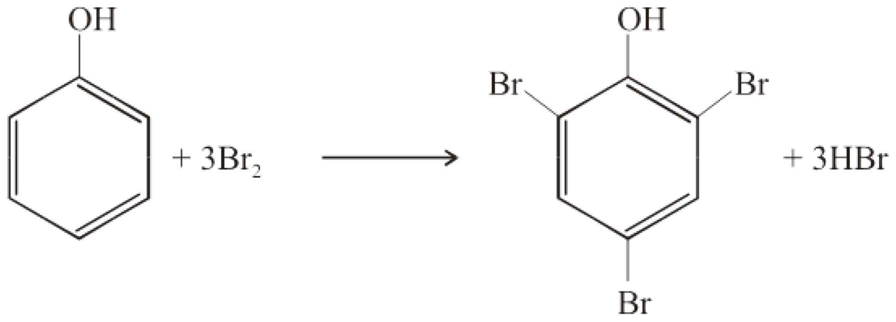



(15%)
o-Hydroxybenzene sulphonic acid

(85%)
p-Hydroxybenzene sulphonic acid

**(3) Halogenation:**

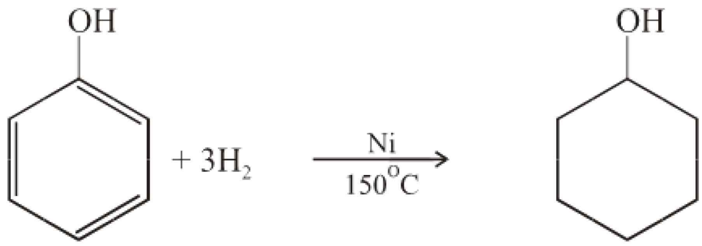
Aqueous solution of phenol reacts with bromine water to give white ppt. of 2, 4, 6 tribromophenol.




2, 4, 6-Tribromophenol

**(4) Hydrogenation:**

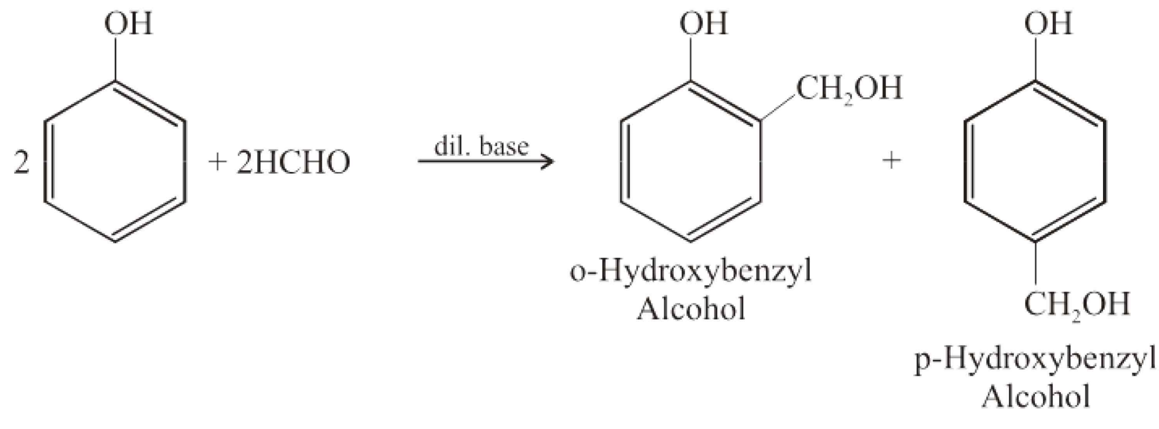
When hydrogen is passed through phenol at 150°C in the presence of Ni catalyst it gives cyclohexanol.

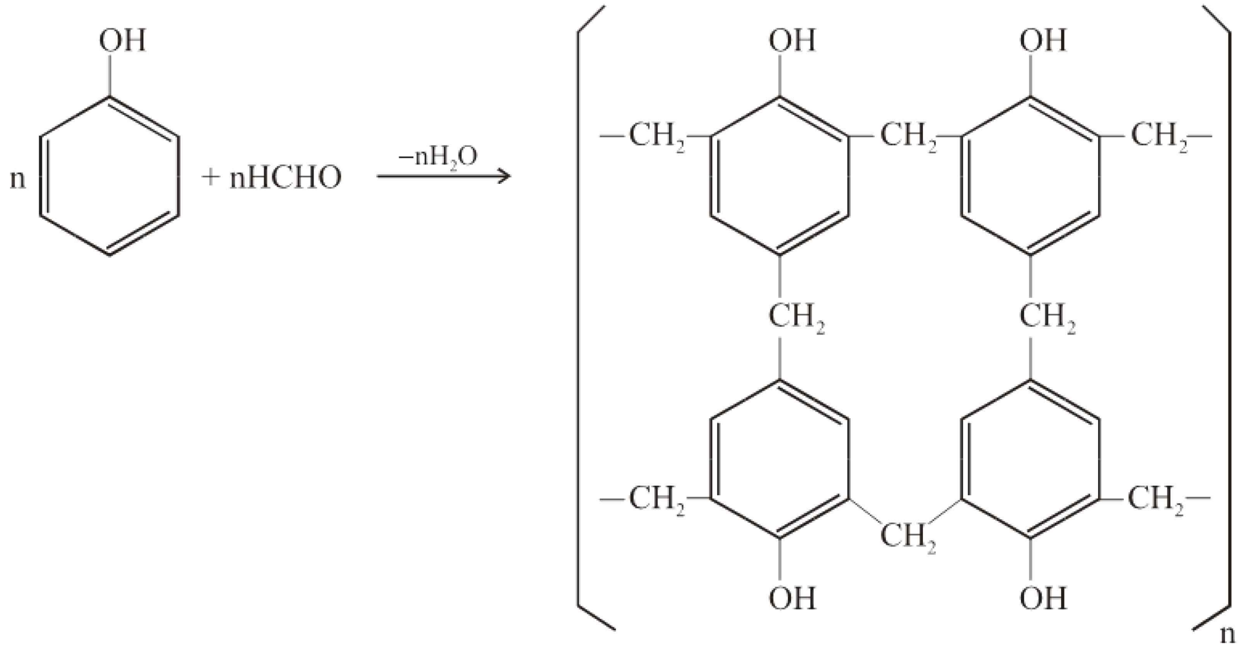



Cyclohexanol

**(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.






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:**

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

(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.

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

(Oxonium ion)

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

$$C_2H_5OH + Hl \longrightarrow C_2H_5l + H_2O$$

***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.