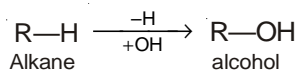


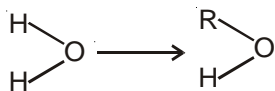
# Alcohol

## 1. Fundamentals of The Subject :

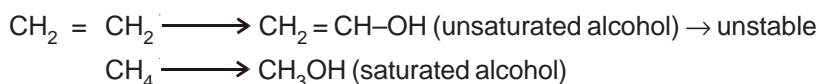
The hydroxy derivatives of alkanes are called alcohols.



or Alcohols are monoalkyl derivative of water



or Alcohols are hydroxy derivative of hydrocarbon

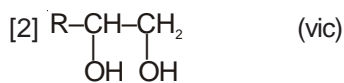
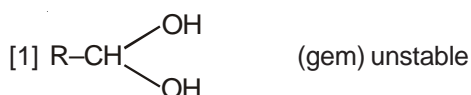


## 2. Classification :

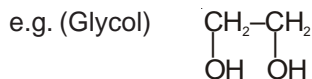
Alcohols are classified according to the Number of 1, 2, 3 or more hydroxy group (-OH) present in the molecule - as

➤ **Monohydric alcohol**  $\longrightarrow$  **R-OH** (one -OH gp)

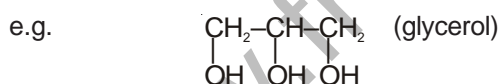
➤ **Dihydric alcohol** -



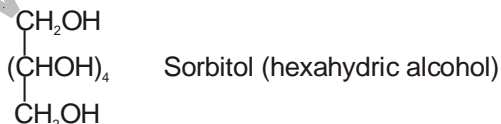
(Two -OH gps.)



➤ **Trihydric alcohol** - (three -OH gps.)



➤ **Polyhydric alcohol** - Containing more than three -OH gp. e.g. Sorbitol

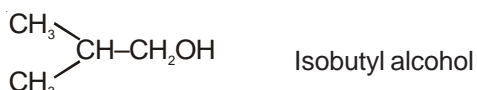
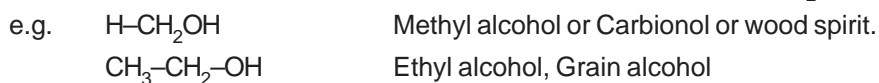


## 3. Monohydric Alcohols :

➤ General formula  $\text{C}_n\text{H}_{2n+1}\text{OH}$  or  $\text{C}_n\text{H}_{2n+2}\text{O}$

➤ Monohydric alcohols are further classified as :

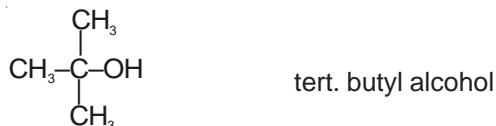
[a] **Primary alcohols** : -OH group attached on  $1^\circ$  carbon atom (gp.  $-\text{CH}_2\text{OH}$ )



[b] **Secondary alcohol** : -OH gp. attached on 2<sup>o</sup> carbon atom (gp. >CH-OH)

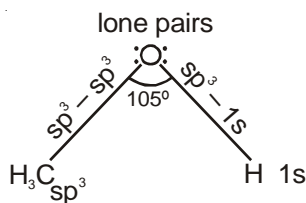


[c] **Tertiary alcohol** : -OH group attached on 3<sup>o</sup> carbon atom, gp.  $\Rightarrow\text{C}-\text{OH}$



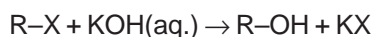
#### 4. Structure of Alcohol :

Alcohols are bent molecules. The carbon atom (linked with 'O' atom of -OH gp.) is sp<sup>3</sup> hybridised. The central 'O' atom is also in sp<sup>3</sup> state of hybridisation. The bond angle is 105°.



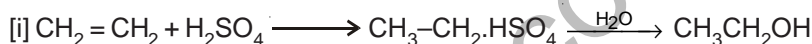
#### 5. General Method of Preparation :

[a] **By the hydrolysis of alkyl halide** : It is a nucleophilic substitution reaction,

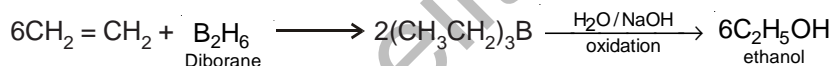


\* Aqueous NaOH or KOH favours substitution. Alcoholic NaOH or KOH favours elimination.

[b] **Hydration of Alkenes** : It is an electrophilic addition of H<sub>2</sub>O.

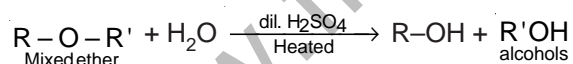


[ii] Hydroboration of alkenes :

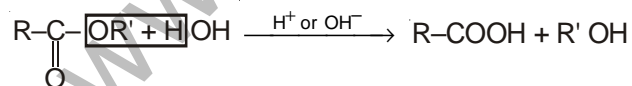


The net result of this reaction is hydration of an alkene against Markownikoff's rule.

[c] **By the hydrolysis of ethers** :

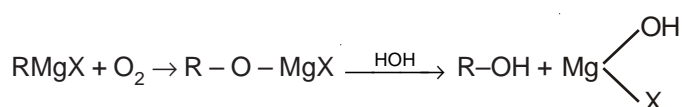


[d] **By the hydrolysis of esters** :

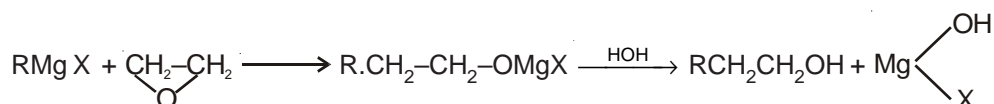


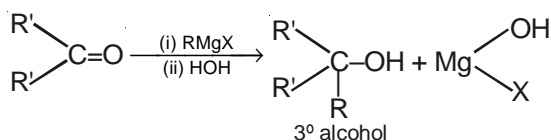
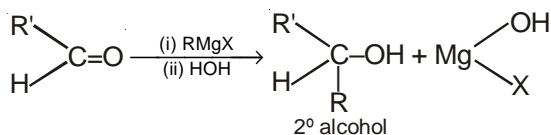
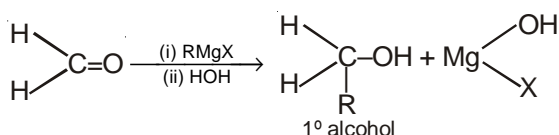
[e] **By Grignard reagent** : All the three types of alcohols (Pr., Sec. & Tert.) can be prepared by this method.

[I] **With Oxygen** :

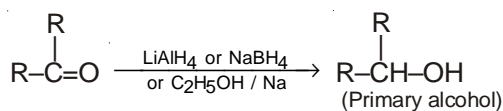


[II] **With epoxide** :

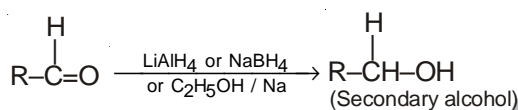


**[iii] With carbonyl compounds :****[f] By the reduction of Carbonyl Compounds :**

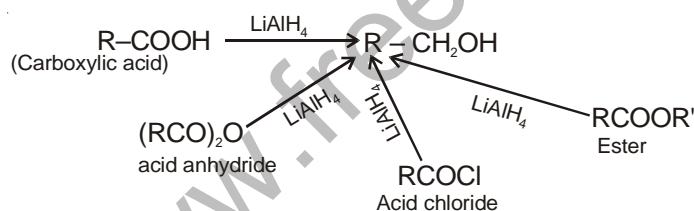
Reduction of aldehyde gives → primary alcohol



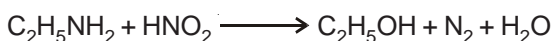
Reduction of ketones gives → Secondary alcohol



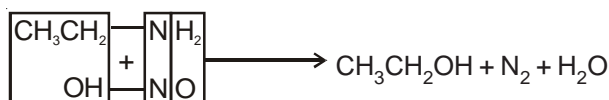
tertiary alcohols can not be obtained by reduction.

**[g] By reduction of carboxylic acids and their derivatives :**

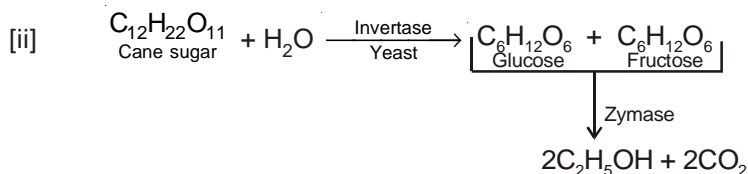
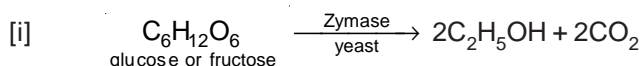
\* Reduction of RCOOR' also give R'-OH with RCH<sub>2</sub>OH

**[h] By the action of nitrous acid on primary amine :**

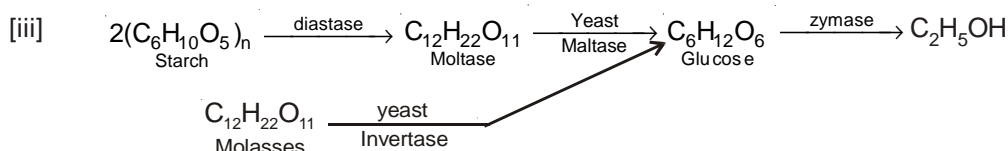
The reaction can be explained as :



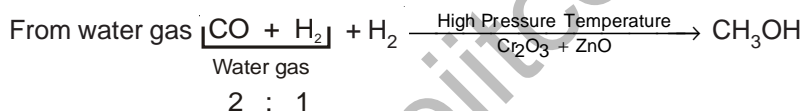
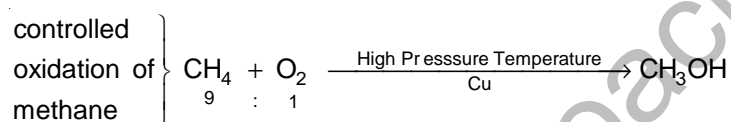
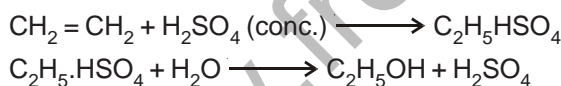
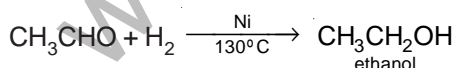
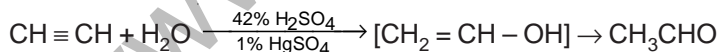
\* But CH<sub>3</sub>NH<sub>2</sub> give CH<sub>3</sub>OCH<sub>3</sub> as a major product with HNO<sub>2</sub>.

**[i] By fermentation of sugar :**

Fermentation is the slow decomposition of complex organic compounds into smaller compounds by the activity of enzymes.

**Favourable conditions for fermentation are :**

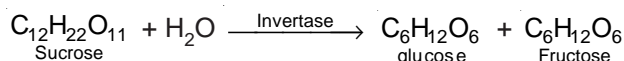
- \* Poptimum temp. 25° – 30°C. At high temp. enzymes get inactivated.
- \* Solution should be dilute
- \* Proper aeration should be maintained in fermentation.

**[j] Methanol can also be prepared as :****[k] Manufacture of ethanol :****[i] From ethylene :****[ii] From Acetylene :****[iii] From fermentation of molasses and starchy materials :****\* Fermentation :**

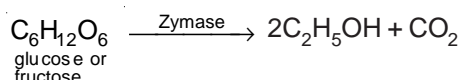
- [i] It is defined as the slow break down of complex organic compound into simpler ones.
- [ii] It is an exothermic reaction.
- [iii] Fermentation takes place in the presence of enzymes.
- [iv] In this process we take yeast cells (living organism containing complex, nitrogenous substances)
- [v] Yeast cell generally contain invertase, Maltase, Zymase, enzymes.

**[A] Preparation of wash from Molasses :**

- [i] 10% to 15% Ethyl alcohol is called wash.
- [ii] Molasses is the waste product obtained after getting cane sugar crystal.
- [iii] Molasses contain 30% cane sugar (sucrose) and 32% invert sugar (mixture of glucose and fructose)
- [iv] Molasses is diluted with water to make about 10% sugar solution.
- [v] In above solution, a small amount of  $(\text{NH}_4)_2\text{SO}_4$  and some yeast cells are added. Here  $(\text{NH}_4)_2\text{SO}_4$  is used as a food for yeast cells.
- [vi] The above solution is taken in large fermentation tank. The temp. of this tank is maintained at about 25 to 35°C.
- [vii] The fermentation takes place and alcohol is formed within 3 to 5 days.
- [viii] The enzyme invertase present in yeast cells converts sucrose to invert sugar.



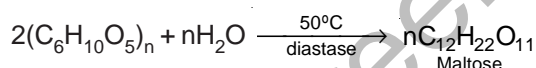
- [ix] the other enzyme zymase converts invert sugar to alcohol



- [x] The alcohol obtained in above method is called as **WASH**.

**[B] Preparation of WASH from starch :**

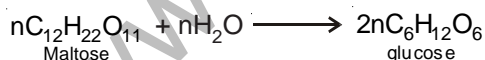
- [i] Wash is obtained from starchy material like rice, potatoes, corn etc.
- [ii] The molecular formula for starch is  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$
- [iii] Starchy materials are heated in superheated steam under pressure at about 140–150°C. The cell walls are ruptured exposing the starch granules producing milky wash. This soln. is called as **Mashing**.
- [iv] Moist barley seeds are spreaded in a dark room, temp is maintained at about 15°C for germination. After 2 or 3 days the temp. of room is raised to 60°C to stop the germination. These germinated barley seeds are technically called as **MALT**. Malt contains an enzyme called as **Diastase**.
- [v] The malt is added to above Mashing solution. The enzyme diastase present in MALT hydrolyses starch to maltose soln. The temp. of this soln. is maintained at about 50°C. The process is called as saccharification.



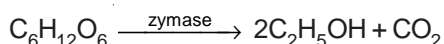
The sweet solution of maltose is called **WORT**.

**[vi] Fermentation of wort solution :**

In above maltose solution yeast cells are added. The temp. is maintained at about 25 to 35°C. The enzyme maltase present in yeast cells hydrolyses maltose to glucose.



The other enzyme zymase present in yeast cells decomposes glucose to  $\text{C}_2\text{H}_5\text{OH}$ .



- [vii] The alcohol obtained in above method is called as **WASH**.

**\*\* Preparation of Raw spirit from WASH**

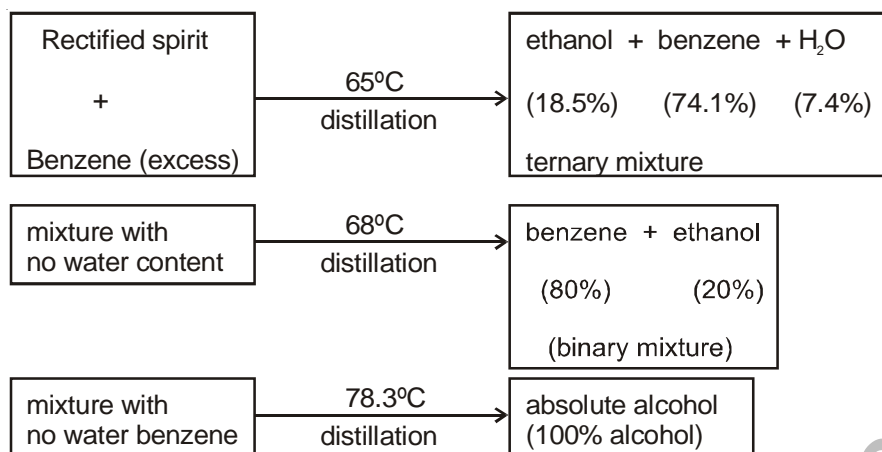
- [i] Wash is now subjected to distillation in Coffey's stills.
- [ii] The alcohol obtained by above method is called as **Raw spirit**. It contains 90% alcohol

**\*\* Preparation of Rectified spirit from Raw spirit :**

Raw spirit  $\xrightarrow{\text{distillation}}$  Rectified spirit (95.5% ethanol)

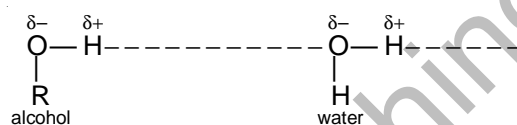
**\*\* Preparation of absolute alcohol from rectified spirit.**

## AZEOTROPIC DISTILLATION

6. **Properties :** Volatile, toxic & inflammable.

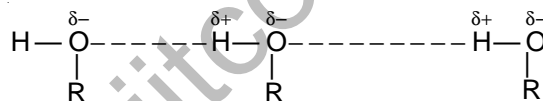
\* Lower alcohols (C<sub>1</sub> – C<sub>11</sub>) are colourless liquid but higher (C<sub>12</sub> & above) are solids.

\* Lower alcohols are soluble in water due to H-bonding.



but solubility falls with rise in molecular wt. as hydrocarbon character of molecule increases.

\* Alcohols have high B.P. than parent alkane, it is due to association of alcohol molecules with H-bonding

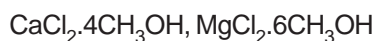


Among isomeric alcohols the decreasing order of M.P. & B.P. is :

pr. alcohol > sec. alc. > tert. alc.

\* Alcohol are neutral substance

thus the alcohols are weaker acid than water, lower alcohols gives solid addition comps. with anhydrous metallic salts like – CaCl<sub>2</sub> & MgCl<sub>2</sub>.



So CaCl<sub>2</sub> can not be used as drying agent of alcohols.

7. **Chemical Properties :**

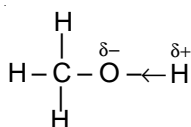
In alcohols the chemical properties are due to hydroxyl gp. (–OH),

\* So in alcohols the reaction may occurs in three ways – as follows –

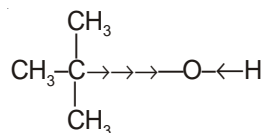
- Reaction involving cleavage of O–H bond i.e. involving only H atom.
- Reaction involving –OH gp as a whole i.e. cleavage of C–OH bond.
- Reaction involving complete molecule of alcohol.

7.1 **Reaction Involving Cleavage of O–H Bond :**

Such reaction involving replacement of H-atom of –OH gp. represent Bronsted acid nature of alcohols. Its decreasing order is – Methyl alcohol > 1° > 2° > 3° alcohols.



(Partial ionic character of  $\overset{\delta-}{\text{O}}-\overset{\delta+}{\text{H}}$ )



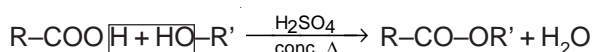
Due to +I effect of  $\text{CH}_3$  gps. -ve charge on O-atom increases and hence tendency to release H-atom decreases.

[1] **Action of active metals :** (Strong electropositive metals like Na, K, Ca & Mg)–

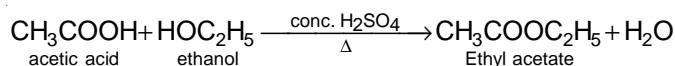


R-ONa (Alkoxides) are not organometallic compounds.

[2] **Esterification :** (Reaction with Carboxylic acids) :



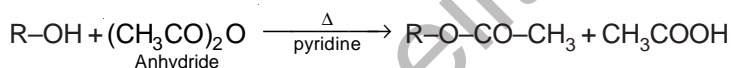
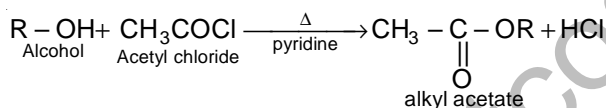
conc.  $\text{H}_2\text{SO}_4$  is used as catalyst as well as dehydrating agent.



Rate of reaction decreases on increasing size of alkyl group (steric effect). Decreasing order is :



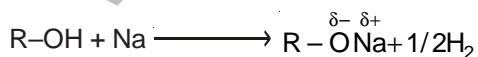
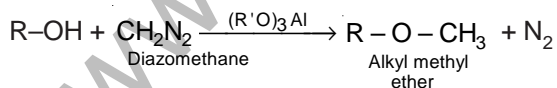
[3] **Acetylation (Reaction with acetyl chloride and acetic anhydride)** – H(of-OH) replaced by  $\text{CH}_3\text{CO}$ -gp.



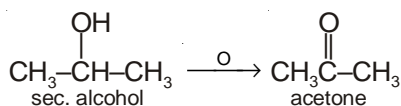
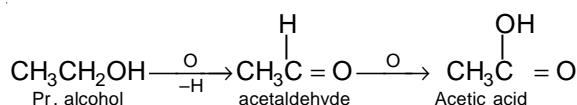
[4] **Action of Grignard's reagent – (Alkane is formed)**



[5] **Replacement of H by alkyl groups :**



[6] **Oxidation :** Into aldehydes and ketons depending upon the alcohol.

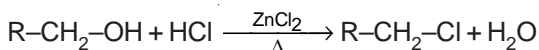


## 7.2 Reaction Involving –OH bonds as the whole i.e. cleavage of C–OH Bond :

The –OH gp. of alcohol having two lone pair of e<sup>-</sup> behaves as Lewis base. The reactivity order of the alcohols is (Basic nature) tert. > sec. > pr.

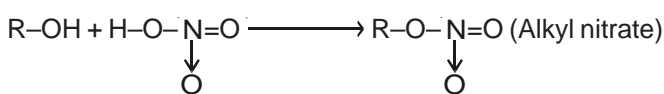
In tert. alcohol –ve charge on O–atom increases due to + I effect of three –CH<sub>3</sub> gps. This increases the tendency of O–atoms to donate electron pair or to show cleavage of C–O bond.

### [1] Action of halogen acids :

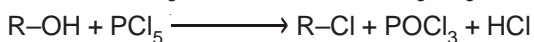


Reactivity of the acids is HI > HBr > HCl > HF

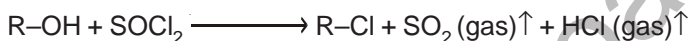
### [2] Reaction with inorganic acids :



### [3] Action of phosphorous halides :



### [4] Reaction with thionyl chloride (SOCl<sub>2</sub>) :



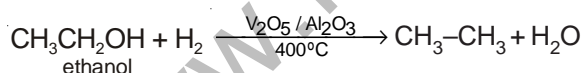
### [5] Reaction with NH<sub>3</sub> :



### [6] Reaction with halogens : Oxidation and chlorination takes place simultaneously :



### [7] Reduction :

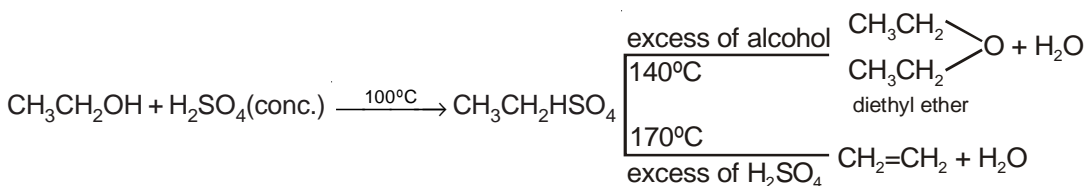


## 7.3 Reaction Involving Complete Molecule of Alcohol :

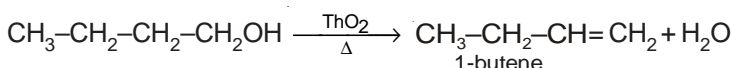
### [1] Dehydration : (Removal of H<sub>2</sub>O)

[i] Intermolecularly removal of H<sub>2</sub>O → form ether

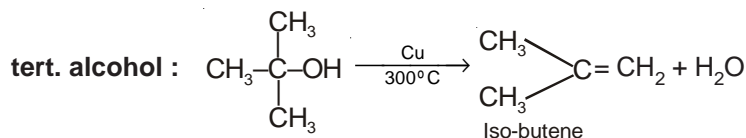
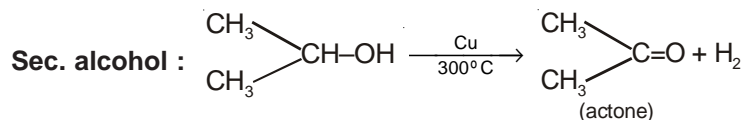
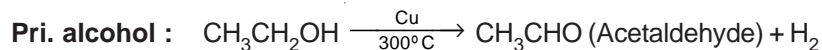
[ii] Intramolecularly removal of H<sub>2</sub>O → form alkene



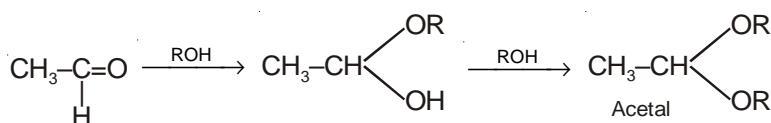
ease of dehydration follows the order : tert. > sec. > pr.





**[2] Dehydrogenation :**

So this reaction is useful in distinction of pr. sec. & tert. alcohols.

**[3] Acetal formation :****8. Uses :**

[i] In beverage industry

[ii] As fuel-spirit lamp

[iii] As antiseptic – spirit

[iv] As solvent for medicine

[v] As an antifreeze

**9. Distinction Between Pr., Sec. & Tert. Alcohols :**

**9.1 Lucas test :** a mixture of  $\text{HCl}_{(\text{conc.})}$  and anhydrous  $\text{ZnCl}_2$  is called Lucas reagent.

Primary alcohol  $\xrightarrow{\text{ZnCl}_2 + \text{HCl}}$  No turbidity at room temp.

Secondary alcohol  $\xrightarrow{\text{ZnCl}_2 + \text{HCl}}$  Turbidity appear in cold after 5–10 minute

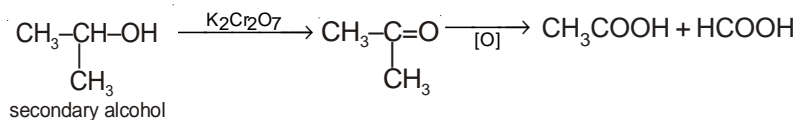
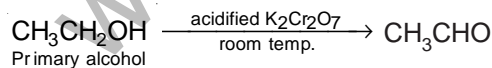
Tertiary alcohol  $\xrightarrow{\text{ZnCl}_2 + \text{HCl}}$  turbidity comes immediately

**9.2 Catalytic dehydrogenation :**

Primary alcohol  $\xrightarrow[300^\circ\text{C}]{\text{Cu}}$  aldehydes +  $\text{H}_2$

Sec. alcohol  $\xrightarrow[300^\circ\text{C}]{\text{Cu}}$  ketones +  $\text{H}_2$

Tert. alcohol  $\xrightarrow[300^\circ\text{C}]{\text{Cu}}$  Alkene +  $\text{H}_2\text{O}$

**9.3 Oxidation test :**

tert. alcohol  $\longrightarrow$  No change [due to no oxidation]

**9.4 Victor – meyer test :** This is colour test for alcohol (pri. sec, & tert.)

Pr. alcohol  $\longrightarrow$  Red colour

sec. alcohol  $\longrightarrow$  Blue colour

tert. alcohol  $\longrightarrow$  No colour

In this test, primary, secondary or tertiary alcohols are first changed into their respective nitro alkanes, which gives different colours on reacting with Nitrous acid.

Primary alcohol	Secondary alcohol	Tertiary alcohol
$\text{CH}_3 - \text{CH}_2 - \text{OH}$	$\text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \text{CH}_3$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\   \\ \text{OH} \end{array}$
$\downarrow P / I_2$	$\downarrow P / I_2$	$\downarrow P / I_2$
$\text{CH}_3 - \text{CH}_2 - \text{I}$	$\text{CH}_3 - \underset{\text{I}}{\text{CH}} - \text{CH}_3$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\   \\ \text{I} \end{array}$
$\downarrow \text{AgNO}_2$	$\downarrow \text{AgNO}_2$	$\downarrow \text{AgNO}_2$
$\text{CH}_3 - \text{CH}_2 - \text{NO}_2$	$\text{CH}_3 - \underset{\text{NO}_2}{\text{CH}} - \text{CH}_3$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\   \\ \text{NO}_2 \end{array}$
$\downarrow \text{HNO}_2$	$\downarrow \text{HNO}_2$	$\downarrow \text{HNO}_2$
$\begin{array}{c} \text{CH}_3 - \text{C} - \text{NO}_2 \\    \\ \text{N} - \text{OH} \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \text{NO}_2 \\   \\ \text{N} = \text{O} \end{array}$	No reaction
Nitrolic acid	Pseudonitrol	$\downarrow \text{NaOH}$
$\downarrow \text{NaOH}$	$\downarrow \text{NaOH}$	Colour less solution
Sod. Salt of nitrolic acid	Blue colour solution	
Blood red colour		

#### 10. Important Facts about Alcohols :

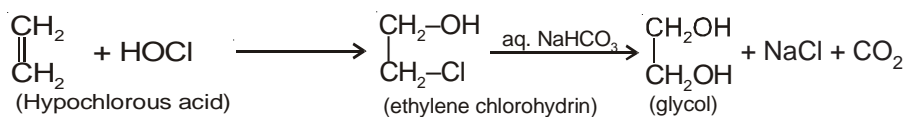
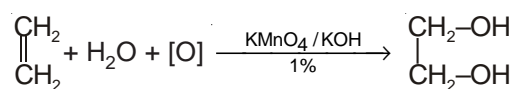
- [1] Toxicity  $\rightarrow$  ethyl alcohol < Iso propyl alcohol < methyl alcohol
- [2] Alcohol contents in drinks :  
Whisky = Rum = Brandy > Undistilled > Beer < Cidar  
35 – 40%      8 – 10%      3–6%      2–6%
- [3] **Rectified spirit** – The content obtained after rectification of fermented liquid.
- [4] **Absolute alcohol** – Ethyl alcohol – 99.5% – 100%
- [5] **Power alcohol** – Rectified spirit +  $\text{C}_6\text{H}_6$  + Petrol for generation of power
- [6] **Methylated spirit** – Methanol + Pyridine + mineral naphtha + Rectified spirit.
- [7] **Proof spirit (P.S.)** the % of alcohol is expressed in term of proof spirit is a mix. of ethanol and  $\text{H}_2\text{O}$  containing 57.1% alcohol by volume.  
–10% under proof means, 100 volume of sample containing 90 volume of P.S.  
–10% over proof means 100 vol. of sample containing 100 volume of P.S.  
–A sample is called over or under proof as it is stronger or weaker than proof spirit.
- [8] 70%  $\text{CH}_3\text{OH}$  is known as **wood spirit**.
- [9] 90%  $\text{C}_2\text{H}_5\text{OH}$  is known as **Raw spirit**.
- [10]  $\text{C}_2\text{H}_5\text{OH}$  is technically called **WASH**.
- [11] **Rectified spirit** contains 95.5% alcohol and 4.5%  $\text{H}_2\text{O}$ .
- [12] **Azeotropic rectified spirit** is known as Azeotrope. It boils at  $78.15^\circ\text{C}$

**DIHYDRIC AND POLYHYDRIC ALCOHOL**

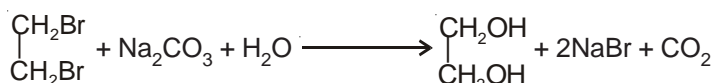
11. **Ethylene Glycol** : (or glycol, 1, 2–ethanediol  $\text{CH}_2\text{OH}.\text{CH}_2\text{OH}$ ) a dihydric alcohol.

11.1 **Preparation** :

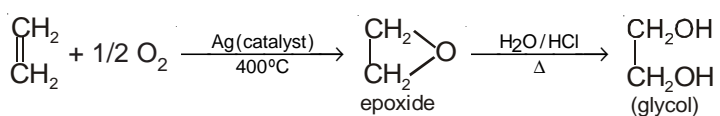
[a] **From ethylene** :



[b] **From ethylene bromide – (Laboratory method)**



[c] **Industrial method** :

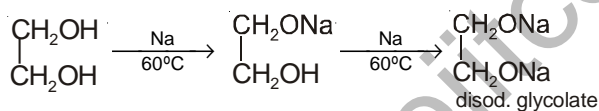


11.2 **Properties** – Colourless, viscous, sweet taste, liquid.

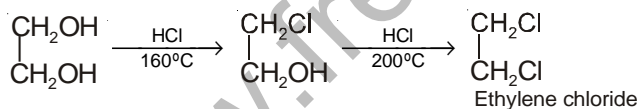
–soluble in water, insoluble in ether.

–B.P.  $197^\circ\text{C}$ .

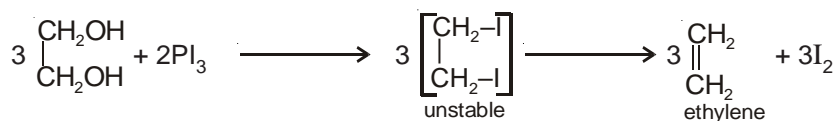
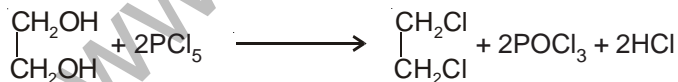
[1] **Reaction with Na** :



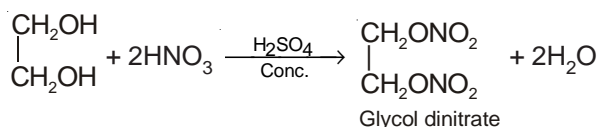
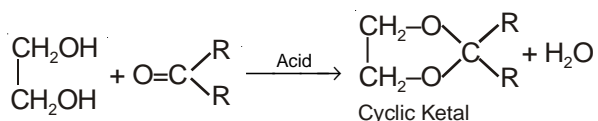
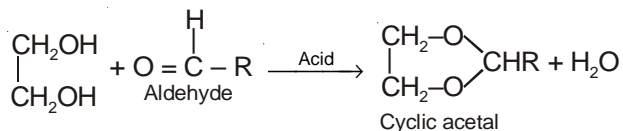
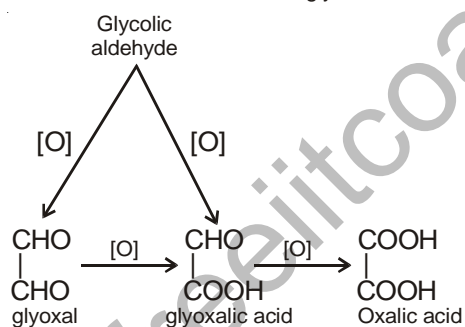
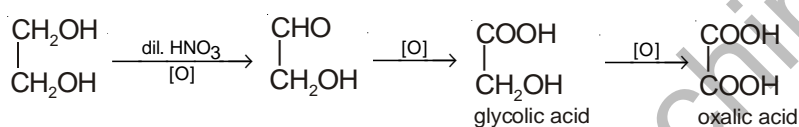
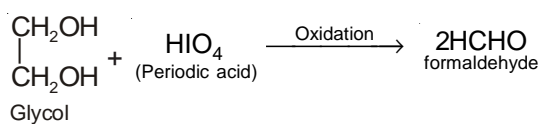
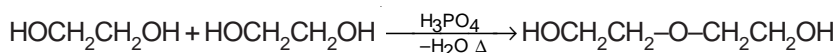
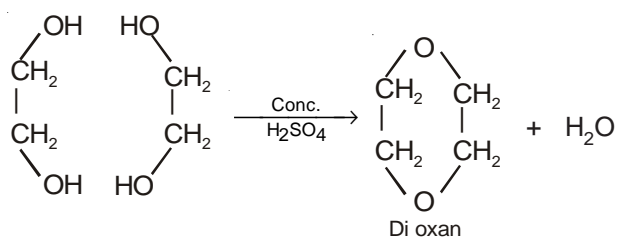
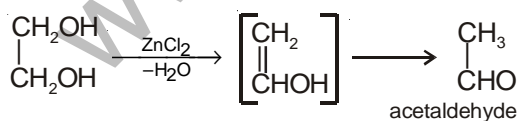
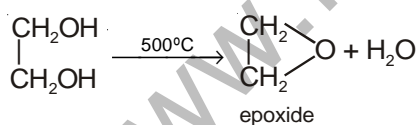
[2] **Reaction with HCl** :



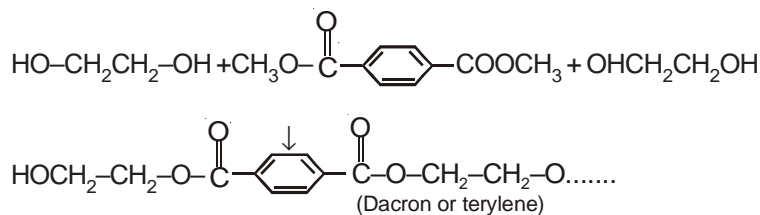
[3] **Reaction with phosphorus halides** :



ethylene iodide is unstable due to big size of Iodine.

**[4] Reaction with  $\text{HNO}_3$  :****[5] Reaction with Aldehyde & Ketone :****[6] Oxidation :****[7] Dehydration :**

[8] **Condensation** : With dimethyl terephthalate gives polymer Dacron or terylene



11.3 **Uses :**

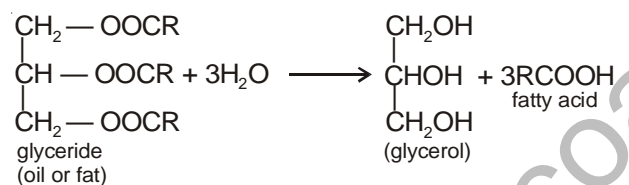
- For making glycol dinitrate (Explosive) dioxan (solvent)
- For making terylene fibre.
- As an antifreeze.

12. **Glycerol** : (glycerine, 1, 2, 3 propantriol)

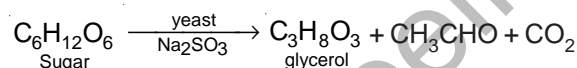
- It is trihydric alcohol.
- It contain two primary and one secondary alcoholic group.
- It is the most viscous liquid.
- It decompose on heating at its B.P. hence purified by vaccum distillation.
- It is found in animal and vegetable fats and oils, which are triesters of glycerol with higher fatty acids.

12.1 **Preparation :**

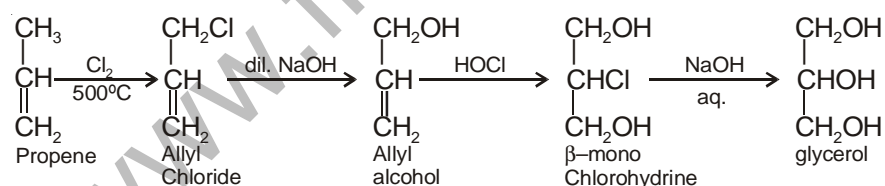
[1] **From fats and oils** : by hydrolysis



[2] **By fermentation of sugars :**



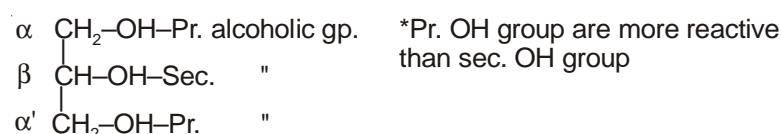
[3] **From propene (Synthesis) :**

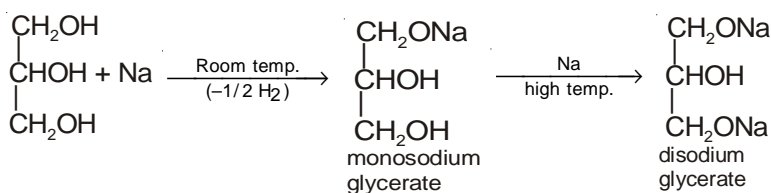
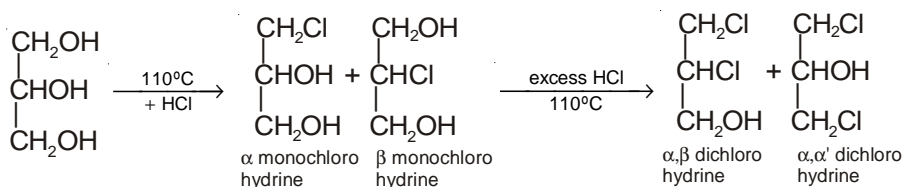
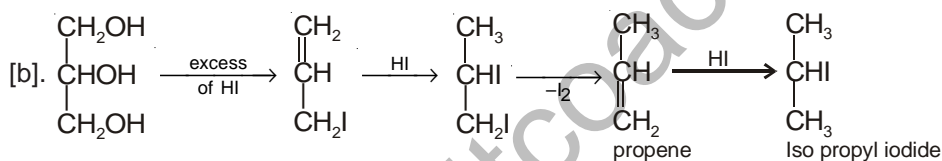
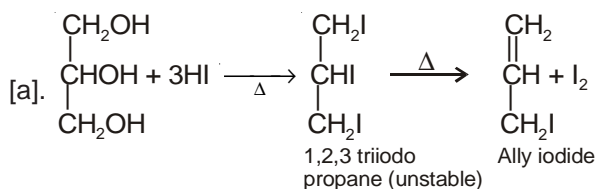
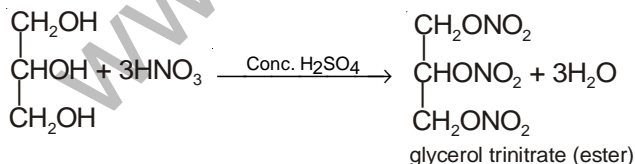


12.2 **Properties :**

- It is colourless, odourless, viscous and hygroscopic liquid, sweet & non-toxic in nature.
- Soluble in water - due to three -OH bond for H-bonding.
- High viscosity & B.P. due to strong H-bonding.

**Chemical** : gives reactions of primary & secondary alcoholic group



**[1] Reaction with sodium :****[2] Reaction with HCl or HBr :****[3] Action of HI → In two ways :****[4] Action of  $\text{PCl}_5$  :****[5] Action of  $\text{HNO}_3$  :**

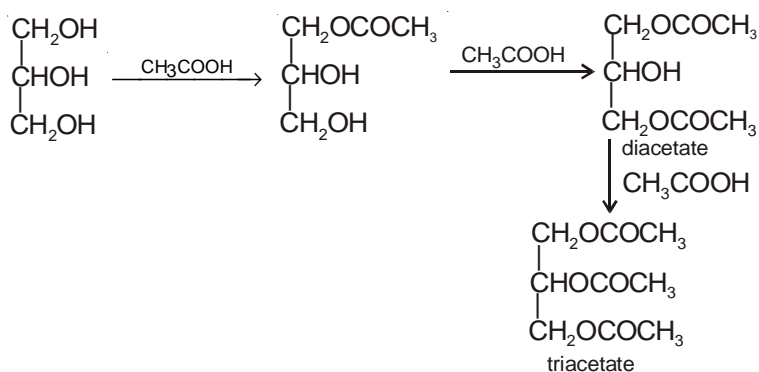
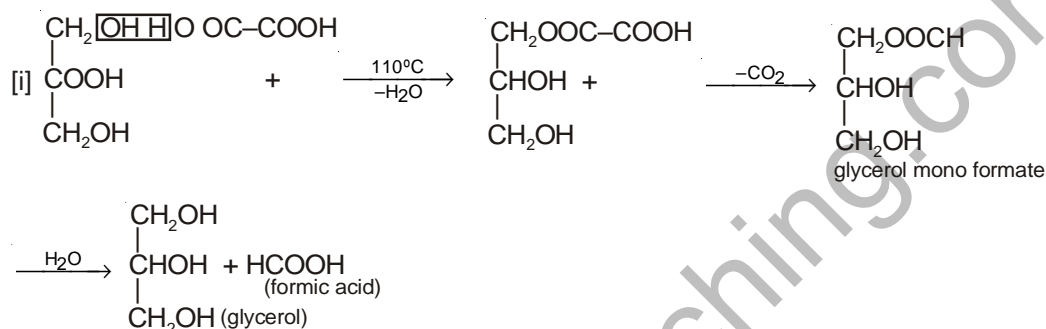
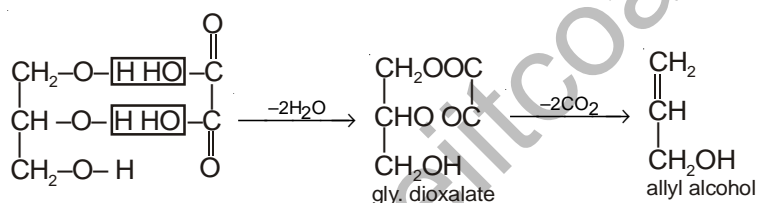
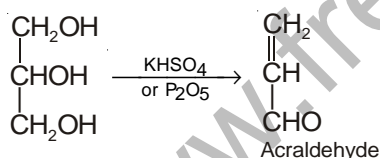
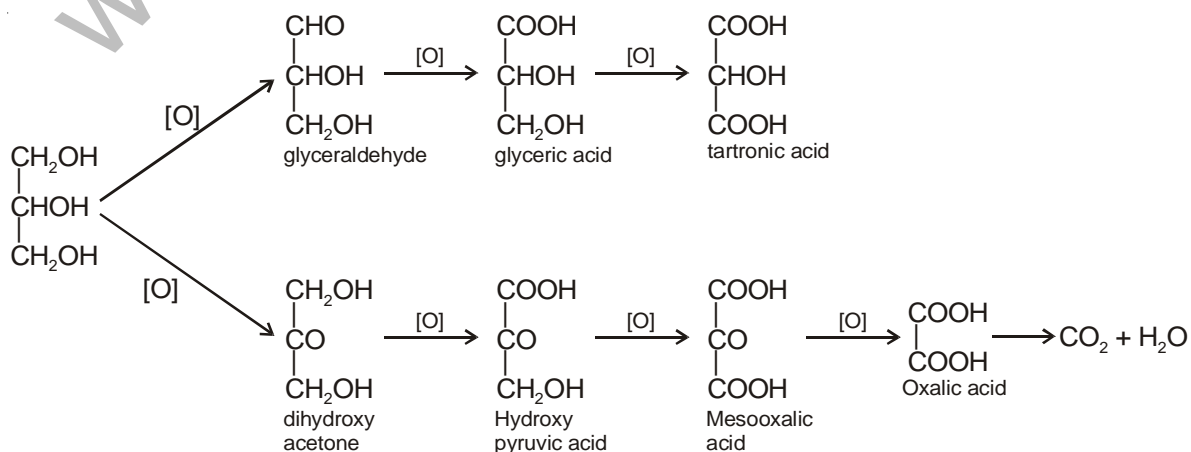
– Glycerol trinitrate is a yellow oily, poisonous liquid and causes headache.

– It explodes violently when heated.

– It is a safer explosive when absorbed on kieselguhr and known as dynamite. Source of other explosive (from glycerol trinitrate) are :

[a] **Blasting gelatin.** a mixture of glycerol trinitrate (GTN) + cellulose nitrate (gum cotton or GC)

[b] **Cordite** → glycerol trinitrate + guncotton + vaseline

**[6] Action of  $\text{CH}_3\text{COOH}$  :****[7] Action of oxalic acid :** different fats are formed at different conditions :**[ii] at  $260^\circ\text{C}$  :****[8] Dehydration :****[9] Oxidation :**

**[10] Oxidation of glycerol with :**

[a] dil.  $\text{HNO}_3 \rightarrow$  glyceric acid

[b] Conc.  $\text{HNO}_3 \rightarrow$  glyceric + tartonic acid

[c] **Bismuth nitrate**  $\rightarrow$  Mesooxalic acid

[d] **Fenton's reagent** ( $\text{H}_2\text{O}_2 + \text{FeSO}_4$ )  $\rightarrow$  glyceraldehyde dihydroxy acetone

[e] Solid  $\text{KMnO}_4 \rightarrow$  Oxalic acid +  $\text{CO}_2$

**12.3 Uses :**

- As freeze
- In the preparation of plastic & synthetic fibre
- In the preparation of explosive like dynamite and cordite.
- As a lubricant in watches.
- In the preparation of good quality of soap hand lotions, shaving cream etc.
- As preservative

**12.4 Dunstan test for glycerol :**

Phenolphthaline drop in borax sol<sup>n</sup>  $\rightarrow$  Pink colour Addition of glycerol  $\rightarrow$  discharge pink colour on heating pink colour again in cold. appears.



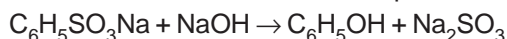
# Phenol (C<sub>6</sub>H<sub>5</sub>OH)

- Phenol is also known as carbolic acid or Benzenol or hydroxy benzene.
- In phenol –OH group is attached to sp<sup>2</sup> – hybridised carbon
- It was discovered by Runge in the middle oil fraction of coaltar distillation and named it carbolic acid (carbo = coal; oleum = oil)
- It is also present in traces in human urine.

## Methods of preparation :

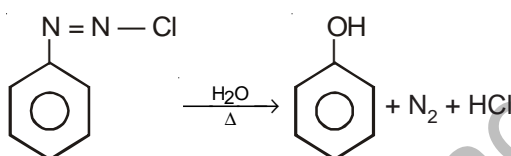
### [1] From Benzene sulphonic acid :

When sodium salt of benzene sulphonic acid is fused with NaOH phenol is obtained.

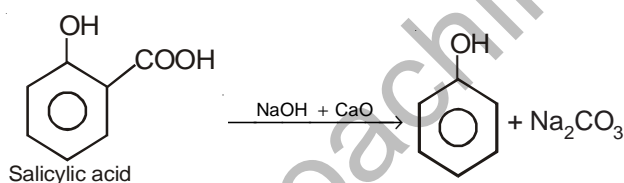


### [2] From benzene diazonium chloride :

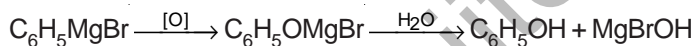
When benzene diazonium chloride solution is warmed phenol is obtained with evolution of nitrogen.



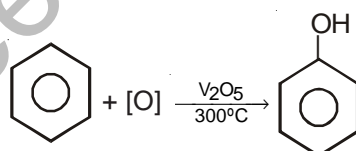
### [3] By distilling a phenolic acid : with sodalime (decarboxylation) :



### [4] From Gignard reagent : The grignard reagent on reaction with oxygen and subsequent hydrolysis by acid yields phenol



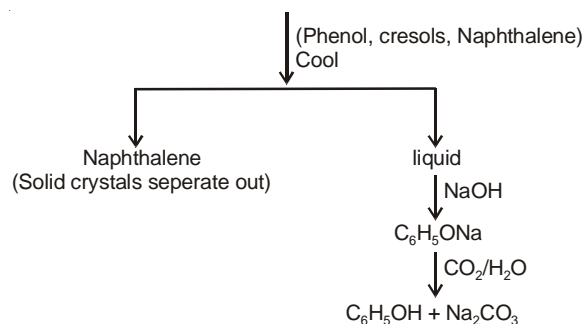
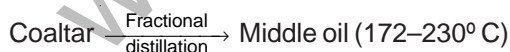
### [5] From benzene :



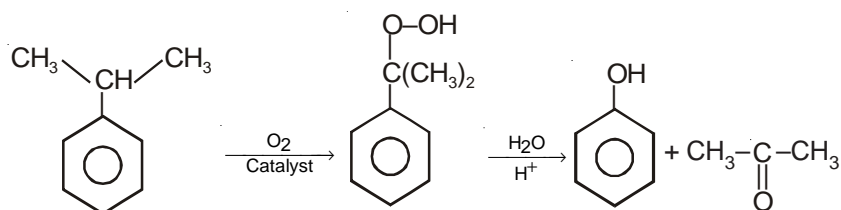
### [6] Industrial preparation of phenol : Phenol can be prepared commercially by :

- |                                                 |                     |
|-------------------------------------------------|---------------------|
| [a] Middle oil fraction of coaltar distillation | [b] Raschig process |
| [c] Dow's process                               | [d] Cumene          |

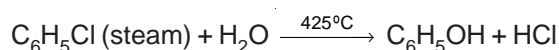
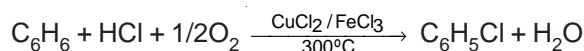
#### [a] Middle oil fraction of coaltar :



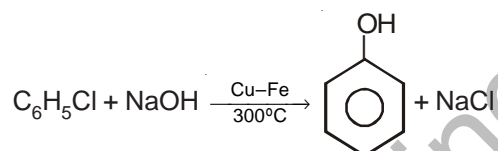
- [b] **From cumene : (Isopropyl benzene) :** Cumene is oxidised with oxygen in to cumene hydro peroxide in presence of a catalyst. This is decomposed by dil.  $\text{H}_2\text{SO}_4$  in to phenol and acetone.



- [c] **Raschig process :** Chlorobenzene is formed by the interaction of benzene  $\text{HCl}$  and air at  $300^\circ\text{C}$  in presence of catalyst  $\text{CuCl}_2 + \text{FeCl}_3$ . It is hydrolysed by superheated steam at  $425^\circ\text{C}$  to form phenol and  $\text{HCl}$ .

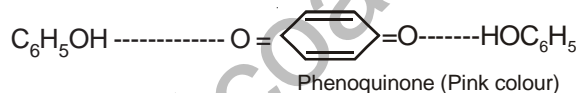


- [d] **Dow process :** This process involves alkaline hydrolysis of chloro benzene



## 2. Physical Properties :

- \* Phenol is a colourless, hygroscopic crystalline solid.
- \* It attains pink colour on exposure to air and light.



- \* It is poisonous in nature but acts as antiseptic and disinfectant.
- \* Phenol is slightly soluble in water, readily soluble in organic solvents.
- \* Solubility of phenol in water is much lower than alcohols because of larger hydrocarbon part in the molecule.
- \* Due to intermolecular H-Bonding, phenol has relatively high B.P. than the corresponding hydrocarbons, aryl halides etc.

## 3 Chemical Properties :

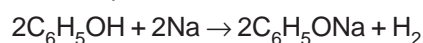
- 3.1 **Acidic Nature :** Phenol is a weak acid. The acidic nature of phenol due to formation of stable phenoxide ion in solution.



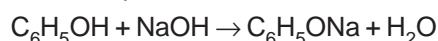
The phenoxide ion is stable due to resonance.

- \* The negative charge is spread through out the benzene ring which is stabilising factor in the phenoxide ion.
- \* Electron withdrawing groups ( $-\text{NO}_2$ ,  $-\text{Cl}$ ) increase the acidity of phenol while electron releasing groups ( $-\text{CH}_3$  etc.) decrease the acidity of phenol.
- \* Phenol is stronger acid than alcohols but weaker than the carboxylic acids and even carbonic acid.
- \* The acidic nature of phenol is observed in the following :

- [i] Phenol changes blue litmus to red.  
[ii] Highly electropositive metals react with phenol.



- [iii] Phenol reacts with strong alkalis to form phenoxides

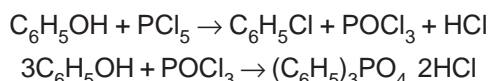


- [vi] However phenol does not decompose  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$  because phenol is weaker acid than carbonic acid.

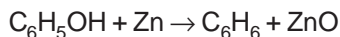


### 3.2 Reaction due to -OH group :

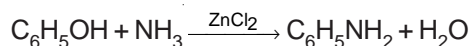
[1] **Reaction with  $\text{PCl}_5$**  : Phenol reacts with  $\text{PCl}_5$  to form chloro benzene. The yield of chlorobenzene is poor and mainly triphenyl phosphate is formed.



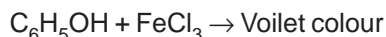
[2] **Reaction with Zn dust** : When phenol is distilled with zinc dust benzene is obtained.



[3] **Reaction with  $\text{NH}_3$**  : Phenol reacts with  $\text{NH}_3$  in presence of anhydrous  $\text{ZnCl}_2$  to form aniline.

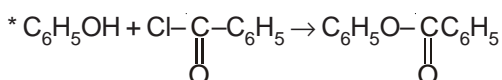
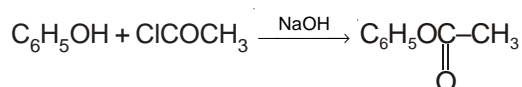


[4] **Reaction with  $\text{FeCl}_3$**  : Phenol gives violet colouration with  $\text{FeCl}_3$  solution (neutral) due to formation of a complex.



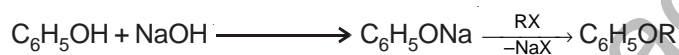
\* This reaction is used to differentiate phenol from alcohols.

[5] **Acetylation** : Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.



This reaction is called **Schotten-Baumann reaction**.

[6] **Ether Formation** : Phenol reacts with alkyl halides in alkali solution to form phenyl ethers.

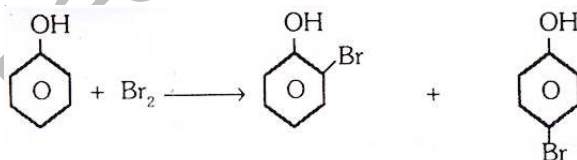


[7] **Reaction with  $\text{P}_2\text{S}_5$**  :

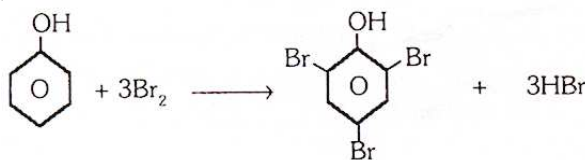


3.3 **Reaction of Benzene Ring** : The -OH group is ortho and para directing. It activates the benzene nucleus.

[1] **Halogenation** : Phenol reacts with bromine in  $\text{CCl}_4$  to form mixture of o- and p-bromo phenol.

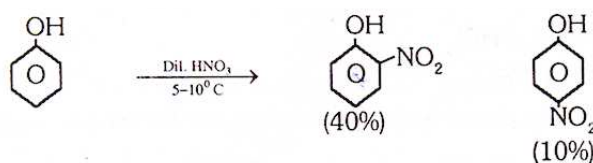


\*Phenol reacts with bromine water to form a white ppt. of 2, 4, 6 tribromo phenol.

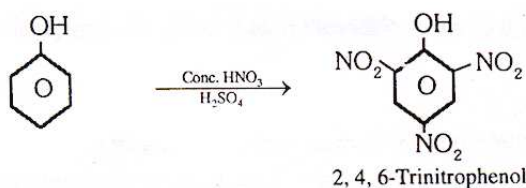


[2] **Nitration** :

[a] Phenol reacts with dil.  $\text{HNO}_3$  at  $5-10^\circ\text{C}$  to form o- and p- nitro phenols.

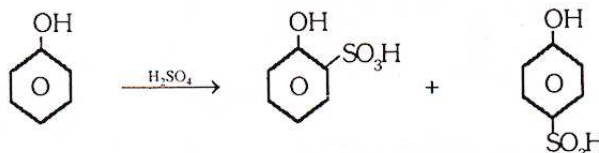


[b] When phenol is treated with conc.  $\text{HNO}_3$  in presence of conc.  $\text{H}_2\text{SO}_4$  2,4,6-trinitro phenol (picric acid) is formed.



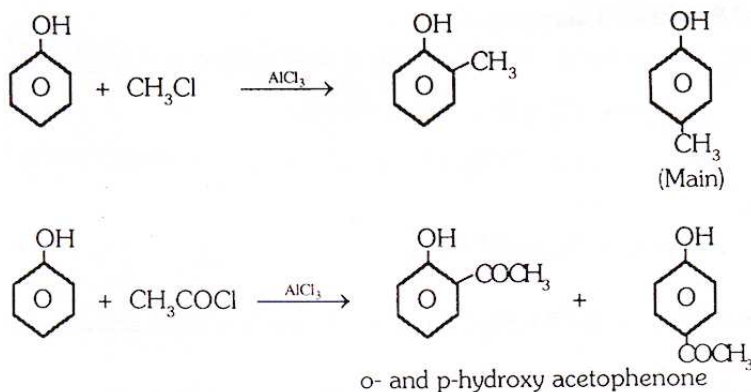
[3] **Sulphonation :**

Phenol reacts with conc.  $\text{H}_2\text{SO}_4$  to form mixture of o- and p- hydroxy benzene sulphonic acid.



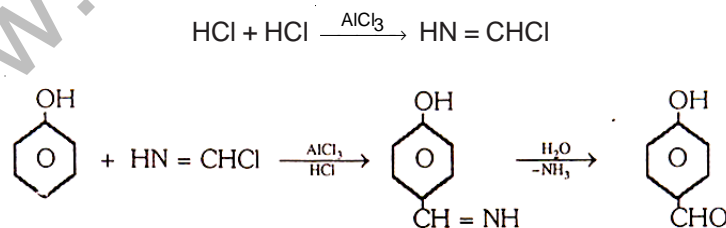
[4] **Friedel-Craft's reaction :**

Phenol when treated with methyl chloride in presence of anhydrous  $\text{AlCl}_3$  p-cresol is main product.

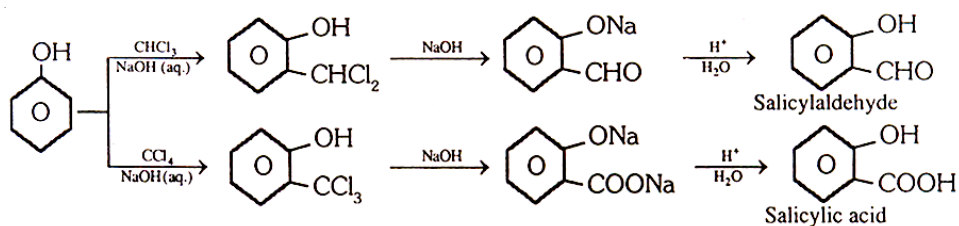


[5] **Gattermann aldehyde synthesis :**

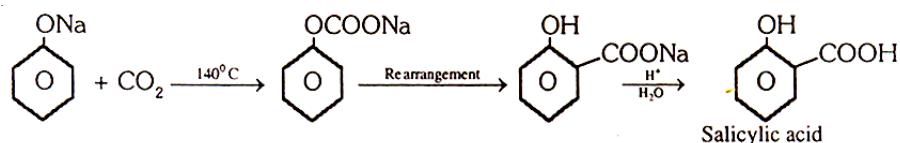
When phenol is treated with liquid HCN and HCl gas in presence of anhydrous  $\text{AlCl}_3$  yields mainly p-hydroxy benzaldehyde.



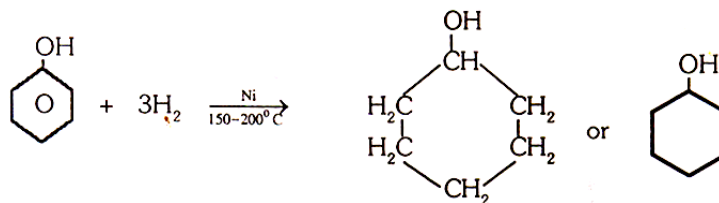
[6] **Reimer-Tiemann reaction :** Phenol on refluxing with chloroform and NaOH (aqueous) followed by acid hydrolysis yields o-hydroxy benzaldehyde. When  $\text{CCl}_4$  is used salicylic acid is formed.



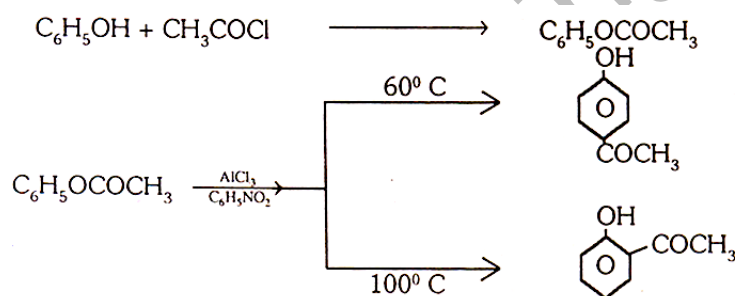
- [7] **Kolbe's Schmidt reaction** : This involves the reaction of  $C_6H_5ONa$  with  $CO_2$  at  $140^\circ C$  followed by acid hydrolysis salicylic acid is formed.



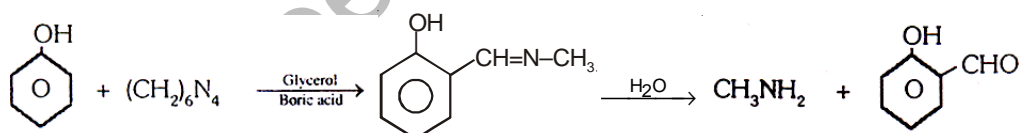
- [8] **Hydrogenation** : Phenol when hydrogenated in presence of Ni at  $150-200^\circ C$  forms cyclohexanol.



- [9] **Fries rearrangement reaction** :

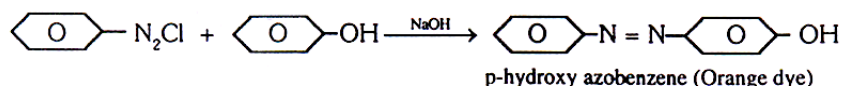


- [10] **Duff's reaction** :

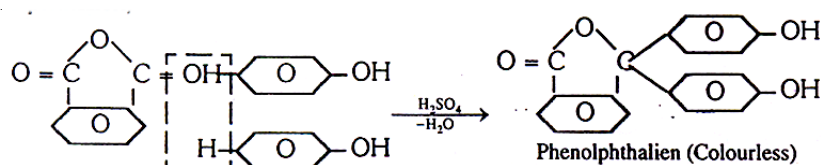


- [11] **Coupling reactions** :

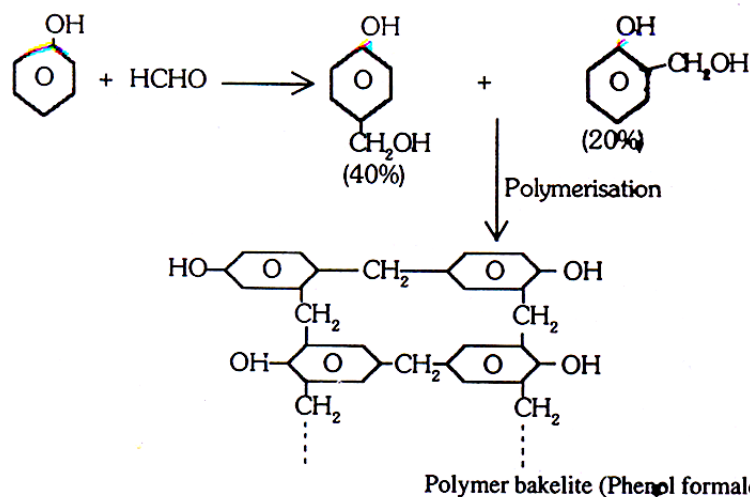
[a] Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a dye (p-hydroxy azobenzene)



[b] Phenol couples with phthalic anhydride in presence of conc.  $H_2SO_4$  to form a dye (phenolphthalein)

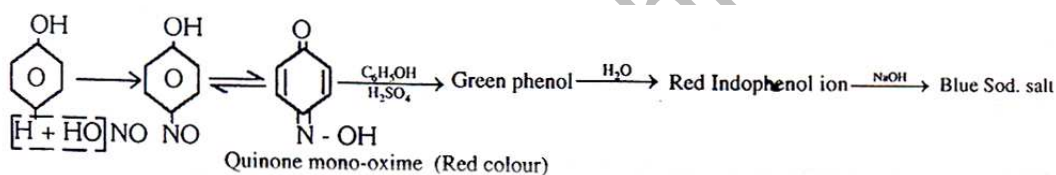


- [12] **Condensation with formaldehyde :** Phenol condenses with HCHO (excess) in presence of NaOH to form a polymer known as bakelite.

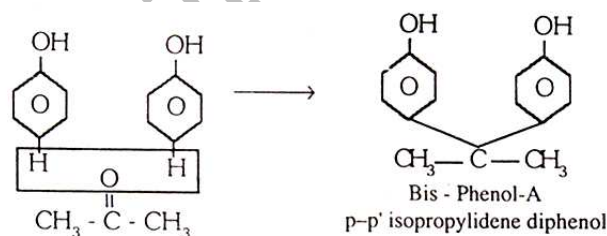


- [13] **Liberman's nitroso reaction :** When phenol is reacted with  $\text{NaNO}_2$  and conc.  $\text{H}_2\text{SO}_4$  it gives a deep green or blue colour which changes to red on dilution with water. When made alkaline with NaOH original green or blue colour is restored.

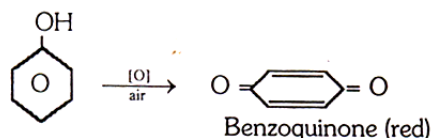
The reaction is used as a test of phenol.



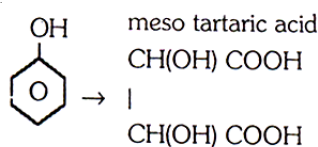
- [14] **Reaction with acetone :**



- [15] **Oxidation :**  
[1] In presence of air :

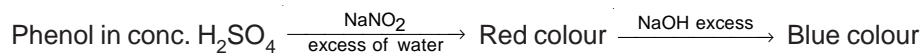


- [2]  $\text{KMnO}_4$  :



**3.4 Test of Phenol :**

- [1] Phenol turns blue litmus to red.
- [2] Aqueous solution of phenol gives a violet colour with a drop of ferric chloride.
- [3] Phenol gives Lieber mann's nitroso test.



- [4] Aqueous solution of phenol gives a white ppt. of 2,4,6 tribromophenol with bromine water.
- [5] Phenol combines with phthalic anhydride in presence of conc.  $\text{H}_2\text{SO}_4$  to form phenolphthalein which gives pink colour with alkali.
- [6] With ammonia and sodium hypochlorite, phenol gives blue colour.

**3.5 Differences between phenol and alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) :**

- [1] Phenol is more acidic than aliphatic alcohol due to resonance in phenoxide ion.
- [2] Phenol gives violet colour with  $\text{FeCl}_3$  while aliphatic alcohol does not give.
- [3] Phenol gives triphenyl phosphate with  $\text{PCl}_5$  while aliphatic alcohol gives alkyl chloride.
- [4] Phenol has phenolic odour whereas alcohol has pleasant odour.
- [5] Phenol on oxidation gives quinone while alcohol gives aldehyde or ketone and acids.

**3.6 Uses of Phenol :**

Phenol is used :

- [1] As an antiseptic in soaps and lotions.
- [2] In manufacture of azodyes, phenolphthalein, picric acid (explosive), cyclohexanol (Solvent for rubber), plastic (bakelite) etc.
- [3] In manufacture of drugs like aspirin, salol, phenacetin etc.
- [4] As preservation for ink.

	<b>Test/ Reaction</b>	<b>Alcohol</b>	<b>Phenol</b>
1	Litmus test	No reaction	Blue litmus red
2	$\text{FeCl}_3$ solution	No reaction	Violet colour
3	Benzene diazonium salt	No reaction	Yellow or orange azo dye
4	$\text{Br}_2$ water	No reaction	2,4, 6 -tribromophenol

# Ether

– Ethers are as dialkyl derivatives of water  $\left( \begin{array}{c} \text{H} \\ \diagdown \\ \text{O} \\ \diagup \\ \text{H} \end{array} \rightarrow \begin{array}{c} \text{R} \\ \diagdown \\ \text{O} \\ \diagup \\ \text{R} \end{array} \right)$  or anhydride of alcohols

ROH + HOR  $\rightarrow$  ROR or mono alkyl derivative of alcohol R–OH  $\rightarrow$  ROR.

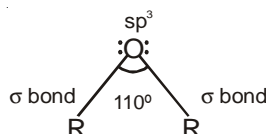
– General formula is  $C_nH_{2n+2}O$

1. **Classification** : These may be classified as :

[a] Simple or symmetrical ether. e.g. R–O–R

[b] Mixed or unsymmetrical ether e.g. R–O–R'

2. **Structure** :



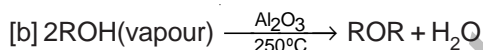
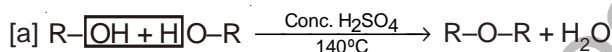
– The molecule of ether is bent due to lone pair of electron – bond electron repulsion.

– The bond angle is  $110^\circ$  It is greater than of water  $105^\circ$  due to the repulsion between bulky alkyl gps.

– Due to bent structure, it posses dipole moment and hence is polar in nature.

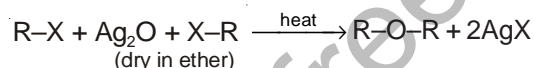
3. **Preparation** :

[1] **By dehydration of alcohols** :

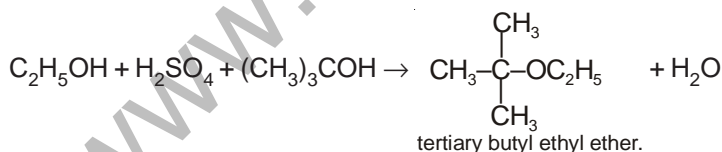


The secondary and tertiary alcohols give  $\rightarrow$  alkenes.

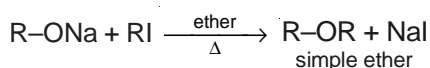
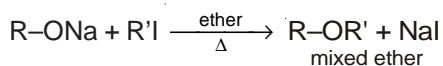
[2] **From alkyl halides** :



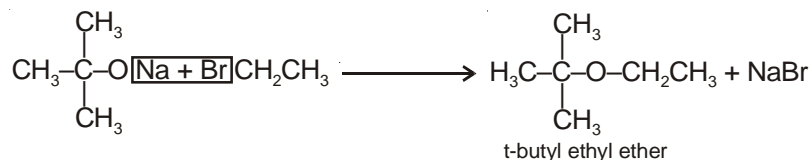
Mixed ethers may also be prepared, e.g.



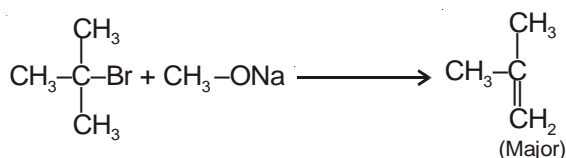
[3] **Williamson synthesis** : This reaction obeys  $\text{SN}^2$  mechanism.



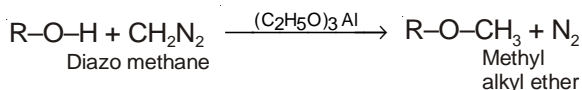
To prepare t-butyl methyl ether, the reaction will be :







[4] By the reaction between an alcohol and diazomethane :



#### 4. Properties :

- Liquid ethers are highly volatile and vapours are highly inflammable.
- Their B.P. are lower than Isomeric alcohols because ether can not associate with H-bonding.
- Sparingly soluble in water, since due to bulky alkyl groups, oxygen of Ether is incapable of forming H-bonding with H<sub>2</sub>O molecules.
- As bond angle of C-O-C 110° thus dipole moment of two C-O bonds does not cancel out each other, As a result ethers are slightly polar and have a net dipole moment.

#### Chemical nature :

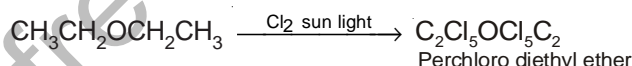
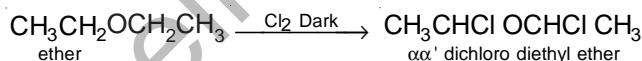
- Ethers are less reactive.
- The chemical properties of ethers are due to
  - Alkyl group.
  - lone pairs of electrons on oxygen
  - Cleavage of C-O bond.

#### 4.1 Reaction due to alkyl group :

##### i. Combustion :

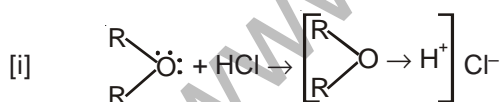


ii. Halogenation : Alkyl group of ethers give substitution reactions, to give α,α'-halogenated ethers.

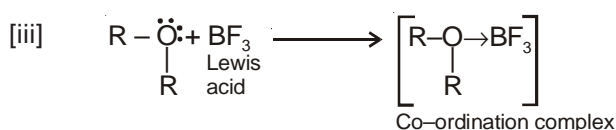
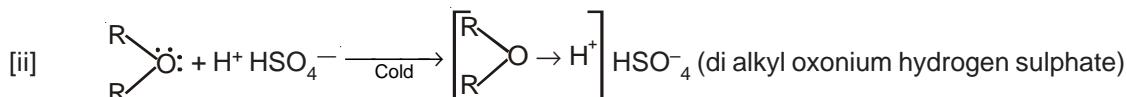


#### 4.2 Reaction due to O-atom :

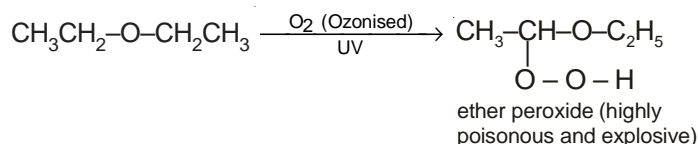
[A] Basic nature : due to presence of two lone pair of electron on oxygen atom ether behaves as Lewis base



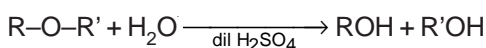
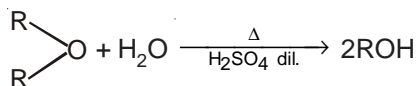
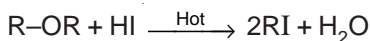
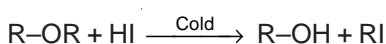
Oxonium salt. ether regeneration



AlCl<sub>3</sub>, RMgX etc. also form such complexes.

**[B] Formation of ether peroxides :**

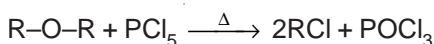
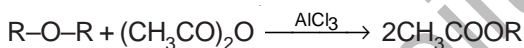
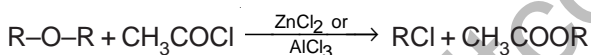
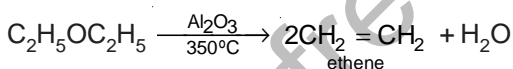
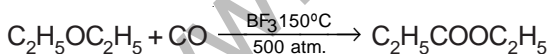
\*Mechanism is free radical

**[C] Reactions involving cleavage of C-O bond – (Hydrolysis)****[i] Action of dil. H<sub>2</sub>SO<sub>4</sub>****[ii] Action of HI :**

In case of mixed ether, halogen atoms attached to simple alkyl gp.



Similar reactions with HCl, HBr take place and the reactivity order is : HI > HBr > HCl

**[iii] Action of PCl<sub>5</sub> :****[iv] Action of acetyl chloride & acetic anhydride :****[v] Dehydration :****[vi] Action of carbon monoxide :****4.3 Uses of ether :**

- [i] General anaesthetic agent.
- [ii] Refrigerant
- [iii] Solvent for oil, fats, resins, Grignard reagent.
- [iv] For providing inert & moisture free medium e.g. Wurtz reactions.
- [v] In perfumery.
- [vi] Di-isopropyl ether → Petrol as an antiknock compound.