

# Chapter-2

## FUNCTIONAL GROUP-I

### Alcohols

Alcohols are hydroxy derivatives of alkanes. Alcohol are classified as mono-, di-, tri- and poly-hydric alcohols according to the number (1, 2, 3 or more) of hydroxyl groups present.

$C_2H_5OH$	$\begin{array}{c} CH_2OH \\   \\ CH_2OH \end{array}$	$\begin{array}{c} CH_2OH \\   \\ CHOH \\   \\ CH_2OH \end{array}$	$\begin{array}{c} CH_2OH \\   \\ (CHOH)_4 \\   \\ CH_2OH \end{array}$
Ethyl alcohol (Monohydric)	Glycol (Dihydric)	Glycerol (Trihydric)	Sorbitol (Polyhydric)

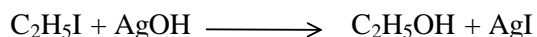
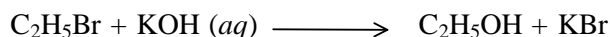
Monohydric alcohols are further divided into primary, secondary and tertiary depending upon the nature of the carbon atom to which the functional group ( $-OH$ ) is attached.

$CH_3CH_2CH_2CH_2OH$	$\begin{array}{c} OH \\   \\ CH_3CH_2CHCH_3 \end{array}$	$(CH_3)_3COH$
n-Butyl alcohol (1-Butanol) 1° alcohol	sec-Butyl alcohol (2-Butanol) 2° alcohol	t-Butyl alcohol (2-Methyl-2-propanol) 3° alcohol

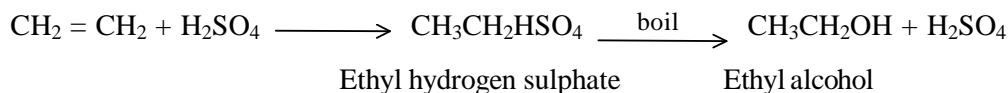
**Structure of alcohols :** It is important to note that in alcohols, carbon as well as oxygen are in  $sp^3$  hybridised state. The  $C-O-H$  bond angle  $105^\circ$  which is less than the normal tetrahedral angle ( $109^\circ 28'$ ). This is because of the presence of two unshared and completely filled  $sp^3$  orbitals of oxygen which repel each other and hence reduce the bond angle.

#### Preparation of Alcohols :

- 1. From Grignard reagents :** reaction of Grignard reagent with formaldehyde, aldehydes other than formaldehyde, and ketones leads to the formation of primary, secondary and tertiary alcohols respectively.
- 2. By the hydrolysis** of alkyl halides with aq. KOH or moist silver oxide ( $Ag_2O + H_2O$ ).



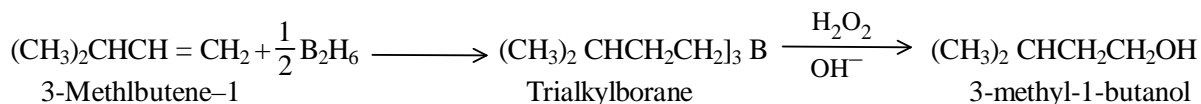
- 3. By the hydration** of olefins by means of 98%  $H_2SO_4$ .



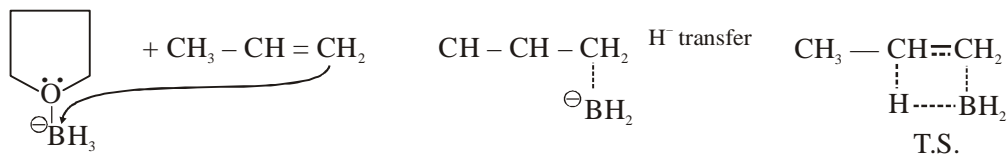
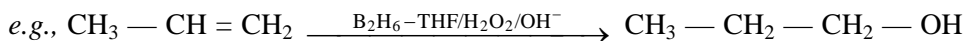
It is important to note that when an unsymmetrical olefin, e.g.  $(CH_3)_2CHCH=CH_2$  is hydrated, different products are formed by different reagents.

- With dil.  $H_2SO_4$ , the expected product is 3-methyl-2-butanol (Markownikoff addition) but in practice the major product is 2-methyl-2-butanol due to rearrangement of the intermediate carbocation.

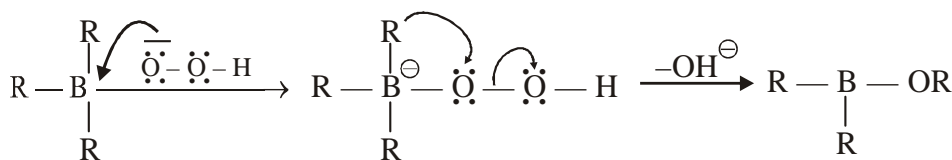
#### 4. Hydroboration oxidation of alkene.



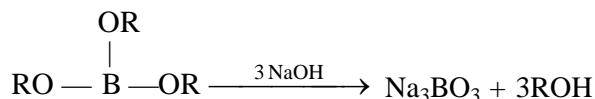
#### Mechanism



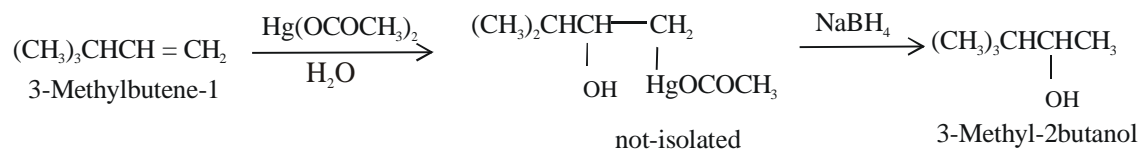
These steps are repeated twice to form  $(\text{CH}_3-\text{CH}_2-\text{CH}_2)_2\text{B}$  and then :



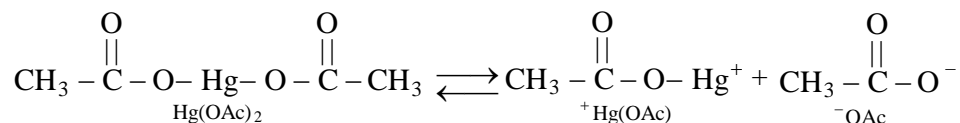
With  $\text{H}_2\text{O}_2$ , finally  $\text{RO}-\overset{\text{OR}}{\text{B}}-\text{OR}$  is formed by above mentioned method



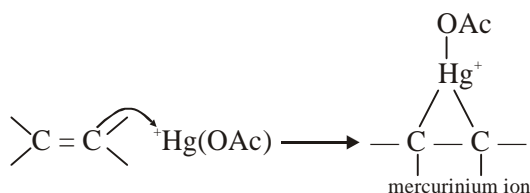
(5) **Oxymercuration and demercuration** with mercuric acetate, the product is 3-methyl-2-butanol (Markownikoff addition with no rearrangement, Oxymercuration demercuration reaction).



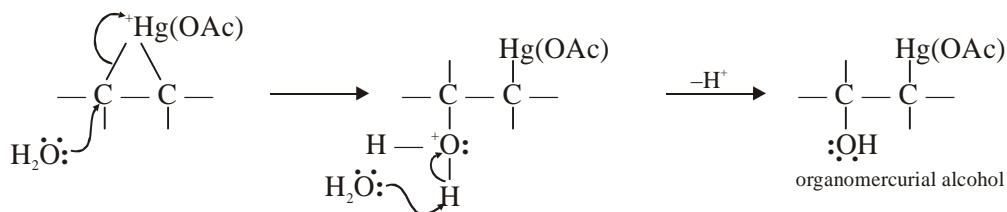
**Mechanism of Oxymercuration demercuration reaction :** The reagent for mercuration is mercuric acetate,  $\text{Hg}(\text{OCOCH}_3)_2$ , abbreviated  $\text{Hg}(\text{OAc})_2$ . There are several theories as to how this reagent acts as an electrophile, but the simplest one is that mercuric acetate dissociates slightly to form a positively charged mercury species,  $^+\text{Hg}(\text{OAc})$



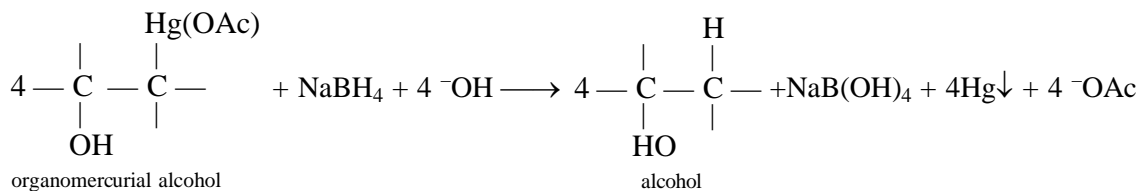
**Oxymercuration** involves an electrophilic attack on the double bond by the positively charged mercury species. The product is a *mercurinium ion*, an organometallic cation containing a three-membered ring.



Mercuration commonly takes place in a solution containing water and an organic solvent to dissolve the alkene. Attack on the mercurinium ion by water gives (after deprotonation) an organomercurial alcohol.

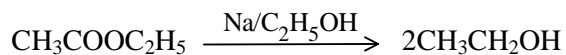
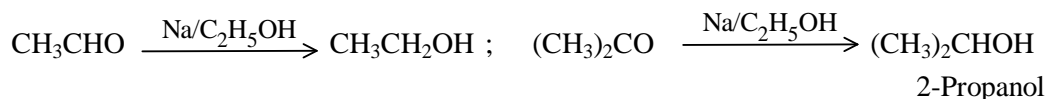


The second step is **demercuration**, to form the alcohol. Sodium borohydride ( $\text{NaBH}_4$ , a reducing agent) replaces the mercuric acetate fragment with hydrogen.

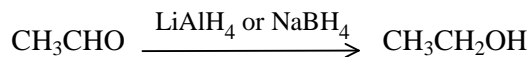


(6) By the catalytic reduction of carbonyl compounds (aldehydes and ketones). Aldehydes give primary alcohols, while ketones give secondary alcohols.

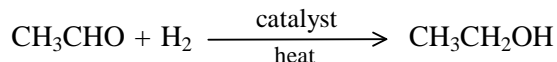
(a) Reduction of carbonyl compounds and ester to alcohols by using alcoholic sodium is called Bouveault-Blanc reduction.



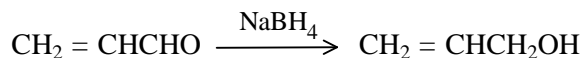
(b) Reduction by  $\text{LiAlH}_4$  or  $\text{NaBH}_4$ .



(c) Catalytic reduction



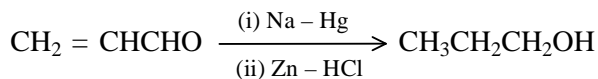
(d) Reduction of unsaturated aldehydes  $\alpha$ ,  $\beta$ -Unsaturated carbonyl compounds may be reduced to unsaturated alcohols by  $\text{LiAlH}_4$ ,  $\text{NaBH}_4$  or best of all by aluminium hydride, e.g.



However, when a phenyl group is attached to the  $\beta$ -carbon atom of an  $\alpha$ ,  $\beta$ -unsaturated carbonyl compound both the double bond and carbonyl group are reduced by  $\text{LiAlH}_4$ , e.g.

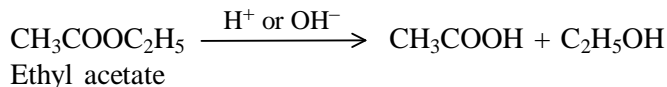


- (e) All  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds can be reduced to saturated alcohols by sodium-amalgam, metal-acid and Ni-H<sub>2</sub> at elevated temperatures.

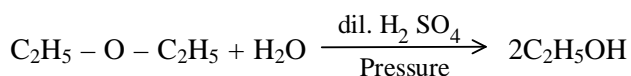


Remember that metal and acid does not reduce a usual double bond unless it is in the  $\alpha$ ,  $\beta$ -position with respect to carbonyl group.

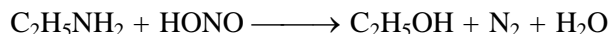
- (7) By the hydrolysis of esters by acids or alkalies. Alkaline hydrolysis of esters is known as saponification.



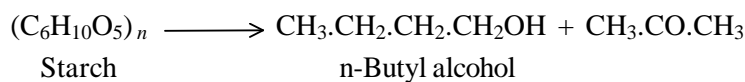
- (8) By the hydrolysis of ethers with hot dil. H<sub>2</sub>SO<sub>4</sub> under pressure.



- (9) By the action of nitrous acid on aliphatic primary amines.

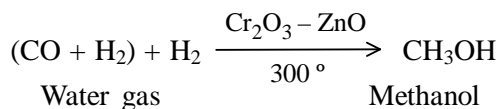


- (10) **By fermentation** : Fermentation is a slow decomposition of complex organic compounds into simpler compounds in the presence of suitable micro-organisms which are the source of biochemical catalyst known as enzymes.



**Industrial preparation** : Ethanol is manufactured by (i) the hydration of ethylene in the presence of H<sub>2</sub>SO<sub>4</sub> and (ii) fermentation of sugars present in the form of starch (e.g. potato, maize, barley, rice, etc.) or cane sugar (e.g., molasses).

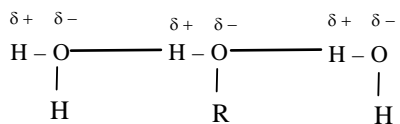
Methanol is manufactured (i) as a by product by the destructive distillation of wood during the manufacture of charcoal or (ii) by heating a mixture of water gas (a mixture of CO and H<sub>2</sub> in equimolar ratio) with half its volume of hydrogen in presence of catalyst.



### Properties :

- (1) The lower alcohols are liquids while higher having more than 12 carbon atoms are solids. They are colourless neutral substances with characteristic sweet alcoholic odour and burning taste.
- (2) The lower alcohols are readily soluble in water and the solubility decreases with the increase in molecular weight.

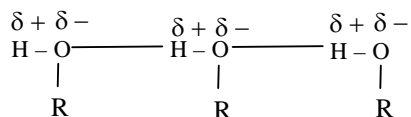
The solubility of alcohols in water can be explained due to the formation of hydrogen bond between the highly polarised -OH groups present both in alcohol and water.



Hydrogen bonding between alcohol and water molecules

However, in higher alcohols the hydrocarbon character (alkyl chain) of the molecule increases and thus alcohols tend to resemble hydrocarbon (which are insoluble in water) and hence the solubility in water decreases. When the ratio of C to OH is more than 4, alcohols have little solubility in water.

- (3) Boiling points of alcohols are much higher than those of the corresponding alkanes. It is again due to the formation of hydrogen bonding between the hydroxyl groups of the two molecules of an alcohols with the result several molecules are associated to form a large molecule.



Hydrogen bonding in alcohol molecules

Among the isomeric alcohols, b.p. and m.p. show the following trend.

Primary > Secondary > Tertiary

This is because of the fact that in secondary and tertiary alcohols, the alkyl part outweighs the -OH group due to branching.

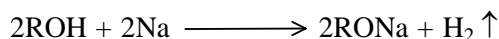
- (4) Lower alcohols form solid addition compounds with anhydrous metallic salts like  $\text{CaCl}_2$  and  $\text{MgCl}_2$ , viz.,  $\text{CaCl}_2 \cdot 4\text{C}_2\text{H}_5\text{OH}$  and  $\text{MgCl}_2 \cdot 6\text{C}_2\text{H}_5\text{OH}$

By analogy to water of crystallisation, these alcohol molecules are referred to as alcohol of crystallisation. For this reason, alcohols cannot be dried over anhydrous calcium chloride.

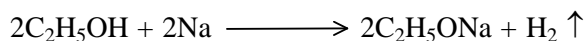
**(A) Reactions involving cleavage of oxygen-hydrogen bond, -O -H. All such reactions (No. 1 to 4) follow the following order of reactivity.**

Primary > Secondary > Tertiary

- (1) Action of alkali metals. Electropositive metals like Na, K, Ca and Mg react with alcohols forming alkoxides with the liberation of hydrogen gas.



Sod. alkoxide

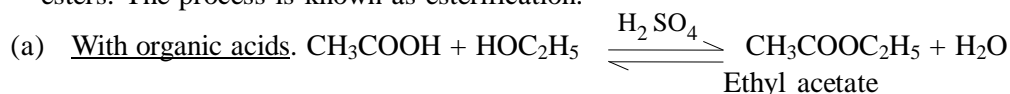


Sod. ethoxide

In this reaction alcohols behave as very weak acids. The decreasing order of acidic character of alcohols in comparison to water is

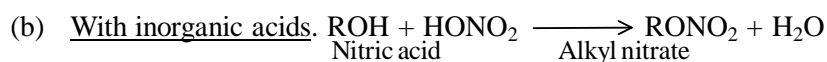
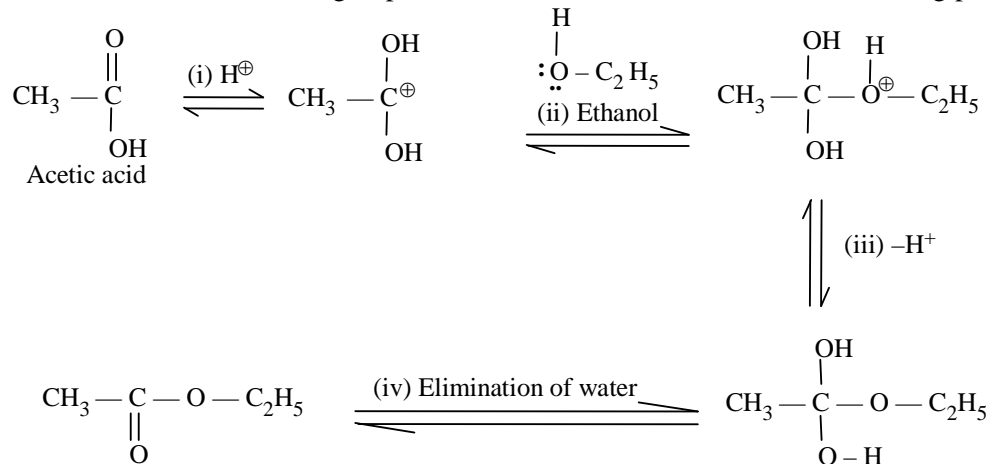


- (2) Action of acids (esterification). Alcohols react with organic and inorganic acids (except halogen acids) in presence of a dehydrating agent like  $\text{H}_2\text{SO}_4$  or dry hydrogen chloride gas to form esters. The process is known as esterification.

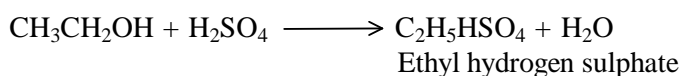




**Mechanism :** It is now proved beyond doubt that esterification with organic acids involved hydrogen atom of the alcohol and –OH group of the acid. The reaction follows the following path.

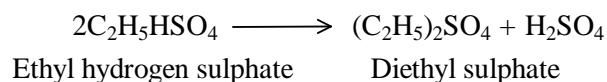


The action of conc.  $\text{H}_2\text{SO}_4$  on alcohols is very interesting as it gives different products under different conditions. Alcohols dissolve in cold conc.  $\text{H}_2\text{SO}_4$  (i.e. at  $0^\circ\text{C}$ ) forming oxonium salts,  $\text{ROH}_2\text{HSO}_4^-$ . At room temperature, esterification takes place to form alkyl hydrogen sulphate.

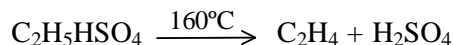


Ethyl hydrogen sulphate now can react in three different ways.

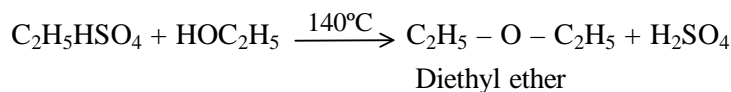
(i) When heated alone, it forms diethyl sulphate.



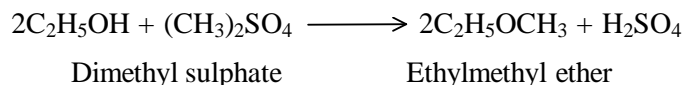
(ii) When heated with excess of  $\text{H}_2\text{SO}_4$  at  $160^\circ\text{C}$ , it forms ethylene.



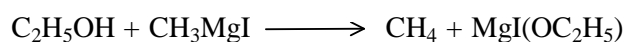
(iii) When heated with excess of ethyl alcohol at  $140^\circ\text{C}$ , it gives diethyl ether.



3. Alkylation (replacement of hydrogen atom by alkyl group).



4. Reaction with Grignard reagents (formation of alkanes).



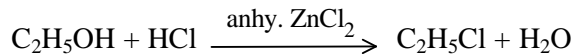
This reaction may be used for the estimation of alcoholic group (Zerewitnoff reaction).

**(B) Reactions involving –OH group as a whole, i.e. reactions involving cleavage of carbon-**

oxygen bond, C – OH. All such reactions follow the following order.

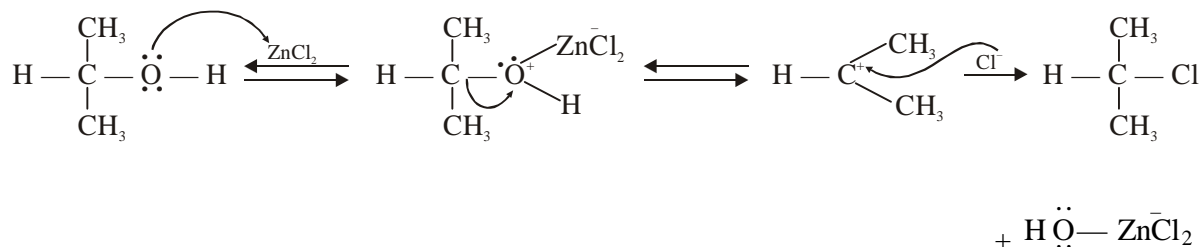
Tertiary > Secondary > Primary

(5) Action of halogen acids

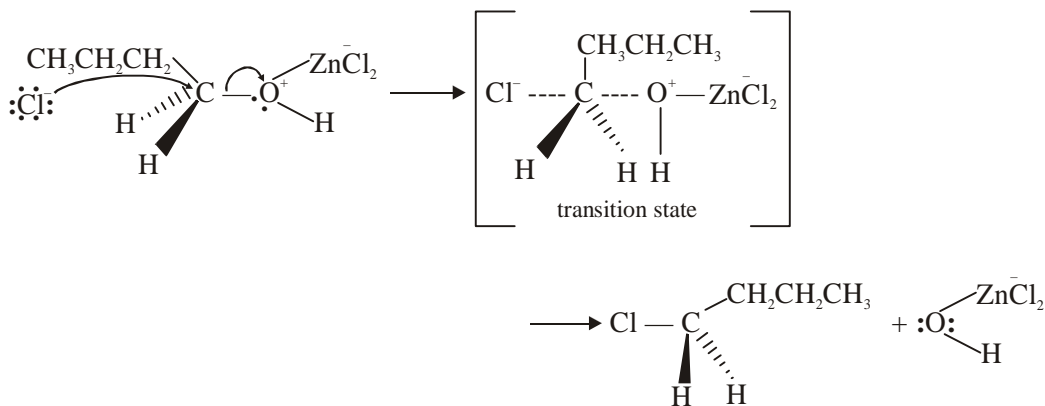


The reactivity of halogen acid is in the order : HI > HBr > HCl.

*S<sub>N</sub>1 reaction with the Lucas reagent (fast)*



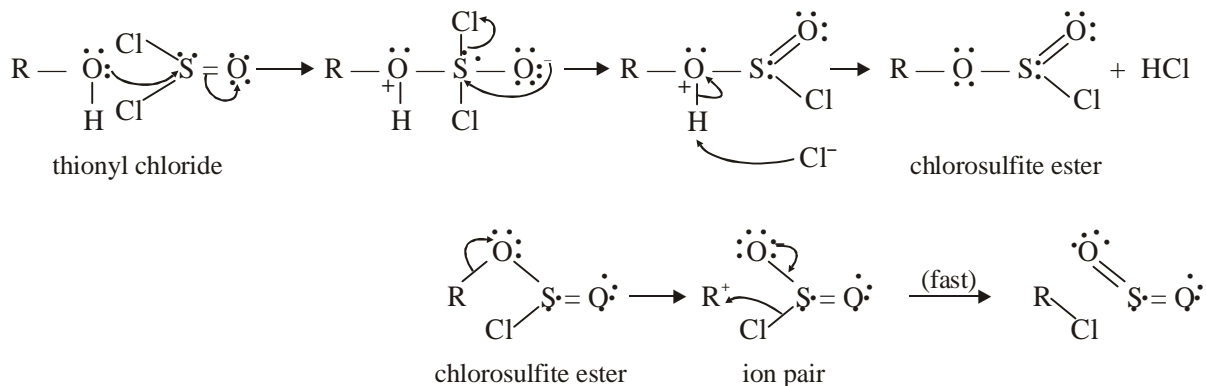
*S<sub>N</sub>2 reaction with the Lucas reagent (slow)*



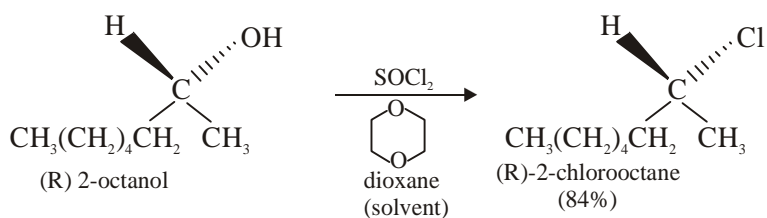
(6) Action of thionyl chloride



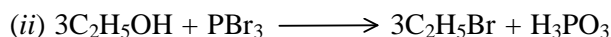
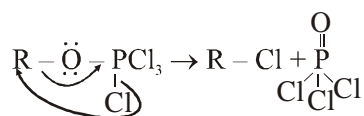
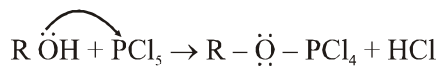
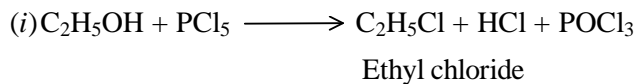
**Mechanism**



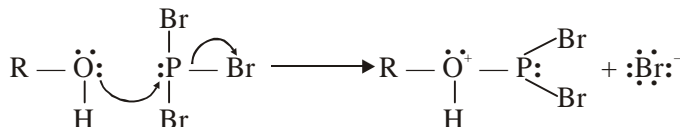
This mechanism resembles the *S<sub>N</sub>1*, except that the nucleophile is delivered to the carbocation by the leaving group, giving retention of configuration as shown in the following example. So called *S<sub>N</sub>i* reaction and in presence of mild base the reaction path is *S<sub>N</sub>2* which gives 100% inversion in configuration.



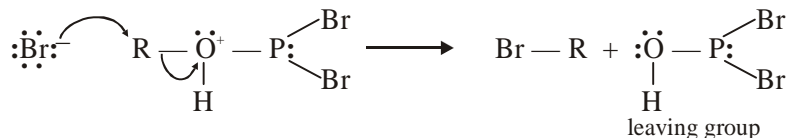
(7) **Action of phosphorus halides (PX<sub>5</sub> and PX<sub>3</sub>).** For example,



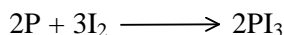
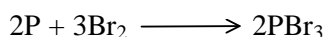
*Displacement of bromide ion*



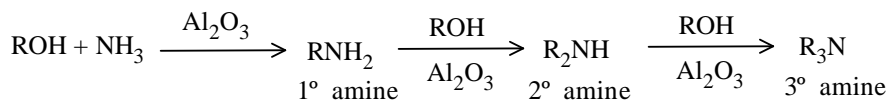
*S<sub>N</sub>2 attack on the alkyl group*



Phosphorus tribromide and phosphorus tri iodide are usually prepared in situ (bromine or iodine is added to red phosphorus and warmed).



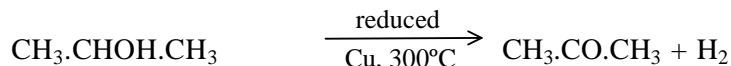
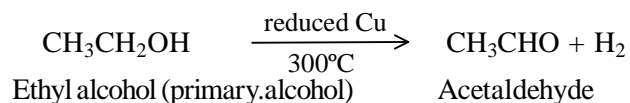
(8) **Action of ammonia**



The ease of dehydration of alcohols is in the order :

Tertiary > Secondary > Primary

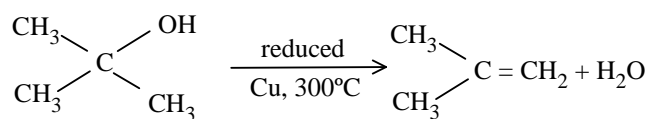
(9) **Action of hot reduced copper :** Primary and secondary alcohols are dehydrogenated to form aldehydes and ketones respectively, while tertiary alcohols are dehydrated to form olefins.





Isopropyl alcohol (sec. alcohol)

Acetone



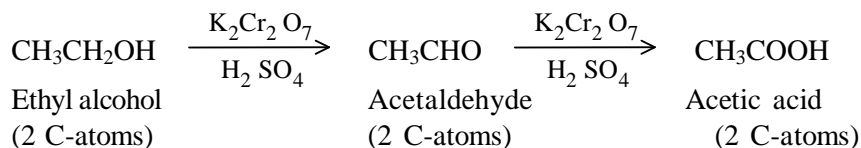
t-Butyl alcohol

Isobutene

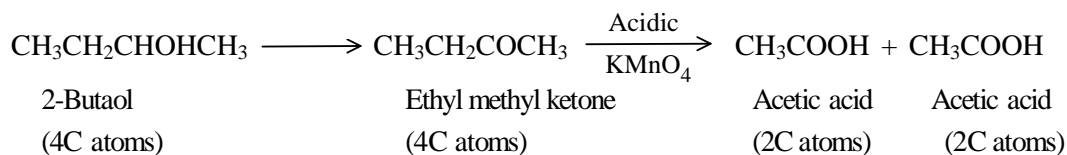
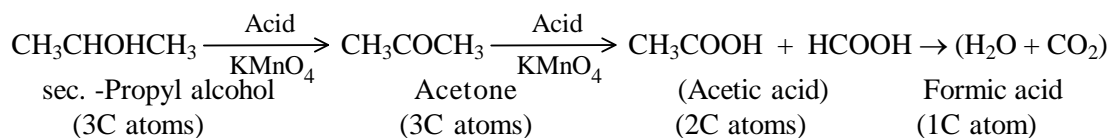
Thus dehydrogenation reaction may be used for distinguishing primary, secondary and tertiary alcohols.

(10) **Oxidation** : Primary, secondary and tertiary alcohols behave differently towards oxidising agents. Primary and secondary alcohols are readily oxidised by a dilute solution of acidic  $\text{K}_2\text{Cr}_2\text{O}_7$ , acidic or alkaline  $\text{KMnO}_4$  or dilute nitric acid. On the other hand, tertiary alcohols are oxidised only by strong oxidising agents under vigorous conditions.

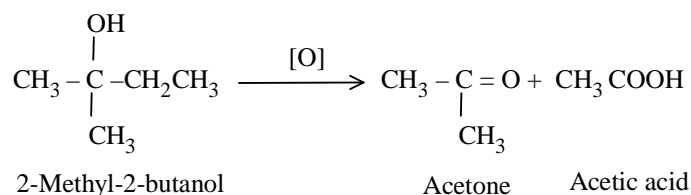
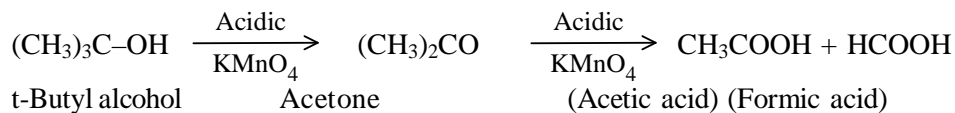
(a) **Primary alcohols** : These are easily oxidised first to aldehydes and then to carboxylic acids, both having the same number of carbon atoms as the parent alcohol.



(b) **Secondary alcohols** : are oxidised to ketones having the same number of carbon atoms as the parent alcohols. Although ketones are difficult to oxidise, these undergo oxidation under drastic conditions giving a mixture of acids containing lesser number of carbon atoms.



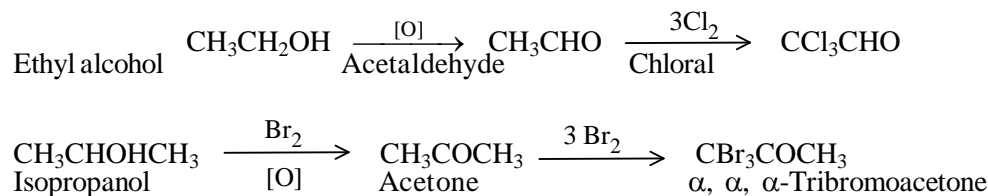
(c) **Tertiary alcohols** are generally resistant to oxidation in neutral or alkaline solution, but are oxidised by acidic oxidising agents (i.e. under drastic conditions) to form first ketones and then acids both having lesser number of carbon atoms than the parent molecule.



Thus oxidation may also be used for distinguishing the three types of alcohols.

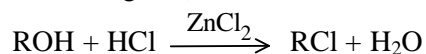
(11) **Action of chlorine or bromine** : Chlorine and bromine, being mild oxidising agents, oxidise primary

and secondary alcohols to aldehydes and ketones respectively which then undergo halogenation.



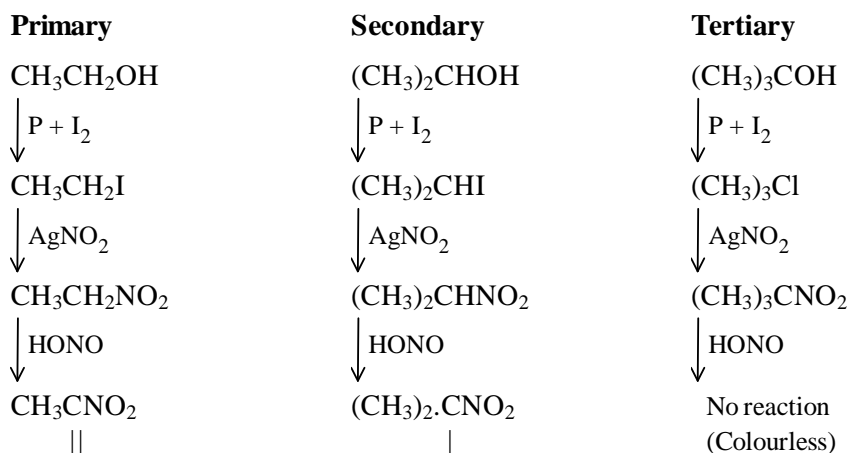
### Distinction Between Primary, Secondary and Tertiary alcohols.

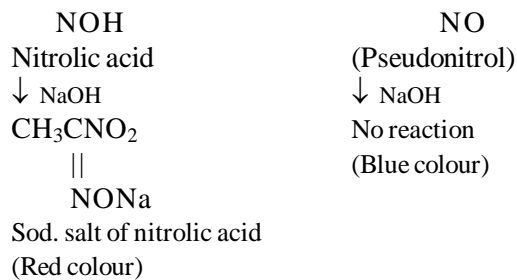
- (1) **Lucas test** : This test is based on the difference in the three types of alcohols (having 6 or less carbon) towards Lucas reagent (a mixture of conc. hydrochloric acid and anhydrous zinc chloride)



Since alkyl halides are insoluble, their formation is indicated by the appearance of a turbidity in the reaction mixture. The order of reactivity is tertiary > secondary > primary, the tertiary alcohols produce turbidity immediately, the secondary alcohols give turbidity within 5 – 10 minutes, and the primary alcohols do not give turbidity at all, at room temperature.

- (2) **Catalytic dehydrogenation** (action of reduced copper at 300°C). Discussed earlier.
- Primary alcohols form aldehydes
  - Secondary alcohols form ketones.
  - Tertiary alcohols form olefins.
- (3) **Victor Meyer test** : This test is based on the different behaviour of primary, secondary and tertiary nitroalkanes towards nitrous acid. The test involves the following steps.
- Alcohol is treated with concentrated hydriodic acid or red phosphorus and iodine to form the corresponding alkyl iodide.
  - Alkyl iodide is reacted with silver nitrite to form the corresponding nitroalkane.
  - The nitroalkane is treated with nitrous acid ( $\text{NaNO}_2 + \text{H}_2\text{SO}_4$ ) followed by treatment with alkali ( $\text{NaOH}$  or  $\text{KOH}$ ). Upon such treatment different alcohols give different colours.
    - Primary alcohols produce a blood red colour
    - Secondary alcohols produce a blue colour.
    - Tertiary alcohols produce no colour.

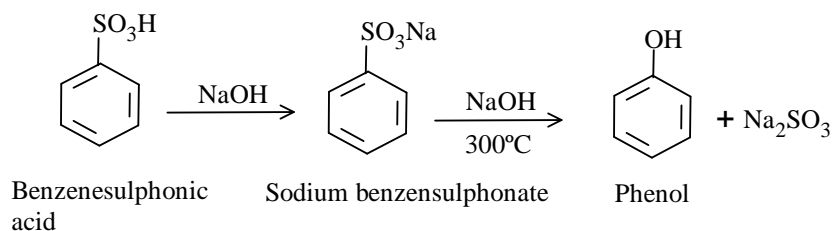




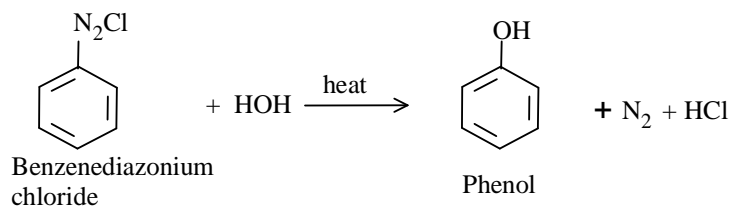
## Phenols

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

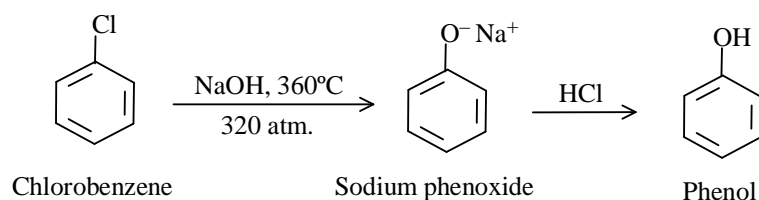
1. By fusing the sodium salt of benzene sulphonic acid with NaOH.



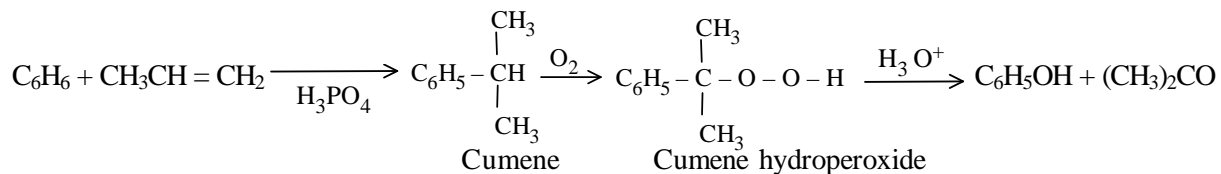
2. By adding benzene diazonium chloride to a large volume of boiling dilute H<sub>2</sub>SO<sub>4</sub>.



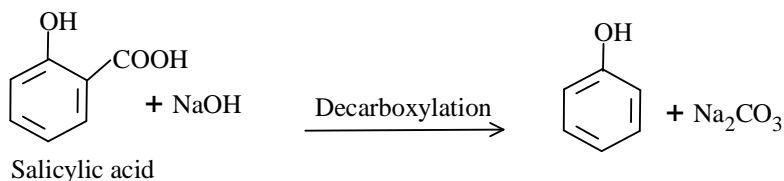
3. By heating chlorobenzene with caustic soda under pressure (Dow's process). This is commercial method. The reaction involves nucleophilic substitution.



4. From cumene hydroperoxide (commercial method).



5. By distilling a phenolic acid with soda lime.

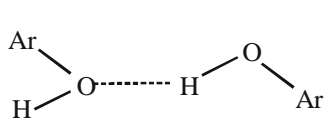


## Properties

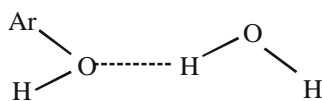
### Physical :

- (i) Pure phenols are generally colourless solids or liquids. The light colour usually associated with phenols is due to its oxidation by air in presence of light.
- (ii) Phenols, in general, are insoluble in water; but phenol itself, and polyhydric phenols are fairly soluble in water which is believed to be due to the formation of hydrogen bonds with water.
- (iii) Due to intermolecular hydrogen bonding, phenols usually have relatively high boiling points than the corresponding hydrocarbons, aryl halides and alcohols. For example, phenol (mol. wt. 94) boils at 182°C while toluene (mol. wt 92) boils at 110°C.

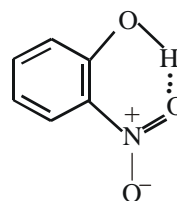
Higher b.p. than alcohols is due to higher polarity of the O – H bond and consequently stronger intermolecular hydrogen bonding in phenols than in alcohols. Appreciable solubilities of the phenol and polyhydric phenols in water is also due to strong hydrogen bonding between phenols and water molecules.



Intermolecular hydrogen bonding in phenols



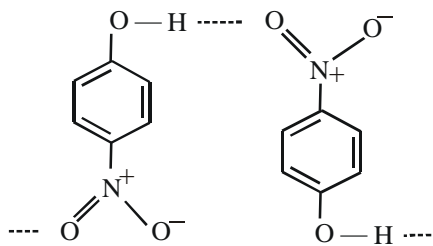
Hydrogen bonding between phenols and water molecules



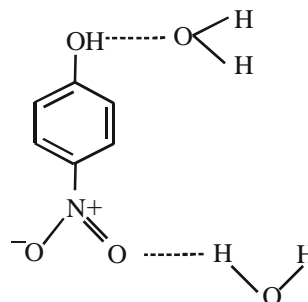
o-Nitrophenol (Intramolecular H-bonding possible due to closeness of –NO<sub>2</sub> and –OH groups)

Phenols containing groups like –NO<sub>2</sub> or –COOH in the ortho position to the –OH group can also form intramolecular hydrogen bonds (e.g. o-nitrophenol) which is responsible for their lower boiling points and less solubility in water than the corresponding meta or para isomer.

Due to possibility of intramolecular hydrogen bonding (also known as chelation) in the ortho isomer, intermolecular hydrogen bonding is not possible and hence the ortho isomer can neither get associated nor can form hydrogen bonding with water with the result it has a low b.p. and less solubility in water than the meta and para isomers which can associate as well as can form hydrogen bonding with water.



p-Nitrophenol (2 molecules) (Intramolecular H-bonding is not possible due to large distance between –NO<sub>2</sub> and –OH groups; hence intermolecular H-bonding is possible)

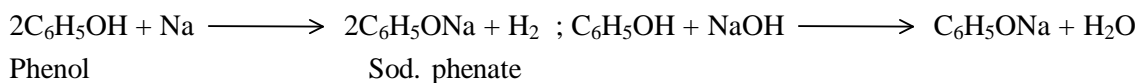


Hydrogen bonding between p-nitrophenol and water

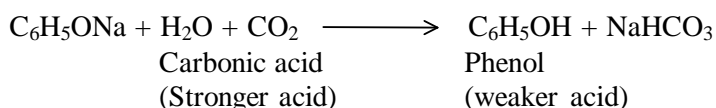
- 
- (iv) They possess characteristic colour. They are highly toxic in nature and possess antiseptic properties. They may produce wounds on skin.

### Chemical Properties of Phenols

1. **Acidic character (Salt formation)** : Phenols are acidic in nature and react with alkali metals and their hydroxides to form salts known as phenoxides or phenates. However, phenols do not react with weak alkalies like carbonates or bicarbonates (difference from carboxylic acids).

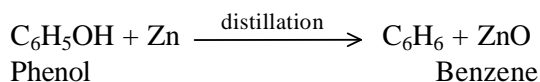


Salts of phenols are decomposed by aqueous mineral acids, carboxylic acids or even carbonic acid to give back free phenols.



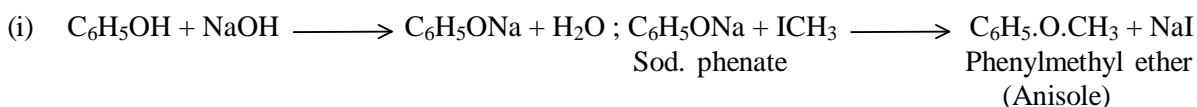
This indicates that phenols are very weak acids; weaker than carboxylic acids or even carbonic acid. In short, phenols are stronger acids than alcohols but weaker than the carboxylic acids and even carbonic acid.

2. **Action of ferric chloride** : Phenols give characteristic colour with neutral ferric chloride solution. The characteristic colour is believed to be due to the formation of coloured co-ordination compounds. Reaction of phenols with ferric chloride is used in analytical chemistry for distinguishing phenols from carboxylic acids.
3. **Reduction with zinc dust** : Phenols, when distilled with zinc dust, give aromatic hydrocarbons (e.g. alcohols are reduced to hydrocarbons with hydriodic acid).

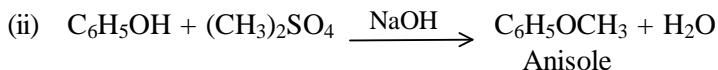


Note that phenols differ from alcohols in the above three reactions numbered 1, 2, and 3.

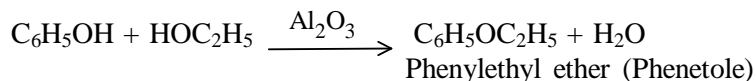
4. **Alkylation** : (Ether formation) : Phenols react with alkyl halides (aryl halides are too inert) or dialkyl sulphates in alkaline medium to form phenolic ethers.



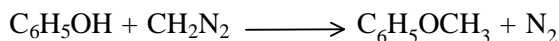
The method resembles Williamson's synthesis for preparing ethers.



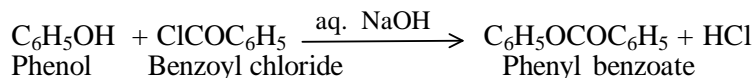
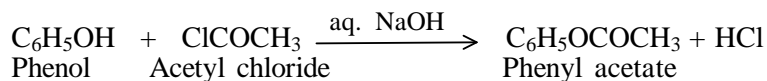
- (iii) Ethers can also be prepared by passing the mixed vapours of phenols and some alcohols over heated alumina or thoria.



- (iv) Methyl ether can also be easily prepared from diazomethane ( $\text{CH}_2\text{N}_2$ ).

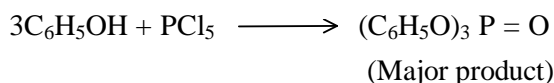
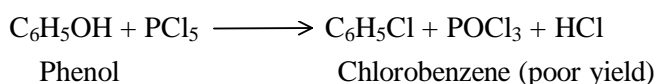


5. **Acylation** : (Ester formation) : Phenols react with acid chlorides or acid anhydrides (but not with acids) in alkaline solution to form esters.

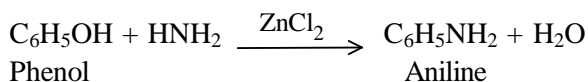


Reaction with benzoyl chloride is known as Schotten-Bauman reaction.

6. **Reaction with phosphorus pentachloride** (Formation of aryl chlorides). Unlike alcohols, it is difficult to replace –OH group of phenols by halogen. For example, halogen acids do not react with phenols, and phosphorus trihalides give phosphorus esters. However, phenols react with  $\text{PCl}_5$  or  $\text{PBr}_5$  forming the corresponding halide.



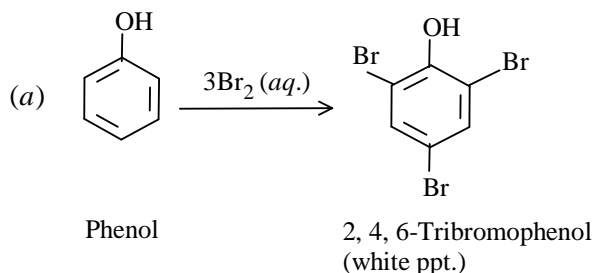
7. **Reaction with ammonia** (Formation of anilines). Phenols when heated with ammonia in presence of anhydrous zinc or calcium chloride gives the corresponding aniline.

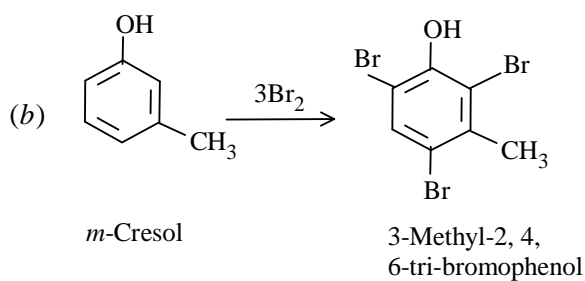


Note that phenols resemble alcohols in the above reactions numbered 4 to 7.

8. **Electrophilic substitution reactions** (halogenation, nitration, sulphonation and Friedel-Craft reaction). The –OH group in phenol, being activating group, facilitates further substitution in the ortho and para positions. In fact, the –OH group is so highly activating that unless precautions are taken, trisubstitution takes place.

- (i) **Halogenation** : Phenols when treated with aqueous solution of halogens undergo halogenation very rapidly to form polyhalogen derivatives. For example,

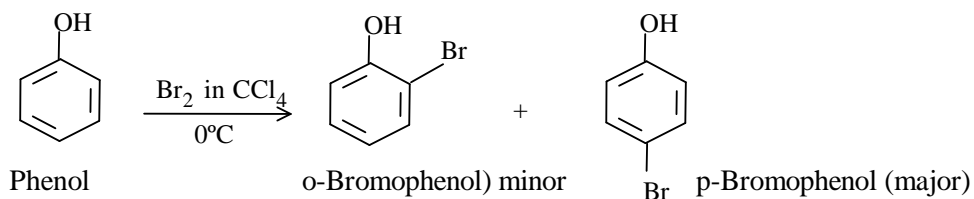




In fact, phenols are so reactive towards bromine water that even substituent like  $-\text{SO}_3\text{H}$ ,  $-\text{NO}_2$ ,  $-\text{COOH}$ , etc. if present, in *o*- and *p*-positions, may be replaced by halogens.

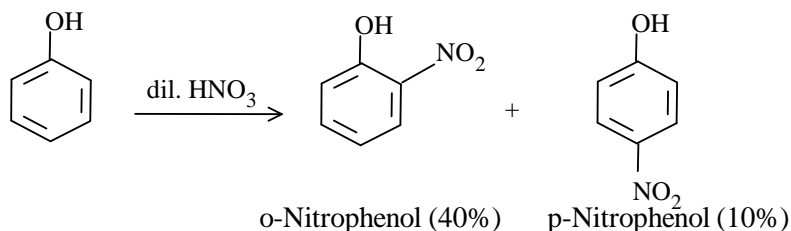
Polyhalogenation while using water as solvent is because of the fact that water (a highly polar solvent) facilitates the ionisation of phenol to phenoxide ion which is more reactive than phenol towards electrophilic substitution.

**For preparing monohalogen derivatives**, halogenation is carried out at low temperature and in non-polar solvents such as carbon tetrachloride ( $\text{CCl}_4$ ) or carbon disulphide. For example,

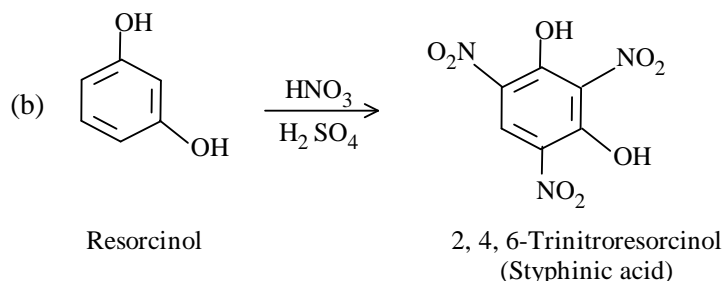
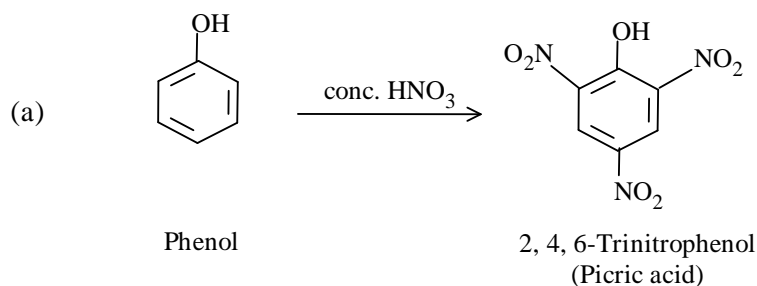


Non-polar solvents ( $\text{CS}_2$ ,  $\text{CCl}_4$ ) decrease the electrophilic character of  $\text{Br}_2$  and minimize ionization of phenol.

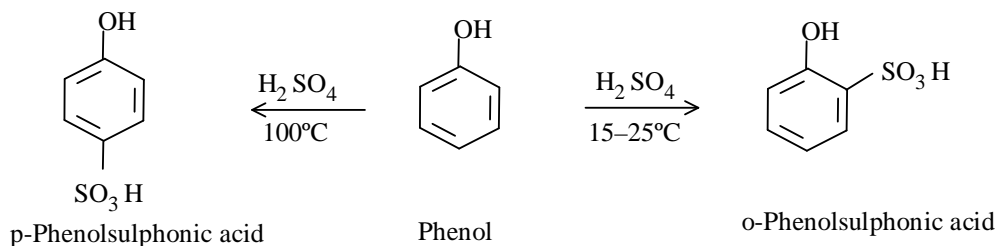
- (ii) **Nitration** : With nitric acid, phenol gives a mixture of *o*- and *p*-nitrophenols. The relatively low yields are due to oxidation of phenol by nitric acid. Since *o*-nitrophenol is more volatile than the *para*, the two isomers can be separated by steam distillation.



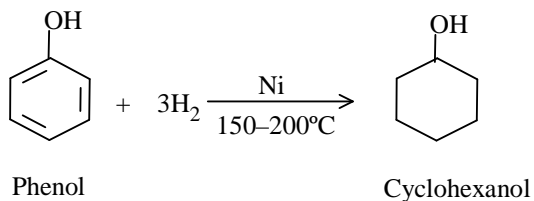
Nitration of phenol with concentrated nitric acid gives 2, 4, 6-trinitrophenol (picric acid). However, the yield is low because of excessive oxidation of phenol.



- (iii) **Sulphonation** : Sulphonation of phenols occurs readily giving a mixture of o- and p- isomers; o-isomer predominates at low temperature while p-isomer at high temperatures. Further, the o-isomer can be changed to p-isomer on heating.

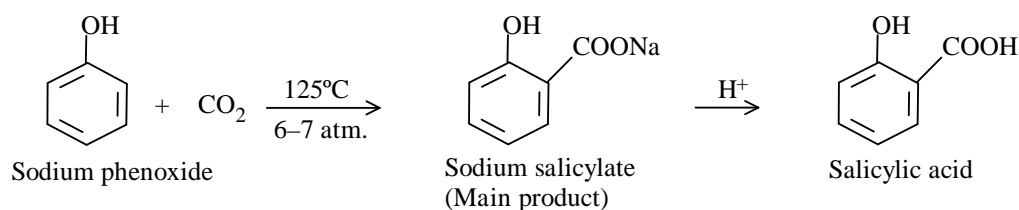


9. **Hydrogenation** : Phenols when hydrogenated in presence of nickel catalyst at about 150–200°C give the corresponding cyclohexanol.

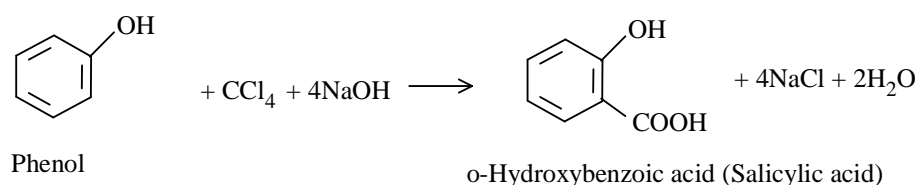
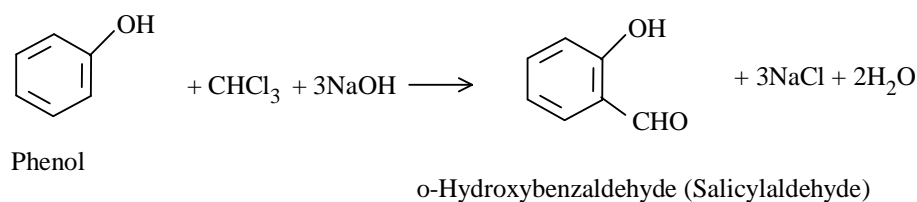


10. **Kolbe reaction** : When sodium salt of a phenol is heated with carbon dioxide gas at 120° – 140°C under pressure (6–7 atmospheres), a carboxyl group is introduced mainly in the ortho position with respect to the phenolic group to form o-hydroxy benzoates. This reaction is known as Kolbe reaction. A small amount of p-isomer is also obtained. However, if the reaction is carried out at high temperature, p-isomer is the main product.



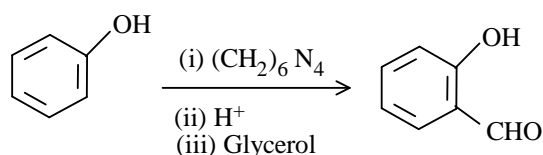


11. **Reimer-Tiemann reaction** (reaction between phenol and alkaline chloroform or carbon tetrachloride to form salicylaldehyde and salicylic acid respectively).

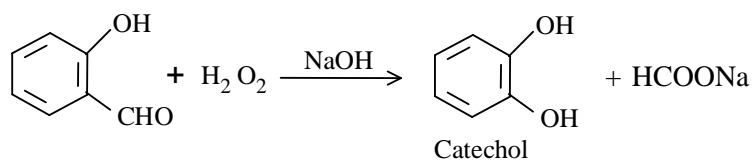


In the Reimer – Tiemann reaction, the electrophile used is :  $\text{CCl}_2$  (dichlorocarbene), an electron deficient species.

**Salicylaldehyde** can also be prepared by heating phenol with hexamethylenetetramine, glycerol and boric acid (Duff reaction).

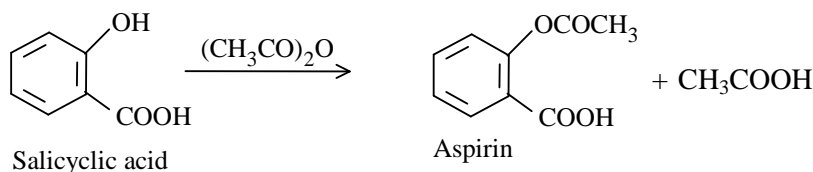


An interesting reaction of salicylaldehyde is its oxidation with alkaline hydrogen peroxide to form 1, 2-dihydroxybenzene (**Dakin reaction**).

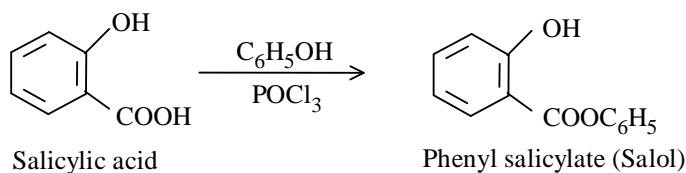


**Salicylic acid** (o-hydroxybenzoic acid) is an important compound. Its three important derivatives are mentioned below.

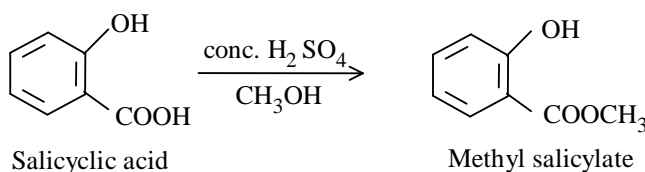
(i) **Aspirin** (Acetyl salicylic acid). It is an important analgesic and antipyretic.



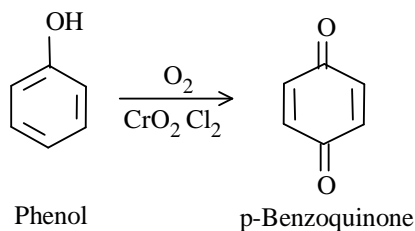
(ii) **Salol (Phenyl salicylate)** : It is used as an internal antiseptic.



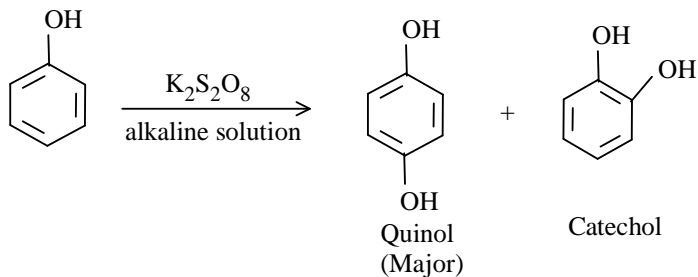
(iii) **Methyl salicylate (Oil of winter green)** : It is used as a flavouring agent.



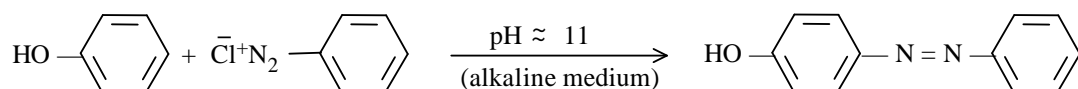
12. **Oxidation** : (i) Oxidation by oxygen in presence of chromyl chloride.



(ii) Oxidation by potassium persulphate (Elbs persulphate reaction).



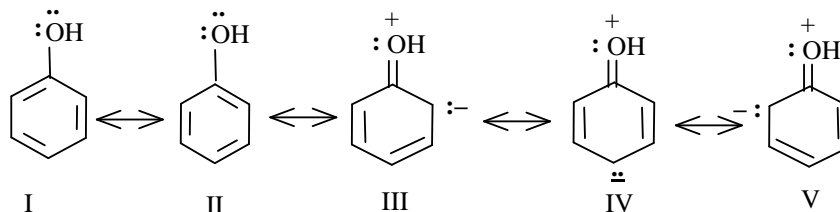
13. **Condensation reaction** : Phenol with benzenediazonium chloride in presence of alkali to form hydroxyazo dyes. The reaction occurs mainly in the para position and known as coupling.



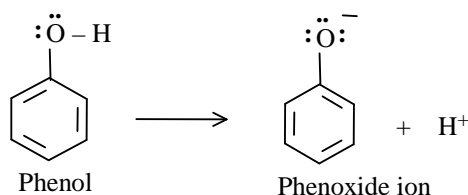
Phenol condenses with formaldehyde in presence of acids to form a polymer called bakelite (used in buttons, electric switches, etc.). Phenol condenses with phthalic anhydride in presence of a few drops of concentrated sulphuric acid or anhydrous  $\text{ZnCl}_2$  to form phenolphthalein (phthalein reaction), a common indicator in acid-alkali titrations.

**Uses of Phenol :** Phenol is used (i) for making bakelite. (ii) as a starting material for manufacturing drugs like salol (phenyl salicylate) used as internal antiseptic, aspirin (acetyl salicylic acid) used as analgesic and antipyretic, phenolphthalein (indicator), picric acid (explosive), etc. (iii) as an antiseptic.

(i) Phenol exists as a resonance hybrid of the following structures.

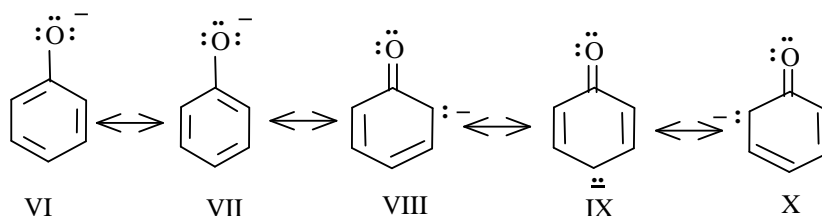


Due to resonance, oxygen atom of the  $-OH$  group acquires a positive charge (see structures III to V) and hence attracts electron pair of the  $O - H$  bond leading to the release of hydrogen atom as proton.



Since resonance is not possible in alcohols (due to absence of conjugation of the lone pair of electron of oxygen with a double bond), the hydrogen atom is more firmly linked to the oxygen atom and hence alcohols are neutral in nature.

(ii) Once the phenoxide ion is formed, it stabilises itself by resonance, actually phenoxide ion is more stable than the parent phenol.



Resonating structures of phenoxide ion (note that all the structures are similar and hence equally stable)

Note that all resonating structures of the phenoxide ion have a negative charge, hence these are almost equally stable; Resonating structures I and II of phenol have no charge hence these are more stable than structures III to V having both positive and negative charges. Thus phenoxide ion is more resonance stabilised than phenol. Since there is no possibility for the delocalisation of negative charge in the alkoxide ion, the latter is not stable and hence alcohols have practically no tendency to ionise to form alkoxide and hydrogen ions.

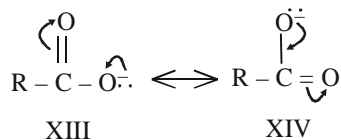
**Comparison of acidity of phenols and carboxylic acids :** Let us draw the required structures for carboxylic acids.



Resonating structures of acids

Ionisation of carboxylic acids

(Note that only structure XII involves charge separation)



Resonating structures of carboxylate anion

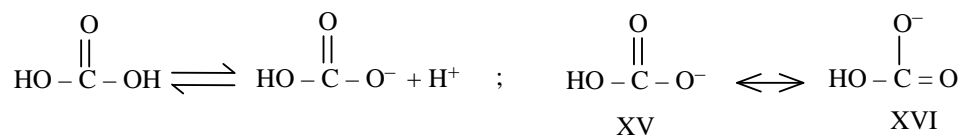
(Note that both structures are similar and hence equally stable)

Note that the resonating structures XI and XII of the carboxylic acid are non-equivalent and hence much less stable than the equivalent resonating structures XIII and XIV for the carboxylate ion.

Hence carboxylic acids have a tendency to undergo ionisation to form more stable carboxylate ions and protons.

Now let us compare the acidic strengths of carboxylic acids and phenols. The resonating structures VI to X of the phenoxide ion are not equivalent, while the resonating structures XIII and XIV of the carboxylate anions are equivalent. Hence the resonance hybrid of the carboxylate anion is relatively more stable than the resonance hybrid of the phenoxide ion. Thus a carboxylic acid is more acidic than a phenol.

**Comparison of acidity of phenols and carbonic acid.** Let us consider the ionisation of carbonic acid.



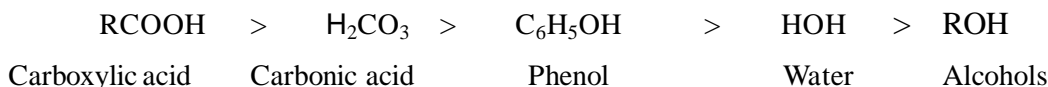
Carbonic acid

Bicarbonate ion

Resonating structures of bicarbonate ion

Here also note that the resonating structures XV and XVI of the bicarbonate ion are equivalent, while the resonating structures VI to X of the phenoxide ion are non-equivalent. Hence bicarbonate ion is relatively more stable than the phenoxide ion. Thus it is reasonable to say that carbonic acid is a stronger acid than a phenol.

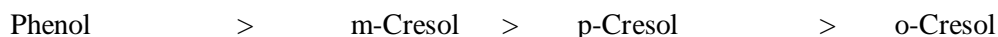
Relative acidity of the various common compounds.



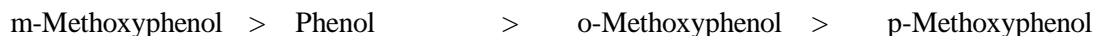
**Effect of substituents on the acidity of phenols:** Presence of deactivating groups (electron-withdrawing groups) like  $-\text{NO}_2$ ,  $-\text{X}$ ,  $-\text{CN}$ , etc. increases the acidity of phenols while the presence of activating groups (electron-releasing groups) like  $-\text{R}$ ,  $-\text{NH}_2$  etc. decreases the acidity of phenols. Further the particular effect is more when a substituent is present in o- or p- position than in m-position to the phenolic group. This explains the following order of acidity.



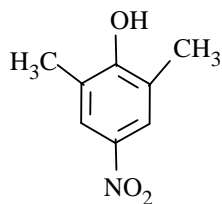
Similarly; the following order of acidity is found in cresols.



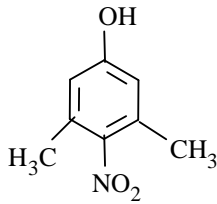
However, m-methoxy and m-amino phenols are stronger acids than the phenol because of presence of  $-I$  effect and absence of  $+R$  effect. Thus



Lastly, acidity of substituted phenols may also be influenced by steric effect and hydrogen bonding. Thus we can explain the low acidity of 3, 5-dimethyl-4-nitrophenol than the isomeric 2, 6-dimethyl-4-nitrophenol.

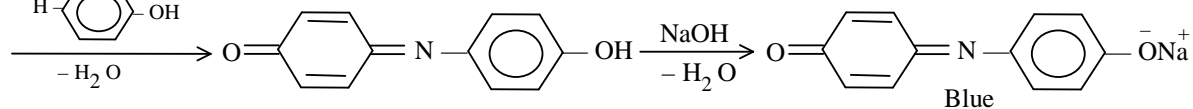
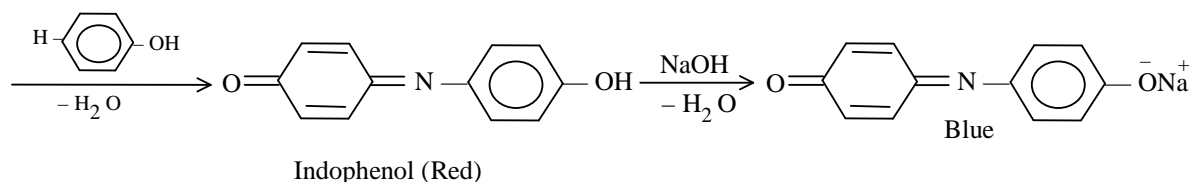
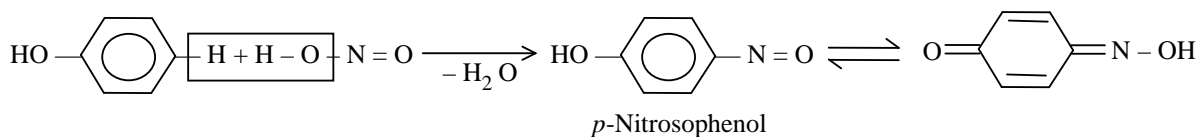
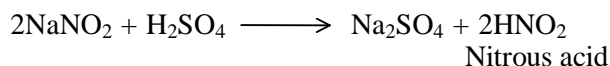


2, 6-Dimethyl-4-nitrophenol  
(more acidic)



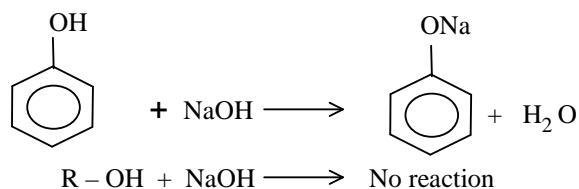
3, 5-Dimethyl-4-nitrophenol (less acidic due to steric inhibition of resonance of  $-\text{NO}_2$  group)

**Libermann's Reaction :** When phenol is treated with sodium nitrite dissolved in conc. Sulphuric acid, a red colouration appears, which changes to blue on adding aqueous NaOH. This reaction is called Libermann's reaction

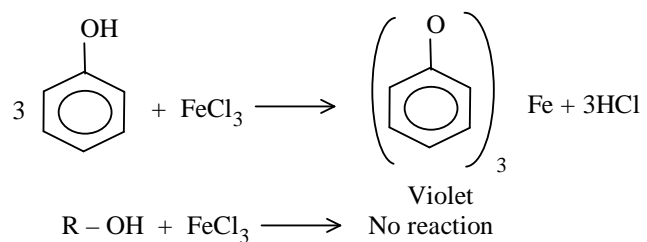


### Distinction between alcohol and phenol.

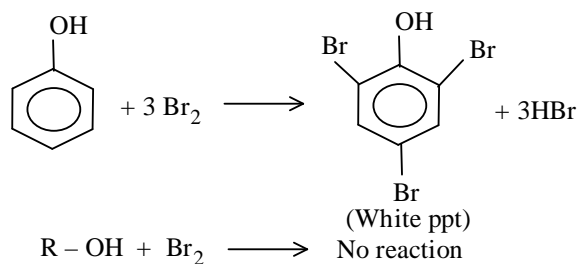
- (i) Phenols turns blue litmus red but alcohols do not.
- (ii) Phenols neutralize base, while alcohols do not.



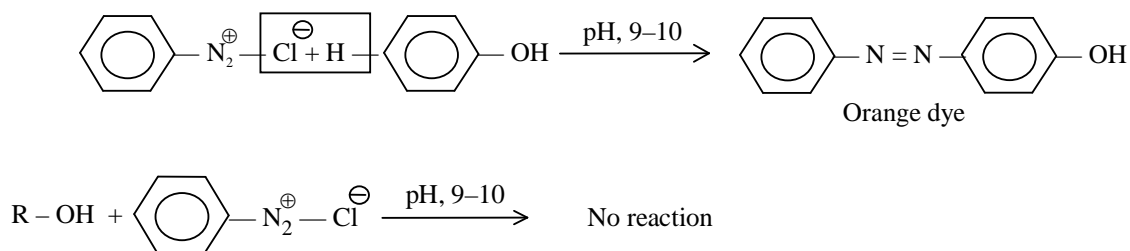
- (iii) Phenols give violet colour with  $\text{FeCl}_3$ , while alcohols do not.



(iv) Phenols give white ppt. with bromine while alcohols do not.

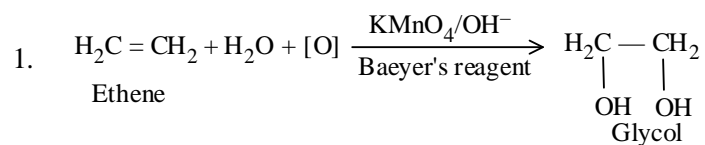


(v) Phenols undergo coupling reactions while alcohols do not.

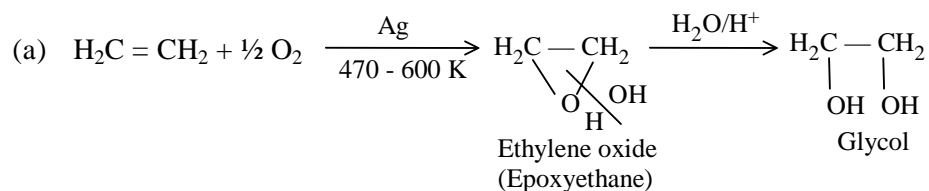


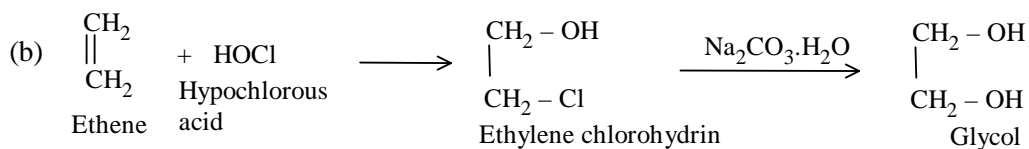
## Glycol

### Methods of Preparation :

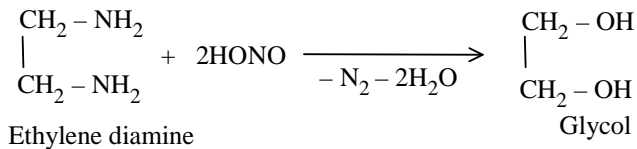


2. From ethene (commercial scale).

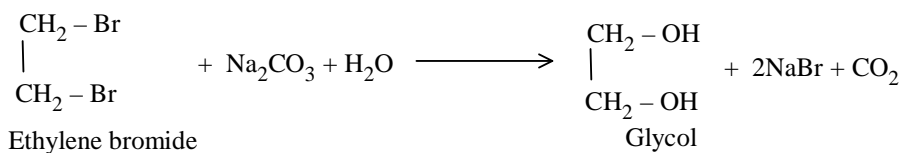




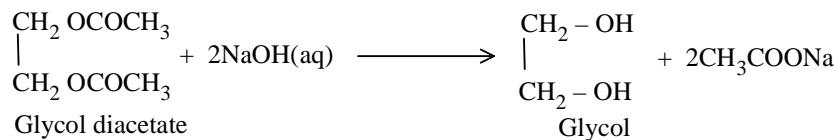
3. From ethylenediamine



4. From ethylene bromide (Laboratory method).



5. From glycol diacetate.

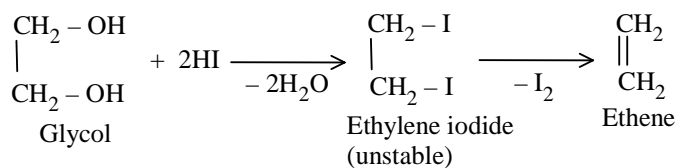


### Physical Properties :

1. Glycol is a colourless, syrupy liquid.
2. It is sweet in taste
3. It is highly soluble in water due to intermolecular hydrogen bonding.

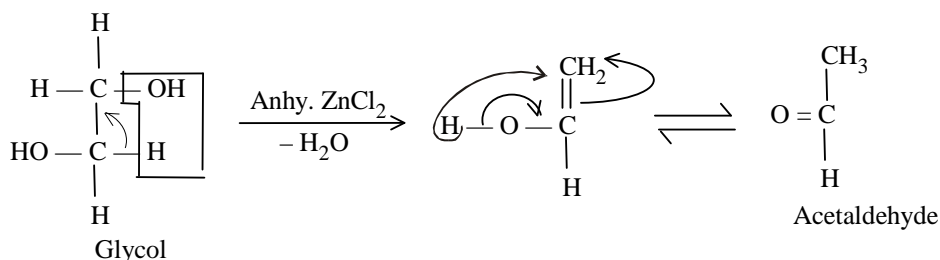
### Chemical Properties :

1. Action with HI.

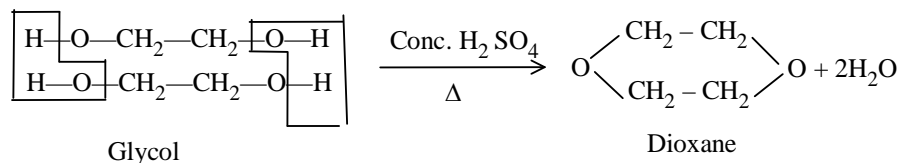


2. Dehydration : Glycol give different products on dehydration with different reagents : -

(i) With anhy.  $\text{ZnCl}_2$

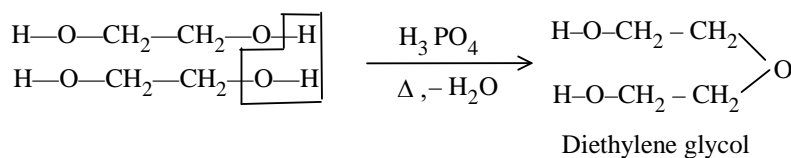


(ii) With conc.  $\text{H}_2\text{SO}_4$ .

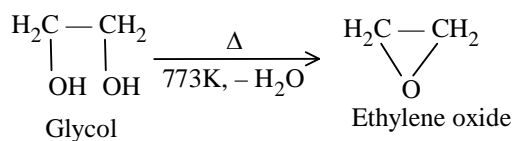


It is used as a solvent in industry.

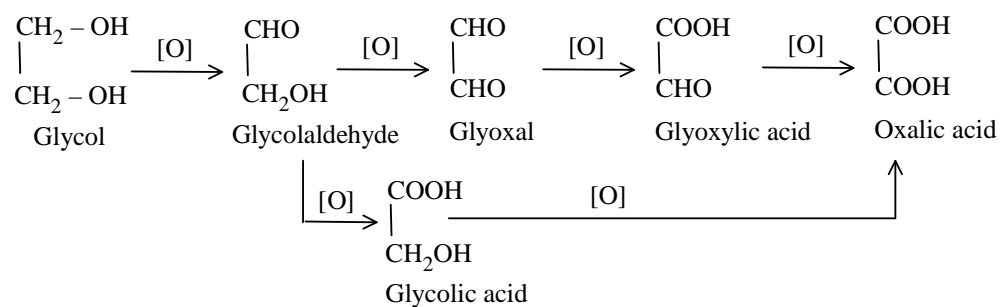
(iii) With phosphoric acid.



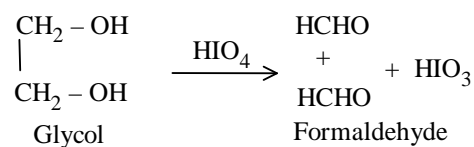
(iv) Heating.



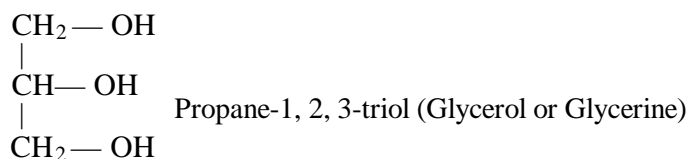
### 3. Oxidation



When is oxidised with nitric acid, glycolic acid and oxalic acid are obtained. On oxidation of glycol with periodic acid, formaldehyde is formed by oxidative cleavage and only one molecule of  $\text{HIO}_4$  is consumed.



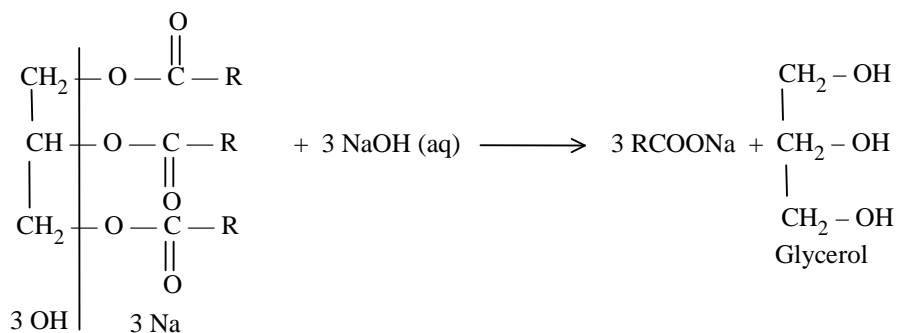
## Glycerol



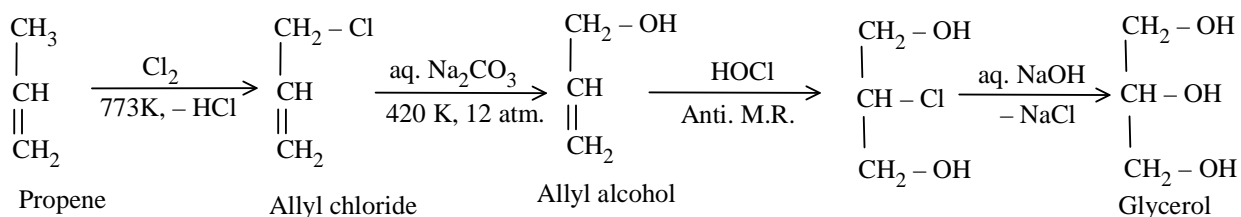


## Methods of preparation

- From glycerides : Triacyl derivatives of glycerol are called glycerides. Glycerol is prepared from glyceride by treating it with aq. NaOH. The reaction is called saponification reaction.



- From propene.



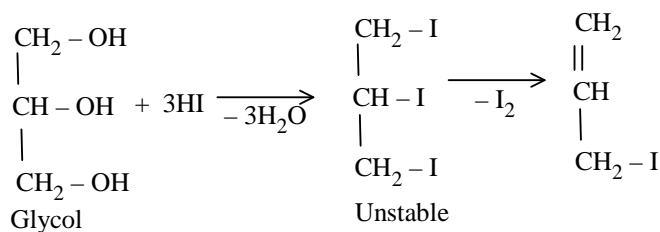
Glycerol prepared from propene is called synthetic glycerol.

## Physical Properties

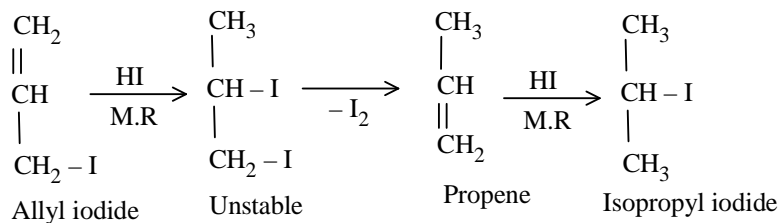
- Glycerol is a colourless, odourless, syrupy liquid.
- It has a sweet taste
- It is more viscous than glycol due to greater extent of hydrogen bonding.

## Chemical Properties :

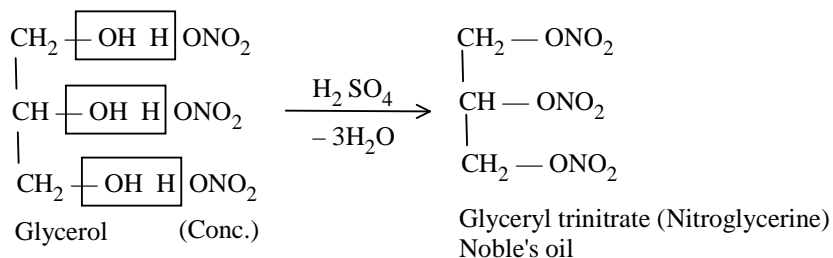
### 1. Action with HI.



If HI is taken in excess, then further reaction takes place.



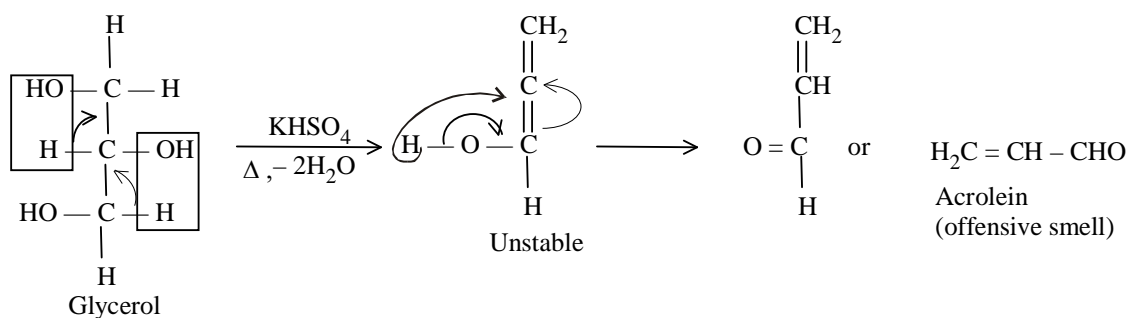
## 2. Nitration



Nitroglycerine is an explosive. It was discovered by Alfred Noble.

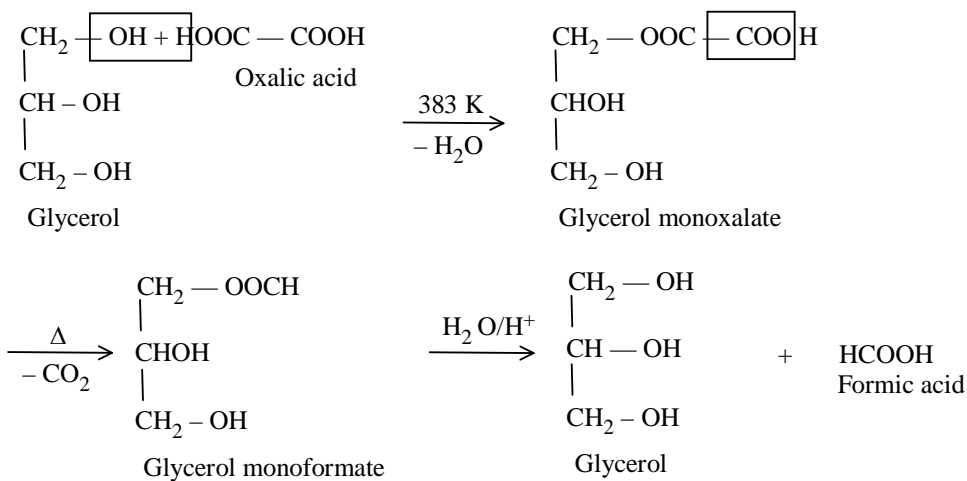
A mixture of glyceryl trinitrate, glyceryl dinitrate and Kieselguhr (a kind of porous clay) is called as dynamite.

## 3. Dehydration.

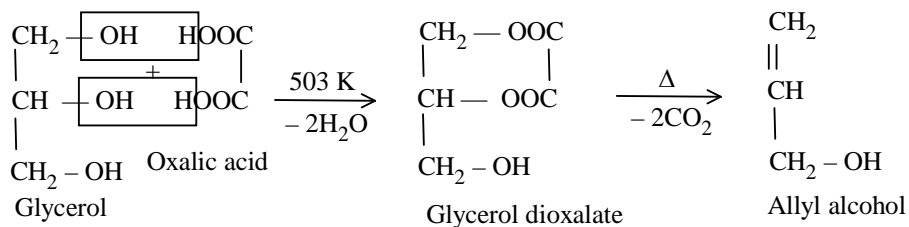


## 4. Reaction with oxalic acid.

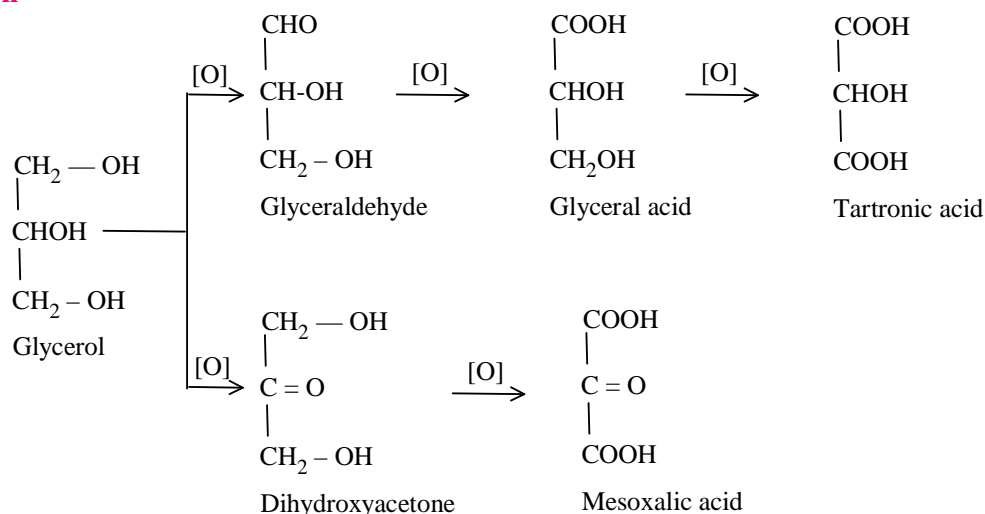
(i) At 383 K.



(ii) At 503 K.



## 5. Oxidation



The different products obtained by different reagents are :

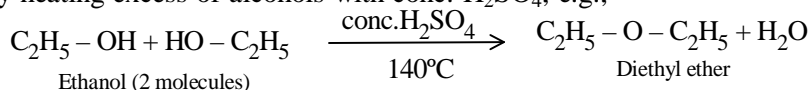
- (i) Conc.  $\text{HNO}_3$  = Glyceric acid
- (ii) Dil.  $\text{HNO}_3$  = Glyceric acid and tartonic acid
- (iii) Fenton's reagent ( $\text{H}_2\text{O}_2 + \text{FeSO}_4$ ) = Glyceraldehyde and dihydroxyacetone.  
(This mixture is called glycerose)
- (iv) Bismuth nitrate  $\text{Bi}(\text{NO}_3)_3$  = Mesoxalic acid

## Ethers

Here the C – O – C bond angle is about  $110^\circ$  which is quite close to the normal tetrahedral ( $109^\circ 28'$ ) and different from that in water ( $105^\circ$ ). This difference is because of the fact that in ethers the repulsion between lone pairs of electrons is counterbalanced by the repulsion between the bulky alkyl groups with the result value near to  $109^\circ 28'$  is retained.

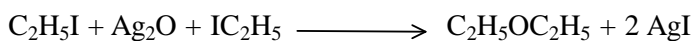
### Preparation of Ethers :

1. By heating excess of alcohols with conc.  $\text{H}_2\text{SO}_4$ , e.g.,



Recall that  $2^\circ$  and  $3^\circ$  alcohols under the above conditions give alkenes as the main product. Moreover, this method is limited only for the preparation of simple ethers.

2. By heating alkyl halide with dry silver oxide (only for simple ethers)

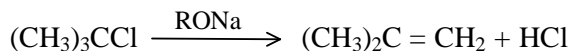


Remember that reaction of alkyl halides with **moist** silver oxide ( $\text{Ag}_2\text{O} + \text{H}_2\text{O} = \text{AgOH}$ ) gives alcohols.

3. By heating alkyl halide with sodium or potassium alkoxides (Williamson synthesis). This is the most important industrial and laboratory method and may be used for preparing simple as well as mixed ethers. For example,



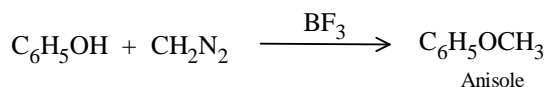
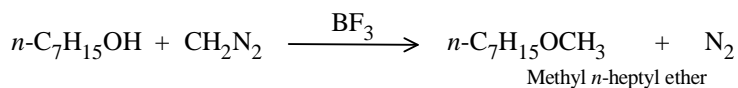
**Note :** Alkyl halides (especially ter. halides) undergo elimination reaction with sodium alkoxides (strong bases).



Hence when one of alkyl groups of the ether to be prepared is ter., it must be introduced as base and not as ter. halide. Thus for preparing  $(\text{CH}_3)_3\text{C} - \text{O} - \text{C}_2\text{H}_5$ , we should start with  $(\text{CH}_3)_3\text{CONa}$  and  $\text{C}_2\text{H}_5\text{Br}$  and not with  $(\text{CH}_3)_3\text{CBr}$  and  $\text{C}_2\text{H}_5\text{ONa}$ .

Ether used in the preparation of Grignard reagent should be free from traces of water and alcohol. This, so-called absolute ether, can be prepared by distilling ordinary ether with conc.  $\text{H}_2\text{SO}_4$  followed by storing over metallic sodium.

4. By reaction of Alcohols with diazomethane to form methyl ethers.



## Properties

### Physical :

1. Their boiling points are much lower than the isomeric alcohols. This is because of absence of  $-\text{OH}$  group in ethers and hence they are incapable of forming intermolecular hydrogen bonds.
2. Since the two  $\text{C} - \text{O}$  bonds in ethers are not linear ( $180^\circ$ ) but they are at an angle of about  $110^\circ$ , i.e., the molecule is bent, the dipole moment of the two  $\text{C} - \text{O}$  bonds do not cancel each other. Consequently, ethers are slightly polar and have a small net dipole moment (e.g. 1.18 D for diethyl ether).

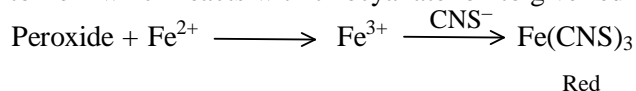
Note that the bond angle in ether is somewhat greater than water ( $105^\circ$ ). It is due to the repulsion between bulky alkyl groups.

### Chemical :

Ethers are much less reactive than compounds containing other functional group. They do not react with active metals like Na, strong base like NaOH, reducing or oxidising agents.

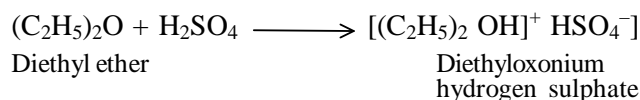
1. **Formation of peroxides :** On standing in contact with air, ethers are converted into unstable peroxides ( $\text{R}_2\text{O} \rightarrow \text{O}$ ) which are highly explosive even in low concentrations. Hence ether is always purified before distillation. Purification (removal of peroxide) can be done by washing ether with a solution of ferrous salt (which reduces peroxide to alcohols) or by distillation with conc.  $\text{H}_2\text{SO}_4$  (which oxidises peroxides).

The presence of peroxides in ether is indicated by formation of red colour when ether is shaken with an aqueous solution of ferrous ammonium sulphate and potassium thiocyanate. The peroxide oxidises  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  which reacts with thiocyanate ion to give red colour of ferric thiocyanate.



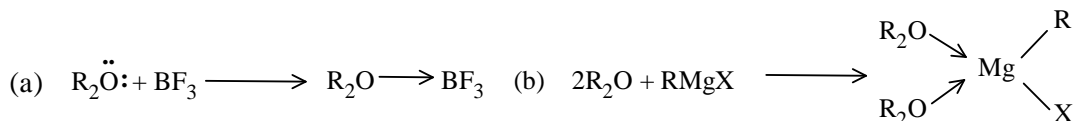
However, the formation of peroxide is prevented by adding a little  $\text{Cu}_2\text{O}$  to it.

2. **Basic nature :** Owing to the presence of unshared electron pairs on oxygen, ethers are basic. Hence they dissolve in strong acids (e.g., HCl, conc. H<sub>2</sub>SO<sub>4</sub>) at low temperature to form oxonium salts.



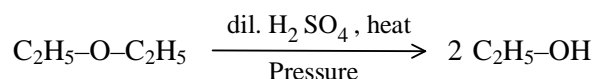
On account of this property, ether is removed from ethyl bromide by shaking with conc. H<sub>2</sub>SO<sub>4</sub>. The oxonium salts are stable only at low temperature and in a strongly acidic medium. On dilution, they decompose to give back the original ether and acid.

Ethers also form coordination complexes with Lewis acids like BF<sub>3</sub>, AlCl<sub>3</sub>, RMgX, etc.

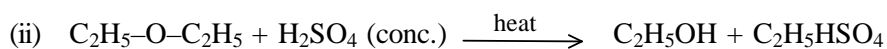
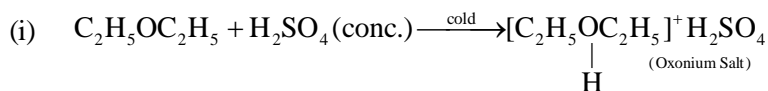


It is for this reason that ethers are used as solvent for Grignard reagents.

3. Action of dilute H<sub>2</sub>SO<sub>4</sub> (hydrolysis).



4. Action of concentrated H<sub>2</sub>SO<sub>4</sub>.



5. Action of conc. HI or HBr.

