

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. Since the compounds containing two or more hydroxyl groups on the same carbon atom are unstable and lose a molecule of water at room temperature. The two or more alcoholic groups must be present on different carbon atoms.

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.

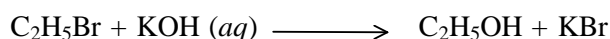
$CH_3CH_2CH_2CH_2OH$	$\begin{array}{c} OH \\ \\ CH_3CH_2CHCH_3 \end{array}$	$(CH_3)_3COH$
n-Butyl alcohol (1-Butanol) 1° alcohol	sec-Butyl alcohol (2-Butanol) 2° alcohol	t-Butyl alcohol (2-Methyl-2-propanol) 3° alcohol

Structure of alcohols : It is important to note that in alcohols, carbon as well as oxygen are in sp^3 hybridised state. However, the four sp^3 hybrid orbitals of oxygen are not similar : two have one electron each and the other two have a pair of electrons each (difference from sp^3 hybridised C atom). The two completely filled sp^3 orbitals do not take part in the bond formation ; while the other two half-filled sp^3 hybrid orbitals of oxygen form bonds with the s orbital of hydrogen (O– H) and the sp^3 orbital of carbon of the alkyl group (C – O). The C – O – H bond angle 105° 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 hybrid orbitals of oxygen which repel each other and hence reduce the bond angle.

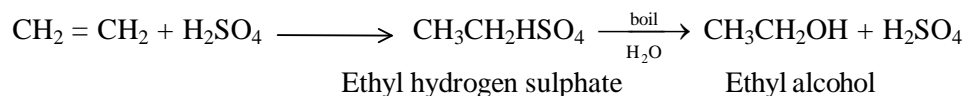
Alkoxy group : The group obtained by the removal of hydrogen atom of the hydroxyl group of alkanols is known as alkoxy group (RO–). For example, methoxy (CH_3O-), ethoxy (C_2H_5O-), etc.

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 ($Ag_2O + H_2O$).

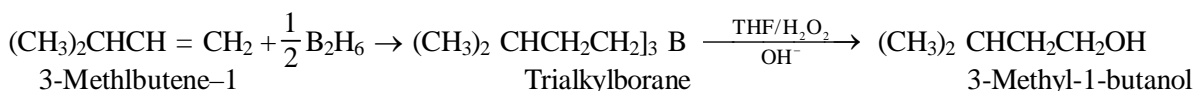


3. By the hydration of olefins by means of 98% H₂SO₄.

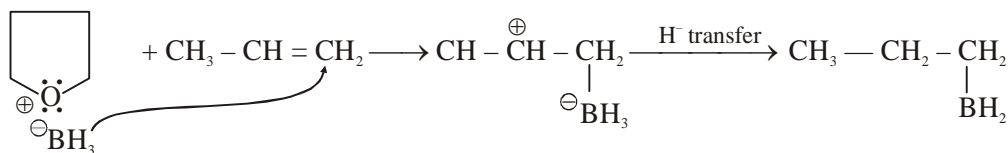
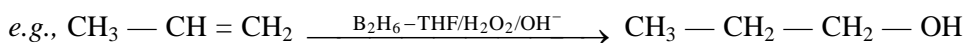


It is important to note that when an unsymmetrical olefin, e.g. (CH₃)₂CHCH = CH₂ is hydrated, different products are formed by different reagents.

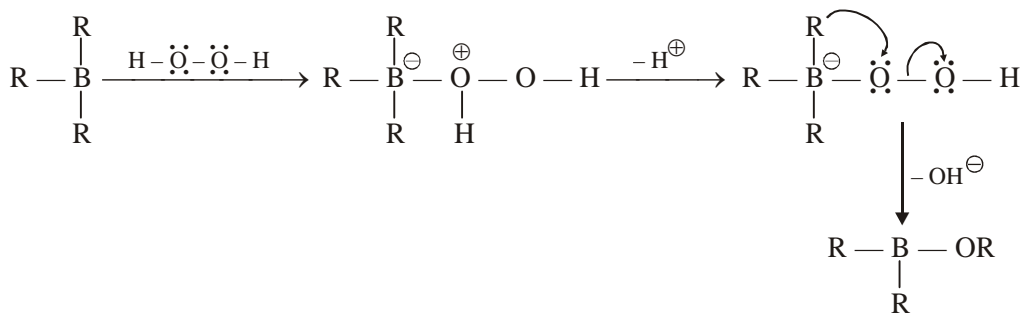
- (i) With dil. H₂SO₄, the expected product is 3-methyl-2-butanol (Markownikoff addition) but in practice the major product is 2-methyl-2-butanol due to rearrangement of the intermediate carbocation.
- (ii) With B₂H₆, hydration gives 3-methyl-1-butanol (anti-Markownikoff addition with no rearrangement, Hydroboration oxidation reaction).



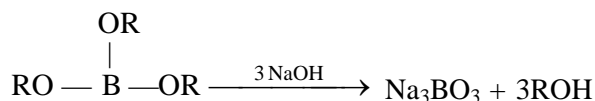
Mechanism of Hydroborations-deboration



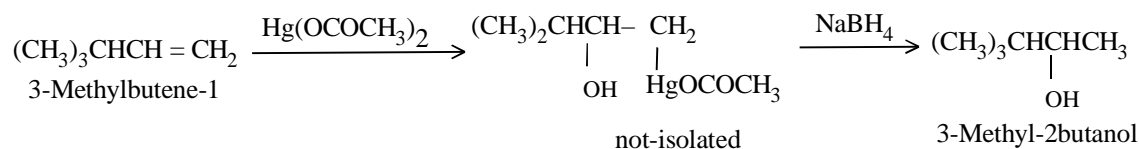
These steps are repeated twice to form (CH₃ - CH₂ - CH₂)₂B and then :



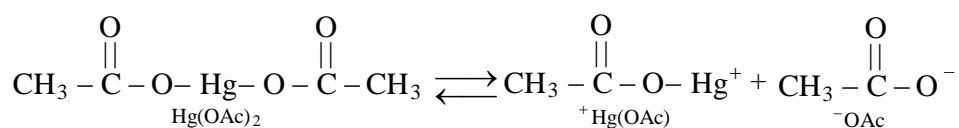
With H₂O₂, finally $\text{RO} - \overset{\text{OR}}{\text{B}} - \text{OR}$ is formed by above mentioned method



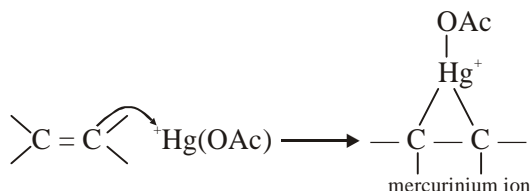
- (iii) With mercuric acetate, the product is 3-Methyl-2-butanol (Markownikoff addition with no rearrangement, Oxymercuration demercuration reaction).



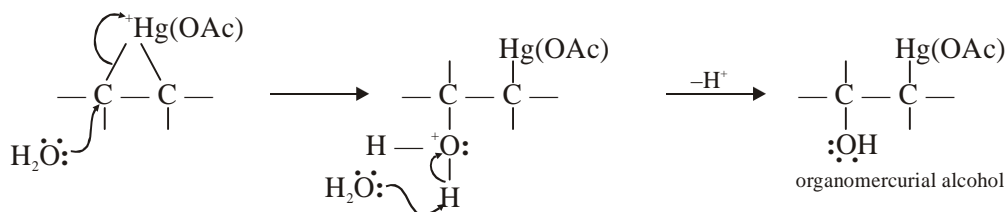
Mechanism of Oxymercuration demercuration reaction : The reagent for mercuriation is mercuric acetate, $\text{Hg}(\text{OCOCH}_3)_2$, abbreviated $\text{Hg}(\text{OAc})_2$. There are several theories as to how this reagent acts as an electrophile, but the simplest one is that mercuric acetate dissociates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



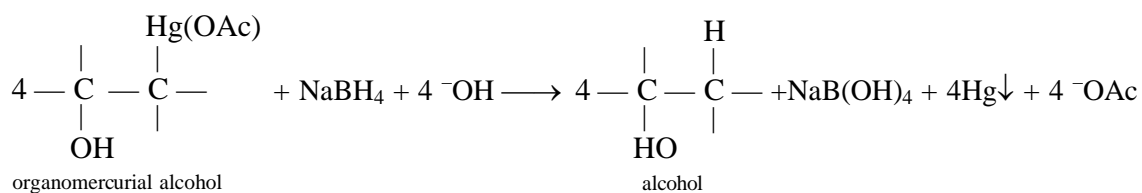
Oxymercuration involves an electrophilic attack on the double bond by the positively charged mercury species. The product is a *mercurinium ion*, an organometallic cation containing a three-membered ring.



Mercuriation 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.

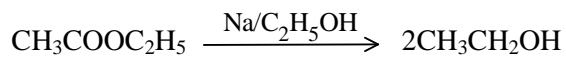
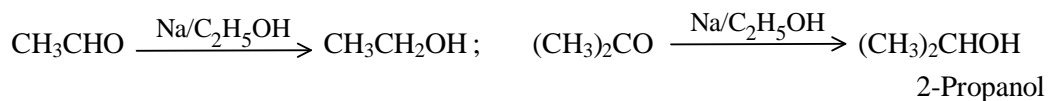


The second step is **demercuration**, to form the alcohol. Sodium borohydride (NaBH_4 , a reducing agent) replaces the mercuric acetate fragment with hydrogen.

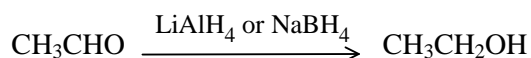


(4) By reduction of carbonyl compounds (aldehydes and ketones). Aldehydes give primary alcohols, while ketones give secondary alcohols.

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



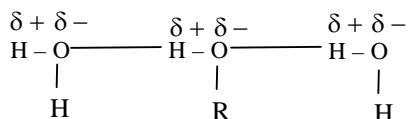
(b) Reduction by LiAlH_4 or NaBH_4 .



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.

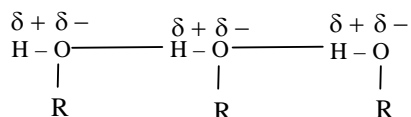
The solubility of alcohols in water can be explained due to the formation of hydrogen bond between the highly polarised –OH groups present both in alcohol and water.



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 as a 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 (hydrocarbon character) outweighs the –OH group due to branching.

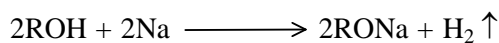
- (4) Lower alcohols form solid addition compounds with anhydrous metallic salts like CaCl_2 and MgCl_2 , viz., $\text{CaCl}_2 \cdot 4\text{C}_2\text{H}_5\text{OH}$ and $\text{MgCl}_2 \cdot 6\text{C}_2\text{H}_5\text{OH}$

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.

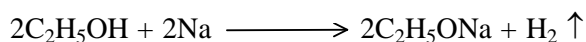
(A) Reactions involving only the hydrogen atom of the –OH group, i.e. reactions involving cleavage of oxygen-hydrogen bond, –O –H. All such reactions (No. 1 to 4) follow the following order.

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

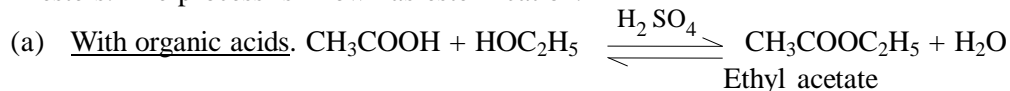


Sod. ethoxide

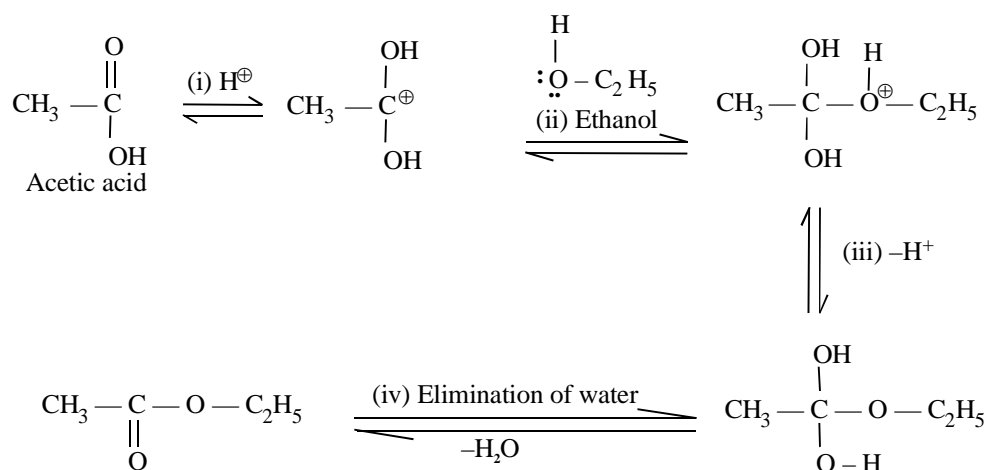
In this reaction alcohols behave as very weak acids. The decreasing order of acidic character of few such allied compounds is



- (2) Action of acids (esterification): Alcohols react with organic and inorganic acids (except halogen acids) in presence of a dehydrating agent like H_2SO_4 or dry hydrogen chloride gas to form esters. The process is known as esterification.

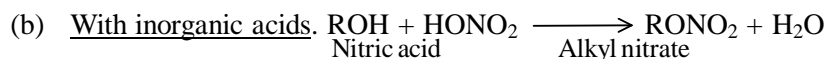


Mechanism : It is now proved beyond doubt that esterification with organic acids involved hydrogen atom of the alcohol and $-\text{OH}$ group of the acid. The reaction follows the following path.

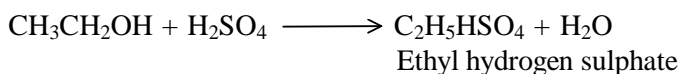


Note that :

- (i) Step is the protonation of carboxylic acid
- (ii) Step is the nucleophilic attack of ROH.
- (iii) Step is the elimination of proton.
- (iv) Step is elimination of water molecule.

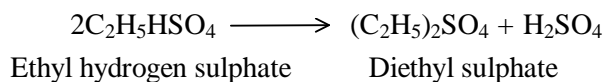


The action of conc. H_2SO_4 on alcohols is very interesting as it gives different products under different conditions. Alcohols dissolve in cold conc. H_2SO_4 (i.e. at 0°C) forming oxonium salts, $\text{ROH}_2\text{HSO}_4^+$. At room temperature, esterification takes place to form alkyl hydrogen sulphate.

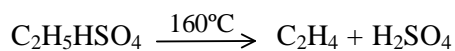


Ethyl hydrogen sulphate now can react in three different ways.

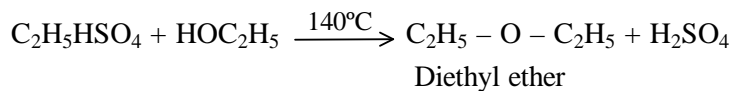
- (i) When heated alone, it forms diethyl sulphate.



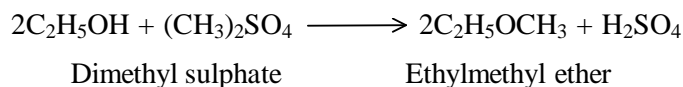
(ii) When heated with excess of H_2SO_4 at 160°C , it forms ethylene.



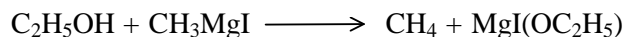
(iii) When heated with excess of ethyl alcohol at 140°C , it gives diethyl ether.



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



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

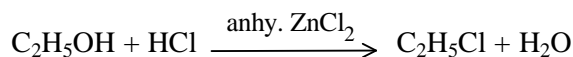


This reaction may be used for the estimation of alcoholic group (Zerewitnoff reaction).

(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.

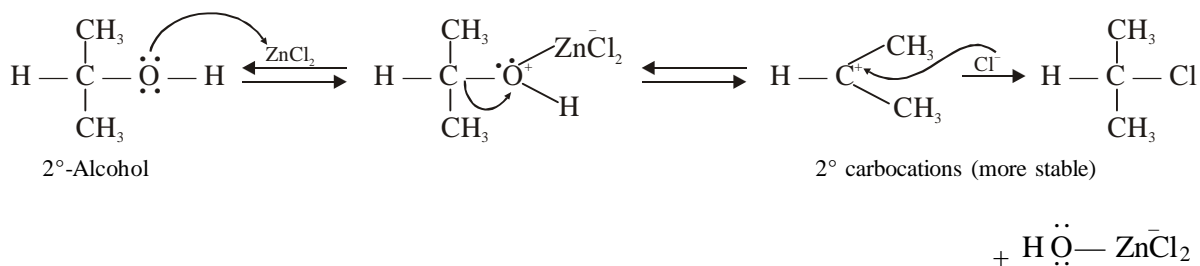
Tertiary > Secondary > Primary

(5) Action of halogen acids

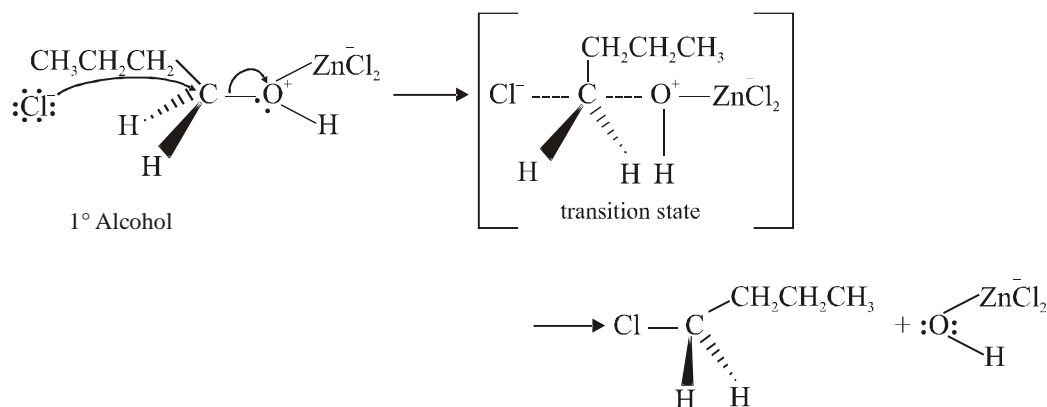


The reactivity of halogen is in the order : $\text{HI} > \text{HBr} > \text{HCl}$.

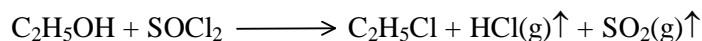
S_N1 reaction with the Lucas reagent (fast)



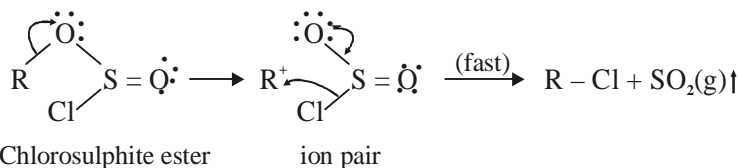
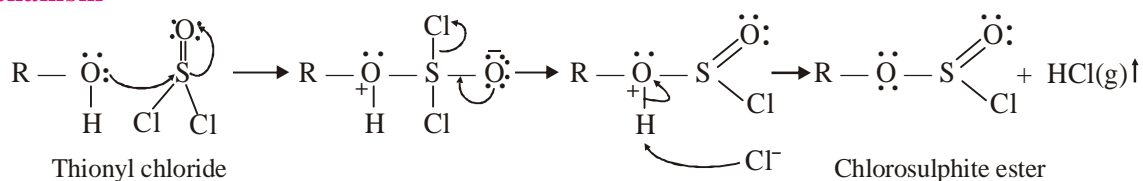
S_N2 reaction with the Lucas reagent (slow)



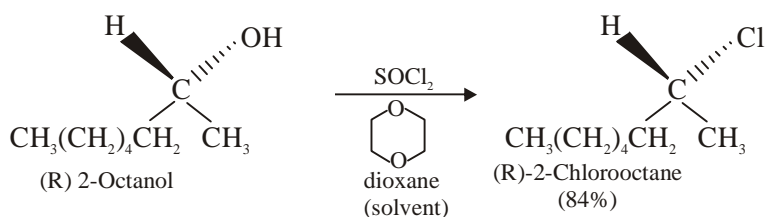
(6) Action of thionyl chloride



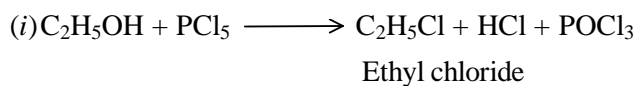
Mechanism



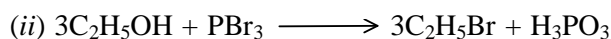
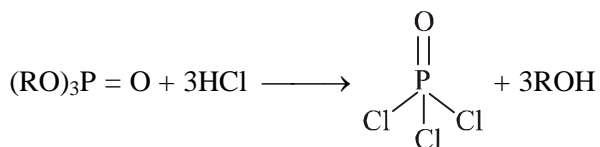
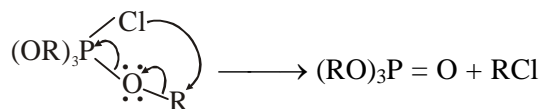
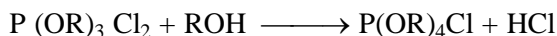
This mechanism resembles the $\text{S}_{\text{N}}1$, except that the nucleophile is delivered to the carbocation by the leaving group, giving retention of configuration as shown in the following example. (Under different conditions, retention of configuration may not be observed.)



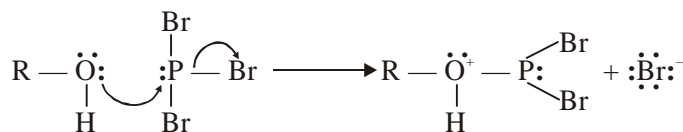
(7) Action of phosphorus halides (PX_5 and PX_3). For example,



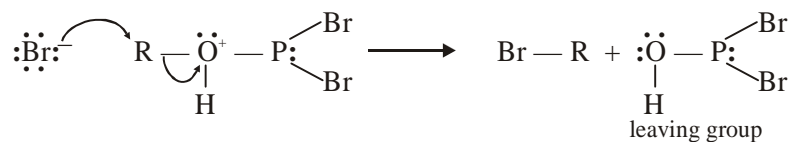
Mechanism



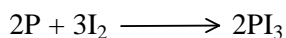
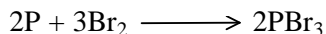
Displacement of bromide ion



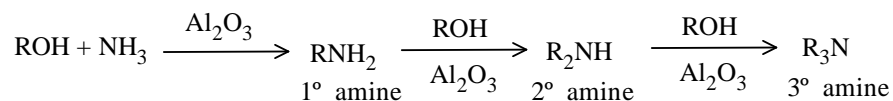
$\text{S}_{\text{N}}2$ attack on the alkyl group



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

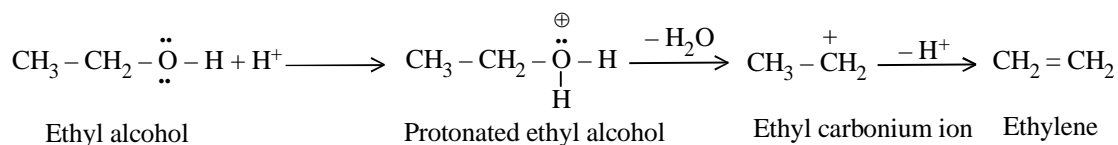


The ease of dehydration of alcohols is in the order :

Tertiary > Secondary > Primary

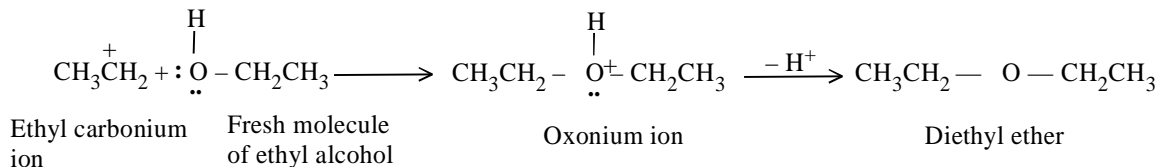
Mechanism of dehydration of alcohols to alkenes involves three steps.

- (i) Protonation of the alcohol molecule forming ROH_2^+ .
- (ii) Elimination of water molecule forming a carbonium ion.
- (iii) Expulsion of a proton from the carbonium ion forming alkene.

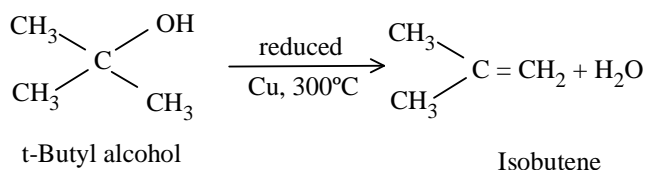
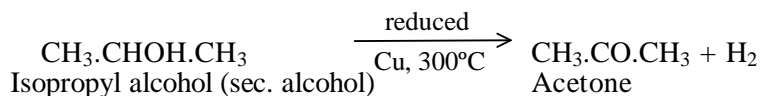
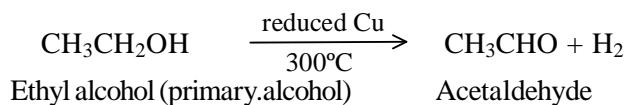


Protonation of $-\text{OH}$ (a poor leaving group) to $-\overset{+}{\text{O}}\text{H}_2$ converts it to a good leaving group. The relative ease of dehydration, i.e. $3^\circ > 2^\circ > 1^\circ$, of alcohols follows the order of stability of carbonium ions.

Mechanism of dehydration of alcohols to ethers. A carbonium ion is formed exactly in the same way as above (i.e. the two steps are same as in above mechanism). Now the nucleophile, a fresh molecule of alcohol attacks on the carbonium ion to form oxonium ion which then loses a proton forming ether as the final product. For example,



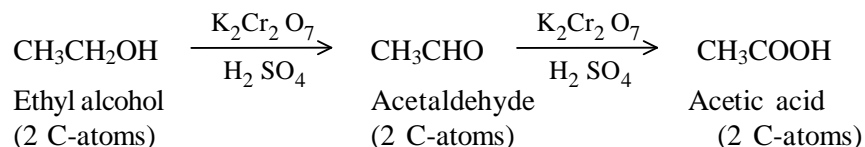
(9) Action of reduced copper : Primary and secondary alcohols are dehydrogenated to form aldehydes and ketones respectively, while tertiary alcohols are dehydrated to form olefins.



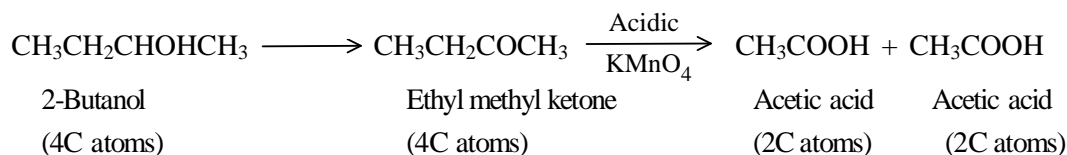
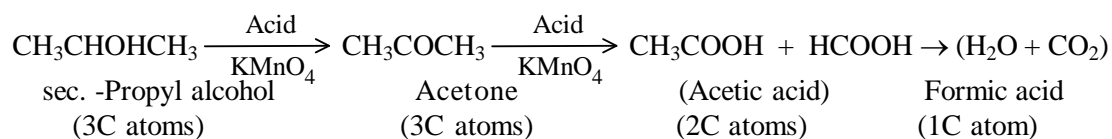
This dehydrogenation reaction may be used for distinguishing primary, secondary and tertiary alcohols.

(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 $K_2Cr_2O_7$, acidic or alkaline $KMnO_4$ or dilute nitric acid. On the other hand, tertiary alcohols are oxidised only by strong oxidising agents under vigorous conditions.

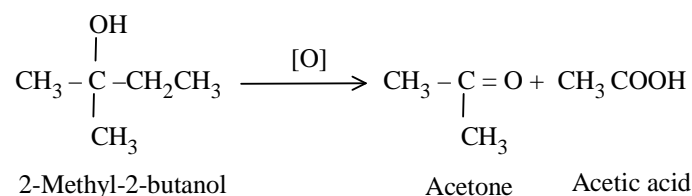
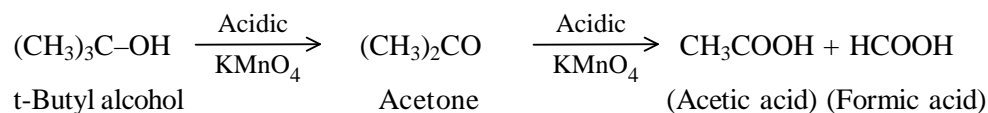
(a) **Primary alcohols** : These are easily oxidised first to aldehydes and then to carboxylic acids both having the same number of carbon atoms as the parent alcohol.



(b) **Secondary alcohols** : These 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.

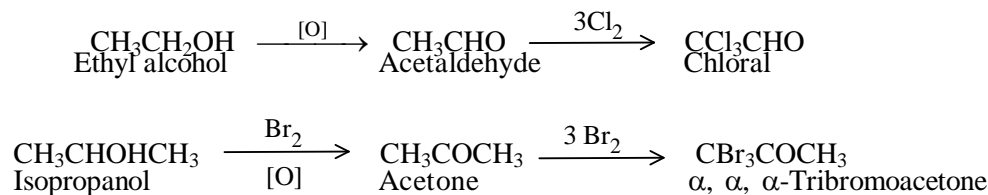


(c) **Tertiary alcohols** are generally resistant to oxidation in neutral or alkaline solution, but are oxidised by acidic oxidising agents (i.e. under drastic conditions) to form first ketones and then acids both having lesser number of carbon atoms than the parent molecule.



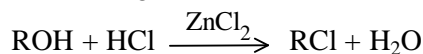
Thus oxidation may also be used for distinguishing the three types of alcohols.

(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)



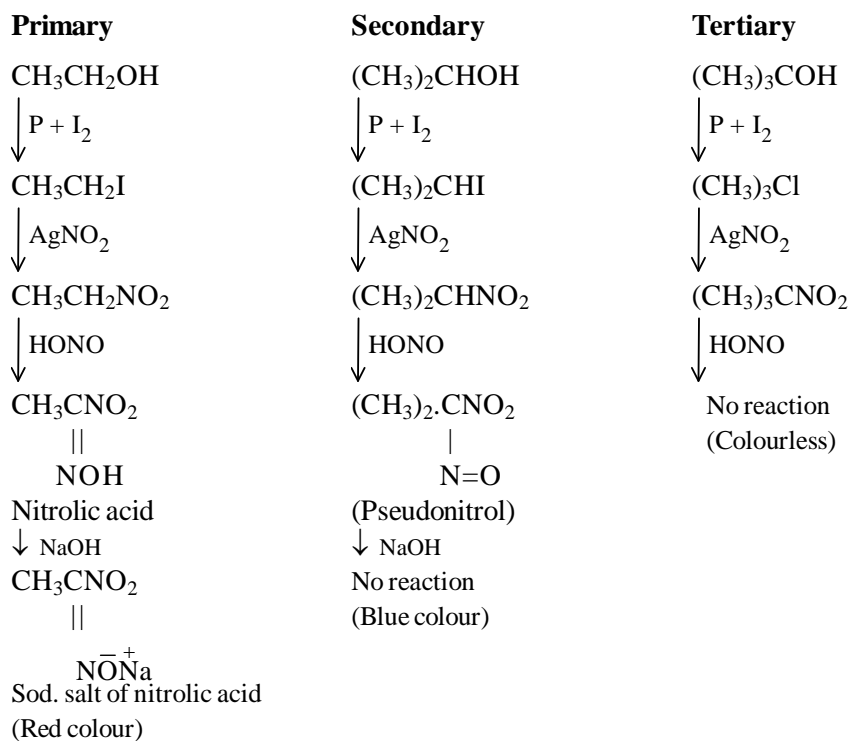
Since alkyl halides are insoluble, their formation is indicated by the appearance of a turbidity in the reaction mixture. The order of reactivity is tertiary > secondary > primary, the tertiary alcohols produce turbidity immediately, the secondary alcohols give turbidity within 5 – 10 minutes, and the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

- (2) **Catalytic dehydrogenation** (action of reduced copper at 300°C). Discussed earlier.

- (i) Primary alcohols form aldehydes
- (ii) Secondary alcohols form ketones.
- (iii) 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.

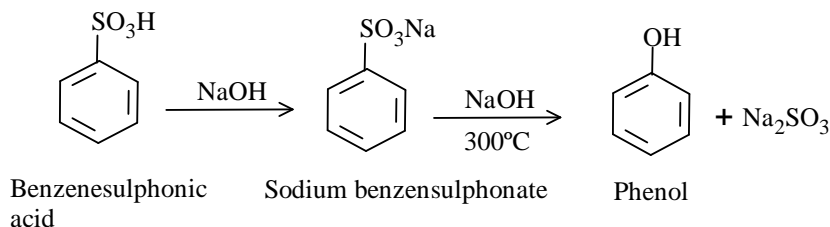
- (i) Alcohol is treated with concentrated hydroiodic acid or red phosphorus and iodine to form the corresponding alkyl iodide.
- (ii) Alkyl iodide is then reacted with silver nitrite to form the corresponding nitroalkane.
- (iii) The nitroalkane is treated with nitrous acid ($\text{NaNO}_2 + \text{H}_2\text{SO}_4$) followed by treatment with alkali (NaOH or KOH). Upon such treatment different alcohols give different colours.
 - (a) Primary alcohols produce a blood red colour
 - (b) Secondary alcohols produce a blue colour.
 - (c) Tertiary alcohols produce no colour.



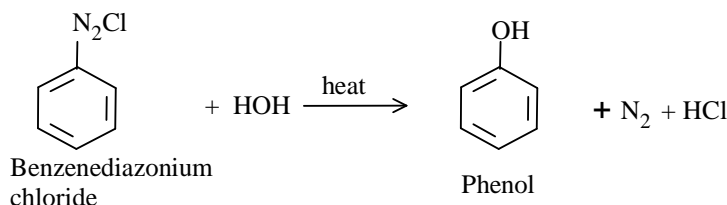
Phenols

Methods of Preparation of Phenol (C₆H₅OH)

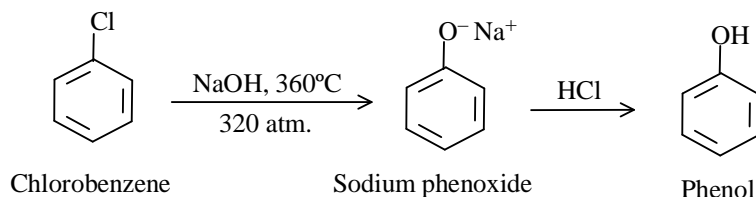
1. By fusing the sodium salt of benzene sulphonic acid with NaOH.



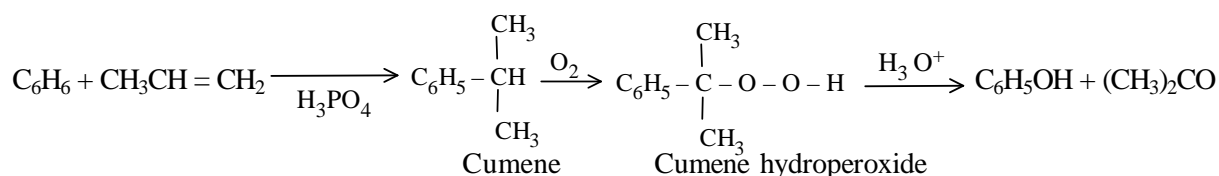
2. By adding benzene diazonium chloride to a large volume of boiling dilute H₂SO₄.



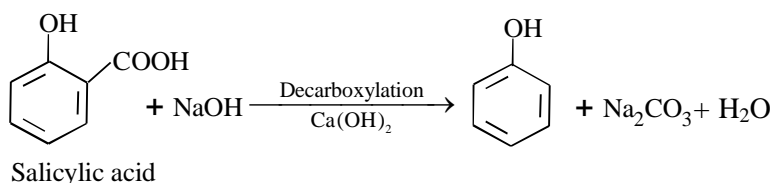
3. By heating chlorobenzene with caustic soda under pressure (Dow's process). This is commercial method. The reaction involves nucleophilic substitution, reaction.



4. From cumene hydroperoxide (commercial method).



5. By distilling a phenolic acid salicylic acid with soda lime.

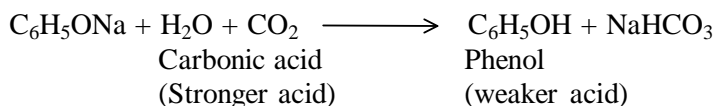


Properties

Physical :

- Pure phenols are generally colourless solids or liquids. The light colour usually associated with phenols is due to its oxidation by air in the presence of light.
 - 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.
-

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

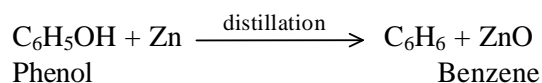


This indicates that phenols are very weak acids; weaker than carboxylic acids or even carbonic acid. In short, phenols are stronger acids than alcohols but weaker than the carboxylic acids and even carbonic acid.

2. **Action of ferric chloride :** Phenols give characteristic colour with neutral ferric chloride solution.

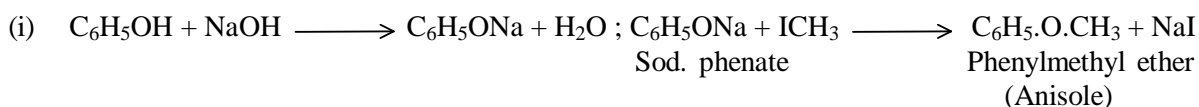
The characteristic colour is believed to be due to the formation of coloured co-ordination compounds. Reaction of phenols with ferric chloride is used in analytical chemistry for distinguishing phenols from carboxylic acids.

3. **Reduction with zinc dust :** Phenols, when distilled with zinc dust, give aromatic hydrocarbons (e.g. alcohols are reduced to hydrocarbons with hydriodic acid).

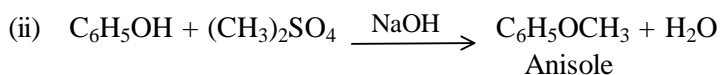


Note that phenols differ from alcohols in the above three reactions numbered 1, 2, and 3.

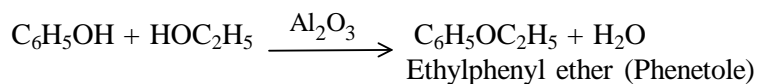
4. **Alkylation :** (Ether formation) : Phenols react with alkyl halides (aryl halides are too inert) or dialkyl sulphates in alkaline medium to form phenolic ethers.



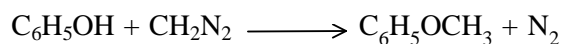
The method resembles Williamson's synthesis for preparing ethers.



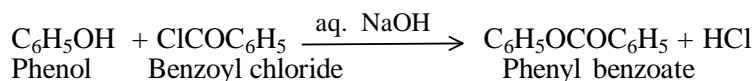
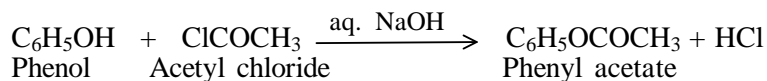
- (iii) Ethers can also be prepared by passing the mixed vapours of phenols and some alcohols over heated alumina.



- (iv) Methyl phenyl ether can also be easily prepared from diazomethane (CH_2N_2).

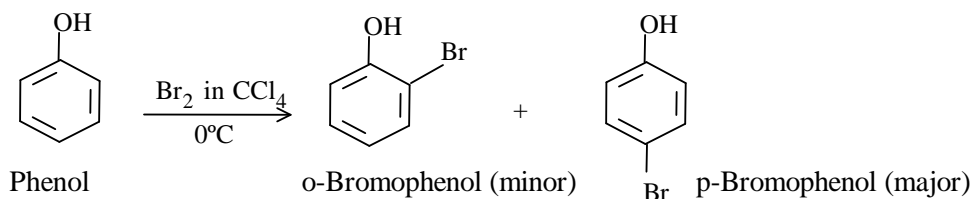


5. **Acylation :** (Ester formation) : Phenols react with acid chlorides or acid anhydrides (but not with acids) in alkaline solution to form esters.



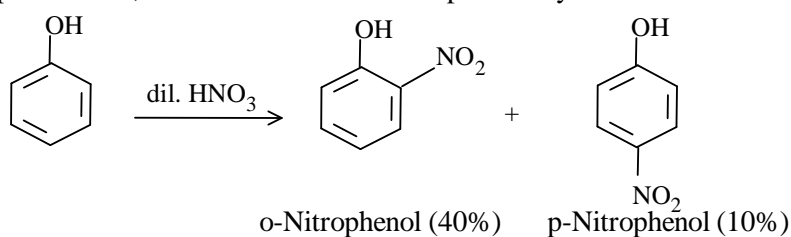
Reaction with benzoyl chloride is known as **Schotten-Bauman** reaction.

For preparing monohalogen derivatives, halogenation is carried out at low temperature and in non-polar solvents such as carbon tetrachloride (CCl₄) or carbon disulphide. For example,

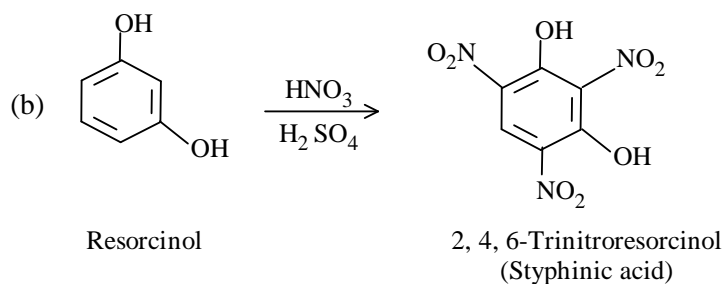
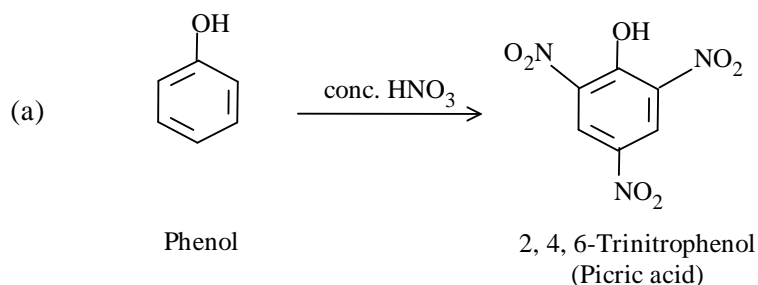


Non-polar solvents (CS₂, CCl₄) decrease the electrophilic character of Br₂ and minimize ionization of phenol.

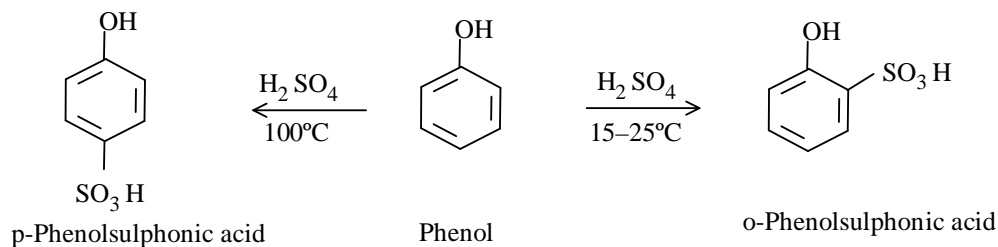
- (ii) **Nitration :** With dilute nitric acid, phenol gives a mixture of o- and p- nitrophenols. The relatively low yields are due to oxidation of phenol by nitric acid. Since o-nitrophenol is more volatile than the para isomer, the two isomers can be separated by steam distillation.



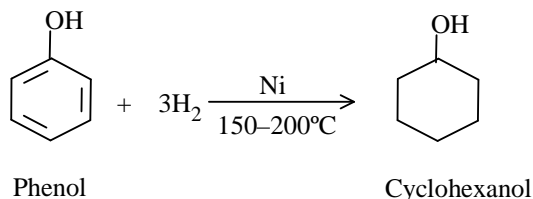
Nitration of phenol with concentrated nitric acid gives 2, 4, 6-trinitrophenol (picric acid). However, the yield is low because of excessive oxidation of phenol.



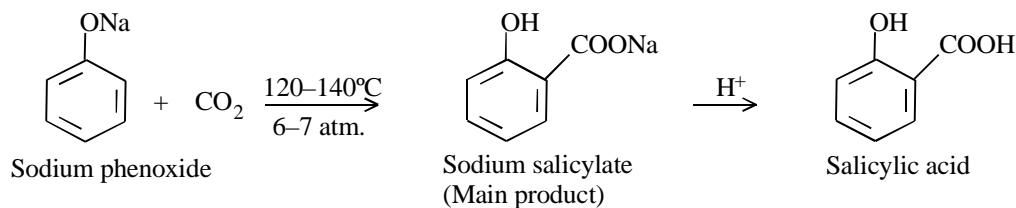
- (iii) **Sulphonation :** Sulphonation of phenols occurs readily giving a mixture of o- and p- isomers. The o-isomer predominates at low temperature while the p-isomer at high temperatures. Further, the o-isomer can be changed to p-isomer on heating at high temperature.



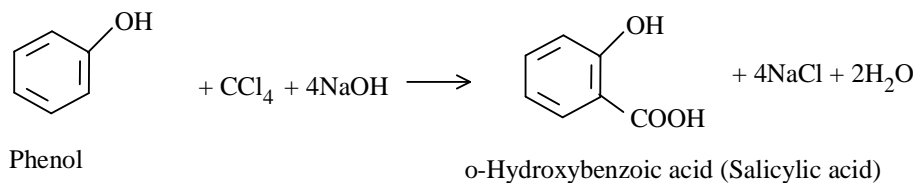
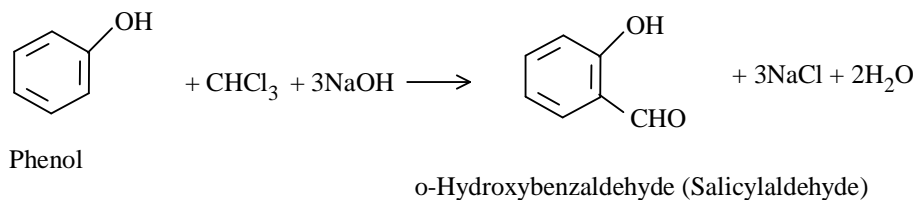
9. **Hydrogenation** : Phenols when hydrogenated in presence of nickel catalyst at about 150–200°C give the corresponding cyclohexanol.



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 benzoic acid. 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.

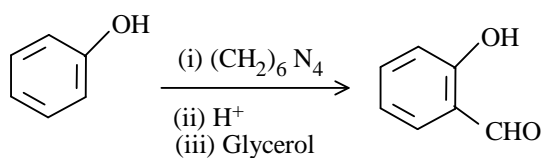


11. **Reimer-Tiemann reaction** (reaction between phenol and alkaline chloroform or carbon tetrachloride to form salicylaldehyde and salicylic acid respectively).

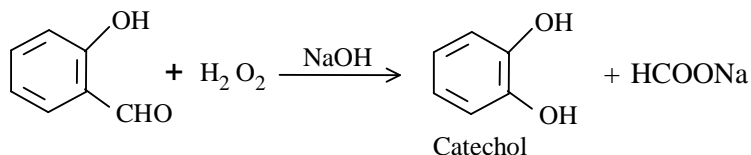


In the Reimer – Tiemann reaction, the electrophile intermediate formed is : CCl_2 (dichlorocarbene), an electron deficient species.

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

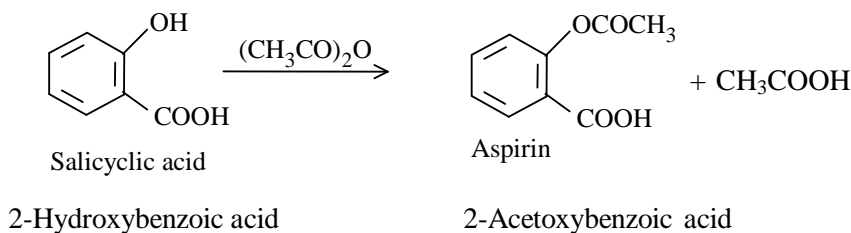


An interesting reaction of salicylaldehyde is its oxidation with alkaline hydrogen peroxide to form 1, 2-dihydroxybenzene (**Dakin reaction**).

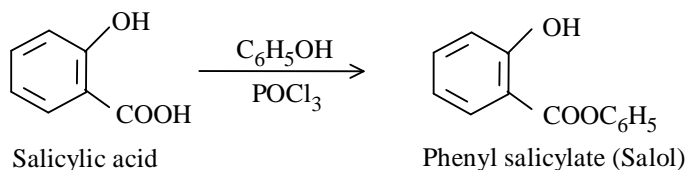


Salicylic acid (o-hydroxybenzoic acid) is an important compound. Its three important derivatives are mentioned below.

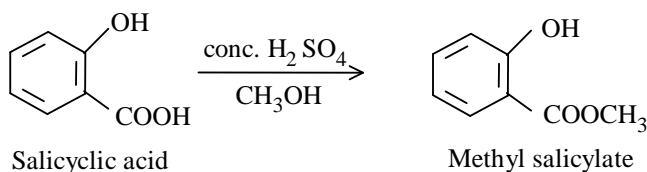
(i) **Aspirin** (Acetyl salicylic acid). It is an important analgesic and antipyretic.



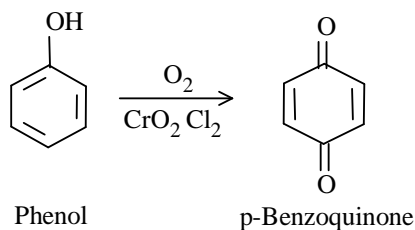
(ii) **Salol** (Phenyl salicylate) : It is used as an internal antiseptic.



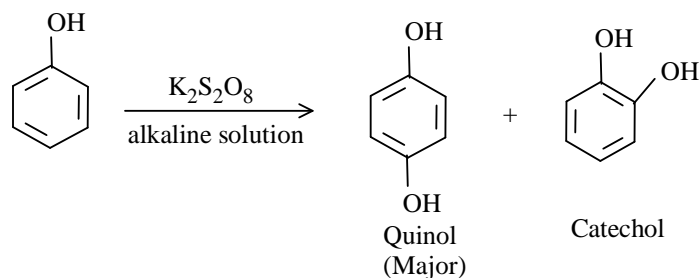
(iii) **Methyl salicylate** (Oil of winter green) : It is used as a flavouring agent.



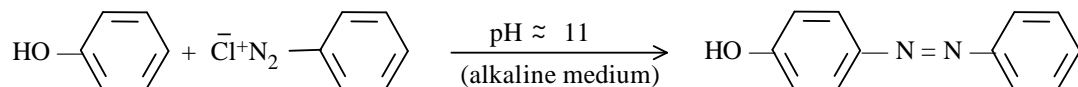
12. **Oxidation** : (i) Oxidation by oxygen in the presence of chromyl chloride.



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



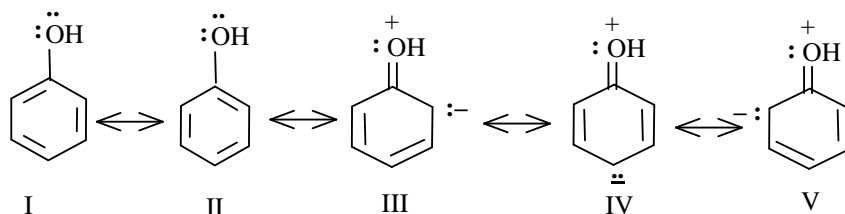
13. **Condensation reaction** : Phenol with benzenediazonium chloride in presence of alkali to form p-hydroxyazo dyes. The reaction occurs mainly at the para position and known as coupling reaction.



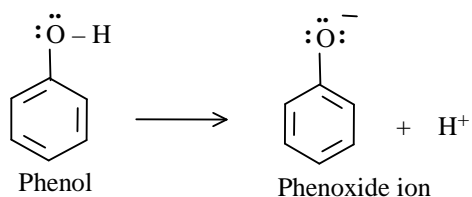
Phenol condenses with formaldehyde in presence of acids to form a polymer called bakelite (used in buttons, electric switches, etc.). Phenol condenses with phthalic anhydride in the presence of a few drops of concentrated sulphuric acid or anhydrous $ZnCl_2$ to form phenolphthalein (phthalein reaction), a common indicator in acid-base 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.

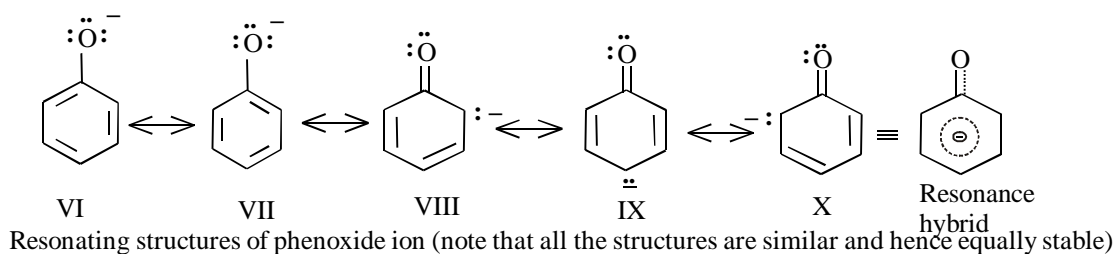


Due to resonance, oxygen atom of the -OH group acquires a positive charge (see structures III to V) and hence attracts electron pair of the O - H bond leading to the release of hydrogen atom as proton.



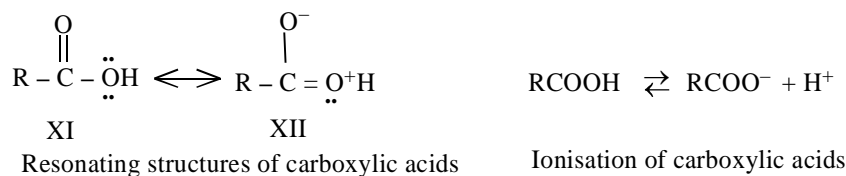
Since resonance is not possible in alcohols (due to absence of conjugation with the lone pair of electrons of oxygen with a double bond), the hydrogen atom is more firmly linked to the oxygen atom and hence alcohols are less acidic than phenols.

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

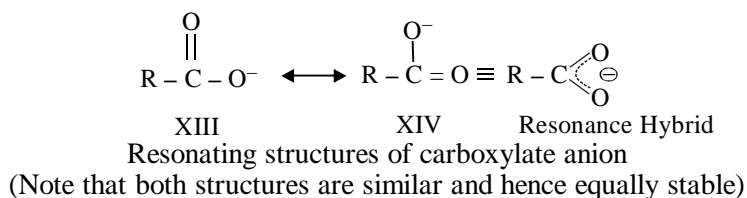


Note that all resonating structures of the phenoxide ion have a negative charge, hence these are almost equally stable; Resonating structures I and II of phenol have no charge hence these are more stable than structures III to V having both positive and negative charges. Thus phenoxide ion is more resonance 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. This conforms the less acidic nature of alcohols w.r.t Phenols.

Comparison of acidity of phenols and carboxylic acids : Let us draw the resonance structures of carboxylic acids.



(Note that only structure XII involves charge separation)

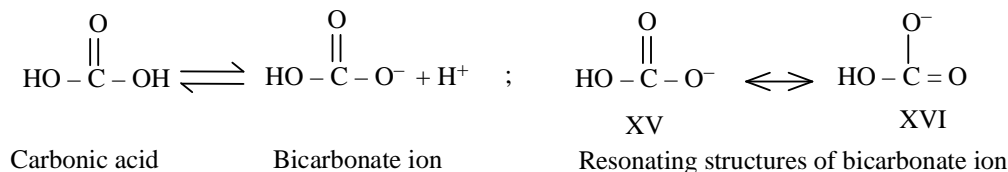


Note that the resonating structures XI and XII of the carboxylic acid are non-equivalent and hence much less stable than the equivalent resonating structures XIII and XIV for the carboxylate ion.

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

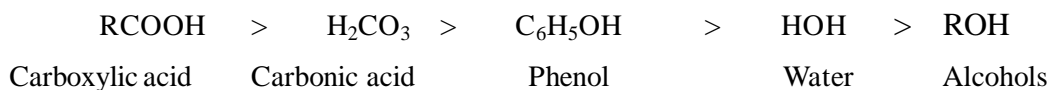
Now let us compare the acidic strengths of carboxylic acids and phenols. The resonating structures VI to X of the phenoxide ions are not equivalent, while the resonating structures XIII and XIV of the carboxylate anions are equivalent. Hence the resonance hybrid of the carboxylate anion is relatively 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.



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 phenol.

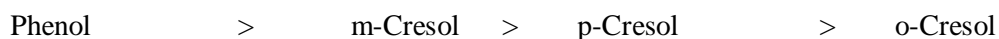
Relative acidity of the various common compounds.



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 at o- or p- position than at m-position to the phenolic group. This explains the following order of acidity.



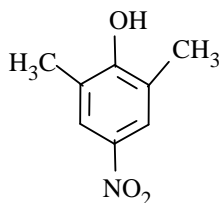
Similarly; the following order of acidity is found in cresols.



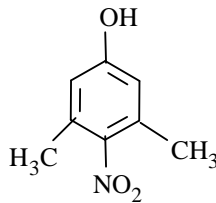
However, m-Methoxy and m-Amino phenols are stronger acids than the phenol because of presence of $-\text{I}$ effect and absence of $+\text{R}$ effect. Thus



At last, 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.

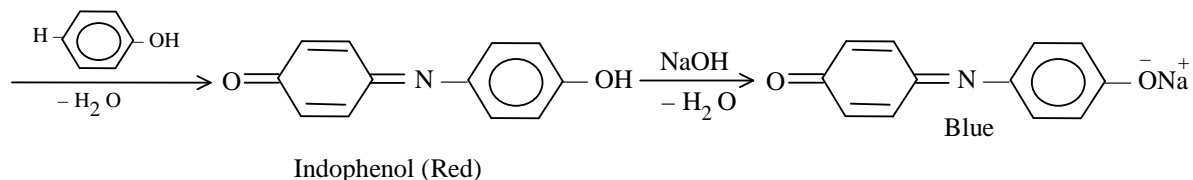
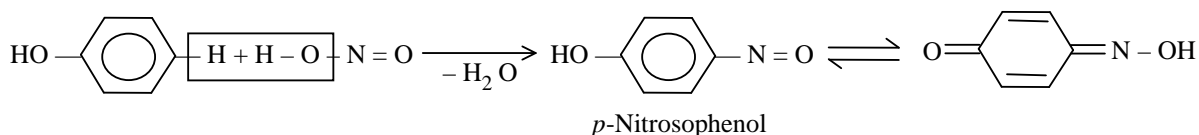
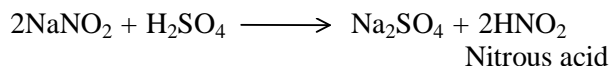


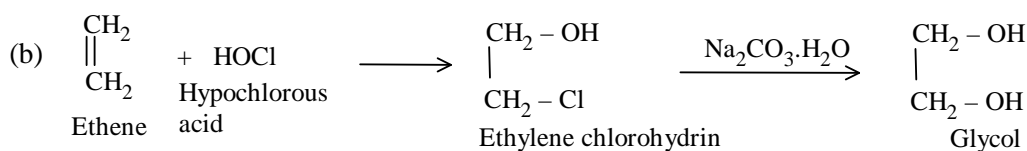
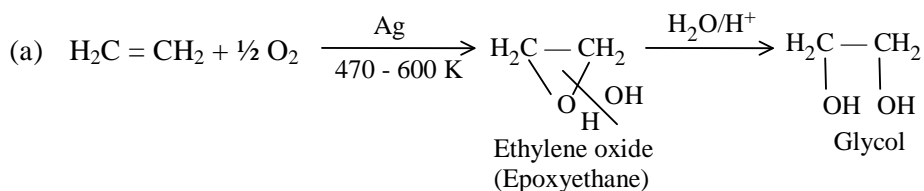
2, 6-Dimethyl-4-nitrophenol
(more acidic)



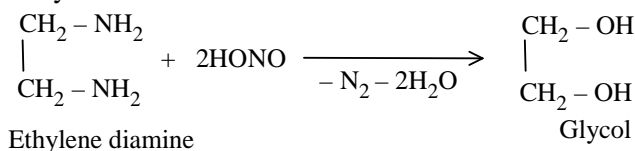
3, 5-Dimethyl-4-nitrophenol (less acidic due to steric inhibition of resonance of $-\text{NO}_2$ group)

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

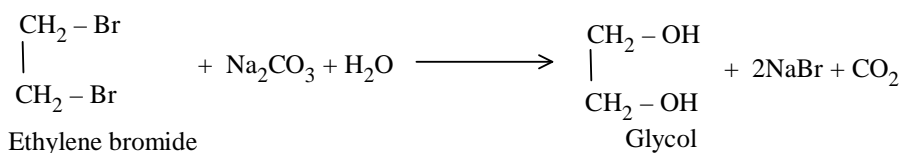




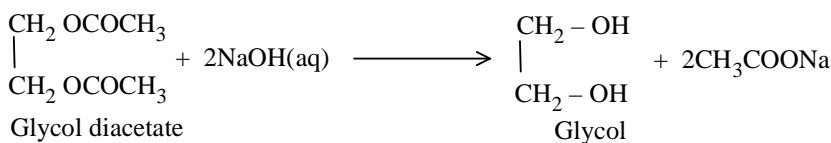
3. From ethylenediamine



4. From ethylene bromide (Laboratory method).



5. From glycol diacetate.

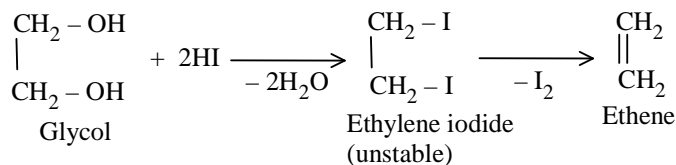


Physical Properties :

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.

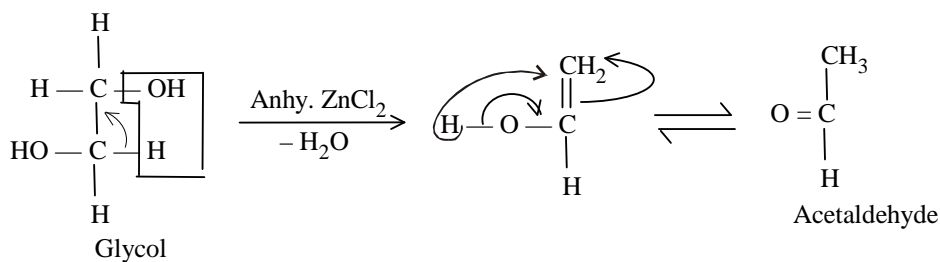
Chemical Properties :

1. Action with HI.

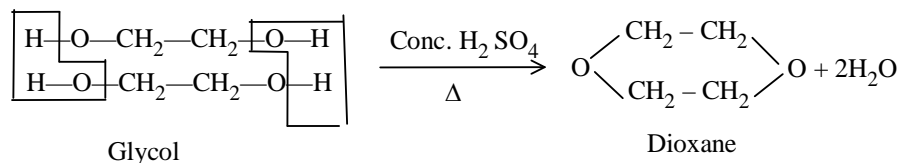


2. Dehydration : Glycol give different products on dehydration with different reagents :-

(i) With anhy. ZnCl_2

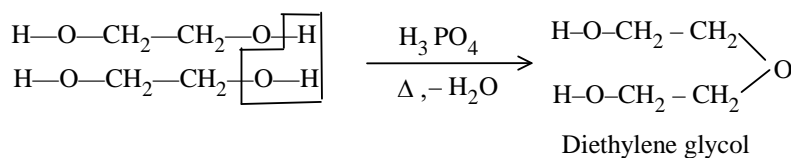


(ii) With conc. H_2SO_4 . (Intermolecular dehydration)

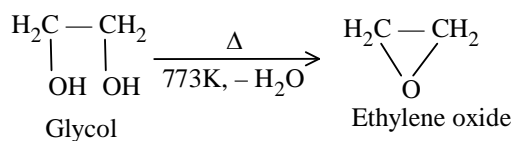


It is used as a solvent in industry.

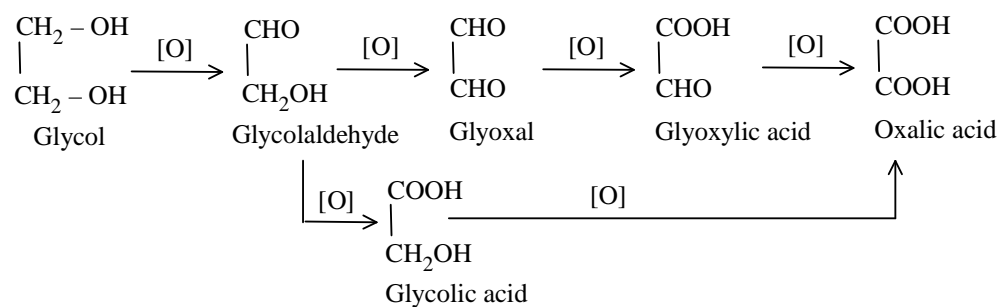
(iii) With phosphoric acid.



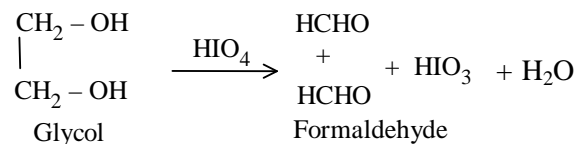
(iv) Heating.



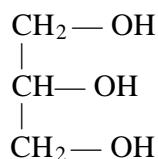
3. Oxidation



When glycol 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 HIO_4 is consumed.



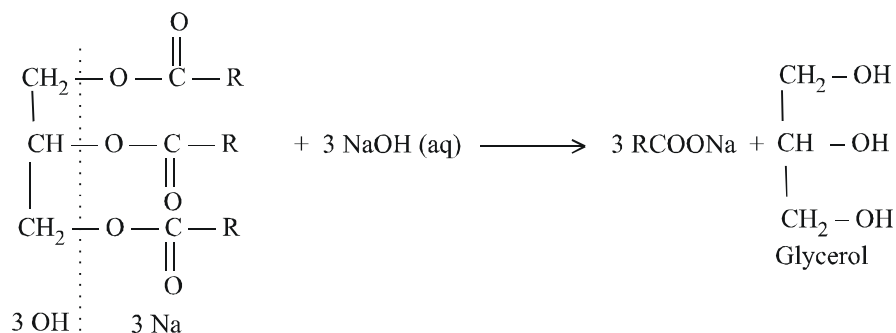
Glycerol



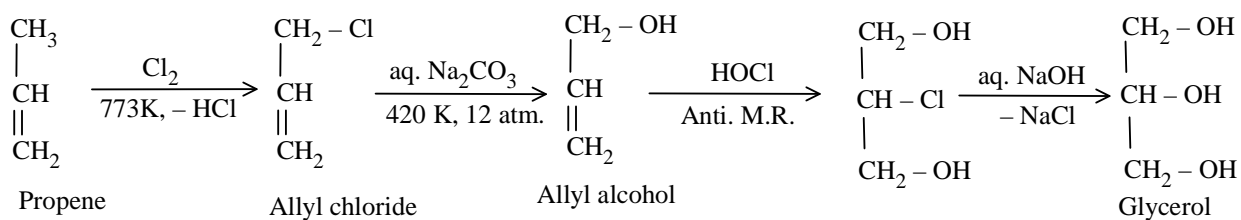
Propane-1, 2, 3-triol (Glycerol or Glycerine)

Methods of preparation

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



- From propene.



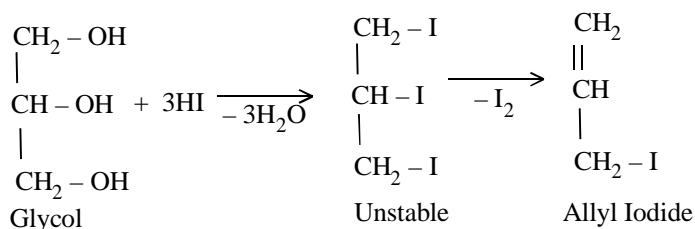
Glycerol prepared from propene is called synthetic glycerol.

Physical Properties

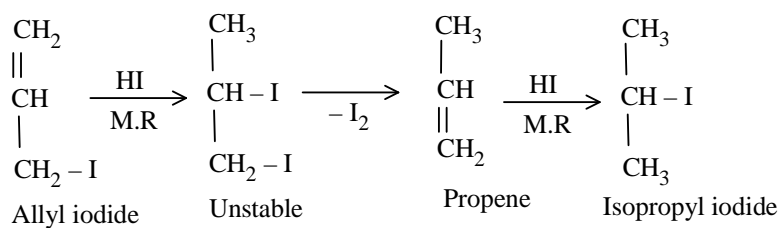
- Glycerol is a colourless, odourless, syrupy liquid.
- It has a sweet taste
- It is more viscous than glycol due to greater extent of hydrogen bonding.

Chemical Properties :

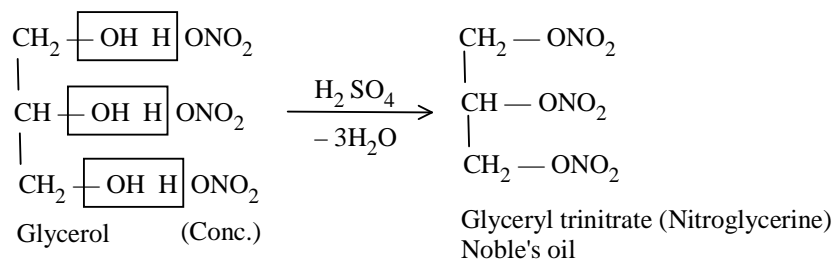
- Action with HI.**



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



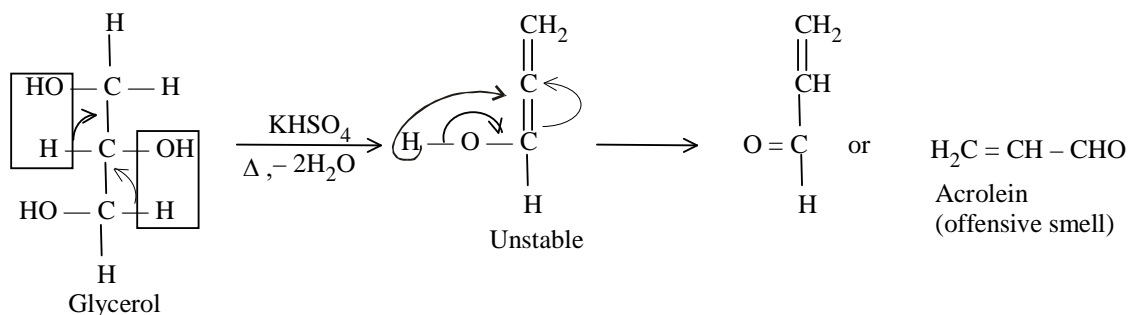
2. Nitration



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

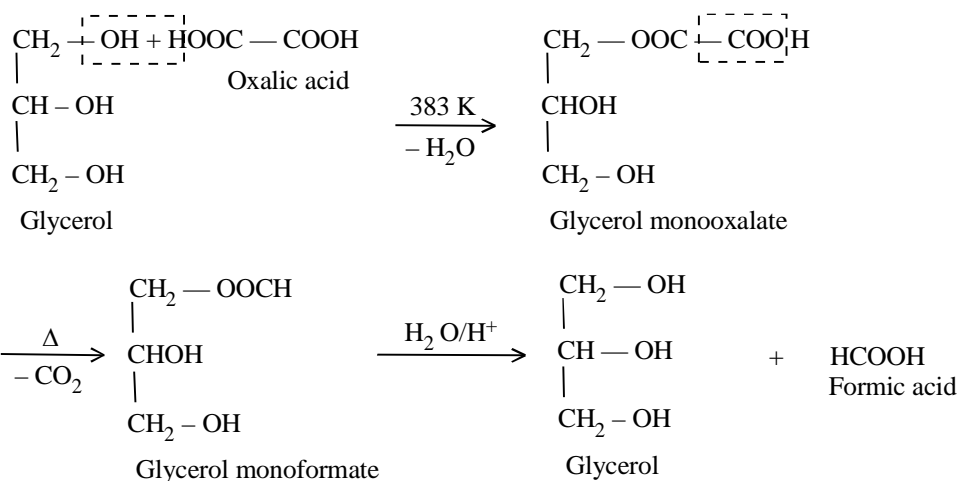
A mixture of glyceryl trinitrate, glyceryl dinitrate and Kieselguhr (a kind of porous clay) is called as dynamite.

3. Dehydration.

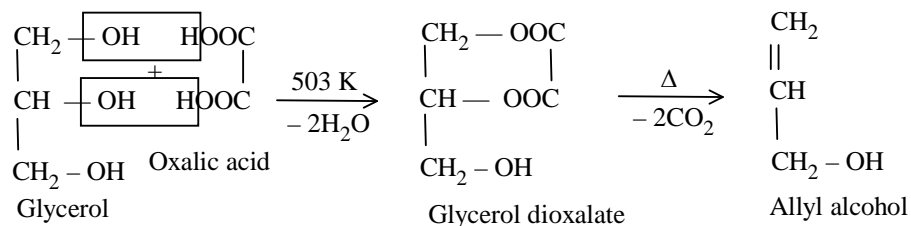


4. Reaction with oxalic acid.

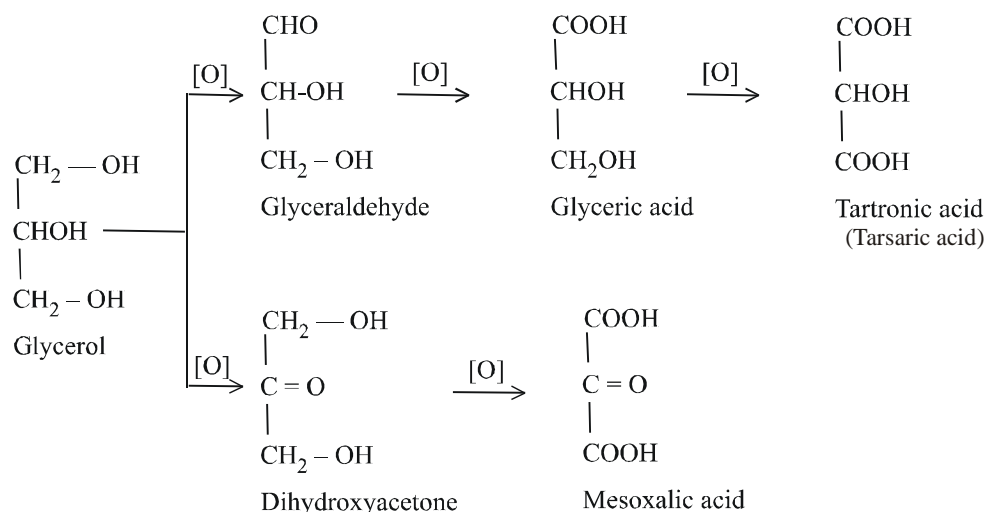
(i) At 383 K.



(ii) At 503 K.



5. Oxidation



The different products obtained by different reagents are :

- (i) Conc. HNO_3 = Glyceric acid
- (ii) Dil. HNO_3 = Glyceric acid and tartaric 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

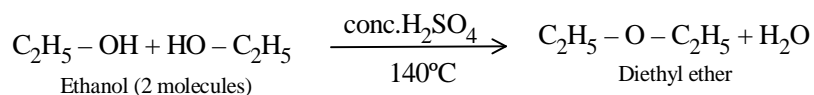
Ethers

The functional group is $\text{R}-\text{O}-\text{R}$. The central atom oxygen is in sp^3 hybridised state; the two half-filled sp^3 orbitals form strong σ ($\text{C}-\text{O}$) bonds with the half-filled sp^3 orbitals of the two carbon atoms of the two alkyl groups. The remaining two completely filled sp^3 orbitals remain free, i.e. they do not form bond with any orbital. Here the $\text{C}-\text{O}-\text{C}$ bond angle is about 110° which is quite close to the normal tetrahedral ($109^\circ 28'$) and different from that in water (105°). This difference is because of the fact that in ethers the repulsion between lone pairs of electrons is counter balanced by the repulsion between the bulky alkyl groups with the result value near to $109^\circ 28'$ is retained.

Ethers may be symmetrical or simple (when both the alkyl groups are identical) and unsymmetrical or mixed (when the two alkyl groups are different) commonly known as ether.

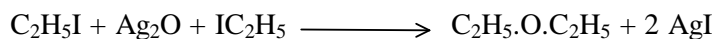
Preparation of Ethers :

1. By heating excess of alcohols with conc. H_2SO_4 , e.g.,



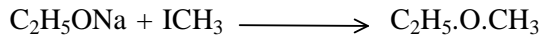
Recall that 2° and 3° alcohols under the above conditions give alkenes as the main product. Moreover, this method is limited only for the preparation of simple ethers.

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

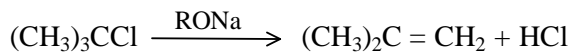


Remember that reaction of alkyl halides with **moist** silver oxide ($\text{Ag}_2\text{O} + \text{H}_2\text{O} = 2\text{AgOH}$) gives alcohols.

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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,



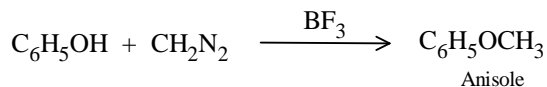
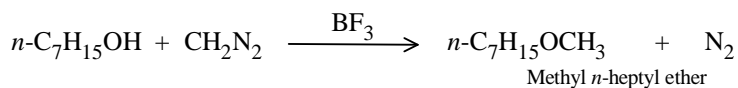
Recall that alkyl halides (especially tertiary alkyl halides) undergo elimination reaction with sodium alkoxides (strong bases).



Hence when one of alkyl groups of the ether to be prepared is tertiary, it must be introduced as base and not as tertiary alkyl 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. H_2SO_4 followed by storing over metallic sodium.

4. By the use of 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°) but they are at an angle of about 110° , 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°). It is due to the repulsion between bulky alkyl groups.

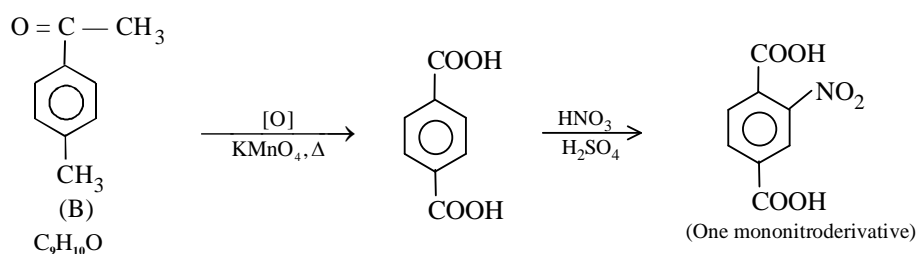
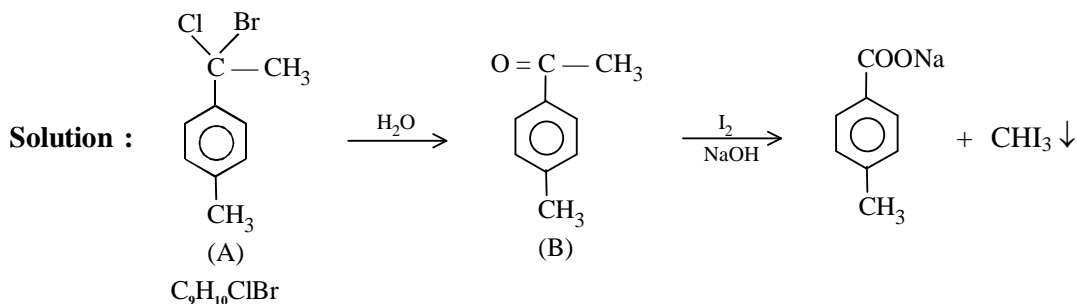
Chemical :

Ethers are much less reactive than compounds containing other functional groups. 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. H_2SO_4 (which oxidises peroxides).
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SOLVED EXAMPLES

Example 1 : Hydrolysis of compound (A) of molecular formula $C_9H_{10}Cl Br$ yields (B) of molecular formula $C_9H_{10}O$. (B) gives the haloform reaction. Strong oxidation of (B) yields a dibasic acid which forms only one mononitro derivative. What is A ?



Example 2 : When Bromobenzene is monochlorinated two isomeric compounds (A) and (B) are obtained. Monobromination of (A) gives several isomeric products of molecular formula $C_6H_3Cl Br_2$, while monobromination of (B) yields only two isomers (C) and (D). Compound (C) is identical with one of the compounds obtained from the bromination of (A). Give the structures of (A), (B), (C) and (D) and also structures of four isomeric monobrominated products of (A). Support your answer with reasoning.

