



Knowledge... Everywhere

Chemistry

# Hydroxy Compounds & Ethers

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## 1. Introduction of hydroxy compounds.

Hydroxy compounds are compounds in which the hydroxy group, – OH is directly linked with the aliphatic or aromatic carbon. Hydroxy compounds can be classified into following three categories.

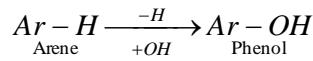
(1) **Aliphatic hydroxy compounds** (alcohols): Alcohols are regarded as hydroxy derivatives of hydrocarbons.



They can be mono, di or tri-hydric alcohols depending upon whether they contain one, two or three hydroxy groups.

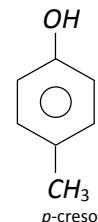
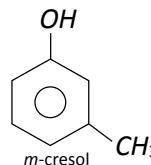
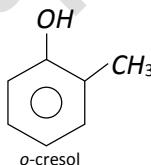
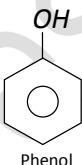
Monohydric alcohols	Dihydric alcohol	Trihydric alcohol	Polyhydric alcohol
$CH_3OH$ Methanol	$CH_2OH$ $\begin{array}{c}   \\ CH_2OH \end{array}$ Glycol	$CH_2OH$ $\begin{array}{c}   \\ CHOH \\   \\ CH_2OH \end{array}$ Glycerol	$CH_2OH$ $\begin{array}{c}   \\ (CHOH)_4 \\   \\ CH_2OH \end{array}$ sorbitol or Mannitol
$C_2H_5OH$ Ethanol			

(2) **Aromatic hydroxy compounds** (Phenols): Phenols are regarded as hydroxy derivatives of aromatic hydrocarbons (arenes).

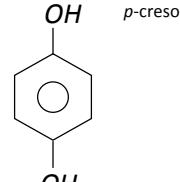
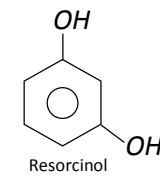
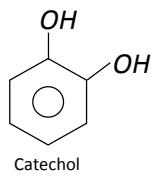


They can be mono, di or tri-hydric phenols depending upon whether they contain one, two or three hydroxy groups.

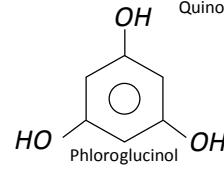
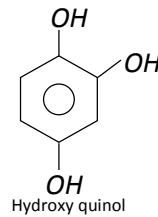
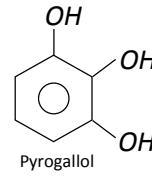
**Monohydric phenols:**



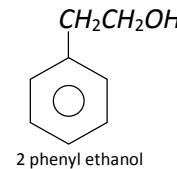
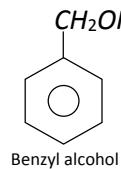
**Dihydric phenols:**



**Trihydric phenols:**

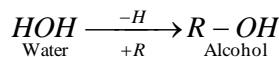


(3) **Aromatic alcohols:** Compounds in which the hydroxy group is present in the side chain are termed aromatic alcohols.



## 2. Monohydric alcohols.

Alcohols containing one hydroxyl group are known as monohydric alcohols. These alcohols may be saturated or unsaturated depending on the nature of hydrocarbon groups. Saturated monohydric alcohols form a homologous series of the general formula  $C_nH_{2n+1}OH$ . They are also represented as R – OH where R represents an alkyl group. They may be regarded as derivatives of water, i.e., one hydrogen atom of the water molecule is replaced by an alkyl group.



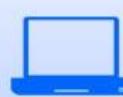
(1) **Classification:** Monohydric alcohols are subdivided into three classes

(i) **Primary alcohols:** In these alcohols, the hydroxyl group is attached with primary ( $1^\circ$ ) carbon atom. They possess a characteristic group –  $CH_2OH$  and their general formula is  $RCH_2OH$ . R may be H in the first member and alkyl group in the rest of the members.

Examples:  $HCH_2OH$ ;  $CH_3CH_2OH$ ;  $CH_3CH_2CH_2OH$ ;  $\overset{CH_3}{CH}_3$   $\overset{CH}{CH_2}OH$   
 Methylalcohol      Ethylalcohol      n-propylalcohol      isobutylalcohol

(ii) **Secondary alcohols:** In these monohydric alcohols, the hydroxyl group is attached with secondary ( $2^\circ$ ) carbon atom. They possess a characteristic group  $CHOH$  and the general formula  $\overset{R}{R'}CHOH$  (R and R' may be same or different).

Example:  $\overset{CH_3OH}{CH_3OH}$ ;  $\overset{CH_3OH}{CH_3CH_2OH}$ ;  $\overset{C_2H_5}{CH_3} \overset{CHOH}{CH_2}$   
 Isopropylalcohol      sec. butylalcohol



(iii) **Tertiary alcohols:** In these monohydric alcohols, the hydroxyl group is attached with tertiary ( $3^\circ$ ) carbon atom. They contain a characteristic group  $\text{COH}$  and have the general formula  $\begin{array}{c} R'' \\ | \\ \text{R}'\text{OH} \\ | \\ R \end{array}$  ( $R, R'$  and  $R''$  may be same or different).

Examples:  $\begin{array}{c} CH_3 \\ | \\ CH_3 - C - OH \end{array}$ ;  $\begin{array}{c} CH_3 \\ | \\ C_2H_5 - C - OH \\ | \\ CH_3 \end{array}$

## (2) Nomenclature

(i) **Common system:** Named as alkyl alcohol.

Note: In higher members, it is always indicated whether the – OH group is attached to primary, secondary and tertiary carbon. By prefixing n for primary sec. for secondary and tert. for tertiary.

Example:  $\begin{array}{c} CH_3 \\ | \\ CH_3CH_2OH \end{array}$ ;  $\begin{array}{c} CH_3 - CH_2 - CH - CH_3 \\ | \\ OH \end{array}$ ;  $\begin{array}{c} CH_3 - C - OH \\ | \\ CH_3 \end{array}$

Ethylalcohol

sec. butylalcohol

tert. butylalcohol

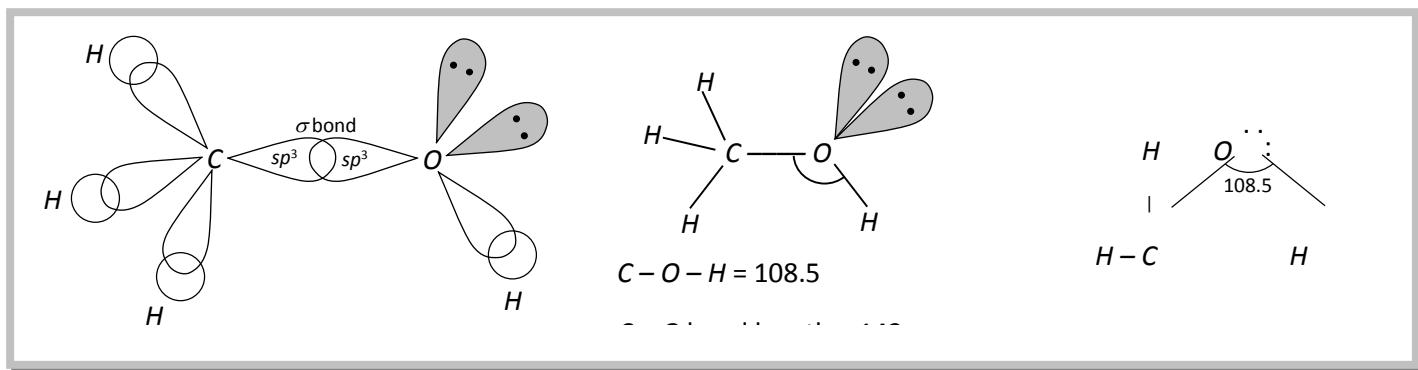
(ii) **Carbinol system:**  $\text{CH}_3\text{OH}$  is called carbinol. All other members are considered its alkyl derivatives.

Example:  $\text{CH}_3\text{OH}$ ;  $\begin{matrix} \text{CH}_3 \\ | \\ \text{CH}_3\text{OH} \end{matrix}$ ;  $\begin{matrix} \text{CH}_3 \\ | \\ \text{CH}_3\text{CH}_2\text{OH} \end{matrix}$

(iii) **IUPAC system:** Named as alkanol.

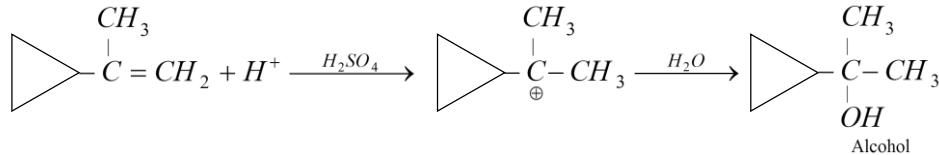
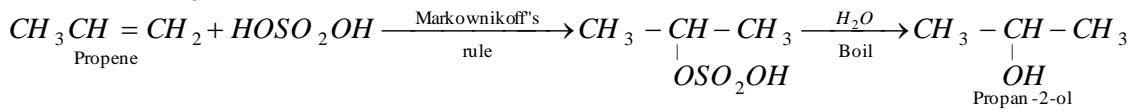
**Example:**  $\text{CH}_3\text{OH}$ ;  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ;  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

(3) **Structure:** Oxygen of – OH group is bonded to  $sp^3$  hybrid carbon by a sigma bond.

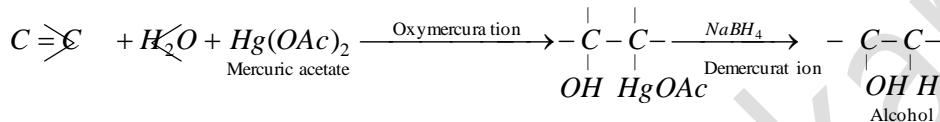




### **In case of unsymmetrical alkenes**

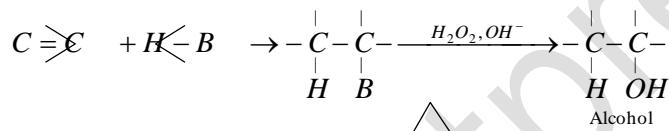


### (b) Oxymercuration-demercuration

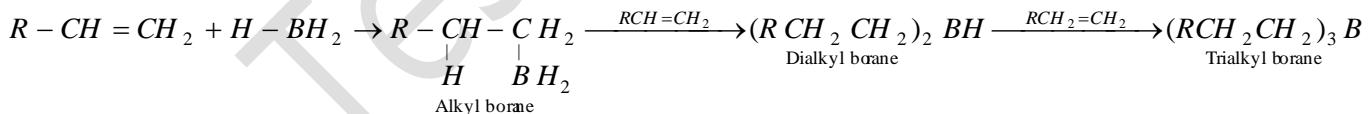


This reaction is very fast and produces the alcohol in high yield. The alcohol obtained corresponds to Markownikoff's addition of water to alkene.

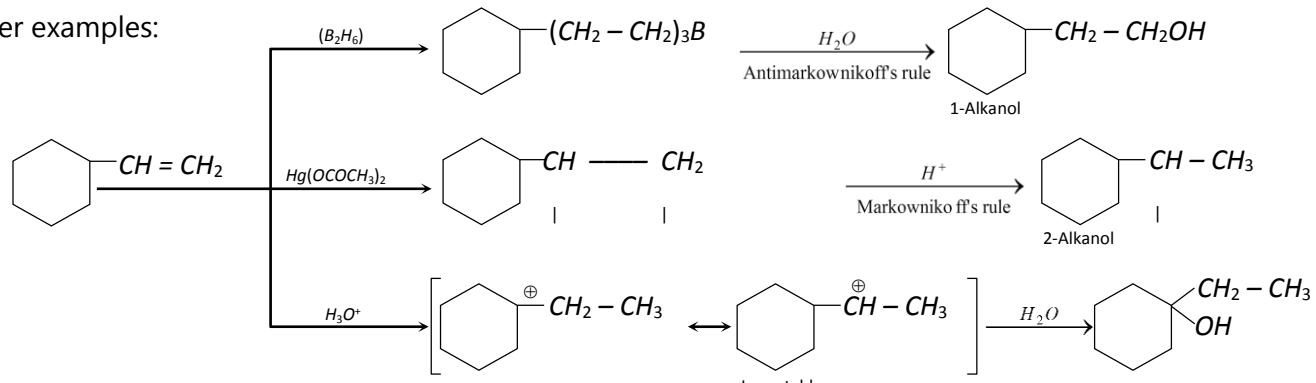
(c) Hydroboration oxidation (HBO): (Antimarkownikoff's orientation)



Diborane is an electron deficient molecule. It acts as an electrophile reacting with alkenes to form alkyl boranes  $R_3B$ .



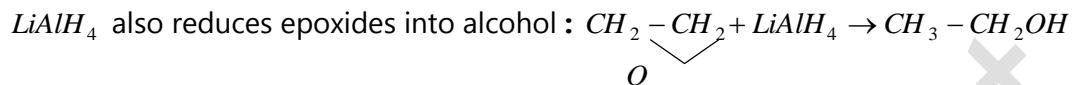
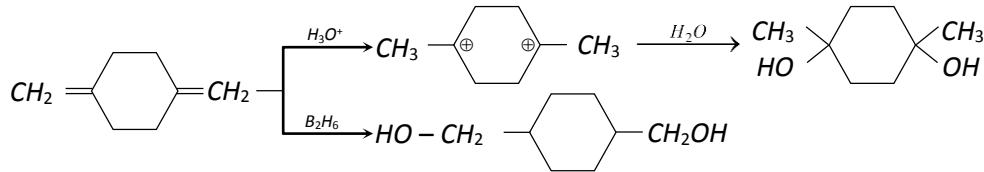
Other examples:



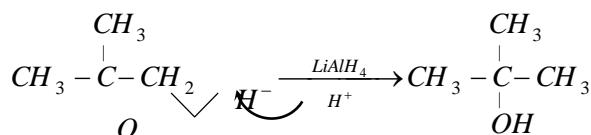
Note: Carbocation are not the intermediate in HBO hence no rearrangement take place. Less stable



### (iii) By reduction of carbonyl compounds: Bouveault Blanc



Hydride selectively attacks the less alkylated carbon of the epoxide.



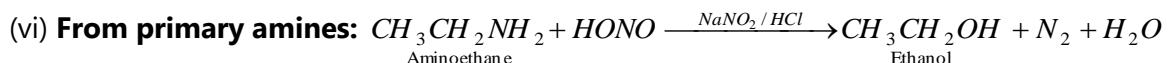
### (iv) By reduction of carboxylic acids and their derivatives



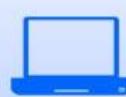
Esters are also reduced to alcohols



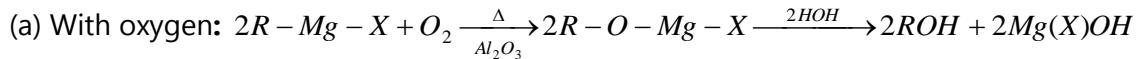
Note: Reduction with aluminium isopropoxide is known as Meerwein-Ponndorff verley reduction (MPV) reduction.



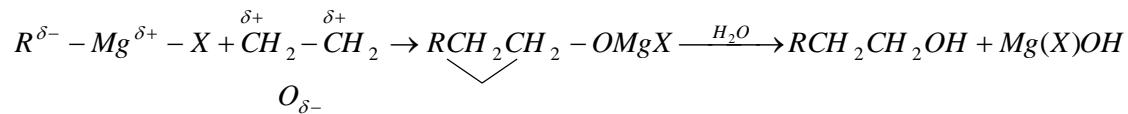
Note: It is not a good method of preparation of alcohols because number of by product are formed like alkyl chloride alkenes and ethers.



## (vii) From Grignard reagent

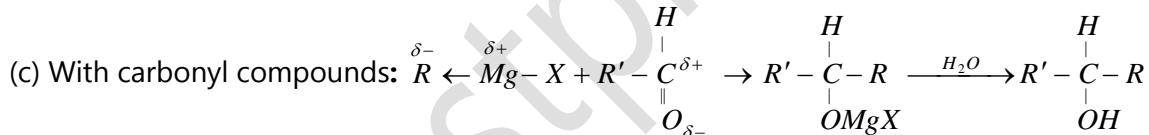
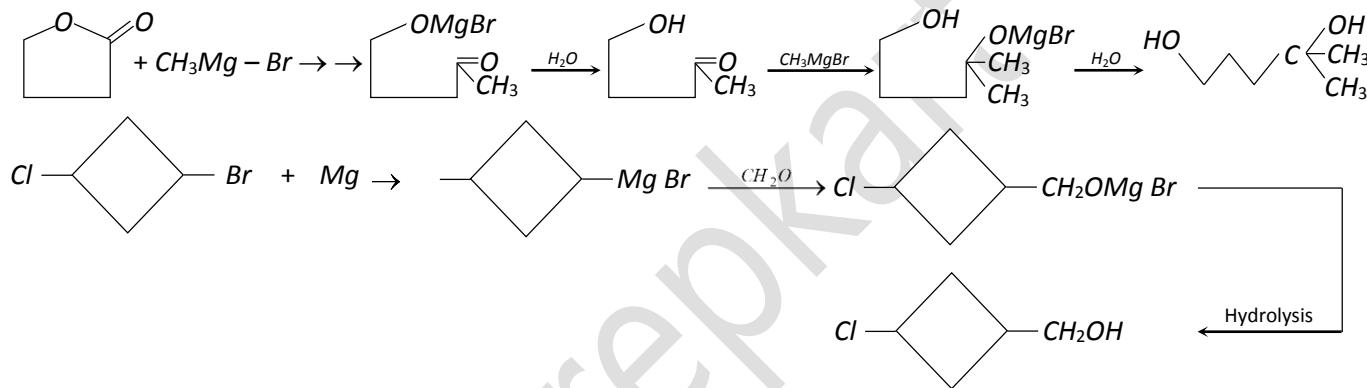


(b) With ethylene oxide



Other examples

### With cyclic ester



Note: If  $R' = H$ , product will be  $1^\circ$  alcohol.

If  $R' = R$ , product will be  $2^\circ$  alcohol.

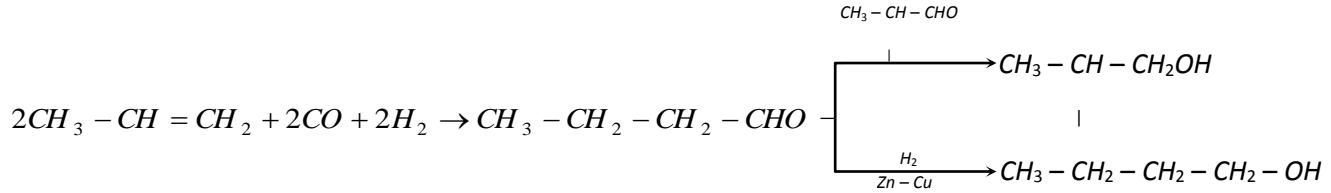
If carbonyl compound is ketone, product will be  $3^\circ$  alcohol.

It is the best method for preparation of alcohols because we can prepare every type of alcohols.

(viii) **The oxo process:** It is also called carbonylation or hydroformylation reaction. A mixture of alkene, carbon monoxide and hydrogen. Under pressure and elevated temperature in the presence of catalyst forms aldehyde.

Catalyst is cobalt carbonyl hydride  $[CoH(CO)_4]$  product is a mixture of isomeric straight chain (major) and branched chain (minor) aldehydes. Aldehydes are reduced catalytically to the corresponding alcohols.





## (6) Physical properties of monohydric alcohols

(i) **Character:** Alcohols are neutral substances. These have no effect on litmus paper. This is analytical test for alcohols.

**(ii) Physical state:** The lower alcohols (upto C<sub>12</sub>) are colourless alcohol with characteristic smell and burning taste. The higher members with more than 12-carbon atoms are colourless and odourless solids.

(iii) **Polar character:** Oxygen atom of the – OH group is more electronegative than both carbon and hydrogen. Thus the electron density near oxygen atom is slightly higher. Hydrogen bonding shown below

$H - O \cdots H - O \cdots H - O \cdots H - O$ . This gives polar character to OH bond.



(iv) **Solubility:** The lower alcohols are miscible in water.



Increase in carbon-chain increases organic part hence solubility in water decreases.

Isomeric 1°, 2°, 3° alcohols have solubility in order 1° > 2° > 3°.

(v) **Boiling points:** Due to intermolecular hydrogen bonding boiling points of alcohols are higher than hydrocarbon and ethers.

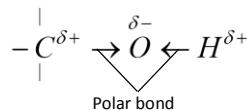
B.P.  $\propto \frac{1}{\text{No. of branches}}$ ; B.P. follows the trends :  $1^\circ$  alcohols >  $2^\circ$  >  $3^\circ$  alcohol

(vi) **Density:** Alcohols are lighter than water. Density  $\propto$  Molecular masses.

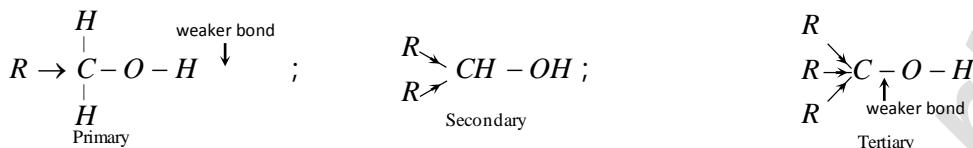
(vii) **Intoxicating effects:** Methanol is poisonous and is not good for drinking purposes. It may cause blindness and even death. Ethanal is used for drinking purposes.



(7) **Chemical properties:** Characteristic reaction of alcohol are the reaction of the – OH group. The reactions of the hydroxyl group consists of either cleavage of C – O bond or the cleavage of O – H bond.



C – O bond is weaker in the case of tertiary alcohols due to +I effect of alkyl groups while – OH bond is weaker in primary alcohols as electron density increase between O – H bond and hydrogen tends to separates as a proton.

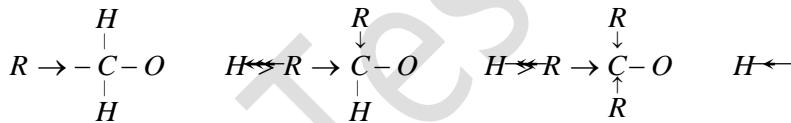


Thus primary alcohols give the most of reaction by cleavage of O – H bond while tertiary alcohols are most reactive because of cleavage of C – O bond. Hence – O – H cleavage reactivity order : Primary > Secondary > Tertiary and C – O – cleavage reactivity order : Tertiary > Secondary > Primary alcohol

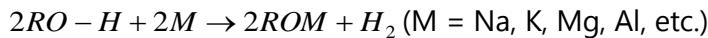
### (i) Reaction involving cleavage of with removal of 'H' as proton

Alcohols are stronger acids than terminal acetylene but are not acidic enough to react with aqueous NaOH or KOH. Acidic nature is in the order  $\text{HOH} > \text{ROH} > \text{CH} \equiv \text{CH} > \text{NH}_3 > \text{RH}$ .

Acidic nature of alcohol decrease with increase of alkyl groups on – OH bonded carbon due to +I (inductive) effect of alkyl group.

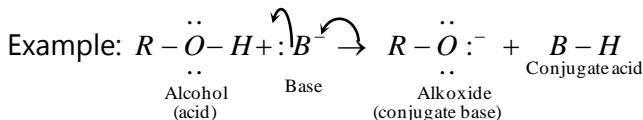


(a) Reaction with Na: (Active metals)



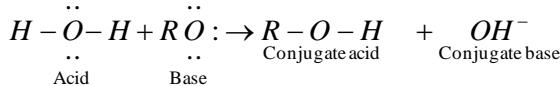
Evolution of  $H_2$  shows the presence of –OH and reaction show that alcohols are acidic in nature.

Alcohols act as Bronsted acids because they donate a proton to a strong base ( $:B^-$ ).



On reaction of alkoxide with water, starting alcohol is obtained.





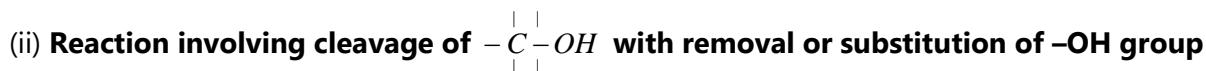
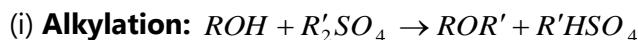
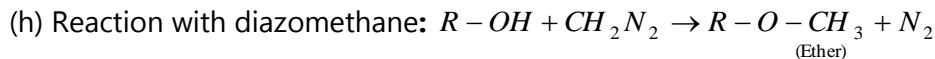
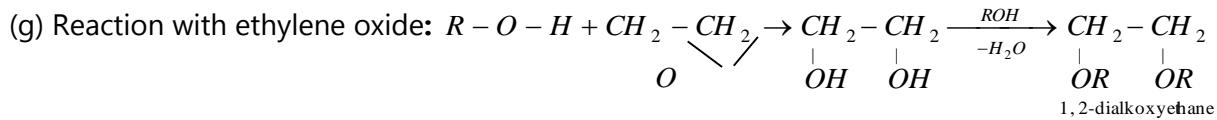
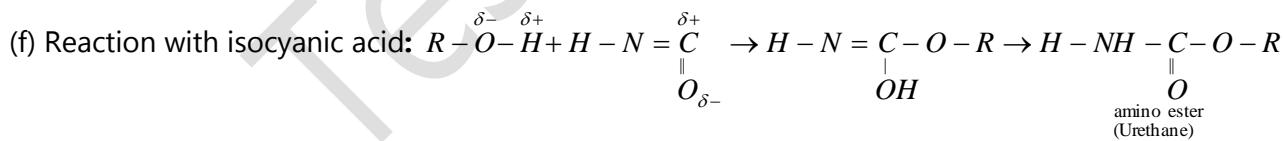
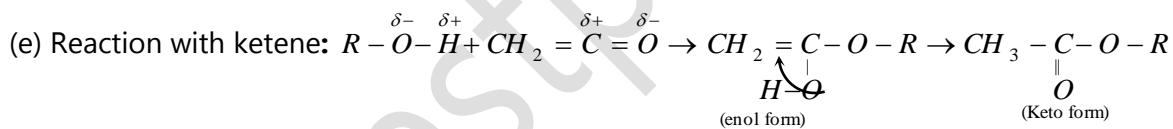
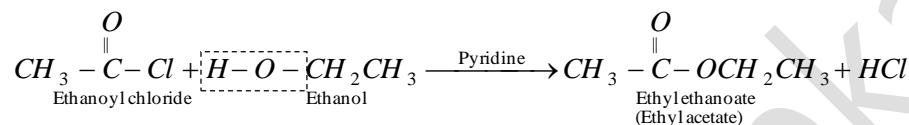
This is the analytical test for alcohols.



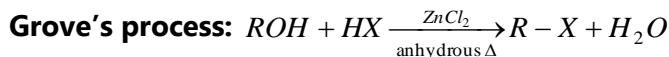
When HCl gas is used as catalyst, the reaction is called fischer-speier esterification.

Presence of bulky group in alcohol or in acid decreases the rate of esterification. This is due to steric hinderence of bulky group. Reactivity of alcohol in this reaction is  $1^\circ > 2^\circ > 3^\circ$ .

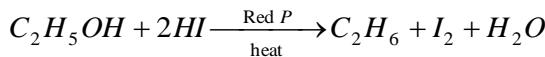
(c) Reaction with acid derivatives: (Analytical test of alcohol)



(a) Reaction with hydrogen halides: Alcohols give alkyl halide. The reactivity of HX is in the order of HI > HBr > HCl and the reactivity of ROH is in the order of allyl, benzyl > 3° > 2° > 1°. The reaction follows a nucleophilic substitution mechanism.

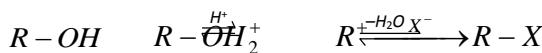


If alcohols react with HI and red phosphorus, alkane will be formed.



Primary alcohols follow  $SN^2$  mechanism.  $R - OH_2^+ + X^- \rightarrow \overset{\text{Protonated}}{R - OH_2^+} \cdots \overset{\delta-}{X} \cdots R \cdots \overset{\delta+}{OH_2^+} \rightarrow R - X + H_2O$

In secondary and tertiary alcohols, the  $SN^1$  mechanism operates



(b) Reaction with  $PCl_5$ :  $ROH + PX_5 \rightarrow RX + POX_3 + HX$ ; X = Cl (Analytical test for alcohols)

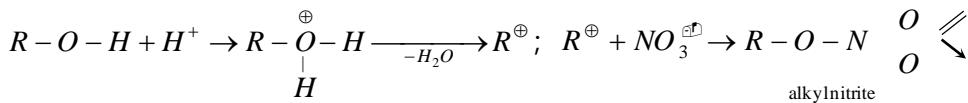
(c) Reaction with  $PCl_3$ :  $3ROH \xrightarrow[\text{Alcohol}]{PCl_3} 3RCl + H_3PO_3$

(d) Reaction with thionyl chloride [ $SOCl_2$ ]:  $ROH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + SO_2 + HCl$

(e) Reaction with ammonia:  $ROH + NH_3 \xrightarrow[360^\circ C]{Al_2O_3} RNH_2 \xrightarrow[\text{Primary amine}]{ROH} R_2NH \xrightarrow[\text{Secondary amine}]{Al_2O_3} R_3N \xrightarrow[\text{Tertiary amine}]{Al_2O_3}$

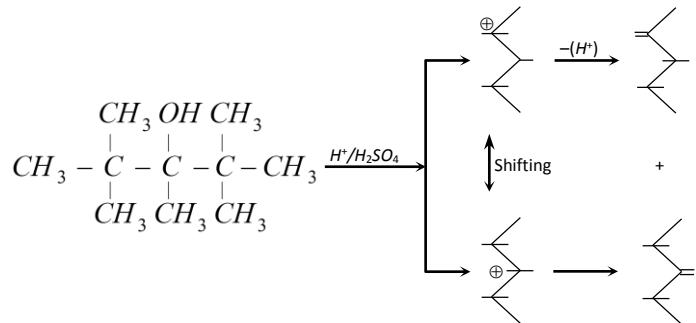
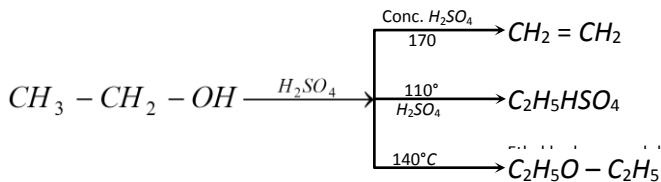
(f) Reaction with  $HNO_3$ :  $R - OH + \text{conc. } HNO_3 \rightarrow R - O - N \begin{array}{c} O \\ || \\ O \end{array} + H_2O$   
alkylnitrite

**Mechanism:**  $HNO_3 \rightarrow H^+ + NO_3^-$

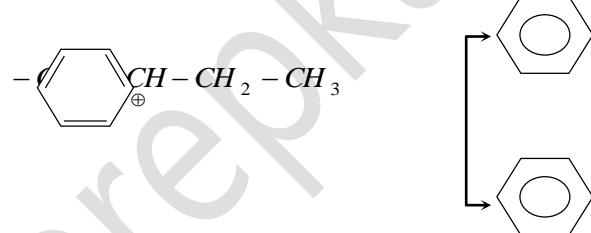
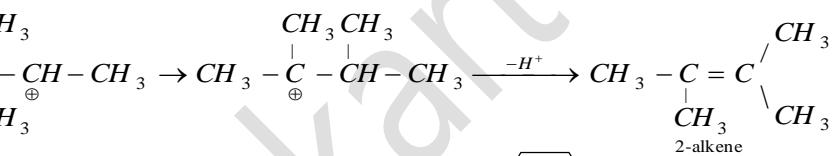
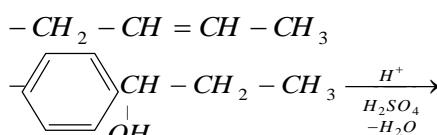
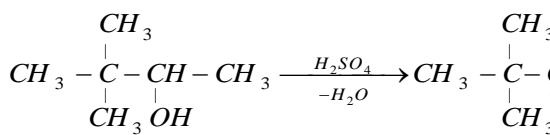
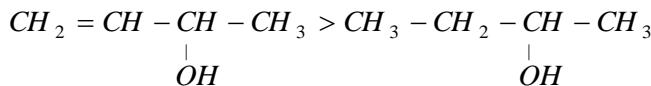


(g) Reaction with  $H_2SO_4$  [Dehydration of alcohol] : The elimination of water from a compound is known as dehydration. The order of ease dehydration is Tertiary > Secondary > primary alcohol. The products of dehydration of alcohols are depend upon the nature of dehydrating agents and temperature.



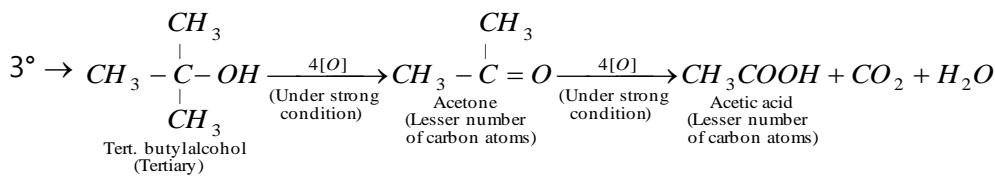
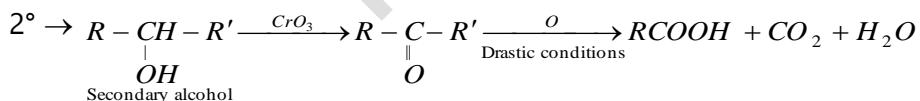
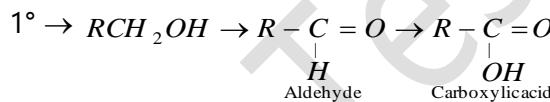


Alcohol leading to conjugated alkene are dehydrated to a greater extent than those of alcohols leading to nonconjugated alkene. Thus dehydration is in order



(a) Reduction:  $R-OH + 2HI \xrightarrow{\Delta} R-H$

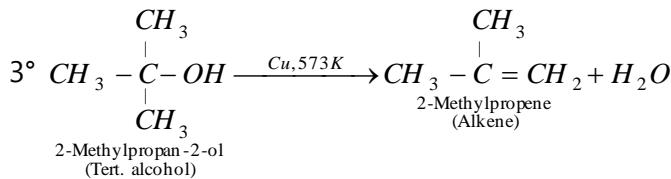
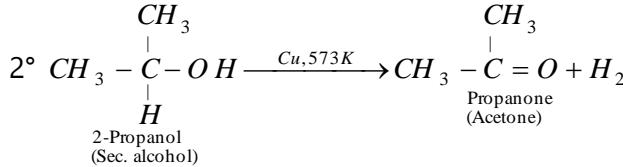
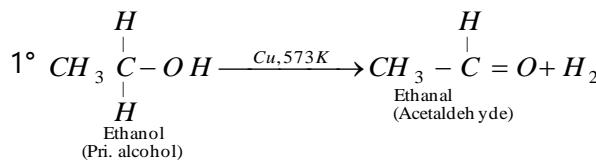
(b) Oxidation: Difference between 1°, 2° and 3° alcohols.



Note: 3° alcohols are resistant to oxidation, but on taking stronger oxidizing agent they form ketone.



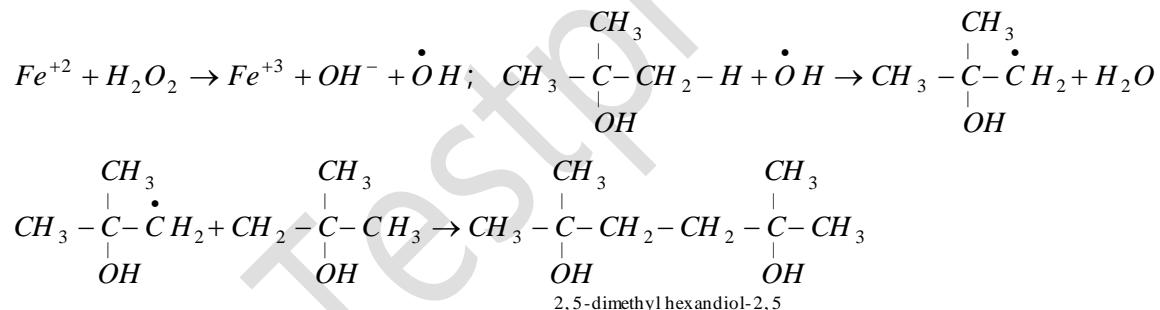
(c) Catalytic oxidation/dehydrogenation



This is dehydration process and difference between 1°, 2° and 3° alcohols.

(d) Oxidation through Fenton's reagent:  $[FeSO_4 + H_2O_2]$

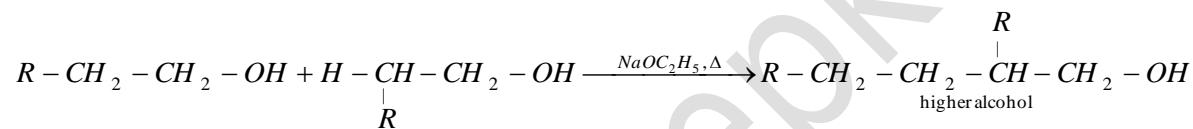
**Mechanism**



### Important reagents used for oxidation of alcohols

- PCC [Pyridinium chloro chromate ( $C_6H_5^+ NH Cl CrO_3^-$ )] to oxidise 1° alcohols to aldehydes and 2° alcohols to ketones.
- PDC [Pyridinium di chromate ( $C_5H_5.NH_2^+ Cr_2O_7^{2-}$ )] to oxidise 1° alcohols to aldehyde and 2° alcohol to ketones.
- $H_2CrO_4$  (chromic acid) to oxidise 1° alcohol to carboxylic acid.
- $CrO_3 \cdot H_2SO_4$  / Acetone to oxidise 2° alcohol to ketones.
- Jones reagents (chromic acid in aqueous acetone solution) oxidise 1° alcohol to aldehyde and 2° alcohol to ketone without affecting (C = C) double bond.
- $MnO_2$  selectively oxidises the –OH group of allylic and benzylic 1° and 2° alcohols to give aldehyde and ketone respectively.
- $N_2O_4$  in  $CHCl_3$  (field's) oxidises primary and secondary benzyl alcohol.

### (e) Self condensation: Guerbet's reaction



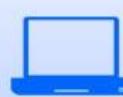
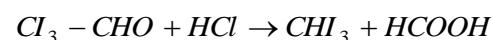
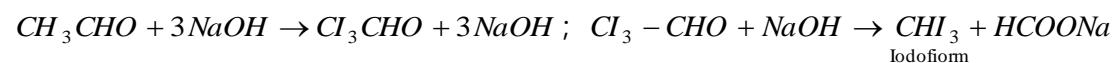
(f) Reaction with ceric ammonium nitrate: Cerrie ammonium nitrate +  $ROH \rightarrow$  Red color solution of Yellow colour complex. This is analytical test for alcohols.

(g) Iodoform test: When a few drops of alcohol are warmed with iodine and KOH yellow precipitate of iodoform with characteristic smell is obtained. Any alcohol consists  $CH_3CHOH$  group give iodoform test.

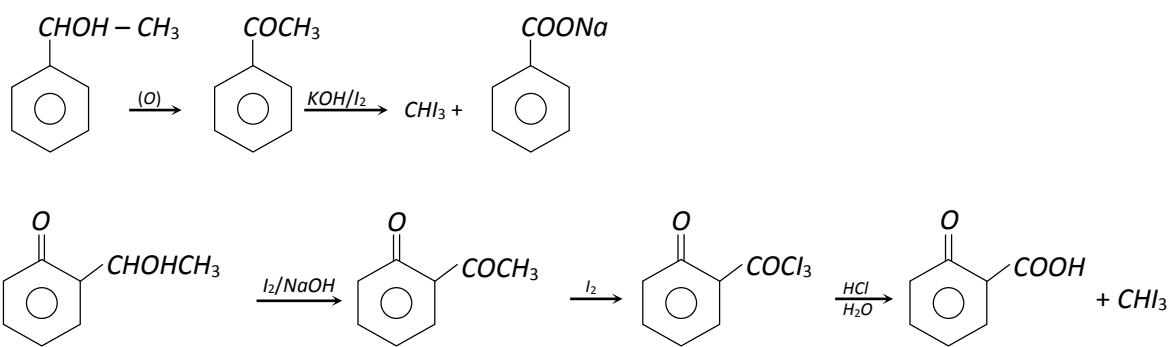
Example:  $CH_3CH_2OH$ ,  $CH_3 - CHO - CH_3$ ,  $C_6H_5 - CHO - CH_3$

Since reaction takes place with alkali solution as one of the reagents hence alkyl halide like

$CH_3 - CH_2Cl$  and  $CH_3 - \underset{Cl}{\overset{|}{CH}} - R$  will also give this test.



### Other example

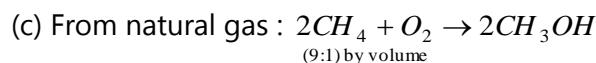
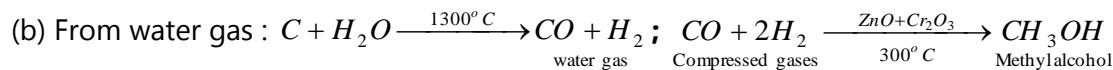
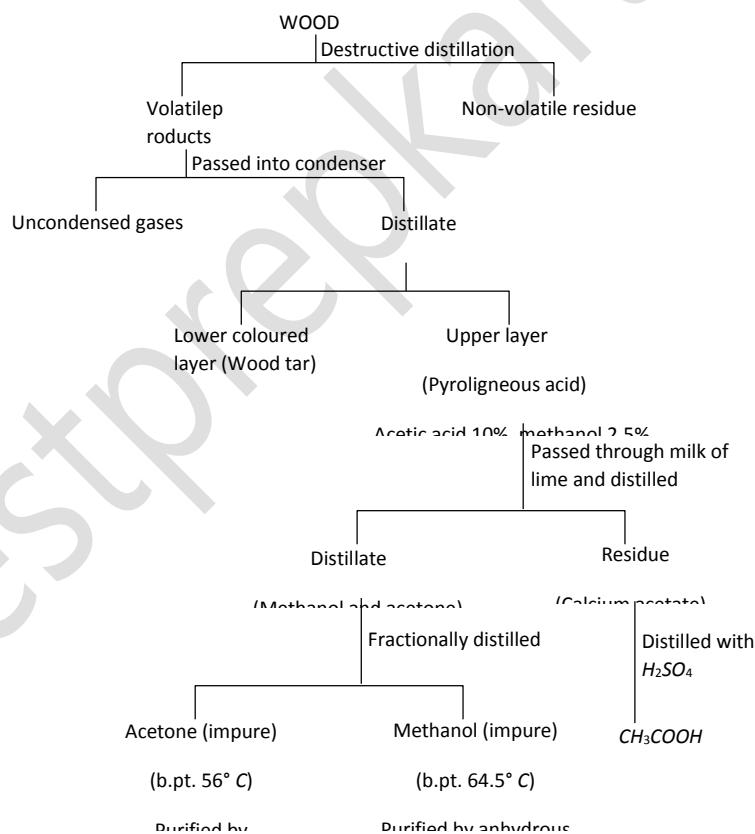


### (8) Individual members of monohydric alcohols

#### Methanol

##### (i) Preparation

##### (a) By destructive distillation



## (ii) Physical properties

- (a) It is a colorless liquid and boils at 64.5° C.
- (b) It is miscible in water, good solvent for fats and oils.
- (c) It is inflammable and burns with a faint luminous flame.
- (d) It has pleasant smell and burning taste.

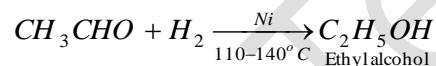
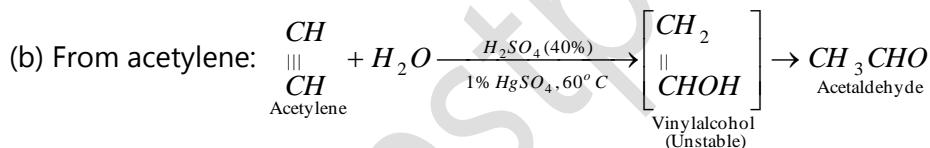
## (iii) Uses

- (a) For the manufacture of formaldehyde and formaline.  $\text{CH}_3\text{OH} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7} \text{CH}_2\text{O} + \text{H}_2\text{O}$
- (b) A 20% mixture of methyl alcohol and gasoline is a good motor fuel.
- (c) Use as an antifreeze for automobile radiators.
- (d) To denature ethyl alcohol, mixture is called methylated spirit.
- (e) In the preparation of dyes, medicines and perfumes.

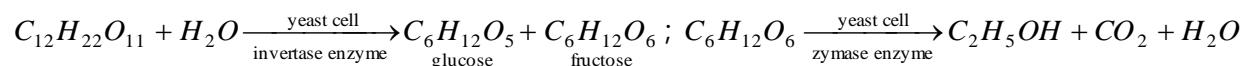
## Ethanol

### (i) Preparation

(a) From Ethylene:  $\text{C}_2\text{H}_4 + \text{H}_2\text{O} \xrightarrow[300^\circ\text{C}, 70\text{ atm}]{\text{H}_3\text{PO}_4} \text{C}_2\text{H}_5\text{OH}$  Yield of ethyl alcohol is 95%.

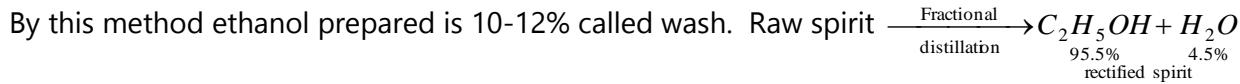
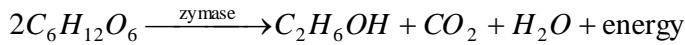
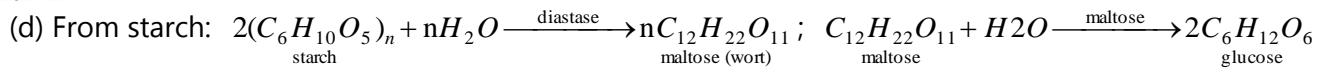


(c) Fermentation: This word is given by Lebeig. Fermentation process is exothermic. Ethanol is prepared by molasses and invert sugar molasses is the waste product in sugar industry. It is a mixture of sugar (30%) and invert sugar (32-40%) combine form of glucose and fructose called invert sugar. Temperature should be 25-30°C. low concentration (8-10%) is favourable.



Certain amounts of inorganic compound such as ammonium sulphate, phosphate should be added. Oxygen is necessary for the growth of ferment. Boric acid, mercury salts etc. should not be present in the solution as these retards the fermentation.





Manufacturing of ethyl alcohol (absolute) from rectified spirit called Azeotropic distillation.

- Absolute alcohol is prepared by distillation rectified spirit with benzene.
- The first fraction consists of constant boiling mixture of ethyl alcohol, water and benzene [18.5% + 7.4% + 74.1%] and distills over at 64.8°C.
- The second fraction consists of a boiling mixture of ethyl alcohol and benzene [32.4% + 67.6%] and distills at 68.2° C.
- Pure alcohol distills at 78.3° C and known as absolute alcohol (100%).

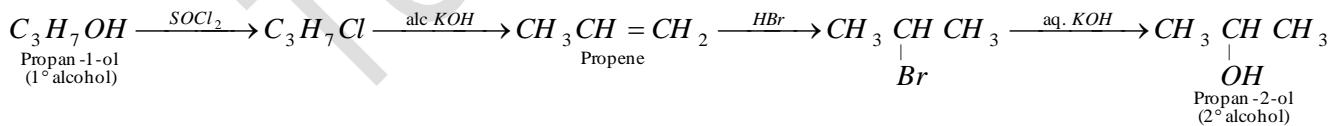
(ii) **Properties:** Same as monohydric alcohols.

(iii) **Uses**

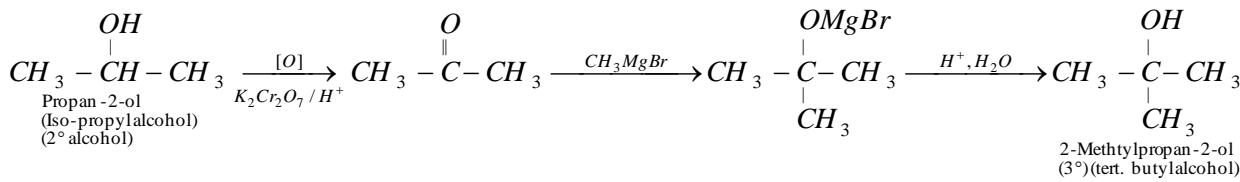
- In the manufacture of alcoholic beverages.
- As a preservative for biological specimens.
- As a low freezing and mobile liquid in scientific apparatus such as thermometers and spirit levels.
- In hospitals as an antiseptic.
- As a petrol substitute (power alcohol).

## (9) Interconversion of monohydric alcohols

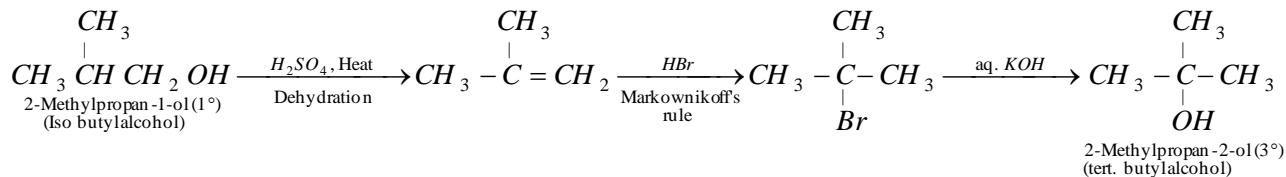
(i) Primary alcohol into secondary alcohols



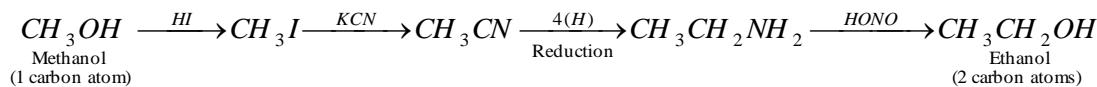
(ii) Secondary alcohol into tertiary alcohol



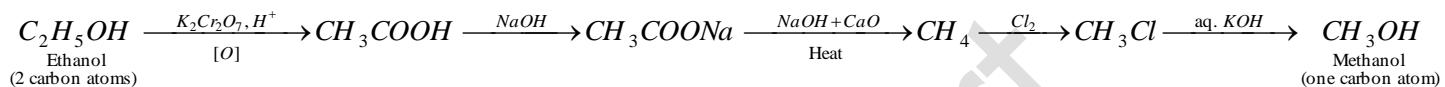
**(iii) Primary alcohol into tertiary alcohol**



**(iv) Lower alcohol into higher alcohol** (ascent of series)



**(v) Higher alcohol into lower alcohol** [Descent series]



**(10) Alcoholic beverages:** Liquors used for drinking purposes containing ethyl alcohol as the principal constituent are called alcoholic beverages. Besides alcohol, these contain large amounts of water, colouring and flavouring materials. Alcoholic beverages are of two types:

**(i) Undistilled beverages:** These are prepared from fruit juices and grains. Those prepared from grapes and other fruit juices are known as wines. Wines contain 18-20% of ethyl alcohol and are used as such after fermentation, i.e., with distillation. The natural wines when made stronger by the addition of rectified alcohol are known as fortified wines.

Name	Undistilled Percentage of alcohol	Source
Beer	<b>3-6</b>	Barley
Cider	<b>2-6</b>	Apples
Wine (Champagne)	<b>8-10</b>	Grapes
Claret	<b>7-13</b>	Grape juice
Port and Sherry (Fortified)	<b>14-24</b>	Grape juice



(ii) **Distilled beverages:** These are prepared by the fermentation of molasses, barley, maize, etc. The fermented liquor is then distilled. These contain a higher percentage of ethyl alcohol which may be as high as 50%.

Name	Distilled Percentage of alcohol	Source
Whisky	<b>35-40</b>	Malt
Rum	<b>45-55</b>	Molasses
Gin	<b>40-45</b>	Maize
Brandy	<b>40-45</b>	Grape juice
Cognac	<b>40-50</b>	Grape juice

(11) **Alcoholometry:** The process of determining the percentage of alcohol in a given sample is known as alcoholometry. An alcohol water mixture having specific gravity 0.91976 at 15°C and containing 57.1% of ethyl alcohol by volume or 49.3% by mass is called proof-spirit. A sample having higher percentage of ethyl alcohol in comparison to proof-spirit is referred to as over-proof (O.P.) and the one having lower alcohol content than proof-spirit is known as under-proof (U.P.). Thus 15 U.P. means that 100 ml of the sample contains as much alcohol as 85 ml of proof spirit. Similarly, 15 O.P. means that 100 ml of the sample contains as much of alcohol as 115 ml of proof spirit.

(12) **Power alcohol:** Alcohol used for the generation of power is called power alcohol. Generally it is a mixture of 80% petrol and 20% absolute alcohol with cosolvent benzene. It is cheaply obtained from waste petrol.

(13) **Methylated spirit:** Ethyl alcohol containing 5 to 10% of methyl alcohol is known as methylated spirit or denatured spirit. Denaturing can also be done by adding 0.5% pyridine, petroleum naptha, rubber distillate (caoutchoucine) or  $CuSO_4$ .

(14) **Toxicity of alcohols:** The toxicity of alcohols is mainly due to their biological oxidation takes place in living organism. Methyl alcohol is highly toxic and its consumption causes, blindness and death. Ethyl alcohol is nontoxic but produces physiological effect disturbing brain activity on drinking. The commercial alcohol is made unfit for drinking by mixing in it copper sulphate (which gives its colour) and pyridine (which makes it foul smelling liquid). It is known as denaturation of alcohol.



**(15) Distinguish between primary, secondary and tertiary monohydric alcohols**

(i) **Lucas test:** A mixture of anhydrous  $ZnCl_2$  + conc.  $HCl$  is called as Lucas reagent.

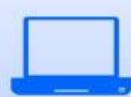
Primary	$R-CH_2-OH \xrightarrow[-H_2O]{\text{conc. } HC / ZnCl_2 \text{ anhy.}} R-CH_2-Cl \rightarrow$ ppt. appears after heating
Secondary	$R_2CH-OH \xrightarrow[-H_2O]{\text{conc. } HCl / ZnCl_2 \text{ anhy.}} R_2-CH-Cl \rightarrow$ ppt. appears with in 5 minutes
Tertiary	$R_3C-OH \xrightarrow{ZnCl_2 / HCl} R_3C-Cl \rightarrow$ ppt. appears immediately

(ii) **Victor mayer test:** Also known as RBW test. RBW → Red, Blue, White test.

Primary	$C_2H_5OH \xrightarrow{P+I_2} C_2H_5I \xrightarrow{AgNO_2} C_2H_5NO_2 \xrightarrow{HONO} CH_3 - \underset{\substack{\parallel \\ NOH}}{C - NO_2} \xrightarrow{NaOH} CH_3 - \underset{\substack{\parallel \\ NONa}}{C - NO_2}$ <p style="text-align: center;">Nitrolicacid</p> <p style="text-align: right;">Sod. salt of nitrolicacid (Red colour)</p>
Secondary	$(CH_3)_2CHOH \xrightarrow{P+I_2} (CH_3)_2CHI \xrightarrow{HONO} (CH_3)_2 - \underset{\substack{  \\ NO}}{C - NO_2} \xrightarrow{NaOH} \text{No reaction (Blue colour)}$
Tertiary	$(CH_3)_3COH \xrightarrow{P+I_2} (CH_3)_3Cl \xrightarrow{AgNO_2} (CH_3)_3CNO_2 \xrightarrow{HONO} \text{No reaction (colourless)}$

## Difference between methanol and ethanol

<b>Methanol</b>	<b>Ethanol</b>
(i) When $\text{CH}_3\text{OH}$ is heated on Cu coil it gives formalin like smell.	(i) It does not give formalin like smell.
(ii) When $\text{CH}_3\text{OH}$ is heated with salicylic acid in $\text{H}_2\text{SO}_4$ (conc.) then methyl salicylate is formed which has odour like winter green oil.	(ii) No such odour is given.
(iii) It does not give haloform or iodoform test.	(iii) It gives haloform test

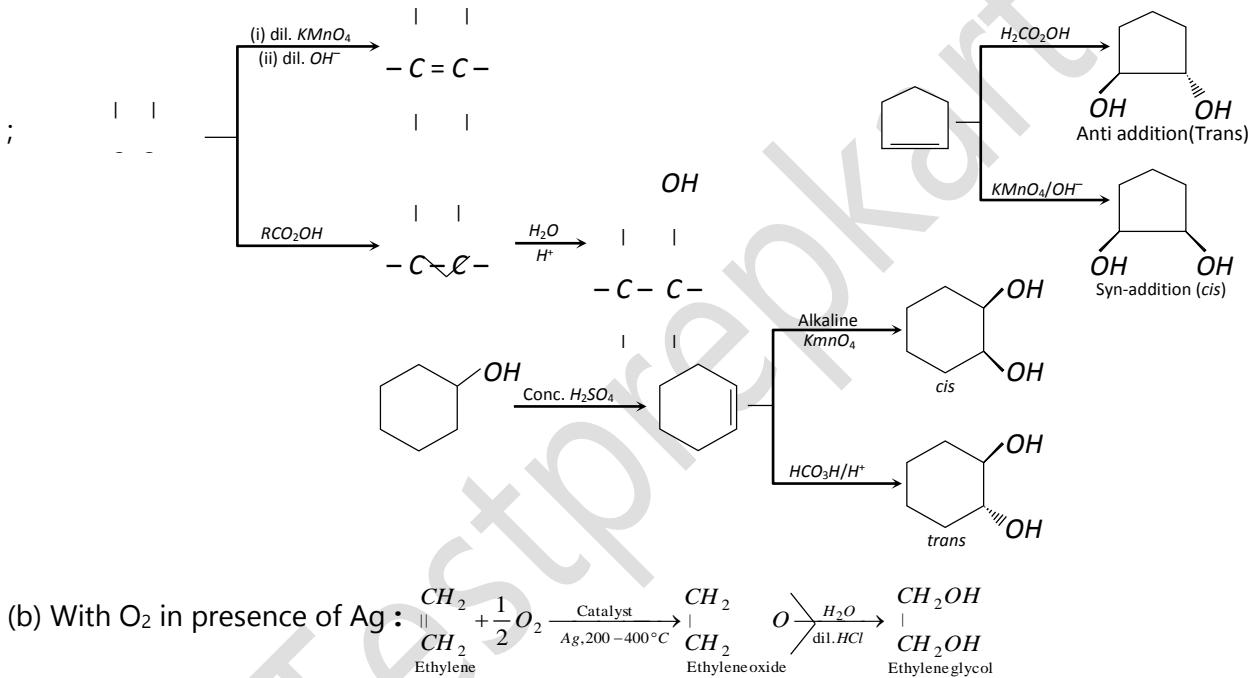


### 3. Dihydric alcohols.

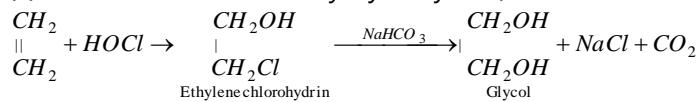
These are compound containing two hydroxyl groups. These are dihydroxy derivatives of alkanes. Their general formula is  $C_nH_{2n+2}O_2$ . The simplest and most important dihydric alcohol is ethylene glycol. They are classified as  $\alpha$ ,  $\beta$ ,  $\gamma$ ..... glycols, according to the relative position of two hydroxyl groups.  $\alpha$  is 1, 2 glycol,  $\beta$  is 1, 3 glycol.

## (1) Preparation

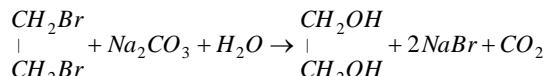
(i) **From ethylene:** (a) Through cold dilute alkaline solution of Bayer's reagent



(c) With HOCl followed by hydrolysis: (Industrial method)



**(ii) From 1, 2 dibromo ethane [Lab method]:**



$$\begin{array}{c} CH_2Br \\ | \\ CH_2Br \end{array} + 2CH_3COOK \xrightarrow[-2KBr]{CH_3COOH} \begin{array}{c} CH_2OOCCH_3 \\ | \\ CH_2OOCCH_3 \end{array} \xrightarrow{NaOH} \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} + 2CH_3COONa$$

Glycoldiacetate

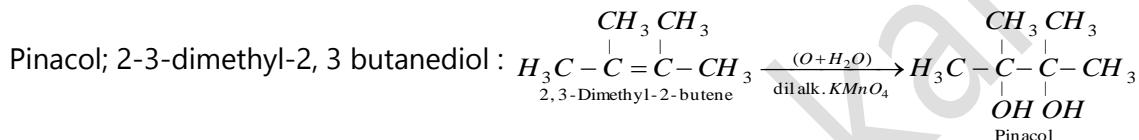


Note: Vinyl bromide is formed as by product.

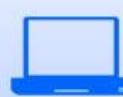
Best yield of glycol can be obtained by heating 1, 2-dibromo ethane with  $CH_3COOK$  in glacial acetic acid.

## (2) Physical properties

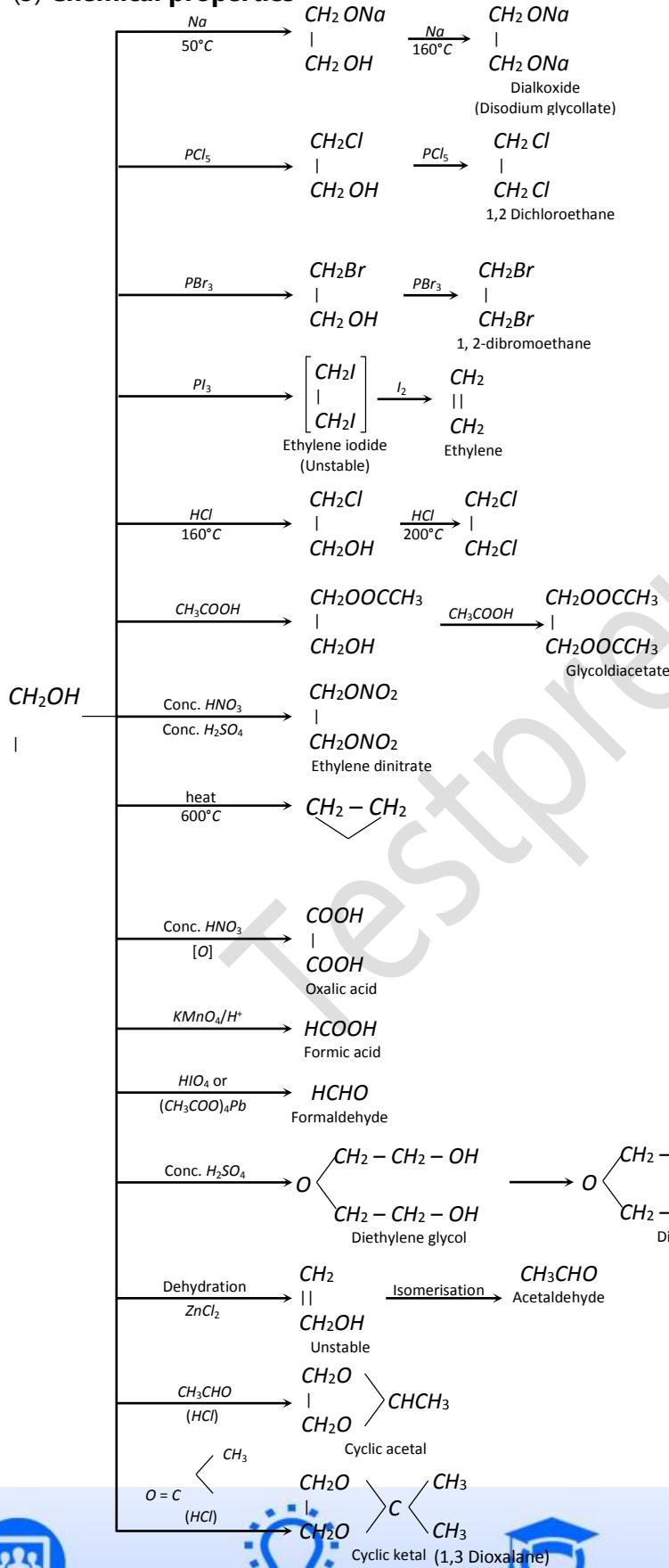
- (i) It is a colourless, syrupy liquid and sweet in taste. Its boiling point is 197°C.
- (ii) It is miscible in water and ethanol in all proportions but is insoluble in ether.
- (iii) It is toxic as methanol when taken orally.
- (iv) It is widely used as a solvent and as an antifreeze agent.



When pinacol react with mineral acid then pinacolone is formed.

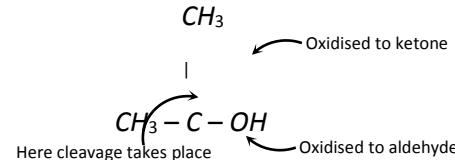


### (3) Chemical properties

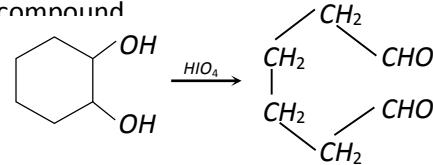


Per iodic oxidation of polyhydroxy alcohol gives following information,

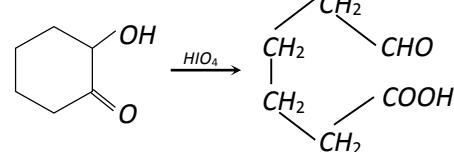
(1) There is cleavage of (C – C) bond. When two –OH–



(2) Both CHO are present in one molecule indicating cyclic compound



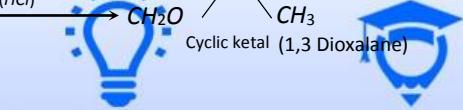
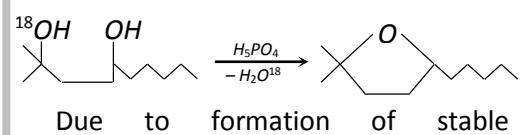
(3) On one side presence of –COOH group indicates keto group adjacent to (C – OH) group in (C).



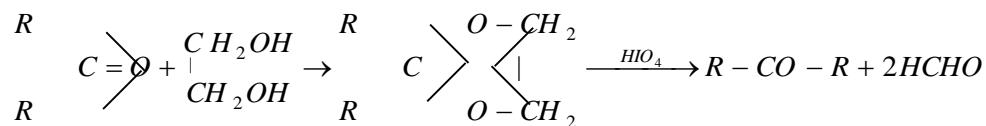
(4) Formation of two molecule of glyoxalic acid indicate that D is cyclic compound of four C- atom with C=O and C-OH groups on both sides



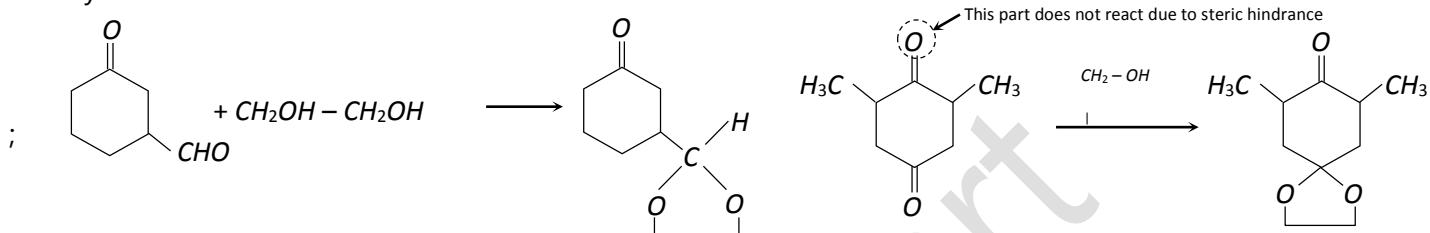
### Dehydration



Dioxalane formation provides a path of protecting a carbonyl group in reaction studied in basic medium in which acetals are not affected. The carbonyl compound may be regenerated by the addition of periodic acid to aqueous solution of the dioxalane or by acidic hydrolysis.



Aldehyde is more reactive than ketone in dioxalane formation.



#### (4) Uses

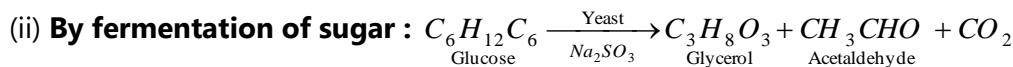
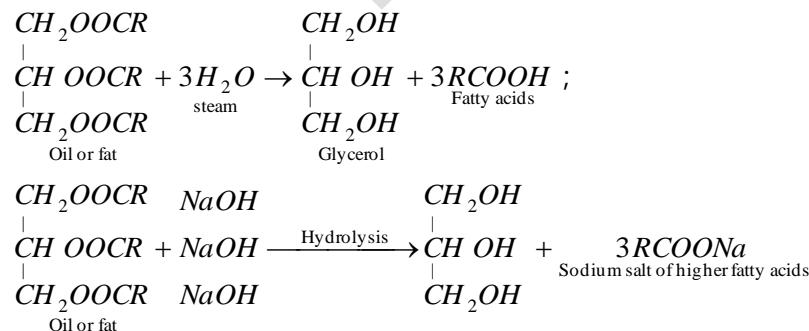
- (i) Used as an antifreeze in car radiators.
- (ii) Used in the manufacture of dacron, dioxan etc.
- (iii) As a solvent and as a preservatives.
- (iv) As a cooling agent in aeroplanes.
- (v) As an explosives in the form of dinitrate.

## 4. Trihydric alcohols.

The only important trihydric alcohol is glycerol (propane-1, 2, 3-triol). It occurs as glycosides in almost all animal and vegetable oils and fats.

#### (1) Preparation

##### (i) From oils and fats



##### (iii) From propene [Modern method]



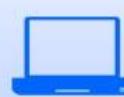
Preparation Classes



Counseling Sessions



Online Test



Free Trial Classes



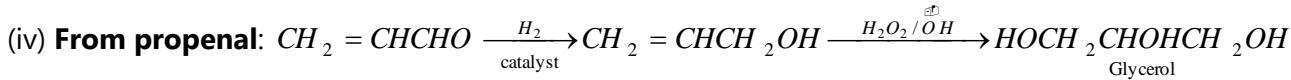
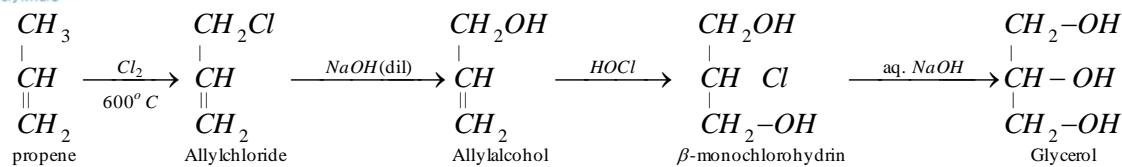
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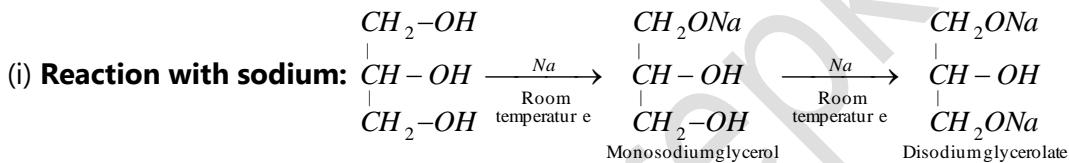
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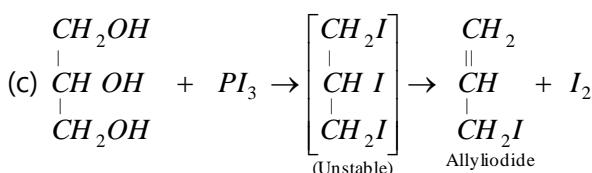
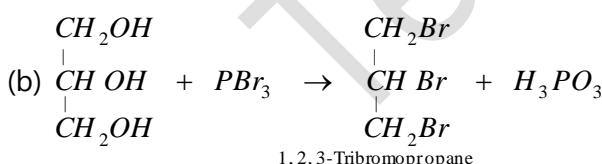
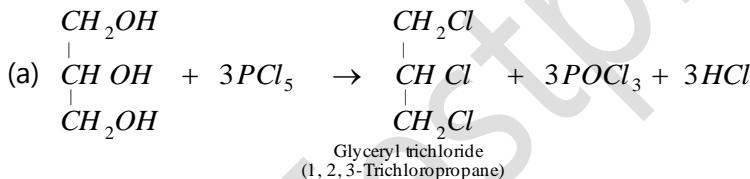
## (2) Physical properties

- (i) It is a colorless, odorless, viscous and hygroscopic liquid.
- (ii) It has high boiling point i.e., 290°C. The high viscosity and high boiling point of glycerol are due to association through hydrogen bonding.
- (iii) It is soluble in water and ethyl alcohol but insoluble in ether.
- (iv) It is sweet in taste and nontoxic in nature.

## (3) Chemical properties



### (ii) Reaction with $\text{PCl}_5$ , $\text{PBr}_3$ and $\text{PI}_3$



Preparation Classes



Counseling Sessions



Online Test



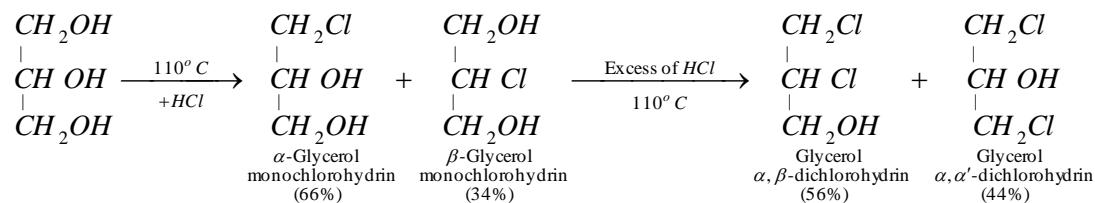
Free Trial Classes


[www.testprepkart.com](http://www.testprepkart.com)

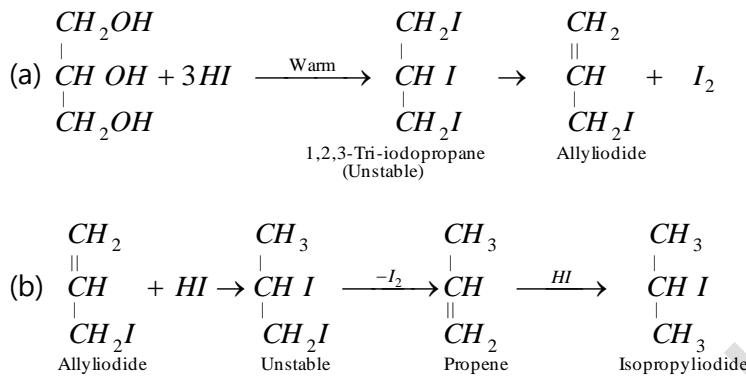
[info@testprepkart.com](mailto:info@testprepkart.com)


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**(iii) Reaction with HCl or HBr**

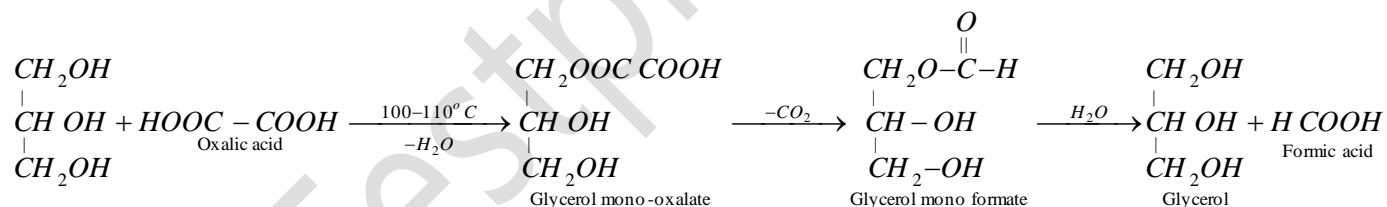


**(iv) Reaction with HI**

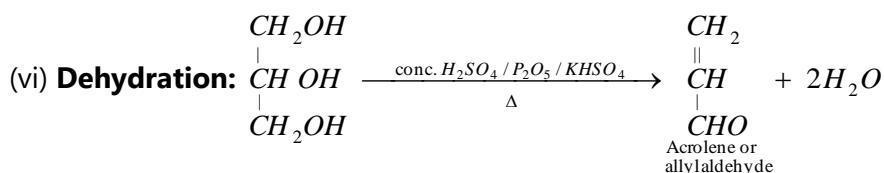
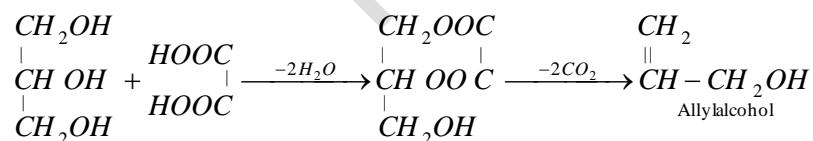


**(v) Reaction with oxalic acid**

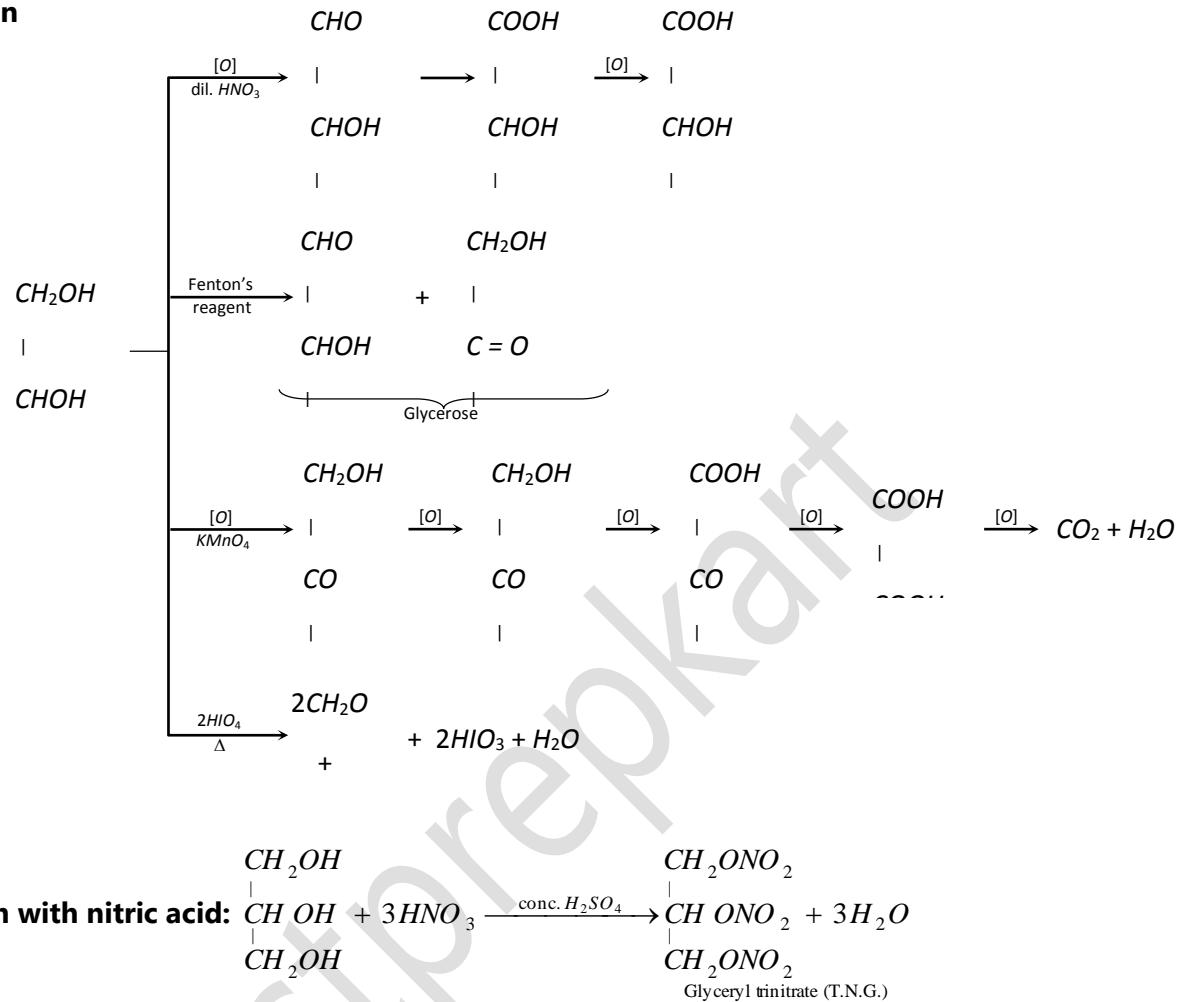
(a) At 110°C Glycerol is formed



(b) At 260°C, allyl alcohol is formed



(vii) **Oxidation**



Dynamite is prepared from T.N.G.

**Dynamite:** A mixture of T.N.G. and glyceryl dinitrate absorbed in kieselguhr is called dynamite. It was discovered by Alfred Nobel in 1867. It releases large volume of gases and occupy 10,900 times the volume of nitroglycerine.



**Blasting gelatin:** A mixture of glyceryl trinitrate and cellulose nitrate (gun cotton).

**Cordite:** It is obtained by mixing glyceryl trinitrate with gun cotton and vaseline it is smokeless explosive.



#### (4) Uses

- (a) As antifreeze in automobile radiator.
- (b) In the preparation of good quality of soap-hand lotions shaving creams and tooth pastes.
- (c) As a lubricant in watches.
- (d) As a preservatives.
- (e) As a sweetening agent in confectionary, beverages and medicines being non-toxic in nature.
- (f) In manufacture of explosives such as dynamite.

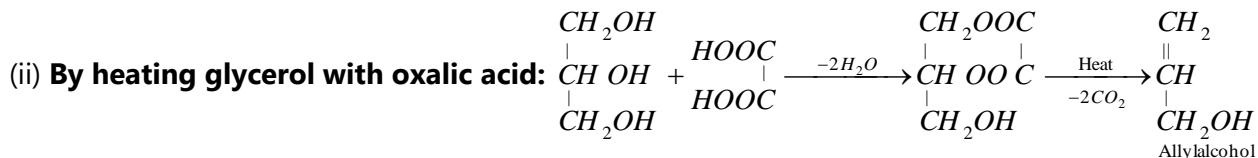
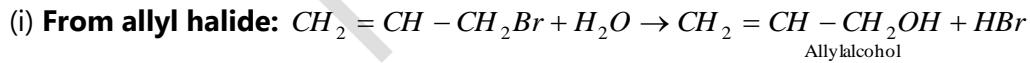
#### (5) Analytical tests of glycerol

- (i) **Acrolein test:** When glycerol is heated with  $KHSO_4$  a very offensive smell is produced due to formation of acrolein. Its aqueous solution restores the colour of schiff's reagent and reduces Fehling solution and Tollen's reagent.
- (ii) **Dunstan's test:** A drop of phenolphthalein is added approximately 5 ml of borax solution. The pink colour appears on adding 2-3 drops of glycerol, pink colour disappears. The pink colour appears on heating and disappears on cooling again.

## 5. Unsaturated alcohols.

#### (1) Preparation

(Allyl alcohol)

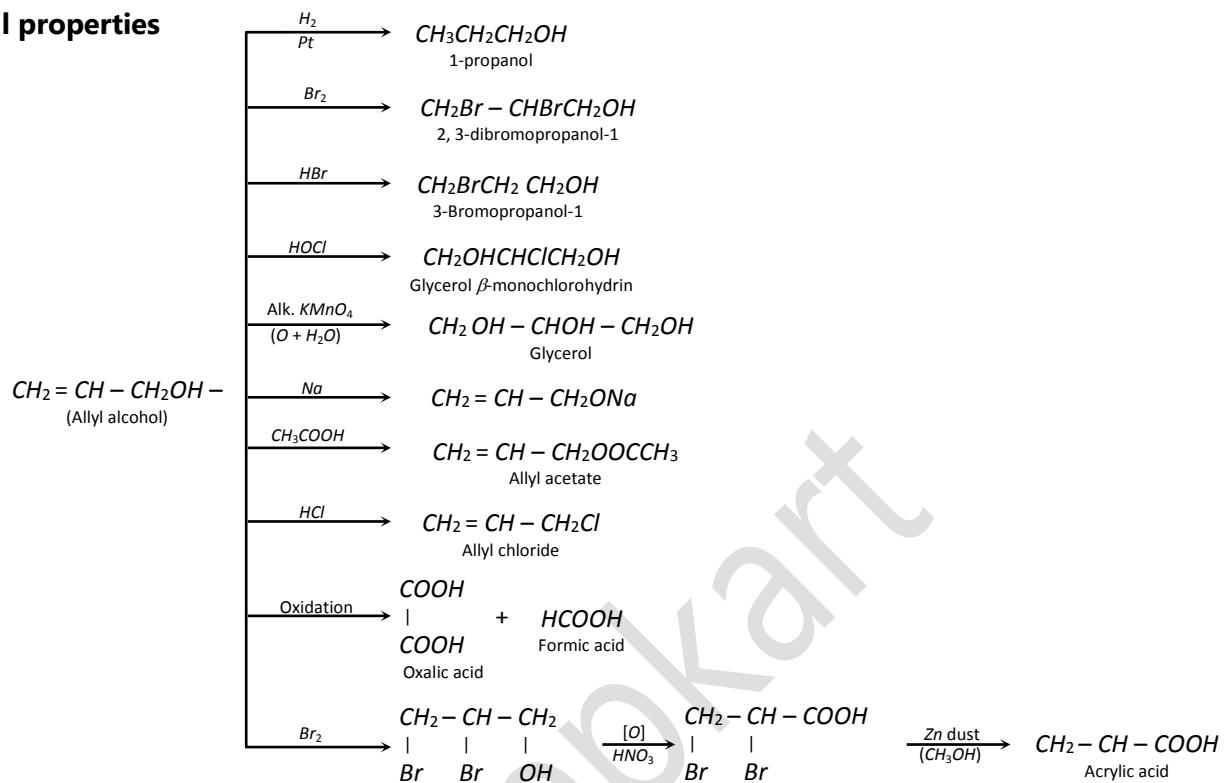


#### (2) Physical properties

- (a) It is colourless, pungent smelling liquid.
- (b) It is soluble in water, alcohol and ether in all proportion.



### (3) Chemical properties

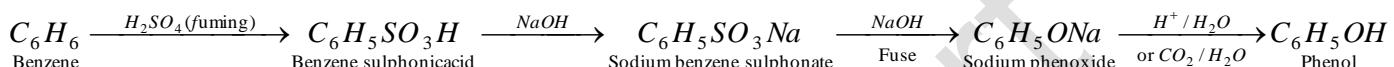


## 6. Phenol (Carbolic acid), $C_6H_5OH$ or Hydroxy benzene.

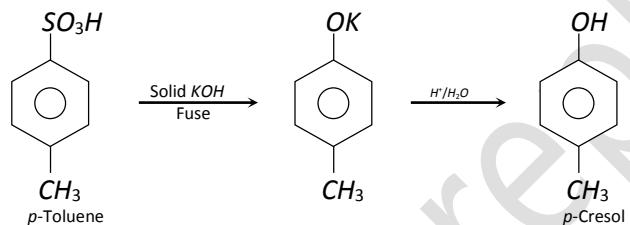
It was discovered by Runge in the middle oil fraction of coal-tar distillation and named it 'carbolic acid' (carbo = coal, oleum = oil) or phenol containing 5% water is liquid at room temperature and is termed as carbolic acid. It is also present in traces in human urine.

## (1) Preparation

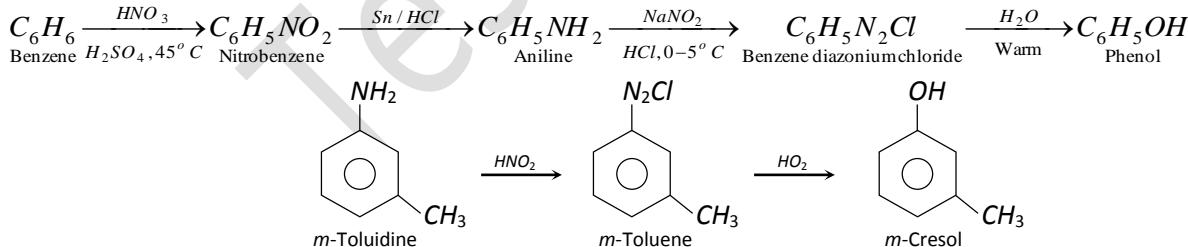
**(i) From benzene sulphonic acid:** Sodium salt of benzene sulphonic acid is fused with sodium hydroxide ( $\text{NaOH}$ ) when sodium phenoxide is formed. Sodium phenoxide on treatment with dilute acid or carbon dioxide yields phenol. The start can be made with benzene.



This is one of the laboratory methods for the preparation of phenol. Similarly methyl phenols (cresols) can be prepared.

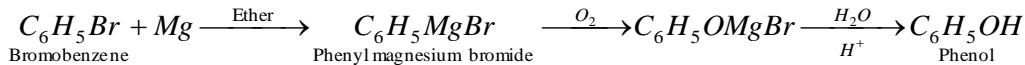


(ii) **From benzene diazonium chloride:** When benzene diazonium chloride solution is warmed, phenol is formed with evolution of nitrogen. The phenol from solution is recovered by steam distillation. In this case also, benzene can be taken as the starting material. This is also a laboratory method.

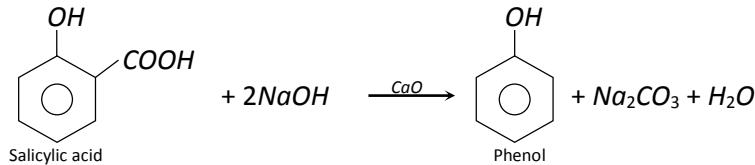


Note: Diazonium salts are obtained from aniline and its derivatives by a process called **diazotisation**.

(iii) **From Grignard reagent:** Chlorobenzene or bromobenzene is first converted into phenyl magnesium halide in presence of dry ether. The Grignard reagent on reaction with oxygen and subsequent hydrolysis by a mineral acid, yields phenol.



(iv) **From salicylic acid:** When salicylic acid or its sodium salt is distilled with soda lime, decarboxylation occurs and phenol is formed.

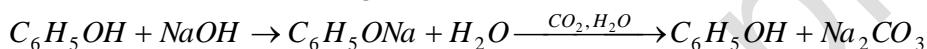


(v) **Middle oil of coal tar distillation:** Middle oil of coal-tar distillation has naphthalene and phenolic compounds. Phenolic compounds are isolated in following steps.

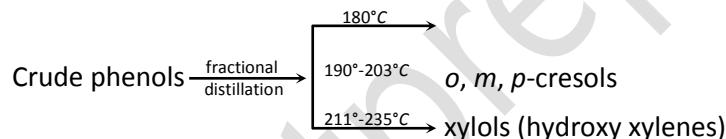
**Step I:** Middle oil is washed with  $H_2SO_4$ . It dissolves basic impurities like pyridine (base).

**Step II:** Excessive cooling separates naphthalene (a low melting solid)

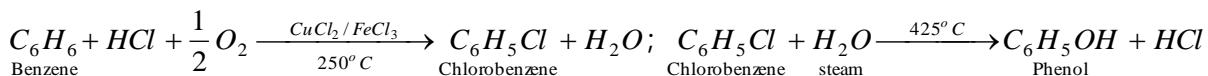
**Step III:** Filtrate of step II is treated with aqueous NaOH when phenols dissolve as phenoxides. Carbon dioxide is then blown through the solution to liberate phenols.



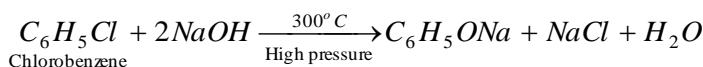
**Step IV:** Crude phenol (of step III) is subjected to fractional distillation.



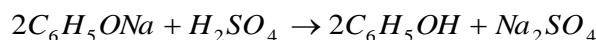
(vi) **Raschig's process:** Chlorobenzene is formed by the interaction of benzene, hydrogen chloride and air at 250°C in presence of catalyst cupric chloride and Ferric chloride it is hydrolysed by superheated steam at 425°C to form phenol and HCl. This is one of the latest methods for the synthesis of phenol. HCl may be again used to convert more of benzene into chlorobenzene.



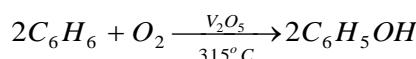
(vii) **Dow process:** This process involves alkaline hydrolysis of chlorobenzene. Large quantities of phenol are formed by heating chlorobenzene with a 10% solution of caustic soda or sodium carbonate at 300°C under a very high pressure (200 atm).



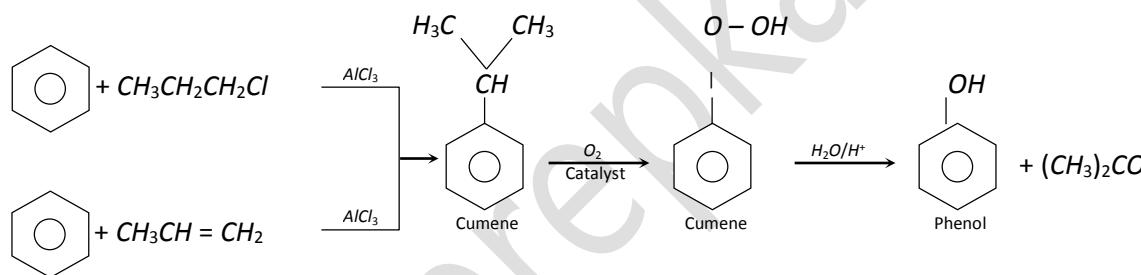
sodium phenoxide on treatment with mineral acid yields phenol.



(viii) **Oxidation of benzene:** This is the latest method for the manufacture of phenol. The mixture of benzene and air is passed over vanadium pentaoxide at 315°C. Benzene is directly oxidised to phenol.

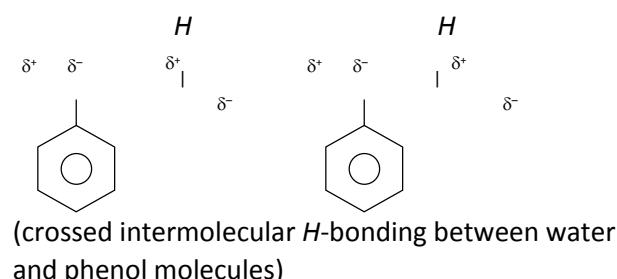
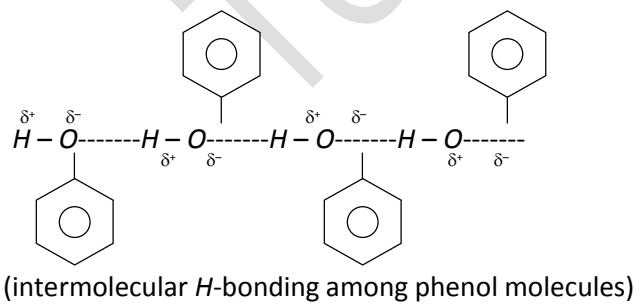


(ix) **Oxidation of isopropyl benzene [Cumene]:** Cumene is oxidised with oxygen or air into cumene hydroperoxide in presence of a catalyst. This is decomposed by dilute sulphuric acid into phenol and acetone.



## (2) Physical properties

- (i) Phenol is a colourless crystalline, deliquescent solid. It attains pink colour on exposure to air and light.
- (ii) They are capable of forming intermolecular H-bonding among themselves and with water. Thus, they have high b.p. and they are soluble in water.



- Due to intermolecular H- bonding and high dipole moment, m.p. and b.p. of phenol are much higher than that of hydrocarbon of comparable molecular weights.

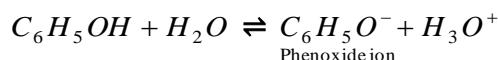


Compounds	Molecular weight	Boiling point	Melting point
Phenol	94 g mol <sup>-1</sup>	182°C	41°C
Toluene	92 g mol <sup>-1</sup>	111°C	-95°C

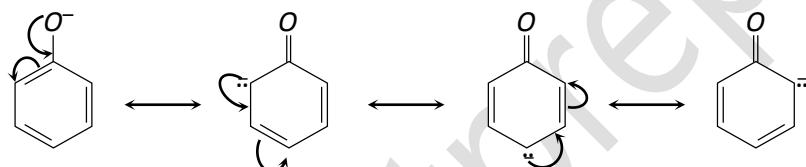
- (iii) It has a peculiar characteristic smell and a strong corrosive action on skin.
- (iv) It is sparingly soluble in water but readily soluble in organic solvents such as alcohol, benzene and ether.
- (v) It is poisonous in nature but acts as antiseptic and disinfectant.

### (3) Chemical properties

(i) **Acidic nature:** Phenol is a weak acid. The acidic nature of phenol is due to the formation of stable phenoxide ion in solution.

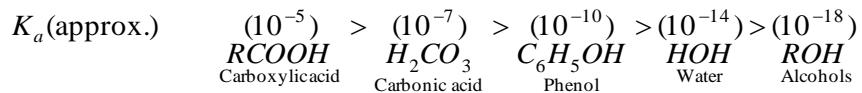


The phenoxide ion is stable due to resonance.



The negative charge is spread throughout the benzene ring. This charge delocalisation is a stabilising factor in the phenoxide ion and increase acidity of phenol. [No resonance is possible in alkoxide ions ( $RO^-$ ) derived from alcohols. The negative charge is localised on oxygen atom. Thus alcohols are not acidic].

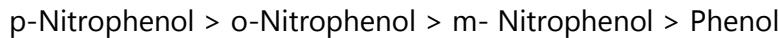
**Note:** Phenols are much more acidic than alcohols but less so than carboxylic acids or even carbonic acid. This is indicated by the values of ionisation constants. The relative acidity follows the following order



**Effects of substituents on the acidity of phenols:** Presence of electron attracting group, (e.g.,  $-NO_2$ ,  $-X$ ,  $-NR_3^+$ ,  $-CN$ ,  $-CHO$ ,  $-COOH$ ) on the benzene ring increases the acidity of phenol as it enables the ring to draw more electrons from the phenoxy oxygen and thus releasing easily the proton. Further, the particular effect is more when the substituent is present on o- or p-position than in m-position to the phenolic group.



The relative strengths of some phenols (as acids) are as follows:



Presence of electron releasing group, (e.g.,  $-CH_3$ ,  $-C_2H_5$ ,  $-OCH_3$ ,  $-NR_2$ ) on the benzene ring decreases the acidity of phenol as it strengthens the negative charge on phenoxy oxygen and thus proton release becomes difficult. Thus, cresols are less acidic than phenol.

However, m-methoxy and m-aminophenols are stronger acids than phenol because of  $-I$  effect and absence of  $+R$  effect.



Greater the value of  $K_a$  or lower the value of  $pK_a$ , stronger will be the acid. Some other examples of acidic nature of phenols are,

Chloro phenols: o- > m- > p-

Cresols : m- > p- > o-

Dihydric phenol: m- > p- > o-

The acidic nature of phenol is observed in the following:

(a) Phenol changes blue litmus to red.

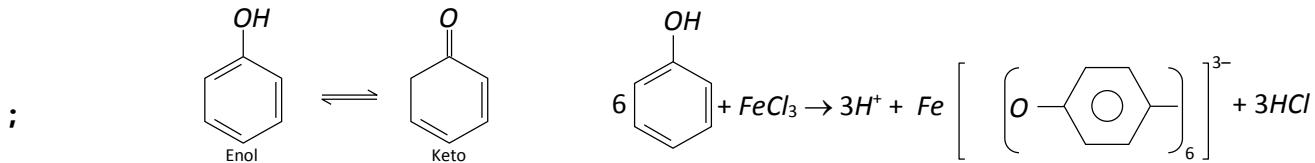
(b) Highly electropositive metals react with phenol.  $2C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2$

(c) Phenol reacts with strong alkalies to form phenoxides.  $C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$

However, phenol does not decompose sodium carbonate or sodium bicarbonate, i.e.,  $CO_2$  is not evolved because phenol is weaker than carbonic acid.

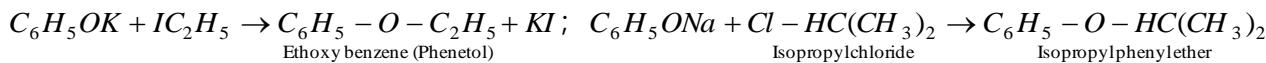
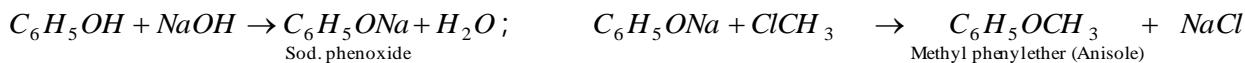
## (ii) Reactions of $-OH$ group

(a) Reaction with  $FeCl_3$  : Phenol gives violet coloration with ferric chloride solution (neutral) due to the formation of a colored iron complex, which is a characteristic to the existence of keto-enol tautomerism in phenols (predominantly enolic form).

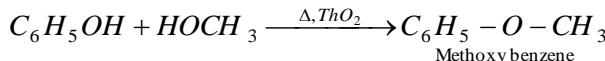


This is the test of phenol.

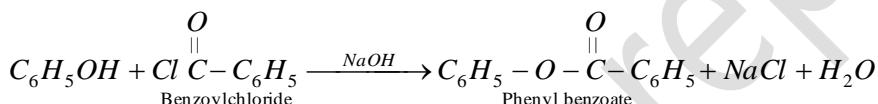
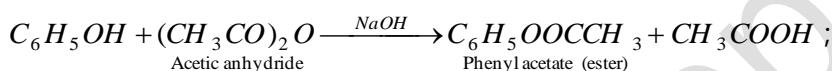
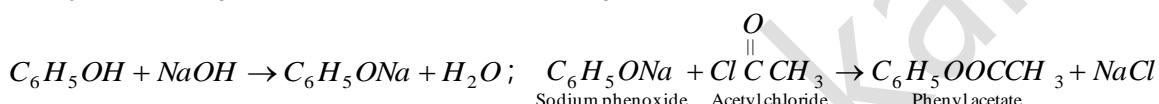
(b) Ether formation: Phenol reacts with alkyl halides in alkali solution to form phenyl ethers (Williamson's synthesis). The phenoxide ion is a nucleophile and will replace halogenation of alkyl halide.



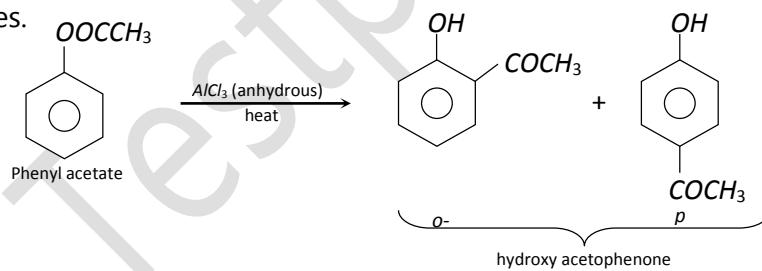
Ethers are also formed when vapours of phenol and an alcohol are heated over thoria ( $\text{ThO}_2$ ) or  $\text{Al}_2\text{O}_3$ .



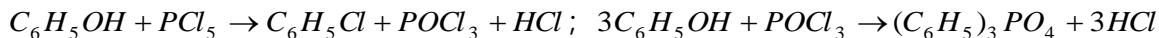
(c) Ester formation: Phenol reacts with acid chlorides (or acid anhydrides) in alkali solution to form phenylesters (**Acylation**). This reaction (**Benzoylation**) is called **Schotten-Baumann** reaction.



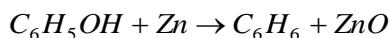
The phenyl esters on treatment with anhydrous  $AlCl_3$  undergoes **Fries rearrangement** to give o- and p- hydroxy ketones.



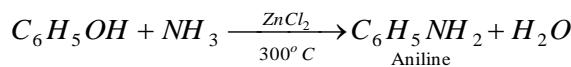
(d) Reaction with  $PCl_5$ : Phenol reacts with  $PCl_5$  to form chlorobenzene. The yield of chlorobenzene is poor and mainly triphenyl phosphate is formed.



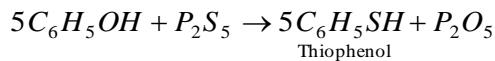
(e) Reaction with zinc dust: When phenol is distilled with zinc dust, benzene is obtained.



(f) Reaction with ammonia: Phenol reacts with ammonia in presence of anhydrous zinc chloride at 300°C or  $(NH_4)_2SO_3 / NH_3$  at 150°C to form aniline. This conversion of phenol into aniline is called **Bucherer reaction.**

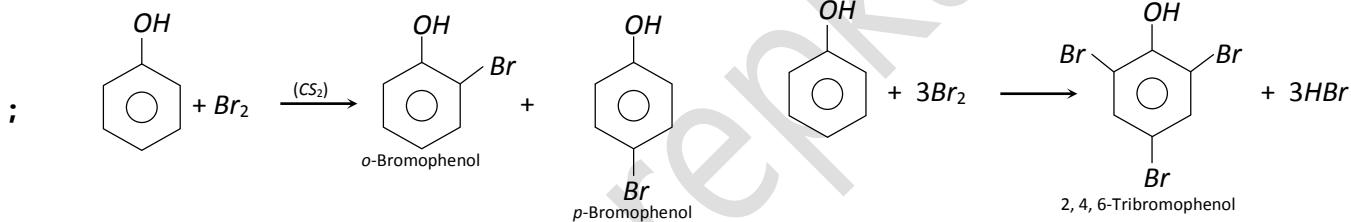


(g) Action of  $P_2S_5$  : By heating phenol with phosphorus penta sulphide, thiophenols are formed.



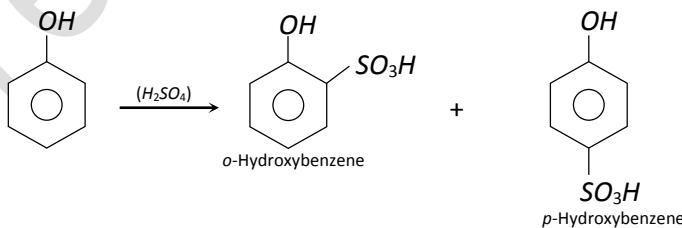
(iii) **Reactions of benzene nucleus:** The –OH group is ortho and para directing. It activates the benzene nucleus.

(a) Halogenation: Phenol reacts with bromine in carbon disulphide (or  $CHCl_3$ ) at low temperature to form mixture of ortho and para bromophenol.



Phenol forms a white precipitate with excess of bromine water yielding 2, 4, 6-tribromophenol.

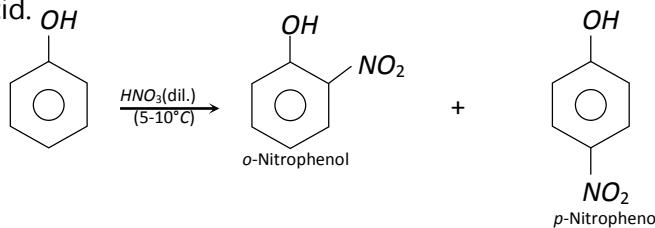
(b) Sulphonation: Phenol reacts with conc.  $H_2SO_4$  readily to form mixture of ortho and para hydroxy benzene sulphonic acids.



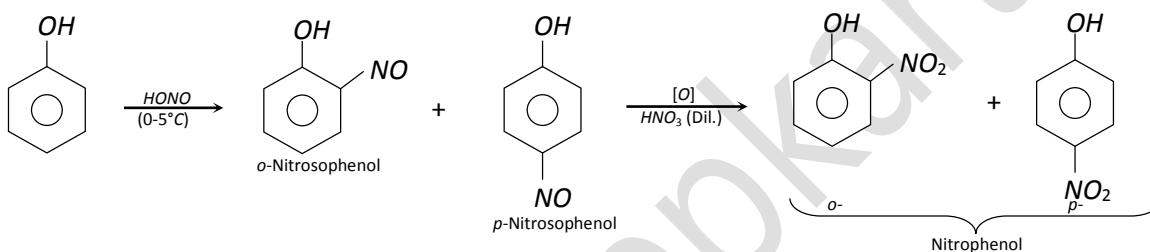
At low temperature (25°C), the ortho-isomer is the major product, whereas at 100°C, it gives mainly the para-isomer.



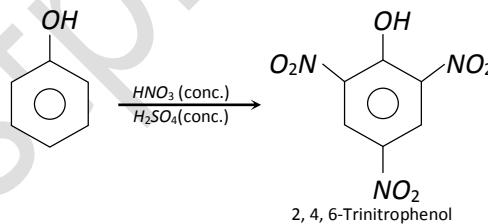
(c) Nitration: Phenol reacts with dilute nitric acid at 5-10°C to form ortho and para nitro phenols, but the yield is poor due to oxidation of phenolic group. The –OH group is activating group, hence nitration is possible with dilute nitric acid.



It is believed that the mechanism of the above reaction involves the formation of *o*- and *p*-nitrosophenol with nitrous acid,  $HNO_2(NaNO_2 + HCl)$  at 0-5°C, which gets oxidised to *o*- and *p*-nitrophenol with dilute nitric acid.

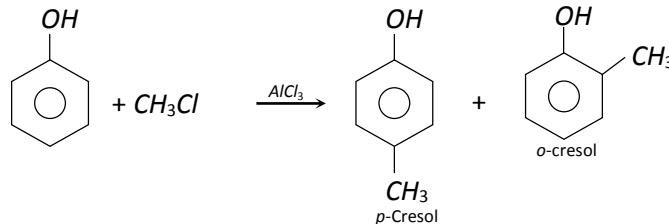


However, when phenol is treated with concentrated  $HNO_3$  in presence of concentrated  $H_2SO_4$ , 2,4,6-trinitrophenol (**Picric acid**) is formed.

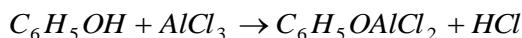


To get better yield of picric acid, first sulphonation of phenol is made and then nitrated. Presence of  $-SO_3H$  group prevents oxidation of phenol.

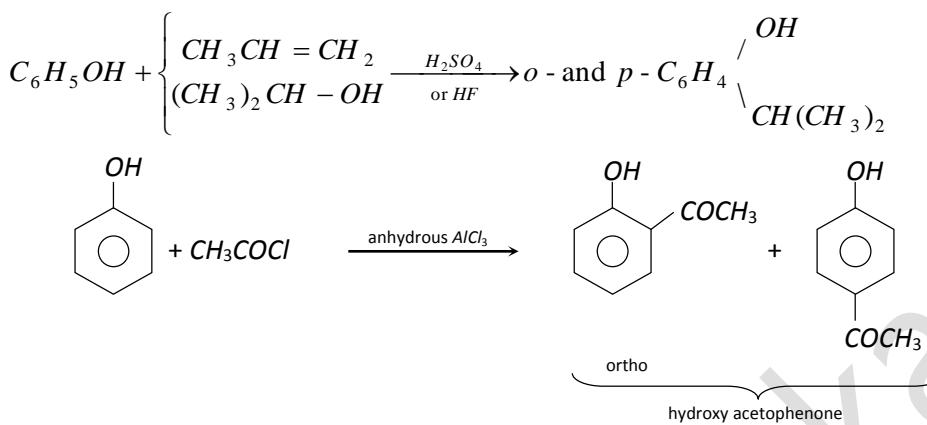
(d) Friedel-Craft's reaction: Phenol when treated with methyl chloride in presence of anhydrous aluminium chloride, *p*-cresol is the main product. A very small amount of *o*-cresol is also formed.



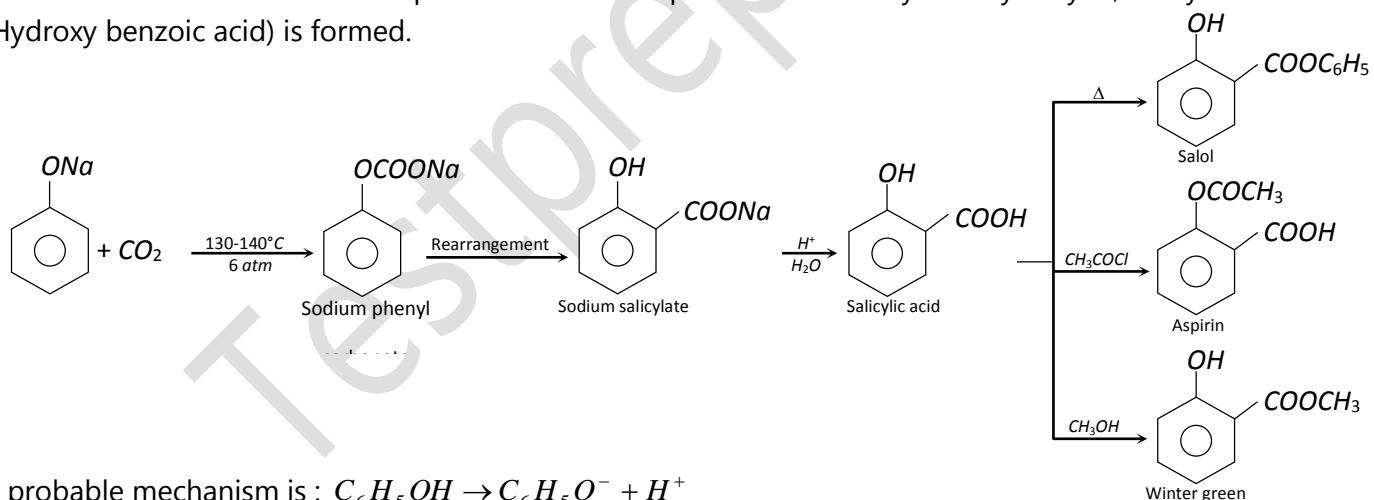
RX and  $AlCl_3$  give poor yields because  $AlCl_3$  coordinates with O. So Ring alkylation takes place as follows,



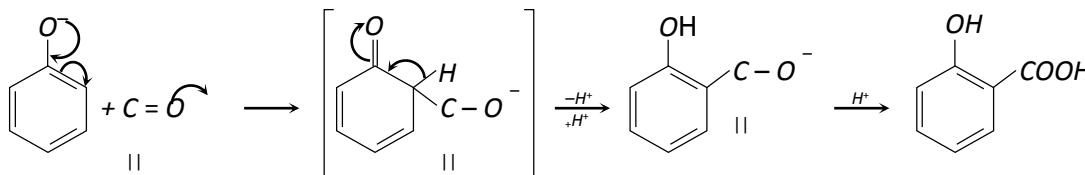
Thus to carry out successful Friedel-Craft's reaction with phenol it is necessary to use a large amount of  $AlCl_3$ . The **Ring alkylation** takes place as follows:



(e) Kolbe-Schmidt reaction (Carbonation) : This involves the interaction of sodium phenoxide with carbon dioxide at  $130-140^\circ C$  under pressure of 6 atmospheres followed by acid hydrolysis, Salicylic acid (o-Hydroxy benzoic acid) is formed.



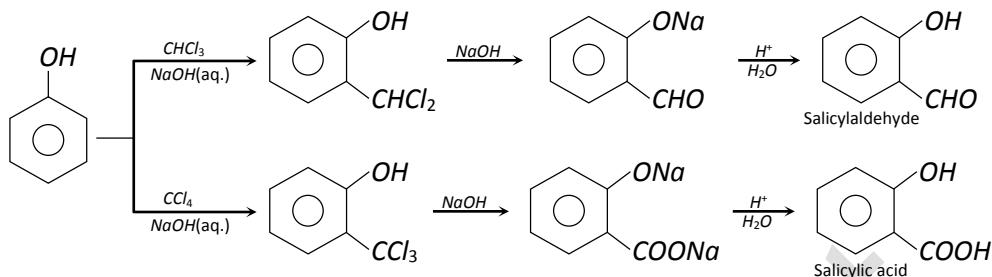
The probable mechanism is :  $C_6H_5OH \rightarrow C_6H_5O^- + H^+$



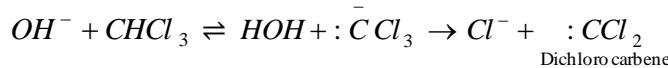
At higher temperature ( $250-300^\circ C$ ), p-isomer is obtained.



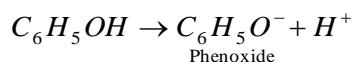
(f) **Reimer-Tiemann reaction:** Phenol, on refluxing with chloroform and sodium hydroxide (aq.) followed by acid hydrolysis yields salicylaldehyde (o-hydroxy benzaldehyde) and a very small amount of p-hydroxy benzaldehyde. However, when carbon tetrachloride is used, salicylic acid (predominating product) is formed.



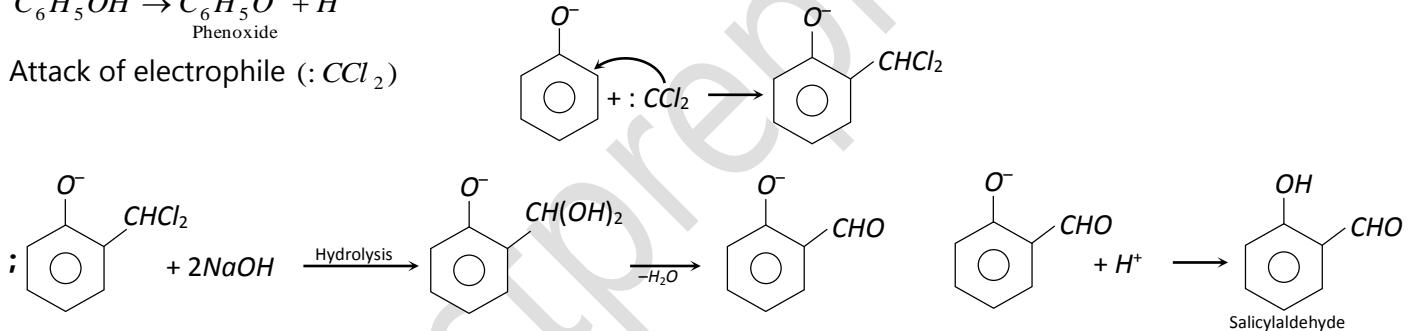
The electrophile is dichloromethylene :  $\text{CCl}_2$  generated from chloroform by the action of a base.



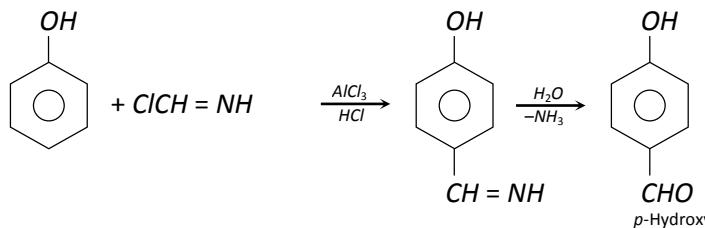
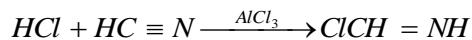
Reimer-Tiemann reaction involves electrophilic substitution on the highly reactive phenoxide ring.



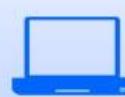
Attack of electrophile ( $: \text{CCl}_2$ )

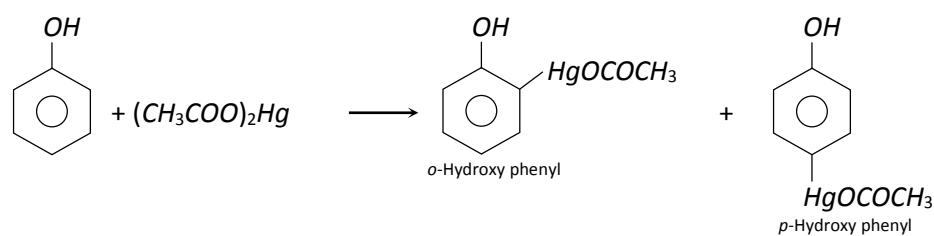


(g) Gattermann's reaction: Phenol, when treated with liquid hydrogen cyanide and hydrochloric acid gas in presence of anhydrous aluminium chloride yields mainly p-hydroxy benzaldehyde (Formylation).

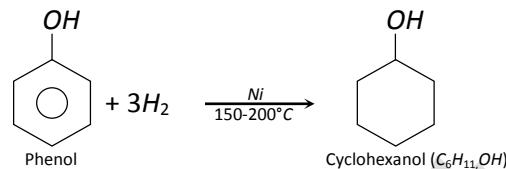


(h) Mercuration : Phenol when heated with mercuric acetate undergoes mercuration to form o- and p-isomers.



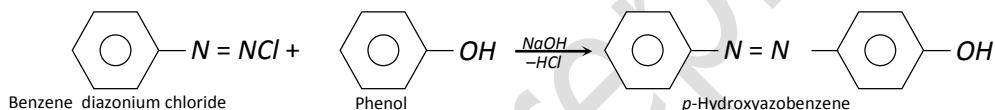


(i) **Hydrogenation:** Phenol, when hydrogenated in presence of a nickel catalyst at about 150-200°C, forms cyclohexanol.

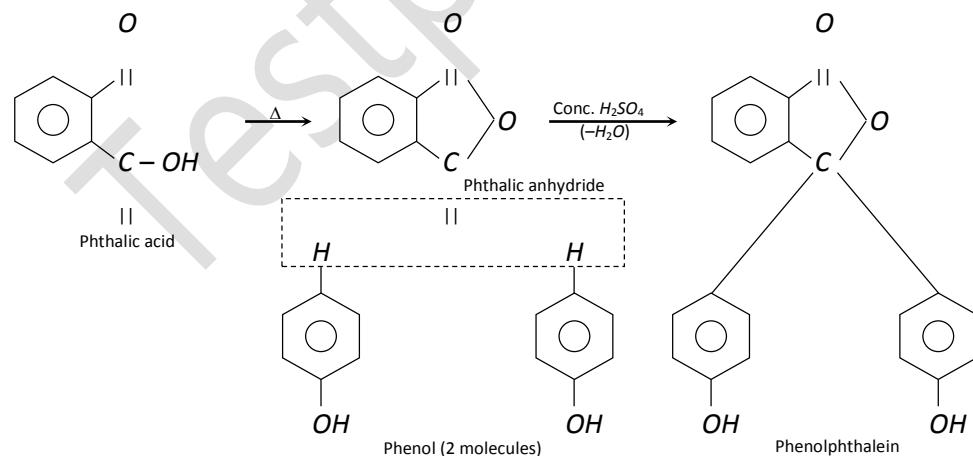


#### (iv) Miscellaneous reactions

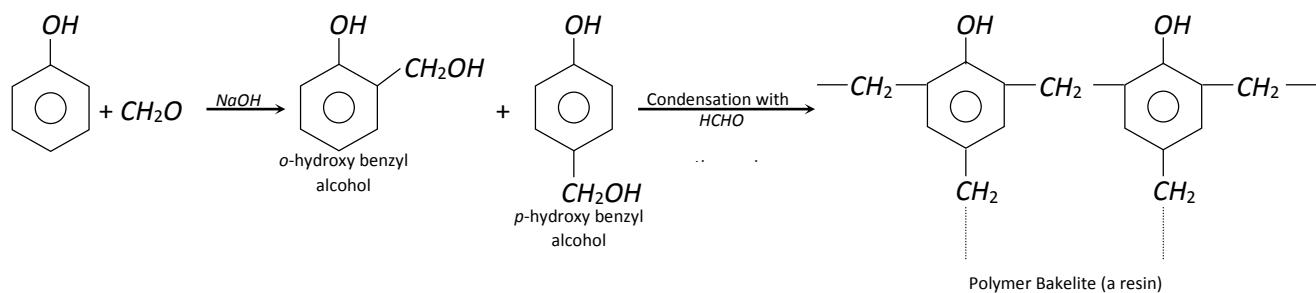
(a) Coupling reactions: Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a red dye (p-hydroxy azobenzene).



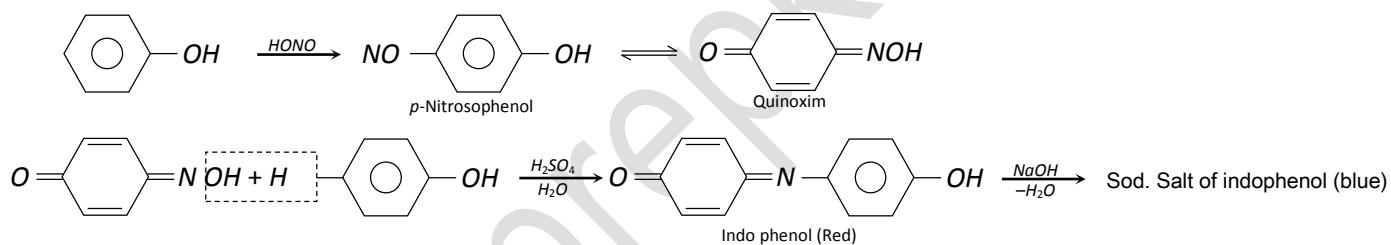
Phenol couples with phthalic anhydride in presence of concentrated  $\text{H}_2\text{SO}_4$  to form a dye, (phenolphthalein) used as an indicator.



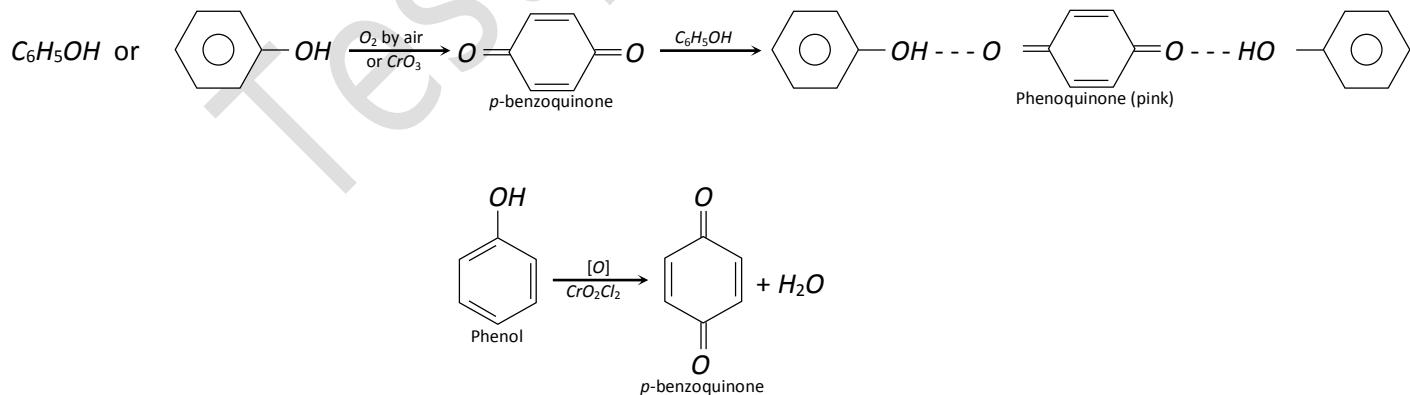
(b) Condensation with formaldehyde: Phenol condenses with formaldehyde (excess) in presence of sodium hydroxide or acid ( $H^+$ ) for about a week to form a polymer known as bakelite (a resin).



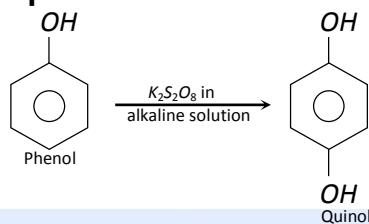
(c) Liebermann's Nitroso reaction: When phenol is reacted with  $NaNNO_2$  and concentrated  $H_2SO_4$ , it gives a deep green or blue color which changes to red on dilution with water. When made alkaline with  $NaOH$  original green or blue color is restored. This reaction is known as Liebermann's nitroso reaction and is used as a test of phenol.



(d) Oxidation: Phenol turns pink or red or brown on exposure to air and light due to slow oxidation. The colour is probably due to the formation of quinone and phenoquinone.



But on oxidation with potassium persulphate in alkaline solution, phenol forms 1, 4-dihydroxy benzene (Quinol). This is known as **Elbs persulphate oxidation**.



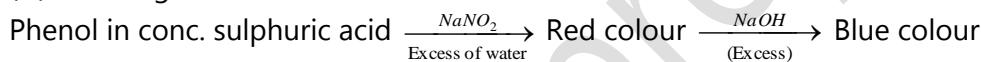
(4) **Uses:** Phenol is extensively used in industry. The important applications of phenol are:

- (i) As an antiseptic in soaps, lotions and ointments. A powerful antiseptic is "Dettol" which is a phenol derivative (2, 4-dichloro-3, 5-dimethyl phenol).
- (ii) In the manufacture of azo dyes, phenolphthalein, etc.
- (iii) In the preparation of picric acid used as an explosive and for dyeing silk and wool.
- (iv) In the manufacture of cyclohexanol required for the production of nylon and used as a solvent for rubber and lacquers.
- (v) As a preservative for ink.
- (vi) In the manufacture of phenol-formaldehyde plastics such as bakelite.
- (vii) In the manufacture of drugs like aspirin, salol, phenacetin, etc.
- (viii) For cauterising wounds caused by the bite of mad dogs.
- (ix) As a starting material for the manufacture of nylon and artificial tannins.
- (x) In the preparation of disinfectants, fungicides and bactericides.

(5) **Tests of phenol:** (i) Aqueous solution of phenol gives a violet colouration with a drop of ferric chloride.

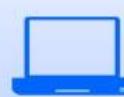
(ii) Aqueous solution of phenol gives a white precipitate of 2, 4, 6-tribromophenol with bromine water.

(iii) Phenol gives **Liebermann's nitroso reaction**.



(iv) Phenol combines with phthalic anhydride in presence of conc.  $H_2SO_4$  to form phenolphthalein which gives pink colour with alkali, and used as an indicator.

(v) With ammonia and sodium hypochlorite, phenol gives blue colour.



## Difference between phenol and alcohol

Property	Phenol ( $C_6H_5OH$ )	Alcohol ( $C_2H_5OH$ )
Odour	Typical phenolic odour	Pleasant alcoholic odour
Nature, reaction with alkali	Acidic, dissolves in sodium hydroxide forming sodium phenoxide.	Neutral, no reaction with alkalies.
Reaction with neutral $FeCl_3$	Gives violet colouration due to formation of complex compound.	No reaction.
Reaction with halogen acids	No reaction with halogen acids.	Forms ethyl halides.
Oxidation	Pink or brown colour due to formation of quinone and phenoquinone.	Undergoes oxidation to give acetaldehyde and acetic acid.
Reaction with $HCHO$	Forms polymer (bakelite).	No reaction.
Liebermann's nitroso reaction	Positive.	Does not show.
Coupling with benzene diazonium chloride	Forms azo dye.	Does not form any dye.
Reaction with $PCl_5$	Mainly forms triphenyl phosphate.	Forms ethyl chloride
Iodoform test	Does not show.	Positive.

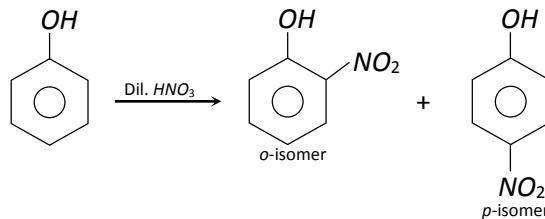
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## 7. Derivatives of phenol.

### NITROPHENOLS

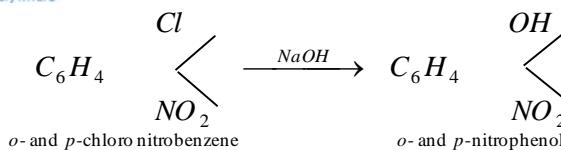
#### (1) Preparation

(i) Phenol easily undergoes nitration. Ortho and para nitrophenols are obtained by nitration of phenol with dilute  $HNO_3$  in cold. Ortho isomer is separated by steam distillation as it is steam volatile.

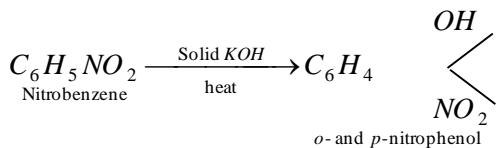


(ii) o- and p-forms are also obtained by treating chloro or bromo nitrobenzene with caustic alkali at  $120^\circ C$ .

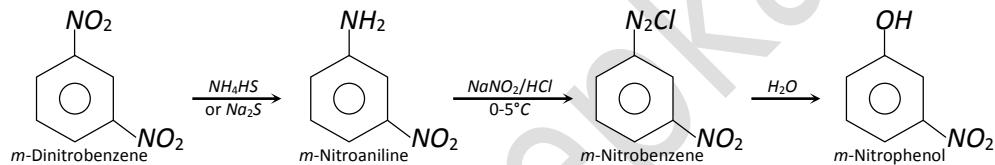




(iii) When heated with solid potassium hydroxide, nitrobenzene produces a mixture of o- and p-nitrophenols.



(iv) m-Nitrophenol is obtained from m-dinitrobenzene. One of the nitrogroup is converted into  $-NH_2$  group which is diazotised. The diazonium compound on boiling yields m-nitrophenol.



(2) **Properties:** o-Nitrophenol is a yellow colored crystalline compound, while m- and p-isomers are colorless crystalline compounds.

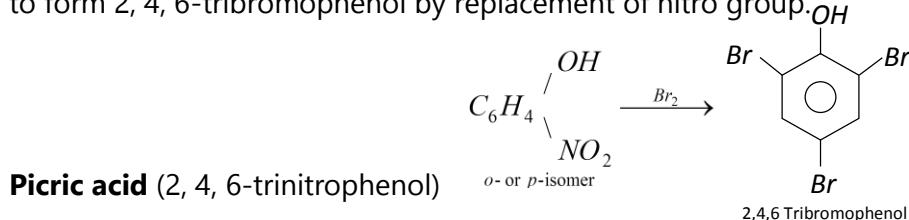
	Isomer	ortho	meta	para
m.pt.(°C)		45	97	114

the lowest melting point of o-isomer is due to **intramolecular hydrogen bonding** whereas meta and para isomers possess **intermolecular hydrogen bonding** and thus, they have higher melting points

They are stronger acids than phenol. The order is:

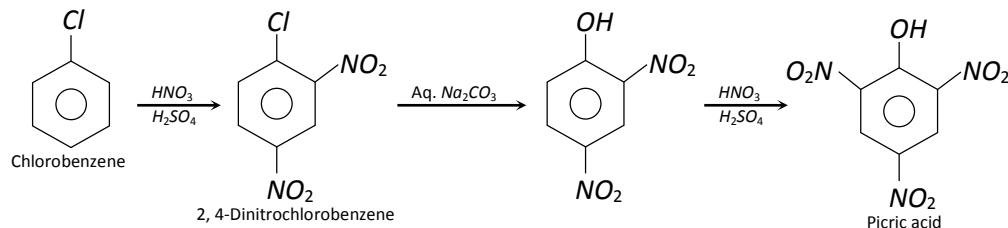
P-isomer > o-isomer > m-isomer > phenol

When reduced, they form corresponding aminophenols. o- and p-Nitrophenols react with bromine water to form 2, 4, 6-tribromophenol by replacement of nitro group.

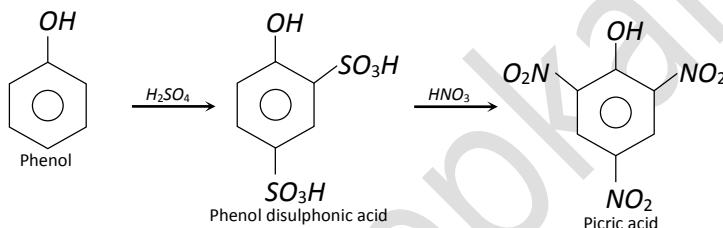


(1) **Preparation:** It is obtained when phenol is treated with conc.  $HNO_3$ . However, the yield is very poor. It is prepared on an industrial scale:

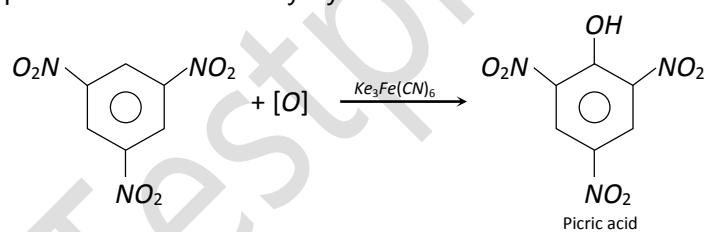
(i) **From chlorobenzene**



(ii) **From phenol through disulphonic acid**

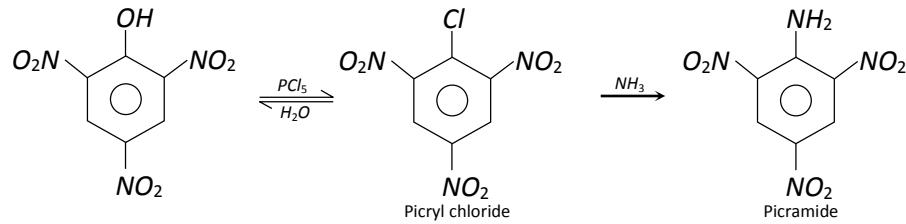


(iii) It may be prepared in the laboratory by oxidation of s-trinitrobenzene (TNB) with potassium ferricyanide.



(2) **Properties:** It is a yellow crystalline solid, m.pt. 122°C. It is insoluble in cold water but soluble in hot water and in ether. It is bitter in taste. Due to the presence of three electronegative nitro groups, it is a stronger acid than phenol and its properties are comparable to the carboxylic acid. It neutralises alkalies and decomposes carbonates with evolution of carbon dioxide.

Dry picric acid as well as its potassium or ammonium salts explode violently when detonated. It reacts with  $PCl_5$  to form picryl chloride which on shaking with  $NH_3$  yields picramide.



When distilled with a paste of bleaching powder, it gets decomposed and yields chloropicrin,  $CCl_3NO_2$ , as one of the products and is thus employed for the manufacture of tear gas.

It forms yellow, orange or red colored molecular compounds called picrates with aromatic hydrocarbons, amines and phenols which are used for characterization of these compounds.

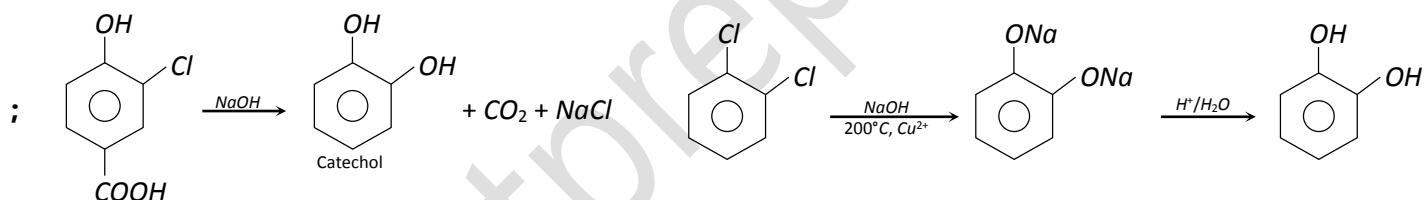
**Note:** Picrates are explosive in nature and explode violently when heated. These are prepared carefully.

(3) **Uses:** It is used as a yellow dye for silk and wool, as an explosive and as an antiseptic in treatment of burns.

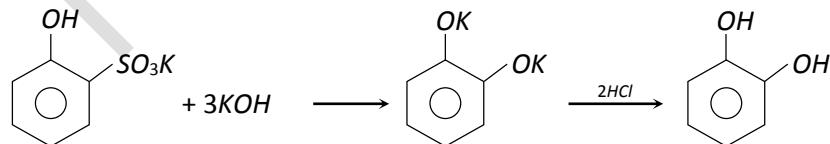
### Catechol (1, 2-Dihydroxy benzene)

#### (1) Preparation

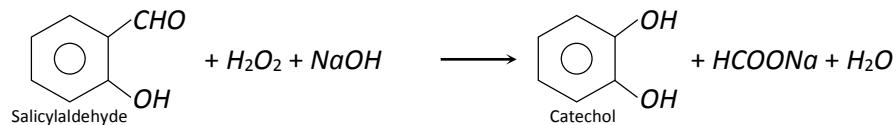
(i) By fusion of chlorosubstituted phenolic acid with caustic soda. or by hydrolysis of o-dichlorobenzene or o-chlorophenol with dilute NaOH solution at  $200^{\circ}C$  and in the presence of copper sulphate catalyst.



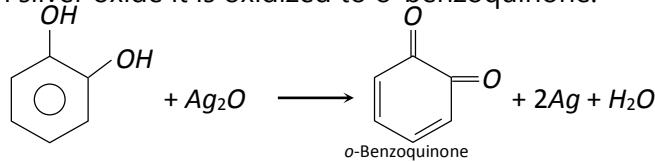
(ii) By fusing alkali salt of o-phenol sulphonic acid with caustic alkali and then hydrolysing the product with mineral acid.



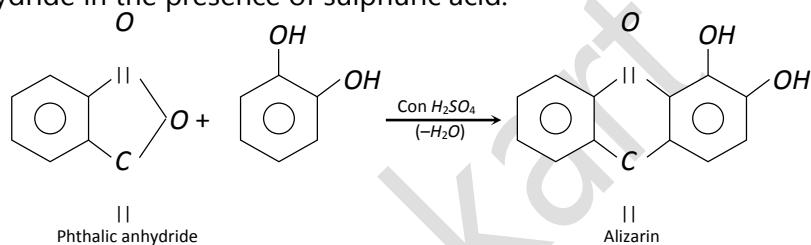
(iii) It may be conveniently prepared in the laboratory by treating salicylaldehyde with alkaline  $H_2O_2$ .



(2) **Properties:** It is a colorless crystalline solid, m.pt. 105°C. It is soluble in water. It is affected on exposure to air and light. It acts as a reducing agent as it reduces Tollen's reagent in cold and Fehling's solution on heating. With silver oxide it is oxidized to o-benzoquinone.



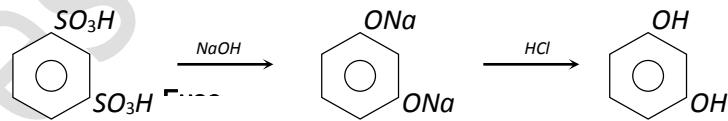
It forms insoluble lead salt (white ppt.) when treated with lead acetate solution and gives green color with  $\text{FeCl}_3$  which changes to red on adding  $\text{Na}_2\text{CO}_3$  solution. It forms alizarin dye stuff when condensed with phthalic anhydride in the presence of sulphuric acid.



(iii) **Uses:** It finds use as photographic developer, in the manufacture of alizarin and adrenaline hormone and as an antioxidant (inhibitor in auto oxidation) for preserving gasoline.

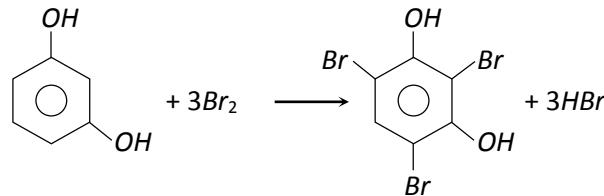
### Resorcinol (1, 3-Dihydroxy benzene)

(1) **Preparation:** It is prepared by alkali fusion of 1,3, benzene disulphonic acid (Industrial method).

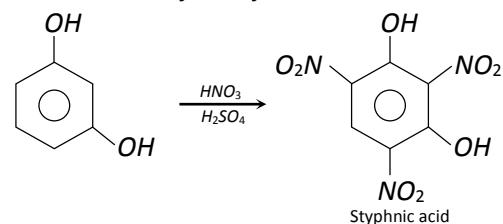


(2) **Properties:** It is a colourless crystalline solid, m.pt. 110°C. it is affected on exposure by air and light. It is soluble in water, alcohol and ether. It shows tautomerism. Its aqueous solution gives violet color with  $\text{FeCl}_3$ . It reduces Fehling's solution and Tollen's reagent on warming.

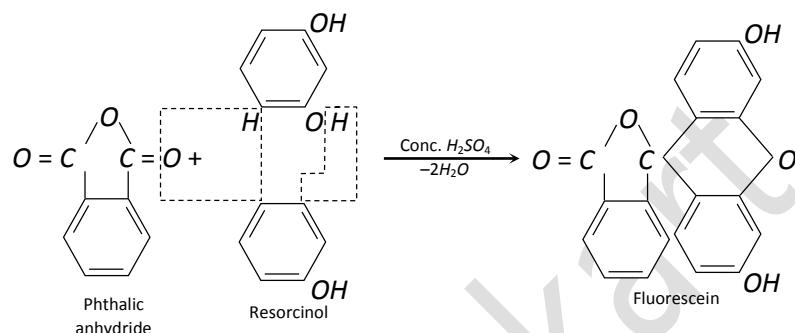
With bromine water, it gives a crystalline precipitate, 2, 4, 6-tribromoresorcinol.



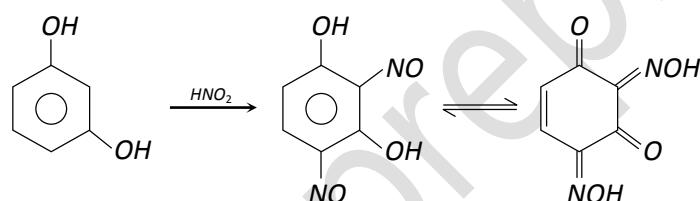
On nitration, it forms 2, 4, 6-trinitro-1, 3-dihydroxybenzene.



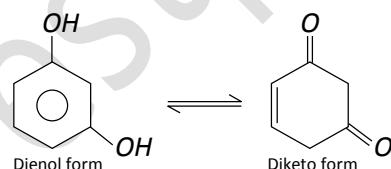
It condenses with phthalic anhydride and forms fluorescein.



With nitrous acid, it forms 2, 4-dinitrosoresorcinol



Resorcinol behaves as a tautomeric compound. This is shown by the fact that it forms a dioxime and a bisulphite derivative.



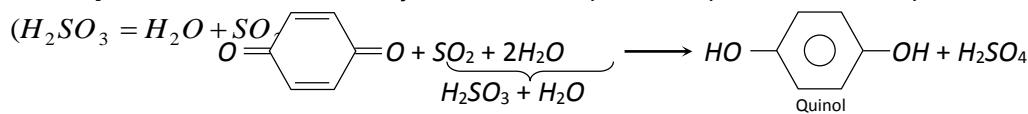
### (3) Uses

- (i) It is used as antiseptic and for making dyes.
- (ii) It is also used in the treatment of eczema. 2, 4, 6-trinitroresorcinol is used as an explosive.

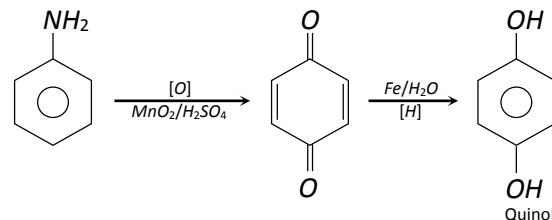
### Hydroquinone or quinol (1, 4-Dihydroxy benzene)



(1) **Preparation:** It is formed by reduction of p-benzoquinone with sulphurous acid

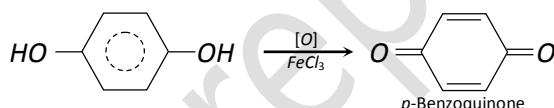


(p-Benzoquinone is obtained by oxidation of aniline)



(2) **Properties:** It is a colorless crystalline solid, m.pt. 170°C. it is soluble in water. It also shows tautomerism. It gives blue color with  $FeCl_3$  solution.

It acts as a powerful reducing agent as it is easily oxidised to p-benzoquinone. It reduces Tollen's reagent and Fehling's solution.

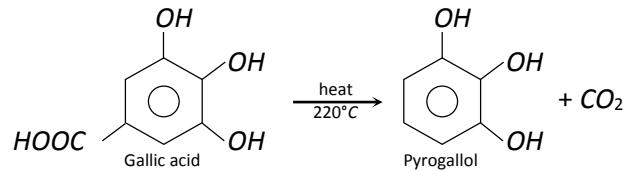


Due to this property, it is used as photographic developer.

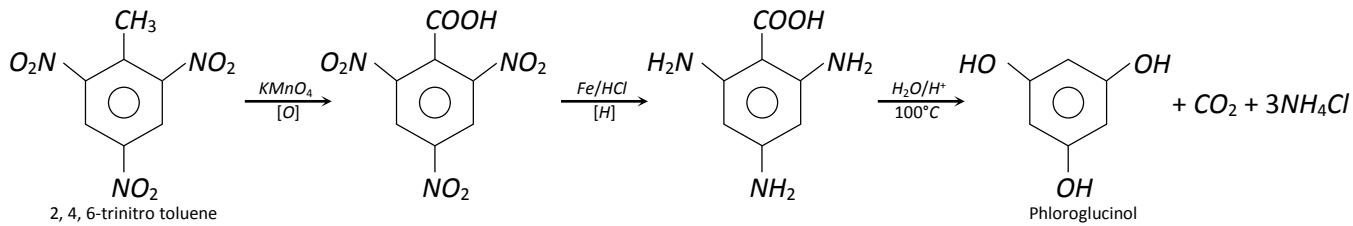
(3) **Uses:** It is used as an antiseptic, developer in photography, in the preparation of quinhydrone electrode and as an antioxidant.

**Trihydric Phenols:** Three trihydroxy isomeric derivatives of benzene are Pyrogallol (1, 2, 3), hydroxyquinol (1, 2, 4) and phloroglucinol (1, 3, 5).

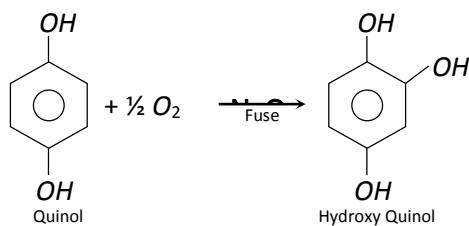
Pyrogallol is obtained by heating aqueous solution of gallic acid at 220°C.



Phloroglucinol is obtained from trinitrotoluene (TNT) by following sequence of reactions.



Hydroxyquinol is prepared by the alkaline fusion of hydroquinone in air.



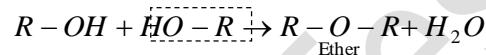
The three isomers are colorless crystalline compounds. All are soluble in water and their aqueous solutions give characteristic color with  $\text{FeCl}_3$ . For example, Pyrogallol-red; Hydroxy quinol-greenish brown; Phloroglucinol-bluish violet. Alkaline solutions absorb oxygen rapidly from air.

### Uses of pyrogallol

- (i) As a developer in photography.
- (ii) As a hair dye.
- (iii) In treatment of skin diseases like eczema.
- (iv) For absorbing unreacted oxygen in gas analysis.

## 8. Introduction of ether.

Ethers are anhydride of alcohols, they may be obtained by elimination of a water molecule from two alcohol molecules.



General formula is  $C_nH_{2n+2}O$

(1) **Classification:** It may be divided in two category.

(i) **Aliphatic ethers:** Both R of ether are alkyl group.

Example:  $CH_3-O-CH_3$ ,  $CH_3-\underset{\substack{| \\ \text{Dimethyl ether}}}{C}-O-CH_2-CH_2-CH_3$ .

$\begin{array}{c} H \\ | \\ CH_3-C-O-CH_2-CH_2-CH_3 \\ | \\ CH_3 \end{array}$ 
  
Isopropylpropylether

(ii) **Aromatic ethers:** In which either one or both R of ether are aryl groups.

Example:  $C_6H_5-O-CH_3$  or  $C_6H_5-O-C_6H_5$

$\begin{array}{c} C_6H_5-O-CH_3 \\ \text{Methyl phenylether} \end{array}$ 
  
 $\begin{array}{c} C_6H_5-O-C_6H_5 \\ \text{Diphenylether} \end{array}$

Aromatic ethers are divided in two category.

(a) Phenolic ethers: Ethers in which one of the group is aryl and other one is alkyl.



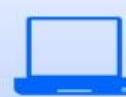
Preparation Classes



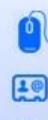
Counseling Sessions



Online Test



Free Trial Classes



[www.testprepkart.com](http://www.testprepkart.com)



[info@testprepkart.com](mailto:info@testprepkart.com)



+91 - 8800 1234 92

Example:  $C_6H_5 - O - CH_3$  .  
methyl phenylether

(b) Diaryl ether: In which both the groups are aryl group.

Example :  $C_6H_5 - O - C_6H_5$   
Diphenylether

### (iii) Symmetrical and unsymmetrical ethers,

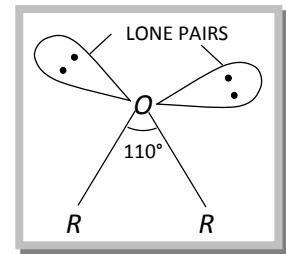
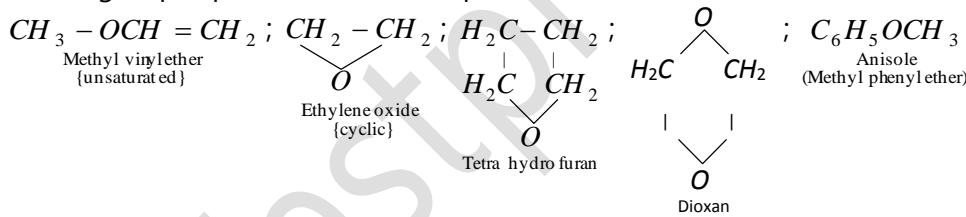
(a) An ether in which both the R are same known as symmetrical ethers.

Example:  $CH_3 - O - CH_3$  ,  $C_6H_5 - O - C_6H_5$  .  
Dimethyl ether Diphenylether

(b) An ether in which the both R are different called unsymmetrical ethers or mixed ethers.

Example:  $CH_3 - O - C_2H_5$  and  $CH_3 - O - C_6H_5$  .  
Ethyl methyl ether Methyl phenylether

(2) **Structure:** The oxygen atom in ether is  $sp^3$  hybridized. Two of the hybrid orbitals overlap with hybrid orbital (one each) of two carbon atoms to form sigma bonds  $\begin{array}{c} \sigma \\ | \\ C - O - C \end{array}$ . The bond angle is  $110^\circ$ . Besides the open chain saturated homologous series, there are numerous organic compounds in which – O – functional group is present. These compounds are also termed ethers.



(3) **Nomenclature:** There are two systems for naming ethers.

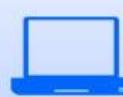
(i) **Common names:** When both the alkyl group are same, the prefix di- is used. In case of unsymmetrical ethers two alkyl groups are named in alphabetical order.

Example:  $CH_3OCH_3$  ,  $C_2H_5OC_3H_7$  .  
Di methyl ether Ethyl propylether

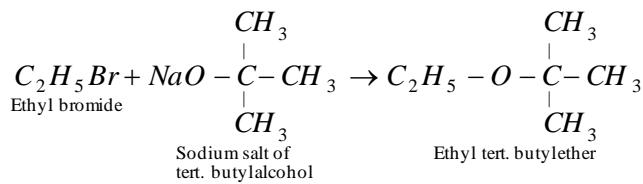
(ii) **IUPAC system:** Ethers are named as **alkoxy alkanes**.

(a) The ethernal oxygen is taken with smaller alkyl group.

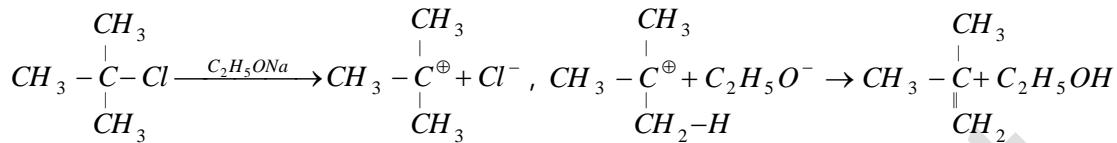
Example:  $CH_3O$  ;  $C_2H_5O$  .  
Methoxy Ethoxy group



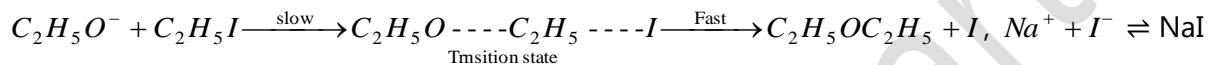




(d) Secondary and tertiary alkyl halides readily undergo  $E_2$  elimination in the presence of a strong base to form alkenes.

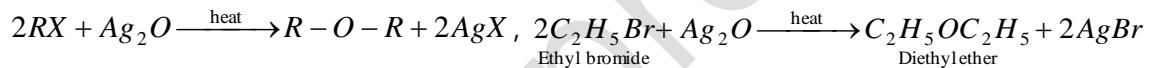


$SN^2$  mechanism:  $C_2H_5ONa \rightleftharpoons C_2H_5O^- + Na^+$ ,



Note: Aryl halide and sodium alkoxide cannot be used for preparing phenolic ethers because aryl halide are less reactive toward nucleophilic substitution reaction than alkyl halides.

(ii) By heating alkyl halide with dry silver oxide



## (2) From alcohols

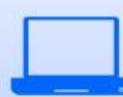
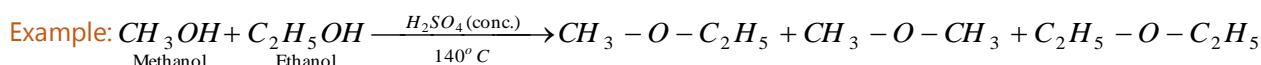
### (i) By dehydration of alcohols



Note: In this reaction alcohol must be present in excess.

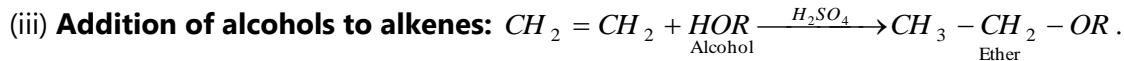
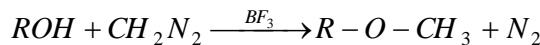
This reaction is mainly applicable for the dehydration of primary alcohols. Secondary and tertiary alcohols form alkenes mainly.

When this reaction is carried out between different alcohols then there is a mixture of different ethers is obtained.

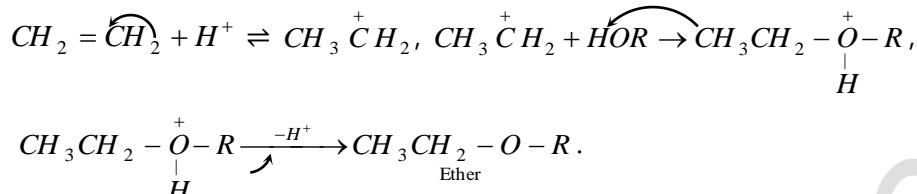




(ii) **By the action of diazomethane on alcohols:** This reaction is in presence of catalyst, boron trifluoride or  $\text{HBF}_4$ .

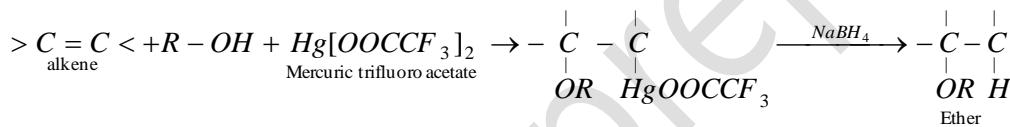


The intermediate is carbonium ion.



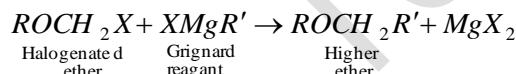
- (a) This method is very useful for preparing mixed ethers.
- (b) In higher cases, there can be 1, 2-hydride or 1, 2-methyl shift to form more stable carbonium ion.

### (3) Alkoxy mercuration-demercuration



Note: This is the best method for the preparation of t-ethers.

### (4) Reaction of lower halogenated ether with grignard reagent



- (i) Higher members can be prepared by the action of grignard reagent on lower halogenated ethers.
- (ii) Ether form soluble coordinated complexes with grignard reagent.



## 10. General properties of ethers.

### Physical properties

(1) **Physical state:** Methoxy methane and methoxy ethane are gases while other members are volatile liquid with pleasant smell.

(2) **Dipole moment (D.M.):** Bond angle of ether is due to  $sp^3$  hybridisation of oxygen atom. Since C – O bond is a polar bond, hence ether possess a net dipole moment, even if they are symmetrical.

D.M. of dimethyl ether is 1.3 D

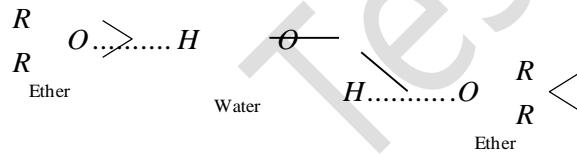
D.M. of di ethyl ether is 1.18 D

Note: The larger bond angle may be because of greater repulsive interaction between bulkier alkyl groups as compared to smaller H-atoms in water.

(3) **Boiling points:** Boiling points of ethers are much lower than those of isomeric alcohols, but closer to alkanes having comparable mass. This is due to the absence of hydrogen bonding in ethers.

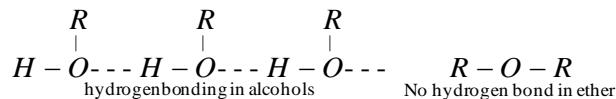
(4) **Solubility:** Solubilities of ethers in water are comparable with those of alcohols.

Example : Di ethyl ether and n-butyl alcohol have approximately the same solubility in water. This is because, ether form hydrogen bond with water much in the same way as alcohol do with water.



Note: Solubility of ether in water decreases with the size of alkyl groups.

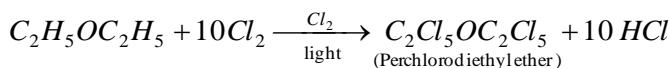
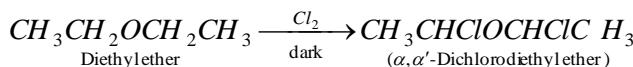
(5) **Hydrogen bonding:** There is no hydrogen directly attach (bonded) to oxygen in ethers, so ethers do not show any intermolecular hydrogen bonding.



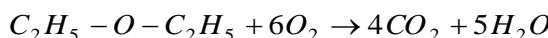
(6) **Density:** Ethers are lighter than water.

**Chemical properties:** Ethers are quite stable compounds. These are not easily attacked by alkalies, dilute mineral acids, active metals, reducing agents or oxidising agents under ordinary conditions.

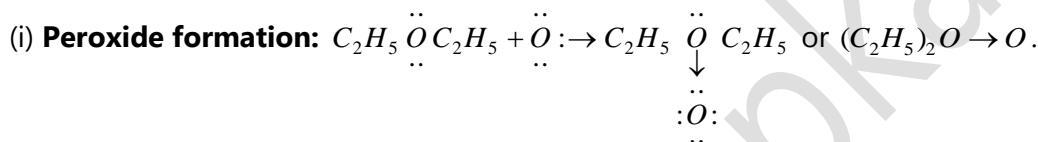
### (1) Reaction due to alkyl group



(ii) **Burning:** Ethers are highly inflammable. They burn like alkanes.



### (2) Reaction due to ethernal oxygen

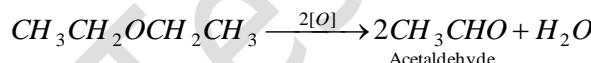


(a) The boiling point of peroxide is higher than that of ether. It is left as residue in the distillation of ether and may cause explosion. Therefore ether may never be evaporated to dryness.

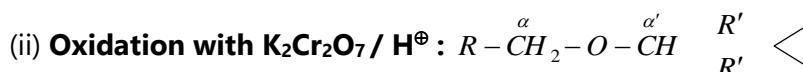
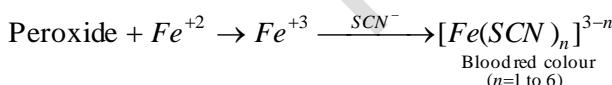
(b) Absolute ether can be prepared by distillation of ordinary ether from conc.  $\text{H}_2\text{SO}_4$  and subsequent storing over metallic sodium.

Note: Formation of peroxide can be prevented by adding small amount of  $\text{Cu}_2\text{O}$  to ether.

With strong oxidising agent like acid, dichromate ethers are oxidised to aldehydes.



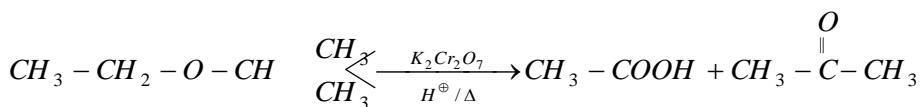
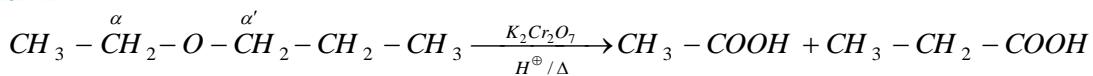
The presence of peroxide can be indicated by the formation of blood red colour complex in the following reaction.



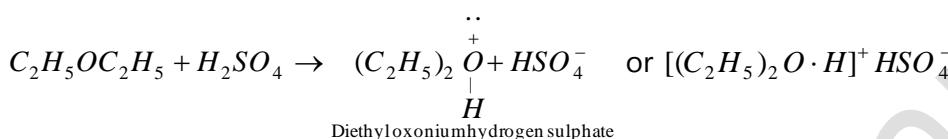
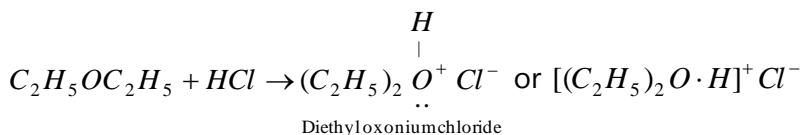
(a) Oxidation of ether can only be possible if any one of the alkyl groups of ether has hydrogen on  $\alpha$ -carbon.

(b)  $\alpha$ -carbon having two hydrogens converts in carboxylic group and  $\alpha$ -carbon having only one hydrogen converts into keto group.





(iii) **Salt formation:** Due to lone pair of electrons on oxygen atom. Ether behaves as Lewis base and form stable oxonium salt with strong inorganic acids at low temperature.



The oxonium salts are soluble in acid solution and ethers can be recovered from the oxonium salts by treatment with water.  $(C_2H_5)_2 \overset{H}{\underset{H}{O}} Cl \xrightarrow{H_2O} (C_2H_5)_2 O + HCl$

Oxonium salt

Note: The formation of oxonium salt is similar to the formation of ammonium salts from ammonia and acids.

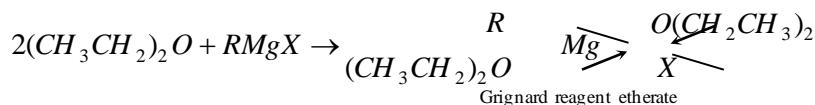
Ether is removed from alkyl halides by shaking with conc.  $H_2SO_4$ .

Ethers can be distinguished from alkanes with the help of this reaction.

(iv) **Reaction with Lewis acids:** Being Lewis bases, ethers form complexes with Lewis acids such as  $BF_3$ ,



Similarly, diethyl ether reacts with Grignard reagent forming Grignard reagent etherate.



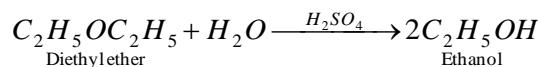
Due to the formation of the etherate, Grignard reagents dissolve in ether. That is why Grignard reagents are usually prepared in ethers. However, they cannot be prepared in benzene, because benzene has no lone pair of electrons and therefore, cannot form complexes with them.



### (3) Reaction involving cleavage of carbon-oxygen bond

### (i) Hydrolysis

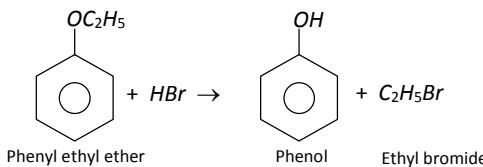
(a) With dil.  $H_2SO_4$  :  $ROR + H_2O \xrightarrow{H_2SO_4} 2ROH$



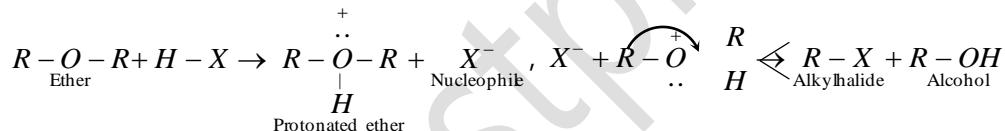
### (ii) Action of hydroiodic acid

(a) **With cold HI:**  $C_2H_5OC_2H_5 + HI \xrightarrow[\text{Diethyl ether}]{\text{Cold}} C_2H_5I + C_2H_5OH$

Note: Same reaction are observed with HBr and HCl. The order of reactivity of halogen acid  $\text{HI} > \text{HBr} > \text{HCl}$ .



## Mechanism of the reaction



- This can be explained on the basis of steric hinderence.
  - The above reaction is a  $SN'$  reaction.
  - The ether molecule gets protonated by the hydrogen of the acid to form protonated ether and the protonated ether undergoes nucleophilic attack by halide ion  $[X^-]$  and form alkyl alcohol and alkyl halide.

(b) **With hot HI:**  $R - O - R' + 2HI \xrightarrow{\text{heat}} RI + R'I + H_2O$

(iii) **Zeisel method:**  $RI + AgNO_3$  (alc.)  $\rightarrow AgI \downarrow + RNO_3$

Note: The silver iodide thus formed can be detected and estimated. This formed the basis of Zeisel method for the detection and estimation of alkoxy group in a compound.



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(iv) **Action of  $PCl_5$ :**  $R-O-R + PCl_5 \xrightarrow{\text{heat}} 2RCl + POCl_3$ . There is no reaction in cold.

(v) **Reaction with acetyl chloride:**  $CH_3COCl + C_2H_5\cdot O\cdot C_2H_5 \xrightarrow[\text{Diethyl ether}]{\text{heat}, ZnCl_2} CH_3COOC_2H_5$   
Acetyl chloride Ethyl acetate

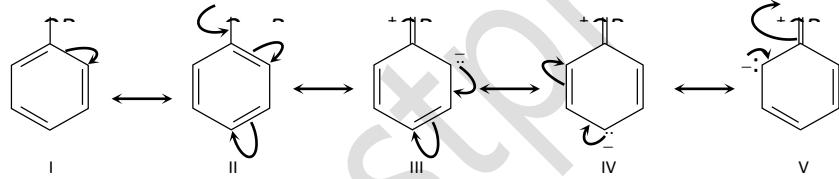
(vi) **Reaction with acid anhydride:**  $CH_3CO\cdot O\cdot OCC_2H_5 + C_2H_5\cdot O\cdot C_2H_5 \xrightarrow[\text{Diethyl ether}]{\text{heat}, ZnCl_2} 2CH_3COOC_2H_5$   
Acetic anhydride Ethyl acetate

(vii) **Dehydration:**  $C_2H_5OC_2H_5 \xrightarrow[300^\circ C]{Al_2O_3} 2CH_2 = CH_2 + H_2O$

(viii) **Reaction with carbon mono oxide:**  $C_2H_5OC_2H_5 + CO \xrightarrow[\text{Diethyl ether}]{BF_3 / 150^\circ C, 500 \text{ atm.}} C_2H_5COOC_2H_5$   
Ethyl propionate

(ix) **Action of bases:**  $Li^+ + CH_3^- + H - CH_2 - CH_2 - O - CH_2 - CH_3 \rightarrow CH_4 + CH_2 = CH_2 + Li^+ + O^- C_2H_5$

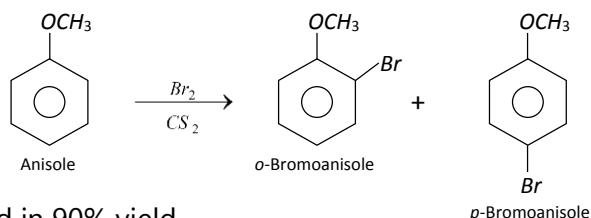
(4) **Ring substitution in aromatic ethers:** Alkoxy group is ortho and para directing and it directs the incoming groups to ortho and para position. It activates the aromatic ring towards electrophilic substitution reaction.



III, IV and V show high electron density at ortho and para position.

(i) **Halogenation:** Phenyl alkyl ethers undergo usual halogenation in benzene ring.

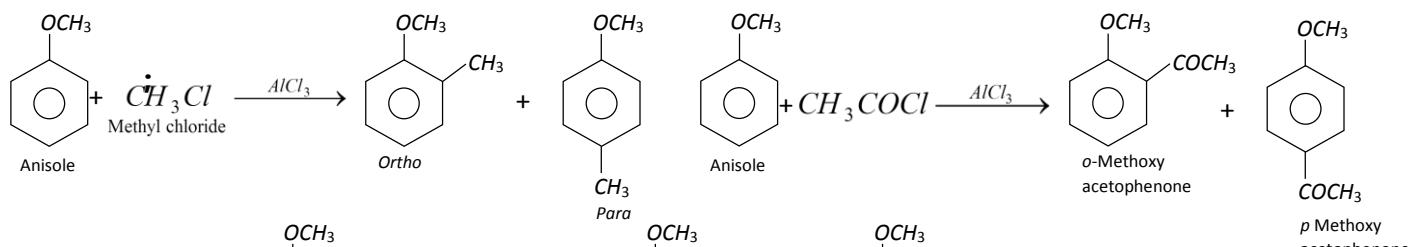
For example, Bromination of anisole gives ortho and para bromo derivative even in the absence of iron (III) bromide catalyst.



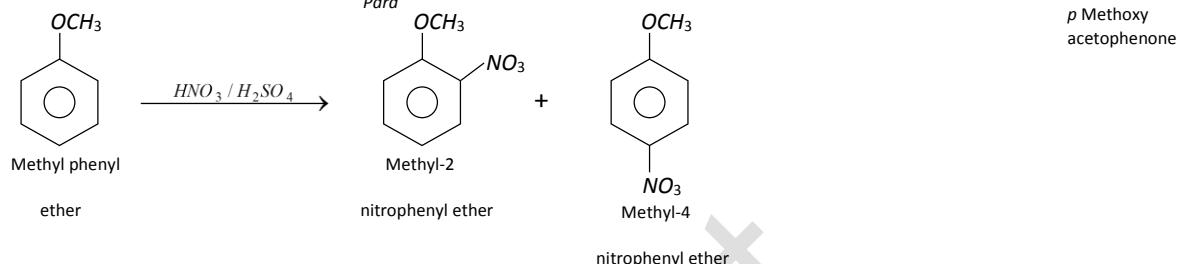
Para isomer is obtained in 90% yield.



**(ii) Friedel craft reaction**



**(iii) Nitration:**



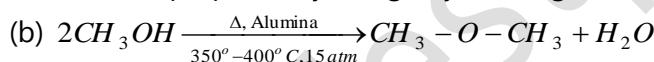
Note: Ethers are relatively less reactive than phenol towards electrophilic substitution reaction.

## 11. Some commercially important compounds of ethers.

**(1) Di methyl ether:** It is the simplest ether.

**(i) Preparation**

(a) It can be prepared by using any of the general method of preparation.



(c) It can be manufactured by dehydration of methyl alcohol with conc.  $H_2SO_4$  at  $140^\circ C$ .

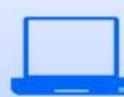
**(ii) Properties**

(a) It is colorless highly inflammable gas having B.P. of  $-24.8^\circ C$ .

(b) It is soluble in water, alcohols and other organic solvents and gives all the characteristic reactions of ethers.

**(iii) Uses**

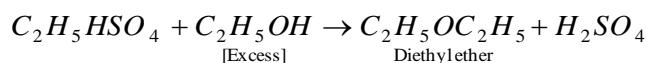
(a) It is used in the form of compressed liquid as a refrigerant, low temperature solvent and propellant for sprays.



- (b) It is used for storing food stuffs by freezing on direct contact because it does not leave any undesirable taste or smell.

(2) **Diethyl ether (Sulphuric ether):** It is the most important member of the ether series and is known as ether. It may also be regarded as an anhydride of  $C_2H_5OH$  (ethanol).

(i) **Preparation:** Laboratory method:  $C_2H_5OH + H_2SO_4 \xrightarrow{\text{heat}} C_2H_5HSO_4 + H_2O$



It is also known as Williamson's etheral continuous process.

### (ii) Properties

- (a) It is a colourless, highly volatile and inflammable liquid having boiling point  $34.5^\circ C$ .
- (b) It has a pleasant smell and burning taste.
- (c) It is only slightly soluble in water but readily soluble in organic solvents.
- (d) Di ethyl ether is itself a very good solvent even for fats and oils.
- (e) It produces unconsciousness when inhaled.

### (iii) Uses

- (a) It is used as a refrigerant.
- (b) It is used as a reaction medium in  $LiAlH_4$  reduction and grignard synthesis.
- (c) It is used as an extracting solvent in laboratory.
- (d) Mixture of alcohol and ether is used as petrol substitute under the trade name Natalite.
- (e) It is used in perfumery and in the manufacture of smokeless powder.

### (3) Di-isopropyl ether

(i) **Preparation:**  $2CH_3CH=CH_2 + H_2O \xrightarrow[75-125^\circ C]{3-7 \text{ atm}, H^+} (CH_3)_2CHOCH(CH_3)_2$

(ii) **Properties:** It is a colourless liquid with a pear like odour having B.P.  $68.5^\circ C$ .

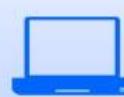
(iii) **Uses:** It is used for reducing knocking of petrol.

### (4) Divinyl ether

(i) **Preparation:**  $CH_2ClCH_2OCH_2ClCH_2 + 2KOH \xrightarrow{\Delta} CH_2=CHO-CH=CH_2 + 2KCl + H_2O$

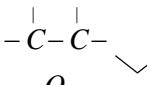
### (ii) Properties

- (a) It is highly inflammable liquid.



(b) It is colorless and boils at  $28.3^{\circ}C$ .

(iii) **Uses:** It is better anaesthetic than di ethyl ether because of its rapid action and rapid recovery from anaesthesia.

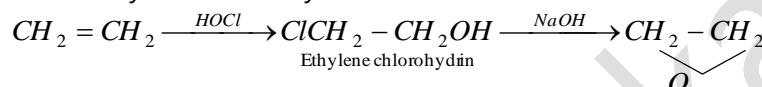
(5) **Epoxides [oxirane] or cyclic ether** - 

#### (i) Preparation

(a) By oxidation of ethylene with oxygen:  $2CH_2 = CH_2 + O_2 \xrightarrow[250^{\circ}C]{Ag} 2CH_2 - CH_2 - O - CH_2 -$

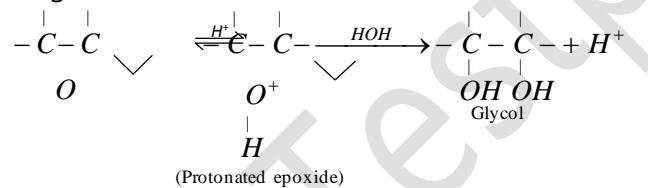
(b) By oxidation of ethylene with peroxy acids:  $RCH = CHR \xrightarrow[\text{or } CF_3CO_3H]{C_6H_5CO_3H} R - CH - CH - R - O -$

(c) By treatment of ethylene chlorohydrin with NaOH



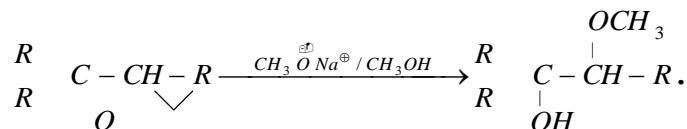
#### (ii) Properties

- (a) It is a poisonous, flammable gas.
- (b) Its B.P. is  $14^{\circ}C$ .
- (c) It is very reactive compound because of its strained configuration.
- (d) An epoxide is converted into protonated epoxide by acid which can undergo attack by any nucleophilic reagent.



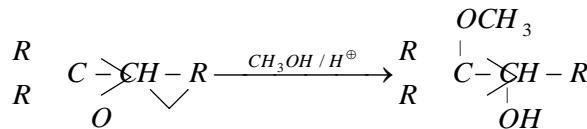
Some of the chemical reactions

(a) Case I: Base catalysed ring opening: In this case nucleophile attack on less hindered carbon of the oxirane ring and reaction is  $SN^2$  mechanism.

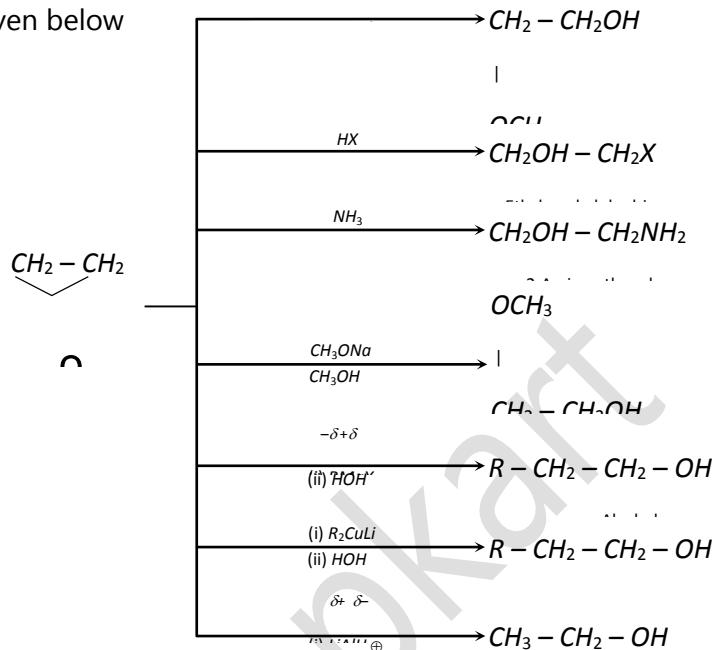


(b) Case II: Acid catalysed ring opening: Nucleophile attacks on carbon of oxirane ring which is highly substituted.  $SN^2$  Reaction is there.





Some reactions of oxirane are given below



## Uses

- (a) It is used in the manufacture of ethylene glycol.
  - (b) It is used in the manufacture of dacron.
  - (c) It is used in the manufacture of solvent ethoxy ethanol used in varnishes and enamels for quick drying.

(6) **Crown ethers:** The crown ethers are heterocyclic poly-ethers usually with at least four oxygen atoms. These are called crown ethers because they have crown like shape.

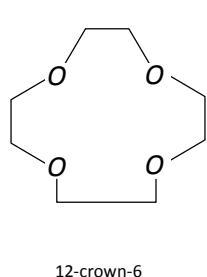
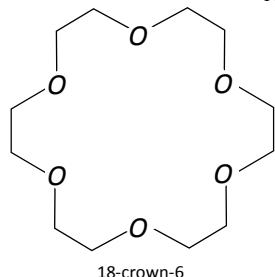
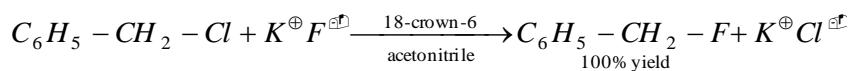
18-crown-6 means compound is eighteen member ring compound out of which  $[18 - 6 = 12]$  12 atoms are carbon [i.e. six ethylene group  $-CH_2 - CH_2 -$ ] and six atoms of oxygen.

Crown ethers have remarkable affinity for metal ions.

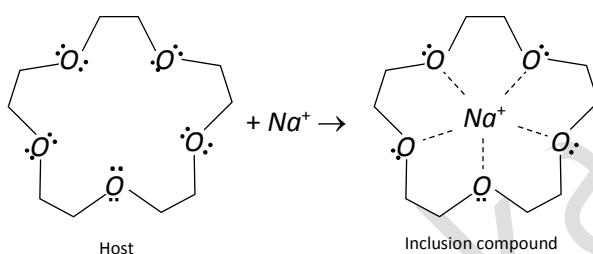
Example: 12-crown-4 has affinity with  $Li^+$  and 18-crown-6 has affinity with  $K^+$ .

Example:  $K^{\oplus} \text{CN} + R - CH_2 - X \xrightarrow[\text{benzene}]{\substack{18\text{-crown-6} \\ \text{100\% yield}}} R - CH_2 - CN + KX$





A crown ether binds certain metal ions depending on the size of the cavity.



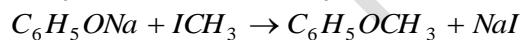
In this reaction, the crown ether is the 'host' and the species it binds is the 'guest'. The crown-guest complex is called an **inclusion compound**.

NNNNM1

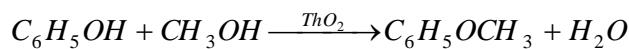
### (7) Anisole (Methyl phenyl ether) $C_6H_5OCH_3$ or (methoxy benzene)

#### (i) Preparation

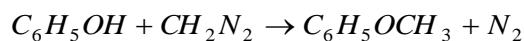
(a) By the action of methyl iodide on sodium phenoxide.



(b) By passing vapours of phenol and methyl alcohol over heated thoria.



(c) By methylation of phenol with diazomethane.



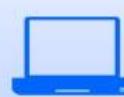
Preparation Classes



Counseling Sessions



Online Test



Free Trial Classes



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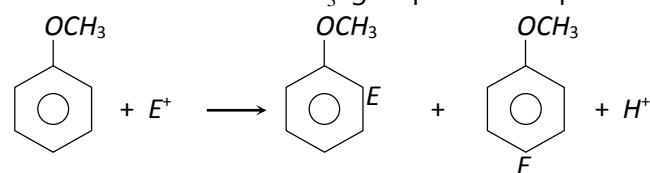


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(ii) **Properties:** It is a pleasant smelling liquid. It is used as a solvent in some organic reactions. Anisole undergoes electrophilic substitution reactions. –OCH<sub>3</sub> group is o- and p- directing.



Anisole is decomposed by conc. hydroiodic acid again into phenol.

