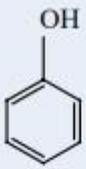
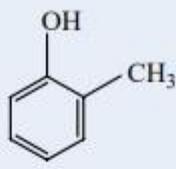
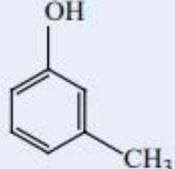
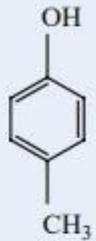
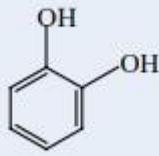
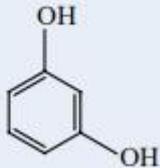
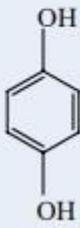
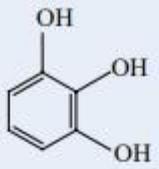
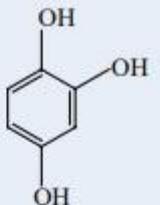
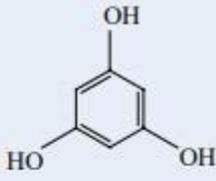
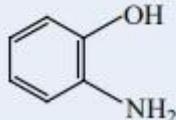
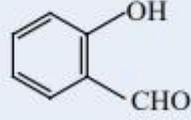
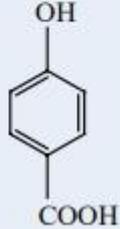
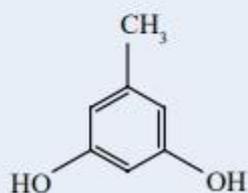


**B.Sc Semester – IV MJC – 6(T) Organic Chemistry**  
**Unit – I Alcohols, Phenols , Esters and Epoxides**

**Phenols: Classification , Nomenclature and Properties**

Phenols are organic compounds in which a -OH group is directly attached to a benzene ring. The carbon bearing the -OH group is  $sp^2$  hybridized.

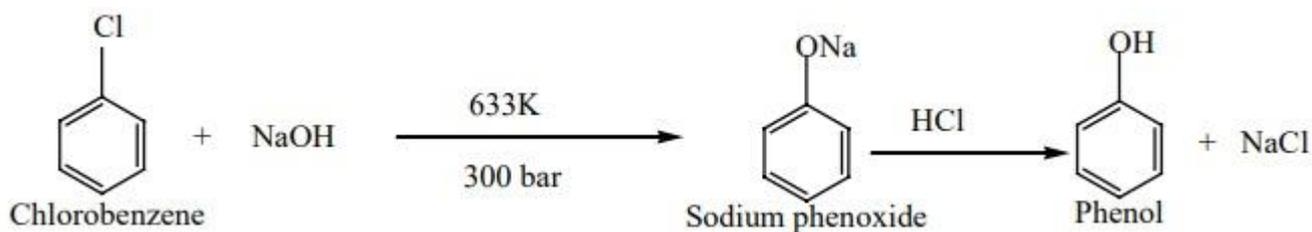
**Table: Classification of phenols**

<p align="center">Monohydric Phenol</p>	<p align="center">Monohydric phenols</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">             Common Name: Phenol            IUPAC Name: Phenol         </div> <div style="text-align: center;">             o -cresol            2-methylphenol         </div> <div style="text-align: center;">             m-cresol            3-methylphenol         </div> <div style="text-align: center;">             p-cresol            4-methylphenol         </div> </div>
<p align="center">Dihydric Phenol</p>	<p align="center">Dihydric phenols</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">             Common Name: Catechol            IUPAC Name: 1,2-dihydroxybenzene         </div> <div style="text-align: center;">             Resorcinol            1,3-dihydroxybenzene         </div> <div style="text-align: center;">             Quinol            1,4-dihydroxybenzene         </div> </div>
<p align="center">Trihydric Phenol</p>	<p align="center">Trihydric phenols</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">             Common Name: Pyrogallol            IUPAC Name: 1,2,3-trihydroxybenzene         </div> <div style="text-align: center;">             Hydroxyquinol            1,2,4-trihydroxybenzene         </div> <div style="text-align: center;">             Phloroglucinol            1,3,5-trihydroxybenzene         </div> </div>
<p align="center">Substituted phenol</p>	<p align="center">Substituted phenols</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">             o-amino phenol         </div> <div style="text-align: center;">             o-hydroxy Benzaldehyde         </div> <div style="text-align: center;">             p-hydroxy benzoic acid         </div> <div style="text-align: center;">             Orcinol(or)            3,5-Dihydroxy toluene         </div> </div>

## Preparation of Phenols

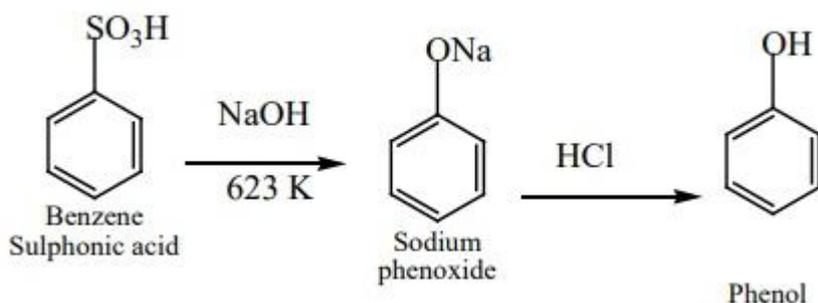
### a) From halo arenes(Dows process)

When Chlorobenzene is hydrolysed with 6-8% NaOH at 300 bar and 633K in a closed vessel, sodium phenoxide is formed which on treatment with dilute HCl gives phenol.



### b) From benzene sulphonic acid

Benzene is sulphonated with oleum and the benzene sulphonic acid so formed is heated with molten NaOH at 623K gives sodium phenoxide which on acidification gives phenol.



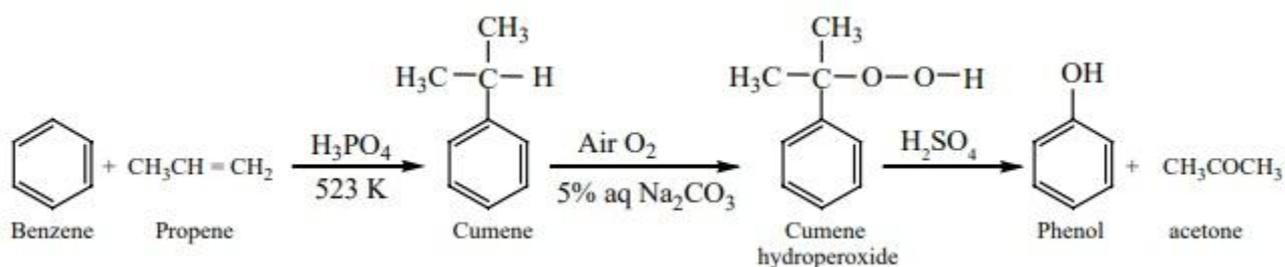
### c) From aniline

Aniline is diazotized with nitrous acid ( NaNO<sub>2</sub> +HCl ) at 273-278K to give benzene diazonium chloride which on further treatment with hot water in the presence of mineral acid gives phenol.



### d) From cumene

A mixture of benzene and propene is heated at 523K in a closed vessel in presence of H<sub>3</sub>PO<sub>4</sub> catalyst gives cumene (isopropylbenzene). On passing air to a mixture of cumene and 5% aqueous sodium carbonate solution, cumene hydro peroxide is formed by oxidation. It is treated with dilute acid to get phenol and acetone. Acetone is also an important byproduct in this reaction.



## Physical Properties

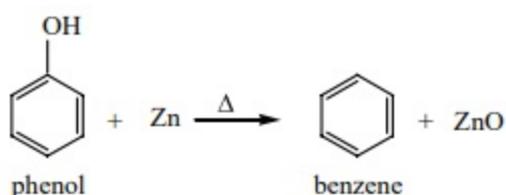
Phenol is colourless, needle shaped crystal, hygroscopic, corrosive and poisonous. It turns pink on exposure to air and light. The simplest phenols are liquids or low melting solids, they have quite high boiling points. Phenol is slightly soluble in water because of hydrogen bonding. However other substituted phenols are essentially insoluble in water.

## Chemical Properties:

Reactions involving -OH group.

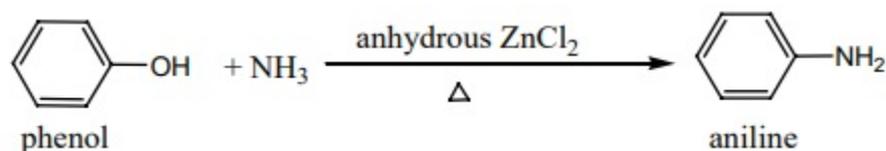
### a) Reaction with Zn dust:

Phenol is converted to benzene on heating with zinc dust. In this reaction the hydroxyl group which is attached to the aromatic ring is eliminated.



### b) Reaction with ammonia:

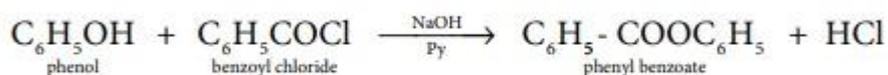
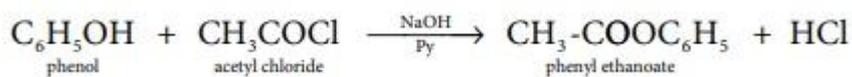
Phenol on heating with ammonia in presence of anhydrous  $\text{ZnCl}_2$  gives aniline.



### c) Formation of esters:

#### Schotten-Baumann reaction :

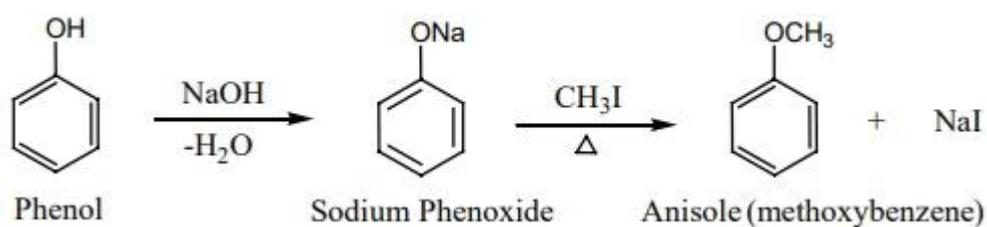
Phenol on treatment with acid chlorides gives esters. The acetylation and benzoylation of phenol are called Schotten-Baumann reaction.



#### d) Formation of ethers:

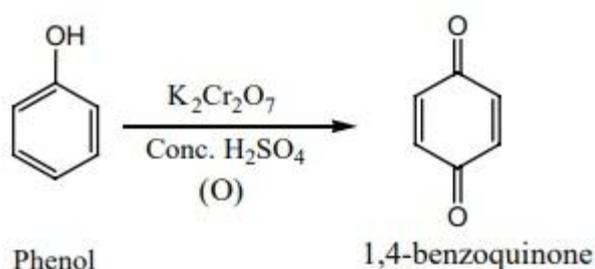
##### Williamson ether synthesis:

An alkaline solution of phenol reacts with alkyl halide to form phenyl ethers. The alkyl halide undergoes nucleophilic substitution by the phenoxide ion in the presence of alkali.



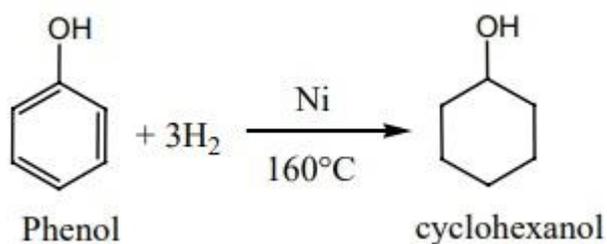
#### d) Oxidation:

Phenol undergoes oxidation with air or acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  with conc.  $\text{H}_2\text{SO}_4$  to form 1,4-benzoquinone.



#### e) Reduction:

Phenol on catalytic hydrogenation gives cyclohexanol.



## Reactions of benzene ring:

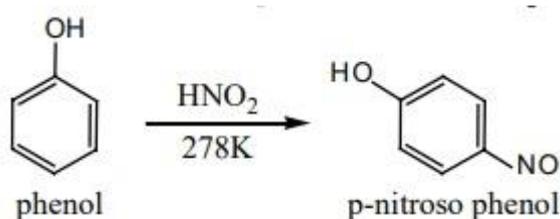
### Electrophilic aromatic substitution:

We have already learnt in XI standard that the groups like  $-\ddot{\text{O}}\text{H}$ ,  $-\ddot{\text{N}}\text{H}_2$ , etc., which when directly attached to the benzene ring, activate the ring towards electrophilic substitution reaction and direct the incoming electrophile to occupy either the ortho or para position.

Common electrophilic aromatic substitutions are as follows:

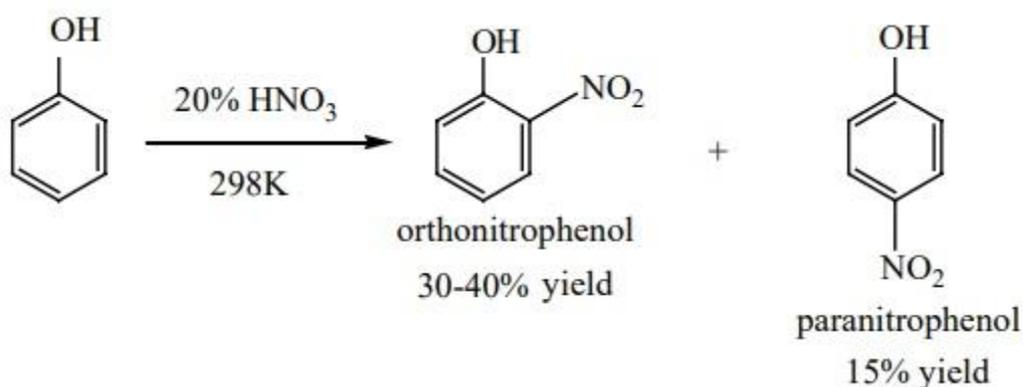
#### i) Nitrosation:

Phenol can be readily nitrosoated at low temperature with  $\text{HNO}_2$ .



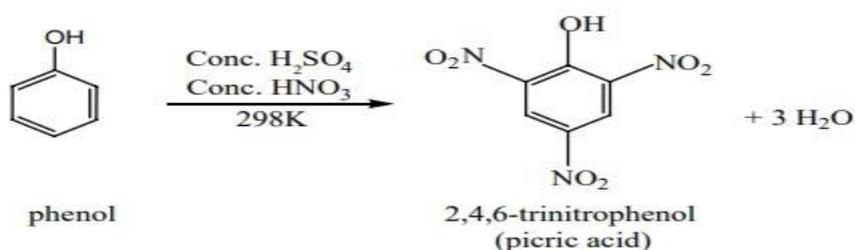
#### ii) Nitration:

Phenol can be nitrated using 20% nitric acid even at room temperature, a mixture of ortho and para nitro phenols are formed.



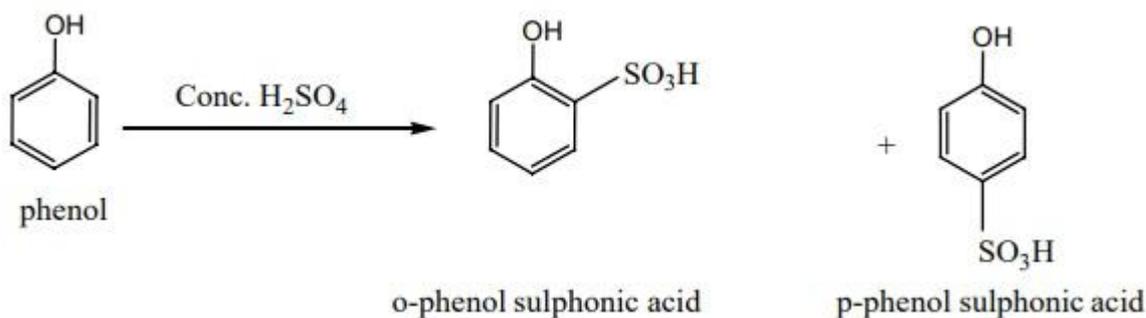
The ortho and para isomers are separated by steam distillation, as o-nitro phenol is slightly soluble in water and more volatile due to intra molecular hydrogen bonding, whereas p-nitro phenol is more soluble in water and less volatile due to intermolecular hydrogen bonding.

Nitration with Conc.  $\text{HNO}_3$  + con.  $\text{H}_2\text{SO}_4$  gives picric acid.



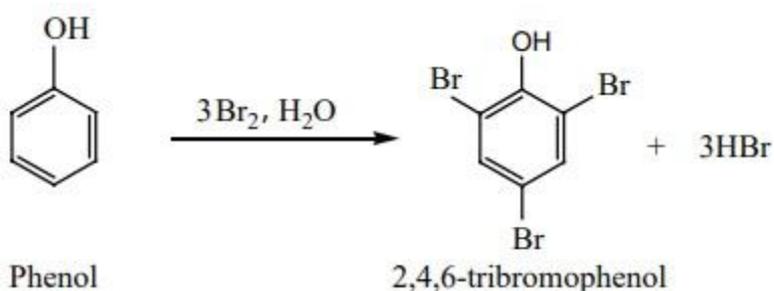
### iii) Sulphonation:

Phenol reacts with  $\text{con. H}_2\text{SO}_4$  at 280K to form o-phenol sulphonic acid as the major product. When the reaction is carried out at 373K the major product is p-phenol sulphonic acid.

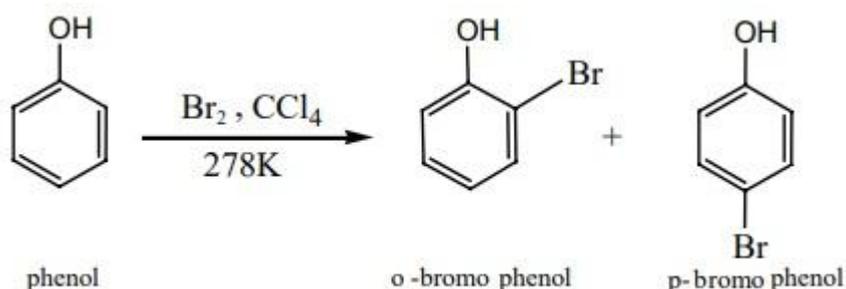


### iv) Halogenation:

Phenol reacts with bromine water to give a white precipitate of 2,4,6-tri bromo phenol.

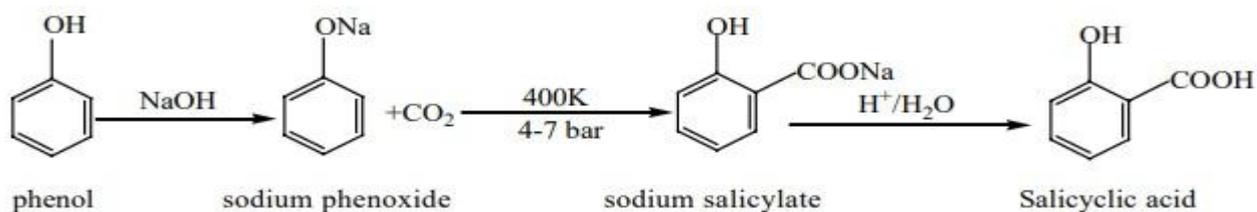


If the reaction is carried out in  $\text{CS}_2$  or  $\text{CCl}_4$  at 278K, a mixture of ortho and para bromo phenols are formed.



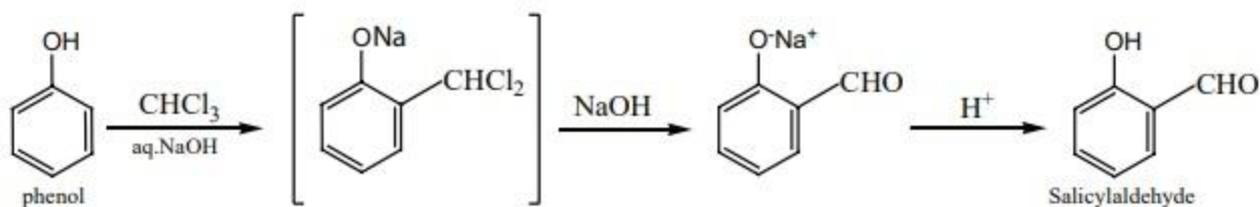
### v) Kolbe's (or) Kolbe's Schmit reaction:

In this reaction, phenol is first converted into sodium phenoxide which is more reactive than phenol towards electrophilic substitution reaction with  $\text{CO}_2$ . Treatment of sodium phenoxide with  $\text{CO}_2$  at 400K, 4-7 bar pressure followed by acid hydrolysis gives salicylic acid.



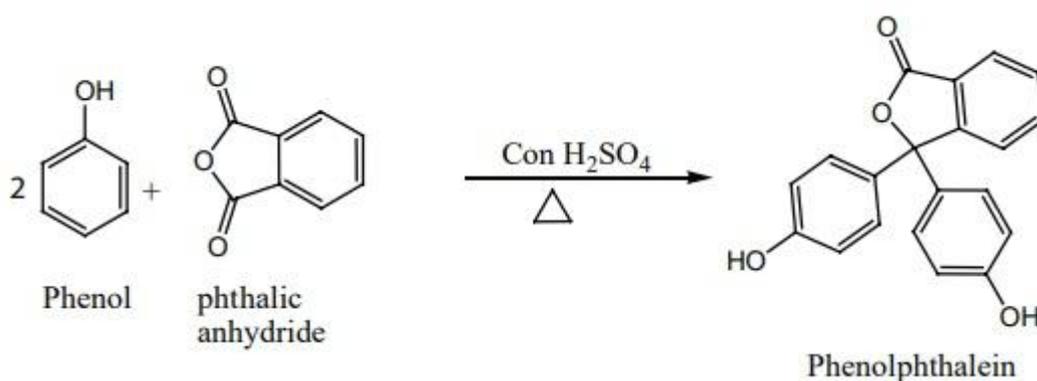
### vi) Riemer – Tiemann Reaction:

On treating phenol with  $\text{CHCl}_3/\text{NaOH}$ , a  $-\text{CHO}$  group is introduced at ortho position. This reaction proceeds through the formation of substituted benzal chloride intermediate.



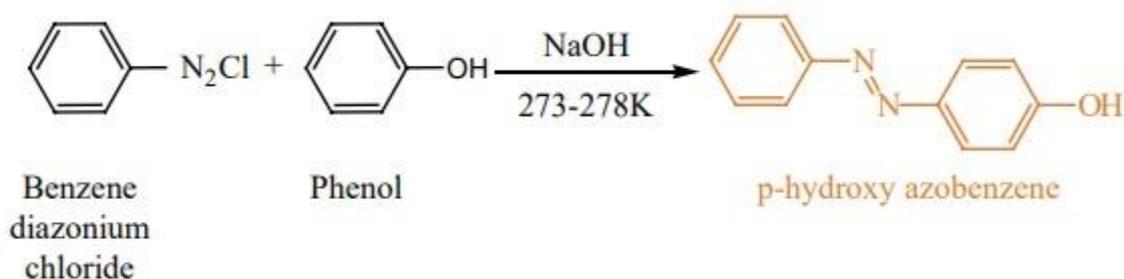
### vii) Phthalein reaction:

On heating phenol with phthalic anhydride in presence of  $\text{con. H}_2\text{SO}_4$ , phenolphthalein is obtained.



### viii) Coupling reaction:

Phenol couples with benzene diazonium chloride in an alkaline solution to form p-hydroxy azobenzene (a red orange dye).



## Test to differentiate alcohol and phenols

i) Phenol reacts with benzene diazonium chloride to form a red orange dye, but ethanol has no reaction with it.

ii) Phenol gives purple coloration with neutral ferric chloride solution, alcohols do not give such coloration with  $\text{FeCl}_3$ .

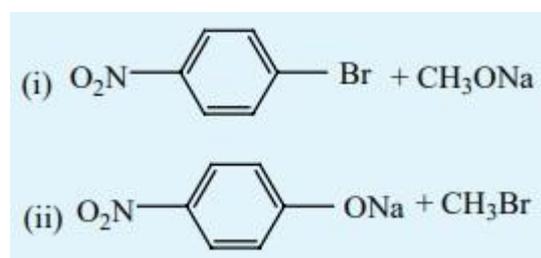
iii) Phenol reacts with  $\text{NaOH}$  to give sodium phenoxide. Ethyl alcohol does not react with  $\text{NaOH}$ .

## Uses of phenol

- 1) About half of world production of phenol is used for making phenol formaldehyde resin. (Bakelite).
- 2) Phenol is a starting material for the preparation of
  - i) drugs such as phenacetin, Salol, aspirin, etc.
  - ii) phenolphthalein indicator.
  - iii) explosive like picric acid.
- 3) It is used as an antiseptic-carbolic lotion and carbolic soaps.

### Evaluate Yourself

1. Which of the following set of reactants will give 1-methoxy-4-nitrobenzene.



2. what happens when m-cresol is treated with acidic solution of sodium dichromate?

3. when phenol is treated with propan-2-ol in the presence of HF, Friedel-Craft reaction takes place . Identify the products.