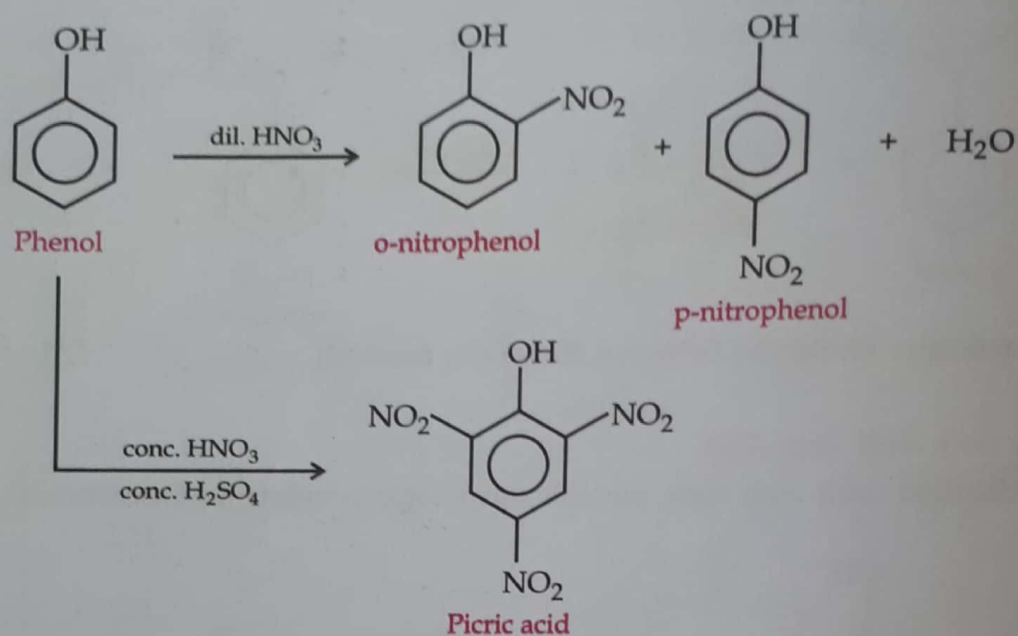


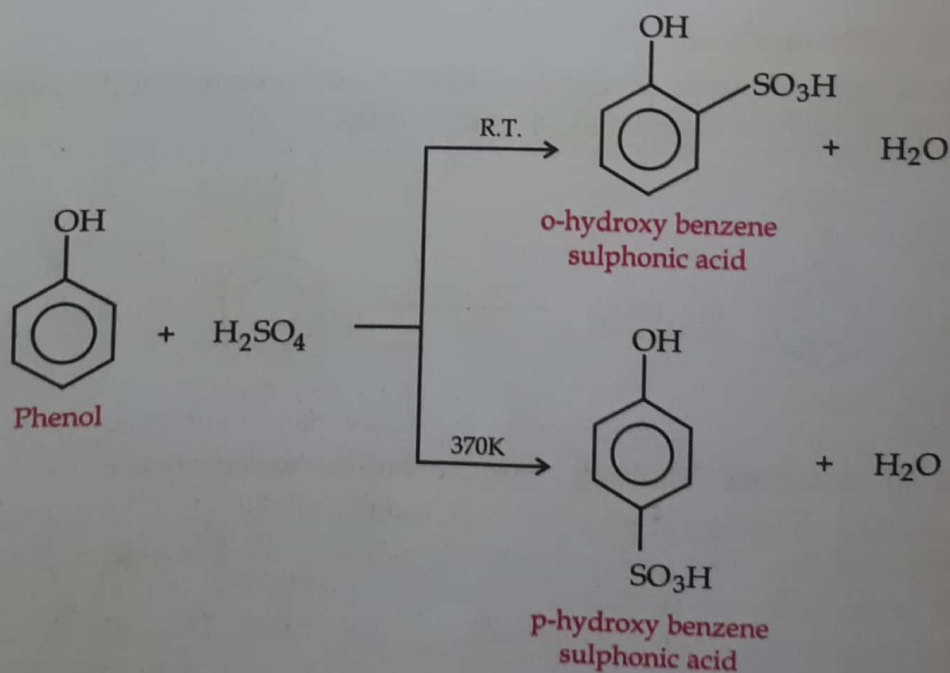
## **B. Reactions of Benzene Nucleus : Electrophilic substitution**

Due to presence of hydroxyl group ( $-OH$ ), further substitution in the benzene ring is very much facilitated. The  $-OH$  group powerfully activates the benzene ring to electrophilic substitution at ortho and para positions. In fact the  $-OH$  group is very powerful activator and unless precautions are taken polysubstitution takes place. Thus phenol undergoes following electrophilic substitution reactions readily as compared to benzene ring to form ortho and para derivatives.

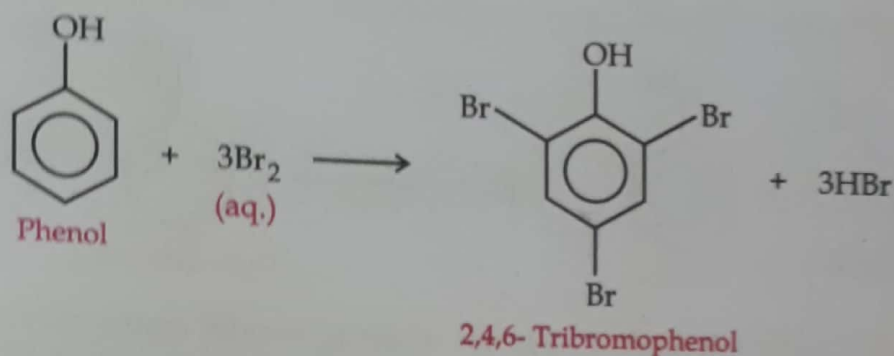
**(i) Nitration :** Phenol when react with dilute nitric acid it gives a mixture of ortho and para nitrophenol, whereas with conc. nitric acid, it forms 2, 4, 6-trinitro phenol (picric acid) but the yield of picric acid is poor due to oxidation of benzene ring by Nitric acid.



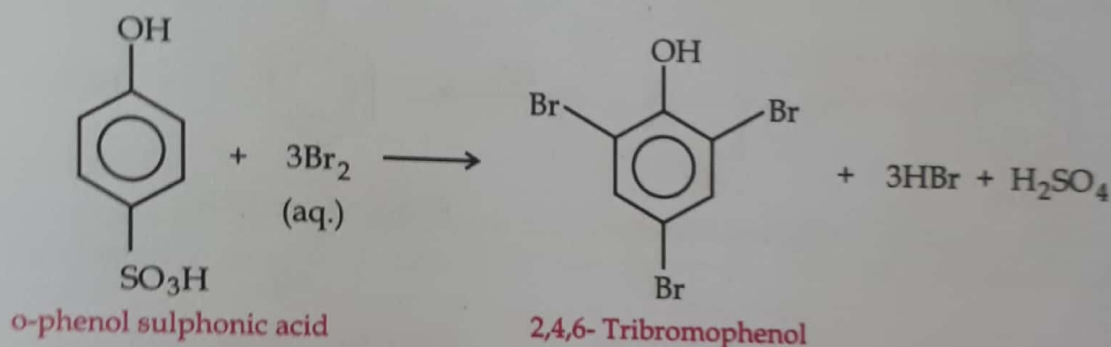
**(ii) Sulphonation :** Sulphonation of phenol occurs readily to yield either the ortho isomer or para isomer depending upon temperature. At low temperature ortho isomer formed while at high temperature (370K) para- isomer formed.



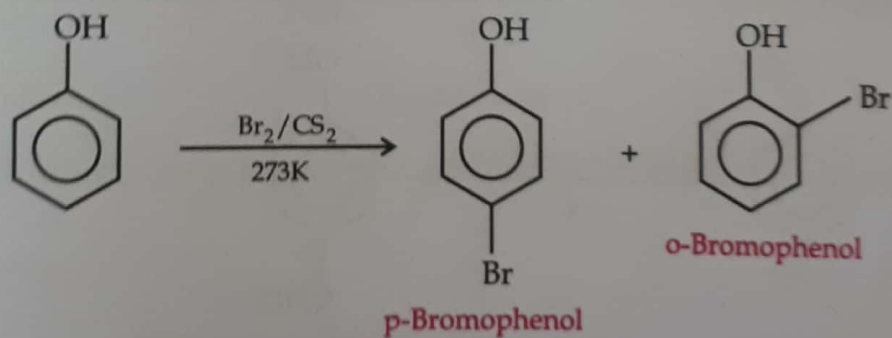
**(iii) Halogenation :** With aqueous solution of bromine phenol readily forms a tribromophenol.



Halogenation may even cause displacement of certain groups like SO<sub>3</sub>H, if present at ortho or para positions.

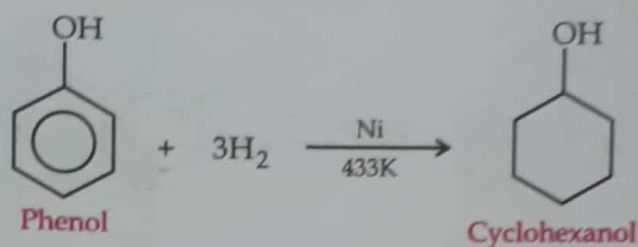


If halogenation is carried out in a solvent of low polarity such as chloroform, CCl<sub>4</sub> or CS<sub>2</sub> reaction can be limited to mono halogenation.

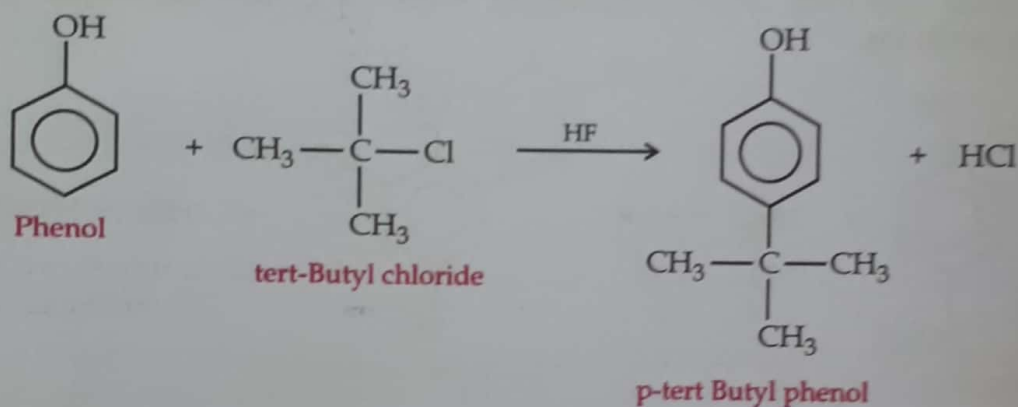


This can be explained by considering the ionization of phenol. In aqueous medium phenol ionizes to give phenoxide ion, which being more reactive than phenol results in the formation of a trisubstituted product. In the non-polar solvents, however, phenol is ionized to a small extent. The OH group in phenol is less electron releasing than the negatively charged oxygen in phenoxide ion. Unionised phenol is therefore less reactive than phenoxide ion towards electrophilic aromatic substitution. The higher proportion of phenol in a non-polar solvent thus result in only monosubstitution.

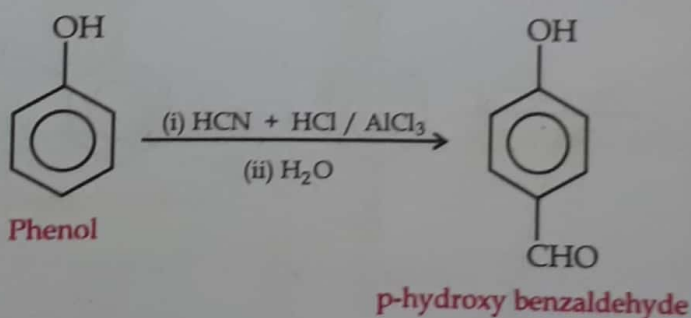
**(iv) Hydrogenation :** When phenol is reduced by hydrogen at 433K in the presence of finely divided nickel (catalyst) phenol forms cyclohexanol.



(v) **Friedel Craft's alkylation** : Phenol undergo Friedel craft's alkylation forming predominant para-isomers. This reaction is carried out in the presence of HF.

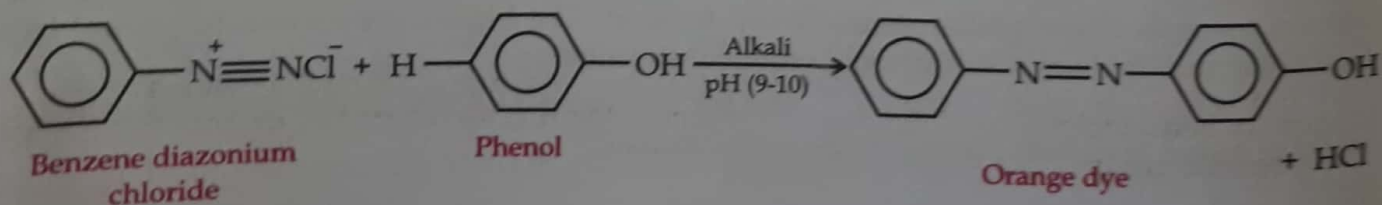


(vi) **Gattermann's synthesis** : Phenol when react with a mixture of hydrogen cyanide and hydrogen chloride in the presence of anhydrous  $\text{AlCl}_3$ , give phenolic aldehydes.

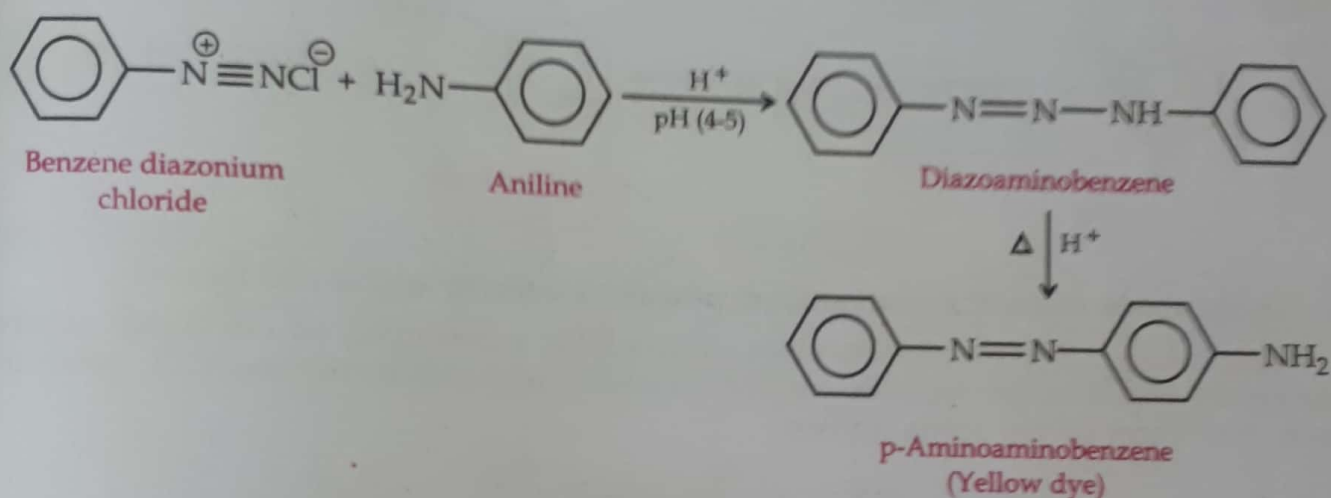


### (C) Special reactions of phenol

(i) **Diazo-coupling reaction** : Phenol couples with benzene diazonium chloride in mild alkaline solution forming an azo dye.

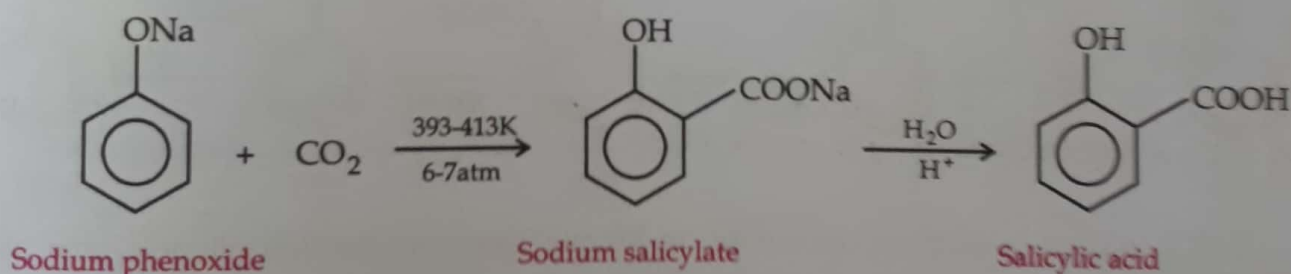


Aromatic amines also couple with benzene diazonium chloride in slightly acid medium (pH=4-5) to form an azo dye.



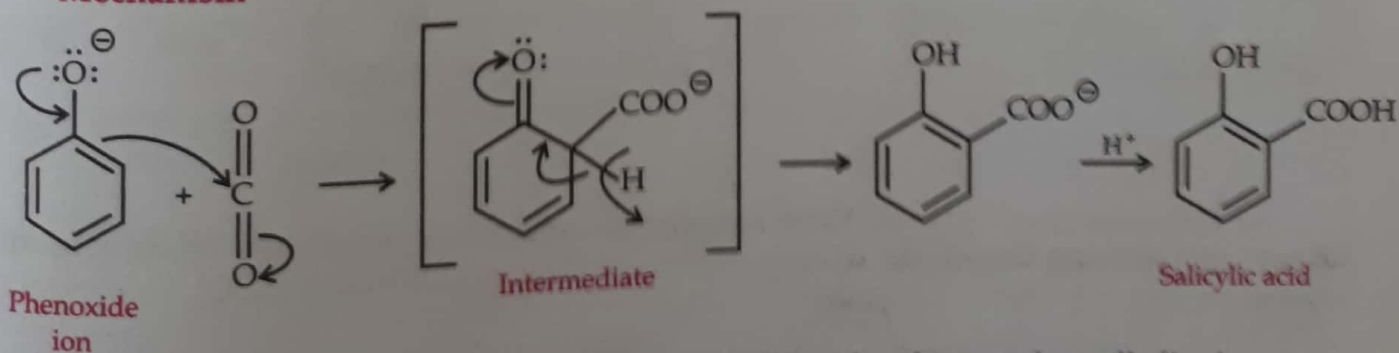
### (ii) Kolbe's reaction :- Carboxylation

When sodium salt of phenol is react with carbon dioxide at 393-413K under pressure (6-7 atm) sodium salicylate is produced. This on further treatment with HCl yields salicylic acid.

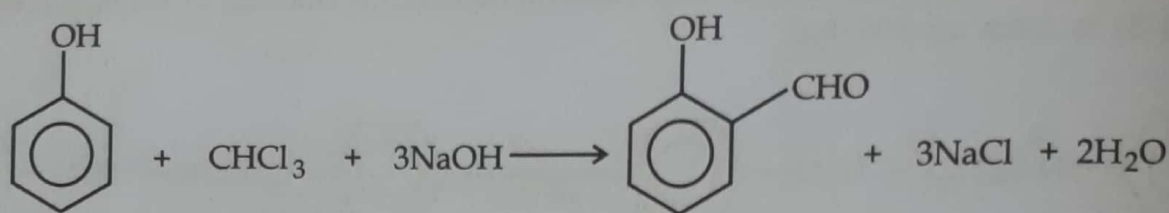


A small amount of p-isomer also obtained. If potassium salt is used, the O-isomer pre-dominates.

#### Mechanism



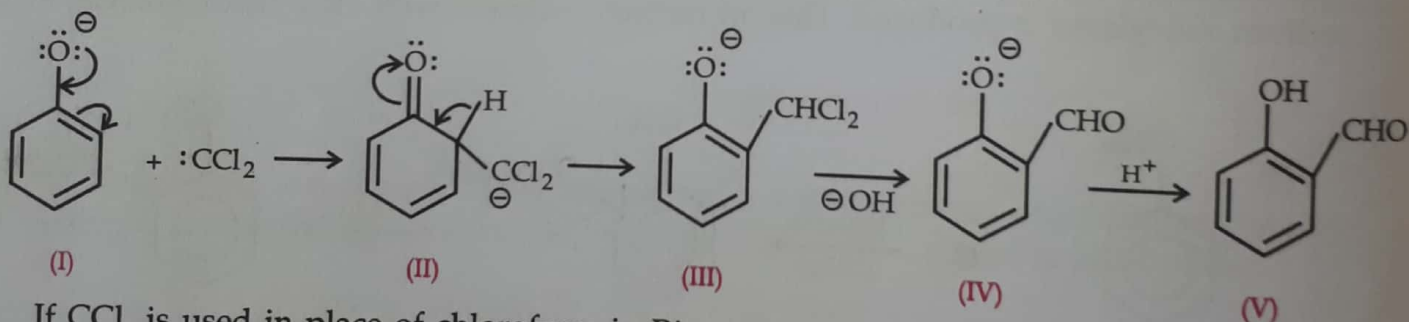
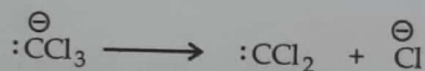
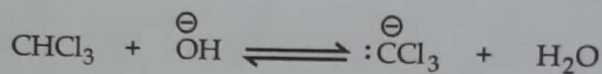
(iii) **Reimer-Tiemann reaction** : Phenols heated with chloroform and an alkali, gives o-hydroxy benzaldehyde an aldehyde group enters the ring in the ortho position with respect to phenolic group.



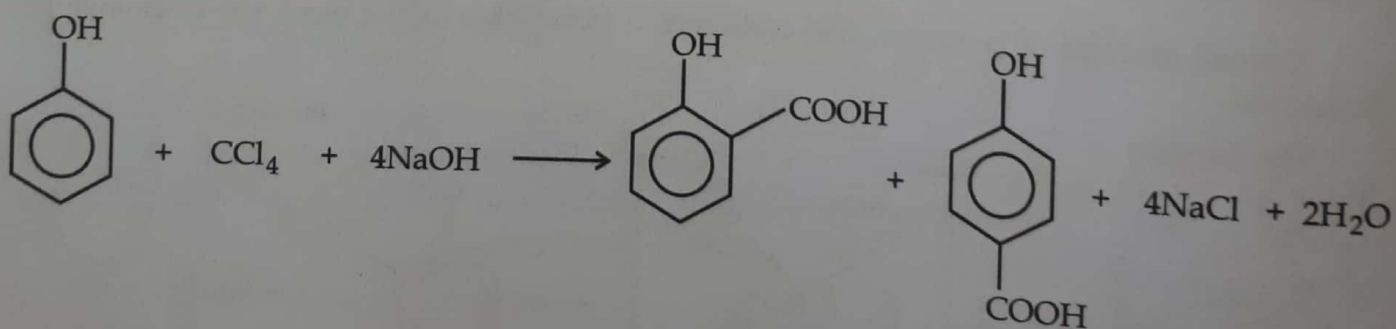
**Salicylaldehyde**  
(Main product)

In the above reaction a small amount p-hydroxy benzoic acid is also formed.

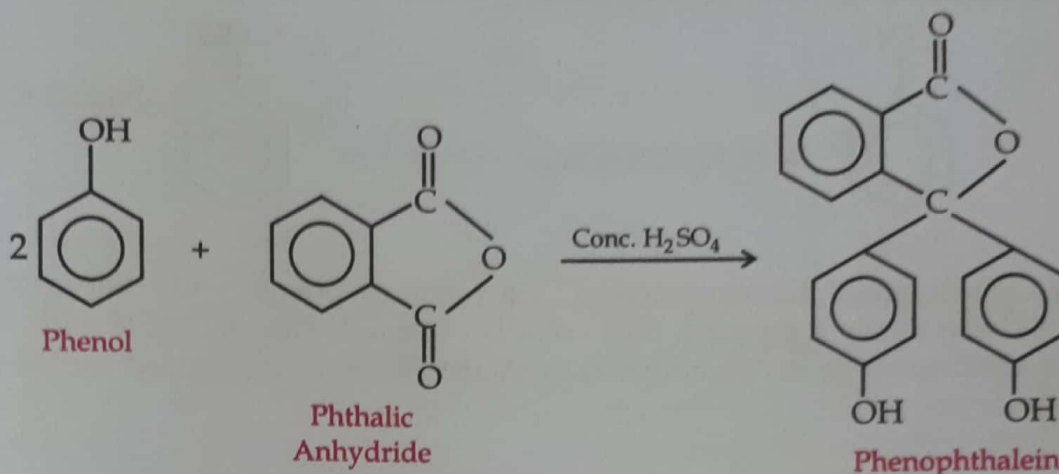
**Mechanism :** The reaction involves electrophilic substitution on the highly reactive phenoxide ring. The electrophilic reagent is carbene, dichloromethylene;  $\text{CCl}_2$  generated from chloroform by the action of base.



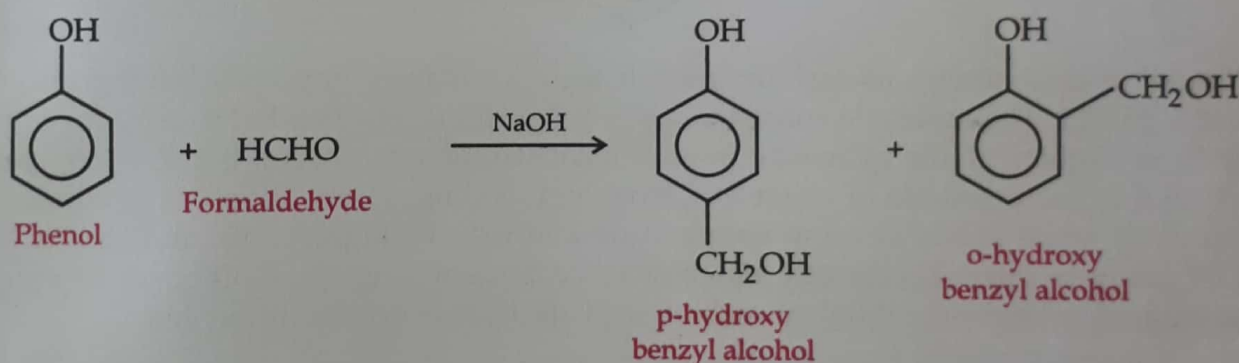
If  $\text{CCl}_4$  is used in place of chloroform in Reimer-Tiemann reaction phenols give rise to phenolic acid.



**(iv) Condensation with phthalic anhydride (phthalein reaction) :** When phenol is heated with phthalic anhydride in the presence of little concentrated  $\text{H}_2\text{SO}_4$ , condensation takes place forming phenolphthalein.



(v) **Condensation with Formaldehyde (Leaderer Manasse reaction)** : Phenol readily condenses with formaldehyde at low temperature and in the presence of dilute acid or alkali. The main product is p-hydroxy benzyl alcohol and a small amount of o-isomer.



Phenol and excess of HCHO slowly form a three-dimensional polymer in the presence of dilute NaOH and this is known as phenol formaldehyde resin (Bakelite).

(vi) **Nitrosation** : When phenol is heated with  $\text{NaNO}_3$  and  $\text{H}_2\text{SO}_4$  below 283K, nitroso group is introduced at the para position to the hydroxy group.

