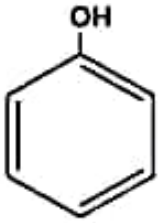
Phenol

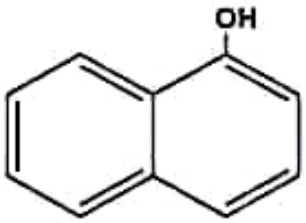
Phenols are hydroxy derivatives of aromatic hydrocarbons. In phenol hydroxy group (-OH) is directly attached to an aromatic ring. The general formula of phenol is;

Ar-OH

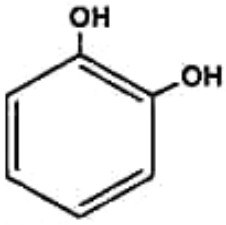
Where Ar- is aryl group. Phenols are classified as mono-, di- , and trihydric phenols according to the numbers of –OH groups attached to aromatic ring.



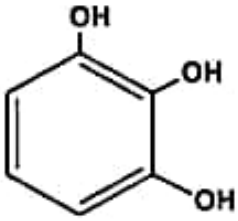
Hydroxy benzene (Phenol) Monohydric



Napthol Monohydric

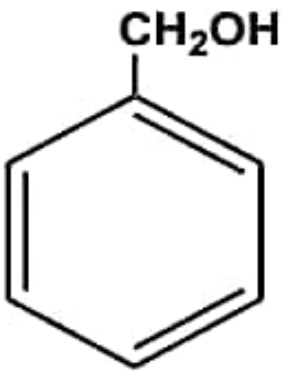


1,2-dihydroxy benzene (Catechol) Dihydric

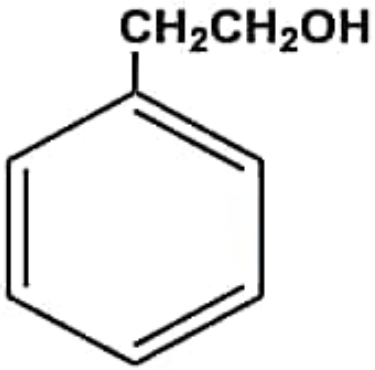


1,2,3-tridihydroxy benzene (Pyrogallol) Trihydric phenol

But The aromatic compound in which –OH is not directly attached to aromatic rings are not phenol, they are aromatic alcohols.



Phenylmethanol (Benzyl alcohol)



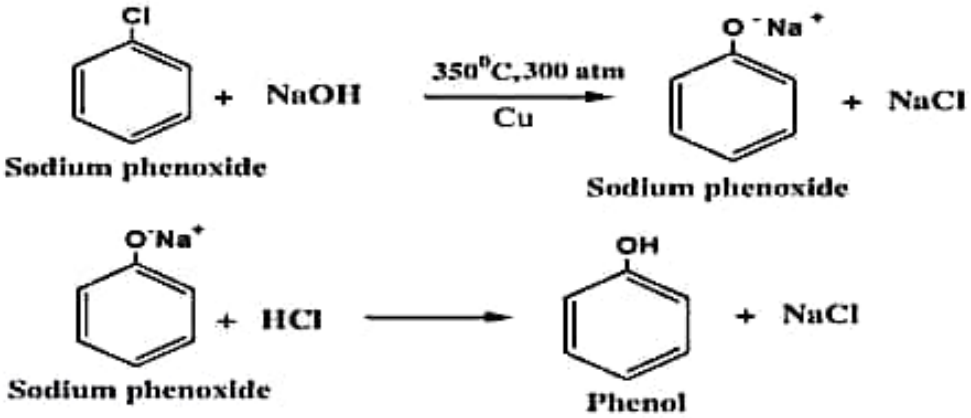
Phenylethanol

Preparation of Phenol

Phenol can be prepared by the following methods.

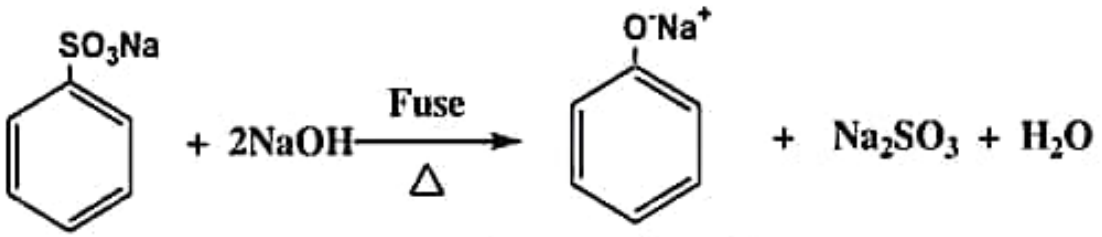
(i) From chlorobenzene (Dow's process)

Phenol is prepared in large scale by heating chlorobenzene with dil. NaOH solution at 350^0C under a pressure of 300 atm. In the presence of copper catalyst. Sodium phenoxide is formed which on acidification gives phenol.

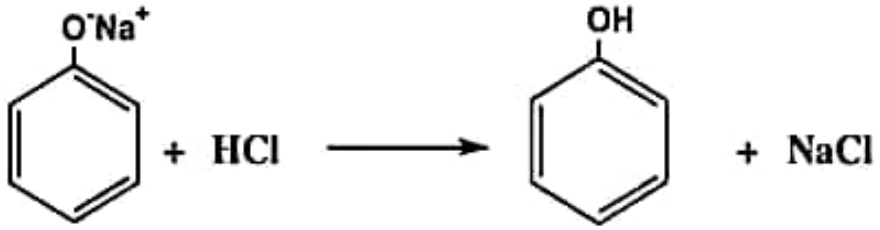


From benzene sulphonic acid

Sodium salt of sulphonic acid on fusion with sodium hydroxide at 300^0C gives sodium phenoxide which on acidification give Phenol.



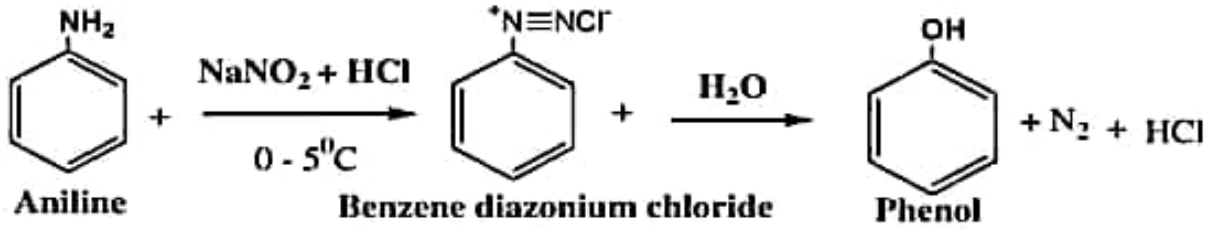
Sodium benzene sulphonate (Benzene sulphonic acid) **Sodium phenoxide**



Sodium phenoxide **Phenol**

From Diazonium salt: (Laboratory preparation)

Phenol is prepared in the laboratory by warming an aqueous solution of benzene diazonium chloride which is obtained by diazotization of aniline.

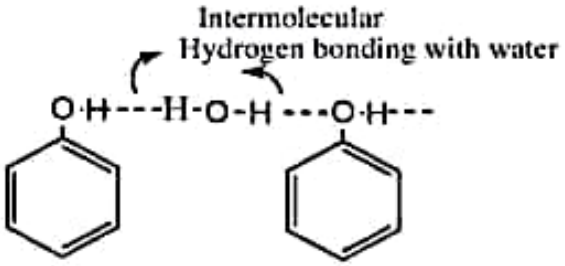


Properties of Phenol

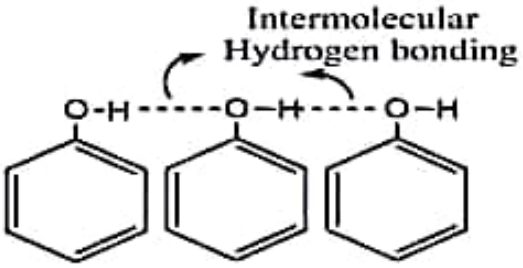
Physical properties of Phenol

1. Phenol is colorless crystalline solid and deliquescent . However, it turns into pink/reddish colour due to slow oxidation with air.
2. Its boiling point is 182^0C and melting point is 41^0C

3. It is slightly soluble in water forming reddish pink colour solution but it is easily soluble in organic solvents like alcohols and ether. The limited solubility is due to presence of polar –OH group (Hydrophilic) which forms hydrogen bond with water and the benzene ring remains hydrophobic (water repealing nature)



3. The boiling point of phenol is high it is because of the intermolecular hydrogen bondings between phenol molecules.



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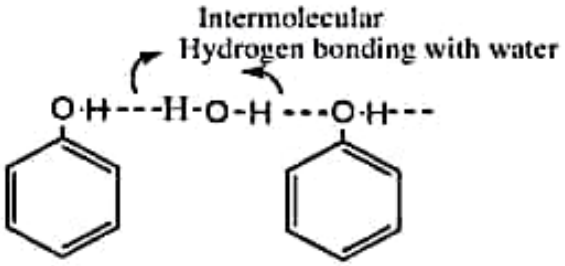

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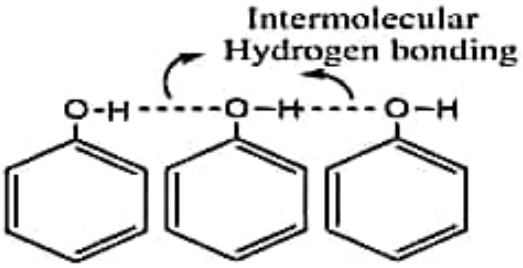


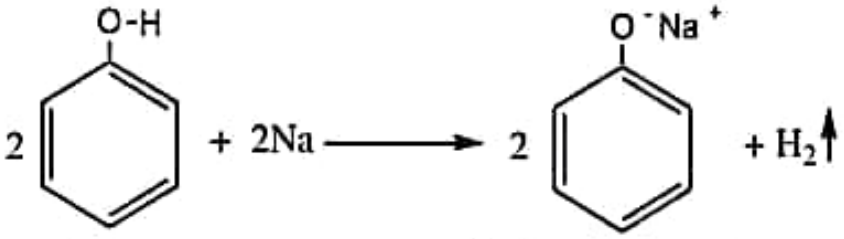
Chemical Properties:

Acidic Nature of Phenol:

Phenol is acidic in nature. It gives H_2 gas with active metals and neutralizes alkalies to give salt and water, and turns also blue litmus paper to red. **Although the phenol is stronger acid than alcohol and water but weaker than carboxylic acids**. They are unable to decompose carbonates or bicarbonates.

Reaction with metals:

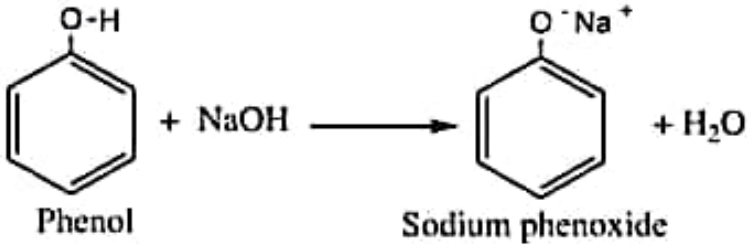
Phenol reacts with the alkali metals like sodium and potassium to form salt and hydrogen gas is liberated.



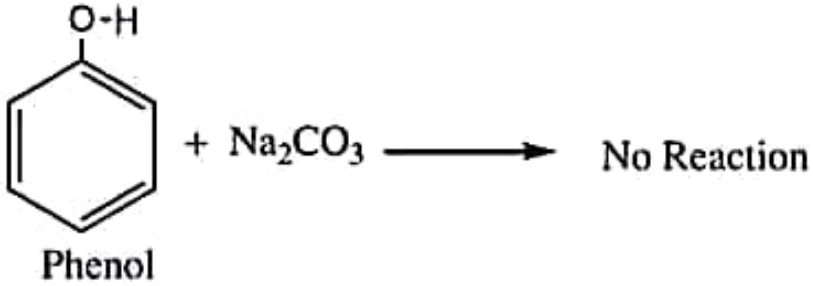
Phenol Sodium phenoxide

(2) **Reaction with alkalies**

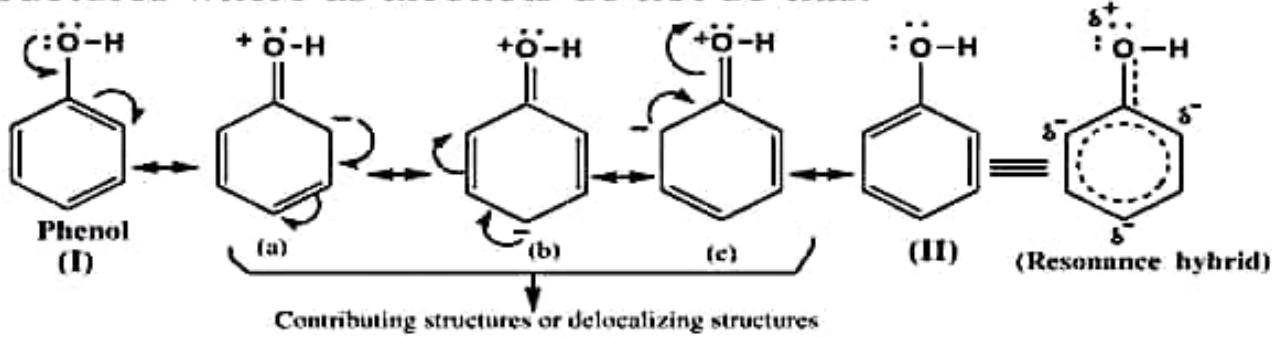
Phenol reacts with alkalies like sodium or potassium hydroxide to form salt and water.



(3) Phenol does not react with sodium carbonates and bicarbonates.

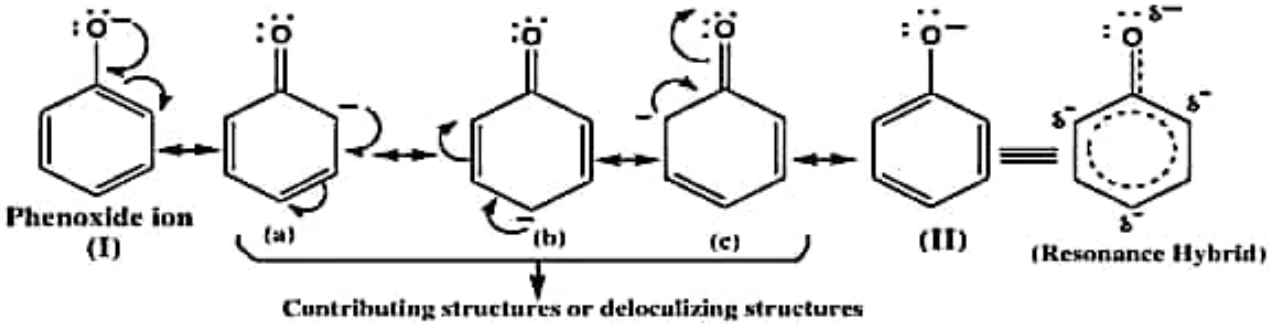


Phenol exist as resonance hybrid of following contributing structures where as alcohols do not do this.



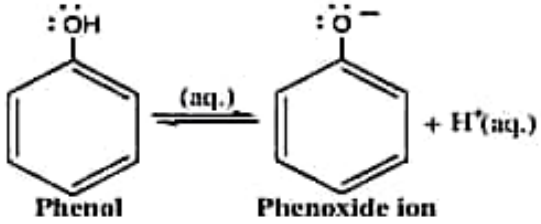
Resonance in Phenol

During the resonance in phenol, the oxygen atom acquires a partial negative positive charge. It weakens the O-H bond and release of proton becomes easier.

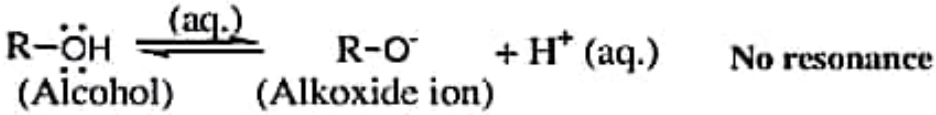


Resonance in Phenoxide ion

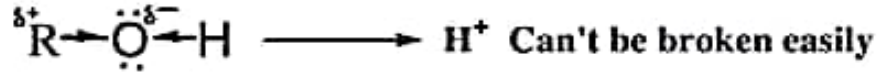
From the above resonance, phenoxide ion is more stabilized by resonance than phenol, there is no charge separation in contributing structures. During the ionization of phenol, equilibrium is very much in favours of phenoxide ion(forward reaction favoured), and concentration of H^+ increases in aq. Solution which increases the acidic strength of phenol and becomes more acidic than alcohols.

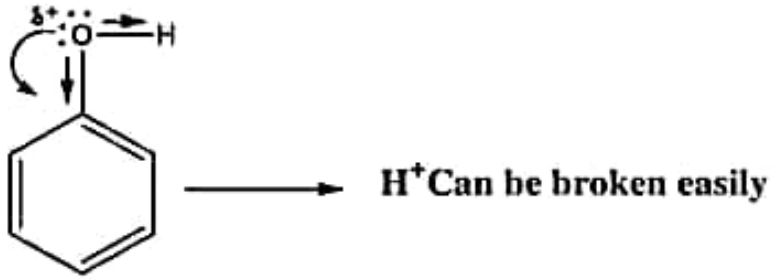


On the other hand, in case of alcohols neither alcohols nor alkoxide ions are stabilized by resonance and they behaves as weaker acids than phenol.



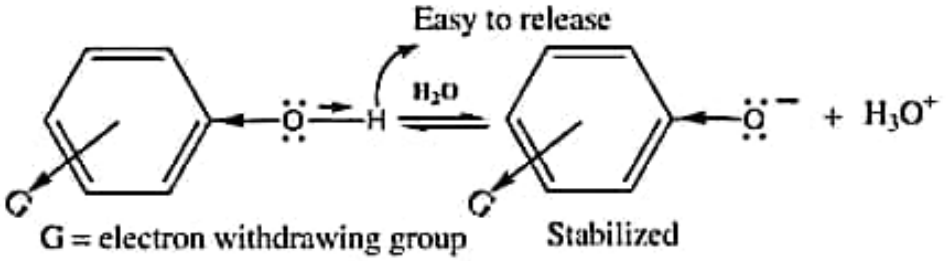
Due to the positive inductive effect of alkyl group in alcohol, electron density increases around oxygen and hydrogen is more strongly attached to oxygen and can't be released in aqueous solution. But in phenol oxygen becomes fractional positive charge due to resonance and electron density around oxygen decreases and bond between oxygen and hydrogen becomes weaken and H^+ can be broken easily and concentration of protons H^+ in aqueous solution increases and acidic strength increases. So due to above evidences, phenols are more acidic than alcohols.



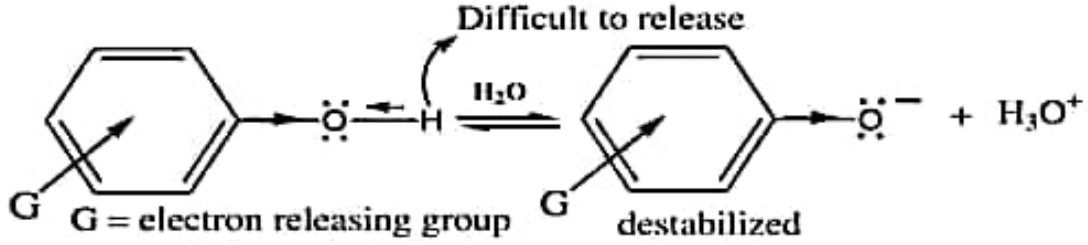


Effect of substituent on the acidic strength of phenol.

The acidic strength of the phenol is effected considerably by the presence of the substituent in the ring. In general, The electron withdrawing group (i.e. $-NO_2$,-CHO, -X etc) increases the acidic strength by stabilizing the phenoxide ion by the dispersal of –ve charge.



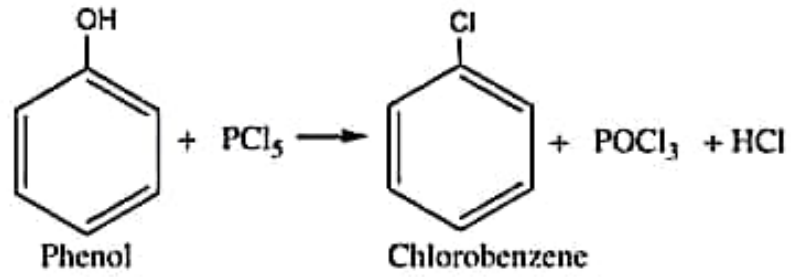
The electron releasing group (i.e. $-R$,-NH_2, -OH etc) decreases the acidic strength by destabilizing the phenoxide ion by intensifying the –ve charge.



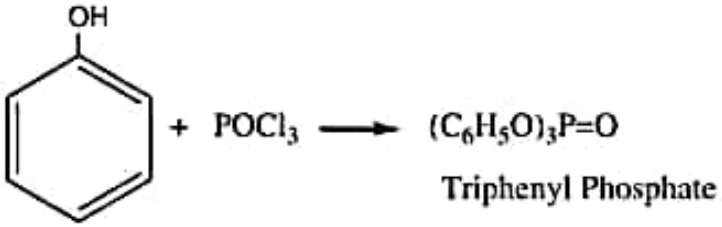
2. Reaction with phosphorous halides

❖ With phosphorous pentachloride:

When phenol is treated with PCl_5, it gives little amount of chlorobenzene because the major product triphenyl phosphate is produced by the reaction between byproduct $POCl_3$ and phenol.



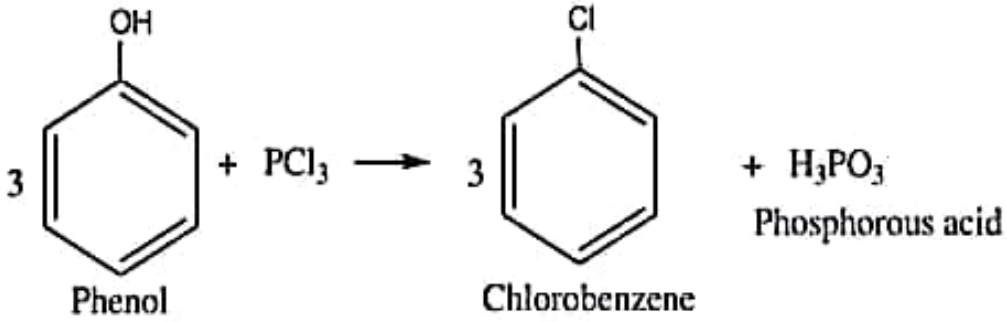
Phenol Chlorobenzene



Triphenyl Phosphate

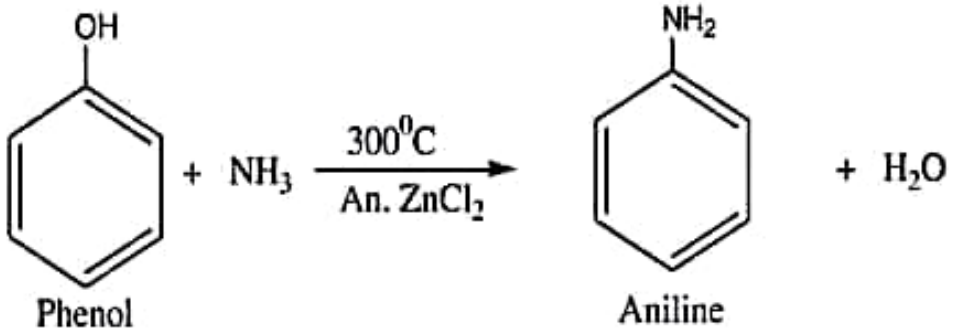
Phenol

❖ **Reaction with PCl_3**



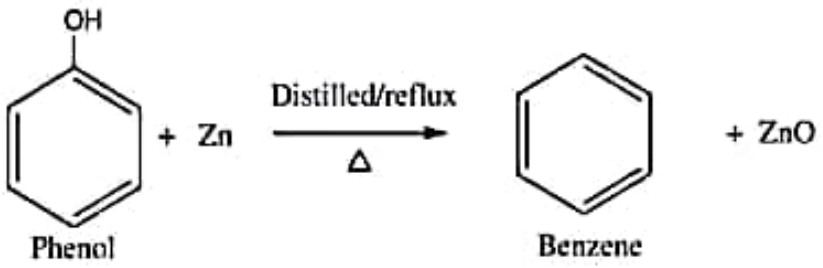
3. Reaction with ammonia:

Phenol reacts with ammonia at 300^0C in the presence of anhydrous $ZnCl_2$ to give aniline.



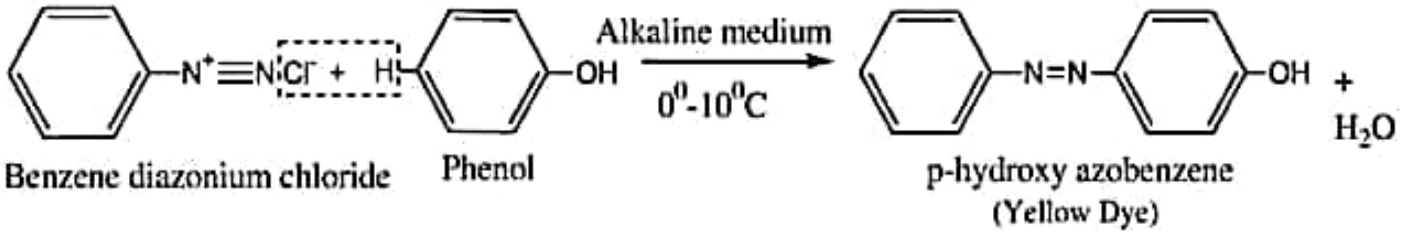
4. Reaction with Zinc dust :

When phenol is refluxed or distilled with zinc dust, it is reduced to benzene.



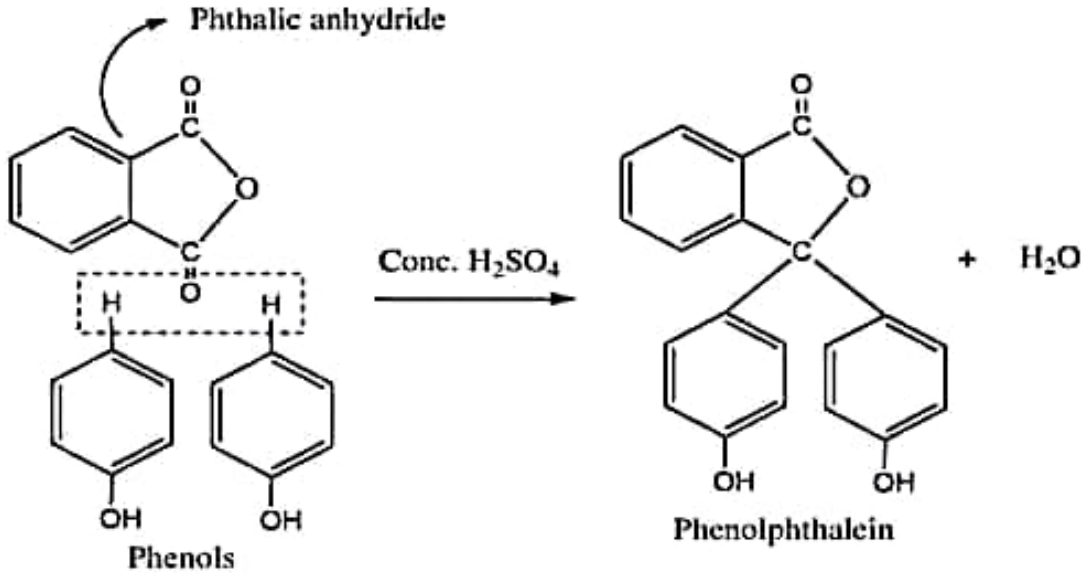
5. Reaction with benzene diazonium chloride:(Lab.Test)

When phenol is condensed with benzene diazonium chloride in slightly alkaline medium, it gives a dye or colored compound called azodye, This reaction is called coupling reaction



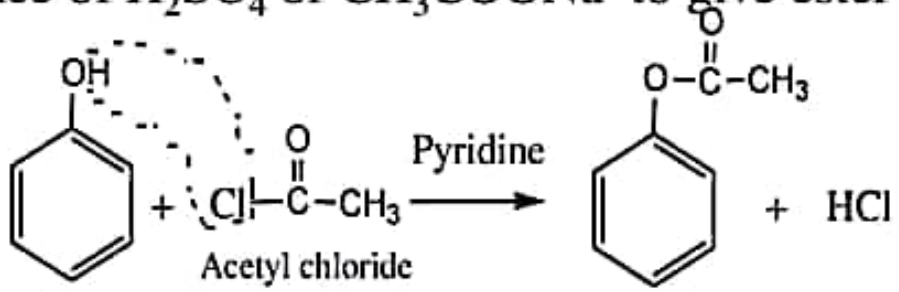
6. Reaction with phthalic anhydride:

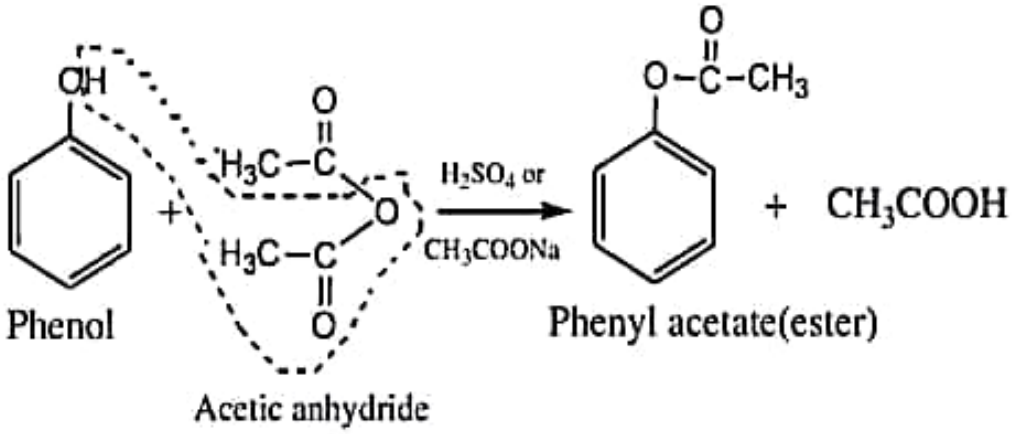
Phenol on condensation with phthalic anhydride in the presence of conc. H_2SO_4 to give phenolphthalein which is an important indicator used in acid base titration. Conc. H_2SO_4 is used as a dehydrating agent.



7. Acylation reaction (Reaction with acid chloride and anhydride)

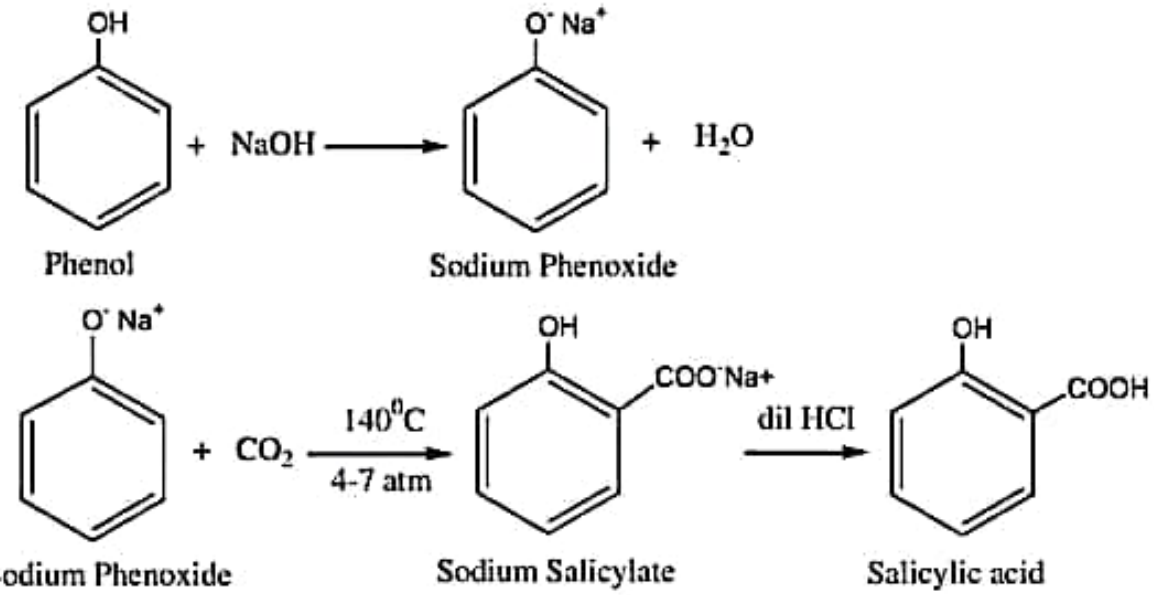
Phenol undergoes acylation reaction on reacting with acid chlorides in the presence of pyridine and with acid anhydride in the presence of H_2SO_4 or CH_3COONa to give ester esters in both cases.



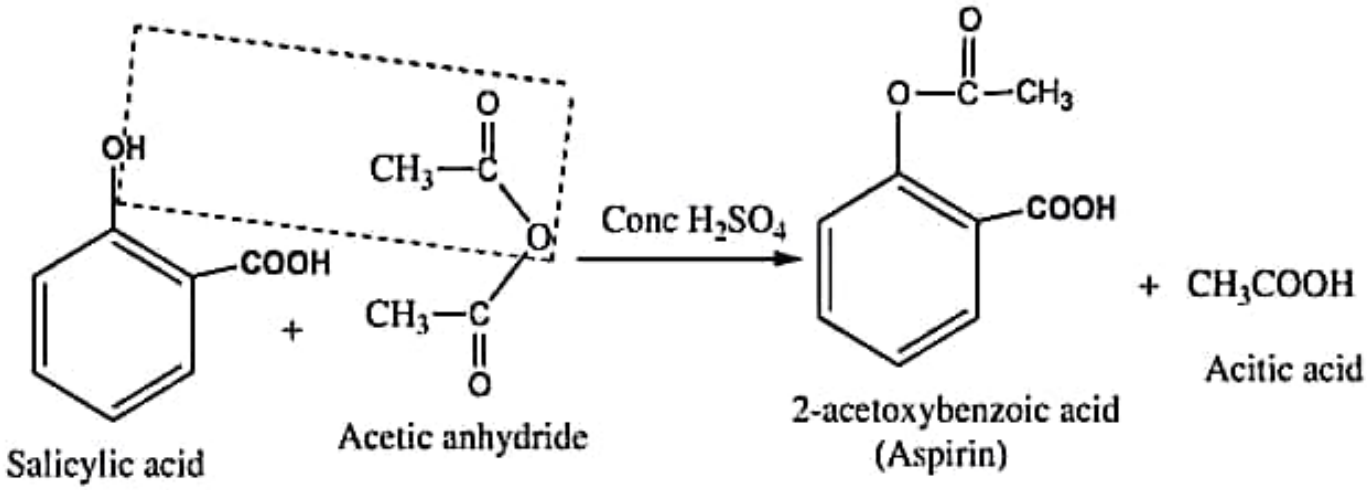


8. Kolbe Reaction (Carboxylation reaction):

When sodium phenoxide is heated with CO_2 at 140^0C under 4-7 atm pressure, sodium salicylate is obtained which on acidification gives salicylic acid. This reaction is known as Kolbe reaction. – COOH group is introduced in this reaction, so this reaction is also called carboxylation reaction.

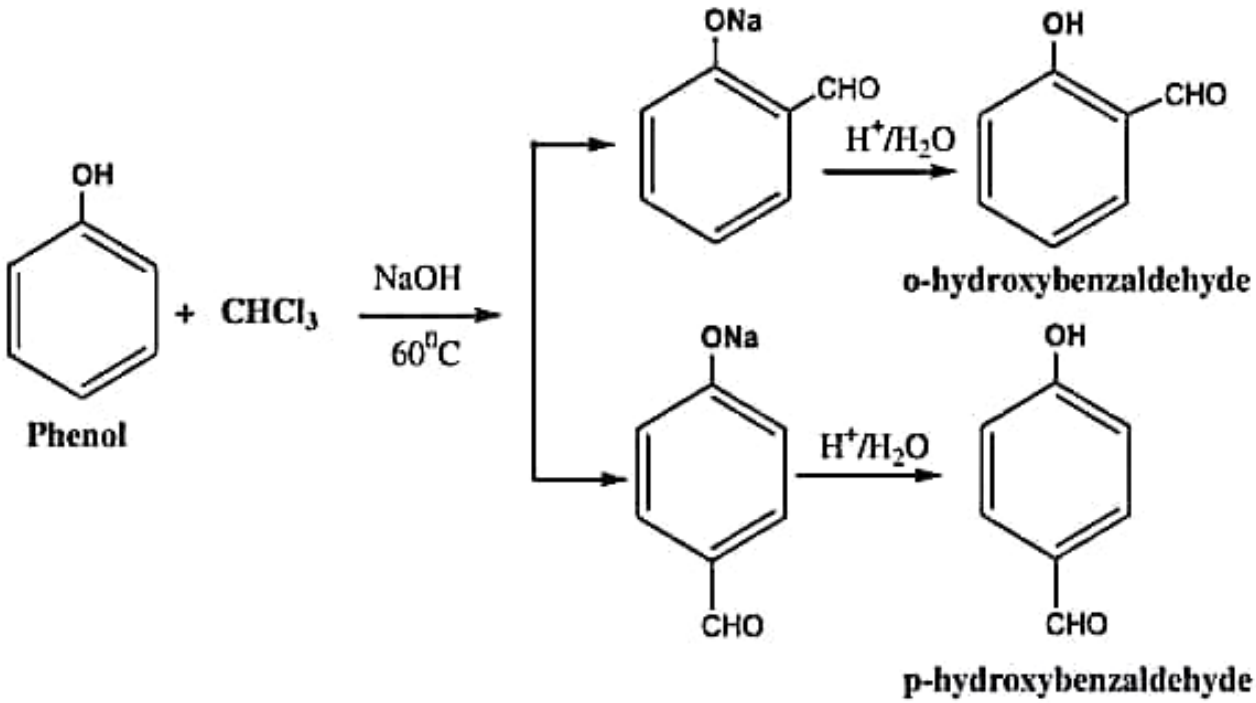


This salicylic acid is raw material to prepare very important medicine 2-acetoxy benzoic acid (Aspirin). This medicine is well known analgesics as well as antipyretic. This is prepared when salicylic acid reacts with acetic anhydride in the presence of conc. H_2SO_4



9. Reimer-Tiemann's reaction:

When phenol is refluxed with chloroform ($CHCl_3$) and NaOH at 60^0C followed by hydrolysis, it gives o-hydroxybenzaldehyde and p-hydroxybenzaldehyde. Both isomers can be separated from by steam distillation. This reaction is known as reimer-Tiemann reaction.



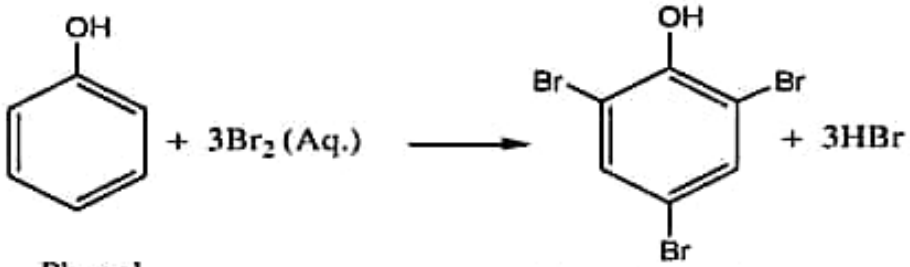
Phenol

Electrophilic Substitution reaction:

Phenol due to the presence of electron releasing -OH group is ortho and para directing or ring activator. During the electrophilic substitution reaction, the incoming electrophile always comes to ortho and para position rather than meta position. Some ring substituting reactions are given as below.

(i) Halogenation(Bromination)

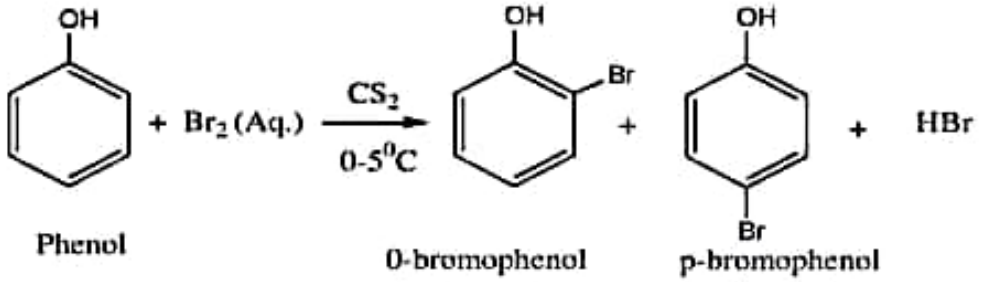
Phenol reacts with halogens to give poly halogen substituted compounds. For example phenol react with bromine to give 2,4,6-tribromophenol (o,p-tribromophenol.)



Phenol

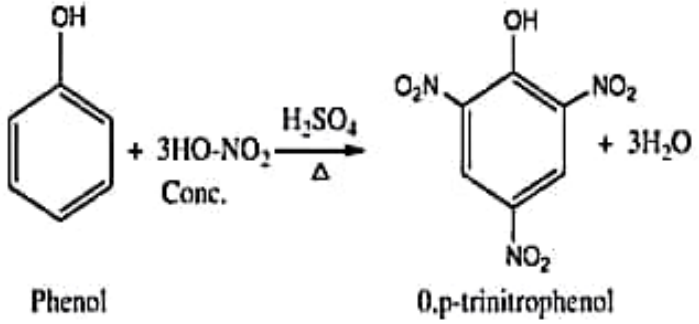
o,p-tribromophenol
(2,4,6-tribromophenol)

If phenol react with bromine in the presence of less polar compounds like CS_2, CCl_4 at low temp. give the mixture of 0-bromophenol and p-bromophenol.

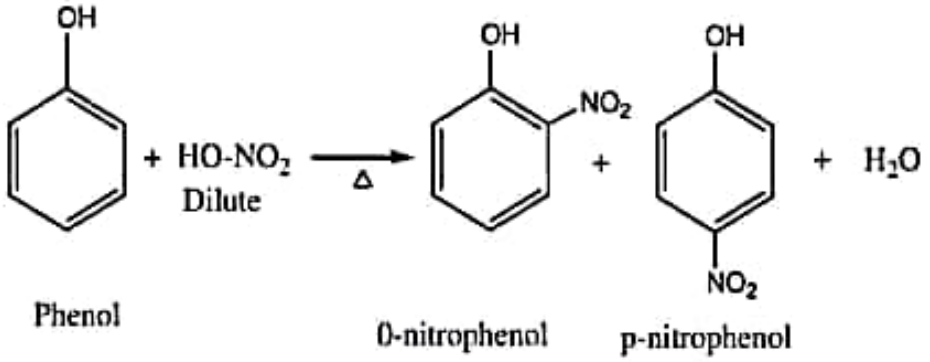


(ii) Nitration Reaction:

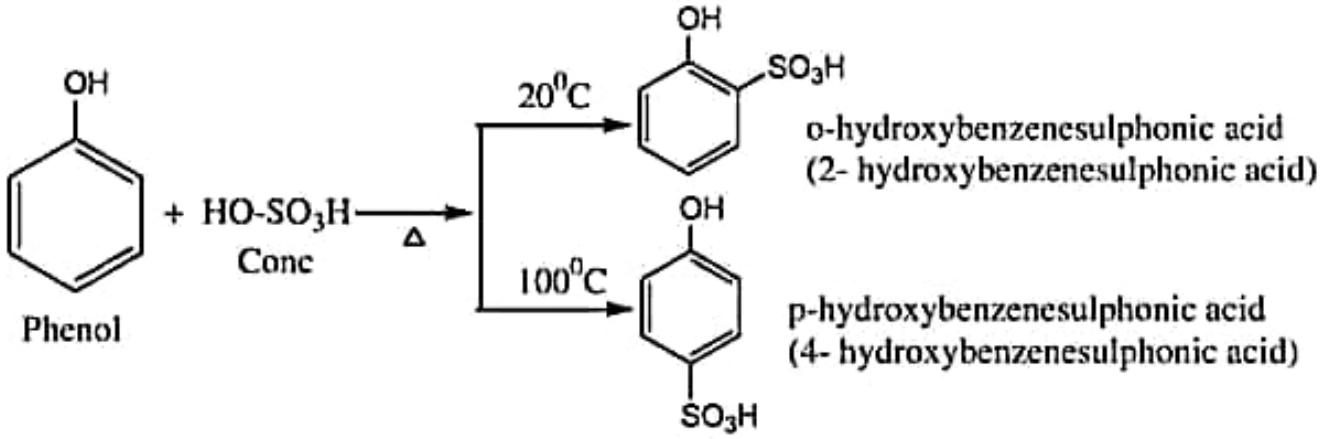
Phenol reacts with conc. Nitric acid in the presence of conc. H_2SO_4 to give 2,4,6-trinitrophenol(o,p-trinitrophenol).



But with dilute nitric acid at low temperature about 20-30^{0}C, a mixture of ortho and para nitrophenol is obtained.

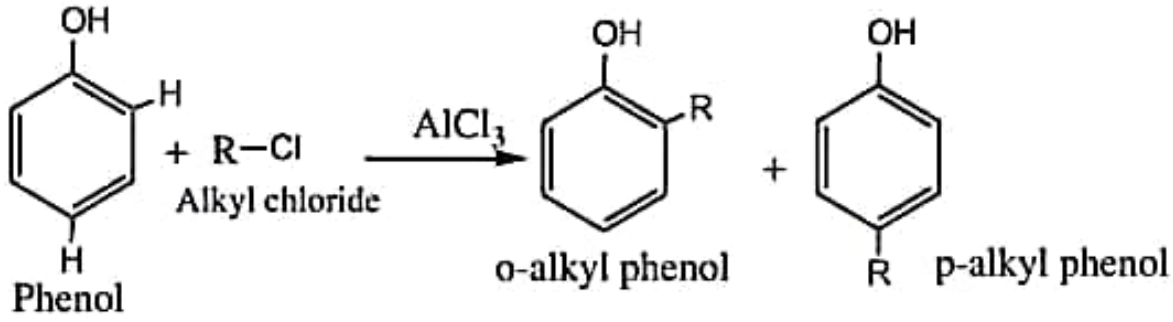


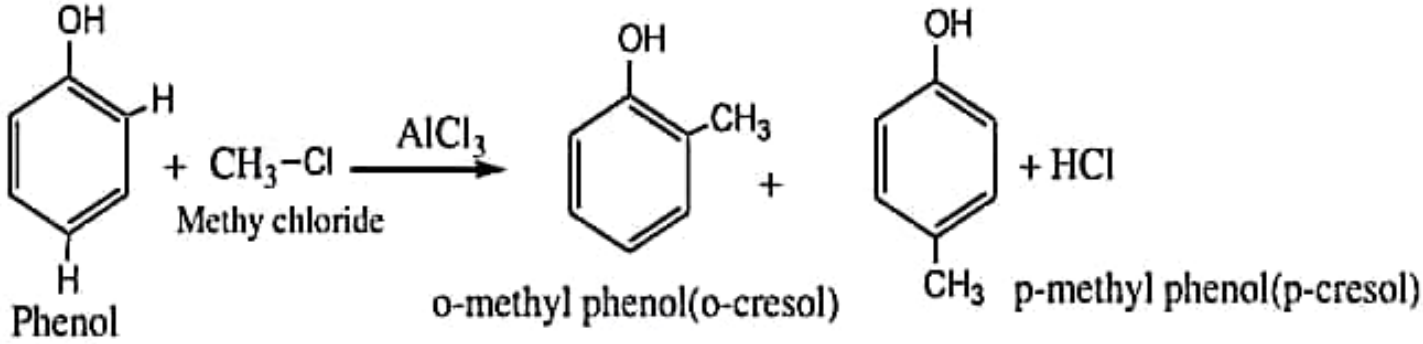
(iii) Sulphonation Reaction:



(iv) Alkylation reaction (Friedel Craft's alkylation)

Phenol react with alkyl halide in the presence of anhydrous $AlCl_3$ to give ortho-alkyl phenol and para-alkyl phenol.





❖ **Reaction with ferric chloride(Lab. Test of Phenol)**

Phenol reacts with ferric chloride solution to form water soluble violet-coloured iron hexaphenoxide ion complex. This is the laboratory test of phenol.

$$3\ C_6H_5OH + FeCl_3 \longrightarrow \left[\{Fe(OC_6H_5)_6\}\right]^{3-} + 3H^+ + 3HCl$$

Phenol — Ironhexaphenoxide ion (Violet colour)

Uses of Phenol

(i) For the manufacture of phenol formaldehyde plastic or bakelite.

(ii) As a raw material to prepare salicylic acid and aspirin (medicine).

(iii) For making phenolphthalein and explosive like picric acid.

(iv) It is used for the preparation of antiseptic, disinfectants, weedicides, insecticides, germicides & also for photographic developer(ortho and para amino phenol.

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Phenol reacts with ferric chloride solution to form water soluble violet-coloured iron hexaphenoxide ion complex. This is the laboratory test of phenol.

$$3\ C_6H_5OH + FeCl_3 \longrightarrow \left[\{Fe(OC_6H_5)_6\}\right]^{3-} + 3H^+ + 3HCl$$

Phenol — Ironhexaphenoxide ion (Violet colour)

Uses of Phenol

(i) For the manufacture of phenol formaldehyde plastic or bakelite.

(ii) As a raw material to prepare salicylic acid and aspirin (medicine).

(iii) For making phenolphthalein and explosive like picric acid.

(iv) It is used for the preparation of antiseptic, disinfectants, weedicides, insecticides, germicides & also for photographic developer(ortho and para amino phenol.