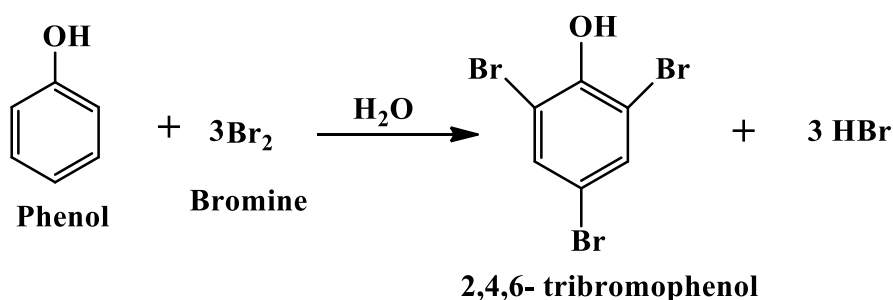


B. Reactions due to the benzene ring (Electrophilic substitution reaction):

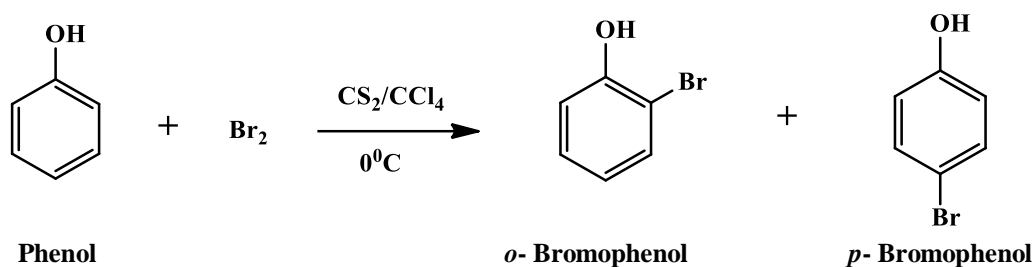
- Phenol undergoes electrophilic substitution reaction much more fastly reactive as compared to benzene ring. The reaction conditions used for monosubstitution in benzene give trisubstitution with phenol. By moderating the reaction conditions, however, can obtain the monosubstitution product.
- OH group in phenol is an ortho-para director and ring activator.

1. Halogenation:

Phenol reacts with bromine water (aqueous bromine) to give **precipitate** of 2,4,6- tribromophenol.



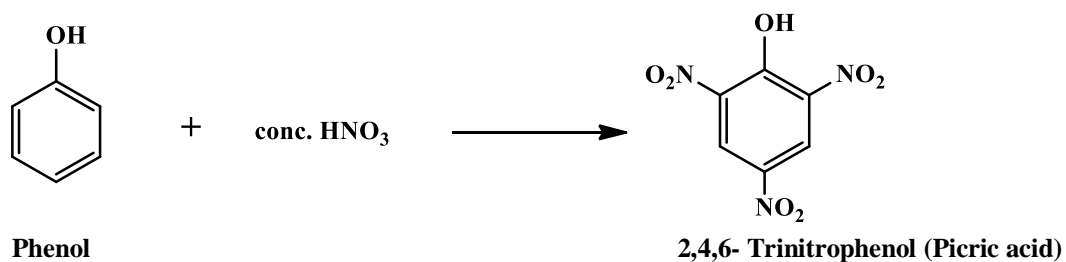
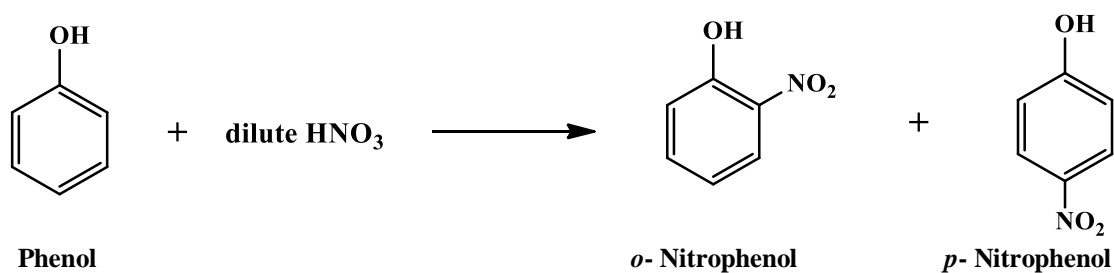
.If the reaction is carried in CS₂ or CCl₄ (non-polar solvent), a mixture of ortho- and para- bromophenol is formed.



Note: Chlorine reacts in the same way.

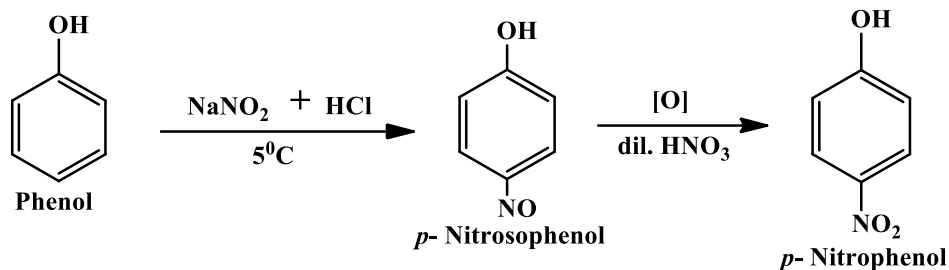
2. Nitration:

.Phenol reacts with dilute HNO₃ to give mixture of ortho- and para- nitrophenol.

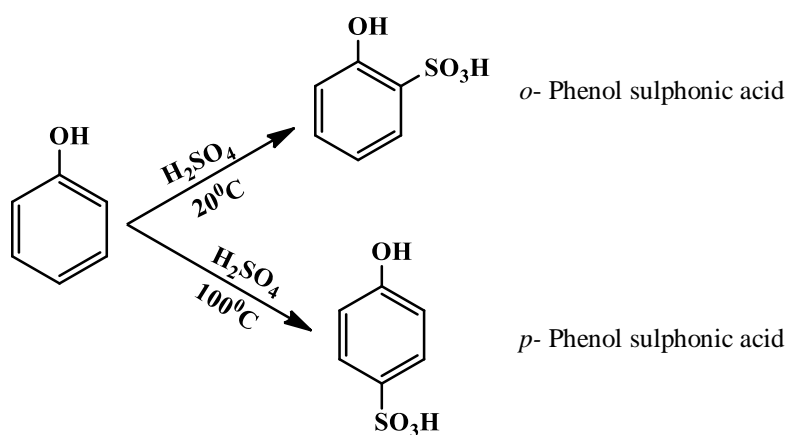


3. Nitrosation:

Phenol reacts with nitrous acid (obtained from NaNO_2/HCl at 5°C) to form *p*-nitrosophenol.



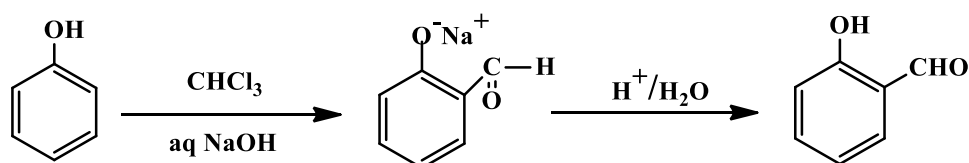
4. Sulphonation:



Phenol

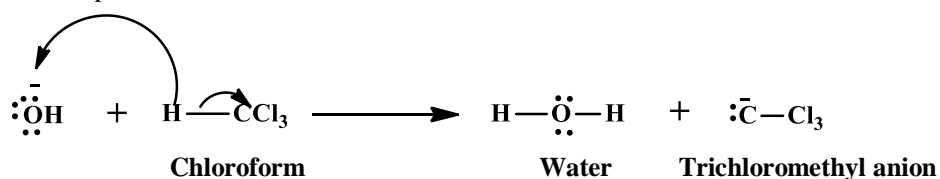
5. Reimer-Tiemann reaction:

This involves the treatment of phenol with chloroform in aqueous NaOH solution followed by acid hydrolysis. Salicylaldehyde is formed.

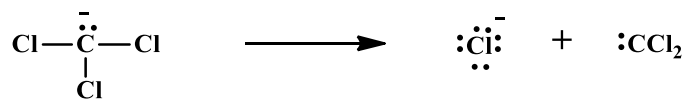


Phenol Mechanism:

Step 1: Removal of a proton from chloroform

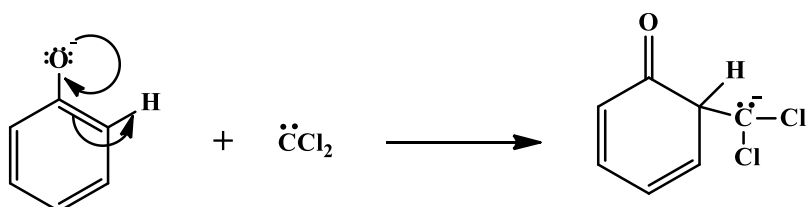


Step 2: Dissociation of trichloromethyl anion

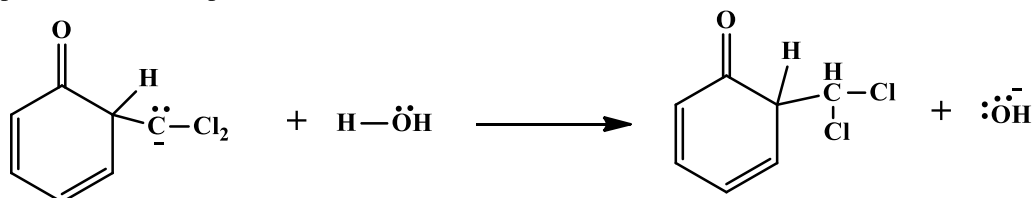


Dichlorocarbene

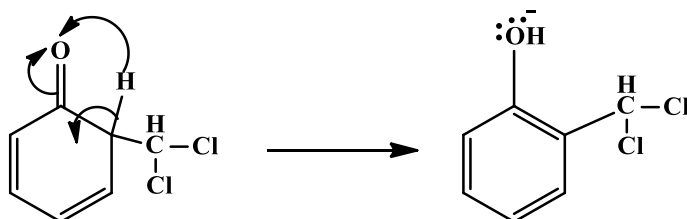
Step 3: Addition of dichlorocarbene to the phenoxide ion



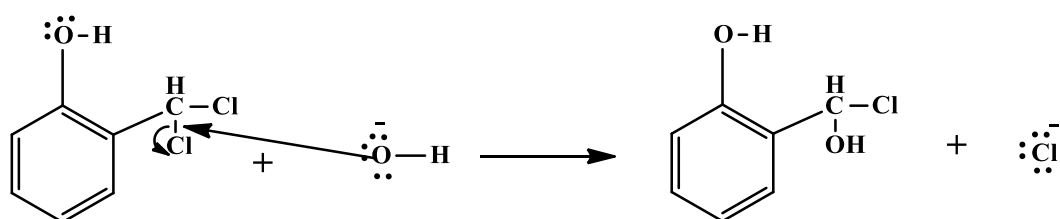
Step 4: Abstraction of proton from water



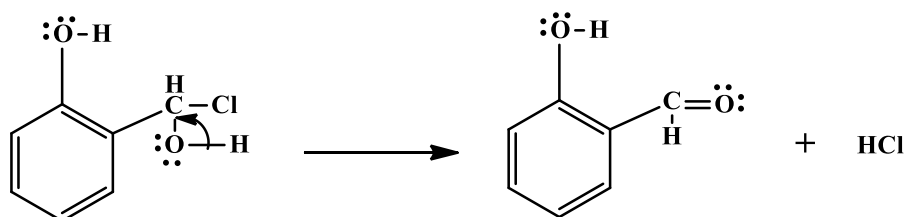
Step 5: Tautomerisation to form substituted phenol



Step 6: Displacement of halide by hydroxy ion



Step 7: Elimination of HCl to form the aldehyde product



Note: 1.If CCl_4 is used in place of CHCl_3 , salicylic acid is formed.

2. The Reimer-Tiemann reaction is also given by other phenols and introduce $-\text{CHO}$ group in ortho- position.