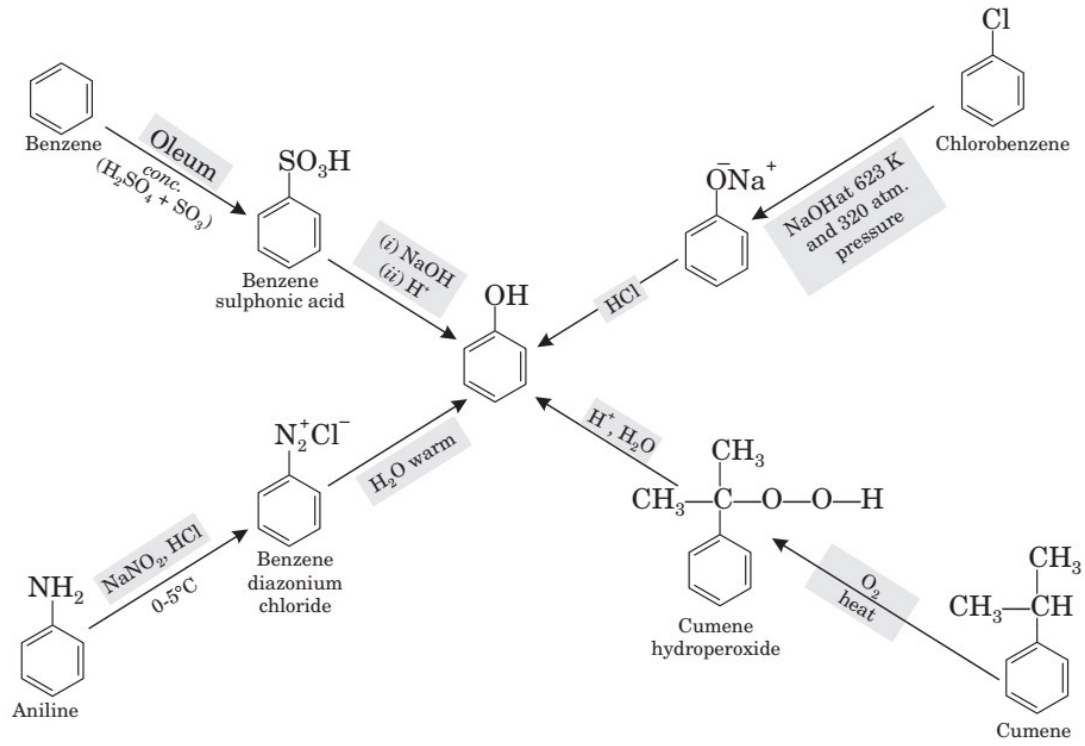
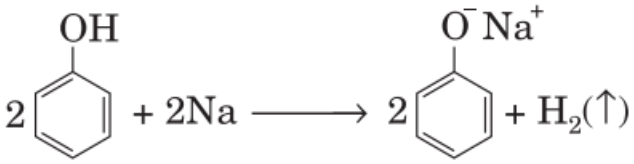
Phenols

Preparation of Phenols



Chemical Properties of Phenols

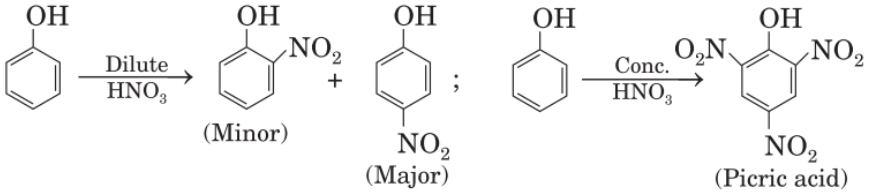
- **Reaction with metals:**



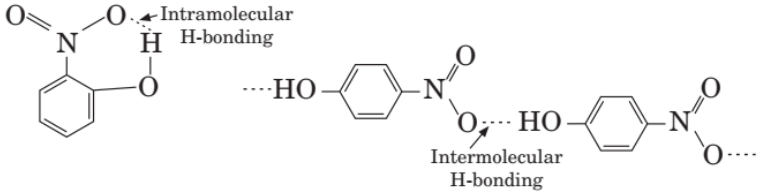
- **Esterification:**

$$C_6H_5OH + CH_3COOH \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{Phenyl ethanoate}}{CH_3COOC_6H_5} + H_2O$$

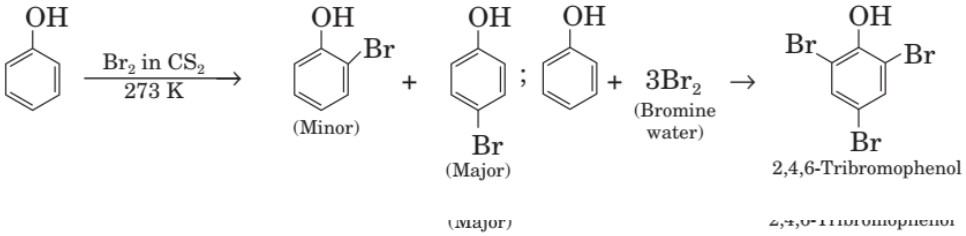
- **Electrophilic aromatic substitution:**



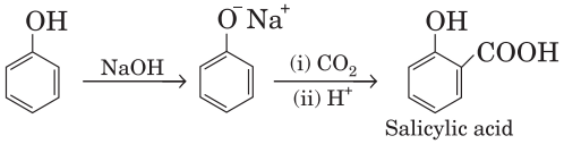
- *o*-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding.



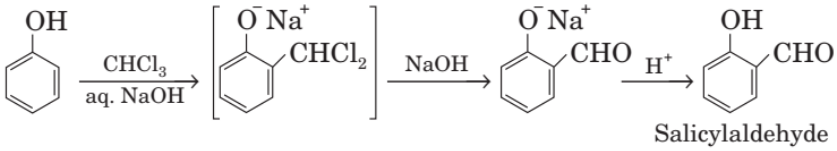
- **Halogenation:**



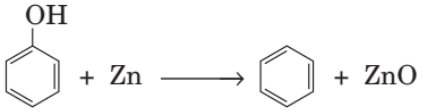
- **Kolbe's Reaction:**



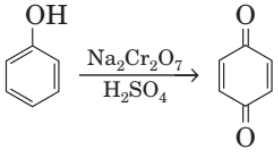
- **Reimer-Teimann Reaction:**



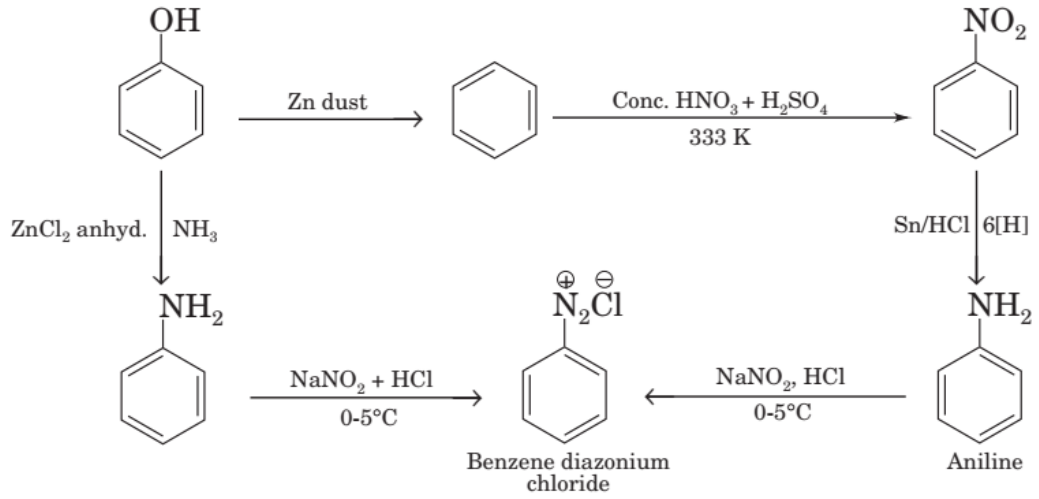
- **Reaction of phenol with Zn-dust:**



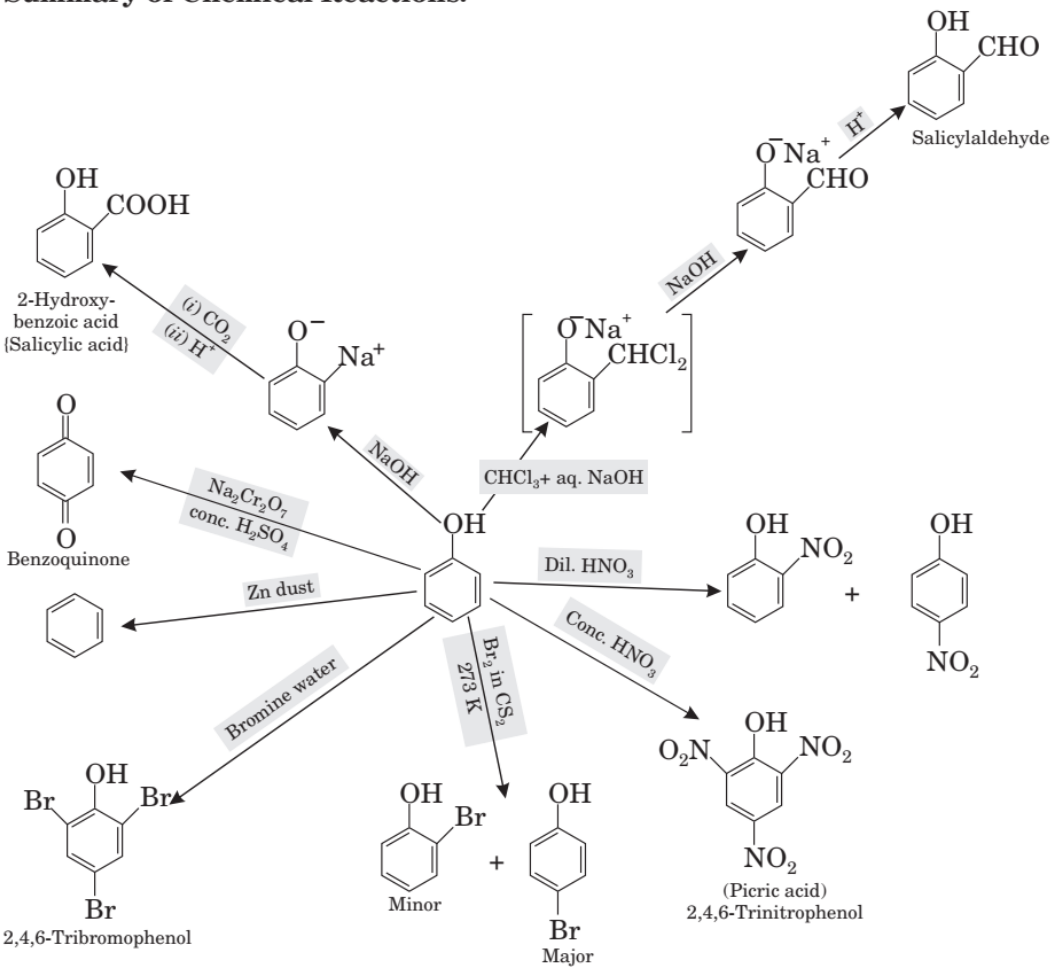
- **Oxidation:**



- **Conversion of Phenol to Benzene diazonium chloride:**



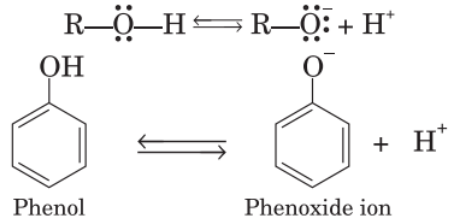
- **Summary of Chemical Reactions:**



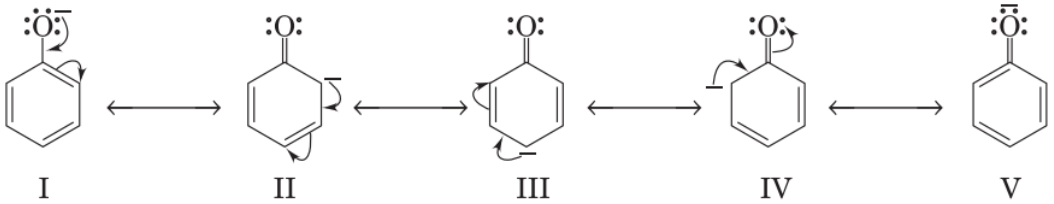
- **Acidic Nature:**
  - ➢ ***Phenol is more acidic than alcohols*:** In phenol, the hydroxyl group is directly attached to the sp^2 hybridised carbon atom of benzene ring. However, in alcohols

the hydroxyl group is attached to the sp^3 hybridised carbon atom of the alkyl group, i.e. less *s*-character. The sp^2 hydridised carbon has higher electronegativity than sp^3 hybridised carbon atom because of having more of *s*-character. Hence, the polarity O–H bond in phenols is higher than those of alcohols. Thus, the extent of ionisation of phenols is higher than that of alcohols.

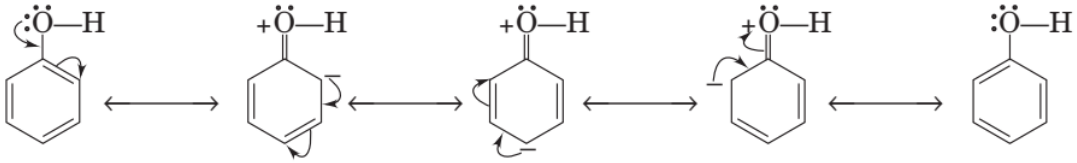
➢ The ionisation of an alcohol and a phenol takes place as follows:



In alkoxide ion, the negative charge is localised over oxygen atom while in phenoxide ion, the charge is delocalised over the benzene ring. Resonating structures of phenoxide ion are shown below:



The delocalisation of negative charge makes phenoxide ion more stable and favours the ionisation of phenol. Although there is also charge delocalisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than phenoxide ion. Resonating structures of phenol are depicted below:



➢ Electrophilic substitution reactions in phenol will take place at *o* and *p*-position ∴ electron density is maximum at *o* and *p*-position. Nucleophilic substitution reactions will not take place easily in phenol due to double bond character in C—O bond.

➢ In substituted phenols, the presence of an electron withdrawing group such as nitro group enhances the acidic strength of phenol. On the other hand, electron releasing groups, such as alkyl group of phenol decreases the acid strength.

Acid Strength:

➢ *p*-nitro phenol > *o*-nitro phenol > *m*-nitro phenol > phenol > *p*-cresol > ethanol