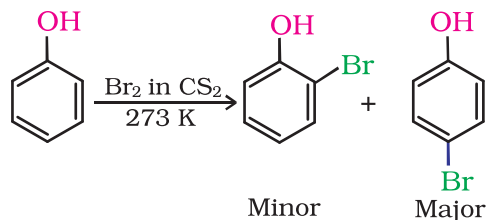


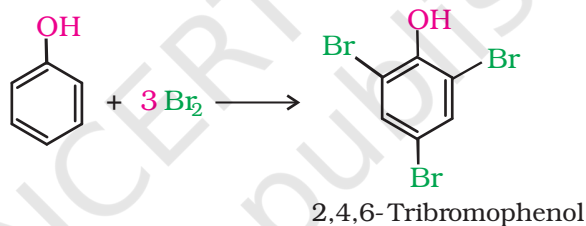
(ii) **Halogenation:** On treating phenol with bromine, different reaction products are formed under different experimental conditions.

(a) When the reaction is carried out in solvents of low polarity such as CHCl_3 or CS_2 and at low temperature, monobromophenols are formed.



The usual halogenation of benzene takes place in the presence of a Lewis acid, such as FeBr_3 (Unit 10, Class XII), which polarises the halogen molecule. In case of phenol, the polarisation of bromine molecule takes place even in the absence of Lewis acid. It is due to the highly activating effect of $-\text{OH}$ group attached to the benzene ring.

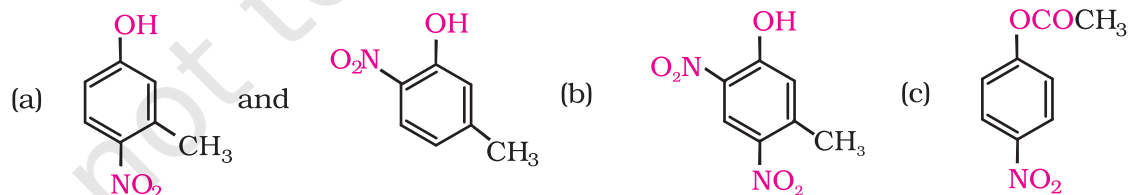
(b) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.



Example 11.5 Write the structures of the major products expected from the following reactions:

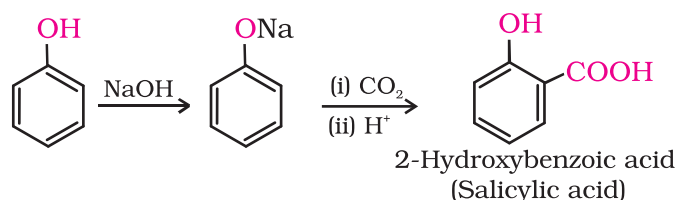
- Mononitration of 3-methylphenol
- Dinitration of 3-methylphenol
- Mononitration of phenyl methanoate.

Solution The combined influence of $-\text{OH}$ and $-\text{CH}_3$ groups determine the position of the incoming group.



2. Kolbe's reaction

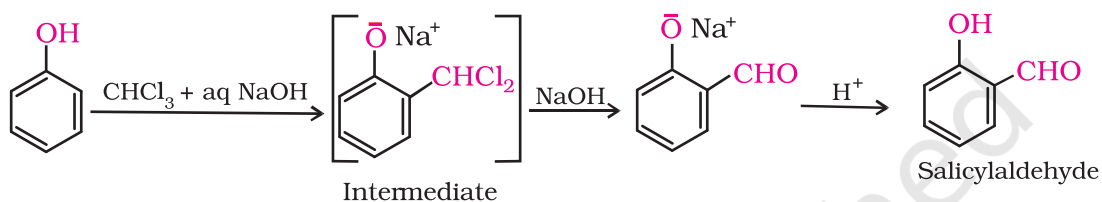
Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. *Ortho* hydroxybenzoic acid is formed as the main reaction product.



3. Reimer-Tiemann reaction

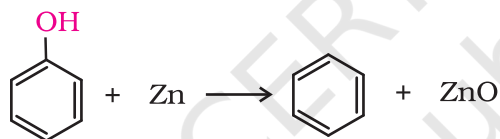
On treating phenol with chloroform in the presence of sodium hydroxide, a $-CHO$ group is introduced at *ortho* position of benzene ring. This reaction is known as *Reimer - Tiemann reaction*.

The intermediate substituted benzal chloride is hydrolysed in the presence of alkali to produce salicylaldehyde.



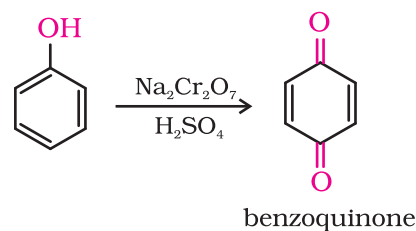
4. Reaction of phenol with zinc dust

Phenol is converted to benzene on heating with zinc dust.



5. Oxidation

Oxidation of phenol with chromic acid produces a conjugated diketone known as benzoquinone. In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinones.



Intext Questions

- 11.6** Give structures of the products you would expect when each of the following alcohol reacts with (a) $HCl - ZnCl_2$ (b) HBr and (c) $SOCl_2$.
- (i) Butan-1-ol (ii) 2-Methylbutan-2-ol
- 11.7** Predict the major product of acid catalysed dehydration of
- (i) 1-methylcyclohexanol and (ii) butan-1-ol
- 11.8** *Ortho* and *para* nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.
- 11.9** Write the equations involved in the following reactions:
- (i) Reimer - Tiemann reaction (ii) Kolbe's reaction