# VIVEKANANDA COLLEGE OF ARTS AND SCIENCE (Women)

THENPATHI-SIRKALI
NAGAPATTINAM (Dt) - 609 111

# Unit-III Aromatic electrophilic substitution reactions of Phenol

**S. Sandhiya**
Asst. Professor
Department of Chemistry

sub: General Chemistry - IV
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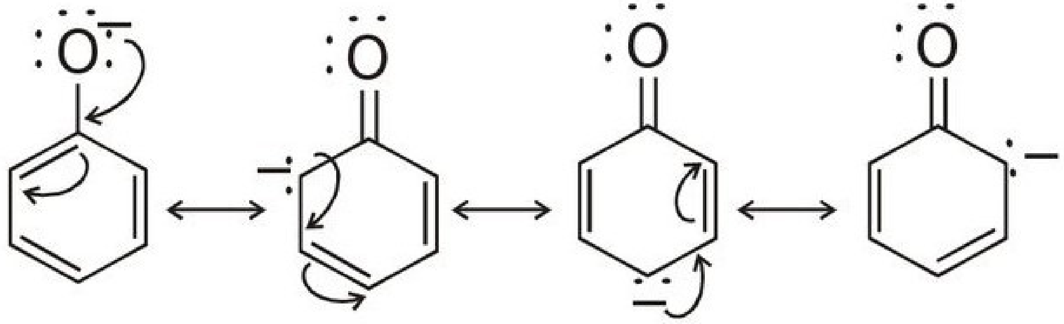
# Aromatic electrophilic substitutution reactions of phenol

- Electrophilic aromatic substitution reactions are the reactions where an electrophile replaces one or more hydrogen atoms attached to the aromatic ring. Phenols are highly prone to electrophilic substitution due to rich electron density
- The hydroxyl group attached to the aromatic ring in phenol facilitates the effective delocalization of the charge in the aromatic ring. Thus, it stabilizes the arenium ion through resonance. The hydroxyl group also acts as ortho para directors. Hence, we acknowledge most of these substitutions at ortho and para positions only.

# Acidity of phenol

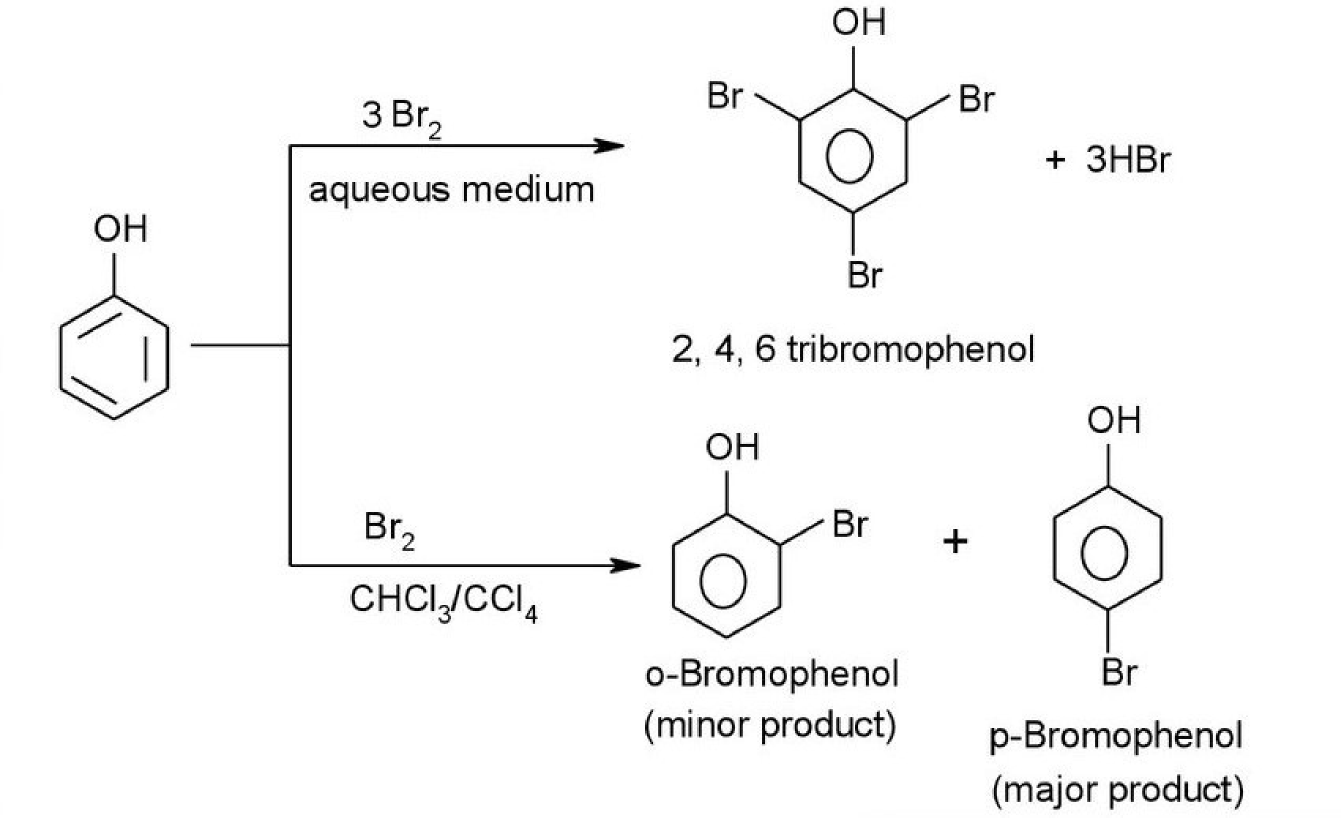
- Acidic nature : Phenol is a weak acid. The acidic nature of phenol is due to the formation of stable phenoxide ion in solution
- The phenoxide ion is stable due to resonance.



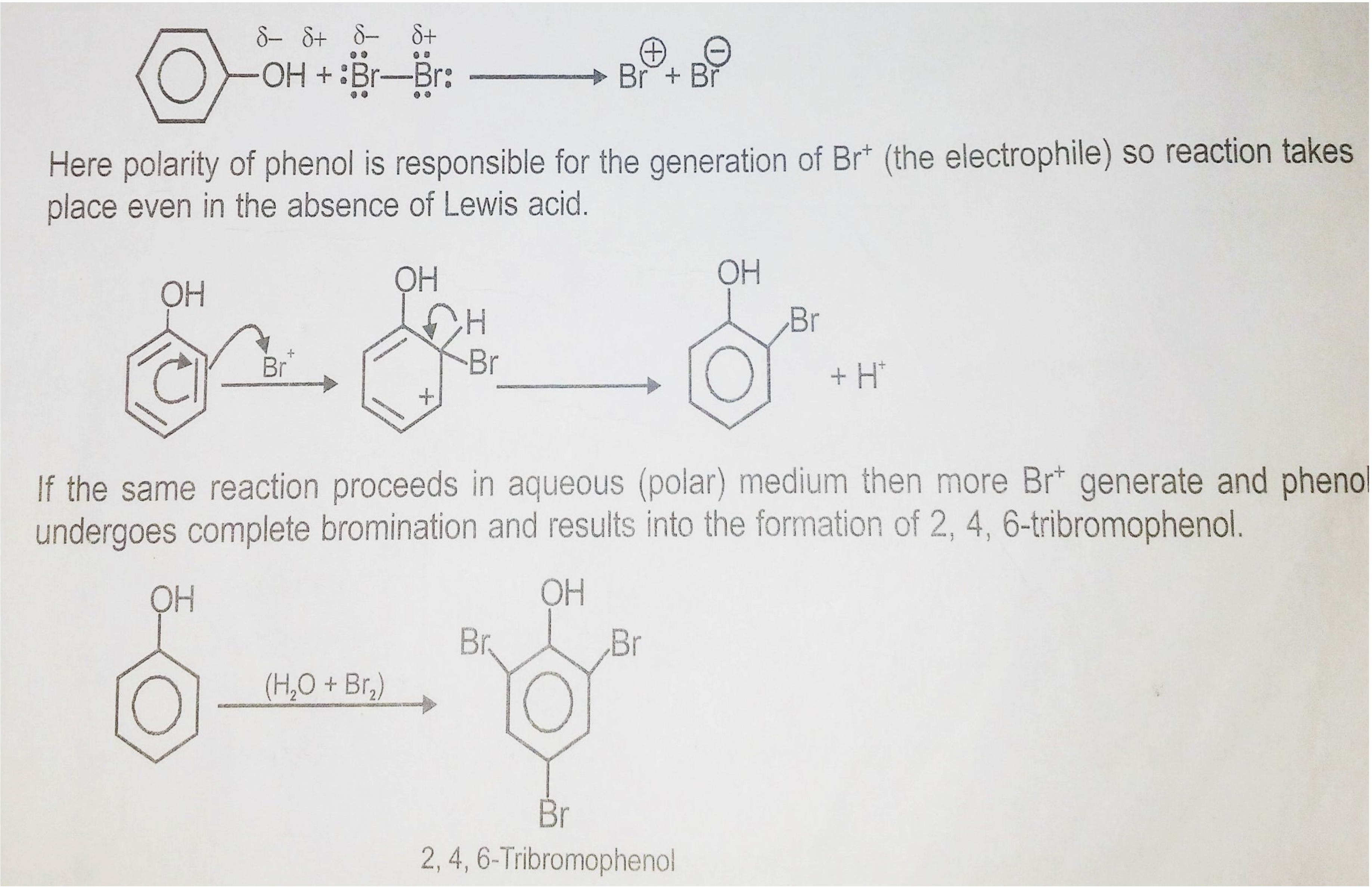
- The negative charge is spread throughout the benzene ring. This charge delocalisation is a stabilising factor in the phenoxide ion and increase acidity of phenol.
- Phenols are much more acidic than alcohols but less so than carboxylic acids or even carbonic acid

# Halogenation reaction of phenols

- **Bromination:** Phenol reacts with bromine in carbon disulphide (or $CHCl_3$) at low temperature to form mixture of ortho and para bromophenol.
- Phenol generates a white precipitate with excess of bromine water yielding 2, 4,6-tribromophenol.



# Mechanism:

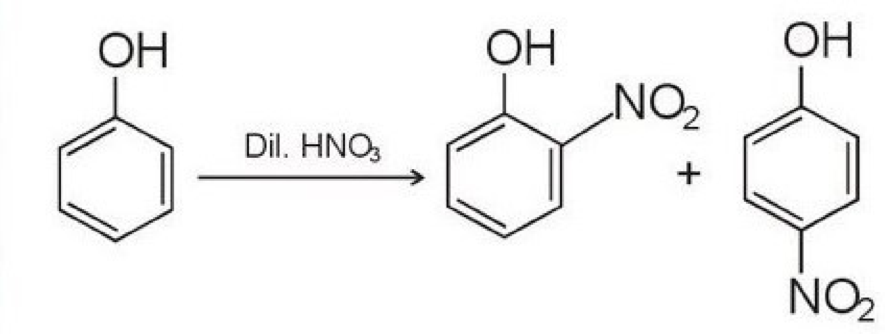


Here polarity of phenol is responsible for the generation of $Br^+$ (the electrophile) so reaction takes place even in the absence of Lewis acid.

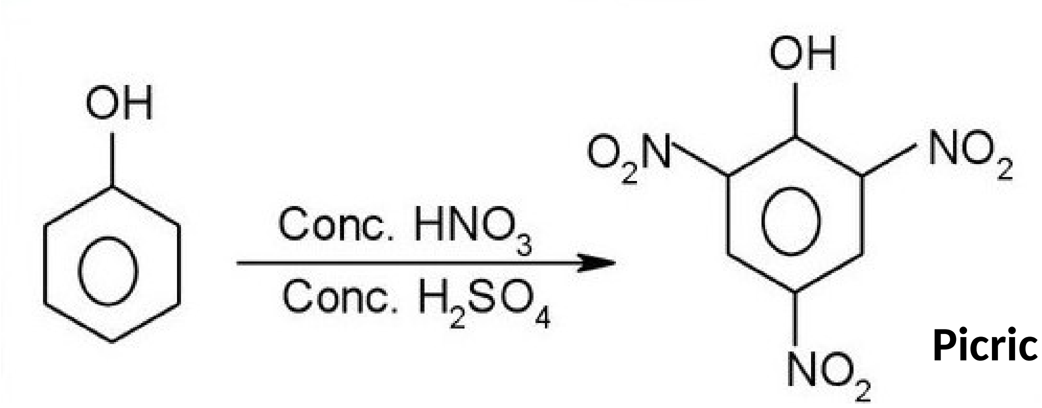
If the same reaction proceeds in aqueous (polar) medium then more $Br^+$ generate and phenol undergoes complete bromination and results into the formation of 2, 4, 6-tribromophenol.

2, 4, 6-Tribromophenol

**Nitration :** Phenol reacts with dilute nitric acid at 5-10°C to form ortho and para nitro phenols, but the yield is meager because of oxidation of phenolic group set. The -OH group is reactivating set, hence nitration is possible with light nitric acid.

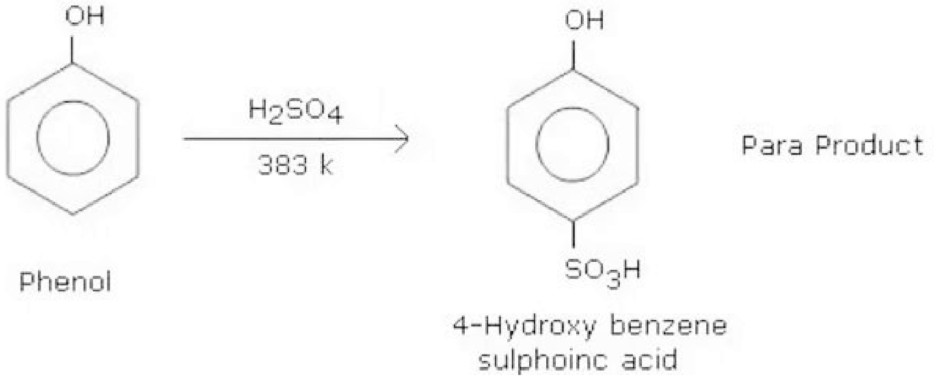


However, when phenol is treated with concentrated $HNO_3$ in presence of concentrated H SO , 2,4,6-trinitrophenol (Picric acid) is formed.

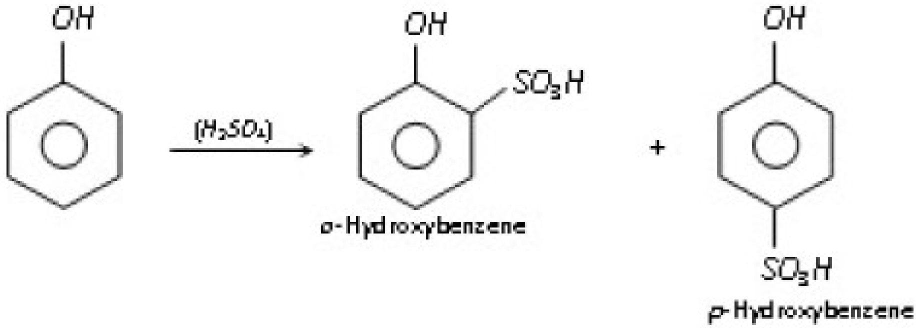


**Picric acid**

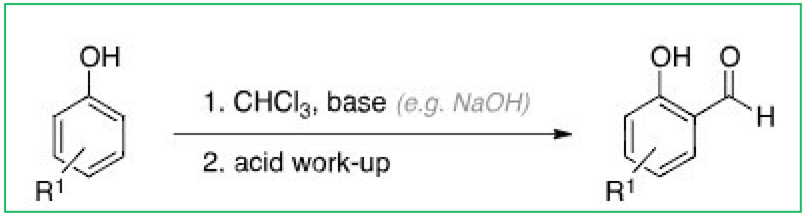
- **Sulphonation :** Phenol reacts with conc. $H_2SO_4$ readily to form mixture of ortho and para hydroxy benzene sulphonic acids

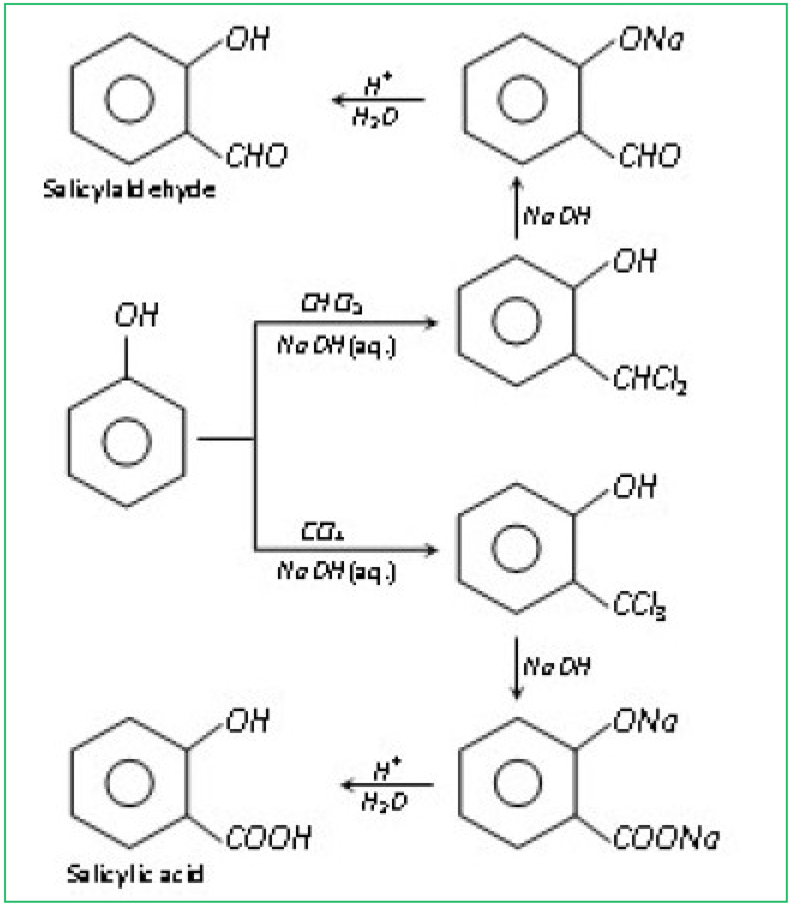


- At low temperature (25°C), the ortho-isomer is the major product, whereas at 100°C, it gives mainly the para-isomer.

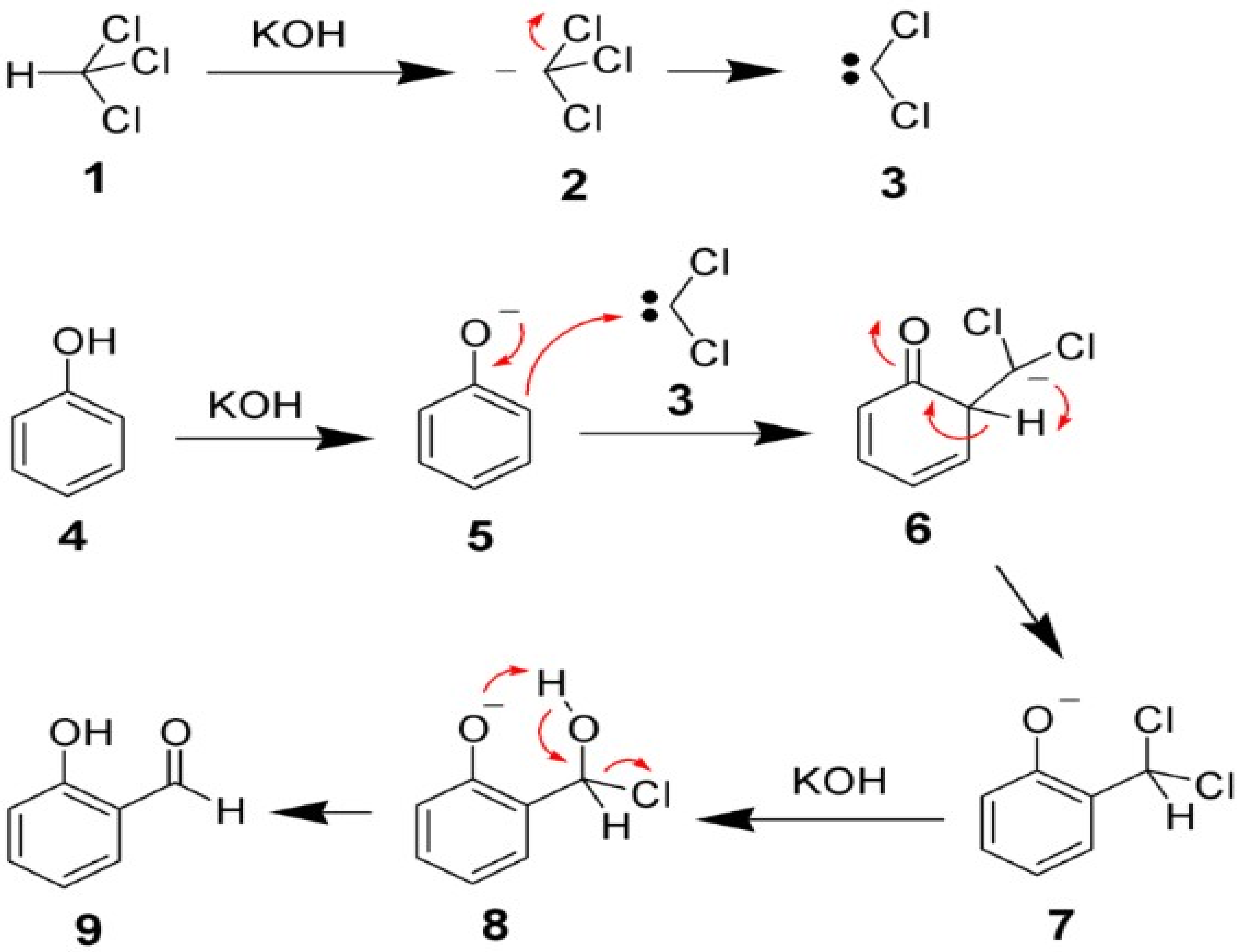


- **Reimer-Tiemann reaction** : Phenol, on refluxing with chloroform and sodium hydroxide (aq.) given by acid hydrolys (o-hydroxy benzaldehyde) and a very small amount of p-hydroxy benzaldehyde. However, when carbon tetrachloride is needed, salicylic acid (predominating product) is formed

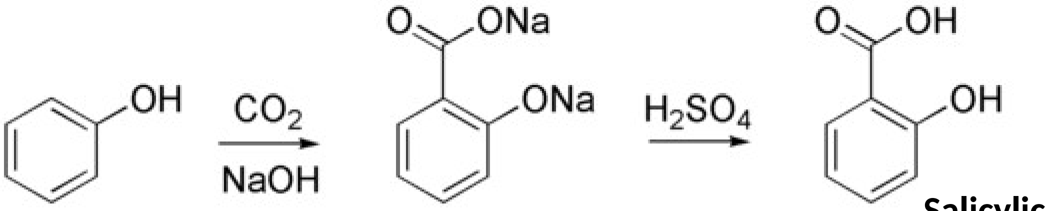




# Reimer-Tiemann reaction (Mechanism)

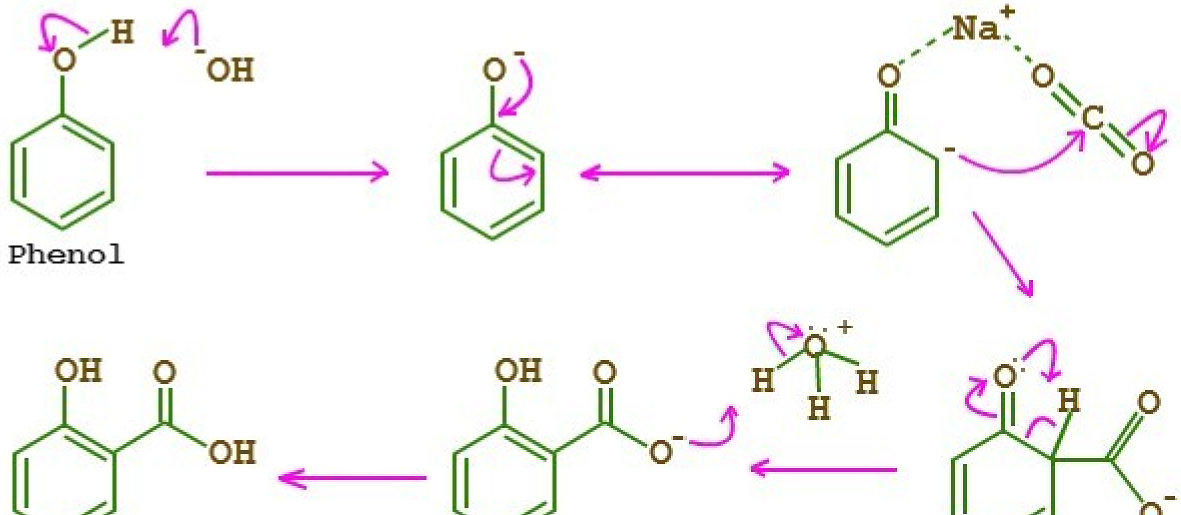


Kolbe’s Reaction: When phenol is treated with sodium hydroxide, phenoxide ion is formed. This phenoxide ion formed is highly reactive towards electrophilic substitution reactions. Upon treatment with a weak electrophile (carbon dioxide), it undergoes electrophilic substitution reaction to form Ortho-hydroxybenzoic acid. This reaction is popularly known as **Kolbe’s reaction**



**Salicylic acid**

## Mechanism:



**Salicylic acid**