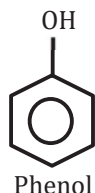


PHENOLS (INTRODUCTION, PREPARATION METHOD AND PROPERTIES)

Phenol Phenols - General Method of Preparation

Formula: C_6H_5OH



Structure

Phenol, known by alternative names such as carbolic acid, benzenol, or hydroxy benzene, has an -OH group linked to a carbon atom with sp^2 hybridization. It was first discovered by Runge in the middle oil fraction obtained from the distillation of coal tar. Initially, it was termed "carbolic acid," combining "carbo" for coal and "oleum" for oil. Interestingly, trace quantities of phenol are also detectable in human urine.

General Methods of Preparation

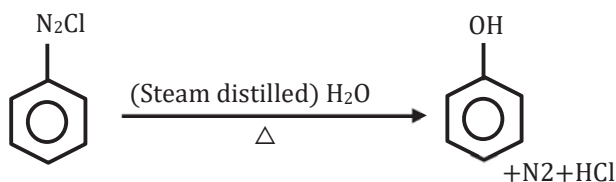
(1) From benzene sulphonic acid

When sodium salt of benzene sulphonic acid is fused with NaOH phenol is obtained.

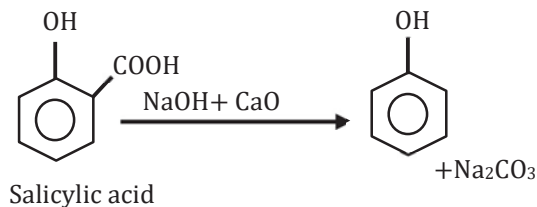


(2) From benzene diazonium chloride

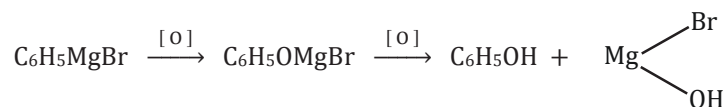
Warming a solution of benzene diazonium chloride results in the production of phenol, accompanied by the release of nitrogen gas.

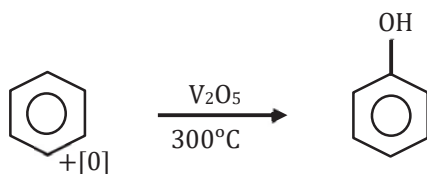
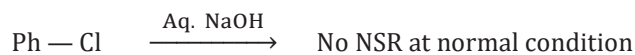


(3) By distilling a phenolic acid with soda lime (decarboxylation)

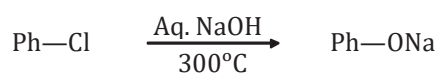
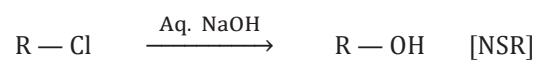


(4) From Grignard reagent: Phenol can be obtained by reacting the Grignard reagent with oxygen, followed by hydrolysis in an acidic environment.

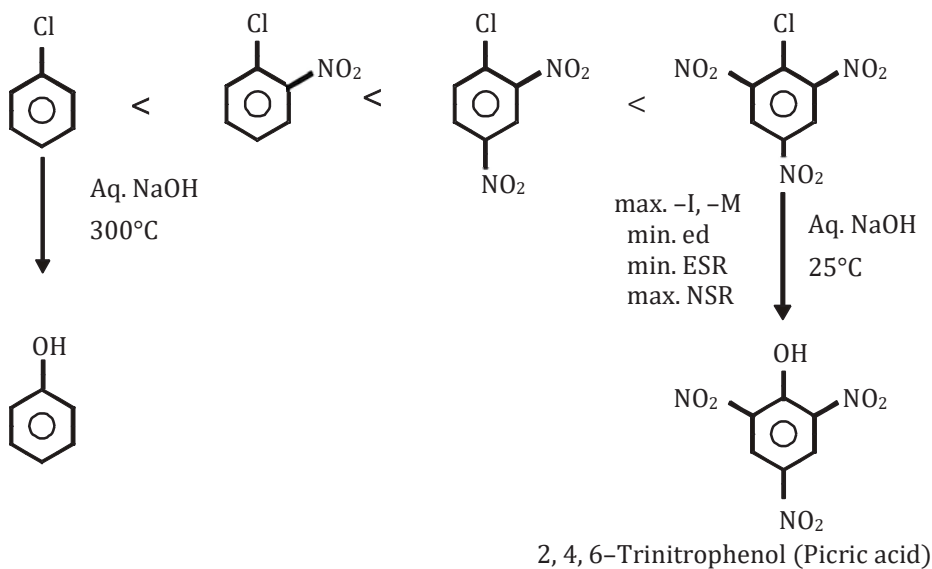


(5) From benzene**(6) From chloro benzene**

Stable by resonance

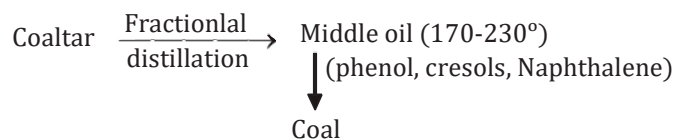


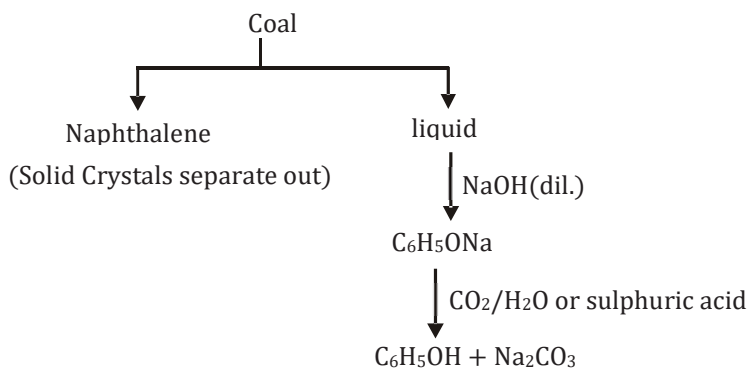
Order of NSR

**(7) Industrial Preparation of Phenol**

Phenol can be industrially synthesized through the following methods:

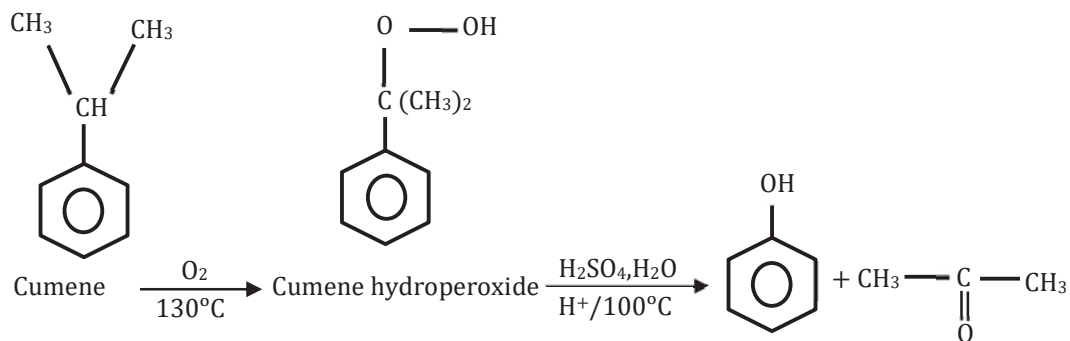
- Middle oil fraction from coal tar distillation
- Cumene
- Raschig process
- Dow's process

(a) Middle oil fraction from coal tar distillation



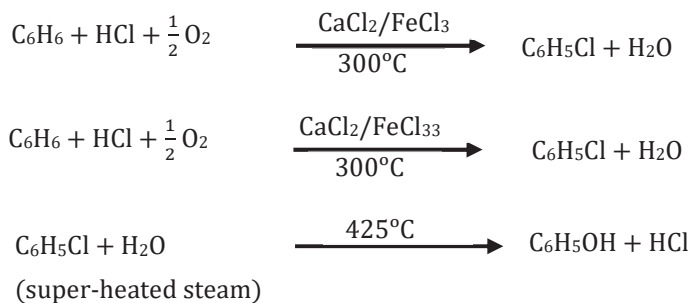
(b) From cumene (Isopropyl benzene)

Cumene is oxidised with oxygen into cumene hydroperoxide in presence of a catalyst. This is decomposed by dil. H_2SO_4 into phenol and acetone.



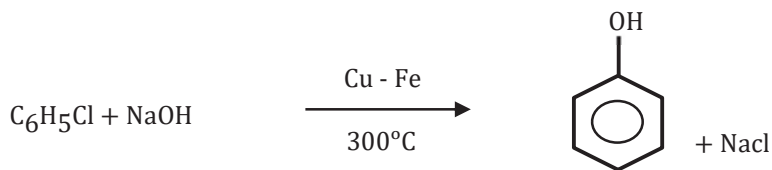
(c) Raschig process

Chlorobenzene is formed by the interaction of benzene, HCl and air at 300°C in presence of catalyst $\text{CuCl}_2 + \text{FeCl}_3$. It is hydrolyzed by superheated steam at 425°C to form phenol and HCl.



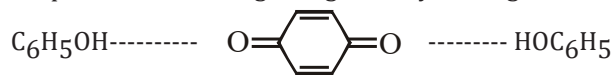
(d) Dow process

This process involves alkaline hydrolysis of chloro benzene-(large quantities of phenol formed).



Physical Properties of Phenols

- (i) Phenol is a transparent, moisture-absorbing crystalline solid.
- (ii) When exposed to air and light, it gradually undergoes oxidation, turning pink in color.



Phenoquinone (pink colour)

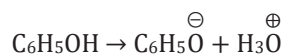
- (iii) While it possesses toxic properties, it serves as an antiseptic and disinfectant.
- (iv) Phenol exhibits limited solubility in water, but readily dissolves in organic solvents.
- (v) The solubility of phenol in water is significantly lower than that of alcohols, primarily due to the larger hydrocarbon component within its molecule.
- (vi) Thanks to intermolecular hydrogen bonding, phenol has a higher boiling point than corresponding hydrocarbons and aryl halides. In contrast, intermolecular hydrogen bonding in ortho-derivatives is utilized in the production of dyes, drugs, bakelite. Its melting point (MP) is 43°C, and its boiling point (BP) is 182°C.

Chemical Properties of Phenols

(A) Phenols – Reactions Due To –OH Group

Acidic Nature

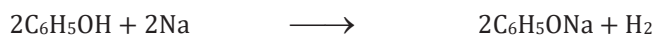
Phenol displays modest acidity, which can be attributed to the creation of a stable phenoxide ion in solution. The stability of the phenoxide ion is achieved through resonance, which disperses the negative charge across the benzene ring, enhancing its stability. Electron-withdrawing groups like -NO₂ and -Cl amplify the acidity of phenol, while electron-releasing groups such as -CH₃ diminish its acidity.



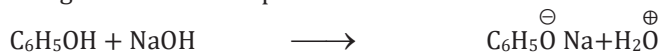
Phenol exhibits greater acidity compared to alcohols but is less acidic than carboxylic acids and even carbonic acid.

This acidic nature of phenol is evident in the following ways:

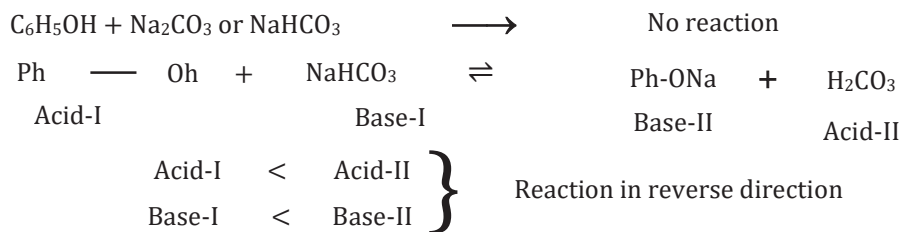
- (i) Phenol changes blue litmus to red.
- (ii) Highly electro positive metals react with phenol.



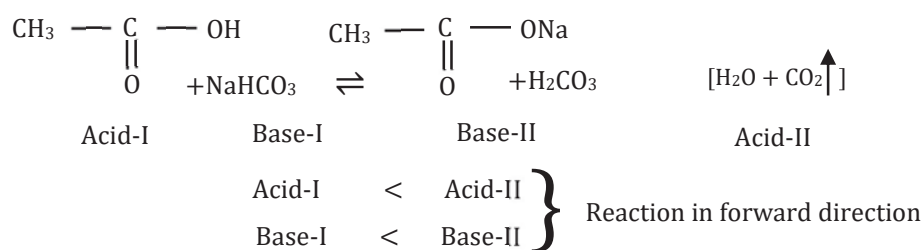
- (iii) Phenol reacts with strong alkalies to form phenoxides.



- (iv) However, phenol does not decompose Na₂CO₃ or NaHCO₃ because phenol is weaker than carbonic acid.

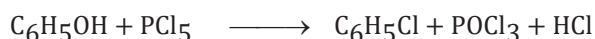


(v) Phenol does not react with NaHCO_3 .



(vi) Acetic acid reacts with NaHCO_3 and gives effervescence of CO_2 .

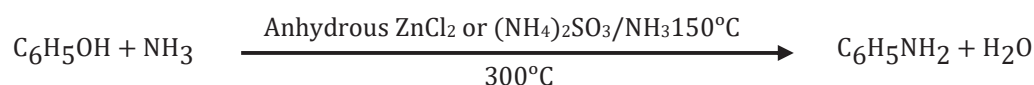
Reaction with PCl_5 : Phenol reacts with PCl_5 to form chloro benzene. The yield of chlorobenzene is poor and mainly triphenyl phosphate is formed.



Reaction with Zn dust: When phenol is distilled with zinc dust benzene is obtained.



Reaction with NH_3 (Butcherer reaction): Phenol reacts with NH_3 in presence of anhydrous ZnCl_2 to form aniline.



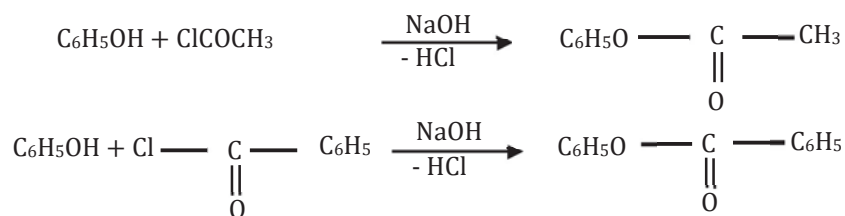
Reaction with FeCl_3

Phenol gives violet colouration with FeCl_3 solution (neutral) due to formation of a complex.



This reaction is used to differentiate phenol from alcohols.

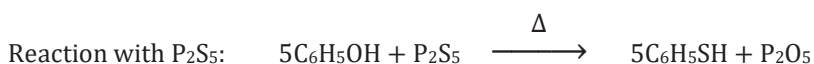
Acetylation (Schotten-Baumann reaction): Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.



Ether formation (Alkylation): Phenol reacts with alkyl halides in alkali solution to form phenyl ethers. (Williamson's synthesis)

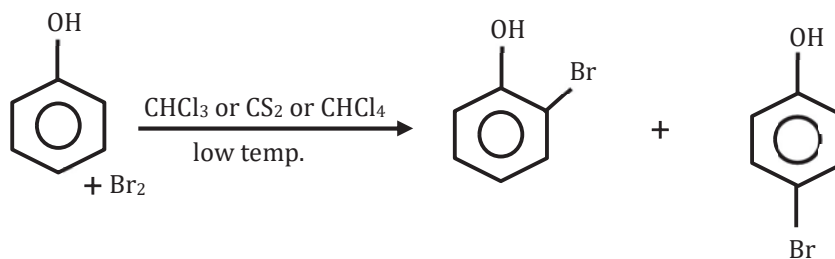


Sodium phenoxide

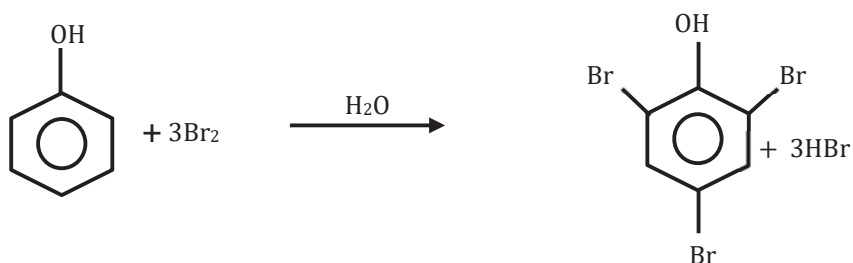


(B) Phenols - Reaction of Benzene Ring

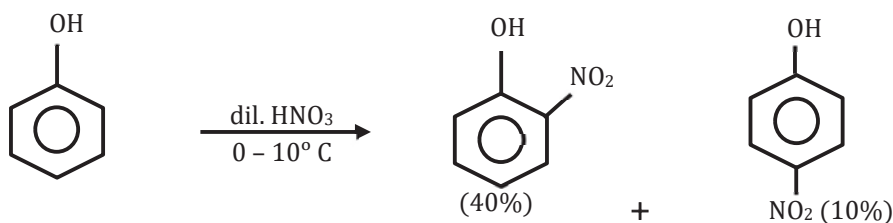
The -OH group exhibits ortho and para directing effects, effectively activating the benzene ring.



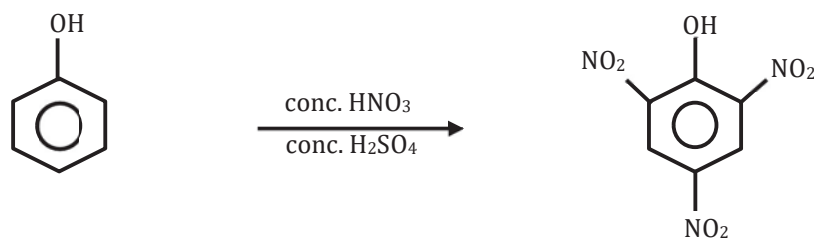
Halogenation: Phenol reacts with bromine in CCl_4 to form mixture of o- and p-bromo phenol.



Phenol reacts with bromine water to form a white ppt. of 2,4,6 tribromo phenol.

**Nitration**

when exposed to diluted HNO_3 at temperatures ranging from 0°C to 10°C , undergoes a reaction that leads to the formation of both o- and p-nitro phenols.

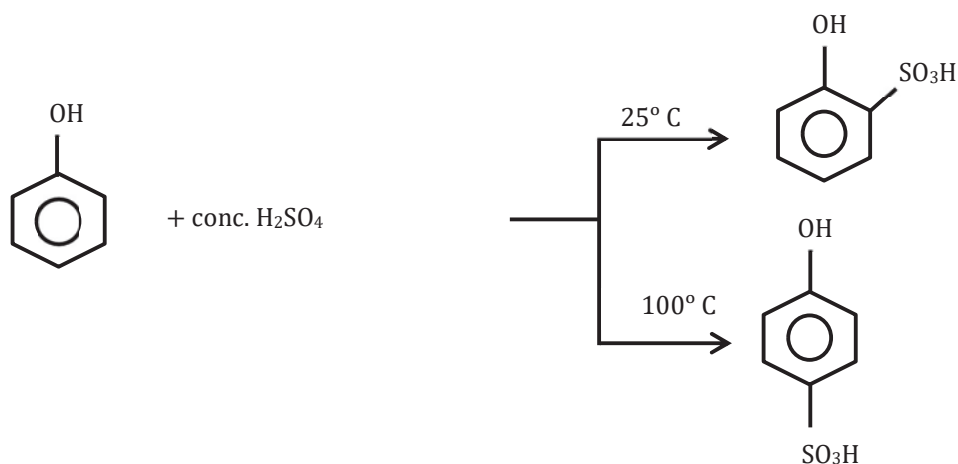


[2, 4, 6-Trinitrophenol (Picric acid)]

Additionally, when phenol is subjected to a nitrating mixture, it results in the production of 2,4,6-trinitro phenol, also known as picric acid.

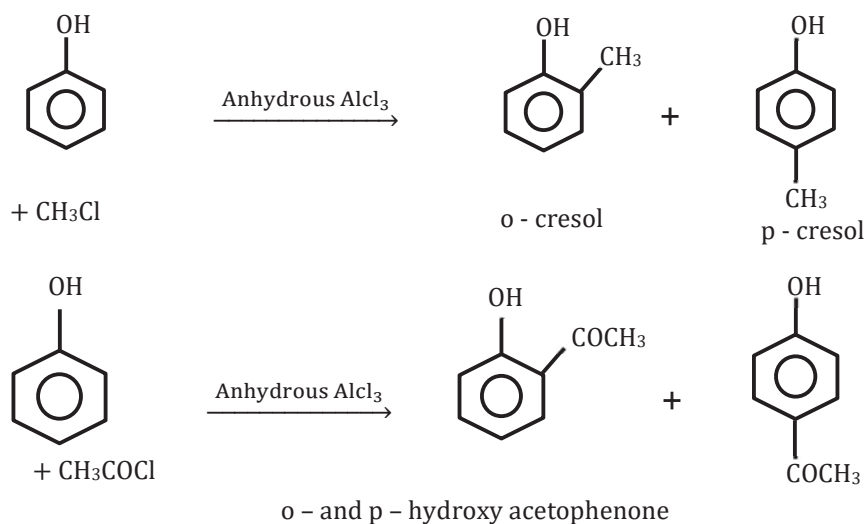
Sulphonation

Phenol reacts with fuming H_2SO_4 to form o- and p-hydroxy benzene sulphonic acid at different temperatures.



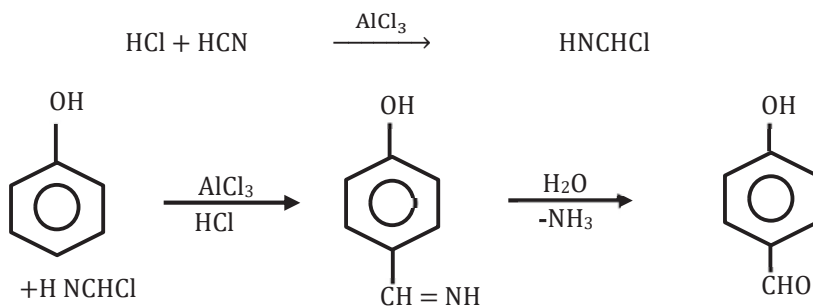
Friedel-Craft's Reaction

Phenol when treated with methyl chloride in presence of anhydrous AlCl_3 p-cresol is main product.



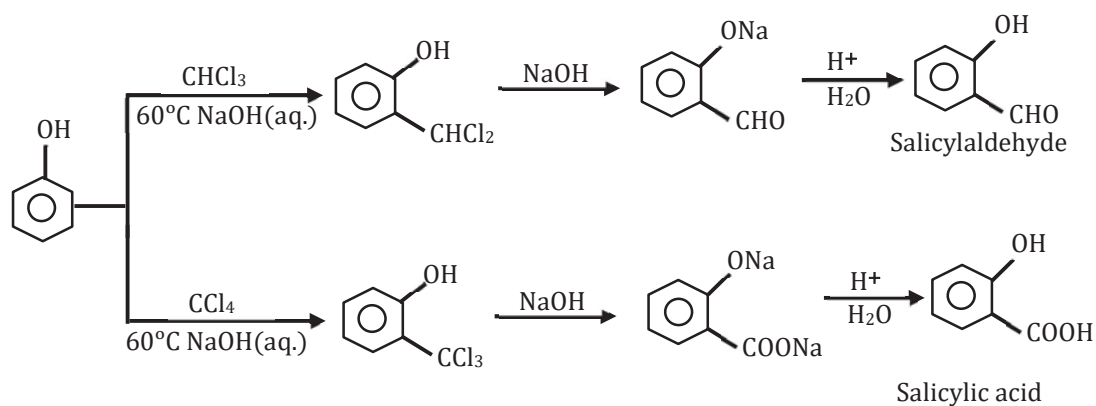
Gattermann Aldehyde Synthesis

The treatment of phenol with liquid HCN and HCl gas in the presence of anhydrous AlCl_3 primarily results in the formation of p-hydroxy benzaldehyde through a formylation reaction.



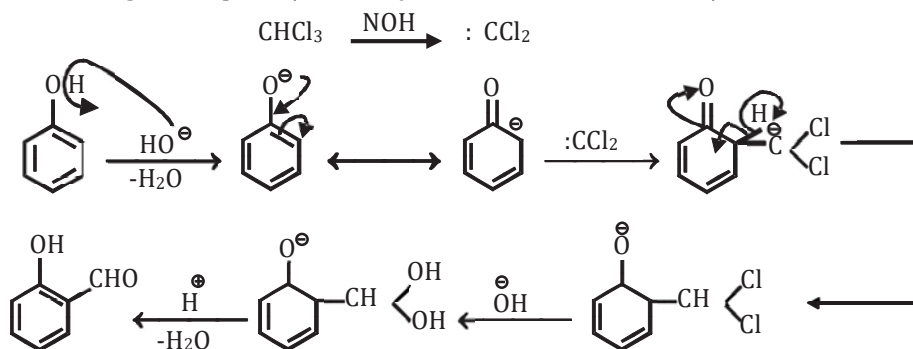
Riemer-Tiemann Reaction

When phenol is subjected to reflux with chloroform and aqueous NaOH, followed by acid hydrolysis, it produces o-hydroxy benzaldehyde. However, if CCl_4 is employed, salicylic acid is generated instead.



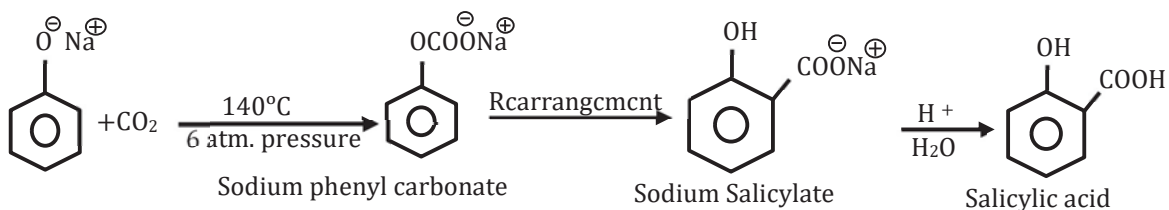
Mechanism

CCl_2 is neutral attacking electrophile (formed by α, α -elimination reaction)

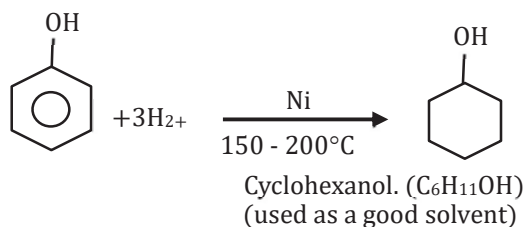


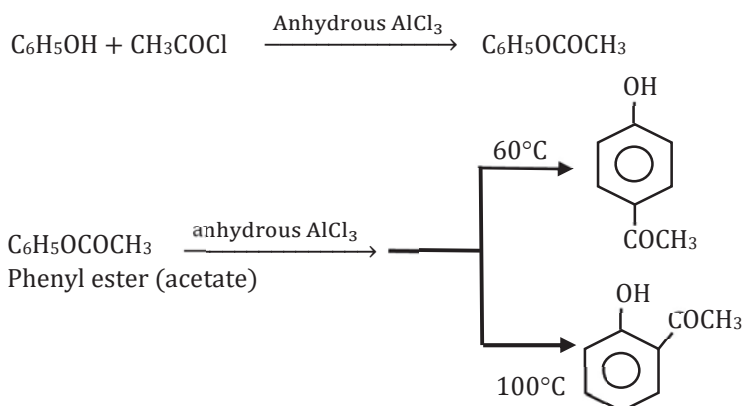
Kolbe's Schmidt Reaction

This process entails the reaction of $\text{C}_6\text{H}_5\text{ONa}$ with CO_2 at 140°C , and it is followed by the formation of salicylic acid through acid hydrolysis.

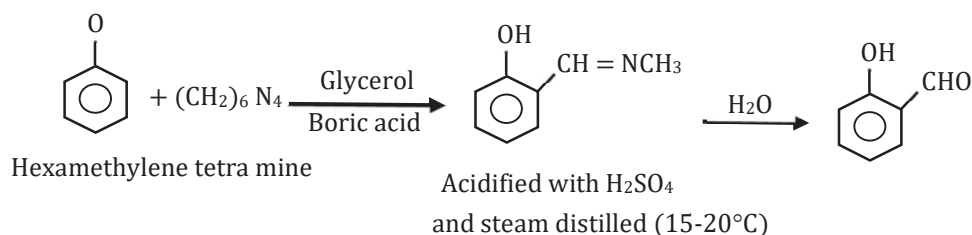


Hydrogenation: When phenol is subjected to hydrogenation in the presence of nickel catalyst at a temperature range of 150 - 200°C , it transforms into cyclohexanol.

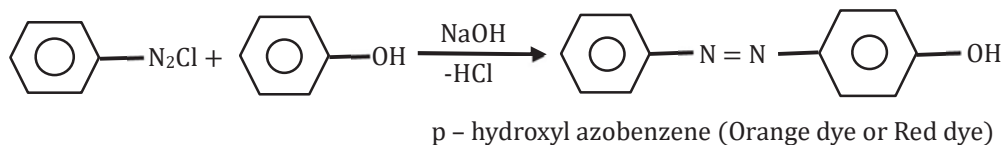


Fries' Rearrangement Reaction

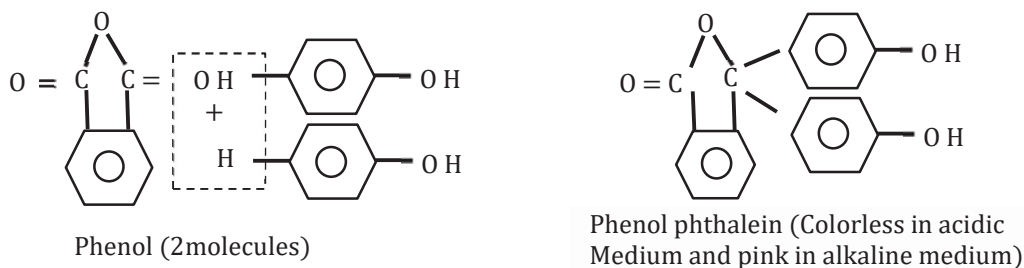
Duff's reaction: This approach exclusively yields the o-compound due to the hindrance caused by the presence of a -I group within the ring.



Coupling reactions: Phenol, in the presence of an alkaline solution, undergoes coupling with benzene diazonium chloride, resulting in the creation of a red dye known as p-hydroxy azobenzene.

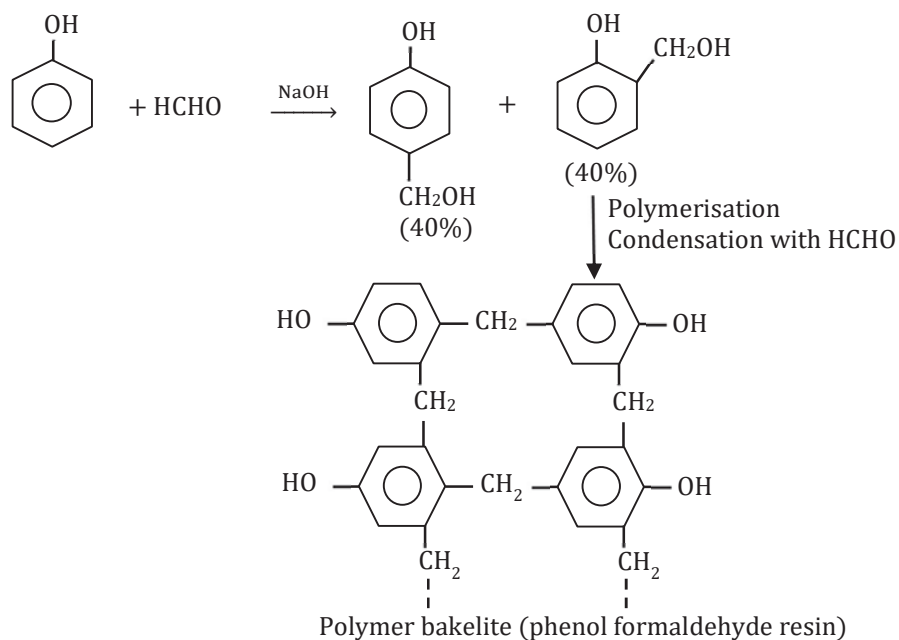


Phenol couples with phthalic anhydride in presence of conc. H_2SO_4 to form a dye (phenol phthalein) used as an indicator.



Lederer Manasse (Condensation with Formaldehyde)

Phenol can polymerize when it reacts with an excess of formaldehyde in the presence of either NaOH or a weak acid

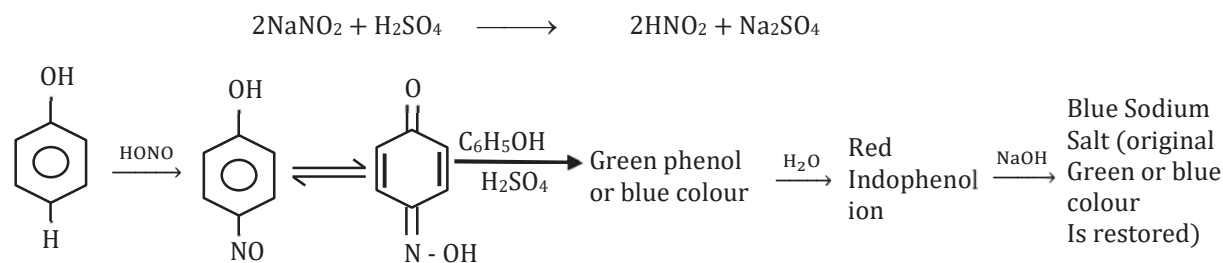
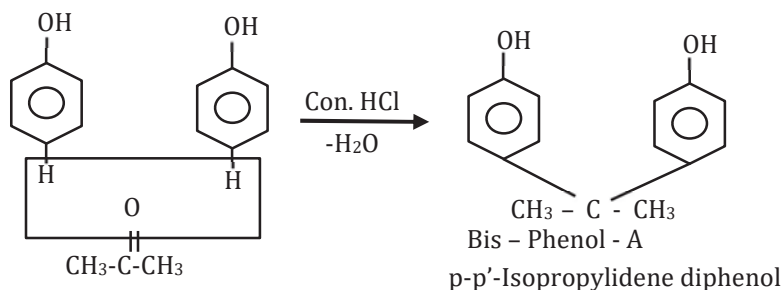


(H^+), leading to the formation of a polymer commonly referred to as bakelite or a resin.

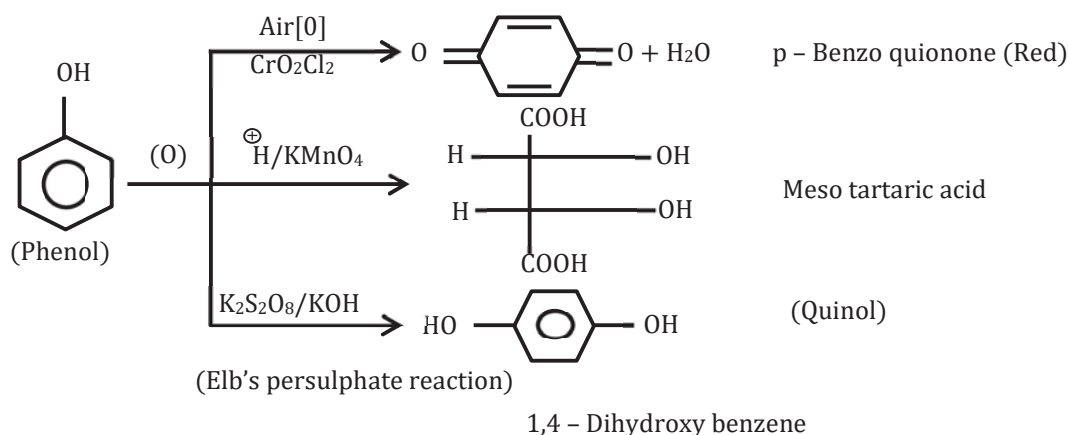
Leibermann's Nitroso Reaction

When phenol undergoes a reaction with NaNO_2 in the presence of concentrated H_2SO_4 , it results in a profound green or blue hue, which subsequently shifts to red when diluted with water. Upon alkaline treatment with NaOH, the initial green or blue color is reinstated.

This reaction is used as a test of phenol.

**Reaction with Acetone
(Condensation with acetone)**

Oxidation

**Test of Phenol and Uses of Phenol****Tests of Phenol**

- Phenol causes blue litmus paper to turn red.
- An aqueous solution of phenol exhibits a violet color when a drop of ferric chloride is added.
- Phenol undergoes Liebermann's nitroso test, resulting in red color in concentrated H_2SO_4 and blue color in dilute H_2SO_4 .
- When an aqueous phenol solution is exposed to bromine water, it forms a white precipitate of 2,4,6-tribromophenol.
- In the presence of concentrated H_2SO_4 , phenol reacts with phthalic anhydride to produce phenolphthalein, which exhibits a pink color in the presence of an alkali.
- When phenol is treated with ammonia and sodium hypochlorite, it produces a blue color.

Differences between Phenol and Alcohol ($\text{C}_2\text{H}_5\text{OH}$)

- Phenol exhibits greater acidity compared to aliphatic alcohols due to the presence of resonance in the phenoxide ion.
- When treated with FeCl_3 , phenol develops a violet color, whereas aliphatic alcohols do not exhibit this reaction.
- Phenol reacts with PCl_5 to form triphenyl phosphate, whereas aliphatic alcohols yield alkyl chlorides.
- Phenol is characterized by a phenolic odor, whereas alcohols have a pleasant odor.
- Upon oxidation, phenol yields quinone, while alcohols produce aldehydes, ketones, or acids.

Uses of Phenol

Phenol is used

- Utilized as an antiseptic in soap and lotion formulations, "Dettol" contains 2,4-Dichloro-3,5-dimethyl phenol.
- Employed in the production of azo dyes, phenolphthalein, picric acid (an explosive), cyclohexanol (used as a solvent for rubber), plastics (such as bakelite), and more.
- Employed in the synthesis of pharmaceuticals like aspirin, salol, phenacetin, and other drugs.
- Serves as a preservative for ink products.