

Phenol

The hydroxyl derivative of benzene is known as Phenol. Its formula is C_6H_5OH .

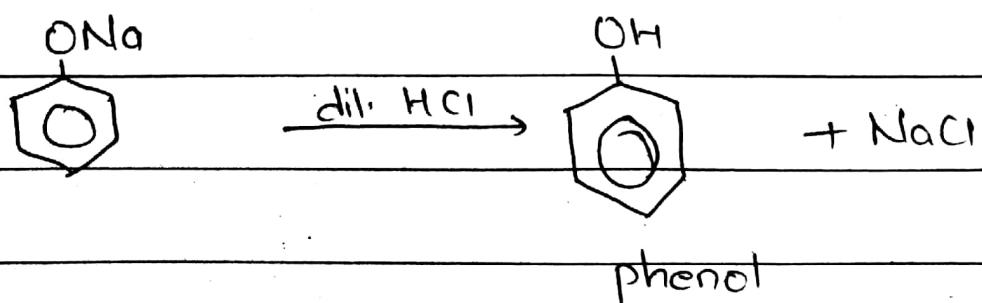
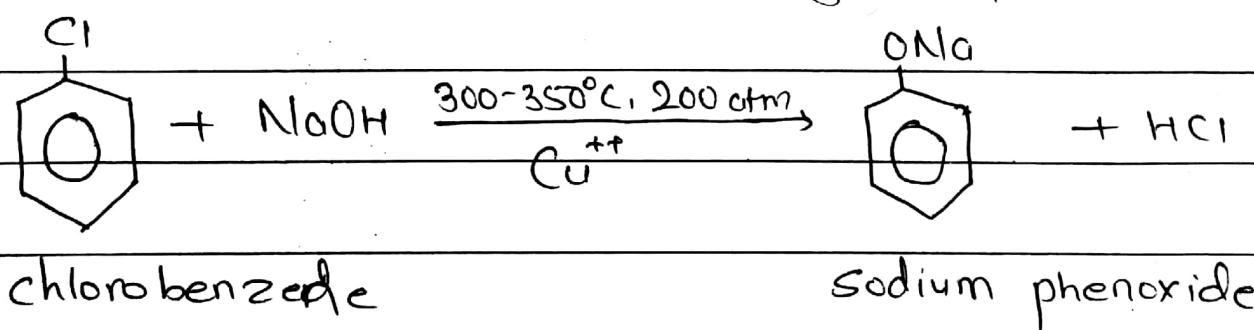


Phenol

General Methods of Preparation of Phenol.

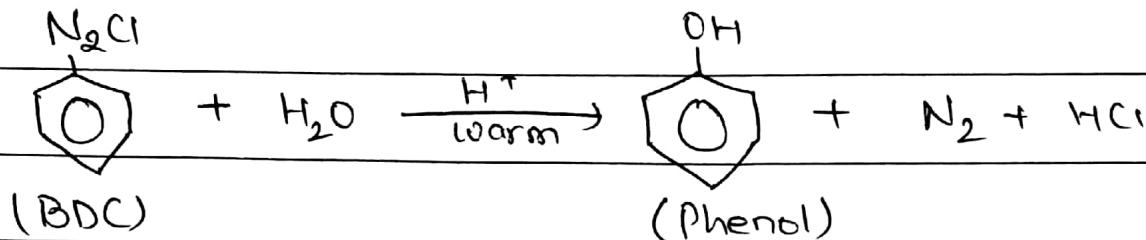
1. From Chlorobenzene (Dow's Process)

When chlorobenzene is heated with 10% Na_2CO_3 or NaOH at $300-350^\circ\text{C}$ under 200 atm pressure in presence of Copper salt then sodium phenoxide is formed which on acidification gives phenol.



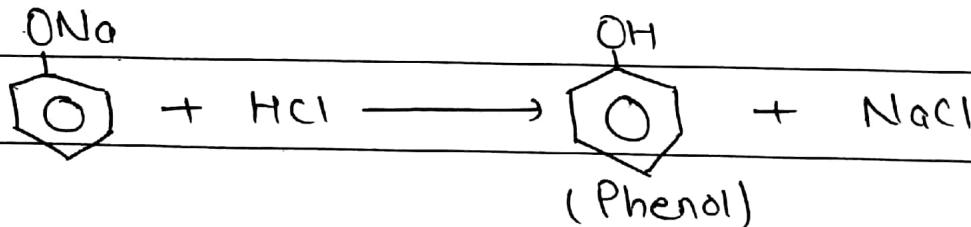
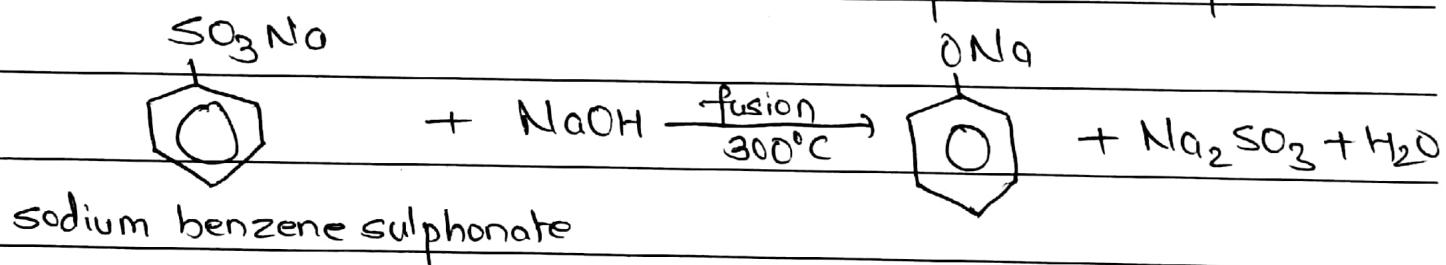
2. From Diazonium Salt

When benzene diazonium salt is treated with warm water in presence of acid then phenol is formed.



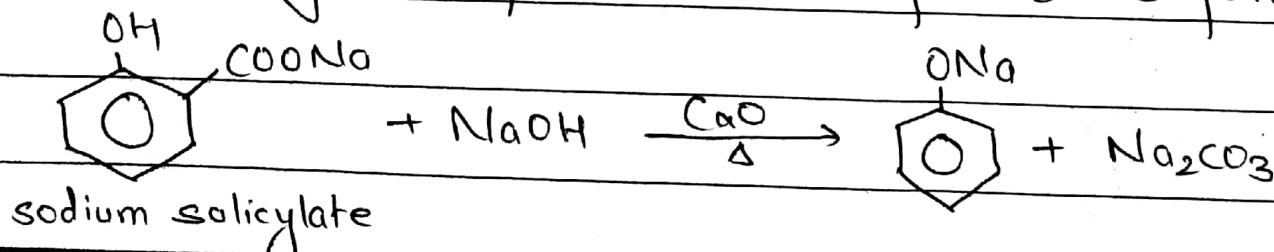
3. From Benzene Sulphonic acid.

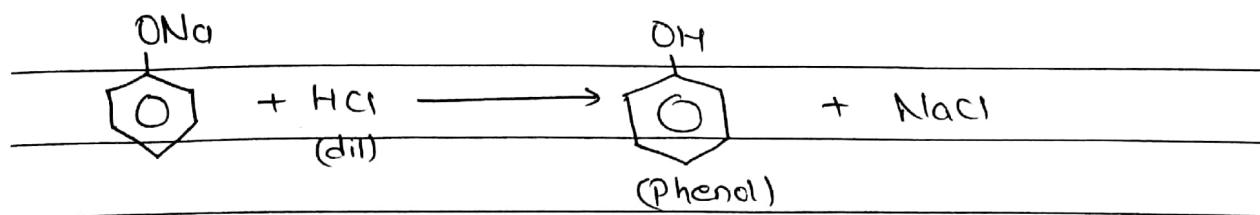
When sodium salt of benzene sulphonic acid is fused with solid NaOH at 300°C followed by treatment with dil. HCl then phenol is formed.



4. From Decarboxylation of sodium salicylate

When sodium salicylate is treated with sodalime followed by acidification then phenol is formed.



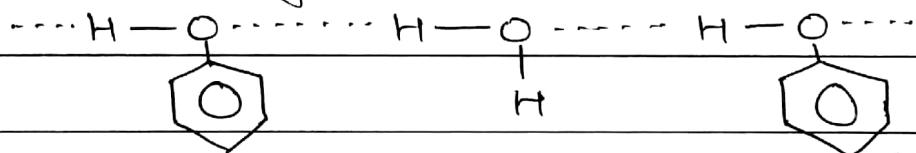


Properties

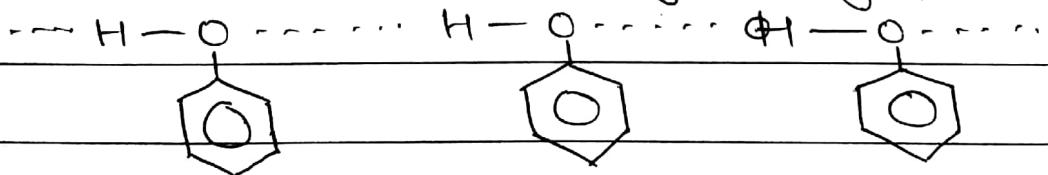
* Physical Properties

1. Phenols are either colourless crystalline solid or liquid having characteristic carbolic smell & antibacterial property.

2. Phenols are slightly soluble in water (due to intermolecular H-bonding with water) but readily soluble in organic solvent.



3. Boiling point of phenols is higher than aromatic hydrocarbons of comparable mol. wt. due to formation of intermolecular H-bonding among phenol molecules.

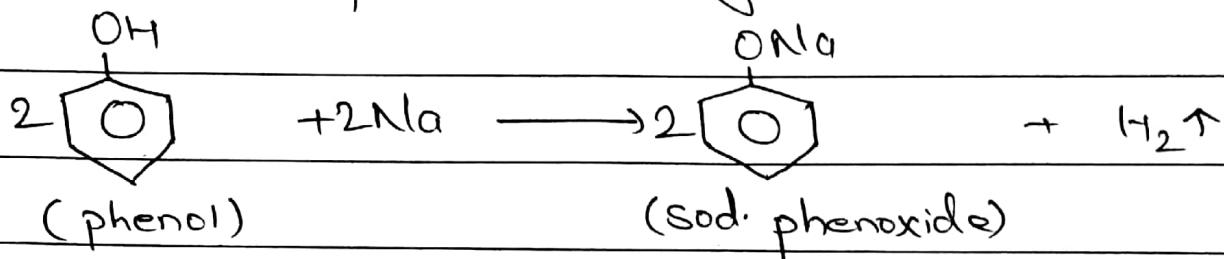


* Chemical Properties

A. Reactions due to $-OH$ group.

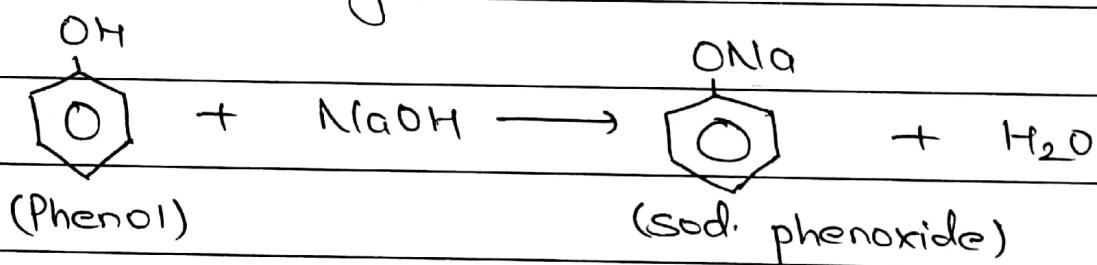
1. Reaction with alkali metal.

Like alcohols, phenol reacts with alkali metals to produce H_2 gas.



2. Reaction with alkali (NaOH or KOH)

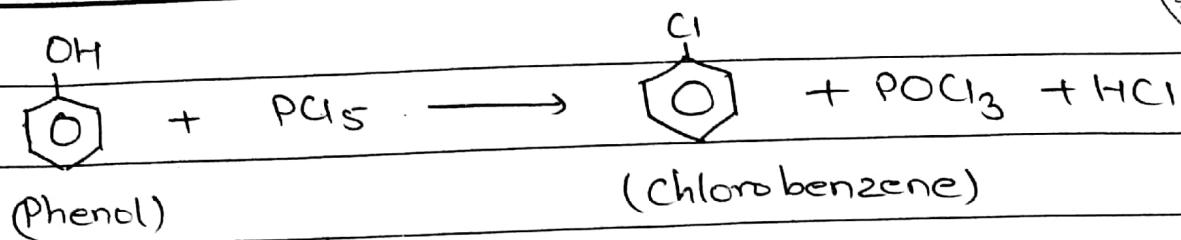
Phenol gives salt & water with alkali



Note: Phenol also does not react with carbonates & bicarbonates like alcohol. So, phenols are weaker acid than carboxylic acid.

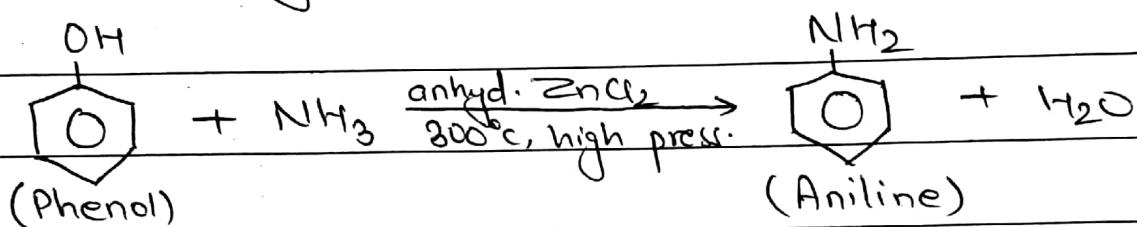
3. Reaction with PCl_5

Like alcohol, phenol reacts with PCl_5 to give chlorobenzene. However, it does not react with PCl_3 , PBr_3 , PI_3 & SOCl_2 .



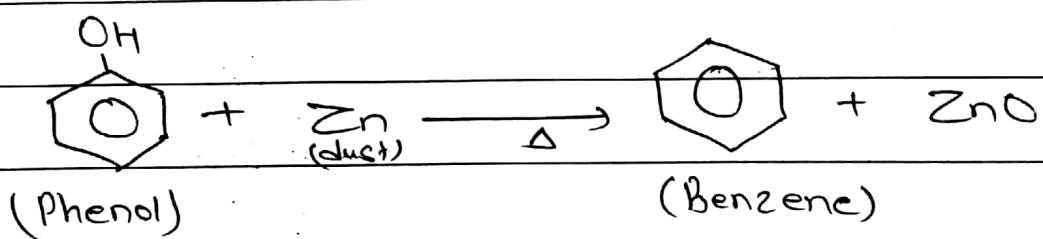
4. Reaction with Ammonia (Bucherer Reaction)

Phenol reacts with ammonia in presence of anhydrous $ZnCl_2$ at $300^\circ C$ temperature & high pressure to give aniline.



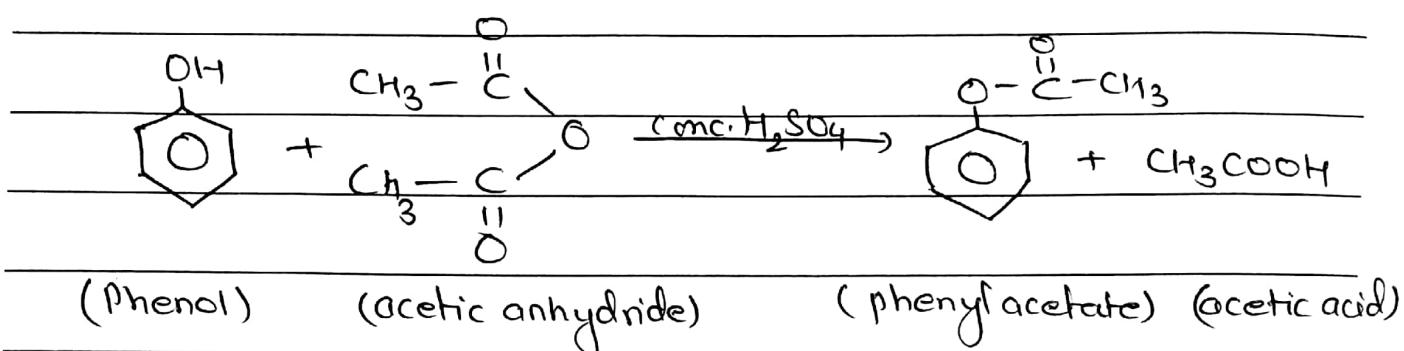
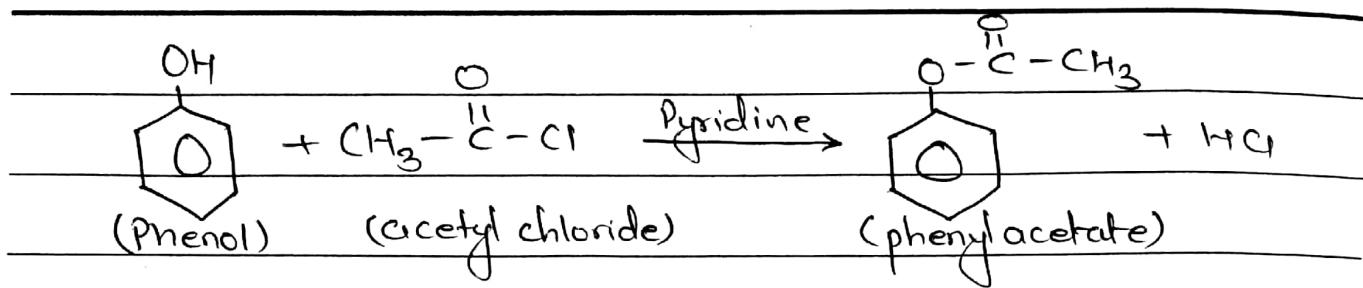
5. Reaction with Zinc dust

Phenol when heated with Zinc dust produces benzene.



6. Reaction with Acid Chloride & Acid Anhydride

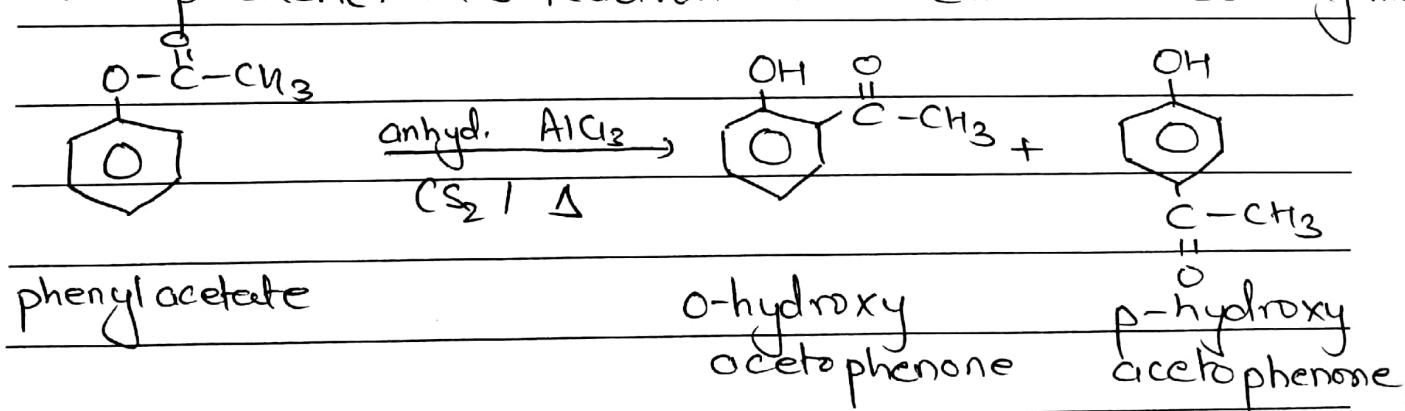
Phenol reacts with acid chloride in presence of pyridine & acid anhydride in presence of conc. H_2SO_4 to give corresponding esters.



~~V. imp~~

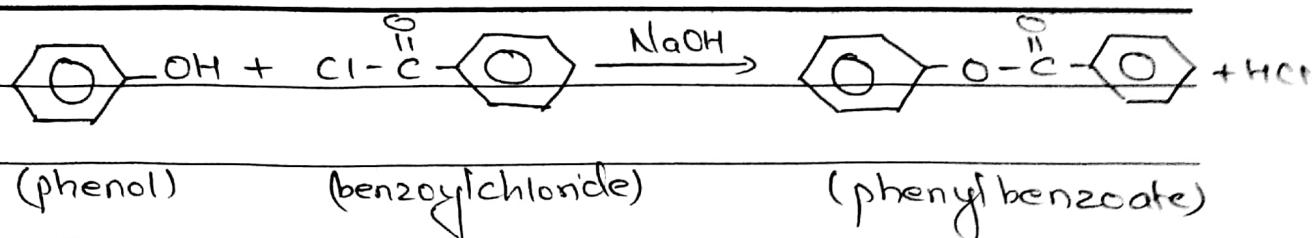
Fries Rearrangement

Phenylacetate when heated with anhydrous AlCl_3 in presence of CS_2 as solvent, it undergoes rearrangement to give ortho- & para-hydroxy acetophenone. This reaction is called Fries rearrangement.



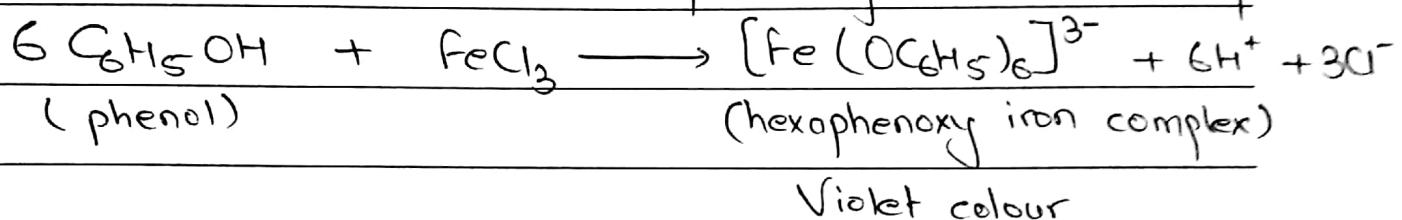
7. Reaction with Benzoylchloride

Phenol reacts with benzoyl chloride in presence of alkali to give phenylbenzoate. This reaction is known as Schotten-Baumann Reaction.



8. Reaction with ferric chloride (Test Reaction of Phenol)

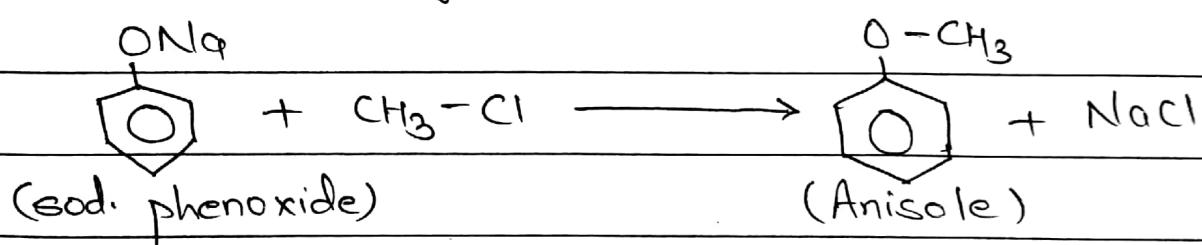
Phenol reacts with neutral FeCl_3 to give water soluble violet coloured hexaphenoxy iron(III) complex.



9. Reaction with alkyl halide (formation of ether)

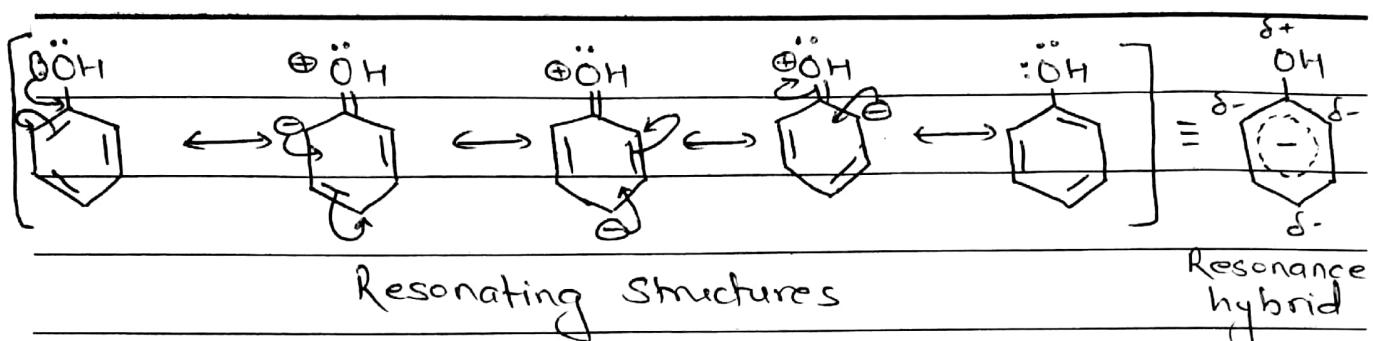
When sodium phenoxide is treated with chloromethane, then anisole is formed.

(Williamson's Synthesis)



B. Reaction involving Benzene Ring.

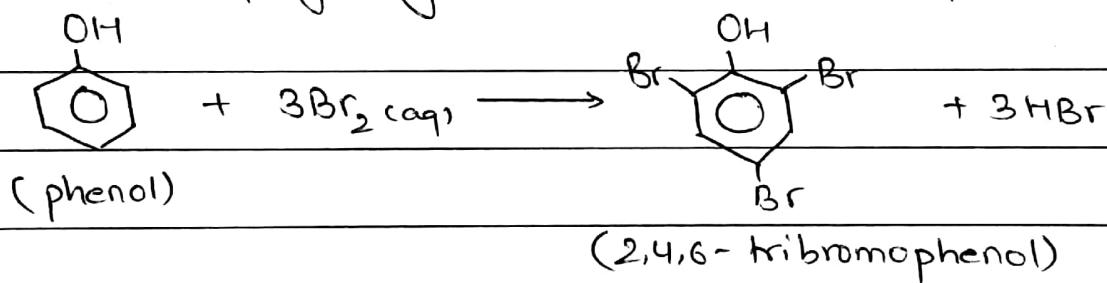
Since $-\text{OH}$ group in phenol is ortho-, para-director so the incoming electrophile in phenol are substituted at ortho- & para- positions.



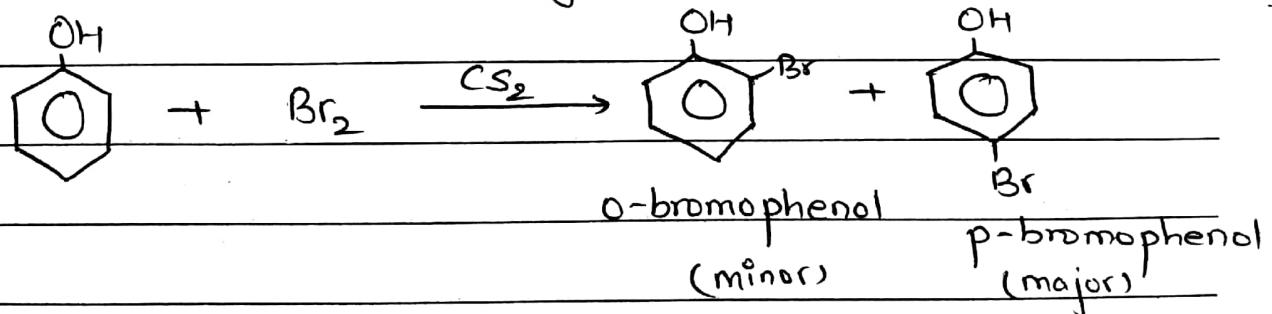
Due to the presence of one charge at ortho- & para- positions in benzene ring, the incoming electrophile are attached at o- & p- position.

1. Halogenation

When phenol is treated with halogen in aqueous solution then polyhalogen substituted compounds.

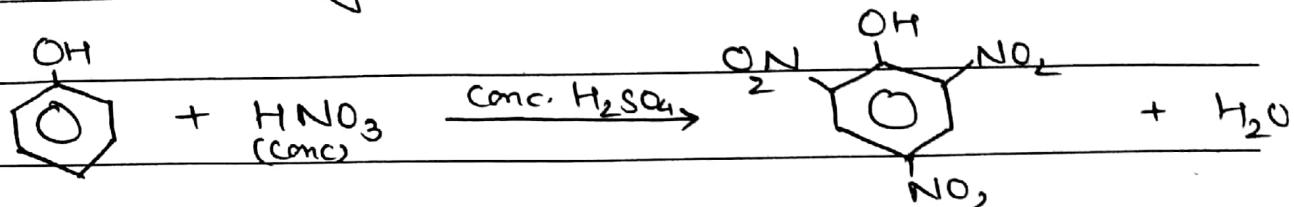


But, if halogenation is carried out in presence of less polar solvent at low temperature then ortho or para monohalogen derivatives are obtained.



2. Nitration

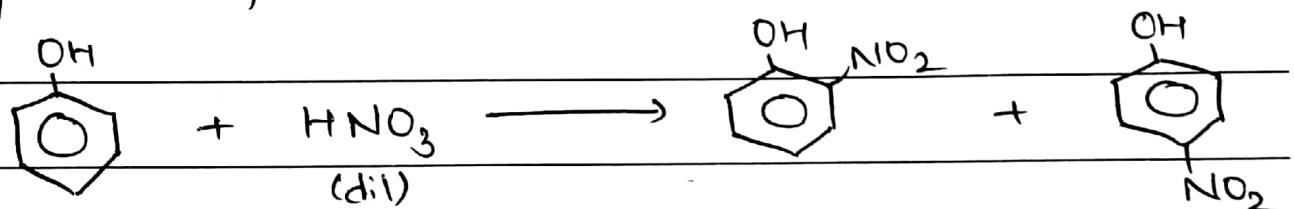
Phenol reacts with conc. HNO_3 in presence of conc. H_2SO_4 to give Picric acid.



(Phenol)

2,4,6-trinitrophenol
(Picric acid)

But, with dil. HNO_3 , phenol gives ortho-nitrophenol & para-nitrophenol.

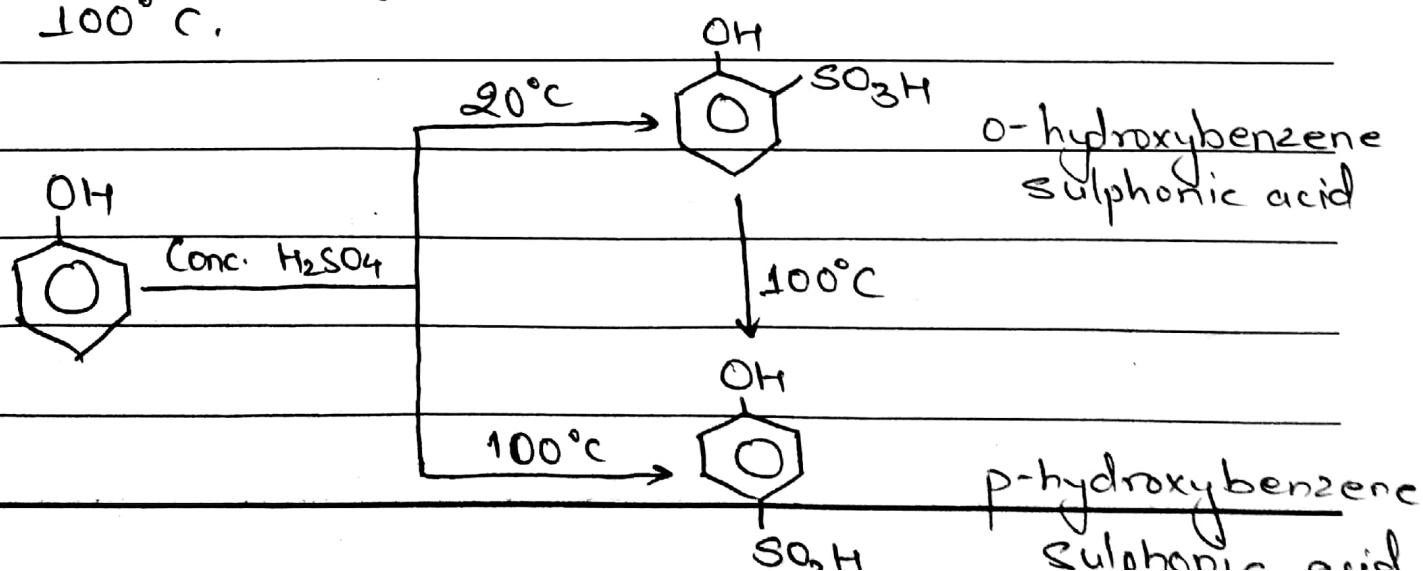


(Phenol)

(o-nitrophenol) (p-nitrophenol)

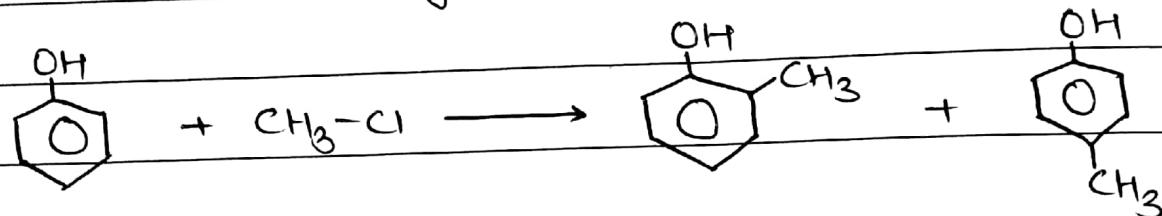
3. Sulphonation

Phenol reacts with conc. sulphuric acid to give ~~α -hydroxysulphur~~ α -hydroxybenzene sulphonic acid at 20°C but gives p -hydroxybenzene sulphonic acid at 100°C .



4. Friedel-Crafts Alkylation

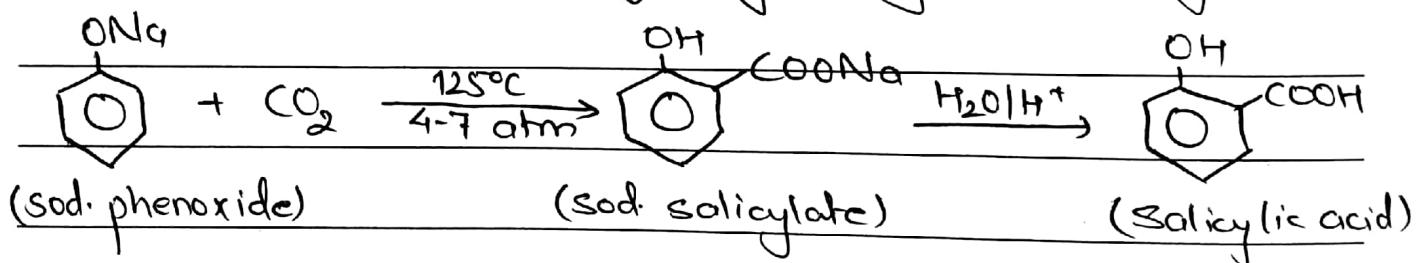
Phenol reacts with alkyl halide in presence of lewis acid to give ortho or para alkylphenol.



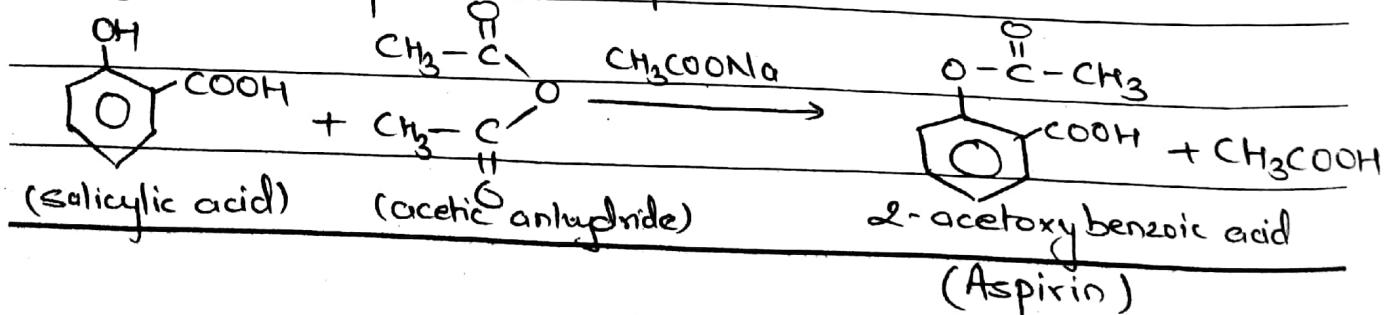
(Phenol)	(chloro methane)	(α -methylphenol)	(4-methylphenol)
		(α -cresol) (minor)	(p -cresol) (major)

S. Kolbe's Reaction

When sod. phenoxide is treated CO_2 at 125°C
under 4-7 atm pressure then carboxylation reaction
occurs to give sodium salicylate which when further
subjected to acidic hydrolysis gives salicylic acid.



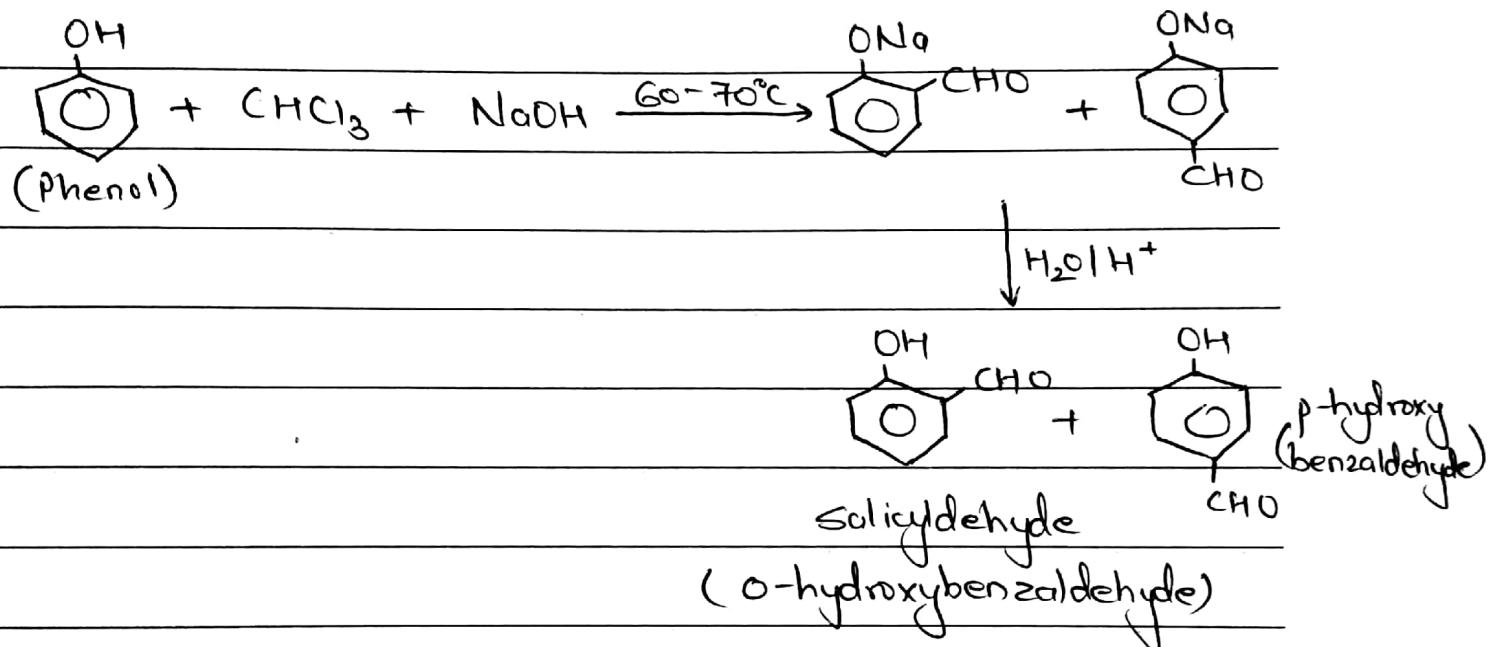
Salicylic acid is the precursor for production of Aspirin which is an analgesic & antipyretic drug.
It is obtained by treating salicylic acid with acetic anhydride in presence of sodium acetate.



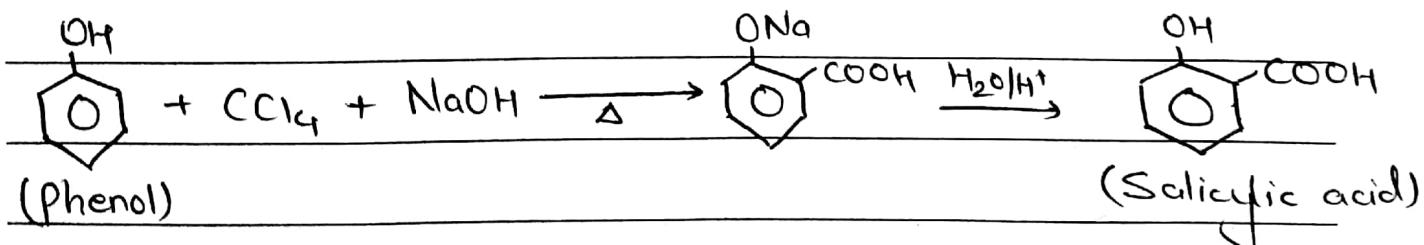
6. Reimer - Tiemann's Reaction

Phenol when refluxed with chloroform in eq.

NaOH at about $60-70^{\circ}\text{C}$ followed by acidic hydrolysis gives salicyldehyde as major product along with p -hydroxybenzaldehyde. This reaction is known as Reimer - Tiemann's Reaction.

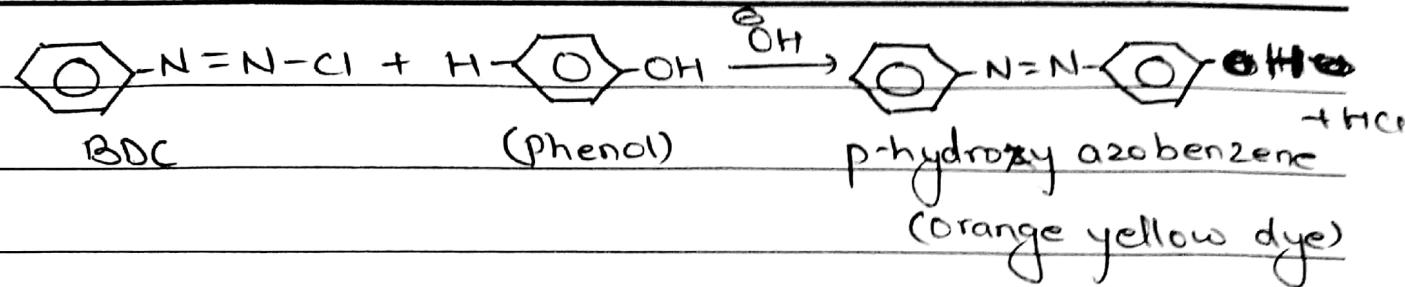


If CCl_4 is used instead of CHCl_3 then salicylic acid is formed.



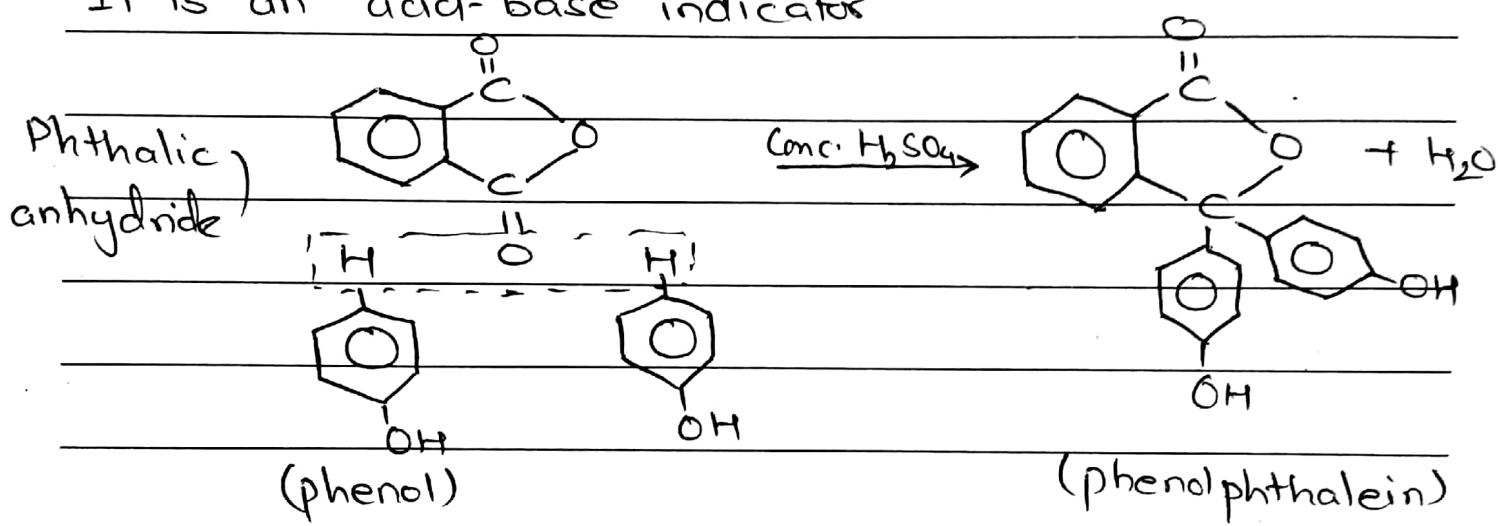
7. Coupling Reaction

Phenol reacts with benzene diazonium salt in presence of base to form coloured compound called azo dye. This reaction is called coupling reaction.



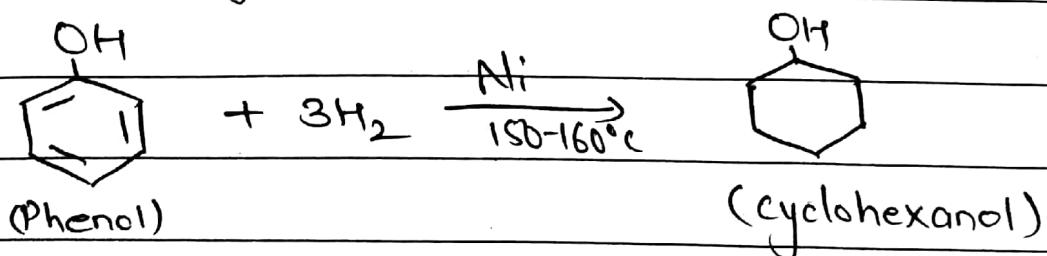
8. Reaction with Phthalic anhydride.

Phenol reacts with phthalic anhydride in presence of dehydrating agent to give phenolphthalein. It is an acid-base indicator.



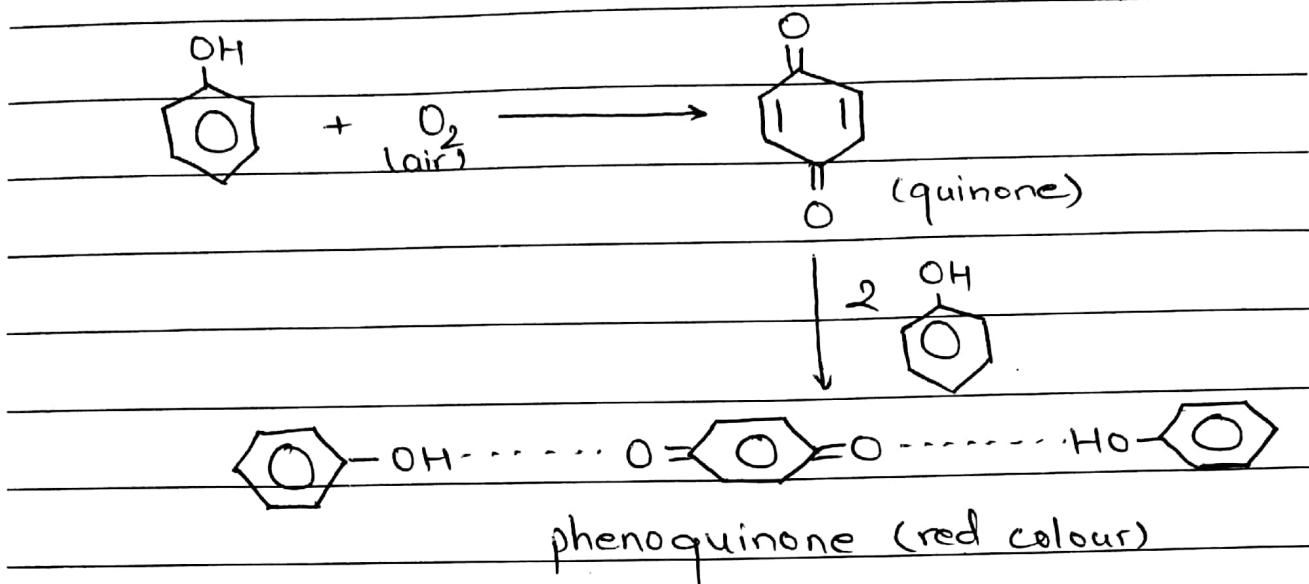
9. Reduction

Phenol is reduced by catalytic hydrogenation to produce cyclohexanol.



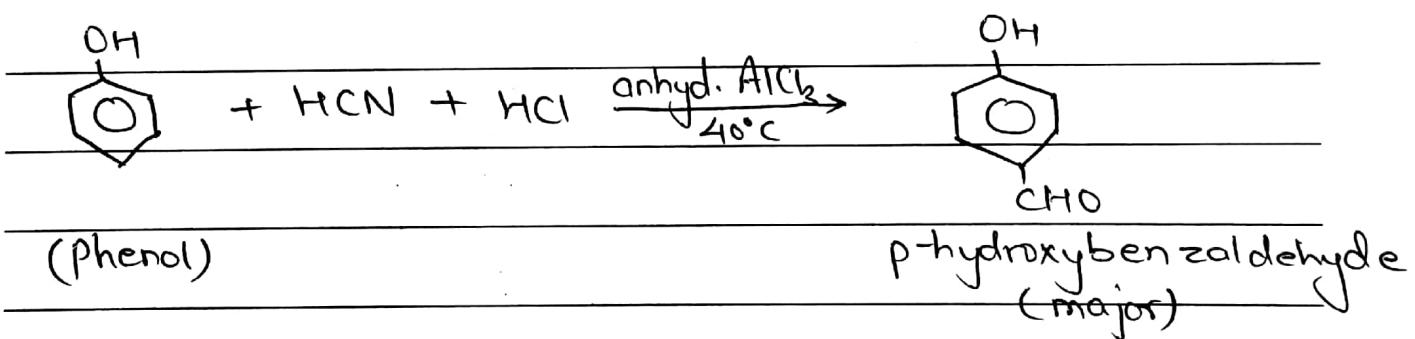
10. Oxidation

Phenol oxidises in atmospheric air to give red coloured product called phenoquinone.



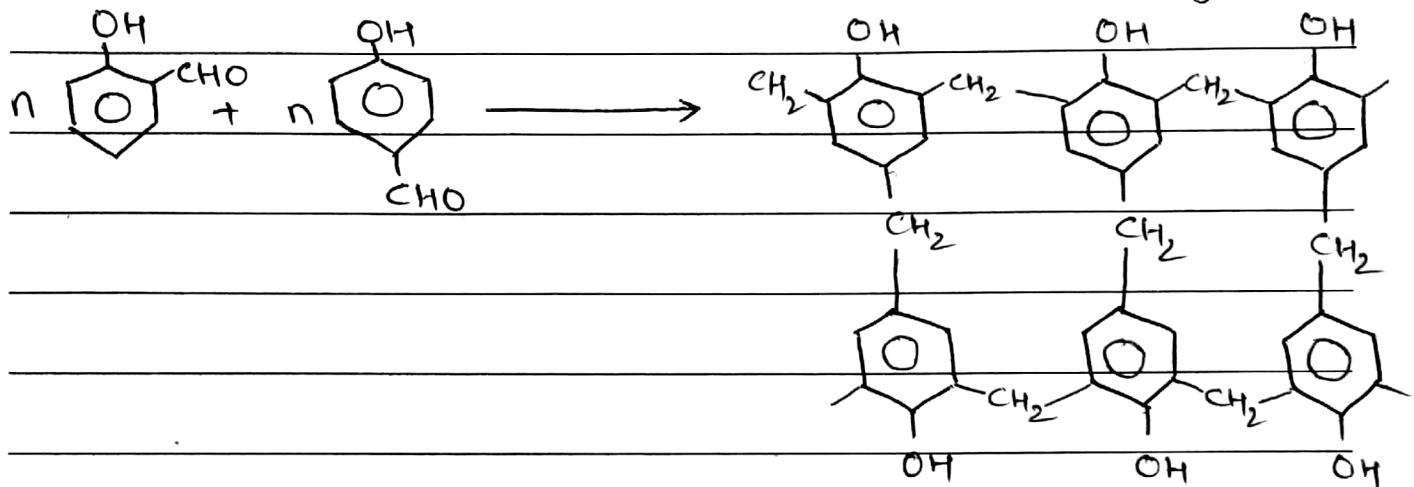
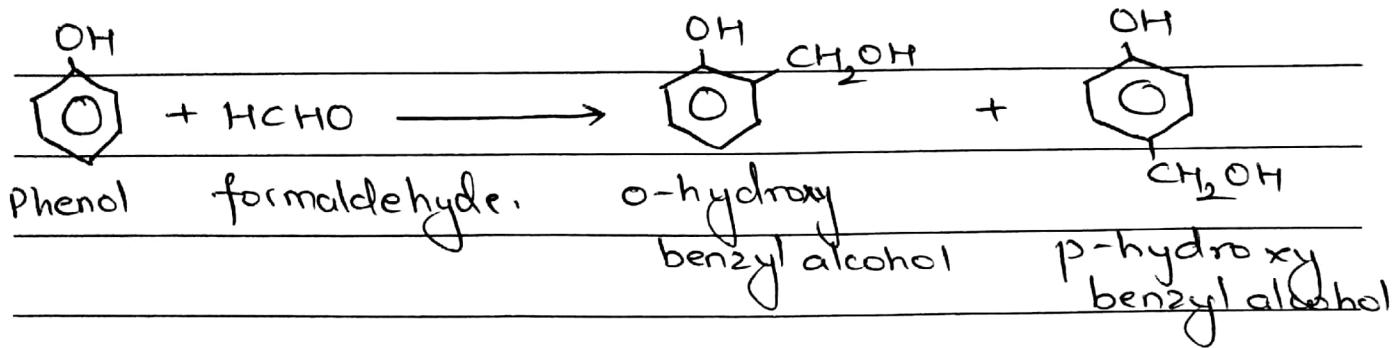
11 Gattermann Reaction

Phenol reacts with liquid HCN & HCl gas in presence of anhydrous $AlCl_3$ to give p-hydroxy benzaldehyde as major product. This reaction is called Gattermann Reaction.



12. Reaction with formaldehyde

Phenol reacts with formaldehyde in presence of alkali or acid as catalyst to form ortho- or para-hydroxy benzyl alcohol which undergoes further cross-linked condensation to form 'bakelite'.



Bakelite

Uses

1. As starting material in manufacture of drugs like aspirin, salol, phenacetin etc.
2. In manufacture of picric acid (explosive), bakelite (resin), phenolphthalein (indicator), dye etc.
3. As an antiseptic & disinfectant
4. As a preservative for ink
5. As gasoline additive
6. for manufacture of cyclohexanol which is used as solvent for rubber & lacquers.