आईएफटीएम विश्वविद्यालय, मुरादाबाद, उत्तर प्रदेश

IFTM University, Moradabad, Uttar Pradesh

NAAC ACCREDITED

E-Content

IFTM University, Moradabad

UNIT 2

TOPIC
PHENOLS

PHENOLS

- The class of organic compounds where one or more hydroxyl groups (-OH) attached to a carbon atom that is part of an aromatic ring is termed as Phenols. The simplest is Phenol (C_6H_5OH).

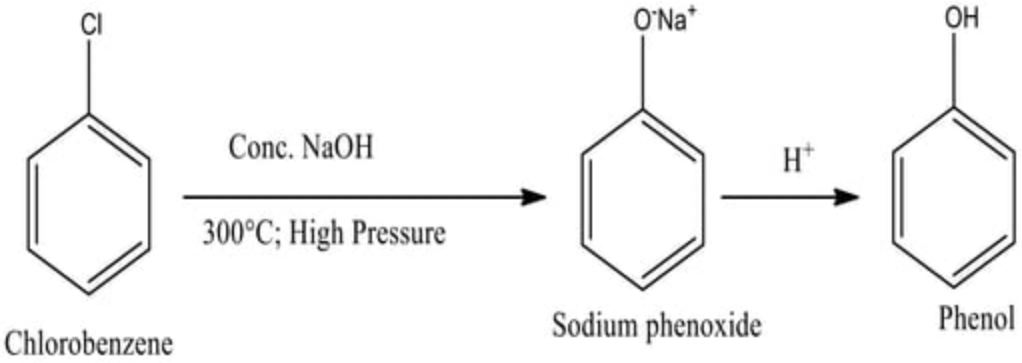
- PHYSICAL PROPERTIES

- Phenols are generally colorless solids at room temperature. On exposure to air, phenol becomes reddish in colour.

- Phenols are slightly soluble in water and their solubility increases with an increase in temperature. Phenol is also known as Carbolic acid.

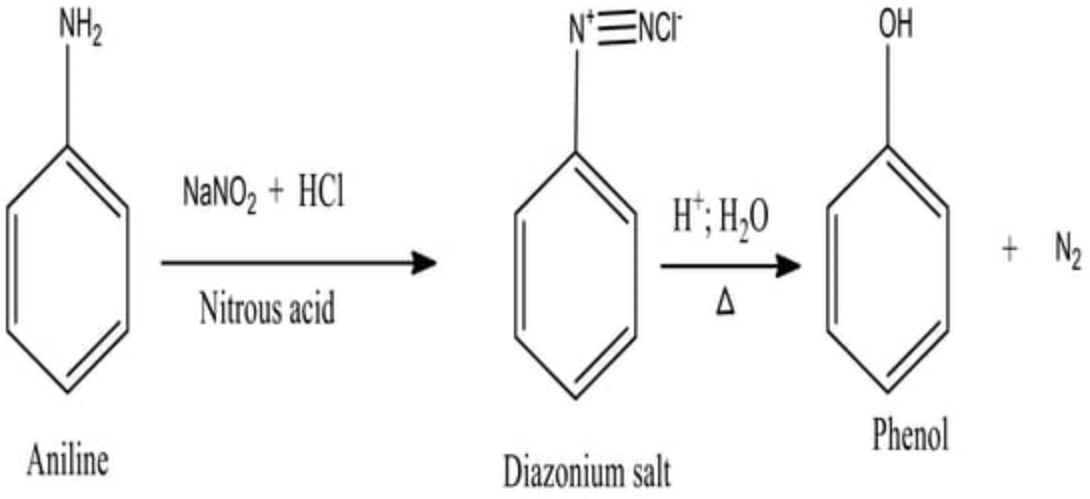
PREPARATION OF PHENOLS

- DOW'S PROCESS- Heating chlorobenzene with conc. NaOH solution at 300°C under high pressure results in the formation of sodium salt of phenol, which in acidic medium liberates free phenol.



- FROM AROMATIC AMINES

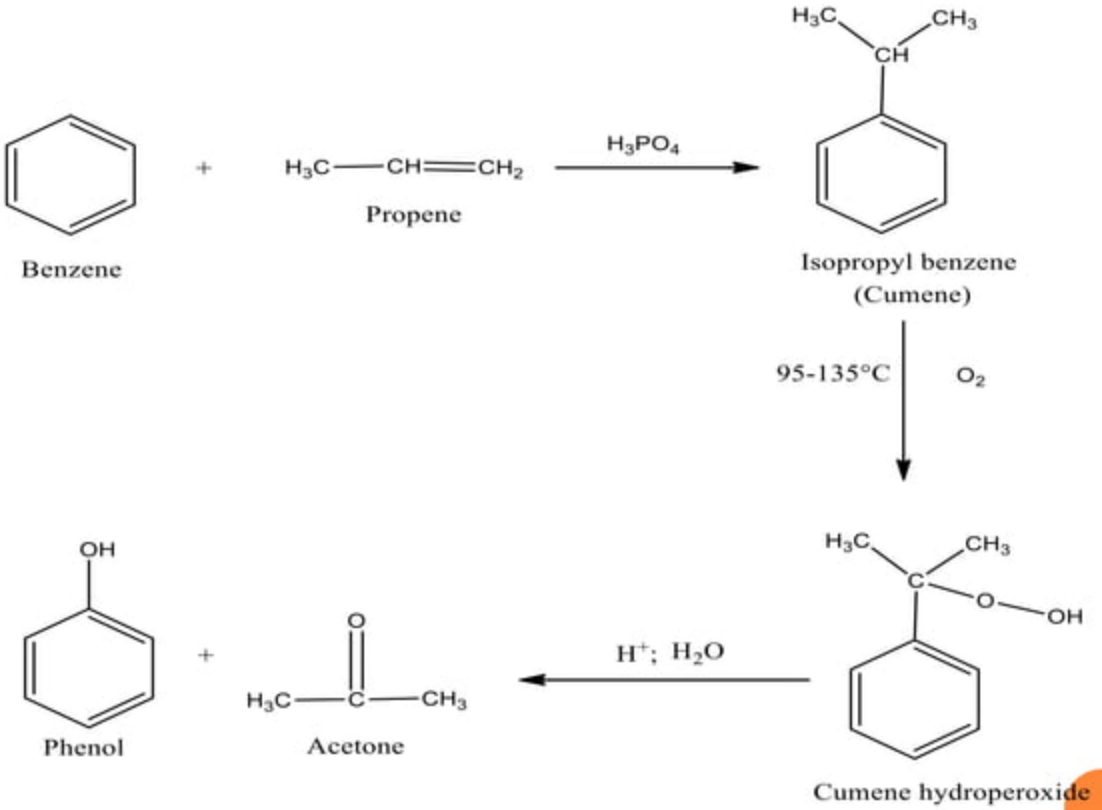
- Aniline in the presence of nitrous acid form diazonium salt; which in the presence of water form phenol.



- FROM CUMEME (AN INDUSTRIAL PROCESS FOR PREPARATION OF PHENOLS)

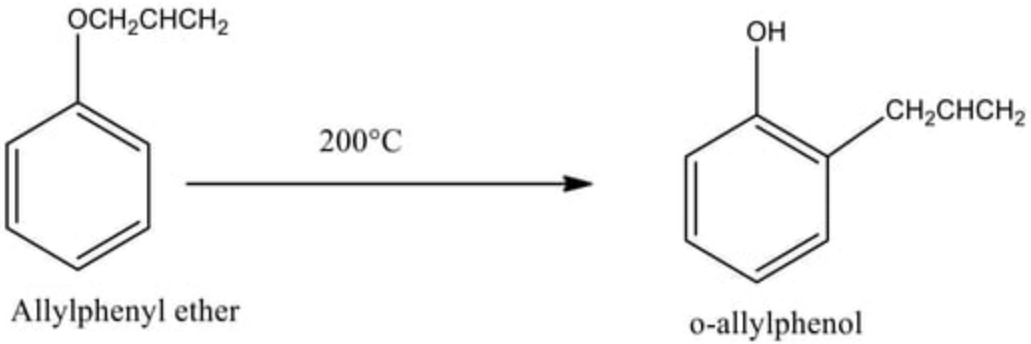
- Benzene on reaction with propene in the presence of phosphoric acid form isopropyl benzene (Cumene).

- The Oxidation of Cumene results in the formation of Cumene Hydroperoxide, which on hydrolysis in acidic medium produces phenol and acetone.


Benzene
+
H3C—CH=CH2
Propene
H3PO4
H3C
CH3
CH
Isopropyl benzene
(Cumene)
95-135°C
O2
Cumene hydroperoxide
H+; H2O
OH
Phenol
+
O
H3C—C—CH3
Acetone

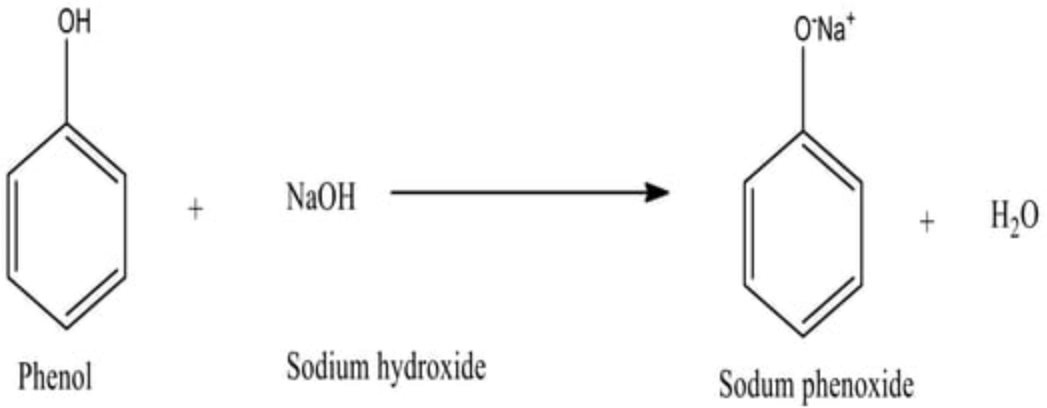
- FROM ALLYL PHENYL ETHER (CLAISEN REARRANGEMENT)

- Allyl Phenyl Ether on heating undergoes an intramolecular rearrangement to form o-allyl phenol and the reaction is known as Claisen rearrangement.



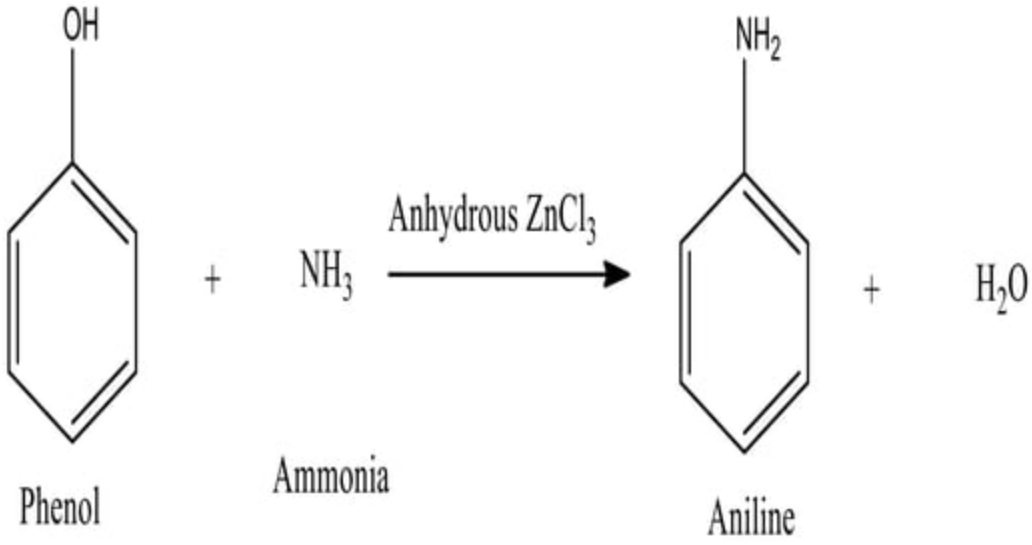
CHEMICAL PROPERTIES

- REACTIONS OF –OH GROUP
  - FORMATION OF SALT
    - Phenol reacts with sodium hydroxide to form salt.



- REACTION WITH AMMONIA

- Phenol reacts with ammonia at high temperature and pressure to form aniline.



- FORMATION OF ESTERS
- Phenol reacts with acid chloride in aqueous alkali solution to give phenyl esters.
- The alkali first forms the phenoxide ion which then reacts with the acid chloride to give phenyl ester.

Phenol — Sodium hydroxide — Sodium phenoxide

Sodium phenoxide — Acetyl chloride — Phenyl acetate — Sodium chloride

Sodium phenoxide — Benzoyl chloride — Phenyl benzoate — NaCl

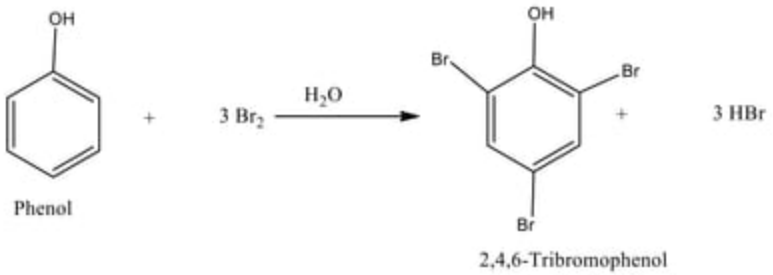
- Reaction of Phenol with Benzoyl chloride is known as **Schotten Baumann reaction.**

- FORMATION OF ETHERS
  - Phenol reacts with Dimethyl sulphate in alkali solution to form anisole (Methoxybenzene).

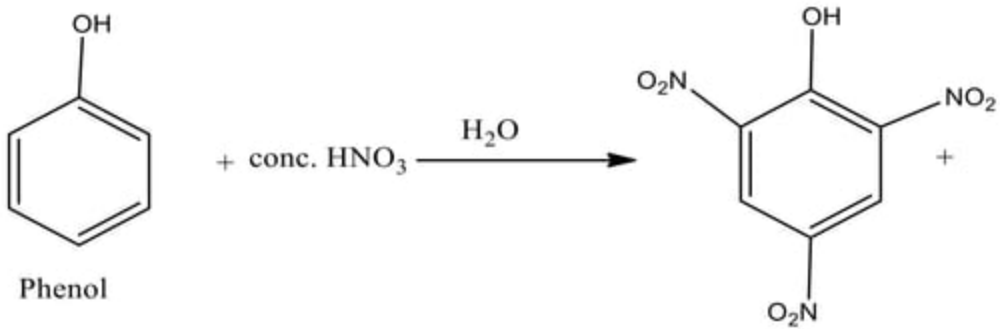
- REACTION WITH ZINC DUST

REACTION OF BENZENE RING

- HALOGENATION
  - Phenol reacts with bromine water (aqueous bromine) to give precipitate of 2,4,6-tribromophenol.



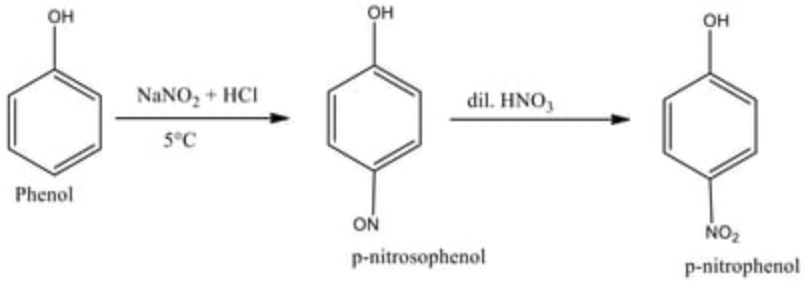
- NITRATION
  - Phenol reacts with concentrated nitric acid to form picric acid.



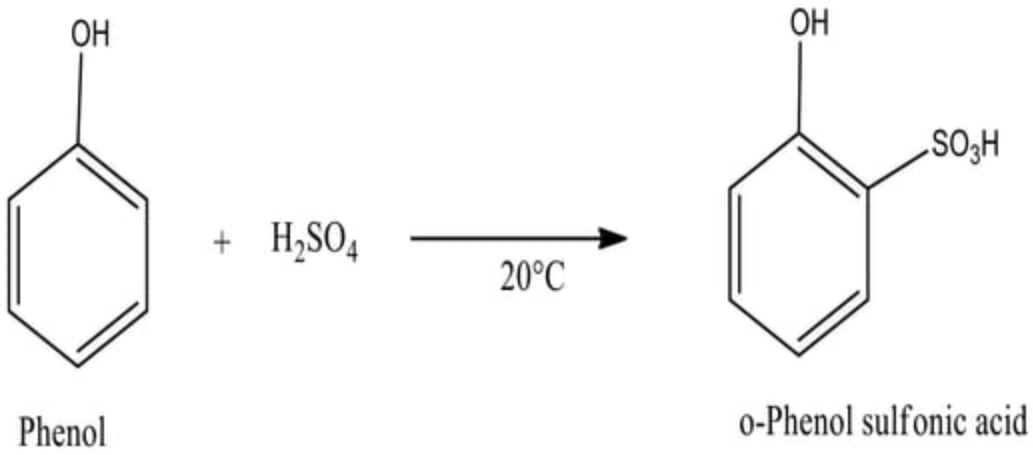
Phenol

2,4,6-Trinitrophenol

- NITROSATION
- Phenol reacts with nitrous acid (obtained from Sodium nitrite and HCl at 5 °C) to form *p*-nitrosophenol.
- *p*-nitrosophenol on oxidation with dil. Nitric acid gives *p*-nitrophenol.

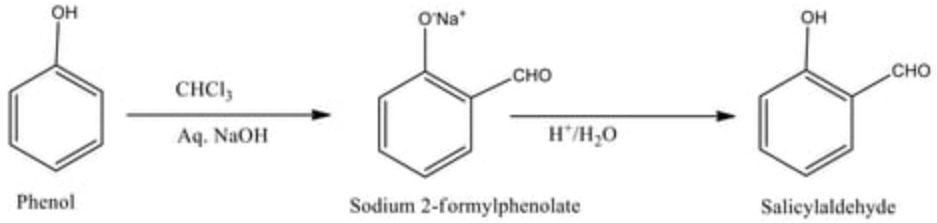


- SULFONATION
  - When Phenol is treated with concentrated sulphuric acid at 20 °C, *o*-phenolsulfonic acid is formed.



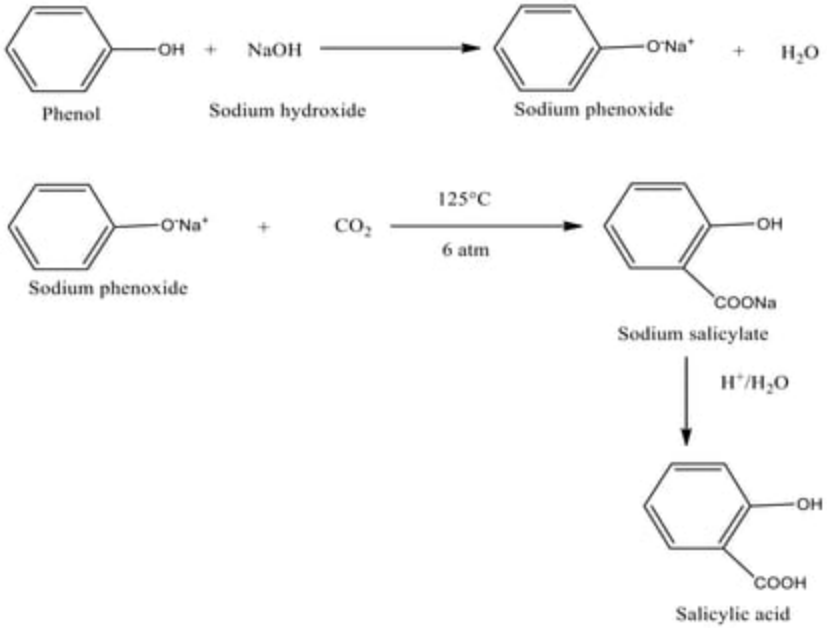
REIMER-TIEMANN REACTION

- This involves treatment of phenol with chloroform in aqueous sodium hydroxide solution followed by acid-hydrolysis. Salicylaldehyde is formed.



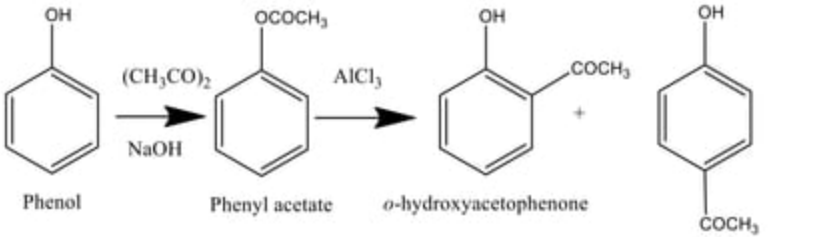
KOLBE REACTION

- Phenol reacts with sodium hydroxide to form sodium phenoxide.
- Sodium phenoxide reacts with carbon dioxide at 125 °C at 6 atm pressure followed by acid hydrolysis to form salicylic acid.



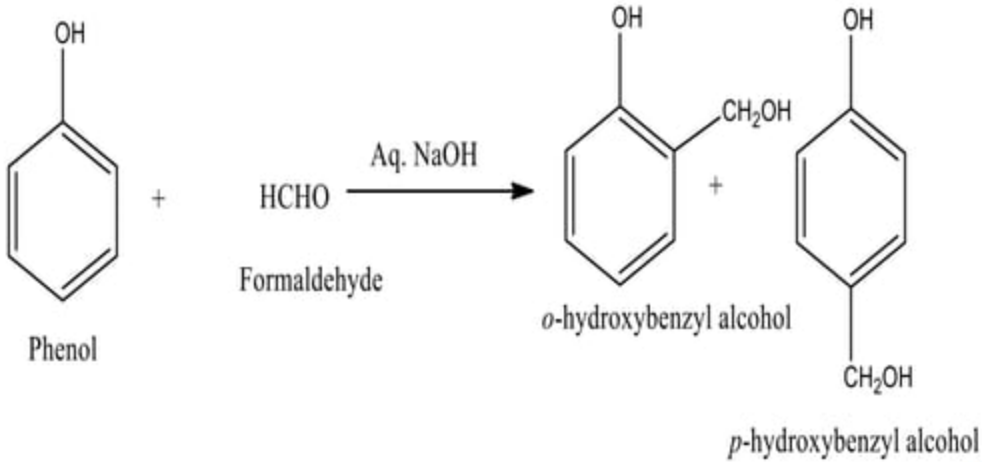
FRIES REARRANGEMENT

- The Phenol is first treated with acetic anhydride in the presence of aqueous NaOH to give phenyl acetate.
- The ester is then heated with aluminium chloride catalyst; the acyl group migrates from the phenolic oxygen to an ortho or para position of the ring.



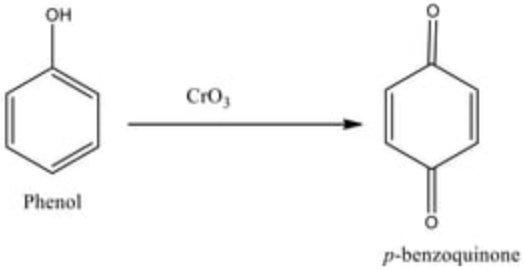
REACTION WITH FORMALDEHYDE

- When Phenol is treated with an alkaline solution of formaldehyde, a mixture of *o*- and *p*-hydroxybenzyl alcohol is formed.



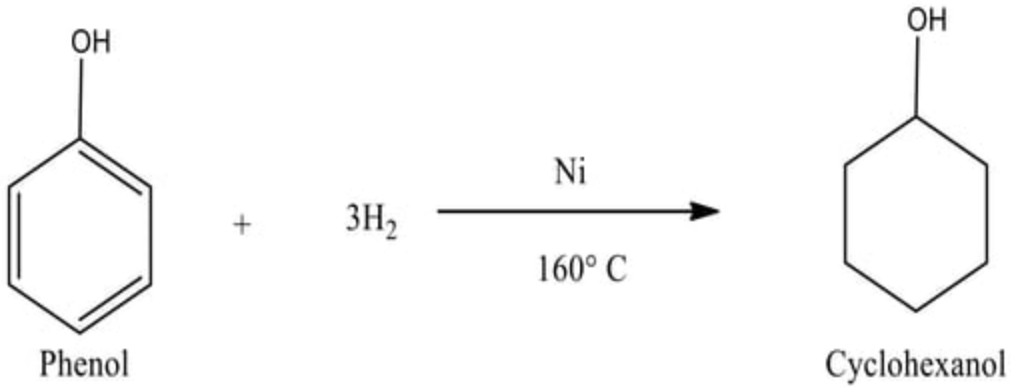
OXIDATION

- Phenol undergoes oxidation in the presence of chromic acid to form *p*-benzoquinone.



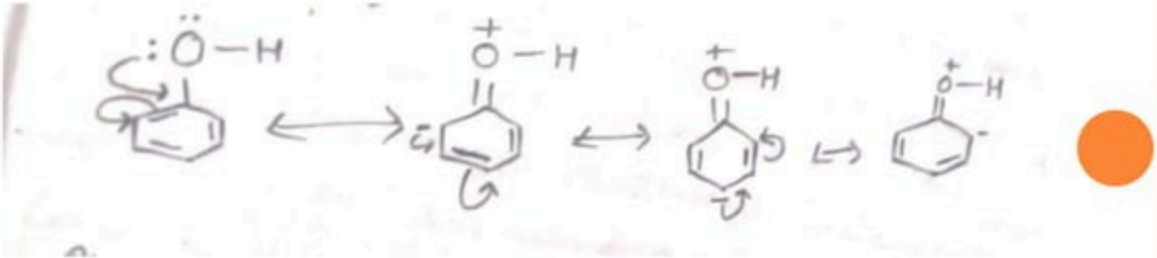
CATALYTIC HYDROGENTION

- Phenol on catalytic hydrogenation gives Cyclohexanol at 160°C.

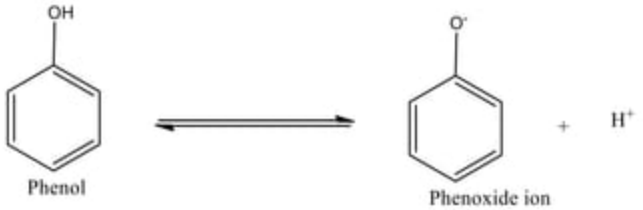


ACIDIC NATURE OF PHENOL: A GENERAL DISCUSSION

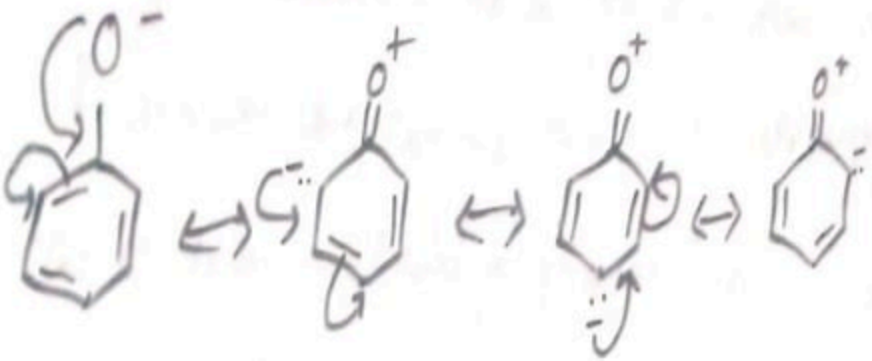
- Phenols are acidic in nature. The acidic nature of phenol is attributed to the +R effect in phenol.
- Due to +R effect, the oxygen develops a positive charge and thereby registers reduced hold on hydrogen.
- This results in the weakening of the O-H bond and makes the removal of hydrogen as proton (H^+) to occur readily thereby making the phenol acidic.



- Phenols are much more acidic than alcohols but less than carboxylic acids.
- Phenols are acidic due to the formation of stable phenoxide ions in aqueous solutions.
- For example, phenol itself gives phenoxide ion on dissociation.

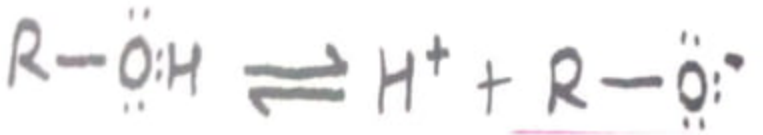


- The phenoxide ion is stable due to resonance.



- Notice that the negative charge is spread throughout the benzene ring and thereby effectively dispersed.
- This charge delocalization is a stabilizing factor in the phenoxide ion.

- On the other hand no resonance is possible in the alkoxide ion (RO^-) derived from the alcohols. The negative charge is localized on a single oxygen atom.



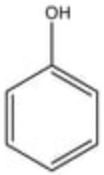
Alkoxide ion

- Consequently alcohol are much weaker acids than phenols.

Effect of substituents on acidic strength of phenol

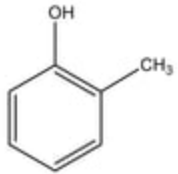
- The electron withdrawing groups (for example -Cl, -CN, -CHO, -COOH) present on aromatic rings increase the acidic strength of phenol.
- The electron withdrawing groups take way the electrons from the ring system and thus increase the positive charge on oxygen of O-H bond. More the positive charge on oxygen, easier the removal of proton and higher the acidic strength.
- The electron releasing groups ($-CH_3$, $-OCH_3$, $-NH_2$) release electrons towards the ring system and this neutralizes or reduces the positive charge on the oxygen atom and makes O-H bond stronger thereby making the removal of proton difficult.
- Lesser the positive charge on oxygen, higher the strength of O-H bond and lesser is the acidic strength of phenol.

STRUCTURE AND USES OF PHENOL

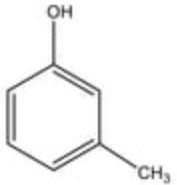


- It is used as powerful antiseptic in soaps and lotions.
- It is used to synthesize bakelite plastic resin.
- It is used in cosmetic surgery as an exfoliant to remove layers of dead skin.
- It is used as a preservative for ink.
- It is used in cosmetic industries in manufacturing of sunscreen, skin lightining creams and hair coloring solutions.

STRUCTURE AND USES OF CRESOLS



o-cresol



m-cresol

p-cresol

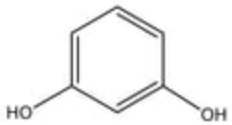
- Alkylation of *o*-cresol gives carvacol which is strong antibacterial agent.
- o-cresol is used in the synthesis of muscle relaxant drug Mephenesin.
- p-cresol is used in the production of butylated hydroxytoluene (BHT) which is an antioxidant.

- *m*-cresol is precursor for various compounds-:
  - Synthetic Vitamin E
  - Amylmetacresol used as antiseptic.
  - Preservative in some insulins.

- *p*-cresol is used in the synthesis of Bupranolol which is a non-selective beta blocker.

- Chloro-*m*-cresol is used as household disinfectant.

STRUCTURE AND USES OF RESORCINOL

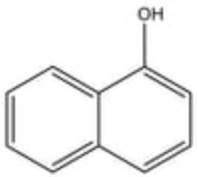


Resorcinol

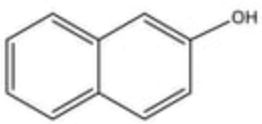
- It is used as antiseptic and disinfectant.
- It is used in antidandruff shampoo ot in sunscream cosmetics.
- Resorcinol has bactericidal effects and can be used as preservatives in cosmetics and dermatological drugs.
- It is used for making wood glue.

- It is used as analytical reagent for determination of ketoses sugar.
- It's ointment (5 to 10 %) is used in the treatment of psoriasis, eczema.
- It is used in the production of plasticizers.

STRUCTURE AND USES OF NAPHTHOLS



1-Naphthol



2-Naphthol

- 1-Naphthol is an ingredient of Molisch's reagent which is used for detecting the presence of carbohydrates.
- 1-Naphthol is a precursor of variety of insecticides like carbanyl.
- 1-Naphthol is used to detect the presence of arginine in proteins by Sakaguchi test.
- 2-Naphthol is a precursor for the preparation of Sudan dye.
- 2-Naphthol is used as an antiseptics and in perfumes.

QUALITATIVE TEST FOR PHENOLS

EXPERIMENT	PROCEDURE	OBSERVATION	INFERENCE
1. Ferric Chloride Test	Take small amount of sample in a test tube and dissolve it in 1 ml of water. Add few drops of ferric chloride solution.	Voilet Color	Phenol present
2. Phthalein Test	Place in a dry test tube 0.5 g each of the sample and phthalic anhydride. Add 2 to 3 drops of conc. sulphuric acid. Heat the tube gently for about 1 minute. Cool and add 10 % solution on NaOH in excess.	Red Color	Phenol Present

EXPERIMENT	PROCEDURE	OBSERVATION	INFERENCE
3. Bromination	Take small amount of sample in a test tube and dissolve it in 1 ml of water. Add bromine water gradually.	First decolouration of bromine takes place and on adding in excess a yellowish –white ppt. forms.	Phenol present
4. Libermann reaction	Take 0.5 g of the sample in a test tube and add few crystals of sodium nitrite. Heat gently for half a minute. Cool and add 1 ml of conc. sulphuric acid.	Deep green or violet coloration develops. Dilute the mixture with water, the solution turns red. Add an excess of NaOH solution, the solution again become green and blue.	Phenol Present

EXPERIMENT	PROCEDURE	OBSERVATION	INFERENCE
5. Benzoylation	Take about 0.2 g of the sample in a beaker and dissolve it in 15 to 20 ml of 10% NaOH solution. Add about 3 ml of benzoyl chloride. Shake it vigorously for 10 minutes.	Solid separates out	Phenol present

THANK YOU