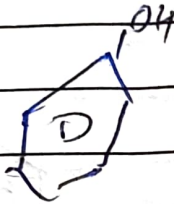


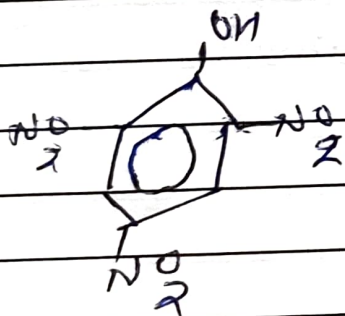
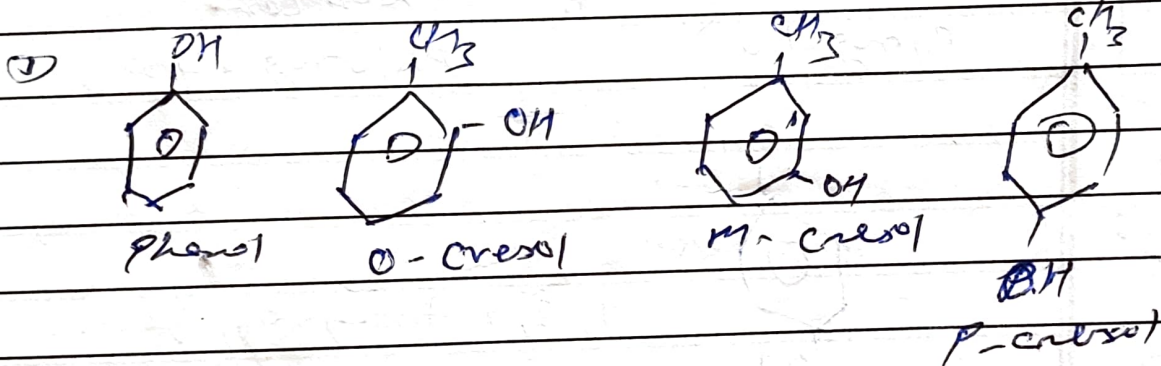
1 PHENOLS

Phenols are aromatic hydroxy compounds in which the hydroxyl group is directly attached to an aromatic ring.

General formula $Ar-OH$ Ar can be phenyl group

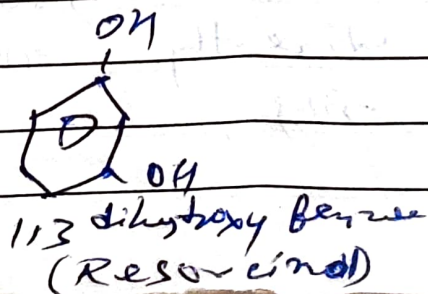
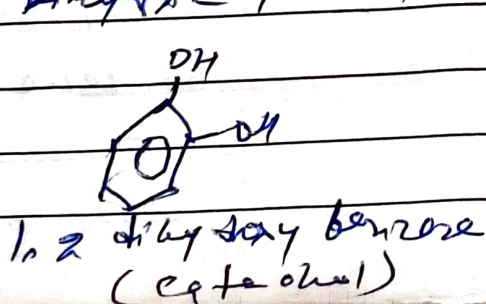


Classification of Phenol & Nomenclature



2,4,6 trinitrophenol (Picric acid)

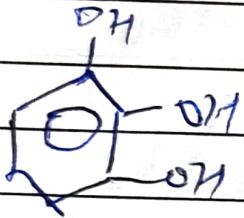
② Dihydroxy phenols



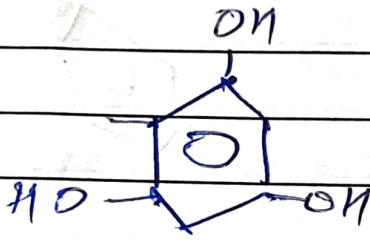


1,4 dihydroxy benzene
(Quinol)

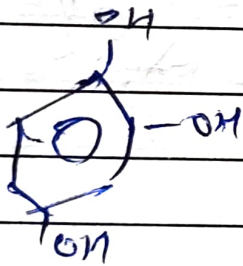
(ii) Trihydroxy Alcohol



1,2,3, trihydroxy benzene
(Pyrogallol)



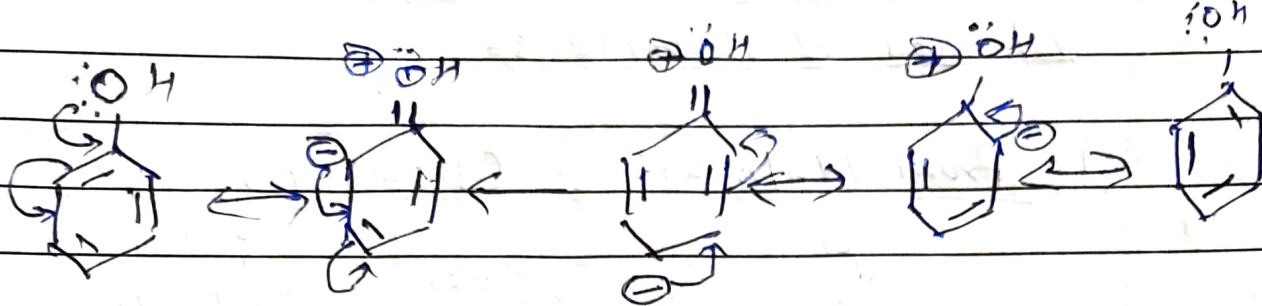
1,3,5-trihydroxy
benzene
(Phloroglucinol)



1,2,4 trihydroxy benzene
(hydroxy quinol)

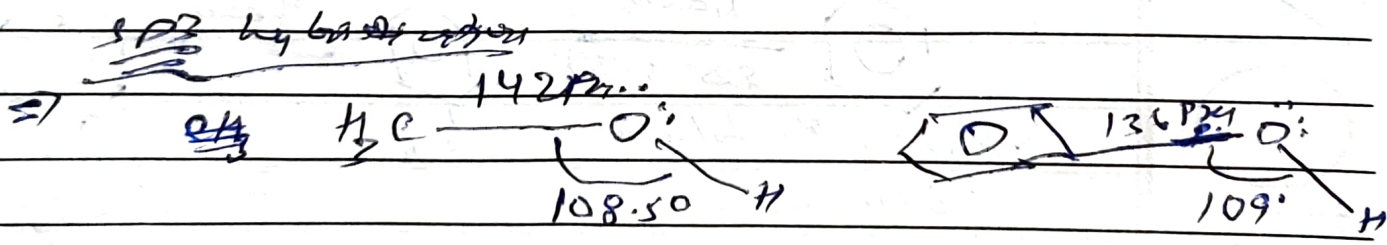
St. of Phenol

Structure of phenol is similar to that of ~~the~~ alcohol. However, since the -OH group in phenol is directly attached to benzene ring,



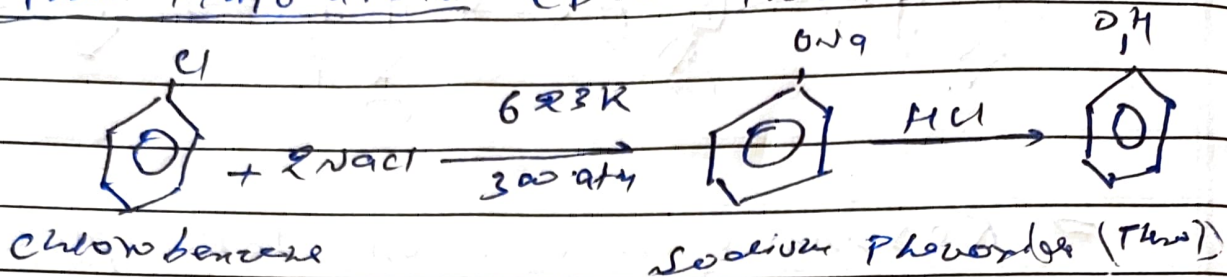
⇒ Resonance interaction take place b/w a lone pair of electron on oxygen and the benzene ring due to which C-O bond acquires some double bond character and becomes shorter and stronger than the C-O-bond in alcohols.

At the same time oxygen acquires a slight +ve charge due to which it attracts the electron pair of ~~the~~ O-H bond. In phenol become more polar than in alcohol.

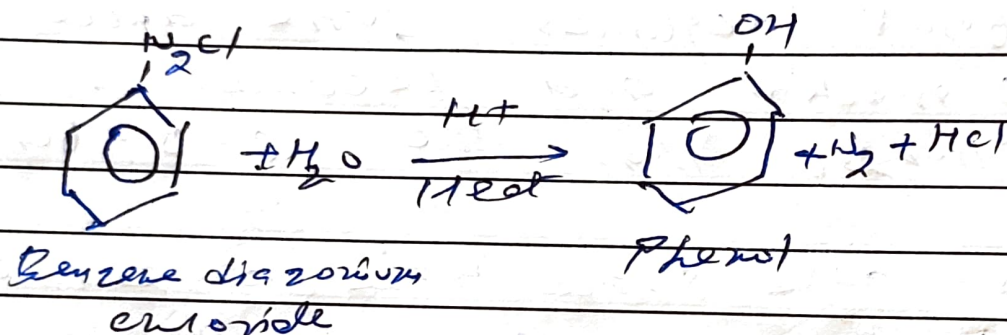


Method of Preparation :-

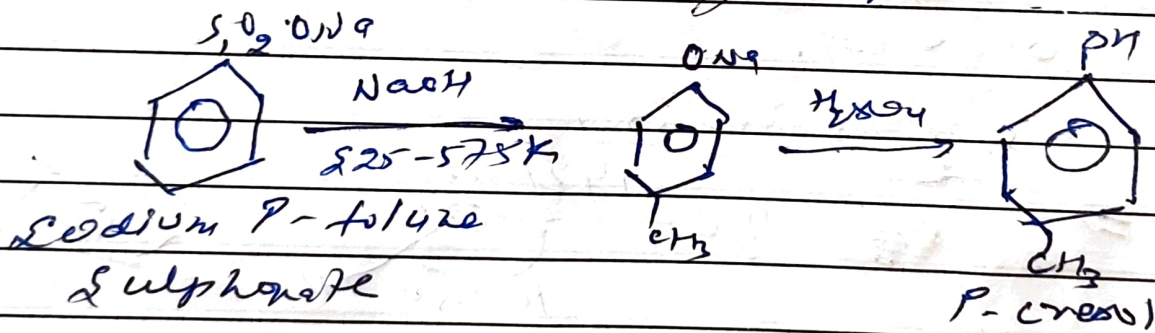
(1) From Halo arenes (Dow's Process)



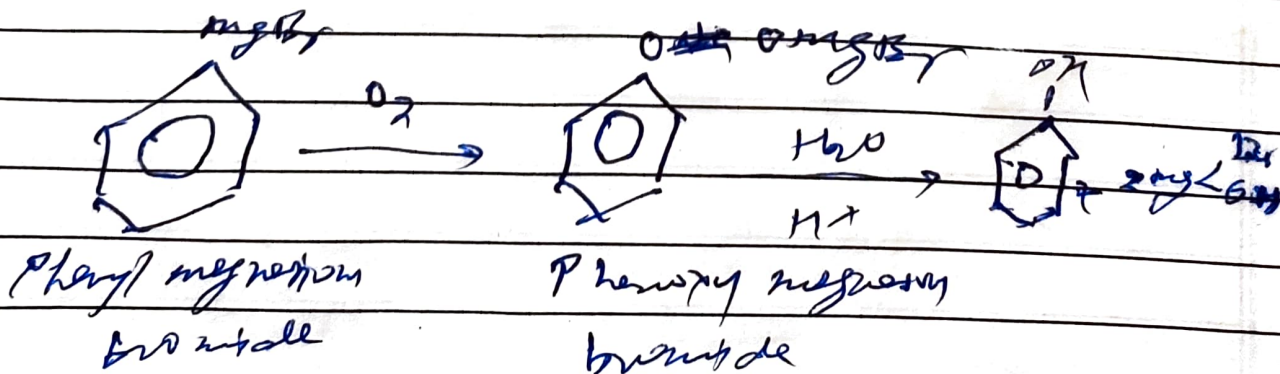
(2) From Diazonium Salts



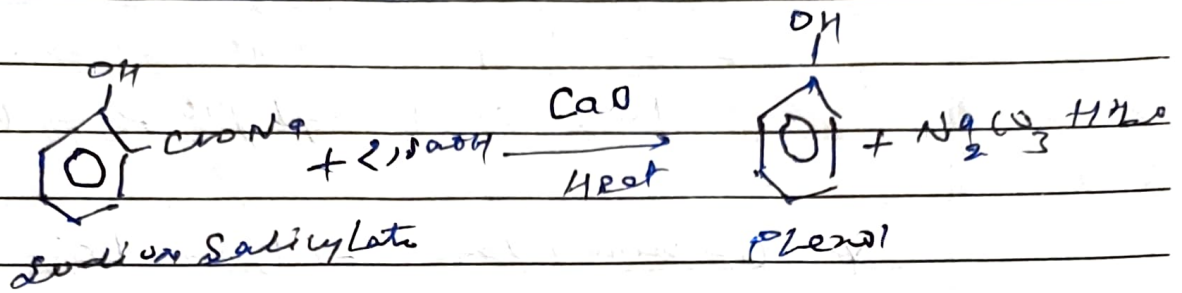
(3) From alkali fusion of sulphates



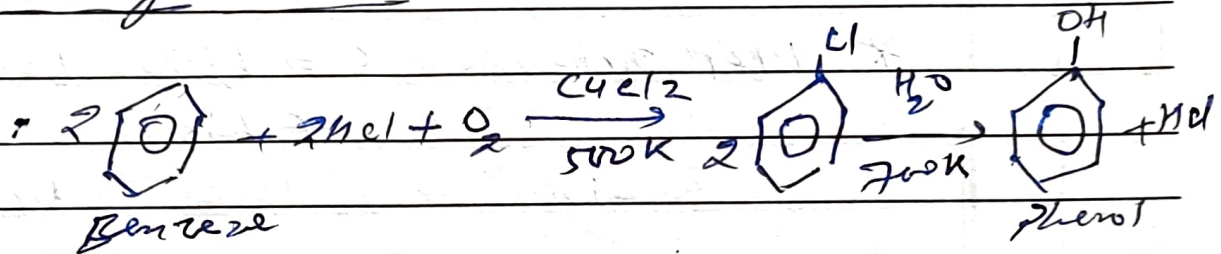
(4) From Grignard reagents



6) From Phenolic acids



7) Raschig's Process



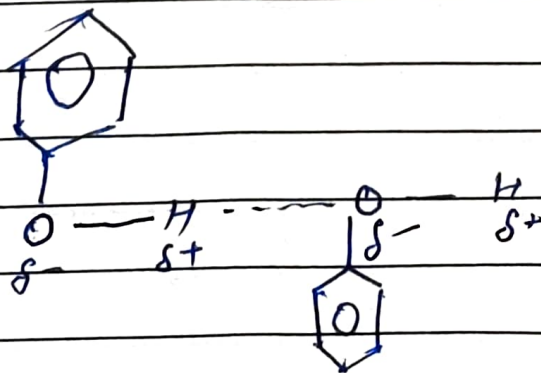
Physical Properties

(i) Physical state - colourless solid/liquid
- pink on exposure to air

(ii) Boiling point

- Due to ~~the~~ stronger association of molecules by intermolecular hydrogen bonding in phenol have high boiling point than hydrocarbon and aryl halide

eg \rightarrow phenol m.wt 94 boils at 455K
 \rightarrow toluene m.wt 92 boils at 284K.



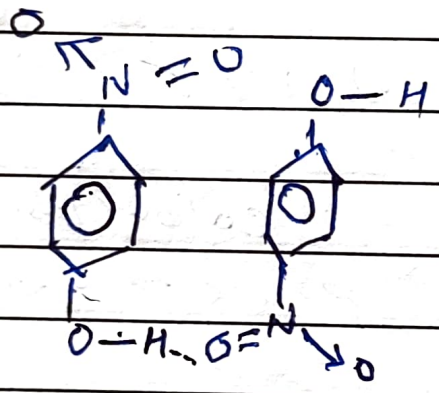
iii) Solubility

- diethyl ether + phenol \rightarrow soluble
- \rightarrow large size phenyl group \rightarrow less soluble

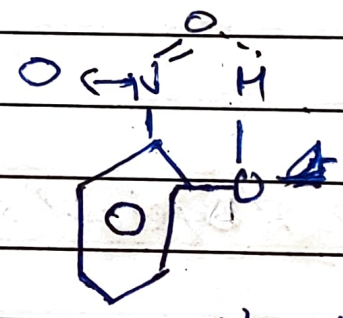
* o-nitro phenol \rightarrow lower boiling pt & lower solubility

~~due to~~ due to inter molecular H-bonding

* m-nitro phenol \rightarrow higher boiling point & higher solubility due to inter molecular hydrogen bonding



p-nitro phenol
(inter molecular H-bonding)



o-nitro phenol
(inter molecular H-bonding)

Chemical properties

Three classes

- Reactions of the OH group
- Reactions of the benzene nucleus
- ~~Reaction~~ special reactions

Reactions of the hydroxyl group

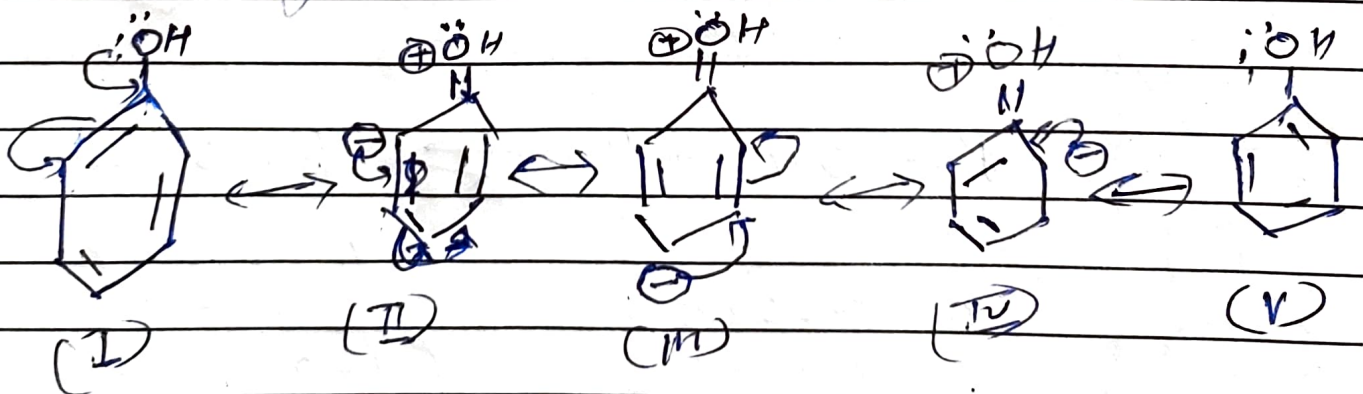
(1) Acidic nature

- Phenol is a weakly acidic ($K_a = 1 \times 10^{-10}$)
- turn blue litmus red
- React with sodium metal & aqueous alkali hydroxide to form salts & phenoxide
- do not react with carbonate or bicarbonate

⇒ Phenols are stronger acids than alcohols.

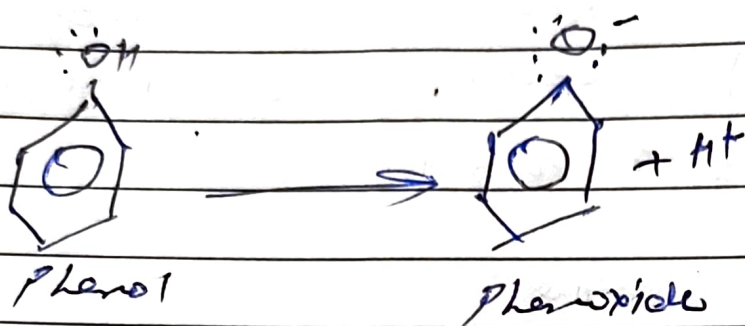
Explanation

Phenols is a resonance hybrid of following canonical structures.



The oxygen atom of phenol acquires a partial positive charge due to resonance contribution of structures II, III & IV. As a result it

attracts the electron pair of the O-H bonds thereby facilitating the release of H^+



The phenoxide ion formed is more stabilized by resonance than phenol, due to ~~dispersion~~ dispersal of negative charge.

But in case of alcohol there is no resonance stabilization of alkoxide ion relative to alcohol since neither the alcohol nor the alkoxide ion exhibits resonance.



Alcohol

Alkoxide ion

(NO resonance stabilization)

(NO resonance stabilization)

So that phenol are more acidic than alcohols.

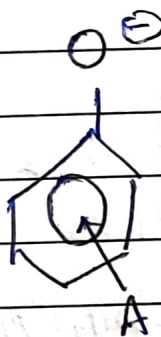
Effect of substituents on acidity of Phenols



Electron withdrawing groups stabilize phenoxide ion

→ more acidic

(A = CN, NO₂, CHO, X, COX, COOK, NR₂)



[A = -NH₂, -OH, -R etc)

Electron releasing groups destabilize phenoxide ion → less acidic

⇒ Position of substituents

The presence of electron withdrawing and electron releasing groups is more pronounced at ortho and para positions than meta position. This is due to the resonance effect.

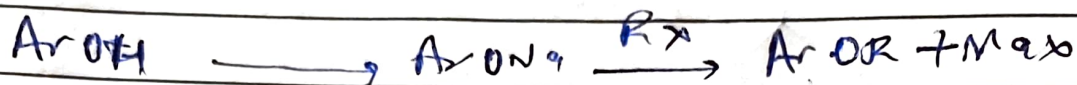
Acidity ↑

p-nitrophenol > o-nitrophenol > m-nitrophenol

2,4,6-trinitrophenol > 2,4-dinitrophenol > 2-nitrophenol

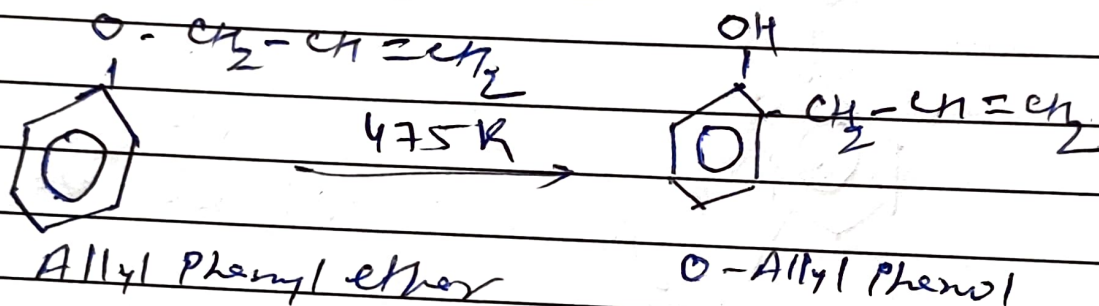
⇒ OH Reaction

Alkylation [Williamson synthesis]

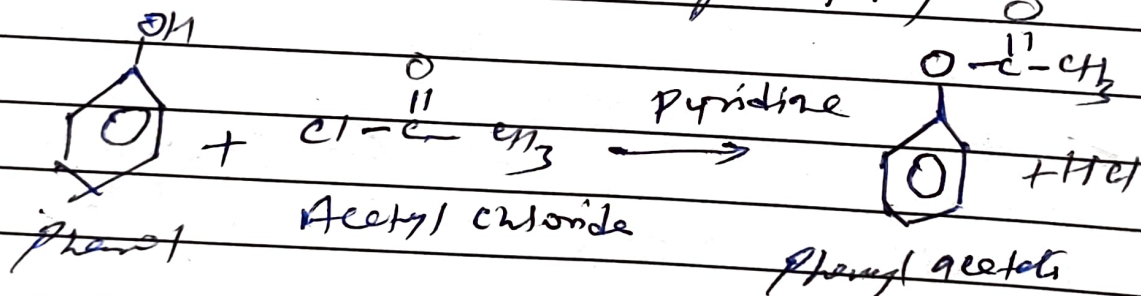


Alkyl halide
Phenolic ether.

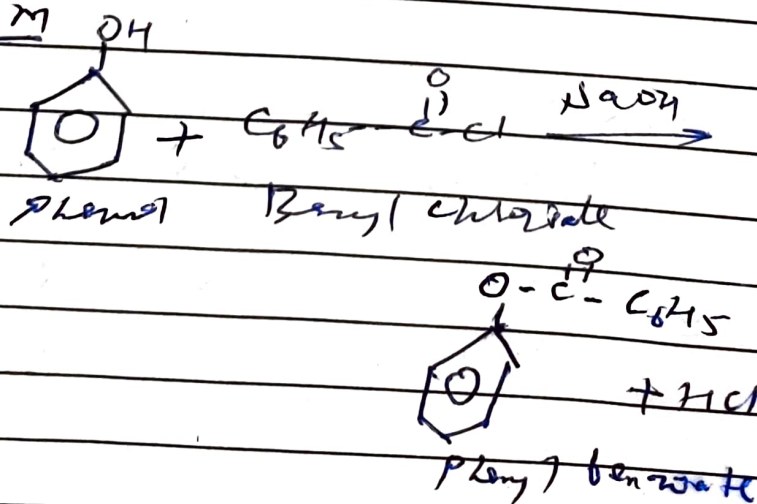
Claisen rearrangement



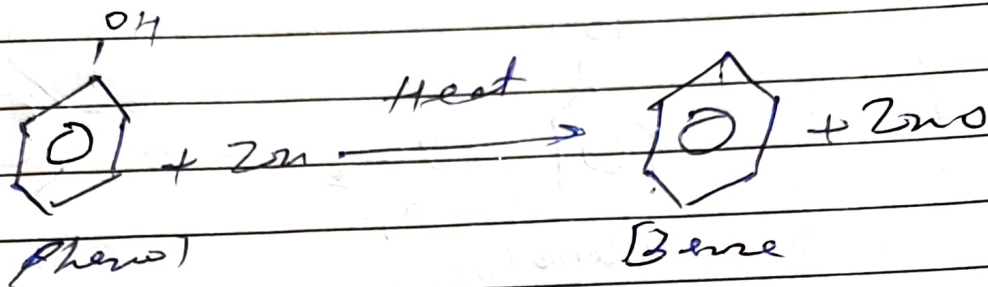
② Acylation [formation of esters]



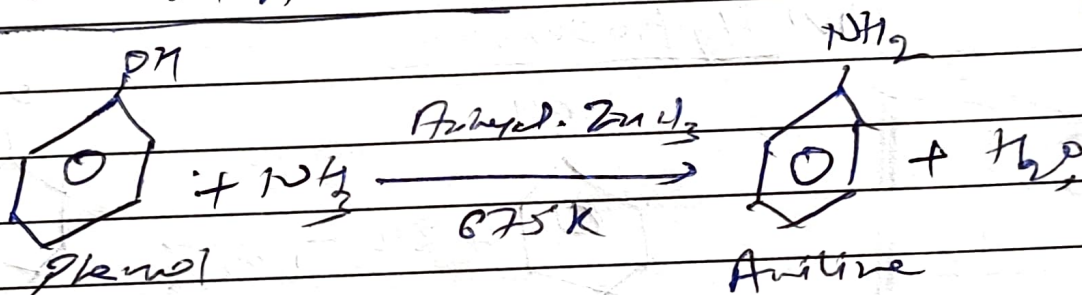
④ Benzoylation



⑤ Reaction with zinc dust

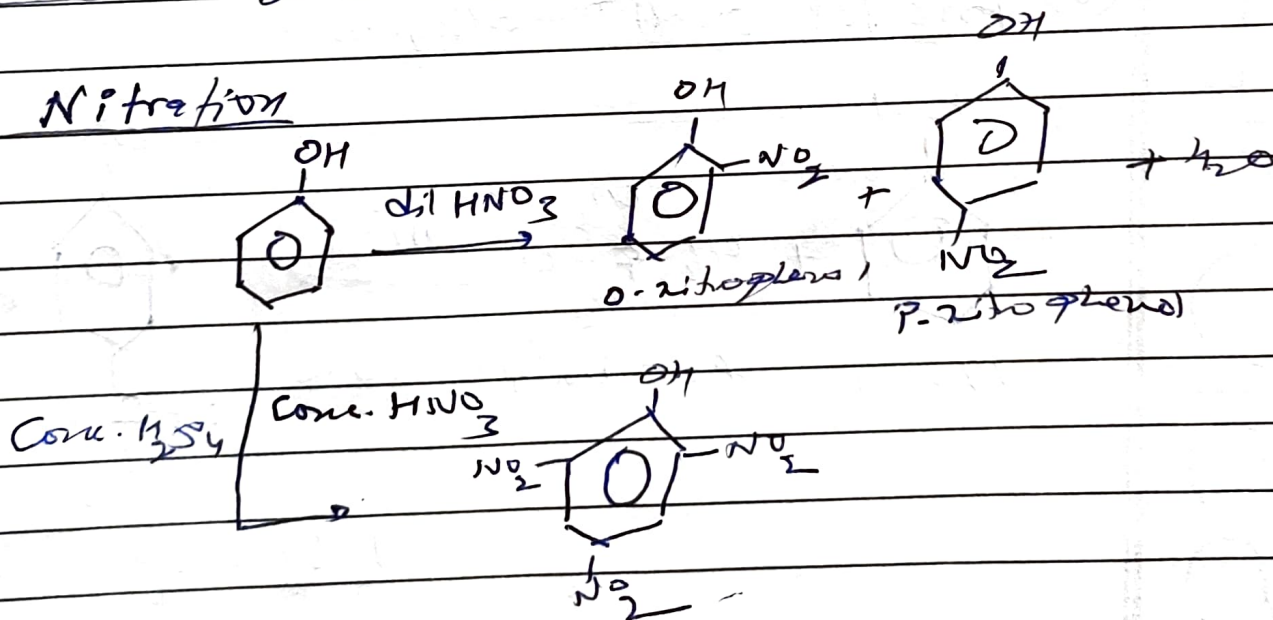


⑥ Reaction with Ammonia ✓

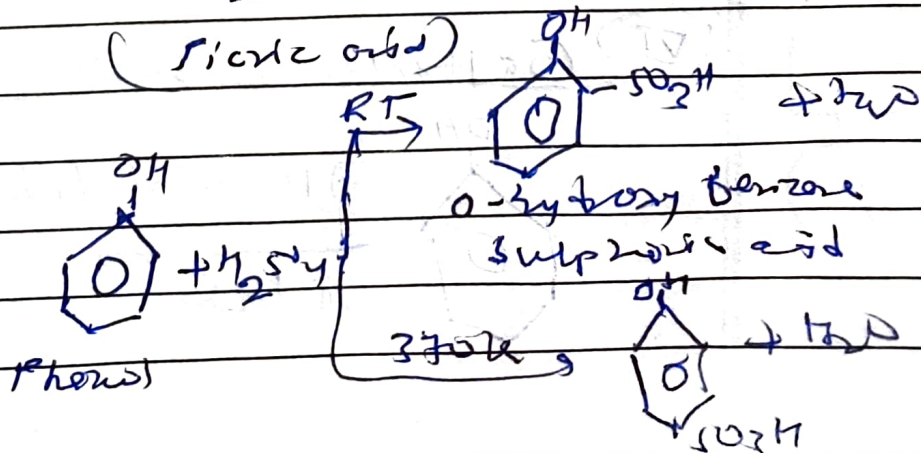


Reactions of Benzene Nucleus

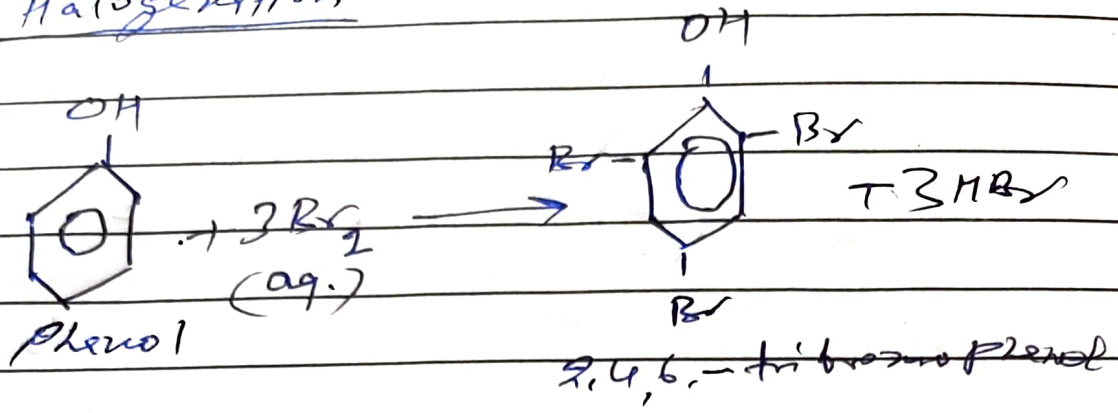
① Nitration



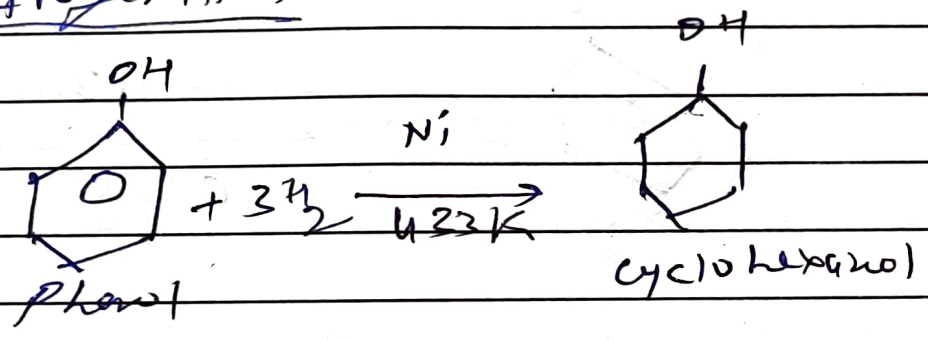
② Sulphonation



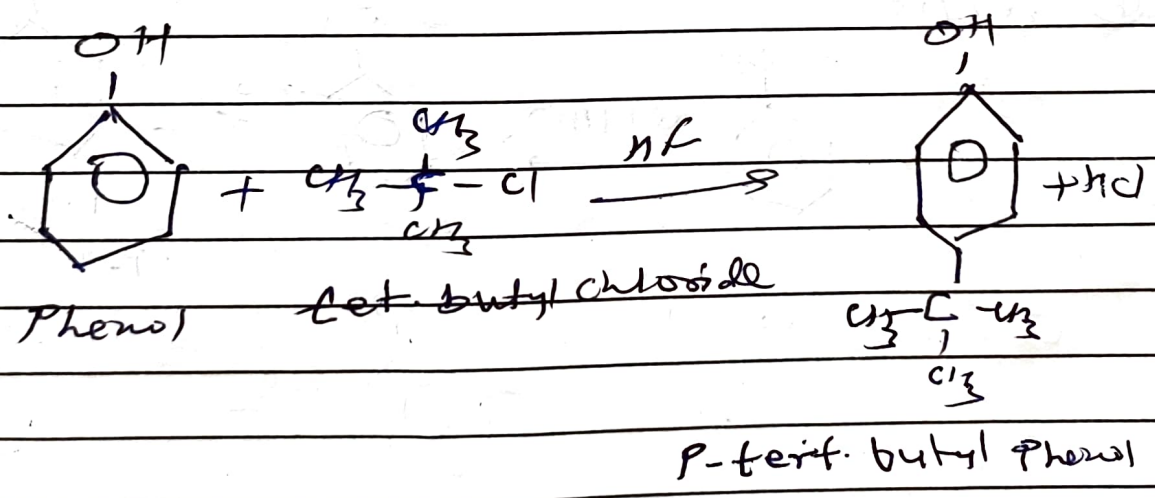
(iii) Halogenation



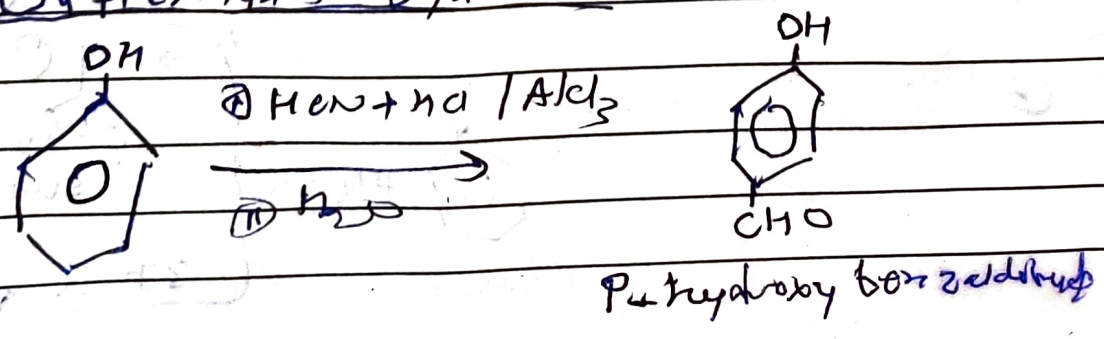
(iv) Hydrogenation



(v) Friedel-Crafts alkylation

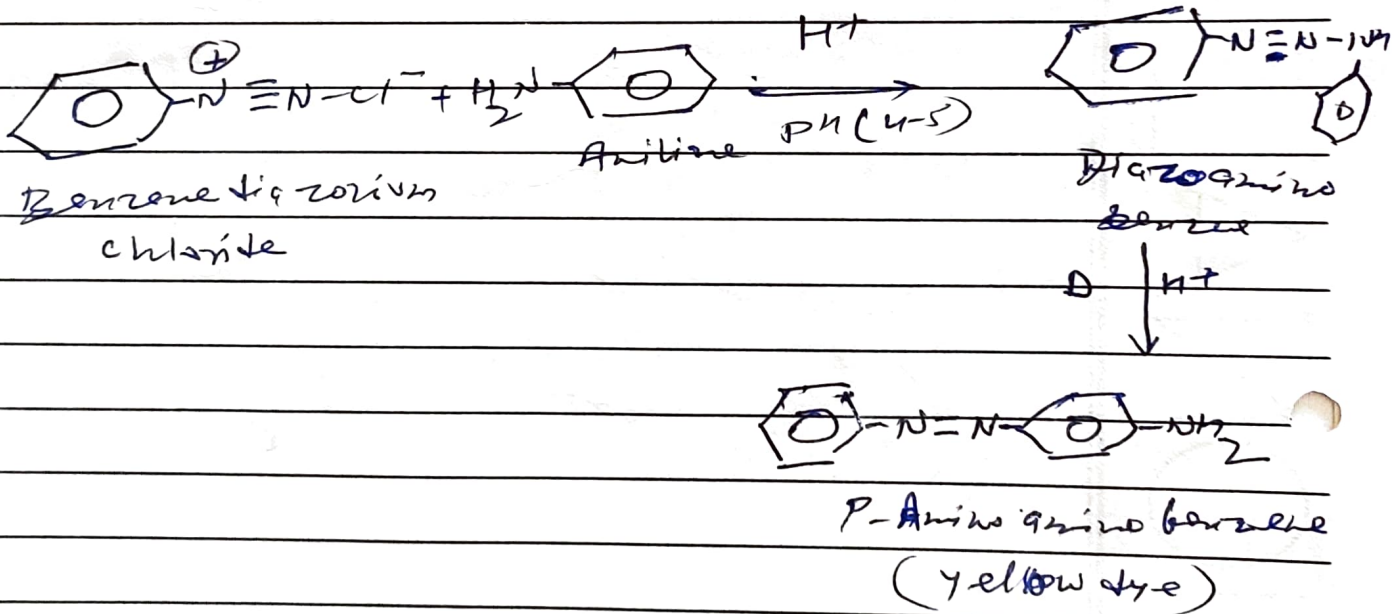
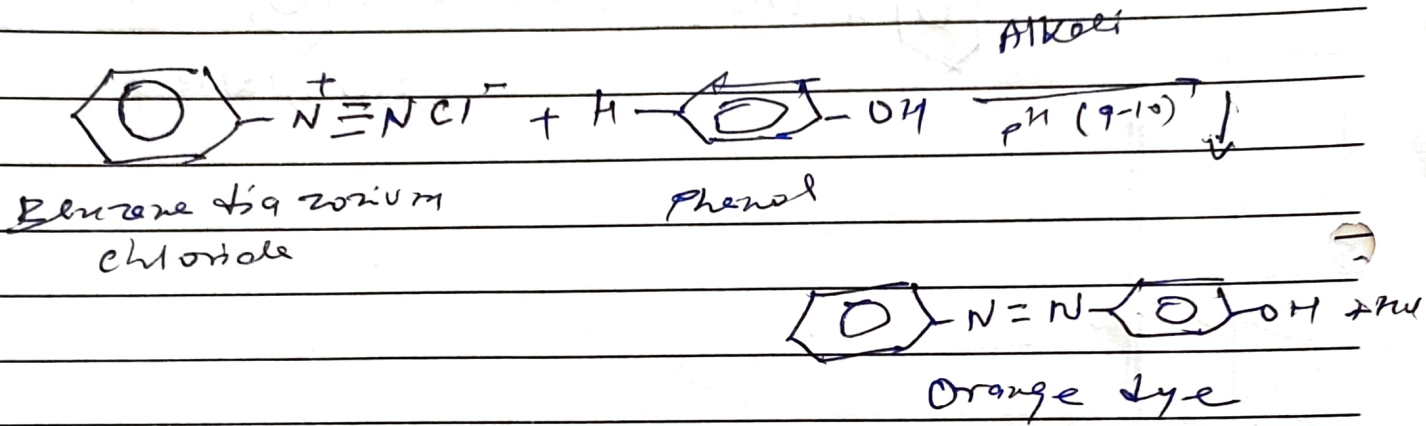


(vi) Gattermann's synthesis

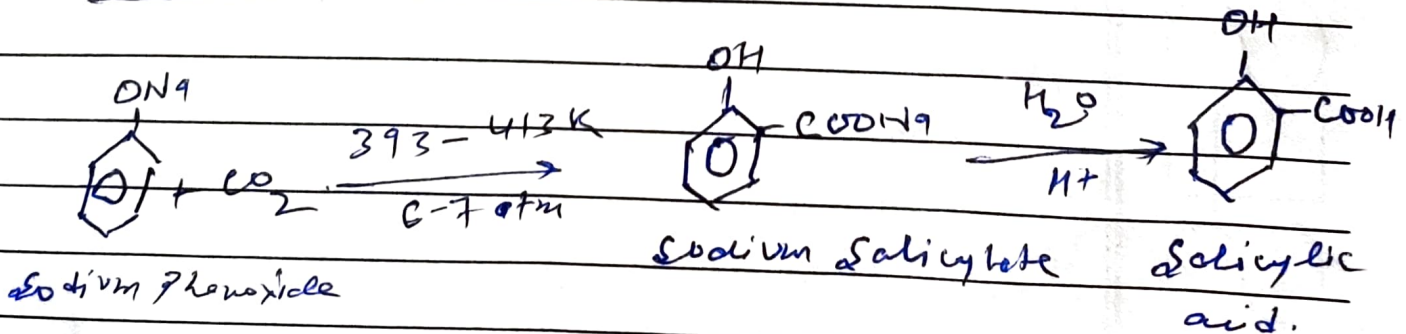


[C] Special reactions of Phenol.

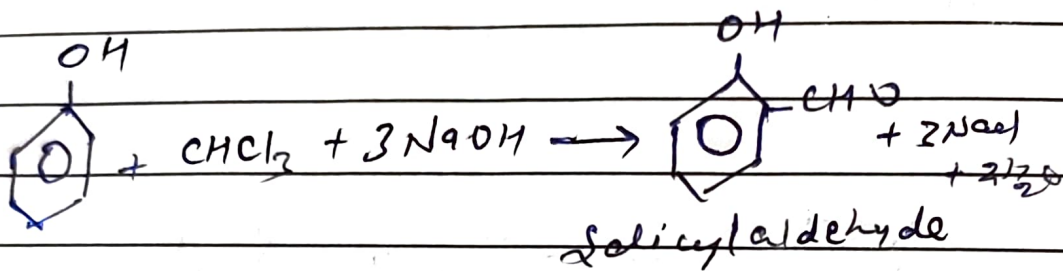
(i) Diazo-coupling reaction



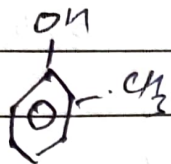
(ii) Kolbe's reaction :- Carboxylation



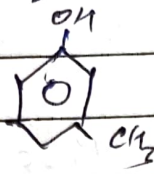
ii) Reimer-Tiemann reaction



CRESOLS $[C_7H_8O]$



o-cresol



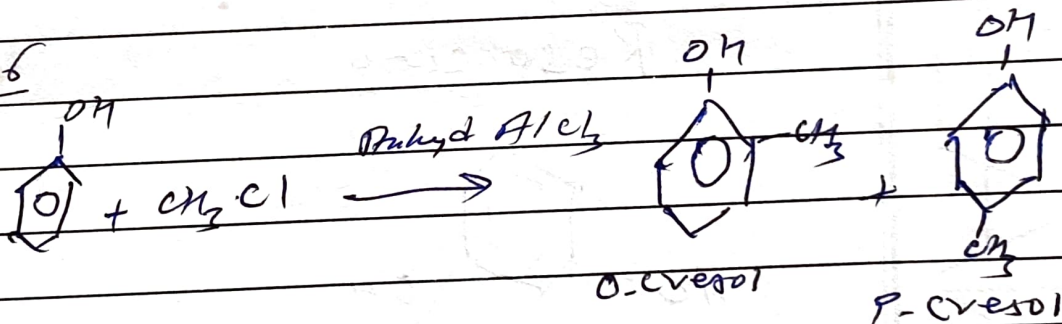
m-cresol



p-cresol

- K₁₀s = hydroxy toluene / methyl phenols
- solid or liquid
- exposure to air yellowish to brown red
- characteristic odour
- three isomer o, p, m.
- the mixture of these isomer is called tricresol

Synthesis



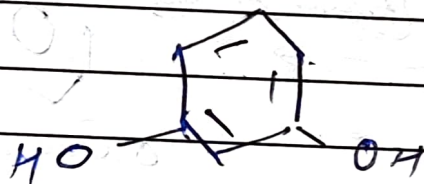
* Exposure to cresol in high conc. can cause irritation and burning of skin, eyes, mouth & throat abdominal pain, vomiting, anemia, liver and kidney damage

Uses

- ① Chlorination & etherification of o-cresol gives 2-methyl 4-chloro phenoxy acetic acid which is used as herbicides
- ② Preparation of Carvacrol which is a strong antibacterial agent
- ③ Preparation of Mephenesin which is muscle relaxant

- ④ production of butylated hydroxy toluene (BHT) which is an antioxidant
- ⑤ m-cresol is a precursor of various compounds like
 - ① fenitrothion → pesticides
 - ② synthesis of vit E.
 - ③ Amyl meta cresol used as antiseptic
 - ④ As a solvent
 - ⑤ preservative in some insulins.
 - ⑥ household disinfectant.

Resorcinol



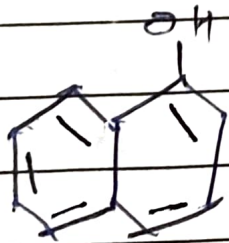
- 150 mer of benzene diol
- Colourless.
- Readily soluble in water, alcohol & ether
- Insoluble in chloroform and CS_2 .
- It condense readily with aldehyde to give formaldehyde.
- It ~~give~~ undergoes electrophillic as well as nucleophillic substitution reaction

- Resorcinol will become pink upon exposure to light and air or contact with iron.
- It has sweet taste
- On exposure irritation of skin and mucous membranes

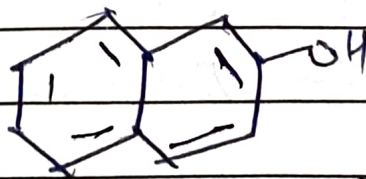
Uses \Rightarrow Antiseptic & Disinfectant

- It is ointment (5 to 10%) used for treatment of psoriasis, eczema
- It is 2% solution is used in hay fever and whooping cough
- anti-dandruff shampoo & sunscreen cosmetic
- treatment of gastric ulcer
- production of diacyte & plasticizer.
- used for determination of ketose sugar
- Preparation of synthetic resin
- Preparation of adhesive agent of tire & wood glue
- determination of zinc, lead, tartaric acid through colorimetric method.
- preservative in cosmetic & dermatology drugs

Naphthols $C_{10}H_7OH$



(1-naphthol)



(2-naphthol)

Naphthol is composed of a hydroxy group bonded to naphthalene ring

It can exist as one of two isomers i.e. 1-naphthol & 2-naphthol.

These two isomers differ by which carbon in the ~~ring~~ naphthalene ring the hydroxyl group is bonded to.

It is aromatic in nature.

Due to more electronegativity of oxygen, than both carbon & hydrogen, naphthol is highly polar in nature.

1-naphthol (α -naphthol) is white solid, fluorescent compound and soluble in alcohol, ethers & chloroform.

2-naphthol (β -naphthol) is colourless or yellow crystalline solid, fluorescent having same solubility as 1-naphthol.

Uses

① 1-Naphthol is an ingredient of molisch's reagent which is ~~used~~ used for detecting the presence of carbohydrates.

② 1-Naphthol is precursor of variety of insecticides like carbaryl.

- ② 1-Naphthol is used for the detection of arginine.
- ④ 2-Naphthol is precursor for preparation of sudan dye
- ⑤ 2-Naphthol is used for synthesis of BINOL [transition metal synthesis]
- ⑥ 2-naphthol used as antiseptics, in perfumes, synthesis of fungicides & anti oxidants for rubber
- ⑦ determination of pesticides content in the body.

—xxx—