Phenol

Introduction to phenol

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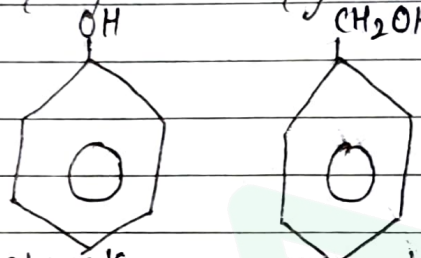
Phenols are hydroxy derivative of aromatic hydrocarbons in which the hydroxy group is directly attached to aromatic ring. Hence phenols are represented by general Ar OH

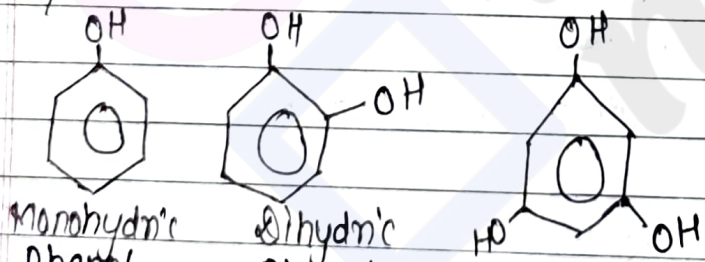
where Ar = Aryl group.

→ Hydroxy derivatives of aromatic hydrocarbon in which the hydroxy group is present in the side chain of aromatic ring are not phenols. They are aromatic alcohols.



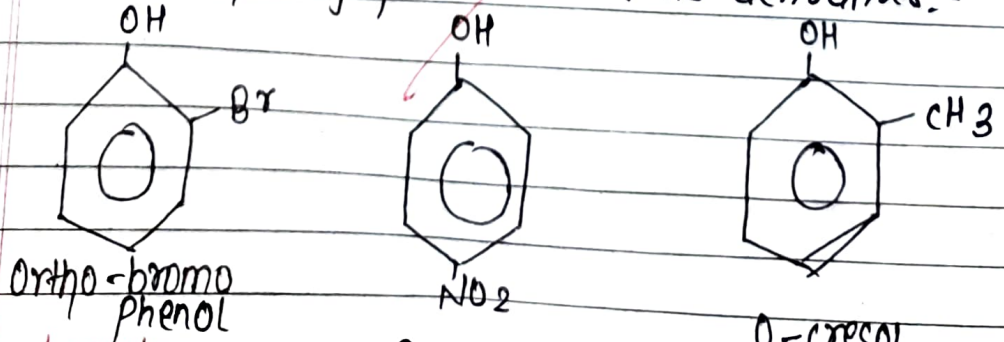
Phenols Aromatic alcohol.

→ phenols may be classified as mono, di, trihydric phenol depending upon the number of hydroxyl group present in the molecules.



Monohydric Phenol Dihydric Phenol Trihydric phenol.

Some example of phenol with its derivatives:-



Ortho-bromo phenol P-nitrophenol O-cresol

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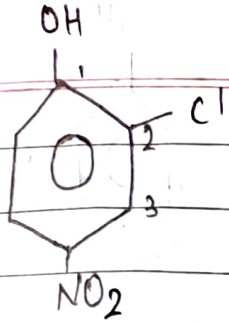
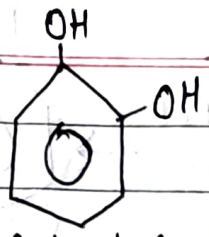
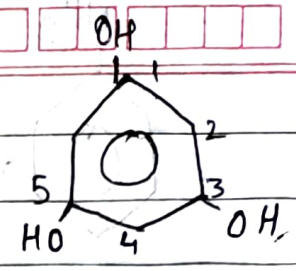


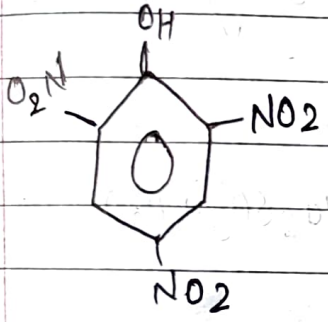
2- chloro - 1 - hydroxy 4- nitrobenzene.



O-hydroxy phenol (o-(catechol)



3,5-dihydroxy phenol (Pyrogold)

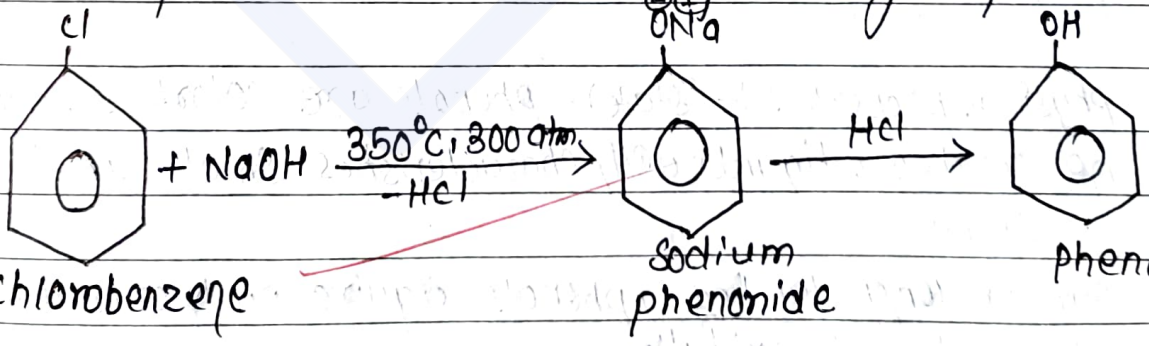


2, 4, 6 - trinitrophenol (Picric acid)

Preparation of phenol →

1. From chloro-benzene → (Dow's process) → (halo arenes)

Chlorobenzene when heated with 10% NaOH solution about 350°C under apressure of 300 atoms gives Sodium phenonide which on acidification gives phenol.

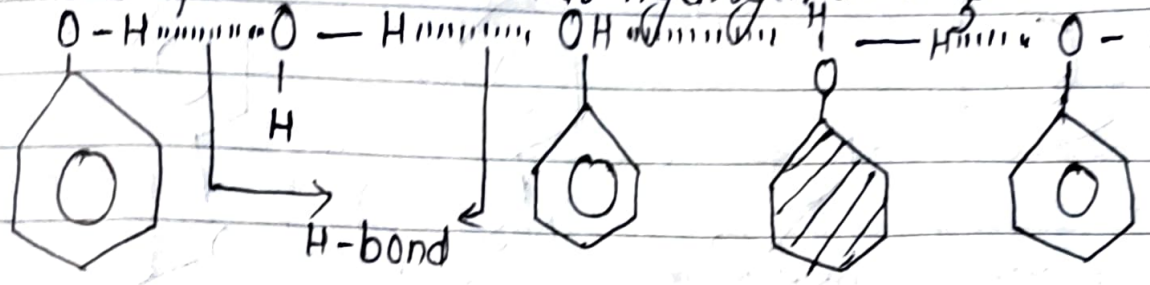


Chlorobenzene — Sodium phenonide — phenol.

2. Diazonium salt → (Laboratory method)

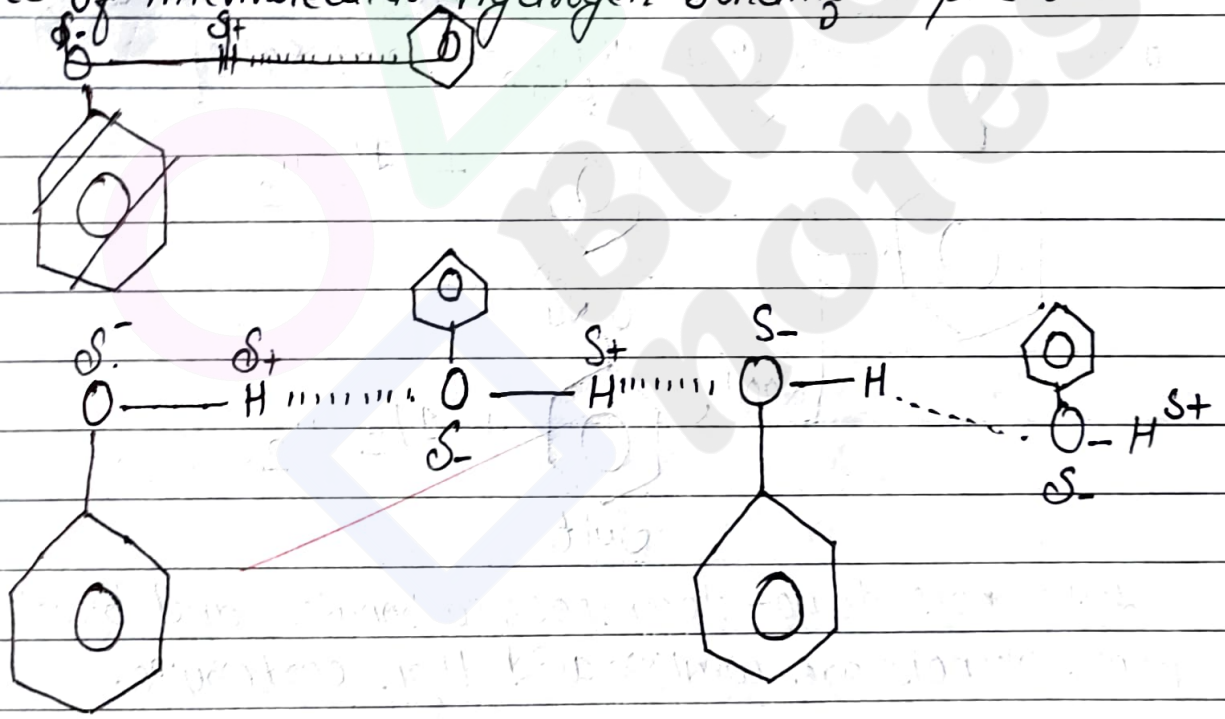
In lab phenol is obtained by warming an aqueous solution of diazonium salts which is prepared by diazotization of aniline

(hydrophilic) and the hydrophilic phenyl group. The -OH group of phenol can form intermolecular hydrogen bonding with water.

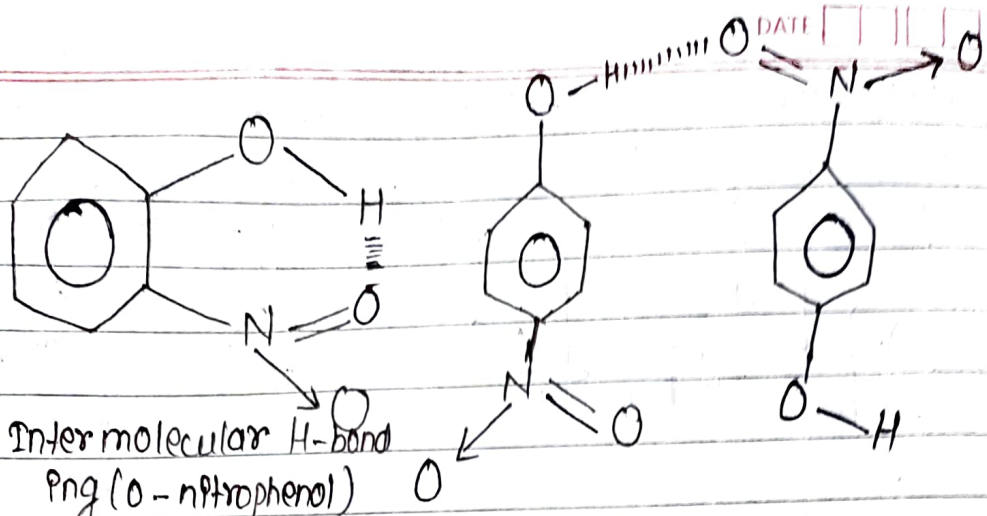


* Due to presence of such hydrophobic phenyl group & hydrophilic -OH group, phenol is slightly soluble in water.

3. Boiling point → ⊛ phenols have higher boiling point then that of corresponding aromatic hydrocarbons, it is due to presence of intermolecular hydrogen bonding in phenols.



Among isomeric nitrophenol the orthoisomer have lower mpt.. bpt, water solubilities and are weaker acids then meta-para isomer. It is because in case of ortho isomer there is intramolecular H-bonding and in case of meta and para isomer there is intermolecular H-bonding.

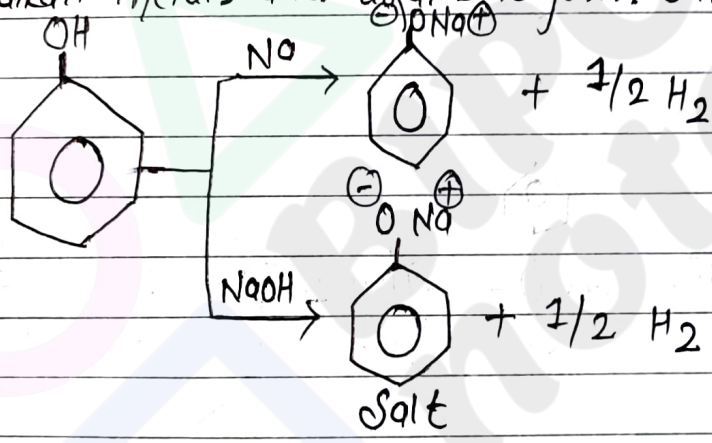


Intermolecular H-bond ing (o-nitrophenol)

Intermolecular H-bonding (p-nitrophenol)

Chemical properties:

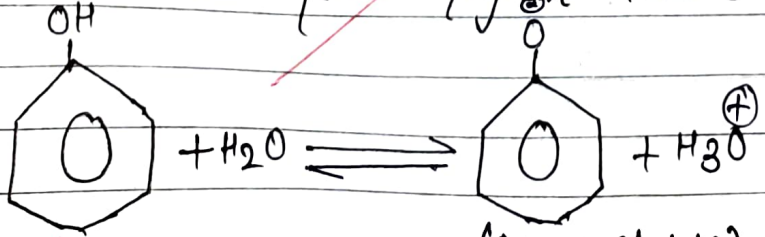
1. Acidic nature of phenol → phenols are weakly acidic in nature. They turn ~~but~~ blue litmus into red and react with alkali metals and alkalis to form salts.



But phenols do not decompose carbonates and bicarbonates hence phenols are weaker acid then carboxylic.

Q.N Why phenol is acidic?

→ phenol is acidic in nature due to the presence of polar -OH group. phenol dissolves in water to form hydronium ion. hence they are acidic in nature.



(More stable)

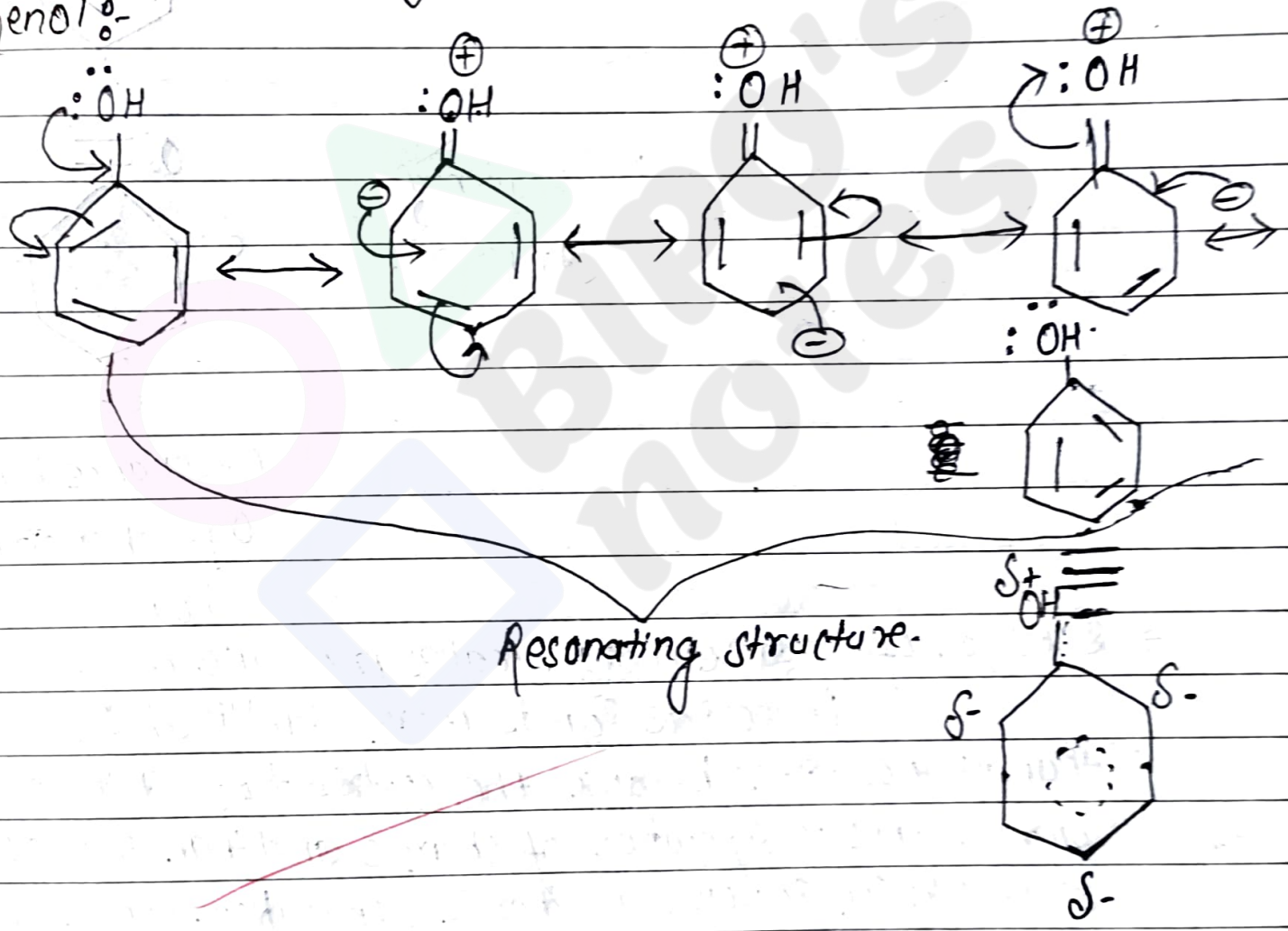
On the other hand alcohols are net neutral to litmus. As a result phenols are stronger acids than alcohols.

Q.N Why phenols are more acidic than alcohols ?

⇒ phenols are more acidic than alcohols this fact can be understoods by considering the relative stabilities of phenol and phenoxide ion compared to alcohols and alkonide ions.

In phenol both phenol and phenonide ions are ~~stabilished~~ stabilized by resonance.

Phenol :-

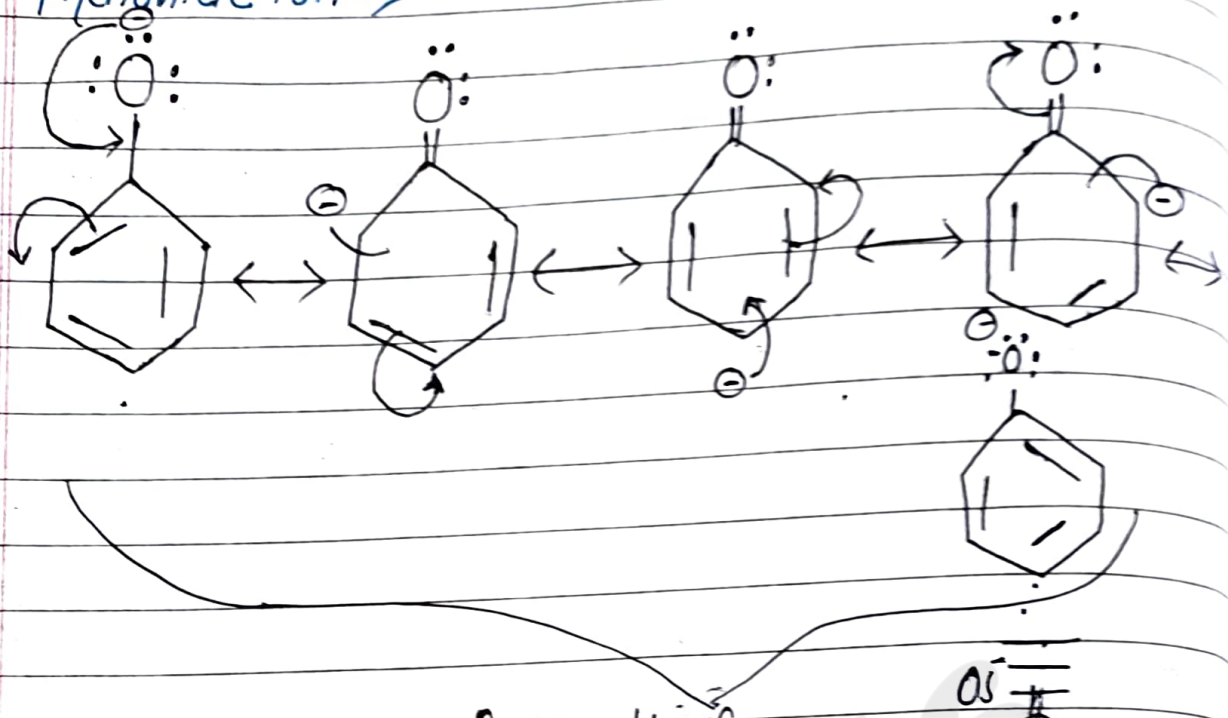


Resonating structure.

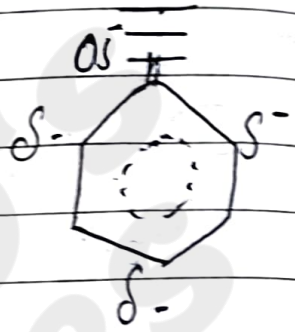
Resonance hybrid of phenol.

Seperation of charge makes molecules less stable.

Phenoxide ion →

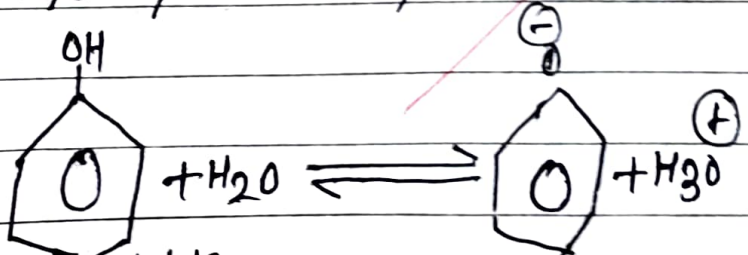


Resonating structure.



Resonance hybrid of phenoxide ion

⇒ Dispersal of negative charge makes molecule more stable. Phenoxide ion is more stabilized by resonance than phenol, it is because the contributing structure of phenols involve seperation of charge and than that of phenoxide ion involve no charge separation. Hence in the dissociation of phenol the equilibrium is very much in the favour of phenoxide ion and produces high concentration of $H^{\oplus}$ ions. As a result phenol are acidic.



less stable

more stable.

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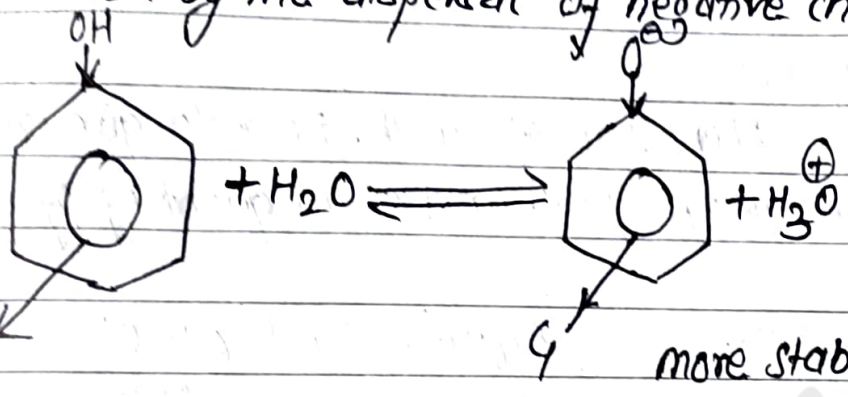
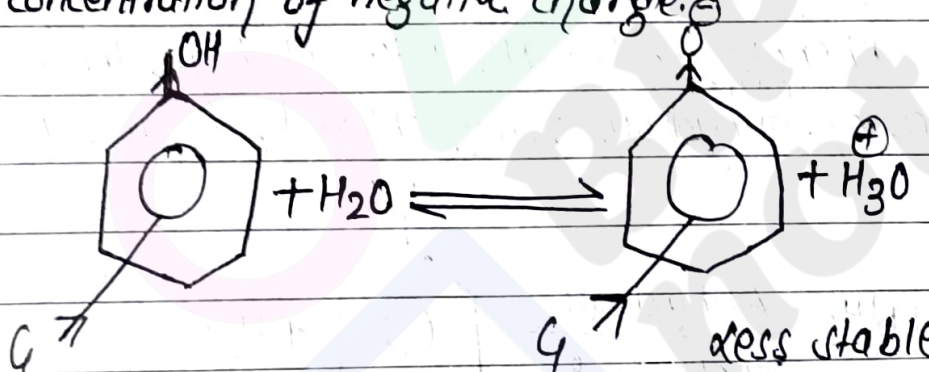
Note :-

Effects of substituent on the acidity of phenol :-

(a) The presence of electron with drawing groups like $-NO_2$, $-CHO$, $-X$ etc increase the acid strength of phenol by stabilising the phenoxide ion by the dispersal of negative charge.

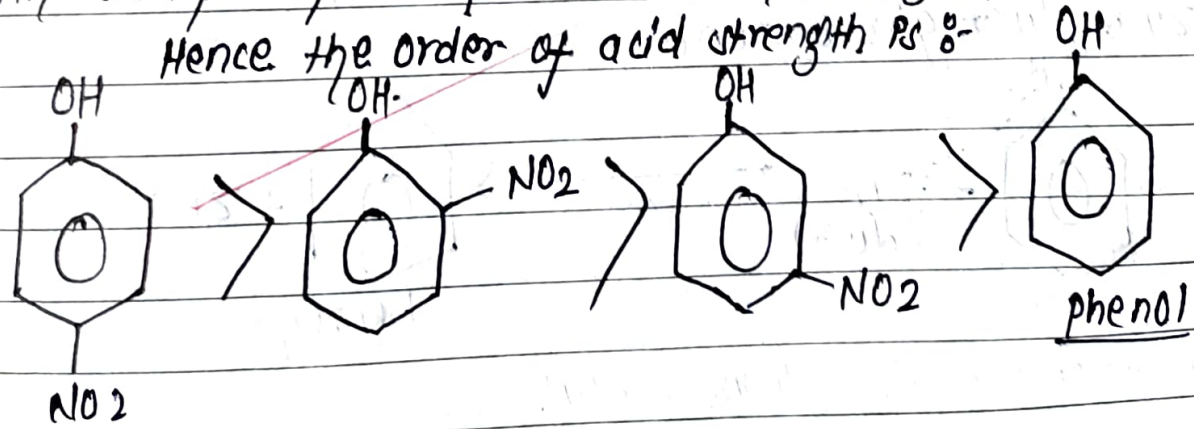


(b) The presence of electron releasing groups like $-OH$, $-NH_2$, $-R$ etc decrease the acid strength by destabilizing the phenoxide ion by concentration of negative charge.



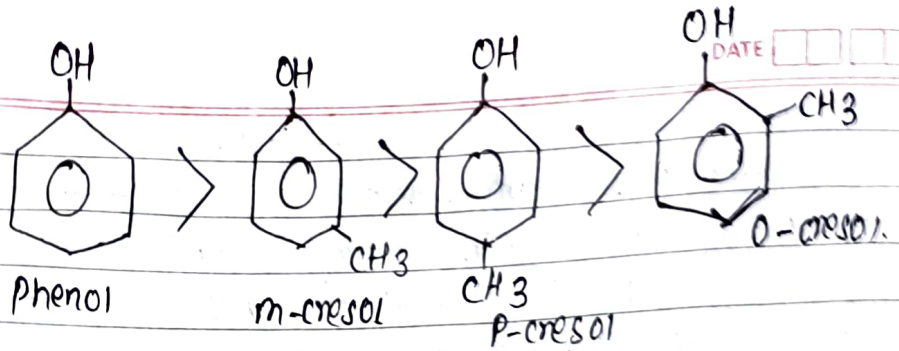
(c) The effect of this group are prominent when they are present at ortho and para position relative to the $-OH$ group.

Hence the order of acid strength is :-



P-nitrophenol

II)



Imp ② Reaction with PCl_5 →

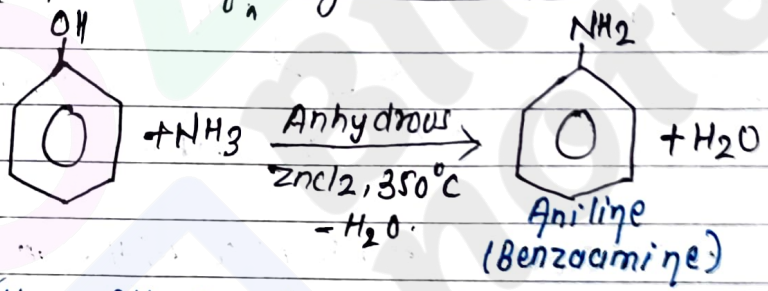
Phenols reacts with PCl_5 to give the phenyl phosphate as major product and small quantity of chlorobenzene

$$4 \cdot C_6H_5OH + PCl_5 \longrightarrow (C_6H_5)_3PO_4 + C_6H_5Cl + 4HCl$$

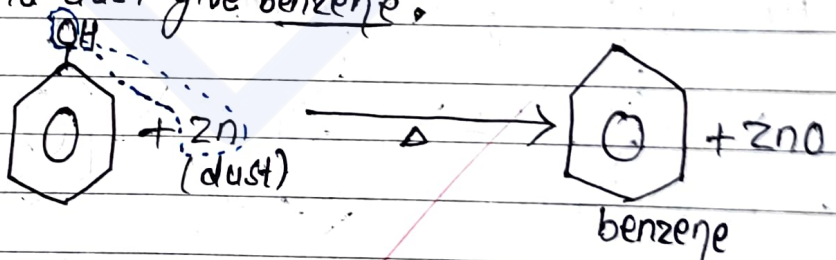
(phosphorous penta-chloride) — major (Tri-phenyl phosphate) — + — 4 HCl. — a little (chlorobenzene)

③ Reaction with NH_3 →

Phenols react with NH_3 at high temperature in the presence of anhydrous zinc chloride (catalyst) to give aniline

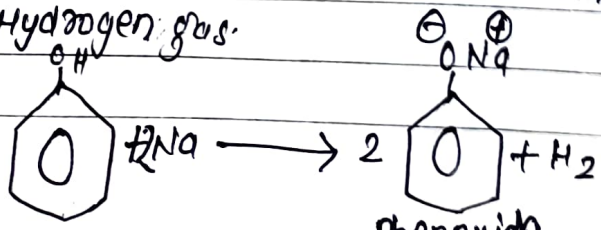


v.imp ④ Reaction with zinc dust :→ Phenols when distilled with zinc dust give benzene.



⑤ Reactions with sodium metals →.

Phenols react with alkali metals evolving Hydrogen gas.



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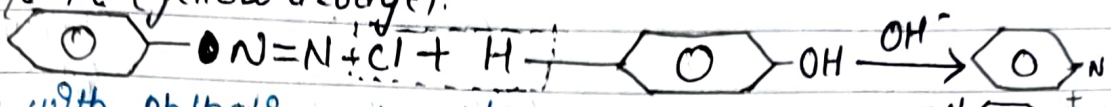
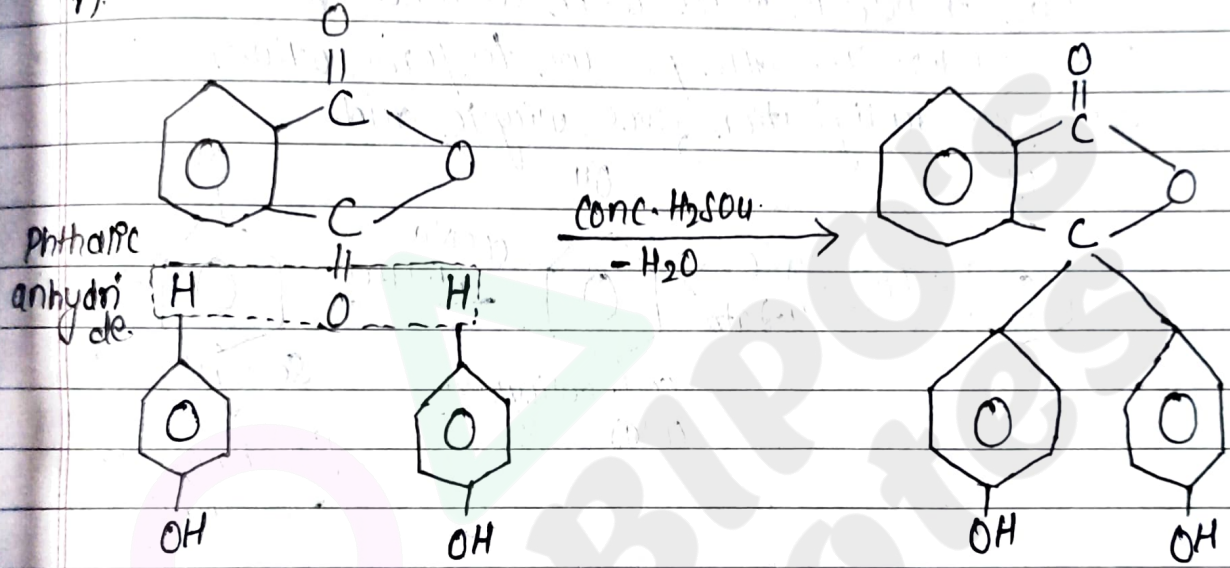
6. Benzene diazonium chloride → phenols reacts with benzene diazonium chloride in slightly alkaline medium to form parahydroxy azobenzene i.e (yellow azodye).



p-hydroxyazobenzene

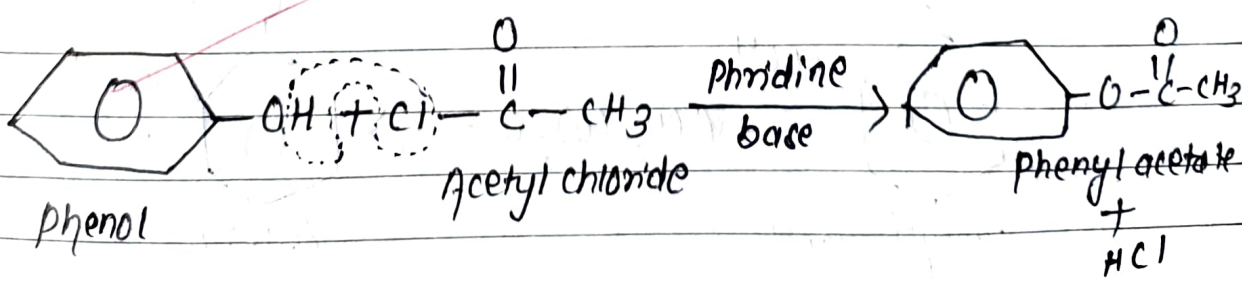
7. Reaction with phthalic anhydride → Phenol condenses with phthalic anhydride in presence of conc H_2SO_4 to give phenophthalein (Indicator).



Phenol

Phenolphthalein (Indicator)

8. Acylation Reaction → phenols reacts with acid chloride or acid anhydride in the presence of acidic or basic catalyst to form aromatic esters



Phenol

Acetyl chloride

Phenyl acetate

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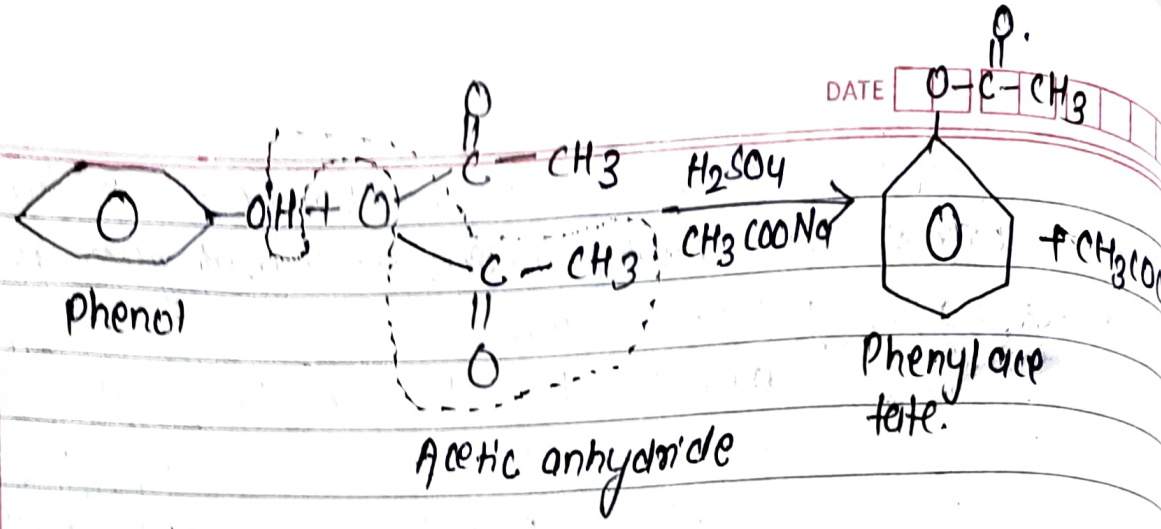
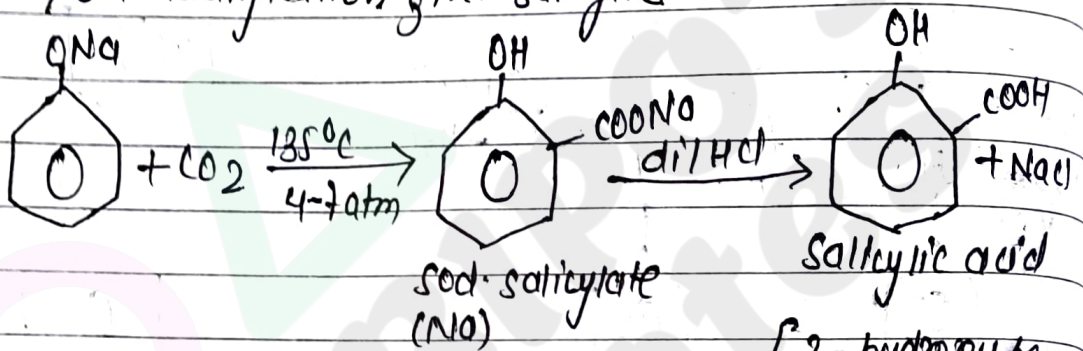
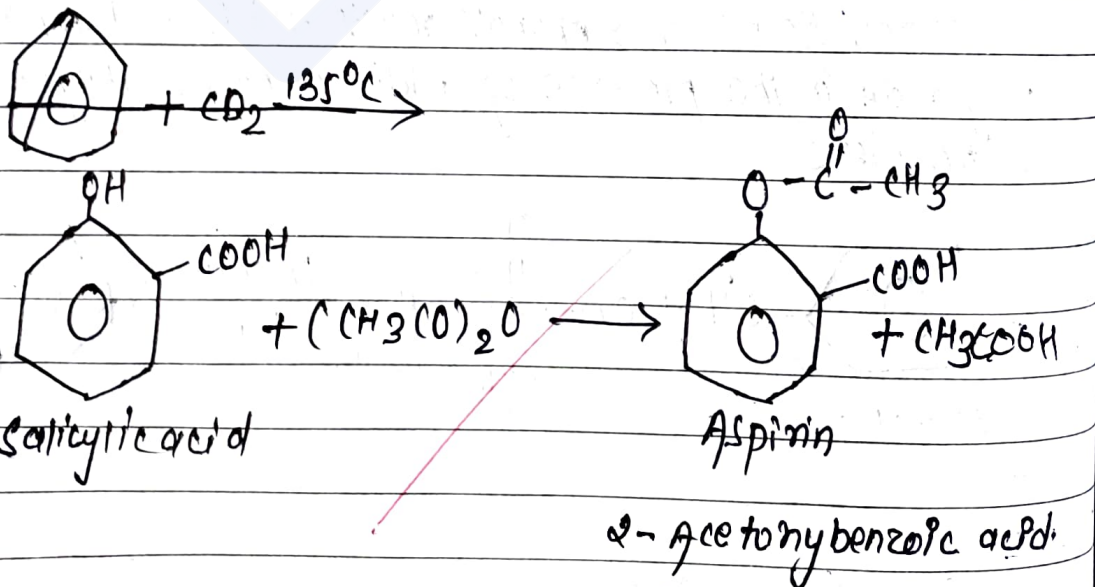


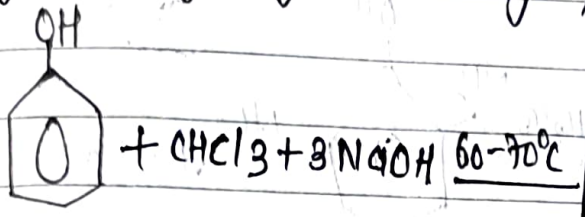
8. Kolbe's reaction (carboxylation) → phenol in the form of sodium phenoxide reacts with carbondioxide (CO_2) at 135°C under 4-7 atm pressure to form sodium salicylate which on acidification gives salicylic acid.

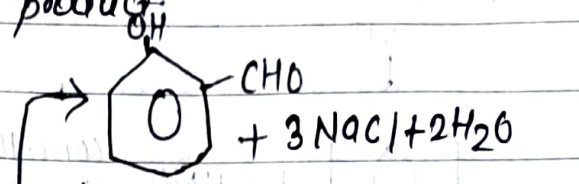


Salicylic acid when acted with acetic anhydride gives Aspirin (analgesic and antipyretic):-

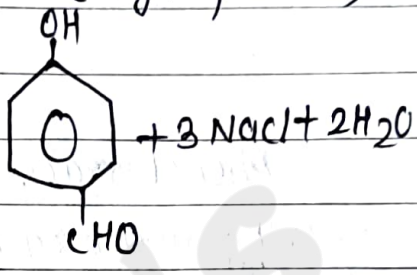


c) Reimer-Tiemann's reaction → Phenol when heated to 60-70°C with chloroform and aqueous NaOH gives ortho hydroxy benzaldehyde (salicylaldehyde) as major product.





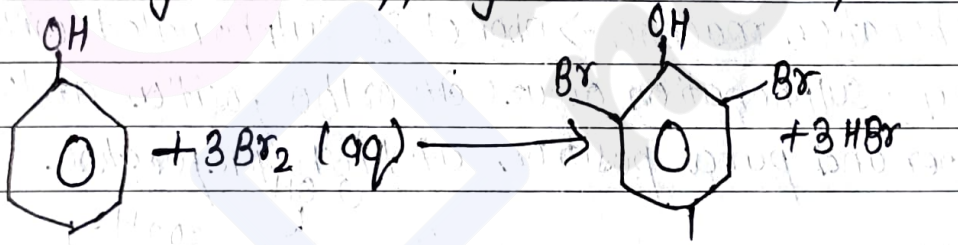
o-hydroxy benzaldehyde (Major product)



p-hydroxy benzaldehyde (minor)

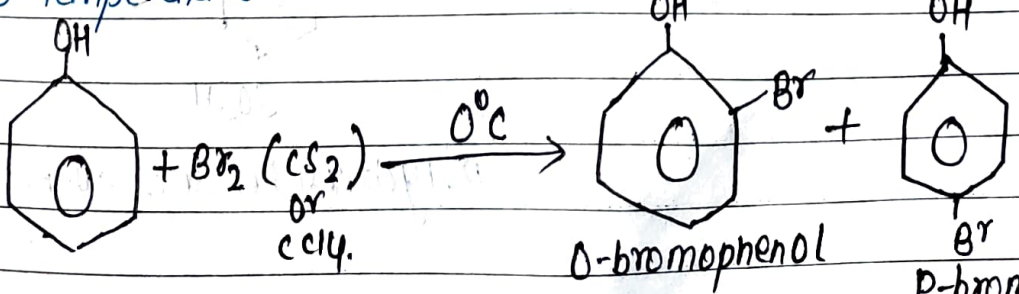
Electrophilic substitution reaction

1. Halogenation reaction → phenol reacts with halogen to form polyhalogen substituted compounds. For eg:- phenols reacts with aqueous bromine to form white ppt of 2,4,6-tribromo phenol.



2,4,6-tribromophenol.

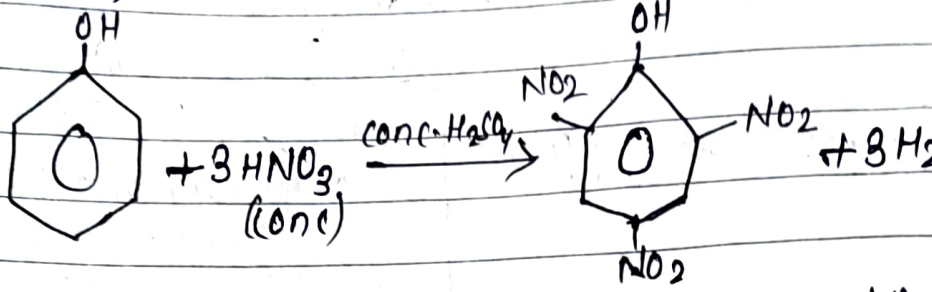
→ Monobromophenol is obtained by reacting phenol with bromine in the presence of carbon disulfide or carbon-tetrachloride at low temperature.



o-bromophenol

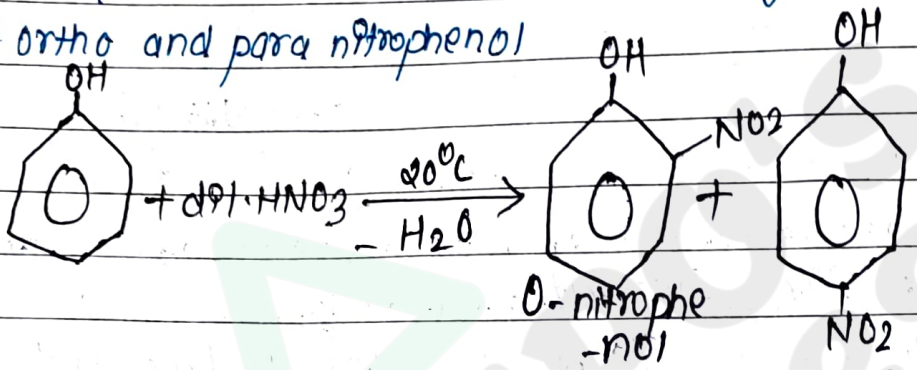
p-bromophenol

2. Nitration reaction → phenol reacts with conc. HNO_3 in the presence of conc. H_2SO_4 to give 2,4,6 – trinitro phenol (picric acid)

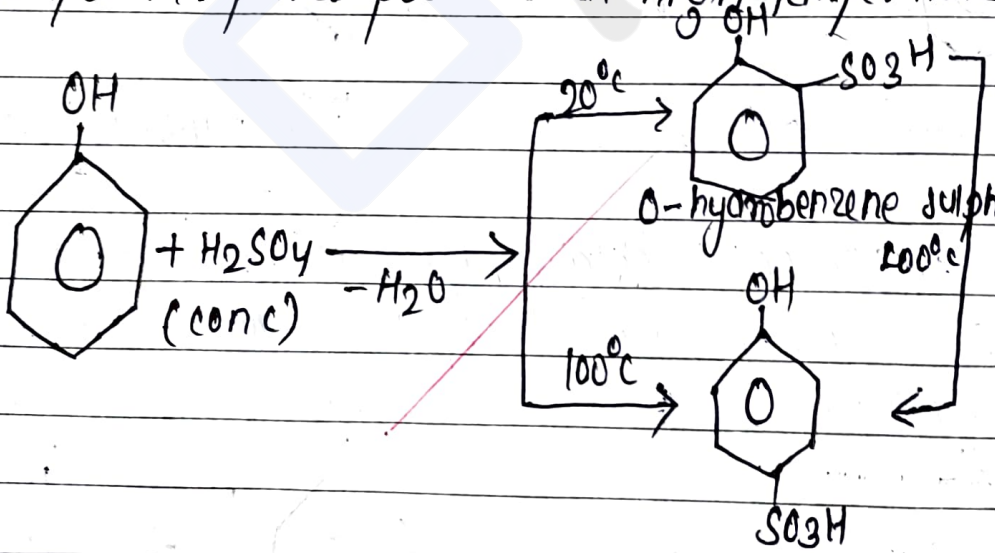


(picric acid)

Phenol reacts with dil. HNO_3 to give a mixture of ortho and para nitrophenol



3. Sulphonation reaction → phenol is sulphonated with conc. H_2SO_4. Sulphonation occurs at ortho position at low temperature and para position at high temperature.



P-hydroxy benzene sulphonide.

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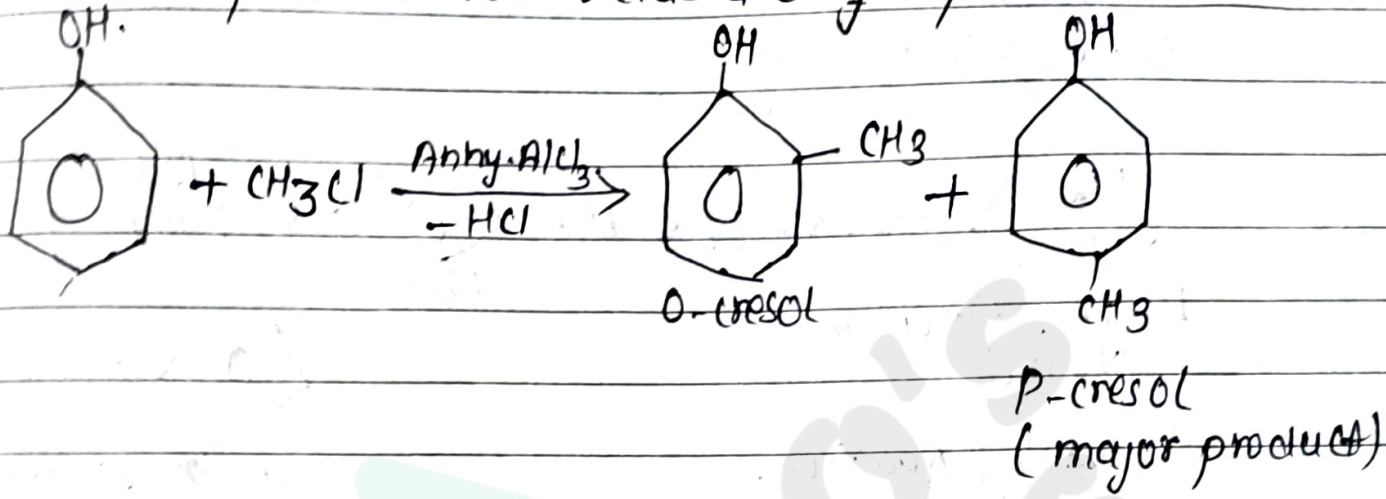
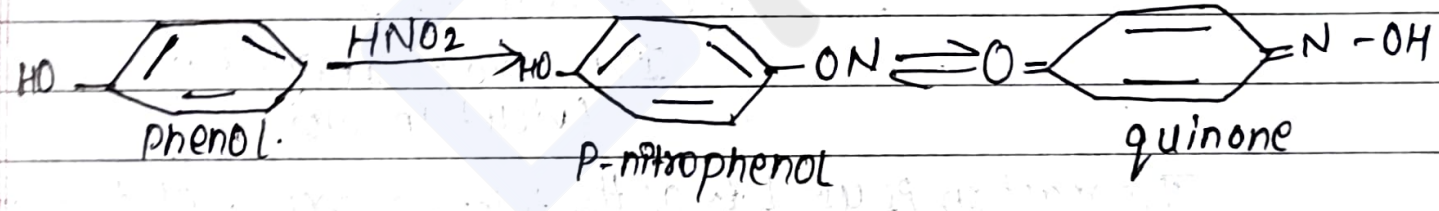
4. Friedal craft's alkylation → phenol reacts with alkyl halides in the presence of anhydrous aluminium chloride to give a mixture of o-cresol and p-cresol ~~xx xx~~ yields are often poor.



Test reaction of phenol →

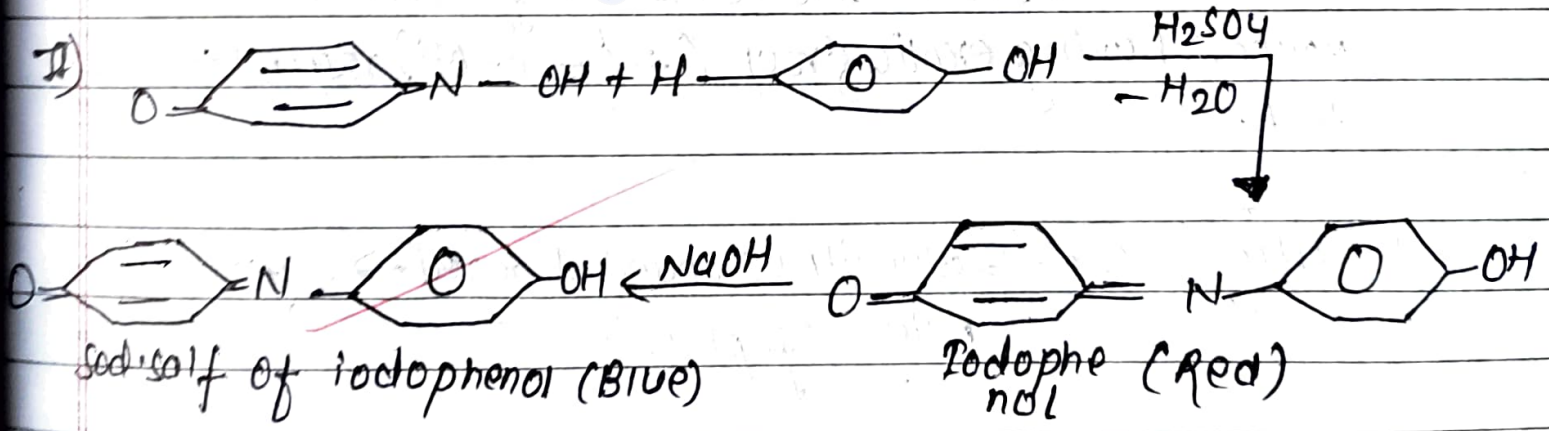
1. Liberman reaction → when phenol is treated with conc. H_2SO_4 and $NaNO_2$ it gives red or brown coloration which turns blue or green on the presence of aqueous sodium ~~hyd~~ hydroxide. Hence this reaction is used for the test of phenol.

I)



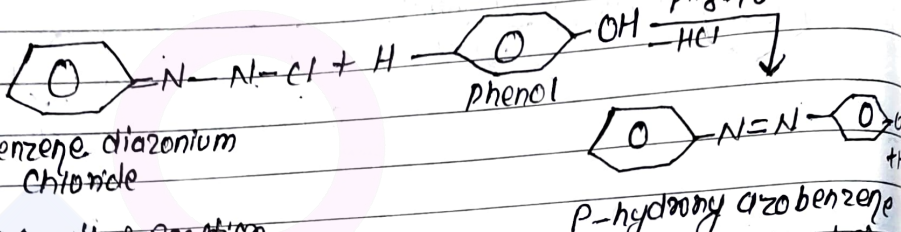
phenol. P-nitrophenol quinone

II)



Sod. salt of iodophenol (Blue) Iodophenol (Red)

2. Azo dye test Reaction (Reaction with diazonium salt)
Phenol react with benzene diazonium chloride in slightly alkaline medium to form parahydroxy azobenzene i.e (a yellow azodye).



benzene diazonium chloride

→ Coupling Reaction.

p-hydroxy azobenzene (yellow azodye)

3. Ferric chloride test →
Phenol reacts with aqueous solution of ferric chloride to give violet colored complex. This complex is co-ordination compound in which iron is hexavalent

$$C_6H_5OH + FeCl_3 \longrightarrow [Fe(OC_6H_5)]^{3-} + 3H^+ + 3HCl$$

Iron hexa phenoxide ion (violet in color)

This reaction is used to as the test for phenol. All the compounds having enolic group (C=C-OH) respond to this test.

4. Litmus test → Blue litmus changed to red → confirmed acidic nature of phenol.

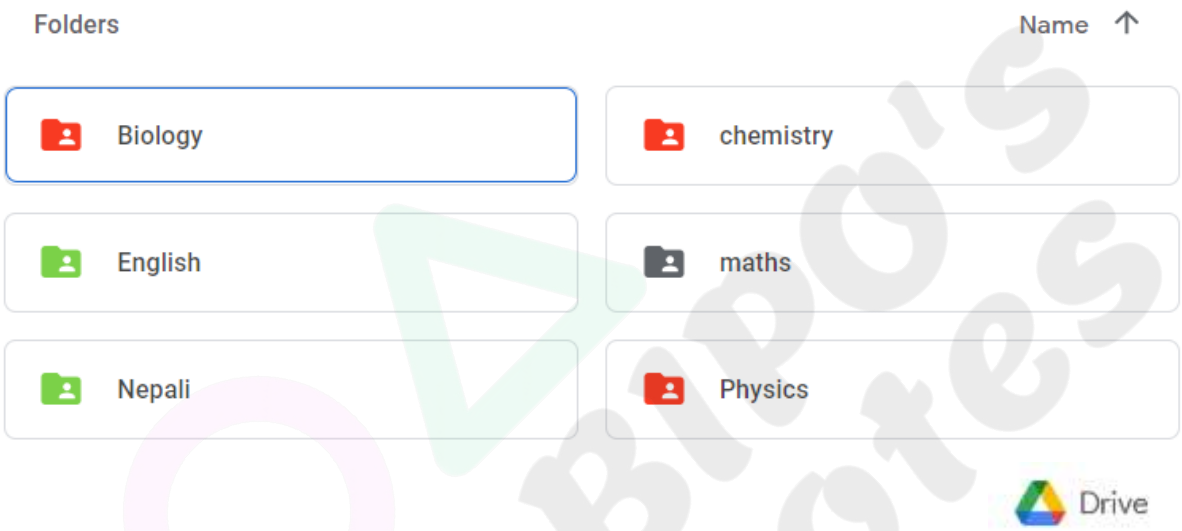
5. Na_2CO_3 or $NaHCO_3$ test → phenols donot give effervescence with it. It can be easily distinguished from carboxylic acid

Uses of phenol → 1) In the manufacture of bakelites.
2. In the manufacture of dyes, drugs, explosive (picric acid)
3. In the preparation of phenolphthalein.
4. As antiseptics in soaps, lotions and ointments.

Bipin Khatri

(Bipo)

Class 12 complete notes and paper collection.



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