



Date: _____

Page: _____

UNIT - II

Phenol are ^{these} compound containing an alcohol (-OH) group attached directly to an aromatic ring

General formula \rightarrow ArOH

Ar = Phenyl, substituted phenyl or other aryl group

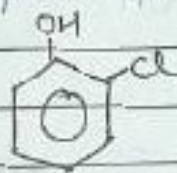
Structure :



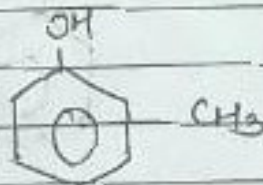
Phenol

Phenols are generally simplest member of family

Eg : Chlorophenol / o-chlorophenol



* Cresols :



* Uses :

- Used as solvent, disinfectant & as chemical intermediate.

.)

→ Meta Cresol : It is used to produce herbicides as a precursor to insecticides.

• It produces anti-oxidant properties.

• It produces explosive.

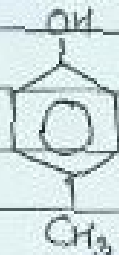
Eg: 2,4,6-trinitrophenol

• It is used in synthesis of drug such as Saliprolol.

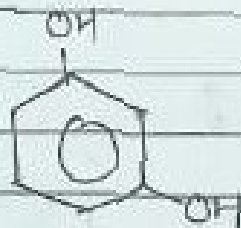
→ Para Cresol : It is used in formulations of anti-oxidant, fragrance & dyes.

• It is used in production of antioxidant such as BHT (Butylated Hydroxy Toluene).

p-cresol



* Resorcinol :



Used

→ Uses : In production of dioxidised and plasticizer.

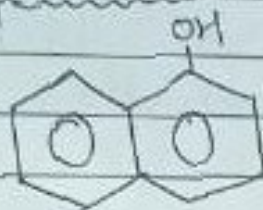
• It is also called Mesercline.

• It is used as UV absorber in sunscreens.

• It is used as antiseptic and disinfectant.

-) It is used as analgesic
-) 5-10% is used in ointment for treatment of chronic skin disease.

* Naphthols :



α -Naphthol



β -Naphthol

- Uses :
-) It is used in biomarker for live stock & human exposed to poly-cyclic aromatic hydrocarbon.
 -) 1-Naphthol is used as precursor to variety of insecticide including pharmaceutical product such as Nadolol.
 -) It is used in detection of presence of carbohydrate as in Melisch Test.
 -) It is used to detect the presence of Arginine in protein, 1-Naphthol react with sodium hydroxide (NaOH) Sakaguchi Test.

* Phenol :



-) Phenol reagent used in plastic manufacturing industry.



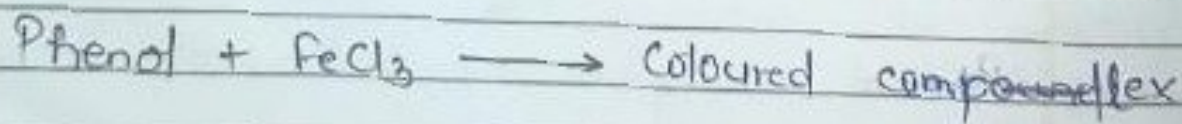
- For commercial preparation of phenolic reagent polymerization phenol with formaldehyde (HCHO) form Bakelite.
- In cosmetic industry, it is used in formation of sunscreens, skin whitening cream & hair colour soft.
- Study an extraction of biomolecule, phenol is used in extraction of nucleic acid from tissue sample.
- It is also used as a versatile precursor for a large variety of drug substance and herbicides.

* Qualitative Test :

1) Litmus Test : Place a trace of organic compound on the moist blue litmus paper. It turns red.

2) Neutral FeCl_3 test : When phenol are treated with neutral FeCl_3 solⁿ, they form coloured complexes. The colour of the complex may be violet, red, blue or green.

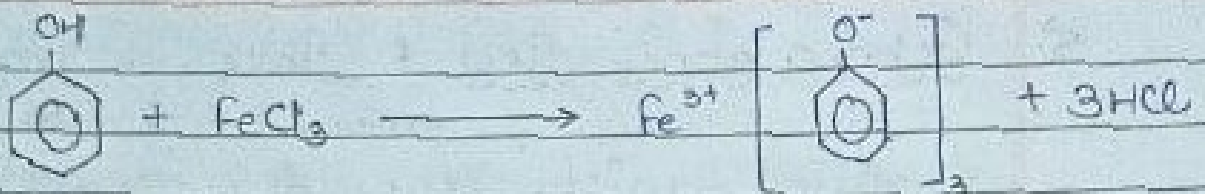
→ This is characteristic reaction of compound having phenolic group.
Fe^{III} stable enols respond to this test.





Date: _____

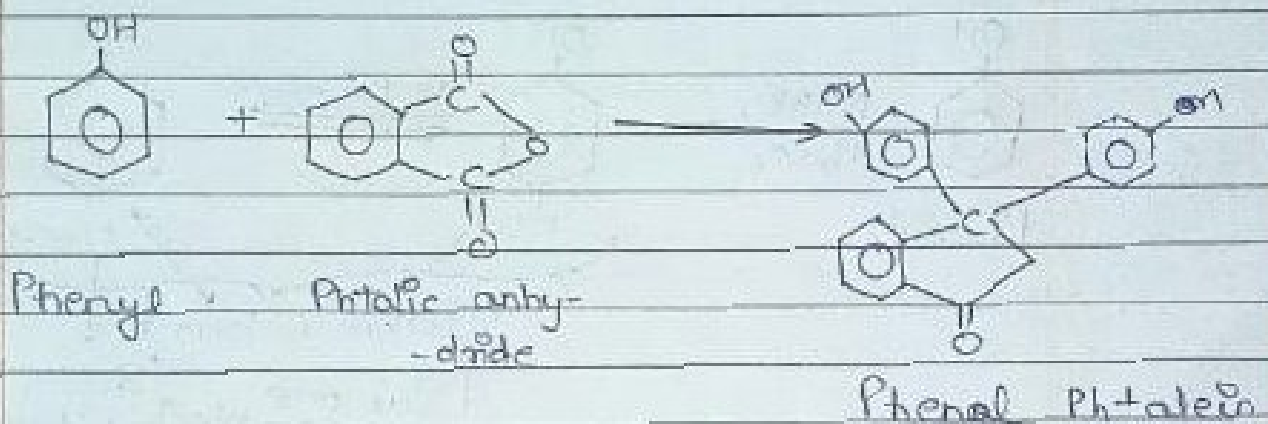
Page: _____



3) Phthalic Test :

or

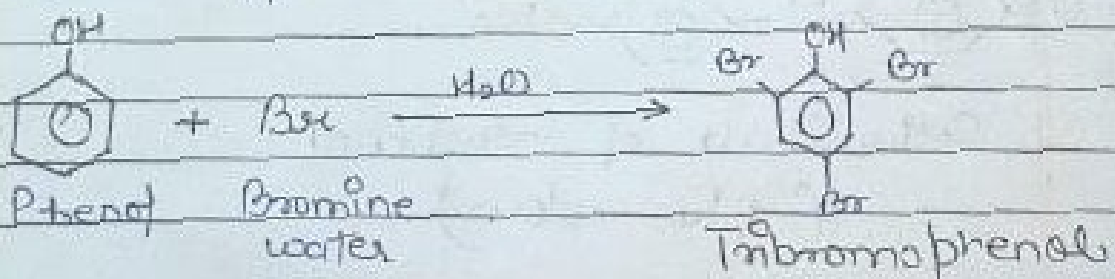
→ Florescence Test : Heat some organic compound + phthalic anhydride with a few drop of concⁿ H₂SO₄ in test tube. pour the heated mixture into water taken in beaker and then add NaOH solⁿ till it become alkaline.



4) Bromine Water Test : Take aq. or alcoholic solⁿ of the organic

compound in a test tube.

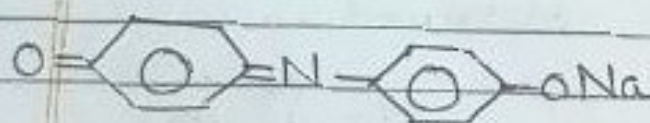
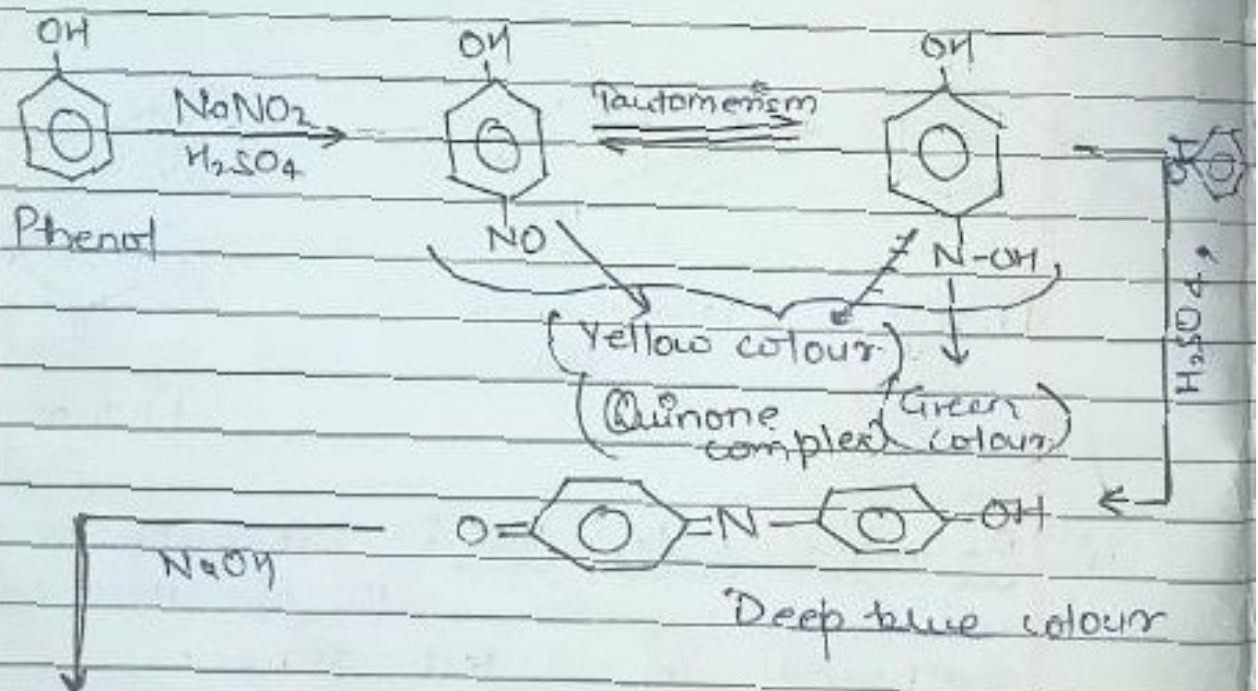
Add excess of Br₂ water a yellowish white ppt. is obtained.



5) Liebermann's Test : Take a small amount of of compound + fused with the few crystals of NaNO_2 in a test tube.

Cool the test tube and add some concⁿ H_2SO_4 . A deep green colour obtain and when poured into large excess of H_2O , green colour changed to red.

When a little NaOH solⁿ is added to the aq. solⁿ the solⁿ become deep blue coloured



Sodium salt of Indophenol
(Blue colour)



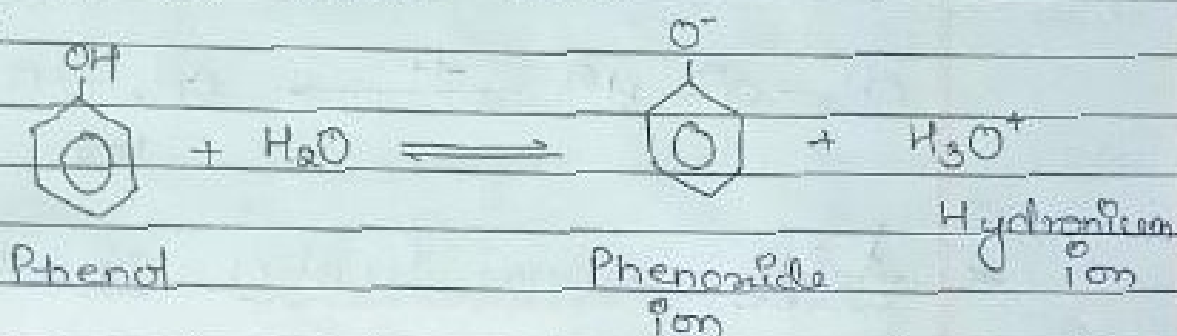
Date: _____

Page: _____

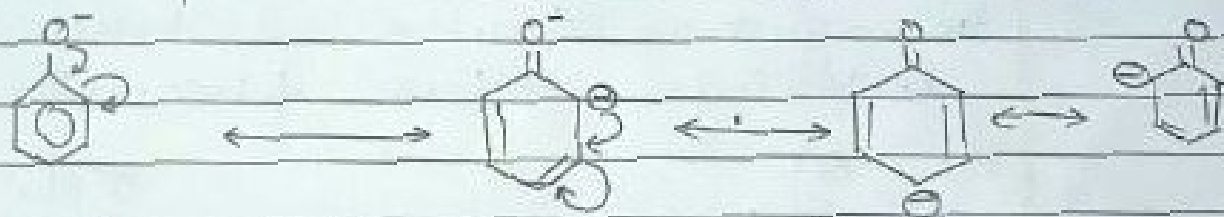
* Acidity of Phenol:

- Phenols are more acidic than alcohol but less acidic than COOH .
- The acidity of phenol is due to its ability of losing H^+ ion to form phenoxide ion.
- Phenol is weak acid.

Eg:



- The $-ve$ charge of phenoxide ion is stabilised by resonance. This makes the phenoxide ion more stable.



Resonating structure of phenoxide ion

Phenols are more acidic than alcohol because the phenoxide anion is resonance stabilised by aromatic ring.

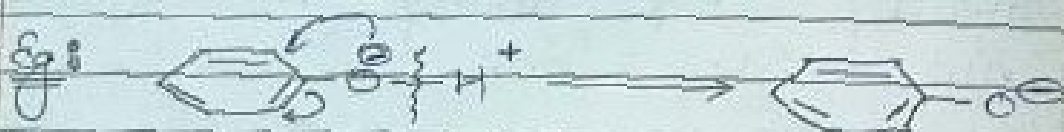
% s character & acidity

5

Date: _____

Page: _____

Sharing the negative charge over the ring increases the stability of phenoxide ion thus increase the tendency of corresponding phenol is dissociate.



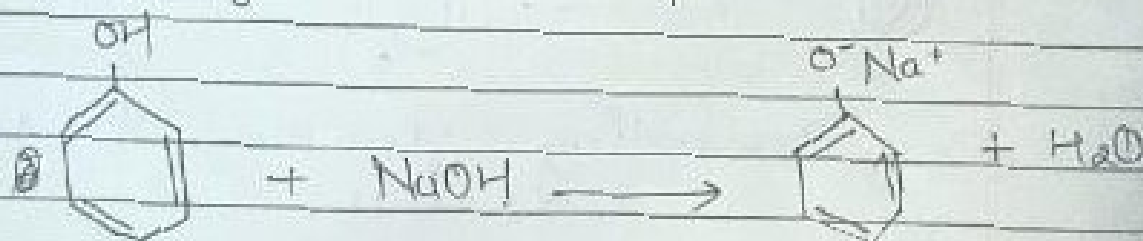
More stable



less stable

* Acidic characteristics of Phenol

- pH of dilute solⁿ of phenol in water raised b/w 5-6
- phenol react with NaOH solⁿ to give colourless solution containing Sodium phenoxide



Phenol
(Acid)

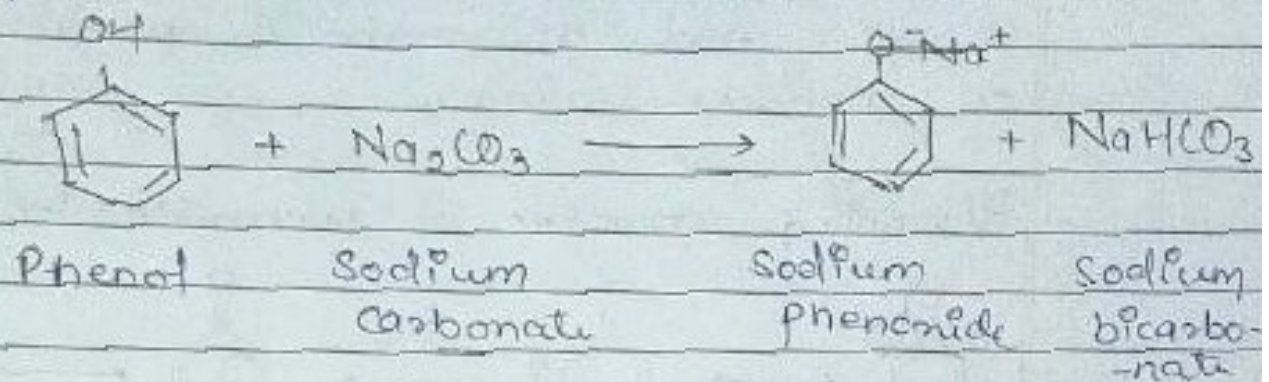
Sodium
hydroxide
(Base)

Sodium
Phenoxide
(Salt)

e density $\propto \frac{1}{\text{Acidity} \propto \text{stability}}$ } Case of +I effect



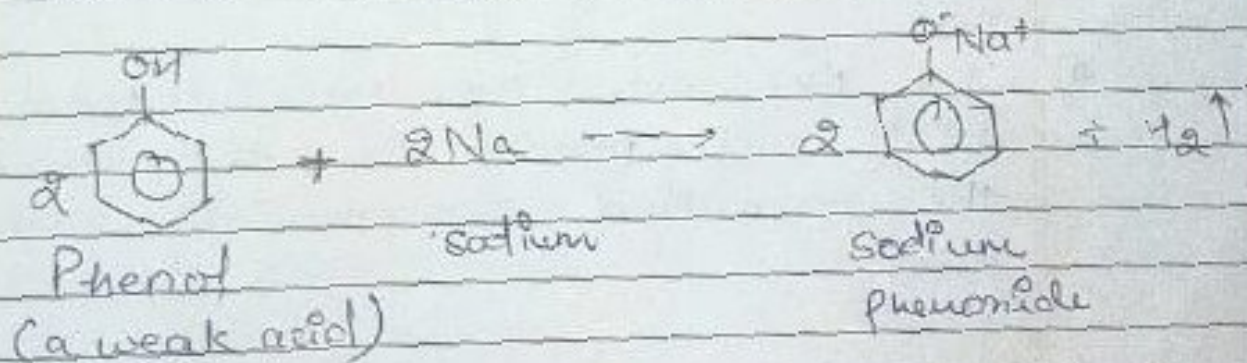
→ Due to weak acidic nature phenol partially react with sodium carbonate to give sodium phenoxide & sodium bicarbonate



* Unlike other COOH, phenol is not acidic enough to react with NaHCO₃ to produce CO₂ & water

→ Like other Acids, phenol react with metallic Na / K to give Hydrogen gas.

→ Phenol being a weak acid it is a slow reaction.



Case of \downarrow e-density \rightarrow \uparrow stability & \uparrow acidity
-Effect



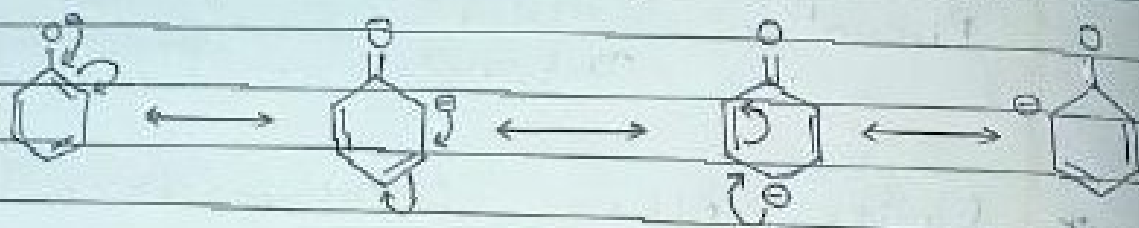
Date: _____

Page: _____

* Effect of Substituents on Acidity

1) The resonance structure of phenoxide ion explain the delocalisation of -ve charge and at ortho & para position of benzene ring.

Resonating structure of phenoxide ion :



2) Substituents particularly those locate ortho and para to through the -OH group can influence the acidity of phenol due to resonance / inductive effect

(-I)

3) Electron withdrawing group like NO_2 , COH increase the stability of phenoxide ion.

(+I)

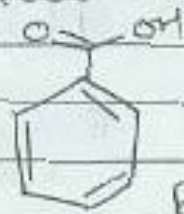
4) EDG like CH_3 , OH , NR_2 decrease the acidity of phenol as they prohibit the formation of phenoxide ion.

* Aromatic Acids : Aromatic acids are a type of aromatic compound including in that class are substance containing an aromatic ring & an organic acid functional group.

There are several categories of aromatic acids including :

- 1) Phenolic Acid : substance containing an aromatic ring, organic carboxylic acid.
- 2) Aromatic amino acid : Phenylalanine, Tryptophan.

* Benzoic Acid : Benzene carboxylic acid.



Benzoic Acid

• Colourless, crystalline solid.

* Uses : • Benzoic acid used as precursor and plasticizer.

• Used as a topical antiseptic.

• Benzoic acid & its salts are used as food preservatives.

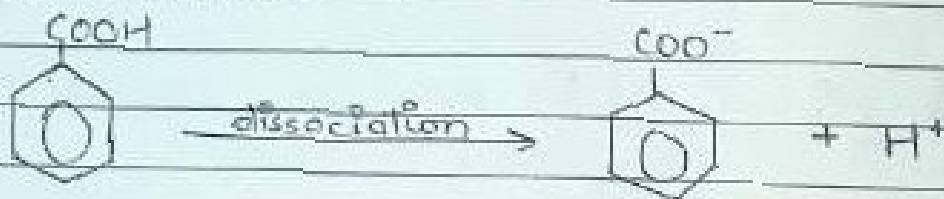
• Benzoic acid is a precursor to benzoyl chloride (C_6H_5COCl) by treatment with thionyl chloride or one of the chloride of phosphorus.



Benzoyl chloride is an important starting material for several benzoic acid derivatives like benzyl benzoate which is used in artificial flavour and insect repellent.

* Acidity of Aromatic Acids :

- These compounds release H^+ which are acidic in nature.
- In aromatic acid after dissociation it releases H^+ ion so they are acidic in nature.

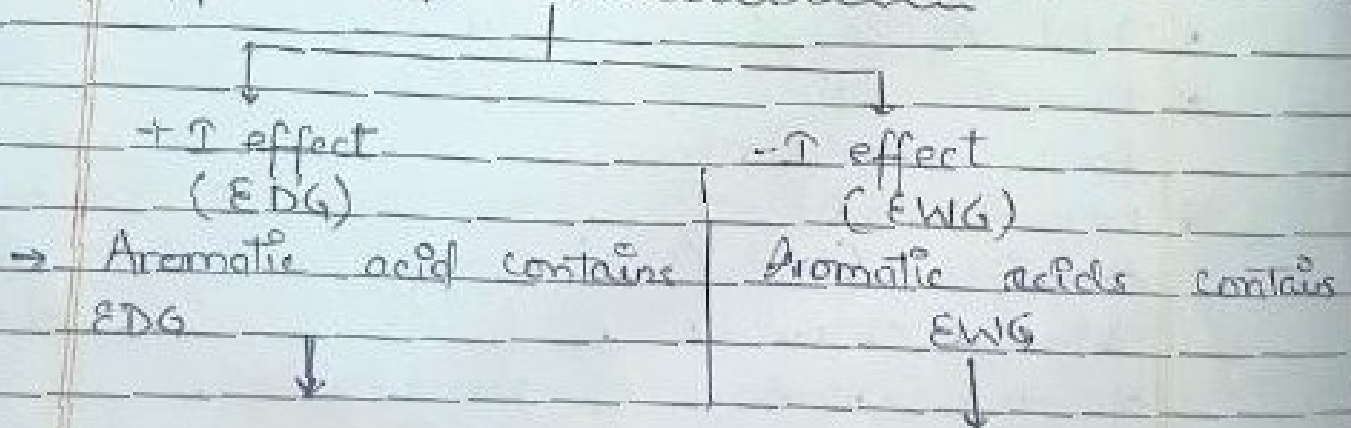


Benzoic acid

Benzoate ion

- Benzoate ion is stable due to sharing of -ve charge, so they are acidic in nature.

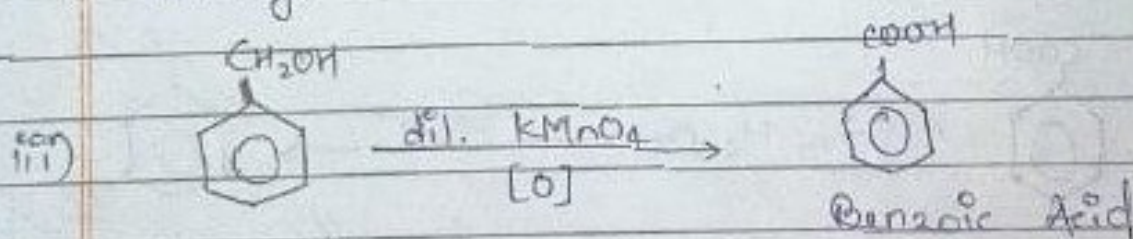
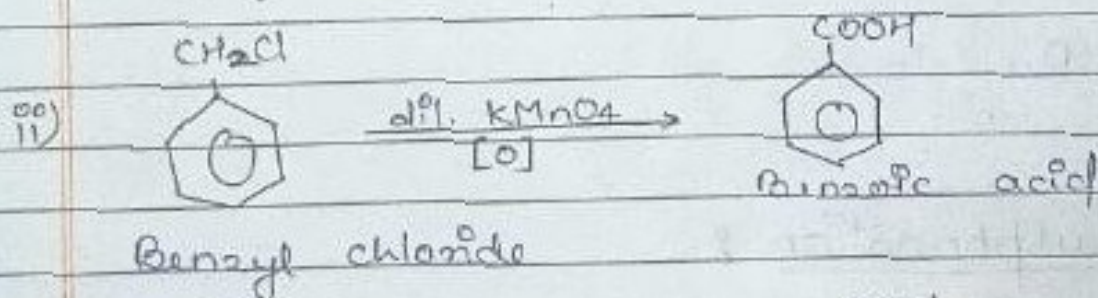
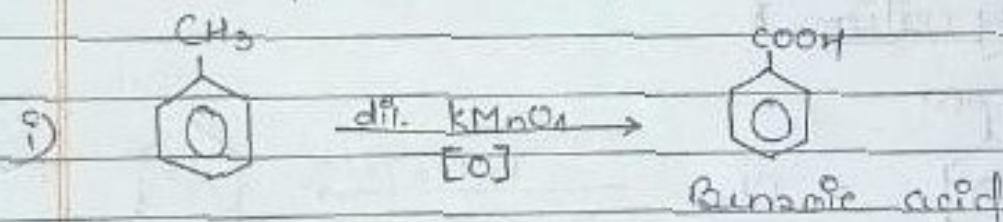
* Effect of Substitution :



<p>→ Increase the e⁻ density</p> <p style="text-align: center;">↓</p> <p>→ Decreases stability or May less stable</p> <p style="text-align: center;">↓</p> <p>→ less acidic nature</p> <p>Eg: Alkyl halide</p>	<p>Decrease the e⁻ density</p> <p style="text-align: center;">↓</p> <p>Increases stability or Highly stability</p> <p style="text-align: center;">↓</p> <p>More acidic nature</p> <p>Eg: Halogen</p>
---	---

* Preparation of Benzoic Acid :

→ By the oxidation of Aromatic compound containing aliphatic side chain in presence of dilute $KMnO_4$ or $K_2Cr_2O_7$

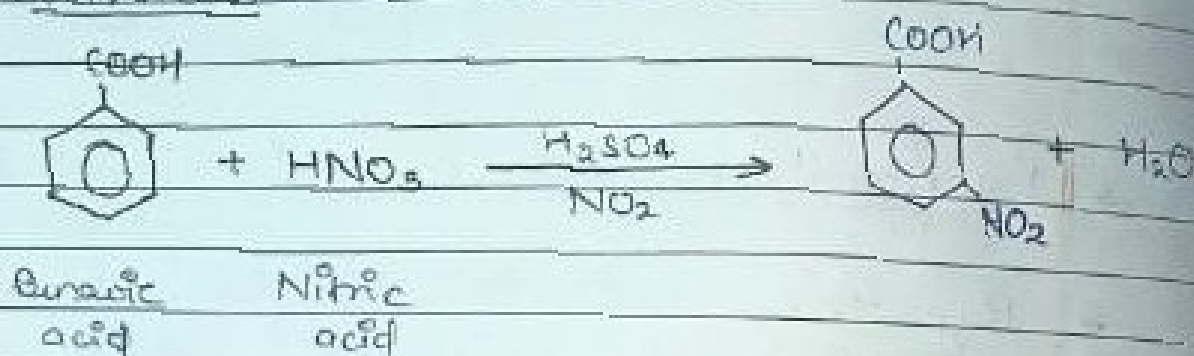


iv) By hydrolysis of Cyano benzoic acid :

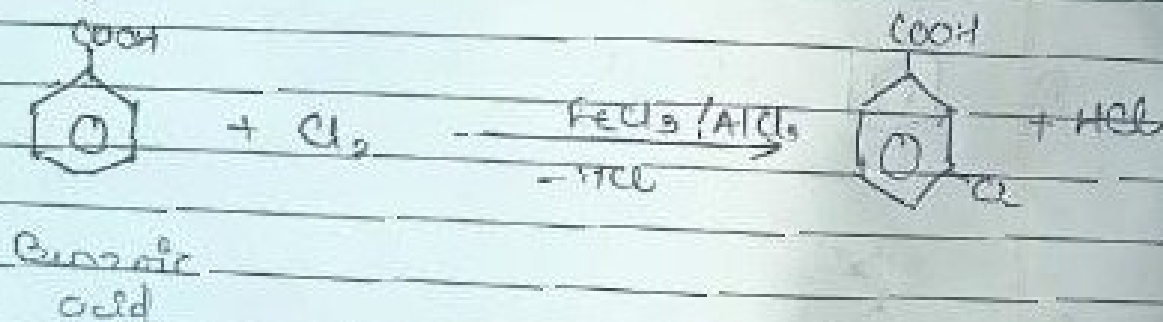


* Important Reaction of A.A :

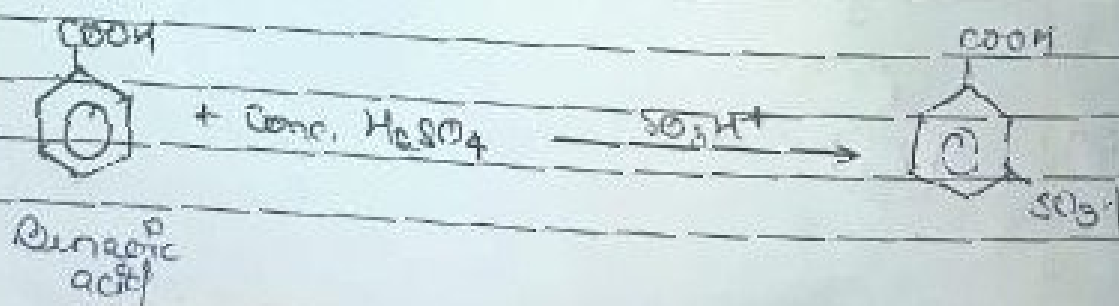
→ Nitration :



→ Halogenation :



→ Sulphonation :

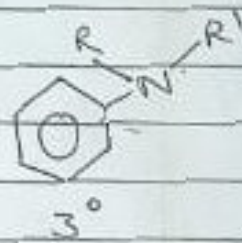
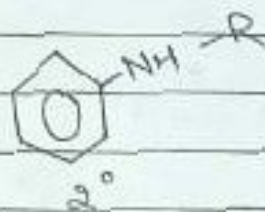


* Aromatic Amine : Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atom of ammonia molecule by alkyl group (Alkyl amine) or aryl group (Aromatic amine) or

OR

Aromatic amine is a organic compound consisting of an aromatic ring attached to amine.

* Aliphatic Amines : Aliphatic amines are those ^{which} are directly linked to one, two or three alkyl group.



* Aromatic Amine : Aromatic amine have an amine ($-NH_2$) attached directly to the aromatic ring.

→ Aromatic amine known as aryl amines



→ Compound with two amine ($-NH_2$) group are named by adding the suffix diamine to the name of the corresponding

alkane or aromatic compound

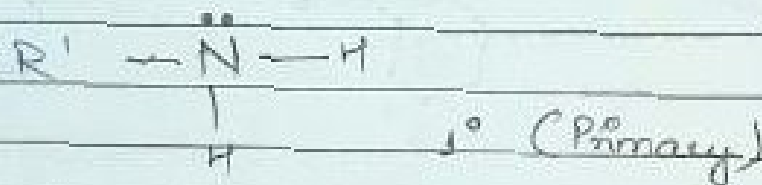
eg 6



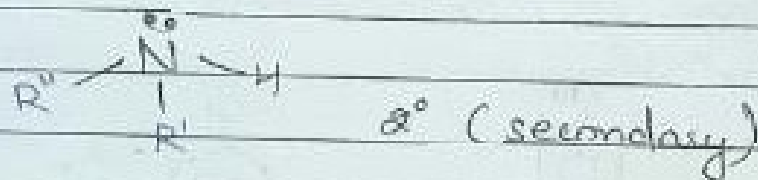
* Classification of Amine

- Primary
- secondary
- Tertiary

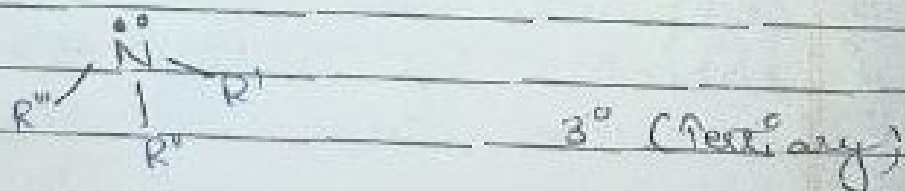
→ Primary Amine : 1-alkyl or aryl (C_6H_5) attached to the nitrogen atom



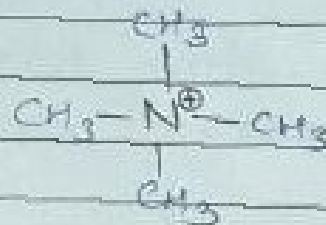
→ Secondary Amine : 2-alkyl or aryl group is attached to the N-atom.



→ Tertiary Amine : 3-alkyl or aryl group is attached to the N-atom



→ Quaternary Amine : An ion in which N is bonded with 4-alkyl or aryl group & bears a +ve charge.



4° (Quaternary)

* Basicity of Amine : A amine can act as a :

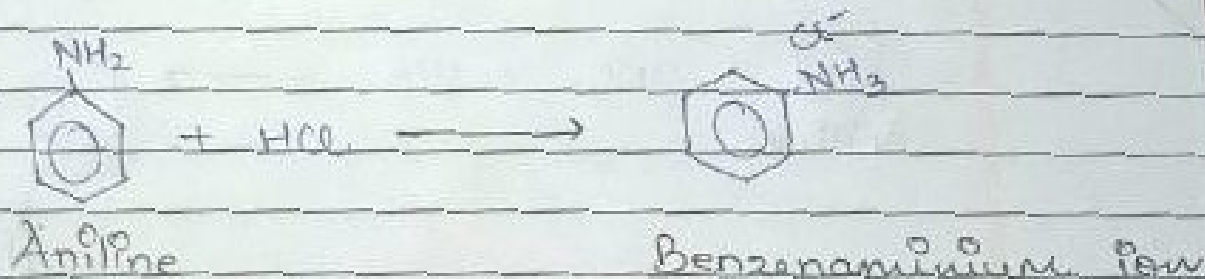
→ A nucleophile (Lewis base) because its lone pair is non-bonding e⁻ can form a bond with an electrophile.

* Reaction of Amine :

→ Reaction of amine with acid will give amine salt, - composed of two types of ion

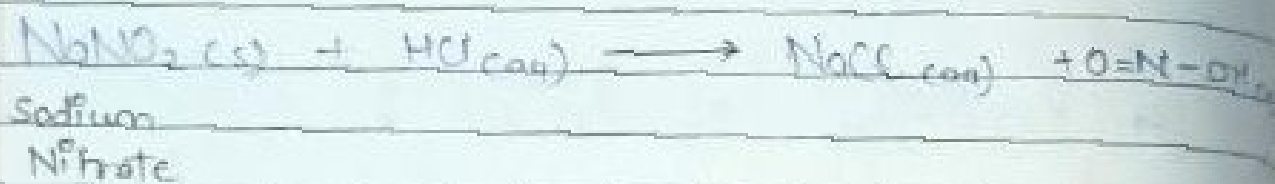
• The protonated amine cation (an ammonium ion)

• Anion derived from the acid



→ Reaction with nitrous acid :

- Nitrous acid is unstable & is prepared in situ by the rxn of dilute HCl or dil. H₂SO₄ with NaNO₂ in the absence of heat.



- Nitrous acid can be used to differentiate primary, secondary, tertiary aliphatic amines.
- Primary aromatic amine react with cold HNO₂ & dissolved in dil. HCl & at 0-5°C to produce diazonium salt. When this cold salt is heated at room temp. N₂ gas will evolve.



N₂ ↑ + mixture product

→ Ring Halogenation of Phenyl Amine :

When Br₂ water is added to phenyl amine (aniline) at room temp. decolorisation of bromine water occurs & a white ppt of 2,4,6-tribromoaniline is obtained.

This reaction is used to test for bromine aniline.

