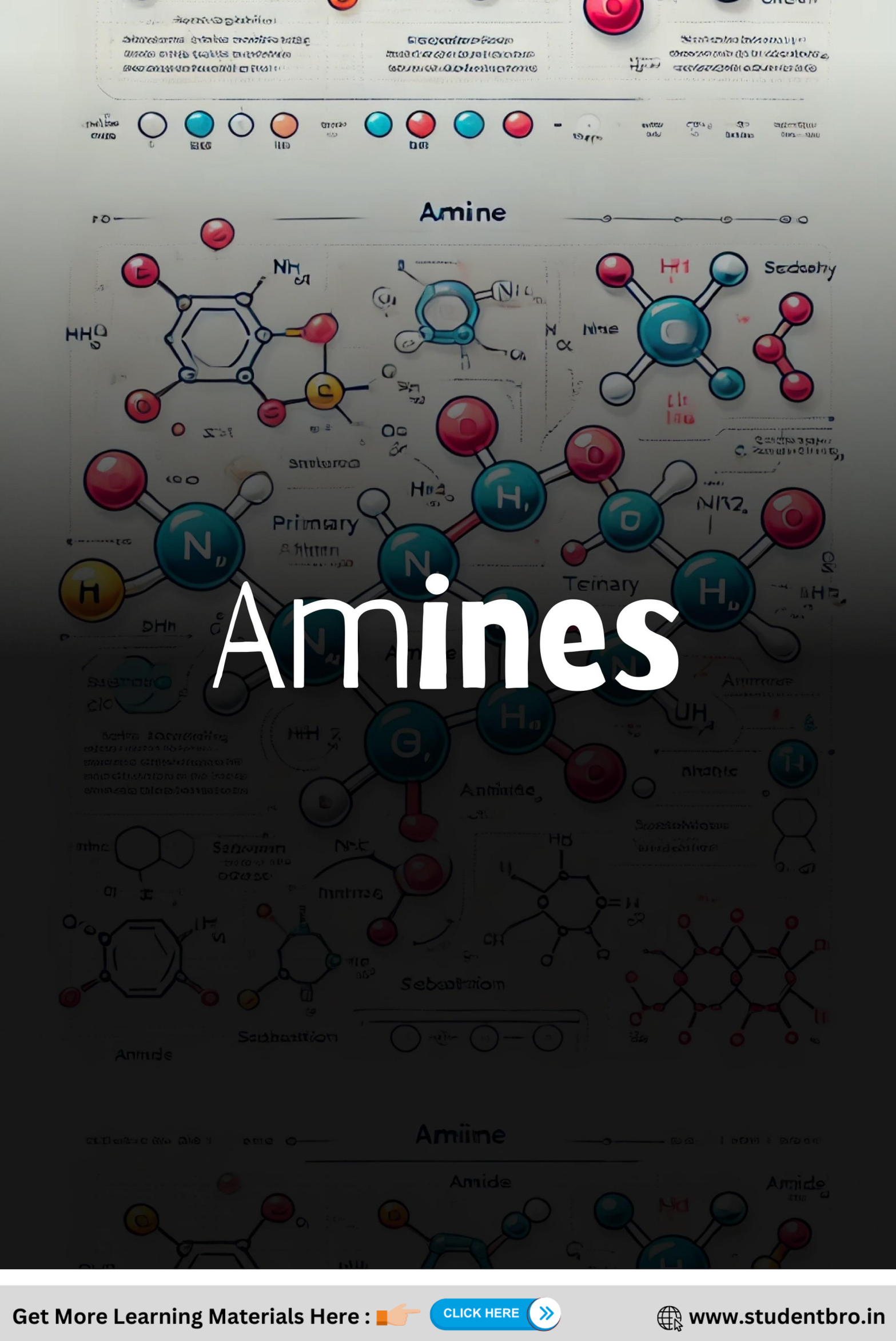


Amines

Amines

① Reduction of nitro compounds.

$-NO_2 \xrightarrow{R\cdot A} -NH_2$

R·A → ① Sn + HCl
② Fe + HCl ★
③ H_2 + Ni
Alcohol (ROH)

② Ammonolysis of alkyl halide.

NH_3 (Ammonia) $\xrightarrow[SN_2]{R-X}$ $R-NH_2$ (1° amine) $\xrightarrow{R-X}$ $R-NH-R$ (2° amine)

$R-X$ ↓

Quaternary ammonium salt $R-\overset{+}{N}(R)(R)-R\ X^-$ $\xleftarrow{R-X}$ $R-N(R)-R$ (3° amine)

③ Reduction of Nitriles.

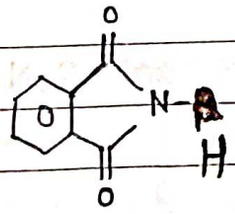
$R-CN \xrightarrow{R\cdot A} R-CH_2-NH_2$

R·A → ① H_2 + Ni
② Na(Hg) + ROH
③ $LiAlH_4$

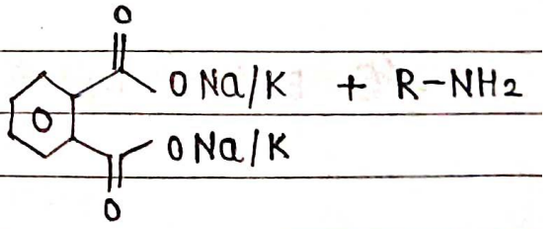
④ Reduction of Amides:

$R-CONH_2 \xrightarrow[H_2O]{LAH} R-CH_2-NH_2$

⑤ Gabriel pthalamide synthesis. (For aliphatic 1° amine)



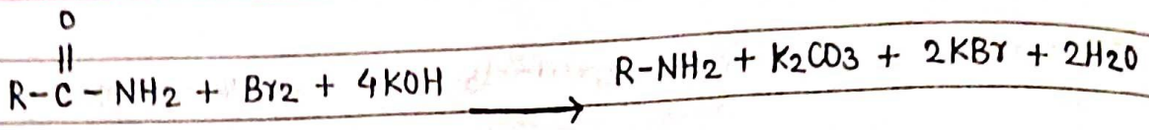
1) NaOH / KOH
2) R-X (1°)
3) NaOH / KOH (aq)



+ $R-NH_2$

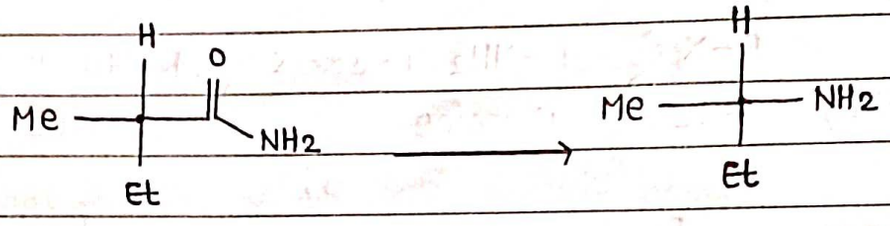
⑥ Hoffman Bromamide degradation.

$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[KOH/NaOH]{Br_2} R-NH_2 + Na_2CO_3 + NaBr + H_2O$

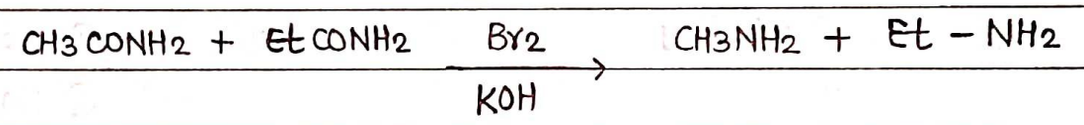


OP POINTS :

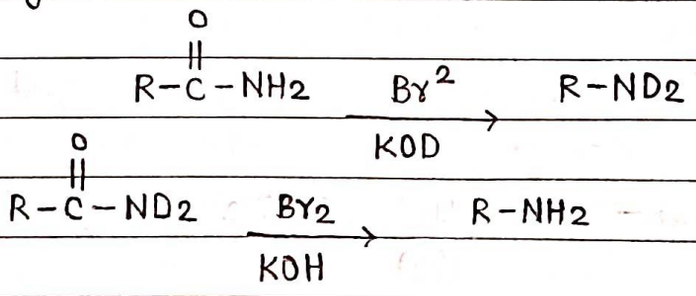
① Rearrangement of R is purely intramolecular (stereochemistry remains same)



② If mix of amides are present then intramolecular migration of alkyls occurs b/w the same amide.



Isotopic change :



Properties of Amines :

✓① Basic strength

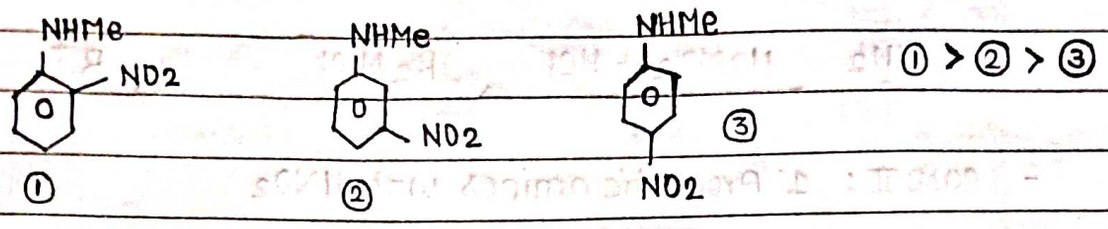
$R-NH_2$	R_2NH	R_3N
1° amine	2° amine	3° amine

Case I : In Gas phase, 3° > 2° > 1°

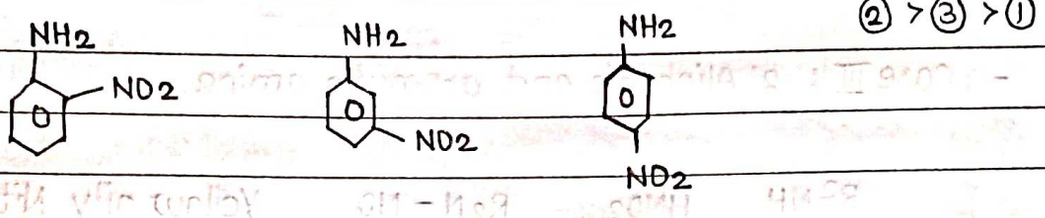
Case II : In aqeous medium, 2° > 1° > 3° (R = Me); 2° > 3° > 1° (R = Et)

- B.S $\propto$ +M $\propto$ +I $\propto \frac{1}{-M} \propto \frac{1}{-I}$

- SIR — B·S Increases — 2° and 3° Aromatic amines:



- SIP — B·S decreases — 1° Aromatic amines.



② Alkylation or Ammonolysis:

$$NH_3 \xrightarrow[SN2]{R-X} R-NH_2 \xrightarrow{R-X} R_2NH \xrightarrow{R-X} R_3N \xrightarrow{R-X} R_4N^+X^-$$

Quaternary ammonium salt

③ Acylation.

$$R-NH_2 \xrightarrow{R-C(=O)-Cl} R-NH-C(=O)-R$$

Amide

$$R-NH_2 \xrightarrow{R-C(=O)-O-C(=O)-R} R-NH-C(=O)-R + RCOOH$$

④ Carbyl amine reaction. (Isocyanide Test For Both Aliphatic and aromatic 1° amine)

$$R-NH_2 \xrightarrow[KOH]{CHCl_3} R-NC$$ (Foul smelling)

⑤ Reaction with nitrous acid.

- Case I: 1° Aliphatic amine with HNO_2

Rearrange if possible

$R\text{-}NH_2 \xrightarrow{HNO_2} R^{\oplus} \xrightarrow{OH^{\ominus}} R\text{-}OH$ or

$R\text{-}NH_2 \xrightarrow{NaNO_2 + HCl} R_2N^{+}Cl^{-} \rightarrow R^{+} \xrightarrow{OH^-} ROH$

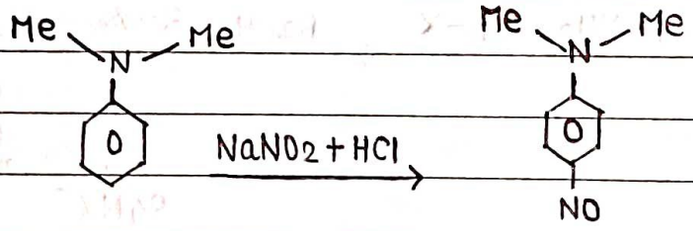
- Case II: 1° Aromatic amines with HNO_2

$ph\text{-}NH_2 \xrightarrow{NaNO_2 + HCl} phN_2^{+}Cl^{-}$

- Case III: 2° Aliphatic and aromatic amine.

$R^2NH \xrightarrow{HNO_2} R_2N - NO$ Yellow oily Nitrosamine.

- Case IV: 3° Aromatic amine.



⑥ Hinsberg's Test.

Hinsberg Reagent: $phSO_2Cl$ – Benzene Sulphonyl chloride

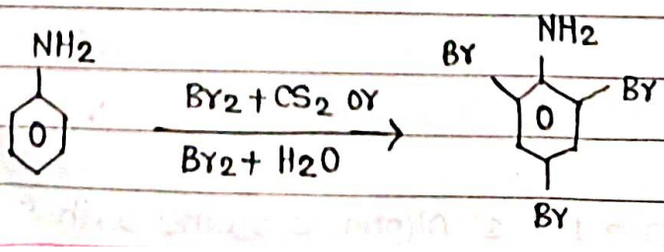
$R_3N \xrightarrow{phSO_2Cl}$ No RXN

$R_2NH \xrightarrow{phSO_2Cl} ph\text{-}S(=O)_2\text{-}N(R)\text{-}R \xrightarrow{alkali}$ Insoluble

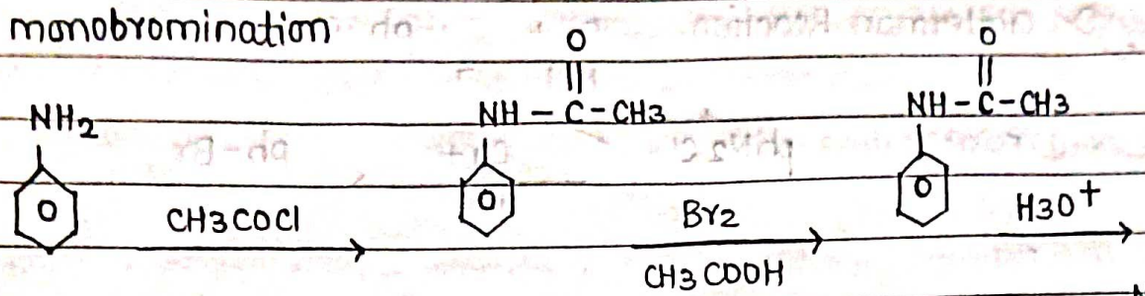
$R\text{-}NH_2 \xrightarrow{phSO_2Cl} ph\text{-}S(=O)_2\text{-}NH\text{-}R \xrightarrow{alkali}$ Soluble.

⑦ ESR

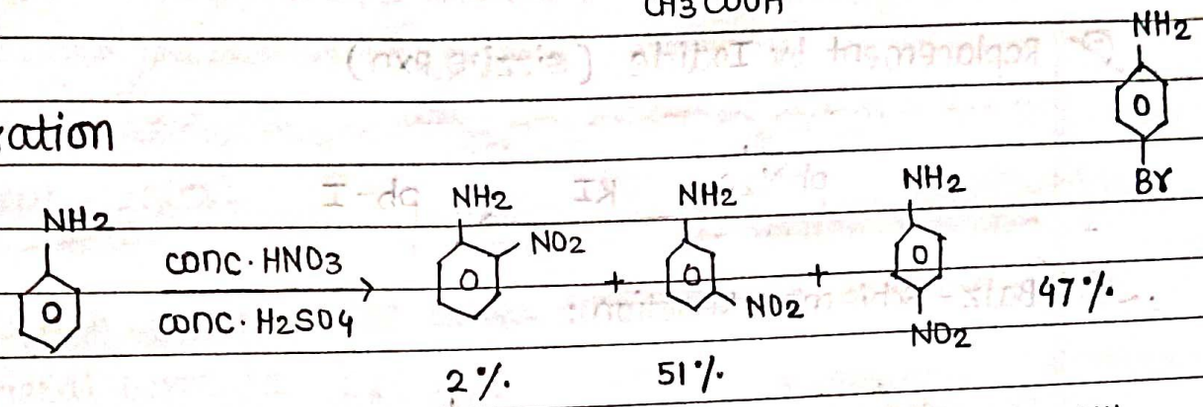
a) Bromination



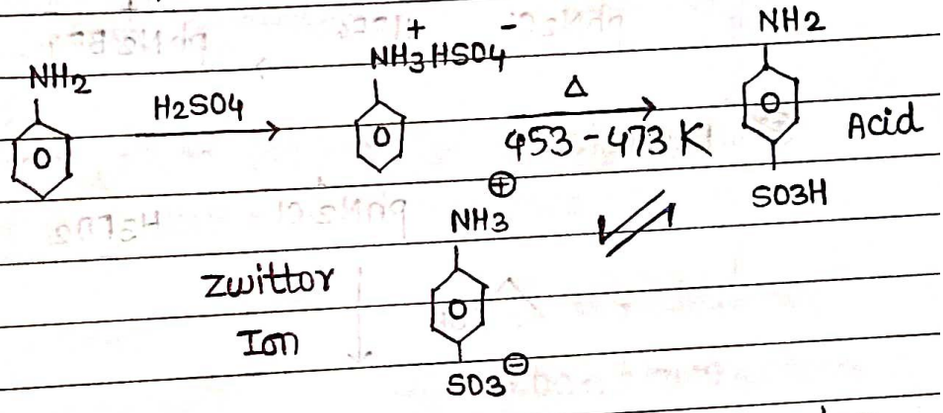
- For monobromination



② Nitration



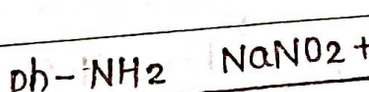
③ Sulphonation



- Aniline does not undergo FCR.

Zwitter Ion

MOP of Diazonium salts:

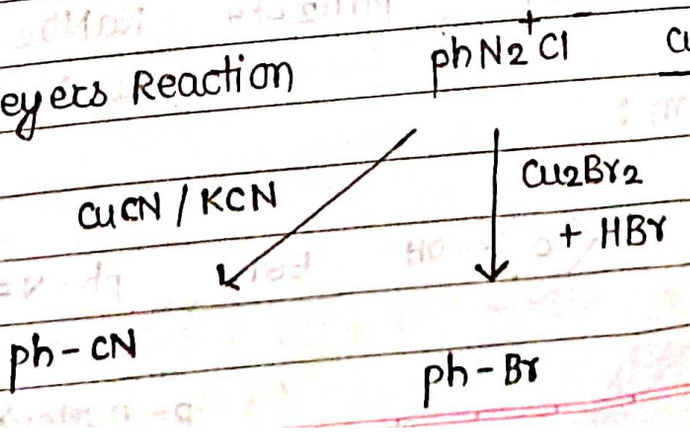


- Other Diazonium salts:

phN2+X-
phN+HSO4-
phN2+BF4-

Properties of diazonium salt

① Sandmeyers Reaction



② Gatterman Reaction

$PhN_2^+Cl^-$ —(Cu + HCl)→ Ph–Cl

$PhN_2^+Cl^-$ —(Cu + HBr)→ Ph–Br

③ Replacement by Iodide (Sizzi's Rxn)

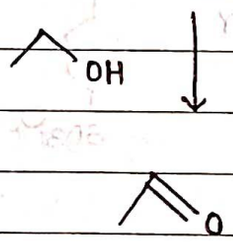
$PhN_2^+Cl^-$ —(KI)→ Ph–I

④ Balz-Schieman Reaction:

$PhN_2^+Cl^-$ —(HBF_4)→ $PhN_2^+BF_4^-$ —(Δ)→ $PhF + BF_3 + N_2$

⑤ Reduction:

$PhN_2^+Cl^-$ —(H_3PO_2)→ $Ph–H + H_3PO_3$



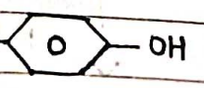
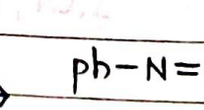
+ Ph–H

⑥ Formation of Phenol: $PhN_2^+Cl^-$ —(H_2O, 283K)→ PhOH

⑦ Formation of NitroBenzene:

$PhN_2^+Cl^-$ —(HBF_4)→ $PhN_2^+BF_4^-$ —($NaNO_2$, Cu, Δ)→ $PhNO_2$

⑧ Coupling Reaction:

$PhN_2^+Cl^-$ +  —(ESR)→ Ph–N=N– 

p- hydroxy azobenzene

(Orange Dye)

p-Amino Azobenzene

(Yellow Dye)