AMINES

MOP of Amines

① Reduction of nitro compounds

$Ph-NO_2 \xrightarrow[\text{or Sn/HCl or Fe/HCl}]{H_2 + Pd/Alcohol} Ph-NH_2$

NO_2 hatao NH_2 lagao

*** OP Point :-**

Aliphatic nitro: $R-NO_2 \xrightarrow{LAH} R-NH_2$

↳ but LAH cannot give NH_2 of aromatic nitro.

② Ammonolysis of alkyl halides

$NH_3 \xrightarrow[1^\circ\ S_N2]{R-X} R-\overset{+}{N}H_3 + X^{\ominus} \longrightarrow R-NH_2 + HX$ (1° Amine)

$R-NH_2 \xrightarrow{R-X} R_2NH$ (2° amine) $\xrightarrow{R-X} R_3N$ (3° amine) $\xrightarrow{R-X} R_4N^+X^-$ (quaternary Ammonium salt)

③ Reduction of nitriles

$R-C\equiv N \xrightarrow[3)\ Na(Hg)/ROH]{1)\ LAH/H_2O \quad 2)\ H_2+Ni} R-CH_2-NH_2$

CN hatao CH_2NH_2 lagao

*** OP Point :-**

↳ LAH can reduce Isocyanide

$R-\overset{+}{N}\equiv\overset{-}{C} \xrightarrow{LAH} R-NH-CH_3$

NC hatao, $NHCH_3$ lagao

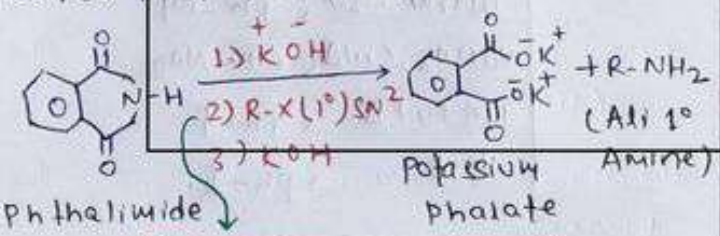
④ Reduction of Amides

$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{LAH} R-CH_2-NH_2$

CO hatao, CH_2 lagao

⑤ Gabriel phthalimide synthesis

↳ For prep 1° Aliphatic amine



Phthalimide → Potassium phalate + $R-NH_2$ (Ali 1° Amine)

X hatao, NH_2 lagao

Intermidiate :- N-alkylated phthalimide

⑥ Hoffmann Bromamide degradation Rxn

$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[KOH]{Br_2} R-NH_2$

CO ko phenk do, uda do jo krna hkro 😊

*** OP Point :-**

① Nitrene intermediate $R-\overset{O}{\overset{\|}{C}}-\ddot{N}:$

② Bromamide " $R-\overset{O}{\overset{\|}{C}}-NH-Br$

③ Overall Rxn

$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4KOH \longrightarrow R-NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

Properties of Amine

① Basic strength

- B.S $\propto$ +M, +H, +I $\propto \frac{1}{-M} \propto \frac{1}{-H} \propto \frac{1}{-I}$
- In gas phase :- $RNH_2 < R_2NH < R_3N$
- In Aq medium :-

$R = Me \rightarrow 2^\circ > 1^\circ > 3^\circ$

$R = Et \rightarrow 2^\circ > 3^\circ > 1^\circ$

$R = Pr \rightarrow 3^\circ > 2^\circ > 1^\circ$

⋮ ⋮

② Alkylation :- (Ammonolysis)

$NH_3 + CH_3-Cl \longrightarrow \underset{1^\circ}{CH_3NH_2} \xrightarrow{CH_3Cl} \underset{2^\circ}{CH_3-NH-CH_3} \xrightarrow{CH_3-Cl} \underset{3^\circ}{CH_3-N(CH_3)_2} \xrightarrow{CH_3-Cl} Me_4N^+Cl^-$ (4° ammonium salt)

③ Acylation :- (only one time)

$R-NH_2 \xrightarrow{CH_3-\overset{O}{\overset{\|}{C}}-Cl} CH_3-\overset{O}{\overset{\|}{C}}-NH-R + HCl$

H hatao, COR lagao

④ Carbyl Amine Test

↳ Isocyanide Test for 1° Amine

$R-NH_2 \xrightarrow[KOH]{CHCl_3} R-NC$

NH_2 hatao NC lagao

⑤ Rxn with Nitrous Acid

ⓐ With 1° Ali amine

$R-NH_2 \xrightarrow[\text{or } NaNO_2+HCl]{HNO_2} RN_2^+Cl^- \longrightarrow R^+ + N_2 + Cl^-$

$R^+ \xrightarrow[H_2O]{-H^+} ROH$; R^+ → Rearrange ; Cl^- → H^+ → HCl ; ↑POS.