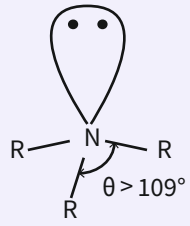
10. AMINES

STRUCTURE

NH_3	Ammonia
$R\text{-}NH_2$	1° Amine
R_2NH	2° Amine
R_3N	3° Amine



Pyramidal geometry

PHYSICAL PROPERTIES

PHYSICAL STATE: Lower aliphatic amines are gases, intermediate members are liquid (fishy odour), while higher members are solid.

SOLUBILITY: Lower aliphatic amines are soluble in water due to H-bonding, while higher amines (> C_6) are insoluble in water.

$$\text{Solubility} \propto \frac{1}{\text{Molecular weight}}$$

BOILING POINT: Primary and secondary amines forms intermolecular H-Bonding while tertiary does not.

1° Amine > 2° Amine > 3° Amine

CHEMICAL PROPERTIES

$R\text{-}NH_2$ +

- $CHCl_3 + KOH$ (Carbylamine test) → R-NC
- HNO_2 → R-OH
- RX → R-NH-R'
- R'-C(=O)-Cl (Acylation) → R-NH-C(=O)-R'

PREPARATION

Reduction of Nitro Compounds.

$$RNO_2 \xrightarrow[\text{or } H_2/Pd]{Sn/HCl \text{ or } Fe/HCl} R\text{-}NH_2$$

Ammonolysis

$$R\text{-}X \xrightarrow{NH_3} R_3N{+}HX^- \xrightarrow{NaOH} R\text{-}NH_2 + H_2O + Na{+}X^-$$

Reduction of Nitriles

$$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R-CH_2-NH_2$$

Reduction of Amides

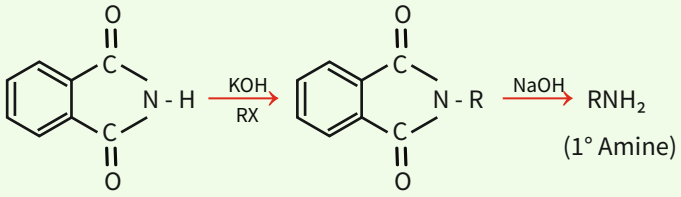
$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[H_2O]{LiAlH_4} R-CH_2-NH_2$$

Hoffmann Bromamide Degradation reaction

one carbon less amine is formed as compared to amide

$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Gabriel Phthalimide synthesis



Aromatic primary amines cannot be prepared by this method

BASIC NATURE

Due to the presence of lone pair on nitrogen amines are basic.

Factors affecting basicity

(i) Inductive effect
(ii) solvation effect
(iii) Steric hinderance

In Gaseous Phase

3° Amine > 2° Amine > 1° Amine > $\ddot{N}H_3$

In Aqueous Phase

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

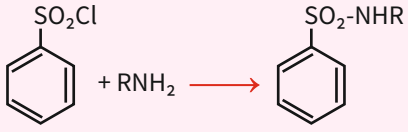
$(C_2H_5)_2NH > (C_2H_5)_3N > (C_2H_5)NH_2 > NH_3$

Overall Basicity Order

Aliphatic Amine > Ammonia > Aromatic Amine

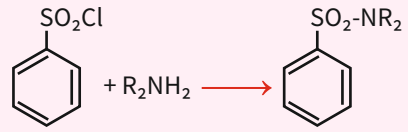
TEST FOR AMINES - HINSBERG'S TEST

Primary Amine



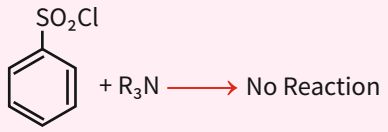
ppt. soluble in alkali

Secondary Amine

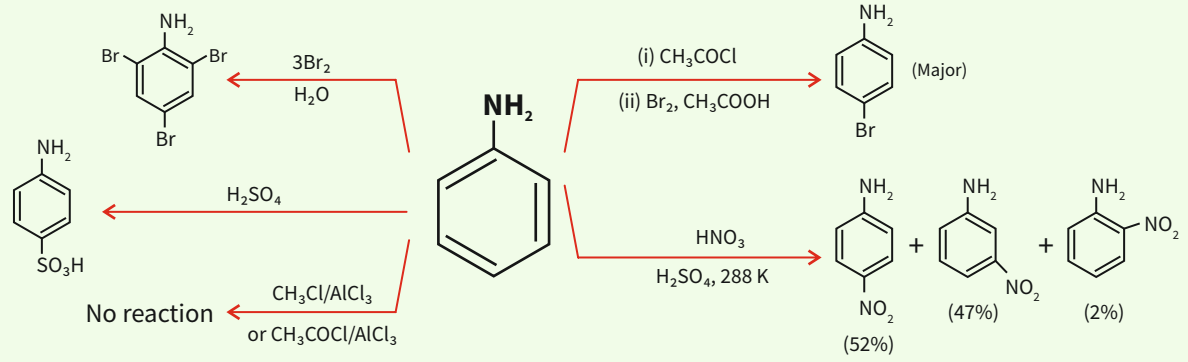


ppt. insoluble in alkali

Tertiary Amine

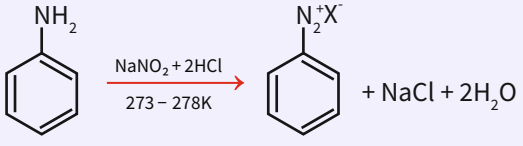


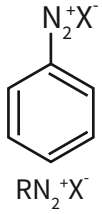
ELECTROPHIC SUBSTITUTION



DIAZONIUM SALTS

PREPARATION



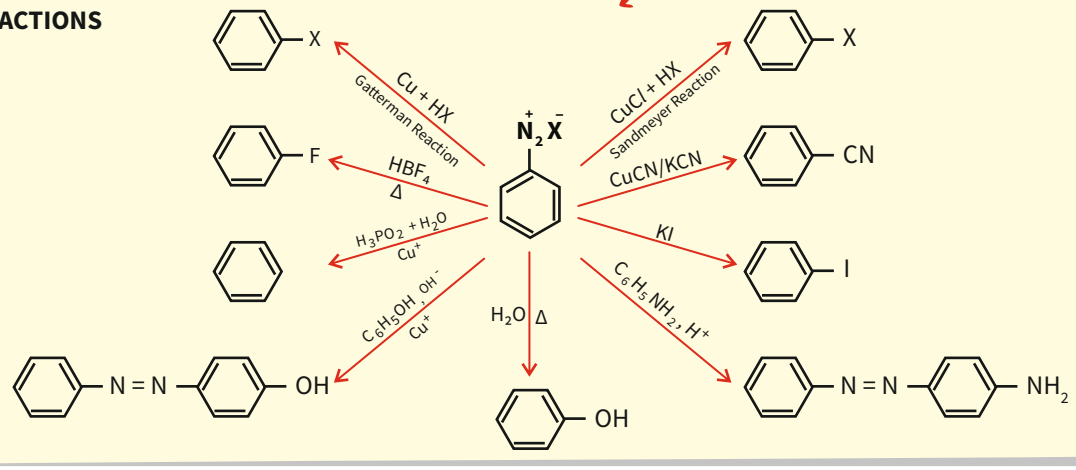


PHYSICAL PROPERTIES

Colourless, soluble in water, decompose in dry state.

$C_6H_5N_2^+Cl^-$ is readily soluble in water.

CHEMICAL REACTIONS



IMPORTANCE

In preparation of substituted aromatic compounds which cannot be prepared by direct substituion in benzene.