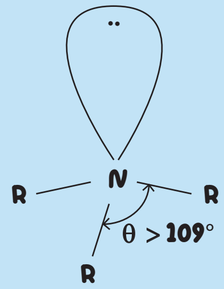
AMINES

atpstar

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.

Primary > Secondary > Tertiary
Amine Amine Amine

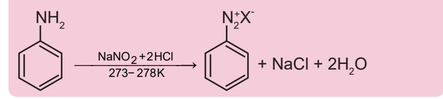
PHYSICAL PROPERTIES

Colourless, soluble in water, decompose in dry state
$C_6H_5N_2^+Cl^-$ is readily soluble in water

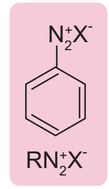
IMPORTANCE

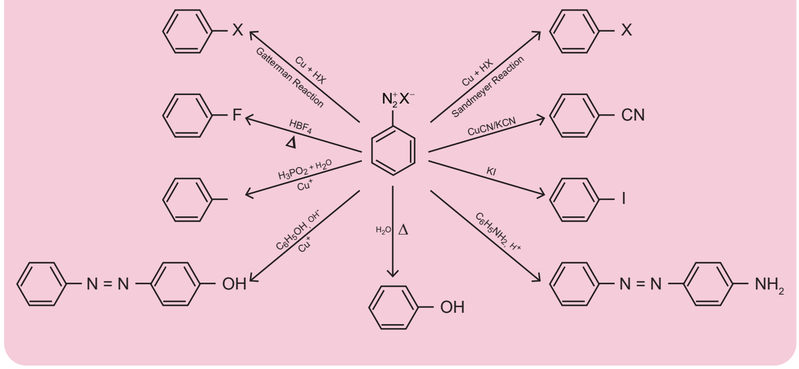
In preperation of substituded aromatic compounds which cannot be prepared by direct substituion in benzene or substistude benzene.

PREPERATION



DIAZONIUM SALTS





PREPARATION

- **Reduction of Nitro Compounds.**

$$RNO_2 \xrightarrow[OrH_2/pd]{Sn/HCl \text{ or } Fe/HCl} RNH_2$$

- **Ammonolysis**

$$R\text{-}X \xrightarrow{NH_3} R\text{-}NH_3X^- \xrightarrow{NaOH} R\text{-}NH_2 + H_2O + Na^+X^-$$

- **Reduction of Nitriles**

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

- **Reduction of Amides**

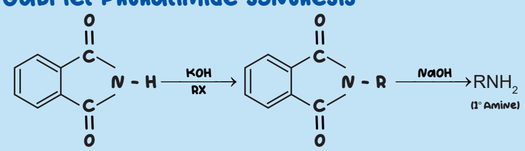
$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 \xrightarrow[(i)\ H_2O]{(i)\ LiAlH_4} R\text{-}CH_2\text{-}NH_2$$

- **Hoffmann Bromamide Degradation reaction**

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

One carbon less amine is formed as compared to amides

- **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

$3° \text{ Amine} > 2° \text{ Amine} > 1° \text{ Amine} > NH_3$

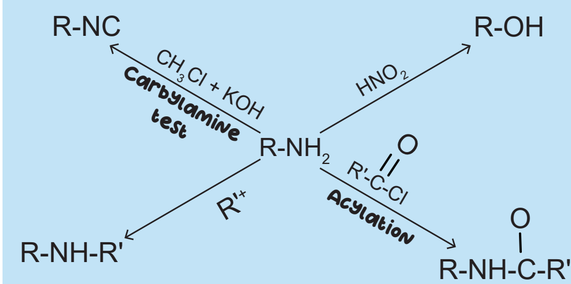
IN AQUEOUS PHASE

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
$(C_2H_5)_2NH > (C_2H_5)_3N > (C_2H_5)NH_2 > NH_3$

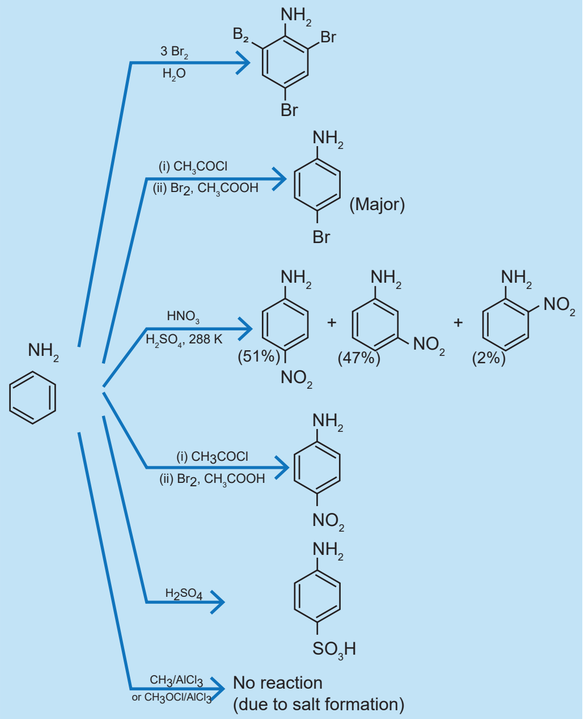
OVERALL BASICITY ORDER

Aliphatic Amine > Ammonia > Aromatic Amine

CHEMICAL REACTION



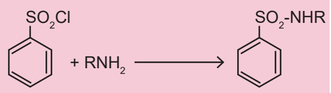
ELECTROPHIC SUBSTITUTION



TEST FOR AMINES

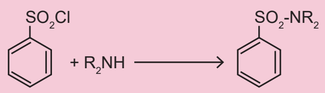
HINSBERG'S TEST

PRIMARY AMINE



Ppt. Soluble in alkali

SECONDARY AMINE



Ppt. insoluble in alkali

TERTIARY AMINE

No Reaction