Amines

Amines:

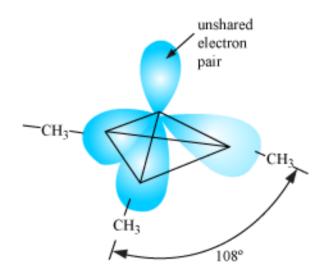
- (i) Derivatives of ammonia
- (ii) Obtained by the replacement of one, two or all the three H-atoms of ammonia by alkyl and/or aryl group

(iii) Structure of Amines

Nitrogen on amines is sp^3 hybridised.

Geometry - Pyramidal

Example: Pyramidal shapes of trimethylamine



Classification: Primary (1), secondary (2) and tertiary (3)

- (i) If one H-atom of NH₃ is replaced by R or Ar, RNH₂ or ArNH₂ is obtained (primary amine, 1°).
- (ii) If two H-atoms of NH_3 or one H-atom of RNH_2 are replaced by alkyl or aryl group (R'), R_2NH is obtained (secondary amine, 2°).

(iii) On the replacement of another hydrogen atom by alkyl or aryl group, R₃N is obtained (tertiary amine, 3°).

$$NH_3 \longrightarrow RNH_2 \longrightarrow R' \longrightarrow N - H \longrightarrow R' \longrightarrow N - R''$$

Primary (1°) Secondary (2°) Tertiary (3°)

Nomenclature

Common System

Aliphatic amine: Named by prefixing alkyl group to amine, i.e., alkylamine. Example: Methylamine (CH₃NH₂)

Secondary and tertiary amines: Prefix di- or tri- is appended before the name of alkyl group when two or more groups are the same.

IUPAC System

Named as alkanamines; derived by replacing the 'e' of alkane with the word amine.

Example: CH₃NH₂ – Methanamine

When more than one amino group is present –

- (i) Suitable prefix such as di-, tri-, etc., is attached to amine.
- (ii) 'e' of the suffix of hydrocarbon is retained.
- (iii) Positions of -NH₂ group are specified by giving numbers to the parent chain.

Example:
$$H_2N - \overset{2}{C}H_2 - \overset{1}{C}H_2 - NH_2$$
 Ethane-1, 2-diamine

(iv) or aryl amines -NH2 group is directly attached to the benzene ring

While naming arylbenzenes by IUPAC system, the suffix 'e' of arene is replaced by 'amine'.

Preparation:

(i) By reduction of nitro compounds -

(ii) By ammonolysis of alkyl halides – Ammonolysis is the process of cleavage of the C–X bond by ammonia molecule.

$$R - \stackrel{+}{N}H_{3}X^{-} + NaOH \longrightarrow R - NH_{2} + NaX + H_{2}O$$

Primary amine obtained behaves as a nucleophile and further reacts as

$$R - NH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4 \stackrel{^+}{N} X^-$$
(1°) (2°) (3°) Quaternary ammonium salt

Order of reactivity of halides with amines – RI > RBr > RCl

(iii) Reduction of Nitrites

$$R - C \equiv N \xrightarrow{LiAlH_4} R - CH_2 - NH_2$$

Nitrile

(iv) Reduction of Amides

(v) Gabriel Pthalimide Synthesis: Used for the preparation of primary amine.

Phthalimide N-Alkylphthalimide

$$\begin{array}{c|c}
O \\
C \\
N-R
\end{array}$$

$$\begin{array}{c|c}
NaOH_{(aq)} \\
\hline
C - ONa \\
C - ONa
\end{array}$$

$$\begin{array}{c|c}
+ R - NH_2 \\
C - ONa \\
C - ONa
\end{array}$$

$$\begin{array}{c|c}
C - ONa \\
C - ONa
\end{array}$$

$$\begin{array}{c|c}
C - ONa \\
C - ONa
\end{array}$$

(vi) Hoffmann Bromamide Degradation Reaction:

Physical properties:

Solubility -

- (i) Lower aliphatic amines are soluble in water, but higher amines are insoluble in water. This is because lower amines can form H-bonds with water, but higher amines cannot.
- (ii) Solubility of amines in water decreases with increase in molar mass of amines as the size of the hydrophobic alkyl part increases.
- (iii) The order of increasing boiling points of isomeric amines is 3^{o} amine $< 2^{o}$ amine $< 1^{o}$ amine. This because of intermolecular association of 1 amines due to H-bonding.

Chemical reactions:

(i) Basic character of amines –

The order of increasing basicity is

(a) Aromatic amines < Ammonia < Aliphatic amines

Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups.

Aromatic amines are weaker bases than ammonia due to electron-withdrawing nature of the aryl group.

Structure-basicity relationship of amines

The increasing order of basicity of amines in the gaseous phase is

$$NH_3 < 1$$
 amine < 2 amine < 3 amine

The increasing order of basic strength in the case of methyl-substituted amines and ethyl-substituted amines in aqueous solution.

$$NH_3 < (CH_3)_3 N < CH_3NH_2 < (CH_3)_2 NH$$

$$NH_3 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$$

The above order is due to the combined effect of steric hindrance of the alkyl group, inductive effect and salvation effect.

In the case of substituted aniline, electron-withdrawing groups ($-NO_2$, $-SO_3$, -COOH, -X) decrease the basicity while electron-donating groups ($-OCH_3$, $-CH_3$) increase the basicity.

(ii) Alkylation

Amines undergo alkylation on reaction with alkyl halides.

Sandmeyer's reaction

NH2
NaNO₂ + HX

Benzene diazonium
halide

$$X = Cl$$
, Br

(iii) Acylation

For example:

(iv) Benzoylation – Reaction of amines with benzoyl chloride (C₆H₅COCl)

$$CH_3NH_2$$
 + C_6H_5COCl \longrightarrow $CH_3NHCOC_6H_5$ + HCl
Methanamine Benzoyl chloride N-methylbenzamide

Carbylamines reaction (or isocyanide test) – Used as test to distinguish 1° , 2° , and 3° amines. As 2° and 3° amines do not react to this test.

Aliphatic/Aromatic primary amines + CHCl₃ + KOH

→ Isocyanides or carbylamines

(foul smelling)

Reaction with nitrous acid –Nitrous acid is prepared in situ from a mineral acid and sodium nitrate.

Primary aliphatic amines:

$$R - NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} \boxed{R - N_2 \ Cl} \xrightarrow{H_2O} R - OH + N_2 + HCl$$
Diazonium salt Alcohol

Aromatic amines:

$$C_6H_5 - NH_2 \xrightarrow{NaNO_2+2HCl} C_6H_5 - N_2 Cl + NaCl + 2H_2O$$
Aniline

Benzenediazonium

chloride

Reaction with arylsulphonyl chloride – Hinsberg's reagent Benzenesulphonyl chloride ($C_6H_5SO_2Cl$). This reaction can be used for distinguishing and separating 1^o , 2^o and 3^o amines

(i) Primary amine: The amide formed is soluble in alkali because the hydrogen attached to nitrogen is strongly acidic due to the presence of a strong electron-withdrawing sulphonyl group.

N – Ethylbenzenesulphonamide (soluble in alkali)

(ii) Secondary amine: The amide formed is insoluble in alkali. As it does not contain any hydrogen atom attached to nitrogen atom, it is not acidic.

N, N – Diethylbenzenesulphonamide (insoluble in alkali)

(iii) Tertiary amines do not react with Hinsberg's reagent.

Electrophilic substitution –

(i) **Bromination:** Electrophilic substitution reaction of aromatic amines is of very high reactivity – tends to occur both at *ortho* and *para* positions.

$$H_2$$
 H_2O H

To prepare monosubstituted aniline, -NH₂ group is protected by acetylation with acetic anhydride; then the desired substitution is carried out, followed by hydrolysis.

NH₂
Aniline

$$H-N-C-CH_3$$
 $H-N-C-CH_3$
 $H-N-C-C-CH_3$
 $H-N-C-C-CH_3$

(ii) Nitration: In strong acidic medium, anilinium ion is formed, which is *meta* directing. Hence, significant amount of *meta* derivative is also formed along with *ortho* and *para* isomers.

By protecting –NH₂ group by acetylation reaction, *para* isomer can be obtained as the major product.

(iii) Sulphonation:

(iv) Aniline does not undergo Friedel-Crafts reaction (alkylation and acelytation).

Diazonium salts: $R \stackrel{+}{N_2} X^-$

Preparation:

Diazotisation: The conversion of primary aromatic amines into diazonium salts.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278 \text{ K}} C_6H_5N_2Cl + NaCl + 2H_2O$$
Aniline

Benzendiazonium

chloride

Chemical reactions:

Reactions that involve displacement of nitrogen

(i) Replacement by halide or cyanide ion

Sandmeyer's reaction

$$ArN_{2}^{+}\bar{X} \xrightarrow{CuCl/HCl} ArCl + N_{2}$$

$$CuBr/HBr \longrightarrow ArBr + N_{2}$$

$$CuCN/KCN \longrightarrow ArCN + N_{2}$$

Gattermann reaction

$$ArN_{2}^{+}\bar{X} - \underbrace{Cu/HCl}_{Cu/HBr} - ArBr + N_{2} + CuX$$

Replacement by iodide ion

$$Ar \overset{+}{N_2} Cl^- + KI \longrightarrow ArI + KCl + N_2$$
 $C_6H_5\overset{+}{N_2} Cl^- + KI \longrightarrow C_6H_5I + KCl + N_2$
Iodobenzene

Replacement by fluoride ion

$$Ar \stackrel{+}{N_2}Cl^- + HBF_4 \longrightarrow Ar - \stackrel{+}{N_2}BrF_4^- \stackrel{Heat}{\longrightarrow} Ar - F + BF_3 + N_2$$

Fluoroboric acid

(ii) Replacement by NO₂ group

$$\begin{array}{c} \stackrel{+}{\overset{+}{\bigvee}}_2 \bar{\text{CI}} \\ \stackrel{+}{\overset{+}{\bigvee}}_2 \bar{\text{DF}}_4 \\ + \text{NaNO}_2 \\ \hline \\ \stackrel{-}{\overset{+}{\bigvee}}_2 \bar{\text{Cu}}, \Delta \end{array} \begin{array}{c} \text{NO}_2 \\ \stackrel{+}{\overset{+}{\bigvee}}_2 + \text{NaBF}_4 \\ \hline \end{array}$$

Fluoroboric acid

Nitrobenzene

(iii) Reactions that involve retention of diazo group:

Coupling reactions (Electrophilic substitution reaction)