AMINES

Class XII Board Exam

- Target 100
- Verified by Top Faculties & CBSE Science Board Toppers
- All PYQ's Integrated
- As per marking scheme

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Amines

Preparation of Amines
- Reduction of Nitro Compounds
- Ammonolysis of alkyl halides
- Reduction of nitriles
- Reduction of amides
- Gabriel phthalimide synthesis
- Hoffmann bromoamide degradation reaction

Chemical reactions
- Basic Character
- Alkylation/Acylation
- Carbylamine Reaction
- Reaction with nitrous acid
- Reaction with Arylsulphonyl chloride
- Electrophilic substitution

Physical Property

Structure Of Amines
Classification
Nomenclature
Amines (-NH₂ group) Prefix: Amino Suffix: Amin

Amines can be considered as derivatives of ammonia.

\[ \text{NH}_3, \quad \text{R-NH}_2, \quad \text{R-NH}, \quad \text{R-N-R} \]

1° Amine 2° Amine 3° Amine

IUPAC Name: Alkane + amine = Alkanamine (R-NH₂)
Alkane + diamine → For two amino group.

Common Name: Alkylamine (R-NH₂) \(_{\text{left}}\) \(\frac{\text{no. of Carbon}}{\text{No. of Carbon}}\) \(\text{R-N-R}'_{\text{right}}\)

Example: \(\text{CH}_2-\text{CH}_2-\text{NH}_2\) \(\text{IUPAC}\) \(\text{N-Alkylalkanamine}\)

\(2\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2\) \(\text{h-Propylamine}\) \(\text{[Propan-1-amine]}\) (Ethylmethylamine)

\(3\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2\) \(\text{Isopropylamine}\) \(\text{[Propan-2-amine]}\)

\(\text{N-N'-dimethyl ethanamine}\) \(\text{[Dellhi 2017]} \quad \text{[M]}\)

\(\text{N-ethyl N-methyl ethanamine}\) \(\text{[Dellhi 2017]} \quad \text{[M]}\)

\(3\text{NH}_2\) \(\text{Prop-2-en-1-amine}\) \(\text{[CBSR 2013]} \quad \text{[M]}\)

\(\text{N-methylthiobamine}: 2\text{CH}_3-\text{CH}_2-\text{NH}-\text{CH}_3\)

\(\text{NH}_2-\text{CH}_2-\text{CH}_2-\text{CH} = \text{CH}_2\) \(\text{But-3-en-1-amine}\) \(\text{[Dellhi 2017]} \quad \text{[M]}\)

Senior functional group marks as suffix and junior functional groups are treated as substituent. For naming of junior functional group we use prefix of that group.

\(3\text{NH}_2\) \(\text{2-Aminobutan-1-ol}\)

\(2\text{CH}_3-\text{CH} = \text{CH}-\text{NH}_2\) \(\text{[CBSR 2014]} \quad \text{[M]}\)

\(5\text{NH}_2\) \(4\text{-Aminopentan-1-oic acid}\)

\(\text{3-Aminobutanal}\)
Preparation of amines

1. Reduction of nitro compounds:

\[ \text{NO}_2 \xrightarrow{\text{H}_2\text{Pd}, \text{H}_2\text{let}} \text{NH}_2 \]

2. Ammonolysis of alkyl halides:

Breaking of bond by ammonia.

Order of reactivity of alkyl halides with amines:

- R–I > R–Br > R–Cl > R–F
- Strong bond, so tough to break.
- Weak bond, so easy to break.

3. Reduction of nitriles:

\[ \text{R–C≡N} \xrightarrow{\text{LiNH}_4, \text{H}_2\text{Ni}} \text{R–C}≡\text{N} \]

4. Reduction of amides:

\[ \text{R–C(=O)NH}_2 \xrightarrow{\text{LiAlH}_4, \text{n} \text{H}_2\text{O}} \text{R–CH}_2\text{–NH}_2 \]

\[ \text{CH}_3–\text{C(=O)NH}_2 \xrightarrow{\text{LiAlH}_4, \text{n} \text{H}_2\text{O}} \text{CH}_3\text{–CH}_2\text{–NH}_2 \]

\[ \text{CH}_3–\text{NH}_2 \xrightarrow{\text{LiAlH}_4, \text{n} \text{H}_2\text{O}} \text{CH}_3\text{–CH}_2\text{–NH}_2 \]
5) **Gabriel Phthalimide Synthesis** — (for preparation of 1° Amines)

\[
\text{Phthalimide} \xrightarrow{\text{KOH}} \text{Phthalimide + K⁺} \xrightarrow{\text{electrophile}} \text{Amide}
\]

- Only aliphatic alkyl groups
- Because in aromatic (as phenyl) group, the double bond character in bond with halogens.

6) **Hoffmann Bromamide Degradation Reaction**:

\[
R\text{-CN} + \text{Br₂} + \text{NaOH} \rightarrow R\text{-NH₂} + \text{Na₂CO₃} + 2 \text{NaBr} + 2\text{H₂O}
\]

- Amide → Amine
- Reduction of nitro to amino

\[
\text{Butanamido} \xrightarrow{\text{HBDR}} \text{Propanamine}
\]

- Benzamide

**Physical Properties:**

- Lower amines are soluble in water because they can form hydrogen bonding with water molecules.

\[
R\text{-NH}_2 \xrightarrow{\text{solubility}} \text{1° Amino} \xrightarrow{\text{H-bonding}} \text{2° Amino} \xrightarrow{\text{3° Amino}}
\]

- Aromatic amines (such as aniline) are insoluble in water due to large hydrocarbon part (non-interactive with water). [CASE 2011] 1M

**Boiling Point:** Order of B.P.: 1° Amine > 2° Amine > 3° Amine

- This is because of order of extent of H-bonding.
This intermolecular association is more in primary amines than in $\text{\textsuperscript{2}}$ amines as there are two hydrogen atoms are available for hydrogen bond formation in it.

Extent of H-bonding in it:

$$R-NH_2 + H_2O \rightleftharpoons R-NH\cdot\cdot\cdot-OH$$

Because $\text{\textsuperscript{3}}$ amines have no hydrogen bond between itself. So, primary amines have higher $\text{B.P.}$, according to $\text{CASSE 2011}$.

For example, $\text{B.P.}$:

- Propanamine $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2 > \text{CH}_3-\text{CH}_2-\text{NH}_3$ [CASSE 2019]

**Basis of amines**

$$R-NH_2 + H_2O \rightleftharpoons R-NH\cdot\cdot\cdot-OH$$ (Salt)

Basicity is represented by $k_B$.

$$pk_B = -\log k_B \quad \text{then} \quad k_B = \frac{1}{pk_B}$$

**Alkanamines vs. Ammonia**:

1. $R-NH_2 + H^+ \rightleftharpoons R-NH_3^+$

Due to stability of $R-NH_3^+$ with respect to $NH_3^+$, equilibrium constant for reaction (1) is more than reaction (ii).

Means that: Aliphatic amines are stronger bases than ammonia. $\text{CH}_3-NH_2 > NH_3$ & $k_B$

Order of basicity in gas phase: Explain it by $\text{I}^+\text{E}$ effect, as there is no solvent.

$$k_B: \text{CH}_3-NH_2 > \text{NH}_3^+ \text{CH}_3 > \text{NH}_2^+\text{R}$$
Basicity of amines in aq. phase: Above order is not true in aqueous medium. The substituted ammonium cations get stabilised not only by electron releasing effect of alkyl group (+I) but also by solvation with water molecules.

The ion having more hydrogen bonds with water molecule, are more stable. So more will be $K_b$ value for that amine.

\[
\begin{align*}
R-\text{-NH}_2 + H_2O & \rightarrow R-\text{-N-H\text{-OH}_2} : 3 \text{ H-bonds} \\
R-\text{-N-H} + H_2O & \rightarrow R-\text{-N-H\text{-OH}_2} : 2 \text{ H-bonds} \\
R-\text{-N+H}_2O & \rightarrow R-\text{-N-H\text{-OH}_2} : 1 \text{ H bond}
\end{align*}
\]

More solvation $\Rightarrow$ More stable ion

According to solvation effect $K_b : 1^\circ > 2^\circ > 3^\circ$

Basic strength in aq. soln

Kb : $\left(\text{C}_2\text{H}_5\right)\text{NH} > \left(\text{C}_2\text{H}_5\right)\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3 : 23 1 \text{ NH}_3$

Kb : $\left(\text{CH}_3\right)\text{NH} > \text{CH}_3\text{NH}_2 > \left(\text{CH}_3\right)\text{N} > \text{NH}_3 : 21 3 \text{ NH}_3$

Asylamines vs. Ammonia:

Kb : $\text{NH}_3$ > $\text{NH}_2\text{C}_6\text{H}_5$

Low pair of nitrogen on ammonia is available for protonation. But in aniline, $\text{O}^\text{+} - \text{NH}_2 + \text{H}^\text{+} \rightarrow \text{O}^\text{+} \text{NH}_3$.

Low pair is not easily available due to resonance with benzene ring.


- **Basicity Order (Kb):**
  \[ \text{CH}_3 \equiv \text{NH}_2 > \text{NH}_2 \equiv \text{CH}_2 > \text{O} \equiv \text{NH}_2 \]  
  - Case 2011: IM

- **Localised lone pair**
  - Localised lone pair, so lone pair is not available for protonation.

- **Kb:**
  - Localised lone pair, so lone pair is not available for protonation.

- **Kb:**
  - Lone pair is in resonance, so not available for protonation.
  - +I effect of alkyl group.

- **Electron donating group in basic N atom**
  - Electron density at nitrogen of aniline.
  - So, it can easily donate lone pair to H⁺.

- **Acylation of amines:**
  - Addition of -R group.
  - Acylation of product of 1°/2° amine.

- **1°/2° Amines**
  - Acylation of product of 1°/2° amine.

- **Replacing of Hydrogen by CH₃**
  - Acylation.
Carbylamine reaction: [Test for 1º Amines: Presence of 2 Hydrogens is necessary]

2º/3º Amines do not give this reaction.

\[ R-\text{NH}_2 + \text{CH}_3\text{CHOH} + 3\text{KOH} \rightarrow R-\text{NC} + 3\text{KOH} + 3\text{H}_2\text{O} \]

This test is also called Isocyanide test.

By using this reaction (test) we can distinguish (1º and 2º amines) and (1º and 3º amine).

\[ \text{CH}_3-\text{NH}_2, \quad \text{CH}_3-\text{NH}-\text{CH}_3 \quad \text{KOH} \]

(1º Amines) No reaction

Foul smelling (\text{CH}_3-\text{NC})

Similarly, Ethylamine (\text{-NH}_2) and Diethylamine (\text{-NCH}_2\text{-}) can be distinguished by carbylamine test. 1º Amine (\text{-NH}_2) gives foul smelling with \text{CH}_3\text{CHOH} and \text{KOH}.

Amiline & N-methylamiline:

[CBSE 2010] [1 M]

\[ \text{O-NH}_2 \quad \text{KOH} \rightarrow \text{O-NC} \quad \text{Foul smelling} \]

[1 M]

\[ \text{O-NH}-\text{CH}_3 \quad \text{KOH} \rightarrow \text{No reaction} \]
Reaction with HNO₂ [Nitrous Acid]:

1. Primary aliphatic amines:
   \[ R-\text{NH}_2 + \text{HNO}_2 \rightarrow R-\text{N}_2 \text{O} + \text{R}-\text{OH} + \text{N}_2 + \text{H}_2\text{O} \]

   → Evolution of nitrogen.

2. Aromatic Amines:
   \[ \text{NH}_2 + \text{HNO}_2 \xrightarrow{0-5^\circ \text{C}} \text{N}_2\text{O} + \text{H}_2\text{O} \]
   \[ \text{NaNO}_2 + \text{HCl} \rightarrow \text{(Benzene diazenium Chloride)} \]
   \[ \text{Salt} \]

→ Aromatic and aliphatic amines can be distinguished by above reaction.

For example:

- Aniline and Ethylamine:
  \[ \text{NH}_2 \xrightarrow{\text{NaNO}_2/\text{HCl}} \text{N}_2 \text{O} + \text{H}_2\text{O} \]
  \[ \text{(Salt)} \]

- Aniline and Benzylamine:
  \[ \text{NH}_2 \xrightarrow{\text{NaNO}_2/\text{HCl}} \text{N}_2 \text{O} + \text{H}_2\text{O} \]
  \[ \text{(Salt)} \]

→ Reaction with Hinsberg Reagent:

- Hinsberg Reagent:
  \[ \text{Cl} - \xrightarrow{\text{NaNO}_2/\text{HCl}} \text{N}_2 \text{O} + \text{H}_2\text{O} \]
  \[ \text{N-ethyl benzene sulphonamide} \]
  \[ \text{Not soluble in alkali because there is no acidic hydrogen.} \]

1° Amine:
\[ \text{NH}_2 + \text{Cl} \xrightarrow{\text{H}_2\text{O}} \text{N}_2 \text{O} + \text{H}_2\text{O} \]
\[ \text{Soluble in NaOH} \]

2° Amine:
\[ \text{NH} + \text{Cl} \xrightarrow{\text{H}_2\text{O}} \text{N}_2 \text{O} + \text{H}_2\text{O} \]
\[ \text{Not soluble in alkali} \]

3° Amine:
\[ \text{No Reaction} \]

→ This reagent can be used to distinguish 1°/2°/3° Amines.
Electrophilic Substitution Reaction:

- The \( \text{NH}_2 \) group is ortho-para directing and powerful activating group.

In resonating structure, the electron density is present at ortho and para position.

It donates electron density to benzene ring, making it more active for electrophilic substitution.

That's why electrophilic substitution takes place more readily in aromatic amines than benzene. [Delhi 2016] (1M)

1. Bromination:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{NH}_2 + \text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_4\text{Br}_2 + \text{H}_3\text{N}\text{Br} \\
\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{C} = \text{O} \rightarrow \text{C}_6\text{H}_4\text{Br} + \text{H}_3\text{N}=\text{O}
\end{align*}
\]

Activating effect of \(-\text{NH}_2\) group is less than that of \(-\text{NH}_2\) group, because in \(\text{NH}_2\text{CH}_3\) the lone pair of nitrogen is shared also with \(-\text{H}\) group. So it can not activate benzene ring as much as \(-\text{NH}_2\) group.

2. Sulphonation:

\[
\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{SO}_4^- \rightarrow \text{C}_6\text{H}_5\text{SO}_3^- + \text{H}_3\text{N}^+
\]

Aniline does not undergo Friedel-Crafts reaction due to salt formation with \(\text{AlCl}_3\). Hence, it acts as a strong deactivating group for further reaction.

[Delhi 2014] (1M)
Complete the following reaction!

\[ \text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{N} \xrightarrow{\text{NaCN}} \text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{N} \xrightarrow{\text{Ni/H}_2} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2 \]

\[ \text{CH}_3 - \text{C} = \text{N} \xrightarrow{\text{NH}_3/\Delta} \text{CH}_3 - \text{NH}_2 \xrightarrow{\text{KOH}} \text{CH}_3 - \text{NH}_2 \xrightarrow{\text{KOH}} \text{CH}_3 - \text{NC} \]

\[ \text{CH}_3 - \text{CH}_2 - \text{CN} \xrightarrow{\text{LiAIH}_4} \text{CH}_3 - \text{CH}_2 - \text{NH}_2 \]

\[ \text{CH}_3 - \text{CH}_2 - \text{CN} \xrightarrow{\text{KCN}} \text{CH}_3 - \text{CN} \xrightarrow{\text{LiAIH}_4} \text{CH}_3 - \text{CH}_2 - \text{NH}_2 \]

An aromatic compound A \( \left[ \text{C}_7\text{H}_6\text{O}_2 \right] \) \xrightarrow{\text{NH}_3/\Delta} \text{C}_6\text{H}_5 - \text{CH}_2 - \text{NH}_2 \]

\[ \text{Br} \xrightarrow{\text{H}_2\text{O}} \text{NH}_2 \xrightarrow{\text{Br}_2} \text{Br}_2 \]

\[ \text{C}_6\text{H}_5 - \text{NH}_2 \xrightarrow{\text{LiAIH}_4} \text{C}_6\text{H}_5 - \text{CH}_2 - \text{NH}_2 \]

\[ \text{Br} \xrightarrow{\text{H}_2\text{O}} \text{NH}_2 \xrightarrow{\text{Br}_2} \text{Br}_2 \]

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\[ \text{H}_2\text{O} \xrightarrow{\text{Br}_2} \text{Br}_2 \]

\[ \text{C}_6\text{H}_5 - \text{NH}_2 \xrightarrow{\text{LiAIH}_4} \text{C}_6\text{H}_5 - \text{CH}_2 - \text{NH}_2 \]

\[ \text{Br} \xrightarrow{\text{H}_2\text{O}} \text{NH}_2 \xrightarrow{\text{Br}_2} \text{Br}_2 \]

\[ \text{C}_6\text{H}_5 - \text{NH}_2 \xrightarrow{\text{LiAIH}_4} \text{C}_6\text{H}_5 - \text{CH}_2 - \text{NH}_2 \]

\[ \text{C}_6\text{H}_5 - \text{CH}_2 - \text{NH}_2 \xrightarrow{\text{Br}_2/\text{KOH}} \text{C}_6\text{H}_5 - \text{NH}_2 \]

JAO AB

[Delhi 2015c] 3M

Amide
Diazonium Salts

General formula:

\[ R \overset{N\equiv N}{\text{Aryl Group}} X^+ \]

\( R \overset{N\equiv N}{\text{Aryl Group}} \) Cl\(^-\) / Br\(^-\) / HSO\(_4^+\) / BF\(_4^-\)

Methods of Preparation:

Diazotisation:

The conversion of primary aromatic amines into diazonium salts is known as diazotisation.

1) Primary aliphatic amines:

\[ R \overset{\text{NH}_2}{\text{Primary aliphatic amines}} + \overset{\text{HNO}_2}{\text{HNO}_2} \rightarrow R \overset{N\equiv N}{\text{Primary aliphatic amines form}} \]

\[ \overset{\text{NaNO}_2 + \text{HCl}}{\text{highly unstable alkyldiazonium salts.}} \]

2) Aromatic Amines:

\[ \overset{\text{NH}_2}{\text{Aromatic Amines}} \overset{\text{Aniline}}{\text{(Aniline)}} + \overset{\text{HNO}_2}{\text{HNO}_2} \rightarrow \overset{\text{Cl}^-}{\text{Benzenediazonium Chloride Salt}} \]

Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (0-5°C).

Reason for stability of arenediazonium: Resonance phenomenon
Physical Properties:

- Colourless crystalline solid
- It is readily soluble in water and is stable in cold but reacts with water when warmed. It decomposes easily in the dry state.

Benzenediazonium fluoroborate is water insoluble and stable at room temperature.

Chemical Reactions

Reactions involving displacement of nitrogen

**Gattermann Reaction**

\[ \text{N}_2 + \text{BrCH}_2\text{Cl} \xrightarrow{\text{Cu/HCl}} \text{BrCH}_2\text{NCl} \]

**Sandmeyer reaction**

\[ \text{N}_2 + \text{BrCH}_2\text{Br} \xrightarrow{\text{Cu/HBr}} \text{BrCH}_2\text{NBr} \]

Other important reactions:

\[ \text{N}_2 + \text{BF}_3 + \text{NO}_2 \xrightarrow{\text{Cu/Heat}} \text{NO}_2\text{BF}_4^- \]

\[ \text{N}_2 + \text{NaBF}_4 + \text{I} \xrightarrow{\text{KI}} \text{I} \text{BF}_4^- + \text{KCl} + \text{N}_2 \]
The azo products obtained have an extended conjugate system having both the aromatic rings joined through the $-\text{N}=\text{N}-$ bond. These compounds are often coloured and are used as dyes.