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Amines

Definition and Classification

Amines are organic compounds derived from ammonia (NH_3) where one or more hydrogen atoms are replaced by alkyl or aryl groups. They are classified as primary (1°), secondary (2°), or tertiary (3°) amines based on the number of carbon-containing groups attached to the nitrogen atom.

Structure and Hybridisation

The nitrogen atom in amines is sp^3 hybridised, resulting in a pyramidal molecular geometry. The lone pair of electrons on nitrogen influences the shape and reactivity of amines.

Nomenclature

Amines are named using common or IUPAC systems. The IUPAC names are systematic and based on the longest carbon chain attached to the amino group.

Preparation Methods

Amines can be prepared by various methods including reduction of nitro compounds, ammonolysis of alkyl halides, reduction of nitriles, Gabriel phthalimide synthesis, reduction of amides, and Hoffmann bromamide degradation.

Physical Properties

Amines exhibit varying physical states depending on molecular weight, have characteristic boiling points influenced by hydrogen bonding, and show solubility trends in water and organic solvents.

Chemical Properties

Amines are basic due to the lone pair on nitrogen and undergo reactions such as alkylation, acylation, carbylamine reaction, bromination, nitration, sulphonation, and reactions with nitrous acid.

Solved Examples

Example 1: Write the structure and IUPAC name of the amide that forms propanamine by Hoffmann bromamide degradation.

Solution: Propanamine has three carbon atoms. Hoffmann bromamide degradation removes one carbon from the amide. Therefore, the amide must have four carbons: butanamide ($CH_3CH_2CH_2CONH_2$).

Example 2: Identify the amine formed by Hoffmann degradation of benzamide.

Solution: Benzamide ($C_6H_5CONH_2$) undergoes Hoffmann degradation to form aniline ($C_6H_5NH_2$), a primary aromatic amine.

Practice Set

- **Level 1 (Easy):** Define primary, secondary, and tertiary amines with examples.
- **Level 2 (Moderate):** Explain the Gabriel phthalimide synthesis and its limitation.
- **Level 3 (Challenging):** Compare the basicity order of methyl-substituted amines in aqueous solution and explain the reason.

Answer Key

- **Level 1:** Primary amines have one alkyl/aryl group attached to nitrogen (RNH_2), secondary have two (R_2NH), tertiary have three (R_3N). Examples: methylamine (1°), dimethylamine (2°), trimethylamine (3°).
- **Level 2:** Gabriel phthalimide synthesis involves formation of potassium phthalimide, reaction with alkyl halide to form N-alkyl phthalimide, and hydrolysis to yield primary amine. It cannot prepare aromatic primary amines.
- **Level 3:** Basicity order for methyl-substituted amines in aqueous solution is $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$. This is due to inductive effect, solvation, and steric hindrance affecting proton acceptance.

Quick Reference Table

- **Classification:** Primary (RNH_2), Secondary (R_2NH), Tertiary (R_3N)
- **Preparation:** Reduction of nitro compounds, ammonolysis of alkyl halides, reduction of nitriles, Gabriel synthesis, Hoffmann degradation
- **Basicity:** Tertiary > Secondary > Primary > Ammonia (gas phase); influenced by inductive and solvation effects in solution
- **Reactions:** Alkylation, acylation, carbylamine test, bromination, nitration, sulphonation, diazotisation
- **Diazonium salts:** Formed by diazotisation of primary aromatic amines; used in synthesis of dyes and aromatic compounds

Common Mistakes and Misconceptions

- Confusing primary, secondary, and tertiary amines based on the number of alkyl groups attached.
- Assuming all amines have the same basic strength; basicity varies with structure and environment.
- Believing Gabriel phthalimide synthesis can prepare aromatic amines; it cannot.
- Overlooking the role of lone pair electrons on nitrogen in determining amine properties.
- Mixing up diazonium salt reactions and their conditions, especially temperature sensitivity.

Glossary

- **Amines:** Organic compounds derived from ammonia by replacement of hydrogen atoms with alkyl or aryl groups.
- **Diazonium Salts:** Compounds containing the diazonium group (N_2^+) attached to an aromatic ring, used as intermediates in organic synthesis.
- **Gabriel Phthalimide Synthesis:** A method to prepare primary amines using phthalimide and alkyl halides.
- **Hoffmann Bromamide Degradation:** Reaction converting amides to primary amines with one less carbon atom.
- **Basicity:** The ability of a compound to accept protons, influenced by electronic and steric factors.
- **sp^3 Hybridisation:** Mixing of one s and three p orbitals to form four equivalent orbitals in a tetrahedral arrangement.