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Class 11
Chemistry

Chapter 20
Nitrogen Compounds
Handwritten Notes

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Ch 20: NITROGEN Compounds Amines

Amines

The group of organic compounds containing nitrogen linked with alkyl or aryl groups with a lone pair on nitrogen atom are called amines. Generally they are derived from ammonia by replacing one or more hydrogen atoms by alkyl or aryl group. Classified into three types according to the no. of carbon atoms directly attached with nitrogen.

- **Primary amines** only one alkyl group is linked with nitrogen atom. They have general formula of $R-NH_2$

- **Secondary amines** two alkyl groups are linked. They have general formula $R-NH-R$

- **Tertiary amines** three alkyl groups are linked. They have general formula $(R)_3N$

Example: For primary amines,

• Methyl amine CH_3-NH_2

• Ethyl amine $CH_3-CH_2-NH_2$

For secondary amines,

• Dimethyl amine $CH_3-NH-CH_3$

• Methyl ethyl amine $CH_3-CH_2-NH-CH_3$

Physical Properties

• The polar nature of N-H bond (due to the electronegativity difference of the two atoms) results in the formation of hydrogen bonds with other amine molecules.

• Because of hydrogen bonding they have high melting and boiling points compared to analogous alkanes and high solubility in water.

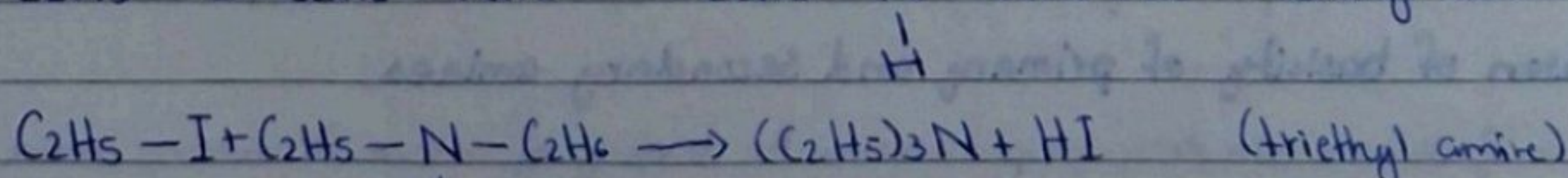
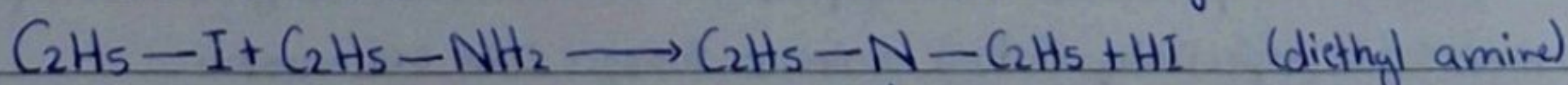
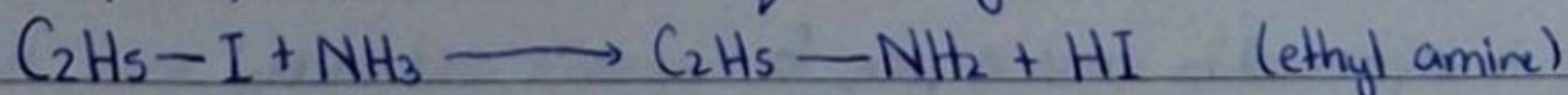
Structure

In amines, nitrogen atom is sp^3 hybridized and has nearly tetrahedral structure. It forms three sigma bonds with its three sp^3 hybrid orbitals while the fourth non-bonding sp^3 hybrid carries a pair of electron. Amine have ability to donate this electron pair. This makes them a base and a nucleophiles.

Preparation of Amines

- **By the reaction of Alkyl Halides with ammonia**

When an alcoholic solution of ammonia is heated with alkyl halide in a sealed tube at $100^\circ C$, a mixture of prim-, sec-, ter-, amines and a quaternary ammonium salt is obtained.



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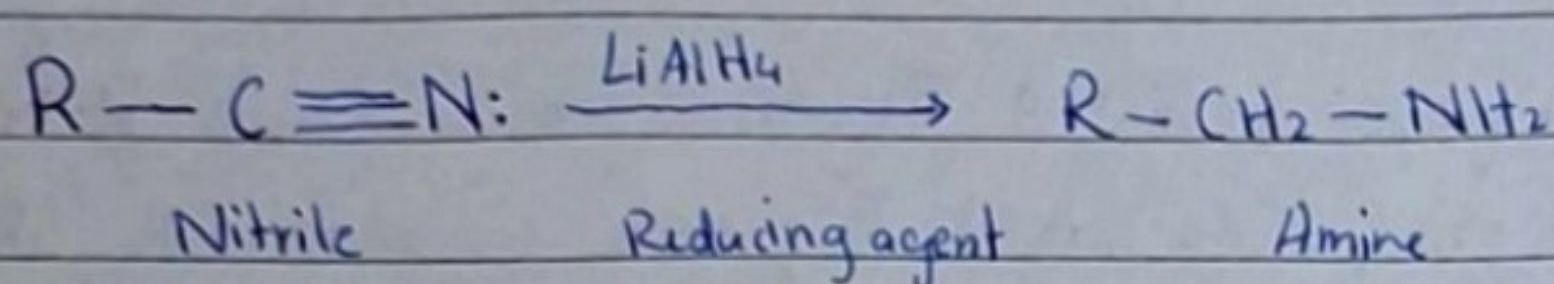
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- By the reductions of nitrogen containing functional groups

Nitrogen containing functional as nitriles, amides and nitro are reduced to amino group by various reducing agents.

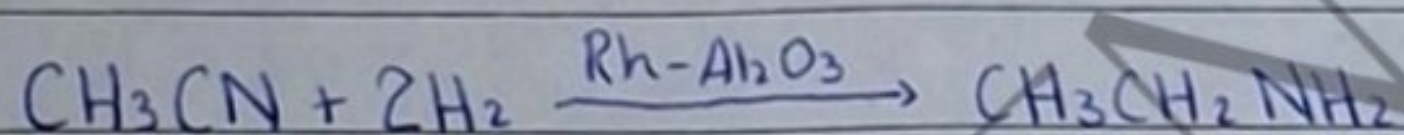
• Reduction of Nitriles

Reduction of alkyl or aryl nitriles gives primary amines. The reduction may be brought by reducing agent i.e. LiAlH_4 , or sodium in ethanol.



• Catalytic Reduction

Nitriles on reaction with hydrogen gas in the presence of catalysts such as $\text{Rh-Al}_2\text{O}_3$, Pt or Raney Nickel gives primary amines.



• Reduction of Nitro-Compounds

Nitro compounds on catalytic or chemical reduction produce primary amines. Nitro benzene can be reduced to Aniline by using reducing agent as tin/iron in the presence of concentrated hydrochloric acid.

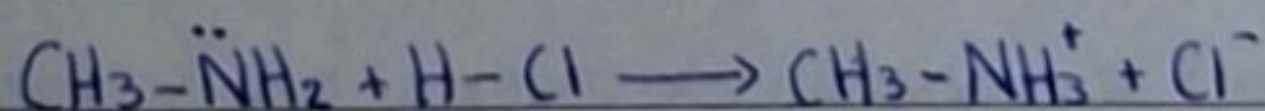
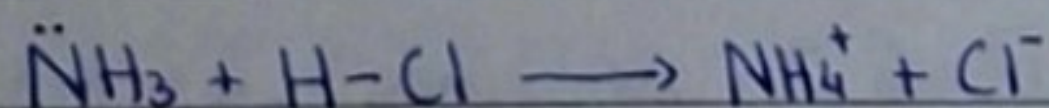
• Reduction of amides

When an amide is treated with reducing agent LiAlH_4 , $-\text{CO}$ group of amide is reduced to $-\text{CH}_2$ and primary amide is formed.

When an amide is treated with bromine in the presence of KOH , degradation of amide takes place leading to the formation of primary amines. This reaction is known as Hoffman degradation reaction.

Basicity of Ammonia and Methyl amine.

Amines are basic and nucleophiles because of non-bonding pair of electrons on nitrogen can easily be donated to an electron-deficient center. Consider the following reaction.



The strength of base is expressed in terms of pK_b , for ammonia and methyl amine, the pK_b values are 4.76 and 3.38 respectively. Methyl amine is stronger base than ammonia.

- Comparison of basicity of primary and secondary amines

The presence of electron-donating group increases the basicity of amines. Secondary amine is stronger

base than primary amine, since it has two electron donating alkyl groups.

Secondary amine > primary amine

Reactions of amines

- Reaction of amine with acid halide

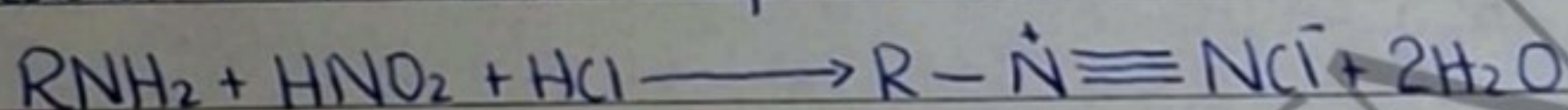
When amine reacts with acid halide, secondary amide is formed.

- Reaction of amine with alkyl halide (alkylation reaction)

Primary amines react with alkyl halide to form secondary, tertiary amine and ammonium salt.

- Reaction with nitrous acid (Preparation of Diazonium Salts)

When amines react with nitrous acid in the presence of hydrochloric acid, diazonium compounds are formed. The reaction mixture must be kept below 10°C .



Alkyl diazonium salts are generally too unstable for practical use.

When the diazonium group is attached to the benzene ring, the delocalized electron in the ring stabilizes the ion to some extent. Because of this, benzene diazonium ion is far more stable than the aliphatic diazonium salt. Benzene diazonium chloride is a colorless crystalline solid. It is stable below 10°C and decomposes easily above 10°C . When combined with phenol, it forms an orange-red dye. Phenyl azo compounds are used as dyes and pigments, they also have antibacterial and antifungal properties.

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