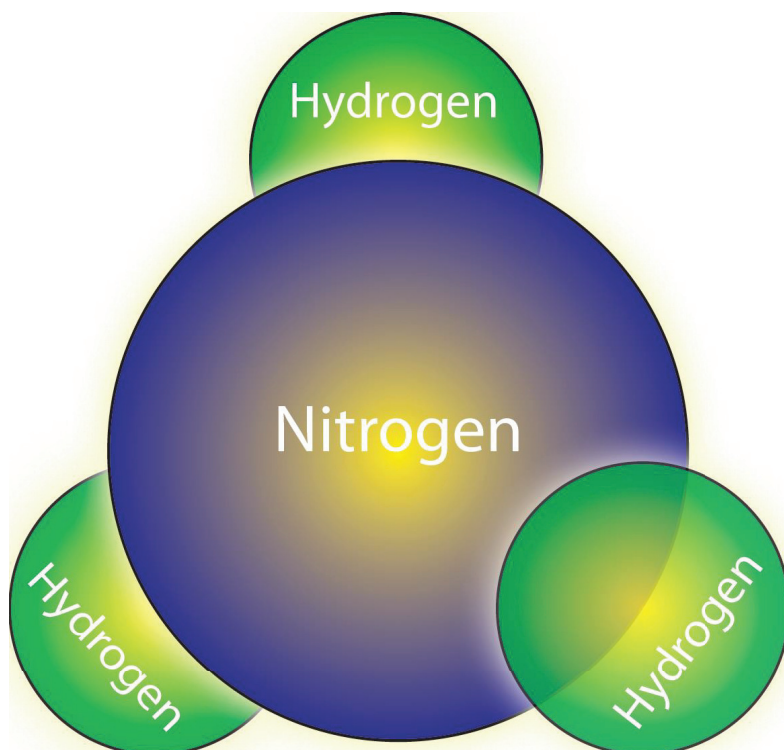


AMINES



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AMINES

Amines are the derivatives of ammonia prepared by the replacement of one, two or all the three hydrogen atoms by alkyl and/or aryl groups.

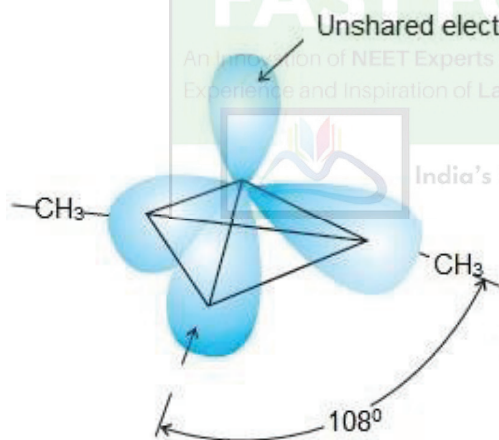
Examples:

(i) $\text{CH}_3\text{-NH}_2$

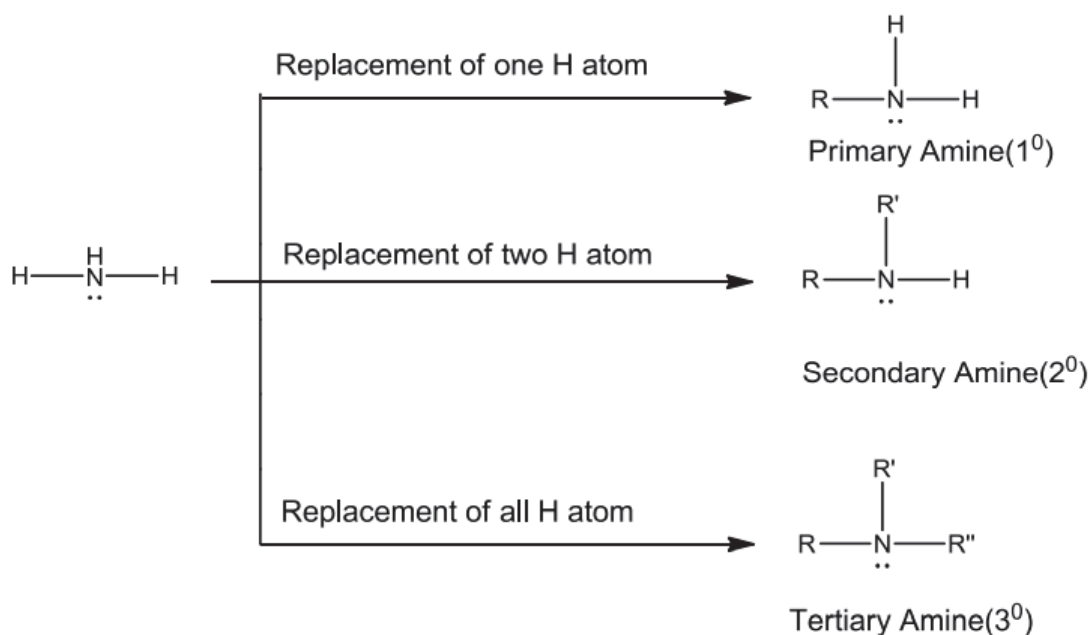
Structure of Amines

- In amines, the nitrogen atom is trivalent and has an unshared pair of electrons. Hence the nitrogen orbitals are sp^3 hybridised with pyramidal geometry.
- The three sp^3 hybrid orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending on the nature of the amines.
- The fourth orbital of nitrogen in all amines contains an unshared pair of electrons. It is due to the presence of unshared pair of electrons, the angle C-N-E is less than 109.5° .

For example: The bond angle for trimethyl amine is 108° .



Classification of Amines

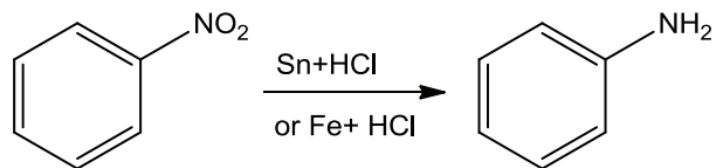
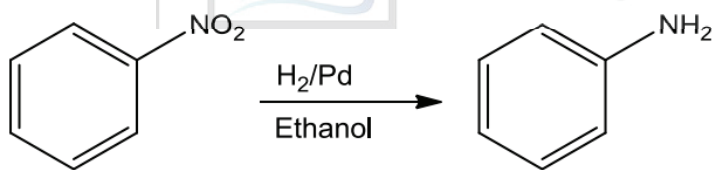
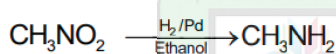


R, R' and R'' can be alkyl or aryl

Preparation of Amines

Reduction of Nitro Compounds

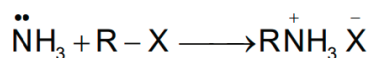
Nitro compounds on reduction with hydrogen gas in the presence of finely divided nickel, palladium or platinum and also on reduction with metals in acidic medium give amines.



Ammonolysis

Alkyl halides or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which halogen

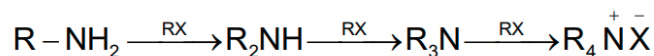
atom is replaced by an amino (-NH₂) group. The process of cleavage of the C-X bond by ammonia molecule is known as ammonolysis.



Nucleophile

Substituted ammonium salt

The primary amine prepared behaves as a nucleophile and reacts with further alkyl halide to form secondary, tertiary amines, and finally quaternary ammonium salt.



(1°)

(2°)

(3°)

Quaternary ammonium salt

The free amine can be obtained from the ammonium salt by treatment with a strong base.

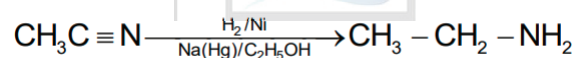


In this method, a mixture of primary, secondary and tertiary and also a quaternary ammonium salt. However a primary amine is prepared by taking large excess of ammonia.

The order of reactivity of halides with amines is RI > RBr > RCl

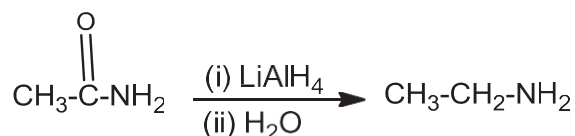
Reduction of Nitriles

Nitriles on reducing with LiAlH₄ or catalytic hydrogenation produce primary amines.



Reduction of Amides

Amides on reducing with LiAlH₄ yield amines.



Gabriel phthalimide synthesis

Phthalimide on reacting with ethanolic solution of KOH forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis yields the corresponding primary amine.



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