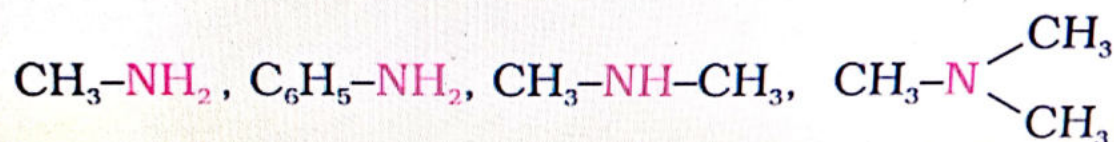


UNIT-V ALIPHATIC AMINES

Aliphatic Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group(s).

For example:

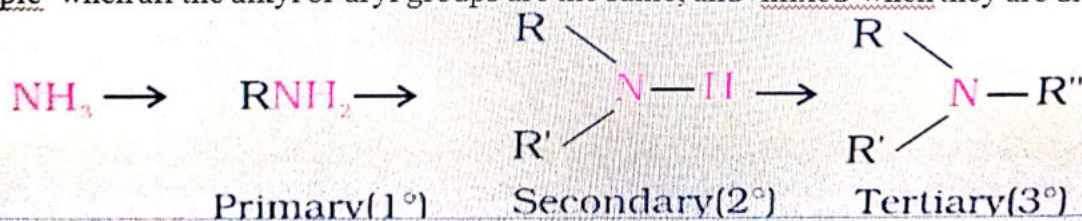


Classification

Amines are classified as primary, secondary and tertiary depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule. If one hydrogen atom of ammonia is replaced by R or Ar, we get RNH₂ or ArNH₂, a primary amine.

If two hydrogen atoms of ammonia or one hydrogen atom of R-NH₂ are replaced by another alkyl/aryl(R') group, we get R-NHR', secondary amine. The second alkyl/aryl group may be same or different. Replacement of another hydrogen atom by alkyl/aryl group leads to the formation of tertiary amine. Amines are said to be

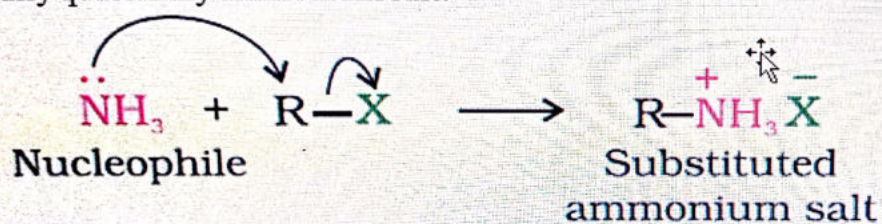
'simple' when all the alkyl or aryl groups are the same, and 'mixed' when they are different.]



Preparation of Amines

1. Ammonolysis of alkyl halides

The process of cleavage of the C-X bond by ammonia molecule is known as ammonolysis. The reaction is carried out in a sealed tube at 373 K. The primary amine thus obtained behaves as a nucleophile and can further react with alkyl halide to form secondary and tertiary amines, and finally quaternary ammonium salt.



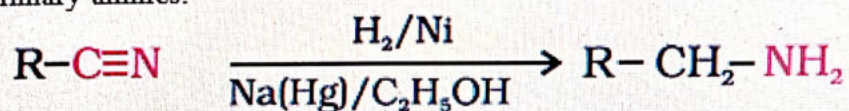
The free amine can be obtained from the ammonium salt by treatment with a strong base:



The order of reactivity of halides with amines is $\text{RI} > \text{RBr} > \text{RCl}$.

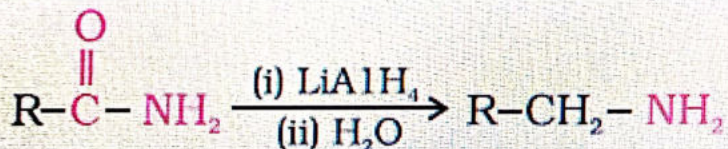
2. Reduction of nitriles

Nitriles on reduction with lithium aluminium hydride (LiAlH₄) or catalytic hydrogenation produce primary amines.



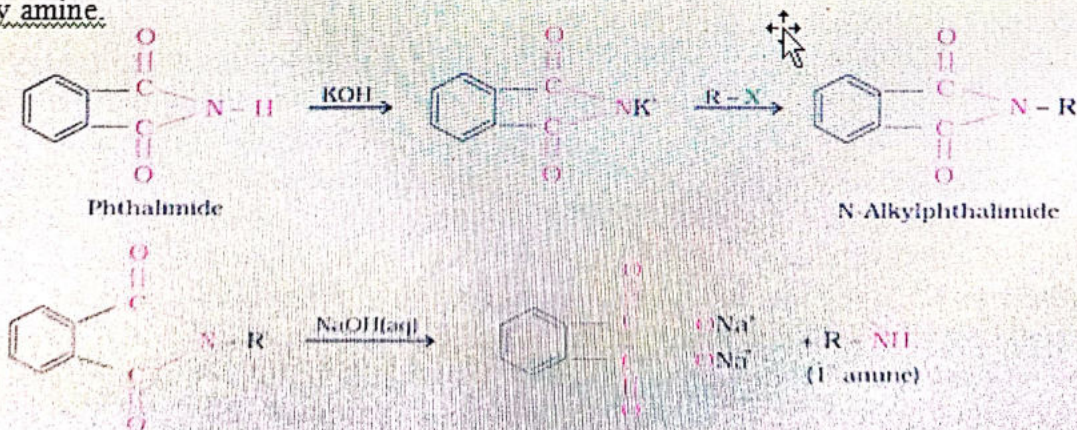
3. Reduction of amides

The amides on reduction with lithium aluminium hydride yield amines.



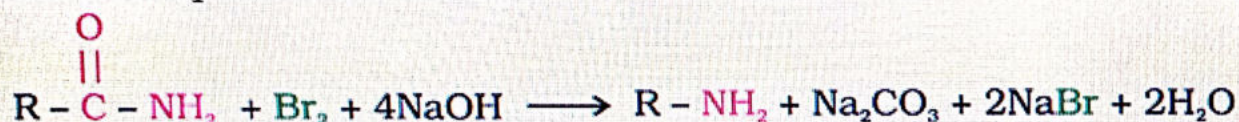
4. Gabriel phthalimide synthesis

Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.



5. Hoffmann bromamide degradation reaction

Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide. In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so formed contains one carbon less than that present in the amide.



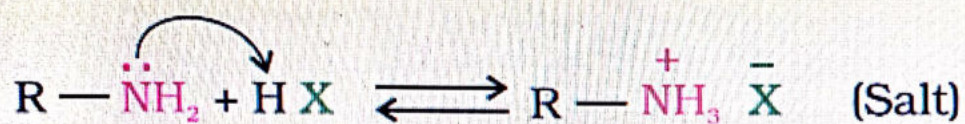
Physical Properties

1. The lower aliphatic amines are gases with fishy odour. Primary amines with three or more carbon atoms are liquid and still higher ones are solid.
2. Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part. Higher amines are essentially insoluble in water. Amines are soluble in organic solvents like alcohol, ether and benzene.
3. Amines have higher boiling points than nonpolar compound of similar molecular weight because they can form intermolecular hydrogen bonds due to their polar nature

CHEMICAL REACTIONS

1. Basic character of amines

Amines, being basic in nature, react with acids to form salts.

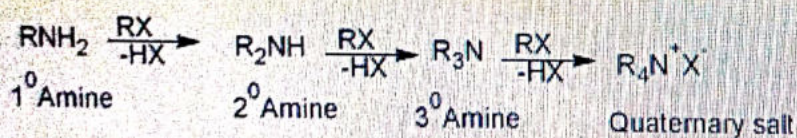


The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. Amines have an unshared pair of electrons on nitrogen atom due to which they behave as **Lewis base**.

Basicity of amines is related to their structure. Basic character of an amine depends upon the ease of formation of the cation by accepting a proton from the acid. The more stable the cation is relative to the amine, more basic is the amine.

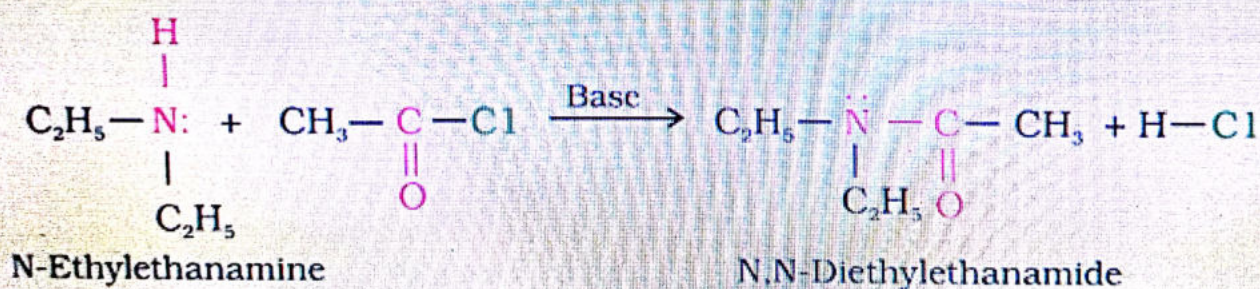
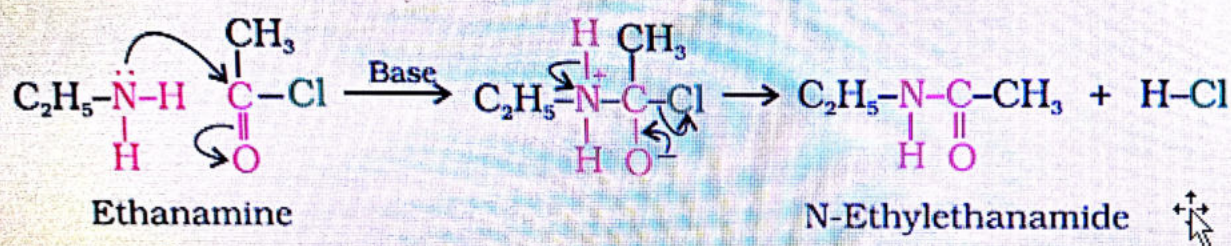
2. Alkylation

Amines undergo alkylation on reaction with alkyl halides.



3. Acylation

Aliphatic amines react with acid chlorides and anhydrides to form N-substituted amide. This reaction is known as acylation. The reaction is carried out in the presence of a base stronger than the amine, like pyridine, which removes HCl so formed and shifts the equilibrium to the right hand side.



Amines also react with benzoyl chloride ($\text{C}_6\text{H}_5\text{COCl}$). This reaction is known as benzoylation.



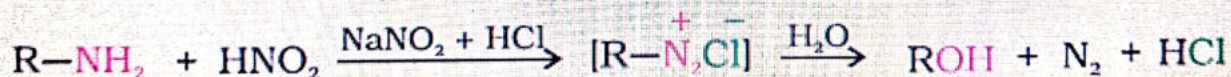
4. Carbylamine reaction

Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamines reaction or isocyanide test and is used as a test for primary amines.



5. Reaction with nitrous acid (NITROUS ACID TEST)

Three classes of amines react differently with nitrous acid which is prepared from a mineral acid and sodium nitrite.



- (a) Primary aliphatic amines react with nitrous acid to liberate nitrogen gas (seen as bubbles).
- (b) Secondary aliphatic amines react with nitrous acid to produce a yellow oily layer.
- (c) Tertiary aliphatic amines react with nitrous acid to form soluble nitrile salts. There is no visible sign of reaction.

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