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**CHEMISTRY**

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CLASS 11 & 12th



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CLASS 12th

# Organic Compounds Containing Nitrogen

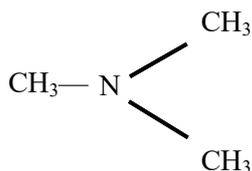
misostudy



## 01. Introduction

Amines can be considered as derivatives of ammonia, obtained by replacement of one or more hydrogen atoms by alkyl and/or aryl groups.

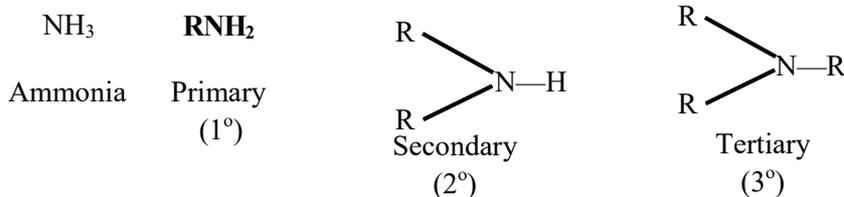
For example:



Like ammonia, nitrogen atom of amines is trivalent and carries an unshared pair of electrons. Nitrogen orbitals in amines are therefore,  $sp^3$  hybridised and the geometry of amines is pyramidal. Each of the three  $sp^3$  hybridised orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending upon the composition of the Amines. The fourth orbitals of nitrogen in all amines contains an unshared pair of electrons. Due to presence of unshared pair of electrons, the angle C—N—E, (where E is C or H) is less than  $109.5^\circ$  ( $109^\circ 28'$ ). For example, it is  $108^\circ$  in case of trimethylamine.

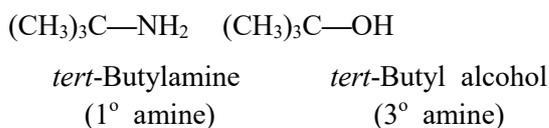
### Classification of amines:

Amines are classified as primary ( $1^\circ$ ), secondary ( $2^\circ$ ) and tertiary ( $3^\circ$ ) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule. Amines are said to be 'simple' when all the alkyl or aryl groups are the same, and 'mixed' when they are different.



### Caution:

For amines,  $1^\circ$ ,  $2^\circ$  or  $3^\circ$  nature of the nitrogen atom of amino group is considered while for all other compounds  $1^\circ$ ,  $2^\circ$  or  $3^\circ$  nature of the carbon atom attached to the functional group is considered. For example, *tert*-butylamine is a  $1^\circ$  amine while *tert*-butyl alcohol is a  $3^\circ$  alcohol.



### Nomenclature of amines:

In common system, an aliphatic amine is named by prefixing alkyl group to amine, *i.e.*, alkylamine as one word (*e.g.*, methylamine). In secondary and tertiary amines, when two or more groups are the same, the prefix di or tri is appended before the name of alkyl group. In IUPAC system, amines are named as alkanamines, derived by replacement of 'e' of alkane by the word amine. For example,  $\text{CH}_3\text{NH}_2$  is named as methanamine. In case, more than one amino group is present at different position in the parent chain, their position are specified by giving number to the carbon atoms bearing  $\text{—NH}_2$  groups and suitable prefix such as di, tri etc. is attached to the amine. The letter 'e' of the suffix of the hydrocarbon part is retained.

For example,  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$  is named as ethane-1,2-diamine.

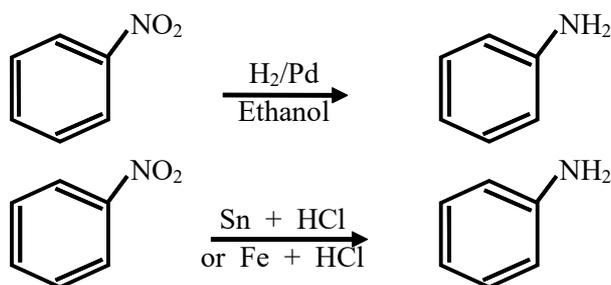
In arylamines,  $-\text{NH}_2$  group is directly attached to the benzene ring.  $\text{C}_6\text{H}_5\text{NH}_2$  is the simplest example of arylamine. In common system, it is known as aniline. It is also an accepted IUPAC name. While naming arylamines according to IUPAC system, suffix 'e' of arene is replaced by 'amine'.

Thus in IUPAC system,  $\text{C}_6\text{H}_5-\text{NH}_2$  is named as benzenamine.

### General methods of preparation of amines.

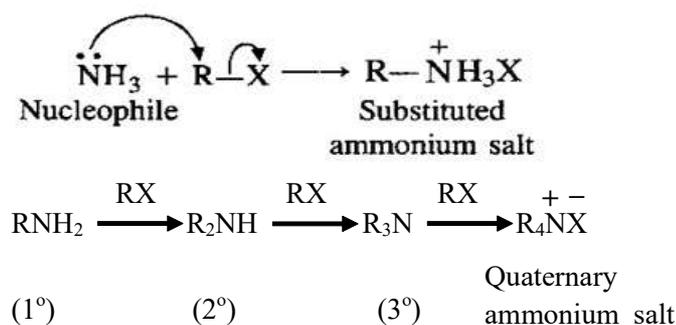
Amines are prepared by the following methods:

- (i) **Reduction of nitro compounds** : Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium. Nitroalkanes can also be similarly reduced to the corresponding alkanamines.



Reduction with iron scrap and hydrochloric acid is preferred because  $\text{FeCl}_2$  formed gets hydrolysed to release hydrochloric acid during the reaction. Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

- (ii) **Ammonolysis of alkyl halides**: The carbon-halogen bond in alkyl or benzyl halides can be easily cleaved by a nucleophile. Hence, an alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino ( $-\text{NH}_2$ ) group. This process of cleavage of the  $\text{C}-\text{X}$  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.

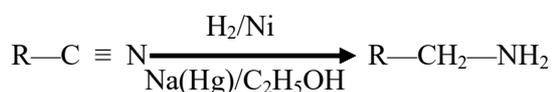


The free amine can be obtained from the ammonium salt by treatment with a strong base:

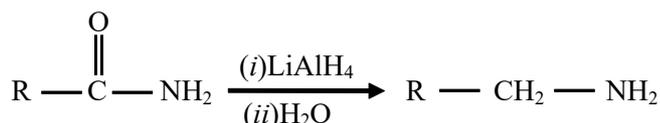


Ammonolysis has the disadvantage of yielding a mixture of primary, secondary and tertiary amines and also a quaternary ammonium salt. However, Primary amine is obtained as a major product by taking large excess of ammonia. The order of ammonia. The order of reactivity of halides with amines is  $\text{RI} > \text{RBr} > \text{RCl}$ .

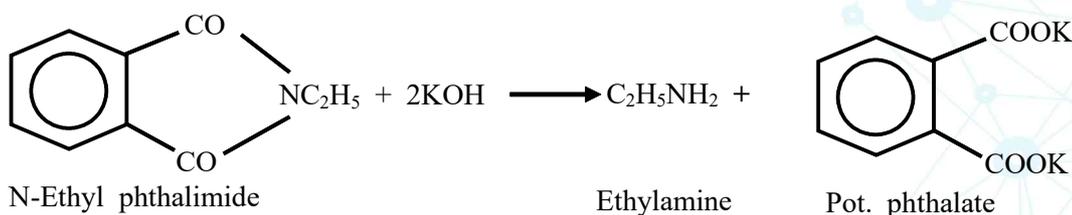
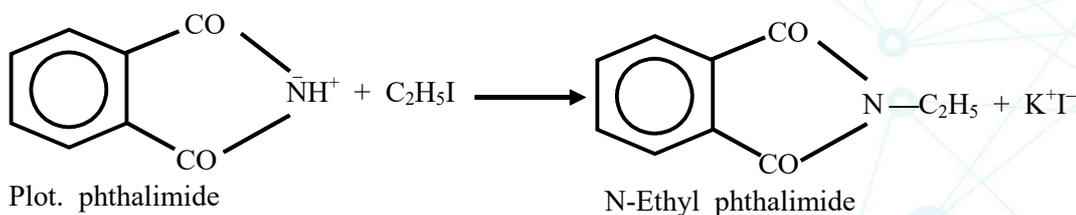
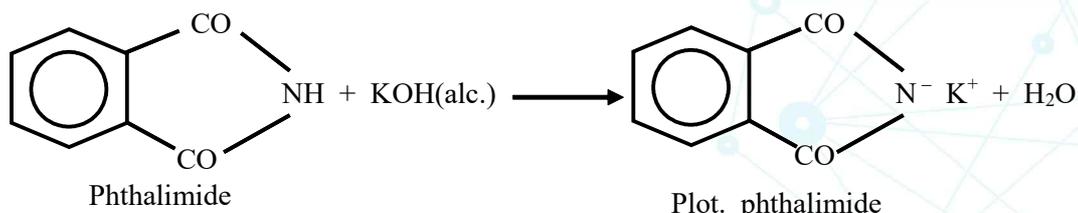
(iii) **Reduction of nitriles or cyanides (Mendius reaction) :**



(iv) **Reduction of amides :**

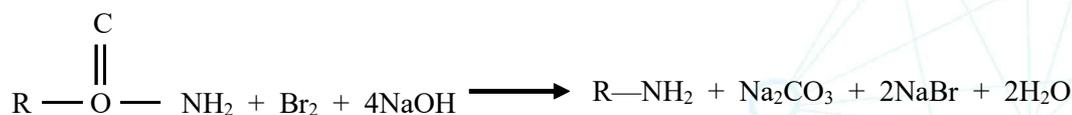


(v) **Gabriel phthalimide synthesis :**



(vi) **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 of amines

- 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.
- Aniline and other arylamines are usually colourless but get coloured on storage due to atmospheric oxidation.