

CHEMISTRY STUDY MATERIALS FOR CLASS 12

(NCERT Based Notes of Chapter - 13)

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Amines

Amines are the derivatives of ammonia. Like ammonia, the nitrogen atom in amines is also sp^3 hybridised with an unpaired electron in one of the sp^3 hybridised orbitals. So the shape of amines is also pyramidal.

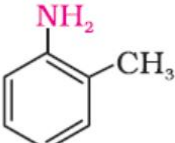

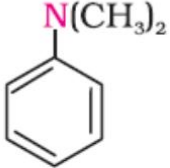
Amines are classified into three types – primary (1^0), secondary (2^0) and tertiary (3^0) amines. If one hydrogen atom of ammonia is replaced by R (alkyl) group, we get 1^0 amine. Their general formula is $R-NH_2$. If two hydrogen atoms of ammonia are replaced by two R or Ar groups, we get 2^0 amine. Their general formula is R_2NH . If three hydrogen atoms of ammonia are replaced by R group, we get 3^0 amine. Their general formula is R_3NH .

If all the alkyl or aryl groups are the same, that amine is called simple amine and if they are different, it is called mixed amine.

Nomenclature:

In common system amines are named by prefixing alkyl group to amine, i.e. alkyl amine. In secondary and tertiary amines, when the alkyl groups are same, the prefix di or tri is used before the name of the alkyl group. In IUPAC system, amines are named by replacing of 'e' of alkane by the word amine, i.e. alkanamine. In the case of secondary and tertiary amines, the alkyl group containing the maximum number of carbon atom is taken as the parent chain and the other alkyl groups are taken as substituents. While naming aryl amines according to IUPAC system, the suffix 'e' of arene is replaced by 'amine', i.e. arenamine. E.g. benzenamine.

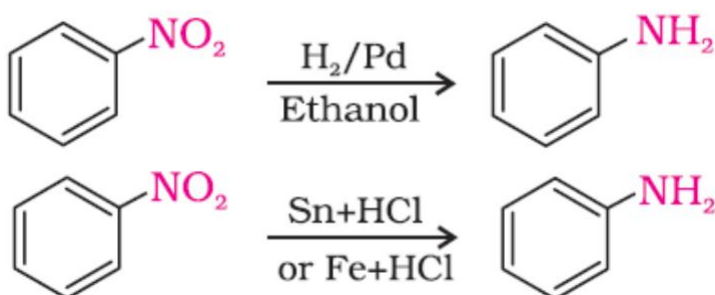
Amine	Common name	IUPAC name
CH_3-NH_2	Methyl amine	Methanamine
$CH_3-CH_2-NH_2$	Ethylamine	Ethanamine
$CH_3-CH_2-CH_2-NH_2$	n-Propylamine	Propan-1-amine

$(\text{CH}_3)_2\text{CH-NH}_2$	Isopropylamine	Propan-2-amine
$\text{CH}_3\text{-NH-CH}_2\text{-CH}_3$	Ethylmethylaniline	N-Methylethanamine
$(\text{CH}_3)_3\text{N}$	Trimethylamine	N,N-Dimethylmethanamine
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-N(C}_2\text{H}_5)_2$	N,N-Diethylbutylamine	N,N-Diethylbutan-1-amine
$\text{CH}_2=\text{CH-CH}_2\text{-NH}_2$	Allylamine	Prop-2-en-1-amine
$\text{NH}_2\text{-(CH}_2)_6\text{-NH}_2$	Hexamethylenediamine	Hexane-1,6-diamine
$\text{C}_6\text{H}_5\text{-NH}_2$	Aniline	Aniline or Benzenamine
	o-Toluidine	2-Aminotoluene
	p-Bromoaniline	4-Bromobenzenamine or 4-Bromoaniline
	N,N-Dimethylaniline	N,N-Dimethylbenzenamine

Preparation of Amines

1. Reduction of nitro compounds:

Nitro compounds when reduced by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum or by reduction with metals in acidic medium, we get amines.



Reduction with iron and hydrochloric acid is preferred because 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.

2. Ammonolysis of alkyl halides:

Alkyl halides when treated with alcoholic solution of ammonia at 373 K, undergo nucleophilic substitution reaction to give a mixture of primary, secondary and tertiary amines and quaternary ammonium salt ($R_4N^+X^-$).

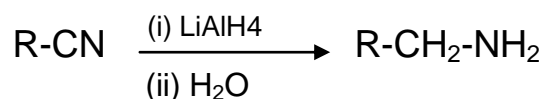
This process of cleavage of C-X bond by ammonia is called **ammonolysis** (Hofmann's Ammonolysis).



If large excess of ammonia is used, primary amine is formed as the major product. The order of reactivity of halides with amines is $RI > RBr > RCl$.

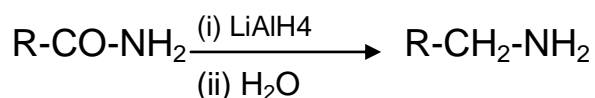
3. Reduction of Nitriles:

Nitriles on reduction with lithium aluminium hydride ($LiAlH_4$) or catalytic hydrogenation produce primary amines. This reaction is used for ascending in amine series, i.e., for preparation of amines containing one carbon atom more than the starting amine.



4. Reduction of amides:

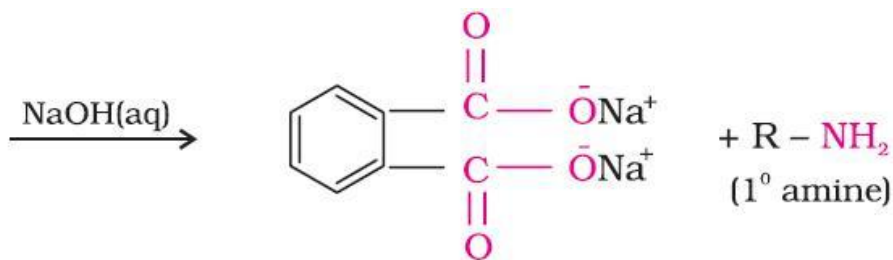
The amides on reduction with lithium aluminium hydride give amines.



5. Gabriel phthalimide synthesis:

This method is used for the preparation of aliphatic primary amines only. Phthalimide when treated with ethanolic solution of potassium hydroxide to form potassium salt of Phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.

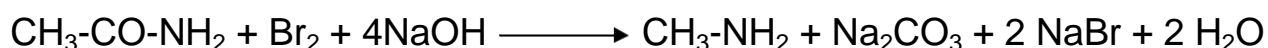
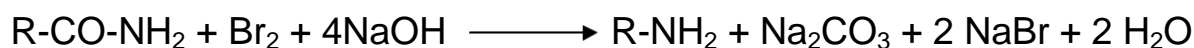




Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by Phthalimide.

6. Hoffmann bromamide degradation reaction:

This method is used for the conversion of an amide to a primary amine with one carbon atom less than that present in the amide. In this method, an amide is treated with Bromine and ethanolic solution of NaOH to give an amine.



Physical Properties: Lower amines have fishy smell.

1. Solubility: 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 insoluble in water. Amines are soluble in organic solvents like alcohol, ether and benzene.

2. Boiling point: Primary and secondary amines are associated through intermolecular hydrogen bonding. This intermolecular association is more in primary amines than in secondary amines. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom.

Therefore, the order of boiling points of isomeric amines is as follows: