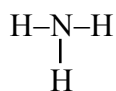


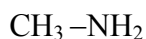


Amines

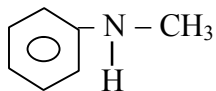
Definition : Amines are defined as organic derivatives of ammonia in which one, two or all the three hydrogen atoms of ammonia are replaced by corresponding number of same or different alkyl/aryl or both radicals.



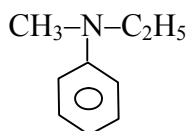
ammonia



methyl amine



methyl phenyl
amine



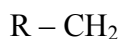
ethyl methyl
phenyl amine

Classification :

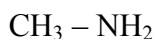
Amines are classified on the basis of number of radicals directly attached to nitrogen.

1) Primary amines (1° amines) :

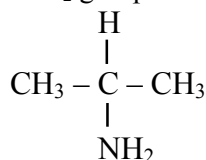
In these compounds only one hydrogen atom of ammonia is replaced by one alkyl or aryl group. The functional group is called amino group denoted as “- NH_2 group”.



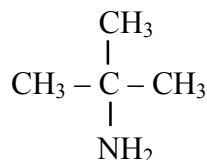
1° amines



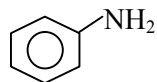
methyl amine



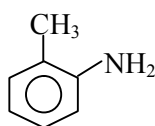
isopropyl amine



t. butyl amine (1° amines)



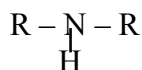
phenyl amine (aniline)



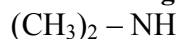
o. toluidine

2) Secondary amines (2° amines):

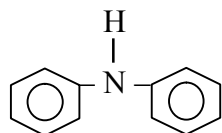
In these compounds two hydrogen atoms of ammonia are replaced by two same or different alkyl/aryl group. The functional group is called **imino group** denoted by $>\text{N}-\text{H}$ group.



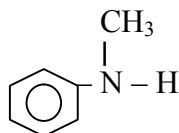
2° amine



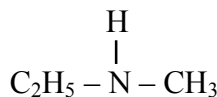
dimethyl amine



dimethyl amine

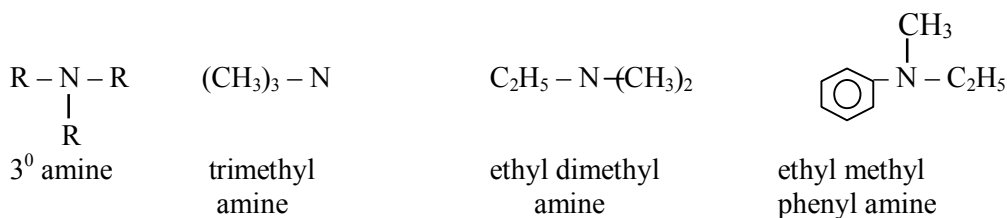


methyl phenyl amine



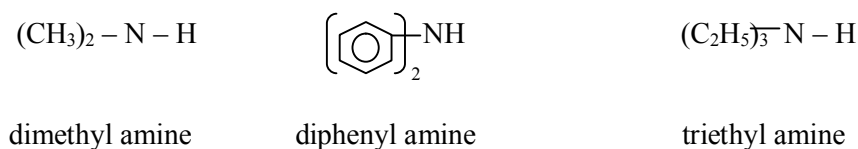
ethyl methyl amine

3) Tertiary amine (3° amine) In these compounds all three hydrogen atoms of ammonia are replaced by three same or different alkyl/aryl radicals. The functional group is called t nitrogen denoted by $\text{N}<$

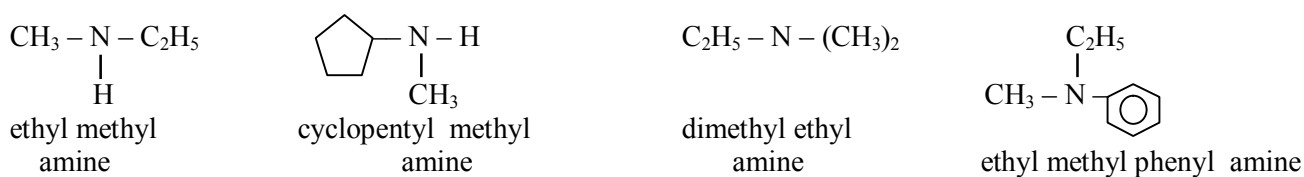


The secondary and tertiary amines are sub classified into two classes.

a) Simple or symmetrical amines :



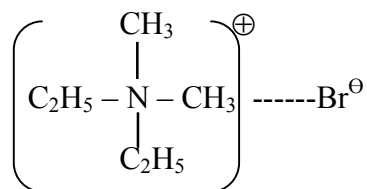
b) Mixed or unsymmetrical amines : They have different radicals.



They have identical radicals.

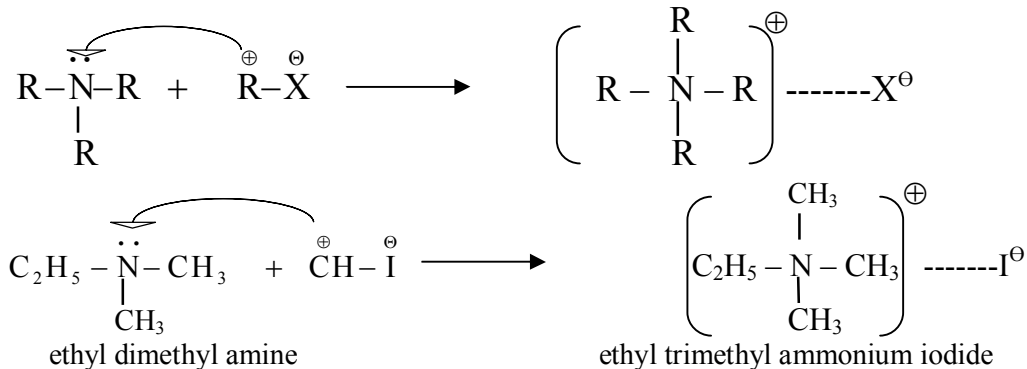
Quaternary Ammonium Salt:

Quaternary Ammonium compounds which all 4 H atoms in NH_4^+ ion are replaced by 4 alkyl radicals, which may be same or different.



diethyl dimethyl ammonium bromide

Q.A. Salt can be obtained by heating 3⁰ amines with alkyl halide.



Nomenclature of Amines

Common names of amines are given on the basis of alkyl radicals attached to nitrogen.

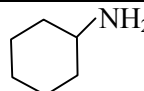
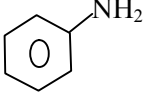
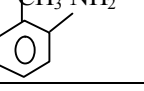
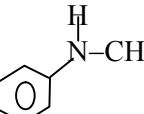
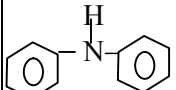
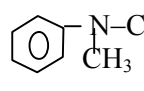
In the case of IUPAC system for primary amines from the name of the parent alkane the last letter 'e' should be replaced by the letters 'amine' along with the locant.

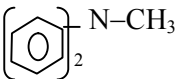

If more than one amino groups are present then prefix di, tri, etc. are applicable to amine. But the last letter 'e' of the parent alkane is retained.

In secondary and tertiary amines the largest alkyl radical is considered as parent alkanamine and remaining groups are named as N-substituent. (N for nitrogen)

The name aniline is retained in the IUPAC system along with benzenamine.

Nomenclature of amines:

Formula	Common Name	IUPAC Name
R-NH ₂	Alkyl amine	Alkanamine
CH ₃ - NH ₂	methylamine	Methanamine
C ₂ H ₅ - NH ₂	ethylamine	Ethanamine
CH ₃ - CH ₂ - CH ₂ NH ₂	n propyl amine	Propan-1-amine
H CH ₃ - C - CH ₃ NH ₂	Isopropyl amine sec. propylamine	Propan-2-amine
CH ₂ - (CH ₂) ₄ - CH ₂ NH ₂ NH ₂	Hexamethylene diamine	Hexane -1,6 diamine
H CH ₂ = C - CH ₂ - NH ₂	Allyl amine	Prop -2-en-1-amine
	Cyclohexylamine	Cyclohexanamine
	Aniline or phenylamine	Aniline or Benzenamine
	O. toluidine	2 amino toluene
(CH ₃) ₂ -N-H	Dimethylamine	N-methyl methanamine
C ₂ H ₅ -N-CH ₃ H	Ethyl methyl amine	N methyl ethanamine
	Methyl phenyl amine	N- methyl aniline Or N- methyl benzanamine
	Diphenyl amine	N- phenyl aniline Or N- phenyl benzanamine
(CH ₃) ₃ -N	Trimethyl amine	N N dimethyl methanamine
(CH ₃) ₂ -N-C ₂ H ₅	Dimethyl ethyl amine	N N dimethylethanamine
	Ethyl methyl aniline	N ethyl N methyl aniline Or N ethyl N methyl benzanamine
(C ₂ H ₅) ₂ -N-CH ₃	Diethyl methyl amine	N ethyl N methyl ethanamine

	Diphenyl methyl amine	N methyl N phenyl aniline
	Benzyl amine	Phenylmethanamine

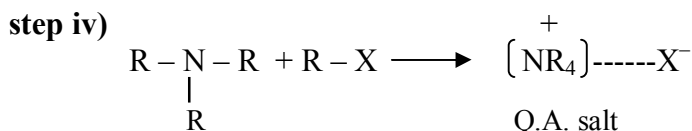
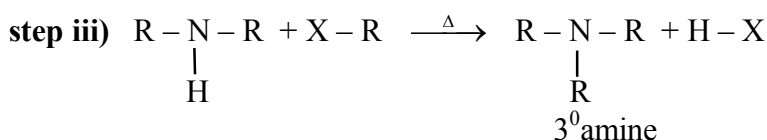
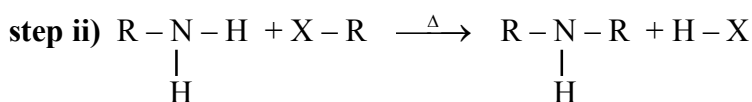
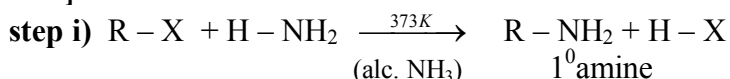
Methods of Preparation

1) From Alkyl halides :

A) By Ammonolysis of alkyl halides (haloalkanes) Hofmann's Ammonolysis:

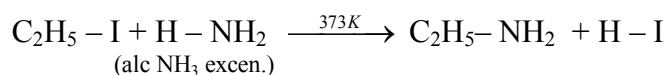
When **large excess of alkyl halide** is heated with alcoholic solution of ammonia at about 373 K it undergoes ammonolysis, in a sealed tube. Ammonolysis occurs in four steps; giving a mixture of primary amines, 2° amines, 3° amines and quaternary ammonium salt.

Ex.1]



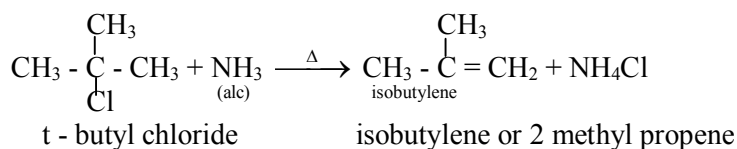
However if ammonia is taken in excess then reactions stops in one step giving primary amine as a major product.

Ex.2]



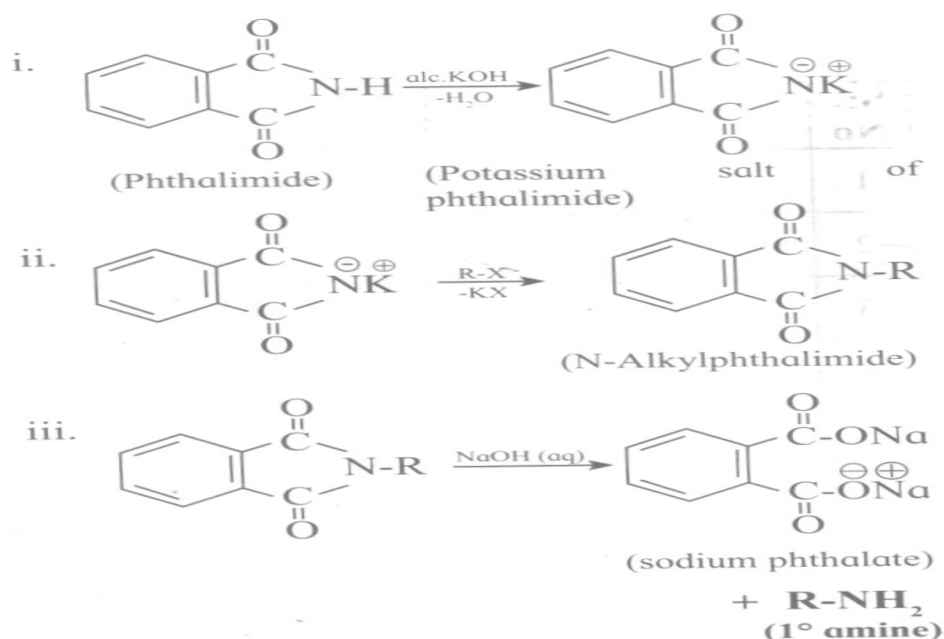
Limitations of method :

1. The method cannot be applied for the preparation of 1° amines only. Because mixture of all amines and Q.A. salt is obtained. However if alcoholic NH₃ is in excess, then 1° amines are the major products.
2. 3° alkyl halides do not undergo ammonolysis. Instead of substitution they prefer to undergo elimination reaction



2. Gabriel phthalimide Synthesis (From alkyl halide & phthalimide) :

Phthalimide reacts with ethanolic potassium hydroxide. During this reaction N-H proton is neutralized with the formation of potassium salt. This potassium salt is heated with alkyl halide to obtain N-alkyl derivative of phthalimide. This derivative on alkaline hydrolysis by caustic soda gives corresponding primary amine along with sodium phthalate.



*** Advantage of Gabriel Synthesis :**

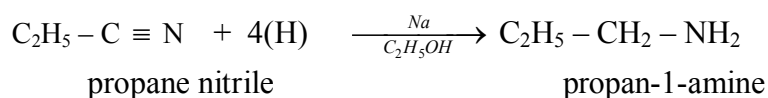
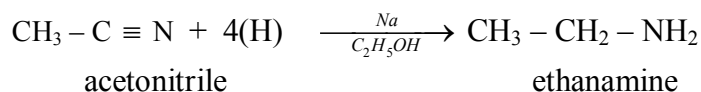
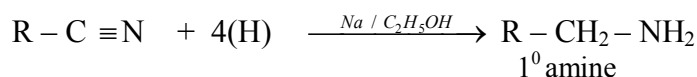
Alkylation of 1° amines giving 2° and 3° amines is prevented in this method. Thus 1° amines are formed only.

*** Limitations :**

Aromatic amines cannot be obtained because aryl halides do not have nucleophilic reaction with potassium salt of phthalimide.

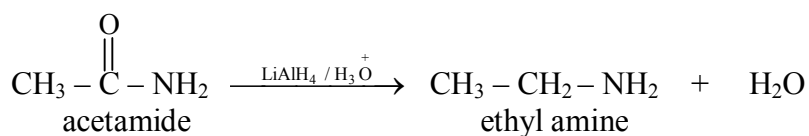
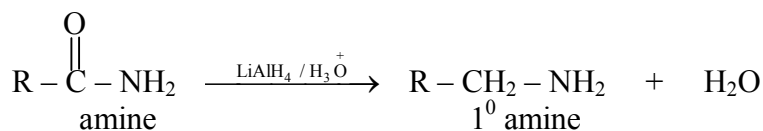
A) Reduction of alkyl cyanides (Nitriles) Mendius Reduction :

Alkyl cyanides or nitriles can be reduced by sodium and alcohol giving primary amines. The reaction is called as **Mendius Reduction**.



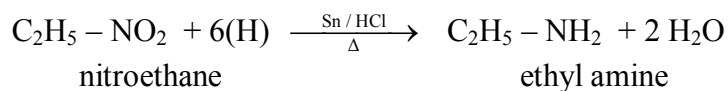
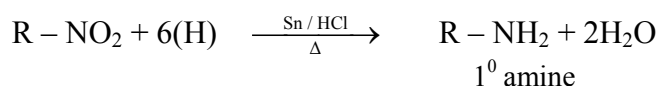
B) Reduction of Amides :

Amides are reduced by strong reducing agent such as LiAlH_4 followed by acidic hydrolysis. On reduction amides give primary amines **containing some no. of carbon atoms**.



C) Reduction of nitro alkanes or nitro paraffins :

Nitro alkane can be reduced by metallic tin and concentrated HCl or by LiAlH_4 followed by acid hydrolysis. On reduction corresponding 1° amines are form.

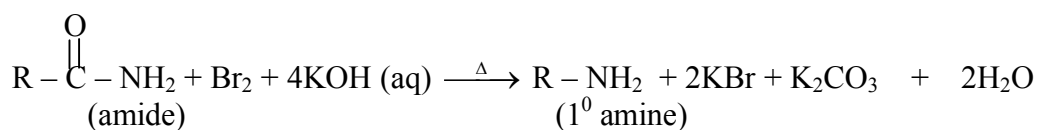


4) Hofmann's broamide degradation :

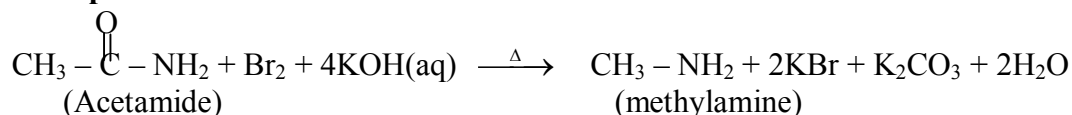
[Preparation of 1° amine from amides]

When the amide is heated with bromine in presence of NaOH Solution corresponding primary amine is formed.

* The 1° amines contain one carbon atom less than the amide. therefore it is called degradation.



For example :

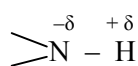


Structure of amino group :

In amines nitrogen atom is in Sp^3 hybridized state. Nitrogen forms 3 sigma bonds using three hybrid orbitals. On the fourth side there is lone pair of electron. This lone pair repells the bonds. Therefore in amine the tetrahedral geometry changes to pyramidal geometry and bond angles are decreased to 107°

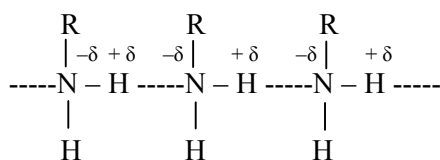
Intermolecular forces in amines

The $\text{N} - \text{H}$ bond is polarized as electronegativity of N is 3.25 & that of Hydrogen is 2.1.



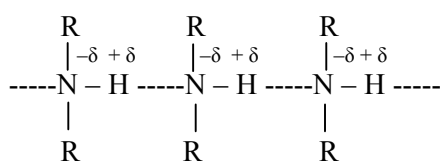
Due to this primary & secondary amines can form intermolecular H bonding.

Primary amines :



The H bonding is highest in 1° amines as there are two $\text{N} - \text{H}$ bonds.

Secondary amines :

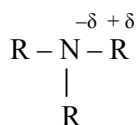




The H bonding is Less in 2^o amine as there is only one N – H bond.

Tertiary amines:

They can not have H bonding as there is no N – H bond. However polarization is there between Nitrogen & carbon. So 3^o amines can have dipole attraction.

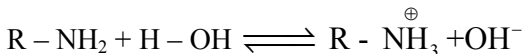


Physical properties :

- (1) First few members of amines are colourless gases having fishy smell. Middle members are liquids while higher members are solids,
- (2) Aniline and other aryl amines are colourless in pure state. But when exposed to air they become coloured. (3) Lower amines are water soluble as they can form hydrogen bonds with water molecules. Solubility decreases with increasing molecular weight. Amongst the isomeric amines solubility in water is in the decreasing order of [1^o > 2^o > 3^o] amines. (No hydrogen bonds in 3^o amines)
- (4) **Boiling Point :** 1^o & 2^o amine can form inter molecular hydrogen bonding but N-H bond is less polar than O-H bond. (electronegativity of O = 3.5 & N = 3.25 ev) therefore the B.P of amines are less than those of alcohols.
order : → R-COOH > R - OH > R - NH₂
Amongst isomeric amines 1^o have the highest B.P. while 3^o has the lowest B.P
→ 1^o amine > 2^o amine > 3^o amine.

Basic Nature of Amines

All amines have a lone pair of electron with nitrogen atom, which make them basic compound. Due to the lone pair they are also nucleophiles. All amines can accept the proton indicating their basic nature. When amine is dissolved in water following equilibrium is obtained.



$$K = \frac{[\text{R} - \text{NH}_3^+][\text{OH}^-]}{[\text{R} - \text{NH}_2][\text{H}_2\text{O}]}$$

But water is taken in a large excess. So its concentration nearly remains constant denoted by K'

$$K = \frac{[\text{R} - \text{NH}_3^+][\text{OH}^-]}{[\text{R} - \text{NH}_2] K'}$$

$$K \times K' = K_b = \frac{[\text{R} - \text{NH}_3^+][\text{OH}^-]}{[\text{R} - \text{NH}_2]}$$

The constant K_b is called dissociation constant or ionisation constant of weak base.

$$\text{PK}_b = -\log K_b$$

Lower the value of pK_b, relatively stronger will be the base.

*** Relative basic strengths of amines :** The basic strength of amines depends upon availability of lone pair of electrons. The basic nature is therefore controlled by three factor.

i) Inductive effect :

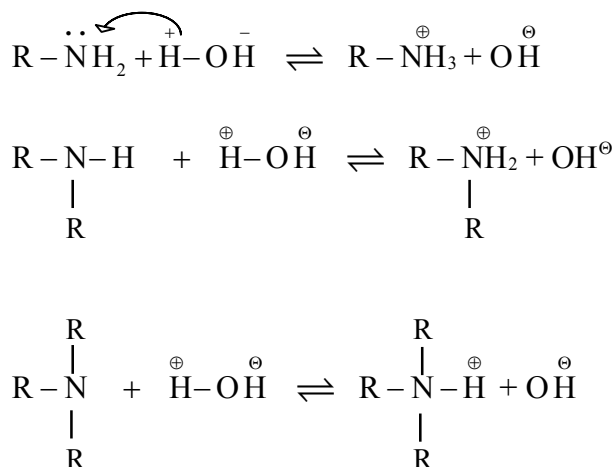
The +I effect increases the electron density over the nitrogen. This increases the basic nature. So all amines are stronger bases than ammonia .

ii) Steric hindrance :

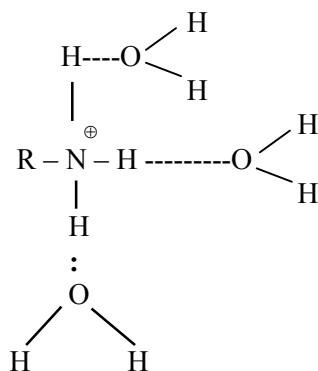
More the steric hindrance, less will be the availability of lone pair. Thus steric hindrance decreases basic nature.

iii) Solvation :

Amines react with water producing alkyl ammonium ions which are conjugate acids of amines.
(Lowry – Bronsted Theory)

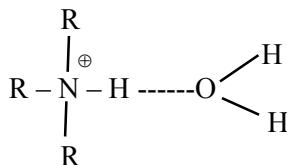


In primary amine conjugate acid ie. $\text{R}-\overset{\oplus}{\text{N}}\text{H}_3$ is highly solvated by water ; SO it is highly stable



In secondary amines $\text{R}-\overset{\oplus}{\text{N}}\text{H}_2$ is less solvated.

And in 3° amines $\text{R}_3\overset{\oplus}{\text{N}}-\text{H}$ is least solvated, so least stable.

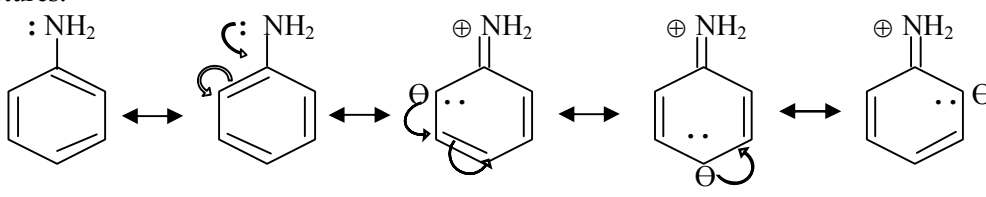


So as per stability, equilibrium of 1° amine in water, should be more shifted in forward direction.

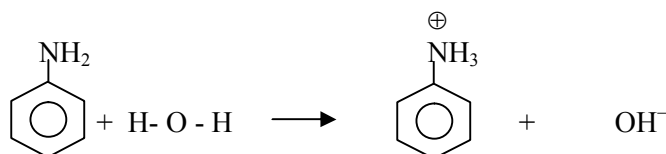
However the combined effect of +I effect, steric hindrance & solvation indicates that 2° amines are most basic & 3° are least.

Order of basic strength $2^\circ \text{ amine} > 1^\circ \text{ amine} > 3^\circ \text{ amine} > \text{NH}_3$.

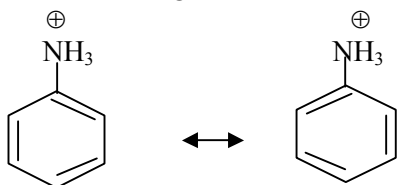
* In aromatic amines NH_2 group is directly attached to benzene ring. The lone pair of electron on the nitrogen is in conjugation with the benzene ring. Therefore it can take part in the resonance. Aniline can have five resonating structures.



If aniline accepts hydrogen ion, it forms anilinium ion ($\text{C}_6\text{H}_5-\text{NH}_3^+$ ion). The lone pair of nitrogen is donated to H^+ ion. It is not available for resonance. So anilinium ion has only two resonating structures. Obviously it is less stable than aniline.



The resonating structures of anilinium ion are two in number



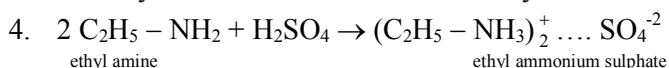
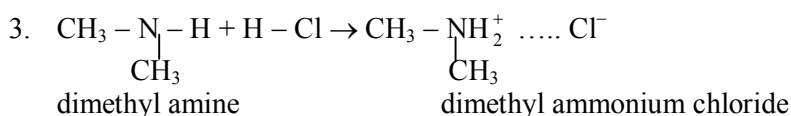
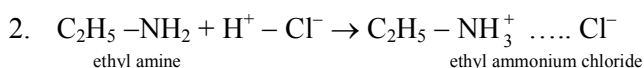
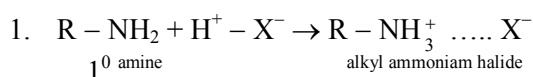
The anilinium ion is less stable than aniline. So equilibrium in aqueous medium is shifted in backward direction. Thus aromatic amines are reluctant to donate the lone pairs of electron. So they are less basic than ammonia and aliphatic amines.

*** Reaction indicating basic nature of amines :**

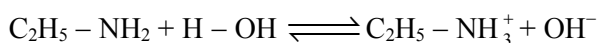
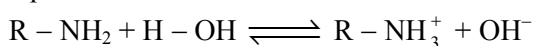
a) Neutralization of amines by acids :

Amines are neutralized by mineral acids giving corresponding salts. This neutralization indicates basic nature of amines.

eg.



b) Reaction of amines with water : Amines react with water giving an equilibrium which contains OH^- ions. So aqueous solution of amines turns red litmus blue.

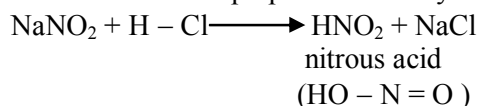


In the above reaction OH^- ions is a stronger base. It has greater affinity for H^+ ions. So above equilibrium is shifted in the backward direction i.e. towards left side. Due to this most of the amine molecule remain undissociated. So amines are weaker bases than NaOH or KOH.

Other chemical Properties :

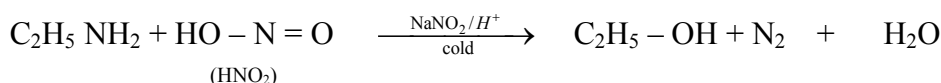
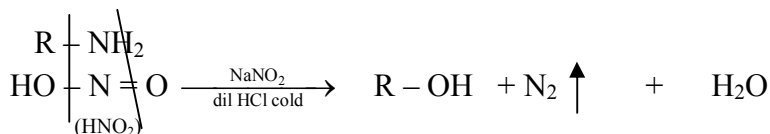
1) Reaction with nitrous acid (HNO₂)

Nitrous acid is prepared in situ by the action of dil HCl on either NaNO₂ or KNO₂.



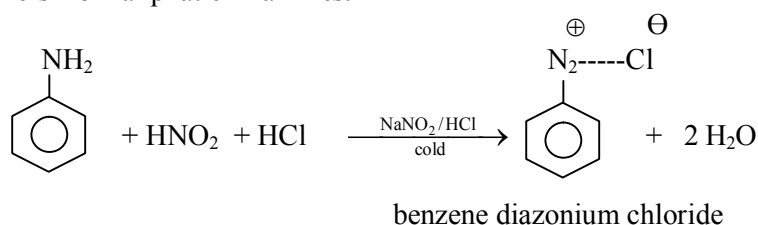
Nitrous acid react with amines in cold condition at about 273 to 278 K. The aliphatic & aromatic amines give different products on treatment with nitrous acid. Therefore it is a distinguishing reaction of them.

Aliphatic primary amine 1^o + HNO₂ A primary aliphatic amine react with nitrous acid giving corresponding alcohol with the evolution of nitrogen gas.



Aniline + HNO₂ :

Aromatic 1^o amine such as aniline reacts with nitrous acid giving benzene diazonium chloride. In this reaction aniline differs from aliphatic 1^o amines.

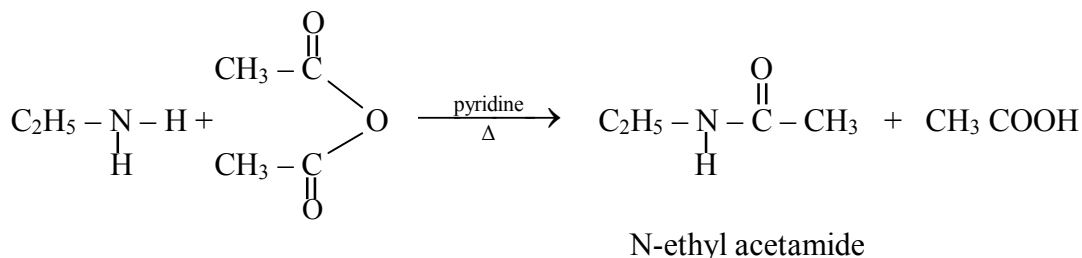
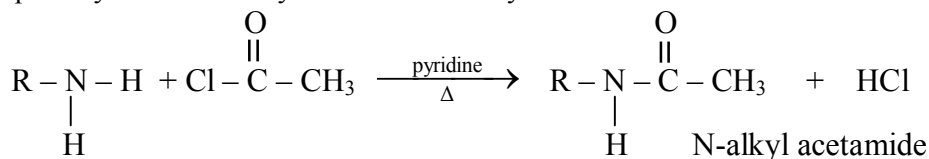


2) Acylation or Acetylation of Amines :

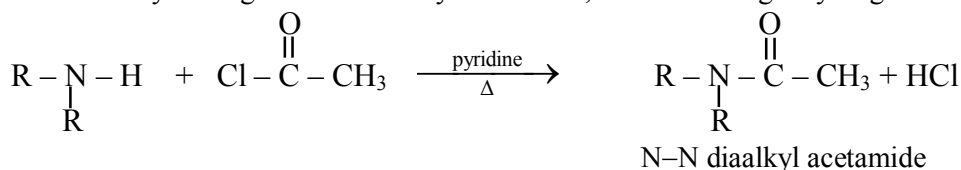
Acylation is a substitution reaction in which hydrogen atoms of amino group are replaced by acyl group (R - CO). The reaction is carried out in the presence of pyridine.

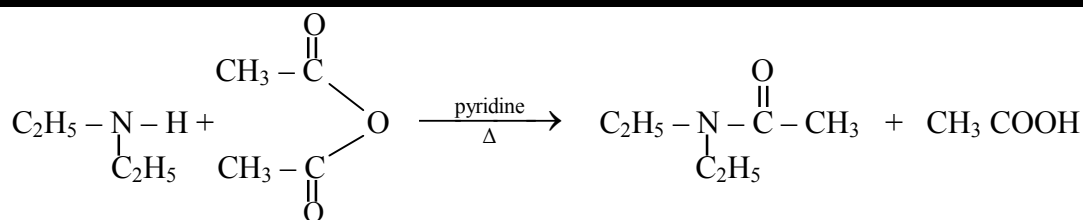
Acetylation is a type of acylation in which hydrogen atom of amino group is replaced by acetyl radical i.e. CH₃ - CO - only primary & secondary amines undergo acetylation by the action of either acetyl chloride or acetic anhydride in the presence of pyridine at high temperature, as they have replaceable H atom.

A primary amine on acetylation forms N alkyl acetamide.



2^o amine on acetylation give N-N diaalkyl acetamide, as there is single hydrogen in imino group.





N-N diethyl acetamide

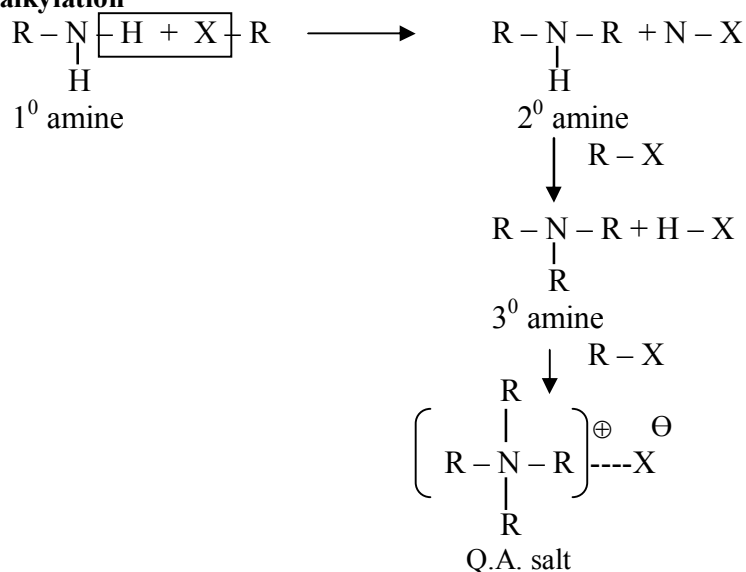
3⁰ amines do not undergo acetylation as there is no replaceable hydrogen.

3) Alkylation of Amines (Hoffmann's Exhaustive Alkylation) :

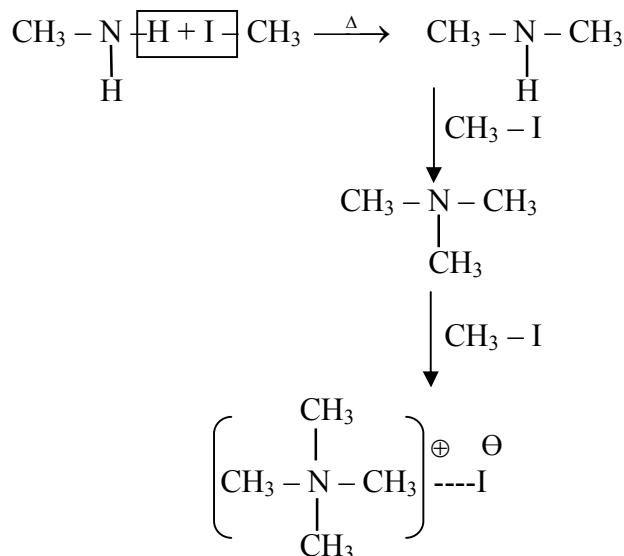
A substitution reaction in which hydrogen atoms of amino group are replaced by alkyl radicals is called alkylation. It is a nucleophilic substitution reaction. Alkylation is carried out by using alkyl halide.

When a primary amine is heated with large excess of alkyl halide stepwise alkylation occurs with the formation of a secondary amine then a tertiary amine and finally quaternary ammonium salt. If the alkyl halide is in very large excess, the reaction stops giving quaternary ammonium salts only. This is called **exhaustive alkylation**.

Ex. :- alkylation

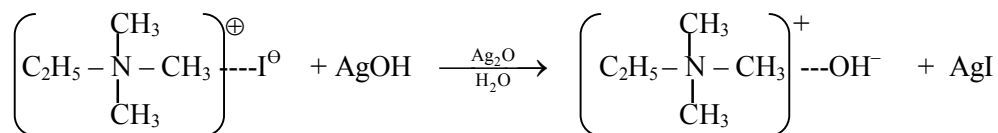


Ex :- Methylation



4) Hoffmann's Elimination:

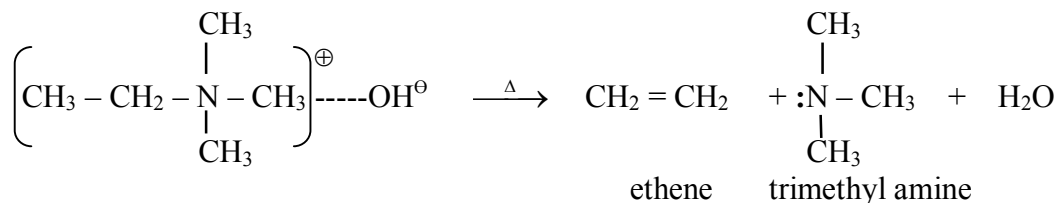
This reaction is shown by quaternary ammonium hydroxide. These hydroxides are strongly basic like NaOH and KOH, Q.A. hydroxides are obtained by hydrolyzing Q.A. salt by using moist silver oxide.



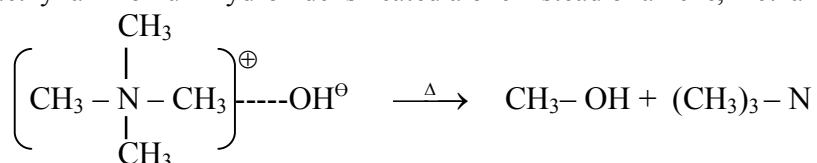
N ethyl NNN trimethyl ammonium iodide

N ethyl NNN trimethyl ammonium hydroxide

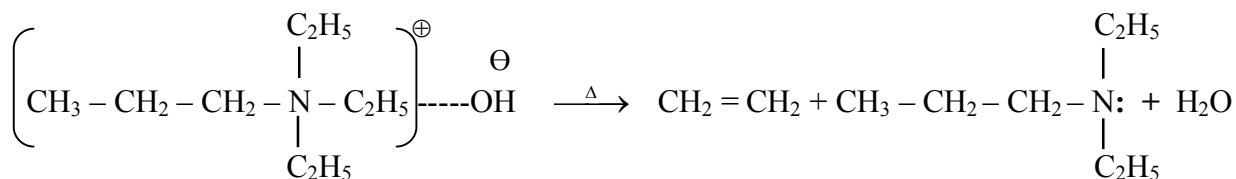
In the Hoffmann elimination, quaternary Ammonium hydroxide is heated alone. It undergoes β elimination producing an alkene and tert. amine.



If tetraethyl ammonium hydroxide is heated alone instead of alkene, methanol and 3^o amines are formed.



If different alkyl radicals are present then least substituted alkene is formed. (opposite to Saytzeff Rule)



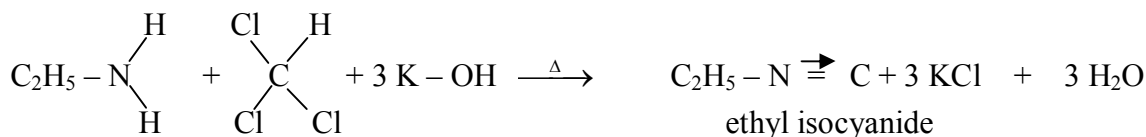
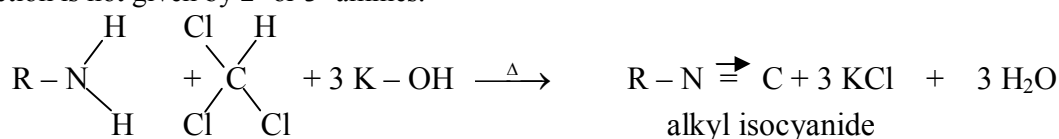
N propyl NNN triethyl ammonium hydroxide

ethene

N propyl NN diethyl amine

5) Hoffmann's Carbylamine Test:

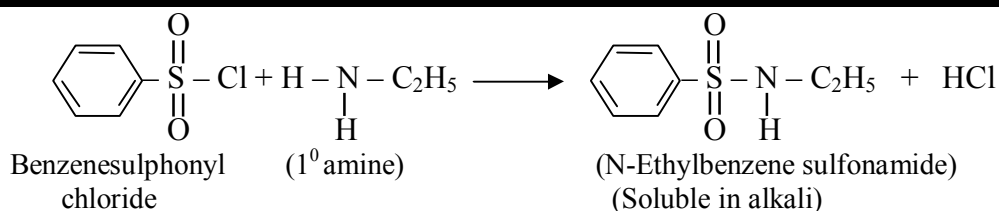
For 1^o amines only : This reaction is given by **aliphatic or aromatic 1^o amines only**. When a 1^o amine is heated with chloroform in the presence of alcoholic potash corresponding isocyanides or carbyl amines are formed. These compound have very foul or obnoxious smell. So the reaction is used as a laboratory test for 1^o amines. The reaction is not given by 2^o or 3^o amines.



6) Reaction with Benzene Sulphonyl chloride (C₆H₅SO₂Cl) Or arene Sulphonyl chloride (Hinsberg's test for 1^o, 2^o, 3^o amines)

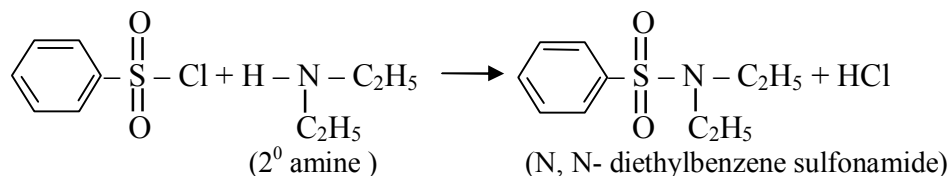
It is a distinguishing test of 1^o, 2^o, 3^o amines.

1^o amine : A 1^o amine reacts with aryl sulphonyl chloride forming N-alkyl benzene sulphonyl amide.



The H attached to Nitrogen is highly acidic, Therefore the amide dissolves in KOH giving clear solution when mineral acid is added to this clear solution, insoluble ppt. of sulphonyl amide is reformed.

2^o Amine: It reacts with aryl sulphonyl chloride giving N-N dialkyl benzene sulphonyl amide.



There is no acidic hydrogen in the product. Therefore this amide is insoluble in KOH as well as insoluble in acid.

3^o amines : The amines have no reaction with benzene sulphonyl chloride. So tertiary amines remain unreacted.

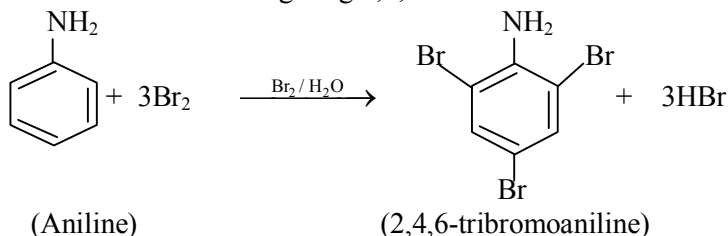
Electrophilic Substitution

In aniline amino group shows the properties of amine while benzene nucleus shows electrophilic substitution. So aromatic amines are bifunctional in nature.

The lone pair of electron in the amino group takes part in the resonance. So amino group is ortho, para directing.

1) Bromination of aniline :

Aniline reacts with bromine water giving 2,4,6 tribromoaniline.



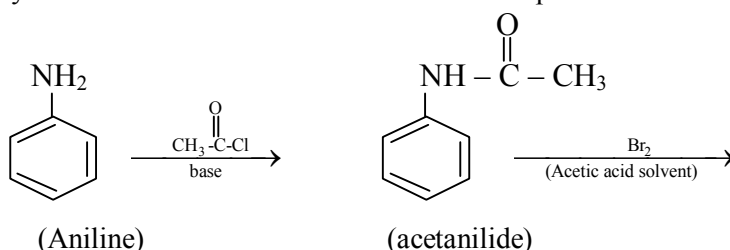
* Preparation of p-bromoaniline :

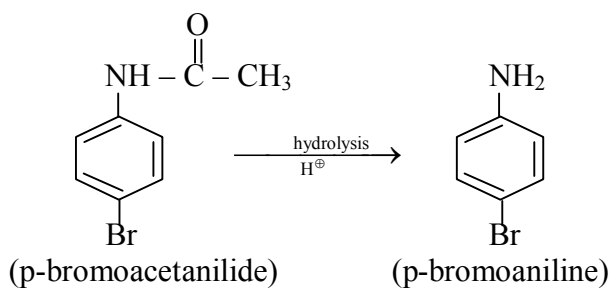
Amino group is highly activating. So monobromination does not occur.

For obtaining monobromo derivative NH₂ group is protected by acetylation.

The acetyl radical ($\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} -$) has -I effect so it decreases activating power of amino group.

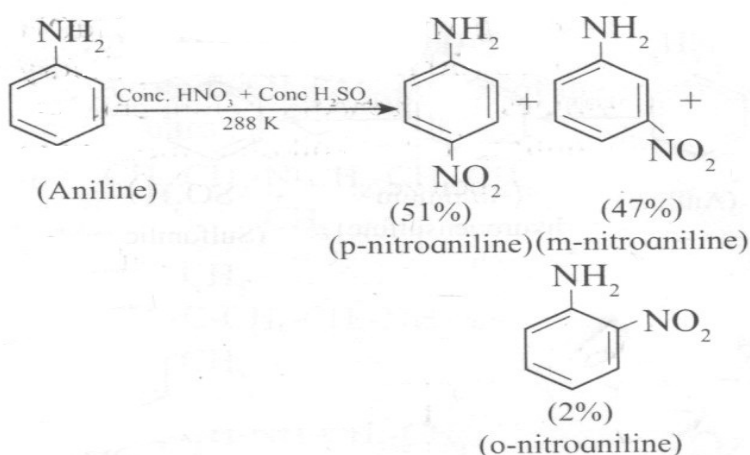
Aniline is treated with acetic anhydride in the presence of pyridine to get acetanilide or N-phenyl acetamide. It reacts with bromine in the presence of acetic acid as a solvent. Bromination occurs at para position. The product is hydrolysed in the acidic or basic medium to obtain para bromoaniline.





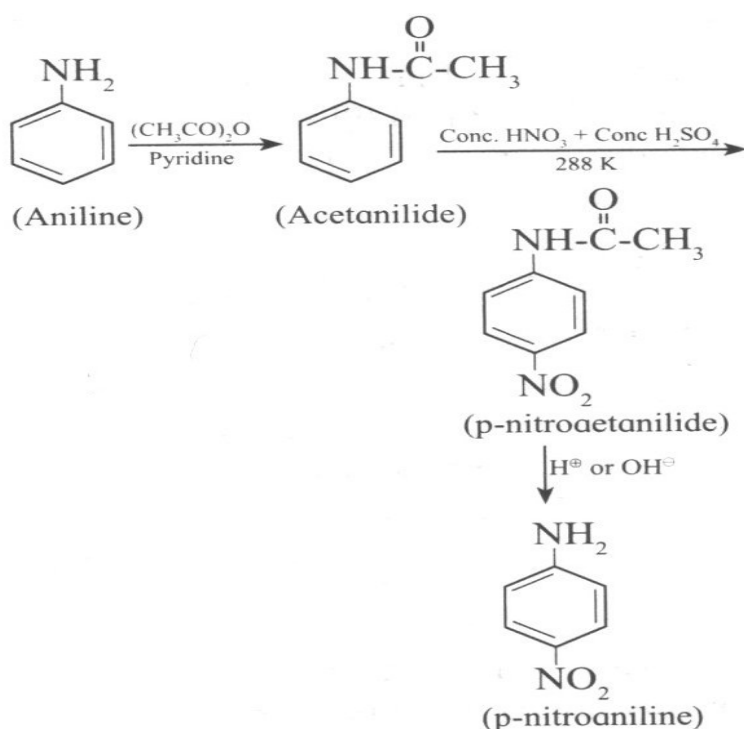
2) Nitration of Aniline :

Aniline directly reacts with nitrating mixture at 288 K giving a mixture of ortho, meta and para nitroaniline, along with black coloured tar (Oxidation product). (Some aniline molecules in the acidic medium converted into anilinium ion i.e, $\text{C}_6\text{H}_5 - \text{NH}_3^+$ where the functional group is deactivating so meta directing.



Preparation of p nitro aniline :

The amino group is first protected by acetylation. Then nitration is carried out by nitrating mixture at 288 k. Nitration occurs at para position. The product is hydrolysed to obtain p nitro aniline.



3) Sulphonation of aniline :

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Aniline reacts with cold conc. H_2SO_4 to obtain anilinium hydrogen sulphate. This salt is heated with conc. H_2SO_4 at 453 – 473 K. This gives p amino benzene sulphonic acid or sulphanilic acid.

Sulphanilic acid undergoes internal neutralization forming a salt which exist as zwitter ion.

