AMINES

INTRODUCTION

In this unit we shall focus our attention on the chemistry of organic compounds with functional groups containing nitrogen. The important functional groups in which nitrogen is present are

Cyanides	$-C\equiv N$
Iso cyanide	$-N\overset{\rightarrow}{\equiv}C$
Nitro Compounds	$-N\begin{matrix}=O\\ \searrow O\end{matrix}$
Nitrite	$-O-N=O$
Amines	$-NH_2$ (Primary)
	$-NH$ (Seconday)
	$-N$ (Tertiary)

Cyanides and isocyanides

Nomenclature

In IUPAC system of nomenclature, cyanides are called as alkanenitriles.

Methods of preparation

Form alkyl halides

When alkyl halide is treated with ethanolic solution of KCN, we get major product alkyl cyanide but when alkyl halide is treated with AgCN, the major product is alkyl isocyanide.

$$\underset{\text{alkyl halide}}{RX} + KCN\ (\text{alcoholic}) \longrightarrow RCN + KX$$

$$RX + AgCN\ (\text{alcoholic}) \longrightarrow RNC + AgX$$

Here CN^- is nucleophile. The cyanide ion has an unshared pair of electrons on both carbon and nitrogen.

$$:\overset{-}{C}\equiv N: \longleftrightarrow :\ddot{C}=\overset{-}{N}:$$

Molecular formula	Common name	IUPAC name
CH_3CN	methyl cyanide or acetonitrile	ethanenitrile
CH_3-CH_2-CN	ethylcyanide or propiononitrile	propane nitrile
$CH_2=CH-CN$	vinylcyanide acrylonitrile	2-propen nitrile
C_6H_5CN	phenyl cyanide or benzonitrile	benzonitrile
$CH_3-CH-CN$ | CH_3	isopropyl cyanide	2-methyl propane nitrile
$CH_3-CH-CH_2-CH_2-CN$ | Cl	---	4-chloropentanenitrile
$CH_3-CH-CH_2-CH_2-CN$ | OC_2H_5	---	4-ethoxy pentane nitrile
CH_3NC	acetoisonitrile	methyl isocyanide
CH_3-CH_2NC	propionoisonitrile	ethyl isocyanide

Here either carbon or nitrogen can act as a nucleophilic centre. Such a nucleophile which can react at two sites is known as an ambident nucleophile. NO_2^- is also an ambident nucleophile.

From acid amides

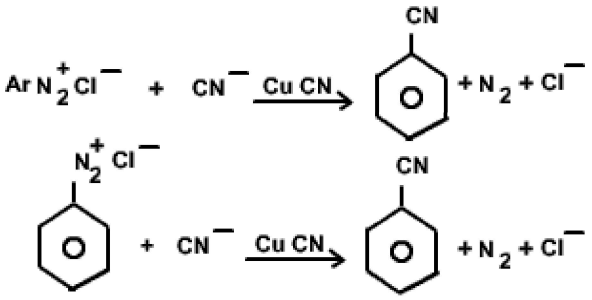
Alkyl and aryl cyanides are prepared by dehydration of acid amides with phosphorous pentaoxide (P_2O_5) or thionyl chloride ($SOCl_2$). In this method pure cyanide is prepared.

$$CH_3CO\ NH_2 \xrightarrow[-H_2O]{P_2O_5\text{ or }SOCl_2} CH_3CN$$

$$C_6H_5CONH_2 \xrightarrow[-H_2O]{P_2O_5\text{ or }SOCl_2} \underset{\text{Phenyl cyanide}}{C_6H_5CN}$$

From diazonium salt

Arenediazonium salt when reacted with a mixture of copper(1) cyanides and NaCN or KCN, lose nitrogen to give aryl cyanides



This method is a special case of Sandmeyer's reaction.

From aldoximes

Dehydration of aldoxmies with P_2O_5 or acetic anhydride gives cyanide

$$\underset{\text{acetaldoxlme}}{CH_3CH=NOH} \xrightarrow[\text{or }(CH_3CO)_2O]{P_2O_5} \underset{\text{Methyl cyanide}}{CH_3CN} + H_2O$$

$$\underset{\text{Benzaldoxime}}{C_6H_5CH=NOH} \xrightarrow[\text{or }(CH_3CO)_2O]{P_2O_5} \underset{\text{Phenyl cyanide}}{C_6H_5C\equiv N} + H_2O$$

From primary animes

Isocyanides are obtained when primary amines are treated with $CHCl_3$ in the persence of KOH.

$$\underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + CHCl_3 + 3KOH \rightarrow \underset{\text{Ethyl Isocyanide}}{CH_3CH_2NC} + 3KCl + 3H_2O$$

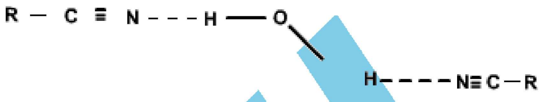
$$\underset{\text{aniline}}{C_6H_5NH_2} + CHCl_3 + 3KOH \rightarrow \underset{\text{Phenyl Isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

The above reaction is also called carbylamine reaction. This reaction is not given by secondary and tertiary amines.

Proparties of Cyanides and Isocyanides

Physical properties

The lower members of the family are colourless liquids and higher members are crystalline solid. Cyanides have generally pleasant odour but isocyanides have very disagreeable odour. Both - CN and - NC groups are highly polar. Both cyanides and isocyanides have high dipole moments resulting in strong intermolecular attraction and have relatively high boiling points. Alkyl cyanides have relatively high boiling point than the corresponding isomeric isocyanides. Alkyl cyanides are more soluble in water than alkyl isocyanides. The solubility of cyanides in water is due to their tendency to form hydrogen bonds with water molecules.



Chemical properties

Hydrolysis

Alkyl cyanides can be hydrolysed under acidic or basic condition to give amides. The further hydrolysis of amides give carboxylic acids and ammonia.

$$CH_3CN \xrightarrow[H_2O]{H_3O^+} CH_3CONH_2 \xrightarrow[H_2O]{HCl} CH_3COOH + NH_4Cl$$

$$CH_3CN \xrightarrow[H_2O]{OH^-} CH_3CONH_2 \xrightarrow[H_2O]{NaOH} CH_3COONa + NH_3$$

Isocyanides can be hydrolysed by dilute acids to form primary amines and formic acid.

$$CH_3NC \xrightarrow[H_2O]{H_3O^+} \underset{\text{Methylamine}}{CH_3NH_2} + \underset{\text{Formic acid}}{HCOOH}$$

Alkyl isocyanides are not hydrolysed by alkalies.

Reduction

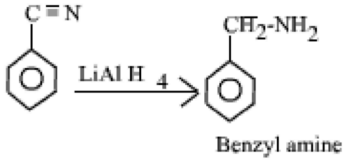
Nitriles undergo reduction to form primary amines as the product. We can use following reagents.

a) H_2 in the presence of Ni or Pt

b) $LiAlH_4$

c) Na + C_2H_5OH

$$CH_3CH_2CN \xrightarrow{LiAlH_4} \underset{\text{propanamine}}{CH_3\text{-}CH_2\text{-}CH_2\text{-}NH_2}$$



On the other hand isocyanides are reduced to secondry amines.

$$CH_3-NC + 2H_2 \xrightarrow{\text{Pt or Ni}} CH_3-NH-CH_3$$

Dimethyl amine.

$$C_6H_5NC + 2H_2 \xrightarrow{\text{Pt or Ni}} C_6H_5NH + CH_3$$

N - methyl aniline

Addition reaction

Isocyanides (but not cyanides) react with halogens, sulphur, mercuric oxide, ozone to give addition compounds.

$$CH_3NC + Cl_2 \longrightarrow CH_3-N=CCl_2$$

Methyl amino Carbonyl Chloride.

$$CH_3NC + S \longrightarrow CH_3N=C=S$$

Methyl Isothio cyanate

$$CH_3NC + 2HgO \longrightarrow CH_3N=C=O + Hg_2O$$

Methyl Isocyanate

$$CH_3-NC + O_3 \longrightarrow CH_3-N=C=O + O_2$$

Methyl Isocyanate.

Methyl Isocyanate gas (MIC) was responsible for the Bhopal gas tragedy.

Isomerism

Alkyl isocynides on heating for a long time rearrange to more stable alkyl cyanides.

$$R-NC \xrightarrow{\text{heat}} RCN$$

alkyl isocyanide alkyl cyanide

Uses

1) Ethane nitrile is used as a solvent in perfume industry.

2) Nitriles are also used in the manufacture of nitrile rubber and in textiles.

3) The alkyl nitriles or cyanides are useful intermediates in organic synthesis.

Nitro compounds

Nitro compounds are characterised by the presence of nitro group ($-NO_2$) in their molecules. They may be aliphatic or aromatic.

$R-NO_2$ $Ar-NO_2$

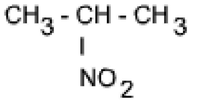
The $-O-N=O$ group is isomeric with nitro group and is known as a nitrite group.

Nomenclature

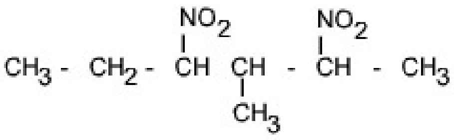
They are named by using the prefix nitro before the name of parent hydrocarbon.

CH_3NO_2 (Nitromethane)

$CH_3CH_2NO_2$ (Nitroethane)

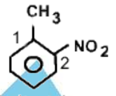


$CH_3-\underset{\displaystyle NO_2}{\underset{|}{CH}}-CH_3$ is 2 - nitropropane

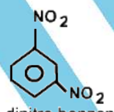


$CH_3-CH_2-\overset{\displaystyle NO_2}{\overset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle NO_2}{\overset{|}{CH}}-CH_3$

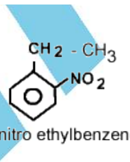
3 - methyl - 2,4 dinitrohexane



2 nitro toluene



1,3 dinitro benzene



2 nitro ethylbenzene

$CH_3-ON=O$

Methyl nitrite

Methods of preparation

Alkyl bromides and alkyl iodides react with silver nitrite and give nitro compounds.

$$C_2H_5I + \underset{\text{(alcoholic)}}{AgNO_2} \longrightarrow \underset{\text{Nitroethane}}{C_2H_5-NO_2} + AgI$$

But with $NaNO_2$ or KNO_2 it gives ethyl nitrite.

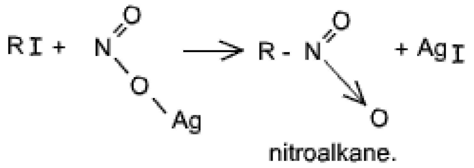
$$C_2H_5I + NaNO_2 \longrightarrow C_2H_5-O-N=O + NaI$$

$$C_2H_5I + KNO_2 \longrightarrow C_2H_5-O-N=O + KI$$

ethyl Nitrite

NO_2 is an ambident nucleophile (having two attacking sites N and O atoms). Attack through N gives nitroalkanes as product and attack through oxygen gives alkylnitrites. Alkali nitrites give alkyl nitrite. Due to ionic nature of alkali nitrites, the attack mostly occurs through oxygen because C-O bond is relatively stronger. In the case of silver nitrite which is covalent in nature, the attack mostly occurs through N atom giving nitro compound as major product.

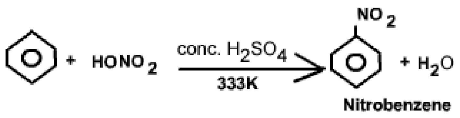
$$RI + [O=N-O]^{-}K^{+} \longrightarrow R-O-N=O + KI$$



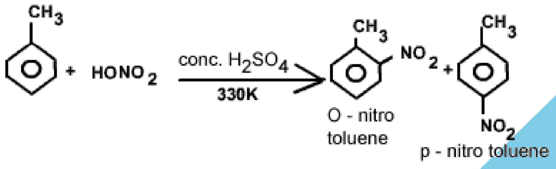
nitroalkane.

By direct nitration

Aromatic nitro compounds are obtained by this method. Nitrobenzene is produced when benzene is allowed to react with a mixture of conc. HNO_3 and conc. H_2SO_4

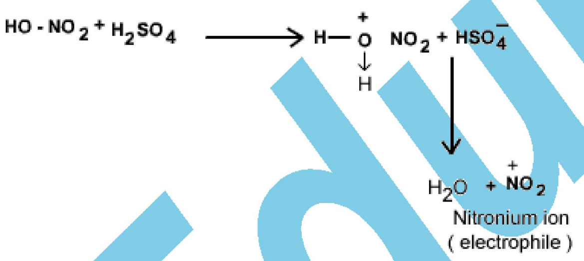


Nitrobenzene



O - nitro toluene p - nitro toluene

Mechanism of Nitration



Nitrobenzene

Direct nitration of alkanes is relatively more difficult in comparison to the nitration of arenes.

High temperature vapour phase reaction of alkanes with HNO_3 gives a mixture of nitroalkanes and products like CO_2, water and oxides of nitrogen.

$$CH_3-CH_3 + HNO_3 \xrightarrow{675K} CH_3-CH_2-NO_2 + CH_3NO_2 + \text{water} + CO_2 + \text{oxide of Nitrogen}$$

Properties

Physical properties

Lower nitroalkanes are colourless liquids with pleasant smell. Aromatic nitro compounds like nitrobenzene have pale yellow colour. Nitrobenzene has a smell of bitter almonds. Nitroalkanes are sparingly soluble in water. Aromatic nitro compounds are not soluble in water at all. Nitro compounds are polar in nature so molecular interaction is more and they have high boiling points as compared to hydrocarbons of comparable molecular masses. Nitroalkanes are relatively more polar than their corresponding alkyl nitrite.

$C_2H_5NO_2$ $C_2H_5-O-N=O$

b.p. = 388 K b.p. = 261 K

(nitro ethane) (ethyl nitrite)

Chemical properties

Reduction

Nitroalkanes can be reduced to corresponding primary amines with $LiALH_4$

$$CH_3CH_2NO_2 \xrightarrow[\text{Ether}]{LiAlH_4} CH_3-CH_2-NH_2$$

Ethyl amine

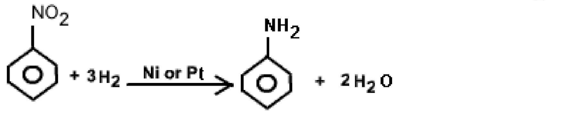
$$2C_6H_5NO_2 \xrightarrow[\text{Ether}]{LiAlH_4} C_6H_5-N=N-C_6H_5$$

Azobenzene

Catalytic reduction

Both aliphatic and aromatic nitro compounds are reduced to primary amines on reaction with H_2/Ni or H_2/Pt or H_2/Pd.

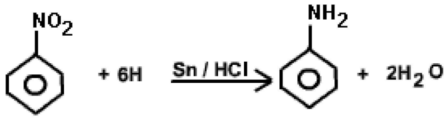
$$CH_3-CH_2-NO_2 + 3H_2 \xrightarrow{\text{Ni or Pt}} CH_3-CH_2-NH_2 + 2H_2O$$



Reduction in acidic medium

On reducing the nitro compounds with Zn/HCl, Fe/HCl or Sn/HCl, the NO_2 group reduced to primary amino group.

$$CH_3CH_2NO_2 + 6H \xrightarrow{\text{Fe/HCl}} CH_3-CH_2-NH_2 + 2H_20$$



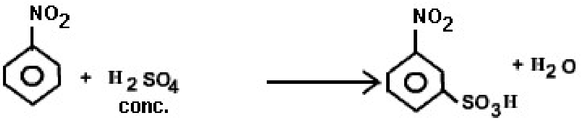
Nitration

By the nitration of nitrobenzene we get m-dinitrobenzene.

M-Dimutrobenzene

Sulphonation

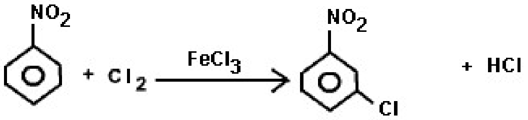
By sulphonation of nitrobenzene we get the following compound



m - nitro benzene sulphonic acid

Halogenation

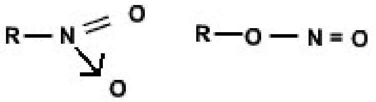
By the halogenation of nitrobenzene we get m-chloronitrobenzene.



m chloro nitrobenzene

Distinction between nitro alkanes and alkyl nitrites

Nitroalkanes and alkyl nitrite are functional isomers having the structural formula



They can be distinguished by the following test,

- Nitroalkanes on reduction with H_2/Ni, Sn/HCl, or $LiAlH_4$ give primary amines while nitrites give primary alcohols.

$$CH_3-CH_2-NO_2 + 6H \xrightarrow{Sn/HCl} CH_3-CH_2NH_2 + 2H_2O$$

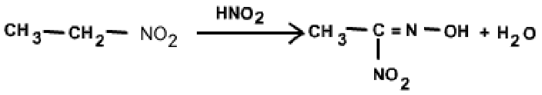
$$CH_3-CH_2-O-N=O + 6H \xrightarrow{Sn/HCl} CH_3CH_2OH + NH_3 + H_2O$$

- Alkyl nitrites on hydrolysis form alcohols while nitroalkanes do not get hydrolysed and form only salts.

$$C_2H_5O-N=O + NaOH \xrightarrow{hydholysis} C_2H_5OH + NaNO_2$$

$$CH_3-CH_2-NO_2 + NaOH \longrightarrow \text{Form salts.}$$

- Nitroalkanes (primary and secondry) react with HNO_2 give nitrolic acid which gives red colour with NaOH aqueous solution.



$$CH_3-CH_2-NO_2 \xrightarrow{HNO_2} CH_3-\underset{NO_2}{\underset{|}{C}}=N-OH + H_2O$$

Nitrolic acid

Ethyl nitrite does not give any color.

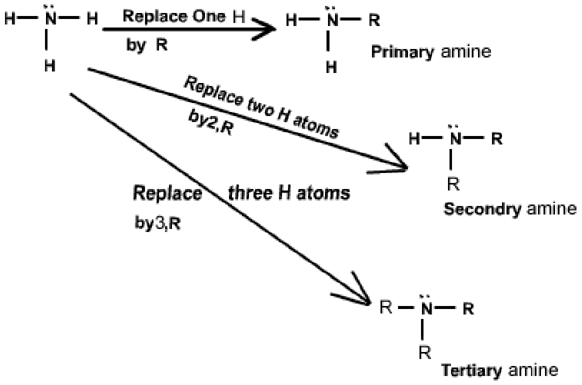
$$CH_3-CH_2-O-NO \xrightarrow[Na\,OH\,(aq)]{HNO_2} \text{No colouration}$$

Uses

- Lower nitroalkanes and nitrobenzene are widely used as industrial solvent for a large numbers of organic compounds.
- These are used as intermediates in the production of explosives, pharmaceuticals etc. 2,4,6, trinitrotoulene (T.N.T.) and 1,3,5, trinitrobenzene (T.N.B.) are popular explosives.
- Chloropicrin is used as insecticide
- Nitroalkanes are used in the manufacture of hydroxylamine

Amines

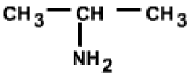
Amines may be regarded as the alkyl or aryl derivatives of ammonia. They can be classified into primary, secondry, or tertiary amines.



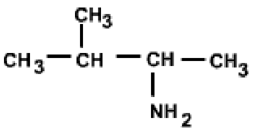
Nomenclature

According to IUPAC system primary amines are named as amino ($-NH_2$) derivatives of the corresponding hydrocarbon and are called aminoalkanes. The secondry and tertiary amines are named as nitrogen substituted primary amine.

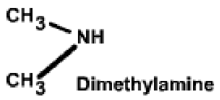
amino ethane



2 aminopropane



2 - methyl - 2 - aminobutane



IUPAC name N methyl aminomethane

Preparation of amines

When an aqueous or alcoholic solution of ammonia is heated with an alkyl halide at 373 K in a sealed tube, all the three types of amines are obtained. This type of reaction is called ammonolysis.

$CH_3I + NH_3 \longrightarrow CH_3NH_2 + HI$

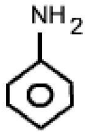
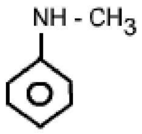
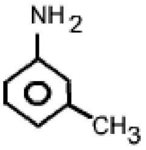
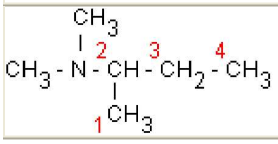
$CH_3NH_2 + CH_3I \longrightarrow CH_3\text{-}NH\text{-}CH_3 + HI$

$CH_3\text{-}\underset{\substack{|\\ CH_3}}{NH} + CH_3I \longrightarrow CH_3\text{-}\underset{\substack{|\\ CH_3}}{N}\text{-}CH_3 + HI$

Tertiary amine also combine with methyl iodide to form quaternary ammonium salts.

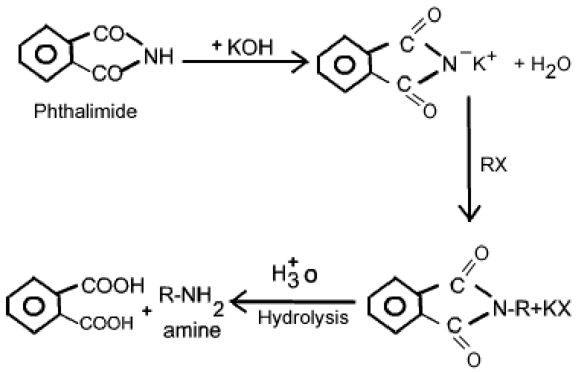
$(CH_3)_3N + CH_3I \longrightarrow [(CH_3)_4N]^+I^-$

This mehtod is not suitable for the preparation of ovylamines.

Amine formula	Common name	IUPAC name
$CH_3\ NH_2$	methylamine	aminomethane
$C_2H_5NH_2$	ethylamine	aminoethane
$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$	n propylamine	1 aminopropane
$CH_3\text{-}\underset{\substack{|\\ NH_2}}{CH}\text{-}CH_3$	isopropylamine	2-aminopropane
$CH_3\text{-}NH\text{-}CH_3$	dimethylamine	N-methylaminomethane
$CH_3\text{-}\underset{\substack{|\\ CH_3}}{N}\text{-}CH_3$	trimethylamine	N,N-dimethylaminomethane
$CH_3\text{-}\underset{\substack{|\\ CH_3}}{N}\text{-}C_2H_5$	ethyldimethylamine	N,N-dimethyl aminoethane
	aniline	benzenamine
	N-methylaniline	N-methylbenzenamine
	3-methylaniline	3-methylbenzenamine
 $CH_3\text{-}\underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{N}}\text{-}CH\text{-}CH_2\text{-}CH_3$	---	2-(N,N dimethylamino)butane

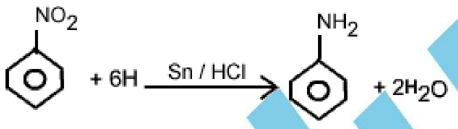
By Gabriel phthalimide synthesis

In this method, phthalimide is first converted into potassium phthalimide by reaction with KOH. The potassium phthalimide on treatment with alkyl halide gives N-alkyl phthalimide which on hydrolysis with 20% HCl gives pure primary amine.



By the reduction of nitro compounds

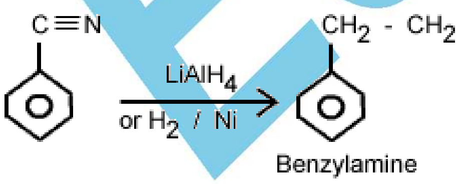
$$CH_3CH_2NO_2 + 6H \xrightarrow{Sn / HCl} C_2H_5NH_2 + 2H_2O$$



Reduction on nitriles and Isonitriles

Nitriles can be reduced to amines using H_2/Ni or Pt, $LiAlH_4$ or Na/C_2H_5OH

$$CH_3CN + 4H \xrightarrow{LiAlH_4} CH_3CH_2NH_2$$



The reduction of isocyanides under similar condition give secondry amines

$$CH_3-N\overset{\rightarrow}{\equiv}C + 4H \xrightarrow[\text{or LiAlH4}]{\text{Pt or Ni}} CH_3-NH-CH_3$$

From amides

$$CH_3CONH_2 + \xrightarrow[\text{ether}]{LiAlH_4} CH_3-CH_2-NH_2 + H_2O$$

Ethylamine

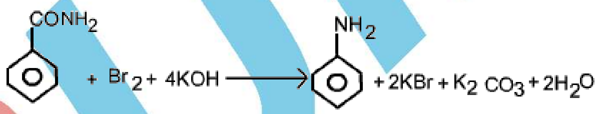
$$C_6H_5CONH_2 + \xrightarrow[\text{ether}]{LiAlH_4} C_6H_5CH_2NH_2$$

Benzylamine

From amides using Hofmann degradation method

By this method primary amide can be converted into primary amines.

$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

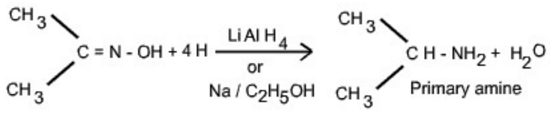


By the reduction of oximes

Primary amimes can be prepared by the reduction of oximes of aldehyde and ketones with Na/C_2H_5OH or $LiAlH_4$

$$CH_3-CH=N-OH + 4(H) \xrightarrow[\text{Na / }C_2H_5OH]{LiAlH_4 \text{ or}} CH_3-CH_2NH_2 + H_2O$$

acetald oxime　　Primary amine



$$(CH_3)_2C=N-OH + 4H \xrightarrow[\text{Na / }C_2H_5OH]{LiAlH_4 \text{ or}} (CH_3)_2CH-NH_2 + H_2O$$

From alcohols (industrial method)

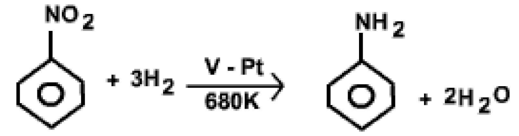
On industrial scale aliphatic amines are prepared by passing vapours of alcohols and ammonia over alumina at 273 k.

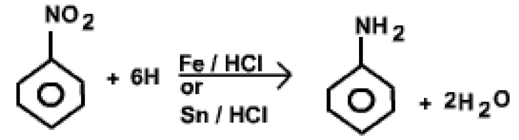
$$\begin{tikzcd} C_2H_5OH + NH_3 \arrow[r, "723K"', "Al_2O_3" below] & C_2H_5NH_2 \arrow[r, "C_2H_5OH", "Al_2O_3"'] & (C_2H_5)_2NH \arrow[d] \\ & \arrow[r, "C_2H_5OH", "Al_2O_3"'] & (C_2H_5)_3N \end{tikzcd}$$

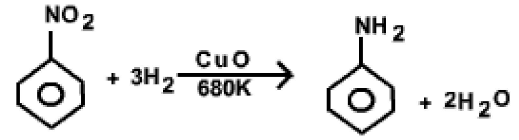
The mixture of three amines are separated by fractional distillation.

Preparatoin of aniline (industrial preparation)

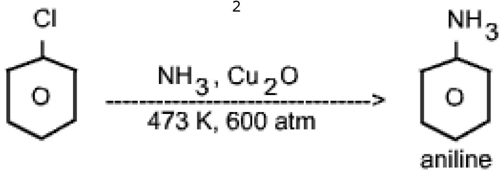
It is prepared by the following way







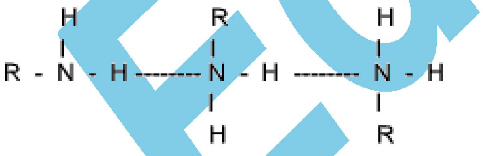
aniline is also prepared on large scale by treating chlorobenzene with ammonia at 473K and 60 atm. pressure using Cu_2O as catalyst.



Properites

Physical properties

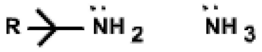
Among aliphatic amines the lower members are gases while higher members are liquids. Among oxylamines the lower members are liquids while higher members are solids. CH_3NH_2 and $C_2H_5NH_2$ have ammonical smell but higher amines have fishy smell. Most of the aromatic amines are colourless in pure form. Aromatic amines are generally toxic. All amines, except the tertiary amines are capable of forming intermolecular hydrogen bonds due to the presence of polar N-H bonds.



As a result of this, amines have higher boiling point than the non polar compounds of comparable molecular masses. Lower aliphatic amines are soluble in water. The higher one with larger alkyl groups are less soluble.

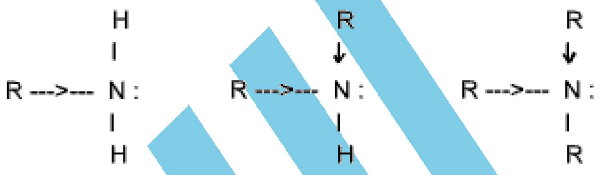
Chemical properties

Like ammonia, primary, secondry, tertiary amines all have a loan pair of electron on nitrogen atom. So they behave as a nucleophile and a base. Alkylamines are stronger base than ammonia because alkyl group is electron pumping group and they will increase the electron density on nitrogen.

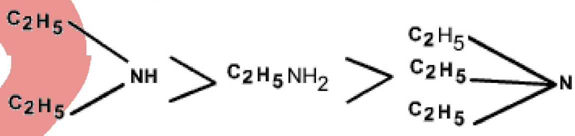


$C_6H_5NH_2$ will be less basic than ammonia because C_6H_5 group is electron attracting group and it will decrease the electron density on nitrogen. So $CH_3NH_2 > NH_3 > C_6H_5NH_2$

Basic strength of primary, secondry, tertiary amines



Among all the three amines the electron pumping effect (+I efect) is maximum in tertiary amines and least in primary amines. So on the basis of +I effect, the basic strength is expected to increase from primary amine to tertiary amine. This is true in gas phase. In aqueous medium, it is observed that basic character of secondry amine is maximum and tertiary amine have least basic character.



⟶ Basic character decreases

Explanation

Basic strength in aqueous solution depends not only upon electron releasing effect but also upon steric and hydration effect.

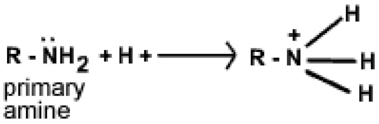
Steric effect

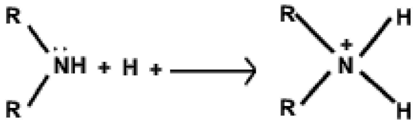
Steric means hinderance by bulky group. If more and more groups are there, then there will be more steric effect. Suppose proton is going to attack on nitrogen atom in a amine, hinderance will be maximum in tertiary amine and so it will be least basic. Thus on the basis of steric effect we can say basic strength of

Primary amine > Secondry amine > Tertiary amine or $1^\circ > 2^\circ > 3^\circ$

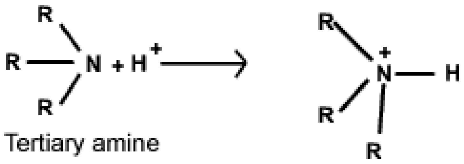
Hydration effect

uppose H^+ is attacking on amine, we get the following protonated amine



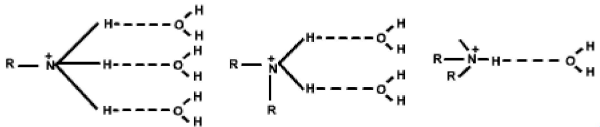


Secondry amine



Tertiary amine

The protonated amine forms hydrogen bond with water and release energy called hydration energy. Now greater the extent of H bonding, more will be its stabilisation and consequently greater will be the basic strength of the corresponding amine.



Protonated cation of 1° amine (maximum hydrocarbon)

Protonated cation of 2° amine (Less hydrocarbon)

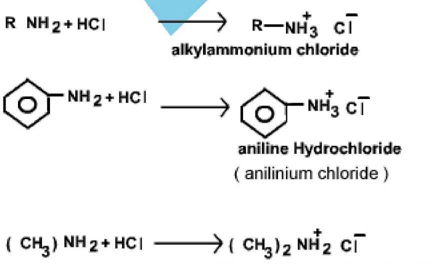
Protonated cation of 3° amine (Least hydrocarbon)

Hydration due to H bonding ------------------> Decreases ---------------->

Hydration energy is maximum in primary amine (1°) and it is minimum in tertiary amine (3°). On the basis of hydration energy basic strength should decrease from 1° > 2° > 3° Thus, we find that in 3° amine, hydration is least and steric hinderance is maximum thus it is least basic inspite of maximum +I effect. In 1° amine (primary amine) steric - hinderance is least and hydration is maxium but +I effect is also minimum. Hence its basic strength is more than 3° amine. The resultant of all factors cause 2° amine to be still more basic than 1° amine thus overall basic strength varies as 2° > 1° > 3° or Secondry amine is more basic > Primary amine > Tertiary amine

Reaction with acid

Amines dissolve readily in acids to form quaternary salts



alkylammonium chloride

aniline Hydrochloride

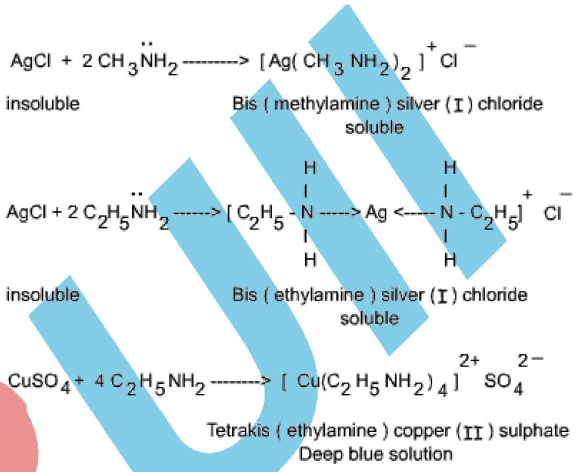
(anilinium chloride)

Dimethyl ammonium chloride

Salts of amines are ionic compounds. They are soluble in water. The amines, which are insoluble in water can be converted to the water soluble quaternary ammonium salts.

Reaction with metal ions

Lower aliphatic amines form co-ordination complexes with metal ions like Ag^+, Cu^{2+}. AgCl dissolves in methylamine solution.



$AgCl + 2CH_3\ddot{N}H_2 \dashrightarrow [Ag(CH_3NH_2)_2]^+Cl^-$

insoluble

Bis (methylamine) silver (I) chloride soluble

$AgCl + 2C_2H_5\ddot{N}H_2 \dashrightarrow [C_2H_5\text{-}NH_2 \rightarrow Ag \leftarrow NH_2\text{-}C_2H_5]^+ Cl^-$

insoluble

Bis (ethylamine) silver (I) chloride soluble

$CuSO_4 + 4C_2H_5NH_2 \dashrightarrow [Cu(C_2H_5NH_2)_4]^{2+} SO_4^{2-}$

Tetrakis (ethylamine) copper (II) sulphate Deep blue solution

Reaction with alkyl halides

Amines react with alkyl halides to form amines of higher class

$RNH_2 \xrightarrow[-HX]{+RX} R_2NH \xrightarrow[-HX]{+RX} R_3N \xrightarrow{+RX} R_4N^+X^-$ tetra alkyl] ammonium halide

$C_2H_5NH_2 + C_2H_5I \longrightarrow (C_2H_5)_2NH + HI$

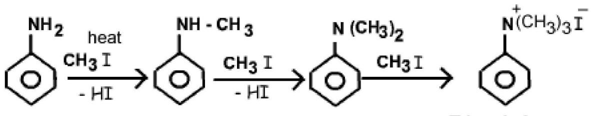
N-ethylamino ethane

$(C_2H_5)_2NH + C_2H_5I \longrightarrow (C_2H_5)_3N + HI$

N,N-diethyl aminoethane

$(C_2H_5)_3N + C_2H_5I \longrightarrow (C_2H_5)_4N^+I^-$

tetra ethylammonium iodide



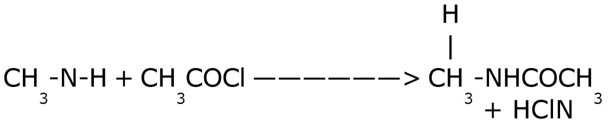
N - methylaniline

N,N dimethyl aniline

Trimethyl anilinium Iodide

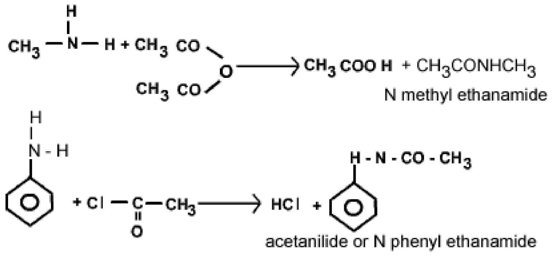
Reactron with acid chlorides and acid anhydrides

Primary and secondry amines react with acid chlorides or acid anhydrides to form substituted amides.



$CH_3\text{-}\overset{H}{\underset{|}{N}}\text{-}H + CH_3COCl \longrightarrow CH_3\text{-NHCOCH}_3 + HClN$

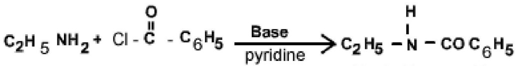
methylethaneamide



Tertiary amines do not undergo this reaction (acylation) because they do not have H atom on the nitrogen.

Benzoylation

When H atom of amino group by benzoyl group (C_6H_5-CO) it is called benzoylation. Primary and secondry amines react with benzoyl chloride (C_6H_5COCl) in the presence of a base like pyridine to form benzoyl derivative.



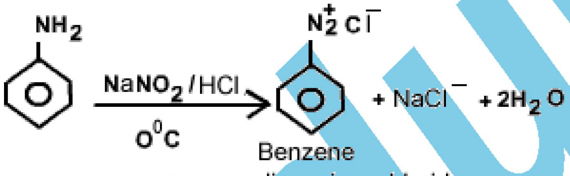
$$C_2H_5NH_2 + Cl-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow[\text{pyridine}]{\text{Base}} C_2H_5-\overset{H}{\overset{|}{N}}-COC_6H_5$$

N ethyl benzamide

Tertiary amines do not give this test.

Reaction with HNO_2

Primary aromatic amines react with HNO_2 at low temperature (0°C) to give aromatic diazonium salts. This reaction is known as diazotisation



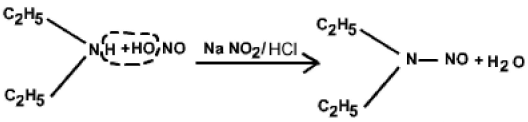
Benzene diazonium chloride

Primary aliphatic amines give alcohol

$$C_2H_5NH_2 + HNO_2 \xrightarrow{NaNO_2/HCl} C_2H_5OH + N_2 + H_2O$$

Secondary aliphatic and aromatic amines react with HNO_2 to produce nitroso amines that are insoluble in the aqueous solution and comes out as a yellow oil and forms a separate layer.

N nitroso N methyl aniline



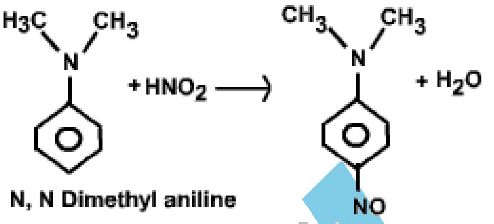
N nitroso diethylamine

Reaction with tertiary aliphatic amines

$$(C_2H_5)_3N + HNO_2 \longrightarrow [(C_2H_5)_3NH]^+NO_2^-$$

triethly ammonium nitrite

Reaction with tertiary aromatic amines

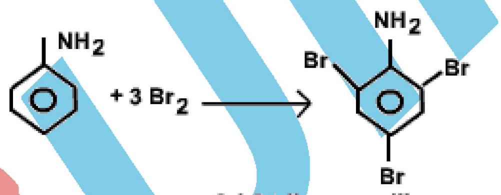


N, N Dimethyl aniline

P nitroso N,N dimethylaniline

Bromination of aniline

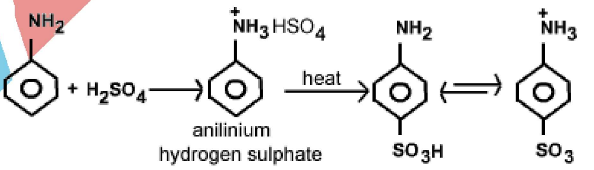
We get 2,4,6, tribromo aniline



2,4,6 tribromoaniline

Sulphonation of aniline

Aniline reacts with H_2SO_4 (conc.) and forms anilinium hydrogen sulphate, which on heating gives p aminobenzene sulphonic acid which is also called sulphanilic acid.



anilinium hydrogen sulphate

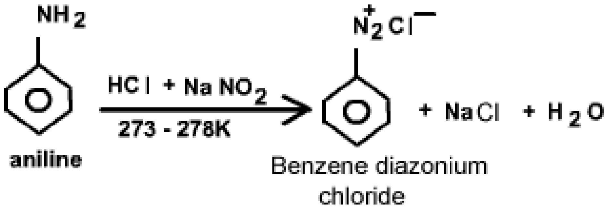
P - amino benzene sulphonic acid (sulphanilic acid)

Zwitter ion structure

Sulphanilic acid exists as zwitter ion ie a dipolar ion which exists in the form of internal salt structure.

Diazonium salts and their reactions

The diazonium salts are represented by $ArN_2^+X^-$. They are prepared as under



Benzene diazonium chloride

EduBull

The above reaction is known as diazotisation. Aromatic diazonium salts undergo a large numbers of reactions. The reaction of arenediazonium salts can be divided into two categories.

(a) Substitution reaction

(b) Coupling reaction

Substitution reaction

$$ArN_2^+Cl^- \xrightarrow{CuCl/HCl} ArCl + N_2$$

$$ArN_2^+Cl^- \xrightarrow{CuBr/HBr} ArBr + N_2 + Cl^-$$

$$ArN_2^+Cl^- \xrightarrow{CuCN/KCN} ArCN + N_2 + Cl^-$$

The above reactions are Sandmeyer's reactions

$$ArN_2^+Cl^- \xrightarrow{Cu/HCl} ArCl + N_2$$

$$ArN_2^+Cl^- \xrightarrow{Cu/HBr]} ArBr + N_2 + Cl^-$$

The above reactions are Gattermann reaction

$$ArN_2^+Cl^- + KI \xrightarrow{Warm} ArI + N_2 + KCl$$

$$ArN_2^+Cl^- \xrightarrow{HBF_4} \underset{\text{(flouroboric acid)}}{ArN_2^+BF_4^-} \xrightarrow{-Heat} ArF + N_2 + BF_3$$

$$ArN_2^+Cl^- + H_2O \xrightarrow{Warm(H^+)} ArOH + N_2 + HCl$$

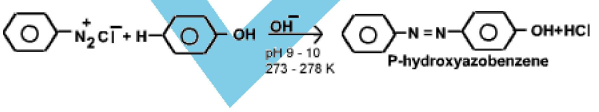
$$ArN_2^+Cl^- + H_3PO_2 + HOH \longrightarrow ArH + N_2 + H_3PO_3 + HCl$$

hypophosphorus acid arene

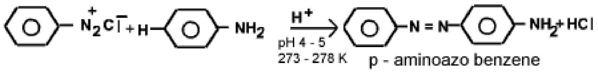
Coupling reaction

Diazonium salts react with highly activated aromatic compounds such as phenols and amines to form azo compounds. Azo compounds are coloured and many of them are used as dyes and indicator.

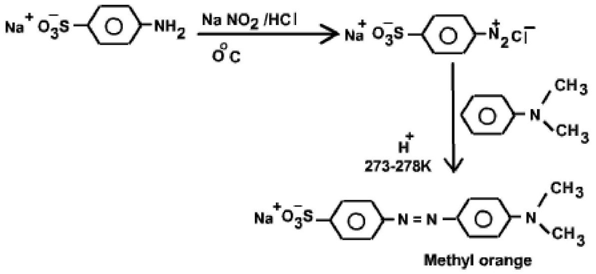
Reaction with phenols



Reaction with aniline



The indicator methyl orange is obtained by coupling the diazonium salt of sulphanilic acid with N, N-dimethylaniline

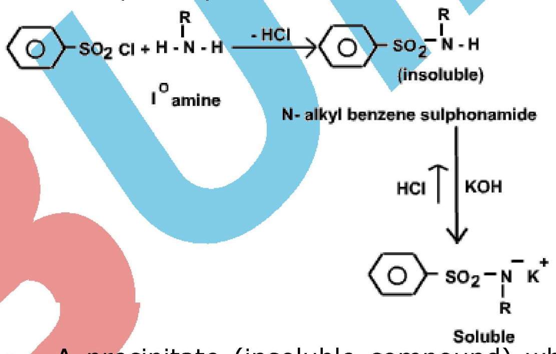


Analysis of amines

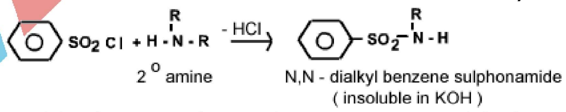
Hinsberg's test

This test helps to distinguish between primary, secondry and tertiary amines. The given amine is treated with benzene sulphonyl chloride in the presence of excess of aqueous KOH.

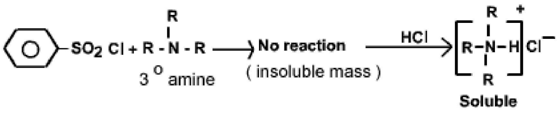
- A clear solution in aqueous KOH which on acidification with HCl gives an insoluble material indicates primary amines.



- A precipitate (insoluble compound) which is insoluble in KOH solution indicates secondry amine.



- Tertiary amines do not react with benzene sulphonyl chloride. An insoluble compound in KOH solution which dissolves by the addition of acid indicates tertiary amine.



Carbylamine test

From this test we can identify primary amine (aliphatic as well as aromatic). In this test compound is warmed with $CHCl_3$ (chloroform) in the presence of alcoholic solution of KOH. The primary amines yield isocyanides which have an extremely unpleasant smell.

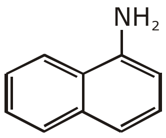
$$RNH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{alkyl isocyanide}}{RNC} + 3KCl + 3H_2O$$

$$ArNH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{aryl isocyanide}}{ArNC} + 3KCl + 3H_2O$$

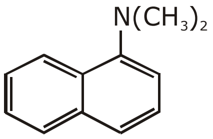
SOLVED PROBLEMS

Q.1 Classify the following amines as primary, secondary and tertiary :

(a)



(b)



(c) $(C_2H_5)_2$ CHNH$_2$ **(d) $(C_2H_5)_2$NH**

Ans. (a) parimary (b) Tertiary

(c) Primary (d) Secondary

Q.2 (a) Write structures of different isomeric amines corresponding to the molecular formula, C_4H_{11}N.

(b) Write IUPAC names of all the isomers.

(c) What type of ismerism is exhibited by different pairs of amines ?

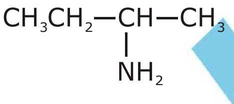
Ans. (a and b)

Primary amines :

(i) $CH_3CH_2CH_2CH_2NH_2$

Butanamine

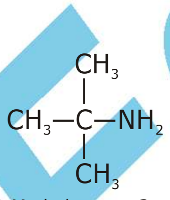
(ii)



$$CH_3CH_2-\underset{\underset{NH_2}{|}}{CH}-CH_3$$

Butan-2-amine

(iii)



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-NH_2$$

2-Methylpropan-2-amine

(iv)

$$\overset{3}{CH_3}-\overset{\overset{CH_3}{2|}}{CH}-\overset{1}{CH_2}-NH_2$$

2-Methylpropanamine

Secondary amines :

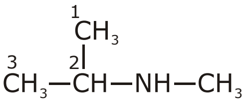
(v) $CH_3-CH_2-NH-CH_2CH_3$

N-Ethylethanamine

(vi) $CH_3CH_2CH_2-NH-CH_3$

N-Methylpropanamine

(vii)

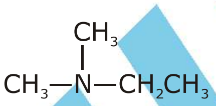


$$\overset{3}{CH_3}-\overset{\overset{\overset{1}{CH_3}}{2|}}{CH}-NH-CH_3$$

N-Methylpropan-2-amine

Tertiary amine :

(viii)



$$CH_3-\overset{\overset{CH_3}{|}}{N}-CH_2CH_3$$

N, N-Dimethylethanamine

(c) Chain isomers :

(i) & (iv), (ii) & (iii), (i) & (iii)

Position isomers : (i) & (ii), (vi) & (vii)

Metamers : (v) & (vi)

Functional isomers : All primary amines are functional isomers of secondary and tertiary amines and vice versa.

Q.3 Give one chemical test to distinguish between the following pairs of compounds

(i) Methylamine and dimethylamine

(ii) Secondary and tertiary amines

(iii) Ethylamine and aniline

Ans. (i) These can be distinguished by the carbylamine test. Methylamine is 1° amine, therefore, it gives carbylamine test, i.e., when heated with an alcholic solutoin of KOH and $CHCl_3$, it gives an offensive smell of methyl carbylamine. In contrast, diethylamine is a secondary amine and hence does not give this test.

$$\underset{\substack{\text{Methylamine}\\ (1^\circ \text{ Amine})}}{CH_3NH_2} + CHCl_3 + \underset{(\text{alc})}{3KOH} \xrightarrow{\text{Heat}} \underset{\substack{\text{Methyl carbylamine}\\ (\text{offensive smell})}}{CH_3NC}$$

$$+ 3KCl + 3H_2O$$

$$\underset{\substack{\text{Diethylamine}\\ (2^\circ \text{ Amin})}}{(CH_3CH_2)_2\ NH} \xrightarrow[\text{Heat}]{CHCl_3/KOH(alc)} \text{NO reaction.}$$

(ii) These can be distinguished by Liebermann nitroamine test since secondary amines give Liebermann nitroamine test while tertiary amines do not.

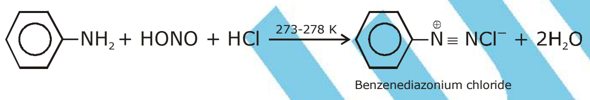
Secondry Amines on treatment with HNO_2 (generated in situ by the action of HCl on $NaNO_2$) gives yellow coloured oily N-nitrosoamine. For example.

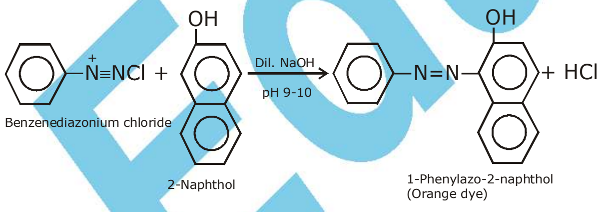
$$\underset{\text{Diethy lamine}}{(CH_3CH_2)_2\,NH} + HO{-}N{=}O \longrightarrow \underset{\substack{\text{N-Nitrodiethylamine}\\ \text{(Yellow colour)}}}{(CH_3CH_2)_2\,N{-}N{=}O} + H_2O$$

N-Nitrosodiethylamine on warming with a crystal of phenol and conc. H_2SO_4, gives a great solution which when made alkaline with aqueous NaOH turns deep blue and then red on dilution. Tertiary amines do not give this test.

(iii) Ethylamine is primary aliphatic amine while alinine is a primary aromatic amine. These may be distinguished by the azo dye test :

Azo dye test : It involves the reaction of any aromatic primary amine with HNO_2 ($NaNO_2$+dil. HCl) at 273–278 K followed by treatment with an alkaline solution of 2-naphthol (β-naphthol) when a brilliant yellow, orange or red coloured dye is obtained.





Aliphatic primary amines under these conditions gives a brisk evolutoin of N_2 gas with the formation of primary alcohols, i.e., the solution remains clear.

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + HONO \xrightarrow{273\text{-}278\ K} \underset{\text{Ethyl alcohol}}{C_2H_5OH} + N_2\uparrow + H_2O$$

These may be distinguished by the following test.

Q.4 Account for the following :

(i) pK_b of aniline is more than that of methylamine.

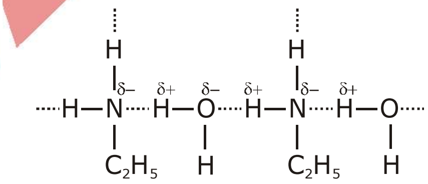
(ii) Ethylamine is soluble in water, whereas aniline is not.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

(iv) Although amino group is o- and p-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

Ans. (i) In aniline, the lone pair of electrons on the N-atom are delocalized over the benzene ring. Resulting, electron density on the nitrogen decreases. On the other hand, in CH_3CH_2. +ve-I-effect of CH_3 increases the electron density on the N-atom. Thus, aniline is a weaker base than methylamine and hence its pK_b value is higher than that of methylamine.

(ii) Ethylamine dissolves in water because it forms H-bonds with water molecule as shown below.



In aniline, due to the large, hydrocarbon part, the extent of H-bonding decreases considerably and hence aniline is insoluble in water.

(iii) Methylamine being more basic than water, accepts a proton from water liberating OH^- ions.

$$CH_3\ddot{N}H_2 + H{-}OH \longrightarrow CH_3{-}\overset{+}{N}H_3 + OH^-$$

These OH^- ions combine with Fe^{3+} ions present in H_2O to form brown precipitate of hydrated ferric oxide.

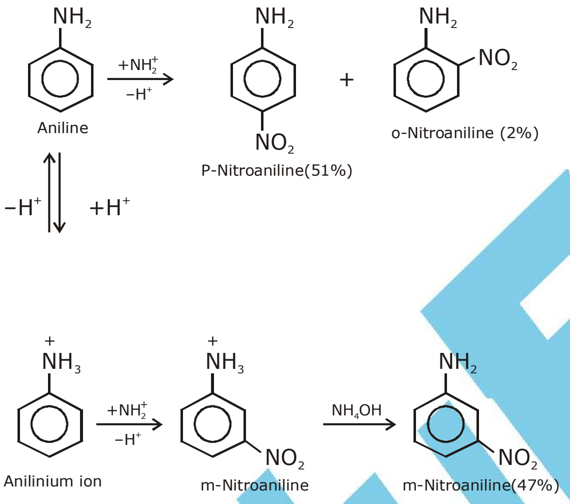
$$FeCl_3 \rightarrow Fe^{3+} + 3Cl^-$$

$$2Fe^{3+} + 6OH^- \rightarrow 2Fe(OH)_3 \text{ or } \underset{\substack{\text{Hydrated ferric oxide}\\ \text{(Brown ppt.)}}}{Fe_2O_3.\,3H_2O}$$

(iv) Nitration is usually carried out with a mixture of conc. HNO_3 and conc. H_2SO_4.

In presence of these acids, most of aniline gets protonated to form anilinium ion. Thus, in presence of acids, the reaction mixture consists of aniline and anilinium ion. Now —NH_2 group in aniline is o, p-directing and activating while the $\overset{+}{N}H_3$ group in anilinium ion is m-directing and deactivating.

On the other hand, nitration of aniline mainly gives p-nitroaniline, the nitration of anilinium ion gives m-nitroaniline.



Thus, nitration of aniline gives a substantial amount of m-nitroaniline due to protonation of the amino group.

Q.5 **Give plausible explanation for each of the following :**

(i) Why are amines less acidic than alcohols of comparable molecular masses ?

(ii) Why are aliphatic amines stronger bases than aromatic amines ?

Ans. (i) Loss of a proton from an amine gives amide ion while loss of a proton from alcohol gives an alkoxide ion as shown below :

$$\underset{\text{Amine}}{R - NH_2} \rightarrow \underset{\text{Amide ion}}{R - NH^{\ominus}} + H^+$$

$$R - O - H \rightarrow R - O^{\ominus} + H^+$$

As O is more electronegative than N, RO^- can accommodate the -ve charge more easily than the $RNH^{\ominus}$ can accommodate the -ve charge. As, $RO^{\ominus}$ is more stable than $RNH^{\ominus}$. Therefore, amines are less acidic than alcohols.

(ii) Aliphatic amines are stronger bases than aromatic amines because :

(a) due to resonance in aromatic amines, the lone pair of electrons on the nitrogen atom gets delocalised over the benzene ring and thus is less easily available for protonation.

(b) The aryl amine ions have lower stability than the corresponding aryl amines. i.e., protonation of aromatic amines is not fovoured.

Q.6 **Mention two important uses of sulphanilic acid.**

Ans. Sulphanilic acid is used in the manufacture of (i) dyes (ii) sulpha drugs.

Q.7 **Aniline gets coloured on standing in air for a long time. Why ?**

Ans. Due to strong electron-donating effect (+R-effect) of NH_2 group, the electron density on the benzene ring increases. As a result, aniline is easily oxidised on standing in air for a long time to form coloured products.

EXERCISE - I UNSOLVED PROBLEMS

Q.1 Direct nitration of aniline is not carried out. Explain why.

Q.2 How can you control the reactivity of aniline in electrophilic substitution reaction ?

Q.3 Arrange the following in decreasing order of their basic strength :
$C_6H_5NH_2$, $C_2H_5NH_2$, $(C_2H_5)_2NH$, NH_3

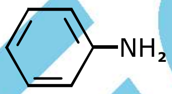
Q.4 Out of n-butylamine (K_b = 4.8) and isobutyl amine (K_b = 3) in aqueous medium, isbutylamine is more basic why ?

Q.5 Basic character of isobutylamine (K_b = 3), sec--butylamine (K_b = 4) and tert-butylamine (K_b = 5) in aqueous medium is in the order tert-Butylamine < sec-Butylamine < Isobutylamines. Why ?

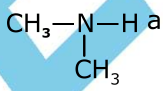
Q.6 Predict, giving reasons, the order of basicity of the following compound in (i) gaseous phase (ii) in aqueous solutions ;
$(CH_3)_3N$, $(CH_3)_2NH$, CH_3NH_2, NH_3

Q.7 Account for the following :
(a) Aniline does not undergo Friedel Crafts alkynation.
(b) Although $—NH_2$ group is ortho and paradirecting group nitration of aniline give along with ortho and para derivative, a good proportion of meta derivative also.

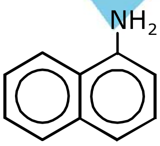
Q.8 How will you distinguish between

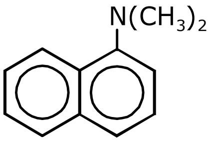
(a) 

and CH_3NH_2,

(b) 
$CH_3—\underset{\displaystyle CH_3}{\underset{|}{N}}—H$
and $(CH_3)_3N$.

Q.9 Classify the following amines as primary secondary or tertiary.

(i) 

(ii) 

(iii) $(C_2H_5)_2CHNH_2$ (iv) $(C_2H_5)_2NH$.

Q.10 (i) Write structures of different isomeric amines corresponding to the molecular formula $C_4H_{11}N$.
(ii) Write IUPAC names of all the isomers.
(iii) What type of isomerism is exhibited by different pairs of amines ?

Q.11 How will you convert
(i) Benzene into aniline
(ii) Benzene into N, N-dimethylaniline
(iii) $Cl—[CH_2]_4—Cl$ into hexane-1, 6-diamine.

Q.12 Write reactions of the final alkynation product of aniline with excess of methyl iodide in the presence of sodium carbonate solution.

Q.13 Write chemical reaction of aniline with benzoyl chloride and write the name of the product obtained.

Q.14 Write structures of different isomers corresponding to the molecular formula C_3H_9N. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

Q.15 Give on chemical test to distinguish between the following pairs of compounds.
(i) Methylamineand dimethylamine
(ii) Secondary and tertiary amines
(iii) Ethylamine and aniline
(iv) Aniline and benzylamine
(v) Aniline and N-methylaniline.

Q.16 How will you convert :
(i) Ethanoic acid into methenamine,
(ii) Hexanenitrile into 1-aminopentane,
(iii) Methanol to ethanoic acid,
(iv) Ethanamine into methanamine,
(v) Ethanoic acid into propanoic acid,
(vi) Methanamine into ethanamine
(vii) Nitromethane into dimethylamine.
(viii) Propanoic acid into ethanoic acid,

Q.17 Describe a method for the identification of primary secondary and tertiary amines. Also write chemical equations of the reactions involved.

Q.18 Write the IUPAC name of $C_6H_5NHCH_3$

EXERCISE - II OLYMPIAD PROBLEMS

Q.1 Why do animes behave as nucleophiles ?

Q.2 Why is an alkylamine more basic than ammonia

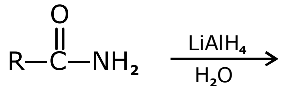
Q.3 Arrange the following compounds in an increasing order of basic strengths in their aqueous solutions.

NH_3, $CHNH_2$, $(CH_3)_2NH$, $(CH_3)_3N$

Q.4 Arrange the following compound in an increasing order of their basic strength in aqueous solutions.

NH_3, RNH_2, R_2NH, R_3N

Q.5 Complete the following reaction equations :

(i) 

$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[H_2O]{LiAlH_4}$

(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(iii) $C_6H_5NH_2 + Br_2(aq) \longrightarrow$

Q.6 How are the following conversions carried out

(i) Aniline to nitrobenzene

(ii) Ethanamine to N-ethylethanamide

(iii) Chloroethane to propan-1-amine

Q.7 In the following cases rearrange the compound as directed :

(i) In an increasing order of basic strength : $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(ii) In a decreasing order of basic strength : Aniline, p-nitroaniline and p-toluidine

(iii) In an increasing order of pK_b values : $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $CH_6H_5NH_2$

Q.8 Give chemical test to distinguish between $C_6H_5CH_2NH_2$ and $C_6H_5NH_2$.

Q.9 Illustrate the following reactions giving a chemical equation in each case :

(i) Gabriel phthanlimide synthesis

(ii) A coupling reaction

(iii) Hoffmann's bromamide reaction.

Q.10 (a) Explain why an alkylamine is more basic than ammonia.

(b) How would you convert

(i) Aniline to nitrobenzene

(ii) Aniline to iodobenzene ?

Q.11 Arrange the following compound in an increasing order of their solubility in water.

$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

Q.12 Rearrange the following in an increasing order of their basic strengths :

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_6H_5)_2NH$ and CH_3NH_2

Q.13 Why is an alkylamine more basic than ammonia

Q.14 State reasons for the following :

(i) pK_b value for aniline is more than that for methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not soluble in water.

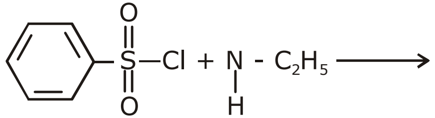
(iii) Primay amines have higher boiling points than tertiary amines.

Q.15 A hydrocarbon 'A', (C_4H_8) on reaction with HCl gives a compound 'B', (C_4H_9Cl), which on reaction with 1 mol of NH_8 gives compound 'C', $(C_4H_{11}N)$. On reacting with $NaNO_2$ and HCl followed by treatment with water, compound 'C' yields as optically active alcohol, 'D'. Ozonolysis of 'A' gives 2 moles of acetaldehyde. Identify compounds 'A' to 'D'. Explain the reactions involved.

Q.16 Write the structure of prop-2-en-1-amine.

Q.17 Write the main products of the following reactions :

(i) $CH_3CH_2NH_2 \xrightarrow[0^oC]{HNO_2}$?

(ii) 

(iii)