

# 5

CHAPTER



# NITROGEN CONTAINING COMPOUNDS

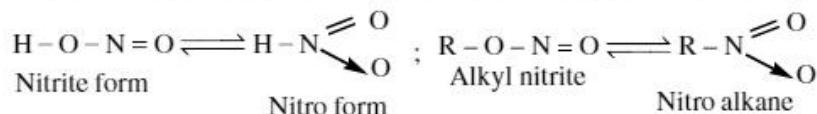
- \* Nitro Compounds
- \* Diazonium Salts
- \* Amines
- \* Cyanides and Isocyanides

## NITRO COMPOUNDS

### 5.1.1

#### Nitro compounds

Nitroalkanes are the derivatives of alkanes. They are isomeric nitrites. It may be noted that  $-NO_2$  group is ambident group and is capable of getting attached to the carbon chain through nitrogen ( $R-N\equiv O$  nitroalkane) as well as through oxygen ( $R-O-N=O$ , alkyl nitrite) atom. Both are alkyl derivatives of nitrous acid ( $HNO_2$ ) which exhibits tautomerism as the two forms are in dynamic equilibrium.



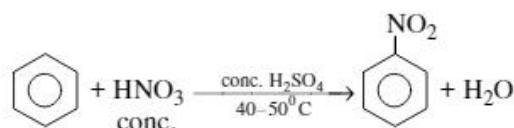
*Nitrobenzene is called oil of mirbane*

Aromatic compounds in which one or more nitro groups are attached directly to the aromatic ring such as benzene are called aromatic nitro compounds.

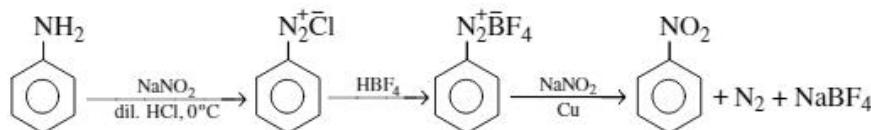
Nitrobenzene is also called as artificial oil of bitter almond or oil of mirbane.

#### Preparation

Nitrobenzene is prepared in the laboratory by heating benzene with a mixture of concentrated nitric acid and concentrated sulphuric acid at  $40-50^\circ C$  (below  $60^\circ C$ ). The temperature should not increase otherwise m-dinitrobenzene is formed. This procedure is also adopted for its industrial preparation. For introducing only one nitro group in ortho position, acetyl nitrate is a good nitrating agent.



Aniline is diazotised first by treating with sodium nitrite and dilute hydrochloric acid at  $0^\circ C$ . The resulting benzene diazonium chloride is treated with tetrafluoroboric acid which when treated with aqueous sodium nitrate and copper powder gives nitrobenzene.



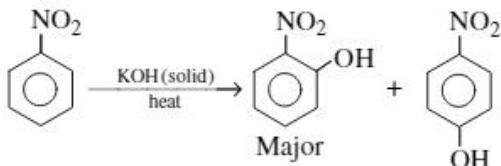
**Physical properties :** Nitrobenzene is a pale yellow oily liquid, with boiling point  $211^\circ C$ . It is insoluble in water but soluble in many organic solvents. It is heavier than water and steam volatile.

*Nitrobenzene is steam volatile*

**Chemical Properties :** Nitrobenzene does not undergo any displacement reaction since the nitro group is firmly linked to the benzene nucleus and shows partial double bond character due to resonance which makes it inert.

The nitro group is a meta-directing group in electrophilic substitution reactions. Nitro group is also strongly deactivating towards electrophilic substitution reactions. Further nitration, halogenation and sulphonation mainly occur at m-position under vigorous conditions. Neither Friedel-Crafts alkylation nor acylation can be carried out on nitrobenzene because the ring is so highly deactivated that it cannot react with alkyl cations ( $R^+$ ) and acyl cations ( $RCO$ ) which are less electrophilic than other common electrophiles.

On heating with solid KOH, nitrobenzene yields a mixture of o- and p-nitrophenols along with some azoxybenzene. It is an example of **nucleophilic substitution**, where the presence of one nitro group is sufficient to activate the benzene nucleus for nucleophilic substitution at o- and p-positions. Due to intra molecular hydrogen bonding, o-nitrophenol is the major product.



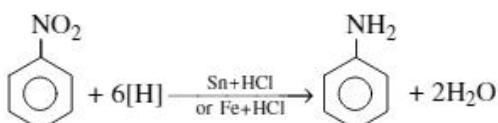
**Reduction properties :** The reduction of the nitro group of nitrobenzene proceeds through the following stages, each involving the transfer of two electrons from the reducing agent to the nitro group or its intermediate reduction product.



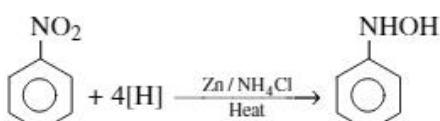
*Reduction of nitrobenzene with Sn and HCl gives aniline*

*Reduction of nitrobenzene in neutral medium gives N-phenyl hydroxylamine*

**Reduction in acidic medium :** Reduction of nitrobenzene in presence of tin and hydrochloric acid or iron and hydrochloric acid yields only the final product aniline and intermediate products, nitrosobenzene and phenyl hydroxylamine do not appear at all.

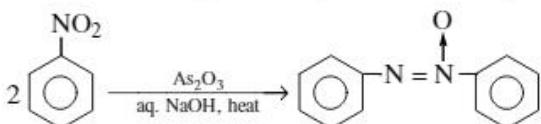


**Reduction in neutral medium :** When nitrobenzene is heated with zinc dust and aqueous ammonium chloride at  $65^\circ\text{C}$ , N-phenyl hydroxylamine is formed. Nitrosobenzene cannot be isolated.

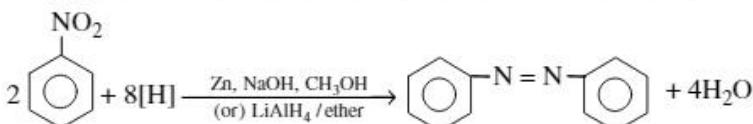


**Reduction in alkaline medium :** Reduction of nitrobenzene in alkaline medium leads to the formation of binuclear products due to addition reaction between nitrosobenzene and N-phenyl hydroxylamine that are formed as intermediate products under these conditions.

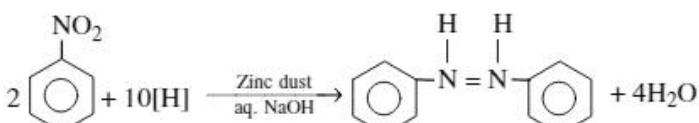
When nitrobenzene is heated with an alkaline solution of sodium arsenite,  $\text{Na}_2\text{AsO}_3$ , azoxybenzene is formed. Reduction with alkaline solution of glucose or methanolic sodium hydroxide yields the same product.



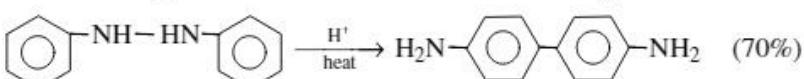
When nitrobenzene is heated with zinc dust and methanolic sodium hydroxide, azobenzene is formed. Alkaline sodium stannite and lithium aluminium hydride in ether also reduce nitrobenzene to azobenzene, but not to aniline.



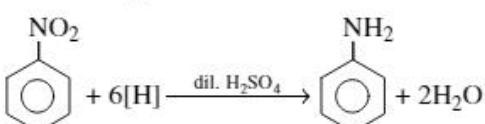
Hydrazobenzene is obtained when reduction of nitrobenzene is carried out with zinc dust and aqueous sodium hydroxide. Hydrazine in presence of ruthenium catalyst and alcoholic KOH leads to the formation of hydrazobenzene.



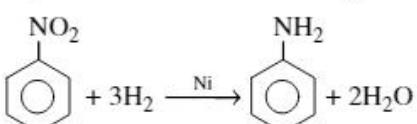
Hydrazobenzene on being treated with aqueous  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  isomerises to benzidine (4,4'-diaminobiphenyl). This reaction involves acid-catalysed intramolecular rearrangement called the **benzidine rearrangement**.



**Electrolytic reduction :** The electrolytic reduction of nitrobenzene in a weakly acidic medium gives aniline.



**Catalytic hydrogenation :** The hydrogenation of nitrobenzene with hydrogen gas in presence of Ni or Pt or Pd gives aniline.

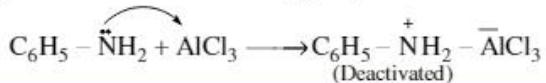


Nitrobenzene is used in the manufacture of aniline and azodyes. It is also used as an oxidising agent and in the preparation of shoe polish and scenting cheap soaps.



**P.5.1** Aromatic rings containing  $-\text{NH}_2$ ,  $-\text{NHR}$  or  $-\text{NR}_2$  groups do not undergo Friedel-Crafts reaction. Why?

**Solution**  $-\text{NH}_2$ ,  $-\text{NHR}$  and  $-\text{NR}_2$  groups are electron releasing groups, but these are converted into powerful electron-attracting groups as a result of Lewis acid-Lewis base reaction with  $\text{AlCl}_3$ .



**P.5.2** Why aryl halides and vinyl halides cannot be used in Friedel-Crafts alkylation reaction?

**Solution** Aryl halides and vinyl halides cannot be used in Friedel-Crafts reaction because aryl cations and vinyl cations, being very unstable, are difficult to form.

### EXERCISE - 5.1.1

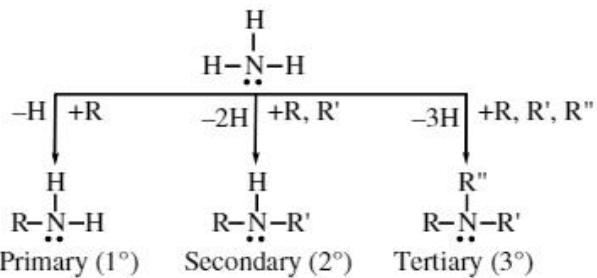
1. Write any two methods of preparation of nitrobenzene.
2. Discuss various reduction properties of nitrobenzene in different media.
3. What happens when nitrobenzene is heated with solid potassium hydroxide?

## AMINES

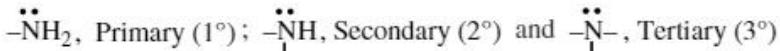
### 5.2.1

#### Classification

Amines are the alkyl or aryl derivatives of ammonia, formed by the replacement of one or more hydrogen atoms by corresponding number of alkyl or aryl or both groups. Amines are three types.

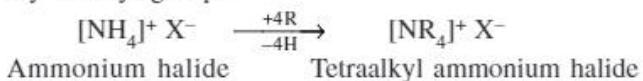


A primary amine has only one alkyl group directly attached to nitrogen atom, a secondary amine has two alkyl groups and a tertiary amine has three alkyl groups directly attached to nitrogen atom. Thus, characteristic functional groups for primary, secondary and tertiary amines are :

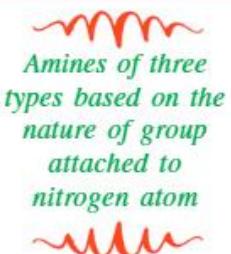


If the two alkyl groups in secondary amine and the three alkyl groups in tertiary amine are same, they are known as simple amines and if the groups are different, they are mixed amines.

In addition to above amines, tetra-alkyl derivatives, similar to ammonium salts also exist which are called quaternary ammonium salts. They are regarded as derivatives of ammonium salts in which all the four hydrogen atoms are replaced by alkyl or aryl groups.



2° or 3° amine  
with same alkyl  
groups is known  
as simple amine

  
**Amines of three types based on the nature of group attached to nitrogen atom**

Depending upon the nature of group attached to nitrogen of amino group, amines are classified as aliphatic, aromatic or arylalkyl amines.

Aliphatic amines :  $\text{CH}_3\text{NH}_2$ ,  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{NH}-\text{CH}_3 \end{array}$ ,  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{N}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$ , etc.

Aromatic amines :  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $(\text{C}_6\text{H}_5)_2\text{NH}$ ,  $(\text{C}_6\text{H}_5)_3\text{N}$ , etc.

Arylalkyl amines :  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{NHCH}_2\text{C}_6\text{H}_5$ , etc.

Trimethyl amine is pyramidal as shown in Fig 5.1. Due to the presence of unshared electron pair on nitrogen atom, the C–N–C bond angle is  $108^\circ$ .

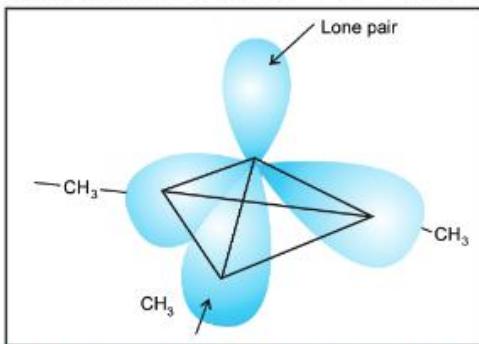


Fig 5.1 Pyramidal shape of trimethyl amine

### 5.2.2

#### Nomenclature

  
**IUPAC name of a 1° amine is alkanamine**

Amines are named as alkylamines in common system. In IUPAC system, they are named as alkanamines. The last latter 'e' in the name of the alkane is omitted.

If more than one  $-\text{NH}_2$  group is present, suitable prefixes like di, tri, etc., are used to indicate the number of such groups. Their positions in the chain are indicated and the letter 'e' in the name of parent alkane is retained.

Secondary and tertiary amines are named as N–substituted derivatives of primary amines like N–alkylalkanamine and N,N-dialkylalkanamine, respectively.

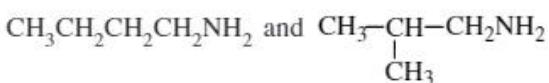
Aryl amine, aniline is named as benzenamine. Toluidine is named as aminotoluene. Common and IUPAC names of some amines are listed in Table 5.1.

### 5.2.3

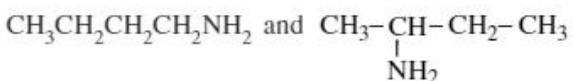
#### Isomerism

Amines exhibit the following types of isomerism.

1. **Chain isomerism** : Aliphatic amines containing four or more carbon atoms exhibit chain isomerism.



2. **Position isomerism** : Alkyl amines with three or more carbon atoms exhibit position isomerism.



3. **Metamerism** : Secondary and tertiary amines may exhibit metamerism.

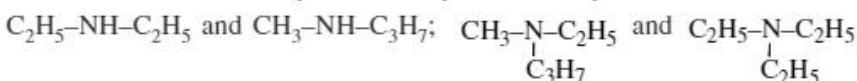
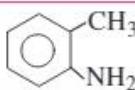
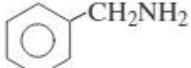


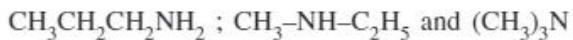
Table 5.1 Common and IUPAC names of some amines

S.No.	Amine	Common name	IUPAC name
1	$\text{CH}_3\text{NH}_2$	Methyl amine	Methanamine
2	$\text{CH}_3\text{CH}_2\text{NH}_2$	Ethyl amine	Ethanamine
3	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	n-Propyl amine	Propan-1-amine
4	$\begin{matrix} \text{CH}_3-\text{CH}-\text{CH}_3 \\   \\ \text{NH}_2 \end{matrix}$	Isopropyl amine	Propan-2-amine
5	$(\text{CH}_3)_3\text{C}-\text{NH}_2$	tert-Butyl amine	2-Methylpropan-2-amine
6	$\text{C}_6\text{H}_5\text{NH}_2$	Aniline	Benzenamine
7		ortho-Toluidine	2-Aminotoluene
8		Benzyl amine	Phenylmethanamine
9	$\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$	Hexamethylenediamine	Hexane-1,6-diamine
10	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2$	Allylamine	Prop-2-ene-1-amine

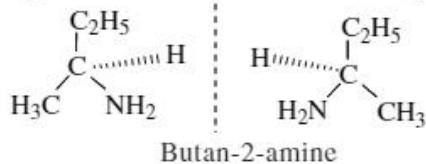
  
 1°, 2° and 3°  
 amines, with same  
 molecular  
 formula, are  
 functional isomers

  
 Amines having  
 chiral structures  
 may show  
 enantiomerism  


4. **Functional isomerism :** Primary, secondary and tertiary amines having same molecular formula are functional isomers of one another.

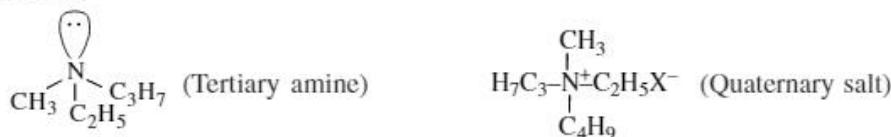


5. **Optical isomerism :** Amines having chiral structures may show enantiomerism.



These enantiomers are stable and do not undergo interconversion. The racemic mixture is resolvable.

Tertiary amines and quaternary salts with different groups also exhibit optical isomerism.



A tertiary amine with a lone pair of electrons is chiral because of its pyramidal geometry, but is optically inactive. A rapid **umbrella** type inversion converts either of the enantiomers to a racemic mixture. This inversion involves very less energy. Thus, reacemisation occurs and enantiomers cannot be isolated.

The nitrogen in quaternary ammonium salts is tetrahedral and is positively charged. A quaternary ammonium salt with four different substituents on nitrogen is chiral. The inversion of configuration is not possible because the nitrogen atom has no lone pair of electrons and cannot adopt a planar transition state. The chiral nitrogen is thus configurationally stable.



**P.5.3** Write the structures of the eight isomeric amines with the formula  $C_4H_{11}N$ .

**Solution** Out of eight isomeric amines with the formula  $C_4H_{11}N$ , four are primary, three are secondary and one is tertiary amine.

- (i)  $CH_3CH_2CH_2CH_2NH_2$ ; (ii)  $CH_3\underset{NH_2}{|}CHCH_2CH_3$ ; (iii)  $CH_3-\underset{CH_3}{|}CH-CH_2NH_2$ ; (iv)  $(CH_3)_3C-NH_2$ ;
- (v)  $CH_3NHCH_2CH_2CH_3$ ; (vi)  $C_2H_5\underset{CH_3}{|}NHC_2H_5$ ; (vii)  $CH_3NHCH(CH_3)_2$  and (viii)  $CH_3-\underset{CH_2CH_3}{|}N-CH_3$



**P.5.4** Write the IUPAC names of (a)  $OHC-\underset{\text{benzene ring}}{\text{---}}NH_2$  and (b)  $CH_3CH_2-\underset{CH_3}{|}N-CH_2CH_2CH_3$

**Solution** IUPAC name of  $OHC-\underset{\text{benzene ring}}{\text{---}}NH_2$  is 4-Aminobenzenecarbaldehyde.

IUPAC name of  $CH_3CH_2-\underset{CH_3}{|}N-CH_2CH_2CH_3$  is N-Ethyl-N-methylpropanamine-1.



**P.5.5** Classification of aliphatic amines and alcohols is different. Comment.

**Solution** Classification of primary, secondary and tertiary alcohols is based on the nature of carbon atom to which hydroxyl group is attached.

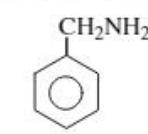
$-CH_2-OH$  ( $1^\circ$  alcohol);  $>CH-OH$  ( $2^\circ$  alcohol) and  $\geqslant C-OH$  ( $3^\circ$  alcohol).

Classification of primary, secondary and tertiary amines is based on the nature of nitrogen atom to which alkyl group is attached :  $-NH_2$  ( $1^\circ$  amine);  $>NH$  ( $2^\circ$  amine) and  $\geqslant N$  ( $3^\circ$  amine).

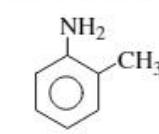


**P.5.6** Give the structures and names of various amines with the formula  $C_7H_9N$ .

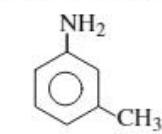
**Solution**



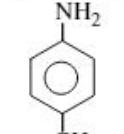
Phenyl-methanamine



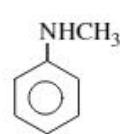
2-Methyl-benzenamine



3-Methyl-benzenamine



4-Methyl-benzenamine



N-methyl-benzenamine

#### 5.2.4

##### Solubility

Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part. Higher amines are essentially insoluble in water. Amines are soluble in organic solvents like alcohol and ether.

Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and hydrogen of another molecule. This intermolecular association is more in primary amines than in secondary amines Fig 5.2. The order of boiling points of isomeric amines is :  $1^\circ > 2^\circ > 3^\circ$ .

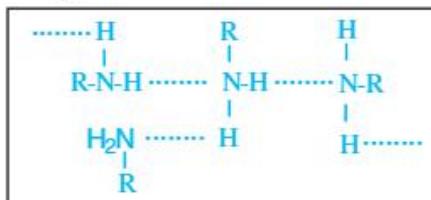


Fig 5.2 Intermolecular hydrogen bonding in primary amines

### 5.2.5 Basic nature of amines

Due to the presence of a lone pair of electrons on nitrogen, amines exhibit basic character. They are stronger bases than water and are, therefore, protonated by water in their aqueous solutions. The basic nature of amines is compared in terms of the equilibrium constant  $K_b$ .



$$\text{At equilibrium, dissociation constant of the base } K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]}$$

As the value of  $K_b$  increases, strength of the base increases. A more convenient method of expressing the basic strength of amines is in terms of their  $pK_b$  values. As the value of  $pK_b$  decreases, strength of the base increases.

The strength of a base depends on the stability of its conjugate acid. As the stability of the conjugate acid of a base increases, the corresponding base is a stronger base.

Larger the value of  $K_b$  or smaller the value of  $pK_b$ , more is the basic strength of amine. The  $K_b$  and  $pK_b$  values for some amines are given in Table 5.2.

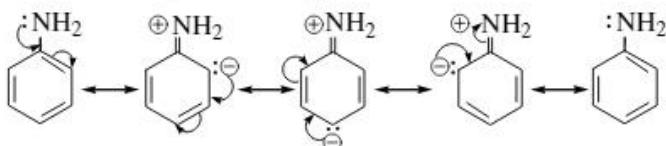
**Table 5.2  $pK_b$  values of some amines**

S.No.	Amine	$pK_b$	S.No.	Amine	$pK_b$
1	Ammonia	4.74	10	Triethylamine	3.24
2	Methylamine	3.36	11	Tri-n-propylamine	3.35
3	Ethylamine	3.36	12	Aniline	9.40
4	n-Propylamine	3.32	13	N-Methylaniline	9.21
5	Isopropylamine	3.40	14	N, N-Dimethylaniline	8.94
6	Benzylamine	4.67	15	p-Toluidine	8.92
7	Dimethylamine	3.28	16	p-Chloroaniline	10.00
8	Diethylamine	3.01	17	p-Methoxyaniline	8.70
9	Trimethylamine	4.26	18	p-Nitroaniline	13.00

*Basic strength  
of amines  
increases with  
increase in  $K_b$*

#### Factors affecting the basic nature of an amine

**Availability of lone pair for donation :** Aliphatic amines are more basic than aromatic amines as the lone pair of aromatic amines is involved in resonance with the benzene ring and not in free state. Ethyl amine is more basic than aniline. In aniline, the lone pair on nitrogen is involved in resonance.



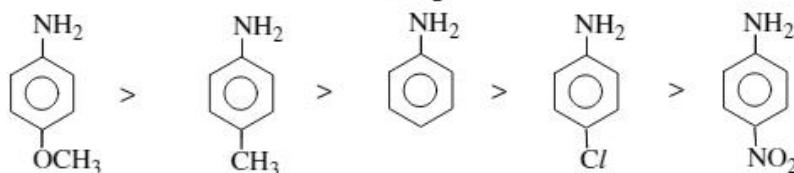
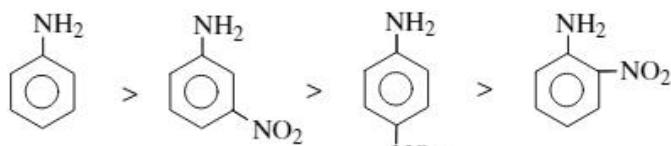
**Stability of conjugate acid of a base decides strength of a base :** The stability of the conjugate acid of a base depends on charge spreading. +I Effect of alkyl groups connected to the nitrogen of a base or +M effect of a group present may decrease the +ve charge formed on nitrogen of a base in its conjugate acid. It is stabilised and the base becomes a strong base.

Alkyl amines are thus more basic than ammonia, as their conjugate acids become more stable due to the +I effect of the alkyl groups. Stability further increases with the number of alkyl groups connected to nitrogen increasing.

In gaseous state, order of basic strength:  $\text{R}-\overset{\cdot\cdot}{\underset{|}{\text{N}}}-\text{R} > \text{R}-\overset{\cdot\cdot}{\text{NH}}-\text{R} > \text{R}-\overset{\cdot\cdot}{\text{NH}_2} > \overset{\cdot\cdot}{\text{NH}_3}$

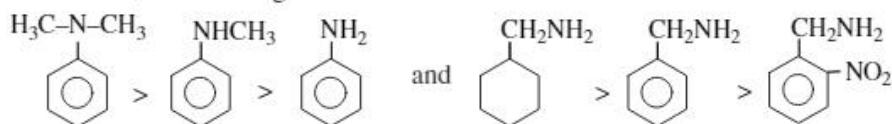
But in aqueous solution, in addition to +I effect of -R groups, hydrogen bonding with water also stabilises the conjugate acid. So the order of basic strength in aqueous solution is:  $\text{C}_2\text{H}_5\text{-NH-C}_2\text{H}_5 > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$ . If the alkyl group is methyl, the order of basic strength is :  $\text{CH}_3\text{-NH-CH}_3 > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$ .

The relative basic strength of various aliphatic amines also depends upon the nature of the alkyl group. Presence of an electron withdrawing group in aromatic amines generally decreases the basic strength, whereas electron releasing group increases the strength of a base. Decreasing order of basic strengths of some amines is given below.

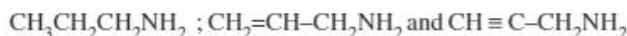


(+ M effect) (hyper conjugation) (-I effect) (-M and -I effects)

The greater extent of hydrogen bonding in protonated amine, more will be its stabilisation and consequently, greater will be the basic strength of the corresponding amine. The hydration due to hydrogen bonding is maximum in monoalkyl ammonium ion. It is less in dialkyl ammonium ion and still less in trialkyl ammonium ion. Therefore, basic strength should decrease in the order :  $1^\circ > 2^\circ > 3^\circ$ .



**P.5.7** Arrange the following in the decreasing order of basic strength :



**Solution** The order of basic strength is :  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 > \text{CH}_2=\text{CH}-\text{CH}_2\text{NH}_2 > \text{CH} \equiv \text{CCH}_2\text{NH}_2$

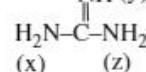
Alkyl group is electron releasing and stabilises the conjugate acid of propyl amine.

Alkenyl and alkynyl groups connected to  $-\text{CH}_2\text{NH}_2$  are electron withdrawing groups and destabilise the conjugate acid of  $\text{CH}_2=\text{CHCH}_2\text{NH}_2$  and  $\text{CH}\equiv\text{CCH}_2\text{NH}_2$ , hence they become weak bases.

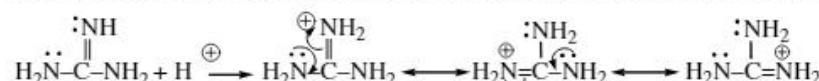


P58

NH<sub>2</sub>(y) has 3 amino groups x, y and z. Which amino group is more basic?



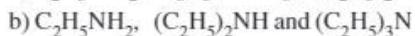
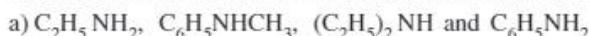
**Solution** Group v is more basic. This is because its conjugate acid is more stable due to resonance.



Conjugate acids of the other two ( $x$  and  $z$ ) are not stabilised.



**P.5.9** Arrange the following in the decreasing order of basic strength :



**Solution** a)  $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{C}_6\text{H}_5\text{NHCH}_3 > \text{C}_6\text{H}_5\text{NH}_2$

b)  $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2$

c)  $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3 > \text{C}_6\text{H}_5\text{NH}_2$ .



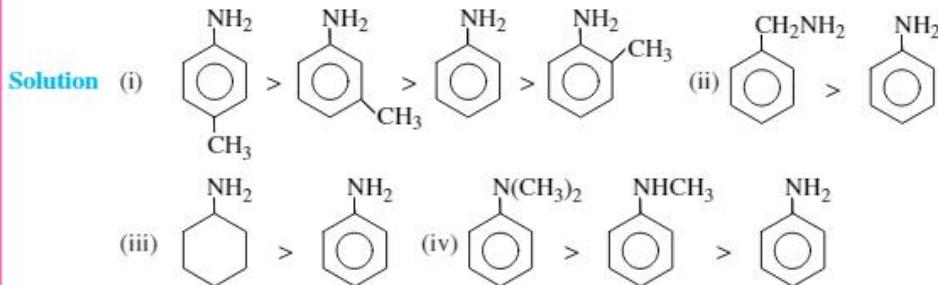
**P.5.10** Arrange the following in the decreasing order of their basic strength :

(i) Aniline, ortho, meta and para toluidines,

(ii) Benzyl amine and aniline,

(iii) Aniline and cyclohexylamine and

(iv) Aniline, N-methylaniline and N, N-dimethylaniline

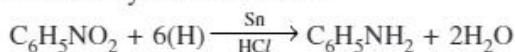


### 5.2.6

#### Aniline Preparation

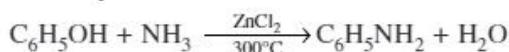
Aniline can also be called as benzenamine. Aniline was prepared by Unverboden for the first time by the destructive distillation of indigo. Hence it is named as aniline as anil means indigo.

**1. From nitro benzene :** Aniline is prepared by the reduction of nitrobenzene with tin and hydrochloric acid.

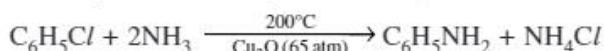


Iron, water and small quantity of hydrochloric acid are used for this reduction on a commercial scale.

**2. From phenol :** Phenol gives aniline when heated with ammonia at  $300^\circ\text{C}$  under pressure in presence of zinc chloride.



**3. From chlorobenzene :** On heating chlorobenzene with ammonia at  $200^\circ\text{C}$  under pressure in presence of cuprous oxide gives aniline. This is called ammonolysis.



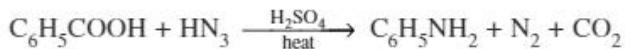
**4. Hofmann hypobromite reaction :** Benzamide gives aniline, when treated with bromine in presence of alkali.



This is the most convenient method for preparing primary amines. This method gives an amine containing one carbon atom less than that in amide.

*In Hofmann hypobromite reaction, amide is converted to amine*

5. From benzoic acid : When a solution of benzoic acid dissolved in conc.  $\text{H}_2\text{SO}_4$  and hydrazoic acid dissolved in chloroform are mixed, aniline is formed. This reaction is called Schmidt reaction.



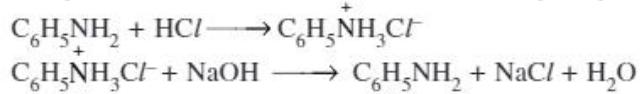
### Physical properties

Aniline is a colourless, oily liquid but turns dark brown on exposure to air due to oxidation. It has characteristic unpleasant odour. It is slightly soluble in water but soluble in organic solvents like ether, acetone, etc. It is steam volatile. The boiling point of aniline is  $183^\circ\text{C}$ .

*Aqueous  
solution of  
 $\text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-$   
is acidic, due to  
the hydrolysis of  
 $\text{C}_6\text{H}_5\text{NH}_3^+$  ion*

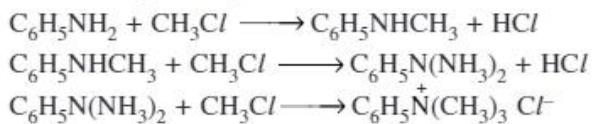
### Chemical properties

1. Basic Nature : Aniline is soluble in dil  $\text{HCl}$ . It forms salts with acids. Aniline is regenerated when alkali is added to aniline hydrochloride. Aqueous solution of aniline hydrochloride is acidic, due to cationic hydrolysis.

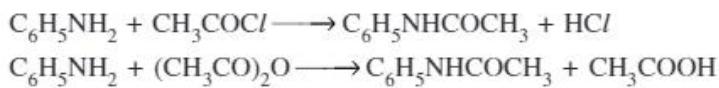


Amines undergo alkylation with alkyl halide to give secondary and tertiary amines and finally quaternary ammonium salts.

2. Alkylation : Aniline reacts with alkyl halide to give secondary and tertiary amines. Quaternary ammonium salt is finally formed. The bi-product in this reaction is neutralised by adding carbonate.



3. Acylation : Aniline reacts with acetic anhydride or acetyl chloride to give acetanilide.



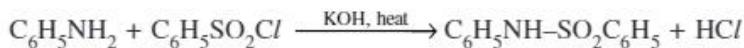
Order of reactivity in acylation :  $\text{CH}_3\text{COCl} > \text{CH}_3\text{COOCOCH}_3 > \text{CH}_3\text{COOC}_2\text{H}_5$

With benzoyl chloride, aniline gives benzylidene. This reaction is called Colom-Baumann reaction.

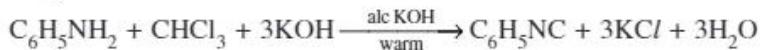


Introduction of  $\text{CH}_3\text{CO}-$  or  $\text{C}_6\text{H}_5\text{CO}-$  group in place of  $-\text{H}$  atom in general is known as acylation. The former is acylation and the latter is benzoylation.

Aniline gives N-phenyl benzenesulphonamide with benzene sulphonyl chloride.

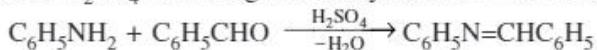


4. Carbylamine reaction : On warming with chloroform in presence of alcoholic potash, aniline forms phenyl carbylamine which has a foul smell. Only primary amines give this test.



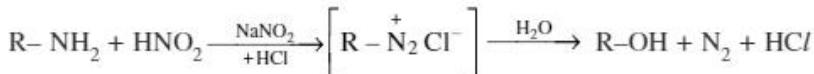
*Only 1° amines  
give carbylamine  
reaction*

5. Reaction with carbonyl compounds : On heating with benzaldehyde in presence of conc.  $\text{H}_2\text{SO}_4$ , aniline gives benzylideneaniline, an imine called Schiff's base.

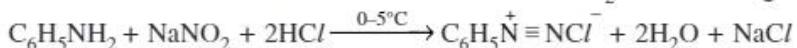


6. Reaction with nitrous acid : Nitrous acid is prepared in situ from a mineral acid and sodium nitrite. Different types of amines react differently with nitrous acid. Primary aliphatic amines react to form unstable diazonium salts liberating nitrogen gas quantitatively and alcohols.

Due to evolution of nitrogen gas quantitatively, this reaction is used in the estimation of amino acids and proteins.

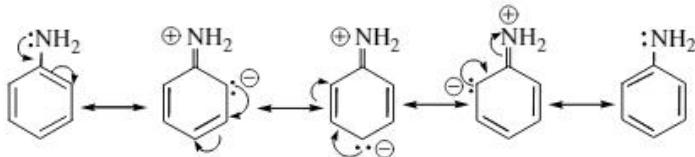


7. Diazotisation : Aniline undergoes diazotisation when treated with nitrous acid at  $0^\circ\text{C}$  and gives benzene diazonium chloride. Introduction of diazo group ( $-\text{N}=\text{N}-$ ) is called diazotisation. Only aromatic primary amines give diazo reaction. Aniline is dissolved in dil  $\text{HCl}$  and a solution of  $\text{NaNO}_2$  is added to give  $\text{HNO}_2$ .

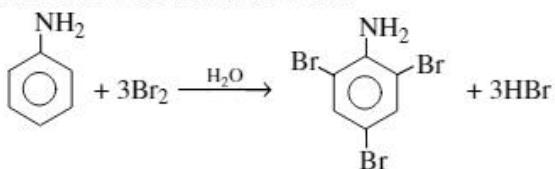


The reaction of secondary and tertiary amines with nitrous acid is different and they don't undergo diazotisation.

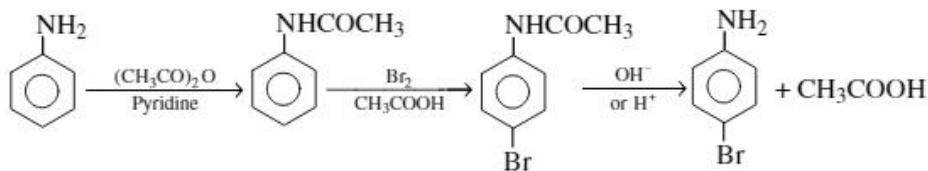
8. Electrophilic substitution in aniline : The amino group in aniline releases electrons by exerting  $+M$  effect and increases the  $\pi$  electron density at the ring carbon atoms. Electrophilic substitution takes place fast in aniline than in benzene due to this activation of the ring. Amino group is ortho and para orienting group as  $\pi$  electron density increases at ortho and para positions than at meta position.



**Bromination :** Aniline forms a white precipitate of symmetrical tribromoaniline when treated with bromine water.

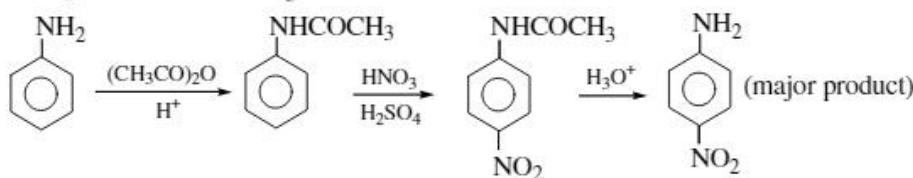


If we have to prepare monosubstituted derivative, the activating effect of  $-\text{NH}_2$  group is to be controlled by protecting the  $-\text{NH}_2$  group by acetylation with acetic anhydride then followed by hydrolysis.



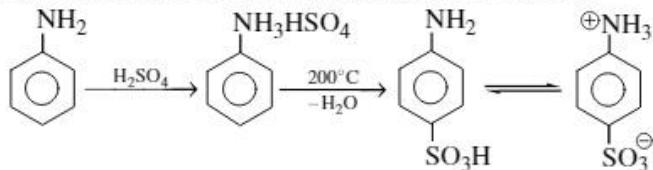
**Nitration :** Direct nitration with conc.  $\text{HNO}_3$ , oxidises aniline and a mixture of o-, m- and p- nitro anilines is formed. If acetanilide is nitrated only o- and p- nitro acetanilides are formed. These are converted to o- and p- nitro anilines by hydrolysis.

Due to resonance, the lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom. Thus the lone pair of electrons on nitrogen is less available for donation to benzene ring. Hence activating effect of amino group is lessened by converting into  $\text{--NHCOCH}_3$ .



Sulphanilic acid exists as zwitter ion

**Sulphonation :** Aniline is sulphonated by heating with conc.  $\text{H}_2\text{SO}_4$ . Anilinium hydrogen sulphate formed rearranges to p-aminobenzene sulphonic acid called sulphanilic acid at  $200^\circ\text{C}$ , which exists as zwitter ion.



**Uses :** Aniline is used to prepare benzene diazonium salt and to prepare Schiff's bases, anti-oxidant in rubber industry. It is used to prepare acetanilide, sulphanilic acid, sulpha drugs and dyes.

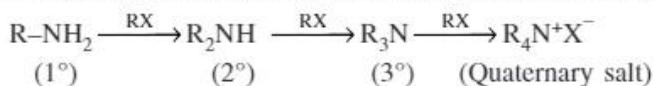
### 5.2.7

#### Other amines

#### Preparation

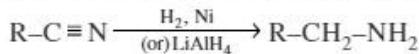
Reduction of nitrile or amide gives 1° amine

**Ammonolysis of alkyl halides :** An alkyl or benzyl halide when treated with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which halogen atom is replaced by an amino group. This process of cleavage of the C-X bond by ammonia molecule is called as ammonolysis. The primary amine thus obtained behaves as a nucleophile and can further react with alkyl halide to form secondary and tertiary amines and finally quaternary ammonium salt.

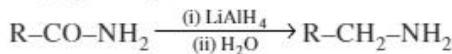


However, primary amine is obtained as a major product by taking large excess of ammonia.

**Reduction of nitriles :** When nitriles are reduced with lithium aluminium hydride or subjected to catalytic hydrogenation, primary amines are formed. Amines containing one carbon atom more than the starting amine can be prepared by this method. This reaction is used for ascent of amine series.



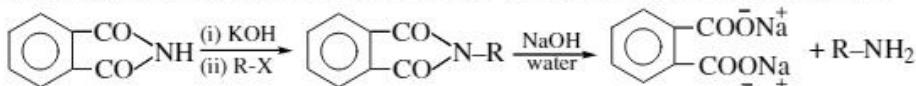
**Reduction of amides :** When amides are reduced with lithium aluminium hydride, primary amines are obtained.



**Gabriel phthalimide synthesis :** Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Gabriel synthesis is used for the preparation of aliphatic primary amines.

Gabriel synthesis is useful to prepare aliphatic primary amines only

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



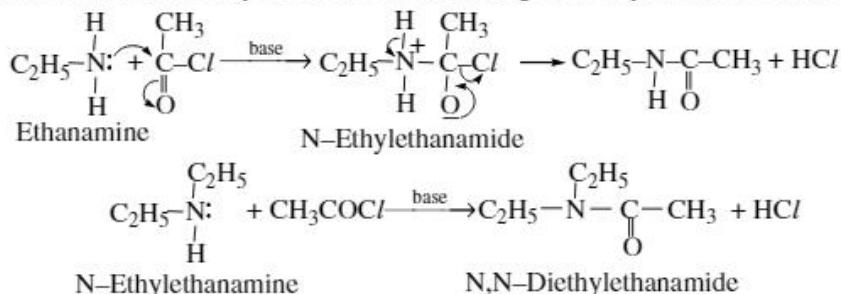
## Physical properties

Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part. Higher amines are essentially insoluble in water. It may be noted that intermolecular hydrogen bonding in amines is weaker than that in alcohols. Boiling point of ethanamine is less than that of ethanol.

Intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in primary amine. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom. Therefore, the order of boiling points of isomeric amines is as follows : primary > secondary > tertiary.

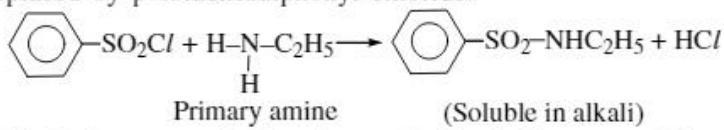
## Chemical properties

**Acylation :** When aliphatic or aromatic primary and secondary amines react with acid chlorides, anhydrides and esters undergo nucleophilic substitution reaction.

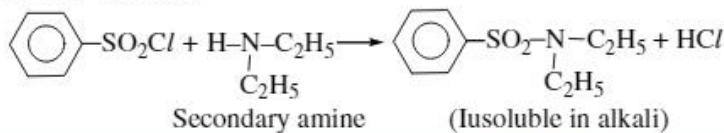


This reaction is carried out in the presence of a base stronger than the amine, like pyridine, which removes  $HCl$  so formed shifts the equilibrium to the right hand side.

**Reaction with benzenesulphonyl chloride :** Benzenesulphonyl chloride which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides. Tertiary amines do not react with this reagent. By using this reagent, primary, secondary and tertiary amines can be distinguished and also can be separated from a mixture of amines. Now-a-days, benzene sulphonyl chloride is replaced by p-toluenesulphonyl chloride.



The hydrogen attached to nitrogen in N-ethyl benzene sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

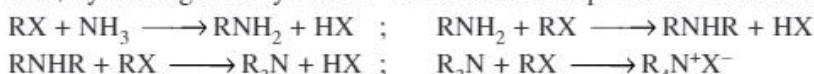


In N,N-diethyl benzene sulphonamide, there is no hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali. Other chemical reactions like alkylation, carbylamine reaction, diazotisation with nitrous acid, etc., were already discussed in aniline.

### 5.2.8

#### Separation of amines

A mixture of all the three types of amines and quaternary ammonium salt is obtained, by heating an alkyl halide with ammonia in presence of alcohol at 100°C.

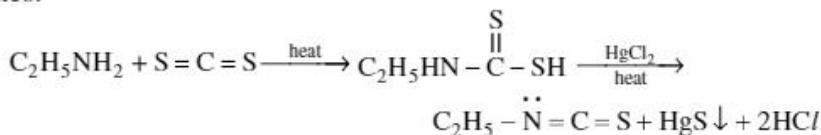


A mixture of all three classes of amines is also formed when an alcohol is heated with ammonia in presence of  $\text{Al}_2\text{O}_3$  or  $\text{ThO}_2$  at 350°C.

**Hinsberg's method :** The mixture of three types of amines along with quaternary salt is distilled with potassium hydroxide. The quaternary salt remains undistilled in the flask.

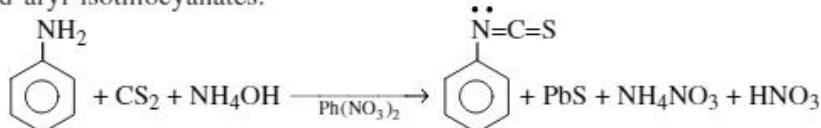
The salt of primary amine dissolves and salt of secondary amine is insoluble. The mixture in the flask is filtered. The salt of primary amine is present in the filtrate and the residue is the salt of secondary amine. They are separately hydrolysed to give primary and secondary amines.

**Reaction with carbondisulphide :** Primary amines react with carbondisulphide to form alkyl derivative of dithiocarbamic acid which when decomposed by mercuric chloride to give alkyl isothiocyanates. This reaction is called **Hofmann mustard oil reaction** which has pungent smell. This reaction is useful for identifying primary amines.



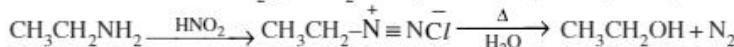
Secondary amines form diakyl dithiocarbamic acid which is not decomposed by mercuric chloride.

Aromatic primary amines react with carbondisulphide in presence of  $\text{NH}_4\text{OH}$  to form ammonium aryl dithiocarbamates which on heating with lead nitrate solution yield aryl isothiocyanates.



**P.5.11** How is aliphatic primary amine distinguished from aromatic primary amine?

**Solution** When treated with  $\text{HNO}_2$  ( $\text{NaNO}_2 + \text{HCl}$ ) at 0°C, aliphatic primary amines give alcohols.



Aromatic primary amines give a stable diazonium salt.



**P.5.12** How a mixture of nitrobenzene and aniline can be separated?

**Solution** The mixture is treated with dil  $\text{HCl}$ . Only aniline dissolves. It is then shaken with ether. Nitrobenzene goes into ether layer. It is separated.

Nitrobenzene is obtained by evaporating ether.

The aqueous layer, on neutralisation with  $\text{NaOH}$  gives aniline. It is also shaken with ether separately and ether is collected. Aniline is obtained by evaporating ether.

Different methods of identifying amines are listed in Table 5.3.

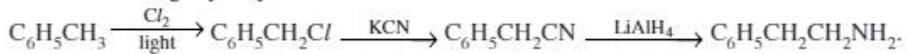
**Table 5.3 Identification of primary, secondary and tertiary amines**

Reaction	Primary amine	Secondary amine	Tertiary amine
1. Hinsberg's test. The amine is treated with benzene sulphonyl chloride, and then with NaOH	N-alkyl benzene sulphonamide formed dissolves in NaOH. $\text{RNH}_2 + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \rightarrow \text{RNHSO}_2\text{C}_6\text{H}_5 + \text{HCl}$	N,N-dialkyl benzene sulphonamide is formed, but insoluble in NaOH. $\text{R}_2\text{NH} + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \rightarrow \text{R}_2\text{NSO}_2\text{C}_6\text{H}_5 + \text{HCl}$	No reaction.
2. Action of $\text{HNO}_2$ .	Aliphatic amines form diazonium ion which is unstable. It decomposes to a carbonium ion which gives alcohol or alkene. $\begin{aligned} \text{RCH}_2\text{NH}_2 + \text{HNO}_2 &\rightarrow \\ &+ \text{RCH}_2\text{N}^+ \text{N}^- \rightarrow \text{RCH}_2^+ + \text{N}_2 \\ &\downarrow \text{H}_2\text{O} \\ &\text{RCH}_2\text{OH} \end{aligned}$	An yellow oily nitroso amine is formed. It gives a green colour on heating with phenol and $\text{H}_2\text{SO}_4$ which changes to red on dilution and then blue on adding alkali. $\text{RNHR} + \text{HNO}_2 \rightarrow \text{R}-\overset{\text{N}}{\underset{\text{R}}{\text{N}}} \text{R} \downarrow \text{NO}$	Tertiary amines give a salt. $\begin{array}{c} \text{R}-\overset{\text{N}}{\underset{\text{R}}{\text{N}}} \text{R} + \text{HNO}_2 \rightarrow \\ \text{R} \quad \text{H} \\ \text{R}-\overset{\text{N}}{\underset{\text{R}}{\text{R}}}^+ \text{NO}_2 \end{array}$
3. Carbonyl amine test. Treated with $\text{CHCl}_3$ and alc. KOH.	Primary amines give carbonyl amine with unpleasant odour. $\text{RNH}_2 + \text{CHCl}_3 \xrightarrow{\text{Alc KOH}} \text{RNC}$	No reaction.	No reaction.
4. Oxidation with $\text{KMnO}_4$ .	Aldehydes and ketones are formed. $\begin{aligned} \text{RCH}_2\text{NH}_2 &\rightarrow \text{RCHO} \\ \text{R}-\overset{\text{CH}}{\underset{\text{NH}_2}{\text{R}}} &\rightarrow \text{RCOR} \end{aligned}$	Tetra alkyl hydrazine is formed. $2\text{R}_2\text{NH} \xrightarrow{(O)} \text{R}-\overset{\text{N}}{\underset{\text{R}}{\text{N}}} \text{R} + \text{H}_2\text{O}$	No reaction.
5. Hofmann mustard oil reaction	Pungent smell of mustard oil	No reaction	No reaction



**P.5.13** How is toluene converted to phenyl ethanamine ?

**Solution** Toluene is converted to benzyl chloride by treating with  $\text{Cl}_2$  in light. It is then treated with KCN and reduced to get phenyl ethanamine.



**P.5.14** Arrange the following in the order of boiling points : (A) n-Butyl amine ; (B) Secondary butyl amine ; (C) Isobutyl amine and (D) Tertiary butyl amine.

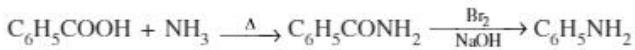
**Solution** The order of boiling points is : D < B < C < A.

As the length of the carbon chain increases, due to van der Waals forces, intermolecular attractions increase and boiling point increases.



**P.5.15** How is benzoic acid converted to aniline and benzylamine?

**Solution** Benzoic acid on heating with ammonia gives benzamide which produces aniline with bromine and alkali.



Benzyl amine is formed when benzamide is reduced.



**P.5.16** How is benzoic acid converted to aniline and benzylamine?

**Solution** Benzoic acid on heating with ammonia gives benzamide which produces aniline with bromine and alkali.

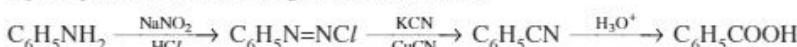


Benzyl amine is formed when benzamide is reduced.



**P.5.17** How is aniline converted to benzyl alcohol?

**Solution** Aniline is converted to benzene diazonium chloride, which in turn is converted to benzonitrile. Hydrolysis of benzonitrile gives benzoic acid.

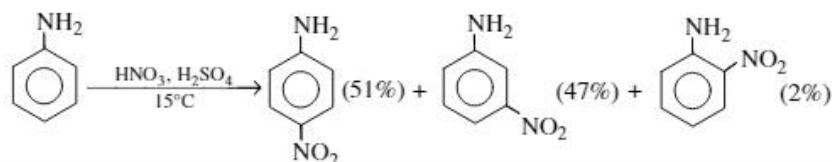


Benzoic acid on reduction gives benzyl alcohol.



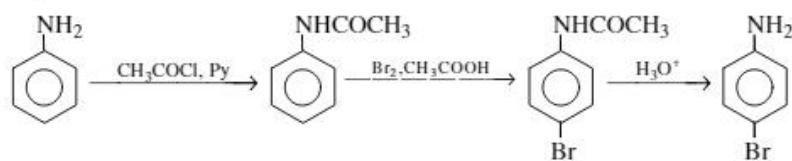
**P.5.18** Amino group in aniline is ortho and para directing. But on nitration, aniline gives an appreciable amount of m-nitroaniline also. Explain.

**Solution** In the strongly acidic medium, aniline is protonated to form the anilinium ion which is meta directing. That is why besides the ortho and para derivatives, significant amount of meta derivative is also formed.



**P.5.19** How to convert aniline to 4-bromoaniline?

**Solution** Monobromoaniline can be prepared by first decreasing the activity of  $-\text{NH}_2$  group through acylation.



**P.5.20** Aniline does not undergo Friedel-Crafts reaction. Justify.

**Solution** Aniline forms salt with Friedel-Crafts catalyst  $\text{AlCl}_3$ .

In this salt 'N' atom acquires positive charge and acts as strong deactivating group. Hence, the reactivity is decreased.

Therefore, aniline does not undergo Friedel-Crafts reaction.

**EXERCISE - 5.1.2**

- How is aniline prepared from nitrobenzene? Discuss the properties of aniline.
- How are (a)  $C_6H_5COOH$  (b)  $C_6H_5OH$  and (c)  $C_6H_5Cl$  converted to aniline?
- What happens when aniline is treated with  $NaNO_2$  and  $HCl$  at  $0^\circ C$ ?
- Write short notes on carbylamine reaction.
- How primary amines are distinguished from secondary and tertiary amines?
- Write short notes on (i) Hoffmann bromamide reaction (ii) Gabriel phthalimide synthesis and (iii) Ammonolysis
- Discuss the mechanism of acetylation of aniline.
- How do you convert  $C_6H_5Cl$  and  $C_6H_5OH$  to aniline?
- Give equation for diazotisation reaction? Give the examples.
- Write the important uses of aniline.

**DAZONIUM SALTS****5.3.1****Introduction**

The  $-N \equiv N^+ \longleftrightarrow N=N^-$  ion is called diazonium ion. The compounds possessing this ion along with  $X^-$  are called diazonium salts. The general formula of diazonium salts is  $R-N \equiv N^+X^-$  (or)  $R-N \equiv N^-X^+$ . If R is an alkyl group, it is alkyl diazonium salt.  $X^-$  may be  $Cl^-$ ,  $Br^-$ ,  $HSO_4^-$ ,  $BF_4^-$ , etc.

Diazonium compounds are named by suffixing diazonium to the name of the hydrocarbon corresponding to  $-R$  group, followed by the name of  $X^-$ .

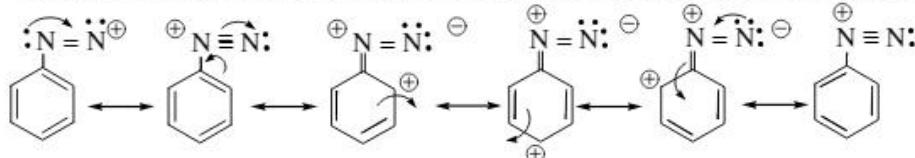
$C_6H_5N \equiv N^+Cl^-$ , Benzene diazonium chloride,

$C_6H_5N \equiv N^+HSO_4^-$ , Benzene diazonium hydrogen sulphate,

$CH_3CH_2N \equiv N^+Br^-$ , Ethane diazonium bromide.

**Stability :** Aliphatic diazonium salts are unstable and dissociate forming a carbocation, releasing nitrogen gas. The carbocation may form alcohol, alkene or alkyl halide.

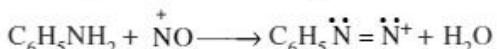
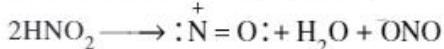
Aromatic diazonium salts are stable as diazonium ion is resonance stabilised.

**5.3.2**

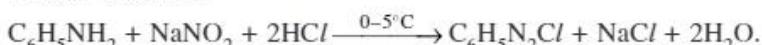
**Aromatic diazonium salts are stable due to resonance**

**Benzene diazonium chloride**

Benzene diazonium chloride is prepared by dissolving aniline in dilute hydrochloric acid and adding a solution of sodium nitrite at  $0-5^\circ C$ .



Overall reaction :



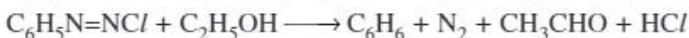
  
**Benzene diazonium chloride is obtained from aniline in HCl medium at 0°C using HNO<sub>2</sub>**  


  
**Substituted aromatic compounds can be prepared directly from diazonium salts**  


**Physical properties :** Benzene diazonium chloride is a colourless crystalline solid. It is soluble in water and stable at 0°C, but reacts with warm water. Benzene diazonium fluoborate is insoluble in water and stable at room temperature. In solid state, diazonium chloride decomposes.

**Chemical reactions :** Diazonium chloride is converted to several compounds and becomes important in organic synthesis.

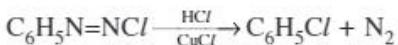
When reduced with hypophosphorus acid or ethanol, it gives benzene.



If the temperature of the diazonium salt solution is allowed to rise upto 10°C, the salt gets hydrolysed to phenol.

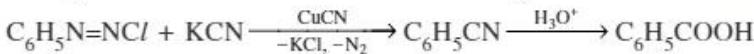


**Sandmeyer reaction :** Benzene diazonium chloride is converted to chlorobenzene when treated with cuprous chloride and hydrogen chloride.

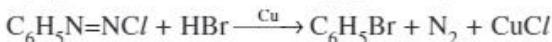
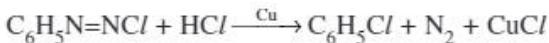


Bromobenzene is formed with cuprous bromide and hydrogen bromide.

Benzene diazonium chloride gives benzonitrile with potassium cyanide and cuprous cyanide. Benzonitrile on acidification gives benzoic acid.



These reactions are called Sandmeyer reactions. The above products can also be prepared by treating benzene diazonium chloride with HCl and Cu or HBr and Cu. This reaction is known as **Gattermann reaction**.



Formation of benzonitrile from benzene diazonium chloride with aqueous KCN and copper powder is called Gattermann reaction.

The yield in Sandmeyer reaction is better than that in Gattermann reaction.

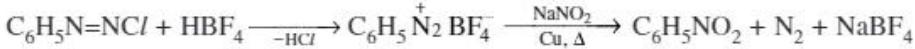
Iodobenzene is formed when benzene diazonium chloride is treated with potassium iodide.



**Schiemann reaction :** Benzene diazonium chloride on treating with hydrofluoroboric acid followed by heat gives fluorobenzene.

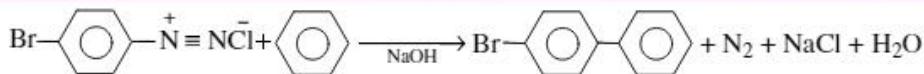


Benzene diazonium chloride on treating with HBF<sub>4</sub> followed by heating with aqueous sodium nitrite solution in the presence of copper, nitrobenzene is formed.



When aryl diazonium chloride is treated with an aromatic hydrocarbon in presence of aqueous NaOH, a biaryl compound is formed which is called **Gomberg reaction**.

*In Sandmeyer reaction, halo-benzenes are prepared from benzene diazonium chloride*



**Importance of diazonium salts :** The replacement of diazo group by other groups is helpful in preparing those substituted aromatic compounds which cannot be prepared by direct substitution in benzene or substituted benzene. These salts provide important link in many synthetic processes.

Diazonium salts can be prepared from almost all primary aromatic amines. One of the significant routes in which diazonium salts provide link during synthesis processes is given below.



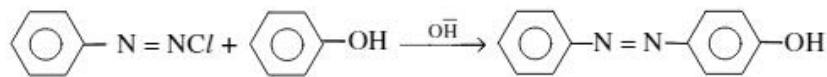
### 5.3.3 Azo-dyes

*Coupling reaction of benzene diazonium salt is used in preparing azo-dyes*

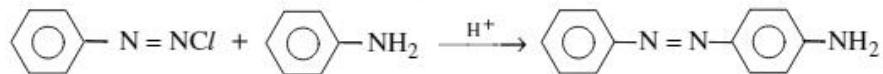
Benzene diazonium chloride undergoes coupling reactions. Coupling reaction is an electrophilic aromatic substitution reaction. Benzene diazonium ion substitutes phenol and aniline in para position.

This reaction is useful in the synthesis of azo-dyes.

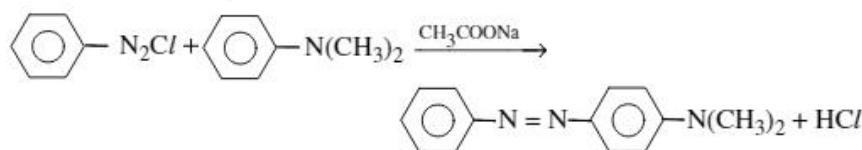
Phenol gives orange coloured p-hydroxy azobenzene when it undergoes coupling with benzene diazonium chloride, at a pH value 9 to 10.



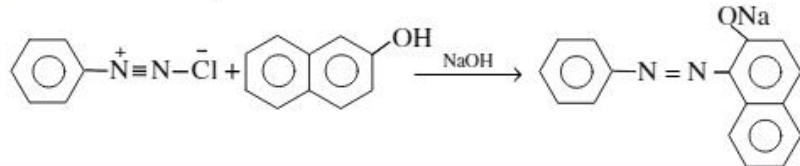
Aniline gives yellow coloured p-amino azobenzene when it undergoes coupling with benzene diazonium chloride, at a pH value 4 to 5.



N,N-Dimethylaniline gives an azo dye (yellow methyl orange) with benzene diazonium chloride in presence of sodium acetate.

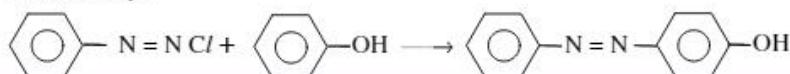


Benzene diazonium chloride gives scarlet red azo dye with  $\beta$ -naphthol in presence of sodium hydroxide solution.



P.5.21 What is the product of the reaction :  $\text{C}_6\text{H}_5\text{N}=\text{NCl} \xrightarrow{\text{Phenol}} ?$

**Solution** p-Hydroxy azobenzene is obtained by the coupling reaction with phenol, which is an orange red colour dye.



- P.5.22** Write Chemical equation for the ammonolysis of benzyl chloride and reaction of amine so formed with two moles of methyl chloride.

**Solution**  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow{\text{NH}_3} \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 \xrightarrow{2\text{CH}_3\text{Cl}} \text{C}_6\text{H}_5-\text{CH}_2-\text{N}-(\text{CH}_3)_2$   
Benzylchloride Benzylamine N,N-Dimethylphenylmethanamine

**P.5.23** How benzyl chloride can be converted to 2-phenylethanamine?

**Solution**  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow[\text{NaCN or KCN}]{\text{ethanolic}} \text{C}_6\text{H}_5\text{CH}_2\text{C}\equiv\text{N} \xrightarrow[\text{Benzylcyanide}]{\text{H}_2/\text{Ni}} \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_2$   
Benzylchloride 2-phenylethanamine

**P.5.24** Write structure and IUPAC name of the amide which gives propanamine by Hoffmann bromamide reaction. Explain.

**Solution** Propanamine contains three carbon atoms. Hence the amide molecule should contain four carbon atoms. It is butanamide. Its structure is  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CONH}_2$ .

**P.5.25** How will you convert 4-nitrotoluene to 2-bromobenzoic acid?

**Solution**  $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_3 \xrightarrow{\text{Br}_2} \text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_3 \xrightarrow[\text{Sn/HCl}]{\text{Br}} \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_3 \xrightarrow[\text{0-5}^\circ\text{C}]{\text{NaNO}_2/\text{HCl}}$   
 $\text{C}_6\text{H}_4-\text{CH}_3 \xrightarrow[\text{H}_3\text{PO}_2]{\text{H}_2\text{O}} \text{C}_6\text{H}_4-\text{CH}_3 \xrightarrow[\text{OH}^-]{\text{KMnO}_4} \text{C}_6\text{H}_4-\text{COOH}$

**P.5.26**  $\text{C}_6\text{H}_5\text{N}_2\text{Cl} \xrightarrow[\text{KCN}]{\text{CuCN}} \text{A} \xrightarrow[\text{H}^+]{\text{H}_2\text{O}} \text{B} \xrightarrow[\text{A}]{\text{NH}_3} \text{C} \xrightarrow[\text{NaOH}]{\text{Br}_2} \text{D}$ . Identify the final product, D .

**Solution**  $\text{C}_6\text{H}_5\text{N}=\text{NCI} \xrightarrow[\text{KCN}]{\text{CuCN}} \text{C}_6\text{H}_5\text{CN} \xrightarrow[\text{(A)}]{\text{H}_2\text{O}, \text{H}^+} \text{C}_6\text{H}_5\text{COOH} \xrightarrow[\text{(B)}]{\text{NH}_3, \Delta} \text{C}_6\text{H}_5\text{CONH}_2$   
 $\text{Benzamide(C) undergoes hypobromite reaction with bromine and alkali. Degradation of benzamide gives aniline. The final product (D) in the given sequence is aniline, C}_6\text{H}_5\text{NH}_2$

**P.5.27** How is aniline converted to benzyl alcohol?

**Solution** Aniline is converted to benzene diazonium chloride, which in turn is converted to benzonitrile. Hydrolysis of benzonitrile gives benzoic acid, which on reduction gives benzyl alcohol.

$\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[\text{HCl}]{\text{NaNO}_2} \text{C}_6\text{H}_5\text{N}=\text{NCI} \xrightarrow[\text{CuCN}]{\text{KCN}} \text{C}_6\text{H}_5\text{CN} \xrightarrow{\text{H}_3\text{O}^+} \text{C}_6\text{H}_5\text{COOH} \xrightarrow{\text{LiAlH}_4} \text{C}_6\text{H}_5\text{CH}_2\text{OH}$

**P.5.28** How is nitrobenzene converted to benzoic acid?

**Solution** Nitrobenzene is converted to aniline which on diazotisation gives benzene diazonium chloride. This on treating with potassium cyanide in the presence of cuprous catalyst gives benzonitrile and it gives benzoic acid on hydrolysis.

$\text{C}_6\text{H}_5\text{NO}_2 \xrightarrow[\text{HCl}]{\text{Sn}} \text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[\text{HCl}]{\text{NaNO}_2} \text{C}_6\text{H}_5\text{N}=\text{NCI} \xrightarrow[\text{CuCN}]{\text{KCN}} \text{C}_6\text{H}_5\text{CN} \xrightarrow{\text{H}_3\text{O}^+} \text{C}_6\text{H}_5\text{COOH}$

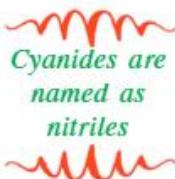
### **EXERCISE - 5.1.3**

1. How is benzene diazonium chloride prepared? What are its properties?
  2. Write short notes on coupling reactions giving azo-dyes.
  3. Discuss the following reactions :
    - a) Sandmeyer reaction, b) Gattermann reaction and c) Schiemann reaction.
  4. How the following are obtained from benzene diazonium chloride?
    - a) Iodobenzene, b) Chlorobenzene, c) Phenyl hydrazine and d) Nitrobenzene.

## CYANIDES AND ISOCYANIDES

### 5.4.1

#### Nomenclature

  
Cyanides are named as nitriles

Hydrogen cyanide exists in two tautomeric forms.



Alkyl or aryl derivatives of these two forms are called cyanides and isocyanides respectively. These two are functional isomers.

$\text{R}-\text{C}\equiv\text{N}$  is cyanide and  $\text{R}-\overset{+}{\text{N}}\equiv\text{C}$  is isocyanide.

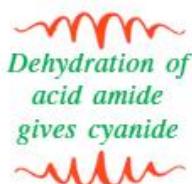
Cyanides are named as ‘nitriles’ based on the corresponding carboxylic acids obtained from them, by hydrolysis. The terminal ‘ic acid’ in the name of acid is replaced by o-nitrile. IUPAC names of cyanides are derived by adding the secondary suffix ‘nitrile’ to the name of the hydrocarbon containing the same number of carbon atoms. Isocyanides are named as carbylamines. Common and IUPAC names of some important cyanides and isocyanides are given in Table 5.4.

**Table 5.4 Names of some cyanides and isocyanides**

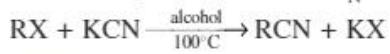
	Common name	IUPAC name
$\text{CH}_3\text{CN}$	Methyl cyanide (or) Acetonitrile	Ethannitrile
$\text{CH}_3\text{CH}_2\text{CN}$	Ethyl cyanide (or) Propionitrile	Propannitrile
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$	Propyl cyanide (or) Butyronitrile	Butannitrile
$\text{C}_6\text{H}_5\text{CN}$	Phenyl cyanide (or) Benzonitrile	Benzennitrile
$\text{CH}_3\text{NC}$	Methyl isocyanide	Methylcarbylamine
$\text{C}_2\text{H}_5\text{NC}$	Ethyl isocyanide	Ethylcarbylamine
$\text{C}_6\text{H}_5\text{NC}$	Phenyl isocyanide	Phenylcarbylamine

### 5.4.2

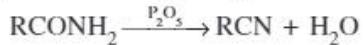
#### Cyanides Preparation

  
Dehydration of acid amide gives cyanide

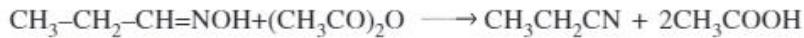
**From alkyl halides :** Alkyl halides on heating with potassium cyanide in alcoholic solution form cyanides. This is  $\text{S}_{\text{N}}^2$  reaction.



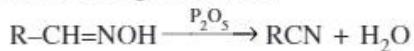
**From acid amides :** Acid amides on heating with phosphorus pentoxide undergo dehydration and give cyanides.



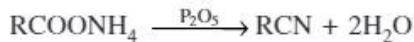
The reaction can also be run in pyridine, which takes up the two acids in the form of their pyridine salts.



**From oximes :** Oximes undergo dehydration on heating with phosphorus pentoxide and give nitriles.



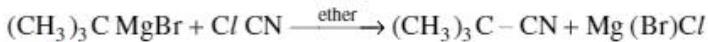
**From ammonium carboxylates :** Ammonium carboxylates on heating with phosphorus pentoxide yield alkyl cyanides.



**From Grignard reagent :** Grignard reagent gives cyanides on treating with cyanogen chloride.



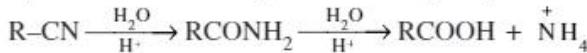
This method is useful for preparing tertiary alkyl cyanides also.



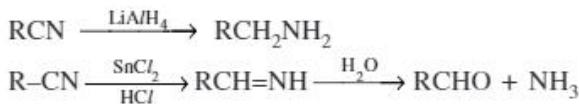
### Properties

Cyanides are neutral substances with pleasant odour. They are soluble in water and organic solvents.

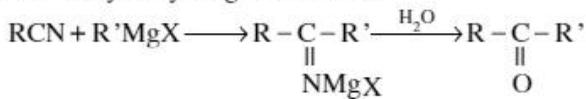
Cyanides form carboxylic acids on hydrolysis either with dil. acid or with alkali.



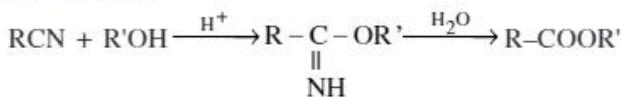
Complete reduction of cyanides gives primary amines.  $\text{LiAlH}_4$ , hydrogen and nickel or sodium and ethyl alcohol can be used as reducing agents. Partial reduction of cyanides with  $\text{SnCl}_2$  and  $\text{HCl}$  followed by hydrolysis forms aldehydes. This is called **Stephen's reaction**.



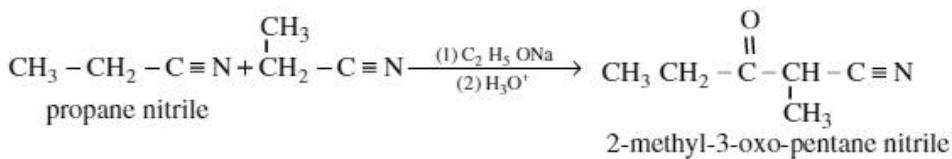
Alkyl or aryl cyanides undergo addition with Grignard reagent. The addition product on hydrolysis gives ketone.



Cyanides give esters when heated with alcohol in acid medium. This is called **Pinner reaction**.



Nitriles containing  $\alpha$ -hydrogens undergo self-condensation, much like the aldol condensation, in presence of sodium ethoxide to form  $\beta$ -imino nitriles. The latter on hydrolysis give  $\beta$ -keto nitriles. The reaction is called the **Thorpe reaction**.

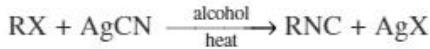


Cyanides are important intermediates in multistep synthesis in the laboratory, e.g., vinyl cyanide (acrylo nitrile) is produced in millions of pounds annually, which is mainly used for the production of rubbers and synthetic textiles.

### 5.4.3

#### Isocyanides Preparation

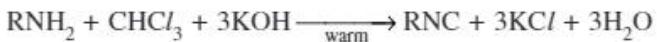
**From alkyl halides :** Alkyl halides produce isocyanides when heated with silver cyanide. A small quantity of cyanide is also formed.



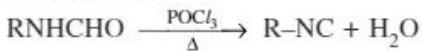
  
**Primary amine  
with chloroform  
in alkali forms  
isocyanide**  


  
**Reduction of  
isocyanide forms  
2° methyl amine**  
  
  
**Oxidation of  
isocyanide with  
HgO gives  
isocyanate**  


**From primary amines :** Primary amines on warming with chloroform in presence of alcoholic KOH form isocyanides.



**From N-alkyl formamides :** N-Alkyl formamide on dehydration with  $\text{POCl}_3$  forms isocyanide.



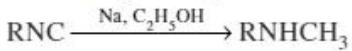
### Properties

Isocyanides possess unpleasant bad odour. Isocyanides are more volatile than corresponding cyanides. These are insoluble in water and soluble in organic solvents. Isocyanides are more toxic than cyanides.

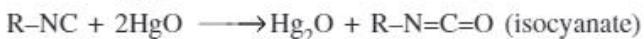
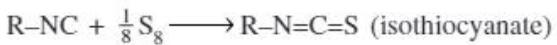
On hydrolysis with dilute acids, isocyanides produce primary amines. They are not hydrolysed by alkali.



On reduction with hydrogen and platinum or sodium and ethanol, isocyanides form secondary methyl amines.



Isocyanides undergo addition with chlorine and sulphur. They are oxidised to isocyanates when treated with  $\text{HgO}$ .

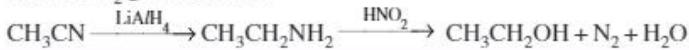


On prolonged heating, isocyanides are converted into more stable cyanides.



**P.5.29** How is methyl cyanide converted to ethanol?

**Solution** Methyl cyanide on reduction gives ethanamine. This is a primary amine which on treatment with  $\text{HNO}_2$  gives ethanol.



**P.5.30** How cyanides are identified from isocyanides?

**Solution** Hydrolysis of cyanides gives carboxylic acids, whereas hydrolysis of isocyanides produces primary amines.

On reduction, cyanides give primary amines whereas isocyanides give secondary methyl amines.

### EXERCISE - 5.1.4

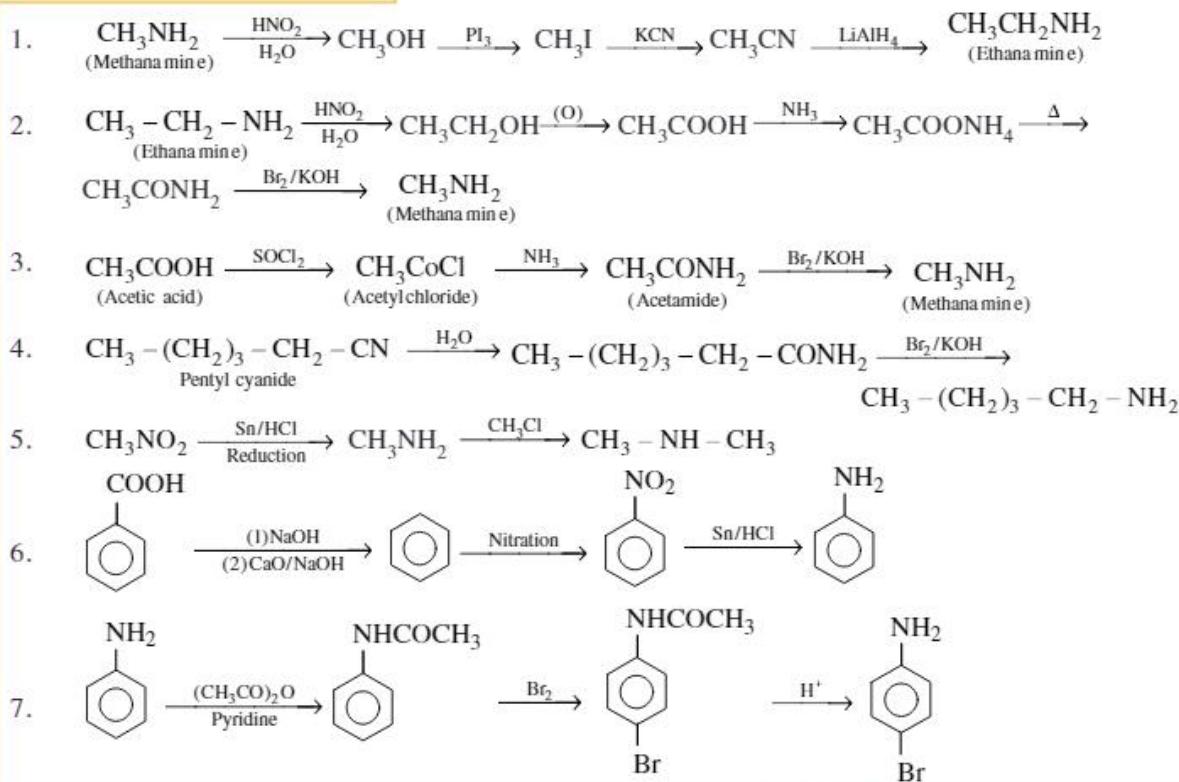
1. How cyanides are distinguished from isocyanides?
2. Write short notes on carbylamine test.
3. Explain why cyanides have higher boiling points and more solubility in water than isocyanides.
4. Write a note on the reduction of cyanides and isocyanides.



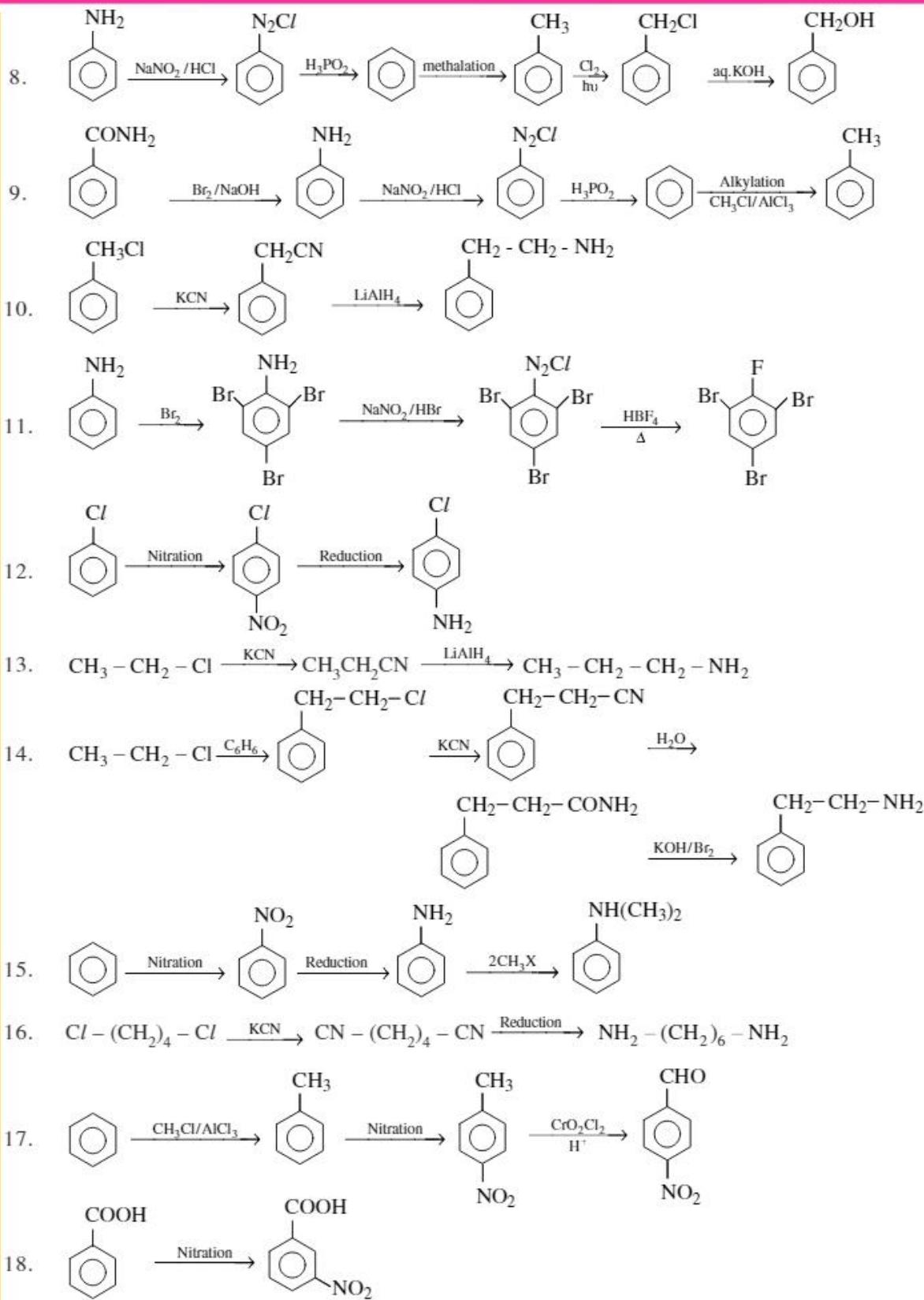
1. Amines are alkyl or aryl derivatives of ammonia. They are classified as primary ( $\text{RNH}_2$ ), secondary ( $\text{R}_2\text{NH}$ ) and tertiary ( $\text{R}_3\text{N}$ ) amines.
2. Amines are basic in nature, as they can donate a lone pair and accept proton. Basic nature depends on availability of lone pair for donation and stability of conjugate acid.
3. Electron releasing groups increase the basic strength and electron withdrawing groups decrease the basic strength.
4. Aliphatic amines are more basic compared to aromatic amines.
5. Primary amines are prepared by the reduction of nitro compounds, cyanides, amides and oximes.
6. Secondary amines are formed by reduction of isocyanides, hydrolysis of p-nitro aniline or N, N-dialkyl aniline and reductive ammoniation of aldehydes with primary amines.
7. Tertiary amines are prepared by Hofmann degradation, reductive ammoniation of aldehydes or ketones with secondary amines.
8. Aniline is prepared by reduction of nitrobenzene, Hofmann reaction of benzamide and by the action of ammonia on phenol or chlorobenzene.
9. Amines are basic. Basic nature in gaseous state is in the order :  $3^\circ > 2^\circ > 1^\circ > \text{NH}_3$ .
10. Primary, secondary and tertiary amines form quaternary salts with alkyl halides. Primary and secondary amines can be acylated.
11. Primary amines give carbylamine reaction with chloroform and alcoholic potash.
12. Amino group is an activating group. It is ortho- and para- orienting group.
13. Benzene diazonium salt is formed by diazotising aniline with nitrous acid at  $0^\circ\text{C}$ . It is stabilised by resonance.
14. Benzenediazonium chloride gives benzene with hypophosphorus acid or ethanol, but phenol with water.
15. Benzenediazonium chloride gives chlorobenzene with cuprous chloride and  $\text{HCl}$ , iodobenzene with potassium iodide and benzonitrile with potassium cyanide and cuprous cyanide.
16. Benzene diazonium chloride undergoes coupling reaction with phenol or aniline and gives azo-compounds.
17. Cyanides and isocyanides are functional isomers. They are formed by the action of  $\text{KCN}$  and  $\text{AgCN}$  respectively, on alkyl halide.
18. On hydrolysis, cyanides give carboxylic acids and isocyanides give amines.
19. On reduction, cyanides give primary amines and isocyanides give secondary amines.

**CONVERSIONS**

1. Ethanamine to methanamine
2. Methanamine to ethanamine
3. Ethanoic acid to aminomethane
4. Pentyl cyanide to 1-aminopentane
5. Nitromethane to N-methylmethanamine
6. Benzoic acid to aniline
7. Aniline to p-bromoaziline
8. Aniline to benzyl alcohol
9. Benzamide to toluene
10. Benzylchloride to 2-phenylethanamine
11. Aniline to sym-tribromofluorobenzene
12. Chlorobenzene to p-chloroaniline
13. Ethylchloride to propanamine-1
14. Ethyl chloride to 2-phenylethanamine
15. Benzene to N,N-Dimethylaniline
16. 1,4-Dichlorobutane to hexane-1,6-diamine
17. Benzene to p-nitrobenzaldehyde
18. Benzoic acid to m-nitrobenzylalcohol

**ANSWERS to CONVERSIONS**

**CHEMISTRY IIB**



**EXERCISE - 5.2**

- Explain the basic nature of amines. What are the factors influencing basic nature?
- Write a note on coupling reactions of benzene diazonium chloride.
- Write resonance structures to explain the nitration of nitrobenzene giving mainly m-dinitrobenzene.
- Why amines are basic. Explain.
- Aliphatic amines are more basic than aromatic amines. Explain.
- Write the effect of substituents on the basic nature of aniline.
- Give the mechanism of Hofmann bromamide reaction.
- Write the behaviour of aliphatic  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  amines towards reaction with nitrous acid.
- How the three types of amines are distinguished?
- Write the reactions of aliphatic and aromatic primary amines with nitrous acid.
- Aniline is insoluble in water, but ethyl amine is soluble. Explain.
- Aniline is less basic than ammonia. Why?
- How is chlorobenzene prepared from aniline ?
- What is Hinsberg's reagent? How it is useful to identify  $1^\circ$ ,  $2^\circ$ ,  $3^\circ$  amines?
- Write resonance structures of benzene diazonium ion.
- Diazonium salts are useful for preparation of halobenzenes. Give reaction.
- Aromatic amines can not be prepared by Gabriel phthalimide method. Justify.
- Comment on the conversion of methyl chloride into acetaldehyde.

(Hint : Stephen's reaction)

- How ethyl cyanide is converted to diethyl ketone? What are the special features of the conversion?

(Hint : Thorpe's condensation)

- $X \xrightarrow{\text{Sn, HCl}} Y \xrightarrow{\text{KNO}_2, \text{HCl}} Z$ . The compound 'Z' reacts with 'Y' at pH value 6 to give an yellow coloured dye. What is 'X'? (Ans : Nitrobenzene)

- How is aniline converted to benzene? Discuss the reactions. (Hint : via diazonium salt)

- $\text{C}_6\text{H}_5\text{N}_2\text{Cl} \xrightarrow[\text{KCN}]{\text{CuCN}} \text{A} \xrightarrow[\text{H}^+]{\text{H}_2\text{O}} \text{B} \xrightarrow[\Delta]{\text{NH}_3} \text{C} \xrightarrow[\text{NaOH}]{\text{Br}_2} \text{D}$ . Identify the final product, D. (Ans: Aniline)

- $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[\text{H}_2\text{O}]{\text{Br}_2} \text{A} \xrightarrow[0^\circ\text{C}]{\text{NaNO}_2, \text{HCl}} \text{B} \xrightarrow{\text{H}_3\text{PO}_2} \text{C}$ . Identify the organic product 'C'. Write the reactions. (Ans : s-tribromobenzene)

- $\text{X} \xrightarrow{\text{CHCl}_3, \text{KOH}} \text{Y} \xrightarrow{\text{H}_3\text{O}^+} \text{X}$ . If 'Y' is a compound with awful odour, identify the starting compound X? (Ans :  $1^\circ$  amine)

