30

COMPOUNDS OF CARBON CONTAINING NITROGEN

In the previous lesson, you have studied the chemistry of organic compounds containing oxygen atom as a part of the functional group. Now, you will learn about organic compounds containing nitrogen atom as a part of the functional group. An historical importance can be associated with these compounds as the first ever organic compound synthesised in the laboratory was urea which contains nitrogen. Nitrogen containing compounds have wide applications in our daily life. They form a part of dyes, drugs, fertilizers, alkaloids, proteins, etc. Only two classes of nitrogen containing compounds, *viz*. amines and nitro compounds are discussed in this lesson. First, the IUPAC nomenclature of amines has been explained followed by their preparation and chemical properties. The difference in the basicities of aliphatic and aromatic amines has also been described. Finally, the chemistry of nitro compounds is briefly discussed.

Objectives

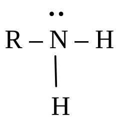
After reading this lesson, you will be able to:

- classify amines as primary, secondary, or tertiary amines;
- write the IUPAC names of amines and nitro compounds;
- describe the general methods of preparation, properties and uses of primary amines and nitro compounds and
- explain the relative basicities of primary, secondary and tertiary aliphatic amines and compare them with the basicities of ammonia and aromatic amines.

30.1 Amines

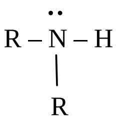
Amines are derivatives of ammonia (NH_3) in which one or more hydrogen atoms are replaced by alkyl or aryl groups. Amines are classified into three different types as primary (1^0), secondary (2^0) and tertiary (3^0) depending on the number of hydrogen atoms replaced by alkyl or aryl groups. In primary amines, only one alkyl or aryl group is attached to the nitrogen atom. In secondary amines, two alkyl or aryl groups are attached to the nitrogen while tertiary amines contain three alkyl or aryl groups attached to the nitrogen atom.

This is illustrated below.



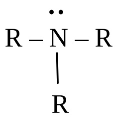
$$\begin{array}{c}\cdot\cdot\\ R-N-H\\ |\\ H\end{array}$$

A primary amine



$$\begin{array}{c}\cdot\cdot\\ R-N-H\\ |\\ R\end{array}$$

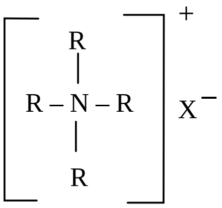
A secondary amine



$$\begin{array}{c}\cdot\cdot\\ R-N-R\\ |\\ R\end{array}$$

A tertiary amine

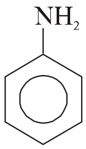
If four alkyl groups are attached to the nitrogen atom, then the quaternary ammonium ion or salt is formed.



$$\left[\begin{array}{c}R\\ |\\ R-N-R\\ |\\ R\end{array}\right]^{+} X^{-}$$

A quaternary ammonium salt

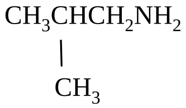
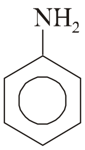
The amino group in aromatic amines is directly bonded to the benzene ring. Aromatic amines are aryl derivatives of ammonia. The parent aromatic amine is known as aniline.



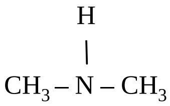
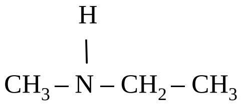
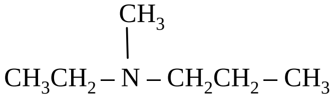
Aniline

30.1.1 IUPAC Nomenclature of Amines

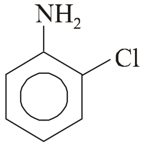
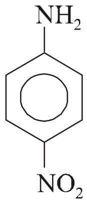
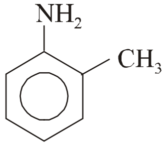
Similar to other classes of compounds which you have studied, amines can also be named according to the IUPAC system. In case of primary aliphatic amines, the longest continuous chain of carbon atoms determines the root name of the compound. The ending –*e* in the name of the corresponding alkane is changed to-*amine*. The other substituents along the carbon chain are given numbers. This is illustrated by the following examples.

Compounds	*IUPAC name*	*Common name*
CH_3NH_2	Methanamine	Methyl amine
$CH_3CH_2NH_2$	Ethanamine	Ethyl amine
$CH_3CH_2CH_2NH_2$	Propan-1-amine	Propyl amine
 $CH_3\underset{\underset{CH_3}{\vert}}{CH}CH_2NH_2$	2-Methyl propan-l-amine	—
	Benzenamine	Aniline

Secondary and tertiary amines are named by using the prefix *N* for each substituent on the nitrogen atom.

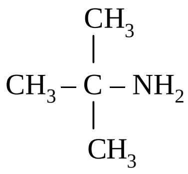
Compound	***IUPAC name***	***Common name***
 $CH_3-\overset{\overset{\displaystyle H}{\vert}}{N}-CH_3$	*N*-Methylmethanamine	Dimethylamine
 $CH_3-\overset{\overset{\displaystyle H}{\vert}}{N}-CH_2-CH_3$	*N*-Methylethanamine	Ethylmethylamine
 $CH_3CH_2-\overset{\overset{\displaystyle CH_3}{\vert}}{N}-CH_2CH_2-CH_3$	*N*-Ethyl-*N*-methylpropan-1-amine	—

The IUPAC names of other aromatic amines are given as derivatives of aniline shown below :

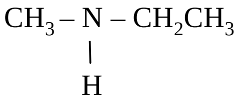
Compound	***IUPAC name***	***Common name***
	2-Chloroaniline	*o*-Chloroaniline
	4-Nitroaniline	*p*-Nitroaniline
	2-Methylaniline	*o*-Toluidine

Intext Questions 30.1

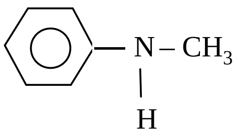
1. Classify the following as primary, secondary, tertiary amines and quaternary ammonium salts :

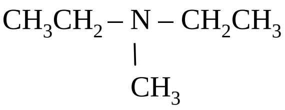
(i) 

$$CH_3-\underset{\underset{\displaystyle CH_3}{\vert}}{\overset{\overset{\displaystyle CH_3}{\vert}}{C}}-NH_2$$

(ii) 

$$CH_3-\underset{\underset{\displaystyle H}{\vert}}{N}-CH_2CH_3$$

(iii) 

(iv) 
$CH_3CH_2-\underset{\underset{CH_3}{|}}{N}-CH_2CH_3$

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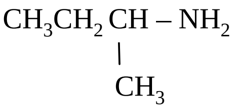
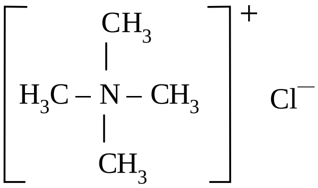
(v) 
$CH_3CH_2\underset{\underset{CH_3}{|}}{CH}-NH_2$

(vi) 
$\left[H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-CH_3\right]^+ Cl^-$

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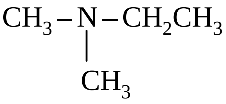
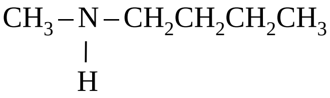
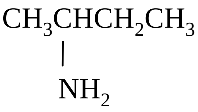
2. Write IUPAC names for the following amines :

(i) $CH_3CH_2CH_2CH_2NH_2$

(ii) 
$CH_3-\underset{\underset{CH_3}{|}}{N}-CH_2CH_3$

....

(iii) 
$CH_3-\underset{\underset{H}{|}}{N}-CH_2CH_2CH_2CH_3$

(iv) 
$CH_3\underset{\underset{NH_2}{|}}{C}HCH_2CH_3$

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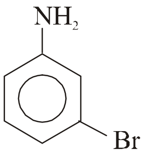
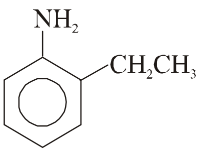
(v) 

(vi) 

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30.1.2 Preparation of Amines

Several methods are available for the preparation of primary aliphatic and aromatic amines. In this section, you will learn some of the methods which are generally used for their perparation.

(i) ***From alkyl halides***

Alkyl halides react with ammonia to form primary amines.

$$R - X + 2\ NH_3 \longrightarrow R\ NH_2 + NH_4X$$

The primary amine so formed may further react to give a secondary amine, tertiary amine or a quaternary ammonium salt. So in order to get good yield of the primary amine, the reaction is carried out using excess of ammonia. For example, bromoethane on reaction with excess of ammonia gives ethanamine.

$$\underset{\textbf{Bromoethane}}{C_2H_5Br} + 2\ NH_3 \longrightarrow \underset{\textbf{Ethanamine}}{C_2H_5NH_2} + NH_4Br$$

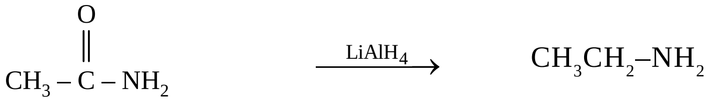
(ii) ***By reduction of nitriles (cyanides), amides and nitro compounds***

Compounds containing cyano, amido or nitro groups can be reduced into the corresponding primary amines.

Nitriles can be reduced by hydrogen in the presence of platinum catalyst or by sodium in presence of ethanol to corresponding primary amines. For example, propanenitrile (cyano ethane) on reduction gives propan-l-amine.

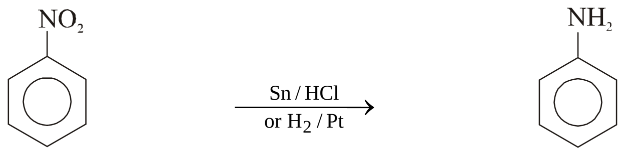
$$\underset{\textbf{Propanenitrile}}{CH_3CH_2C{\equiv}N} \xrightarrow[\text{or Na / }C_2H_5OH]{H_2\text{ / Pt}} \underset{\textbf{Propan-l-amine}}{CH_3CH_2CH_2{-}NH_2}$$

Similarly, amides are reduced by $LiAlH_4$ to primary amines having same number of carbon atoms as in the starting amide. For example, ethanamide gives ethanamine on reduction.



$$\underset{\textbf{Ethanamide}}{CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2} \xrightarrow{LiAlH_4} \underset{\textbf{Ethanamine}}{CH_3CH_2{-}NH_2}$$

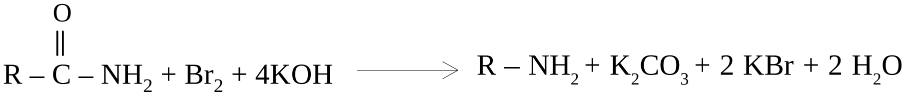
Reduction of nitro compounds can be carried out by using hydrochloric acid and a metal such as Sn or Fe. They can also be reduced with hydrogen in presence of Ni or Pt as catalyst. Such a reduction of nitrobenzene by any of these methods provides aniline.



Nitrobenzene **Aniline**

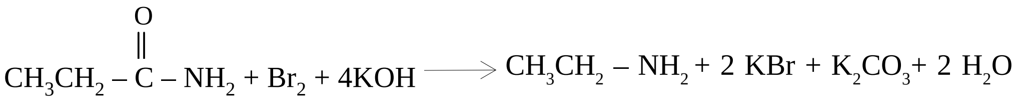
(iii) ***By Hofmann bromamide reaction***

Aliphatic amides on treatment with bromine and a strong base like potassium hydroxide are converted into primary amines having one carbon less than those present in the starting amide.



$$\underset{\textbf{Amide}}{R - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2} + Br_2 + 4KOH \longrightarrow \underset{\textbf{Amine}}{R - NH_2} + K_2CO_3 + 2\ KBr + 2\ H_2O$$

Thus, ethanamine is obtained by treating propanamide with bromine and KOH.



$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow CH_3CH_2-NH_2 + 2\,KBr + K_2CO_3 + 2\,H_2O$$

Propanamide **Ethanamine**

30.1.3 Physical Properties of Amines

Aliphatic amines containing up to three carbon atoms are gases whereas higher amines are liquids. Some higher aromatic amines are even solids. Methyl and ethyl amines have smell like ammonia. Amines have higher boiling points than the corresponding hydrocarbons because they form hydrogen bonds amongst themselves. Lower amines are soluble in water and the solubility decreases with the increase in size of the alkyl group. This solubility is because of the presence of hydrogen bonding between the amino group and water molecules. All amines are soluble in organic solvents like benzene, alcohol, ether etc.

30.1.4 Chemical Properties of Amines

(i) ***Basic Character***

Amines are basic in nature due to the presence of a lone pair of electrons on nitrogen. You know that the strength of a base depends upon the availability of electrons. Basicities of amines can be compared with respect to ammonia, by comparing the availability of pair of electrons on nitrogen. Ammonia and amines, both when dissolved in water, attract a proton from water to form an ammonium or alkylammonium ion, respectively, and a hydroxide ion.

$$\ddot{N}H_3 + H-O-H \longrightarrow \underset{\textbf{Ammonium ion}}{NH_4^+} + OH^-$$

$$R-\ddot{N}H_2 + H-O-H \longrightarrow \underset{\textbf{Alkylammonium ion}}{R-NH_3^+ + OH^-}$$

You know that aliphatic amines contain one or more alkyl groups in place of hydrogen atoms of ammonia. Since alkyl groups are electron releasing groups, they increase the electron density on nitrogen. This makes the lone pair of electrons on nitrogen atom to be easily available for sharing and hence, this increases the basicity of the amine. So, we expect that the basicities of the amines would increase as we move from primary to secondary to tertiary amines.

But the order of the basicities has been found to be

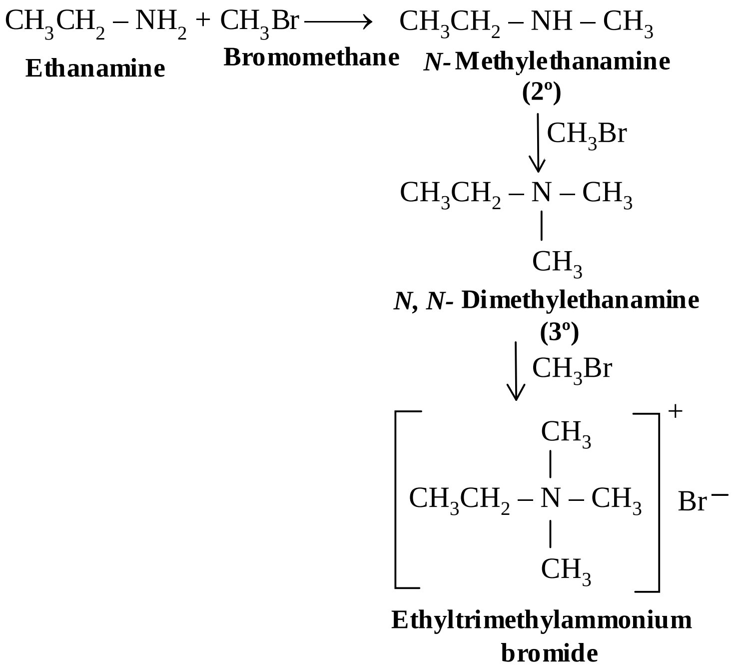
$$\underset{\textbf{Primary }(1^0)}{R-NH_2} < \underset{\textbf{Secondary }(2^0)}{R_2\,NH} > \underset{\textbf{Tertiary }(3^0)}{R_3N}$$

The tertiary amines are less basic than secondary amines. The reason is that a tertiary amine, though has three alkyl groups which can donate electrons to the nitrogen atom but they also cause crowding (also called *steric hinderance*) around nitrogen. This hinders the protonation at nitrogen atom and hence, reduces the basicity.

The aromatic amines are weaker bases than ammonia because the aromatic ring is electron withdrawing. It reduces the electron density at nitrogen and makes the aromatic amines less basic. So we can express the basic character of aliphatic and aromatic amines as shown below.

Aromatic amines < Ammonia < Aliphatic amines

(ii) ***Alkylation :*** Primary amines react with alkyl halides to give secondary amines. The reaction may continue further to form a tertiary amine and a quaternary ammonium salt. For example, the reaction of ethanamine with bromomethane proceeds as shown below.



$$CH_3CH_2-NH_2 + CH_3Br \longrightarrow CH_3CH_2-NH-CH_3$$

Ethanamine **Bromomethane** ***N*-Methylethanamine (2°)**

$$\downarrow CH_3Br$$

$$CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$$

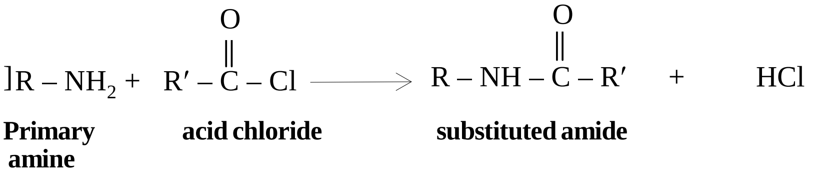
***N, N*- Dimethylethanamine (3°)**

$$\downarrow CH_3Br$$

$$\left[CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{N}}}}-CH_3\right]^+ Br^-$$

Ethyltrimethylammonium bromide

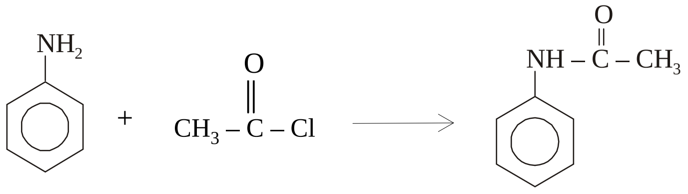
(iii) ***Acylation :*** Primary amines on reaction with acid chlorides or acid anhydrides give *N*-substituted amides.



$$R-NH_2 + R'-\overset{\displaystyle O}{\overset{||}{C}}-Cl \longrightarrow R-NH-\overset{\displaystyle O}{\overset{||}{C}}-R' + HCl$$

Primary amine **acid chloride** **substituted amide**

For example, aniline on reaction with ethanoyl chloride (acetyl chloride) gives acetanilide.



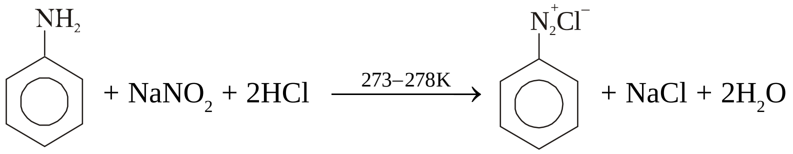
Aniline **Ethanoyl chloride** **Acetanilide**

(iv) ***Carbylamine reaction :*** When a primary amine is heated with chloroform in the presence of alcoholic potassium hydroxide, then the corresponding isocyanide is formed. Isocyanides are also known as **carbylamines**, hence this reaction is called as **carbylamine reaction**. For example, aminoethane on undergoing this reaction, gives ethyl carbylamine.

$$\underset{\textbf{Ethylamine}}{CH_3CH_2-NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\textbf{Ethyl carbylamine}}{CH_3CH_2\,N \equiv C} + 3KCl + 3H_2O$$

Isocyanides give a very offensive odour, so this reaction is also used as a test for primary amines.

(v) ***Reaction with nitrous acid :*** Primary aromatic amines react with nitrous acid to give diazonium salts and this reaction is known as **diazotisation**. Nitrous acid is an unstable compound and can not be stored, so it is prepared during the reaction by mixing sodium nitrite and hydrochloric acid. The reaction is specifically carried out at low temperature between 273 – 278 K. For example, aniline reacts with nitrous acid to give benzene diazonium chloride.



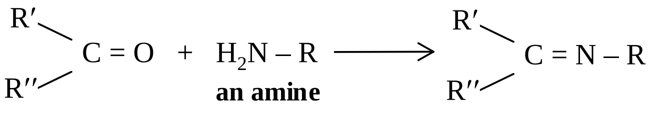
Aniline

Benzene diazonium chloride
(a diazonium salt)

Primary aliphatic amines also react in a similar way but the diazonium salts formed are unstable and decompose to give alcohols and nitrogen gas. Thus, ethanamine gives ethanol when subjected to this reaction.

$$\underset{\textbf{Ethanamine}}{CH_3CH_2-NH_2} \xrightarrow{NaNO_2\,/\,HCl} \underset{\substack{\textbf{Ethyldiazonium chloride}\\ \textbf{Unstable diazonium salt}}}{[CH_3CH_2N_2^+\ Cl^-]} \xrightarrow{H_2O} \underset{\textbf{Ethanol}}{CH_3CH_2-OH} + N_2\uparrow + HCl$$

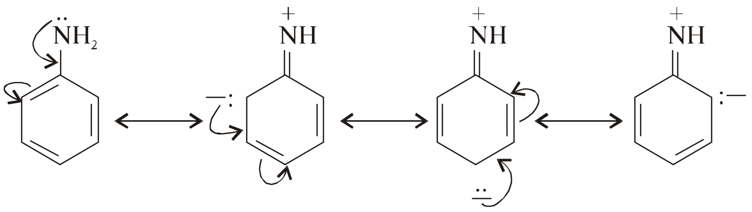
(vi) Primary amines undergo condesnsation with aldehydes or ketones to form **imines**. These products are also called **Schiff's bases**. The reaction can be shown as follows :



$$\begin{matrix}R' \\ R''\end{matrix}\!\!>C=O + \underset{\textbf{an amine}}{H_2N-R} \longrightarrow \begin{matrix}R' \\ R''\end{matrix}\!\!>C=N-R$$

a Schiff's base

(vii) ***Ring substitution in aromatic amines :*** You know that – NH_2 group is a strong activating and *ortho*-, *para*- directing group for electrophilic aromatic substitution reactions. This directive influence can be explained by the following resonating structures of aniline.

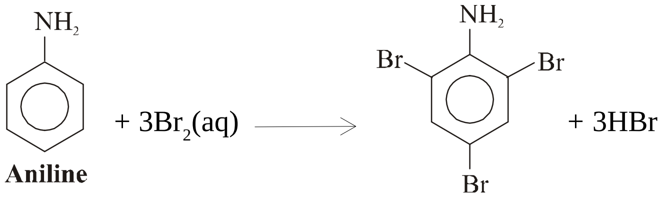


Resonance structures of aniline

As a result of this resonance, the electron density is more at *ortho*- and *para*- positions; hence, the electrophilic substitution occurs at these positions.

Some important ring substitution reactions of aromatic amines are halogenation, nitration and sulphonation.

(a) ***Halogenation :*** Aniline on treatment with an aqueous solution of bromine gives 2,4,6 - tribromoaniline.



Aniline

2,4,6-Tribromoaniline

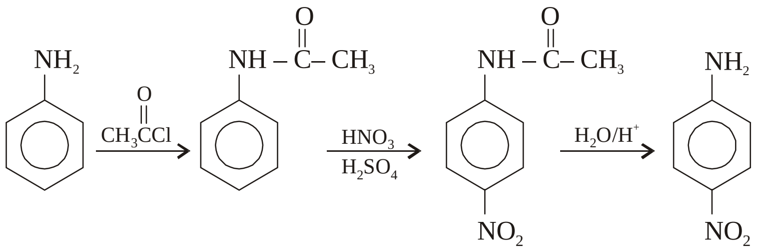
Aniline is very reactive and all the three hydrogen atoms at *ortho*- and *para*- positions are substituded with bromine atoms.

(b) ***Nitration :*** Nitration of aniline is carried out on the acetylated amine (acetanilide) rather than on the free amine itself. There are two reasons for this.

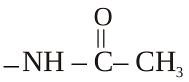
(i) The free amine is very susceptible to oxidation and thus much of it is lost in the form of a black-sticky material which is fomed as result of its oxidation.

(ii) The free amine is very reactive but acetyl the group protects it and reduces its reactivity.

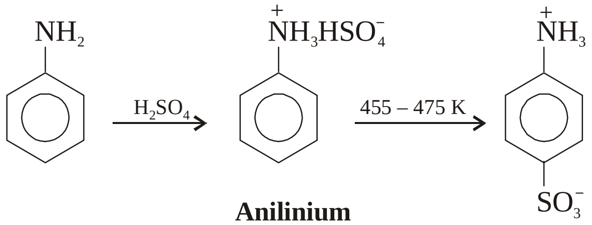
The nitration of aniline with the protection of the amino group is shown below:



Aniline **Acetanilide** ***p*-Nitroacetanilide** ***p*-Nitroaniline**

The first step consists of acetylation of the amino group in aniline. The conversion of $-NH_2$ to  $-NH-\overset{O}{\overset{||}{C}}-CH_3$, lowers the activity of $-NH_2$ group because of electron withdrawal by $-\overset{\displaystyle O}{\overset{||}{C}}-CH_3$. This step is followed by nitration (conc. HNO_3 / H_2SO_4) which gives mainly the *p*-nitroacetanilide. This, 'on acid hydrolysis' yields the desired product *p*-nitroaniline.

(c) ***Sulphonation :*** Sulphonation is carried out in the presence of sulphuric acid. The amino group in aniline is a basic group. Therefore, an acid-base reaction takes place to form anilinium hydrogensulphate salt. This salt undergoes rearrangement at a high temperature to give sulphanilic acid.



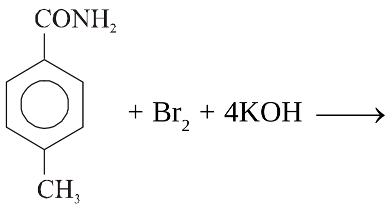
Aniline **Anilinium hydrogensulphate** **Sulphanilic acid**

30.1.5 Uses of Amines

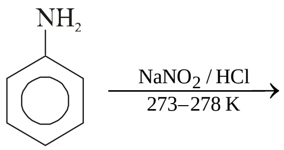
Amines are very useful compounds. They are used for a variety of purposes in the laboratory as well as in the industry. Some aliphatic amines are used as solvents and intermediates in drug synthesis. The quaternary ammonium salts derived from long chain aliphatic tertiary amines are widely used as detergents. Aromatic amines e.g. aniline and its derivatives, are used for the production of dyes, drugs and photographic developers. 1,4-Diaminobenzene is the main ingredient of all hair dyes. Many dithiocarbamates which are the compounds derived from primary amines, are used as herbicides. Diazonium salts obtained from primary aromatic amines form the basis of synthesis of many other organic compounds.

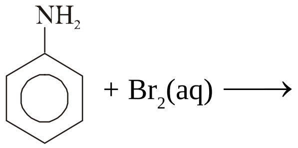
Intext Questions 30.2

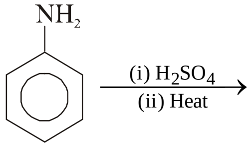
1. Predict the major product of the following reactions :

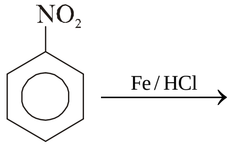
(a) 

(b) $CH_3CH_2NH_2 \xrightarrow{NaNO_2 / HCl}$

(c) 

(d) 

(e) 

(f) 

....

2. Why is aniline very reactive towards bromination?

....

3. Name the test which uses potassium hydroxide and chloroform for identifying a primary amine.

....

4. Can aniline be nitrated directly?

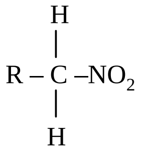
....

5. How will you obtain sulphanilic acid from benzene?

....

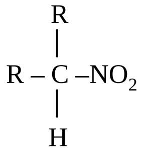
30.2 Nitro Compounds

Nitro compounds are those derivatives of hydrocarbons in which a hydrogen atom is replaced by a nitro ($–NO_2$) group. They may be aliphatic or aromatic. Nitroalkanes are divided into primary (1^0), secondary (2^0) or tertiary (3^0) nitro alkanes depending upon the attachment of nitro group to primary, secondary or tertiary carbon atom, respectively.



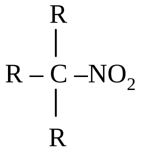
$$R - \overset{\displaystyle H}{\underset{\displaystyle H}{C}} - NO_2$$

***p*-nitroalkane**



$$R - \overset{\displaystyle R}{\underset{\displaystyle H}{C}} - NO_2$$

sec-nitroalkane

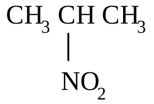
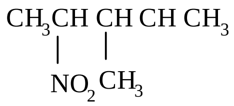
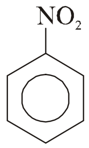
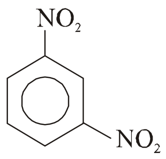


$$R - \overset{\displaystyle R}{\underset{\displaystyle R}{C}} - NO_2$$

tert-nitroalkane

30.2.1 IUPAC Nomenclature of Nitro Compounds

According to IUPAC system, nitro compounds are named by prefixing the word nitro before the name of the parent hydrocarbon. The number of nitro groups and their positions are suitably indicated as shown in some examples given below.

Compound	IUPAC Name
CH_3-NO_2	Nitromethane
$CH_3CH_2-NO_2$	Nitroethane
 $CH_3\underset{\displaystyle NO_2}{\underset{\mid}{CH}}CH_3$	2-Nitropropane
 $CH_3\underset{\displaystyle NO_2}{\underset{\mid}{CH}}\underset{\displaystyle CH_3}{\underset{\mid}{CH}}CH\,CH_3$	2-Nitro - 3- methylbutane
	Nitrobenzene
	1, 3 - Dinitrobenzene (*m* - Dinitrobenzene)

30.2.2 Preparation of Nitro Compounds

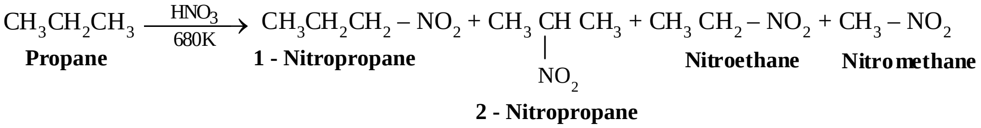
(i) ***From alkyl halides :*** Nitroalkanes are prepared by heating an alkyl halide with aqueous ethanolic solution of silver nitrite. In this reaction, a small amount of isomeric alkyl nitrites (R–O–N = O) is also obtained.

$$R-X + AgNO_2 \longrightarrow R-NO_2 \quad + \quad AgX$$

For example. bromoethane on reaction with silver nitrite gives nitroethane.

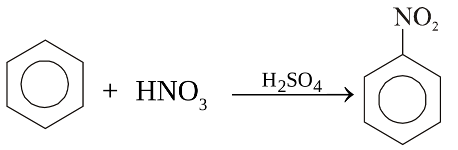
$$\underset{\textbf{Bromoethane}}{CH_3CH_2Br} + AgNO_2 \longrightarrow \underset{\textbf{Nitroethane}}{CH_3CH_2NO_2} + AgBr$$

(ii) ***By nitration of alkanes :*** Nitroalkanes can also be prepared by the nitration of alkanes in vapour phase. For this reaction, a mixture of the alkane and nitric acid is passed through a metal tube at about 680 K. This reaction always yields a mixture of compounds due to the cleavage of the starting alkane. For example, propane on nitration gives a mixture of following compounds.



$$\underset{\textbf{Propane}}{CH_3CH_2CH_3} \xrightarrow[680K]{HNO_3} \underset{\textbf{1 - Nitropropane}}{CH_3CH_2CH_2-NO_2} + \underset{\textbf{2 - Nitropropane}}{CH_3\underset{\displaystyle NO_2}{\underset{\mid}{CH}}CH_3} + \underset{\textbf{Nitroethane}}{CH_3CH_2-NO_2} + \underset{\textbf{Nitromethane}}{CH_3-NO_2}$$

(iii) ***By nitration of aromatic compounds :*** Aromatic nitro compounds are almost always prepared by direct nitration. For example, nitration of benzene gives nitrobenzene. The reaction is generally carried out with a mixture of concentrated nitric acid and concentrated sulphuric acid.



Benzene **Nitrobenzene**

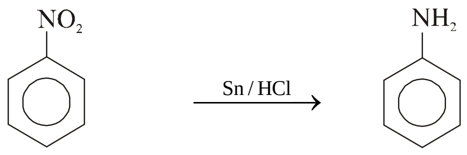
30.2.3 Physical Properties of Nitro Compounds

Nitroalkanes are colourless oily liquids in the pure state. They have pleasant smell. They possess higher boiling points than the corresponding alkanes because of their polar nature. Amongst the aromatic nitro compounds, nitrobenzene is a yellow liquid with the smell of bitter almonds. Most other aromatic nitro compounds are yellow crystalline solids. All the nitro compounds are heavier than water and insoluble in it. They are, however, soluble in organic solvents like alcohol, ether, benzene, chloroform etc.

30.2.4 Chemical Properties of Nitro Compounds

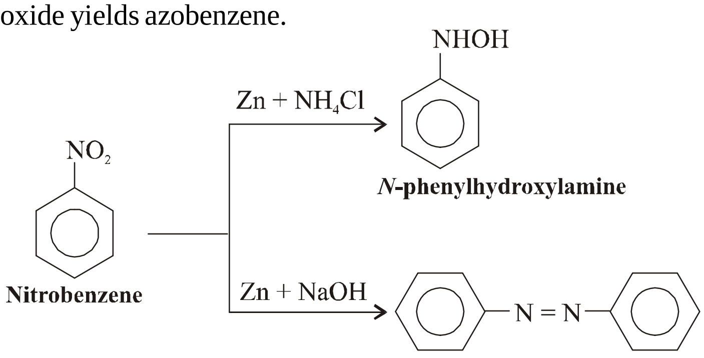
(i) ***Reduction :*** One of the important reactions of nitro compounds is reduction. Nitro compounds can be readily reduced to primary amines by a variety of reducing agents. For example, (a) hydrogen in presence of catalyst like nickel or platinum (b) a metal like tin or iron in presence of hydrochloric acid and (c) lithium aluminium hydride. Reduction of nitroethane and nitrobenzene provides ethanamine and aniline, respectively.

$$\underset{\textbf{Nitroethane}}{CH_3CH_2-NO_2} + 3H_2 \xrightarrow{Ni} \underset{\textbf{Ethanamine}}{CH_3CH_2-NH_2} + 2H_2O$$



Nitrobenzene **Aniline**

Nitrobenzene on reduction in neutral medium, using zinc dust and ammonium chloride yields *N*-phenylhydroxylamine whereas its reduction in alkaline medium using zinc and sodium hydroxide yields azobenzene.



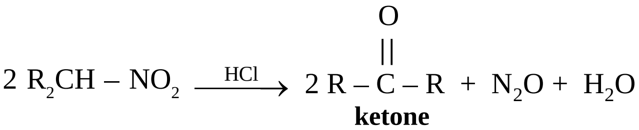
Nitrobenzene ***N*-phenylhydroxylamine** **Azobenzene**

(ii) ***Hydrolysis :*** Primary nitroalkanes on reaction with dilute hydrochloric acid or sulphuric acid undergo hydrolysis to produce carboxylic acids and hydroxylamine.

$$RCH_2 - NO_2 + H_2O \xrightarrow{HCl} R - COOH + NH_2OH$$

A carboxylic acid **Hydroxylamine**

Secondary nitroalkanes on hydrolysis form ketones.



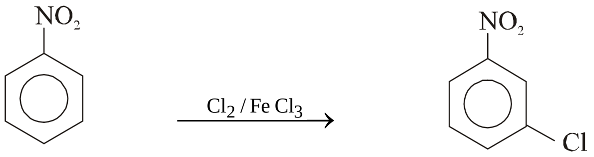
$$2\ R_2CH - NO_2 \xrightarrow{HCl} 2\ R - \overset{\overset{\displaystyle O}{||}}{C} - R + N_2O + H_2O$$

ketone

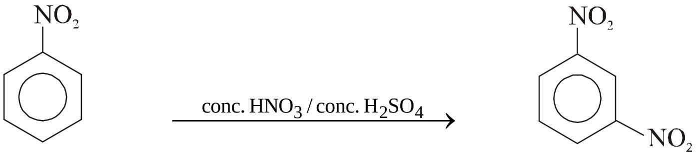
(iii) ***Thermal decomposition :*** Nitroalkanes decompose with explosion on heating. Advantage is taken of this reaction in the commercial use of nitroalkanes as explosives. It is due to the formation of large volume of gaseous products on heating which produce high pressure.

$$2\ CH_3NO_2 \xrightarrow{\Delta} N_2 + 2\ CO_2 + 3\ H_2$$

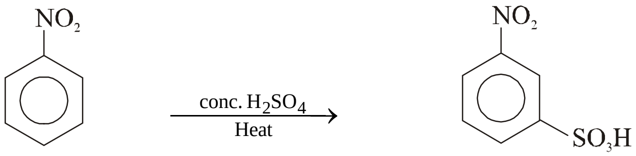
(iv) ***Ring substitution in aromatic nitro compounds*** : You know that $-NO_2$ group is a deactivating and *meta* - directing group for electrophilic substitution reactions. It is due to the electron withdrawing tendency of $-NO_2$ group. Thus, nitrobenzene on halogenation, nitration or sulphonation gives the *meta*-substituted products as shown below.



Nitrobenzene **3-Chloronitrobenzene**



Nitrobenzene **1, 3-Dinitrobenzene**



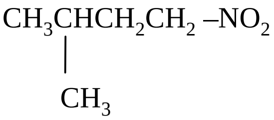
Nitrobenzene **3-Nitrobenzenesulphonic acid**

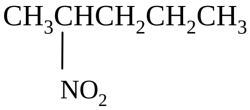
30.2.5 Uses of Nitro Compounds

1. Nitroalkanes are used as solvents for rubber, cellulose acetate etc.
2. They are used as intermediates in the industrial production of explosives, detergents, medicines, amines etc.
3. Nitro compounds are also used as fuel in small engines and rockets.

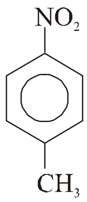
Intext Questions 30.3

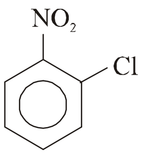
1. Write IUPAC names of the following :

(a)

$CH_3CH(CH_3)CH_2CH_2-NO_2$

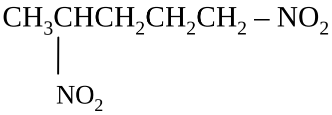
(b)

$CH_3CH(NO_2)CH_2CH_2CH_3$

....

(c)


(d)


....

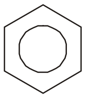
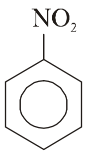
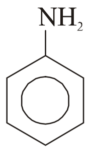
(e)

$CH_3CH(NO_2)CH_2CH_2CH_2-NO_2$

....

2. Write the product formed when 1,3 - dinitrobenzene is treated with tin and hydrochloric acid.

....

3. Arrange the following compounds in increasing order of their reactivity towards halogenation.


,

,


....

4. Which reaction of nitroalkanes makes them suitable to be used as rocket fuel?

....

What You Have Learnt

- Amines are considered as derivatives of ammonia. They are classified as primary, secondary or tertiary based on how many alkyl groups have replaced the hydrogen atoms of ammonia.
- Reaction of alkyl halides with ammonia produces a mixture of primary, secondary or tertiary amines alongwith quaternary ammonium salts.

- Reduction of nitriles, amides and nitro compounds gives amines having the same number of carbon atoms.
- In Hofmann bromamide reaction, the amine formed has one carbon less than the starting amide.
- Both aliphatic and aromatic amines are basic in nature. But aromatic amines are less basic and aliphatic amines are more basic than ammonia. An aliphatic secondary amine is more basic than primary and tertiary amines.
- Primary amines can be differentiated from secondary and tertiary amines by carbylamine reaction.
- Aliphatic primary amines undergo diazotisation to form alcohols whereas aromatic primary amines form diazonium salts.
- The amino group ($–NH_2$) is an activating and *ortho*-, *para*-directing group towards the electrophilic aromatic substitution reactions.
- Nitroalkanes are obtained by the reaction of alkyl halides with alcoholic silver nitrite.
- Nitrobenzene is obtained by the direct nitration of benzene with conc. HNO_3 in the presence of conc. H_2SO_4.
- Primary nitroalkanes are hydrolysed in acidic medium to give carboxylic acids whereas secondary nitroalkanes give ketones.
- All nitro compounds are reduced into amino compounds by (i) hydrogen in presence of catalyst or (ii) tin or iron in presence of hydrochloric acid.
- Nitro group is deactivating and *meta*-directing group towards electrophilic aromatic substitution reactions.

Terminal Exercise

1. Write the structural formula of the following compounds :

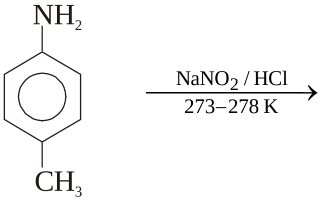
   (i) 2-Methylpropan - 2-amine (ii) Butan - 2-amine

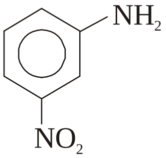
   (iii) *N* - Ethyl - *N* - methylbutan - 1- amine (iv) 2 - Methyl - 2-nitropropane

   (v) 4 - Nitrotoluene

2. What do you understand by diazotisation? Write the product of following reactions.

(8)

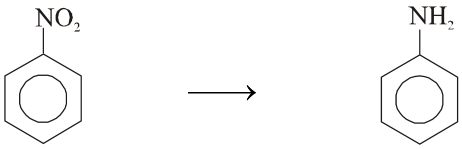


(ii)  $\xrightarrow[273-278\ K]{NaNO_2\ /\ HCl}$

(iii) $CH_3–CH_2–CH_2–NH_2 \xrightarrow[273-278\ K]{NaNO_2\ /\ HCl}$

3. How will you prepare butan-1-amine starting from a suitable amide? Name the reaction involved.

4. What different reagents can be used for the following conversion?



5. Arrange the following amines in increasing order of their basicities :

   Ethanamine, *N*-Methylethanamine, Aniline

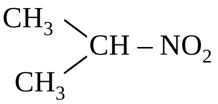
6. How will you prepare sulphanilic acid from nitrobenzene?

7. What happens when ethanamine is treated with excess of chloroethane?

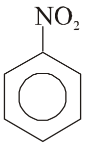
8. Write the reaction sequence to convert nitromethane into ethanamine.

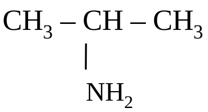
9. How will you prepare *para*-bromoaniline from nitrobenzene? Can this compound be obtained by direct bromination of aniline with aqueous solution of bromine? Explain.

10. Complete the following reactions :

(i)  $(CH_3)_2CH-NO_2 \xrightarrow{dil.\ HCl}$?

(ii) $CH_3CH_2CH_2CONH_2 \xrightarrow{Br_2\ /\ KOH}$? $\xrightarrow[273-278\ K]{NaNO_2\ /\ HCl}$?

(iii)  $\xrightarrow[heat]{HNO_3\ /\ H_2SO_4}$

(iv)  $CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3 \xrightarrow{CHCl_3\ /\ KOH}$?

(v) $CH_3CH_2CH_2– Br + AgNO_2 \xrightarrow{alcohol}$?

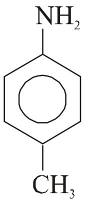
Answers to Intext Questions

30.1

1. (i) Primary amine (ii) Secondary amine (iii) Secondary amine
   (iv) Tertiary amine (v) Primary amine (vi) Quaternary ammonium salt
2. (i) Butan-1-amine
   (ii) *N*, *N*-Dimethylethanamine
   (iii) *N*-Methylbutan-1- amine
   (iv) Butan-2-amine
   (v) 3-Bromoaniline
   (vi) 2-Ethylaniline

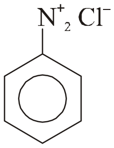
30.2

1. (i)

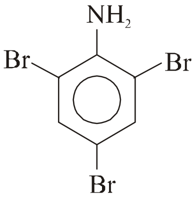


(ii) CH_3CH_2OH

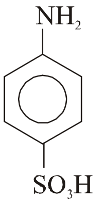
(iii)



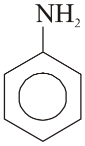
(iv)



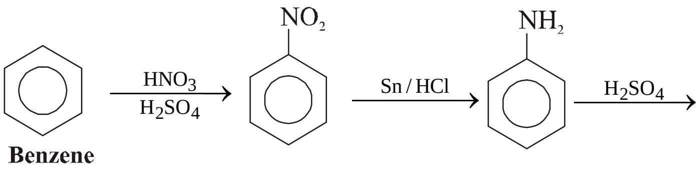
(v)

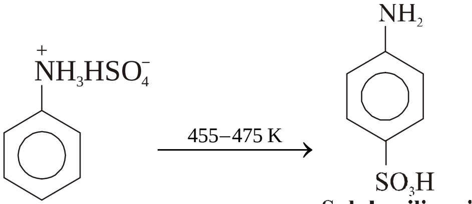


(vi)



2. Aniline is very reactive towards bromination because the –NH_2 group is a highly activating group.
3. Carbylamine test.
4. No
5.





Sulphanilic acid

30.3

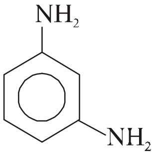
1. (i) 3-Methyl-1-nitrobutane

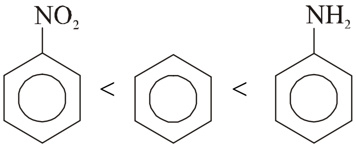
   (ii) 2-Nitropentane

   (iii) 4- Nitrotoluene

   (iv) 2-Chloronitrobenzene

   (v) 1,4 –Dinitropentane

2. 

3. 

4. Nitroalkanes decompose on heating and produce large volume of gases. The formation of gaseous products at high pressure produces the thrust which is necessary for the movement of rocket.