

30

Compounds of Carbon Containing Nitrogen

30.1 INTROCUCTION

In the previous lesson you have studied 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. Nitrogen containing compounds have wide applications in our daily life. They form a part of dyes, drugs, fertilizers, alkaloids, proteins, etc. Three types of the compounds, viz. amines, amides and nitro compounds will be discussed. The IUPAC nomenclature of amines will be discussed first, followed by their preparation and chemical proeprties. A difference in the basicity of aliphatic and aromatic amines is also intended. The amides and nitro compounds will be taken up later

30.2 OBJECTIVES

After reading this lesson you will be able to:

- identify the different functional groups containing nitrogen,
- distinguish between primary, secondary and tertiary amines,
- write the IUPAC names of amines, amides and the nitro compounds,
- describe the preparation of ethanamine and aniline,
- explain the chemical reactions of amines and
- differentiate between the basicity of ethanamine and aniline.

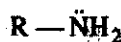
30.3 AMINES

Amines contain the functional group $-NH_2$ as a part of the molecule. The nitrogen atom forms three covalent bonds that are typical of ammonia. There are two remaining electrons on the nitrogen atom. Amines are derivative of ammonia in which one or more hydrogen atoms are replaced by alkyl or aryl groups. The amino group is present in a number of substances as stated earlier. amines are classified into three different types as primary (1°), secondary (2°) and tertiary (3°) depending on the number of hydrogen atoms displaced. In primary amines, N- is attached directly to one alkyl or aryl group, in secondary two alkyl groups are attached to N while tertiary cont. three alkyl groups attached to N atom.

This is exemplified below.



Primary amines

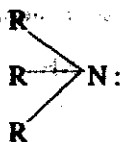


Ammonia

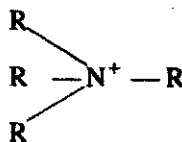
Secondary amines



Tertiary amines

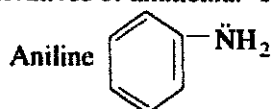


If four alkyl groups are attached to nitrogen atom, then it is called quaternary ammonium salt.



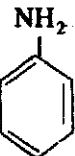
A quaternary ammonium salt

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



30.3.1 IUPAC Nomenclature of Amines

Similar to other classes of compounds you have studied, amines can be named on the basis of IUPAC system. Amines are named similar to alcohols. The longest continuous chain of carbon atoms determine the root name. The e-ending of the name is changed to *-amine*. Substituents along the carbon chain are given numbers. This is illustrated by the following examples.

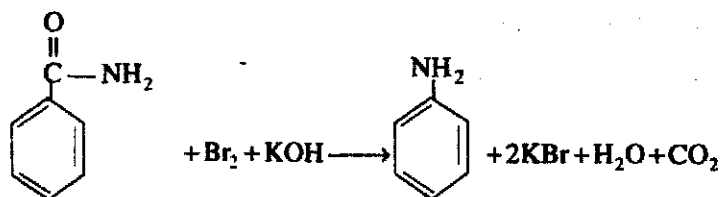
<i>Amines</i>	<i>IUPAC name</i>	<i>Common name</i>
CH_3NH_2	Methanamine	Methyl amine
$\text{CH}_3\text{CH}_2\text{NH}_2$	Ethanamine	Ethyl amine
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	Propanamine	Propyl amine
$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{NH}_2 \\ \\ \text{CH}_3 \end{array}$	2-Methyl-1-propanamine	
	Benzenamine	Aniline

Primary and secondary amines are named by using the prefix N for each substituent on the nitrogen atom.

From the above reaction, it is observed that the starting amide has three carbons but the product ethanamine has only two. This reaction can thus be employed to step-down the homologous series.

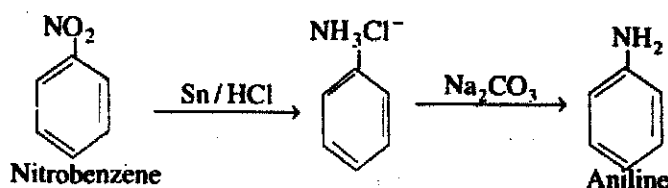
(ii) Preparation of Aniline from Benzamide:

Aniline can similarly be obtained by the Hofmann amide reagent using benzamide



(iii) Preparation of Aniline from nitrobenzene:

Nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) on treatment with tin and hydrochloric acid (a reducing agent) or iron and hydrochloric acid yields aniline.

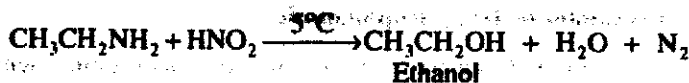


30.3.3 Properties of Ethanamine and Aniline

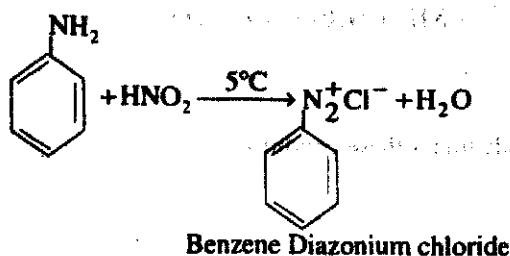
Both aliphatic and aromatic amines are basic. This makes them soluble as salts in dil. hydrochloric acid. The simplest aliphatic amines are gases soluble in water and have strong ammonia-like odour. Aniline is a liquid and insoluble in water.

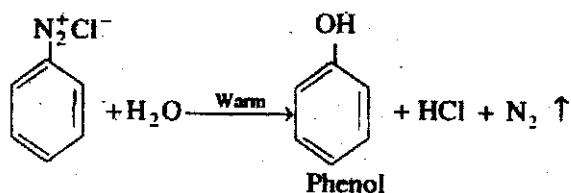
Chemical Properties

(i) Reaction with Nitrous acid: Both ethanamine and aniline react with nitrous acid ($\text{NaNO}_2 + \text{HCl}$) at low temperature. Aliphatic amines form alcohol while aniline yields a stable benzene diazonium salt.



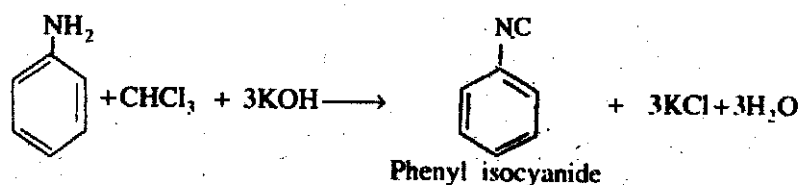
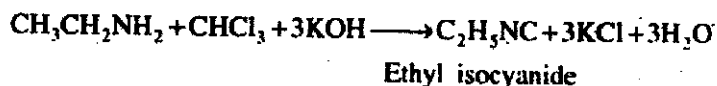
Aniline under these conditions yields a stable diazonium salt. This salt on warming is hydrolyzed to phenol.



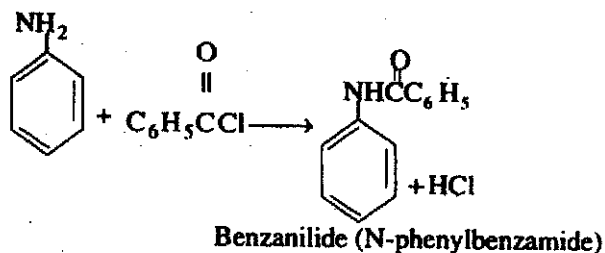
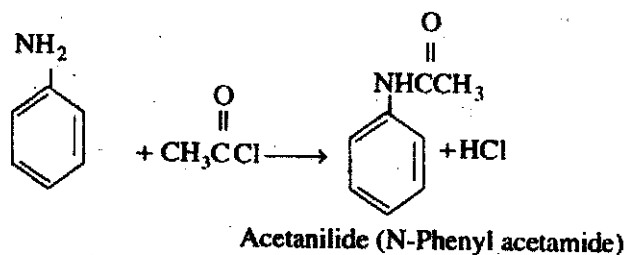
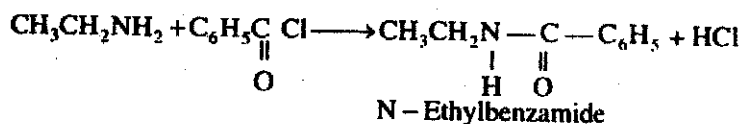
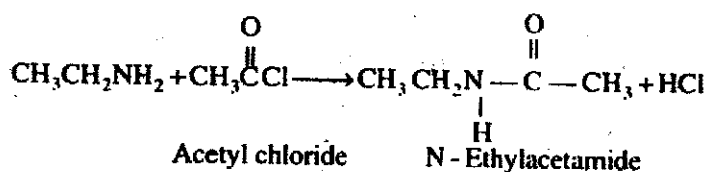


The process of formation of a diazonium salt from an aromatic amine is called *diazotization*.

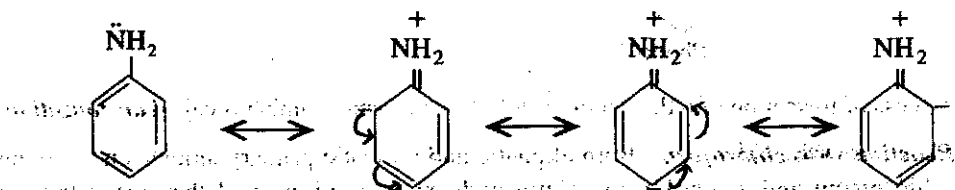
(ii) **Reaction with chloroform:** Both aliphatic and aromatic primary amines on warming with chloroform and alcoholic potassium hydroxide solution yield the corresponding isocyanides (carbylamines). The isocyanides give a very foul smell and thus this reaction is employed as a test for detecting primary amines and is called the *carbylamine test*.



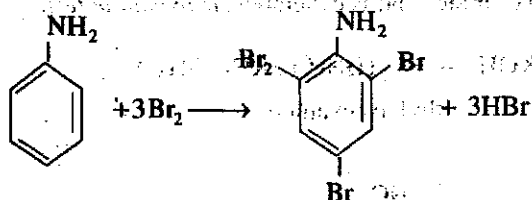
(iii) **Reaction with Acid Chlorides:** Both types of amines react with acid chlorides namely, acetyl chloride and benzoyl chloride to give alkyl or aryl substituted amides.



(iv) **Ring Substitution in Aniline:** The aromatic amine (aniline) undergoes the typical substitution reactions of the benzene ring. The most important reactions are halogenation, nitration and sulphonation. The -NH_2 group in aniline is *ortho*- and *para*-directing.

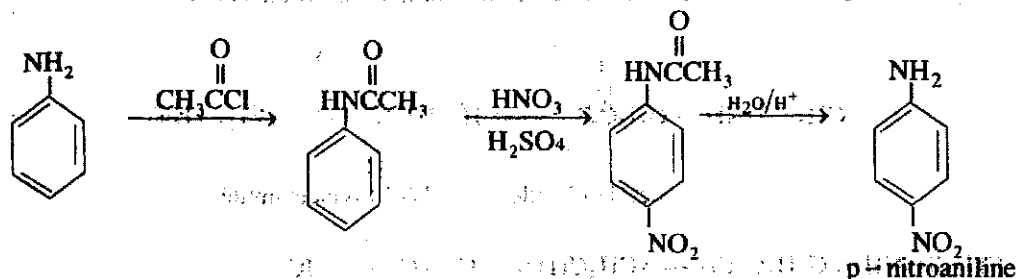


(i) **Halogenation:** On treatment of aniline with an aqueous solution of bromine, tribromoaniline (2,4,6-tribromoaniline) is obtained.



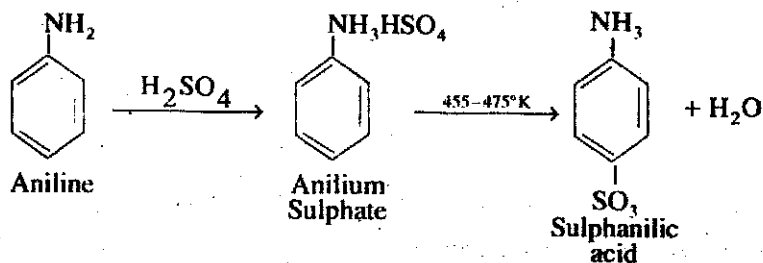
Aniline is very reactive and all the three *ortho*- and *para* positions are substituted with bromine.

(ii) **Nitration of Aniline:** Nitration of aniline is carried out on the acetylated amine (N-phenylacetamide) rather than on the free amine itself. There are two reasons for this (i) free amine is very susceptible to oxidation and thus much of it is lost in the form of tarry material. (ii) the free amine is very reactive but acetylation controls its reactivity. The reaction of aniline with the protection of amino group is shown below:



The first step consists of acetylation of the amino group in aniline. The conversion of -NH_2 to $\text{-NH}-\overset{\text{O}}{\parallel}{\text{C}}\text{CH}_3$, lowers the activity of -NH_2 group because of electron withdrawal of $\text{-C}(=\text{O})\text{CH}_3$ group. This step is followed by nitration ($\text{HNO}_3/\text{H}_2\text{SO}_4$) which gives mainly the *p*-nitro acetanilide. This on acid hydrolysis yields the desired product *p*-nitroaniline.

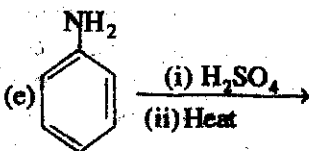
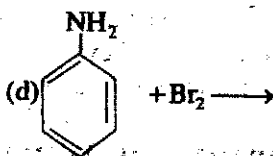
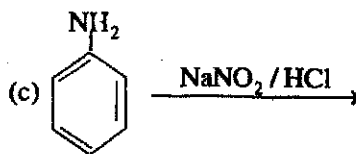
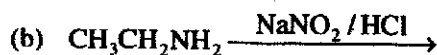
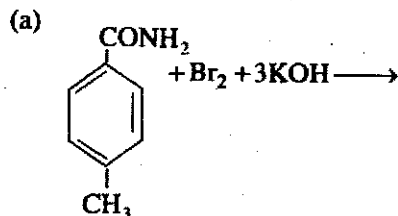
(iii) **Sulphonation:** Sulphonation is carried out in the presence of sulphuric acid. The amino group in aniline is a basic group therefore, an acid-base reaction takes place to form anilinium sulphate salt. This salt undergoes rearrangement at a high temperature to give sulphanilic acid.

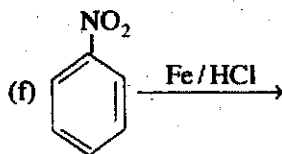


Sulphanilic acid has a high boiling point 573K and is soluble in water because of its dipolar or *zwitter ionic* structures.

INTEST QUESTION 30.2

1. Predict the major product in the following reactions:





-
2. Why is aniline very reactive towards bromination?
.....
 3. Name the test which uses potassium hydroxide and chloroform for testing a primary amine.
.....
 4. State whether an amino group in aniline is:
 - (i) only *ortho* directing
.....
 - (ii) only *para* directing
.....
 - (iii) only *meta* directing
.....
 - (iv) both *ortho* and *para* directing
.....
 5. Can aniline be nitrated directly ?
.....
 6. How will you obtain sulphanilic acid from benzene ?
.....

30.4 BASIC NATURE OF AMINES

Ethanamine is aliphatic while aniline is aromatic amine. Both of these amines are basic. Both of these forms water soluble salts with dilute hydrochloric acid. They react with acetyl chloride and benzoyl chloride. Both have characteristic ammonia like odour.

30.4.1 Comparison of Basic Nature of Aliphatic and Aromatic Amines

Both aliphatic amines and aromatic amines are basic in nature. The aliphatic amines particularly are more basic than the aromatic amines. For instance between ethanamine and aniline, the former is more basic because of the inductive electron donating effect by the alkyl group on the nitrogen atom. This increases the electron density on nitrogen and as a result gets protonated easily. Aniline is less basic because the non-bonding electron pair on the nitrogen atom is involved in resonance with the benzene ring. This tends to decrease the electron density on the nitrogen atom in aniline.

Among the primary, secondary and tertiary aliphatic amines the order of basicity is the following:

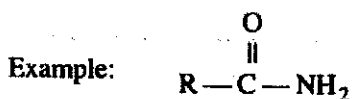
Secondary amine (2°) > Primary amine (1°) > Tertiary amine (3°)

A secondary amine is more basic than a primary amine because it has two alkyl group which donate electrons inductively to the nitrogen atom. The tertiary amine is less basic than the other two. The reason is that a tertiary amine though has three alkyl groups which can donate electrons to the nitrogen atoms, but this atom is sterically hindered for protonation due to the presence of three sizeable alkyl groups.

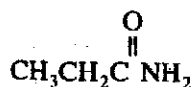
30.5 IUPAC NOMENCLATURE OF AMIDES AND NITRO COMPOUNDS

The amides are ammonia derivatives and formally similar to acid chloride ($\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$)

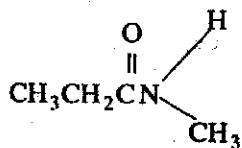
in which the $-\text{Cl}$ group is replaced by the $-\overset{\text{H}}{\underset{\text{H}}{\text{N}}}$ group.



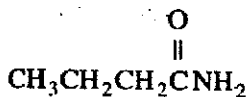
The IUPAC name of amide is obtained by simply changing -oic acid to -amide as shown below.



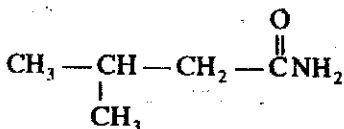
Propanamide



N-Methylpropanamide



Butanamide

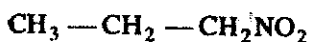


3-Methylbutanamide

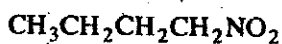
The IUPAC names of nitro compounds are derived by prefixing the word nitro to the parent carbon chain.



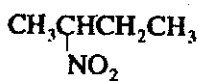
1-Nitroethane



1-Nitropropane



1-Nitrobutane

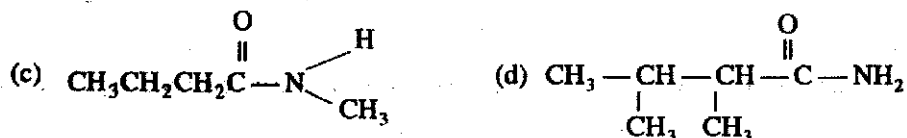
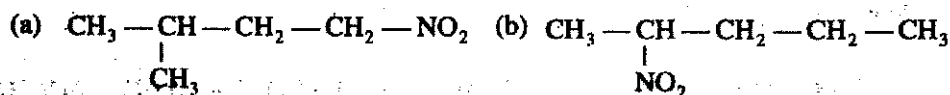


2-Nitrobutane

INTEXT QUESTION 30.3

1. Are aliphatic amines more basic than aromatic amines?

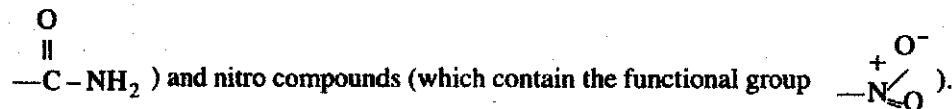
2. Write IUPAC names of the following:



30.6 WHAT YOU HAVE LEARNT?

- There are three types of important organic compounds that contain nitrogen atom as the part of their functional group. These compounds are amines (which contain the

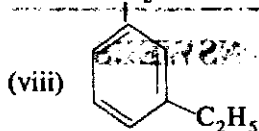
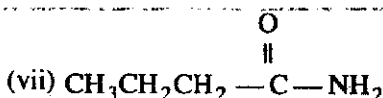
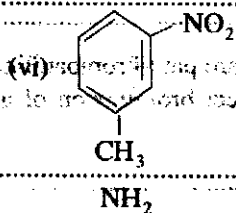
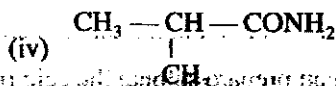
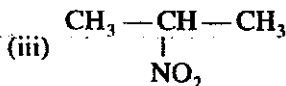
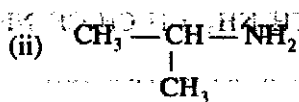
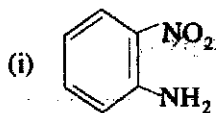
functional group $-\overset{\cdot\cdot}{\text{N}}\text{H}_2$, $\overset{\cdot\cdot}{\text{N}}\text{H}$, $-\overset{\cdot\cdot}{\text{N}}:$), amides (which contain the functional group



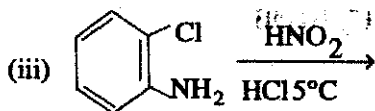
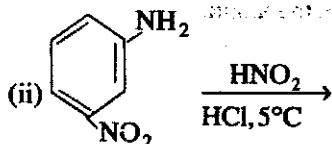
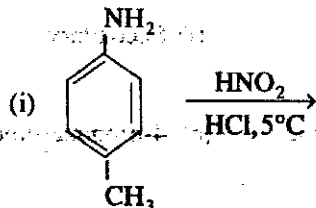
- Both aliphatic and aromatic amines are basic.
- Ethanamine (aliphatic amine) is obtained from amide by Hofman bromamide reaction. Aniline can be obtained from benzamide from Hofmann bromamide reaction and reduction (Sn/HCl) of nitrobenzene.
- Both ethanamine and aniline react with nitrous acid, chloroform and acid chloride.
- Primary amines react with chloroform in the presence of strong base to form isocyanides (carbylamines). This is called the *carbylamine test*.
- Aniline reacts with nitrous acid at 5°C to form benzene diazonium chloride.
- Aniline is aromatic and the ring substitution takes place (halogenation) at the ortho and para position. The amino group ($-\text{NH}_2$) being *ortho* and *para* directing.
- The amino group in aniline is very reactive, therefore, nitration is carried out first by protecting the amino group by acetylation.
- Aniline on sulphonation does not yield the ortho and para derivatives.
- A Secondary amine is more basic than primary which is more basic than tertiary amine.
- The amides and nitro alkanes follow the usual IUPAC system of nomenclature.

30.7 TERMINAL EXERCISE

1. Write the IUPAC names of the following compounds:

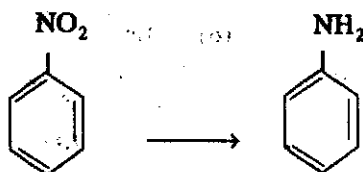


2. What do you understand by diazotization? Write the product of following reactions.



3. How will you prepare butanamine starting from an amide? Name the reaction involved.

4. State the different conditions for the following reaction.



5. Write the steps involved in the preparation of 4-bromophenol from 4-bromoaniline.
.....
6. Arrange the following amines in increasing order of basicity
 $\text{CH}_3\text{CH}_2\text{NH}_2$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, $\text{CH}_3\text{CH}_2\text{CH}_2$, CH_2NH_2

7. Write the chemical reaction for the acetylation and benzylation of propanamine and 2-methylaniline.

8. How will you prepare sulphanilic acid from aniline?

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.

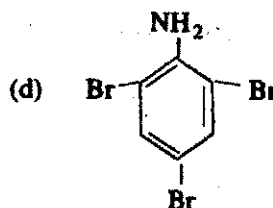
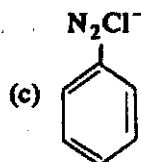
CHECK YOUR ANSWERS

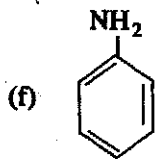
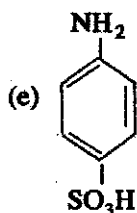
INTEXT QUESTIONS 30.1

1. (a) Primary (b) Secondary (c) Secondary
 (d) Tertiary (e) Primary (f) Secondary
 (g) Quaternary ammonium salt.
2. (a) Butanamine (b) Cyclohexanamine (c) 4-bromoaniline
 (d) 3-Methylbutanamine (e) Pentanamine
 (f) Cyclopropanamine (g) N,N-dimethylethanamine
 (h) N-Methyl propanamine

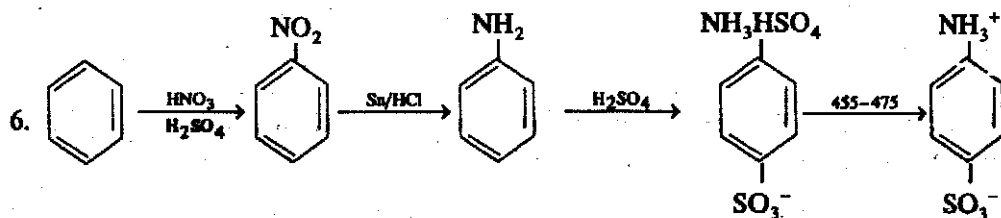
INTEXT QUESTIONS 30.2

1. (a) NH_2 (b) $\text{CH}_3\text{CH}_2\text{OH}$





2. Aniline is very reactive towards bromination because the —NH_2 group is a highly activating group.
3. Carbylamine test
4. (iv) Both ortho and para directing
5. No

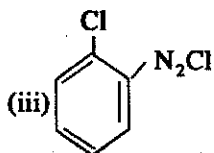
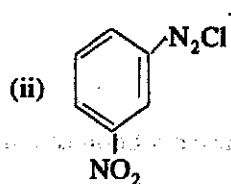
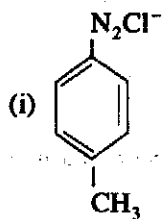
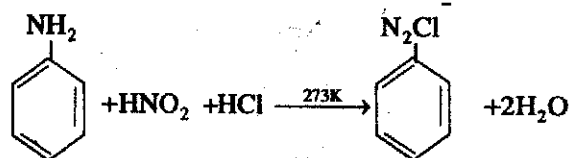


INTEXT QUESTIONS 30.3

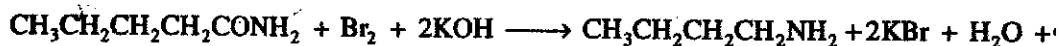
1. Yes
2. (a) 1-Nitro-3-Methylbutane
- (b) 2-Nitropentane
- (c) N-Methylbutanamide
- (d) 2,3-Dimethylbutanamide

TERMINAL EXERCISE

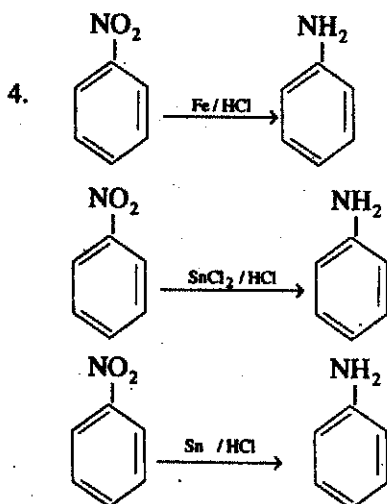
1. (i) 2-Nitroaniline
- (ii) 2-Propanamine
- (iii) 2-Nitropropane
- (iv) 2-Methylpropanamide
- (v) Butanamine
- (vi) 3-nitrotoluene
- (vii) Butanamide
- (viii) 3-Ethylaniline
2. Reaction of an aromatic primary amine with nitrous acid and dil HCl at 5°C to form a diazonium salt is called **diazotization**. Aniline on treatment under similar condition yields benzene diazonium chloride. This salt on warming with water yields phenol.



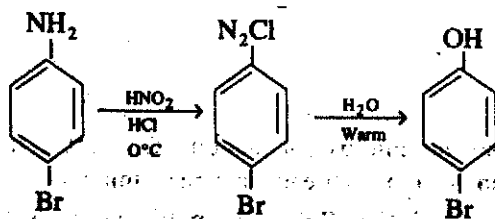
3. Butanamine may be prepared by the reaction of pentanamide with bromine and potassium hydroxide.



This reaction is called Hofmann bromamide reaction.



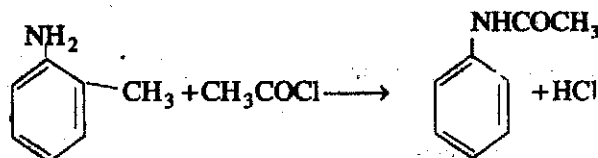
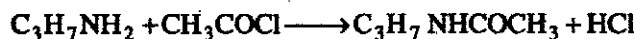
5. 4-bromoniline undergoes diazotization with HNO_2 to form diazonium salt. This salt when warmed with water forms phenol.



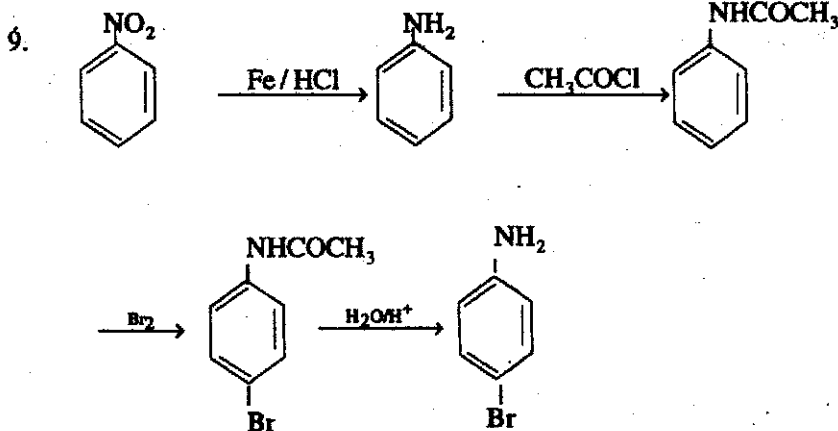
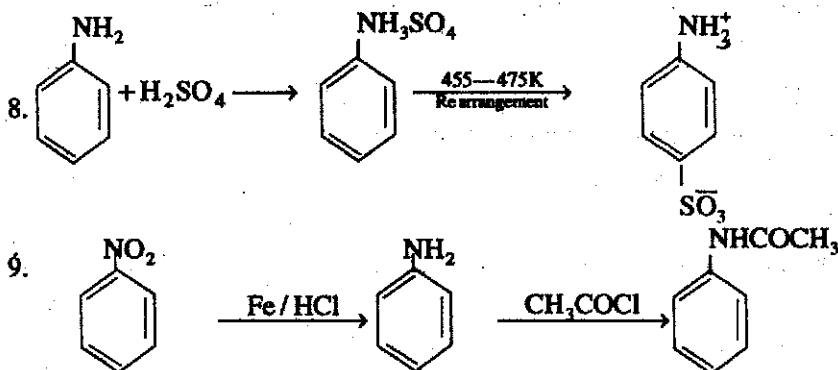
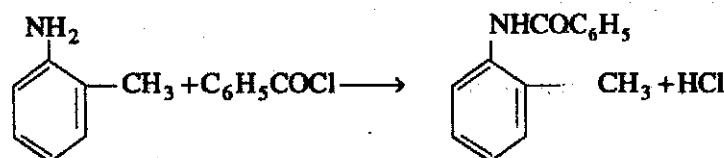
6. Butanamine ($K_b = 4.8 \times 10^{-4}$) is more basic than propanamine ($K_b = 4.7 \times 10^{-4}$) which is more so than ethanamine ($K_b = 4.4 \times 10^{-4}$). The reason is that butanamine has inductively more electron donating carbon chain than the other two. This increases the electron density on the nitrogen atom and this makes the amine more basic. So the order is



7. Acetylation:



Benzoylation:



No, para - bromoaniline cannot be obtained by direct bromination of aniline as it is very reactive towards bromine and instead gives 2,4,6-tribromoaniline.