24 ORGANIC NITROGEN COMPOUNDS

Student Learning Outcomes

[C-12-D-79 to C-12-D-97]

- **Part 1: Amines - Fundamentals and Classification**
- Define primary and secondary amines, and explain their basic properties and reactivity.
- Identify the differences between primary and secondary amines in terms of their structure and chemical properties.
- Define the basicity of aqueous solutions of amines.
- **Part 2: Synthesis of Amines and Related Nitriles**
- Describe the reactions by which nitriles can be produced: reaction of a halogenoalkane with KCN in ethanol and heat.
- Recall the reactions by which hydroxy nitriles can be produced: the reaction of aldehydes and ketones with HCN, KCN as catalyst, and heat.
- Describe the hydrolysis of nitriles with dilute acid or dilute alkali followed by acidification.
- Describe the preparation methods of primary and secondary amines, including nucleophilic substitution reactions and reduction of nitro compounds.
- Recall the reactions (reagents and conditions) by which primary and secondary amines are produced: a) reaction of halogenoalkanes with NH_3 in ethanol heated under pressure; b) reaction of halogenoalkanes with primary amines in ethanol, heated in a sealed tube / under pressure. c) The reduction of amides with $LiAlH_4$; d) The reduction of nitriles with $LiAlH_4$ or H_2 / Ni.
- **Part 3: Phenylamine and Azo Compounds (Aromatic Amines)**
- Explain the relative basicity of aqueous ammonia, ethylamine and phenylamine.
- Explain the properties and reactivity of phenylamine and azo compounds, including their use as dyes and pigments.
- Define the reaction of phenylamine with $Br_{2(aq)}$ at room temperature.
- Define the reaction of phenylamine with HNO_2 or $NaNO_2$ and dilute acid below 1°C to produce the diazonium salt; further warming of the diazonium salt with H_2O to give phenol.
- Identify the properties of azo compounds (some examples include: a) Describe the coupling of benzene-diazonium chloride with phenol in $NaOH_{(aq)}$ to form an azo compound; b) Identify the azo group; c) State that azo compounds are often used as dyes; d) Recognize that other azo dyes can be formed via a similar route).
- **Part 4: Amides and Amino Acids**
- Identify the reactions (reagents and conditions) by which amides are produced (some examples include: a) The reaction between ammonia and an acyl chloride at room temperature; b) The reaction between a primary amine and an acyl chloride at room temperature).
- Describe the reactions of amides (some examples include: a) Hydrolysis with aqueous alkali or

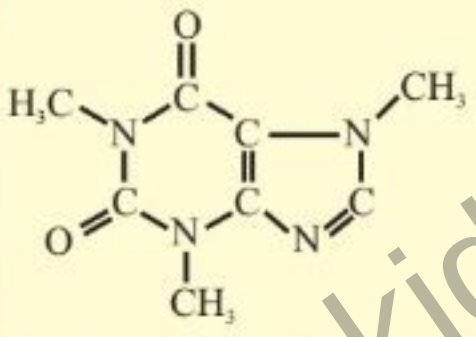
aqueous acid; b) The reduction of the CO group in amides with $LiAlH_4$ to form an amine).

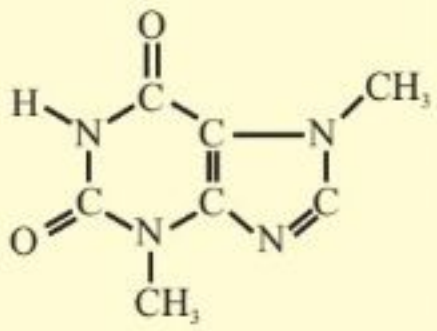
- Explain why amides are much weaker bases than amines.
- Describe the acid / base properties of amino acids and the formation of zwitterions.
- Describe the formation of amide (peptide) bonds between amino acids to give di- and tripeptides.
- Predict the results of electrophoresis on mixtures of amino acids and dipeptides at varying pHs.

Organic nitrogen compounds are essential to life and the modern world. They form the basis of life in the form of amino acids and nucleotides, making the most vital compounds for life, i.e. proteins. Amines and nitro compounds have the pivotal significance in the dye industry and medicines. Nylon, Kevlar®, and polyurethane are the nitrogen containing polymers, which are found in every home and office. Apart from these, nitrogen compounds are also part of our food, fertilisers, explosives, etc.

MORE INFO Interesting Information

Caffeine in coffee and theobromine in chocolate both are organic nitrogen compounds. These are active compounds that make our mode happy. What is the difference between these two?





24.1 AMINES

Amines are considered as organic derivatives of ammonia, where alkyl or aryl groups may replace one, two or three hydrogen atoms of ammonia. The number of hydrogen atoms replaced by alky or aryl groups provides a foundation for the classification of amines as primary, secondary and tertiary amines. In the primary amines one alky or aryl group is attached to -NH_2 group. In IUPAC nomenclature system, amines are referred to as alkanamines.

$CH_3 — NH_2$ methanamine

$CH_3 — CH_2 — NH_2$ ethanamine

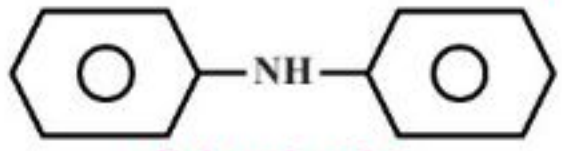
$CH_3 — CH_2 — CH_2 — NH_2$ propan-1-amine

phenyl amine (aniline)

In secondary amines, two alky or aryl groups are attached to NH group e.g.

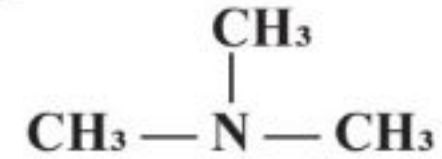
$CH_3 — NH_2 — CH_3$ N-methylmethanamine

$CH_3 — NH_2 — CH_2 — CH_3$ N-methylethanamine



diphenyl amine

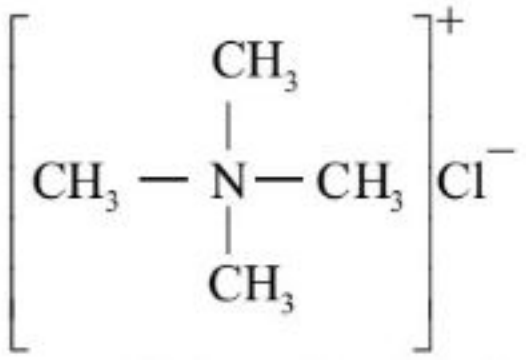
In tertiary amines, three alkyl or aryl groups are attached to the same nitrogen atom e.g.



N-N-dimethylmethanamine

triphenylamine

Tetra-substituted nitrogen derivatives are also known, and are termed as quaternary ammonium salts e.g.



tetramethylammonium chloride

It is important to note that the branching takes place at the nitrogen atom, rather than at the carbon atom attached to it, that determines whether an amine is primary, secondary or tertiary. This is not the same as in the case of the alcohols or monohaloalkanes (alkyl halides).

Quick Check 24.1

a) Give IUPAC names of the following compounds.

i) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - CH_2 - CH_2 - NH_2$

ii) $CH_3 - CH_2 - \underset{\displaystyle NH}{\underset{|}{CH}} - CH_3$ (note: likely intended to be NH_2 for 2-butanamine)

iii) $CH_3 - CH_2 - \underset{\displaystyle CH_2-CH_3}{\underset{|}{CH}} - \underset{\displaystyle CH_2-CH_3}{\underset{|}{CH}} - NH - CH_2 - CH_3$

b) Draw a structure corresponding to each amine.

i) 2,4 dimethylhexan -3- amine

ii) N-methylpentan -1- amine

iii) 2-methylcyclohexan-1-amine

iv) N, N -dimethylethanamine

24.2 PREPARATION OF AMINES

A) Aliphatic Primary Amines

i) Primary amines can be prepared by the nucleophilic substitution reactions of halogenoalkanes with ammonia. Excess of ethanolic ammonia under pressure is used to avoid the formation of secondary amines or a mixture of products.

If NH_3 is in excess, the major product will be primary amine and if halogenoalkane is in excess, tertiary amine is the major product.

$$CH_3 - CH_2 - Br + NH_3 \xrightarrow[\text{Highy Pressure}]{\text{ethanol}} CH_3 - CH_2 - NH_2 + HBr$$

bromoethane (excess) (ethanamine)

ii) Primary amines are prepared by the reduction of alkanenitriles. For example, propanenitrile is reduced with H_2/Ni or $LiAlH_4$ ro prepare propane-1-amine

$$CH_3 - CH_2 - C \equiv N + 4[H] \xrightarrow{LiAlH_4} CH_3 - CH_2 - CH_2 - NH_2$$

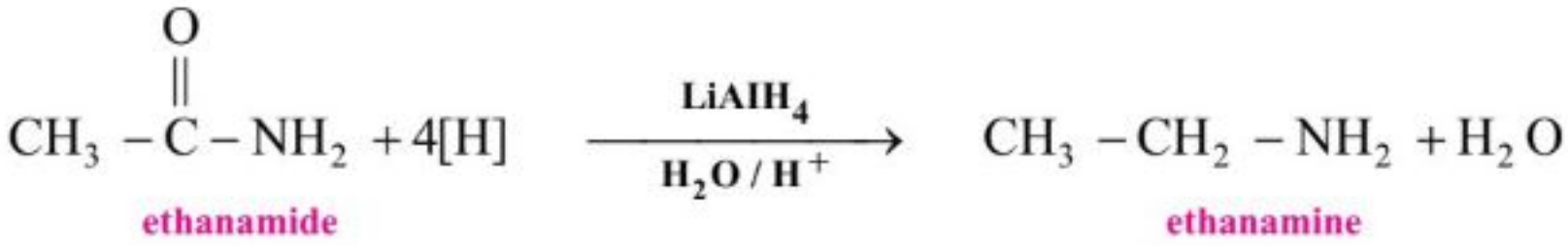
propanenitrile propan-1-amine

iii) Nitroalkanes are reduced in the presence of $LiAlH_4$ resulting in the formation of primary amines.

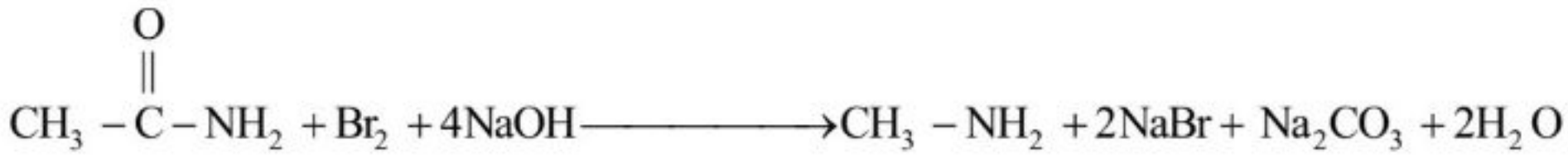
$$CH_3 - CH_2 - NO_2 + 3H_2 \xrightarrow{LiAlH_4} CH_3 - CH_2 - NH_2 + 2H_2O$$

nitroethane ethanamine

iv) Alkanamides are reduced by $LiAlH_4$ to form primary amines in good yield since no byproduct is formed in this reaction.



v) Primary alkanamine can also be prepared by the Hofmann reaction.

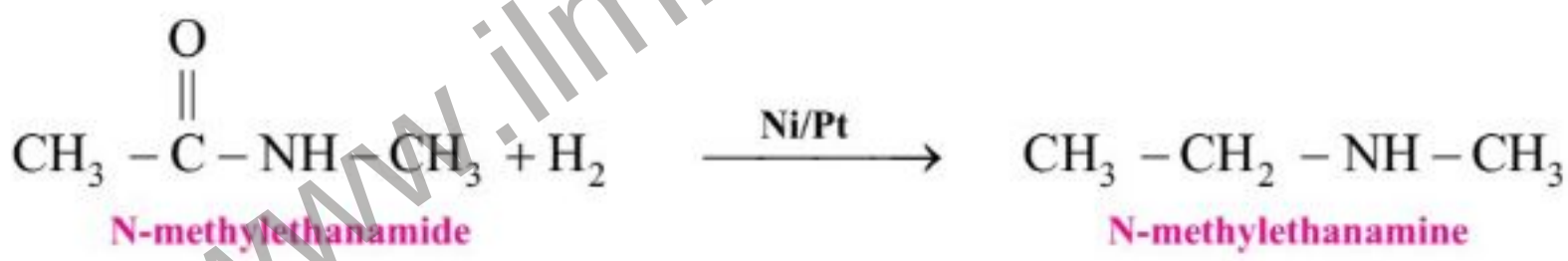


This reaction yields the amine with one carbon less than the starting amide.

B) Aliphatic Secondary Amines

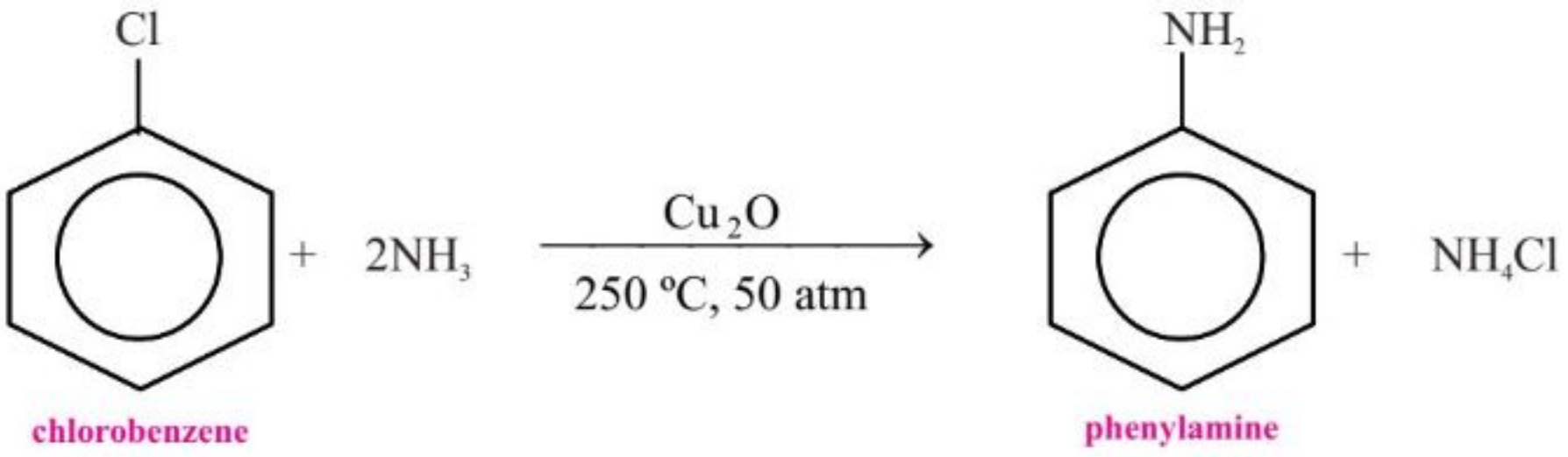
I) Secondary amines can be prepared by the alkylation of primary amines. When a halogenolkane reacts with a primary amine in the presence of ethanol under pressure secondary amine is formed.

ii) Secondary amines are also prepared by the reduction of N-substituted amides

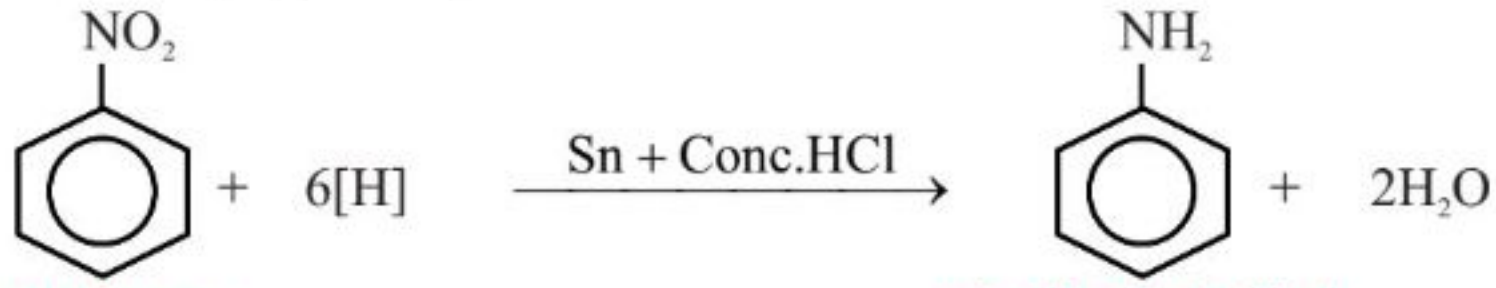


C) Phenyl Amine (Aromatic Amine)

i. Phenyl amine can be prepared by ammonolysis of chlorobenzene. Ammonylsis is a reaction in which an ammonia molecule is broken down to react with another compound.

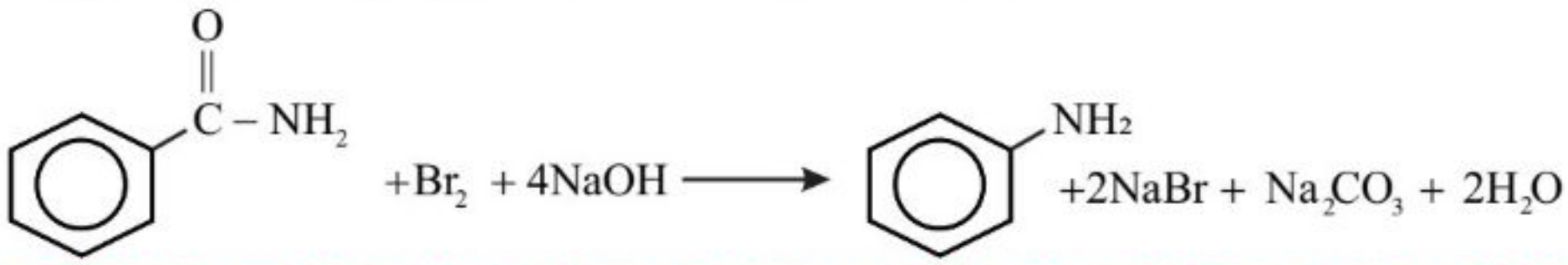


iii. Phenyl amine can also be prepared by the reduction of nitrobenzene.



nitrobenzene — phenyl amine (aniline)

iv. Phenyl amine can be prepared by the Hofmann reaction.



Quick Check 24.2

a) The "feel good factor" in chocolate has been identified as 2-phenylethanamine, $C_6H_5CH_2CH_2NH_2$. Suggest a synthesis of this compound from chloromethylbenzene, $C_6H_5CH_2Cl$.

b) What nitro compound, nitrile and amide are reduced to yield each of the following amine compound?

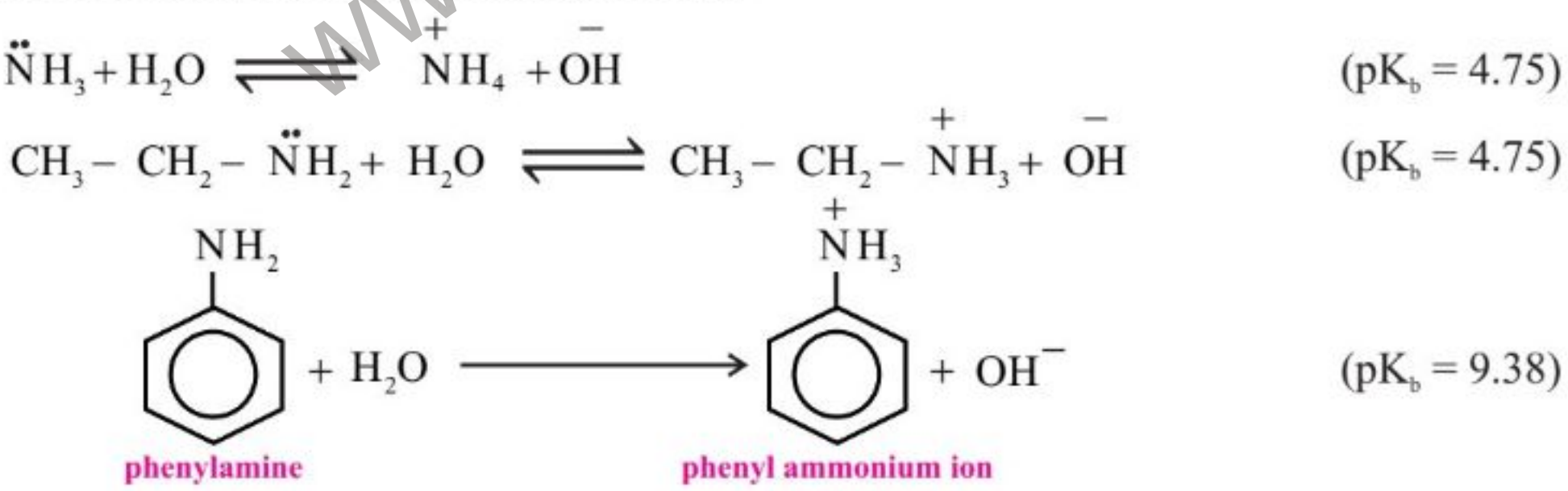
I) For the primary amine: $CH_3 — \underset{\displaystyle CH_3}{\underset{|}{CH}} — CH_2 — Nh_2$ (determine the structures of nitro compound,nitrile , and amide that would produce this amine upon reduction

ii) For the secondary amine: $CH_3 — CH_2 — CH_2 — CH_2 — NH — Ch_3$

24.3 REACTIONS OF AMINES

24.3.1 Basicity of Amines

The amines which are soluble in water form weakly alkine solutions, just as ammonia does due to partial reaction with solvent forming OH ions.



phenylamine — phenyl ammonium ion

The basicity of amines depends on the availability of the "lone pair" of electrons on the nitrogen atom. Reactions of different amines and ammonia with water show their pK_b values. The Larger the K_b (or smaller the pK_b), the stronger is the base. It is clear that electron-donating alkyl groups attached to the nitrogen atom increase the basicity of amines, whereas the electron-withdrawing groups decrease it. Basicity is also an indicator of the stronger nucleophilic character of a compound, mostly. Following this, we can infer that:

- Etahanamine is a stronger base than ammonia and methanamine (primary amine). Likewise, alkyl amines are stronger base than ammonia as well.
- Ammonia is a stronger base than aromatic amines like phenyl-amine. This is because in phenylamine, the lone pair of electrons on the nitrogen atom is delocalized over the benzene ring as shown in **Figure 24.1**. The nitrogen atom is planar, with its lone pair in a p orbital. This can overlap with the delocalized π electrons of benzene ring.

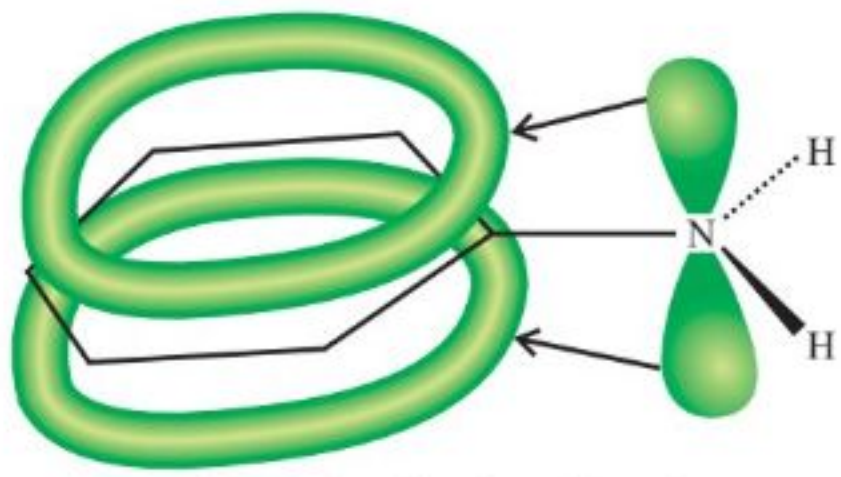


Figure 24.1 Delocalisation of the nitrogen lone pair in phenylamine

Table 24.1 The basicity of some amines

Sr.No.	Amine	Formula	Kb	pKb
1	Ammonia	NH_3	1.8×10^{-5}	4.75
2	Ethanamine	$CH_3\text{-}CH_2\text{-}NH_2$	5.1×10^{-4}	3.29
3	Phenylamine (Aniline)		4.2×10^{-10}	9.38

Ammonia and ethanamine react with an acid to form salts due to their basic nature. In this reaction, the nitrogen atom donates an electron pair to form a dative bond with a proton, forming a salt.

$$\ddot{N}H_3 + H^{+\delta} - Cl^{-\delta} \longrightarrow NH_4^+Cl^-$$

$$CH_3-CH_2-\ddot{N}H_2 + H^{+\delta} - Cl^{-\delta} \longrightarrow CH_3-CH_2-\overset{+}{N}H_3Cl^-$$

Did You Know?

The foul smell from fish is due to N,N– dimethylmathanamine (trimethylamine). When lemon juice is sprinkled on fish its acid (citric acid) reacts with the amine making it less smelly. The same happens when the fish is processed with vinegar.

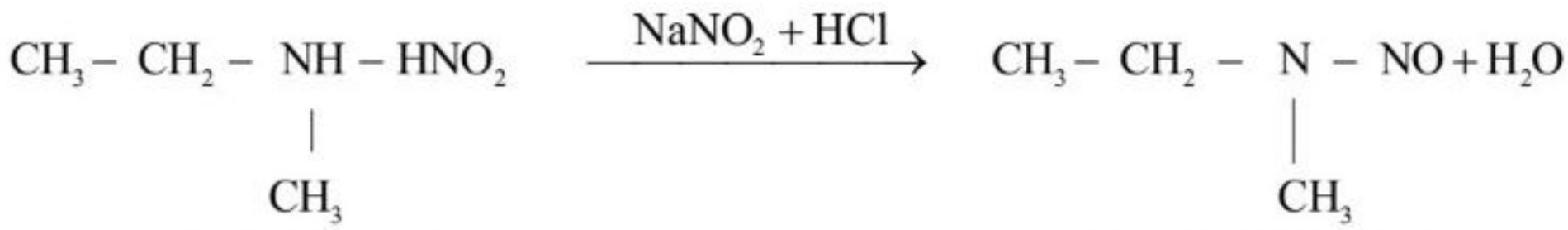
24.3.2 Distinction between primary and secondary amines

Primary, secondary and tertiary aliphatic amines are identified and distinguished by reacting them with nitric (III) acid (nitrous acid). Primary amines react with nitrous acid to form diazonium salts. The process is called diazotization.

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

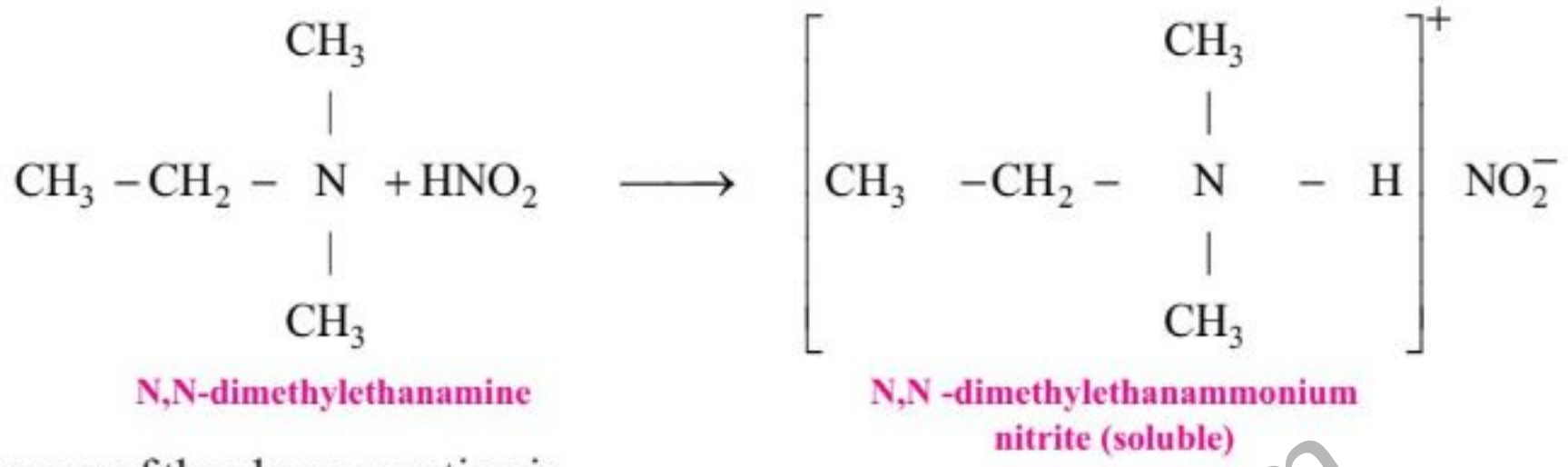
$$\underset{\text{ethaneamine}}{CH_3-CH_2-NH_2} + HNO_2 + HCl \longrightarrow \underset{\text{ethane diazonium chloride}}{CH_3-CH_2-\overset{+}{N}\equiv N\bar{Cl}} + 2H_2O$$

Secondary amines form N-nitrosoamines (yellow oily liquid) on reaction with nitrous acid.)



N-methylethanamine — N-methyl-N-nitrosoethanamine

Tertiary amines react with nitrous acid to form soluble salt.



N,N-dimethylethanamine — N,N -dimethylethanammonium nitrite (soluble)

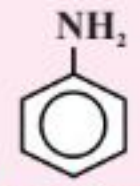
The summary of the above reaction is

i. Primary amines react with nitrous acid to produce nitrogen gas (seen as bubbles).
ii. Secondary amines react with nitrous acid to produce yellow oily liquid.

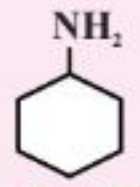
Tertiary amines react with nitrous acid to form soluble nitrite salts. There is no visible sign of reaction.

Quick Check 24.3

a) Phenylamine is about a million times less basic than cyclohexylamine. Give reason.



phenylamine
Kb = 4.2 x 10⁻¹⁰



cyclohexylamine
Kb = 3.3 x 10⁻⁴

b) Which of ethanamine and propan-2-amine is more basic? Explain.

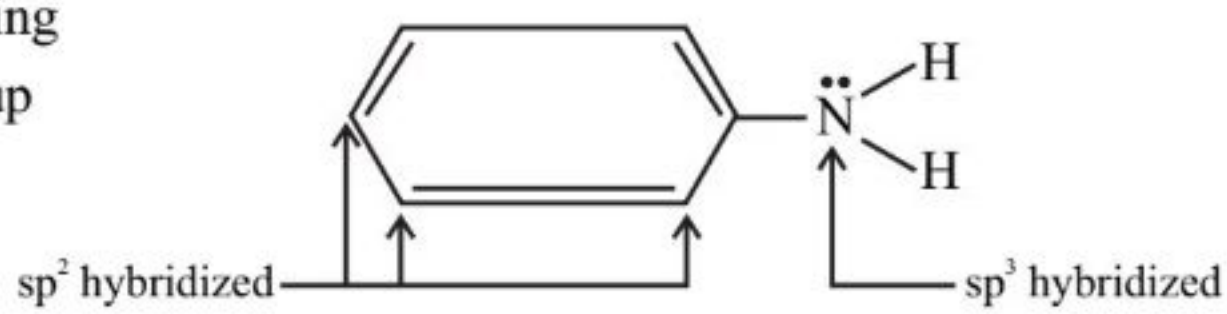
c) Show the reaction of propan-2-amine with HCl. Name the salt formed.

d) Which acid reacts with N,N-dimethylammine in fish when it is treated with vinegar? Write a chemical equation to show this reaction.

24.3.3 Reactions of Phenylamine (Aromatic Amine)

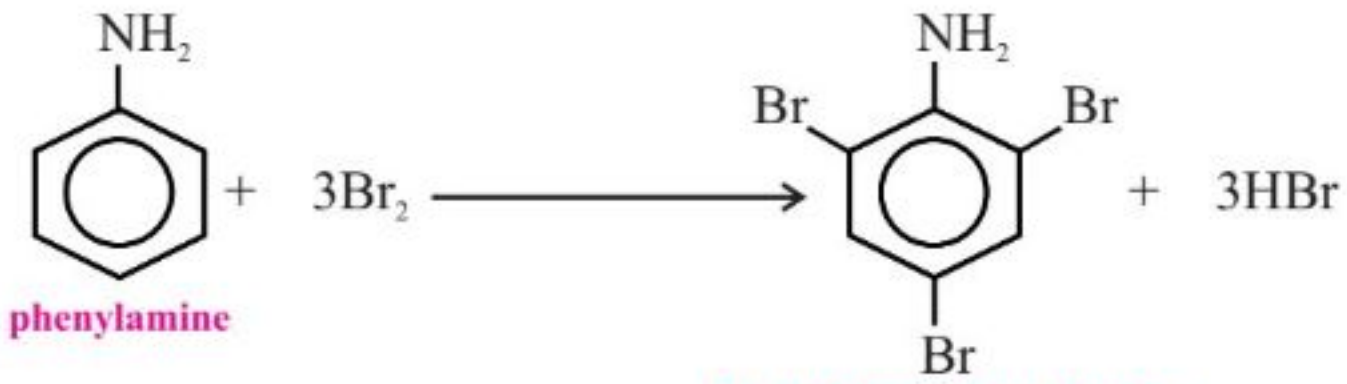
Phenylamine gives two types of reactions:

a) due to benzene ring
b) due to -NH_2 group



a) Reaction with bromine water

The amino group (–$\ddot{N}H_2$) is an ortho-para directing group. Therefore, the incoming electrophile attacks at "o" and "p" positions. The presence of the amino group makes benzene ring fairly reactive, especially at these position. Hence, bromination of phenylamine is faster than benzene, and its two ortho and the para positions, all are occupied in a single reaction.



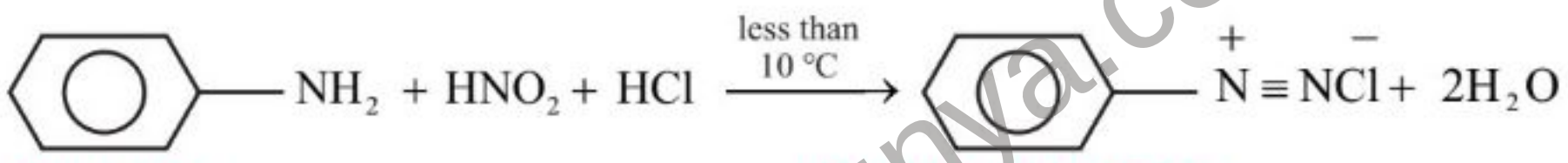
phenylamine

2,4,6-tribromophenylamine
(White precipitates)

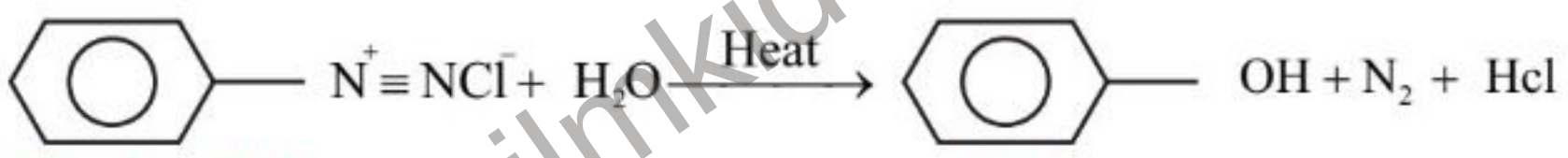
b) Reaction with Nitrous Acid and Formation of Azo Compounds

Phenylamine being a primary amine reacts with nitrous acid to form phenyldiazonium salt. This reaction is called diazotization. The organic compounds having diazonium ion, $-\overset{+}{N}\equiv N$(diazo group) as a functional group are called diazo compounds. Both aliphatic and aromatic primary amines react with nitrous acid to yield diazonium salts. Nitrous acid is unstable and is prepared *in situ* by the reaction of sodium nitrite and HCl. The reaction mixture is kept below 10°C using ice. This is because the diazonium salts are unstable and will decompose easily, giving off nitrogen gas, N_2, even at room temperature.

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

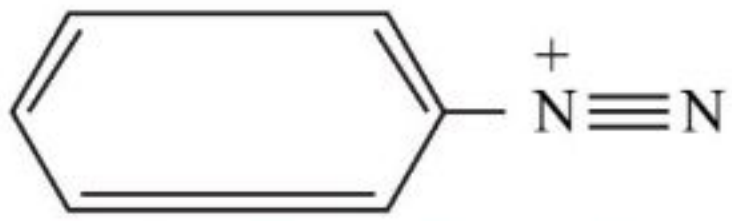


phenylamine — phenyldiazonium chloride



phenyldiazonium chloride — phenol

The alkyl diazonium salts are highly unstable under all conditions and therefore cannot be isolated. The aryl diazonium salts are however fairly stable at low temperatures. The extra stability of aromatic diazo compounds compared to aliphatic diazo compounds is due to the delocalization of the positive charge over the aromatic ring. Benzene diazonium salts are the important intermediates in the synthesis of many organic compounds.

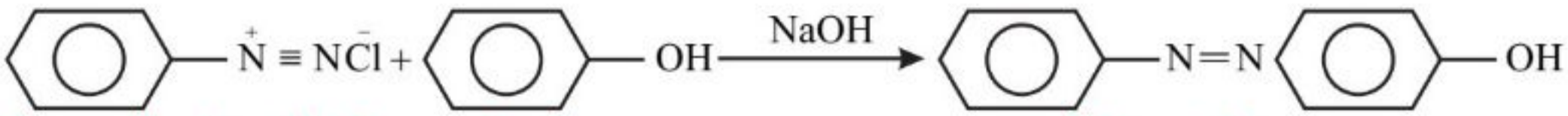


Structure of benzene diazonium ion

Coupling reactions of diazonium compounds

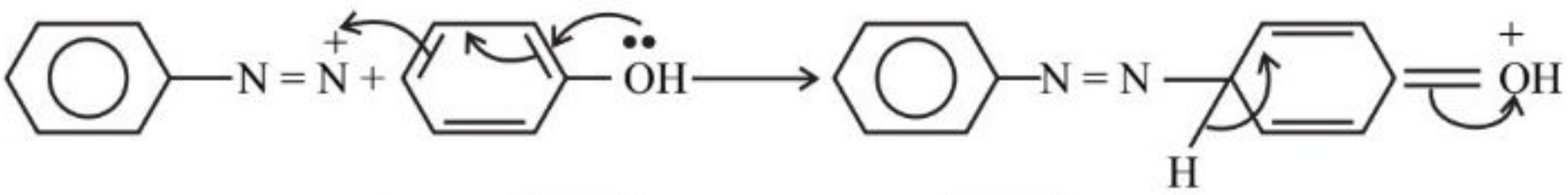
The reactions of aryl diazonium salts with strongly activated aromatic compounds, such as phenols and amines, are called coupling reactions. The products of such reactions containing a –N=N- bond are called azo compounds. In the coupling reaction, the positively charged diazonium ion acts as an electrophile. It substitutes into the benzene ring of phenol at the para position.

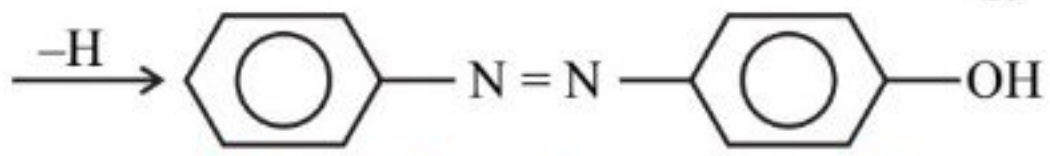
Coupling with phenol occurs in mild alkaline solution and with aromatic amines in mild acidic conditions.



benezenediazonium chloride phenol p-hydroxyazobenzene (orange solid)

Mechanism

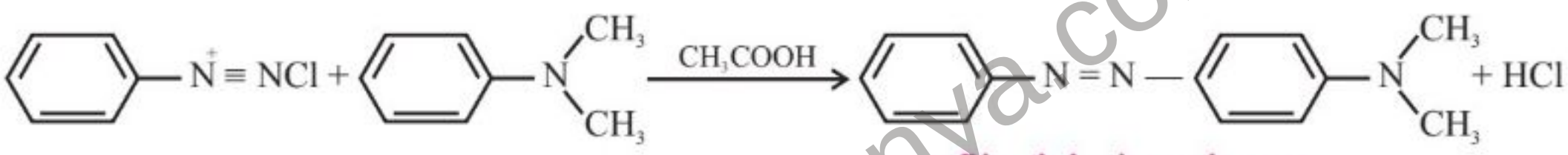




p-hydroxyazobenzene (an azo compound)

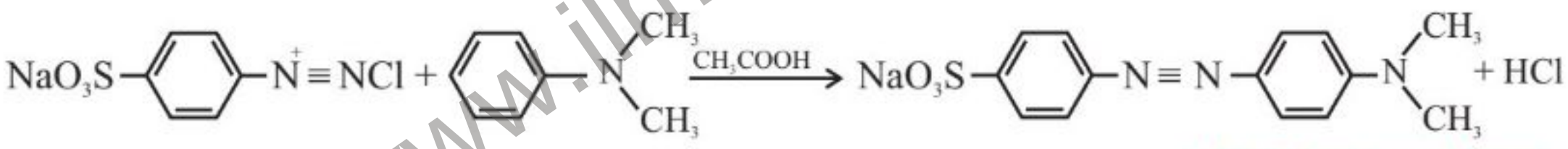
Formation of Dyes

Coupling reaction can be used to form different types of azo dyes. p-Dimethylaminoazo benzene is called Butter yellow, which was previously used in food. However, due to its carcinogenic nature, its use in food is now forbidden.



p-Dimethylaminoazo benzene (butter yellow)

Methyl orange is an acid-base indicator and is prepared from diazotized sulfanilic acid and N, N-diamethylphenylamine as follows.



p-dimethylaminoazo benzene

The azo group (Ph-N=N-Ph) in azo dyes is called a chromophore. This group is responsible for the intense colour of the dyes ranging from yellow and orange to red, blue and green depending upon what other groups are attached to the benzene rings.

Different food colours often contain azo dyes

Quick Check 24.4

Azo dyes are the coloured compounds which are prepared by the reaction of diazonium salt of phenylamine and some aryl compound having activated benzene ring.

i) How will you prepare a dye from phenylamine and 2-methylphenol.

ii) Give equations stepwise along with reaction conditions.

24.4 Alkanenitriles

The organic compounds containing -CN functional group are called alkanenitriles. For example

CH_3-CN — ethanenitrile

CH_3-CH_2-CN — propanenitrile

Preparation of alkanenitriles has been given in chapter 21.

Alkanenitriles are important compounds in many chemical reactions. However, the most important application s of alkanenitriles is their hydrolysis to produce carboxylic acids through hydrolysis. Hydrolysis of nitriles can occur with both dilute acid and dilute alkali.

Acid hydrolysis of nitriles

When a nitrile is heated with a dilute acid, such as dilute hydrochloric acid or dilute sulphuric acid, a carboxylic acid is formed.

$$CH_3CN_{(aq)} + 2H_2O_{(l)} + HCl_{(aq)} \longrightarrow CH_3COOH_{(aq)} + NH_4Cl_{(aq)}$$

ethanenitrile — ethanoic acid

Alkaline hydrolysis of nitriles

When a nitrile is heated with a dilute sodium hydroxide solution, a salt of carboxylic acid is produced, which on acidification with dilute hydrochloric acid gives free carboxylic acid.

$$CH_3CN_{(aq)} + H_2O_{(l)} + NaOH_{(aq)} \longrightarrow CH_3COONa_{(aq)} + NH_{3(g)}$$

$$CH_3COONa_{(aq)} + HCl_{(aq)} \longrightarrow CH_3COOH_{(aq)} + NaCl_{(aq)}$$

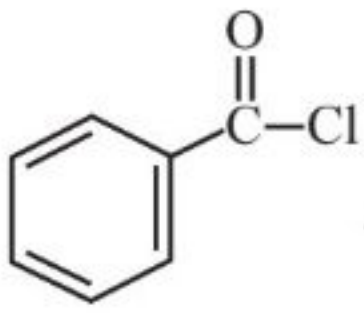
24.5 AMIDES

Amides contain the functional group $-\overset{\overset{O}{\|}}{C}-NH_2$. Since they are prepared from carboxylic acids that is why amides are still sometimes called as "acid amides".

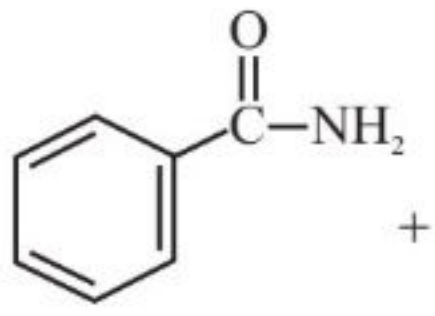
Amides can be prepared by the following methods.

1. By the reaction of acyl chlorides with ammonia

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + NH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + HCl$$



benzoyl chloride

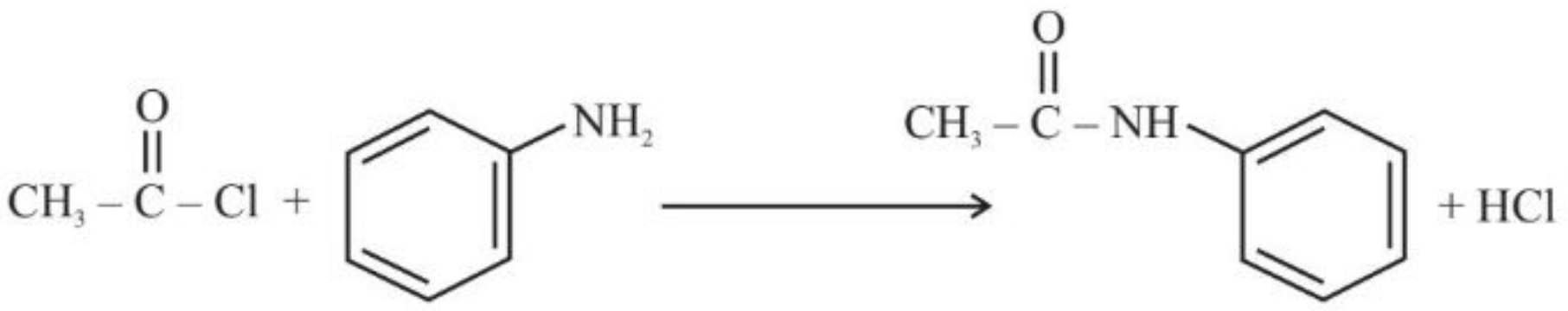


benzamide

2. By the reaction of acyl chlorides with primary amines

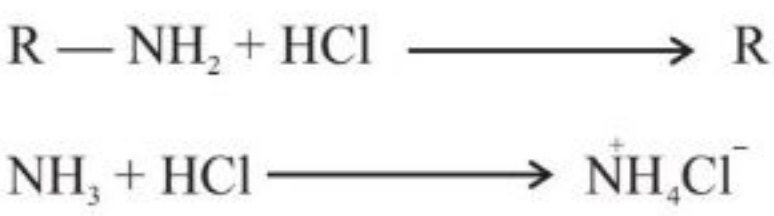
$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + CH_3-CH_2-NH_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-NH-CH_2-CH_3 + HCl$$

ethanoyl chloride — N-ethyl ethanamide



phenyl amine — N– phenyl ethanamide

In the above two methods, all the reactions take place at room temperature, releasing white fumes of hydrogen chloride (HCl). The HCl produced reacts with another molecule of ammonia or amine to form a salt.



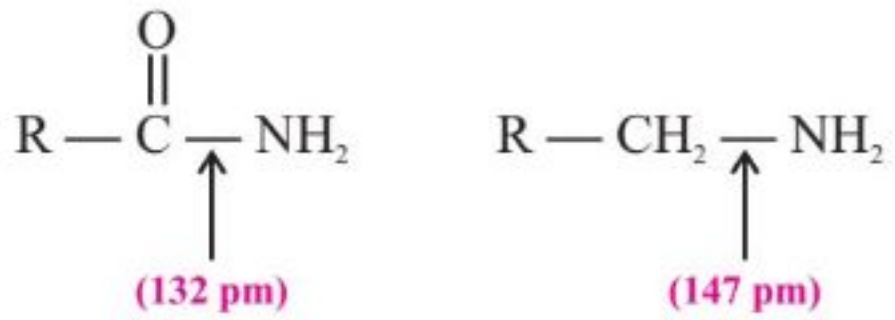
All amides except methanamide, which is a liquid, are solid with sharp melting point. They have quite high boiling points which is a consequence of strong intermolecular hydrogen bonding. However, in case of N-substituted amides, the melting and boiling points decrease as the sites for hydrogen bonding diminish with increasing number of alkyl substituents.

Therefore, an excess of ammonia or amine is used to ensure complete reaction.

Basic Properties of Amides

Amides are less basic than aliphatic amines. Unlike amines, amides form neutral solutions in water. They exhibit resonance where the lone pair on nitrogen participates in delocalization with oxygen of carbonyl group. This reduces the availability of electrons on nitrogen, thereby decreasing the basicity.

The introduction of double bond character between carbon and nitrogen reduces the C—N bond length less than the usual C—N single bond length.



Reactions of Amides

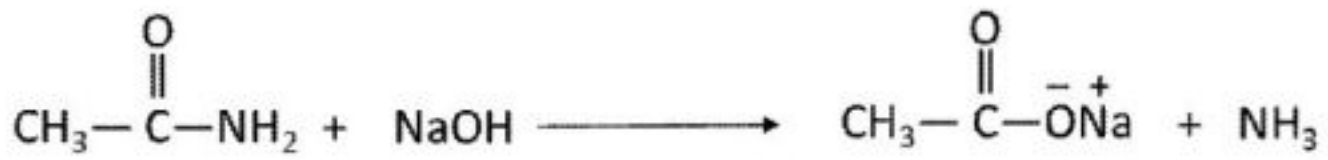
Amides are the least reactive of all acid derivatives, because lone pair of nitrogen is delocalized over the oxygen of carbonyl group, thus decreasing the electrophilic power (+δ charge) of the carbonyl carbon.

Reactions of amides are generally slow and require prolonged heating or catalysts (acid or base) for them to take place. Some of them are given as under:

1. Hydrolysis

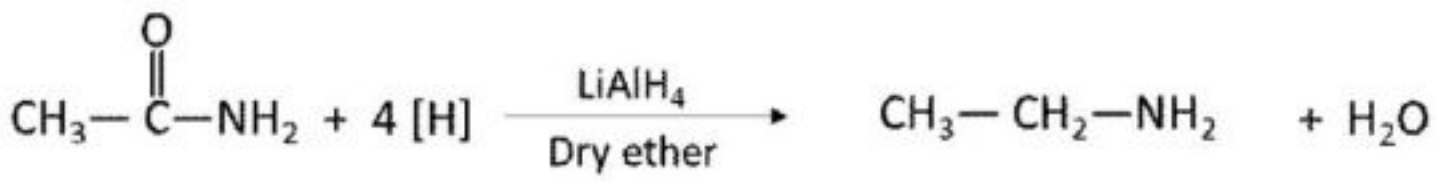
Unsubstituted amides yield carboxylic acids ammonium salt.

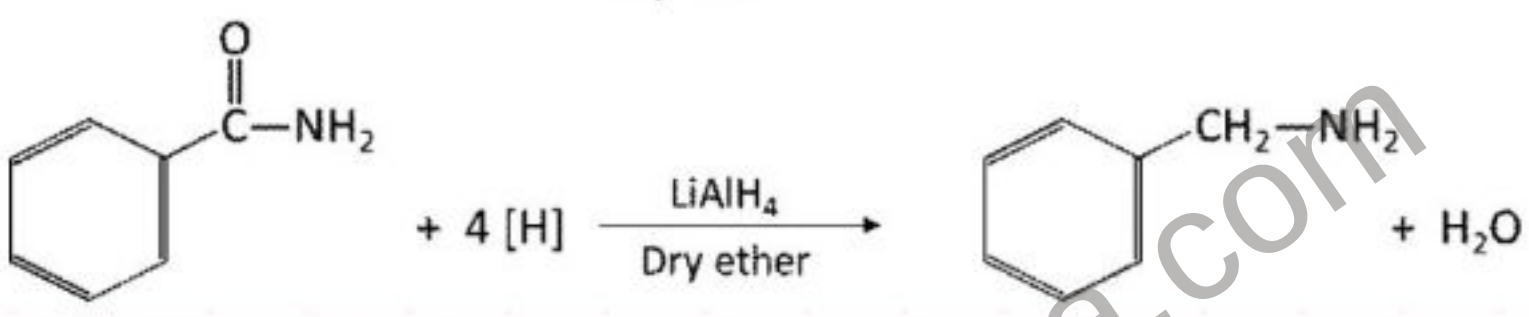
In the base-catalyzed reaction, the products are the salts of carboxylic acids and ammonia. The free carboxylic acid is obtained when this salt is treated with dilute hydrochloric acid.



2. Reduction

Amides are reduced to primary amines with lithium tetrahydridoaluminate (III) in dry ethoxyethane (ether).



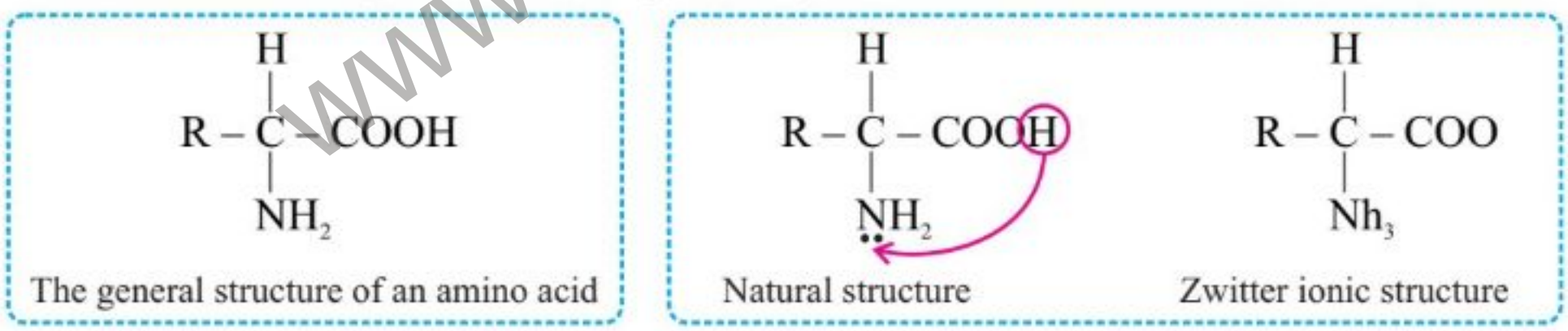


24.6 AMINO ACIDS

Amino acids are an important group of compounds that contain:

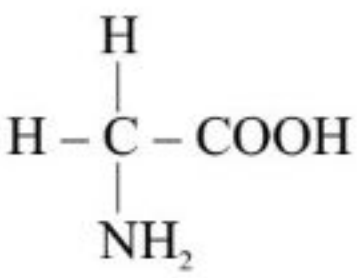
the basic amino group ($-NH_2$), and
the acidic carboxylic acid group (-COOH).

This makes amino acids amphoteric, as they can behave as both an acid and a base. The general structure of amino acids (2-aminocarboxylic acid), also called α-amino acids, is shown as.

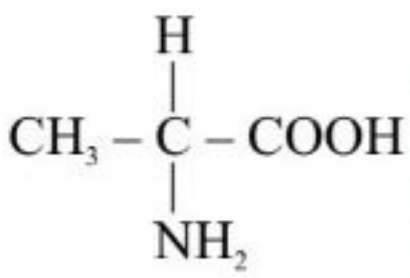


An α-amino acid exists as a dipolar ion called Zwitter ion, having a positive and a negative end within the same molecule. In the formation of a Zwitter ion, the proton goes from the carboxyl group to the amino group. The dipolar structure is also called the internal salt.

The R group is the part of the amino acid that can vary in different amino acids. The simplest amino acid is glycine (aminoethanoic acid) in which R is a hydrogen atom. Alanine (2-amino propanoic acid) is an amino acid in which the R group is the methyl group, $-CH_3$.



glycine



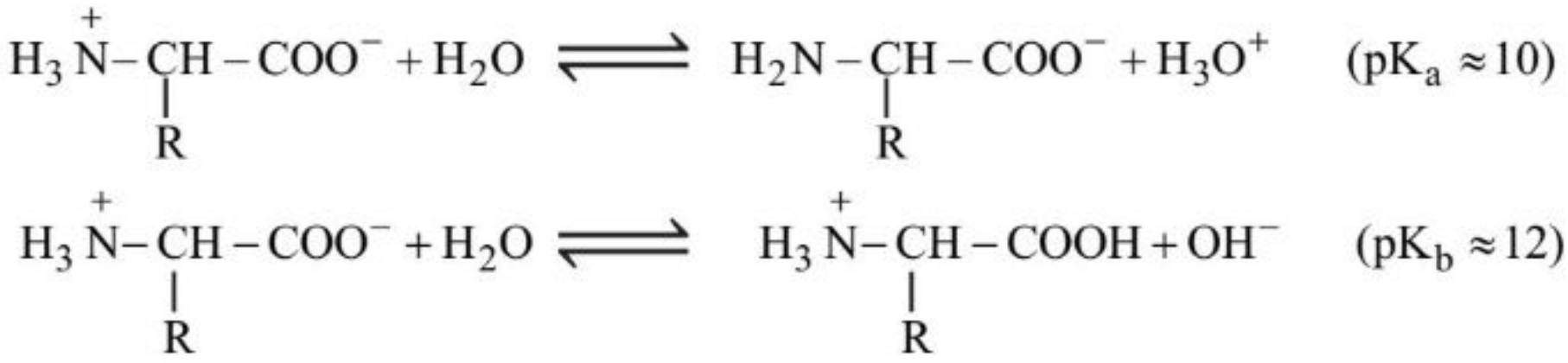
alanine

Except glycine all α-amino acids are chiral.

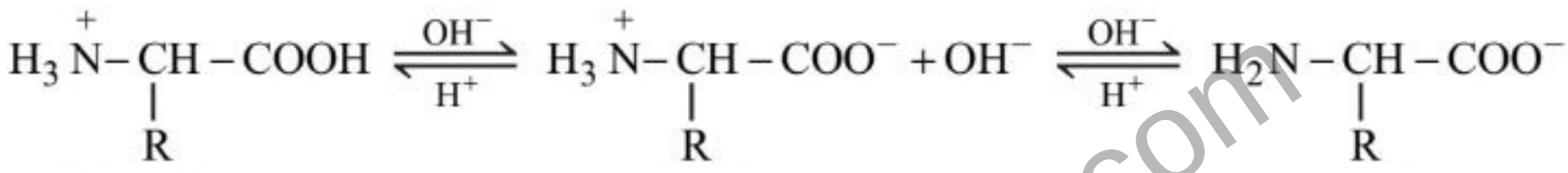
Out of 20 α-amino acids, 10 are essential (body cannot synthesis) and 10 are non-essential (body can synthesis) amino acids.

24.6.1 Acidic and Basic Properties of Amino Acids

Amino acids are amphoteric, i.e., they show both acidic and basic properties. However, they are less acidic than most carboxylic acids, and are less basic than most amines. In fact, the acidic part of the amino acid molecule is $-NH_3^+$, group, not $-COO^-$ group, and the basic part is $-COO^-$ group, not $-NH_2$, group. RNH_3^+ is a weaker acid than RCOOH, as shown below:



In the aqueous solution, an equilibrium exists between the dipolar ion and a cationic and an anionic form of an amino acid.



Cationic form (Predominant at low pH) — **Dipolar ion** (Predominant at isoelectric pH) — **Anionic form** (Predominant at high pH)

For each amino acid, there is specific pH at which the concentration of the zwitter ion reaches its maximum value. This pH is called the isoelectric point (pI), and each amino acid has its own unique pI.

24.6.2 Separation of Amino Acids via Electrophoresis

Amino acids can be separated from each other by a variety of techniques. One method, called electrophoresis, is used to separate amino acid in a mixture based on their charge. In this technique, a few drops of the mixture are applied to a filter paper or gel that is placed in a buffered solution between two electrodes. When an electric field is applied, the amino acids separate based on their different pI values. If the pI of an amino acid is greater than the pH of the solution, the amino acid will exist predominantly in a form that bears a positive charge and will migrate toward the cathode. The greater the difference between pl and pH, the faster it will migrate. An amino acid with a pI that is lower than the pH of the solution exists predominantly in a form that bears a negative charge and will migrate toward the anode. The greater the difference between pl and pH, the faster it will migrate (**Figure 24.2**). If two amino acids have very similar pI values (such as glycine and leucine), the amino acid with the larger molecular weight will move more slowly, because the charge has to carry a greater mass.

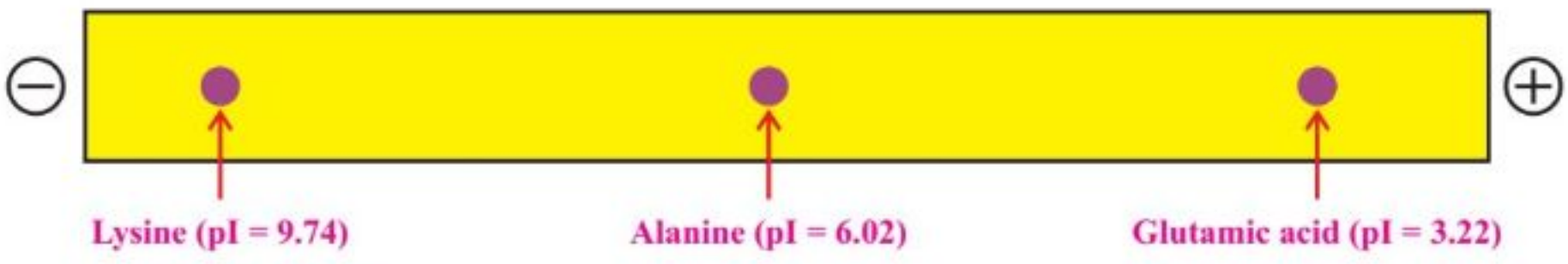
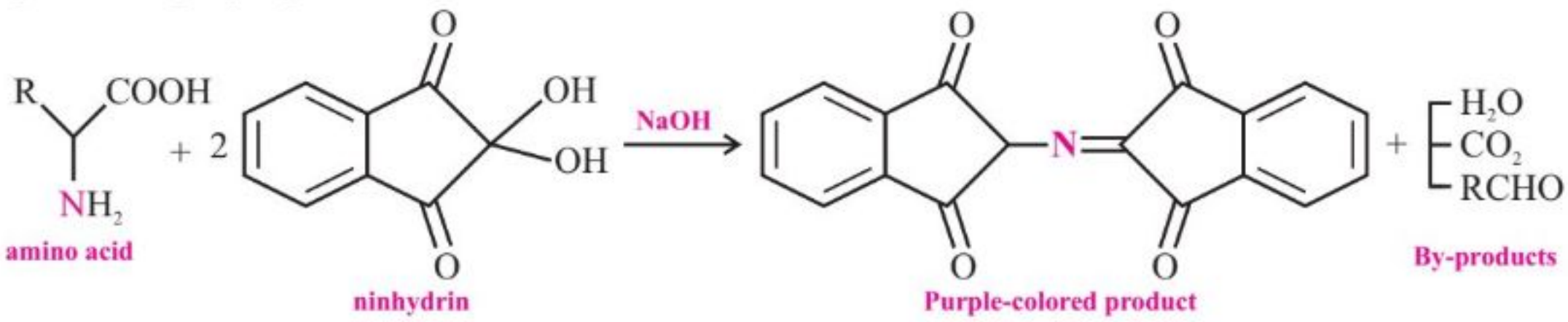


Figure 24.2 Separations of amino acids at pH 6 by electrophoresis

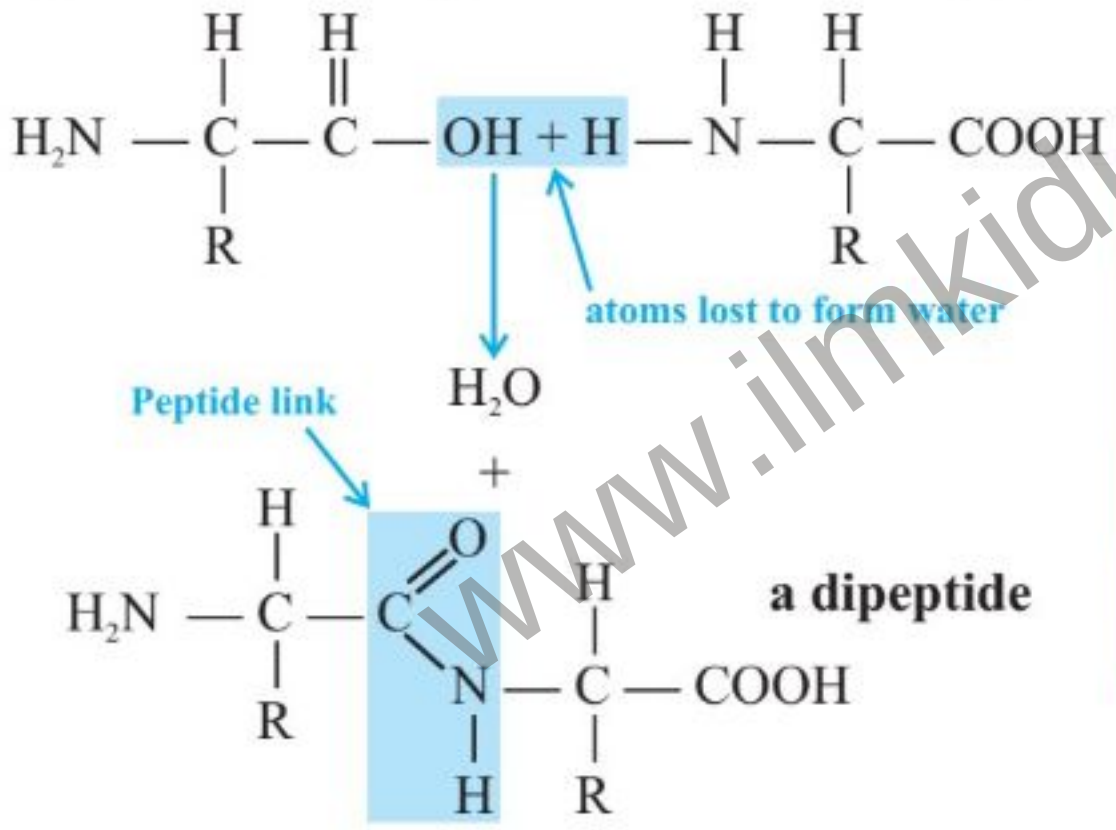
Amino acids are colorless, so a detection technique is necessary in order to visualize the location of the various spots. Ninhydrin is used as a locating agent, which reacts with amino acids to produce a purple product.



Electrophoresis cannot be used to separate large quantities of amino acids. It is used just as an analytical method for determining the number of amino acids in a mixture. In order to actually separate an entire mixture of amino acids, other laboratory techniques are used, such as column chromatography.

24.6.3 Peptides

Amino acid molecules can also react with each other. The acidic -COOH group in one amino acid molecule reacts with the basic-NH, group in another molecule. When two amino acids react together, the resulting molecule is called a dipeptide.



isoelectric point: the pH value at which there is no overall charge on a particular amino acid in its aqueous solution.

tripeptide: a compound formed from the condensation reaction between three amino acids.

polypeptide: a compound formed from the condensation between a large number of amino acids.

Note that the shaded area is the amide bond between the two amino acids. An amide bond between two amino acid molecules is also called a peptide bond or peptide link. The reaction is a condensation reaction, as a small molecule, in this case water is eliminated when the reactant molecules join together.

Quick Check 24.5

The R groups in the amino acids aspartic acid and lysine are ($-CH_2-COOH$) and ($-CH_2-(CH_2)_3NH_2$ respectively.

a) Draw the displayed formulae of these amino acid.

b) Draw the structures of their Zwitter ions.

c) Draw the structures of their ions in acidic conditions.

d) Draw the structures of their ions in basic conditions.

Discuss with what we mean by the isoelectric point of these amino acids.

Exercise

Q1. Multiple Choice Questions:

I. Primary, secondary and tertiary amine are regarded as:

a) Tautomers
b) Metamers
c) Functional group isomers
d) Position isomers

II. General formula for secondary amines is:

a) RNH_2
b) RNHR
c) R_3N
d) $RCONH_2$

III. Which one of the following bases is a strongest one?

a) Ammonia
b) Ethyl amine
c) Phenyl amine
d) Diethyl amine

IV. Acid hydrolysis if nitriles produces:

a) Alcohol
b) Ketone
c) Carboxylic acid
d) Ester

V. phenyl amine areacts with aqueous Br to form:

a) Phenol
b) 2,4,6-Tribromophenylamine
c) An azo compound
d) None of these

VI. Benzenediazonium chloride reacts with phenol in NaOH to form:

a) Phenyl hydrozine
b) Nitro compound
c) Azo compound
d) Alcohol

VII. What is the structure of an azo compound:

a) R_1-N=N-R_2
b) R_1-NH-R_2
c) R-O-R
d) R-C≡N

VIII. When diazonium salt is heated with water, the gas evolved is:

a) Nitrogen
b) Ammonia
c) Nitric oxide
d) Nitrogen dioxide

IX. An aqueous solution of glycine is neutral because of the formation of:

a) Carbanion
b) Carbocation
c) Zwitterion
d) Free radical

X. Which amines are produced by the reduction of amides?

a) Primary
b) Secondary
c) Tertiary
d) None of these

Q2. SHORT ANSWER QUESTIONS:

a) Give two preparations of phenyl amine

b) Give two preparations of secondary amines.

c) What is the chromophore in azo dyes? What is its function in dyes?

d) Why amides are less basic than ammonia.

e) What is zwitter ion?

f) Differentiate between primary, secondary & tertiary amines.

g) Write names & structures of four isomeric amines having the molecular formula C_3H_9N.

h) Convert ethanamine into methanamine.

i) How will you synthesize ethanal from ethanenitrile?

j) Define peptide bond. How many peptide bonds are there in a tripeptide?

k) Give all the tripeptides that could possibly be synthesized from glycine (Gly), alanine (Ala).

Q3. CONSTRUCTED RESPONSE QUESTIONS:

Complete the following reaction sequence by giving the structures of the compounds.

a) 1, 3, 5-tribromobenzene from benzene.

$$\text{benzene} \xrightarrow[H_2SO_4]{HNO_3} (A) \xrightarrow[HCl]{Sn} (B) \xrightarrow[FeBr_3]{Br_2\ (excess)} (C) \xrightarrow[HCl]{NaNO_2} (D) \xrightarrow[-N_2]{H_3PO_2} (E)$$

b) 1, 3, 5-Tribromobenzene from benzene.

$$\text{benzene ring} \xrightarrow[H_2SO_4]{HNO_3} (A) \xrightarrow[FeCl_3]{Cl_2} (B) \xrightarrow[HCl]{Sn} (C) \xrightarrow[HCl]{NaNO_2} (D) \xrightarrow[-N_2]{H_2O} (E)$$

c) Keep in view the scheme, devise a reaction sequence to prepare 4-Hydroxybenzoic acid from benzene.

LONG QUESTIONS

Q4. Describe the relative basicity of aqueous ammonia, ethyl amine and phenyl amine.

Q5. Give two preparation methods of each of the following.

i) Primary amines ii) Secondary amines

Q6. Write a note on electrophoresis.

Q7. Explain the formation of azo compounds from phenylamine and illustrate the preparation of a dye using this?