Amines

EXERCISE [PAGES 296 - 297]

Exercise | Q 1.01 | Page 296

Choose the most correct option.

The hybridisation of nitrogen in primary amine is _____.

1. sp
2. sp^2
3. **sp^3**
4. sp^3d

Solution: The hybridisation of nitrogen in primary amine is **sp^3**.

Exercise | Q 1.02 | Page 296

Choose the most correct option.

Isobutylamine is an example of _____.

1. 2° amine
2. 3° amine
3. **1° amine**
4. quaternary ammonium salt

Solution: Isobutylamine is an example of **1° amine**.

Exercise | Q 1.03 | Page 296

Choose the most correct option.

Which one of the following compounds has the highest boiling point?

1. **n-Butylamine**
2. sec-Butylamine
3. isobutylamine
4. tert-Butylamine

Solution: n-Butylamine

Exercise | Q 1.04 | Page 296

Choose the most correct option.

Which of the following has the highest basic strength?

1. Trimethylamine
2. Methylamine
3. Ammonia
4. **Dimethylamine**

Solution: Dimethylamine

Exercise | Q 1.05 | Page 296

Choose the most correct option.

Which type of amine does produce N_2 when treated with HNO_2?

1. **Primary amine**
2. Secondary amine
3. Tertiary amine
4. Both primary and secondary amines

Solution: Primary amine

Exercise | Q 1.06 | Page 296

Choose the most correct option.

Carbylamine test is given by _____.

1. **Primary amine**
2. Secondary amine
3. Tertiary amine
4. Both secondary and tertiary amines

Solution: The Carbylamine test is given by **Primary amine**.

Exercise | Q 1.07 | Page 296

Choose the most correct option.

Which one of the following compounds does not react with acetyl chloride?

1. $CH_3 - CH_2 - NH_2$
2. $(CH_3 - CH_2)_2NH$
3. **$(CH_3 - CH_2)_3N$**
4. $C_6H_5 - NH_2$

Solution: $(CH_3 - CH_2)_3N$

Exercise | Q 1.08 | Page 296

Choose the most correct option.

Which of the following compounds will dissolve in aqueous NaOH after undergoing reaction with Hinsberg reagent?

1. **Ethylamine**
2. Triethylamine
3. Trimethylamine
4. Diethylamine

Solution: Ethylamine

Exercise | Q 1.09 | Page 296

Choose the most correct option.

Identify 'B' in the following reactions

$$CH_3 - C \equiv N \xrightarrow{Na/C_2H_5OH} A \xrightarrow{NaNO_2/dilHCl} B$$

1. $CH_3 - CH_2 - NH_2$
2. $CH_3 - CH_2 - NO_2$
3. **$CH_3 - CH_2N_2^+Cl^-$**
4. $CH_3 - CH_2 - OH$

Solution: $CH_3 - CH_2N_2^+Cl^-$

Exercise | Q 1.1 | Page 296

Choose the most correct option.

Which of the following compounds contains azo linkage?

1. Hydrazine
2. **p-Hydroxyazobenzene**
3. N-Nitrosodiethylamine
4. Ethylenediamine

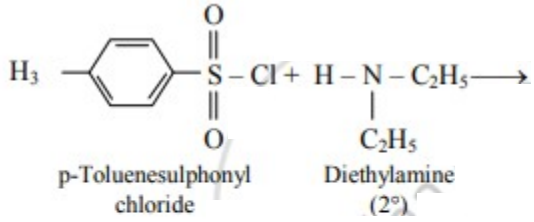
Solution: p-Hydroxyazobenzene

Exercise | Q 2.01 | Page 296

Answer in one sentence.

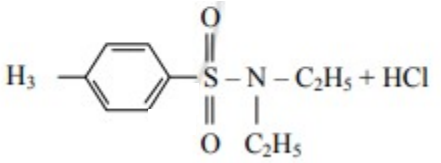
Write the reaction of p-toluenesulphonyl chloride with diethylamine.

Solution:



p-Toluenesulphonyl chloride

Diethylamine (2°)



N,N-Diethylbenzene p-toluenesulphonamide

Exercise | Q 2.02 | Page 296

Answer in one sentence.

How many moles of methylbromide is required to convert ethanamine to N, N-dimethyl ethanamine?

Solution:

Two moles of methyl bromide are required to convert ethanamine to N,N-dimethylethanamine.

Exercise | Q 2.03 | Page 297

Answer in one sentence.

Which amide does produce ethanamine by Hofmann bromamide degradation reaction?

Solution:

Propanamide ($C_2H_5CONH_2$) produces ethanamine by Hofmann bromamide degradation reaction.

Exercise | Q 2.04 | Page 297

Answer in one sentence.

Write the order of the basicity of aliphatic alkylamine in the gaseous phase.

Solution:

Order of basicity of aliphatic alkylamine in gaseous phase: 3° amines > 2° amines >1° amine.

Exercise | Q 2.05 | Page 297

Answer in one sentence.

Why are primary aliphatic amines stronger bases than ammonia?

Solution:

i. This is due to the presence of an alkyl group that exerts electron releasing inductive effect (+I effect). This stabilizes the positive charge on the atom bonded to it.

ii. The conjugate acid of ammonia is (NH_4^+) and that of 1° amine is (RNH_3^+). The presence of the alkyl group results in increased stability of RNH_3^+ □ as compared to NH_4^+ . Thus, primary aliphatic amines are stronger bases than ammonia.

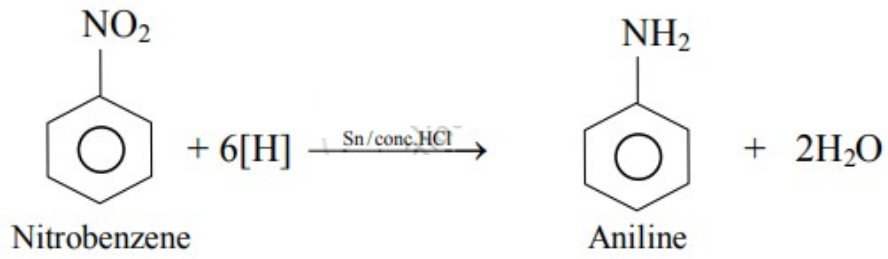
Exercise | Q 2.06 | Page 297

Answer in one sentence.

Predict the product of the following reaction.

$$\text{Nitrobenzene} \xrightarrow{\text{Sn/conc} \cdot \text{HCl}} ?$$

Solution:



Exercise | Q 2.07 | Page 297

Answer in one sentence.

Write the IUPAC name of benzylamine.

Solution: IUPAC name of benzylamine is phenylmethanamine.

Exercise | Q 2.08 | Page 297

Answer in one sentence.

Arrange the following amines in increasing order of boiling points.

n-propylamine, ethylmethyl amine, trimethylamine.

Solution: Trimethylamine (3°) < ethylmethyl amine (2°) < n-propylamine (1°)

Exercise | Q 2.09 | Page 297

Answer in one sentence.

Write the balanced chemical equations for the action of dil H_2SO_4 on diethylamine.

Solution: The action of dil. sulphuric acid on diethylamine gives diethylammonium sulphate.

$$\underset{\text{Diethylamine}}{2\,(C_2H_5)_2NH} + \underset{\text{Sulphuric acid}}{H_2SO_4} \rightleftharpoons \underset{\text{Diethylammonium sulphate}}{[(C_2H_5)_2]NH_2^+]_2SO_4^{2-}}$$

Exercise | Q 2.1 | Page 297

Answer in one sentence.

Arrange the following amines in the increasing order of their pK_b values.

Aniline, Cyclohexylamine, 4-Nitroaniline

Solution: Cyclohexylamine < aniline < 4-nitroaniline.

Exercise | Q 3.01 | Page 297

Answer the following

Identify A and B in the following reactions.

$$C_6H_5CH_2Br \xrightarrow[KCN]{\text{alco}\cdot} A \xrightarrow{Na/\text{ethanol}} B\cdot$$

Solution:

$$\underset{\text{Benzyl bromide}}{C_6H_5-CH_2-Br} \xrightarrow{\text{alcoholic KCN}} \underset{\text{Phenylacetonitrile (A)}}{C_6H_5-CH_2-C\equiv N} \xrightarrow{Na/\text{ethanol}} \underset{\text{2-Phenylethylamine (B)}}{C_6H_5-CH_2-CH_2-NH_2}$$

Exercise | Q 3.02 | Page 297

Answer the following

Explain the basic nature of amines with a suitable example.

Solution:

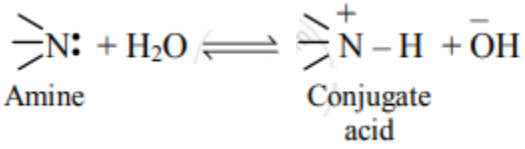
The basic nature of amines is due to the presence of a lone pair of electrons on the nitrogen atom.

i. Lewis theory: In terms of Lewis theory, amines are bases because they can share a lone pair of electrons on ‘N’ atom with an electron-deficient species.

For example, trimethylamine shares its lone pair of electrons with the electron-deficient boron trifluoride.

$Me_3N: + BF_3 \rightarrow Me_3N^+ – B^-F_3$

ii. Lowry-Bronsted theory: The basic nature of amines is explained by writing the following equilibrium.



a. In this equilibrium amine accepts H+, hence an amine is a LowryBronsted base.
b. For a stronger base, this equilibrium shifts towards the right, thereby, for stronger bases, the K_b value is larger or the pK_b value is smaller.

Exercise | Q 3.03 | Page 297

Answer the following

What is diazotisation ?

Solution:

Aliphatic/aromatic primary amines react with nitrous acid to form corresponding diazonium salts. This reaction is called as diazotisation.

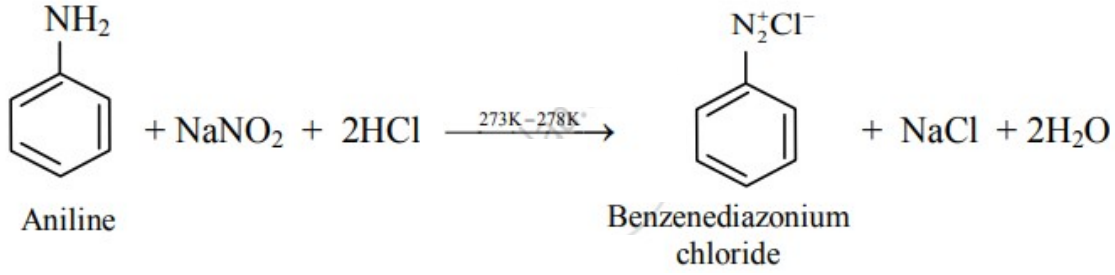
Exercise | Q 3.03 | Page 297

Answer the following

Write diazotisation reaction of aniline?

Solution:

Diazotisation reaction of aniline:



Exercise | Q 3.04 | Page 297

Answer the following

Write a reaction to convert acetic acid into methylamine.

Solution:

$$\underset{\text{Acetamide}}{CH_3-\overset{\overset{O}{\|}}{C}-NH_2} + Br_2 + 4\,KOH_{(aq)} \xrightarrow{\Delta} \underset{\text{Methylamine}}{CH_3-NH_2} + 2\,KBr + K_2CO_3 + 2\,H_2O$$

Exercise | Q 3.05 | Page 297

Answer the following

Write a short note on coupling reactions.

Solution:

The reaction involves the retention of diazo groups.

i. Arenediazonium salts when treated with certain reactive aromatic compounds such as phenols or aromatic amines, give azo compounds.

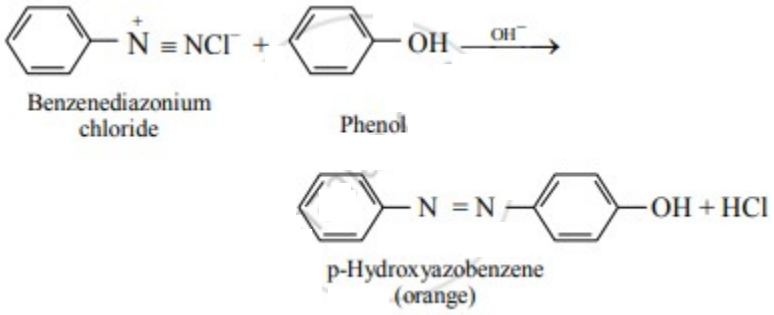
ii. These have extended conjugated system of double bonds in which two aromatic rings are joined through the azo group – N = N–. This reaction is called azo coupling.

iii. Azo compounds are brightly coloured and are used as dyes.

iv. This is an example of an electrophilic aromatic substitution reaction. Here, the electrophiles are positively charged diazonium ions.

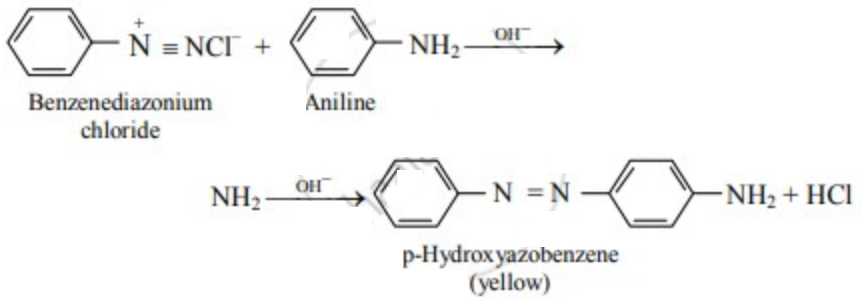
v. Substitution usually occurs para to the ring activating group.

e.g. Benzenediazonium chloride reacts with phenol in mild alkaline medium to give p-hydroxyazobenzene (orange dye).



vi. Azo coupling with β-naphthol in NaOH is used as a confirmatory test for primary aromatic amines.

vii. Benzenediazonium chloride reacts with aniline in mild alkaline medium to give p-aminoazobenzene (yellow dye.)



Exercise | Q 3.06 | Page 297

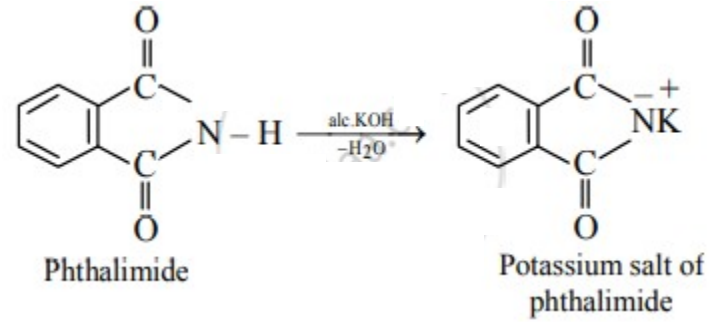
Answer the following

Explain Gabriel phthalimide synthesis.

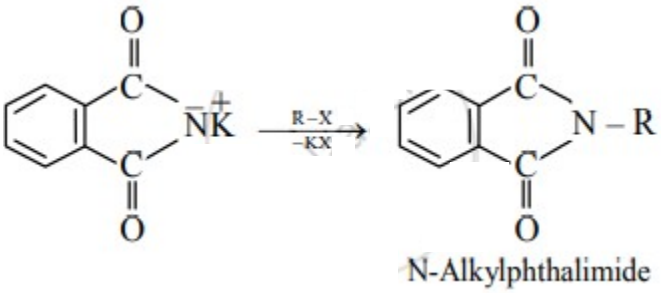
Solution:

This method is used for the synthesis of primary amine. It involves the following three stages.

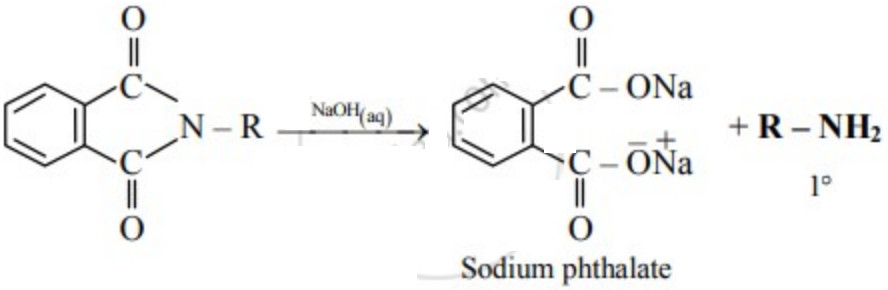
i. Formation of the potassium salt of phthalimide from phthalimide on reaction with alcoholic potassium hydroxide.



ii. Formation of N-alkyl phthalimide from the potassium salt by reaction with an alkyl halide.



iii. Alkaline hydrolysis of N-alkyl phthalimide to form the corresponding primary amine.



Exercise | Q 3.07 | Page 297

Answer the following

Explain carbylamine reaction with suitable examples.

Solution:

Carbylamine reaction:

i. Aliphatic or aromatic primary amines on heating with chloroform give foul (offensive) smelling products called alkyl/aryl isocyanides or carbylamines.

ii. This reaction is a test for primary amines. Secondary and tertiary amines do not give this test.

$$\underset{1^\circ}{R-NH_2} + CHCl_3 + 3\,KOH \xrightarrow{\Delta} \underset{\text{Alkyl isocyanide}}{R-NC} + 3\,KCl + 3\,H_2O$$

e.g.

a.

$$\underset{\text{Ethylamine}}{CH_3-CH_2-NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3\,KOH \xrightarrow{\Delta} \underset{\text{Ethyl isocyanide}}{C_2H_5-NC} + 3\,KCl + 3\,H_2O$$

b.

$$\underset{\text{Aniline}}{C_6H_5-NH_2} + \underset{\text{Chloroform}}{CHCl_3} + 3\,KOH \xrightarrow{\Delta} \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3\,KCl + 3\,H_2O$$

Exercise | Q 3.08 | Page 297

Answer the following

Write a reaction to convert methanamine into ethanamine.

Solution:

Methanamine into ethanamine:

$$\underset{\text{Methanamine}}{CH_3-NH_2} \xrightarrow[273-278\ K]{NaNO_2/HCl} [CH_3-N_2^+Cl^-] \xrightarrow{H_2O} CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow{\text{Ethanolic NaCN}} CH_3CN \xrightarrow{Na/C_2H_5OH} \underset{\text{Ethanamine}}{CH_3CH_2NH_2}$$

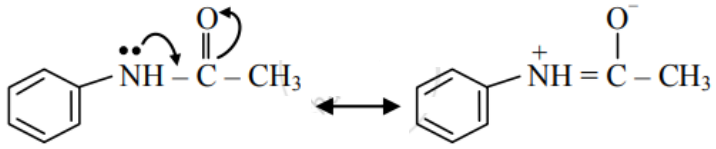
Exercise | Q 3.08 | Page 297

Answer the following

Write a reaction to convert Aniline into p-bromoaniline.

Solution:

–NH_2 group in aniline is highly ringing activating and o-/p- directing due to the involvement of the lone pair of electrons on 'N' in resonance with the ring. As a result, on reaction with Br_2, it gives 2,4,6-tribromoniline. To get a monobromo product, it is necessary to decrease the ring activating effect of -NH_2 group. This is done by acetylation of aniline. The lone pair of 'N' in acetanilide is also involved in resonance in the acetyl group. To that extent ring activation decreases.



Hence, acetanilide on bromination gives a monobromo product p-bromoacetanilide. After monobromination, the original -NH_2 group is regenerated. The protection of the -NH_2 group in the form of acetyl group is removed by acid-catalyzed hydrolysis to get p-bromoaniline, as shown in the following scheme.