

# Amines

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## 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<sub>2</sub> when treated with HNO<sub>2</sub>?

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<sub>3</sub> - CH<sub>2</sub> - NH<sub>2</sub>
2. (CH<sub>3</sub> - CH<sub>2</sub>)<sub>2</sub>NH
3. **(CH<sub>3</sub> - CH<sub>2</sub>)<sub>3</sub>N**
4. C<sub>6</sub>H<sub>5</sub> - NH<sub>2</sub>

**Solution:**  $(\text{CH}_3 - \text{CH}_2)_3\text{N}$

**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?

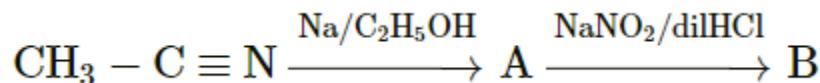
1. Ethylamine
2. Triethylamine
3. Trimethylamine
4. Diethylamine

**Solution:** Ethylamine

**Exercise | Q 1.09 | Page 296**

**Choose the most correct option.**

Identify 'B' in the following reactions



1.  $\text{CH}_3 - \text{CH}_2 - \text{NH}_2$
2.  $\text{CH}_3 - \text{CH}_2 - \text{NO}_2$
3.  **$\text{CH}_3 - \text{CH}_2\text{N}_2^+\text{Cl}^-$**
4.  $\text{CH}_3 - \text{CH}_2 - \text{OH}$

**Solution:**  $\text{CH}_3 - \text{CH}_2\text{N}_2^+\text{Cl}^-$

**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

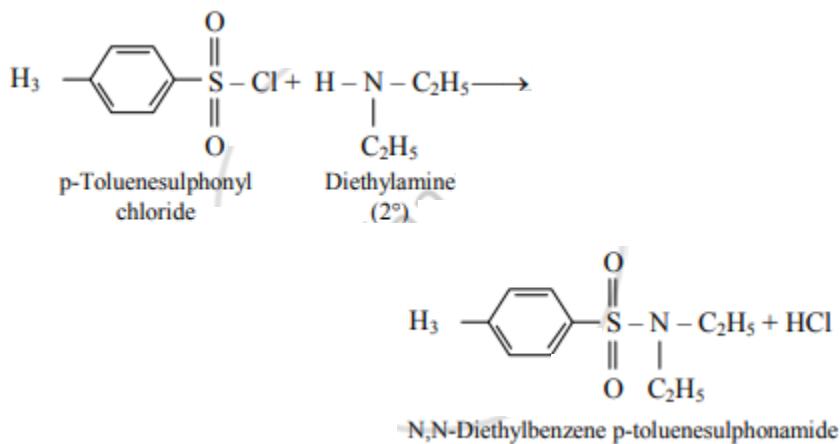
**Solution:** p-Hydroxyazobenzene

**Exercise | Q 2.01 | Page 296**

**Answer in one sentence.**

Write the reaction of p-toluenesulphonyl chloride with diethylamine.

**Solution:**



**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<sub>2</sub>H<sub>5</sub>CONH<sub>2</sub>) 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?

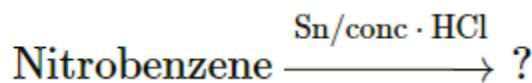
**Solution:**

- 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 ( $\text{NH}_4^+$ ) and that of 1° amine is ( $\text{RNH}_3^+$ ). The presence of the alkyl group results in increased stability of  $\text{RNH}_3^+$  as compared to  $\text{NH}_4^+$ . Thus, primary aliphatic amines are stronger bases than ammonia.

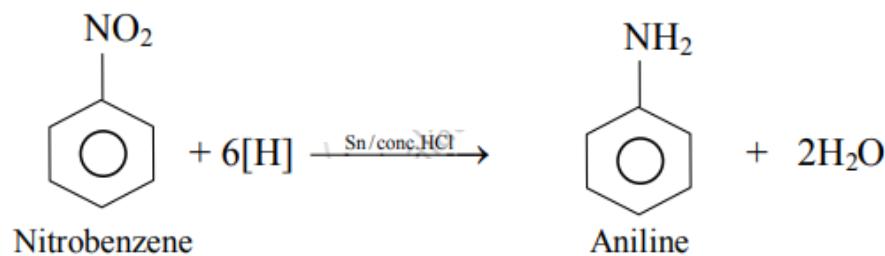
**Exercise | Q 2.06 | Page 297**

**Answer in one sentence.**

Predict the product of the following reaction.



**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.

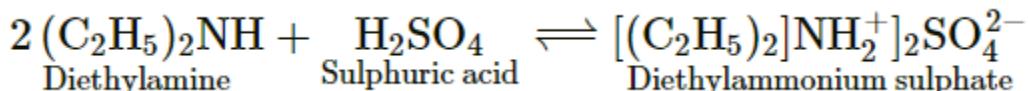
**Solution:** Trimethylamine ( $3^\circ$ ) < ethylmethyl amine ( $2^\circ$ ) < n-propylamine ( $1^\circ$ )

### 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.



### Exercise | Q 2.1 | Page 297

**Answer in one sentence.**

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

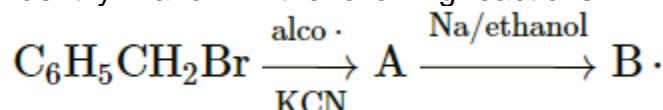
Aniline, Cyclohexylamine, 4-Nitroaniline

**Solution:** Cyclohexylamine < aniline < 4-nitroaniline.

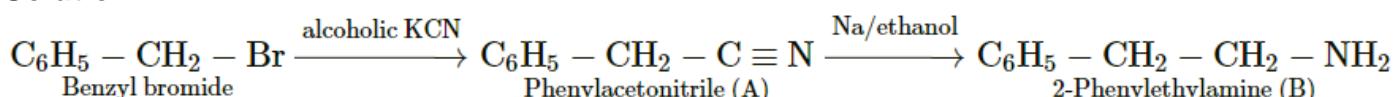
### Exercise | Q 3.01 | Page 297

**Answer the following**

Identify A and B in the following reactions.



**Solution:**



### Exercise | Q 3.02 | Page 297

**Answer the following**

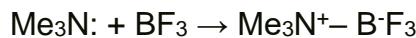
Explain the basic nature of amines with a suitable example.

**Solution:**

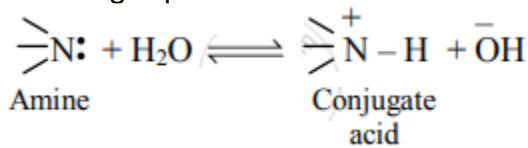
The basic nature of amines is due to the presence of a lone pair of electrons on the nitrogen atom.

**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.



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



- In this equilibrium amine accepts H<sup>+</sup>, hence an amine is a Lowry-Bronsted base.
- For a stronger base, this equilibrium shifts towards the right, thereby, for stronger bases, the K<sub>b</sub> value is larger or the pK<sub>b</sub> 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.

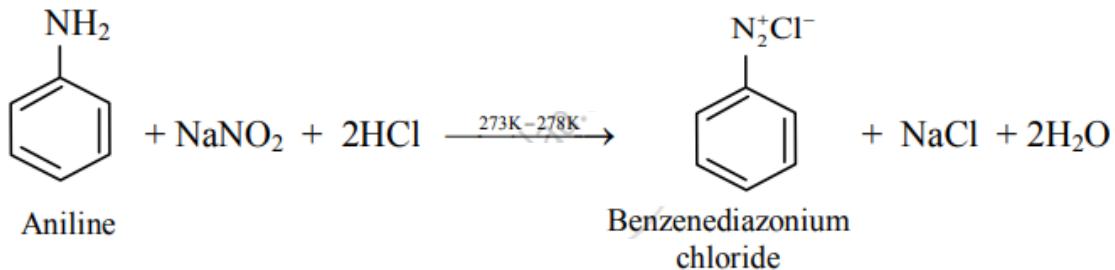
### Exercise | Q 3.03 | Page 297

**Answer the following**

Write diazotisation reaction of aniline?

**Solution:**

**Diazotisation reaction of aniline:**

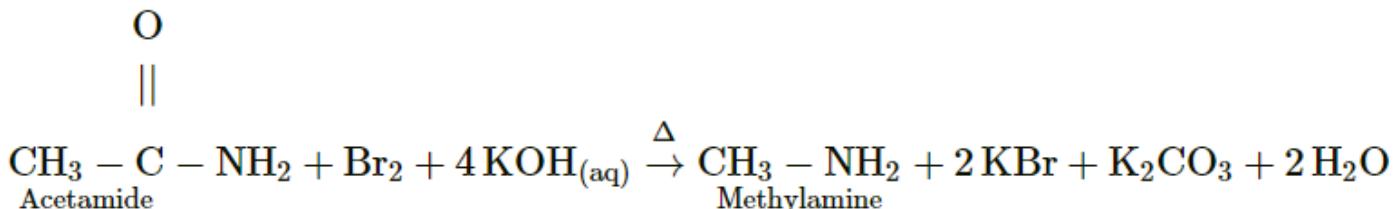


### Exercise | Q 3.04 | Page 297

**Answer the following**

Write a reaction to convert acetic acid into methylamine.

**Solution:**



### Exercise | Q 3.05 | Page 297

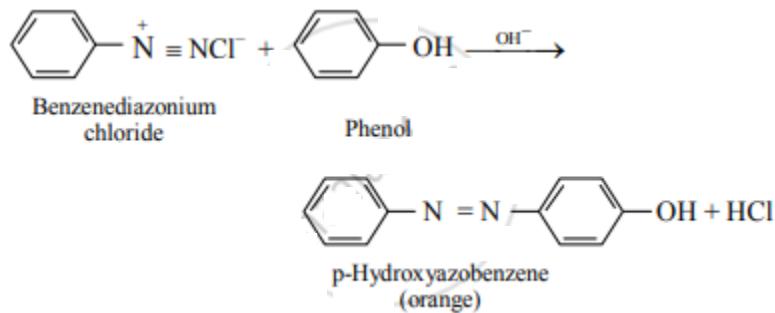
#### Answer the following

Write a short note on coupling reactions.

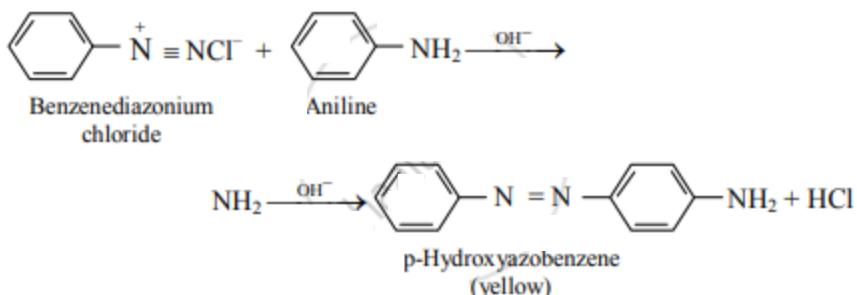
#### Solution:

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

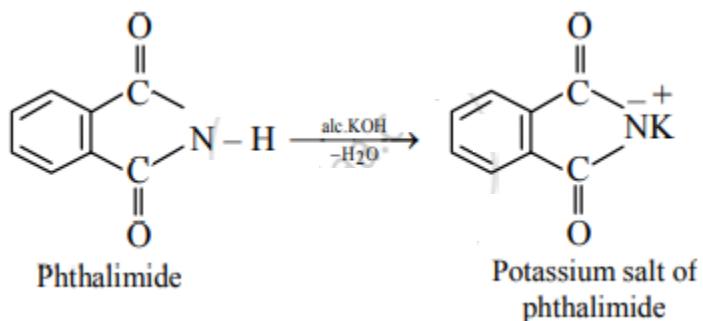
#### Answer the following

Explain Gabriel phthalimide synthesis.

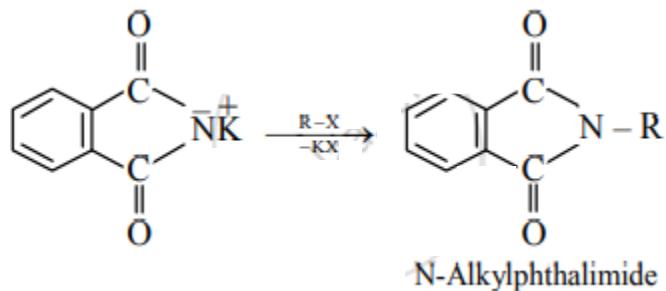
#### Solution:

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

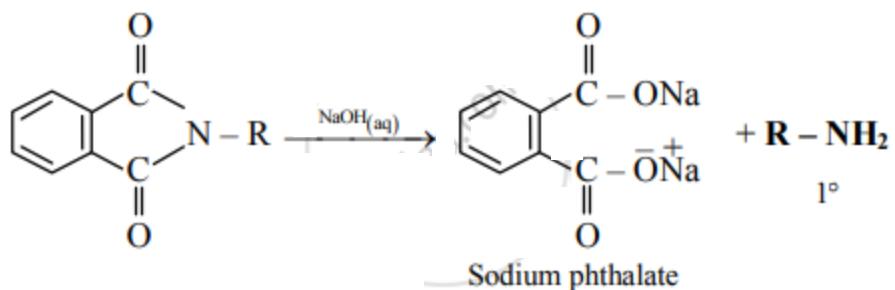
- i. **Formation of the potassium salt of phthalimide** from phthalimide on reaction with alcoholic potassium hydroxide.



- 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

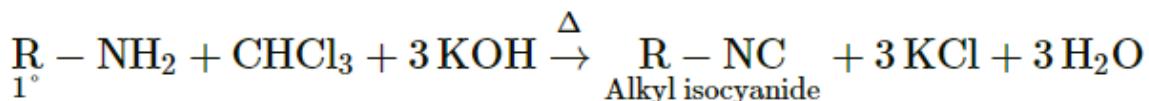
**Answer the following**

Explain carbylamine reaction with suitable examples.

**Solution:**

**Carbylamine reaction:**

- Aliphatic or aromatic primary amines on heating with chloroform give foul (offensive) smelling products called alkyl/aryl isocyanides or carblylamines.
- This reaction is a test for primary amines. Secondary and tertiary amines do not give this test.

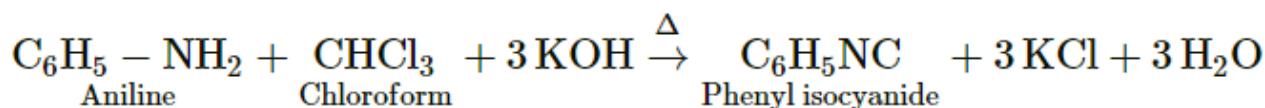


**e.g.**

**a.**



**b.**



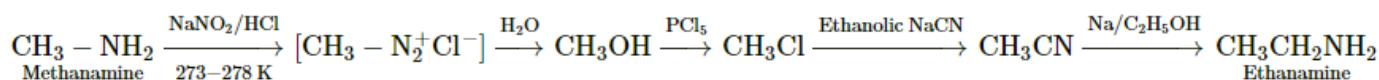
### Exercise | Q 3.08 | Page 297

**Answer the following**

Write a reaction to convert methanamine into ethanamine.

**Solution:**

### Methanamine into ethanamine:



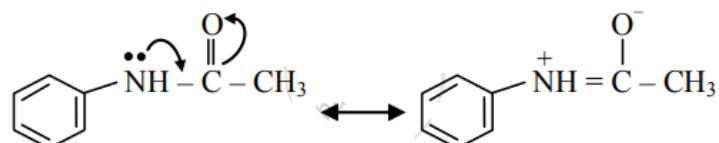
Exercise | Q 3.08 | Page 297

## **Answer the following**

Write a reaction to convert Aniline into p-bromoaniline.

**Solution:**

$-\text{NH}_2$  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  $\text{Br}_2$ , it gives 2,4,6-tribromoniline. To get a monobromo product, it is necessary to decrease the ring activating effect of  $-\text{NH}_2$  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  $\text{-NH}_2$  group is regenerated. The protection of the  $\text{-NH}_2$  group in the form of acetyl group is removed by acid-catalyzed hydrolysis to get p-bromoaniline, as shown in the following scheme.

