Aryl Diazonium Salts

Topics Covered

- Preparation of Benzene Diazonium Chloride
- Properties

 Importance of Diazonium Salts in Synthesis of Aromatic Compounds

Diazonium salts are formed when primary aryl amines or their salt react with nitrous acid in ice cold solution. They have the general formula, $\operatorname{ArN}_{2}^{+}X^{-}$, where X may be Cl⁻, Br⁻, HSO₄⁻, NO₃⁻, etc.

The N_2^+ (i.e. $-N \equiv N$) is called **diazo group**. They are named by adding the suffix diazonium to the name of the parent hydrocarbon from which they are derived.

and $H_3C \longrightarrow N \equiv N HSO_4^-$ is benzene diazonium hydrogen sulphate.

Preparation of Benzene Diazonium Chloride

Benzene diazonium chloride is prepared by the reaction of aniline with nitrous acid (which is produced by the reaction of sodium nitrite and HCl) at 273-278 K.

$$NaNO_2 + HCl \xrightarrow{273-278 \text{ K}} NaCl + HNO_2$$

$$\begin{array}{c} C_{6}H_{5}NH_{2} + HNO_{2} + HCI \xrightarrow{273 \cdot 278 \text{ K}} & C_{6}H_{5}N_{2}CI + 2H_{2}O \\ \text{Aniline} & \text{Benzene diazonium} \end{array}$$

This process of conversion of a primary aromatic amine into their diazonium salts is called **diazotisation**. The reaction is carried out at a low temperature $(0-5^{\circ}C)$ because, both nitrous acid and diazonium salt would decompose at higher temperature.

Properties

Physical Properties

Dry aryl diazonium salts are unstable crystalline solids and readily explode liberating N_2 gas. Therefore, they are not isolated and are used in the solution in which they are prepared.

Chemical Properties

The chemical reactions of diazonium salts are given below:

 (i) Replacement by hydrogen: Synthesis of benzene When benzene diazonium salt solution is treated with hypophosphorous acid, the diazo group is replaced by hydrogen and benzene is formed.

 $\begin{array}{c} \mathrm{C_6H_5N_2^-Cl^-} + \mathrm{H_3PO_2} + \mathrm{H_2O} \longrightarrow \\ \mathrm{Benzene} \\ \mathrm{diazonium} \\ \mathrm{chloride} \\ & \mathrm{C_6H_6} + \mathrm{H_3PO_3} + \mathrm{HCl} + \mathrm{N_2} \uparrow \\ \mathrm{Benzene} \end{array}$

This process is known as de-amination.

(ii) Replacement by halogen: Synthesis of chlorobenzene, bromobenzene and iodobenzene

Sandmeyer reaction In this reaction replacement of the diazonium group by chloride, bromide takes place. Nucleophiles such as Cl⁻ and Br⁻ replace the diazonium group, if appropriate cuprous salt is added to the solution containing diazonium group.



Bromobenzene

Nucleophiles, such Cl^- or Br^- can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder. This reaction is known as **Gattermann reaction**.



Iodine is not easily introduced into the benzene ring directly but when the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.



(iii) Replacement by cyano group: Synthesis of aryl cyanides (Sandmeyer's reaction)

Benzene diazonium chloride when heated with cuprous cyanide, it gives phenyl cyanide.



This method is used for introducing — CN group and hence —CH, —NH $_2$ and — COOH groups in benzene.

 $\begin{array}{ccc} C_{6}H_{5}CH_{2}NH_{2} & \xrightarrow{H_{2}/Ni} & C_{6}H_{5}CN \xrightarrow{H_{2}O/H^{+}} & C_{6}H_{5}COOH \\ & & \text{Phenyl} & & \text{Benzoic acid} \\ & & & \downarrow & \text{SnCl}_{2}/\text{conc.HCl} \\ & & & C_{6}H_{5}CHO \\ & & & \text{Benzaldehyde} \end{array}$

(iv) Replacement by hydroxyl group: Synthesis of phenol When benzenediazonium salt solution is boiled with water containing H₂SO₄, it undergoes hydrolysis and diazo group is replaced by — OH group and phenol is formed.

$$\begin{array}{c} C_{6}H_{5}N_{2}^{+}Cl^{-}+H_{2}O \xrightarrow[Boil]{Boil} C_{6}H_{5} \xrightarrow[Phenol]{OH} + N_{2}\uparrow + HCl \\ Benzene \\ diazonium \\ chloride \end{array}$$

(v) Replacement by fluorine: Synthesis of fluorobenzene When arene diazonium chloride is treated with fluoroboric acid, arene diazonium fluoroborate is precipitated which on heating decomposes to yield aryl fluoride.



This reaction is called **Balz-Schiemann reaction**.

(vi) Replacement by nitro $(-NO_2)$: Synthesis of

nitrobenzene When arene diazonium fluoroborate combines with $NaNO_2$ followed by heat then nitrobenzene is formed.



Reactions involving Retention of Diazo Group or Coupling Reactions

Benzene diazonium chloride reacts with electron rich aromatic compounds, like phenol and amine to give the product azobenzene compounds, Ar— N = N—Ar. The reaction is known as coupling reaction.

The azo products obtained have both the aromatic rings joined through the -N=N- bonds, are coloured and used as dyes. Coupling with benzene substrates occur preferentially at less sterically hindered *p*-position to the hydroxy or amino group. But, if this position is blocked then *o*-coupling occurs.

Coupling with phenols occurs in the basic medium (pH 9-10) at 273-298 K.



Similarly, the reaction of diazonium salt with aniline gives p-aminoazobenzene (yellow dye).

Coupling with amines occur in the acidic medium. (pH 4-5) at 273-298 K.



Azo dyes always contain one or more than one SO₃⁻Na⁺ groups, so that they are soluble in water.



Importance of Diazonium Salts in Synthesis of Aromatic Compounds

Diazonium salts are important in synthesis of aromatic compounds due to following facts:

- (i) Diazonium salts are very good intermediates for the introduction of —F, —Cl, —OH, —CN, —NO₂, etc. into the aromatic ring.
- (ii) Similarly, aryl fluorides and iodides cannot be prepared by direct halogenation. Cyano group cannot be introduced by nucleophilic substitution but cyanobenzene can be prepared from diazonium salts.
- (iii) Thus, replacement of diazo group by other group is helpful in preparing those aromatic compounds which cannot be prepared by direct substitution in benzene.

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK Questions

Important Questions

- Q.1 The diazonium salts are the reaction products of the reaction of nitrous acid with [Textbook]
 - (a) primary aliphatic amines
 - (b) primary aromatic amines
 - (c) secondary aliphatic amines
 - (d) secondary aromatic amines
- **Sol** (b) The diazonium salts are the reaction products of the reaction of nitrous acid with primary aromatic amines.

$$NaNO_2 + HCl \xrightarrow{0.5 \circ C} NaCl + HNO_2$$

Nitrous
acid

 C_6H_5 —NH₂ + HNO₂ + HCl $\xrightarrow{0.5 \circ C}$ Aniline (primary aromatic amine)

 $C_6H_5N_2^+Cl^- + 2H_2O$ (1) Benzene diazonium chloride

(1)

- Q.2 Preparation of a diazonium salt from a primary aromatic amine is known as [Textbook] (a) coupling reaction (c) diazotisation (d) Corey-House synthesis
- **Sol** (c) Preparation of diazonium salt from a primary aromatic amine is known as diazotisation.

$$\begin{array}{c} \text{NaNO}_2 + \text{HCl} & \xrightarrow{0.5^{\circ} \text{ C}} \text{NaCl} + \text{HNO}_2 \\ & \text{Nitrous acid} \\ \text{C}_6\text{H}_5 & -\text{NH}_2 + \text{HNO}_2 + \text{HCl} & \xrightarrow{0.5^{\circ} \text{ C}} \\ \text{Aniline} & & \text{C}_6\text{H}_5 \overset{+}{\text{N}_2}\text{Cl}^- & + 2\text{H} \end{array}$$

ine
$$C_6H_5\overset{+}{N_2}Cl^- + 2H_2O$$

Benzene diazonium chloride (1)

Q.3 Benzene diazonium chloride reacts with hypophosphorus acid to form [Textbook] (a) phenol (b) benzaldehyde

(c) aniline	(d) benzene
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Sol (d) Benzene diazonium chloride reacts with hypophosphorous acid to form benzene.

 C_6H

Benzene

$$\begin{array}{l} & \stackrel{+}{_{5}} \overset{+}{_{N_{2}}} \mathrm{Cl}^{-} &+ \mathrm{H}_{3} \mathrm{PO}_{2} + \mathrm{H}_{2} \mathrm{O} \longrightarrow \\ & \text{diazonium} \\ & \text{aloride} \\ & & \mathrm{C}_{6} \mathrm{H}_{6} + \mathrm{H}_{3} \mathrm{PO}_{3} + \mathrm{HCl} + \mathrm{N}_{2} \\ & & \text{Benzene} \end{array}$$

- Q.4 Benzene diazonium chloride reacts with phenol
 - to form[Textbook](a) p-chlorophenol(b) chlorobenzene

(c) *p*-hydroxyazobenzene (d) DDT

Sol (c) Benzene diazonium chloride reacts with phenol to form *p*-hydroxyazobenzene.

$$\underbrace{\bigcirc}_{\text{Phenol}}^{+} \mathbb{N} \mathbb{C} \mathbb{I}^{-} + \mathbb{H} - \underbrace{\bigcirc}_{\text{Phenol}}^{-} \mathbb{O} \mathbb{H} \xrightarrow{273 \cdot 278 \text{ K}}$$

$$\underbrace{\bigcirc}_{\text{Phenol}}^{-} \mathbb{N} = \mathbb{N} - \underbrace{\bigcirc}_{p \cdot \text{hydroxyazobenzene}}^{-} \mathbb{O} \mathbb{H} + \mathbb{H} \mathbb{C} \mathbb{I}$$

$$\underbrace{p \cdot \text{hydroxyazobenzene}}_{p \cdot \text{hydroxyazobenzene}}$$

$$(1)$$

- Q.5 Chlorobenzene can be prepared by treatment of aniline with [Textbook]
 - (a) cuprous chloride
 - (b) chlorine in the presence of UV light

(c) nitrous acid followed by treatment with CuCl (d) chlorine in the presence of \mbox{FeCl}_3

Sol (c) Chlorobenzene is prepared by treatment of aniline with nitrous acid followed by treatment with CuCl.



- **Q.6** Iodobenzene can be prepared by [Textbook] (a) treating chlorobenzene with I_2 using FeCl₃ catalyst
 - (b) treating phenol with I_2 in NaOH solution
 - (c) treating benzene diazonium chloride with KI
 - (d) treating benzene with CH_3I using $AlCl_3$ catalyst
- **Sol** (c) Iodine is not easily introduced into the benzene ring directly but when the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.



(1)

Q.7 Benzene diazoniur	7 Benzene diazonium chloride reacts with warm		
water to give	[Textbook]		
(a) aniline	(b) phenol		
(c) benzene	(d) chlorobenzene		

Sol (b) When benzene diazonium chloride reacts with warm water to give phenol.

Q.8 Bromobenzene can be prepared by treating aniline with [Textbook] (a) conc.HBr (b) Br₂/FeBr₃ (c) CuBr (d) nitrous acid then CuBr

dia

Sol (d) Bromobenzene is prepared by treating aniline with nitrous acid then CuBr.



Q.9 Which of the following reagents is used to prepare benzene diazonium chloride from aniline? [Textbook]
(a) NaNO₂ + HCl
(b) LiAlH₄

(c) $NH_2NH_2 + KOH$ (d) NaOH

Sol (a) Benzene diazonium chloride is prepared by the reaction of aniline with nitrous acid which is produced by the reaction of sodium nitrite and HCl at 0.5°C temperature.



- Q.10 Which of the following are optimum temperature conditions for making benzene diazonium chloride from aniline? [Textbook]
 (a) 0°C to 10°C
 (b) 20°C to 25°C
 (c) 30°C to 40°C
 (d) 45°C to 50°C
- Sol (a) The reaction is carried out at low temperature (0°C to 10°C) because both nitrous acid and diazonium salt would decompose at higher temperature. (1)
- Q.11 Write the structure of benzene diazonium chloride.

Sol
$$\sqrt{}$$
 $\stackrel{+}{N=}$ NCl⁻ (1)

Q.12	Aqueous solution of benzene diazonium chloride	
	on heating yields	[Textbook]
Sol	phenol.	(1)
Q.13	Benzene diazonium chloride reacts wit	th $ m H_3PO_2$
	to form	[Textbook]
Sol	benzene.	(1)
Q.14	Benzene diazonium chloride reacts with medium to form an orange dye.	h phenol in [Textbook]
Sol	alkaline.	(1)
Q.15	Complete the following reaction.	[Textbook]
	$C_6H_5N_2^+Cl^-$ — H_2O	\rightarrow

Sol
$$C_6H_5N_2^+Cl^- \xrightarrow{H_2O} C_6H_5OH + N_2^+ + HCl$$

Benzene diazonium $\Delta \xrightarrow{Phenol} Phenol$ (1)

2 MARK Questions

Exams' Questions

Q.16 What is Sandmeyer's reaction? Give equation.
[2015]

Sol When solution of benzene diazonium chloride is added to $CuCl_2$ or $CuBr_2$, we get the corresponding halobenzene. The reaction is called Sandmeyer's reaction.

$$\begin{array}{c}
\overbrace{\mathbf{N}}^{\mathbf{N}} \stackrel{\mathbf{N} \stackrel{\mathbf{Cu} \mathcal{Cl}_{2}}{\longrightarrow}} & \overbrace{\mathbf{O}}^{\mathbf{Cl}} + \mathcal{N}_{2} \\
\begin{array}{c}
\text{Benzene diazonium} & \text{Chlorobenzene} \\
\overbrace{\mathbf{Cu} \mathcal{Br}_{2}}^{\mathbf{V}} \stackrel{\mathbf{Cl}}{\xrightarrow{\mathbf{Cu} \mathcal{Br}_{2}}} & \overbrace{\mathbf{O}}^{\mathbf{Br}} + \mathcal{N}_{2} \\
\end{array}$$

$$\begin{array}{c}
\text{Benzene diazonium} & \text{Bromobenzene} \\
\end{array}$$
(1)

Benzene diazonium chloride

(1)

Q.17 What do you mean by coupling reaction? [2014]

Sol Arene diazonium salts react with electron rich aromatic compounds such as phenols and amines to form coloured azo compounds, Ar - N = N—Ar.

This reaction is known as **coupling reaction**.

$$Ar \longrightarrow N = N \overline{Cl} \xrightarrow{Coupling} Ar \longrightarrow N = N \longrightarrow OH$$

$$Ar \longrightarrow OH$$

$$Ar$$

Q.18 What is diazo reaction? Give equation. [2011]

Sol The reaction between a 1° arylamine and $NaNO_2$ in the presence of a mineral acid to produce aryldiazonium salt is called diazo reaction. (1)

$$C_6H_5NH_2 + HNO_2 + HCl \xrightarrow{0.5^{\circ}C} C_6H_5N_2^+Cl^- + 2H_2O$$
(1)

Important Questions

- **Q.19** How would you prepare cyanides from benzene diazonium chloride?
- *Sol* By the action of KCN in the presence of Cu powder, aromatic cyano compounds are formed.



- Q.20 How would you convert benzene diazonium chloride to iodobenzene?
 - **Sol** By treating benzene diazonium chloride with potassium iodide.



<u>3 MARK</u> Questions

Exams' Questions

Q.21 What is coupling reaction? Explain with example.

Or What is coupling reaction? Give two examples.
[Textbook]

Sol Coupling Reaction Coupling reactions are given by benzene diazonium salt. When reacts with electron rich aromatic compounds, like phenol and aniline to give coloured azo compounds,

Ar — N = N — Ar. In these reactions, the azo group (-N=N-) of diazonium salt is retained in the product. Coupling reactions generally take place at *p*-position. e.g.

Benzene diazonium chloride reacts with phenol and aniline, where they are at molecule at *para*-position coupled with diazonium salt to give the product p -hydroxyazobenzene.







Important Question



7 MARK Questions

Exams' Questions

[2015]

- Q.23 Starting from nitrobenzene how will you prepare benzene diazonium chloride? Give the method of synthesis of (i) *p*-hydroxy azobenzene and (ii) fluorobenzene from benzene diazonium chloride. (2019)
- Sol Benzene diazonium chloride from nitrobenzene

Reduction of $C_6H_5\cdot NO_2$ by Sn/HCl give aniline, which on reaction with $NaNO_2$ + HCl at low temperature gives benzene diazonium chloride as follows :



(i) Synthesis of *p*-hydroxy azobenzene from benzene diazonium chloride



(ii) Fluorobenzene from benzene diazonium chloride



(2)

- **Q.24** What is diazo reaction ? Write the structure of the product of this reaction. Using this reaction how the following compounds are prepared? (ii) Fluorobenzene (i) Benzene [2016]
 - Sol The reaction between a 1° arylamine and NaNO₂ in the presence of a mineral acid to produce aryldiazonium salt is called diazo reaction. $C_6H_5NH_2 + HNO_2 + HCl \xrightarrow{0.5 \circ C} C_6H_5N_2Cl + 2H_2O$

Structure of C₆H₅N₂Cl is

(i) **Preparation of benzene**





Benzene



- diazonium chloride. Write its synthetic applications for preparation of (i) chlorobenzene (ii) phenol (iii) benzene (iv) iodobenzene [2014]
- Sol (i) Preparation of chlorobenzene Refer to text on page 319. (1) (ii) **Preparation of phenol** Refer to text on page 319. (1)(iii) Preparation of benzene Refer to text on page 319. (1) (iv) Preparation of iodobenzene Refer to text on page 319. (1)

- **Q.26** How is benzene diazonium chloride prepared from aniline? How are the following compounds prepared from it? [2014, 2012] (a) Benzene (b) Phenol (c) Iodobenzene (d) Phenylcyanide
 - Sol Preparation Aniline reacts with nitrous acid produced in situ from NaNO₂ and HCl at 0-5°C to give benzene diazonium chloride. This reaction is known as diazotisation reaction.

NaNO₂ + HCl
$$\longrightarrow$$
 HNO₂ + NaCl
C₆H₅ \longrightarrow NH₂ + HNO₂ + HCl $\xrightarrow{0.5 \circ C}$
Aniline
C₆H₅ \longrightarrow N⁺₂Cl + 2H₂O
Benzene diazonium
chloride (3)
Refer to text on page 319. (3 + 4 = 7)

- Q.27 How can benzene diazonium chloride be prepared from nitrobenzene? Starting from diazonium salt how can (i) benzene (ii) iodobenzene and (iii) benzoic acid be prepared? [2012, 2008, Textbook]
 - Sol Preparation of nitrobenzene from diazonium chloride.



Form (i) to (ii) Refer to page 319. Refer to text on page 319.

(1 + 2 + 2 + 2 = 7)

Q.28 (i) Illustrate the following reactions with an example. (a) Sandmeyer reaction

- (b) Coupling reaction
- (ii) How benzene diazonium chloride is converted to (a) benzene? (b) anisole? (c) phenol?

Or

Write notes on	
(i) Sandmeyer reaction	
(ii) Coupling reaction	[Textbook]
Sol (i) Refer to text on page 319.	(4)
(ii) Refer to text on page 320.	(3)

Chapter Test

1 MARK Questions

- 1 Benzene diazonium chloride reacts with KI to form [Textbook]
 - (a) benzene diazonium iodide
 - (b) *m*-diiodobenzene
 - (c) iodobenzene
 - (d) o-, m-and p-diiodobenzene [Ans. (c)]
- **2** Write the structure of benzene diazonium chloride.
- **3** Which compound is formed when benzene diazonium chloride reacts with phenol in basic medium?
- 4 Write Balz-Schiemann reaction.
- **5** Write one synthetic importance of diazonium salts.
- **6** Complete the following reaction:

$\underbrace{\bigcirc}^{\stackrel{\stackrel{\stackrel{\scriptstyle}}{}}{N_2Cl}} \underbrace{\stackrel{\stackrel{\scriptstyle}{}}{\underbrace{}}_{HCl}}_{HCl} A'$

- 7 Benzene diazonium fluoroborate is water and stable at room temperature. [*Ans.* insoluble]
- 8 What should be the nature of medium (neutral/acidic/basic) for diazotisation of arylamines? [Textbook]

2 MARK Questions

9 How will you convert? [Textbook]
(i) Aniline to nitrobenzene
(ii) Aniline to iodobenzene

- **10** Give one chemical test to distinguish between ethylamine and aniline.
- 11 Suggest reason, why excess mineral acid is used in diazo reaction? [Textbook]

- 12 Accomplish the following conversion:(i) Aniline to 2, 4, 6 tribromofluorobenzene(ii) Nitrobenzene to benzoic acid
- **13** Write conversion of benzene to 1, 3, 5 tribromobenzene.

3 MARK Questions

- 14 (i) List some important applications of diazonium salts.
 - (ii) Explain physical properties of diazonium salts.
- **15** Give two reaction involving retention of diazo group.
- **16** Identify the compounds *A*, *B*, *C*, *D*, *E* and *F* required for the following conversion.

$$\begin{array}{c} \mathbf{C}_{6}\mathbf{H}_{5}\mathbf{NO}_{2} \xrightarrow{[A]} \mathbf{C}_{6}\mathbf{H}_{5}\mathbf{NH}_{2} \xrightarrow{[B]} \mathbf{C}_{6}\mathbf{H}_{5}\mathbf{N}_{2}^{+}\mathbf{Cl}^{-} \\ \\ \hline \end{array}$$

$$\xrightarrow{[C]} \mathbf{C}_{6}\mathbf{H}_{5}\mathbf{Cl} \xrightarrow{[D]} \mathbf{C}_{6}\mathbf{H}_{5}\mathbf{OH} \xrightarrow{\mathbf{H}_{2}\mathbf{SO}_{4}} [E] + [F]$$

7 MARK Questions

- 17 Write notes on
 - (i) Coupling reaction
 - (ii) Gattermann reaction
- **18** Give the products of following reactions :

(i)
$$\langle \bigcup \rangle - \dot{N}_2 \bar{X} + CuNO_2 \xrightarrow{\Delta} p$$

(ii) $C_6H_5 \dot{N}_2 \bar{X} \xrightarrow{C_2H_5OH + \Delta} p$
(iii) $C_6H_5 \dot{N}_2 \bar{X} \xrightarrow{CuBr + HBr} p$
(iv) $C_6H_5 \dot{N}_2 \bar{X} \xrightarrow{Zn + HCl} p$

(v)
$$C_6H_5 \overset{+}{N}_2\bar{X} + \beta$$
-naphthol $\xrightarrow{\circ_{OH}} p$