Long Answer Questions

Long Answer Questions (PYQ)

Q.1. An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions:

[CBSE Delhi 2015] [HOTS]

Ans.

$$A = \bigcup_{\substack{C - NH_2 \\ Benzamide}} ; B = \bigcup_{\substack{N = NC1 \\ Benzene \\ diazonium \\ chloride}} ; C = \bigcup_{\substack{Benzene \\ Benzene}} ; D = \bigcup_{\substack{NC \\ Phenyl \\ isocyanide}} ; E = \bigcup_{\substack{Iodobenzene \\ Iodobenzene}}$$

Q. Write the structures of A, B, C, D and E in the following reactions:

[CBSE (F) 2017]

$$C_{6}H_{5}NO_{2} \xrightarrow{Sn/HCl} A \xrightarrow{(CH_{3}CO)_{2}O} B \xrightarrow{HNO_{3} + H_{2}SO_{4}} C \xrightarrow{O\overline{H} \text{ or } \overline{H}^{\dagger}} D$$

$$\downarrow H_{2}SO_{4}$$

$$E$$

$$A = \bigcup_{\text{Aniline}}^{\text{NH}_2}, B = \bigcup_{\text{Acetanilide}}^{\text{NHCOCH}_3}, C = \bigcup_{\text{NO}_2}^{\text{NHCOCH}_3}, C = \bigcup_{\text{NO}_2}^{\text{NHCO$$

Q.3. Answer the following questions

[CBSE Delhi 2015]

Q. Write the structures of main products when aniline reacts with the following reagents:

(a) Br₂ water (b) HCl c) (CH₃CO)₂O/pyridine

Acetic anhydride

Q. Arrange the following in the increasing order of their boiling point:

$C_2H_5NH_2$, C_2H_5OH , $(CH_3)_3N$

Ans. $(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$

Q. Give a simple chemical test to distinguish between the following pair of compounds:

(CH₃)₂NH and (CH₃)₃N

Ans. Dimethyl amine and trimethyl amine can be distinguished by using Hinsberg's reagent, *i.e.*, C₆H₅SO₂Cl. When treated with Hinsberg's reagent dimethylamine being a 2° amine gives N, N-dimethyl benzene sulphonamide which is insoluble in aqueous KOH solution while trimethyl amine being a 3° amine does not react with Hinsberg's reagent.

Q.4. Answer the following questions

[CBSE (F) 2015]

Q. Write the structures of main products when benzene diazonium chloride ($C_6H_5N_2^+Cl^-$) reacts with the following reagents:

(b) Cu/HBr

Ans. (a)

$$N_2C1 + HBF_4 \longrightarrow N_2BF_4 \xrightarrow{\Delta} F + BF_3 + N_2$$

(b)

$$N_2\bar{C}l$$
 $N_2\bar{C}l$ $N_2\bar{C}l$ $N_2\bar{C}l$ $N_2\bar{C}l$ $N_2\bar{C}l$ $N_2\bar{C}l$ $N_2\bar{C}l$ $N_2\bar{C}l$

Q. Write the structures of A, B and C in the following reactions:

(a)
$$C_6H_5\operatorname{NO}_2 \stackrel{\operatorname{Sn/HCl}}{\longrightarrow} A \stackrel{\operatorname{NaNO}_2+\operatorname{HCl}}{\longrightarrow} B \stackrel{H_2O}{\longrightarrow} C$$

(b)
$$\operatorname{CH}_3\operatorname{Cl} \stackrel{\scriptscriptstyle{\mathrm{KCN}}}{ o} A \stackrel{\scriptscriptstyle{\mathrm{LialH}_4}}{ o} B \stackrel{\scriptscriptstyle{\mathrm{HNO}_2}}{\overset{\scriptscriptstyle{\mathrm{LialH}_4}}{ o}} C$$

Ans. (a)

$$A = \bigcup_{\text{Aniline}}^{\text{NH}_2}$$
; $B = \bigcup_{\text{Benzene diazonium}}^{\text{+}}$; $C = \bigcup_{\text{Phenol}}^{\text{-}}$

(b)

$$A = \operatorname{CH}_3 - \operatorname{C} \equiv \operatorname{N} \; ; \qquad B = \operatorname{CH}_3 - \operatorname{CH}_2 - \operatorname{NH}_2; \qquad C = \operatorname{CH}_3 - \operatorname{CH}_2 - \operatorname{OH}_2$$
 Ethanonine

Q.5. An aromatic compound 'A' of molecular formula $C_7H_6O_2$ undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions:

[CBSE Allahabad 2015]

$$(C_7H_6O_2) \xrightarrow{NH_3/\text{heat}} C_6H_5CONH_2 \xrightarrow{Br_2 + \text{NaOH}} B \xrightarrow{(CH_3CO)_2O} C$$

$$\downarrow LiAlH_4/\text{ether} \qquad \downarrow Br_2(aq)$$

$$\downarrow D$$

Ans.

$$A = \bigcup_{\text{Benzoic acid}}^{\text{O}} ; B = \bigcup_{\text{Aniline}}^{\text{NH}_2} ; C = \bigcup_{\text{N-Phenyl}}^{\text{N-Phenyl}} ; D = \bigcup_{\text{Benzylamine}}^{\text{O}} ; E = \bigcup_{\text{Br}}^{\text{NH}_2} \text{Br}$$

$$= \bigcup_{\text{Senzylamine}}^{\text{NH}_2} ; C = \bigcup_{\text{Senzylamine}}^{\text{N-Phenyl}} ; D = \bigcup_{\text{Senzylamine}}^{\text{NH}_2} ; E = \bigcup_{\text{Senzylamine}}^{\text{NH}_2} \text{Br}$$

$$= \bigcup_{\text{Senzylamine}}^{\text{N}_2} ; D = \bigcup_{\text{Senzylamine}}^{\text{N}_2} ; D = \bigcup_{\text{Senzylamine}}^{\text{N}_2} ; E = \bigcup_{\text{Senzylamine}}^{\text{N}_2} ;$$

Q.6. Answer the following questions

- Q. Illustrate the following reactions giving suitable example in each case:
 - a. Hoffmann bromamide degradation reaction
 - b. Diazotisation
 - c. Gabriel phthalimide synthesis

Ans. (a) Hoffmann bromamide reaction: When a primary acid amide is heated with an aqueous or ethanolic solution of NaOH or KOH and bromine (*i.e.*, NaOBr or KOBr), it gives a primary amine with one carbon atom less.

$$R$$
—CONH₂ + Br₂ + 4NaOH \rightarrow R —NH₂ + Na₂CO₃ + 2NaBr + 2 H_2 O

Acid amide
CONH₂ + Br₂ + 4KOH \longrightarrow NH_2 + Na₂CO₃ + 2KBr + 2 H_2 O

Benzamide Aniline

(b) Diazotization:

(c) Gabriel phthalimide synthesis: This reaction is used for the preparation of aliphatic primary amines. In this reaction, phthalimide is first of all treated with ethanolic KOH to form potassium phthalimide. Potassium phthalimide on treatment with alkyl halide gives N-alkyl phthalimide, which on hydrolysis with dilute hydrochloric acid gives a primary amine as the product.

- Q. Distinguish between the following pairs of compounds:
 - a. Aniline and N-methylaniline
 - b. $(CH_3)_2NH$ and $(CH_3)_3N$

Ans. (a). Aniline being a primary amine gives carbylamine test, *i.e.*, when heated with an alcoholic solution of KOH and CHCl₃, it gives foul smell of phenyl carbylamine whereas N-methylaniline being a secondary amine does not give this test.

(b). Dimethyl amine and trimethyl amine can be distinguished by using Hinsberg's reagent, *i.e.*, C₆H₅SO₂CI. When treated with Hinsberg's reagent dimethylamine being a 2° amine gives N, N-dimethyl benzene sulphonamide which is insoluble in aqueous KOH solution while trimethyl amine being a 3° amine does not react with Hinsberg's reagent.

Long Answer Questions (OIQ)

- Q.1. Answer the following questions:
- Q. How will you bring about the following conversions?
 - a. Ethanamine into methanamine
 - b. Aniline into 1,3,5-tribromobenzene
 - c. Aniline into 4-bromoaniline

Ans. (a).

(b).

(c).

Q. Account for the following:

- a. Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
- b. Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

Ans. (a). Methylamine being more basic than water, accepts a proton from water, liberating OH⁻ ions.

$$CH_3NH_2 + HOH$$
 \longrightarrow $CH_3-NH_3 + OH$

These OH⁻ ions combine with Fe³⁺ ions present in H₂O to form brown precipitate of hydrated ferric oxide.

(b) The diazonium salts of aromatic amines are more stable than those of aliphatic amines due to dispersal of the positive charge on the benzene ring as shown below:

Q.2. [A], [B], [C], [D], [E], [F] and [G] are amines each of which forms a hydrochloride containing 32.42% chlorine. [A], [B], [C] and [D] evolve N_2 on reaction with HNO₂, but [E], [F], [G] and [H] do not. Give structures of [A] to [H] with reasons.

[HOTS]

Ans. Let the molecular formula of the six amines be $C_nH_{2n+1}NH_2$, where n = 1, 2, 3, etc.

As all the seven amines react with HCl to form hydrochlorides, therefore, the molecular formula of their hydrochloride is

$$C_nH_{2n+1}NH_2 + HCl \longrightarrow C_nH_{2n+1}NH_3Cl^-$$

As all these hydrochlorides contain 32.4% of CI, therefore molecular mass of amines

$$\frac{100 \times 35.5}{32.42} = 109.5$$

Now, molecular mass of = 109.5

$$12n + 2n + 1 + 14 + 3 + 35.5 = 109.5$$

or
$$14n = 56 \Rightarrow n = 4$$

∴ Molecular formula of the six amines = C₄H₉NH₂

As amines [A], [B], [C] and [D] evolve N₂ on treatment with HNO₂, they must be primary amines

$$C_nH_{2n+1}NH_2 + HCl \longrightarrow C_nH_{2n+1}NH_3Cl^-$$

The four primary amines having molecular formula C₄H₉NH₂ are

$$\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2\\ \text{Butana mine [A]} \end{array} \qquad \begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_3\\ \text{NH}_2\\ \text{Butan - 2- amine [B]} \end{array}$$

$$\begin{array}{c} \text{CH}_3\\ \text{CH}_3\\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{NH}_2\\ \text{2-Methyl propana mine [C]} \end{array} \qquad \begin{array}{c} \text{CH}_3-\text{CH}_3-\text{CH}_3\\ \text{CH}_3-\text{CH}_3-\text{CH}_3\\ \text{NH}_2\\ \text{2-Methyl propan - 2- amine [D]} \end{array}$$

As amines [E], [F], [G] and [H] do not react with HNO₂, to evolve N₂, therefore, they must be either secondary or tertiary amines.

Q.3. A hydrocarbon 'A', (C₄H₈) on reaction with HCl gives a compound 'B', (C₄H₉Cl), which on reaction with 1 mol of NH₃ gives compound 'C', (C₄H₁₁N). On reacting with NaNO₂ and HCl followed by treatment with water, compound 'C' ields an optically active alcohol, 'D'. Ozonolysis of 'A' gives 2 moles of acetaldehyde. Identify the compounds 'A' to 'D'. Explain the reactions involved.

[HOTS]

Ans.

(A)
$$\xrightarrow{\text{Ozonolysis}}$$
 2CH₃CHO

 $C_4H_8 \xrightarrow{\text{HCl}} C_4H_9\text{Cl}$ Addition of HCl has occurred on 'A'. This implies 'A' is an alkene.

 $C_4H_9\text{Cl} \xrightarrow{\text{NH}_3} C_4H_{11}\text{N}$ Cl in compound 'B' is substituted by NH₂ to give 'C'.

(C) $\xrightarrow{\text{NaNO}_2/\text{HCl}}$ (D) 'C' gives a diazonium salt with

NaNO₂/HCl that liberates N₂ to give optically active alcohol. This means that 'C' is a primary amine. Number of carbon atoms in amine is same as compound 'A'.

Since products of ozonolysis of compound 'A' are CH₃—CH=O and O=CH—CH₃. Therefore, the compound 'A' is CH₃—CH=CH—CH₃.

On the basis of structure of 'A', the reactions can be explained as follows:

$$\begin{array}{c} \text{CH}_{3}\text{--CH} \stackrel{=}{\underset{(A)}{=}} \text{CH}\text{--CH}_{3} & \stackrel{\text{HCl}}{\xrightarrow{}} \text{CH}_{3}\text{CH}_{2}\text{--CH}\text{--CH}_{3} \\ & & & & & & \\ \text{Cl} & & & & & \\ \text{Cl} & & & & & \\ \text{Cl} & & & & & \\ \text{B)} & & & & & \\ \text{CH}_{3}\text{--CH}_{2}\text{--CH}\text{--CH}_{3} & \stackrel{\text{NaNO}_{2}/\text{HCl}}{\xrightarrow{}} & \text{CH}_{3}\text{--CH}_{4} \\ \text{CH}_{3}\text{--CH}_{2}\text{--CH}\text{--CH}_{3} & \stackrel{\text{NaNO}_{2}/\text{HCl}}{\xrightarrow{}} & \text{CH}_{3}\text{--CH}_{4} \\ \text{CH}_{3}\text{--CH}_{2}\text{--CH} & \stackrel{\text{NaNO}_{2}/\text{HCl}}{\xrightarrow{}} & \text{CH}_{3}\text{--CH}_{4} \\ \text{OH} & & & & & \\ \text{(C)} & & & & & & \\ \end{array}$$

Q.4. Predict the reagents or the products in the following reaction sequence:

[HOTS]

1. Sn–HCl (conc.) 2. NO₂ 3.
$$\text{H}_2\text{O/H}^+$$
 4. NO₂ 5. $\text{H}_3\text{PO}_2/\text{H}_2\text{O}$ NHCOCH₃

Q.5. Write the structures of reagents/organic compounds (A to F) in the following sequence of reactions:

[HOTS]

$$A \xrightarrow{\text{NaOH/Br}_2} B \xrightarrow{\text{NaNO}_2/\text{HCl}} C \xrightarrow{D} E \xrightarrow{\text{Cl}_2/\text{Fe}} F$$

$$\downarrow^{\text{H}_2/\text{Pt}}$$

$$CH_2\text{NH}_2$$

$$A = \bigcirc \\ \bigcirc \\ Benzamide \\ Aniline \\ Aniline \\ Aniline \\ Benzene diazonium \\ Cloride \\ Aniline \\ Benzene diazonium \\ Chloride \\ Chlorobenzene \\$$