Short Answer Questions-II (PYQ)

Q.1. Complete the following reaction equations:

[CBSE (AI) 2009]

Q.
$$C_6H_5N_2Cl + CH_3COCl \longrightarrow$$

Ans.
 $\stackrel{\hat{N}_2\bar{Cl}}{\longrightarrow} + CH_3 \longrightarrow \stackrel{\hat{N}_2\bar{Cl}}{\longrightarrow} + CH_3 \longrightarrow C-Cl \longrightarrow \stackrel{\hat{N}_2\bar{Cl}}{\longrightarrow} -COCH_3$
Q. $C_2H_5NH_2 + C_6H_5SO_2Cl \longrightarrow$

Ans. $C_2H_5NH_2 + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_2NHC_2H_5$

 $Q. C_2H_5NH_2 + HNO_2 \longrightarrow$

Ans. $C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5 - OH + H_2O + N_2$

Q.2. Give the structures of *A*, *B* and *C* in the following reactions:

[CBSE Delhi 2014]

Q.

$$CH_{3}Br \xrightarrow{KCN} A \xrightarrow{LiAIH_{4}} B \xrightarrow{HNO_{2}} C$$

Ans.

Ans.

Q.3. Write the structures of *A*, *B* and *C* in the following:

[CBSE Delhi 2016]

Q.

$$C_6H_5$$
— $CONH_2 \xrightarrow{Br_2/aq. KOH} A \xrightarrow{NaNO_2 + HCl} B \xrightarrow{KI} C$

Ans.

$$A = \bigotimes_{\text{Aniline}} \text{NH}_2, \quad B = \bigotimes_{\text{N} = 1}^{+-} \text{N} = \bigwedge_{\text{N} = 1}^{+-} \text{N} = \bigwedge_{\text{Iodobenzene}} \text{Iodobenzene}$$

Q.

$$CH_3 \longrightarrow Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{CHCl_3 + alc.KOH} C$$

Ans.

$$A = CH_3CN, B = CH_3 - CH_2 - NH_2, C = CH_3 - CH_2 - N \cong C$$

Methyl Ethyl amine Ethyl isocyanide

Q.4. Complete the following reactions:

[CBSE East 2016]

Q.

$$C_6H_5$$
—COOH $\xrightarrow{NH_3}$ $A \xrightarrow{Heat}$ $B \xrightarrow{Br_2/KOH}$ C

Ans.



Q.

$$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{NaNO_2 + HCl} B \xrightarrow{CuCN} C$$

Ans.



Q. Complete the following chemical equations:

[CBSE Delhi 2010]

Q.
$$C_6H_5N_2Cl + C_6H_5NH_2 \longrightarrow$$

Ans.



$$Q. C_6H_5N_2Cl + CH_3CH_2OH \longrightarrow$$

Ans.
$$C_6H_5N_2Cl^- + CH_3 \longrightarrow CH_2 \longrightarrow C_6H_6 + N_2 + CH_3 \longrightarrow CHO + HCl$$

 \mathbf{Q} . \mathbf{RNH}_2 + \mathbf{CHCl}_3 + $\mathbf{KOH} \longrightarrow$

Ans.

 $R - NH_2 + CHCl_3 + 3KOH (alc.) \xrightarrow{\Delta} R - NC + 3KCl + 3H_2O$

Q.6. How are the following conversions carried out:

Q. Aniline to fluorobenzene

Ans. Aniline to fluorobenzene



Q. Benzene diazonium chloride to benzene

Ans. Benzene diazonium chloride to benzene

 $\underbrace{\bigcirc}^{+}_{N_2Cl^-}_{PO_2} + H_3PO_2 + H_2O \longrightarrow \bigcirc + N_2 + H_3PO_3 + HCl$ Benzene diazonium
chloride
Benzene

Q. Methyl chloride to ethylamine

[CBSE (F) 2013]

Ans. Methyl chloride to ethylamine

 CH_3 —Cl $\xrightarrow{alc, KCN}$ CH_3 —CN $\xrightarrow{LiAlH_4}$ $CH_3CH_2NH_2$

Q.7. Write chemical equations for the following conversions:

[CBSE Delhi 2012]

Q. Nitrobenzene to benzoic acid

Ans.



Q. Benzyl chloride to 2-phenylethanamine

Ans.



Q. Aniline to benzyl alcohol

Ans.



Alternatively,



Q.9. Answer the following questions:

Q. Explain why an alkylamine is more basic than ammonia.

Ans.



Due to electron releasing nature, the alkyl group (R) pushes electrons towards nitrogen in alkyl amine and thus makes the unshared electron pair more available for sharing with the proton of the acid. Therefore, alkyl amines are more basic than ammonia.

Q. How would you convert

- a. Aniline to nitrobenzene?
- b. Aniline to iodobenzene?

[CBSE Delhi 2011]







Q.9. Give reasons:

Q. Acetylation of aniline reduces its activation effect.

Ans. Due to resonance the lone pair of electrons on nitrogen of acetanilide gets delocalised towards carbonyl group.



Hence the electrons are less available for donation to benzene ring by resonance. Therefore, activation effect of aniline is reduced.

Q. CH_3NH_2 is more basic than $C_6H_5NH_2$.

Ans. In CH₃—NH₂, +I-effect of —CH₃ group increases the electron density on the nitrogen atom making lone pair more available for donation. On the other hand, in aniline lone pair of electron on the nitrogen atom is delocalised over benzene ring due to resonance and thus making it less available for donation. That is why CH₃NH₂ is more basic than C₆H₅NH₂.

Q. Although --NH₂ is o/p directing group, yet aniline on nitration gives a significant amount of *m*-nitroaniline.

[CBSE Delhi 2017]

Ans. This is because in a strongly acidic medium aniline is protonated to form the anilinium ion which is meta directing.

Q.10. Give reasons for the following:

[CBSE Central 2016]

Q. Aniline does not undergo Friedal-Crafts reaction.

Ans. Aniline being a Lewis base, reacts with Lewis acid AICI₃ to form a salt.

 $C_6H_5NH_2 + AlCl_3 \longrightarrow C_6H_5NH_2AlCl_3^+$ Lewis acid As a result, N of aniline acquires positive charge and hence it acts as a strong deactivating group for electrophilic substitution reaction. Consequently, aniline does not undergo Friedel–Crafts reaction.

Q. (CH₃)₂NH is more basic than (CH₃)₃N in an aqueous solution.

Ans. This is due to combination of three factors, +ve I effect, solvation effect and steric hindrance of alkyl groups in aqueous solutions.

Q. Primary amines have higher boiling point than tertiary amines.

Ans. In primary amines, two hydrogen atoms are present on N-atom and they undergo extensive intermolecular hydrogen bonding which results in association of molecules while in tertiary amines, no hydrogen atom is present on N-atom. Hence, there is no hydrogen bonding in tertiary amines. As a result of this primary amines have higher boiling point than tertiary amines.

Q.11. Account for the following:

[CBSE (AI) 2014] [HOTS]

Q. pK_b of aniline is more than that of methylamine.

Ans. In aniline due to resonance, the lone pair of electrons on the N-atom are delocalised over the benzene ring. Due to this, electron densit on the nitrogen decreases. On the other hand, in CH₃NH₂, +I-effect of CH₃increases the electron density on the N-atom. Consequently aniline is a weaker base than methylamine and hence its pK_b value is higher than that of methylamine.

Q. Although trimethylamine and *n*-propylamine have the same molecular weight, but the former boils at a lower temperature (276 K) than the latter (322 K). Explain.

Ans. *n*-Propylamine has two H-atoms on the N-atom and hence undergoes intermolecular H-bonding, thereby raising its boiling point. Trimethylamine, (CH₃)₃N, being a tertiary amine does not have any H-atom on the N-atom. As a result, it does not undergo H-bonding and hence its boiling point is low.

Q. (CH₃)₂NH is more basic than (CH₃)₃N in an aqueous solution.

Ans. The basicity of amine in aqueous solution depends upon the stability of the substituted ammonium cation. Here the combination of three factors, +ve I effect of CH₃ groups, hydrogen bonding and steric hindrance favour greater stability for ammonium cation of dimethyl amine than ammonium cation of trimethyl amine. Hence dimethylamine is stronger base than trimethyl amine.

Q.12. In the following cases rearrange the compounds as directed:

Q. In an increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2$ NH and CH_3NH_2

Ans. Increasing order of basic strength is:

 $C_{6}H_{5}NH_{2} < C_{6}H_{5}N(CH_{3})_{2} < CH_{3}NH_{2} < (C_{2}H_{5})_{2}NH_{3}$

Q.12. In a decreasing order of basic strength:

Aniline, *p*-nitroaniline and *p*-toluidine

Ans. *p*-Toluidine > Aniline > *p*-nitroaniline

Q.13. In an increasing order of pK_b values:

 $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

Ans. $(C_2H_5)_2NH < C_2H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2$

Q.13. Give one chemical test each to distinguish between the compounds in the following pairs:

[CBSE (F) 2009]

Q. Methylamine and dimethylamine

Ans. Methylamine on treatment with alcoholic KOH and CHCl₃ gives offensive smell of methyl isocyanide but dimethyl amine does not.

 $\begin{array}{c} CH_3NH_2 \\ Methylamine \\ (1^{\circ} amine) \end{array} + \begin{array}{c} CHCl_3 + 3KOH \\ (alc.) \end{array} \xrightarrow[(alc.)]{Heat} \\ Heat \\ (alc.) \\ Methyl carbylamine \\ (offensive smell) \end{array} + 3KCl + 3H_2O$

Q. Aniline and benzylamine

Ans. Aniline on treatment with NaNO₂/HCI (HNO₂) at 0–5°C followed by treatment with an alkaline solution of β -naphthol gives an orange coloured azodye while benzylamine does not give this test.



Q. Ethylamine and aniline

Ans. On adding $Br_2(aq)$, aniline forms white ppt. while ethyl amine does not form such ppt.



Q.14. Illustrate the following reactions giving a chemical equation in each case:

[CBSE (F) 2011]

Q. Gabriel phthalimide synthesis

Ans. 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. A coupling reaction

Ans. Coupling reaction: The reaction of diazonium salts with phenols and aromatic amines to form azo compounds of the general formula, Ar - N = N - Ar is called coupling reaction. The mechanism is basically that of electrophilic substitution where the diazonium ion is electrophile. In this reaction, the nitrogen atoms of the diazo group are retained in the product. The coupling with phenols takes place in mildly alkaline medium



Coupling generally occurs at the *p*-position, w.r.t., the hydroxyl or the amino group, if free, otherwise it takes place at the *o*-position.

Q. Hoffmann's bromamide reaction

Ans. 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.

Q.15. How will you convert the following:

[CBSE (F) 2013]

Q. Aniline to chlorobenzene

Ans. Aniline to chlorobenzene



Q. Ethanoic acid to methanamine

Ans. Ethanoic acid to methanamine

 $\begin{array}{ccc} CH_{3}COOH & \xrightarrow{NH_{3}} & CH_{3}CONH_{2} & \xrightarrow{Br_{2}/KOH} & CH_{3}NH_{2} \\ \hline (Hoffmann \ bromamide \ reaction) & Methanamine \end{array}$

Q. Benzene diazonium chloride to phenol

Ans. Benzene diazonium chloride to phenol



Short Answer Questions-II (OIQ)

Q.1. Answer the following questions:

[CBSE Sample Paper 2017]

Q. Illustrate the following reactions:

- a. Hoffmann bromamide degradation reaction.
- b. Coupling reaction.

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.

(b) Reactions involving retention of diazo group:

Coupling reaction: The reaction of diazonium salts with phenols and aromatic amines to form azo compounds of the general formula, Ar - N = N - Ar is called coupling reaction. The mechanism is basically that of electrophilic substitution where the diazonium ion is electrophile. In this reaction, the nitrogen atoms of the diazo group are retained in the product. The coupling with phenols takes place in mildly alkaline medium while with amines, it occurs under faintly acidic conditions. For example,



Coupling generally occurs at the *p*-position, w.r.t., the hydroxyl or the amino group, if free, otherwise it takes place at the *o*-position.

Q. Write a chemical test to distinguish between aniline and methylamine.

Ans.



Q.2. Give the structures of A, B and C in the following reactions:

Q.

$$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{HNO_2;273 K} B \xrightarrow{C_6H_5OH} C$$

Ans.



Q.

$$C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3;\Delta} C$$

Ans.



Q.3. In the following pairs which one is more basic and why?



Ans.

- i. In CH₃NH₂, the +I effect of —CH₃ group makes lone pair of electrons on N-atom more available for donation. On the other hand in C₆H₅NH₂, the resonance effect causes delocalisation of lone pair of electrons over benzene ring and makes it less available for donation. Hence, CH₃NH₂ is more basic than C₆H₅NH₂.
- ii. CH₃NH₂ is more basic than NH₃. CH₃ group due to its +ve I effect pushes electron towards nitrogen in $CH_3 \dot{N}H_2$ and this makes the unshared electron pair more available for sharing with the proton of the acid.



Q.4. Answer the following questions:

[NCERT Exemplar]

Q. Arrange the following compounds in increasing order of dipole moment.

CH₃CH₂CH₃, CH₃CH₂NH₂, CH₃CH₂OH

Ans. CH₃CH₂CH₃ < CH₃CH₂NH₂ < CH₃CH₂OH

Q. Give possible explanation for each of the following:

- a. The presence of a base is needed in the ammonolysis of alkyl halides.
- b. Amides are more acidic than amines.

Ans. (a). To remove HX formed so that the reaction shifts in the forward direction.

(b)

Due to +R effect, availability of lone pair of electron on N of —NH₂ group decreases. As a result, acid amide is much weaker base than amines. Because of the positive charge on N, as a result of resonance, N can easily lose a proton and behaves, as a weak acid.