

OPEN STUDENT FOUNDATION

Chapters: 9

STD: 12th Chemistry

Date : 01/03/24

PRACTICE SHEET 9

Section A

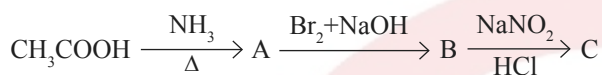
● Choose correct answer from the given options. [Each carries 1 Mark]

[10]

1. Which salt is insoluble in water ?

- (A) $C_6H_5N_2^+ Br^-$ (B) $C_6H_5N_2^+ BF_4^-$ (C) $C_6H_5N_2^+ Cl^-$ (D) $C_6H_5N_2^+ HSO_4^-$

2. Identify the compound 'C' from following reaction. ?

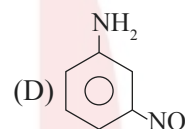
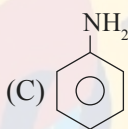
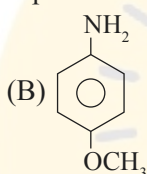
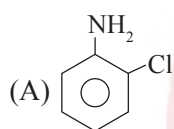


- (A) $CH_3 - CH_2 N_2^+ Cl^-$ (B) $CH_3 - CH_2OH$ (C) CH_3OH (D) $CH_3 - CH_2 - NH_2$

3. The number of σ (singma) and π (pie) bonds in orange azodye is and respectively.

- (A) 27 and 7 (B) 24 and 7 (C) 26 and 7 (D) 26 and 6

4. Which of the following compound is the most basic ?



5. Which of the following reaction is not taking place ?

- (A) Tripropyl amine + Benzene sulphonyl chloride (B) Dipropyl amine + Benzene sulphonyl chloride
(C) Propyl amine + Benzene sulphonyl chloride (D) Propyl amine + para toluene sulphonyl chloride

6. Compare boiling point of isomeric alkyl amines.

- (A) $1^\circ > 2^\circ > 3^\circ$ (B) $1^\circ > 2^\circ < 3^\circ$ (C) $1^\circ < 2^\circ < 3^\circ$ (D) $1^\circ < 2^\circ > 3^\circ$

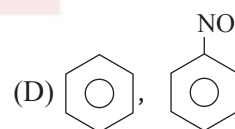
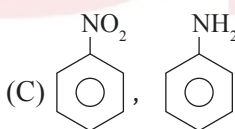
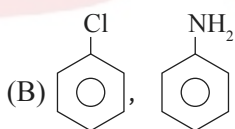
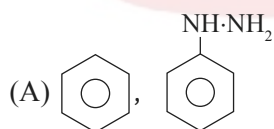
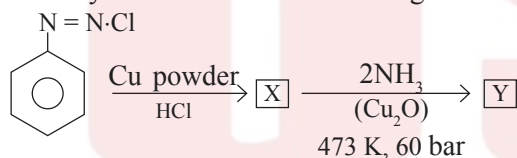
7. IUPAC name of vinyl cyanide is

- (A) Ethane nitrile (B) Prop-2-en-nitrile (C) Butane nitrile (D) Propane nitrile

8. In which of the following reaction N atom is changing its hybridization ?



9. Identify X and Y in the following reaction.



10. Which compound will not give ethanamine on reduction ?

- (A) Ethanolyl chloride (B) Ethanamide (C) Ethanenitrile (D) Nitroethane

Section B

- **Write the answer of the following questions. [Each carries 2 Marks]** **[12]**
- Write note on solubility of amine compounds. Explain which of the amine and alcohol compounds has higher solubility ? Why ?
 - Short note : Sulphonation of Aniline.
 - Describe the physical properties of benzenediazonium salts.
 - Explain the displacement of diazonium group of benzene diazonium salt by hydrogen with equation.
 - Write chemical equations for the following conversions : Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of
 - Convert :
 - 3-Methylaniline into 3-nitrotoluene
 - Aniline into 1, 3, 5 tribromo benzene.

Section C

- **Write the answer of the following questions. [Each carries 3 Marks]** **[15]**
- Write structures of different isomers corresponding to the molecular formula, C_3H_9N . Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.
 - Describe a method for the identification of primary secondary and tertiary amines. Also write chemical equations of the reactions involved.
 - Short note on : Sandmeyer reaction and Gattermann reaction.
 - Explain nitration of aniline. Explain what is done by this process to obtain the para nitro derivative as the major product.
 - Explain the displacement equation of the diazonium group of benzene diazonium salt by the hydroxyl group as well as by the nitro group.

Section D

- **Write the answer of the following questions. [Each carries 4 Marks]** **[12]**
- Arrange the following :
 - In decreasing order of the pK_b values : $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$
 - In increasing order of basic strength : $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2
 - In increasing order of basic strength :
 - Aniline, P-nitroaniline and P-toluidine,
 - $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$
 - In decreasing order of basic strength in gas phase : $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3
 - In increasing order of boiling point : C_2H_5OH , $(CH_3)_2NH$, $C_2H_5NH_2$
 - In increasing order of solubility in water : $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$
 - Short note on : Coupling reactions.
 - Complete the following reactions :

(i) $C_6H_5NH_2 + CHCl_3 + \text{Alcoholic KOH} \rightarrow$	(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$
(iii) $C_6H_5NH_2 + H_2SO_4 \text{ (Concentrated)} \rightarrow$	(iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$
(v) $C_6H_5NH_2 + Br_2 \text{ (aq)} \rightarrow$	(vi) $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$
(vii) $C_6H_5N_2Cl \xrightarrow{\text{(i) } HBF_4}$	
(ii) $NaNO_2/Cu, \Delta$	

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Section A

● Choose correct answer from the given options. [Each carries 1 Mark]

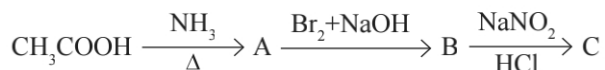
[10]

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⇒ Ans : (B)

2. Identify the compound 'C' from following reaction. ?



- (A) $CH_3 - CH_2 N_2^+ Cl^-$ (B) $CH_3 - CH_2OH$ (C) CH_3OH (D) $CH_3 - CH_2 - NH_2$

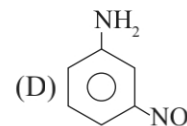
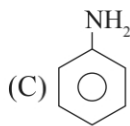
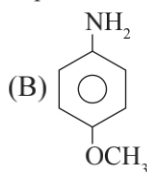
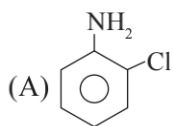
⇒ Ans : (C)

3. The number of σ (singma) and π (pie) bonds in orange azodye is and respectively.

- (A) 27 and 7 (B) 24 and 7 (C) 26 and 7 (D) 26 and 6

⇒ Ans : (C)

4. Which of the following compound is the most basic ?



⇒ Ans : (B)

5. Which of the following reaction is not taking place ?

- (A) Tripropyl amine + Benzene sulphonyl chloride (B) Dipropyl amine + Benzene sulphonyl chloride
(C) Propyl amine + Benzene sulphonyl chloride (D) Propyl amine + para toluene sulphonyl chloride

Ans (A)

⇨ 3° - amine does not react with Hinsberg reagent.

6. Compare boiling point of isomeric alkyl amines.

- (A) $1^\circ > 2^\circ > 3^\circ$ (B) $1^\circ > 2^\circ < 3^\circ$ (C) $1^\circ < 2^\circ < 3^\circ$ (D) $1^\circ < 2^\circ > 3^\circ$

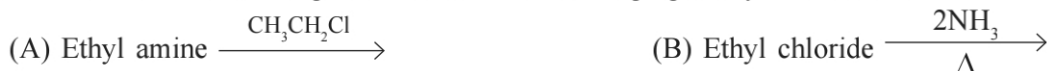
⇒ Ans : (A)

7. IUPAC name of vinyl cyanide is

- (A) Ethane nitrile (B) Prop-2-en-nitrile (C) Butane nitrile (D) Propane nitrile

⇒ Ans : (B)

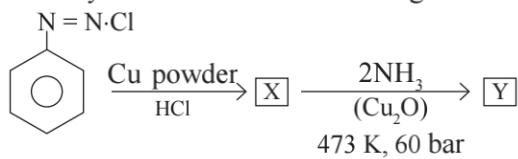
8. In which of the following reaction N atom is changing its hybridization ?



Ans (D)



9. Identify X and Y in the following reaction.



Ans : (B)

10. Which compound will not give ethanamine on reduction ?



Ans : (A)

Section B

● Write the answer of the following questions. [Each carries 2 Marks]

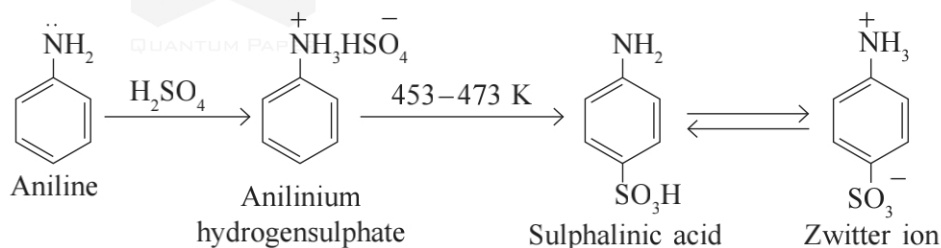
[12]

1. Write note on solubility of amine compounds. Explain which of the amine and alcohol compounds has higher solubility ? Why ?

- ⇨ Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecule.
- ⇨ However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part.
- ⇨ Higher amines are essentially insoluble in water.
- ⇨ Considering the electro negativity of nitrogen of amine and oxygen of alcohol as 3.0 and 3.5 respectively. This means that since the oxygen atom is more electrogative than the nitrogen atom, alcohol compounds can form strong hydrogen bonds with water. Hence, amine compounds have lower water solubility than alcohol compounds.
- ⇨ Amines are soluble in organic solvents like alcohol, ether and benzene.

2. Short note : Sulphonation of Aniline.

- ⇨ Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate which on heating with Sulphuric acid of 453–473K produces P-amino benzene sulphonic acid commonly known as sulphanilic acid as the major product.

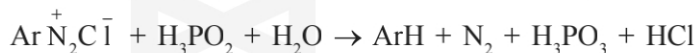


3. Describe the physical properties of benzenediazonium salts.

- ⇨ Benzene diazonium chloride is a colourless crystalline solid.
- ⇨ It is readily soluble in water and is stable in cold but reacts with water when warmed.
- ⇨ It decomposes easily in the dry state.
- ⇨ Benzene diazonium fluoborate is water insoluble and stable at room temperature.

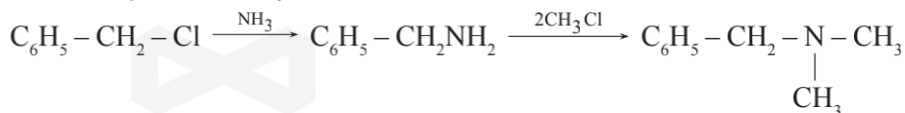
4. Explain the displacement of diazonium group of benzene diazonium salt by hydrogen with equation.

⇒ Certain mild reducing agents like hypophosphorous acid (phosphinic acid) or ethanol reduce diazonium salts to arenes and themselves get oxidised to phosphorous acid and ethanol, respectively.



5. Write chemical equations for the following conversions : Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of

⇒ Ammonolysis of benzyl chloride and reaction of amine so formed with two moles of

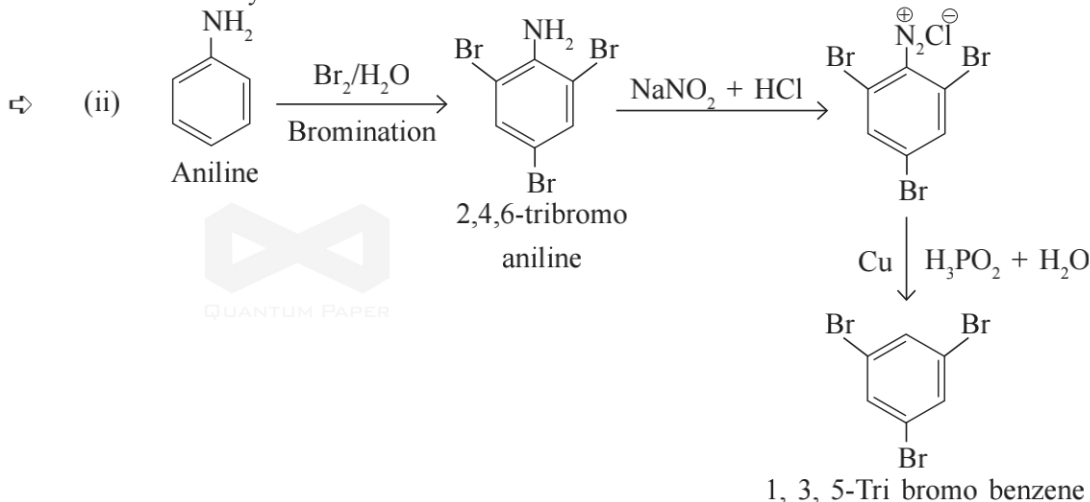
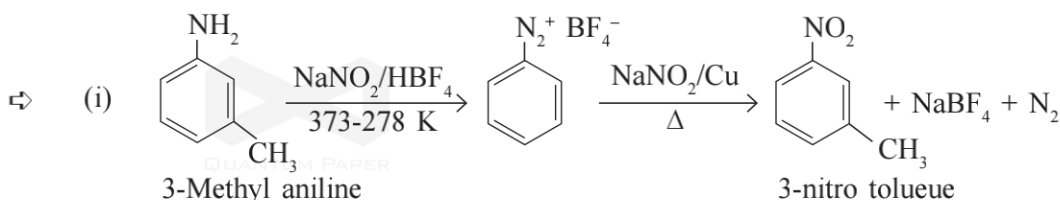


Benzylchloride Benzylamine N, N-Dimethylphenylmethanamine

6. Convert :

(i) 3-Methylaniline into 3-nitrotoluene

(ii) Aniline into 1, 3, 5 tribromo benzene.



Section C

● Write the answer of the following questions. [Each carries 3 Marks]

[15]

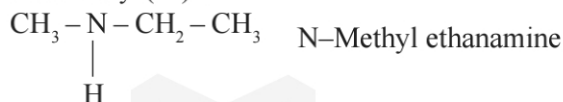
7. Write structures of different isomers corresponding to the molecular formula, $\text{C}_3\text{H}_9\text{N}$. Write IUPAC names of the isomers which will liberate nitrogen gas on treatment with nitrous acid.

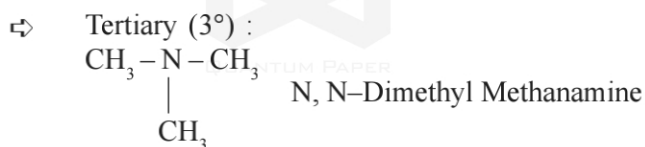
⇒ Total 5 structures of different isomers corresponding to the molecular formula $\text{C}_3\text{H}_9\text{N}$ given below.

⇒ Primary (1°) :



⇒ Secondary (2°) :





⇒ Only primary amine compounds will react with nitrous acid and liberate nitrogen gas, their IUPAC names are Propane-1-amine, Propane-2-amine

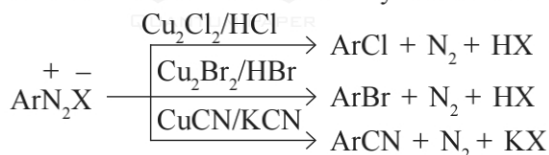
8. Describe a method for the identification of primary secondary and tertiary amines. Also write chemical equations of the reactions involved.

9. Short note on : Sandmeyer reaction and Gattermann reaction.

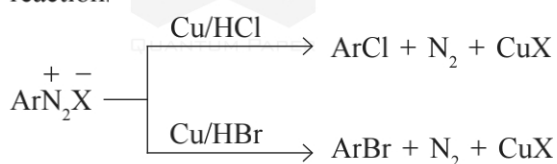
⇒ Replacement by halide or cyanide ion :

⇒ The Cl^- , Br^- and CN^- nucleophiles can easily be introduced in benzene ring in the presence of Cu(I) ion.

⇒ This reaction is called sandmeyer reaction.



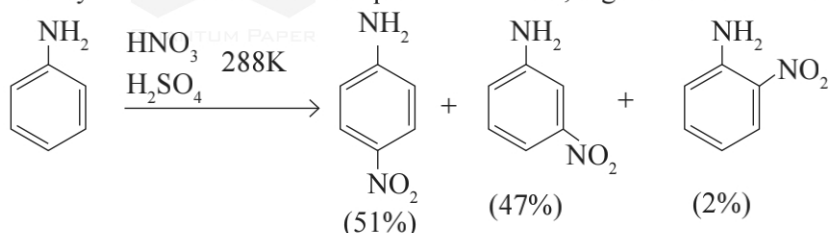
⇒ Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as Gattermann reaction.



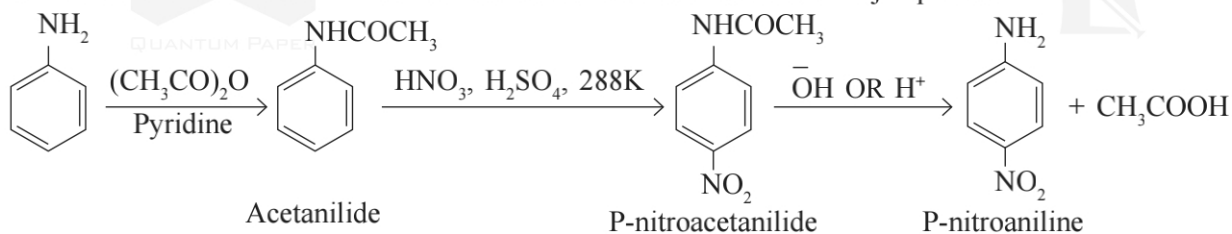
⇒ The yield in sandmeyer reaction is found to be better than Gattermann reaction.

10. Explain nitration of aniline. Explain what is done by this process to obtain the para nitro derivative as the major product.

⇨ Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives. Moreover in the strongly acidic medium aniline is protonated to form the anilinium ion which is meta directing. That is why besides the ortho and para derivatives, significant amount of meta derivative is also formed.



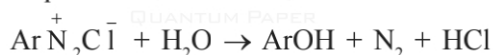
⇨ However by protecting the $-\text{NH}_2$ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the P-nitro derivative can be obtained as the major product.



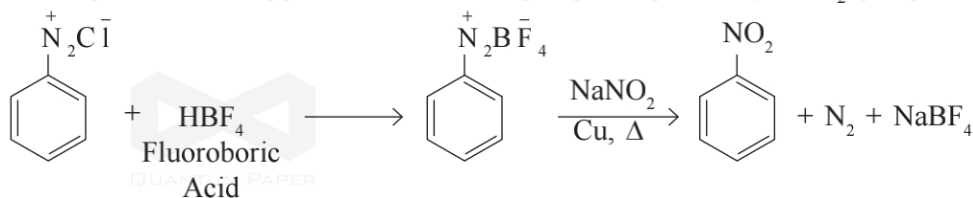
11. Explain the displacement equation of the diazonium group of benzene diazonium salt by the hydroxyl group as well as by the nitro group.

⇨ Replacement by hydroxyl group :

⇨ If the temperature of the diazonium salt solution is allowed to rise upto 283 K, the salt gets hydrolysed to phenol.



⇨ Replacement by nitrogroup : When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by $-\text{NO}_2$ group.



Section D

● Write the answer of the following questions. [Each carries 4 Marks]

[12]

12. Arrange the following :

(i) In decreasing order of the pK_b values : $\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NHCH}_3$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and $\text{C}_6\text{H}_5\text{NH}_2$

(ii) In increasing order of basic strength : $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and CH_3NH_2

(iii) In increasing order of basic strength :

(a) Aniline, P-nitroaniline and P-toluidine,

(b) $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NHCH}_3$, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

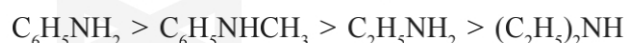
(iv) In decreasing order of basic strength in gas phase : $\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $(\text{C}_2\text{H}_5)_3\text{N}$ and NH_3

(v) In increasing order of boiling point : $\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$

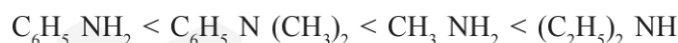
(vi) In increasing order of solubility in water : $\text{C}_6\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$

⇨ (i) In $\text{C}_6\text{H}_5\text{NH}_2$ only one $-\text{C}_2\text{H}_5$ group is present while in $(\text{C}_2\text{H}_5)_2\text{NH}$, two $-\text{C}_2\text{H}_5$ groups are present. Thus, the +I effect is more in $(\text{C}_2\text{H}_5)_2\text{NH}$ than in $\text{C}_2\text{H}_5\text{NH}_2$. Therefore, the electron density over the

N-atom is more in $(C_2H_5)_2NH$ than in $C_2H_5NH_2$. Hence, $(C_2H_5)_2NH$ is more basic than $C_2H_5NH_2$. Also, both $C_6H_5NHCH_3$ and $C_6H_5NH_2$ are less basic than $(C_2H_5)_2NH$ and $C_2H_5NH_2$ due to the delocalization of the lone pair in the former two. Further among $C_6H_5NHCH_3$ and $C_6H_5NH_2$, the former will be more basic due to +I effect of $-CH_3$ group. Hence the order of increasing basicity of the given compounds is as follows $C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$ we know that the higher the basic strength, the lower is the pK_b values.



- ⇒ (ii) $C_6H_5N(CH_3)_2$ is more basic than $C_6H_5NH_2$ due to the presence of the +I effect of two $-CH_3$ groups in $C_6H_5N(CH_3)_2$. Further, CH_3NH_2 contains one $-CH_3$ group while $(C_2H_5)_2NH$ contains two $-C_2H_5$ groups. Thus $(C_2H_5)_2NH$ is more basic than CH_3NH_2 . Now $C_6H_5N(CH_3)_2$ is less basic than CH_3NH_2 because of the $-R$ effect of $-C_6H_5$ group. Hence the increasing order of the basic strengths of the given compounds is as follows :



- ⇒ (iii) (a) In p-toluidine, the presence of electron donating $-CH_3$ group increases the electron density on the N atom. Thus, p-toluidine is more basic than aniline. On the other hand, the presence of electron withdrawing $-NO_2$ group decreases the electron density over the N-atom in p-nitroaniline. Thus p-nitroaniline is less basic than aniline. Hence the increasing order of the basic strengths of the given compounds is as follows :



- (b) $C_6H_5NHCH_3$ is more basic than $C_6H_5NH_2$ due to the presence of electron donating $-CH_3$ group in $C_6H_5NHCH_3$. Again in $C_6H_5NHCH_3$ the $-R$ effect of $-C_6H_5$ group decreases the electron density over the N-atom. Therefore; $C_6H_5CH_2NH_2$ is more basic than $C_6H_5NHCH_3$. Hence the increasing order of the basic strengths of the given compounds is as follows :



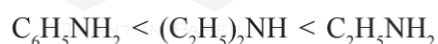
- ⇒ (iv) In the gas phase, there is no solvation effect. As a result, the basic strength mainly depends upon the +I effect. The higher the +I effect, the stronger is the base. Also the greater the number of Alkyl groups, the higher is the +I effect. So, the given compounds can be arranged in the decreasing order of their basic strengths in the gas phase as follows :



- ⇒ (v) The boiling points of compounds depend on the extent of H bonding present in that compound. The more extensive the H-bonding in the compound, the higher is the boiling point. $(CH_3)_2NH$ contains only one H-atom where as $C_2H_5NH_2$ contains two H-atoms. Then $C_2H_5NH_2$ undergoes more extensive H-bonding than $(CH_3)_2NH$. Hence the boiling point of $C_2H_5NH_2$ is higher than that of $(CH_3)_2NH$. Further O is more electronegative than N. Thus C_2H_5OH forms stronger H-bonds than $C_2H_5NH_2$. As a result the boiling point of C_2H_5OH is higher than that of $C_2H_5NH_2$ and $(CH_3)_2NH$. Increasing order of boiling point :



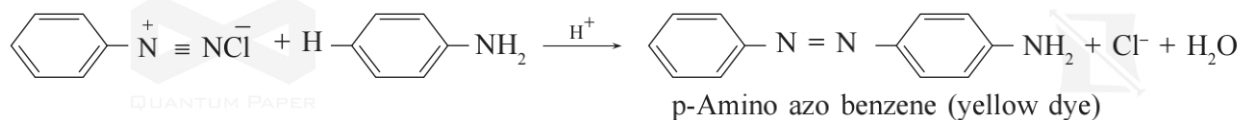
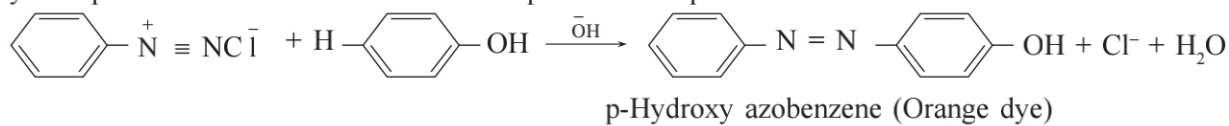
- ⇒ (vi) The solubility of amines decreases with increase in the molecular mass. This is because the molecular mass of amines increases with an increase in size of the hydrophobic part. The molecular mass of $C_6H_5NH_2$ is greater than that of $C_2H_5NH_2$ and $(C_2H_5)_2NH$. Hence the increasing order of their solubility in water is as follows :



13. Short note on : Coupling reactions.

- ⇒ The azo products obtained have an extended conjugate system having both the aromatic rings joined through the $-N=N-$ bond.

- ⇨ These compounds are often coloured and are used as dyes.
- ⇨ Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form p-Hydroxyazo benzene.
- ⇨ This type of reaction is known as coupling reaction. Similarly the reaction of diazonium salt with aniline yields p-aminoazobenzene. This is an example of electrophilic substitution reaction.



14. Complete the following reactions :

