

for Board Examination

AMINES

Time Allowed: 2 Hrs. Maximum Marks: 35 1. Write the IUPAC name of (1)2. Arrange the following in order of their basic strength in aqueous solution. aniline, p-nitroaniline, p-toluidine. (1)3. How will you convert aniline into chlorobenzene? Give equation. (1)4. Why do amines act as nucleophiles? (1)Aniline dissolves in aqueous HCl. Why? (1)Explain: (i) Why does the reactivity of —NH₂ group get reduced in acetanilide? (ii) Why does methylamine has lower boiling point than methanol? (2)Convert the following: (i) 3-Methylaniline to 3-nitrotoluene (2)(ii) Aniline into 1, 3, 5-tribromobenzene. 8. What is Gabriel phthalimide synthesis? Why aromatic primary amines cannot be prepared by this method? (2) 9. How do aromatic and aliphatic primary amines react with nitrous acid? (2)10. Why are aromatic amines weaker bases than aliphatic amines? (2)11. How will you convert: (ii) Aniline to p-bromoaniline (i) Benzyl chloride to 2-phenylethanamine (iii) Benzoic acid to aniline? (3)12. Explain the following reactions by giving one example: (i) Carbylamine reaction (ii) Sandmeyer's reaction (iii) Balz-Schiemann reaction (3)13. Explain the following: (a) Ethylamine is soluble in water, whereas aniline is not. (b) Although amino group is o- and p-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline. (c) Aniline does not undergo Friedel Crafts reaction. (3)14. Convert the following: (i) 4-Nitrotoluene to 2-bromobenzoic acid (ii) p-toluidine into 2-bromo-4-methylaniline (iii) acetaldehyde to ethylamine. (3)15. Starting with aniline and using suitable reagents, outline the synthesis of (3)(i) m-bromochlorobenzene (ii) p-nitrobenzene (iii) 1, 2, 3-tribromobenzene 16. (a) How does benzene diazonium chloride react with (ii) aniline (b) Describe the method for the identification of primary, secondary and tertiary amines. Also write chemical equations for the reactions involved. (5)

3. O-5°C HCl

4. Amines act as nucleophiles because of the presence of a lone pair of electrons on nitrogen.

$$R - \ddot{N} - H$$

5. Aniline dissolves in aqueous HCl due to the formation of water soluble salt.

$$C_6H_5NH_2 + HCl \longrightarrow C_6H_5NH_3^+Cl^-$$
Anilinium chloride
(Water soluble)

6. (i) In acetanilide, the amide group withdraws electrons from NH, group:

As a result, the electron pair on nitrogen gets displaced towards carbonyl group and becomes less available.

1,3,5-Tribromo benzene

(ii) Tendency to form hydrogen bonding in methylamine is less than that in methanol.

7. (i) NaNO₂, HCl
$$\sim$$
 NaNO₂, HCl \sim NaNO₂ NoO₂ \sim NaNO₂ NoO₂ \sim NaNO₂, HCl \sim Br \sim NaNO₂, HCl \sim Br \sim B

$$\mathbf{11.} \quad (i) \quad \overset{\mathbf{CH_2Cl}}{\longleftarrow} \quad \overset{\mathbf{CH_2CN}}{\longleftarrow} \quad \overset{\mathbf{CH_2NH_2}}{\longleftarrow} \quad \overset{\mathbf{LiAlH_4}}{\longleftarrow} \quad \overset{\mathbf{CH_2NH_2}}{\longleftarrow} \quad \overset{\mathbf{CH_2NH_2}}$$

$$(ii) \begin{picture}(200,10) \put(0.5,0.5){\ooliga} \put(0.5,0.5){\ool$$

$$(iii) \begin{picture}(200) \put(0.5,0){\line(1,0){100}} \put(0.5,0){\line(1,0$$

13. (a) Ethylamine dissolves in water due to intermolecular hydrogen bonding as shown below:

However, because of large hydrophobic part (i.e., hydrocarbon part) of aniline, the extent of hydrogen bonding is less and therefore, aniline is insoluble in water.

(b) Under strongly acidic conditions of nitration (in the presence of a mixture of conc. $HNO_3 + H_2SO_4$), aniline gets protonated and is converted into anilinium ion having $-NH_3^+$ group. This group is deactivating group and is m-directing. So, the nitration of aniline gives o, p-nitroaniline (mainly p-product) while the nitration of anilinium ion gives m-nitroaniline.

Thus, nitration of aniline gives a substantial amount of m-nitroaniline due to protonation of aniline.

(c) Aniline being a Lewis base reacts with Lewis acid such as AlCl_s to form a salt.

As a result, N of aniline acquires +ve charge and hence it acts as a strong deactivating group for electrophilic substitution reaction. Hence aniline does not undergo Friedel Crafts reaction.