Unit 13-NITROGEN CONTAINING ORGANIC COMPOUNDS

Two marks:

- 1. Name the product obtained when a nitrile is reduced by H_2/Ni , Δ . Give the equation. Ans. Primary amine: RCN $\xrightarrow{H_2/Ni,\Delta}$ R-CH₂NH₂.
- 2. How is nitrobenzene converted into aniline. Give the equation.

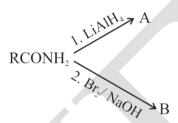
Ans. By reduction using Sn/ HCl

NO₂ Sn/ HCl

NH

NH

3. What are A and B?



Ans. A is RCH₂NH₂, B is R-NH₂

4. Give the equation which will be an example for Hofmann bromamide reaction.

Ans.
$$CH_3CONH_2 + Br_2 + 4NaOH \longrightarrow CH_3NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

Acetamide methanamine

5. Gabriel phthalimide synthesis is used to prepare which class of organic compound? Aniline cannot be prepared by this method. Give reason.

Ans. 1° aliphatic amine

Aryl halides are not reactive towards nucleophilic substitution reaction.

6. Name the reaction by which a 1° amine is prepared from an amide having one carbon atom more than 1° amine. Give the general equation.

Ans. Hofmann bromamide degradation reaction

$$R-CONH_2 + Br_2 + 4KOH \longrightarrow 2NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

7. Between $CH_3CH_2CH_2NH_2$ and $(CH_3)_3N$, which has higher boiling point and why?

Ans. CH₃CH₂CH₂NH₂ has higher boiling point. CH₃CH₂CH₂NH₂ has more H atoms on N to form intermolecular hydrogen bonding.

- 8. Give reason: i) Amines have lower boiling point than alcohol of same molar mass.
 - ii) Amines are insoluble in water.
- Ans. i) Nitrogen in amines is less electronegative than oxygen in alcohol. Hence amines do not form H-bonds among them.
 - ii) Amines do not form H bonds with water.
- 9. Amines are both Bronsted base and Lewis base. How?

Ans. Amines can accept H⁺, hence Bronsted bases. Amines can donate a pair of electrons hence Lewis bases.

- 10. Give reason: aniline is a weaker base than ammonia but methanamine is a stronger base than ammonia.
- Ans. Aniline is weaker base because the pair of electron on nitrogen gets delocalized towards benzene ring. Methanamine is stronger base, because -CH₃ group is electron releasing group and makes pair of electrons on nitrogen more available for protonation.
- 11. Arrange 1°, 2°, 3° methylamines in decreasing order of their base strength i) in gaseous phase ii) in aqueous medium.
- Ans. i) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$
 - ii) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$
- 12. Name two factors that effect the basic strengths of 1°, 2°, 3° methyl amines in water.
- Ans. i) Solvation (hydration)
- ii) steric hindrance
- 13. What is the final product obtained when 1° amine is alkylated? Give its general formula.
- Ans. Quaternary ammonium salt: R₄ NX
- 14. Give equation for the reaction between ethanamine and acetylchloride. Name the product obtained.

Ans.
$$C_2H_5NH_2 + CH_3COCl \longrightarrow CH_3CONHC_2H_5 + HCl$$

N-ethylacetamide

- 15. What is benzoylation of 1° amine? Give the equation with methanamine.
- Ans. Reaction of amine with benzoyl chloride is benzoylation.

$$CH_3NH_2 + C_6H_5COC1 \longrightarrow C_6H_5CONHCH_3 + HCl$$

- 16. Name the family of compounds that answers carbylamine test. Give the equation.
- Ans. 1° amine

$$RNH_2 + CHCl_3 + alc. 3KOH \xrightarrow{\Delta} RNC + 3KCl + 3H_2O$$

- 17. How does a 1° aliphatic amine react with nitrous acid? Give the equation.
- Ans. 1° aliphatic amine reacts with nitrous acid to form respective alcohol.

$$R-NH_2+HNO_2 \xrightarrow{NaNO_2/HCl} \left[R \stackrel{+}{N_2} \stackrel{-}{Cl}\right] \xrightarrow{H_2O} R-OH+HCl+N_2.$$

- 18. Name the reaction by which aniline is converted into phenyl isocyanide. Give the equation.
- Ans. Carbylamine reaction

$$C_6H_5NH_2 + CHCl_3 + Alc.3KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O$$

- 19. Complete the following equations:
 - i) $CH_3NH_2 + CH_3COCl \longrightarrow HCl + _$
 - ii) $RNH_2 \xrightarrow{\text{1 mole R-X} \atop \text{-HX}} \longrightarrow$
- Ans. i) CH₃CONHCH₃
- ii) R-NH-R

20. Identify the main organic product in the following reactions:

i)
$$C_6H_5NH_2 + HNO_2 \xrightarrow{\text{NaNO}_2/\text{HCl}} \longrightarrow$$

$$ii)$$
 $C_6H_5CONH_2 \xrightarrow{\text{Br}_2/\text{NaOH}} \longrightarrow$

Ans. i)
$$C_6H_5N_2Cl$$

ii)
$$C_6H_5NH_2$$

- 21. What is benzene sulphonyl chloride also known as? An amine with benzene sulphonyl chloride forms a compound insoluble in an alkali. Identify the class of the amine.

 Ans. Hinsberg's reagent. 2° amine.
- 22. How does Hinsberg's reagent help to distinguish 1° amine and a 2° amine? Explain.

Ans. The given amine is treated with Hinsberg's reagent. If the product formed is soluble in an alkali, the amine is 1°. If the product formed is insoluble in an alkali, the amine is 2°.

23. Complete the following equations:

i)
$$O$$
 + $3Br_2$ O + O +

ii)
$$O$$
 1. conc.H₂SO₄ 2. heat to 473 K

Sulphanilic acid Zwitter ion

- 24. What is the significance of acetylation of aniline before nitrating it?
- Ans. When aniline is treated with concentrated HNO₃, much of the aniline gets oxidized, aniline gets protonated and the major product is meta-nitroaniline. Hence to avoid all this aniline is acetylated. Acetylated aniline, avoids oxidation of aniline and controlled nitration yields p-nitro aniline as the major product.
- 25. Give reasons: i) aniline does not undergo Friedel-Crafts reaction. ii) aniline with concentrated HNO₃ forms meta nitro compound in significant amounts.
- Ans. i) Aniline reacts with AlCl₃ to form a salt, which makes nitrogen of aniline to get a positive charge, which becomes a strongly deactivating group.
 - ii) Aniline with conc. HNO₃ forms anilinium ion which is meta directing.
- 26. What is diazotization? Give the general formula of a diazonium salt.

Ans. Conversion of 1° aromatic amine into diazonium salt is diazotization.

General formula: $\operatorname{Ar} \operatorname{N}_{2} \operatorname{X}$ or $\operatorname{R} \operatorname{N}_{2} \operatorname{X}$, where $\operatorname{R} = \operatorname{Ar}$

27. How is benzene diazonium chloride prepared from aniline? Give the equation.

Ans. It is prepared by the reaction of aniline with nitrous acid (NaNO₂/ HCl) at 0°C

$$C_6H_5NH_2 + NaNO_2 + 2HC1 \xrightarrow{0^{\circ}C} C_6H_5 \stackrel{+}{N_2} \stackrel{-}{Cl} + NaCl + 2H_2O$$

28. What is Sandmeyer's reaction? Give an example.

Ans. Replacement of diazonium group by Cl⁻/Br⁻ in presence of Cu(I) ion.

E.g.: Ar
$$N_2$$
 $\stackrel{-}{X} \xrightarrow{Cu_2Cl_2/HCl} Ar-Cl + N_2$

29. Name the organic products obtained in the following reactions:

i) Ar
$$\stackrel{+}{N_2}$$
 $\stackrel{-}{X}$ $\stackrel{\text{CuCN/KCN}}{\longrightarrow}$ $+ N_2$

ii) Ar
$$N_2$$
 $\stackrel{-}{\text{Cl}}$ + H_3PO_2 + $H_2O \longrightarrow M_2 + N_2 + CH_3CHO + HCl$

Ans. i) Aryl cyanide

ii) Benzene

30. How is a diazonium salt converted into iodobenzene? Give the equation.

Ans. By treating diazonium salt with potassium iodide.

$$Ar N_2^{\dagger} X + KI \longrightarrow ArI + KCl + N_2$$
iodobenzene

31. Give an example for a coupling reaction with an equation.

Ans. Benzene diazonium chloride reacts with phenol to form p-hydroxyazobenze. This is an example for coupling reaction.

32. How is benzene diazonium chloride converted into an azo dye? Give an example for an azo dye.

Ans. Azo dyes are the products obtained when reaction of benzene diazonium chloride with phenol or aniline takes place with retention of diazo group. E.g.: benzene diazonium chloride couples with aniline to form an azo dye p-amino azo benzene (yellow dye)

33. Mention the importance of diazonium salt in synthetic organic chemistry.

Ans. i) Aryl fluoride and iodides that cannot be prepared by direct halogenation can be synthesized.

ii) It helps to introduce many functional groups into aromatic ring, which cannot be done by direct methods.

THREE MARKS:

34. Identify the X, Y, Z in the following:

$$\underbrace{\text{CONH}_{2}}_{\text{Br}_{2}/\text{NaOH}} X \xrightarrow{\text{NaNO}_{2}/\text{HCl}} Y \xrightarrow{\text{KI}} Z$$

Ans. X is aniline, Y is benzene diazonium chloride, Z is iodobenzene

35. Give equations for the preparation of methylamine (methanamine) by Gabriel-phthalimide synthesis.

Ans.
$$O$$
 CO
 $NH \xrightarrow{alc. KOH} O$
 CO
 $NK \xrightarrow{R-X, \Delta} O$
 CO
 $N-R + KX$

Phthalimide

Potassium phthalimide

N-alkyl phthalimide

$$CO$$
 $N-R$
 $N-R$

36. $RCN \xrightarrow{H_2/N_{i,\Delta}} X \xrightarrow{CHCl_3/Alc.KOH} Y$. Y is a three carbon compound. What is R in RCN, X and Y?

Ans.
$$R = CH_3$$
, $X = CH_3CH_2NH_2$, $Y = CH_3CH_2NC$

37. Give equation for the conversion of aniline into 4-bromoaniline.

- 38. An organic compound with formula C_2H_7N does not answer carbylamine test, but give a product that is insoluble in an alkali, with Hinsberg reagent. Give the IUPAC name of X and to what class of organic compound does it belong to?
- Ans. X is CH₃NHCH₃. IUPAC name: N-methylmethanamine. It is a 2° amine.
- 39. $X \xrightarrow{\text{NaNO}_2/\text{HCI}} Y \xrightarrow{\text{warm}} Z$. $Y + Z \longrightarrow orange \ dye \ (p-hydroxyazobenzene)$. What are X, Y and Z?

Ans. X is aniline, Y is \bigcirc N_2Cl Z is phenol