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## NCERT Solutions for Class 12 Chemistry Chapter 9: Amines – Free PDF Download

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## About NCERT Class 12 Chemistry Chapter 9: Amines

Amines are organic derivatives of ammonia ( $\text{NH}_3$ ) formed by replacing one, two or three hydrogen atoms with alkyl or aryl groups, giving primary ( $1^\circ$ ), secondary ( $2^\circ$ ) and tertiary ( $3^\circ$ ) amines respectively. This chapter builds on the carbonyl and carboxylic-acid chemistry of Chapter 8 and introduces nitrogen-based functional group interconversions that are heavily tested in board exams: basicity comparisons (and why the naive “more alkyl groups = stronger base” rule fails in water), the Hinsberg test for identifying amine class, and the rich chemistry of aromatic diazonium salts — including the Sandmeyer, Gattermann, and Balz–Schiemann reactions, azo-dye coupling, Hofmann’s bromamide degradation, and Gabriel phthalimide synthesis. These reactions form the backbone of many multi-step organic conversion questions.

## NCERT Solutions for Class 12 Chemistry Chapter 9: Amines – All Exercises

**Q9.1 Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines:**

- (i)  $(\text{CH}_3)_2\text{CHNH}_2$
- (ii)  $\text{CH}_3(\text{CH}_2)_2\text{NH}_2$
- (iii)  $\text{CH}_3\text{NHCH}(\text{CH}_3)_2$
- (iv)  $(\text{CH}_3)_3\text{CNH}_2$
- (v)  $\text{C}_6\text{H}_5\text{NHCH}_3$
- (vi)  $(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$
- (vii)  $m\text{-BrC}_6\text{H}_4\text{NH}_2$

Ans: (i) Propan-2-amine — **primary**. (ii) Propan-1-amine — **primary**. (iii) N-Methylpropan-2-amine — **secondary**. (iv) 2-Methylpropan-2-amine — **primary**. (v) N-Methylaniline (N-methylbenzenamine) — **secondary**. (vi) N-Ethyl-N-methylethanamine — **tertiary**. (vii) 3-Bromoaniline (3-bromobenzenamine) — **primary**.

**Q9.2 Give one chemical test to distinguish between the following pairs of compounds:**

- (i) Methylamine and dimethylamine
- (ii) Secondary and tertiary amines
- (iii) Ethylamine and aniline
- (iv) Aniline and benzylamine
- (v) Aniline and N-methylaniline

Ans: (i) **Carbylamine test** ( $\text{CHCl}_3 + \text{alc. KOH}$ , heat): methylamine ( $1^\circ$ ) gives a foul-smelling isocyanide; dimethylamine ( $2^\circ$ ) gives no reaction. (ii) **Hinsberg’s test** (benzenesulfonyl chloride,  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ ): the secondary amine forms an N,N-dialkylsulfonamide that is **insoluble in KOH** (no acidic N–H left); the tertiary amine does not react at all and separates as an unreacted oily layer. (iii) **Diazotisation** ( $\text{NaNO}_2/\text{HCl}$ , 273–278K): aniline forms a stable diazonium salt (clear solution, gives a coloured dye on coupling with alkaline  $\beta$ -naphthol); ethylamine’s diazonium salt decomposes instantly with **brisk evolution of  $\text{N}_2$  gas**. (iv) **Bromine water test**: aniline gives an immediate white precipitate of 2,4,6-tribromoaniline (its  $-\text{NH}_2$  is directly conjugated with the ring); benzylamine ( $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ ) gives no such precipitate, since its  $-\text{NH}_2$  is not attached to the ring. (v) **Carbylamine test**: aniline ( $1^\circ$ ) gives a positive test (foul-smelling phenyl isocyanide); N-methylaniline ( $2^\circ$ ) gives no reaction.

**Q9.3 Account for the following:**

- (i)  $pK_b$  of aniline is more than that of methylamine.
- (ii) Ethylamine is soluble in water, whereas aniline is not.
- (iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.
- (iv) Although the amino group is o- and p-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.
- (v) Aniline does not undergo Friedel-Crafts reaction.
- (vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
- (vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

Ans: (i) In aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance, making it far less available for protonation than methylamine's fully localised lone pair — a higher  $pK_b$  means a weaker base. (ii) Ethylamine forms strong intermolecular hydrogen bonds with water; aniline's bulky hydrophobic ring dominates its behaviour, and its weakly basic, resonance-delocalised nitrogen forms far fewer effective hydrogen bonds, so it is only sparingly soluble. (iii) Methylamine, though a weak base, generates enough hydroxide ion in water ( $\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$ ) to precipitate  $\text{Fe}^{3+}$  as hydrated  $\text{Fe}_2\text{O}_3$  (ferric hydroxide). (iv) In the strongly acidic nitrating mixture, most aniline is protonated to the anilinium ion ( $-\text{NH}_3^+$ ), which is meta-directing and deactivating; the m-nitroaniline arises from this protonated form, while only the small residual free-aniline fraction gives the o-/p-products. (v) The Lewis acid catalyst  $\text{AlCl}_3$  complexes with aniline's basic lone pair, converting  $-\text{NH}_2$  into a bulky, strongly electron-withdrawing  $-\text{NH}_2 \rightarrow \text{AlCl}_3$  group that deactivates the ring rather than activating it, so the Friedel-Crafts reaction fails. (vi) The positive charge on an aromatic diazonium ion is delocalised into the ring by resonance, stabilising it enough to isolate at low temperature; aliphatic diazonium ions have no such stabilisation and decompose instantly, even at 273K, releasing  $\text{N}_2$ . (vii) Gabriel synthesis proceeds through an  $\text{S}_\text{N}2$  attack of the phthalimide anion on an alkyl halide, which cleanly gives only a primary amine on hydrolysis with no risk of over-alkylation to secondary/tertiary amines (unlike direct ammonolysis of alkyl halides).

#### Q9.4 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  $\text{CH}_3\text{NH}_2$
- (iii) In increasing order of basic strength: aniline, p-nitroaniline and p-toluidine; also  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{NHCH}_3$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$
- (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  $\text{NH}_3$
- (v) In increasing order of boiling point:  $\text{C}_2\text{H}_5\text{OH}$ ,  $(\text{CH}_3)_2\text{NH}$  and  $\text{C}_2\text{H}_5\text{NH}_2$
- (vi) In increasing order of solubility in water:  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$  and  $\text{C}_2\text{H}_5\text{NH}_2$

Ans: (i) Decreasing  $pK_b$  (weakest base first):  $\text{C}_6\text{H}_5\text{NH}_2 > \text{C}_6\text{H}_5\text{NHCH}_3 > \text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_2\text{NH}$ . (ii) Increasing basicity:  $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 < \text{CH}_3\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH}$ . (iii) p-Nitroaniline < aniline < p-toluidine (the  $-\text{NO}_2$  group withdraws electron density and weakens basicity;  $-\text{CH}_3$  donates and strengthens it); and  $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{NHCH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  (benzylamine's nitrogen is not conjugated with the ring, so it behaves like a simple aliphatic amine and is the most basic). (iv) In the gas phase, with no solvation effects, basicity rises steadily with alkyl substitution:  $(\text{C}_2\text{H}_5)_3\text{N} > (\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$ . (v) Increasing boiling point:  $(\text{CH}_3)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{OH}$  (alcohols hydrogen-bond more strongly than amines; a secondary amine has one fewer N-H than a primary amine of similar mass, so it boils lowest). (vi) Increasing solubility:  $\text{C}_6\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2$ .

#### Q9.5 How will you convert:

- (i) Ethanoic acid into methanamine
- (ii) Hexanenitrile into 1-aminopentane
- (iii) Methanol into ethanoic acid
- (iv) Ethanamine into methanamine
- (v) Ethanoic acid into propanoic acid
- (vi) Methanamine into ethanamine
- (vii) Nitromethane into dimethylamine
- (viii) Propanoic acid into ethanoic acid

Ans: (i)  $\text{CH}_3\text{COOH} \rightarrow (\text{NH}_3, \Delta) \rightarrow \text{CH}_3\text{CONH}_2 \rightarrow (\text{Br}_2/\text{KOH}, \text{Hofmann degradation}) \rightarrow \text{CH}_3\text{NH}_2$ . (ii)  $\text{CH}_3(\text{CH}_2)_4\text{CN} \rightarrow (\text{H}_2\text{O}/\text{H}^+, \text{partial hydrolysis}) \rightarrow \text{CH}_3(\text{CH}_2)_4\text{CONH}_2 \rightarrow (\text{Br}_2/\text{KOH}) \rightarrow \text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{NH}_2$  (one carbon is lost in the Hofmann step, giving the pentylamine). (iii)  $\text{CH}_3\text{OH} \rightarrow (\text{PBr}_3) \rightarrow \text{CH}_3\text{Br} \rightarrow (\text{KCN}) \rightarrow \text{CH}_3\text{CN} \rightarrow (\text{H}_2\text{O}/\text{H}^+, \text{hydrolysis}) \rightarrow \text{CH}_3\text{COOH}$ . (iv)  $\text{CH}_3\text{CH}_2\text{NH}_2 \rightarrow (\text{HNO}_2) \rightarrow \text{CH}_3\text{CH}_2\text{OH} \rightarrow (\text{oxidation, alk. KMnO}_4) \rightarrow \text{CH}_3\text{COOH} \rightarrow (\text{NH}_3, \Delta) \rightarrow \text{CH}_3\text{CONH}_2 \rightarrow (\text{Br}_2/\text{KOH}) \rightarrow \text{CH}_3\text{NH}_2$ . (v)  $\text{CH}_3\text{COOH} \rightarrow (\text{LiAlH}_4) \rightarrow \text{CH}_3\text{CH}_2\text{OH} \rightarrow (\text{PBr}_3) \rightarrow \text{CH}_3\text{CH}_2\text{Br} \rightarrow (\text{KCN}) \rightarrow \text{CH}_3\text{CH}_2\text{CN} \rightarrow (\text{H}_2\text{O}/\text{H}^+) \rightarrow \text{CH}_3\text{CH}_2\text{COOH}$ . (vi)  $\text{CH}_3\text{NH}_2 \rightarrow (\text{HNO}_2) \rightarrow \text{CH}_3\text{OH} \rightarrow (\text{PBr}_3) \rightarrow \text{CH}_3\text{Br} \rightarrow (\text{KCN}) \rightarrow \text{CH}_3\text{CN} \rightarrow (\text{LiAlH}_4) \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2$ . (vii)  $\text{CH}_3\text{NO}_2 \rightarrow (\text{Fe}/\text{HCl} \text{ or } \text{Sn}/\text{HCl}, \text{reduction}) \rightarrow \text{CH}_3\text{NH}_2 \rightarrow (\text{CHCl}_3/\text{alc. KOH}, \text{carbylamine}) \rightarrow \text{CH}_3\text{NC} \rightarrow (\text{H}_2/\text{Ni}, \text{reduction}) \rightarrow \text{CH}_3\text{NHCH}_3$ . (viii)  $\text{CH}_3\text{CH}_2\text{COOH} \rightarrow (\text{NH}_3, \Delta) \rightarrow \text{CH}_3\text{CH}_2\text{CONH}_2 \rightarrow (\text{Br}_2/\text{KOH}) \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 \rightarrow (\text{HNO}_2) \rightarrow \text{CH}_3\text{CH}_2\text{OH} \rightarrow (\text{oxidation}) \rightarrow \text{CH}_3\text{COOH}$ .

### Q9.6 Describe a method for the identification of primary, secondary and tertiary amines.

Ans: **Hinsberg's test** uses benzenesulfonyl chloride ( $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ ) with KOH. A **primary amine** forms an N-alkylbenzenesulfonamide ( $\text{C}_6\text{H}_5\text{SO}_2\text{NHR}$ ) that still has one acidic N-H (made acidic by the strongly electron-withdrawing  $-\text{SO}_2-$  group), so it **dissolves in excess KOH** as its potassium salt. A **secondary amine** forms a fully N,N-disubstituted sulfonamide ( $\text{C}_6\text{H}_5\text{SO}_2\text{NR}_2$ ) with no acidic hydrogen left, so it **remains insoluble** in KOH. A **tertiary amine** has no N-H to begin with and does not react with benzenesulfonyl chloride at all, separating out unreacted as an oily layer.

### Q9.7 Write short notes on the following:

(i) Carbylamine reaction (ii) Diazotisation (iii) Hofmann's bromamide reaction (iv) Coupling reaction (v) Ammonolysis (vi) Acetylation (vii) Gabriel phthalimide synthesis

Ans: (i) **Carbylamine reaction:** a primary amine (aliphatic or aromatic) heated with  $\text{CHCl}_3$  and alcoholic KOH forms a foul-smelling isocyanide (carbylamine),  $\text{RNC}$  — a test specific to primary amines only. (ii)

**Diazotisation:** an aromatic primary amine treated with  $\text{NaNO}_2 + \text{HCl}$  at 273–278K forms a diazonium salt,  $\text{ArN}_2^+\text{Cl}^-$ . (iii) **Hofmann's bromamide reaction:** an amide treated with  $\text{Br}_2$  and  $\text{NaOH}/\text{KOH}$  degrades to a primary amine with **one carbon fewer** than the starting amide, via an isocyanate intermediate. (iv)

**Coupling reaction:** a diazonium salt reacts with a phenol (mildly alkaline medium) or an aromatic amine (mildly acidic medium) to give a brightly coloured azo compound ( $\text{Ar-N=N-Ar'}$ ), the basis of azo dyes. (v)

**Ammonolysis:** an alkyl halide reacts with excess ammonia (in a sealed tube) to give an amine, via nucleophilic substitution; the product can further react with more alkyl halide, so ammonolysis often gives a mixture of 1°, 2°, 3° amines and a quaternary salt. (vi) **Acetylation:** an amine reacts with acetic anhydride or acetyl chloride to form an N-substituted acetamide, converting a reactive amine into a less nucleophilic, protected amide (used, e.g., to moderate aniline's ring-activating power before nitration/halogenation). (vii)

**Gabriel phthalimide synthesis:** potassium phthalimide reacts with a primary alkyl halide ( $\text{S}_{\text{N}}2$ ), and the resulting N-alkylphthalimide is hydrolysed to give a pure primary amine with no over-alkylation.

### Q9.8 Accomplish the following conversions:

- Nitrobenzene to benzoic acid
- Benzene to m-bromophenol
- Benzoic acid to aniline
- Aniline to 2,4,6-tribromofluorobenzene
- Benzyl chloride to 2-phenylethanamine
- Chlorobenzene to p-chloroaniline
- Aniline to p-bromoaniline
- Benzamide to toluene
- Aniline to benzyl alcohol

Ans: (i)  $\text{C}_6\text{H}_5\text{NO}_2 \rightarrow (\text{Fe}/\text{HCl}) \rightarrow \text{C}_6\text{H}_5\text{NH}_2 \rightarrow (\text{NaNO}_2/\text{HCl}, 273\text{K}) \rightarrow \text{C}_6\text{H}_5\text{N}_2\text{Cl} \rightarrow (\text{CuCN}, \text{then } \text{H}_2\text{O}/\text{H}^+) \rightarrow \text{C}_6\text{H}_5\text{COOH}$ . (ii)  $\text{C}_6\text{H}_6 \rightarrow (\text{Br}_2/\text{FeBr}_3) \rightarrow \text{C}_6\text{H}_5\text{Br} \rightarrow (\text{fuming } \text{H}_2\text{SO}_4) \rightarrow \text{m-BrC}_6\text{H}_4\text{SO}_3\text{H} \rightarrow (\text{fuse with } \text{NaOH}, \text{then } \text{H}^+) \rightarrow \text{m-bromophenol}$ . (iii)  $\text{C}_6\text{H}_5\text{COOH} \rightarrow (\text{NH}_3, \Delta) \rightarrow \text{C}_6\text{H}_5\text{CONH}_2 \rightarrow (\text{Br}_2/\text{NaOH}, \text{Hofmann}) \rightarrow \text{C}_6\text{H}_5\text{NH}_2$ . (iv)  $\text{C}_6\text{H}_5\text{NH}_2 \rightarrow (\text{Br}_2(\text{aq}), \text{excess}) \rightarrow 2,4,6\text{-tribromoaniline} \rightarrow (\text{NaNO}_2/\text{HCl},$

273K)  $\rightarrow$  2,4,6-tribromobenzenediazonium chloride  $\rightarrow$  (HBF<sub>4</sub>, then  $\Delta$ , Balz–Schiemann)  $\rightarrow$  2,4,6-tribromofluorobenzene. (v)  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} \rightarrow (\text{KCN}) \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CN} \rightarrow (\text{LiAlH}_4 \text{ or } \text{H}_2/\text{Ni}) \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_2$ . (vi)  $\text{C}_6\text{H}_5\text{Cl} \rightarrow (\text{conc. HNO}_3/\text{H}_2\text{SO}_4) \rightarrow \text{p-O}_2\text{NC}_6\text{H}_4\text{Cl} \rightarrow (\text{Fe/HCl or Sn/HCl, reduction}) \rightarrow \text{p-ClC}_6\text{H}_4\text{NH}_2$ . (vii)  $\text{C}_6\text{H}_5\text{NH}_2 \rightarrow ((\text{CH}_3\text{CO})_2\text{O, acetylation}) \rightarrow \text{C}_6\text{H}_5\text{NHCOCH}_3 \rightarrow (\text{Br}_2/\text{CH}_3\text{COOH, then } \text{H}_3\text{O}^+/\text{OH}^- \text{ hydrolysis}) \rightarrow \text{p-BrC}_6\text{H}_4\text{NH}_2$  (acetylation moderates  $-\text{NH}_2$ 's activating power so bromination stays mono-substituted and para-selective). (viii)  $\text{C}_6\text{H}_5\text{CONH}_2 \rightarrow (\text{Br}_2/\text{NaOH, Hofmann}) \rightarrow \text{C}_6\text{H}_5\text{NH}_2 \rightarrow (\text{NaNO}_2/\text{HCl, 273K}) \rightarrow \text{C}_6\text{H}_5\text{N}_2\text{Cl} \rightarrow (\text{H}_3\text{PO}_2/\text{H}_2\text{O}) \rightarrow \text{C}_6\text{H}_6 \rightarrow (\text{CH}_3\text{Cl/anhyd. AlCl}_3, \text{Friedel-Crafts}) \rightarrow \text{C}_6\text{H}_5\text{CH}_3$ . (ix)  $\text{C}_6\text{H}_5\text{NH}_2 \rightarrow (\text{NaNO}_2/\text{HCl, 273K}) \rightarrow \text{C}_6\text{H}_5\text{N}_2\text{Cl} \rightarrow (\text{CuCN, then } \text{H}_2\text{O/H}^+) \rightarrow \text{C}_6\text{H}_5\text{COOH} \rightarrow (\text{LiAlH}_4) \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{OH}$ .

### Q9.9 Give the structures of A, B and C in the following reactions:

- $\text{CH}_3\text{CH}_2\text{I} \rightarrow (\text{NaCN}) \rightarrow \text{A} \rightarrow (\text{partial hydrolysis, OH}^-) \rightarrow \text{B} \rightarrow (\text{NaOH} + \text{Br}_2) \rightarrow \text{C}$
- $\text{C}_6\text{H}_5\text{N}_2\text{Cl} \rightarrow (\text{CuCN}) \rightarrow \text{A} \rightarrow (\text{H}_2\text{O/H}^+) \rightarrow \text{B} \rightarrow (\text{NH}_3, \Delta) \rightarrow \text{C}$
- $\text{CH}_3\text{CH}_2\text{Br} \rightarrow (\text{KCN}) \rightarrow \text{A} \rightarrow (\text{LiAlH}_4) \rightarrow \text{B} \rightarrow (\text{HNO}_2, 273\text{K}) \rightarrow \text{C}$
- $\text{C}_6\text{H}_5\text{NO}_2 \rightarrow (\text{Fe/HCl}) \rightarrow \text{A} \rightarrow (\text{NaNO}_2 + \text{HCl, 273K}) \rightarrow \text{B} \rightarrow (\text{H}_2\text{O/H}^+, \Delta) \rightarrow \text{C}$
- $\text{CH}_3\text{COOH} \rightarrow (\text{NH}_3, \Delta) \rightarrow \text{A} \rightarrow (\text{NaOBr}) \rightarrow \text{B} \rightarrow (\text{NaNO}_2/\text{HCl}) \rightarrow \text{C}$
- $\text{C}_6\text{H}_5\text{NO}_2 \rightarrow (\text{Fe/HCl}) \rightarrow \text{A} \rightarrow (\text{HNO}_2, 273\text{K}) \rightarrow \text{B} \rightarrow (\text{C}_6\text{H}_5\text{OH}) \rightarrow \text{C}$

Ans: (i)  $\text{A} = \text{CH}_3\text{CH}_2\text{CN}$  (propanenitrile),  $\text{B} = \text{CH}_3\text{CH}_2\text{CONH}_2$  (propanamide),  $\text{C} = \text{CH}_3\text{CH}_2\text{NH}_2$  (ethanamine, via Hofmann degradation). (ii)  $\text{A} = \text{C}_6\text{H}_5\text{CN}$  (benzonitrile),  $\text{B} = \text{C}_6\text{H}_5\text{COOH}$  (benzoic acid),  $\text{C} = \text{C}_6\text{H}_5\text{CONH}_2$  (benzamide). (iii)  $\text{A} = \text{CH}_3\text{CH}_2\text{CN}$  (propanenitrile),  $\text{B} = \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  (propan-1-amine),  $\text{C} = \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  (propan-1-ol, via deamination). (iv)  $\text{A} = \text{C}_6\text{H}_5\text{NH}_2$  (aniline),  $\text{B} = \text{C}_6\text{H}_5\text{N}_2\text{Cl}$  (benzenediazonium chloride),  $\text{C} = \text{C}_6\text{H}_5\text{OH}$  (phenol). (v)  $\text{A} = \text{CH}_3\text{CONH}_2$  (acetamide),  $\text{B} = \text{CH}_3\text{NH}_2$  (methanamine, via Hofmann degradation with NaOBr),  $\text{C} = \text{CH}_3\text{OH}$  (methanol, via deamination). (vi)  $\text{A} = \text{C}_6\text{H}_5\text{NH}_2$  (aniline),  $\text{B} = \text{C}_6\text{H}_5\text{N}_2\text{Cl}$  (benzenediazonium chloride),  $\text{C} = \text{p-HOC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5$  (p-hydroxyazobenzene, via coupling with phenol).

### Q9.10 An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B', which on heating with Br<sub>2</sub> and KOH forms a compound 'C' of molecular formula C<sub>6</sub>H<sub>7</sub>N. Write the structures and IUPAC names of compounds A, B and C.

Ans:  $\text{A} = \text{C}_6\text{H}_5\text{COOH}$  (benzoic acid)  $\rightarrow \text{B} = \text{C}_6\text{H}_5\text{CONH}_2$  (benzamide)  $\rightarrow \text{C} = \text{C}_6\text{H}_5\text{NH}_2$  (aniline, IUPAC name benzenamine). The Hofmann bromamide degradation of benzamide ( $\text{C}_7\text{H}_7\text{NO}$ ) removes the carbonyl carbon, giving aniline ( $\text{C}_6\text{H}_7\text{N}$ ) — matching the molecular formula given.

### Q9.11 Complete the following reactions:

- $\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + \text{alc. KOH} \rightarrow$
- $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \rightarrow$
- $\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{SO}_4(\text{conc.}) \rightarrow$
- $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow$
- $\text{C}_6\text{H}_5\text{NH}_2 + \text{Br}_2(\text{aq}) \rightarrow$
- $\text{C}_6\text{H}_5\text{NH}_2 + (\text{CH}_3\text{CO})_2\text{O} \rightarrow$
- $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{HBF}_4, \text{ then } \Delta; \text{ and } \text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{NaNO}_2/\text{Cu}, \Delta \rightarrow$

Ans: (i)  $\text{C}_6\text{H}_5\text{NC}$  (phenyl isocyanide) +  $3\text{KCl} + 3\text{H}_2\text{O}$  (carbylamine reaction). (ii)  $\text{C}_6\text{H}_6$  (benzene) +  $\text{N}_2 + \text{H}_3\text{PO}_3 + \text{HCl}$  (reduction of the diazonium group). (iii)  $\text{C}_6\text{H}_5\text{NH}_3^+\text{HSO}_4^-$  (anilinium hydrogen sulphate — simple acid-base salt formation). (iv)  $\text{C}_6\text{H}_6$  (benzene) +  $\text{N}_2 + \text{CH}_3\text{CHO} + \text{HCl}$  (reduction of the diazonium group by ethanol). (v) 2,4,6-tribromoaniline (white precipitate) +  $3\text{HBr}$ . (vi)  $\text{C}_6\text{H}_5\text{NHCOCH}_3$  (acetanilide) +  $\text{CH}_3\text{COOH}$ . (vii) With  $\text{HBF}_4$  then heat:  $\text{C}_6\text{H}_5\text{F}$  (fluorobenzene) +  $\text{BF}_3 + \text{N}_2$  (Balz–Schiemann reaction). With  $\text{NaNO}_2/\text{Cu}$  and heat:  $\text{C}_6\text{H}_5\text{NO}_2$  (nitrobenzene) +  $\text{N}_2$  (a Cu-catalysed replacement of the diazonium group by  $-\text{NO}_2$ , alongside the more commonly tested halogen/cyanide Sandmeyer substitutions).

### Q9.12 Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

Ans: Gabriel synthesis requires an  $\text{S}_{\text{N}}2$  attack of the phthalimide anion on an alkyl halide. An **aryl halide cannot undergo this step**: its C–X bond has partial double-bond character from resonance with the ring,

and the  $sp^2$  carbon is geometrically shielded against backside nucleophilic attack. Since aryl halides are unreactive towards nucleophilic substitution under these conditions, the phthalimide anion cannot be alkylated with them, so aromatic primary amines cannot be made this way.

**Q9.13 Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.**

Ans: (i) **Aromatic primary amines** (e.g. aniline) react with  $HNO_2$  (from  $NaNO_2 + HCl$ ) at 273–278K to form a reasonably stable **diazonium salt**:  $C_6H_5NH_2 + HNO_2 + HCl \rightarrow C_6H_5N_2Cl + 2H_2O$ , which can be isolated and used in a wide range of substitution and coupling reactions. (ii) **Aliphatic primary amines** react with  $HNO_2$  to form an **unstable** diazonium salt that decomposes immediately, even in the cold, evolving nitrogen gas and forming a carbocation that goes on to give a mixture of an alcohol (major), alkene and alkyl halide:  $RNH_2 + HNO_2 \rightarrow ROH + N_2 + H_2O$ . This brisk, quantitative-with-effervescence reaction is itself used as a test to detect primary aliphatic amines.

**Q9.14 Give plausible explanations for each of the following:**

(i) Why are amines less acidic than alcohols of comparable molecular mass?

(ii) Why do primary amines have a higher boiling point than tertiary amines?

(iii) Why are aliphatic amines stronger bases than aromatic amines?

Ans: (i) Nitrogen (electronegativity  $\approx 3.0$ ) is less electronegative than oxygen ( $\approx 3.5$ ), so it holds the N–H bonding electrons less tightly; the resulting amide-ion-like conjugate base ( $R-NH^-$ ) is far less stable than an alkoxide ion ( $R-O^-$ ), making amines much weaker acids than alcohols. (ii) A primary amine ( $R-NH_2$ ) has two N–H bonds available for intermolecular hydrogen bonding, so its molecules associate strongly; a tertiary amine ( $R_3N$ ) has no N–H bonds at all and cannot hydrogen-bond with other amine molecules, so it has a noticeably lower boiling point than an isomeric primary amine. (iii) In aromatic amines, the nitrogen lone pair is delocalised into the ring by resonance, making it far less available to accept a proton; in aliphatic amines the lone pair remains fully localised on nitrogen (and is further pushed towards N by the +I effect of alkyl groups), so aliphatic amines are consistently stronger bases than aromatic ones.

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