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Collegedunia NCERT Solutions

Step-by-step solutions, alternate methods & exam tips for Class 12 Chemistry

Chapter 9: Amines

About this Chapter

This chapter studies **amines**: organic derivatives of ammonia in which one, two or three hydrogens are replaced by alkyl or aryl groups. We learn IUPAC naming, the pyramidal structure of the nitrogen centre, and three big families of reactions: preparation (**ammonolysis**, **Gabriel synthesis**, **Hofmann bromamide**), chemical behaviour (basicity, alkylation, acylation, carbylamine test, **Hinsberg's test**), and diazonium-salt chemistry (**Sandmeyer**, Gattermann, coupling). The role of inductive, steric, and solvation effects on basicity is the recurring theme.

Topics covered: Structure • Classification • IUPAC Nomenclature • Preparation • Basicity • Hinsberg's Test • Carbylamine • Diazotisation • Sandmeyer / Gattermann • Coupling reactions

Quick Formula Sheet

Basicity (aqueous):

$2^\circ > 1^\circ > 3^\circ > \mathrm{NH_3}$ (for $\mathrm{CH_3}$)

Basicity (gas phase):

$3^\circ > 2^\circ > 1^\circ > \mathrm{NH_3}$

pK_b relation:

$\mathrm{p}K_b = -\log_{10} K_b$

Carbylamine test (1° only):

$\mathrm{R{-}NH_2 + CHCl_3 + 3\,KOH \xrightarrow{\Delta} R{-}NC + 3\,KCl + 3\,H_2O}$

Hofmann bromamide:

$\mathrm{R{-}CONH_2 + Br_2 + 4\,NaOH \longrightarrow R{-}NH_2}$

Diazotisation (0–5 °C):

$\mathrm{ArNH_2 + HNO_2 + HCl \longrightarrow ArN_2^+Cl^- + 2\,H_2O}$

Sandmeyer:

$\mathrm{ArN_2^+Cl^- \xrightarrow{CuCl/HCl} ArCl + N_2}$

Chapter 9 Exercises

Q 9.1 **Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines:**

(i) $(CH_3)_2CHNH_2$ (ii) $CH_3(CH_2)_2NH_2$ (iii) $CH_3NHCH(CH_3)_2$

(iv) $(CH_3)_3CNH_2$ (v) $C_6H_5NHCH_3$ (vi) $(CH_3CH_2)_2NCH_3$

(vii) m-$BrC_6H_4NH_2$

SOLUTION

Concept used. An **amine** is a derivative of ammonia (NH_3) in which one, two, or three of its hydrogens are replaced by alkyl or aryl groups, denoted $R{-}NH_2$, R_2NH, R_3N respectively. The number of carbon-containing groups directly bonded to the nitrogen decides the class:

- **Primary (1°):** one R on N, so structure is $R{-}NH_2$.
- **Secondary (2°):** two R groups on N, so R_2NH.
- **Tertiary (3°):** three R groups on N, so R_3N.

For IUPAC naming we use the **substitutive system**: replace the $-e$ of the parent alkane name with $-amine$ and place the lowest possible locant before the suffix. For secondary and tertiary amines, the largest alkyl chain is the parent, and the smaller groups are named as N-substituents (the letter N written in italics). Arylamines based on benzene use *aniline* as the retained IUPAC name (or *benzenamine*).

☞ **How to count R on nitrogen**

Only the carbon atoms *directly bonded* to N count. The chain attached to that carbon can be long, but for classification we look only at the C–N bonds.

Primary (1°)	Secondary (2°)	Tertiary (3°)
$R{-}NH_2$ one C–N	R_2NH two C–N	R_3N three C–N
Example: CH_3NH_2	Example: $(CH_3)_2NH$	Example: $(CH_3)_3N$

Step 1. **(i) $(CH_3)_2CHNH_2$.** The carbon attached to NH_2 is a propan-2-yl group (isopropyl). Parent chain has 3 carbons, so parent alkane is propane → propan*e* ends with the amino group on C-2. IUPAC name: **propan-2-amine**. Only one R (the isopropyl carbon skeleton) is on N ⇒ *primary amine*.

Step 2. **(ii) $CH_3(CH_2)_2NH_2$.** Expand: $CH_3-CH_2-CH_2-NH_2$. Three carbons in the longest chain, $-NH_2$ on C-1. IUPAC name: **propan-1-amine**. One R on N ⇒ *primary amine*.

Step 3. **(iii) $CH_3NHCH(CH_3)_2$.** The N has two carbons bonded directly: a CH_3 group and a $(CH_3)_2CH^-$ group. Choose the larger one (the 3-carbon isopropyl) as the parent → propan-2-amine. The methyl on N is an N-*methyl* substituent. IUPAC name: **N-methylpropan-2-amine**. Two R on N ⇒ *secondary amine*.

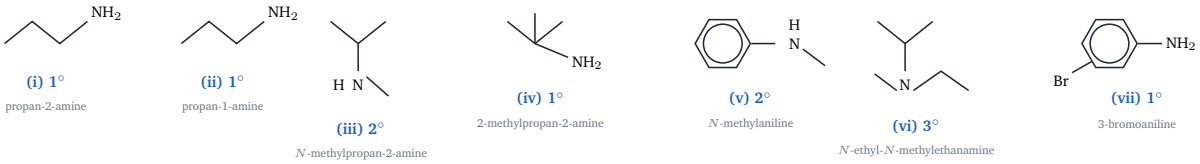
Step 4. **(iv) $(CH_3)_3CNH_2$.** The C attached to NH_2 is a *tert*-butyl carbon ($C(CH_3)_3$). Parent is butane, $-NH_2$ on C-2 of the 4-carbon skeleton $CH_3-C(CH_3)_2-NH_2$. Numbering: the parent chain that contains the amino group with lowest locant is 2-methylpropane. The NH_2 is on C-2 of 2-methylpropane. IUPAC name:

2-methylpropan-2-amine. One R on N $\Rightarrow$ *primary amine*.

Step 5. **(v) $C_6H_5NHCH_3$.** The N carries a phenyl group (C_6H_5) and a methyl group. Treat as aniline with an N-methyl substituent. IUPAC name: **N-methylaniline** (also N-methylbenzenamine). Two R on N $\Rightarrow$ *secondary amine*.

Step 6. **(vi) $(CH_3CH_2)_2NCH_3$.** The N has two ethyl groups and one methyl group. Take the larger group as parent: ethane $\rightarrow$ ethanamine. The second ethyl and the methyl become N-substituents. IUPAC name: **N-ethyl-N-methylethanamine**. Three R on N $\Rightarrow$ *tertiary amine*.

Step 7. **(vii) m-$BrC_6H_4NH_2$.** A bromine on the meta position of aniline. Number the ring with C-1 carrying the principal group (NH_2); meta is C-3. IUPAC name: **3-bromoaniline** (also 3-bromobenzenamine). One R (the benzene ring) on N $\Rightarrow$ *primary amine*.



Final Answer: (i) Propan-2-amine, 1°. (ii) Propan-1-amine, 1°. (iii) N-methylpropan-2-amine, 2°. (iv) 2-methylpropan-2-amine, 1°. (v) N-methylaniline, 2°. (vi) N-ethyl-N-methylethanamine, 3°. (vii) 3-bromoaniline, 1°.

☞ Step-by-step IUPAC naming

1. Find the longest carbon chain attached to N. 2. Drop the final $-e$ of that alkane and add *-amine*. 3. Number the chain so the $-NH_2$ gets the lowest locant. 4. Name any other groups on N with the N- prefix. 5. For aryl primary amines use *aniline* as the retained parent.

☞ Quick alternative: count N–H bonds

A faster classification trick: count the hydrogens still on N. Three N–H = ammonia (no arms); two N–H = 1° ($R-NH_2$); one N–H = 2° (R_2NH); zero N–H = 3° (R_3N). Since the total valency is fixed at 3, "arms" and "N–H" add to 3 every time. JEE/NEET MCQs often hide this in a condensed formula like $C_6H_5N(CH_3)_2$ (zero N–H $\Rightarrow$ 3°).

EXPERT'S SOLUTION *: Pranav Iyer, M.Sc Chemistry, IIT Kanpur*

Structural observation. Treat every C–N bond as one "arm" hanging off the nitrogen. Counting arms gives the class immediately: one arm = primary, two = secondary, three = tertiary. The number of hydrogens still on the nitrogen is $3 - (\text{arms})$, so the two counts are equivalent and you can use whichever is easier to read off the condensed

formula.

Alternative approach (the N–H count). For each compound, try to count the H on N directly: in $(CH_3)_2CHNH_2$ the N still carries NH_2 (two H) $\Rightarrow 1^\circ$; in $CH_3NHCH(CH_3)_2$ the N carries NH (one H) $\Rightarrow 2^\circ$; in $(CH_3CH_2)_2NCH_3$ the N carries no H $\Rightarrow 3^\circ$.

IUPAC strategy in three lines. (1) Pick the carbon group with the longest chain as the parent. (2) Replace the final $-e$ of that alkane by $-amine$, with the locant of the $-NH_2$ inserted before it. (3) Every other carbon group on the same N is named as an N-substituent (italic N in print), listed alphabetically.

Concept linkage. The class fixed in this question controls *every* downstream reaction in the chapter: only 1° amines give the carbylamine test (Q 9.2, 9.11(i)), only 1° aromatic amines give a stable diazonium salt (Q 9.13), and only 1° and 2° amines acetylate (Q 9.7(vi)). So getting (i)–(vii) right is the gateway to reading the rest of the paper correctly.

Step 1. (i) $(CH_3)_2CHNH_2$: amino-bearing carbon has two methyls $\Rightarrow$ propan-2-amine. One C on N (two H) $\Rightarrow 1^\circ$.

Step 2. (ii) $CH_3(CH_2)_2NH_2$: a straight chain of three carbons with NH_2 at the terminal carbon $\Rightarrow$ propan-1-amine, 1°.

Step 3. (iii) $CH_3NHCH(CH_3)_2$: two carbon arms (methyl and isopropyl) on N; pick isopropyl as parent $\Rightarrow$ N-methylpropan-2-amine, 2°.

Step 4. (iv) $(CH_3)_3CNH_2$: a quaternary carbon ($C(CH_3)_3$) bonded to a single NH_2. The chain "2-methylpropan-2-yl" carries NH_2 at C-2 $\Rightarrow$ 2-methylpropan-2-amine. Still one C on N $\Rightarrow 1^\circ$.

Step 5. (v) $C_6H_5NHCH_3$: phenyl and methyl on N; aniline is the retained parent, methyl becomes N-methyl $\Rightarrow$ N-methylaniline, 2°.

Step 6. (vi) $(CH_3CH_2)_2NCH_3$: three arms, two ethyls and one methyl. Largest arm (ethyl) is the parent (ethanamine); the second ethyl and the methyl are N-substituents listed alphabetically $\Rightarrow$ N-ethyl-N-methylethanamine, 3°.

Step 7. (vii) m-$BrC_6H_4NH_2$: bromo at meta on aniline ring (position 3) $\Rightarrow$ 3-bromoaniline, 1°.

Exam relevance. JEE/NEET MCQ writers love disguised tertiary amines like $C_6H_5N(CH_3)_2$ (N,N-dimethylaniline) and ask whether they show the carbylamine test. The answer is no, because they are 3°. A frequent CBSE 1-mark question asks: "identify the nitrogen class in $(CH_3CH_2)_2NCH_3$"$= 3^\circ$.

Why this matters. Class (1°, 2°, 3°) controls which reactions an amine can do. Only 1° amines give the carbylamine reaction and the Hofmann mustard-oil test; only 2° amines give a yellow oil (N-nitrosamine) with nitrous acid; 3° amines do neither but still alkylate or coordinate to Lewis acids. Getting the class right in one glance saves time in every later question.

Final Answer: (i) Propan-2-amine, 1°; (ii) Propan-1-amine, 1°; (iii) N-methylpropan-2-amine, 2°; (iv) 2-methylpropan-2-amine, 1°; (v) N-methylaniline, 2°; (vi) N-ethyl-N-methylethanamine, 3°; (vii) 3-bromoaniline, 1°.

Q 9.2 **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.

SOLUTION

Concept used. Three signature tests distinguish amine classes:

- **Carbylamine test**: 1° amines (both alkyl and aryl) on warming with chloroform and alcoholic KOH give an *isocyanide* (R−NC) with a foul, penetrating smell. 2° and 3° amines give no reaction.

$$\mathrm{R{-}NH_2 + CHCl_3 + 3\,KOH \xrightarrow{\Delta} R{-}NC + 3\,KCl + 3\,H_2O.}$$

- **Hinsberg's test**: amines react with benzenesulphonyl chloride ($C_6H_5SO_2Cl$). 1° amines give a sulphonamide soluble in alkali; 2° amines give a sulphonamide insoluble in alkali; 3° amines do not react (no N–H).
- **Diazotisation**: 1° aromatic amines with $NaNO_2$/HCl at 0–5 °C form a stable diazonium salt $ArN_2^+Cl^-$. 1° aliphatic amines under the same conditions liberate N_2 (vigorous effervescence). The diazonium salt then couples with phenol or 2-naphthol in alkaline medium to give an orange/red **azo dye**.

Hinsberg's Test ($C_6H_5SO_2Cl$)

1° amine	2° amine	3° amine
$R{-}NH{-}SO_2C_6H_5$ soluble in NaOH (clear soln.)	$R_2N{-}SO_2C_6H_5$ insoluble in NaOH (solid stays)	No reaction (no N–H) layer separates

Step 1. **(i) Methylamine vs dimethylamine: carbylamine test.** CH_3NH_2 (1°) on heating with $CHCl_3$ + alcoholic KOH gives methyl isocyanide CH_3NC (offensive smell).

$$\mathrm{CH_3NH_2 + CHCl_3 + 3\,KOH \xrightarrow{\Delta} CH_3NC + 3\,KCl + 3\,H_2O.}$$

Dimethylamine $(CH_3)_2NH$ (2°) gives *no* reaction. Smell test confirms 1°.

Step 2. **(ii) Secondary vs tertiary amines: Hinsberg's test.** Shake with $C_6H_5SO_2Cl$ in KOH. The 2° amine forms a sulphonamide $R_2N{-}SO_2C_6H_5$ which has no N–H and is therefore *insoluble in NaOH*. The 3° amine has no N–H to start with and does not react; on acidifying, the tertiary amine dissolves in dilute HCl while the sulphonamide from the secondary amine does not.

Step 3. **(iii) Ethylamine vs aniline: azo-dye test.** Aniline (1° aromatic) with cold $NaNO_2$/HCl at 0–5 °C gives benzenediazonium chloride, which couples with alkaline 2-naphthol to give a bright **orange/red azo dye**. Ethylamine (1° aliphatic) under the same conditions evolves N_2 gas (effervescence) and gives ethanol; no dye forms.

$$C_6H_5NH_2 + HNO_2 + HCl \xrightarrow{273\text{–}278\,K} C_6H_5N_2^{+}Cl^{-} + 2\,H_2O,$$

$$C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2\uparrow + H_2O.$$

Step 4. **(iv) Aniline vs benzylamine: same azo-dye test.** Aniline is aryl-1° and forms a stable diazonium salt → orange dye on coupling with 2-naphthol/NaOH. Benzylamine $C_6H_5CH_2NH_2$ is alkyl-1° (the amino group is on the CH_2, not on the ring) and behaves like ethylamine: liberates N_2, no dye.

Step 5. **(v) Aniline vs *N*-methylaniline: carbylamine test.** Aniline is 1° and gives the foul smell of phenyl isocyanide C_6H_5NC:

$$C_6H_5NH_2 + CHCl_3 + 3\,KOH \xrightarrow{\Delta} C_6H_5NC + 3\,KCl + 3\,H_2O.$$

N-methylaniline $C_6H_5NHCH_3$ is 2° and gives no reaction.

Final Answer: Use the carbylamine test for 1° vs 2° (i, v); Hinsberg's test for 2° vs 3° (ii); and cold $NaNO_2$/HCl + 2-naphthol coupling to distinguish aryl-1° from alkyl-1° amines (iii, iv).

✗ Tertiary amines do enter Hinsberg's reagent

A common slip is to say 3° amines "react but the product dissolves in acid". In fact 3° amines do not form a bond with $C_6H_5SO_2Cl$ at all (no N–H). The 3° amine simply remains as a free base, distinguishable on later acidification.

☞ Reagent cheat-sheet for amine tests

Carbylamine: $CHCl_3 + \text{alc}\cdot KOH,\ \Delta$ (smells confirm 1°). Hinsberg: $C_6H_5SO_2Cl + KOH$ (solubility separates class). Cold diazotisation: $NaNO_2/HCl$ at 273–278 K (stable salt for aryl, $N_2\uparrow$ for alkyl). β-naphthol/NaOH: orange-red azo dye couples only with aryl diazonium.

EXPERT'S SOLUTION *: Karan Bhat, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. The five pairs reduce to three test "cases": (a) 1° vs 2°: use a test that needs an N–H on *one* carbon ⇒ carbylamine. (b) 2° vs 3°: use a test that distinguishes one N–H from zero N–H ⇒ Hinsberg's. (c) Aryl-1° vs alkyl-1°: use diazotisation ⇒ stable salt vs N_2 burst.

Alternative approach (one test for three classes). If you are given a single unknown amine and want to settle 1°/2°/3° in one shot, Hinsberg's test alone does the job: KOH-soluble sulphonamide ⇒ 1°; KOH-insoluble solid ⇒ 2°; no reaction (but dissolves in dilute HCl) ⇒ 3°. The carbylamine test then confirms 1°, and cold diazotisation splits aryl-1° from alkyl-1°.

Concept linkage. Each pair maps onto a different "N–H count" or "ring vs no ring" contrast, the same two ideas that control basicity (Q 9.3, 9.4) and diazotisation stability (Q 9.13). Notice that two of the five pairs (i, v) use carbylamine, and two others (iii, iv) use diazotisation. So the whole question rests on just three reagents.

Step 1. (i) Methylamine vs dimethylamine ⇒ *carbylamine*. CH_3NH_2 (1°) gives CH_3NC (foul smell); $(CH_3)_2NH$ (2°) gives no reaction.

Step 2. (ii) Secondary vs tertiary ⇒ *Hinsberg's*. 2° amine + $C_6H_5SO_2Cl \rightarrow R_2N{-}SO_2C_6H_5$ (no N–H left) ⇒ insoluble in alkali. 3° amine (no N–H to start) ⇒ no reaction at all, but dissolves in dilute HCl on acidification.

Step 3. (iii)/(iv) Aryl-1° vs alkyl-1° ⇒ *cold diazotisation + 2-naphthol*. Aniline (or its benzylamine cousin in (iv)) forms a stable diazonium that couples to give a red/orange azo dye. Ethylamine and benzylamine, both alkyl-1°, liberate N_2 with effervescence and give the alcohol.

Step 4. (v) Aniline vs N-methylaniline ⇒ *carbylamine* again. Aniline (1°) gives C_6H_5NC (offensive smell); N-methylaniline (2°) gives no isocyanide.

Exam relevance. NEET often phrases this as MCQ-II: "Which reagent does NOT distinguish $C_6H_5NH_2$ and $C_6H_5NHCH_3$?" Answer: Hinsberg (because both react), so the right pick is the carbylamine test. A common JEE Mains twist is to ask about benzylamine vs aniline (pair iv): students wrongly try carbylamine (both 1° and react!) and need to recall diazotisation as the decisive test.

Why this matters. Telling amine classes apart is a routine practical-exam task. The three tests above can identify any unknown amine when used in sequence: Hinsberg's → separates the three classes; carbylamine → confirms 1°; diazotisation → splits aryl from alkyl 1°.

Final Answer: Carbylamine test for (i) and (v); Hinsberg's test for (ii); cold diazotisation + 2-naphthol coupling for (iii) and (iv).

Q 9.3 **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 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.

SOLUTION

Concept used. The basicity of an amine in water reflects the position of the equilibrium

$$\mathrm{R{-}NH_2 + H_2O \rightleftharpoons R{-}NH_3^+ + OH^-}, \qquad K_b = \frac{[\mathrm{RNH_3^+}][\mathrm{OH^-}]}{[\mathrm{RNH_2}]},$$

with $\mathrm{p}K_b = -\log_{10} K_b$. A *larger* $\mathrm{p}K_b$ means a *weaker* base. Three effects decide K_b:

- **Inductive effect (+I)**: alkyl groups push electron density onto N, raising the availability of its lone pair for protonation ⇒ *more* basic.
- **Resonance/mesomeric effect**: in arylamines the lone pair of N is delocalised into the ring through resonance, making it less available ⇒ *less* basic.
- **Solvation by water**: the conjugate acid $\mathrm{RNH_3^+}$ is stabilised by hydrogen bonding with water. More N–H bonds on the cation ⇒ better H-bond solvation ⇒ more basic.

CH_3NH_2: lone pair free, p$K_b = 3.38$ $C_6H_5NH_2$: lone pair delocalised, p$K_b = 9.38$

Step 1. **(i) pK_b of aniline** (≈ 9.38) **> pK_b of methylamine** (≈ 3.38)**.** In methylamine the methyl group has a $+I$ effect, pushing electron density toward N, so the lone pair on N is more available to bind a proton. In aniline the nitrogen lone pair is conjugated into the benzene ring through resonance (it forms part of the π-system), so it is much less available for protonation. The result: aniline is a

much weaker base than methylamine, and a weaker base has a *larger* pK_b.

Step 2. **(ii) Solubility.** Ethylamine has only two carbon atoms and one $-NH_2$. The amino group hydrogen-bonds vigorously with water (both as donor: N–H$\cdots$O, and as acceptor: N$\cdots$H–O). The hydrophobic alkyl part is small, so ethylamine is freely soluble. In aniline the hydrophobic part is the entire benzene ring; the ring is large, non-polar, and cannot form H-bonds. The size of the hydrophobic part dominates, so aniline is sparingly soluble in water (about $3.5\,g/100\,mL$).

Step 3. **(iii) Methylamine + $FeCl_3$ $\rightarrow$ $Fe(OH)_3$.** Methylamine in water gives OH^-:

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-.$$

These hydroxide ions react with the Fe^{3+} from $FeCl_3$:

$$Fe^{3+} + 3\,OH^- \longrightarrow Fe(OH)_3\downarrow \quad \text{(brown ppt., hydrated ferric oxide)}.$$

The strong basicity of methylamine raises $[OH^-]$ enough to exceed the solubility product of $Fe(OH)_3$, so it precipitates.

Step 4. **(iv) Aniline + HNO_3/H_2SO_4 $\rightarrow$ substantial meta-isomer.** The $-NH_2$ is strongly activating and o/p-directing. But the nitration mixture contains conc. H_2SO_4, which protonates the very basic $-NH_2$ to form the anilinium ion $C_6H_5NH_3^+$. The $-N^+H_3$ group is now *deactivating and m-directing* (it has no lone pair to donate and carries a $+$ charge that withdraws electrons through induction). So a portion of anilinium ion in the mixture gives m-nitroaniline while the unprotonated aniline gives the o/p-products. Overall the product mixture contains a substantial fraction of m-nitroaniline ($\sim 47\%$).

Step 5. **(v) No Friedel–Crafts on aniline.** Friedel–Crafts uses a Lewis acid catalyst, typically $AlCl_3$. The basic lone pair on the nitrogen of aniline forms a complex with the Lewis acid:

$$C_6H_5NH_2 + AlCl_3 \longrightarrow C_6H_5NH_2^+{-}AlCl_3^-.$$

The nitrogen now carries a positive charge, so the $-NH_2$ becomes strongly deactivating (like $-NO_2$) and the ring is no longer nucleophilic enough to react with the carbocation electrophile generated from RX/RCOCl. Hence no Friedel–Crafts product forms.

Step 6. **(vi) Stability of ArN_2^+ vs $R{-}N_2^+$.** Aromatic diazonium ions are stabilised by extensive *resonance* delocalisation: the positive charge on $-N_2^+$ spreads onto the ortho and para carbons of the benzene ring (the same ring can be drawn with charges at C-2, C-4 etc.). Aliphatic diazonium ions cannot delocalise this way, so they lose N_2 almost immediately at room temperature to form an alcohol / alkene / alkyl halide mixture. Aromatic salts can be isolated and stored at 0–5 °C.

Step 7. **(vii) Why Gabriel synthesis is preferred for 1° amines.** Direct ammonolysis ($\mathrm{RX} + \mathrm{NH_3}$) gives a mixture: the 1° amine formed first reacts further with RX to give 2°, 3°, and quaternary ammonium salts, so the yield of pure 1° amine is low. In the **Gabriel phthalimide synthesis**, potassium phthalimide reacts with RX to give an N-alkylphthalimide. This intermediate has *no* free N–H, so further alkylation is impossible. Hydrolysis (or hydrazinolysis) then liberates a pure 1° amine and phthalic acid. The route avoids any over-alkylation.

> **Final Answer:** (i) Resonance delocalises N lone pair into the ring. (ii) Hydrophobic phenyl dominates, no H-bonding. (iii) Methylamine raises $[\mathrm{OH^-}]$, precipitates $\mathrm{Fe(OH)_3}$. (iv) In $\mathrm{H_2SO_4}$, $-\mathrm{NH_2}$ is protonated to $-\mathrm{N^+H_3}$ which is m-directing. (v) Lone pair complexes with $\mathrm{AlCl_3}$, deactivating the ring. (vi) Aryl diazonium ion is resonance-stabilised. (vii) Phthalimide blocks over-alkylation, giving only 1° amine.

♥ Resonance in arylamines vs alkylamines

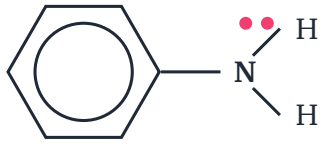
The single biggest reason aromatic chemistry diverges from aliphatic chemistry is the ability of the ring to share electron density. The $-\mathrm{NH_2}$ group is a very different beast on benzene than on a methyl group, and the same is true of $-\mathrm{OH}$, $-\mathrm{OR}$ and $-\mathrm{NHR}$. Recognising that the lone pair gets "pulled into the ring" explains directing effects, basicity, solubility, and diazonium-salt stability all at once.

☞ Account-for questions: name the effect first

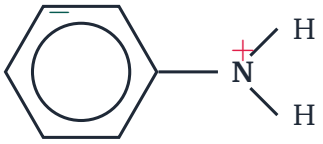
For every "account for" line, write the single *name* of the effect responsible ($+I$, $-I$, $+R$, $-R$, resonance delocalisation, H-bond solvation, K_{sp} argument) in the first sentence. Then elaborate. CBSE markers award the mark for naming the right cause before the explanation.

☞ Phenol acidity vs amine basicity: same idea, opposite sign

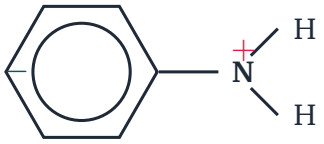
The same resonance that makes aniline a *weaker base* (lone pair delocalised *into* the ring) makes phenol a *stronger acid* (negative charge of $\mathrm{C_6H_5O^-}$ delocalised *into* the ring). Conjugation with the benzene ring helps whichever species is happiest to share charge: aniline gives the lone pair, phenoxide gives the negative charge. Useful for cross-chapter MCQs that compare amine pK_b with phenol pK_a.



Resonance I



Resonance II



Resonance III

N lone pair delocalised into ortho and para ring carbons

EXPERT'S SOLUTION *: Aanya Reddy, M.Sc Physical Chemistry, IIT Madras*

Strategic angle. Seven parts, but only two ideas: how an $-NH_2$ behaves when the lone pair is free vs when it is locked into a π-system or bound to a Lewis acid. Use these ideas in turn.

- **Lone pair free** ($R-NH_2$, R_2NH): strong base, o/p-directing, can react with electrophiles.
- **Lone pair locked** (aniline, anilinium ion, aniline + $AlCl_3$): weak base or deactivating substituent on ring.

Alternative approach: numerical anchor. For (i), put numbers on the comparison: $pK_b(CH_3NH_2) \approx 3.38$ and $pK_b(C_6H_5NH_2) \approx 9.38$. The difference of 6 pK_b units is a factor of $K_b \approx 10^{-6}$: aniline is *a million times* weaker as a base than methylamine in water. That is the size of the resonance-stabilisation effect.

Concept linkage. Parts (iv) and (v) are different faces of the same idea: a basic nitrogen lone pair binding to anything electrophilic (proton in (iv), Lewis acid $AlCl_3$ in (v)) turns $-NH_2$ into a strongly deactivating $-N^+H_3$ / $-N^+H_2-AlCl_3$ group. Once you see this pattern you can predict that aniline will also fail in any other reaction needing a strongly acidic medium: sulphonation gives only sulphanilic acid (Q 9.11(iii)), not the Friedel-Crafts equivalent.

Step 1. (i) Free lone pair in CH_3NH_2 + $+I$ from methyl $\Rightarrow$ strong base ($pK_b \approx 3.38$). Lone pair in aniline locked by resonance into the ring $\Rightarrow$ weak base ($pK_b \approx 9.38$). Hence aniline has the larger pK_b.

Step 2. (ii) Compare hydrophobic/hydrophilic balance. Ethylamine: small C_2H_5 + NH_2; aniline: bulky C_6H_5 + NH_2. Hydrogen-bond gain from the amino group outweighs the hydrophobic cost only when the carbon part is small. Net: ethylamine is fully miscible with water; aniline is only ~ 3.5 g/100 mL.

Step 3. (iii) Methylamine is basic enough to leave free hydroxide in water, which scavenges Fe^{3+}: $Fe^{3+} + 3\,OH^- \longrightarrow Fe(OH)_3\downarrow$. The driving force is the very low K_{sp} of $Fe(OH)_3$ ($\approx 6 \times 10^{-38}$): even a tiny $[OH^-]$ exceeds the solubility threshold and precipitates the hydrated oxide.

Step 4. (iv) In conc. H_2SO_4, almost every $-NH_2$ is protonated to $-N^+H_3$. This positively charged group *withdraws* electrons, deactivating the ring and steering

the nitronium ion NO_2^+ to the meta position. Yield of meta isomer climbs to nearly half.

Step 5. (v) The Friedel–Crafts catalyst $AlCl_3$ is a Lewis acid. The nitrogen lone pair binds to Al, converting $-NH_2$ into a positively charged, strongly deactivating substituent. The ring can no longer attack the acylium / carbocation electrophile, so no Friedel–Crafts product is obtained.

Step 6. (vi) Resonance structures of $C_6H_5N_2^+$ place the positive charge on N, ortho, para carbons; aliphatic analogues cannot delocalise, so $R-N_2^+$ rapidly loses N_2 (ΔG of the loss is large because N_2 is very stable, with a bond enthalpy near 945 kJ mol^{-1}).

Step 7. (vii) Gabriel: $R-X$ + potassium phthalimide $\rightarrow$ N-alkyl phthalimide via SN_2. The blocked nitrogen cannot react twice. Hydrolysis releases a single 1° amine, so no 2°/3° contamination.

Exam relevance. Part (iv) is a classic CBSE 2-mark question that often catches students unprepared — the answer "protonation in H_2SO_4 converts $-NH_2$ to $-N^+H_3$, a meta-director" is exactly what the marker wants. Part (vi) appears nearly every year in NEET MCQs: "Why are aryl diazonium salts stable but alkyl diazonium salts decompose?" $\Rightarrow$ resonance with the ring.

Why this matters. The same toolkit (resonance, induction, solvation, Lewis-acid binding) accounts for every odd observation about amines. Once you recognise which effect dominates for a given compound, the answer follows in one line, and you can predict the behaviour of compounds you have never seen.

> **Final Answer:** All seven observations follow from the same theme: alkyl groups donate electrons (boosting basicity, o/p-direction); aryl rings, protonation, and Lewis-acid binding all lock the N lone pair, making the amine a weaker base or the ring less reactive.

Q 9.4 **Arrange the following:**

(i) In decreasing order of the pK_b values:

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

(ii) In increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(iii) In increasing order of basic strength:

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

(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$

(iv) In decreasing order of basic strength in gas phase:

$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(v) In increasing order of boiling point:

C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

(vi) In increasing order of solubility in water:

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

SOLUTION

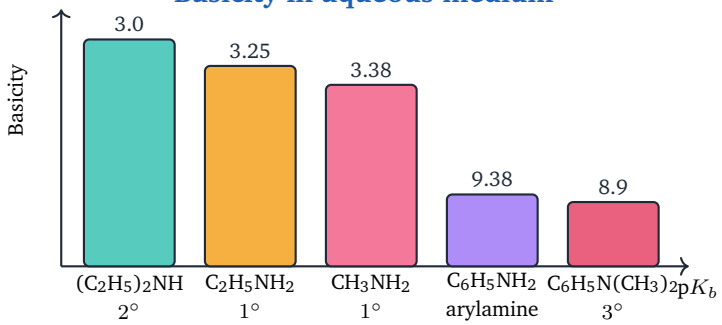
Concept used. Comparing amine basicity in water requires balancing three effects:

- **Inductive (+I) effect of alkyl groups.** More or larger alkyl groups on N push more electron density onto N, raising basicity.
- **Steric crowding around N.** A nitrogen surrounded by bulky groups is harder to approach by a proton or by water: decreases effective basicity.
- **Solvation of the conjugate acid $R_nNH_{(4-n)}^+$ by water.** Each remaining N–H of the cation hydrogen-bonds with water. More N–H bonds ⇒ better solvation ⇒ more stable cation ⇒ equilibrium shifts forward, raising basicity. So the order of H-bonds is 1° (3 N–H) $>$ 2° (2 N–H) $>$ 3° (1 N–H).

The observed aqueous order for methyl-substituted amines is $2^\circ > 1^\circ > 3^\circ > NH_3$ (a non-monotonic order: the $+I$ effect would predict $3^\circ > 2^\circ > 1^\circ$, but steric crowding and weaker solvation pull tertiary amines down). In ethyl amines the order shifts: the ethyl groups are larger, so crowding matters more and the order can become $2^\circ > 3^\circ > 1^\circ$. **In the gas phase**, where there is no solvent, only the $+I$ and steric effects matter, so the order reduces to $3^\circ > 2^\circ > 1^\circ > NH_3$.

For arylamines the lone pair is delocalised into the ring, so they are always weaker bases than alkylamines. Electron-donating substituents on the ring ($-CH_3$) increase basicity; electron-withdrawing substituents ($-NO_2$) decrease it.

Basicity in aqueous medium



Step 1. **(i) Decreasing pK_b = increasing basicity in reverse.** $(C_2H_5)_2NH$ (2° aliphatic) has the smallest pK_b (≈ 3.0). $C_2H_5NH_2$ (1° aliphatic) has the next-smallest pK_b (≈ 3.25). Then come the arylamines: $C_6H_5NHCH_3$ has a methyl that donates electrons, so it is more basic than $C_6H_5NH_2$. Hence $C_6H_5NHCH_3$ has a smaller pK_b than aniline. Decreasing pK_b (weakest to strongest base):

$$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH.$$

Step 2. **(ii) Increasing basic strength.** Aniline is the weakest because its lone pair is delocalised. Adding two methyls on N (giving $C_6H_5N(CH_3)_2$) donates more electrons but the lone pair is still partly tied up in the ring, so it is more basic than aniline but still weaker than any alkylamine. Among alkyls, CH_3NH_2 (1°) is weaker than $(C_2H_5)_2NH$ (2°) because the second ethyl raises the $+I$ effect. Increasing basic strength:

$$C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH.$$

Step 3. **(iii)(a) Aniline vs p-toluidine vs p-nitroaniline.** $-CH_3$ on the para position donates electrons by $+I$ and $+H$ (hyperconjugation), increasing electron density at N $\Rightarrow$ p-toluidine (i.e. 4-methylaniline) is the *most* basic. $-NO_2$ at the para position withdraws electrons strongly by $-I$ and $-R$, pulling the lone pair away from N $\Rightarrow$ p-nitroaniline is the *least* basic. Aniline lies in the middle.

$$p\text{-nitroaniline} < \text{aniline} < p\text{-toluidine}.$$

Step 4. **(iii)(b)** $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$**.** In $C_6H_5CH_2NH_2$ (benzylamine) the $-NH_2$ is on the CH_2, NOT directly on the ring, so the lone pair is *not* delocalised into the ring. It behaves like an aliphatic amine $\Rightarrow$ most basic of the three. Between $C_6H_5NH_2$ and $C_6H_5NHCH_3$, the methyl on N donates electrons by $+I$, raising basicity $\Rightarrow$ $C_6H_5NHCH_3 > C_6H_5NH_2$.

$$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2.$$

Step 5. **(iv) Gas-phase decreasing basicity.** No solvent, no solvation; only $+I$ and steric effects survive. The $+I$ effect rises monotonically with the number of alkyl groups, so the order is determined purely by alkyl count:

$$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3.$$

This is the "natural" order of basicity, recovered when the complications of aqueous solvation are removed.

Step 6. **(v) Increasing boiling point.** $(CH_3)_2NH$ is 2° and has only one N–H, so weak H-bonding. $C_2H_5NH_2$ is 1° and has two N–H bonds, so stronger H-bonding $\Rightarrow$ higher b.p. C_2H_5OH has an O–H whose H-bond is even stronger (O is more electronegative than N) $\Rightarrow$ highest b.p.

$$(CH_3)_2NH\,(7\,^\circ C) < C_2H_5NH_2\,(17\,^\circ C) < C_2H_5OH\,(78\,^\circ C).$$

Step 7. **(vi) Increasing solubility in water.** Aniline is sparingly soluble (large hydrophobic ring). Among the two alkylamines, the smaller, more polar one solvates better: $C_2H_5NH_2$ (1°, two N–H) hydrogen-bonds with water more vigorously than $(C_2H_5)_2NH$ (2°, larger hydrophobic part, only one N–H).

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

Final Answer: (i) $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$. (ii) $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$. (iii)(a) p-nitroaniline < aniline < p-toluidine; (b) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$. (iv) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$. (v) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$. (vi) $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$.

★ Why gas-phase order differs from aqueous

In the gas phase only $+I$ counts; tertiary amines win because they have the most alkyl groups pushing electrons onto N. In water, solvation by H-bonding becomes important and primary amines partly catch up because their conjugate acid RNH_3^+ has three N–H bonds to donate H-bonds. The compromise lands at $2^\circ > 1^\circ > 3^\circ$ for methyl, and shifts for ethyl.

☞ Two competing orders to memorise

In water (aqueous): for methyl amines, the order is $2^\circ > 1^\circ > 3^\circ > NH_3$; for ethyl amines it shifts to $(C_2H_5)_2NH > C_2H_5NH_2 \approx (C_2H_5)_3N > NH_3$. **In the gas phase:** the monotonic $3^\circ > 2^\circ > 1^\circ > NH_3$ holds. A frequent JEE/NEET trick is to drop the words "in water" silently and expect you to remember the aqueous order.

☞ Comparing arylamines: ring substituents matter

When a ring carries $-NO_2$, $-COOH$ or $-CN$ (all electron-withdrawing), the amine is *less* basic than aniline. When a ring carries $-CH_3$, $-OCH_3$ or $-NH_2$ ($+I/+M$), it is *more* basic. Para substitution gives the strongest effect because resonance is fully aligned with the $-NH_2$ group.

EXPERT'S SOLUTION *: Vivaan Joshi, Ph.D Organic Chemistry, IISc Bangalore*

Picture-first. Think of three knobs:

- Lone-pair availability (resonance, $+I$).
- Cation solvation (number of N–H bonds in $R_nNH_{4-n}^+$).
- Steric crowding around N.

Aqueous data integrate all three; gas-phase data show only the first and third.
Alternative approach: tabulate the three effects. For each amine in the pool, write down (a) the number of $+I$ alkyl groups on N (more = stronger base), (b) the number of N–H bonds in the *cation* (more = better solvation = stronger base in water), and (c) the relative steric bulk (more = weaker base). The *net* basicity is the sum of these three contributions. For methyl amines the three terms compromise at $2^\circ > 1^\circ > 3^\circ$; for ethyls they shift slightly because $+I$ from ethyl is a touch larger and bulk from three ethyls is much greater.

Numerical anchor. The aqueous pK_b values are: $(C_2H_5)_2NH$ 3.00; $C_2H_5NH_2$ 3.25; CH_3NH_2 3.38; $(C_2H_5)_3N$ 3.25; $C_6H_5NHCH_3 \approx 9.30$; $C_6H_5NH_2$ 9.38; $C_6H_5N(CH_3)_2 \approx 8.90$; p-toluidine 9.30; p-nitroaniline ≈ 13.0. Lower pK_b = stronger base.

Concept linkage. The "flip" from aqueous to gas phase illustrates that solvation is not a footnote: it actively reshuffles the order of basicity. The same principle is used in solvation effects on SN_1 vs SN_2 pathways (Chapter 6) and on hydration enthalpies of alkali metal ions (Chapter on s-block).

Step 1. (i) Rank by basicity (descending): $(C_2H_5)_2NH$ (best $+I$ without too much sterics) $\rightarrow C_2H_5NH_2 \rightarrow C_6H_5NHCH_3 \rightarrow C_6H_5NH_2$. Flip for p$K_b$: $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$.

Step 2. (ii) Same logic, reversed direction: aniline weakest, then its N,N-dimethyl cousin, then methylamine (1° alkyl), then diethylamine (2° alkyl). So $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$.

Step 3. (iii)(a) Electron-donating $-CH_3$ pushes density into N; $-NO_2$ drains it through $-I$ and $-R$. So p-nitroaniline is the worst, then aniline, then p-toluidine. (b) Benzylamine is essentially alkylic ($-NH_2$ is one CH_2 away from the ring), so its lone pair is *not* delocalised. N-methylaniline beats aniline because of the $+I$ from the N-methyl group.

Step 4. (iv) Without water, only the $+I$/sterics balance applies; more ethyls = more $+I$ on a flat scale. $(C_2H_5)_3N$ wins decisively. Order: $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$.

Step 5. (v) Boiling points scale with H-bond strength: O–H (~ 21 kJ/mol per H-bond) > N–H on a 1° amine (~ 13 kJ/mol, two donor bonds per molecule) > N–H on a 2° amine (one donor bond) > no N–H at all. $(CH_3)_2NH$ (7 °C) < $C_2H_5NH_2$ (17 °C) < C_2H_5OH (78 °C).

Step 6. (vi) Aqueous solubility scales with the ratio of hydrophilic to hydrophobic surface area. Ethylamine wins (small C_2H_5 + two N–H donors); diethylamine middle (two ethyls, one N–H); aniline loses (large C_6H_5 ring, two N–H but blocked lone pair, ring is hydrophobic). $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$.

Exam relevance. The aqueous-vs-gas-phase contrast is a favourite JEE Mains MCQ: "Which is the strongest base in gas phase?" $\Rightarrow$ tertiary, always. "Which is the strongest base in aqueous solution?" $\Rightarrow$ secondary (for methyl), with the order $2° > 1° > 3° > NH_3$. Skipping the words "in water" is a classic trap. Part (iii)(b) is a regular CBSE board question — the trap is treating $C_6H_5CH_2NH_2$ as an arylamine.

Why this matters. The aqueous vs gas-phase mismatch shows why "intrinsic" chemical properties of molecules can differ from their behaviour in solution. The same idea is the basis for the Hammett analysis of organic reactivity at higher level, and explains why textbook "trends" must always be tagged with the medium.

Final Answer: Orders as in the main solution.

Q 9.5 **How will you convert:**
(i) Ethanoic acid into methanamine (ii) Hexanenitrile into 1-aminopentane
(iii) Methanol to 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?

SOLUTION

Concept used. Three key chain-length operations recur in amine syntheses:

- **Hofmann bromamide rearrangement**: an amide is degraded by $Br_2/NaOH$ to give a primary amine with *one carbon less*:

$$R{-}CONH_2 + Br_2 + 4\,NaOH \longrightarrow R{-}NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O.$$

- Nitrile reduction (Mendius / $LiAlH_4$ / catalytic H_2):

$$R{-}C{\equiv}N + 2\,H_2 \xrightarrow{\text{Ni or } LiAlH_4} R{-}CH_2{-}NH_2.$$

  This *adds one carbon* compared to the starting alkyl halide (because RX → RCN adds the C of CN^-).

- Carbylamine elimination and chain shortening of acids: a carboxylic acid is converted to its amide (with NH_3 / Δ), then Hofmann-degraded to the next lower amine; or an acid is converted to its potassium salt and treated with NaOH/CaO (**decarboxylation**, soda-lime) to lose one carbon as CO_2.

Hofmann bromamide ladder (chain shortens by 1)

Step 1. **(i) Ethanoic acid → methanamine.** Ethanoic acid has 2 C; methanamine has 1 C ⇒ chain shortens by one. Use Hofmann bromamide.

$$CH_3COOH \xrightarrow{NH_3,\,\Delta} CH_3CONH_2 \xrightarrow{Br_2,\,NaOH} CH_3NH_2.$$

Step 2. **(ii) Hexanenitrile → 1-aminopentane.** Hexanenitrile is $CH_3(CH_2)_4{-}CN$ (5 C in the chain + 1 C of CN = 6 C in total). 1-aminopentane = $CH_3(CH_2)_4{-}NH_2$ has only 5 C, so the route must *lose* the cyanide carbon. Hydrolyse the nitrile to the amide, then Hofmann-degrade:

$$CH_3(CH_2)_4{-}CN \xrightarrow{H_2O/H^+} CH_3(CH_2)_4{-}CONH_2 \xrightarrow{Br_2,\,NaOH} CH_3(CH_2)_4{-}NH_2.$$

$CH_3(CH_2)_4{-}NH_2$ is 1-aminopentane (pentan-1-amine).

Step 3. **(iii) Methanol $\rightarrow$ ethanoic acid.** Methanol has 1 C; ethanoic acid has 2 C. Need to *add* one C. First convert methanol to methyl iodide, then SN_2 with cyanide, then hydrolyse:

1. $CH_3OH \rightarrow CH_3I$ (PI_3 or HI)
2. $CH_3I \rightarrow CH_3CN$ (KCN)
3. $CH_3CN \rightarrow CH_3COOH$ (H_2O, H^+).

Step 4. **(iv) Ethanamine $\rightarrow$ methanamine.** Both are 1° amines; we need to lose one C. Convert ethanamine to ethanenitrile is not possible directly; instead, oxidise ethanamine carefully to ethanoic acid (or hydrolyse via diazonium on the alkyl version): nitrous acid converts ethanamine to ethanol, which is oxidised to ethanoic acid; then proceed as in (i):

1. $C_2H_5NH_2 \rightarrow C_2H_5OH$ (using HNO_2)
2. $C_2H_5OH \rightarrow CH_3COOH$ (using $K_2Cr_2O_7/H_2SO_4$)
3. $CH_3COOH \rightarrow CH_3CONH_2$ (using NH_3, Δ)
4. $CH_3CONH_2 \rightarrow CH_3NH_2$ (using Br_2, NaOH: Hofmann).

Step 5. **(v) Ethanoic acid $\rightarrow$ propanoic acid.** Need to add one C. Reduce to ethanol, convert to ethyl bromide, substitute with cyanide, hydrolyse:

1. $CH_3COOH \rightarrow CH_3CH_2OH$ ($LiAlH_4$)
2. $CH_3CH_2OH \rightarrow CH_3CH_2Br$ (PBr_3)
3. $CH_3CH_2Br \rightarrow CH_3CH_2CN$ (KCN)
4. $CH_3CH_2CN \rightarrow CH_3CH_2COOH$ (H_2O/H^+).

Step 6. **(vi) Methanamine $\rightarrow$ ethanamine.** Need to add one C to the amine chain. Convert to methanol via nitrous acid, then as in (iii) and (v):

1. $CH_3NH_2 \rightarrow CH_3OH$ (HNO_2)
2. $CH_3OH \rightarrow CH_3I$ (HI)
3. $CH_3I \rightarrow CH_3CN$ (KCN)
4. $CH_3CN \rightarrow CH_3CH_2NH_2$ ($LiAlH_4$).

(Direct alkylation of methylamine with CH_3I would also *form* ethyl-substituted amines, but C_2H_5 on N means the C is on N not in the chain, so that route does not give ethanamine. Hence the longer sequence above.)

Step 7. **(vii) Nitromethane $\rightarrow$ dimethylamine.** Reduce nitromethane to methanamine first, then alkylate:

$$CH_3NO_2 \xrightarrow{Sn/HCl} CH_3NH_2 \xrightarrow{CH_3I,\,\Delta} (CH_3)_2NH.$$

Step 8. **(viii) Propanoic acid $\rightarrow$ ethanoic acid.** Need to lose one C. Use Hofmann route via the amide, then re-oxidise the resulting amine back to the acid:

1. $C_2H_5COOH \rightarrow C_2H_5CONH_2$ (NH_3, Δ)
2. $C_2H_5CONH_2 \rightarrow C_2H_5NH_2$ (Br_2, NaOH: Hofmann removes the $-CONH_2$ carbon)
3. $C_2H_5NH_2 \rightarrow C_2H_5OH$ (HNO_2, 273 K)
4. $C_2H_5OH \rightarrow CH_3COOH$ ($K_2Cr_2O_7/H_2SO_4$).

Carbon balance: propanoic acid (3 C) $\rightarrow$ propanamide (3 C) $\rightarrow$ ethanamine (2 C, Hofmann drops the carbonyl C) $\rightarrow$ ethanol (2 C) $\rightarrow$ ethanoic acid (2 C). Net change: -1 C as required.

Final Answer: Use Hofmann bromamide whenever chain shortens by one carbon, and a cyanide $\rightarrow$ nitrile hydrolysis whenever chain lengthens by one carbon.

☞ Carbon-count first

Before drawing any arrow, count carbons. If product has fewer C than reactant, plan around Hofmann (amide $\rightarrow$ amine) or decarboxylation. If product has more C than reactant, plan around a KCN / NaCN step or a Wurtz / Grignard chain extension.

✗ Direct alkylation of amines is messy

Students often write $CH_3NH_2 + CH_3I \longrightarrow (CH_3)_2NH$ in one clean step, but the actual reaction gives a mixture of 1°, 2°, 3° and quaternary salts because each new N–H is itself nucleophilic. To make a specific class of amine, use Gabriel (clean 1°), Hofmann (clean 1°, one C less), or stoichiometry control with excess of the lower amine plus low $R-X$.

♥ The Hofmann ladder and the cyanide ladder

Two "ladders" run through almost every multi-step synthesis in this chapter. The *Hofmann ladder* (acid $\rightarrow$ amide $\rightarrow$ amine, chain shortens by 1 each rung) walks you down. The *cyanide ladder* (alcohol $\rightarrow$ halide $\rightarrow$ nitrile $\rightarrow$ amine or acid, chain lengthens by 1 each rung) walks you up. Together they connect any C_n-amine to any other C_m-amine via a single starting alcohol or acid, no matter how large $|n-m|$ is.

EXPERT'S SOLUTION *: Rohit Verma, M.Sc Chemistry, IIT Kanpur*

Strategic angle. Eight conversions but only three motifs:

- **Add 1 C:** $R-X \xrightarrow{KCN} R-CN \xrightarrow{H_2O/H^+} R-COOH$ (carboxylic acid) or $R-CN \xrightarrow{LiAlH_4} R-CH_2NH_2$ (amine).
- **Subtract 1 C:** $R-CONH_2 \xrightarrow{Br_2/NaOH} R-NH_2$ (Hofmann).
- **Convert functional group at the same carbon count:** nitro $\rightarrow$ amine (Sn/HCl),

alcohol → acid ($K_2Cr_2O_7/H_2SO_4$), amine → alcohol (HNO_2, aliphatic), alcohol → halide (HX or PX_3).

Alternative approach: write the carbon-count arrow first. Before any reagent, set up the carbon balance: e.g. (i) is 2 C → 1 C (subtract one, so Hofmann); (iii) is 1 C → 2 C (add one, so cyanide); (v) is 2 C → 3 C (add one, cyanide); (viii) is 3 C → 2 C (subtract one, Hofmann). Once the carbon-count arrow is drawn, the choice of route is automatic.

Concept linkage. Every step in this question is a named reaction we will meet again: Hofmann bromamide (Q 9.7(iii), 9.10), nitrile hydrolysis (Q 9.9), HNO_2 deamination (Q 9.13), and nitro reduction (Q 9.8(i), Q 9.9(iv), 9.9(vi)). Treat this question as revision for the entire chapter's mechanistic toolkit.

Step 1. (i) Acid → amine, 1 C less: Hofmann via amide ($CH_3COOH \rightarrow CH_3CONH_2 \rightarrow CH_3NH_2$).

Step 2. (ii) Hexanenitrile (6 C) → 1-aminopentane (5 C): hydrolyse the nitrile to hexanamide, then Hofmann to lose the carbonyl C. Equivalent: nitrile → acid → amide → amine.

Step 3. (iii) Methanol → ethanoic acid: classic add-1-C ladder $CH_3OH \longrightarrow CH_3I \longrightarrow CH_3CN \longrightarrow CH_3COOH$, with HI or PI_3, KCN, then H_2O/H^+.

Step 4. (iv) Ethanamine → methanamine: deaminate to ethanol, oxidise to ethanoic acid, then Hofmann as in (i). Four-step sequence.

Step 5. (v) Ethanoic acid → propanoic acid: reduce ($LiAlH_4$) to ethanol, convert to ethyl bromide (PBr_3), cyanide substitution, hydrolyse to acid. Four steps; net +1 C.

Step 6. (vi) Methanamine → ethanamine: deaminate to methanol, HI to methyl iodide, KCN to methyl cyanide, $LiAlH_4$ reduction to ethanamine. Avoids alkylation side-products.

Step 7. (vii) Nitromethane → dimethylamine: Sn/HCl reduction gives methanamine; carefully controlled methyl iodide alkylates to give dimethylamine (limit CH_3I to avoid tri-methylation and quaternary salt).

Step 8. (viii) Propanoic acid → ethanoic acid: amide → ethylamine (Hofmann) → ethanol (HNO_2) → ethanoic acid (oxidation). One full step down the Hofmann ladder followed by a deamination + oxidation pair.

Exam relevance. JEE/NEET multi-step synthesis questions almost always pivot on (a) the Hofmann ladder going down or (b) the cyanide ladder going up. CBSE board favorites are (i) acid → amine, (vi) methanamine → ethanamine, and (vii) nitromethane → dimethylamine. The trap in (vi) is to write $CH_3NH_2 + CH_3I \longrightarrow C_2H_5NH_2$ in one step, which is wrong: that route gives *N*-methylmethanamine ($(CH_3)_2NH$), not ethanamine, because the new C goes on N not

on the chain.

Why this matters. The Hofmann ladder is the standard way to walk down the amine homologous series by one carbon at a time, while $\mathrm{R{-}X} + \mathrm{KCN}$ is the standard way to walk up. Together they make every C_n-amine reachable from a single starting acid.

Final Answer: Same routes as the main solution.

Q 9.6 Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.

SOLUTION

Concept used. The standard laboratory method is **Hinsberg's test**, which uses **benzenesulphonyl chloride** ($\mathrm{C_6H_5SO_2Cl}$, also called Hinsberg's reagent). The reagent reacts only with N–H bonds, and the solubility of the resulting sulphonamide in alkali separates the three amine classes cleanly.

- **Primary amine + Hinsberg's reagent.** The two N–H bonds allow loss of one HCl and formation of a sulphonamide $\mathrm{R{-}NH{-}SO_2C_6H_5}$. The N–H *still left* on the sulphonamide is acidic (because of the electron-withdrawing sulphonyl) and is removed by KOH/NaOH to give a salt that is **soluble in alkali**.
- **Secondary amine + Hinsberg's reagent.** Only one N–H is available; after substitution, the sulphonamide $\mathrm{R_2N{-}SO_2C_6H_5}$ has *no* N–H. Hence it does not dissolve in alkali $\Rightarrow$ a solid **insoluble in alkali**.
- **Tertiary amine + Hinsberg's reagent.** No N–H to lose $\Rightarrow$ **no reaction**. The amine forms a separate layer; on acidifying, the tertiary amine dissolves in dilute HCl as $\mathrm{R_3NH^+Cl^-}$.

Hinsberg's test ($\mathrm{C_6H_5SO_2Cl + KOH}$)

1° amine	2° amine	3° amine
Reacts. Soluble in KOH (clear soln.)	Reacts. Insoluble in KOH (solid stays)	No reaction. Separate layer; dissolves in HCl

Step 1. **Step 1: Mix.** Add a few drops of Hinsberg's reagent ($\mathrm{C_6H_5SO_2Cl}$) to the unknown amine, then add aqueous KOH (excess) and shake.

Step 2. **Step 2: Reaction with 1° amine.** The amine substitutes on the sulphur, losing HCl:

$$\mathrm{R{-}NH_2 + C_6H_5SO_2Cl \longrightarrow R{-}NH{-}SO_2C_6H_5 + HCl.}$$

The N–H of the sulphonamide is acidic. KOH deprotonates it:

$$\mathrm{R{-}NH{-}SO_2C_6H_5 + KOH \longrightarrow R{-}N(K){-}SO_2C_6H_5 + H_2O.}$$

The potassium salt is ionic and dissolves $\Rightarrow$ *clear solution*.

Step 3. **Step 3: Reaction with 2° amine.**

$$\mathrm{R_2NH + C_6H_5SO_2Cl \longrightarrow R_2N{-}SO_2C_6H_5 + HCl.}$$

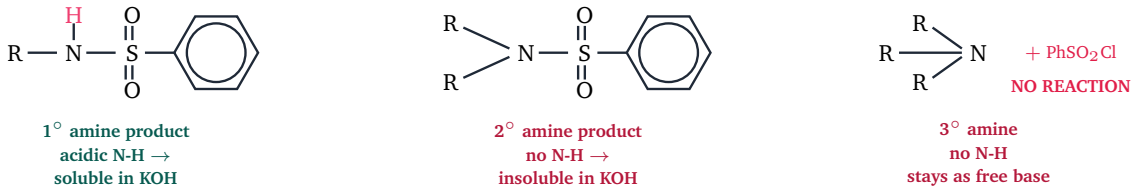
The sulphonamide has *no* N–H, so KOH cannot deprotonate it. It stays as an undissolved solid $\Rightarrow$ *insoluble in alkali*.

Step 4. **Step 4: Reaction with 3° amine.** No N–H, so no reaction with the sulphonyl chloride. On acidifying with dilute HCl,

$$\mathrm{R_3N + HCl \longrightarrow R_3N^+HCl^-} \quad \text{(dissolves)},$$

and the tertiary amine goes into the aqueous layer.

Step 5. **Step 5: Recover the pure amine.** The 1° amine salt in alkali, on acidifying with HCl, releases the sulphonamide solid; further hydrolysis with concentrated HCl regenerates the original 1° amine. The 2° sulphonamide is filtered off and similarly hydrolysed to give back the 2° amine.



Final Answer: Hinsberg's test: 1° → soluble in KOH; 2° → insoluble in KOH; 3° → no reaction with the reagent but dissolves in dilute HCl.

★ Why the 1° sulphonamide is acidic

The sulphonyl group $-\mathrm{SO_2}^-$ is strongly electron-withdrawing by $-I$ and $-R$. It pulls electron density from the N–H, weakening that bond and lowering its pK_a to about 10. KOH (a strong base) then removes the proton easily. By contrast, the N–H of a free amine has pK_a near 35 and KOH cannot touch it.

✗ A 3° amine never reacts with $\mathrm{C_6H_5SO_2Cl}$

A common error in answer scripts: "the 3° amine reacts and gives a sulphonamide which dissolves in HCl". *Wrong.* A 3° amine has *no* N–H, so it cannot form the S–N bond. It stays as a free base in the tube. The dissolution in dilute HCl happens with the unreacted 3°

amine itself ($R_3N + HCl \longrightarrow R_3NH^+Cl^-$), not with any product of Hinsberg's reagent. Wording matters in CBSE markers' rubrics.

☞ Hinsberg test in one tabular line

1° amine $+C_6H_5SO_2Cl + KOH \rightarrow$ clear solution (soluble sulphonamide). 2° amine $\rightarrow$ solid (insoluble in KOH). 3° amine $\rightarrow$ no reaction (free amine layer, soluble in dilute HCl).

EXPERT'S SOLUTION *: Aditi Kapoor, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. Hinsberg's test is a clever decision tree that depends on one feature: how many N–H bonds survive after the amine substitutes once on S. Three N–H $\rightarrow$ 2 left (acidic); two N–H $\rightarrow$ 1 left (acidic); one N–H $\rightarrow$ 0 left (neutral); zero N–H $\rightarrow$ no substitution at all.

Alternative approach: the "count N–H, then check acidity" recipe. Step 1, count the N–H on the amine. Step 2, do the substitution: one N–H is replaced by $-SO_2C_6H_5$, the rest stay. Step 3, check whether the remaining N–H is acidic enough for KOH (the sulphonyl is so electron-withdrawing that any remaining N–H drops to p$K_a \approx 10$). The class then reveals itself: 1° has 1 N–H after $\Rightarrow$ acidic, soluble; 2° has 0 N–H after $\Rightarrow$ neutral, insoluble; 3° never reacted $\Rightarrow$ free base.

Concept linkage. The same "how many N–H bonds" question also controls (a) carbylamine (needs 2 N–H), (b) Hofmann mustard-oil test (needs 2 N–H), (c) acylation (needs at least 1 N–H), and (d) boiling-point comparisons (Q 9.14(ii), donors per molecule). Hinsberg is the cleanest example of the family because it gives *three* distinguishable outcomes from *one* reagent.

Step 1. Primary amine has 2 N–H. After substitution, 1 acidic N–H remains. KOH abstracts it (p$K_a \approx 10$). The potassium salt is ionic and dissolves $\Rightarrow$ clear solution.

Step 2. Secondary amine has 1 N–H. After substitution, 0 N–H remain. KOH has nothing to abstract. The solid sits there.

Step 3. Tertiary amine has 0 N–H. Substitution does not happen. The amine separates as a free base layer; on acidifying with HCl, it dissolves as the ammonium salt.

A back-up test: **nitrous acid test**. 1° aliphatic amines give N_2 burst + alcohol; 1° aromatic amines give a stable diazonium salt at 0–5 °C; 2° amines give a yellow oil (N-nitrosamine); 3° aliphatic amines give a soluble salt; 3° aromatic amines (e.g. N, N-dimethylaniline) give a green/yellow p-nitroso compound.

Exam relevance. CBSE board exams ask either "identify the classes by Hinsberg" or "why does the 2° sulphonamide not dissolve". The complete answer needs both equations and the solubility statement. NEET sometimes asks the reverse: "Which amine will dissolve on adding $C_6H_5SO_2Cl/KOH$?" $\Rightarrow$ primary.

Why this matters. A practical-exam question may ask you to identify an unknown

amine from its physical and chemical behaviour. The Hinsberg + nitrous acid sequence cracks every case in two test tubes.

Final Answer: Hinsberg's test, with confirming nitrous acid test if needed.

Q 9.7 **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.

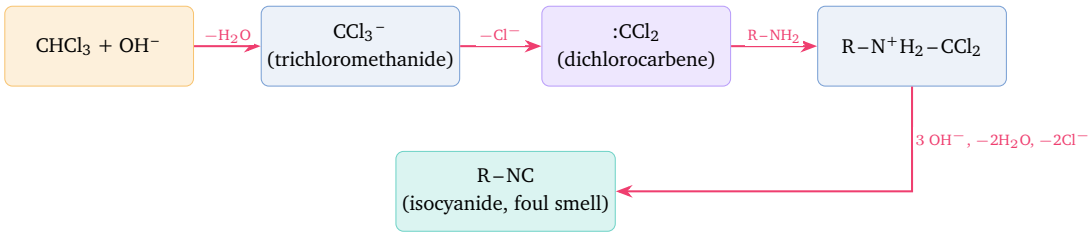
SOLUTION

Concept used. Each named reaction has a single signature step plus a defining set of reagents.

Step 1. **(i) Carbylamine reaction.** *Test for 1° amines.* A 1° amine (aliphatic or aromatic) on heating with chloroform and alcoholic KOH gives an isocyanide (carbylamine) with a foul, penetrating smell. 2° and 3° amines do not react.

$$\mathrm{R{-}NH_2 + CHCl_3 + 3\,KOH \xrightarrow{\Delta} R{-}NC + 3\,KCl + 3\,H_2O.}$$

Mechanism summary: KOH dehydrohalogenates $\mathrm{CHCl_3}$ to give **dichlorocarbene** ($\mathrm{CCl_2}$ with a lone pair); the amine attacks the carbene, loses HCl twice to give the isocyanide.



Step 2. **(ii) Diazotisation.** The conversion of a 1° aromatic amine into an arenediazonium salt with cold $\mathrm{NaNO_2/HCl}$ (the mixture supplies nitrous acid *in situ*, since $\mathrm{HNO_2}$ is too unstable to store):

$$\mathrm{ArNH_2 + HNO_2 + HCl \xrightarrow{273\text{–}278\,K} Ar{-}N{\equiv}N^+\,Cl^- + 2\,H_2O.}$$

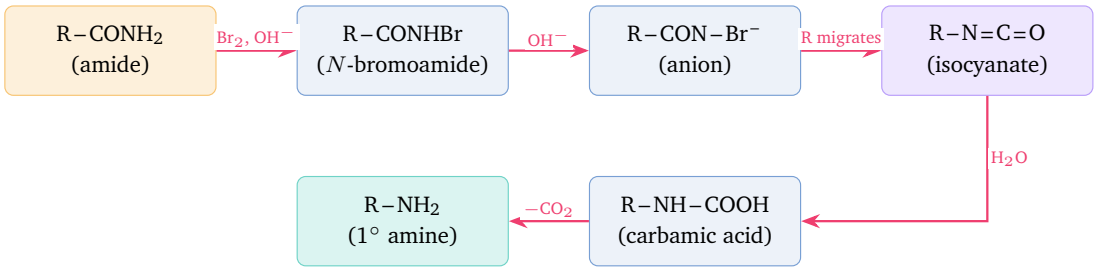
Aliphatic primary amines undergo the same first step but the resulting diazonium ion is unstable and at once loses $\mathrm{N_2}$, giving an alcohol. Aryl diazonium salts can be isolated and stored cold (resonance-stabilised).

Step 3. **(iii) Hofmann's bromamide reaction.** An amide is degraded with bromine

and alkali to give a 1° amine with *one carbon less* than the starting amide:

$$\mathrm{R{-}CONH_2 + Br_2 + 4\,NaOH \xrightarrow{\Delta} R{-}NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O.}$$

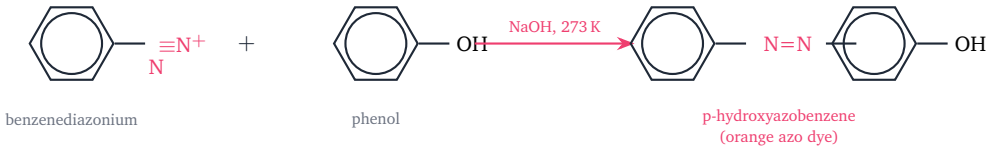
The mechanism proceeds through an N-bromoamide $\mathrm{R{-}CONHBr}$, loss of HBr to a nitrene-like intermediate, migration of R from C to N (giving an isocyanate $\mathrm{R{-}N{=}C{=}O}$), and finally hydrolysis of the isocyanate to the amine and $\mathrm{CO_2}$.



Step 4. **(iv) Coupling reaction.** An aryl diazonium salt reacts with an electron-rich aromatic compound (phenol, naphthol, aniline) to give an azo compound containing the $-\mathrm{N{=}N^-}$ bridge. The azo compound is intensely coloured (orange, red or yellow) because $-\mathrm{N{=}N^-}$ extends the π-conjugation.

$$\mathrm{C_6H_5N_2^+Cl^- + C_6H_5OH \xrightarrow{NaOH/cold} HO{-}C_6H_4{-}N{=}N{-}C_6H_5 + HCl.}$$

The reaction is electrophilic aromatic substitution: $\mathrm{ArN_2^+}$ is a weak electrophile and attacks only highly activated rings (phenol, naphthol, N,N-dimethylaniline).



Step 5. **(v) Ammonolysis (of alkyl halides).** Direct heating of an alkyl halide with alcoholic ammonia under pressure gives a primary amine:

$$\mathrm{R{-}X + NH_3 \longrightarrow R{-}NH_2 + HX.}$$

Drawback: the 1° amine formed is itself nucleophilic and competes with $\mathrm{NH_3}$ for the next $\mathrm{R{-}X}$, giving 2°, 3° and quaternary ammonium salts (a mixture). A large excess of $\mathrm{NH_3}$ biases the product toward 1°.

Step 6. **(vi) Acetylation.** 1° and 2° amines react with acetic anhydride (or acetyl chloride) in pyridine to give an N-acetyl derivative (an amide):

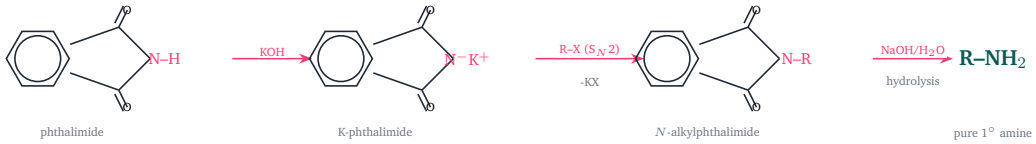
$$\mathrm{R{-}NH_2 + (CH_3CO)_2O \longrightarrow R{-}NHCOCH_3 + CH_3COOH.}$$

The amide is less reactive than the parent amine (the lone pair is delocalised onto the carbonyl), which is why acetylation is used as a *protecting group* for $-\mathrm{NH_2}$ during electrophilic aromatic substitution (e.g. bromination of aniline must protect $-\mathrm{NH_2}$ first or all three positions get brominated).

Step 7. **(vii) Gabriel phthalimide synthesis.** A clean method for pure 1° amines, free of 2°/3° contamination. The steps:

- Treat phthalimide with KOH to form potassium phthalimide (the N–H is acidic, p$K_a \approx 8$, because of the two flanking $-\mathrm{CO}-$ groups).
- React with $\mathrm{R}-\mathrm{X}$: an SN_2 substitution gives an N-alkylphthalimide. The new C–N bond has no N–H left, so further alkylation cannot occur.
- Hydrolyse with aqueous NaOH (or with hydrazine, the Ing–Manske variant) to release the pure 1° amine and phthalic acid (or phthalhydrazide).

Important caveat: aryl primary amines cannot be made this way because aryl halides do not undergo SN_2 substitution with the soft phthalimide nucleophile.



Final Answer: All seven name reactions concisely covered above with reagents, products, and a one-line mechanism.

☞ Memorising the reagents

Carbylamine → $CHCl_3$ + alc. KOH. Diazotisation → cold $NaNO_2/HCl$, 0–5 °C. Hofmann → $Br_2/NaOH$. Coupling → ArN_2^+ + phenol/naphthol, mildly alkaline. Acetylation → $(CH_3CO)_2O$ (in pyridine).

☞ Carbon-count change for each reaction

Carbylamine: same C count (replaces $-NH_2$ by $-NC$). Diazotisation: same C count ($-NH_2 \to -N_2^+$). Hofmann bromamide: *lose 1 C* (carbonyl C of amide is lost as CO_3^{2-}). Coupling: *gain a whole aryl* ring. Ammonolysis: *gain N* (replaces $-X$ by $-NH_2$). Acetylation: *gain* CH_3CO^-. Gabriel: *net add 1 C* per $\mathrm{R}-\mathrm{X}$ unit installed.

♥ Seven reactions, three jobs

This question gathers reactions that do three different jobs: (a) *tests* for amine class (carbylamine), (b) *preparations* of amines (Hofmann, ammonolysis, Gabriel), (c) *transformations* of amines into other useful groups (diazotisation → aryl halides / phenols, coupling → dyes, acetylation → protected amines). Once you label each one by its job, multi-step syntheses (Q 9.5, 9.8, 9.9) read off in seconds.

EXPERT'S SOLUTION *: Siddharth Pillai, M.Sc Chemistry, IIT Kanpur*

Quick reading. For an exam answer, organise the seven reactions by purpose:

- **Tests:** carbylamine (1° amine), Hinsberg (class).
- **Preparations:** Hofmann bromamide (1° amine, -1 C), Gabriel (1° alkyl amine, clean), ammonolysis (1° amine, with side-products).
- **Functional-group conversions:** diazotisation (gateway to many aryl halides, phenols, nitriles); coupling (azo dyes); acetylation (protection of $-NH_2$).

Alternative approach: associate each reaction with its "signature reagent". Carbylamine $\Leftrightarrow$ $CHCl_3$/alc. KOH. Diazotisation $\Leftrightarrow$ $NaNO_2/HCl$, 273 K. Hofmann $\Leftrightarrow$ $Br_2/NaOH$ on an amide. Coupling $\Leftrightarrow$ ArN_2^+ on phenol/naphthol/aniline in mild alkali. Ammonolysis $\Leftrightarrow$ alcoholic NH_3, pressure. Acetylation $\Leftrightarrow$ $(CH_3CO)_2O$ in pyridine. Gabriel $\Leftrightarrow$ K-phthalimide $+$ R$-$X, then aqueous NaOH. Reading a reagent on an exam paper $\Rightarrow$ instant recall of the reaction name.

Concept linkage. Carbylamine and Hinsberg both probe N–H bonds (the same idea as in Q 9.6). Hofmann and Gabriel both walk between amides/imides and 1° amines (Q 9.5, 9.8). Diazotisation and coupling form the diazonium-salt switchboard (Q 9.8, 9.11). Ammonolysis is the cheap industrial route used when product purity is not critical; Gabriel is the laboratory route for clean 1° amines.

Step 1. Carbylamine confirms 1°; foul smell of R$-$NC is diagnostic.

Step 2. Diazotisation produces ArN_2^+, useful for further substitution (Sandmeyer with CuCl/CuBr/CuCN, Gattermann with Cu/HX, H_3PO_2 reduction, H_2O hydrolysis to phenol, coupling).

Step 3. Hofmann gives a 1-C-shorter primary amine cleanly via the nitrene-like rearrangement of an N-bromoamide to an isocyanate.

Step 4. Coupling extends the diazonium into intensely coloured azo dyes used in textile, food, and pH-indicator industries (e.g. methyl orange).

Step 5. Ammonolysis is the simplest route to amines but is messy: the primary amine itself attacks more R$-$X, producing 2°, 3° and quaternary salts.

Step 6. Acetylation protects $-NH_2$ when the ring is to be attacked by strong electrophiles (used in Q 9.8(vii) to make p-bromoaniline cleanly).

Step 7. Gabriel is the cleanest laboratory route to 1° alkyl amines; aryl amines are not accessible because Ar$-$X cannot undergo SN_2 (Q 9.12).

Exam relevance. CBSE board pattern: 7–mark question gives five name reactions; the answer must include reagent, equation, and a one-line statement of the product type. NEET MCQ: "Reagent for carbylamine?" $\Rightarrow$ $CHCl_3$/alc. KOH. JEE Mains MCQ: "What is the gateway intermediate to aryl halides?" $\Rightarrow$ ArN_2^+.

Why this matters. Once you can map each reaction to its purpose, multi-step syntheses (Q 9.5, 9.8, 9.9) become much easier: you simply read off the right transform from the

toolbox.

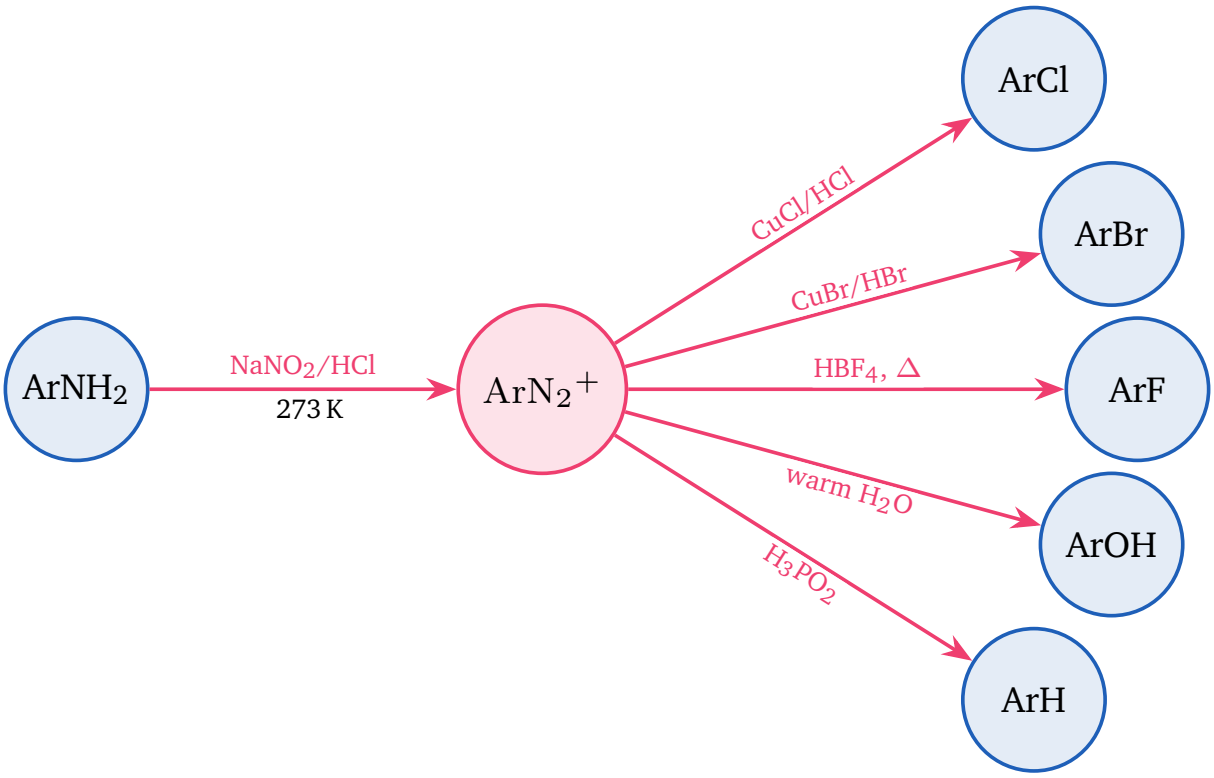
> **Final Answer:** Carbylamine, diazotisation, Hofmann bromamide, coupling, ammonolysis, acetylation and Gabriel synthesis: covered above with reagents and equations.

Q 9.8 **Accomplish the following conversions:**
(i) Nitrobenzene to benzoic acid (ii) Benzene to m-bromophenol
(iii) Benzoic acid to aniline (iv) Aniline to 2,4,6-tribromofluorobenzene
(v) Benzyl chloride to 2-phenylethanamine (vi) Chlorobenzene to p-chloroaniline
(vii) Aniline to p-bromoaniline (viii) Benzamide to toluene
(ix) Aniline to benzyl alcohol.

SOLUTION

Concept used. Three big handles run through all nine routes:

- **Diazonium chemistry**: ArN_2^+ is converted to $ArCl$ (CuCl/HCl, Sandmeyer), $ArBr$ (CuBr/HBr), ArF (HBF_4, then heat $-$ Balz–Schiemann), $ArOH$ (warm water), $ArCN$ (CuCN, Sandmeyer), or $Ar-H$ (H_3PO_2, reduction).
- **$-NH_2$ protection (acetylation)** before electrophilic aromatic substitution. The bare $-NH_2$ is too activating and gives 2,4,6-trisubstitution. Acetylation masks it as $-NHCOCH_3$, a moderate o/p-director.
- Hofmann (amide $\rightarrow$ amine, -1 C) and Clemmensen / Wolff reductions ($C{=}O \rightarrow CH_2$) for chain editing.



Step 1. **(i) Nitrobenzene → benzoic acid.** Reduce to aniline, diazotise, replace by $-\mathrm{CN}$ (Sandmeyer), then hydrolyse the nitrile:

1. $\mathrm{C_6H_5NO_2} \rightarrow \mathrm{C_6H_5NH_2}$ (Sn/HCl)
2. $\mathrm{C_6H_5NH_2} \rightarrow \mathrm{C_6H_5N_2^+Cl^-}$ ($\mathrm{NaNO_2}$, HCl, 273 K)
3. $\mathrm{C_6H_5N_2^+Cl^-} \rightarrow \mathrm{C_6H_5CN}$ (CuCN, Sandmeyer)
4. $\mathrm{C_6H_5CN} \rightarrow \mathrm{C_6H_5COOH}$ ($\mathrm{H_2O}$, $\mathrm{H^+}$).

Step 2. **(ii) Benzene → m-bromophenol.** The $-\mathrm{Br}$ and $-\mathrm{OH}$ are meta to each other. Use diazonium: start with benzene, nitrate to nitrobenzene, brominate (the $-\mathrm{NO_2}$ is m-directing) to get m-bromonitrobenzene, reduce to m-bromoaniline, diazotise, hydrolyse to phenol:

1. $\mathrm{C_6H_6} \rightarrow \mathrm{C_6H_5NO_2}$ ($\mathrm{HNO_3/H_2SO_4}$)
2. $\mathrm{C_6H_5NO_2} \rightarrow \mathrm{m\text{-}BrC_6H_4NO_2}$ ($\mathrm{Br_2/FeBr_3}$)
3. $\mathrm{m\text{-}BrC_6H_4NO_2} \rightarrow \mathrm{m\text{-}BrC_6H_4NH_2}$ (Sn/HCl)
4. $\mathrm{m\text{-}BrC_6H_4NH_2} \rightarrow \mathrm{m\text{-}BrC_6H_4N_2^+Cl^-}$ ($\mathrm{NaNO_2}$, HCl, 273 K)
5. $\mathrm{m\text{-}BrC_6H_4N_2^+Cl^-} \rightarrow \mathrm{m\text{-}BrC_6H_4OH}$ ($\mathrm{H_2O}$, Δ).

Step 3. **(iii) Benzoic acid → aniline.** Convert to amide, Hofmann-degrade:

$$\mathrm{C_6H_5COOH} \xrightarrow{\mathrm{NH_3},\,\Delta} \mathrm{C_6H_5CONH_2} \xrightarrow{\mathrm{Br_2,\,NaOH}} \mathrm{C_6H_5NH_2}.$$

Step 4. **(iv) Aniline → 2,4,6-tribromofluorobenzene.** Brominate aniline in aqueous $\mathrm{Br_2}$ (very activated ring, all three o/p-positions react) to get 2,4,6-tribromoaniline. Diazotise, treat with $\mathrm{HBF_4}$ (Balz–Schiemann):

1. $C_6H_5NH_2 \rightarrow 2,4,6\text{-}Br_3C_6H_2NH_2$ (Br_2/H_2O)
2. $2,4,6\text{-}Br_3C_6H_2NH_2 \rightarrow 2,4,6\text{-}Br_3C_6H_2N_2{}^+Cl^-$ ($NaNO_2$, HCl, 273 K)
3. $2,4,6\text{-}Br_3C_6H_2N_2{}^+Cl^- \rightarrow 2,4,6\text{-}Br_3C_6H_2N_2{}^+BF_4{}^-$ (HBF_4)
4. $2,4,6\text{-}Br_3C_6H_2N_2{}^+BF_4{}^- \rightarrow 2,4,6\text{-}Br_3C_6H_2F + N_2 + BF_3$ (Δ, Balz–Schiemann).

Step 5. **(v) Benzyl chloride $\rightarrow$ 2-phenylethanamine.** Substitute with cyanide, reduce the nitrile:

$$C_6H_5CH_2Cl \xrightarrow{KCN} C_6H_5CH_2CN \xrightarrow{H_2/Ni \text{ or } LiAlH_4} C_6H_5CH_2CH_2NH_2.$$

Step 6. **(vi) Chlorobenzene $\rightarrow$ p-chloroaniline.** Direct amination of chlorobenzene needs very harsh conditions, so we go via nitration: the $-Cl$ is mildly o/p-directing, so nitration gives a mixture of o- and p-isomers; separate and reduce:

$$C_6H_5Cl \xrightarrow{HNO_3/H_2SO_4} p\text{-}ClC_6H_4NO_2 \xrightarrow{Sn/HCl} p\text{-}ClC_6H_4NH_2.$$

Step 7. **(vii) Aniline $\rightarrow$ p-bromoaniline.** Direct bromination of aniline gives 2,4,6-tribromoaniline (over-bromination). Protect $-NH_2$ first by acetylation; then brominate (acetanilide gives mainly p-product); finally hydrolyse the amide back:

$$C_6H_5NH_2 \xrightarrow{(CH_3CO)_2O} C_6H_5NHCOCH_3 \xrightarrow{Br_2/CH_3COOH} p\text{-}BrC_6H_4NHCOCH_3 \xrightarrow{H^+/H_2O} p\text{-}BrC_6H_4NH_2.$$

Step 8. **(viii) Benzamide $\rightarrow$ toluene.** The standard NCERT route uses Hofmann to make aniline, the diazonium switchboard to strip the nitrogen, and Friedel–Crafts alkylation to add the methyl group:

1. $C_6H_5CONH_2 \rightarrow C_6H_5NH_2$ (Br_2, NaOH; Hofmann, -1 C)
2. $C_6H_5NH_2 \rightarrow C_6H_5N_2{}^+Cl^-$ ($NaNO_2$/HCl, 273 K)
3. $C_6H_5N_2{}^+Cl^- + H_3PO_2 + H_2O \rightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$ (reductive deamination)
4. $C_6H_6 + CH_3Cl \xrightarrow{\text{anhyd. } AlCl_3} C_6H_5CH_3 + HCl$ (Friedel–Crafts alkylation).

Net: benzamide (7 C) $\rightarrow$ aniline (6 C) $\rightarrow$ benzene (6 C) $\rightarrow$ toluene (7 C). The first step trims the amide carbon with Hofmann; the last step reinstalls a methyl on the ring.

Step 9. **(ix) Aniline $\rightarrow$ benzyl alcohol.** Diazotise, treat with $CuCN$ (Sandmeyer) to put a $-CN$ on the ring, hydrolyse to benzoic acid, reduce to benzyl alcohol:

1. $C_6H_5NH_2 \rightarrow C_6H_5N_2{}^+Cl^-$ ($NaNO_2$/HCl, 273 K)
2. $C_6H_5N_2{}^+Cl^- \rightarrow C_6H_5CN$ (CuCN, Sandmeyer)

3. $C_6H_5CN \rightarrow C_6H_5COOH$ (H_2O/H^+)
4. $C_6H_5COOH \rightarrow C_6H_5CH_2OH$ ($LiAlH_4$).

> **Final Answer:** Each conversion uses one or two of: diazonium replacement (Sandmeyer / Gattermann / Balz–Schiemann / H_3PO_2 / coupling), $-NH_2$ protection by acetylation, or Hofmann bromamide for -1 C chain change.

♥ Diazonium salts as the synthetic switchboard

The $-N_2^+$ group is a leaving group that lets you swap a single position on a benzene ring for almost any other substituent ($-Cl$, $-Br$, $-I$, $-F$, $-CN$, $-OH$, $-H$, $-N{=}N-Ar$). No other functional group has this breadth. Routing a synthesis through aniline $\rightarrow$ diazonium is often the shortest path.

☞ Always protect $-NH_2$ before electrophilic attack on the ring

The bare $-NH_2$ is so strongly activating that all three of the o/p-positions react. To stop at a single substitution, convert $-NH_2$ to $-NHCOCH_3$ (acetylation), perform the substitution (now only o/p at moderate rate), then hydrolyse the amide back. This is the key trick for p-bromoaniline ((vii)) and the only way to avoid the tribromide.

✗ Direct halogenation of aniline gives the tribromide

A common slip in (vii) is to write $C_6H_5NH_2 + Br_2 \longrightarrow$ p-$BrC_6H_4NH_2$. *Wrong.* Aqueous Br_2 on aniline gives 2,4,6-tribromoaniline (white precipitate) because $-NH_2$ is too activating. The clean p-bromoaniline product requires protection of $-NH_2$ via acetylation first. Forgetting the protection step loses marks every year in board papers.

EXPERT'S SOLUTION *: Krishna Nair, Ph.D Organic Chemistry, IISc Bangalore*

Strategic angle. Use the diazonium "switchboard" first. For each conversion, ask: can I make an aryl amine somewhere on the ring near the right position? If yes, diazotise and swap.

Alternative approach: retrosynthetic disconnection. For each product, write the last functional group as a leaving handle and walk backwards. Examples: benzoic acid $\Leftarrow$ benzonitrile (hydrolyse) $\Leftarrow ArN_2^+ + CuCN \Leftarrow$ aniline $\Leftarrow$ nitrobenzene. Phenol $\Leftarrow ArN_2^+ + H_2O$. Aryl fluoride $\Leftarrow ArN_2^+BF_4^-$ (Balz–Schiemann). Once each disconnection is named, the synthesis writes itself.

Concept linkage. Five of the nine conversions go through ArN_2^+ (i, ii, iv, viii, ix), proving the "diazonium switchboard" theme. The remaining four use either Hofmann (iii, indirectly viii), cyanide chain extension (v), aromatic nitration with chloro directing (vi), or acetylation protection (vii). These are the same five named reactions from Q 9.7,

applied in series.

Step 1. (i) $NO_2 \longrightarrow NH_2 \longrightarrow N_2^+ \longrightarrow CN \longrightarrow COOH$. Four steps; Sn/HCl, $NaNO_2/HCl/_{273}\,K$, $CuCN$, H_2O/H^+.

Step 2. (ii) Start from benzene; nitrate, brominate (meta-director), then $NO_2 \longrightarrow NH_2 \longrightarrow N_2^+ \longrightarrow OH$. The meta relationship between $-Br$ and $-OH$ is built in the second step (brominate m to $-NO_2$).

Step 3. (iii) Standard Hofmann ladder downwards from acid: $C_6H_5COOH \longrightarrow C_6H_5CONH_2 \longrightarrow C_6H_5NH_2$.

Step 4. (iv) Brominate aniline first (saturates ring with three Br), then Balz–Schiemann to plug fluorine in place of $-NH_2$: $NH_2 \longrightarrow N_2^+Cl^- \longrightarrow N_2^+BF_4^- \xrightarrow{\Delta} F$.

Step 5. (v) Cyanide chain extension on benzyl chloride; reduce the nitrile with $LiAlH_4$ to give the amine. Chain grows by one carbon overall.

Step 6. (vi) Nitrate chlorobenzene; $-Cl$ is mildly o/p-directing, so the para-nitro isomer is the major product. Reduce $-NO_2$ to $-NH_2$ with Sn/HCl.

Step 7. (vii) Acetylate $-NH_2$ to protect (now $-NHCOCH_3$, a moderate o/p-director); brominate; hydrolyse the amide back to $-NH_2$.

Step 8. (viii) Hofmann on benzamide $\rightarrow$ aniline; diazotise to $C_6H_5N_2^+Cl^-$; reduce with H_3PO_2 (or hot ethanol) to give benzene; finally Friedel–Crafts alkylation with $CH_3Cl/AlCl_3$ installs the methyl group, giving toluene. Four steps total.

Step 9. (ix) Sandmeyer with $CuCN$ to put $-CN$ on the ring, hydrolyse to benzoic acid, reduce with $LiAlH_4$ to benzyl alcohol.

Exam relevance. CBSE board examiners reuse these conversions nearly every year. Common 3–5 mark routes: **aniline** $\rightarrow$ **p-bromoaniline** (vii, classic) needs the protection trick; **aniline** $\rightarrow$ **benzyl alcohol** (ix) tests the Sandmeyer step; **benzene** $\rightarrow$ **m-bromophenol** (ii) tests the meta-direction logic. JEE often combines two routes in one question and asks for the missing intermediate, e.g. "aniline $\rightarrow$ 2,4,6-tribromofluorobenzene" with the diazonium-tetrafluoroborate intermediate as the blank.

Why this matters. Half of all multi-step Class 12 exam syntheses come down to spotting where to insert a $-NH_2$ (to diazotise) and where to protect/deprotect it. Mastering the diazonium switchboard plus the acetylation-protection trick is enough for roughly 80% of the organic synthesis paper.

Final Answer: Each route given above; the diazonium step is the common pivot.

Q 9.9 Give the structures of A, B and C in the following reactions:

(i) $CH_3CH_2I \rightarrow$ A (NaCN); A $\rightarrow$ B (OH^-, partial hyd.); B $\rightarrow$ C (NaOBr).
(ii) $C_6H_5N_2^+Cl^- \rightarrow$ A (CuCN); A $\rightarrow$ B (H_2O/H^+); B $\rightarrow$ C (NH_3, Δ).
(iii) $CH_3CH_2Br \rightarrow$ A (KCN); A $\rightarrow$ B ($LiAlH_4$); B $\rightarrow$ C (HNO_2, 273 K).
(iv) $C_6H_5NO_2 \rightarrow$ A (Fe/HCl); A $\rightarrow$ B ($NaNO_2$/HCl, 273 K); B $\rightarrow$ C (H_2O/H^+).
(v) $CH_3COOH \rightarrow$ A (NH_3, Δ); A $\rightarrow$ B (NaOBr); B $\rightarrow$ C ($NaNO_2$/HCl).
(vi) $C_6H_5NO_2 \rightarrow$ A (Fe/HCl); A $\rightarrow$ B (HNO_2, 273 K); B $\rightarrow$ C (C_6H_5OH).

SOLUTION

Concept used. Each sequence chains together standard transformations: nucleophilic substitution by cyanide ($+1$ C), nitrile hydrolysis to acid or amide, amide to amine (Hofmann), nitro to amine (reduction), amine to diazonium (cold $NaNO_2$/HCl), diazonium to phenol / coupling product.
Read each step's reagent and "unfold" the structure of the intermediate.

Step 1. **(i)** Start: CH_3CH_2I. With NaCN (SN_2): $A = CH_3CH_2CN$ (propanenitrile). Partial alkaline hydrolysis (one equivalent of water on C≡N): the nitrile becomes an amide, $B = CH_3CH_2CONH_2$ (propanamide). Treatment with NaOBr (i.e. Br_2/NaOH, Hofmann bromamide): $C = CH_3CH_2NH_2$ (ethanamine). Net: 2 C $\rightarrow$ 3 C $\rightarrow$ 3 C $\rightarrow$ 2 C (the Hofmann step removes the carbonyl carbon). $\boxed{A = CH_3CH_2CN,\ B = CH_3CH_2CONH_2,\ C = CH_3CH_2NH_2}$

Step 2. **(ii)** Start: $C_6H_5N_2^+Cl^-$. With CuCN (Sandmeyer): $A = C_6H_5CN$ (benzonitrile). Hydrolysis with H_2O/H^+: $B = C_6H_5COOH$ (benzoic acid). With NH_3 and Δ: ammonium salt $\rightarrow$ amide, $C = C_6H_5CONH_2$ (benzamide).
$\boxed{A = C_6H_5CN,\ B = C_6H_5COOH,\ C = C_6H_5CONH_2}$

Step 3. **(iii)** Start: CH_3CH_2Br. With KCN: $A = CH_3CH_2CN$. Reduction with $LiAlH_4$ adds two hydrogens to the C of C≡N: $B = CH_3CH_2CH_2NH_2$ (propan-1-amine). Cold HNO_2 (i.e. $NaNO_2$/HCl) on an aliphatic 1° amine gives the alcohol with loss of N_2: $C = CH_3CH_2CH_2OH$ (propan-1-ol).
$\boxed{A = CH_3CH_2CN,\ B = CH_3CH_2CH_2NH_2,\ C = CH_3CH_2CH_2OH}$

Step 4. **(iv)** Start: $C_6H_5NO_2$. With Fe/HCl: $A = C_6H_5NH_2$ (aniline). Cold $NaNO_2$/HCl at 273 K: $B = C_6H_5N_2^+Cl^-$ (benzenediazonium chloride). H_2O/H^+ (warm): $C = C_6H_5OH$ (phenol). $\boxed{A = C_6H_5NH_2,\ B = C_6H_5N_2^+Cl^-,\ C = C_6H_5OH}$

Step 5. **(v)** Start: CH_3COOH. With NH_3 and Δ: $A = CH_3CONH_2$ (acetamide). With NaOBr (Hofmann): $B = CH_3NH_2$ (methanamine). $NaNO_2$/HCl on a 1° aliphatic amine: $C = CH_3OH$ (methanol).
$\boxed{A = CH_3CONH_2,\ B = CH_3NH_2,\ C = CH_3OH}$

Step 6. **(vi)** Start: $C_6H_5NO_2$. With Fe/HCl: $A = C_6H_5NH_2$. Cold HNO_2 at 273 K: $B = C_6H_5N_2^+Cl^-$. With phenol C_6H_5OH in mildly alkaline solution: *coupling reaction*, giving the *p*-hydroxyazobenzene dye, $C = p\text{-}HOC_6H_4{-}N{=}N{-}C_6H_5$ (an orange dye).

$$\boxed{A = C_6H_5NH_2,\ B = C_6H_5N_2{}^+Cl^-,\ C = \text{p-HO}{-}C_6H_4{-}N{=}N{-}C_6H_5}$$

Final Answer: See the six boxed answers above.

☞ Track three things at each arrow

For chained-reaction questions, write three labels on every arrow: (a) the reagent name, (b) the carbon count of the intermediate, and (c) the functional group at the reacting carbon. This three-label method catches almost every silly arithmetic or functional-group error before you write the final boxed structure.

☞ Reagent dictionary for chain syntheses

$NaCN/KCN$: $+1$ C, gives nitrile. $LiAlH_4$: reduces $-CN$ to $-CH_2NH_2$, or $-COOH$ to $-CH_2OH$. $Br_2/NaOH$ on amide = Hofmann, -1 C. Sn/HCl or Fe/HCl: $-NO_2 \to -NH_2$. $NaNO_2/HCl$, 273 K: $-NH_2 \to -N_2{}^+$ (stable for aryl, decomposes for alkyl). $CuCN$: $-N_2{}^+ \to -CN$ (Sandmeyer).

EXPERT'S SOLUTION *: Aarav Gupta, M.Sc Chemistry, IIT Kanpur*

Quick reading. Six chains; each one is a guided tour of the chapter. Track the carbon count and the functional group at every arrow.

Alternative approach: tabulate carbon count. For each sub-part, make a tiny ledger showing the C-count and the functional group of each intermediate. Example for (i): CH_3CH_2I (2 C, alkyl iodide) $\to A = CH_3CH_2CN$ (3 C, nitrile) $\to B = CH_3CH_2CONH_2$ (3 C, amide) $\to C = CH_3CH_2NH_2$ (2 C, primary amine). The C-count rises by 1 at the cyanide step and falls by 1 at the Hofmann step — net 0 change. This bookkeeping makes the Hofmann step in (i) visible and prevents the wrong product $CH_3CH_2CH_2NH_2$.

Concept linkage. Two of the six chains use "acid $\to$ amide $\to$ amine" (Hofmann descent, parts (i) and (v)), while three use diazonium chemistry (Sandmeyer, hydrolysis to phenol, coupling) on the aryl side (parts (ii), (iv), (vi)). The remaining chain (part (iii)) is the up-step cyanide chain extension. So this question is a compact menu of the entire chapter's named transformations.

Step 1. (i) $R{-}I \longrightarrow R{-}CN$ ($+1$ C, SN_2); $R{-}CN \longrightarrow R{-}CONH_2$ (partial hydrolysis with OH^-); $R{-}CONH_2 \longrightarrow R{-}NH_2$ (-1 C, Hofmann). Net: $A = CH_3CH_2CN$, $B = CH_3CH_2CONH_2$, $C = CH_3CH_2NH_2$ (ethanamine).

Step 2. (ii) Sandmeyer with $CuCN$ gives benzonitrile. Hydrolysis $\to$ benzoic acid. Ammonia/heat $\to$ benzamide. Three named reactions in one chain.

Step 3. (iii) $R{-}X + KCN \longrightarrow R{-}CN$, then $LiAlH_4$ adds 4 H to the $C{\equiv}N$ triple bond, giving $R{-}CH_2NH_2$ (now 3 C). Aliphatic 1° amine + $HNO_2 \to$ alcohol ($CH_3CH_2CH_2OH$).

Step 4. (iv) Nitro $\rightarrow$ amine (Fe/HCl). Cold HNO_2 $\rightarrow$ diazonium. Warm water hydrolyses the diazonium to phenol. Classic "three-step from nitrobenzene to phenol".

Step 5. (v) Acid $\rightarrow$ amide (NH_3, Δ) $\rightarrow$ Hofmann amine (chain shrinks by 1 C). Then HNO_2 deaminates the 1° aliphatic amine to the alcohol.

Step 6. (vi) Nitro $\rightarrow$ amine $\rightarrow$ diazonium $\rightarrow$ coupling with phenol gives a *p*-hydroxyazobenzene dye (an orange solid).

Exam relevance. CBSE board favorites: "Identify A, B, C" chains worth 3–5 marks. The trap in (i) is recognising the Hofmann step at the end (one C drops out). NEET frequently tests "what is the final product when aniline is treated with cold HNO_2/HCl and then warmed in water?" $\Rightarrow$ phenol (chain iv above).
Why this matters. Practising these chains is the single best preparation for the chapter, because the AISSCE often quotes one of them verbatim and the recurring named reactions appear in combination on every board paper.

Final Answer: See the boxed structures above.

Q 9.10 **An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.**

SOLUTION

Concept used. The clue is the final product's molecular formula, C_6H_7N. Degree of unsaturation:

$$\text{DBE} = \frac{2(6) + 2 - 7 + 1}{2} = 4,$$

which is exactly the DBE of a benzene ring with no other unsaturations. C_6H_7N with one ring is aniline, $C_6H_5NH_2$.
Working backwards: the last step is Br_2/KOH, a **Hofmann bromamide** reaction. So B must be a benzamide, $C_6H_5CONH_2$, which on Hofmann gives aniline (chain shortens by one C). The first step, "aromatic + aqueous NH_3 + heat" $\rightarrow$ amide, points to a benzoic-acid derivative. The simplest fit is benzoic acid itself.

Step 1. **Identify C.** Molecular formula C_6H_7N with one ring and one nitrogen $\Rightarrow$ aniline ($C_6H_5NH_2$). IUPAC name: *aniline* (or benzenamine).

Step 2. **Identify B.** The reaction $B + Br_2 + KOH \rightarrow C$ is Hofmann bromamide. C has 6 carbons; the amide precursor has 7 carbons (C_n + carbonyl C). So B is

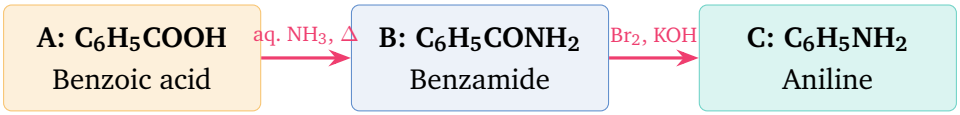
$C_6H_5CONH_2$, benzamide. IUPAC name: *benzamide*.

$$C_6H_5CONH_2 + Br_2 + 4\,KOH \xrightarrow{\Delta} C_6H_5NH_2 + K_2CO_3 + 2\,KBr + 2\,H_2O.$$

Step 3. **Identify A.** "A + aqueous NH_3 + heat $\rightarrow$ benzamide" is the standard route from an acid (or acid chloride / ester) to an amide. The simplest aromatic precursor is benzoic acid:

$$C_6H_5COOH + NH_3 \xrightarrow{\Delta} C_6H_5CONH_2 + H_2O.$$

IUPAC name of A: *benzoic acid*.



Final Answer: $A = C_6H_5COOH$ (benzoic acid); $B = C_6H_5CONH_2$ (benzamide); $C = C_6H_5NH_2$ (aniline).

☞ DBE = the molecular-formula shortcut

For any $C_aH_bN_cO_d$ structure puzzle, compute the degree of bond equivalents (DBE):

$$\text{DBE} = \frac{2a + 2 - b + c}{2}.$$

A DBE of 4 on a C_6 skeleton with one N practically forces a benzene ring with no extra unsaturation: only $C_6H_5NH_2$ (aniline) fits. This single calculation locks the identity of one unknown in seconds.

☞ Work backwards from the last step

When a problem gives the molecular formula of the *final* product, identify that product first (here $C = C_6H_7N$ = aniline), then read the last reagent set (Br_2/KOH on an amide = Hofmann) to deduce the immediate precursor (benzamide). Continue upstream one step at a time. This "finish-line first" strategy beats forward chaining when the puzzle hints come at the end.

EXPERT'S SOLUTION *: Yash Mehta, M.Sc Chemistry, IIT Kanpur*

Quick reading. The trick is to recognise the last step (Br_2/KOH on an amide = Hofmann) and back-solve from the final formula.

Alternative approach: DBE + atom budget. For C_6H_7N,
DBE $= (2 \cdot 6 + 2 - 7 + 1)/2 = 4$. The only common C_6N structures with DBE $= 4$ are aniline ($C_6H_5NH_2$, 1°) and pyridine (C_5H_5N, which has only 5 C). Since C has 6 carbons, the answer is forced to aniline. No mechanism required at this stage — pure formula bookkeeping.

Concept linkage. The puzzle uses the two most exam-friendly transformations of the chapter back-to-back: the *acid→amide* step (NH_3, Δ) and the *Hofmann bromamide* (amide → amine, -1 C, Br_2/KOH). This is exactly the Hofmann ladder pattern used in Q 9.5(i) and Q 9.8(iii).

Step 1. DBE of C_6H_7N is 4 ⇒ benzene ring + 0 extra unsaturation. Therefore C is aniline ($C_6H_5NH_2$).

Step 2. Hofmann bromamide on an amide → amine; one C is lost. Therefore B is the corresponding amide, benzamide ($C_6H_5CONH_2$, 7 C). The Hofmann step removes the carbonyl C as Na_2CO_3.

Step 3. NH_3 + heat converts an acid (or acid derivative) to its amide. Therefore A is benzoic acid (C_6H_5COOH).

Step 4. Verification: $C_6H_5COOH \xrightarrow{NH3,\Delta} C_6H_5CONH_2 \xrightarrow{Br2,KOH} C_6H_5NH_2$. Each step is a textbook transformation, and the carbon count $7 \to 7 \to 6$ matches.

Exam relevance. CBSE 3-mark question: "identify the three compounds A, B, C". Marker rubric: (1) name + structure of each, (2) reasoning that links the last formula to aniline via DBE, (3) recognition of the Hofmann step. A common JEE Mains variant gives a C_7H_9N instead — the answer is then N-methylaniline or p-toluidine, and the upstream chemistry differs (no Hofmann; instead N-methylation or p-methyl substitution).

Why this matters. Reading reactions backwards is a key skill for synthesis problems. The molecular-formula clue is often the quickest way to lock the identity of the last unknown, and a quick DBE saves you from guessing among isomers.

> **Final Answer:** A: benzoic acid; B: benzamide; C: aniline.

Q 9.11 Complete the following reactions:

(i) $C_6H_5NH_2 + CHCl_3 + \text{alc}\cdot\ KOH \longrightarrow$

(ii) $C_6H_5N_2{}^+Cl^- + H_3PO_2 + H_2O \longrightarrow$

(iii) $C_6H_5NH_2 + H_2SO_4\ (\text{conc}\cdot) \longrightarrow$

(iv) $C_6H_5N_2{}^+Cl^- + C_2H_5OH \longrightarrow$

(v) $C_6H_5NH_2 + Br_2\ (aq) \longrightarrow$

(vi) $C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow$

(vii) $C_6H_5N_2{}^+Cl^- \to$ **X (i.** HBF_4**); X →** $NaNO_2/Cu, \Delta$**).**

SOLUTION

Concept used. Each reaction is one of the named amine / diazonium transformations. The required products follow directly from the reagent set.

Step 1. **(i) Carbylamine reaction.** Aniline + $CHCl_3$ + alc. KOH on heating gives phenyl isocyanide (a foul-smelling liquid):

$$C_6H_5NH_2 + CHCl_3 + 3\,KOH \xrightarrow{\Delta} C_6H_5NC + 3\,KCl + 3\,H_2O.$$

Step 2. **(ii) Reduction of diazonium with hypophosphorous acid.** H_3PO_2 replaces the $-N_2^+$ group by $-H$, liberating N_2:

$$C_6H_5N_2^+Cl^- + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2 + H_3PO_3 + HCl.$$

Step 3. **(iii) Aniline + conc. H_2SO_4 → anilinium bisulphate, then sulphonation.** On warming, the salt rearranges and sulphonation occurs at the para position. The final product is **sulphanilic acid** (p-aminobenzenesulphonic acid), which exists as a zwitterion:

$$C_6H_5NH_2 + H_2SO_4\ (\text{conc}\cdot) \xrightarrow{\Delta} \text{p-}NH_2C_6H_4SO_3H\ \text{(sulphanilic acid)}.$$

Step 4. **(iv) Diazonium + ethanol.** Ethanol acts as a reducing agent (like H_3PO_2): replaces $-N_2^+$ by $-H$ and is itself oxidised to acetaldehyde:

$$C_6H_5N_2^+Cl^- + C_2H_5OH \longrightarrow C_6H_6 + N_2 + CH_3CHO + HCl.$$

Step 5. **(v) Aniline + aqueous Br_2.** The $-NH_2$ group is so strongly activating that all three free o/p-positions get brominated, giving the white precipitate 2,4,6-tribromoaniline:

$$C_6H_5NH_2 + 3\,Br_2 \xrightarrow{\text{aq}} 2,4,6\text{-}Br_3C_6H_2NH_2 + 3\,HBr.$$

Step 6. **(vi) Acetylation.** Aniline + acetic anhydride gives acetanilide (N-phenylethanamide):

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH.$$

Step 7. **(vii) Two-step sequence ((i) HBF_4, then (ii) $NaNO_2/Cu$, Δ).** Step (i) converts benzenediazonium chloride to the stable, isolable benzenediazonium tetrafluoroborate $C_6H_5N_2^+BF_4^-$ (HCl is released). Step (ii) is a Sandmeyer-type substitution: the warm $NaNO_2$/Cu pair replaces the $-N_2^+$ group with $-NO_2$, giving nitrobenzene with evolution of N_2. Net transformation:

$$C_6H_5N_2^+Cl^- + HBF_4 \longrightarrow C_6H_5N_2^+BF_4^- + HCl,$$

$$C_6H_5N_2^+BF_4^- + NaNO_2 \xrightarrow{\text{Cu},\,\Delta} C_6H_5NO_2 + N_2\uparrow + NaBF_4.$$

Overall final product: *nitrobenzene* ($C_6H_5NO_2$).

> **Final Answer:** (i) Phenyl isocyanide. (ii) Benzene. (iii) Sulphanilic acid. (iv) Benzene + acetaldehyde. (v) 2,4,6-tribromoaniline. (vi) Acetanilide. (vii) Nitrobenzene ($C_6H_5NO_2$) + N_2 + $NaBF_4$ (the diazonium tetrafluoroborate intermediate is decomposed by warm $NaNO_2/Cu$, substituting $-N_2^+$ by $-NO_2$).

☞ Spotting the named reaction by reagents

$CHCl_3$ + alc. KOH on amine = carbylamine. H_3PO_2 on ArN_2^+ = reductive deamination. Conc. H_2SO_4 on aniline = sulphanilic acid. Ethanol on ArN_2^+ = reductive deamination (like H_3PO_2). Br_2 in water on aniline = tribromoaniline. $(CH_3CO)_2O$ on amine = amide. HBF_4 on $ArN_2^+ \rightarrow$ heat = aryl fluoride.

☞ Quick map: reagent → product on aniline

$CHCl_3$/alc. KOH: phenyl isocyanide. $NaNO_2$/HCl, 273 K: benzenediazonium chloride. Conc. H_2SO_4, Δ: sulphanilic acid. $Br_2(aq)$: 2,4,6-tribromoaniline. $(CH_3CO)_2O$: acetanilide. HNO_3/H_2SO_4 (cold): mainly p- and m-nitroaniline mix. $AlCl_3 + RX$: *no reaction* (Friedel-Crafts fails).

✗ Br_2 in water on aniline gives the TRIbromide, not the monobromide

A frequent answer-script slip in part (v): writing the product as p-bromoaniline. *Wrong.* Aniline is so strongly activated by the $-NH_2$ that aqueous Br_2 brominates all three free o/p-positions, giving 2,4,6-tribromoaniline as a white precipitate. To get the mono-product cleanly, the $-NH_2$ must first be protected as $-NHCOCH_3$ (see Q 9.8(vii)).

EXPERT'S SOLUTION *: Ishaan Desai, M.Sc Physical Chemistry, IIT Madras*

Quick reading. Pair each reagent set with the named reaction it specifies, then write the product.

Alternative approach: "reagent first, product second". Train yourself to read the reagent list in a single glance and recall the named reaction it identifies. $CHCl_3$ + alc. KOH on an amine is *always* carbylamine (whether the amine is aniline or ethylamine). H_3PO_2 on ArN_2^+ is *always* reductive deamination. Conc. H_2SO_4 on aniline is *always* sulphonation to sulphanilic acid. The pattern recognition halves your working time on aniline-reaction MCQs.

Concept linkage. Every one of these seven reagents appears again in Q 9.7 (named reactions) and Q 9.8 (multi-step syntheses). This question doubles as flashcards for the reagent-to-product dictionary that runs through the whole chapter. Note also: parts (ii) and (iv) are mechanistically the same reaction (reductive deamination of ArN_2^+), with H_3PO_2 and ethanol acting as alternative hydride donors.

Step 1. (i) $CHCl_3$/alc. KOH: carbylamine; product C_6H_5NC (phenyl isocyanide). Foul smell is diagnostic.

Step 2. (ii) H_3PO_2 on $C_6H_5N_2{}^+Cl^-$: deaminating reduction; product C_6H_6 (benzene) + $N_2\uparrow$ + H_3PO_3.

Step 3. (iii) Conc. H_2SO_4, Δ: anilinium hydrogen sulphate $\rightarrow$ sulphanilic acid (p-aminobenzenesulphonic acid, an internal salt / zwitterion).

Step 4. (iv) C_2H_5OH on $C_6H_5N_2{}^+Cl^-$: reductive deamination; C_6H_6 + CH_3CHO + $N_2\uparrow$. Ethanol is oxidised to acetaldehyde.

Step 5. (v) Aqueous Br_2 on aniline: 2,4,6-tribromoaniline (white precipitate). The $-NH_2$ is too activating for clean monobromination.

Step 6. (vi) $(CH_3CO)_2O$ on aniline: $C_6H_5NHCOCH_3$ (acetanilide). The reaction uses pyridine as a proton-scavenger in the lab.

Step 7. (vii) The two reagent sets are applied sequentially, not as alternatives. Step (i) HBF_4 converts $C_6H_5N_2{}^+Cl^-$ to the isolable crystalline solid $C_6H_5N_2{}^+BF_4{}^-$ (benzenediazonium tetrafluoroborate). Step (ii) warm $NaNO_2/Cu$ then performs a Sandmeyer-style substitution that replaces $-N_2{}^+$ with $-NO_2$, liberating N_2 and giving nitrobenzene $C_6H_5NO_2$ as the final product.

Exam relevance. NEET and JEE Mains repeatedly test "what is the product of aniline + reagent X?" for X = $Br_2(aq)$, $CHCl_3/KOH$, HNO_2 cold, $(CH_3CO)_2O$. The 2024 JEE paper, for example, asked the product of $C_6H_5N_2{}^+ + H_3PO_2 \Rightarrow$ benzene. CBSE board often gives the conc. H_2SO_4 option (iii) and expects the structure of sulphanilic acid as a zwitterion.

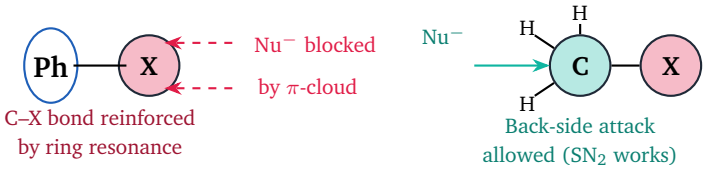
Why this matters. Reaction identification by reagent is a fast-fire skill for MCQ-style sub-questions and is the building block for multi-step syntheses (Q 9.5, 9.8, 9.9).

Final Answer: See products above.

Q 9.12 Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

SOLUTION

Concept used. The Gabriel phthalimide synthesis proceeds by an SN_2 reaction between potassium phthalimide (the soft, stabilised nitrogen nucleophile) and an alkyl halide R–X. The mechanism is bimolecular, requiring backside attack of the nucleophile on the carbon bearing the leaving group.



Step 1. **Step 1: Identify the required mechanism.** Gabriel needs the phthalimide anion to displace the halide from $\mathrm{R-X}$ in an $\mathrm{SN_2}$ step.

Step 2. **Step 2: Examine the aryl halide.** In an aryl halide $\mathrm{Ar-X}$, the halogen is bonded to an sp^2-hybridised carbon of the benzene ring. The C–X bond has *partial double-bond character* because of resonance: the lone pair on the halogen donates into the ring. This makes the C–X bond shorter, stronger and harder to break.

Step 3. **Step 3: $\mathrm{SN_2}$ on sp^2 carbon is forbidden.** The nucleophile must approach from the back of the C–X bond, but on a benzene ring the back side is occupied by the ring's π-electron cloud, which repels any incoming nucleophile. Hence aryl halides do not undergo $\mathrm{SN_2}$ substitution with phthalimide.

Step 4. **Step 4: Conclusion.** Since Gabriel needs $\mathrm{SN_2}$ and aryl halides cannot give $\mathrm{SN_2}$, the synthesis is not applicable to aryl-1° amines (like aniline). They are prepared by other routes (reduction of nitrobenzene with Fe/HCl, or Hofmann bromamide from benzamide).

Final Answer: Aryl halides do not undergo $\mathrm{SN_2}$ substitution (the C–X bond is shortened/strengthened by resonance, and the back side is blocked by the ring's π-cloud), so the phthalimide anion cannot displace the halide. Hence aniline and other aryl-1° amines are not accessible by Gabriel synthesis.

★ $\mathrm{SN_2}$ on aryl C: a hard "no".

The same rule rules out aryl halides as starting materials for Williamson ether synthesis, for Wurtz, for the malonate ester synthesis, and for the acetoacetic ester synthesis. The only standard ways to put a nucleophile on a benzene ring are via diazonium chemistry (Sandmeyer/Gattermann) or via aromatic nucleophilic substitution (needs very activating groups like multiple $-\mathrm{NO_2}$).

♥ Why we route through nitrobenzene for aryl amines

The standard route to aniline is *nitration of benzene* (puts $-\mathrm{NO_2}$ on by electrophilic substitution, which *does* work on aromatic rings) followed by *reduction* of $-\mathrm{NO_2}$ to $-\mathrm{NH_2}$ with $\mathrm{Sn/HCl}$ or $\mathrm{Fe/HCl}$. This two-step route is the universal workaround for the "no $\mathrm{SN_2}$ on aryl C" problem. The same logic underlies the synthesis of all $\mathrm{Ar-NH_2}$ compounds in

this chapter (Q 9.8(i), (vi)).

☞ Two reasons, write both

A CBSE 2-mark question expects you to name *two* reasons why Gabriel fails for aryl-1° amines: (1) the C–X bond of $\mathrm{Ar{-}X}$ has partial double-bond character (resonance with the ring), so it is shorter, stronger, and reluctant to break; (2) backside $\mathrm{SN_2}$ attack is geometrically blocked by the π-electron cloud of the ring. Writing only one reason often costs you a mark.

EXPERT'S SOLUTION *: Tara Banerjee, Ph.D Organic Chemistry, IISc Bangalore*

Structural angle. Two reasons, both pinning the same conclusion:

Step 1. The C–X bond in an aryl halide is partially double-bonded due to delocalisation of the halogen lone pair into the ring. Bond length is shorter (e.g. C–Cl in chlorobenzene is $\sim 1.69\,\text{Å}$ vs $\sim 1.78\,\text{Å}$ in methyl chloride), and the bond dissociation energy is higher.

Step 2. Aryl halides have no sp^3 leaving-group geometry, so backside $\mathrm{SN_2}$ is geometrically impossible. Front-side attack is electronically repelled by the ring's π-cloud.

Alternative approach: orbital-overlap picture. For an $\mathrm{SN_2}$ reaction, the incoming nucleophile must overlap with the σ^* orbital of the C–X bond from the side opposite the leaving group. In a methyl halide, this back-side lobe sits in empty space and the nucleophile slips in easily. In an aryl halide, the back-side lobe of $\sigma^*_{\text{C–X}}$ is squeezed against the π-cloud of the ring; even if the nucleophile reaches it, the geometry forces unfavorable overlap. So $\mathrm{SN_2}$ at aryl C is forbidden by orbital geometry, not merely slow.

Concept linkage. The same restriction governs other nucleophile-on-aryl-halide failures: Williamson ether synthesis (alkoxide + $\mathrm{Ar{-}X} \rightarrow$ aryl ether? *no*), Wurtz coupling, malonate ester synthesis, and acetoacetic ester alkylation. To make a nucleophile sit on an aromatic ring you must either (a) route through diazonium (Q 9.7(ii), 9.8) or (b) use SNAr on rings activated by multiple electron-withdrawing groups (very limited scope at Class 12).

The phthalimide anion is too soft and too sterically demanding to force an SNAr without strong activating groups on the ring. Therefore the Gabriel synthesis simply does not get off the ground.

Exam relevance. CBSE board question 2023, 2-mark: "Why cannot aniline be prepared by Gabriel synthesis?" Marker rubric: (1) $\mathrm{Ar{-}X}$ does not undergo $\mathrm{SN_2}$, (2) reasoned by partial double-bond character or by π-blocking of backside attack. JEE Mains style: pick the amine that *cannot* be made by Gabriel $\Rightarrow$ aniline (any aryl-1° amine).

Why this matters. This restriction extends to almost every "nucleophile + halide" synthesis you have seen. To install $-\mathrm{NH_2}$ on a benzene ring, the standard route is

reduction of $-NO_2$, which you put on by nitration of benzene. Recognising the boundary of SN_2 chemistry saves you from proposing routes that examiners will reject without working through them.

> **Final Answer:** Aryl halides do not react with the phthalimide anion in an SN_2 step, so Gabriel synthesis fails for aryl primary amines.

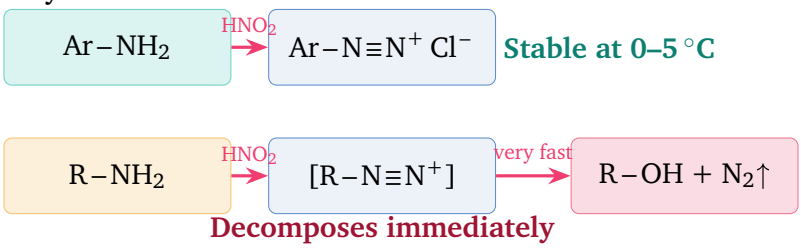
Q 9.13 Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

SOLUTION

Concept used. Nitrous acid is generated *in situ* from sodium nitrite and a mineral acid (HCl or H_2SO_4) at 0–5 °C:

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl.$$

The reaction proceeds by formation of the nitrosonium ion NO^+, which attacks the lone pair of the primary amine.



Step 1. **(i) Aromatic primary amines + HNO_2.** Aniline (and other aryl-1° amines) with cold $NaNO_2/HCl$ at 273–278 K give a stable arenediazonium chloride. The $-N_2^+$ ion in $C_6H_5N_2^+$ is stabilised by resonance delocalisation of the $+$ charge into the ring:

$$C_6H_5NH_2 + HNO_2 + HCl \xrightarrow{273\text{–}278\,K} C_6H_5N_2^+\,Cl^- + 2\,H_2O.$$

The salt is isolable and is the key intermediate for Sandmeyer, Gattermann, Balz–Schiemann and coupling reactions.

Step 2. **(ii) Aliphatic primary amines + HNO_2.** An alkyl-1° amine reacts with HNO_2 to form the same type of diazonium ion, but the aliphatic $R-N_2^+$ is *not* stabilised by any π-system and falls apart at once, releasing N_2 and giving an alcohol (with rearranged / minor olefin / halide side-products):

$$R-NH_2 + HNO_2 \longrightarrow R-OH + N_2\uparrow + H_2O.$$

For example, ethanamine gives ethanol with vigorous effervescence of N_2:

$$C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O.$$

The brisk effervescence of N_2 is a positive test for aliphatic 1° amines.

Final Answer: (i) $C_6H_5NH_2 + HNO_2 + HCl \xrightarrow{273\text{–}278\,K} C_6H_5N_2^+Cl^- + 2\,H_2O$ (stable salt). (ii) $R{-}NH_2 + HNO_2 \longrightarrow R{-}OH + N_2\uparrow + H_2O$ (effervescence of N_2).

★ Why aryl diazonium ions are special

The benzene ring is a built-in stabiliser for positive charge: the $-N_2^+$ group is conjugated with the ring, and the positive charge can be drawn on N and on three ring carbons (ortho and para). Aliphatic $R{-}N_2^+$ has no such delocalisation, so it loses N_2 in a unimolecular (SN_1-like) step almost as soon as it forms.

✗ Diazotisation must be COLD

Forgetting the temperature requirement (273–278 K, i.e. 0–5 °C) is the single most common slip. At room temperature, even the aryl diazonium salt loses N_2 rapidly and gives phenol instead. CBSE markers strictly check for the "cold" condition in any diazotisation equation; missing it costs a mark.

☞ Use the N_2 effervescence as a positive test

The vigorous evolution of N_2 gas when an aliphatic 1° amine meets HNO_2 is a *positive identification test* for that class. The aryl 1° amine gives the stable diazonium salt at cold and only releases N_2 on warming or coupling. The 2° amine gives a yellow *N*-nitrosamine oil — no gas. 3° aliphatic gives a soluble salt; 3° aryl gives a *p*-nitroso compound (green/yellow). One reagent, five different observations, one test for each amine class.

Resonance I Resonance II Resonance III Resonance IV

Positive charge spreads over terminal N and three ring carbons (stabilises ArN_2^+)

EXPERT'S SOLUTION *: Neha Chatterjee, M.Sc Chemistry, IIT Kanpur*

Strategic angle. A clean dichotomy on a single reagent (HNO_2).

- Aryl 1° amine ⇒ stable diazonium salt, isolable, useful synthetic handle.
- Alkyl 1° amine ⇒ ephemeral diazonium ion, immediately loses N_2, gives the alcohol.

Alternative approach: stability argument by resonance count. For $C_6H_5N_2^+$, four resonance structures can be drawn: the positive charge sits on the terminal N (parent form), and three forms push the positive onto the ortho, para, and other ortho ring

carbons. Four resonance structures ⇒ substantial delocalisation ⇒ stable cation. For $R-N_2^+$, no π-system is available, so only one Lewis structure exists ⇒ no delocalisation ⇒ unstable cation that breaks the σ-bond to release N_2.

Numerical anchor. The half-life of $C_6H_5N_2^+Cl^-$ at $0\,^\circ C$ is several hours (isolable as a crystalline solid); the half-life of methyldiazonium $CH_3N_2^+$ at the same temperature is microseconds. The huge gap ($> 10^{10}$ in lifetime) is the quantitative face of the resonance-stability argument.

Concept linkage. This is the same "ring locks the lone pair / delocalises the charge" theme that explains aniline's weaker basicity (Q 9.3, 9.4, 9.14), the failure of aniline's Friedel-Crafts (Q 9.3(v)), and the meta-direction in nitration of anilinium ion (Q 9.3(iv)). The ring's π-system is the master tool of the chapter.

Step 1. Aryl: $Ar-NH_2 + HNO_2/HCl \xrightarrow{273\,K} Ar-N_2^+Cl^-$, isolable below $5\,^\circ C$. Resonance makes $Ar-N_2^+$ a real molecule, used as the launching pad for Sandmeyer, Gattermann, Balz–Schiemann and coupling chemistry.

Step 2. Alkyl: $R-NH_2 + HNO_2 \longrightarrow [R-N_2^+] \longrightarrow R-OH + N_2$. The decomposition is so fast that $R-N_2^+$ is never observed; the brisk effervescence of N_2 is the visible test. Example: $C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O$.

Exam relevance. JEE/NEET MCQ writers love this contrast. Typical question: "A 1° amine reacted with cold $NaNO_2/HCl$. The mixture evolved a colourless, odourless gas. Identify the amine class." ⇒ aliphatic 1° (because aryl would have given the stable diazonium without gas evolution at 273 K). CBSE board sometimes asks: "Why is aryl diazonium more stable than alkyl diazonium?" ⇒ resonance with the ring.

Why this matters. The behaviour with HNO_2 is the classic "aryl vs alkyl" diagnostic for 1° amines. Combined with the carbylamine test (for the amine class) and Hinsberg (for 1°/2°/3°), the chemistry of unknown amines can be cracked in three steps.

> **Final Answer:** Aryl 1° amine → stable $ArN_2^+Cl^-$; alkyl 1° amine → alcohol with $N_2\uparrow$.

Q 9.14 **Give plausible explanation for each of the following:**

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

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

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

SOLUTION

Concept used. Three different acid/base/physical comparisons, each resting on a single electronic or H-bonding argument.

Step 1. **(i) Acidity of amines vs alcohols.** The acidity of $\mathrm{R{-}Z{-}H}$ depends on the stability of the conjugate base $\mathrm{R{-}Z^-}$. For an alcohol the conjugate base is $\mathrm{R{-}O^-}$ (alkoxide); for an amine it is $\mathrm{R{-}N{-}H^-}$ (amide ion). *Oxygen is more electronegative than nitrogen* (3.5 vs 3.0 on the Pauling scale), so $\mathrm{O^-}$ holds the negative charge much more comfortably than $\mathrm{N^-}$:

- pK_a of ethanol ≈ 16 (mildly acidic).
- pK_a of ethylamine ≈ 35 (essentially not acidic in water).

Comparing molecules of similar molar mass (e.g. ethanol vs propylamine, both around 60 g/mol), the alcohol is far more acidic because the alkoxide is much more stable than the corresponding aminide. Hence amines are less acidic.

Step 2. **(ii) Boiling point: 1° vs 3° amines.** Boiling point is largely set by intermolecular forces, the strongest of which (for similar molar mass) is **hydrogen bonding**. Hydrogen bonding requires an N–H (donor) and an N lone pair (acceptor).

- A primary amine has *two* N–H bonds per molecule: it can act as a donor twice, forming a 3D H-bond network. Boiling point is high.
- A tertiary amine has *zero* N–H bonds (the N is fully substituted): it can only *accept* H-bonds, not donate them. So tertiary amines form no H-bond network and rely only on dipole-dipole and London forces. Boiling point is much lower.

Numerical example: propan-1-amine ($\mathrm{CH_3CH_2CH_2NH_2}$, $M = 59$) b.p. $\approx 49\,^\circ$C; trimethylamine ($\mathrm{(CH_3)_3N}$, same $M = 59$) b.p. $\approx 3\,^\circ$C. A 46-°C difference at identical mass shows the dominant role of N–H hydrogen bonding.

Step 3. **(iii) Aliphatic amines $>$ aromatic amines in basicity.** Basicity reflects the availability of the nitrogen lone pair for protonation, plus stabilisation of the conjugate acid $\mathrm{R{-}NH_3^+}$.

- In aliphatic amines (e.g. $\mathrm{CH_3NH_2}$), alkyl groups push electrons toward N by the $+I$ effect, making the lone pair more available, and the conjugate acid $\mathrm{CH_3NH_3^+}$ is well solvated by water (three N–H donor bonds).
- In aromatic amines (e.g. aniline, $\mathrm{C_6H_5NH_2}$), the lone pair on N is conjugated into the benzene ring and delocalised over the o and p carbons. So the lone pair is much less available for protonation. Furthermore, on protonation the aniline loses this resonance stabilisation (the N is now sp^3 with no free lone pair), so the conjugate acid is destabilised relative to the free base. Both effects make aniline a weaker base than methylamine (pK_b 9.38 vs 3.38, a factor of 10^6).

> **Final Answer:** (i) Alkoxide $\mathrm{RO^-}$ is more stable than amide $\mathrm{RNH^-}$ because O is more electronegative than N, so alcohols are far more acidic. (ii) Primary amines form a 3D H-bond network via two N–H donors each; tertiary amines have no N–H donors and rely only on weaker forces. (iii) The aromatic ring delocalises the N lone pair in arylamines, lowering basicity by orders of magnitude.

♥ Three concepts, three observations

Electronegativity, H-bonding and lone-pair conjugation together explain almost all of the comparisons you meet in this chapter. Once you internalise these three knobs, no comparison problem can take more than two lines to answer.

EXPERT'S SOLUTION *: Riya Singh, M.Sc Chemistry, IIT Kanpur*

Quick reading. Three sub-questions, three different arguments:

Step 1. (i) *Electronegativity of O vs N*: more electronegative atoms hold a negative charge better; $\mathrm{RO^-}$ beats $\mathrm{RNH^-}$. Hence pK_a of alcohols is ~ 16, of amines ~ 35.

Step 2. (ii) *N–H donors available*: 1° amine has 2 donor N–H per molecule; 3° amine has 0. H-bond network strength drops, so the b.p. drops by tens of degrees between primary and tertiary at equal mass.

Step 3. (iii) *Resonance lock on the lone pair*: aniline's lone pair is part of the ring's π-system; on protonation the ring loses this delocalisation, so the conjugate acid is relatively unstable. Net basicity drops by 6 pK_b units compared to methylamine.

Why this matters. These are the three favourite comparison questions for boards. Knowing the one-line reason for each is enough to write a complete answer worth 3–4 marks.

> **Final Answer:** (i) Electronegativity gap. (ii) Number of donor N–H bonds. (iii) Lone-pair delocalisation into the ring.

Key Takeaways

- **Classification** of amines (1°, 2°, 3°) depends only on the number of carbon arms on N; the rest of each arm can be anything.
- **IUPAC nomenclature**: pick the largest carbon arm as the parent alkane $\rightarrow$ replace $-e$ with $-amine$; the rest of the arms on N are N-prefixes; aniline is the retained parent

for arylamines.

- Basicity in water depends on three competing knobs: $+I$ from alkyls, lone-pair conjugation into rings, and H-bond solvation of $\mathrm{RNH_3^+}$. The aqueous order ($2^\circ > 1^\circ > 3^\circ > \mathrm{NH_3}$ for methyl) is the compromise; in the gas phase only $+I$ matters, so the order becomes monotonic ($3^\circ > 2^\circ > 1^\circ > \mathrm{NH_3}$).
- **Aniline** is a much weaker base than methylamine ($\sim 10^6$ times) because its lone pair is delocalised into the ring.
- Preparation: **Gabriel** synthesis gives pure 1° alkyl amines via $\mathrm{S_N2}$ on phthalimide anion; cannot give aryl amines (no $\mathrm{S_N2}$ on aryl halides). **Hofmann bromamide** converts $\mathrm{R{-}CONH_2}$ to $\mathrm{R{-}NH_2}$ losing one carbon. Direct **ammonolysis** of $\mathrm{R{-}X}$ is messy.
- **Hinsberg's test** cleanly separates the three amine classes by solubility of the sulphonamide in alkali. **Carbylamine test** identifies 1° amines by the foul smell of $\mathrm{R{-}NC}$.
- **Diazonium chemistry** is the synthetic switchboard for aromatic substitution: $-\mathrm{N_2^+}$ can be replaced by $-\mathrm{Cl}$, $-\mathrm{Br}$, $-\mathrm{I}$, $-\mathrm{F}$, $-\mathrm{CN}$, $-\mathrm{OH}$, $-\mathrm{H}$, or $-\mathrm{N{=}N{-}Ar}$ (azo dye). Aryl diazonium salts are stable at 0–5 °C; aliphatic ones fall apart at once with loss of $\mathrm{N_2}$.
- Protection of $-\mathrm{NH_2}$ as $-\mathrm{NHCOCH_3}$ (acetylation) is often needed before halogenation, nitration or sulphonation of aniline to avoid over-substitution.

End of Chapter 9 Exercises