



Collegedunia NCERT Formula Sheet

The Ultimate Formula Reference for Class 12 (12th) Chemistry — NCERT 2026-27

Chapter 9: Amines

Classification · Nomenclature · Preparations · Basicity · Chemical Reactions ·
Diazonium Salts · Azo Coupling · JEE & NEET

Quick Reference — Amine Classes, Symbols & Key Data

Symbol / Class	Type	General formula & key feature
R-NH ₂	1° (primary) amine	One H of NH ₃ replaced by R/Ar; e.g. CH ₃ NH ₂ , C ₆ H ₅ NH ₂
R ₂ NH	2° (secondary) amine	Two H of NH ₃ replaced; simple if R = R', mixed otherwise
R ₃ N	3° (tertiary) amine	All three H of NH ₃ replaced; no N-H bond
R ₄ N ⁺ X ⁻	Quaternary ammonium salt	All four valences of N as N-C; ionic salt; e.g. (CH ₃) ₄ N ⁺ I ⁻
Ar-NH ₂	Aryl (aromatic) amine	-NH ₂ on benzene ring; e.g. aniline C ₆ H ₅ NH ₂
C-N-C bond angle	≈ 108° (CH ₃) ₃ N	N is sp ³ , pyramidal; one lone pair on N (Fig. 9.1)
pK _b (NH ₃)	4.75	Reference base; in water at 298 K
pK _b (CH ₃ NH ₂)	3.38	Stronger base than NH ₃ (+I of -CH ₃)
pK _b ((CH ₃) ₂ NH)	3.27	Strongest among methylamines in water
pK _b ((CH ₃) ₃ N)	4.22	Weaker than 2° in water (solvation > +I effect)
pK _b (C ₆ H ₅ NH ₂)	9.38	Much weaker than NH ₃ — lone pair delocalised into ring
pK _b ((C ₆ H ₅) ₂ NH)	13.21	Two aryl groups; almost neutral
pK _b (C ₆ H ₅ NHCH ₃)	9.30	N-methylaniline; slightly stronger than aniline
b.p. CH ₃ NH ₂	266.8 K	1° amine; N-H...N H-bonding
b.p. (CH ₃) ₃ N	276 K	3° amine; no N-H, only dipole-dipole
Aniline	b.p. 457 K	Colourless oil → brown on air oxidation; slightly soluble in H ₂ O
HNO ₂ source	NaNO ₂ + HCl, 273–278 K	Generates HNO ₂ <i>in situ</i> ; used for amine differentiation
Diazonium salt	Ar-N ₂ ⁺ X ⁻	Stable below 278 K; loses N ₂ readily; drawn as Ar-N≡N ⁺ X ⁻

1 Structure & Classification of Amines (9.1)

NCERT Section 9.1 derives every amine as an N-alkyl or N-aryl substituted ammonia. The N atom is sp³-hybridised with one lone pair, so amines are pyramidal (Fig. 9.1) and act both as Lewis bases (donate lone pair) and as Brønsted bases (accept H⁺).

Classification (9.1.1)

Replace 1, 2 or 3 H atoms of NH₃ by R/Ar to get:

- **Primary (1°):** R-NH₂ (e.g. CH₃NH₂, C₆H₅NH₂).
- **Secondary (2°):** R₂NH or RR'NH (e.g. (CH₃)₂NH, C₆H₅NHCH₃).
- **Tertiary (3°):** R₃N or RR'R''N (e.g. (CH₃)₃N).

- **Quaternary ammonium salt:** $R_4N^+X^-$ (e.g. $(CH_3)_4N^+I^-$).

Simple amines have identical R groups, **mixed** amines have different R groups. Counting rule: *number of H atoms of NH_3 replaced by R/Ar = degree of the amine.*

Structure of the N atom in amines (9.1.2, Fig. 9.1)

N is sp^3 -hybridised: three σ -bonds (to H/C) plus one lone pair occupy a roughly tetrahedral arrangement, so amines are **pyramidal**.

Bond-angle data: NH_3 $\angle H-N-H = 107^\circ$; $(CH_3)_3N$ $\angle C-N-C \approx 108^\circ$; aniline C-N-H plane $\approx 108-112^\circ$ — close to tetrahedral 109.5° but compressed by lone-pair repulsion.

In aniline, the N-H plane is sometimes drawn *flatter* than in alkylamines because the lone pair is partially in a p -type orbital that conjugates into the ring. The lone pair makes amines **nucleophilic and basic** — the central fact that drives the entire chapter.

Why pyramidal, not planar

A planar N would mean sp^2 + the lone pair in a pure p -orbital. The sp^3 pyramidal geometry is energetically preferred because (a) all four electron pairs are kept farthest apart, and (b) lone pair in sp^3 has more s -character ($\approx 25\%$) so it sits closer to N. **Inversion** of the pyramid is fast at room temperature — like an umbrella flipping — so chiral amines (3 different R + lone pair) cannot be resolved.

2 Nomenclature of Amines (9.2)

NCERT Section 9.2 sets out both *common* (alkyl + amine) and IUPAC (*N*-substituent prefix + parent alkanamine / benzenamine) systems. Mastering both is critical for naming/identification questions.

Common system (9.2)

Rule: list R groups in alphabetical order + word “amine” (one word for 1°).

- $CH_3NH_2 \rightarrow$ methylamine; $(CH_3)_2NH \rightarrow$ dimethylamine; $(CH_3)_3N \rightarrow$ trimethylamine.
- $CH_3NHC_2H_5 \rightarrow$ ethylmethylamine.
- $C_6H_5NH_2 \rightarrow$ aniline (retained IUPAC + common).

Use *di-*, *tri-* for identical R groups; for unequal R groups, alphabetical order with no multiplier.

IUPAC system (Table 9.1)

Aliphatic 1° : parent alkane \rightarrow alkan-**amine** (locant inserted before -amine).

- $CH_3CH_2CH_2NH_2 \rightarrow$ propan-1-amine.
- $(CH_3)_2CHNH_2 \rightarrow$ propan-2-amine.

Aromatic 1° : benzenamine (= aniline).

2° & 3° : *N*-(smaller chain)-*N*(...)-(parent chain)-amine.

- $CH_3NHC_2H_5 \rightarrow$ *N*-methylethan-1-amine (parent = ethane, larger).
- $(CH_3)_2NC_2H_5 \rightarrow$ *N,N*-dimethylethanamine.
- $C_6H_5NHCH_3 \rightarrow$ *N*-methylbenzenamine (\equiv *N*-methylaniline).

Choose the longest carbon chain as the parent; the *smaller* R group(s) on N go as *N*-prefix. Locant of $-NH_2$ on parent gets the lowest number.

Don't confuse *N*-methylaniline with *p*-toluidine

N-methylaniline = C₆H₅-NH-CH₃ (-CH₃ on N, 2° amine). *p*-Toluidine = 4-CH₃-C₆H₄-NH₂ (-CH₃ on ring, 1° amine). Position of the methyl group decides the class.

3 Preparation of Amines (9.3)

Section 9.3 lists six standard routes. Each starts from a readily available functional group (-NO₂, -CN, -CONH₂, R-X) and ends at an amine. Memorise the reagent + degree of amine produced.

Reduction of nitro compounds (9.3.1)**General:**

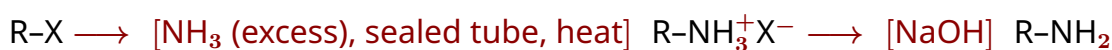
Two common ways: catalytic H₂ over Pd/Pt/Ni in alcohol (gives free amine directly) or metal/acid (gives the ammonium salt; basify with NaOH to release amine). **Fe/HCl** is industrial — FeCl₂ regenerates HCl, making it catalytic in HCl.

Reduction of nitriles (9.3.2) — Mendius reduction

Adds two H₂ across C≡N. **Carbon count goes up by 1** (R-X → R-CN → R-CH₂NH₂) — this is the standard *ascent of series* for converting RX into the next-higher 1° amine. Gives only **1° amine**, never 2° or 3°.

Reduction of amides (9.3.3)

Distinct from Hoffmann bromamide: in amide reduction the C of -CONH₂ is reduced from C=O to CH₂, so the **same number of carbons** are retained between starting amide and product amine. LiAlH₄ is the only common reagent. Gives 1° amine.

Ammonolysis of alkyl halides (9.3.4)**Successive alkylation chain:**

Reactivity of R-X: R-I > R-Br > R-Cl.

Mechanism = S_N2 by NH₃ on R-X. Each amine product is itself nucleophilic and competes for more R-X, so the reaction gives a **mixture of 1°, 2°, 3° amines and quaternary salt**. Using a large excess of NH₃ favours the 1° amine.

Gabriel phthalimide synthesis (9.3.5) — pure 1° amine**Three steps:**

(2) K-phthalimide + R-X \longrightarrow [Δ] N-alkylphthalimide + KX.

(3) N-alkylphthalimide \longrightarrow [NaOH/H₂O or H₃O⁺, Δ] R-NH₂ + phthalate.

Phthalimide N-H is acidic (two adjacent C=O); KOH deprotonates it to a soft nucleophile that does S_N2 once on R-X. Hydrolysis releases the pure 1° amine. **Restriction: aromatic amines (Ar-NH₂) cannot be made this way** — aryl halides do not undergo S_N2 in step (2).

Hoffmann bromamide degradation (9.3.6)

R-CONH₂ + Br₂ + 4 NaOH \longrightarrow [] R-NH₂ + Na₂CO₃ + 2 NaBr + 2 H₂O

Carbon count drops by 1 (amide R-CONH₂ has $n + 1$ C, product amine R-NH₂ has n C). The reaction proceeds via an N-bromoamide \rightarrow nitrene-like intermediate \rightarrow **isocyanate (R-N=C=O)** \rightarrow hydrolysis to R-NH₂. Works for both alkyl and aryl amides; gives **only 1° amine**.

JEE/NEET Extension — distinguishing carbon-count rules

- Ammonolysis, amide reduction, Gabriel: *same* carbon count.
 - Nitrile reduction (Mendius): carbon count goes *up* by 1 (R-X \rightarrow R-CH₂NH₂).
 - Hoffmann bromamide: carbon count goes *down* by 1 (R-CONH₂ \rightarrow R-NH₂).
- Use this to spot the right method in JEE multi-step synthesis questions.

"GAS-HAN" — the six amine prep methods

Gabriel phthalimide, **A**mmunolysis of R-X, **S**n/HCl — reduction of nitro, **H**offmann bromamide, **A**midate reduction (LiAlH₄), **N**itrile reduction (Mendius). Six routes — learn one carbon-count change per pair.

4 Physical Properties — Boiling Points & Solubility (9.4)

Section 9.4 explains how N-H bonds drive amine boiling points and water solubility: 1° has two N-H, 2° has one, 3° has none. Hence the b.p. order **1° > 2° > 3°** for equal carbon count.

Boiling-point trend (9.4)

For amines of similar molecular mass:

R-NH₂ (1°) > R₂NH (2°) > R₃N (3°).

Example (M.W. \approx 59):

n-propylamine (b.p. 322 K) > ethyl(methyl)amine (310 K) > trimethylamine (276 K).

Comparison with neighbours:

alkane < ether < amine < alcohol < carboxylic acid.

Strength of intermolecular H-bonding rises with number of N-H bonds. Tertiary amines have *no* N-H so they only exchange dipole-dipole forces — their b.p. falls below comparable alcohols and even some 2° amines.

Water solubility

- Lower amines (C_1 – C_3) of all three classes are **miscible** with water — they form $N \cdots H-O$ and $O \cdots H-N$ bonds.
- Solubility **decreases as the carbon chain grows** (hydrophobic R dominates).
- Aniline and higher aromatic amines are only slightly soluble in water but freely soluble in organic solvents (alcohol, ether, benzene).

Smell: lower amines smell of fish/ammonia; many higher amines have foul odours — putrescine ($NH_2(CH_2)_4NH_2$) and cadaverine ($NH_2(CH_2)_5NH_2$) are formed in decaying protein.

5 Basic Character of Amines (9.5)

Section 9.5 is the most heavily tested topic in this chapter. Amines accept H^+ via their lone pair: stronger lone-pair availability \Rightarrow stronger base \Rightarrow larger K_b / smaller pK_b .

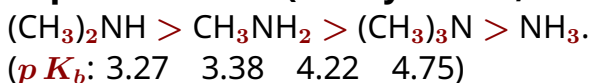
Basicity in water — K_b & pK_b (9.5.1)

$$K_b = \frac{[R-NH_3^+][OH^-]}{[R-NH_2]} \quad pK_b = -\log_{10} K_b$$

Conjugate-acid pK_a data (methylamines, 298 K):

- $CH_3NH_3^+$: $pK_a = 10.62$ • $(CH_3)_2NH_2^+$: $pK_a = 10.77$
- $(CH_3)_3NH^+$: $pK_a = 9.80$ • NH_4^+ : $pK_a = 9.25$

Stronger base \Rightarrow larger $K_b \Rightarrow$ **smaller** pK_b . Conjugate-acid relation: $pK_a(RNH_3^+) + pK_b(RNH_2) = 14$ at 298 K — so the conjugate-acid pK_a order matches the basicity order.

Basicity order in water (9.5.1, Table 9.3)**Aliphatic amines (methyl series, in water):****Ethyl series in water:****Aromatic vs aliphatic:**

Aryl amines are far weaker bases than aliphatic amines or even NH_3 because the N lone pair is delocalised into the ring (Fig. 9.3, five resonance structures), so it is less available for H^+ .

Three structural factors (9.5.1)

The basicity of an amine in aqueous solution is a balance of:

(1) Inductive (+I) effect: alkyl R groups push electron density onto N \Rightarrow increase basicity. So 3° should be most basic in gas phase: $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$.

(2) Solvation (H-bonding) of conjugate acid: $R-NH_3^+$ (3 N-H) $>$ $R_2NH_2^+$ (2 N-H) $>$ R_3NH^+ (1 N-H) in stabilisation by water. More H-bonds \Rightarrow more stable cation \Rightarrow stronger base.

(3) Steric hindrance: bulky R groups around N hinder protonation, reducing basicity in 3° amines.

In water the three effects oppose each other. Net order for methylamines: $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$.

Why aryl amines are weak bases

Aniline \Rightarrow five resonance structures (Fig. 9.3): in two of them the N lone pair sits on the *ortho* or *para* ring carbon, so it is **not available** to grab H^+ .

Energy comparison:

- Aniline: 5 resonance structures (lone-pair delocalised).
- Anilinium ($PhNH_3^+$): only 2 (Kekulé) resonance structures.

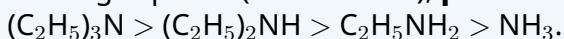
Loss of resonance stabilisation on protonation makes aniline much weaker than CH_3NH_2 .

Ring substituent effect (anilines, *p*-substituted):

- *p*- CH_3 (+I, weak +H): **more basic** than aniline (*p*-toluidine $pK_b \approx 8.92$).
- *p*- OCH_3 (+M dominates): **more basic** than aniline.
- *p*- NH_2 (strong +M): clearly more basic than aniline.
- *p*-Cl, *p*-Br (–I dominates over weak +M): **less basic** than aniline.
- *p*- NO_2 , *p*-CN (strong –M / –I): **much less basic** (*p*-nitroaniline $pK_b = 13.0$, almost neutral).

Gas phase vs solution

In the gas phase (no solvation), **pure +I effect** determines basicity:



In water, solvation reshuffles the order so that 2° often beats 3° . NCERT presents only the aqueous order — but JEE often asks for the gas-phase order, so remember both.

6 Chemical Reactions of Amines (9.6)

Section 9.6 collects the reactions of the lone-pair on N (alkylation, acylation, with HNO_2 , carbylamine) and the ring reactions of arylamines (electrophilic substitution). All of these are NCERT-exam staples.

Salt formation with mineral acids (9.6)



Every amine (1° , 2° , 3°) is protonated by HCl , H_2SO_4 , HNO_3 etc. to give a water-soluble ammonium salt. **Adding NaOH regenerates the free amine** — exploited in extraction (basify \rightarrow amine separates as oil/solid; acidify \rightarrow salt dissolves back).

Alkylation (9.6.1)

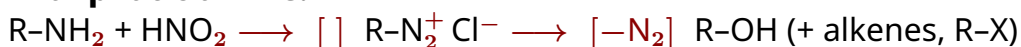
Each amine is more nucleophilic than the last, so the reaction does not stop — always gives a **mixture**. Same logic as in ammonolysis (Section 9.3.4).

Acylation (9.6.2)

1° and 2° amines give substituted amides; 3° amines (no N-H) **do not acylate**. Pyridine traps the HCl byproduct; acetanilide is itself a substrate-protector in aniline ring chemistry.

Carbylamine test (9.6.3) — 1° amine only

Foul-smelling **isocyanide (R-NC)** is the test for any 1° amine (alkyl or aryl). 2° and 3° amines give no isocyanide. The carbylamine reaction is a classical distinguishing test.

Reaction with HNO₂ (nitrous acid) (9.6.4)**1° aliphatic amine:****1° aromatic amine (273–278 K):**

2° amine (alkyl or aryl): $R_2NH + HNO_2 \rightarrow R_2N-N=O$ (yellow *N*-nitrosamine).

3° amine: $R_3N + HNO_2 \rightarrow R_3NH^+NO_2^-$ (no reaction beyond salt formation).

HNO₂ is the master distinguishing reagent — 1° aliphatic effervesces N₂, 1° aromatic gives stable diazonium, 2° gives yellow oil, 3° just neutralises. Always written with NaNO₂ + HCl at 273–278 K.

Hinsberg test (9.6.5) — benzenesulphonyl chloride

C₆H₅SO₂Cl (*Hinsberg reagent*) reacts with:

- **1° amine:** gives *N*-alkyl benzenesulphonamide — soluble in KOH (N-H is acidic due to two adjacent -SO₂).
- **2° amine:** gives *N,N*-dialkyl benzenesulphonamide — insoluble in KOH (no N-H).
- **3° amine:** no reaction (no N-H to lose).

Tests in one tube: dissolve all three; treat with PhSO₂Cl + KOH. 1° dissolves clear; 2° floats as a solid; 3° remains as a separate liquid layer.

Electrophilic substitution on arylamine (9.6.6)

-NH₂ is **strongly activating** and **ortho/para directing**.

Bromination of aniline:

$C_6H_5NH_2 + 3 Br_2 \longrightarrow [H_2O]$ 2,4,6-tribromoaniline + 3 HBr
(White ppt, no catalyst needed.)

Nitration:

$C_6H_5NH_2 \longrightarrow [conc. HNO_3/H_2SO_4]$ 47% m-nitroaniline + 51% p- + 2% o-
(In strong acid, $-NH_2$ becomes $-NH_3^+$ which is **meta-directing** — hence m-isomer forms.)

To make pure p-nitroaniline, protect $-NH_2$ as acetanilide:

$C_6H_5NH_2 \longrightarrow [(CH_3CO)_2O]$ $C_6H_5NHCOCH_3 \longrightarrow [HNO_3/H_2SO_4]$ p-O₂N-
 $C_6H_4NHCOCH_3 \longrightarrow [H_3O^+]$ p-nitroaniline

Sulphonation:

$C_6H_5NH_2 \longrightarrow [conc. H_2SO_4, 453-473 K]$ sulphanilic acid (p-aminobenzenesulphonic acid, zwitterion).

Friedel-Crafts (alkylation/acylation) **fails on aniline** — the basic $-NH_2$ complexes with $AlCl_3$, deactivating the ring. Acylate first (acetanilide) to do F-C reactions cleanly.

 $-NH_2$ becomes meta-directing in strong acid

In conc. HNO_3/H_2SO_4 aniline is protonated to the anilinium ion ($-NH_3^+$). The cation is electron-withdrawing ($-I$), so it **deactivates and meta-directs**. That is why direct nitration of aniline gives 47% *meta* isomer, not the expected *ortho/para*. Protecting $-NH_2$ as acetanilide preserves the +M activating, *p*-directing character.

7 Diazonium Salts — Preparation & Properties (9.7)

Section 9.7 introduces the diazonium salt $Ar-N_2^+X^-$ — the most synthetically useful organic intermediate in benzene chemistry. It is made cold from a 1° aromatic amine and acts as a placeholder for almost any other functional group on the ring.

Preparation — Diazotisation (9.7.1)

$C_6H_5NH_2 + NaNO_2 + 2 HCl \longrightarrow [273-278 K]$ $C_6H_5N_2^+Cl^- + NaCl + 2 H_2O$

Generates HNO_2 *in situ* ($NaNO_2 + HCl$). Below 278 K (0–5 °C) the diazonium ion is stable; above 283 K it decomposes to phenol + N_2 . **Only 1° aromatic amines** give stable diazonium salts; 1° aliphatic amines give unstable $R-N_2^+$ that decomposes immediately.

Structure & stability

$Ar-N_2^+Cl^-$ drawn as $Ar-N \equiv N^+ Cl^-$.

Stability comes from **resonance delocalisation** of the positive charge into the benzene ring: positive charge spreads from N to the *ortho* and *para* ring carbons, with $N=N$ shifting to $N-N$ along the way.

Solid $Ar-N_2^+X^-$ is **explosive when dry**; always handle as the cold aqueous solution. Aliphatic $R-N_2^+$ has no such ring resonance, hence decomposes immediately.

8 Reactions of Diazonium Salts — Loss of N₂ (9.8)

Section 9.8 lists the substitution reactions of Ar-N₂⁺, where N₂ is the leaving group. Almost every common aromatic functional group (-Cl, -Br, -I, -CN, -F, -OH, -H) can be installed via this route — this is why diazonium chemistry is central to aromatic synthesis.

Sandmeyer reactions — Cl, Br, CN (9.8.1)



Catalysed by Cu(I) salts; mechanism is radical. The Cu salt provides the nucleophile (Cl⁻/Br⁻/CN⁻). Yields are generally 70–90%. Note: Ar-CN can be hydrolysed to Ar-COOH (carbon count goes up by 1 from starting Ar-NH₂).

Gattermann reaction — Cu/HX (9.8.1)



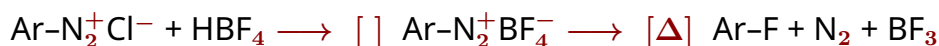
Same outcome as Sandmeyer but uses **copper metal (Cu⁰) in halogen acid** instead of Cu(I) salt. Gives slightly lower yields and is simpler to set up; Sandmeyer is generally preferred at industrial scale.

Replacement by I and F (9.8.1)

Iodination (no catalyst needed):



Balz-Schiemann fluorination:



Direct halogenation of benzene gives only Cl/Br products via electrophilic substitution; **the Ar-F and Ar-I aromatics are only conveniently prepared via the diazonium route.**

Replacement by -OH & -H

Hydroxylation (Ar-OH):



Reduction (Ar-H):



Hydrolysis to phenol works on warming (above 283 K). Reduction to Ar-H is the only way to **remove an -NH₂/-NO₂ group from a benzene ring** (used as a directing handle that is then deleted).

JEE/NEET Extension — diazonium retrosynthesis

Whenever a target arene has Ar-F, Ar-I, Ar-CN, or a specific substitution pattern that direct E.A.S. can't deliver, **work backwards through the diazonium salt:** target \leftarrow Ar-N₂⁺ \leftarrow Ar-NH₂

← Ar-NO₂ ← benzene (HNO₃/H₂SO₄). This is the standard 5-step JEE problem.

9 Diazonium Coupling & Azo Dyes (9.8.2)

Section 9.8.2 covers reactions where Ar-N₂⁺ keeps the N₂ unit and adds it to another aromatic ring as -N=N-. These *azo* compounds are the basis of dye chemistry — bright yellow/orange/red colours from extended N=N-C=C conjugation.

Coupling with phenol (alkaline pH 9-10)



(*p*-hydroxyazobenzene, orange dye)

Couples preferentially at the *para* position; coupling at *ortho* occurs if *para* is blocked. Alkaline conditions deprotonate phenol to PhO⁻, the more reactive coupling component.

Coupling with aniline (mildly acidic pH 4-5)



(*p*-aminoazobenzene, yellow dye)

Slightly acidic conditions: too acidic protonates -NH₂ to -NH₃⁺ (ring deactivated, no coupling); too basic destroys Ar-N₂⁺. The optimum pH window is 4-5.

Why azo compounds are coloured

The -N=N- bridge connects two aromatic rings into a conjugated π-system. The extended chromophore absorbs in the visible region (350-550 nm), so transmitted light appears **yellow** → **orange** → **red** depending on the substituents on the rings. Pushing electron-donor groups (-NH₂, -OH) deeper into the conjugation shifts absorption to longer wavelengths (bathochromic shift).

Diazonium as a synthetic "hub"

From a single Ar-NH₂ (made from Ar-NO₂) you can build:

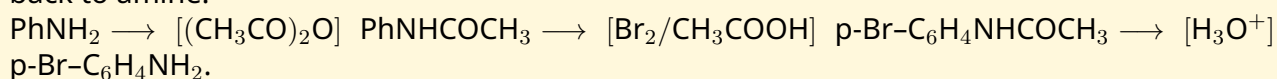
- Ar-Cl, Ar-Br (Sandmeyer/Gattermann);
- Ar-I (KI), Ar-F (HBF₄/Δ);
- Ar-CN → Ar-COOH (hydrolysis);
- Ar-OH (H₂O/Δ);
- Ar-H (H₃PO₂);
- Ar-N=N-Ar' azo dyes (coupling).

The diazonium ion is the most versatile synthetic handle in aromatic chemistry — almost any group can be installed in two steps via Ar-N₂⁺. This is why NCERT devotes a separate section to it.

JEE/NEET Extension — selective *para* bromination of aniline

To make pure *p*-bromoaniline, **acetylate first** to acetanilide — this lowers the activating power of -NH₂ from very-strong to moderate, so monobromination gives selectively *p*-Br. Hydrolyse

back to amine:



10 Quick Recap — Distinguishing Tests

A condensed lookup for the most-asked NCERT distinguishing tests on amines.

Test / reagent	1°	2° & 3° behaviour
HNO_2 ($\text{NaNO}_2 + \text{HCl}$, 273–278 K)	$\text{R-NH}_2 \rightarrow \text{N}_2 \uparrow + \text{R-OH}$ (alkyl); Ar-N_2^+ stable (aryl)	2°: yellow oil $\text{R}_2\text{N-NO}$; 3°: only salt formation
Carbylamine ($\text{CHCl}_3 + \text{KOH}/\Delta$)	Foul-smelling R-NC (positive)	No reaction
Hinsberg ($\text{PhSO}_2\text{Cl} + \text{KOH}$)	PhSO_2NHR — soluble in KOH	2°: PhSO_2NR_2 insoluble in KOH ; 3°: no reaction
Acylation ($\text{R}'\text{COCl}$, pyridine)	$\text{R-NHCOR}'$ (amide)	2°: $\text{R}_2\text{NCOR}'$; 3°: no reaction
Acid/base solubility	All amines soluble in dilute HCl	3° amine $\rightarrow \text{R}_3\text{NH}^+\text{Cl}^-$, regenerated on adding NaOH
$\text{Br}_2/\text{H}_2\text{O}$ on aniline	White ppt of 2,4,6-tribromoaniline (only Ar-NH_2)	No ppt for aliphatic 1° amines

Ascent vs descent of series

Ascent (+1 C): $\text{R-X} \rightarrow \text{R-CN} \rightarrow \text{R-CH}_2\text{NH}_2$ (Mendius reduction).

Descent (–1 C): $\text{R-CONH}_2 \rightarrow \text{R-NH}_2$ (Hoffmann bromamide).

Same C count: amide reduction (LiAlH_4) and Gabriel synthesis.