

Chapter 9 · Amines

CBSE Class 12 Chemistry (043) · Organic · Unit 9 = 6 marks · Ultimate Revision Sheet

60-SECOND RECALL

Basicity in water	$2^\circ > 1^\circ > 3^\circ > \text{NH}_3$ (for ethyl; the order is a balance of three effects)
Aromatic vs aliphatic	Aniline is much WEAKER — lone pair delocalised into the ring
Carbylamine test	1° amine only → foul-smelling isocyanide
Hinsberg	Distinguishes 1°, 2°, 3°
Gabriel	Gives pure 1° amine — fails for aromatic amines
Hofmann bromamide	Amide → amine with ONE carbon less
Diazotisation	$\text{NaNO}_2 + \text{HCl}$, 273–278 K
Coupling	Diazonium + phenol/aniline → azo dye (orange/yellow)

1. Structure and Classification

THE BASICS Amines are derivatives of ammonia with one, two or three H atoms replaced — 1°, 2°, 3°. Nitrogen is sp^3 and the shape is **pyramidal** with a lone pair.
Boiling points: $1^\circ > 2^\circ > 3^\circ$, because 3° amines have **no N–H bond** and therefore **no** intermolecular hydrogen bonding.

2. Preparation

THE FOUR METHODS

1. **Reduction of nitro compounds:** H_2/Pd , or Sn/HCl — nitrobenzene → aniline.
2. **Ammonolysis of alkyl halides:** gives a mixture of 1°, 2°, 3° and quaternary salt. Using a large excess of ammonia favours the 1° amine.
3. **Gabriel phthalimide synthesis:** gives a pure primary amine. It cannot be used for aromatic amines, because aryl halides do not undergo the required nucleophilic substitution with the phthalimide anion.
4. **Hofmann bromamide degradation:** amide + Br_2/KOH → primary amine with **one carbon fewer**. Watch for questions that need a carbon removed — this is the reaction.

Also: reduction of nitriles (LiAlH_4) gives an amine with the **same** number of carbons.

3. Basicity — the heart of the chapter

THE THREE COMPETING EFFECTS

1. **+I effect:** alkyl groups push electron density onto N → **more basic**.
2. **Steric hindrance:** too many bulky groups block the proton → **less basic**.
3. **Solvation:** the more N–H bonds the cation has, the better it is **stabilised by hydrogen bonding with water** → more basic.

Net result in water: $2^\circ > 1^\circ > 3^\circ > \text{NH}_3$ for ethylamines. In the gas phase, where solvation is absent, it is simply $3^\circ > 2^\circ > 1^\circ$.

WHY ANILINE IS A WEAK BASE — guaranteed question In aniline, the lone pair on nitrogen is delocalised into the benzene ring by resonance, so it is less available for donation to a proton. The anilinium ion formed has no such stabilisation.

Order: aliphatic amine > ammonia > aniline.

Substituents: electron-donating groups ($-\text{CH}_3$, $-\text{OCH}_3$) increase basicity; electron-withdrawing groups ($-\text{NO}_2$) decrease it sharply. So *p*-toluidine > aniline > *p*-nitroaniline.

4. Reactions

THE IDENTIFICATION TESTS Carbylamine (isocyanide) test: amine + CHCl_3 + alcoholic KOH $\rightarrow$ foul-smelling isocyanide. Given only by 1° amines, aliphatic or aromatic.

Hinsberg's test with benzenesulphonyl chloride: 1° gives a product soluble in alkali (it still has an acidic N-H); 2° gives one insoluble in alkali; 3° does not react.

With HNO_2 : 1° aliphatic $\rightarrow$ alcohol + N_2 gas; 1° aromatic $\rightarrow$ diazonium salt; $2^\circ \rightarrow$ nitrosamine (yellow oily); $3^\circ \rightarrow$ salt.

ACYLATION AND RING SUBSTITUTION Acetylation of aniline with acetic anhydride gives acetanilide. This is used to protect the $-\text{NH}_2$ group before nitration or bromination, because the free amino group is so strongly activating that it would give the trisubstituted product.

Aniline + bromine water $\rightarrow$ 2,4,6-tribromoaniline (white precipitate) — the activating $-\text{NH}_2$ makes control impossible without protection.

Aniline does not undergo Friedel-Crafts, because AlCl_3 bonds to the lone pair on nitrogen, making it a deactivating group.

5. Diazonium Salts

PREPARATION AND THE REACTION MAP Diazotisation: aniline + NaNO_2 + HCl at 273–278 K $\rightarrow$ benzenediazonium chloride. The low temperature is essential — the salt decomposes above about 278 K.

Reagent	Product
CuCl/HCl or CuBr/HBr (Sandmeyer)	Chlorobenzene / bromobenzene
Cu powder + HX (Gattermann)	Chloro / bromobenzene
KI	Iodobenzene
HBF_4, then heat	Fluorobenzene
H_2O, warm	Phenol
H_3PO_2 or ethanol	Benzene (removes the group entirely)
Phenol / aniline in mild alkali	Azo dye — coupling reaction

Coupling occurs at the *para* position and produces intensely coloured **azo compounds** used as dyes.

TRAP The diazonium route is the **only practical way to put -I or -F on a benzene ring**, and the only way to make phenol or benzene from aniline. Any question asking for an aryl iodide almost certainly wants diazotisation.

Diazonium salt — the junction box



$CuCl / HCl$
chlorobenzene **SANDMEYER**

$CuBr / HBr$
bromobenzene **SANDMEYER**

KI , warm
iodobenzene **no copper**

H_2O , warm
phenol N_2 gas released

H_3PO_2
benzene $-N_2^+ \rightarrow H$

phenol / OH^-
orange azo dye **COUPLING, para**

WHAT THE MAP IS FOR Temperature is part of the answer. The salt is made at 273–278 K; above 278 K it decomposes to phenol on its own.

This route is the **only practical way to put -I or -F on a benzene ring**, and the only way to make phenol or benzene from aniline. Any question asking for an aryl iodide almost certainly wants diazotisation.

Basicity in water: $2^\circ > 1^\circ > 3^\circ > NH_3$ for aliphatic amines — 3° drops because it is too crowded to hydrate. **Aromatic amines are far weaker:** the lone pair is delocalised into the ring.

Carbylamine test ($CHCl_3 + alc. KOH$, foul smell) is given by **1° amines only**; Hinsberg's test separates all three.

6. Question Triggers what the reagent tells you

Reagent / observation	Conclusion
$CHCl_3 + alc. KOH$, foul smell	1° amine (carbylamine test)
Br_2/KOH on an amide	Hofmann → amine, one carbon less
Phthalimide route	Gabriel → pure 1° aliphatic amine
$NaNO_2 + HCl$ at 273–278 K	Diazonium salt
Orange dye formed	Coupling reaction

CuCl / HCl

"why is aniline a weaker base"

"why acetylate before nitration"

SandmeyerLone pair **delocalised into the ring**To **control** the strongly activating -NH_2 **MOST-ASKED BOARD QUESTIONS**

1. [3M] Arrange amines in order of **basic strength** and justify, in water and in the gas phase.
2. [3M] Write the **Gabriel** and **Hofmann bromamide** reactions; why does Gabriel fail for aromatic amines?
3. [3M] Give the reactions of **benzenediazonium chloride** with any three reagents.
4. [2M] How do you distinguish 1° , 2° and 3° amines?
5. [2M] Why is **aniline acetylated** before nitration?
6. [1M] Which test is given only by primary amines? $\rightarrow$ **Carbylamine**

THE HABIT THAT SCORES — Draw the diazonium reaction map as a wheel with the salt at the centre. Almost every aromatic conversion question in the paper — aniline to phenol, to iodobenzene, to benzene, to a dye — is one spoke of that wheel.