



LOGIC BLOOM · CHEMISTRY · CLASS 12

Amines

Structure · basicity · preparation · reactions · diazonium salts

NEET, JEE Main and JEE Advanced

Every question in this chapter asks one thing: what is the nitrogen's lone pair doing? Free, it makes a strong base and a good nucleophile. Shared with a ring or a C=O, it does far less.

13 Sections

16 Diagrams

Advanced Tier

Practice Set

Fact Sheet

Contents

1	Structure and Classification	<i>a pyramid with a lone pair</i>
2	Names and Isomers	<i>common, IUPAC, and how to count</i>
3	Preparation	<i>six routes and the carbon count</i>
4	Physical Properties	<i>hydrogen bonds decide boiling point</i>
5	Basicity	<i>three effects, one order</i>
6	Reactions of the Amino Group	<i>acylation, carbylamine, HNO_2, Hinsberg</i>
7	Aniline and the Ring	<i>too reactive, so protect it</i>
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9	Basicity Beyond the Basics	<i>JEE Advanced tier begins</i>
10	Mechanisms	<i>Hofmann, carbylamine, diazotisation</i>
11	Synthesis Strategy	<i>use N as a temporary tool</i>
12	Advanced Worked Problems	<i>five problems, five techniques</i>
13	Practice Set	<i>fifteen questions with traps explained</i>
★	One-Page Fact Sheet	<i>every result for revision day</i>

How to Read This Set

Sections 1 to 8 cover the full syllabus for **NEET** and **JEE Main**. Sections 9 to 12 are the **JEE Advanced** layer. Section 13 is a practice set across all three exams.

THE WHOLE CHAPTER IN ONE LINE

Follow the nitrogen's lone pair.

Basicity and nucleophilic reactions come from that one pair of electrons. So do the reactivity of aniline's ring and the diazonium salt.



THINK IT
THROUGH

WHAT THIS CHAPTER IS WORTH

- It appears in **every NEET and JEE paper**, often as a conversion or a basicity order.
- Diazonium conversions are a favourite for two-step and three-step questions.
- The tests here (carbylamine, Hinsberg, nitrous acid) also come up in board practicals.



TRAP ALERT

THE HABIT THAT FIXES THIS CHAPTER

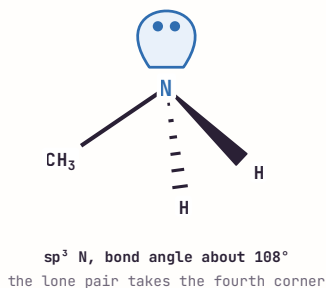
- **Before ranking or predicting, ask where the lone pair is.**
- Is it free on an sp^3 N? Shared with a benzene ring? Shared with a C=O? Part of an aromatic ring?
- That single answer settles most questions before any memorised order.

1 Structure and Classification

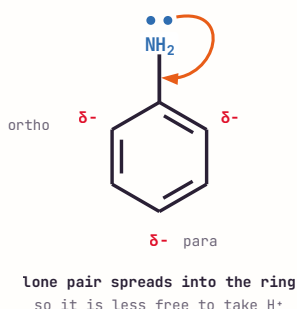
An amine is ammonia with one or more H atoms replaced by carbon groups. The nitrogen is sp^3 . Three corners hold bonds and the fourth holds the lone pair.

WHAT AN AMINE LOOKS LIKE: A PYRAMID WITH A LONE PAIR ON TOP

METHYLAMINE



ANILINE



CLASSIFY BY CARBONS ON N

1° $R-NH_2$
one R

2° R_2NH
two R

3° R_3N
three R

4° $R_4N^+ X^-$
a salt

1°, 2°, 3° count carbons on N, not on the carbon (unlike alcohols). $(CH_3)_3C-NH_2$ is 1°.

The lone pair is the business end of every amine. In aniline it leaks into the ring.

TYPE	GENERAL FORMULA	EXAMPLE
primary (1°)	$R-NH_2$	CH_3NH_2 , methanamine
secondary (2°)	R_2NH	$(CH_3)_2NH$, N-methylmethanamine
tertiary (3°)	R_3N	$(CH_3)_3N$, N,N-dimethylmethanamine
quaternary salt	$R_4N^+ X^-$	$(CH_3)_4N^+ I^-$
aryl amine	N on a benzene ring	$C_6H_5NH_2$, aniline



THINK IT
THROUGH

WHY MOST AMINES ARE NOT OPTICALLY ACTIVE

- An amine with three different groups and a lone pair looks chiral.
- But the nitrogen flips inside out very fast, like an umbrella in the wind.
- The two mirror forms swap too fast to separate. Quaternary salts cannot flip, so they can be resolved.



TRAP ALERT

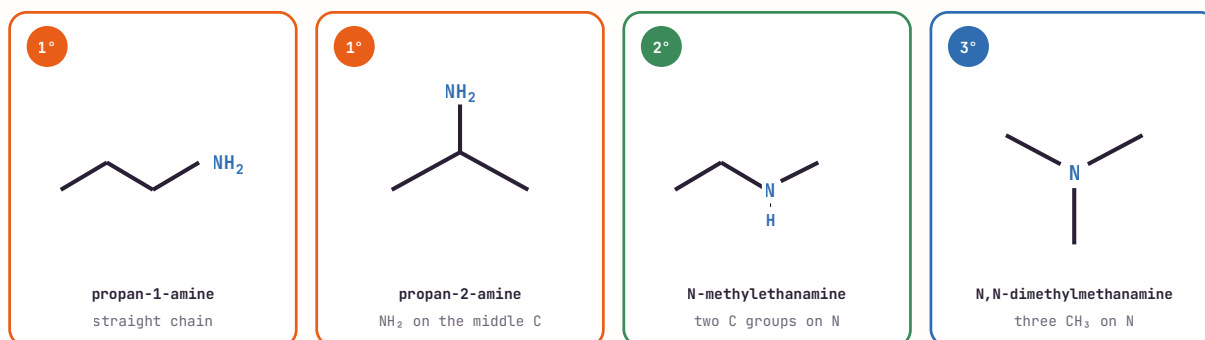
1°, 2°, 3° MEAN SOMETHING DIFFERENT HERE

- **For amines, count the carbons on N, not on the carbon carrying N.**
- $(CH_3)_3C-NH_2$ is a primary amine, though its carbon is tertiary. For alcohols it would be called tertiary.

IUPAC names replace the final -e of the alkane with -amine. Groups on N get the prefix N-.

FORMULA	COMMON NAME	IUPAC NAME
$\text{CH}_3\text{CH}_2\text{NH}_2$	ethylamine	ethanamine
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$	n-propylamine	propan-1-amine
$(\text{CH}_3)_2\text{CHNH}_2$	isopropylamine	propan-2-amine
$\text{CH}_3\text{NHC}_2\text{H}_5$	ethylmethylaniline	N-methylethanamine
$(\text{CH}_3)_3\text{N}$	trimethylamine	N,N-dimethylmethanamine
$\text{H}_2\text{N}-\text{CH}_2\text{CH}_2-\text{NH}_2$	ethylenediamine	ethane-1,2-diamine
$\text{C}_6\text{H}_5\text{NHCH}_3$	N-methylaniline	N-methylbenzenamine
$\text{CH}_3-\text{C}_6\text{H}_4-\text{NH}_2$ (para)	p-toluidine	4-methylaniline

FOUR AMINES, ONE FORMULA: THE ISOMERS OF $\text{C}_3\text{H}_9\text{N}$



$\text{C}_4\text{H}_{11}\text{N}$ has 8 amines: 4 primary, 3 secondary, 1 tertiary. Count them the same way.

Same atoms, four molecules. Two are primary, one secondary, one tertiary.

WORKED EXAMPLE

How many amines have the formula $C_4H_{11}N$? Sort them by type.

Primary: butan-1-amine, butan-2-amine, 2-methylpropan-1-amine, 2-methylpropan-2-amine. That is 4.

Secondary: N-methylpropan-1-amine, N-methylpropan-2-amine, N-ethylethanamine. That is 3.

Tertiary: N,N-dimethylethanamine. That is 1.

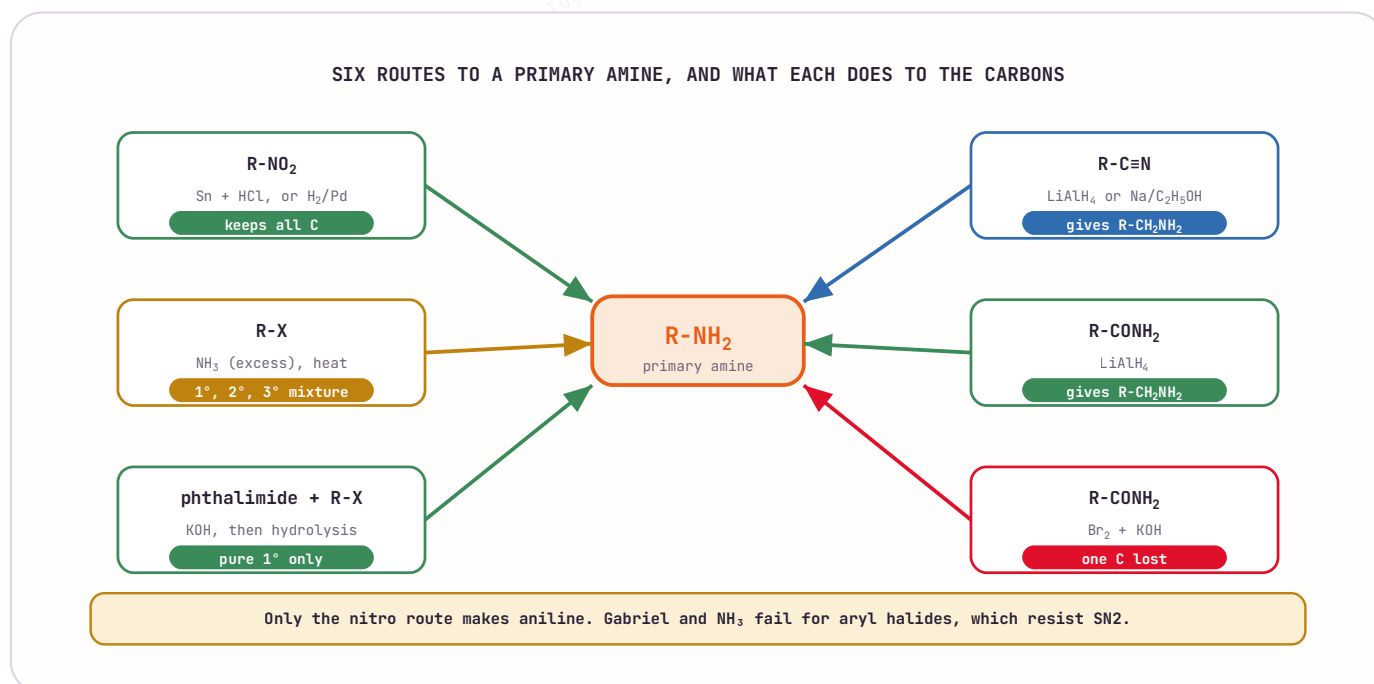
Answer: 8 amines, or 9 if you count both mirror forms of butan-2-amine



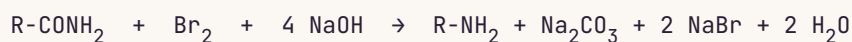
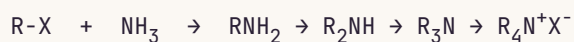
METAMERS ARE STILL ISOMERS

- **N-methylpropan-1-amine and N-ethylethanamine are different molecules.**
- The groups on N differ in size. Such isomers are called metamers. Count each one.

Six routes lead to amines. Choose by two things: the starting material you have, and whether the carbon count must change.



Each route keeps, adds or removes carbon. Questions on conversions turn on exactly that.



ROUTE	GOOD FOR	WATCH OUT
nitro reduction	aryl amines like aniline	Fe/HCl is preferred: the FeCl_2 formed regenerates HCl
ammonolysis of R-X	quick, cheap	gives a mixture; excess NH_3 favours 1°
nitrile reduction	adding one C to a halide	the C of CN becomes CH_2
Gabriel phthalimide	pure 1° amines	fails for aryl amines: aryl halides resist $\text{S}_{\text{N}}2$
Hoffmann bromamide	dropping one C	the C=O carbon leaves as carbonate

WORKED EXAMPLE 1

Convert ethanoic acid into methanamine.

The target has one carbon fewer. That points to the Hoffmann bromamide route.



Answer: make the amide, then use Br_2 and KOH

WORKED EXAMPLE 2

Convert bromoethane into propan-1-amine.

The target has one carbon more. A cyanide adds exactly one.



Answer: KCN , then LiAlH_4



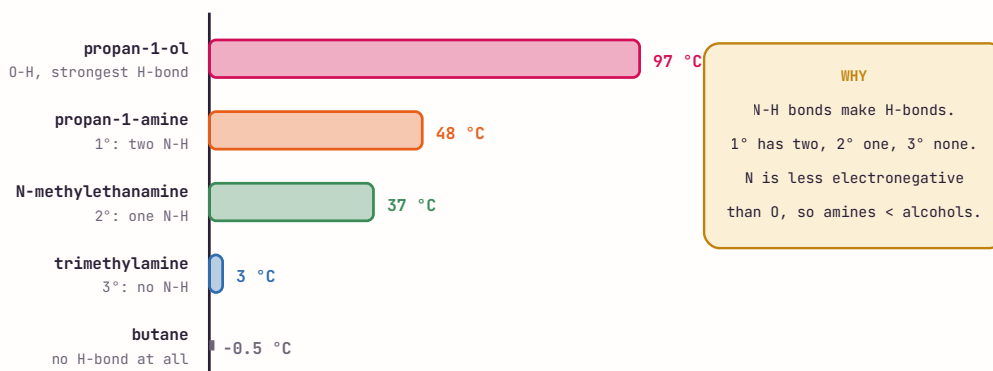
TRAP ALERT

GABRIEL CANNOT MAKE ANILINE

- **The Gabriel route needs an $\text{S}_{\text{N}}2$ step.** An aryl halide will not do $\text{S}_{\text{N}}2$, so no aryl amine forms.
- For aniline and its relatives, reduce the nitro compound instead.

Primary and secondary amines can hydrogen bond through their N-H bonds. Tertiary amines have none to give.

HYDROGEN BONDS DECIDE BOILING POINT: SAME MASS, VERY DIFFERENT bp



All five have nearly the same mass (58 to 60). Only the hydrogen bonding changes.

Same mass, same shape of chain. The number of N-H bonds sets the boiling point.

PROPERTY	WHAT HAPPENS	WHY
boiling point	1° > 2° > 3° for isomers	more N-H, more hydrogen bonds
against alcohols	amines boil lower	N is less electronegative than O, so N-H...N is weaker
solubility in water	small amines dissolve; it falls with size	H-bonds to water, but a larger carbon chain repels it
smell	small amines smell fishy	volatile and basic
colour of aniline	colourless when pure, darkens in air	slow oxidation in air



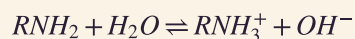
TRAP ALERT

TERTIARY AMINES STILL DISSOLVE IN WATER

- A 3° amine cannot donate an H-bond, but its lone pair can accept one from water.
- So trimethylamine is soluble. It just cannot H-bond to itself, so it boils low.

An amine is a base because its lone pair can take a proton. The more available the lone pair, the stronger the base.

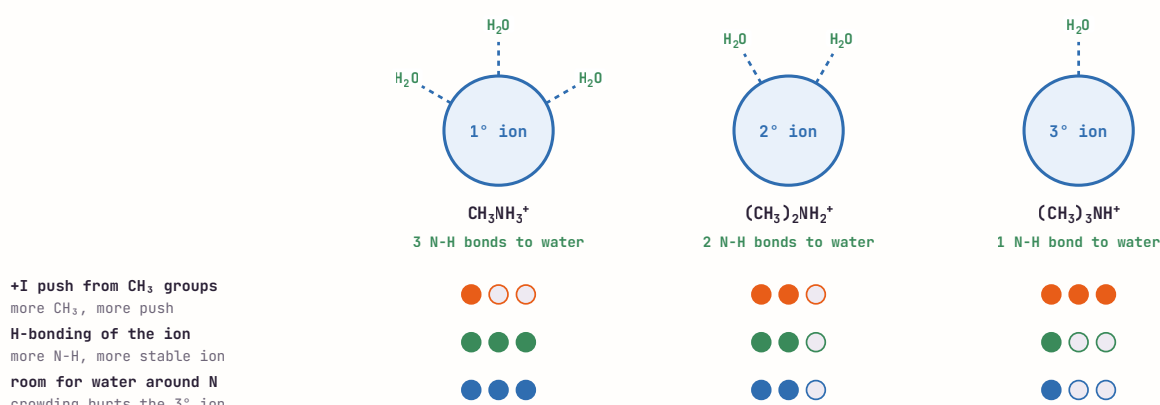
MEASURING BASE STRENGTH



$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]} \quad pK_b = -\log K_b$$

A lower pK_b means a **stronger base**.

WHY $(CH_3)_2NH$ IS THE STRONGEST BASE IN WATER: THREE EFFECTS PULL DIFFERENT WAYS



Net in water: 2° (pK_b 3.27) > 1° (3.38) > 3° (4.22) > NH_3 (4.75). In the gas phase, 3° wins.

Three effects, scored for each methylamine ion. No single effect predicts the order. The balance does.



▶ PLAY

BASICITY ORDERS FEEL RANDOM?

Watch the three effects compete.

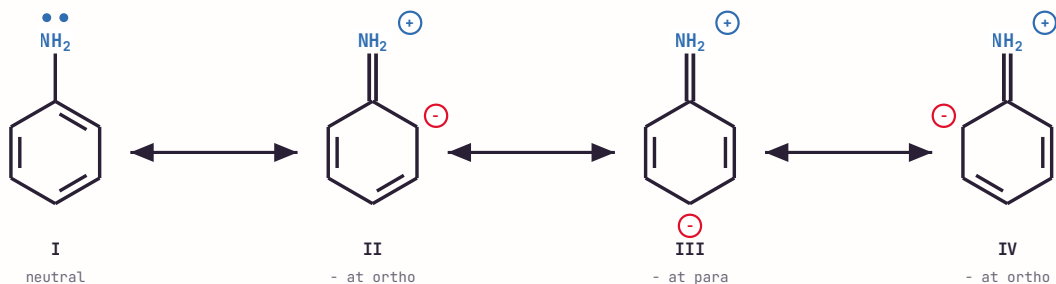
Add CH_3 groups one at a time. See the push grow, the hydrogen bonding fall, and the order flip from gas to water. logicbloom.co.in/download · Free to start.



SCAN

SERIES	ORDER IN WATER	pK_b VALUES
methyl	$2^\circ > 1^\circ > 3^\circ > NH_3$	3.27, 3.38, 4.22, 4.75
ethyl	$2^\circ > 3^\circ > 1^\circ > NH_3$	3.00, 3.25, 3.29, 4.75
gas phase, any series	$3^\circ > 2^\circ > 1^\circ > NH_3$	only the +I effect counts

ANILINE'S LONE PAIR IS SHARED WITH THE RING: FOUR RESONANCE STRUCTURES

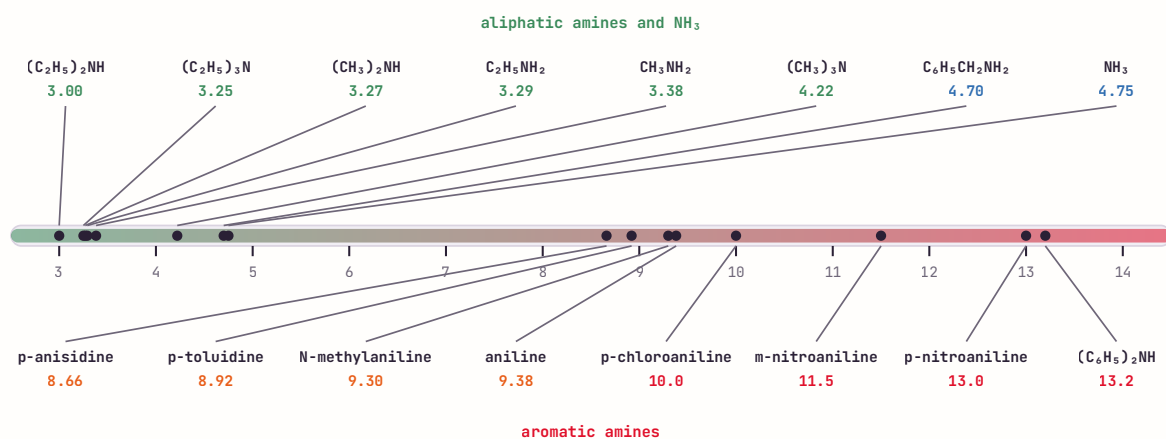


The lone pair is busy in the ring, so aniline holds H^+ weakly: pK_b 9.38 against 3.38 for CH_3NH_2 .
The anilinium ion $C_6H_5NH_3^+$ has no lone pair left, so it has no such resonance. Losing it costs nothing.

Charge piles up at ortho and para. That is also why the ring reacts so fast with electrophiles.

Structures II to IV use the lone pair inside the ring. The proton finds it less available.

THE pK_b LADDER: LOWER pK_b MEANS A STRONGER BASE



A gap of 6 units between CH_3NH_2 and aniline is a million-fold difference in K_b .

Aliphatic amines sit near pK_b 3 to 5. Aromatic amines sit near 9 to 13.

GROUP ON THE RING	EFFECT ON ANILINE'S BASICITY	EXAMPLE
$-CH_3$, $-OCH_3$ at para	raises it: they push electrons in	p-toluidine 8.92, p-anisidine 8.66
$-Cl$ at para	lowers it: -I wins	p-chloroaniline 10.0
$-NO_2$ at para	lowers it a lot: -M and -I	p-nitroaniline 13.0
$-NO_2$ at meta	lowers it less: only -I reaches	m-nitroaniline 11.5
CH_2 between ring and N	behaves like an aliphatic amine	benzylamine 4.70

WORKED EXAMPLE

Arrange in increasing basicity in water: NH_3 , CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$, $\text{C}_6\text{H}_5\text{NH}_2$.

Aniline's lone pair is shared with the ring, so it is the weakest.

Among the rest, use the water order for methyl amines: $2^\circ > 1^\circ > 3^\circ > \text{NH}_3$.

Answer: $\text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < (\text{CH}_3)_3\text{N} < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH}$



THINK IT
THROUGH

SALTS LET YOU SEPARATE AMINES

- Aniline does not dissolve in water. It does dissolve in dilute HCl, as anilinium chloride.
- Add NaOH and the free aniline comes back out.
- This is how amines are pulled out of a mixture with neutral compounds.



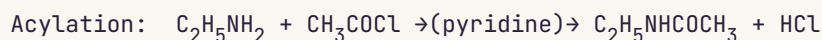
TRAP ALERT

WATER ORDER AND GAS ORDER DIFFER

- **Gas phase:** $3^\circ > 2^\circ > 1^\circ$. **In water:** $2^\circ > 1^\circ > 3^\circ$ **for methyl**. Read which the question asks.
- Do not use the methyl order for ethyl amines. With ethyl groups, 3° beats 1° .

Reactions of the Amino Group

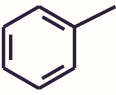
The lone pair makes N a nucleophile. Most reactions here start with N attacking something.



Acylation needs an N-H, so it works for 1° and 2° amines only. Pyridine soaks up the HCl and pushes the reaction forward. The carbylamine test gives a foul-smelling isocyanide. Only primary amines give it.

AMINE	WITH NITROUS ACID ($\text{NaNO}_2 + \text{HCl}$)	WHAT YOU SEE
1° aliphatic	$\text{RNH}_2 \rightarrow \text{ROH} + \text{N}_2$	bubbles of N_2
1° aromatic	$\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ at 0 to 5 °C	no gas when cold; the salt couples to dyes
2°, either kind	$\text{R}_2\text{NH} \rightarrow \text{R}_2\text{N-N=O}$	yellow oily nitrosamine
3° aliphatic	forms a soluble salt	no visible change
3° aromatic	$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 \rightarrow \text{para-nitroso product}$	green solid

HINSBERG TEST: BENZENESULPHONYL CHLORIDE SORTS 1°, 2° AND 3° AMINES



$\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$
Hinsberg reagent
then add KOH

1° amine



dissolves in KOH
 $\text{C}_6\text{H}_5\text{SO}_2\text{-NH-R}$
N-H left: acidic

2° amine



stays insoluble
 $\text{C}_6\text{H}_5\text{SO}_2\text{-NR}_2$
no N-H left

3° amine



no reaction
no product
no N-H to replace

The N-H left on the 1° product is acidic, so KOH pulls it off and the salt dissolves.

One reagent and one base give three different outcomes. The difference is the N-H left behind.

WORKED EXAMPLE

Three bottles hold aniline, N-methylaniline and N,N-dimethylaniline. Tell them apart with nitrous acid.

Aniline is 1° aromatic. Cold HNO_2 gives a diazonium salt. Added to alkaline 2-naphthol, it gives a red dye.

N-methylaniline is 2°. It gives a yellow oily N-nitroso compound.

N,N-dimethylaniline is 3° aromatic. It gives a green p-nitroso compound.

Answer: red dye, yellow oil, green solid

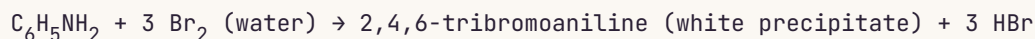


TWO TESTS, TWO TRAPS

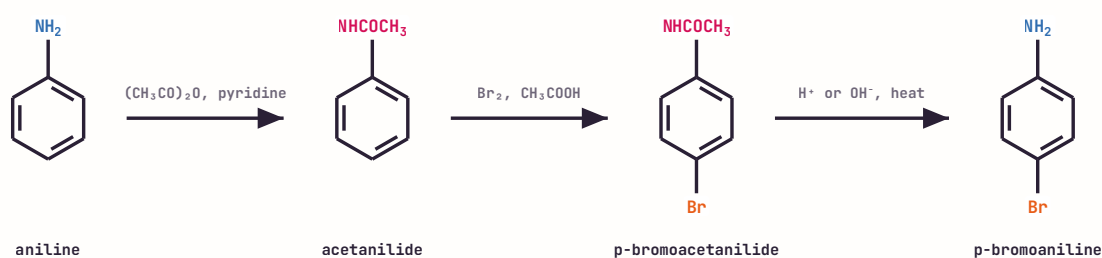
- **Only 1° amines give the carbylamine smell.** A 2° amine gives nothing, not a weaker smell.
- **In the Hinsberg test, 3° amines do not react at all.** They do dissolve in acid, which tells them apart from 2° products.

Aniline and the Ring

The -NH_2 group pushes its lone pair into the ring. That makes aniline react with electrophiles very fast, at ortho and para. Often too fast.



TAMING ANILINE: ACETYLATE, SUBSTITUTE, THEN REMOVE THE ACETYL GROUP

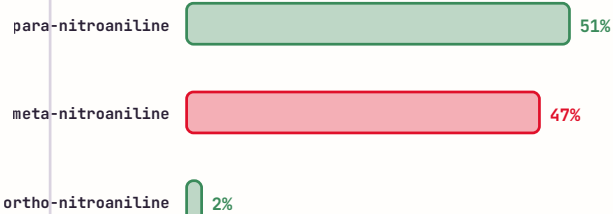
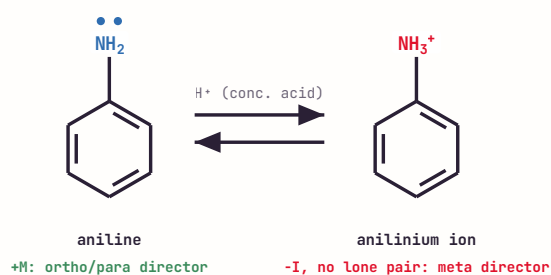


The C=O pulls on N's lone pair, so the ring is only mildly activated.
One Br goes in, at para. The bulky group also blocks ortho.

Br_2 water on plain aniline gives 2,4,6-tribromoaniline at once, as a white precipitate.

Acetylation slows the ring down. After the substitution, the acetyl group comes off and NH_2 returns.

NITRATING ANILINE GIVES 47% META. THE ACID TURNS IT INTO A DIFFERENT GROUP



only 2% ortho: bulk and the charge both push away

Much of the aniline is protonated, and that ion directs meta. Protect the NH_2 to get clean para product.

In strong acid, aniline and anilinium compete. Each directs to different positions.

REACTION	WHAT HAPPENS	REASON
bromine water	2,4,6-tribromoaniline at once	the ring is strongly activated
nitration, direct	51% para, 47% meta, 2% ortho; some oxidation	anilinium ion forms and directs meta
sulphonation	sulphanilic acid on heating at 453 to 473 K	forms a zwitterion, $\text{H}_3\text{N}^+\text{-C}_6\text{H}_4\text{-SO}_3^-$

REACTION	WHAT HAPPENS	REASON
Friedel-Crafts	does not work	N's lone pair binds AlCl_3 , and the ring is deactivated

WORKED EXAMPLE

Make p-nitroaniline from aniline in good yield.

Direct nitration gives a mixture and oxidation. So protect N first.

Aniline $\rightarrow ((\text{CH}_3\text{CO})_2\text{O}) \rightarrow$ acetanilide $\rightarrow (\text{conc. HNO}_3, \text{H}_2\text{SO}_4) \rightarrow$ p-nitroacetanilide $\rightarrow (\text{H}^+, \text{heat}) \rightarrow$ p-nitroaniline.

Answer: acetylate, nitrate, then hydrolyse



TRAP ALERT

FRIEDEL-CRAFTS FAILS, AND SO DOES DIRECT NITRATION

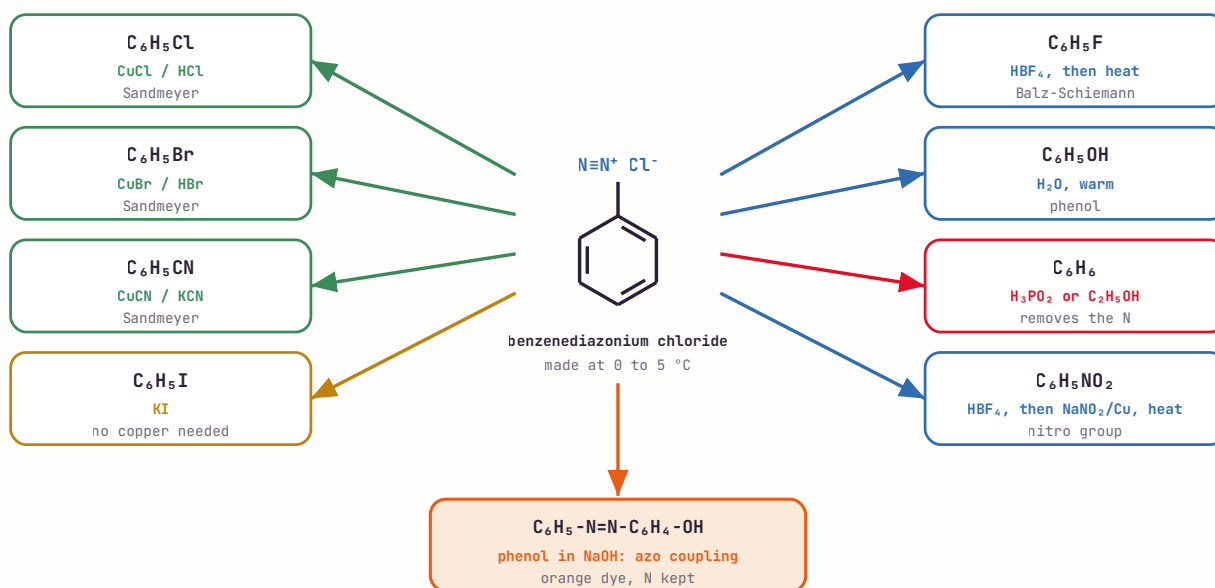
- **Aniline is a Lewis base.** It grabs AlCl_3 and turns into a deactivated salt.
- In nitrating acid it is protonated. Expect lots of meta product, not pure para.

A primary aromatic amine with cold nitrous acid gives a diazonium salt. This one salt can be turned into almost anything.



Aryl diazonium ions are stable in the cold because the positive charge spreads into the ring. Alkyl diazonium ions have no ring to help, so they fall apart at once to N_2 and a carbocation.

ONE DIAZONIUM SALT, NINE PRODUCTS: N_2 LEAVES, OR STAYS AS $\text{N}=\text{N}$



Above 5 °C the salt decomposes to phenol and N_2 , so make it cold and use it at once.

Eight routes replace the N_2 group. In coupling, the $\text{N}=\text{N}$ stays and joins two rings.



▶ PLAY

TOO MANY REAGENTS TO REMEMBER?

Spin the diazonium wheel.

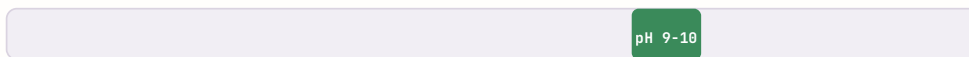
Pick a product and the reagent lights up. Then try it the other way round, from reagent to product. logicbloom.co.in/download · Free to start.



SCAN

AZO COUPLING WORKS ONLY IN A pH WINDOW, AND THE WINDOW DEPENDS ON THE PARTNER

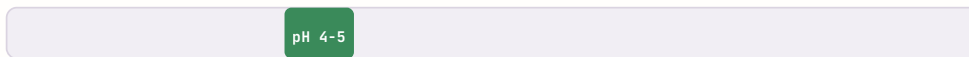
with phenol



phenol not ionised: too slow

ArN_2^+ turns to diazotate

with aniline



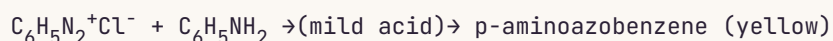
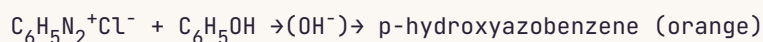
anilinium: no free lone pair

diazotate forms



Phenol needs a base to become phenoxide. Aniline needs mild acid, not strong acid. The salt must survive both.

Too acidic and the partner loses its push. Too basic and the diazonium salt is destroyed.



WORKED EXAMPLE 1

Make fluorobenzene from benzene.

Fluorine cannot be put on directly. Go through the diazonium salt.

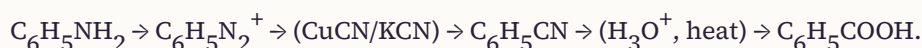
Benzene $\rightarrow$ (HNO_3 , H_2SO_4) $\rightarrow$ nitrobenzene $\rightarrow$ (Sn , HCl) $\rightarrow$ aniline $\rightarrow$ (NaNO_2 , HCl , 0°C) $\rightarrow$ diazonium salt $\rightarrow$ (HBF_4 , heat) $\rightarrow$ fluorobenzene.

Answer: four steps, ending with the Balz-Schiemann reaction

WORKED EXAMPLE 2

Make benzoic acid from aniline.

Diazotise, then swap N_2 for CN with CuCN . Then hydrolyse the nitrile.



Answer: diazotise, CuCN , then hydrolyse



TRAP ALERT

THREE DIAZONIUM SLIPS

- **Diazotise at 0 to 5°C .** Warm, the salt turns into phenol before you can use it.
- Iodine needs only KI . Fluorine needs HBF_4 and heat. Neither is a Sandmeyer reaction.
- In coupling, the N_2 is not lost. The product keeps $-\text{N}=\text{N}-$.

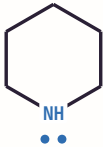
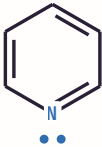
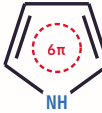
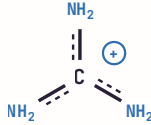
The JEE Advanced layer

Everything so far is complete for NEET and JEE Main. From here each problem needs a route you build yourself. No single formula reaches the answer.

9 Basicity Beyond the Basics

JEE Advanced mixes nitrogen types that the simple rules do not cover. One question settles all of them: where does the lone pair sit, and is it busy?

WHERE THE LONE PAIR SITS DECIDES BASICITY

piperidine  sp^3 N pK_b 2.88	pyridine  sp^2 N, lone pair in plane pK_b 8.75	pyrrole  lone pair is part of the 6 π almost no basicity	guanidine  cation shares + over 3 N pK_b 0.4
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More s-character holds the lone pair tighter. A lone pair used in aromaticity is not for sale.

Same atom, four situations. The pK_b spans from 0.4 to almost no basicity at all.

EFFECT	WHAT IT DOES	EXAMPLE
more s-character	lone pair held closer to N, so less basic	pyridine (sp^2) 8.75 against piperidine (sp^3) 2.88
lone pair in an aromatic ring	not available at all	pyrrole is almost non-basic
lone pair on C=O	shared with oxygen	amides are almost neutral
cation spread over 3 N	the ion is very stable	guanidine, pK _b about 0.4
ortho effect	any ortho group weakens an aniline	o-toluidine 9.56, weaker than aniline 9.38
steric inhibition of resonance	ortho groups twist NMe ₂ out of the ring plane	N,N-dimethyl-o-toluidine is stronger than N,N-dimethylaniline

WORKED EXAMPLE

Arrange in increasing basicity: acetamide, aniline, pyridine, piperidine, guanidine.

Acetamide's lone pair is shared with C=O. It is the weakest.

Aniline (9.38) is weaker than pyridine (8.75). Pyridine's sp^2 lone pair is free; aniline's is shared with the ring.

Piperidine (2.88) is a normal sp^3 amine. Guanidine (0.4) forms a cation spread over three N atoms.

Answer: acetamide < aniline < pyridine < piperidine < guanidine



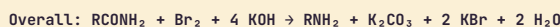
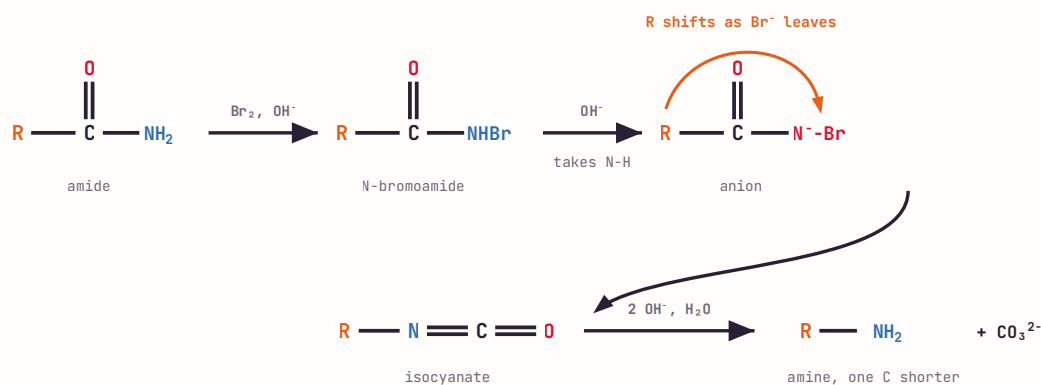
TRAP ALERT

PYRIDINE IS STRONGER THAN ANILINE

- **Most students rank pyridine last because of sp^2 .** But aniline's lone pair is busy in the ring.
- Pyridine's lone pair points out, in the plane, and is not part of the aromatic sextet.

JEE Advanced asks why a product forms, not just what forms. Four mechanisms cover this chapter.

HOFMANN BROMAMIDE: THE R GROUP MOVES FROM CARBON TO NITROGEN

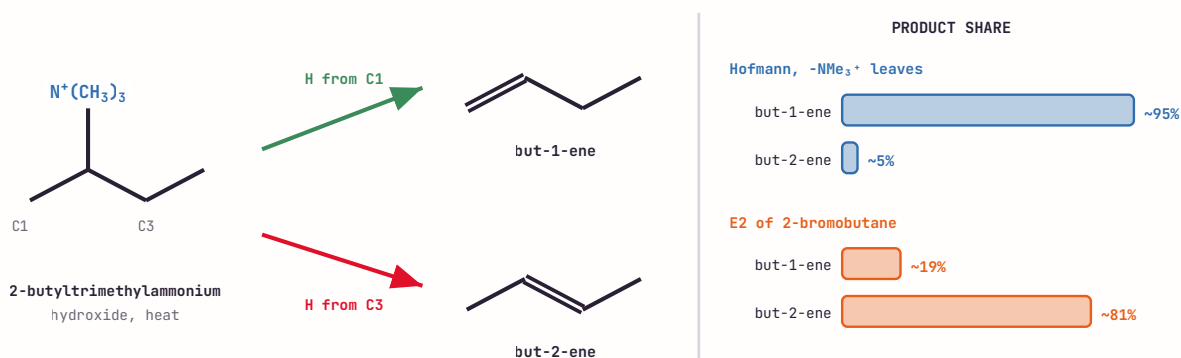


The C=O carbon leaves as carbonate. R moves with its bonds intact, so a chiral R keeps its configuration.

R moves from carbon to nitrogen in one step. That is why a chiral R keeps its configuration.

REACTION	KEY INTERMEDIATE	WHAT IT EXPLAINS
Hofmann bromamide	isocyanate, $R-N=C=O$	one C lost; configuration kept
carbylamine	dichlorocarbene, $:CCl_2$, from $CHCl_3$ and base	only 1° amines can lose two H to form an isocyanide, $R-NC$
diazotisation	nitrosonium ion, NO^+ , from HNO_2 and acid	needs N-H bonds to lose, so only 1° gives N_2^+
Gabriel	phthalimide anion, an N nucleophile	SN_2 , so it fails with aryl and 3° halides

HOFMANN ELIMINATION GIVES THE LESS SUBSTITUTED ALKENE, THE OPPOSITE OF SAYTZEFF



The big NMe_3^+ group crowds C3, and the C1 hydrogens are more acidic. So the base takes H from C1.

A bulky, positive leaving group sends the base to the most accessible hydrogen.

WORKED EXAMPLE

N,N,N-trimethylpentan-2-aminium hydroxide is heated. Which alkene forms mainly? What would 2-bromopentane give with ethoxide?

The leaving group is the bulky $\text{-N(CH}_3)_3^+$. The base takes H from the CH_3 end, C1, which is easiest to reach.

2-bromopentane with ethoxide follows Saytzeff and gives mostly pent-2-ene.

Answer: pent-1-ene from the ammonium salt; pent-2-ene from the bromide



TRAP ALERT

HOFMANN RULE VERSUS SAYTZEFF RULE

- **A quaternary ammonium leaving group gives the less substituted alkene.**
- A halide leaving group with a small base gives the more substituted alkene. Same skeleton, opposite answer.

In ring synthesis, the nitrogen group is a tool. You put it on to steer, then change it or remove it.

TOOL	USE
-NH_2 , then remove with H_3PO_2	a strong ortho/para director that can vanish afterwards
-NO_2 , then reduce	a meta director that later becomes NH_2
-NHCOCH_3	a milder ortho/para director; gives one substitution, at para
the diazonium salt	places F, I, CN, OH or H where no direct reaction can

WORKED EXAMPLE 1

Make m-bromophenol from nitrobenzene.

OH and Br must be meta. NO_2 is a meta director, so brominate first.

Nitrobenzene $\rightarrow (\text{Br}_2, \text{FeBr}_3) \rightarrow \text{m-bromonitrobenzene} \rightarrow (\text{Sn}, \text{HCl}) \rightarrow \text{m-bromoaniline}$.

$\rightarrow (\text{NaNO}_2, \text{HCl}, 0^\circ\text{C}) \rightarrow \text{diazonium salt} \rightarrow (\text{H}_2\text{O}, \text{warm}) \rightarrow \text{m-bromophenol}$.

Answer: brominate, reduce, diazotise, then warm with water

WORKED EXAMPLE 2

Make 1,3,5-tribromobenzene from aniline.

The three Br atoms sit meta to each other. No single group directs like that.

But NH_2 sends Br to 2, 4 and 6, which are meta to each other. Then remove the NH_2 .

Aniline $\rightarrow (\text{Br}_2, \text{water}) \rightarrow 2,4,6\text{-tribromoaniline} \rightarrow (\text{NaNO}_2, \text{HCl}, 0^\circ\text{C}) \rightarrow (\text{H}_3\text{PO}_2) \rightarrow 1,3,5\text{-tribromobenzene}$.

Answer: brominate, diazotise, then remove N with H_3PO_2



TRAP ALERT

ORDER MATTERS

- **Decide the order by which group directs the next step.** Swap two steps and the product changes.
- In Example 1, reducing first would make NH_2 the director, and Br would go ortho and para.

Each problem uses a different technique. None of them can be solved by recalling one reaction.

PROBLEM 1 • MECHANISM AND STEREOCHEMISTRY

(S)-2-methylbutanamide is treated with Br_2 and KOH. Name the product, with its configuration.

What it demands: knowing the R group migrates with retention, then checking that the CIP label does not change

Hofmann bromamide removes the C=O carbon. The group $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)-$ moves from C to N. So the product is butan-2-amine.

The group moves with its bonds intact, so the arrangement in space is kept.

Now re-check the label. Before, $-\text{CONH}_2$ ranked first at the stereocentre. After, $-\text{NH}_2$ ranks first, in the same place. The other three groups keep their ranks.

Answer: (S)-butan-2-amine

PROBLEM 2 • TWO CHAPTERS

0.59 g of a saturated primary amine gives 224 mL of N_2 at STP with nitrous acid. The alcohol formed gives a yellow precipitate with I_2 and NaOH. Identify the amine. Assume one N_2 per NH_2 group.

What it demands: mole counting from a gas volume, then an alcohol test to pick the isomer

Moles of $\text{N}_2 = \frac{224}{22400} = 0.01$. One amine gives one N_2 , so the molar mass is $\frac{0.59}{0.01} = 59$ g/mol.

A saturated amine $\text{C}_n\text{H}_{2n+3}\text{N}$ with mass 59 has $n = 3$. So it is propan-1-amine or propan-2-amine.

The iodoform test needs a $\text{CH}_3\text{-CH}(\text{OH})-$ group. Only propan-2-ol has it.

Answer: propan-2-amine

PROBLEM 3 • DEDUCTION

An aromatic amine A, $\text{C}_7\text{H}_9\text{N}$, is diazotised in the cold. The product gives a red dye with alkaline 2-naphthol. With bromine water, A gives $\text{C}_7\text{H}_6\text{Br}_3\text{N}$. Identify A.

What it demands: using the dye test to fix the amine type, then turning a bromine count into a position count

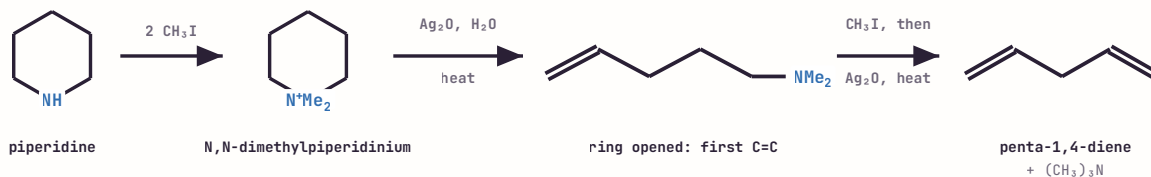
A stable diazonium salt means A is a primary aromatic amine. That rules out benzylamine and N-methylaniline. So A is a toluidine.

Three Br atoms need three free positions ortho and para to NH_2 : 2, 4 and 6.

In o-toluidine CH_3 blocks 2. In p-toluidine it blocks 4. Only in m-toluidine are all three free.

Answer: m-toluidine (3-methylaniline)

TWO HOFMANN ELIMINATIONS OPEN THE PIPERIDINE RING AND REMOVE THE NITROGEN



CH₃I used: 2 + 1 = 3. Each elimination needs a quaternary N first.
Counting the CH₃I tells you how many C-N bonds the nitrogen started with.

Each round of methylation and elimination breaks one C-N bond. Two rounds free the nitrogen.

PROBLEM 4 • WORKING BACKWARDS

Amine X, C₅H₁₁N, has no C=C. It takes 2 mol of CH₃I to become a quaternary salt. Two rounds of Hofmann elimination, with one more CH₃I between them, give penta-1,4-diene and trimethylamine. Identify X.

What it demands: counting CH₃I to find how many C-N bonds N had, then rebuilding the ring from the product

C₅H₁₁N has one degree of unsaturation and no C=C. So X has one ring.

Two CH₃ groups to reach N⁺ means N had two C-N bonds. X is a secondary amine.

All five carbons end up in one unbranched chain with a C=C at each end. So they formed a ring, joined to N at both ends.

Answer: piperidine

PROBLEM 5 • DESIGN A SEPARATION

A mixture holds aniline, N-methylaniline and N,N-dimethylaniline. Plan how to get each one back, pure.

What it demands: using the acidity of one product and the basicity of another to split three similar compounds

Add benzenesulphonyl chloride and aqueous KOH. Aniline's sulphonamide still has an acidic N-H, so it dissolves as a salt. N-methylaniline's sulphonamide has no N-H and stays as a solid. N,N-dimethylaniline does not react.

Separate the alkaline solution and acidify it. Aniline's sulphonamide comes out. Heat it with acid to get aniline back.

Shake the rest with dilute HCl. N,N-dimethylaniline dissolves as its salt; NaOH frees it again. The solid left is N-methylaniline's sulphonamide; acid hydrolysis frees it.

Answer: Hinsberg reagent, then acid for the 3° amine, then hydrolyse each sulphonamide

Questions 1 to 9 are NEET and JEE Main level. Questions 10 to 15 are JEE Advanced, in its real formats. Try each one before reading the answers.

NEET and JEE Main

Q1 NEET • LEVEL 2 • SINGLE CORRECT

The correct order of basic strength in water is:

- (A) $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3$ (B) $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N} > \text{NH}_3$
(C) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$ (D) $\text{NH}_3 > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$

Q2 JEE MAIN • LEVEL 2 • SINGLE CORRECT

Which pair can be told apart by the carbylamine test?

- (A) ethylamine and aniline (B) methylamine and dimethylamine
(C) aniline and benzylamine (D) propan-1-amine and propan-2-amine

Q3 JEE MAIN • LEVEL 2 • SINGLE CORRECT

Which amide gives propan-2-amine with Br_2 and KOH?

- (A) 2-methylpropanamide (B) butanamide
(C) propanamide (D) 2-methylbutanamide

Q4 JEE MAIN • LEVEL 2 • SINGLE CORRECT

An amine $\text{C}_4\text{H}_{11}\text{N}$ gives a Hinsberg product that does not dissolve in KOH. The amine could be:

- (A) butan-1-amine (B) 2-methylpropan-2-amine
(C) N,N-dimethylethanamine (D) N-ethylethanamine

Q5 NEET • LEVEL 2 • SINGLE CORRECT

Direct nitration of aniline gives about 47% meta product because:

- (A) $-\text{NH}_2$ is a meta director (B) the anilinium ion formed in acid is a meta director
(C) the ortho positions are blocked by bulk (D) NO_2^+ attacks N first, then moves to meta

Q6 JEE MAIN • LEVEL 2 • NUMERICAL

Methylamine has $\text{pK}_b = 3.38$. Find the pH of a 0.1 M solution at 25 °C. Give $10 \times \text{pH}$, rounded off to the nearest integer.

Q7 NEET • LEVEL 2 • SINGLE CORRECT

The Gabriel phthalimide synthesis can be used to make:

- (A) aniline and benzylamine (B) ethylamine and N-methylethanamine
(C) benzylamine and ethylamine (D) aniline and ethylamine

Q8 JEE MAIN • LEVEL 2 • SINGLE CORRECT

Which sequence turns aniline into benzonitrile?

- (A) NaNO_2/HCl at 0 to 5 °C, then CuCN/KCN (B) CuCN/KCN directly
(C) NaNO_2/HCl at 40 °C, then CuCN/KCN (D) NaNO_2/HCl at 0 to 5 °C, then warm water

Q9 NEET • LEVEL 2 • SINGLE CORRECT

Benzenediazonium chloride couples best with phenol at:

- (A) pH 1 to 2 (B) pH 4 to 5
(C) pH 13 to 14 (D) pH 9 to 10

JEE Advanced

Q10 JEE ADVANCED • LEVEL 3 • ONE OR MORE CORRECT

Which of the following are correct?

- (A) pyrrolidine is a stronger base than pyrrole (B) p-anisidine is a stronger base than aniline
(C) o-toluidine is a stronger base than p-toluidine (D) guanidine is a stronger base than ethylamine

Q11 JEE ADVANCED • LEVEL 3 • NUMERICAL

8.7 g of butanamide is fully converted to propan-1-amine by Br_2 and KOH . What mass of KOH , in grams, does the balanced reaction use? Round off to one decimal place. ($K = 39$, $O = 16$, $H = 1$)

Q12 JEE ADVANCED • LEVEL 3 • SINGLE CORRECT

Aniline is treated in turn with $(\text{CH}_3\text{CO})_2\text{O}$; Br_2 in CH_3COOH ; H_3O^+ and heat; NaNO_2/HCl at 0 °C; then H_3PO_2 . The final product is:

- (A) bromobenzene (B) 1,4-dibromobenzene
(C) 1,3,5-tribromobenzene (D) 4-bromophenol

Q13 JEE ADVANCED • LEVEL 3 • SINGLE CORRECT

An aromatic amine $\text{C}_8\text{H}_{11}\text{N}$ does not react with benzenesulphonyl chloride. With nitrous acid it gives a green solid. It is:

- (A) N-ethylaniline (B) N,N-dimethylaniline
(C) 2,4-dimethylaniline (D) N-methylbenzylamine

Q14 JEE ADVANCED • LEVEL 3 • ONE OR MORE CORRECT

About coupling of benzenediazonium chloride, which of the following are correct?

- (A) With phenol it is done in mild alkali, because phenoxide is more strongly activated. (B) With aniline it is done at pH 12, so that the amine stays free.
(C) p-cresol still couples, at the position ortho to its OH group. (D) The diazonium ion acts as the electrophile.

Q15 JEE ADVANCED • LEVEL 3 • NUMERICAL

Benzylamine (pK_b 4.70) and aniline (pK_b 9.38) are each made 0.1 M. Find $\log_{10}$ of $[\text{OH}^-]_{\text{benzylamine}} / [\text{OH}^-]_{\text{aniline}}$, to two decimal places.

Practice Set: Answers and Traps

Each answer shows the reasoning, then what each wrong option gets wrong. If you chose a wrong option, find your mistake there.

Q1 • (C). In water, +I, hydrogen bonding of the ion and crowding all count. For methyl amines the balance gives $2^\circ > 1^\circ > 3^\circ > \text{NH}_3$. **Traps:** (A) is the gas-phase order, +I alone. (B) counts only hydrogen bonding. (D) counts only crowding.

Q2 • (B). Only 1° amines give the isocyanide smell. Methylamine gives it; dimethylamine does not. **Traps:** (A), (C) and (D) are pairs of 1° amines. Both give the smell, so the test cannot split them.

Q3 • (A). Hoffmann removes the C=O carbon. Putting it back on propan-2-amine's N gives $(\text{CH}_3)_2\text{CH-CONH}_2$. **Traps:** (B) gives propan-1-amine. (C) gives ethylamine. (D) gives butan-2-amine.

Q4 • (D). A sulphonamide that will not dissolve in KOH has no N-H. So the amine is 2° . N-ethylethanamine is the only 2° amine listed. **Traps:** (A) and (B) are 1° : their products dissolve. (C) is 3° : it gives no product at all.

Q5 • (B). Strong acid protonates much of the aniline. The $-\text{NH}_3^+$ group has no lone pair and pulls electrons, so it directs meta. **Traps:** (A) is false: NH_2 directs ortho and para. (C) explains the small ortho share, not the meta share. (D) invents a mechanism.

Q6 • 118. For a weak base, $\text{pOH} = \frac{1}{2}(\text{pK}_b - \log C) = \frac{1}{2}(3.38 + 1) = 2.19$. So $\text{pH} = 14 - 2.19 = 11.81$. **Traps:** Using pK_b as pOH gives 10.62. Forgetting the $\frac{1}{2}$ gives 9.62.

Q7 • (C). Gabriel needs $\text{S}_\text{N}2$ on an alkyl halide and gives only 1° amines. Benzylamine and ethylamine both qualify. **Traps:** (A) and (D) include aniline: aryl halides do not do $\text{S}_\text{N}2$. (B) includes a 2° amine, which Gabriel cannot make.

Q8 • (A). First make the diazonium salt in the cold. Then CuCN swaps N_2 for CN . **Traps:** (B) skips diazotisation. (C) is too warm: the salt becomes phenol. (D) makes phenol on purpose.

Q9 • (D). Phenol must be ionised to phenoxide, which needs mild alkali. Too much alkali destroys the diazonium salt. **Traps:** (B) is aniline's window. (A) is too acidic for phenol to react. (C) turns the salt into an unreactive diazotate.

Q10 • (A), (B) and (D). Pyrrolidine has a free sp^3 lone pair; pyrrole's is in the ring. OCH_3 at para pushes electrons in (8.66 against 9.38). Guanidine (0.4) is far stronger than ethylamine (3.29). **Traps:** (C) is false: the ortho effect makes o-toluidine (9.56) weaker than p-toluidine (8.92).

Q11 • 22.4. $\text{RCONH}_2 + \text{Br}_2 + 4 \text{KOH} \rightarrow \text{RNH}_2 + \text{K}_2\text{CO}_3 + 2 \text{KBr} + 2 \text{H}_2\text{O}$. Butanamide is 87 g/mol, so 8.7 g is 0.1 mol. $\text{KOH used} = 0.4 \text{ mol} \times 56 \text{ g/mol}$. **Traps:** Using 1 KOH per amide gives 5.6. Using 2 gives 11.2. The carbonate and the two KBr need all four.

Q12 • (A). The acetyl group lets one Br in, at para. Hydrolysis gives p-bromoaniline. Diazotising and H_3PO_2 then remove the N. **Traps:** (B) forgets that H_3PO_2 gives H, not Br. (C) assumes the ring was not protected. (D) assumes water replaced N_2 .

Q13 · (B). No reaction with the Hinsberg reagent means 3°. A green p-nitroso product means 3° aromatic. $C_6H_5N(CH_3)_2$ fits $C_8H_{11}N$. **Traps:** (A) and (D) are 2°: they react, and give yellow oils with HNO_2 . (C) is 1°: it would form a diazonium salt.

Q14 · (A), (C) and (D). Phenoxide is a stronger electron donor than phenol. If para is blocked, as in p-cresol, coupling goes ortho. The diazonium ion is the electrophile. **Traps:** (B) is false: at pH 12 the diazonium salt is destroyed. Aniline couples in mildly acidic solution.

Q15 · 2.34. For each weak base, $[OH^-] = \sqrt{K_b C}$. At equal C, the log of the ratio is $\frac{1}{2}(9.38 - 4.70)$. **Traps:** Forgetting the square root gives 4.68.

★ Amines • Fact Sheet

Every rule for revision day. Print this page alone.

STRUCTURE

sp^3 N, pyramid, about 108°

1° , 2° , 3° = C atoms on N.
(CH_3)₃C-NH₂ is 1° .

PREPARATION

Nitro + Fe/HCl: aniline

Gabriel: pure 1° , no aryl.
Hoffmann: one C lost.

BOILING POINT

$1^\circ > 2^\circ > 3^\circ$ for isomers

Amines boil below alcohols.
 3° still dissolves in water.

BASICITY IN WATER

Methyl: $2^\circ > 1^\circ > 3^\circ > \text{NH}_3$

Ethyl: $2^\circ > 3^\circ > 1^\circ > \text{NH}_3$
Gas phase: $3^\circ > 2^\circ > 1^\circ$

AROMATIC AMINES

Aniline pK_b 9.38

Ring donors raise basicity.
NO₂ at para lowers it most.

CARBYLAMINE

1° only: $\text{R-NH}_2 + \text{CHCl}_3 + \text{KOH}$

Foul isocyanide smell.
 2° and 3° give nothing.

NITROUS ACID

1° aliphatic: N₂ gas

1° aromatic: diazonium, 0 to 5°C
 2° : yellow oil. 3° aryl: green.

HINSBERG

1° : dissolves in KOH

2° : insoluble solid
 3° : no reaction

ANILINE RING

Br₂ water: 2,4,6-tribromo

Nitration: 47% meta
No Friedel-Crafts. Protect N.

DIAZONIUM

**CuCl, CuBr, CuCN:
Sandmeyer**

KI: iodo. HBF₄, heat: fluoro
H₃PO₂: H. Warm water: OH.

COUPLING

Phenol: pH 9 to 10

Aniline: pH 4 to 5
Para first; ortho if para is taken.

LONE PAIR SITE

$sp^3 > sp^2$: piperidine > pyridine

Pyrrole: almost non-basic
Guanidine: strongest, pK_b 0.4

ORTHO EFFECT

Any ortho group weakens aniline.

o-toluidine 9.56 > aniline 9.38
Twisted NMe₂ gets stronger.

HOFMANN BROMAMIDE

R moves C to N, kept intact.

Uses 4 KOH per amide.
Isocyanate in the middle.

HOFMANN ELIMINATION

Least substituted alkene.

One CH₃I round per C-N bond.
Opposite of Saytzeff.



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★ AMINES STILL FEEL LIKE A LIST OF TESTS?

Play it. Then practice it.

Open Amines in the Logic Bloom app. Watch the lone pair move. Run the Hinsberg test on any amine. Spin the diazonium wheel until every reagent sticks. Free to start.

SCAN → PLAY • READ • PRACTICE