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CH 09

Amines & Diazonium Salts — Basicity, Tests & Synthesis

09

Classification and structure, every preparation route including Gabriel and Hofmann bromamide, basicity orders in water and gas phase, carbylamine, Hinsberg and nitrous acid tests, ring substitution of aniline with protection, diazonium salts, Sandmeyer and coupling reactions — with conversions, an exam trap gallery, graded MCQs and a one-page revision sheet.

WHAT YOU WILL BE ABLE TO DO

- Classify amines and prepare them by reduction, ammonolysis, Gabriel synthesis and Hofmann bromamide degradation
- Explain basicity orders of aliphatic and aromatic amines in water and in the gas phase
- Distinguish 1°, 2° and 3° amines by the carbylamine, Hinsberg and nitrous acid tests
- Predict ring substitution of aniline and use acetylation to control it
- Use diazonium salts in Sandmeyer, Gattermann, replacement and coupling reactions, and plan conversions

INSIDE

HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

The big picture

A

One lone pair runs the chapter.

IN ONE LINE

The nitrogen lone pair makes amines basic and nucleophilic and makes aniline's ring highly reactive; converting $-NH_2$ to $-N_2^+$ (diazotisation) turns it into an excellent leaving group that can be replaced by almost anything.

Class	Structure	Example
Primary (1°)	$R-NH_2$	CH_3NH_2, aniline $C_6H_5NH_2$
Secondary (2°)	R_2NH	$(CH_3)_2NH$, N-methylaniline
Tertiary (3°)	R_3N	$(CH_3)_3N$, N,N-dimethylaniline
Quaternary salt	$R_4N^+ X^-$	$(CH_3)_4N^+ I^-$

THINK OF IT LIKE THIS

Think of the nitrogen lone pair as a hand held out. In an alkylamine the hand is free and eager to grab a proton (strong base). In aniline the benzene ring holds that hand (resonance), so it is less available for protons — but the ring itself gets stronger and grabs electrophiles easily.

SECTION B

Structure and physical properties

B

Pyramidal nitrogen and hydrogen bonding.

- Nitrogen is **sp^3** with one lone pair: pyramidal. The C–N–C angle in trimethylamine is 108°.
- In aniline the lone pair is partly delocalised into the ring, so N is slightly flattened toward sp^2.
- **Hydrogen bonding:** 1° amines (two N–H) > 2° (one N–H) > 3° (none). So boiling points: **1° > 2° > 3°** for isomers, e.g. butan-1-amine (350.8 K) > N-ethylethanamine (329.3 K) > N,N-dimethylethanamine (310.5 K).
- Amines boil lower than alcohols of similar mass, because N is less electronegative than O and forms weaker H bonds.

- Lower aliphatic amines are water-soluble and smell fishy; aniline is a colourless liquid that darkens in air by oxidation.

SECTION C

Preparing amines

C

Seven routes and what each is good for.

Route	Reagent	Product	Note
Reduction of nitro compounds	Fe/HCl (preferred), Sn/HCl, H_2/Pd	$ArNH_2$ / RNH_2	Fe/HCl: $FeCl_2$ formed is hydrolysed, releasing HCl, so little acid is needed
Ammonolysis of halides	NH_3 (alcoholic), heat in sealed tube	Mixture of 1°, 2°, 3° amines and $R_4N^+X^-$	Excess NH_3 favours 1°; aryl halides do not react easily
Reduction of nitriles	$LiAlH_4$ or H_2/Ni; Na/ethanol (Mendius)	$R–CH_2NH_2$	Adds one carbon to the halide R–X used to make R–CN
Reduction of amides	$LiAlH_4$, then H_2O	$R–CH_2NH_2$	Same carbon count as the amide
Gabriel phthalimide synthesis	Phthalimide + KOH; then R–X; then NaOH (hydrolysis)	Pure 1° aliphatic amine	Not for aryl amines (ArX does not undergo SN2)
Hofmann bromamide degradation	$RCONH_2 + Br_2 + 4NaOH$	$R–NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$	One carbon fewer than the amide; via isocyanate
Reductive amination	Aldehyde/ketone + NH_3, then H_2/Ni	1° amine	Via the imine

KEY IDEA

Count the carbons. Nitrile reduction adds one carbon (relative to RX); amide reduction keeps the count; Hofmann bromamide loses one. Questions on “ascending” and “descending” a series test exactly this.

SOLVED EXAMPLE 01 — HOFMANN BROMAMIDE

What amine is obtained from benzamide with Br_2 and NaOH? How many carbons does it lose?

SOLUTION

1. $C_6H_5CONH_2 + Br_2 + 4NaOH \rightarrow C_6H_5NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$.
2. The carbonyl carbon leaves as CO_3^{2-}.

ANSWER Aniline; one carbon fewer ($C_7 \rightarrow C_6$).

SOLVED EXAMPLE 02 — WHY GABRIEL FAILS FOR ANILINE

Why can aniline not be prepared by the Gabriel phthalimide synthesis?

SOLUTION

1. The key step is SN2 attack of the phthalimide anion on an alkyl halide.
2. Aryl halides do not undergo SN2 (partial double-bond character of C–X, sp^2 carbon, ring repels the nucleophile).

ANSWER The phthalimide ion cannot substitute the halogen of an aryl halide.

CHECK YOURSELF

C1 Which method gives a pure primary amine free of 2° and 3° amines?

C2 Starting from CH_3Br, how would you get ethanamine?

Answers at the end of the chapter.

SECTION D

Basicity

D

The most-asked topic in this chapter.

Amines are bases because the nitrogen lone pair accepts H^+: $R–NH_2 + H_2O \rightleftharpoons R–NH_3^+ + OH^-$. A **smaller pKb means a stronger base**.

Amine	pKb (in water)
Diethylamine $(C_2H_5)_2NH$	3.00
Triethylamine $(C_2H_5)_3N$	3.25
Dimethylamine $(CH_3)_2NH$	3.27
Ethanamine $C_2H_5NH_2$	3.29
Methanamine CH_3NH_2	3.38

Amine	pKb (in water)
Trimethylamine $(CH_3)_3N$	4.22
Benzylamine $C_6H_5CH_2NH_2$	4.70
Ammonia	4.75
N,N-Dimethylaniline	8.92
N-Methylaniline	9.30
Aniline	9.38

- **Aliphatic amines are stronger bases than NH_3:** alkyl groups push electron density onto N (+I).
- **In the gas phase** only the +I effect matters: 3° > 2° > 1° > NH_3.
- **In water** three effects compete — +I, solvation of the ammonium ion by H bonding (best for 1°, worst for 3°), and steric hindrance. Results: $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ and $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$.
- **Aryl amines are much weaker bases:** the lone pair is delocalised into the ring, and the anilinium ion has fewer resonance structures than aniline. Electron-donating groups (–CH_3, –OCH_3) on the ring raise basicity; electron-withdrawing groups (–NO_2, –Cl) lower it — p-nitroaniline is a very weak base.
- **Benzylamine** (CH_2 between ring and N) behaves like an aliphatic amine — the lone pair is not conjugated.

SOLVED EXAMPLE 03 — ORDERING BASICITY IN WATER

Arrange CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, NH_3 and $C_6H_5NH_2$ in decreasing basicity in aqueous solution.

SOLUTION

1. Aniline is weakest: lone pair delocalised.
2. NH_3 is weaker than all methylamines.
3. Among methylamines in water, 2° > 1° > 3° (solvation and steric effects).

ANSWER $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3 > C_6H_5NH_2$.

CHECK YOURSELF

C3 Which is the stronger base: aniline or benzylamine?

C4 Why is $(CH_3)_3N$ a weaker base than CH_3NH_2 in water but stronger in the gas phase?

Answers at the end of the chapter.

SECTION E

Reactions of amines

E

At nitrogen.

Reaction	Reagent	1°	2°	3°
Alkylation	R–X	→ 2°, 3°, $R_4N^+X^-$	→ 3°, $R_4N^+X^-$	→ $R_4N^+X^-$
Acylation	RCOCl or $(RCO)_2O$, pyridine	Amide RNHCOR	Amide	No reaction (no N–H)
Benzoylation (Schotten–Baumann)	C_6H_5COCl, aq. NaOH	N-substituted benzamide	Benzamide	No reaction
Carbylamine	$CHCl_3$ + alc. KOH, heat	Isocyanide (foul smell)	No reaction	No reaction
Hinsberg	$C_6H_5SO_2Cl$	Sulphonamide, soluble in alkali	Sulphonamide, insoluble in alkali	No reaction
Nitrous acid ($NaNO_2$ + HCl)	HNO_2	Aliphatic: alcohol + N_2 (bubbles); aromatic (273–278 K): diazonium salt	Yellow oily N-nitrosamine	Aliphatic: soluble salt

$$R–NH_2 + CHCl_3 + 3KOH \rightarrow R–NC + 3KCl + 3H_2O$$

Carbylamine (isocyanide) test — given only by primary amines, aliphatic and aromatic

KEY IDEA

Hinsberg logic: the sulphonamide from a 1° amine still has an N–H, made acidic by the strongly electron-withdrawing SO_2 group, so it dissolves in KOH. The 2° sulphonamide has no N–H left, so it does not. A 3° amine has no N–H to react at all.

SOLVED EXAMPLE 04 — IDENTIFYING THE CLASS

Three isomeric amines C_3H_9N are tested. A gives a foul smell with $CHCl_3$/KOH; B forms a sulphonamide insoluble in alkali with Hinsberg's reagent; C does not react with Hinsberg's reagent. Identify them.

SOLUTION

1. A: carbylamine positive → 1°: propan-1-amine (or propan-2-amine).
2. B: 2° → N-methylethanamine.
3. C: 3° → N,N-dimethylmethanamine (trimethylamine).

ANSWER A 1° (propan-1-amine), B 2° (N-methylethanamine), C 3° (trimethylamine).

SECTION F

Ring substitution of aniline

F

A very reactive ring — and how to tame it.

Reaction	Conditions	Product	Note
Bromination	Bromine water, room temperature	2,4,6-Tribromoaniline (white ppt)	Too fast to stop at one Br
Controlled bromination	Acetylate → Br_2/CH_3COOH → hydrolyse	p-Bromoaniline	$-NHCOCH_3$ is a weaker activator and bulky
Direct nitration	conc. HNO_3 + H_2SO_4	p- (51%), m- (47%), o- (2%) nitroaniline + tar	Anilinium ion ($-NH_3^+$) is a meta director; ring also oxidised
Controlled nitration	Acetylate → nitrate → hydrolyse	p-Nitroaniline (major)	Protection again
Sulphonation	conc. H_2SO_4, heat at 453–473 K	Sulphanilic acid (p-aminobenzenesulphonic acid)	Exists as a zwitterion
Friedel–Crafts	RCl / $AlCl_3$	No reaction	$-NH_2$ (Lewis base) complexes $AlCl_3$ and deactivates the ring

KEY IDEA

Why acetylation works: in acetanilide the N lone pair is shared with the C=O of the acetyl group, so it donates less to the ring (moderate activation, monosubstitution); the bulky $-NHCOCH_3$ group also favours the para position. Hydrolysis afterwards regenerates $-NH_2$.

SOLVED EXAMPLE 05 — **WHY M-NITROANILINE APPEARS**

Direct nitration of aniline gives 47% of the meta product, although $-NH_2$ is an o/p director. Explain.

SOLUTION

1. The nitrating mixture is strongly acidic; most aniline is protonated to the anilinium ion $C_6H_5NH_3^+$.
2. $-NH_3^+$ has no lone pair and withdraws electrons: it is a meta director.

ANSWER Substitution on the anilinium ion gives the meta product.

CHECK YOURSELF

C5 How would you prepare p-bromoaniline from aniline?

C6 Why does aniline not undergo Friedel–Crafts reactions?

Answers at the end of the chapter.

SECTION G

Diazonium salts

G

Making them and why aryl ones survive.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \rightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

Diazotisation at 273–278 K; the salt is used at once in solution

- **Aryl diazonium salts are stable at 0–5 °C** because the positive charge is delocalised over the ring; aliphatic diazonium ions decompose at once to carbocations and N_2.
- Benzenediazonium fluoroborate is stable enough to be isolated as a solid; the chloride is used in solution.
- The $-N_2^+$ group is an excellent leaving group (N_2 gas is very stable), so it can be replaced by many nucleophiles.

SECTION H

Reactions of diazonium salts

H

Replacement and coupling.

Replace $-N_2^+$ by	Reagent	Name
–Cl	CuCl / HCl	Sandmeyer
–Br	CuBr / HBr	Sandmeyer

Replace $-N_2^+$ by	Reagent	Name
–CN	CuCN / KCN	Sandmeyer
–Cl or –Br	Cu powder + HCl or HBr	Gattermann
–I	KI (no catalyst)	—
–F	HBF_4, then heat the fluoroborate	Balz–Schiemann
–H	H_3PO_2 (or ethanol)	Reduction / deamination
–OH	Warm water	Hydrolysis
$-NO_2$	HBF_4, then $NaNO_2$/Cu, heat	—

Coupling reactions — azo dyes

- With **phenol** in mildly alkaline solution: p-hydroxyazobenzene (orange dye).
- With **aniline** in mildly acidic solution: p-aminoazobenzene (yellow dye).
- Coupling happens at the para position of the activated ring; the –N=N– group is retained (the electrophile is the diazonium ion).

SOLVED EXAMPLE 06 — BENZENE TO IODOBENZENE

Convert benzene into iodobenzene.

SOLUTION

1. Nitrate: benzene + conc. HNO_3/H_2SO_4 → nitrobenzene.
2. Reduce: Sn/HCl (or Fe/HCl) → aniline.
3. Diazotise: $NaNO_2$ + HCl, 273–278 K → benzenediazonium chloride.
4. Add KI → iodobenzene + N_2.

ANSWER Benzene → nitrobenzene → aniline → diazonium salt → iodobenzene.

SOLVED EXAMPLE 07 — 1,3,5-TRIBROMOBENZENE

Make 1,3,5-tribromobenzene from aniline — a product that direct bromination of benzene cannot give.

SOLUTION

1. Bromine water → 2,4,6-tribromoaniline.
2. Diazotise ($NaNO_2$/HCl, 273–278 K).
3. H_3PO_2 replaces $-N_2^+$ by H.

ANSWER The $-NH_2$ is used to place three Br atoms meta to each other, then removed.

SECTION I

Conversions

I

The problems examiners love.

SOLVED EXAMPLE 08 — ETHANAMINE TO METHANAMINE

Convert ethanamine into methanamine (descending the series).

SOLUTION

1. $C_2H_5NH_2 + HNO_2 \rightarrow C_2H_5OH + N_2 + H_2O$.
2. Oxidise: $C_2H_5OH \rightarrow CH_3COOH$ ($K_2Cr_2O_7/H^+$).
3. $CH_3COOH \rightarrow CH_3COCl$ ($SOCl_2$) $\rightarrow CH_3CONH_2$ (NH_3).
4. Hofmann bromamide: $CH_3CONH_2 + Br_2 + 4NaOH \rightarrow CH_3NH_2$.

ANSWER Via ethanol, ethanoic acid and ethanamide; Hofmann removes one carbon.

SOLVED EXAMPLE 09 — METHANAMINE TO ETHANAMINE

Convert methanamine into ethanamine (ascending the series).

SOLUTION

1. $CH_3NH_2 + HNO_2 \rightarrow CH_3OH$.
2. $CH_3OH \rightarrow CH_3Br$ (PBr_3) $\rightarrow CH_3CN$ (KCN).
3. Reduce: $LiAlH_4 \rightarrow CH_3CH_2NH_2$.

ANSWER Via methanol, bromomethane and ethanenitrile; nitrile reduction adds one carbon.

SOLVED EXAMPLE 10 — ANILINE TO BENZOIC ACID

Convert aniline into benzoic acid.

SOLUTION

1. Diazotise: $NaNO_2$ + HCl, 273–278 K.
2. Sandmeyer: CuCN/KCN → benzonitrile.
3. Hydrolyse: H_3O^+ → benzoic acid.

ANSWER Aniline → diazonium salt → $C_6H_5CN \rightarrow C_6H_5COOH$.

SOLVED EXAMPLE 11 — NITROBENZENE TO PHENOL

Convert nitrobenzene into phenol.

SOLUTION

1. Reduce: Sn/HCl → aniline.
2. Diazotise at 273–278 K.
3. Warm with water → phenol + N_2.

ANSWER Nitrobenzene → aniline → diazonium salt → phenol.

SECTION J

Exam trap gallery

J

Where marks are lost in this chapter.

✗ TRAP 01 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Aniline is a stronger base than methylamine.	Methylamine is far stronger (pKb 3.38 vs 9.38).

WHY Aniline's lone pair is delocalised into the ring.

✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
In water, 3° amines are the strongest bases.	In water 2° is usually strongest; 3° can be weaker than 1°.

WHY Solvation and steric effects oppose +I.

✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Gabriel synthesis gives aniline.	It gives only 1° aliphatic amines.

WHY Aryl halides do not undergo SN2.

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Hofmann bromamide gives an amine with the same number of carbons.	One carbon fewer.

WHY The C=O carbon leaves as carbonate.

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Secondary amines give the carbylamine test.	Only primary amines.

WHY Isocyanide needs two N–H.

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
The 2° sulphonamide in the Hinsberg test dissolves in alkali.	It is insoluble; the 1° sulphonamide dissolves.

WHY No acidic N–H on the 2° product.

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Aniline + bromine water gives p-bromoaniline.	It gives 2,4,6-tribromoaniline.

WHY Protect by acetylation for monobromination.

✗ TRAP 08 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Direct nitration of aniline gives only o- and p-products.	About 47% meta forms.

WHY Anilinium ion is a meta director.

✗ TRAP 09 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Aniline undergoes Friedel–Crafts alkylation.	It does not.

WHY $-NH_2$ forms a complex with $AlCl_3$.

✗ TRAP 10 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Aliphatic diazonium salts are stable at 0–5 °C.	Only aryl diazonium salts are.

WHY Resonance with the ring stabilises the aryl ion.

✗ TRAP 11 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Sandmeyer converts diazonium salt to iodobenzene with CuI.	KI alone is enough for –I.

WHY I^- is a good enough nucleophile.

✗ TRAP 12 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Benzylamine is as weak a base as aniline.	Benzylamine (pKb 4.70) is much stronger.

WHY Its lone pair is not conjugated with the ring.

MEMORY HOOK

"Nitrile adds one, amide keeps, Hofmann takes one."

"Carbylamine for 1° only — follow your nose."

"Hinsberg: 1° dissolves, 2° stays, 3° ignores."

"Protect, substitute, deprotect" — acetanilide route.

SECTION K

Practice MCQs

K

Levels: Easy, Moderate, Tough.

Q01 Carbylamine test is given by: [EASY]

(a) 1° amines
(b) 2° amines
(c) 3° amines
(d) all amines

Q02 Hinsberg's reagent is: [EASY]

(a) C_6H_5COCl
(b) $C_6H_5SO_2Cl$
(c) $CHCl_3$
(d) $NaNO_2$ + HCl

Q03 Aniline is less basic than ammonia because: [EASY]

(a) it has a higher molar mass
(b) its lone pair is delocalised into the ring
(c) N is sp
(d) it is a liquid

Q04 Aniline + bromine water gives: [EASY]

(a) o-bromoaniline
(b) p-bromoaniline
(c) 2,4,6-tribromoaniline
(d) bromobenzene

Q05 Diazotisation is carried out at: [EASY]

(a) 273–278 K
(b) 373 K
(c) 298 K
(d) 573 K

Q06 Benzenediazonium chloride + KI gives: [EASY]

(a) chlorobenzene
(b) iodobenzene
(c) phenol
(d) benzene

Q07 Gabriel synthesis is used to prepare: [EASY]

(a) 1° aliphatic amines
(b) 2° amines
(c) 3° amines
(d) aryl amines

Q08 Hofmann bromamide reaction of propanamide gives: [MODERATE]

(a) propanamine
(b) ethanamine
(c) methanamine
(d) butanamine

Q09 Strongest base in water: [MODERATE]

(a) CH_3NH_2
(b) $(CH_3)_2NH$
(c) $(CH_3)_3N$
(d) NH_3

Q10 Strongest base in the gas phase: [MODERATE]

(a) NH_3
(b) CH_3NH_2
(c) $(CH_3)_2NH$
(d) $(CH_3)_3N$

Q11 Reduction of CH_3CN with $LiAlH_4$ gives: [MODERATE]

(a) CH_3NH_2 (b) $CH_3CH_2NH_2$
(c) CH_3CONH_2 (d) CH_3CH_2OH

Q12 Sandmeyer reaction converts ArN_2^+ to ArCl using: [MODERATE]

(a) Cu/HCl (b) CuCl/HCl
(c) KCl (d) Cl_2

Q13 Benzenediazonium chloride + H_3PO_2 gives: [MODERATE]

(a) phenol (b) benzene
(c) aniline (d) chlorobenzene

Q14 A 2° amine with HNO_2 gives: [MODERATE]

(a) alcohol (b) diazonium salt
(c) N-nitrosamine (d) no reaction

Q15 Coupling of benzenediazonium chloride with phenol gives: [MODERATE]

(a) p-aminoazobenzene (b) p-hydroxyazobenzene
(c) azobenzene (d) biphenyl

Q16 Acetylation of aniline before nitration is done to: [MODERATE]

(a) increase activation (b) protect $-NH_2$ and get the p-product
(c) make it soluble (d) remove the ring

Q17 Sulphanilic acid exists as: [MODERATE]

(a) a neutral molecule (b) a zwitterion
(c) a cation only (d) an anion only

Q18 Which amine does not react with Hinsberg's reagent? [MODERATE]

(a) CH_3NH_2 (b) $(CH_3)_2NH$
(c) $(CH_3)_3N$ (d) $C_6H_5NH_2$

Q19 Weakest base: [TOUGH]

(a) aniline (b) p-toluidine
(c) p-nitroaniline (d) benzylamine

Q20 Direct nitration of aniline gives a large amount of m-nitroaniline because of: [TOUGH]

(a) steric hindrance (b) formation of the anilinium ion
(c) oxidation (d) hydrolysis

Q21 Fluorobenzene is made from benzenediazonium chloride by: [TOUGH]

(a) KF (b) HBF_4 then heating
(c) CuF (d) F_2

Q22 Number of carbons in the amine from Hofmann degradation of hexanamide: [TOUGH]

(a) 4 (b) 5
(c) 6 (d) 7

Q23 Correct basicity order in water: [TOUGH]

(a) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2$ (b) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2$
(c) $C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N$ (d) all equal

Q24 1,3,5-Tribromobenzene can be made from aniline by: [TOUGH]

(a) $Br_2/FeBr_3$ (b) Br_2 water, then diazotisation and H_3PO_2
(c) NBS (d) HBr

Q25 Aniline + $CHCl_3$ + alc. KOH gives: [TOUGH]

(a) phenyl isocyanide (b) benzonitrile
(c) chlorobenzene (d) benzaldehyde

Answer key with explanations

Q01 **(a) 1° amines** — Two N–H needed.

Q02 **(b) $C_6H_5SO_2Cl$** — Benzenesulphonyl chloride.

Q03 **(b) its lone pair is delocalised into the ring** — Resonance.

Q04 **(c) 2,4,6-tribromoaniline** — Highly activated ring.

Q05 **(a) 273–278 K** — Diazonium salt is unstable when warm.

Q06 **(b) iodobenzene** — Replacement by I.

Q07 **(a) 1° aliphatic amines** — Pure 1°.

Q08 **(b) ethanamine** — One carbon fewer.

Q09 **(b) $(CH_3)_2NH$** — 2° in water.

Q10 **(d) $(CH_3)_3N$** — +I only.

Q11 **(b) $CH_3CH_2NH_2$** — Adds one carbon.

Q12 **(b) CuCl/HCl** — Cu(I) salt.

Q13 **(b) benzene** — $-N_2^+ \rightarrow H$.

Q14 **(c) N-nitrosamine** — Yellow oil.

Q15 **(b) p-hydroxyazobenzene** — Orange dye.

Q16 **(b) protect $-NH_2$ and get the p-product** — Controlled substitution.

Q17 **(b) a zwitterion** — $-SO_3^-$ and $-NH_3^+$.

Q18 **(c) $(CH_3)_3N$** — No N–H.

Q19 **(c) p-nitroaniline** — $-NO_2$ withdraws.

Q20 **(b) formation of the anilinium ion** — $-NH_3^+$ meta director.

Q21 **(b) HBF_4 then heating** — Balz–Schiemann.

Q22 **(b) 5** — 6 - 1.

Q23 **(b) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2$** — pKb 3.00, 3.25, 3.29.

Q24 **(b) Br_2 water, then diazotisation and H_3PO_2** — Use and remove $-NH_2$.

Q25 **(a) phenyl isocyanide** — Carbylamine test.

Check-yourself answers

C1 Gabriel phthalimide synthesis (or Hofmann bromamide degradation).

C2 CH_3Br + KCN → CH_3CN; reduce with $LiAlH_4$ (or Na/C_2H_5OH) → $CH_3CH_2NH_2$.

C3 Benzylamine — its lone pair is not delocalised into the ring.

C4 In water, the $(CH_3)_3NH^+$ ion has only one N–H for H bonding with water and is poorly solvated, and the three methyl groups crowd the nitrogen; in the gas phase only the +I effect counts, so 3° is strongest.

C5 Acetylate (acetic anhydride) → acetanilide; brominate (Br_2 in ethanoic acid) → p-bromoacetanilide; hydrolyse (acid or base) → p-bromoaniline.

C6 The $-NH_2$ group (a Lewis base) forms a salt with $AlCl_3$, making nitrogen positive and deactivating the ring.

QUICK REVISION

One-page revision

Read this page the night before the exam.

Preparation

- Nitro + Fe/HCl → amine
- RCN + $LiAlH_4$ → RCH_2NH_2 (+1 C)
- Gabriel: pure 1° aliphatic only
- Hofmann: $RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2$ (−1 C)

Basicity

- Aliphatic > NH_3 > aryl
- Water: 2° > 1° ≈ 3° (Et: 2° > 3° > 1°)
- Gas: 3° > 2° > 1°
- EDG ↑, EWG ↓ basicity of anilines

Tests

- Carbylamine: 1° only, foul RNC
- Hinsberg: 1° soluble in KOH; 2° insoluble; 3° none
- HNO_2: 1° aliphatic → ROH + N_2
- 2° → yellow N-nitrosamine

Aniline ring

- Br_2 water → 2,4,6-tribromoaniline
- Acetylate to get mono / para
- Direct nitration: 47% meta (anilinium)
- No Friedel–Crafts; sulphanilic acid zwitterion

Diazonium

- $ArNH_2 + NaNO_2 + HCl$ at 273–278 K
- CuCl, CuBr, CuCN: Sandmeyer
- KI → ArI; HBF_4 → ArF; H_3PO_2 → ArH
- Warm H_2O → phenol

Coupling and conversions

- Phenol → p-hydroxyazobenzene (orange)
- Aniline → p-aminoazobenzene (yellow)
- Ascend: via nitrile; descend: via Hofmann
- $-NH_2$ as a removable director

END OF NOTES · RAMGOVINDYADAV.COM