JEE MAIN · PAPER 1 · CHEMISTRY

18 Organic Compounds Containing Nitrogen

Formula & concept sheet

Amines and their relatives: structure and classification, every NCERT method of preparation (reduction, ammonolysis, Gabriel, Hofmann), basicity orders and the reasons, reactions (acylation, carbylamine, Hinsberg, nitrous acid), electrophilic substitution of aniline and the protecting-group trick, diazonium salts and the whole family of replacement and coupling reactions, with nitro compounds and cyanides. Each idea is explained first, then the reactions drawn as schemes.

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READ ALONGSIDE NCERT XII · Amines

CHAPTER 18

Organic Compounds Containing Nitrogen

NCERT XII · Amines

Covers: classification, structure, nomenclature · preparation of amines (nitro reduction, ammonolysis, nitrile and amide reduction, Gabriel, Hofmann bromamide) · basicity · alkylation, acylation, carbylamine, Hinsberg, HNO_2 · electrophilic substitution of aniline · diazonium salts: Sandmeyer, Gattermann, Balz-Schiemann, coupling · nitro compounds, cyanides and isocyanides.

1 Structure, classification and basicity

- **Amines** are derivatives of NH_3: 1° (RNH_2), 2° (R_2NH), 3° (R_3N); 4° ammonium salts $R_4N^+X^-$. The nitrogen is sp^3 with a lone pair (pyramidal, C−N−C about 108°); amines are polar, 1° and 2° form H bonds (b.p. $1^\circ > 2^\circ > 3^\circ$ of the same mass, all below alcohols). A saturated amine is $C_nH_{2n+3}N$.
- Names: alkanamine ($CH_3CH_2NH_2$ ethanamine), N-alkyl for substituents on N ($CH_3NHC_2H_5$ N-methylethanamine); aromatic: benzenamine (aniline), N,N-dimethylaniline.
- The **lone pair** makes amines basic and nucleophilic. Basicity in water is a balance of the $+I$ effect (raises), **solvation** of the ammonium ion (more N−H gives more H-bonding, better) and steric hindrance.

BASICITY: pK_b IN WATER (NCERT VALUES; LOWER pK_b IS THE STRONGER BASE)

AMINE	pK_b	AMINE	pK_b
$(C_2H_5)_2NH$	3.00	CH_3NH_2	3.38
$(C_2H_5)_3N$	3.25	$(CH_3)_3N$	4.22
$C_2H_5NH_2$	3.29	NH_3	4.75
$(CH_3)_2NH$	3.27	$C_6H_5CH_2NH_2$	4.70
$C_6H_5N(CH_3)_2$	8.92	$C_6H_5NHCH_3$	9.30
$C_6H_5NH_2$ (aniline)	9.38		

BASICITY ORDERS

SERIES	ORDER
ethylamines (aqueous)	$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$
methylamines (aqueous)	$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ (the tertiary amine is hindered and poorly solvated)
gas phase	$3^\circ > 2^\circ > 1^\circ > NH_3$ (only the $+I$ effect acts)
aliphatic vs aromatic	aliphatic amine $> NH_3 >$ aniline $>$ diphenylamine $>$ triphenylamine; benzylamine behaves as aliphatic
substituted anilines	electron-donating groups raise the basicity, electron-withdrawing groups lower it: m- and p-toluidine $>$ aniline (o-toluidine is weaker: ortho effect) $>$ p-chloroaniline $>$ m-nitroaniline $>$ p-nitroaniline; ortho-substituted anilines are weaker (ortho effect)
others	amides are nearly neutral (the lone pair is conjugated with C=O); guanidine is the strongest neutral organic base; pyridine (pK_b 8.8) $>$ aniline; pyrrole is not basic



aniline — ortho — para — anilinium ion (no resonance of N)

aniline: the lone pair is delocalised into the ring (less available, weak base); in the anilinium ion there is no lone pair, so the ring is not activated and the $-NH_3^+$ group directs meta

WHY IT WORKS

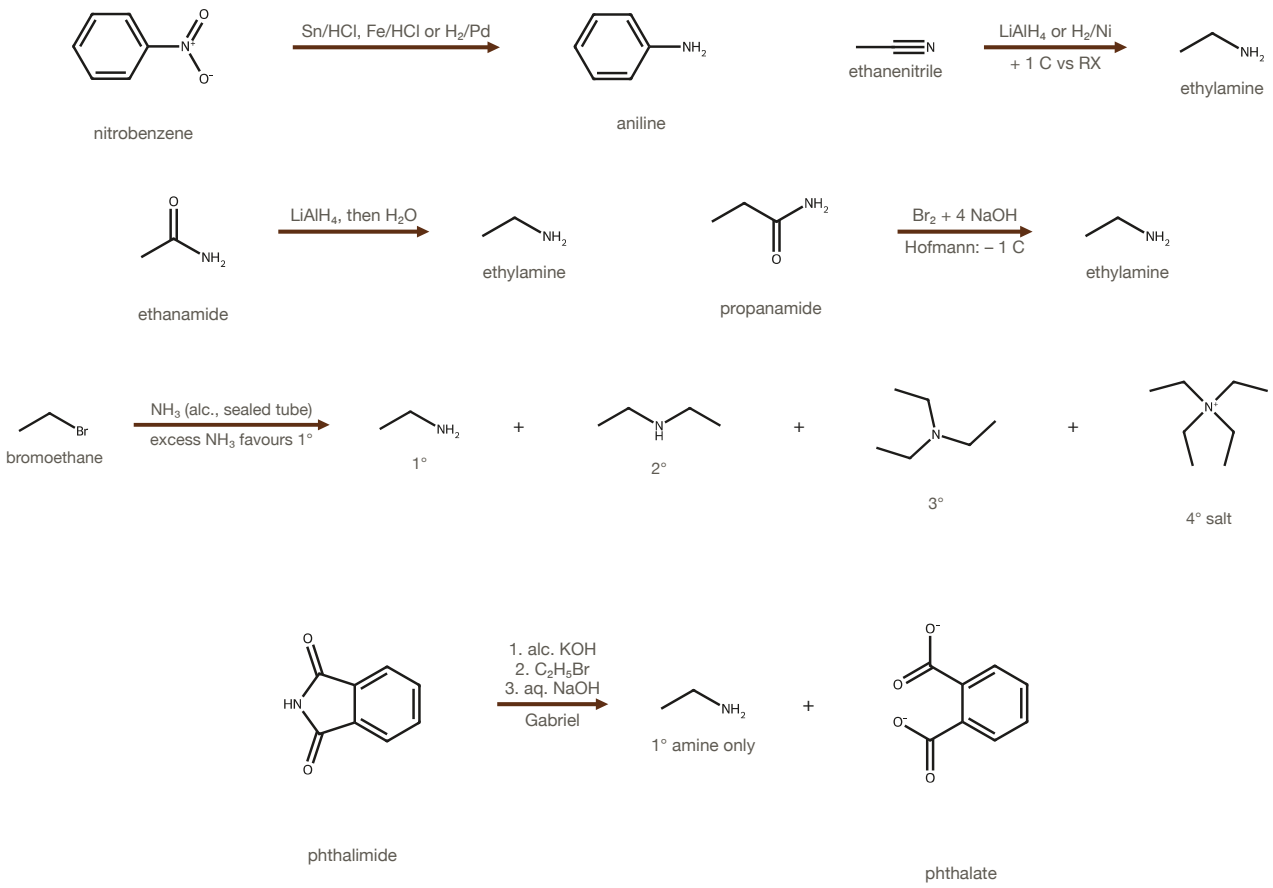
In aniline the nitrogen lone pair overlaps with the ring, so it is shared (resonance) and less available to accept H^+; the anilinium ion has no such delocalisation, so the equilibrium lies towards the free base. Electron-releasing groups push electron density back on N (stronger base), electron-withdrawing groups pull it away.

QUICK CHECK

Arrange by basicity in water: CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$.

Answer: $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > C_6H_5NH_2$ (pK_b 3.27, 3.38, 4.22, 9.38).

2 Preparation of amines



preparation of amines: reduction of nitro compounds, nitriles and amides, ammonolysis of halides (a mixture), Gabriel phthalimide (pure 1°, aliphatic) and Hofmann bromamide (one carbon fewer)

PREPARATION: SUMMARY AND TRAPS

ROUTE	DETAIL
nitro reduction	$\mathrm{ArNO_2 + 6\,[H] \xrightarrow{Sn/HCl,\ Fe/HCl,\ or\ H_2/Pd} ArNH_2 + 2\,H_2O}$; $\mathrm{Fe/HCl}$ is preferred (the $\mathrm{FeCl_2}$ formed hydrolyses and regenerates HCl, so little acid is needed)
ammonolysis	$\mathrm{RX + NH_3 \longrightarrow RNH_2 \longrightarrow R_2NH \longrightarrow R_3N \longrightarrow R_4N^+X^-}$ (successive alkylation): a mixture; a large excess of $\mathrm{NH_3}$ favours the 1° amine; aryl halides do not react
nitrile reduction	$\mathrm{RC{\equiv}N + 4\,[H] \xrightarrow{LiAlH_4\ or\ H_2/Ni} RCH_2NH_2}$ (also $\mathrm{Na/C_2H_5OH}$, Mendius): one carbon **more** than the halide used to make the nitrile
amide reduction	$\mathrm{RCONH_2 \xrightarrow{LiAlH_4,\ then\ H_2O} RCH_2NH_2}$ (same carbon count)
Gabriel phthalimide	phthalimide $\rightarrow$ potassium salt (alc. KOH) $\rightarrow$ N-alkylphthalimide (RX, S_N2) $\rightarrow$ $\mathrm{RNH_2}$ (aq. NaOH or $\mathrm{N_2H_4}$): only **pure** 1° **aliphatic** amines; not aniline (aryl halides do not undergo S_N2)
Hofmann bromamide	$\mathrm{RCONH_2 + Br_2 + 4\,NaOH \longrightarrow RNH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O}$; one carbon **fewer**; through an isocyanate by a $1,2$-shift of R from C to N (the migrating group keeps its configuration)

KEY IDEA

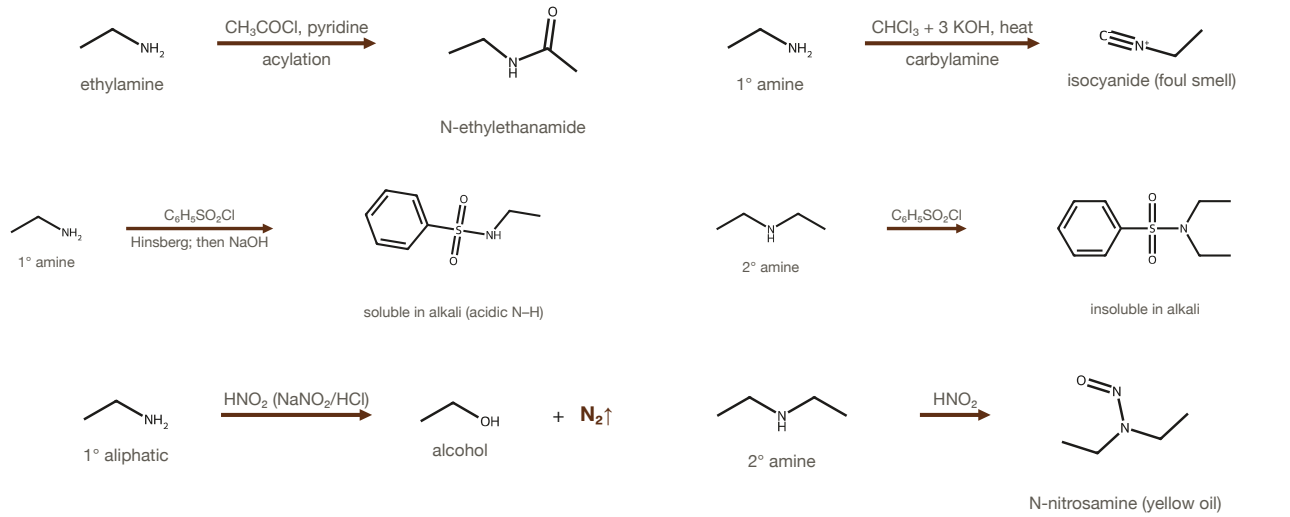
Carbon count decides the route: Hofmann removes one C, nitrile reduction adds one C (to the halide), amide reduction and Gabriel keep the same carbon skeleton. To get a pure 1° amine: Gabriel (aliphatic) or nitro reduction (aromatic).

QUICK CHECK

Propanamide, propanenitrile and 1-bromopropane: which route gives (a) propylamine, (b) ethylamine, (c) butylamine?

Answer: (a) $\mathrm{CH_3CH_2CH_2Br}$ by Gabriel or propanamide + $\mathrm{LiAlH_4}$; (b) propanamide by Hofmann; (c) propanenitrile + $\mathrm{LiAlH_4}$ gives propylamine, but butylamine needs butanenitrile (from propyl bromide + KCN).

3 Reactions of amines and the tests



reactions of amines: acylation (1° and 2° only), carbylamine test (1° only), Hinsberg test, reaction with nitrous acid

REACTIONS OF AMINES

REACTION	DETAIL
salt formation	$\mathrm{RNH_2 + HCl \longrightarrow RNH_3^+Cl^-}$; water-insoluble amines dissolve in dilute acid, NaOH regenerates them
alkylation	with RX $1^\circ \to 2^\circ \to 3^\circ \to$ quaternary ammonium salt
acylation	1° and 2° only (3° has no N−H): $\mathrm{RNH_2 + CH_3COCl \xrightarrow{pyridine} RNHCOCH_3 + HCl}$; benzoylation with $\mathrm{C_6H_5COCl}$ (Schotten-Baumann); pyridine removes HCl and drives it forward
carbylamine	$\mathrm{RNH_2 + CHCl_3 + 3\,KOH \xrightarrow{heat} RNC + 3\,KCl + 3\,H_2O}$: 1° amines only (aliphatic and aromatic), foul-smelling isocyanide; the carbene : $\mathrm{CCl_2}$ is the reagent
nitrous acid ($\mathrm{NaNO_2 + HCl}$)	1° aliphatic: $\mathrm{RNH_2 + HNO_2 \longrightarrow ROH + N_2 + H_2O}$ (bubbles); 1° aromatic at 273 to 278 K: diazonium salt; 2°: yellow oily N-nitrosamine $\mathrm{R_2N-N=O}$; 3° aliphatic: soluble nitrite salt; 3° aromatic ($\mathrm{PhNMe_2}$): p-nitroso compound (green)
Hinsberg ($\mathrm{C_6H_5SO_2Cl}$)	1°: sulphonamide with an acidic N−H, **soluble** in alkali; 2°: sulphonamide with no N−H, **insoluble**; 3°: no reaction

TELLING 1°, 2° AND 3° AMINES APART

TEST	1°	2°	3°
Hinsberg	soluble in KOH	insoluble in KOH	no reaction
carbylamine	foul smell	none	none
$\mathrm{HNO_2}$ (aliphatic)	$\mathrm{N_2}$ gas + alcohol	yellow nitrosamine	nitrite salt
acetylation	yes	yes	no
azo dye (aromatic 1° only)	diazotise, then β-naphthol: orange-red dye	none	none

TRAP

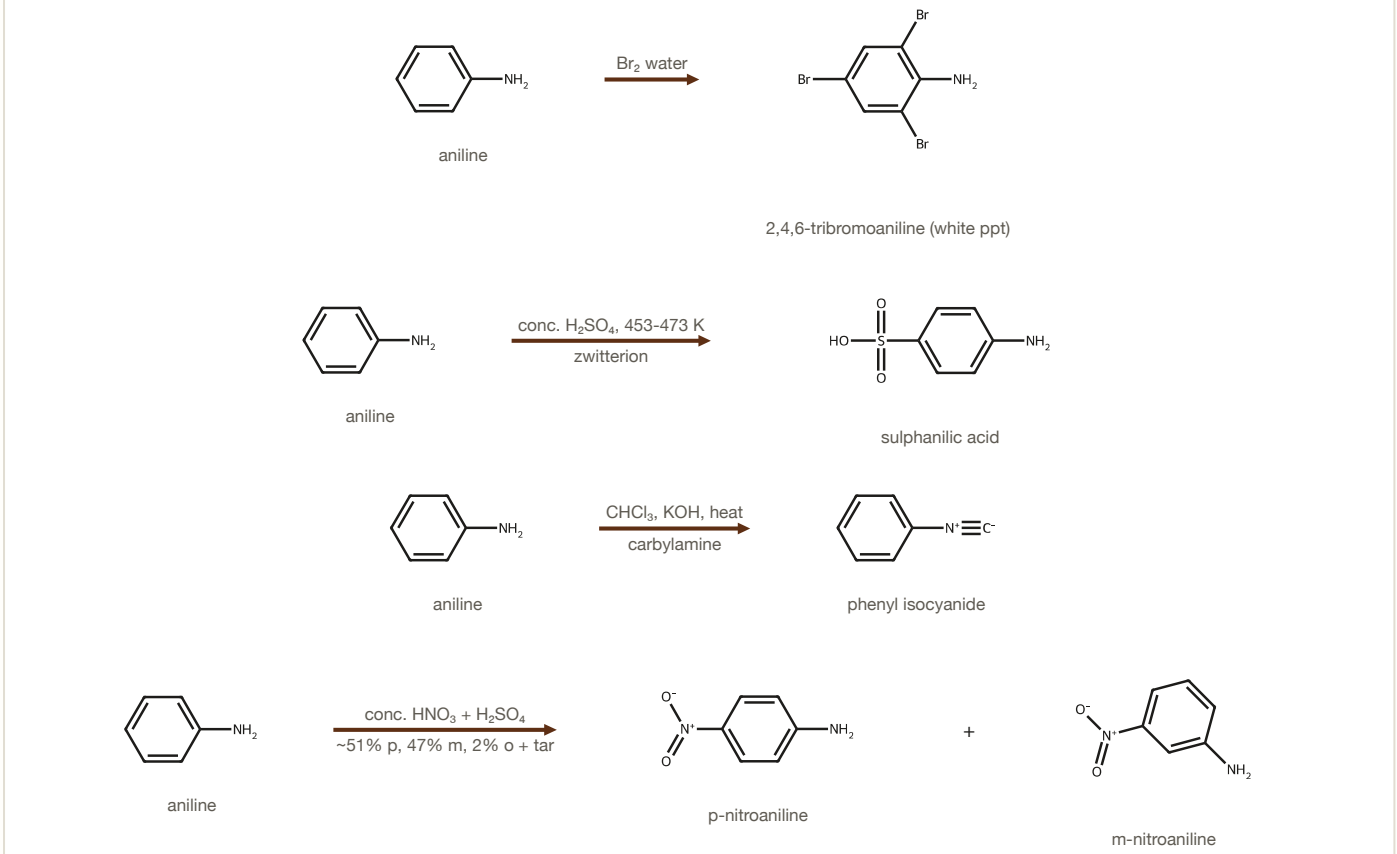
Both aliphatic and aromatic 1° amines give the carbylamine test; the statement "1° amines do not give diazonium salts" is false for aromatic ones. A 3° amine does not react with Hinsberg's reagent nor with acid chlorides. A clear solution after adding alkali to the Hinsberg product means a 1° amine.

QUICK CHECK

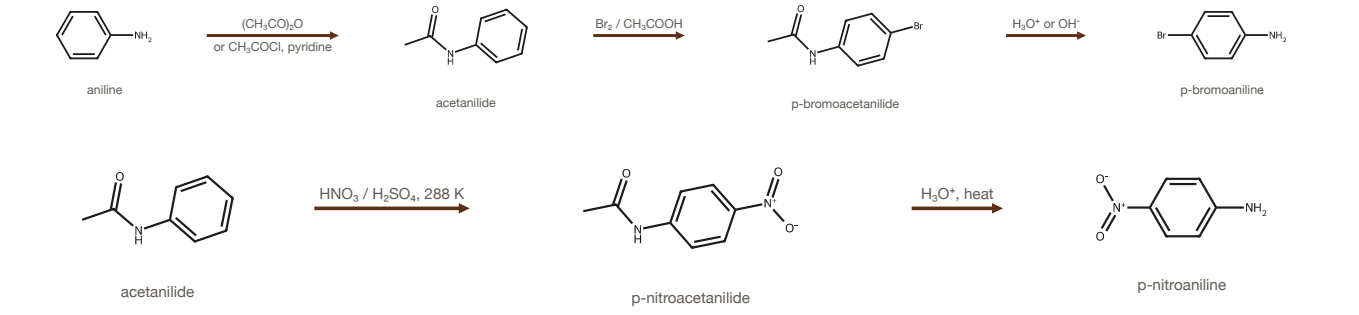
A compound $\mathrm{C_3H_9N}$ forms a sulphonamide soluble in KOH and gives a foul smell with $\mathrm{CHCl_3/KOH}$. Identify it.

Answer: A 1° amine: propan-1-amine or propan-2-amine (both fit; $\mathrm{C_3H_9N}$ with 1° means $\mathrm{CH_3CH_2CH_2NH_2}$ or $\mathrm{(CH_3)_2CHNH_2}$).

4 Aniline: electrophilic substitution and protection



aniline: electrophilic substitution (strongly activated), nitrous acid at 273 K, carbylamine; sulphanilic acid on baking with conc. H_2SO_4



protecting the amino group: acetylation tames the activating NH_2, allows a clean para substitution, then hydrolysis returns the amine

ANILINE AND ELECTROPHILIC SUBSTITUTION

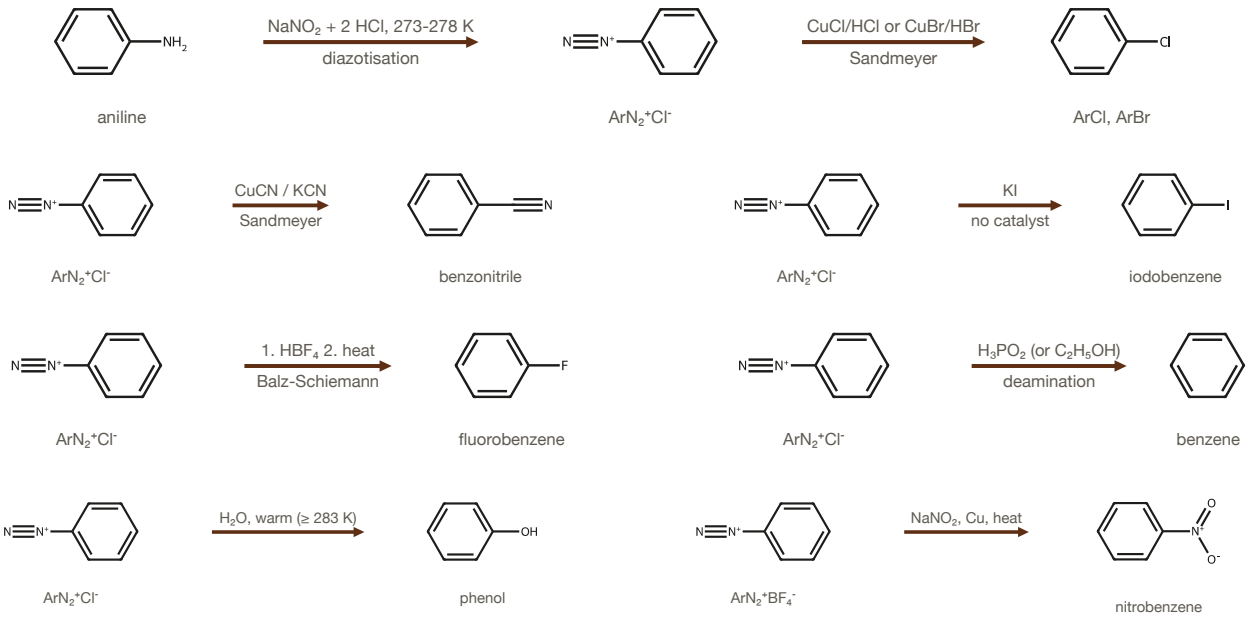
- $-NH_2$ is a strong o/p activator: bromine water gives 2,4,6-tribromoaniline at once (white precipitate).
- Direct nitration gives tarry oxidation products and a large meta fraction (about 51% para, 47% meta, 2% ortho), because in the acid the amine is protonated to $C_6H_5NH_3^+$, a meta director.
- **Protection** by acetylation ($-NHCOCH_3$, a milder o/p activator whose lone pair is shared with C=O) allows clean para bromination or nitration; hydrolysis then frees the amine.

TRAP

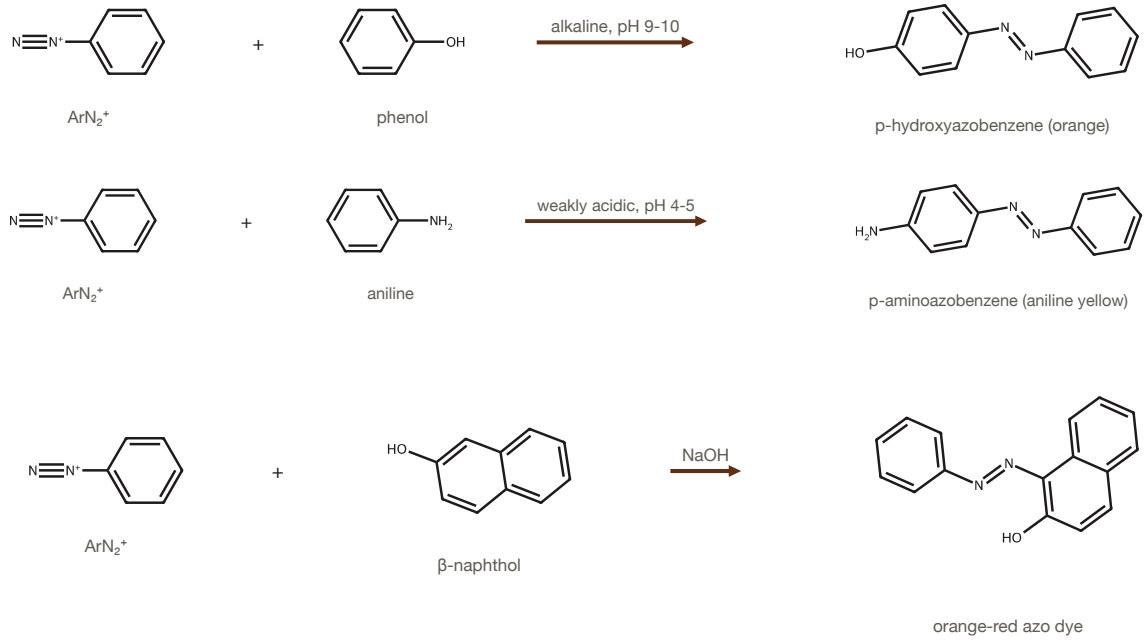
Aniline gives no Friedel-Crafts reaction: the N lone pair binds $AlCl_3$ and the ring becomes strongly deactivated. Sulphonation with conc. H_2SO_4 goes through anilinium hydrogensulphate; heating at 453 to 473 K gives sulphanilic acid, a zwitterion ($H_3N^+-C_6H_4-SO_3^-$).

5 Diazonium salts

- Primary aromatic amines react with $NaNO_2 + HCl$ at 273 to 278 K to give **diazonium salts** $ArN_2^+X^-$ ($C_6H_5NH_2 + NaNO_2 + 2\,HCl \longrightarrow C_6H_5N_2^+Cl^- + NaCl + 2\,H_2O$). Aryl diazonium ions are stable only in cold solution because the $Ar-N_2^+$ is stabilised by resonance with the ring; aliphatic ones decompose at once to the alcohol and N_2. On warming, ArN_2^+ loses N_2.
- Two kinds of reaction: **replacement** of N_2 (gives Cl, Br, CN, I, F, H, OH, NO_2 on the ring where direct substitution fails) and **coupling** (the N_2 is kept: azo dyes).



benzenediazonium chloride (made at 273-278 K): replacement of N_2 (Sandmeyer, Gattermann, iodide, Balz-Schiemann, deamination, hydrolysis)



coupling of the diazonium ion (the electrophile keeps N_2) at the para position of an activated ring: phenols in alkaline, anilines in weakly acidic medium; β-naphthol gives an orange-red dye (test for an aromatic 1° amine)

REPLACEMENT AND COUPLING: REAGENTS AT A GLANCE

REAGENT	PRODUCT	NAME
$CuCl/HCl$, $CuBr/HBr$	$ArCl$, $ArBr$	Sandmeyer
$CuCN/KCN$	$ArCN$	Sandmeyer
Cu powder + HCl or HBr	$ArCl$, $ArBr$	Gattermann
KI (no Cu needed)	ArI	
HBF_4, then heat	$ArN_2{}^+BF_4- \rightarrow ArF + BF_3 + N_2$	Balz-Schiemann
H_3PO_2 or C_2H_5OH	ArH (ethanol gives ethanal)	deamination
H_2O, warm	$ArOH$	hydrolysis
HBF_4, then $NaNO_2/Cu$, heat	$ArNO_2$	
phenol, aniline, β-naphthol	azo dyes (coupling)	phenol: alkaline pH 9-10; aniline: pH 4-5; β-naphthol: alkaline

WHY IT WORKS

The diazonium ion is a weak electrophile: it attacks only strongly activated rings (phenoxide, aniline, naphthol) at the para position (ortho if para is blocked). In strongly acidic solution the aniline is protonated and does not couple; in strongly alkaline solution the diazonium ion is converted to inactive diazotate: hence the pH windows. Diazonium chemistry puts F, I, CN, OH, H on a ring where direct substitution fails, e.g. 1,3,5-tribromobenzene from aniline (brominate, diazotise, H_3PO_2).

QUICK CHECK

Aniline to 1,3,5-tribromobenzene, and aniline to iodobenzene.

Answer:

$C_6H_5NH_2 \xrightarrow{Br_2/H_2O} 2,4,6\text{-}C_6H_2Br_3NH_2 \xrightarrow[273\,K]{NaNO_2/HCl} \text{diazonium} \xrightarrow{H_3PO_2} 1,3,5\text{-}C_6H_3Br_3$; iodobenzene: diazotise, then KI.

6 Nitro compounds, cyanides and isocyanides

NITRO COMPOUNDS

ITEM	REACTION
nitroalkane	$RX + AgNO_2 \longrightarrow RNO_2 + AgX$ (KNO_2 gives the nitrite ester $RONO$ instead); also from nitration of alkanes at high T
nitrobenzene	$C_6H_6 + HNO_3 \xrightarrow{\text{conc}\cdot H_2SO_4,\ 333\ K} C_6H_5NO_2 + H_2O$; m-dinitrobenzene with fuming HNO_3 at higher T; pale yellow oil of bitter-almond smell
reduction in acid	$ArNO_2 \xrightarrow{Sn/HCl} ArNH_2$ (aniline)
reduction by medium	neutral (Zn/NH_4Cl): $ArNHOH$ (phenylhydroxylamine); alkaline: azoxybenzene $\rightarrow$ azobenzene $\rightarrow$ hydrazobenzene ($Zn/NaOH$)
acidity	nitroalkanes with α-H show nitro-aci tautomerism and dissolve in alkali

CYANIDES AND ISOCYANIDES

ITEM	REACTION
alkyl cyanide (nitrile)	$RX + KCN \longrightarrow RCN + KX$ (KCN is ionic: C attacks); hydrolysis $RCN \xrightarrow{H_3O^+} RCONH_2 \longrightarrow RCOOH$; reduction to RCH_2NH_2; Stephen (to aldehyde); Grignard (to ketone)
alkyl isocyanide	$RX + AgCN \longrightarrow RNC + AgX$ (covalent $AgCN$: N attacks); carbylamine reaction; hydrolysis with dilute acid gives $RNH_2 + HCOOH$ (isocyanides are stable to alkali); reduction gives the N-methyl amine $RNHCH_3$
difference	cyanide: R–C≡N (sweet smell, hydrolysed by acid and alkali); isocyanide: R–N⁺≡C⁻ (offensive smell, not hydrolysed by alkali)

REMEMBER

- Stephen reduction of a nitrile ($SnCl_2/HCl$, then H_2O) gives an **aldehyde**, not an amine; $LiAlH_4$ gives the amine.
- KCN gives nitrile, $AgCN$ gives isocyanide; KNO_2 gives nitrite, $AgNO_2$ nitro compound.
- N-benzylphthalimide has $8\ \pi$ bonds (2 C=O + two benzene rings $\times 3$).

QUICK CHECK

279 g of aniline is coupled with 1 equivalent of benzenediazonium chloride at pH 4-5. Mass of the dye ($C_{12}H_{11}N_3$, $M = 197$)?

Answer: $279/93 = 3$ mol aniline, 3 mol aniline yellow: $3 \times 197 = 591$ g.

7 Worked examples

HOFMANN

Amine from propanamide by Hofmann bromamide, and its carbon count change.

$CH_3CH_2CONH_2 + Br_2 + 4\,NaOH \longrightarrow CH_3CH_2NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O$; ethylamine, one C fewer

CONVERSION

Benzene to aniline to p-bromoaniline.

$C_6H_6 \xrightarrow{HNO_3/H_2SO_4} C_6H_5NO_2 \xrightarrow{Sn/H}$

GABRIEL LIMITS

Can Gabriel's synthesis make aniline or isopropylamine?

aniline: no (aryl halide does not undergo S_N2); isopropylamine: poor (2° halide, E2 competes); best for methylamine, ethylamine and other 1° alkyl halides

PRODUCT OF COUPLING

Product when benzenediazonium chloride is added to a mixture of phenol and aniline in acid, in base?

in acidic medium it couples with aniline (p-aminoazobenzene, phenol coupling is slow in acid); in alkaline medium with phenoxide (p-hydroxyazobenzene)

HINSBERG RESULT

An amine gives a sulphonamide that dissolves in KOH. Which class? And with HNO_2 at 273 K, the amine is aliphatic and evolves a gas: product?

1° amine (acidic N−H);
$RNH_2 + HNO_2 \longrightarrow ROH + N_2 + H_2O$ (nitrogen gas)

BASICITY RANKING

Order $C_6H_5NH_2$, p-$O_2NC_6H_4NH_2$, p-$CH_3C_6H_4NH_2$, $C_6H_5CH_2NH_2$.

$C_6H_5CH_2NH_2 > p$-toluidine $>$ aniline $>$ p-nitroaniline

8 Last-minute checklist

BEFORE YOU ANSWER

Aliphatic or aromatic? 1°, 2° or 3°? Does the question want one carbon fewer (Hofmann), one more (nitrile) or the same (Gabriel, amide reduction)? Which pH for coupling?

- Prep: Sn/HCl, Fe/HCl, H_2/Pd on $ArNO_2$; ammonolysis mixes; nitrile and amide reduction ($LiAlH_4$); Gabriel (pure 1° aliphatic); Hofmann $RCONH_2 + Br_2 + 4\,NaOH$ (-1 C).
- Basicity (aq.): $R_2NH > R_3N > RNH_2 > NH_3$ (ethyl), $Me_2NH > MeNH_2 > Me_3N$; aliphatic $> NH_3 >$ aniline; EDG raises, EWG lowers; amide neutral.
- Tests: carbylamine (1°, foul smell), Hinsberg (1° soluble in alkali, 2° insoluble, 3° none), HNO_2 (1° aliphatic N_2; 2° nitrosamine; 1° aromatic diazonium); acylation 1° and 2° only.
- Aniline: tribromo with bromine water; nitration gives meta (anilinium); acetylation protects; no Friedel-Crafts; sulphanilic acid is a zwitterion.
- Diazonium (273-278 K): Sandmeyer (Cu(I)), Gattermann (Cu), KI, HBF_4 (F), H_3PO_2 (H), H_2O warm (OH), coupling (phenol alkaline, aniline weakly acidic, naphthol dye); KCN nitrile vs AgCN isocyanide; Stephen gives an aldehyde.

Now test it. Practise this chapter with past-paper and bank questions on Prep Vault. **Practice this chapter →**