

Organic Chemistry

Class 12 Notes | reactions, reasons, mnemonics and practice

What is inside

- 1. Haloalkanes and Haloarenes
- 2. Alcohols, Phenols and Ethers
- 3. Aldehydes, Ketones and Carboxylic Acids
- 4. Amines (with diazonium salts)
- 5. Biomolecules: carbohydrates, proteins, vitamins, nucleic acids
- 6. Quick sheets: named reactions, distinguishing tests, mnemonic wall
- 7. Practice: MCQs, 'why' questions, conversions, with an answer key

REMEMBER: How to study organic: do not memorise paragraphs. For every reaction write four things: **what goes in, which reagent, what comes out, and the one-line reason.** If you cannot give the reason, you will forget it by the exam.

REMEMBER: Three questions to ask before any reaction: (1) What is the functional group? (2) Is the reagent an acid, a base, a nucleophile or an electrophile? (3) Which carbon is attacked, and which bond breaks?

Reaction arrows are written with a single arrow. Conditions are given after the reagent. 1° , 2° , 3° mean primary, secondary, tertiary.

Haloalkanes and Haloarenes

Alkyl or aryl groups carrying a halogen (F, Cl, Br, I). Major themes: preparation, SN1 vs SN2, elimination, why haloarenes are lazy.

Types and reactivity

- **Haloalkane:** halogen on an sp^3 carbon. **Haloarene:** halogen on an sp^2 carbon of a benzene ring.
- **Allylic and benzylic** halides are very reactive (the carbocation or transition state is stabilised by the double bond or ring).
- **Vinyllic and aryl** halides are sluggish (the C-X bond has partial double-bond character through resonance).

Preparation

$R-OH + SOCl_2 \rightarrow R-Cl + SO_2\uparrow + HCl\uparrow$ (best method: both by-products are gases, product comes out pure)

$R-OH + HCl$ (anhydrous $ZnCl_2$) $\rightarrow R-Cl + H_2O$; $R-OH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl$; $3R-OH + PCl_3 \rightarrow 3R-Cl + H_3PO_3$

$R-OH + \text{red P}/Br_2 \rightarrow R-Br$ (and red P/I₂ for R-I)

Alkene + HX $\rightarrow$ Markovnikov product. HBr + peroxide $\rightarrow$ anti-Markovnikov (works for HBr only)

Finkelstein: $R-Cl/R-Br + NaI$ (dry acetone) $\rightarrow R-I + NaCl\downarrow$ (NaCl and NaBr do not dissolve in acetone, so the reaction is driven forward)

Swarts: $R-Cl/R-Br + AgF$ (or Hg_2F_2 , CoF_2 , SbF_3) $\rightarrow R-F$

Sandmeyer: $ArN_2^+Cl^- + CuCl/HCl \rightarrow ArCl + N_2$. **Gattermann:** same idea with copper powder + HCl

Benzene + Cl_2 (anhy. $FeCl_3$) $\rightarrow$ chlorobenzene. For iodination an oxidising agent (HNO_3) is needed to remove the HI formed

REMEMBER: Fluorides by Swarts (S for Silver), iodides by Finkelstein (F-I: Finkelstein-Iodide).

Free-radical halogenation of alkanes is never the method of choice: it gives a messy mixture.

Physical properties

- Boiling point order for the same alkyl group: **R-I > R-Br > R-Cl > R-F** (bigger halogen, bigger polarisability, stronger van der Waals forces). Branching lowers boiling point.
- Insoluble in water: they cannot form hydrogen bonds strong enough to break water's own hydrogen bonds. Soluble in organic solvents.
- Among the dihalobenzene isomers the **para** isomer has the highest melting point because it packs best in the crystal.

Nucleophilic substitution: SN1 vs SN2

	SN1	SN2
Steps	Two steps (slow ionisation, then fast attack)	One concerted step
Rate law	rate = $k[R-X]$ (first order)	rate = $k[R-X][Nu]$ (second order)
Key species	Carbocation intermediate	Five-coordinate transition state
Substrate order	$3^\circ > 2^\circ > 1^\circ > CH_3X$	$CH_3X > 1^\circ > 2^\circ > 3^\circ$
Stereochemistry	Racemisation (attack from both faces)	Inversion of configuration (Walden inversion)
Best solvent	Polar protic (water, alcohols)	Polar aprotic (acetone, DMF, DMSO)
Nucleophile	Weak is fine	Strong needed
Leaving group	$I > Br > Cl > F$ (same for both)	$I > Br > Cl > F$

REMEMBER: The numbers swap: SN1 has 2 steps, SN2 has 1 step. SN1 has one species in the rate law, SN2 has two. **Tertiary goes SN1** (the cation loves crowding), **primary goes SN2** (the nucleophile needs room). SN2 inversion = an umbrella flipping in the wind.

Ambident nucleophiles (a favourite 2-mark question)

Reagent	Attacks through	Product
KCN (ionic)	Carbon	R-CN (alkyl cyanide)
AgCN (covalent)	Nitrogen	R-NC (isocyanide)
KNO ₂ (ionic)	Oxygen	R-O-N=O (alkyl nitrite)
AgNO ₂ (covalent)	Nitrogen	R-NO ₂ (nitroalkane)

REMEMBER: K-cyanide: Carbon attacks. K-nitrite: Oxygen attacks. Silver flips both.

Reactions of haloalkanes

$R-X + \text{aq. KOH} \rightarrow R-OH$ (substitution) $R-X + \text{alc. KOH} \rightarrow \text{alkene}$ (elimination, loses a β -hydrogen, Saytzeff product)

$R-X + NH_3 \rightarrow R-NH_2$ (plus 2° , 3° amines and a salt) $R-X + KCN \rightarrow R-CN$

Grignard: $R-X + Mg$ (dry ether) $\rightarrow R-MgX$; $R-MgX + H_2O \rightarrow R-H + Mg(OH)X$ (so reagents must be perfectly dry)

Wurtz: $2R-X + 2Na$ (dry ether) $\rightarrow R-R + 2NaX$. **Wurtz-Fittig:** $Ar-X + R-X + 2Na \rightarrow Ar-R$. **Fittig:** $2Ar-X + 2Na \rightarrow Ar-Ar$

REMEMBER: Alcoholic KOH = Alkene. Aqueous KOH = Alcohol. Saytzeff: the more substituted (more stable) alkene is the major product.

Haloarenes: why they refuse nucleophilic substitution

- Resonance:** the lone pair on Cl delocalises into the ring, giving the C-Cl bond partial double-bond character (shorter, stronger).
- Hybridisation:** carbon is sp^2 , more electronegative than sp^3 , so it holds the bond tighter.
- No SN1:** the phenyl cation is not stabilised by resonance. **No SN2:** the ring's π cloud repels the incoming nucleophile.

Haloarenes

Dow process: chlorobenzene + NaOH at 623 K, 300 atm $\rightarrow$ sodium phenoxide $\rightarrow (H^+) \rightarrow$ phenol

-NO₂ at the ortho or para position makes substitution easier: one NO₂ needs 443 K, two need 368 K, three (2,4,6-trinitrochlorobenzene) react with warm water alone

Electrophilic substitution: halogen is ortho-para directing (resonance) but ring-deactivating (-I effect). Nitration, halogenation, sulphonation and Friedel-Crafts all work, slowly

REMEMBER: More NO₂ = easier substitution: 443 K, 368 K, warm water. A meta nitro group does nothing.

Stereochemistry in four lines

- A **chiral carbon** has four different groups. Mirror-image, non-superimposable molecules are **enantiomers**; they rotate plane-polarised light by equal amounts in opposite directions.
- A 50:50 mixture of the two is a **racemic mixture**: optically inactive (the rotations cancel).
- Retention** = bond to the chiral centre is not broken. **Inversion** = configuration flips (SN2). **Racemisation** = both forms appear (SN1).

Polyhalogen compounds

Compound	Use	Catch
CHCl ₃ (chloroform)	Solvent, earlier an anaesthetic	In air and light it oxidises to phosgene (COCl ₂), a poisonous gas. Store in dark, filled-to-the-top bottles; 1% ethanol is added to convert phosgene to harmless ethyl carbonate
CHI ₃ (iodoform)	Antiseptic	The antiseptic action is due to liberated iodine
CCl ₄	Solvent, once in fire extinguishers	Damages liver; contributes to ozone depletion
Freons (e.g. CCl ₂ F ₂)	Refrigerants, aerosol propellants	Ozone depletion in the stratosphere
DDT	Insecticide	Not biodegradable, accumulates in fat tissue

REMEMBER: Chloroform + light + air = phosgene. Keep it dark, keep it full, add a pinch of alcohol.

Alcohols, Phenols and Ethers

R-OH, Ar-OH and R-O-R. Major themes: preparation by reduction and Grignard, acidity, Lucas test, dehydration, phenol substitution.

Preparation of alcohols

Alcohols

Hydration: alkene + $\text{H}_2\text{O}/\text{H}^+$ → alcohol (Markovnikov)

Hydroboration-oxidation: alkene + B_2H_6 , then $\text{H}_2\text{O}_2/\text{NaOH}$ → alcohol (**anti**-Markovnikov; terminal alkene gives 1° alcohol)

Reduction: RCHO → 1° alcohol; R-CO-R' → 2° alcohol (with NaBH_4 , LiAlH_4 or H_2/Pd). RCOOH and esters → 1° alcohol need the strong LiAlH_4 (NaBH_4 is too mild)

Grignard: HCHO → 1° alcohol; other RCHO → 2°; ketone → 3° (then add water or dilute acid)

$\text{R-X} + \text{aq. KOH} \rightarrow \text{R-OH}$

REMEMBER: Grignard counting: H-1, Ald-2, Ket-3. Formaldehyde gives 1°, other aldehydes 2°, ketones 3°. **NaBH_4 is the gentle one** (aldehydes and ketones only); LiAlH_4 reduces almost everything and must be used in dry ether.

Preparation of phenol

Cumene process (industrial): cumene (isopropylbenzene) + $\text{O}_2 \rightarrow$ cumene hydroperoxide → (H_3O^+) phenol + acetone

From chlorobenzene: NaOH , 623 K, 320 atm, then H^+ . **From benzene sulphonic acid:** fuse with NaOH , then H^+

From diazonium salt: $\text{ArN}_2^+ + \text{warm water} \rightarrow \text{ArOH} + \text{N}_2$

Physical properties and acidity

- Alcohols boil much higher than ethers and alkanes of similar mass because of **intermolecular hydrogen bonding**. Ethers cannot hydrogen-bond to each other. Branching lowers the boiling point.
- Solubility in water drops as the alkyl chain grows (the hydrocarbon part outweighs the OH).
- Acidity of alcohols:** $\text{CH}_3\text{OH} > 1^\circ > 2^\circ > 3^\circ$. Alkyl groups push electrons towards oxygen (+I), making the alkoxide less stable.
- Phenol is far more acidic than alcohols:** the phenoxide ion is stabilised by resonance, spreading the negative charge into the ring.
- Electron-withdrawing groups ($-\text{NO}_2$, $-\text{X}$) at ortho/para increase phenol's acidity. Electron-donating groups ($-\text{CH}_3$, $-\text{OCH}_3$) decrease it.

REMEMBER: Acid ladder: carboxylic acid > phenol > water > alcohol. Phenol dissolves in NaOH but **not** in NaHCO_3 ; a carboxylic acid does both. That is how you tell them apart.

Reactions of alcohols

Alcohol reactions

$2\text{R-OH} + 2\text{Na} \rightarrow 2\text{R-ONa} + \text{H}_2\uparrow$ Esterification: $\text{R-OH} + \text{R'COOH} \leftrightarrow \text{ester} + \text{water (H}^+)$

Dehydration: conc. H_2SO_4 at **443 K** $\rightarrow$ alkene. Same acid at **413 K** with excess 1° alcohol $\rightarrow$ ether. Ease of dehydration: $3^\circ > 2^\circ > 1^\circ$

Dehydrogenation: Cu, 573 K: $1^\circ \rightarrow$ aldehyde, $2^\circ \rightarrow$ ketone, $3^\circ \rightarrow$ alkene

REMEMBER: Hot = alkene (443 K), cooler = ether (413 K). Ether formation works for 1° alcohols only; 3° alcohols just eliminate.

Oxidising agent	1° alcohol	2° alcohol	3° alcohol
PCC (in CH_2Cl_2)	Aldehyde (stops here)	Ketone	No reaction
Acidified KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$	Carboxylic acid	Ketone	No reaction under mild conditions

Lucas test (separates 1° , 2° , 3° alcohols)

Reagent: conc. HCl + anhydrous ZnCl_2 . The alcohol turns into an insoluble alkyl chloride, seen as turbidity. Rate follows carbocation stability.

Alcohol	Observation
3°	Turbid immediately
2°	Turbid in about 5 minutes
1°	No turbidity at room temperature (only on heating)

REMEMBER: Tertiary: Today (instantly). Secondary: Soon (5 min). Primary: Pending (never, at room temperature).

Reactions of phenol

Phenol reactions

$\text{ArOH} + \text{NaOH} \rightarrow \text{ArONa} + \text{H}_2\text{O}$ (alcohols do not do this). $\text{ArOH} + \text{Zn dust} \rightarrow$ benzene. Oxidation with chromic acid $\rightarrow$ benzoquinone

Nitration: dilute $\text{HNO}_3 \rightarrow$ o- and p-nitrophenol (separated by steam distillation: the ortho isomer, with intramolecular H-bonding, is steam volatile). Conc. $\text{HNO}_3 \rightarrow$ **2,4,6-trinitrophenol (picric acid)**

Bromination: Br_2 in CS_2 at low temperature $\rightarrow$ o/p-bromophenol. Bromine water $\rightarrow$ **2,4,6-tribromophenol**, white precipitate

Kolbe: sodium phenoxide + CO_2 (400 K, 4-7 atm), then $\text{H}^+ \rightarrow$ **salicylic acid**

Reimer-Tiemann: phenol + CHCl_3 + aq. NaOH (340 K), then $\text{H}^+ \rightarrow$ **salicylaldehyde**

FeCl_3 test: neutral ferric chloride gives a violet colour with phenol. Aspirin: salicylic acid + acetic anhydride

REMEMBER: Kolbe: CO_2 gives COOH . Reimer-Tiemann: CHCl_3 gives CHO . Both add the new group mainly ortho to OH. The -OH group is a strong activator, which is why bromine water needs no catalyst.

Ethers

Ethers

Williamson synthesis (SN2): $R-ONa + R'-X \rightarrow R-O-R' + NaX$. Use a **primary** alkyl halide; a tertiary one eliminates and gives an alkene

Cleavage with HI: $R-O-R' + HI \rightarrow R-I + R'-OH$; excess HI gives two R-I. Iodide attacks the **smaller** alkyl group (SN2); if one group is **tertiary** it leaves as the 3° iodide (SN1)

Aryl alkyl ethers: $C_6H_5-O-CH_3 + HI \rightarrow C_6H_5-OH + CH_3I$. The Ar-O bond has partial double-bond character and never breaks

Anisole ($C_6H_5OCH_3$): $-OCH_3$ activates the ring, ortho-para directing. Friedel-Crafts, nitration and bromination work (mainly para)

REMEMBER: Bulky group on the alkoxide, small group on the halide. To make tert-butyl methyl ether use sodium tert-butoxide + CH_3Br , never $NaOCH_3$ + tert-butyl bromide.

Aldehydes, Ketones and Carboxylic Acids

The C=O family. Major themes: named preparations, nucleophilic addition, aldol vs Cannizzaro, tests, acidity of acids.

Preparation of aldehydes and ketones

Reaction	Reagent and conditions	Gives
Oxidation of 1° alcohol	PCC, or Cu at 573 K	RCHO
Rosenmund reduction	$\text{RCOCl} + \text{H}_2$, Pd on BaSO_4 (poisoned catalyst, stops at aldehyde)	RCHO
Stephen reduction	$\text{RCN} + \text{SnCl}_2/\text{HCl}$, then H_3O^+	RCHO
DIBAL-H	Nitrile or ester + DIBAL-H, then water	RCHO
Etard reaction	Toluene + CrO_2Cl_2 in CS_2 , then H_3O^+	Benzaldehyde
Gattermann-Koch	Benzene + CO + HCl, anhy. $\text{AlCl}_3/\text{CuCl}$	Benzaldehyde
Friedel-Crafts acylation	Benzene + RCOCl , anhy. AlCl_3	Aryl ketone
Hydration of alkynes	$\text{HgSO}_4/\text{H}_2\text{SO}_4$: ethyne gives CH_3CHO ; other alkynes give ketones	Aldehyde / ketone
Oxidation of 2° alcohol, or ozonolysis	$\text{K}_2\text{Cr}_2\text{O}_7$; or O_3 then $\text{Zn}/\text{H}_2\text{O}$	Ketone
Acyl chloride + dialkylcadmium	$2\text{RCOCl} + \text{R}'_2\text{Cd} \rightarrow 2\text{RCOR}' + \text{CdCl}_2$	Ketone

REMEMBER: Every Student Reads Good books = E S R G: Etard (CrO_2Cl_2), Stephen (SnCl_2), Rosenmund (H_2 , Pd- BaSO_4), Gattermann-Koch (CO + HCl). All four make aldehydes.

Physical properties

- The C=O bond is polar (C is δ^+ , O is δ^-). Aldehydes and ketones have dipole-dipole attraction but **no** hydrogen bonding with themselves, so they boil lower than alcohols and higher than ethers and alkanes.
- Lower members dissolve in water because the oxygen hydrogen-bonds with water. Solubility falls as chain length grows.

REMEMBER: Boiling point ladder (similar mass): Acids > Alcohols > Aldehydes/Ketones > Ethers > Alkanes. First letters: A-A-A-E-A. Acids win because they form hydrogen-bonded dimers.

Nucleophilic addition: the signature reaction

The nucleophile attacks the δ^+ carbon, which changes from sp^2 (planar) to sp^3 ; the oxygen picks up the negative charge and is then protonated.

- Aldehydes are more reactive than ketones:** (1) only one alkyl group, so less crowding; (2) two alkyl groups in a ketone push electrons (+I) and reduce the δ^+ on carbon.
- Aromatic aldehydes are less reactive than aliphatic ones:** the ring donates electrons by resonance, lowering the δ^+ on carbon.

REMEMBER: Reactivity: $\text{HCHO} > \text{other aldehydes} > \text{ketones} > \text{aromatic ketones}$. Small and electron-poor carbon wins.

Reagent	Product	Note
HCN (trace base)	Cyanohydrin (hydroxynitrile)	Adds one carbon
NaHSO ₃	Bisulphite addition compound	Crystalline, reversible; used to purify carbonyls
R'OH, dry HCl	Hemiacetal, then acetal	Ketone + ethylene glycol gives a cyclic ketal (protecting group)
NH ₂ OH	Oxime	Ammonia derivatives, all with C=N
NH ₂ NH ₂	Hydrazone	
C ₆ H ₅ NHNH ₂	Phenylhydrazone	
2,4-DNP	2,4-dinitrophenylhydrazone	Orange/yellow precipitate: test for any carbonyl
Semicarbazide	Semicarbazone	
Grignard reagent	Alcohol (see chapter 2)	

Reduction, oxidation and tests

Reduction and oxidation

To alcohol: NaBH₄, LiAlH₄ or H₂/Ni. **To alkane (C=O → CH₂):**

Clemmensen: Zn-Hg + conc. HCl (acidic). **Wolff-Kishner:** NH₂NH₂, then KOH in ethylene glycol, heat (basic)

Tollens' test: RCHO + 2[Ag(NH₃)₂]⁺ + 3OH⁻ → RCOO⁻ + 2Ag↓ + 4NH₃ + 2H₂O (silver mirror). Aldehydes only; ketones do not respond

Fehling's test: Cu²⁺ (tartrate complex, alkaline) → red-brown Cu₂O↓. Aliphatic aldehydes only; **benzaldehyde does not respond**

Iodoform test: I₂/NaOH gives yellow CHI₃↓ with CH₃CO- (methyl ketones, acetaldehyde) and CH₃CH(OH)- (ethanol, propan-2-ol, etc.)

REMEMBER: Clemmensen = acid (Zinc-mercury, HCl). Wolff-Kishner = base (KOH). Choose the one the rest of your molecule can survive. **Tollens = mirror, Fehling = red.** Benzaldehyde: Tollens yes, Fehling no. HCOOH also gives both.

Aldol vs Cannizzaro

Two carbonyl classics

Aldol: 2CH₃CHO (dilute NaOH) → CH₃CH(OH)CH₂CHO (3-hydroxybutanal, 'aldol') → heat → CH₃CH=CHCHO (but-2-enal) + water

Cannizzaro: 2HCHO + conc. NaOH → CH₃OH + HCOONa; 2C₆H₅CHO + conc. NaOH → C₆H₅CH₂OH + C₆H₅COONa

	Aldol condensation	Cannizzaro reaction
Needs	At least one α-hydrogen	No α-hydrogen (HCHO, benzaldehyde, 2,2-dimethylpropanal)
Base	Dilute NaOH	Concentrated NaOH
What happens	Carbanion attacks another carbonyl, new C-C bond forms	Disproportionation: one molecule oxidised (acid salt), one reduced (alcohol)

REMEMBER: Aldol needs Alpha-H. Cannizzaro: No Alpha-H. Cross-aldol between two different enolisable partners gives four products; it works well only if one partner has no α-H.

Carboxylic acids

Preparation

RCH_2OH or RCHO oxidised (KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$) $\rightarrow$ RCOOH . **Alkylbenzene + KMnO_4/KOH , heat**, then $\text{H}_3\text{O}^+ \rightarrow$ benzoic acid (any side chain with a benzylic H shrinks to just $-\text{COOH}$)

RCN or $\text{RCONH}_2 + \text{H}_3\text{O}^+$ (or OH^- then H^+) $\rightarrow$ RCOOH . **Grignard + dry ice:** $\text{RMgX} + \text{CO}_2$, then $\text{H}_3\text{O}^+ \rightarrow$ RCOOH (one carbon more)

Acidity: pull makes it stronger

Carboxylic acids are acidic because the carboxylate ion is resonance-stabilised (two equivalent structures). Anything that pulls electrons away stabilises the ion further; anything that pushes electrons destabilises it.

- **Electron-withdrawing groups** ($-\text{F}$, $-\text{Cl}$, $-\text{NO}_2$, $-\text{CN}$) increase acidity. More of them, or closer to COOH , means stronger acid.
- Order: $\text{FCH}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ICH}_2\text{COOH} > \text{CH}_3\text{COOH}$. And $\text{Cl}_3\text{CCOOH} > \text{Cl}_2\text{CHCOOH} > \text{ClCH}_2\text{COOH}$.
- $\text{HCOOH} > \text{C}_6\text{H}_5\text{COOH} > \text{CH}_3\text{COOH}$. Electron-donating alkyl groups reduce acidity.

Reactions

$\text{RCOOH} + \text{NaHCO}_3 \rightarrow \text{RCOONa} + \text{H}_2\text{O} + \text{CO}_2\uparrow$ (brisk effervescence: standard test for $-\text{COOH}$)

Esterification (Fischer): $\text{RCOOH} + \text{R}'\text{OH} \rightleftharpoons \text{RCOOR}' + \text{H}_2\text{O}$ (conc. H_2SO_4 , reversible)

$\text{RCOOH} + \text{SOCl}_2 \rightarrow \text{RCOCl} + \text{SO}_2 + \text{HCl}$ (or PCl_5). $\text{RCOOH} + \text{NH}_3 \rightarrow \text{RCOONH}_4$, heat $\rightarrow$ RCONH_2 (amide)

Reduction: LiAlH_4 or $\text{B}_2\text{H}_6 \rightarrow \text{RCH}_2\text{OH}$. **Decarboxylation:** $\text{RCOONa} + \text{NaOH}$ (soda lime, heat) $\rightarrow$ $\text{R-H} + \text{Na}_2\text{CO}_3$

Hell-Volhard-Zelinsky: $\text{RCH}_2\text{COOH} + \text{X}_2$ (red P) $\rightarrow$ RCHXCOOH (α -halo acid)

Benzoic acid: $-\text{COOH}$ deactivates the ring and is **meta**-directing; Friedel-Crafts does not work

REMEMBER: HVZ: Red P + halogen puts the halogen on the Alpha carbon. ("A hell of a halogen lands on alpha.")

Amines

$R-NH_2$, R_2NH , R_3N and $Ar-NH_2$. Major themes: basicity order, Hofmann vs Gabriel, Hinsberg, diazonium chemistry.

Preparation

Methods

Reduction of nitro compounds: $R-NO_2 + 3H_2$ (Ni/Pt/Pd) or Sn/HCl or Fe/HCl $\rightarrow R-NH_2 + 2H_2O$. Fe/HCl is preferred in industry (the $FeCl_2$ formed hydrolyses and regenerates HCl)

Reduction of nitriles: $R-CN + LiAlH_4$ or $H_2/Ni \rightarrow R-CH_2NH_2$ (**one carbon more**). **Amides:** $RCONH_2 + LiAlH_4 \rightarrow RCH_2NH_2$

Ammonolysis: $R-X + NH_3 \rightarrow$ mixture of 1°, 2°, 3° amines and a quaternary salt (use excess NH_3 to favour 1°)

Gabriel phthalimide synthesis: phthalimide + KOH $\rightarrow$ potassium phthalimide; + R-X $\rightarrow$ N-alkylphthalimide; alkaline hydrolysis $\rightarrow R-NH_2$ + sodium phthalate. **Pure 1° aliphatic amines only;** aryl halides cannot be used (no nucleophilic substitution), so no aromatic amines

Hofmann bromamide degradation: $RCONH_2 + Br_2 + 4NaOH \rightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$ (**one carbon less**, the carbonyl carbon leaves as carbonate)

REMEMBER: Hofmann Hacks one carbon off. The nitrile route Adds one. Gabriel gives only 1° aliphatic amines.

Physical properties

- 1° and 2° amines hydrogen-bond with each other; 3° cannot. Boiling point: **1° > 2° > 3°** (for the same mass). Amines boil lower than alcohols because N-H...N bonds are weaker than O-H...O.
- Lower amines dissolve in water through H-bonding with water. Aniline is colourless but darkens in air (oxidation).

Basicity: the most-asked topic in this chapter

Basicity = availability of the nitrogen lone pair. Three forces fight: the +I effect (pushes electron density to N, helps), solvation of the ammonium ion by water (more N-H bonds, better solvation, helps), and steric hindrance (hurts).

Situation	Order of basic strength
Methylamines in water	$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
Ethylamines in water	$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$
Gas phase (no solvation)	$3^\circ > 2^\circ > 1^\circ > NH_3$ (pure +I effect)
Aromatic vs aliphatic	Aliphatic amines $> NH_3 >$ aniline (pK_b : CH_3NH_2 3.38, NH_3 4.75, aniline 9.38)

- Why aniline is weak:** its lone pair is delocalised into the ring by resonance, so it is less available.
- Substituents on aniline:** electron-donating groups ($-CH_3$, $-OCH_3$) increase basicity; electron-withdrawing groups ($-NO_2$, $-CN$, halogens) decrease it.

REMEMBER: Methyl: 2-1-3. Ethyl: 2-3-1. The secondary amine always wins in water, and NH_3 is always last. Gas phase is the simple one: more alkyl groups, more basic.

Reactions

Reactions common to amines

Acylation: $\text{R-NH}_2 + \text{R'COCl} \rightarrow \text{R-NH-COR'} + \text{HCl}$; pyridine is added to absorb the HCl and push the reaction on. With benzoyl chloride this is **benzoylation** (Schotten-Baumann)

Carbylamine (isocyanide) test: 1° amine (aliphatic or aromatic) + CHCl_3 + alc. KOH, heat $\rightarrow$ R-NC (foul-smelling isocyanide). **2° and 3° amines do not respond**

With nitrous acid: aliphatic 1° amine $\rightarrow$ alcohol + $\text{N}_2 \uparrow$ (effervescence). Aromatic 1° amine at 273-278 K $\rightarrow$ diazonium salt

Hinsberg test ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$): 1° gives a sulphonamide that **dissolves** in alkali (acidic N-H); 2° gives a sulphonamide **insoluble** in alkali; 3° does not react

REMEMBER: Hinsberg: 1° Dissolves, 2° Doesn't, 3° has no reaction. Carbylamine is the 1°-only test: if it stinks, it is primary.

Aniline: electrophilic substitution

- **Bromine water** gives **2,4,6-tribromoaniline** (white precipitate) at once. $-\text{NH}_2$ activates the ring very strongly.
- **Direct nitration** gives a mixture including a large meta product, because in strong acid aniline is protonated to the anilinium ion ($-\text{NH}_3^+$ is meta directing). **Fix:** protect by acetylation (acetanilide), nitrate (mainly para), then hydrolyse.
- **Friedel-Crafts fails:** the basic $-\text{NH}_2$ reacts with the AlCl_3 catalyst and the ring is deactivated.
- **Sulphonation** (aniline hydrogensulphate heated at 453-473 K) gives sulphanilic acid, which exists as a zwitterion.

REMEMBER: Protect the NH_2 : acetylate, react, hydrolyse. That one trick solves every 'control the substitution' question.

Diazonium salts

Prepared by **diazotisation**: aniline + NaNO_2 + HCl at 273-278 K gives $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$. Benzene diazonium chloride is stable only in the cold (and aromatic ones are more stable than aliphatic ones because of resonance with the ring). It is the most useful intermediate in aromatic chemistry. **Colour test:** cold NaNO_2/HCl , then alkaline β -naphthol gives an orange-red azo dye with aromatic 1° amines; aliphatic amines just fizz out N_2 .

Reagent	Product	Reaction name
CuCl/HCl , CuBr/HBr , CuCN/KCN	ArCl , ArBr , ArCN	Sandmeyer
Cu powder + HCl or HBr	ArCl , ArBr	Gattermann
KI	ArI	(no copper needed)
HBF_4 , then heat	ArF	Balz-Schiemann
Warm water	ArOH	Hydrolysis
H_3PO_2 (hypophosphorous acid) or ethanol	ArH (removes the amino group)	Reduction
Phenol, pH 9-10	p-hydroxyazobenzene (orange dye)	Coupling
Aniline, pH 4-5	p-aminoazobenzene (yellow dye)	Coupling

REMEMBER: Sandmeyer = Cu(I) salts. Gattermann = Cu powder. KI, HBF_4 , H_3PO_2 and water need no copper. **Coupling keeps the N_2 (as $-\text{N}=\text{N}-$); every other reaction throws it away.** Coupling pH: phenol in the alkaline range, aniline in the weakly acidic range.

Biomolecules

Carbohydrates, proteins, vitamins and nucleic acids. Mostly structure, linkage and examples: learn the tables.

Carbohydrates

Polyhydroxy aldehydes or ketones (or compounds that give them on hydrolysis). Classified as monosaccharides (do not hydrolyse), oligosaccharides (2-10 units) and polysaccharides. **Aldoses** carry -CHO, **ketoses** carry C=O. Glucose is an **aldohexose**; fructose is a **ketohexose**. Sugars with a free (hemiacetal) carbonyl are **reducing** (Tollens, Fehling positive).

Observation about glucose	What it proves
Prolonged heating with HI gives <i>n</i> -hexane	Six carbons in an unbranched chain
Forms oxime with NH_2OH and cyanohydrin with HCN	Carbonyl group present
Bromine water gives gluconic acid; nitric acid gives saccharic acid	-CHO group, and a primary -OH at the other end
Acetic anhydride gives a pentaacetate	Five -OH groups
No Schiff's test, no NaHSO_3 addition; two forms with different rotation (mutarotation)	Free -CHO is absent in the ring form: cyclic hemiacetal (pyranose)

- D/L** tells the position of the -OH on the carbon farthest from the carbonyl (C-5 in glucose), nothing to do with the direction of rotation. **(+)/(-)** or **d/l** tells the direction.
- Anomers:** α -D-glucose and β -D-glucose differ only at C-1 (the new chiral centre made on ring closure). α : $[\alpha] = +111^\circ$, β : $+19.2^\circ$; in solution both settle to $+52.5^\circ$. This drift is **mutarotation**.
- Fructose** is laevorotatory (-92.4°) yet reducing, because it tautomerises to glucose-like forms in alkali.

Sugar	Made of	Linkage	Reducing?
Sucrose	α -D-glucose + β -D-fructose	C1 to C2 (both reducing groups tied up)	No
Maltose	α -D-glucose + α -D-glucose	C1 to C4	Yes
Lactose (milk sugar)	β -D-galactose + β -D-glucose	C1 to C4	Yes

- Invert sugar:** sucrose is dextrorotatory ($+66.5^\circ$). Hydrolysis gives glucose ($+52.5^\circ$) and fructose (-92.4°). Fructose's larger negative rotation makes the mixture laevorotatory: the sign has 'inverted'.
- Starch** (plant store): **amylose** (15-20%, unbranched, α -1,4, water soluble, blue with iodine) + **amylopectin** (80-85%, branched, α -1,4 and α -1,6, insoluble).
- Cellulose:** unbranched β -1,4 chains of β -D-glucose; humans lack the enzyme to digest it. **Glycogen:** animal starch, even more branched, stored in liver and muscle.

REMEMBER: Sucrose = Sweet + glucose + fructose (the only non-reducing one). Maltose = Malt: glucose + glucose. Lactose = Look at the Galaxy: galactose + glucose. Starch is α (Apple, food). Cellulose is β (Bark, wood).

Amino acids and proteins

- α -Amino acids:** $\text{H}_2\text{N}-\text{CHR}-\text{COOH}$; exist as **zwitterions** ($\text{H}_3\text{N}^+-\text{CHR}-\text{COO}^-$) and are amphoteric. At the isoelectric point the net charge is zero. Glycine is the only achiral one ($\text{R} = \text{H}$).
- Peptide bond:** the amide link $-\text{CO}-\text{NH}-$ between the COOH of one amino acid and the NH_2 of the next. Essential amino acids cannot be made by the body and must come from food.

REMEMBER: PVT TIM HALL = the essential amino acids: **P**henylalanine, **V**aline, **T**hreonine, **T**ryptophan, **I**soleucine, **M**ethionine, **H**istidine, **A**rginine (semi-essential), **L**eucine, **L**ysine.

Level	What it is	Held together by
Primary	Sequence of amino acids	Peptide bonds
Secondary	α -helix (right-handed, intra-chain) or β -pleated sheet (inter-chain)	Hydrogen bonds
Tertiary	Overall folding of one chain	H-bonds, disulphide bridges, ionic and hydrophobic interactions
Quaternary	Several chains assembled (e.g. haemoglobin)	Same weak forces between chains

- **Fibrous proteins** (keratin, myosin): long, insoluble, structural. **Globular proteins** (insulin, albumin): compact, water soluble.
- **Denaturation**: heat, acid or other agents destroy secondary and tertiary structure; the **primary structure survives**. Examples: boiling an egg, curdling milk.
- **Enzymes** are biological catalysts (nearly all proteins): highly specific, work under mild conditions, names often end in -ase.

REMEMBER: Denaturation breaks the shape, never the sequence. No peptide bonds are cut.

Vitamins

Vitamin	Source	Deficiency disease
A	Fish liver oil, carrots, milk	Night blindness, xerophthalmia
B ₁	Yeast, cereals, pulses	Beriberi
B ₂	Milk, eggs, liver	Cheilosis (cracks at mouth corners)
B ₆	Yeast, milk, cereals	Convulsions
B ₁₂	Meat, fish, eggs	Pernicious anaemia
C	Citrus fruits, amla, green leafy vegetables	Scurvy
D	Sunlight, fish liver oil, egg yolk	Rickets (children), osteomalacia (adults)
E	Vegetable oils, nuts	Fragile red blood cells, muscular weakness
K	Green leafy vegetables	Increased blood clotting time

REMEMBER: Fat-soluble: A, D, E, K = 'A Dog Eats Kibble'. Stored in the body. Water-soluble: B-complex and C (not stored, needed daily). Night = A, bones = D, scurvy = C, clotting = K.

Nucleic acids

Nucleoside = base + sugar. **Nucleotide** = base + sugar + phosphate. Nucleotides join through phosphodiester linkages between C-3' and C-5' of sugars.

	DNA	RNA
Sugar	2-Deoxyribose	Ribose
Bases	A, G, C, T	A, G, C, U
Structure	Double helix	Single strand
Role	Stores genetic information; replication	Protein synthesis: mRNA, rRNA, tRNA

- **Base pairing in DNA:** A pairs with T through **2** hydrogen bonds; G pairs with C through **3**. Equal amounts of A and T, and of G and C (Chargaff's rule). In RNA, A pairs with U.
- **Purines** (double ring): A, G. **Pyrimidines** (single ring): C, T, U.

REMEMBER: Pure As Gold = Purines are A and G. **CUT the pie** = Pyrimidines are C, U, T. **A-T has 2 (at-two)**, **G-C has 3 (Great Cat, 3 lives)**.

Quick Sheets

Final-week revision: named reactions, distinguishing tests, and every mnemonic in one place.

Named reactions at a glance

Name	Converts	Key reagent
Finkelstein	$\text{R-Cl/Br} \rightarrow \text{R-I}$	NaI , dry acetone
Swarts	$\text{R-Cl/Br} \rightarrow \text{R-F}$	AgF , Hg_2F_2 , SbF_3
Sandmeyer / Gattermann	$\text{ArN}_2^+ \rightarrow \text{ArCl, ArBr, ArCN}$	Cu(I) salt / Cu powder
Wurtz / Wurtz-Fittig / Fittig	$\text{R-X} \rightarrow \text{R-R} / \text{Ar-R} / \text{Ar-Ar}$	Na , dry ether
Williamson	$\text{RONa} + \text{R}'\text{X} \rightarrow \text{ether}$	Primary $\text{R}'\text{X}$ ($\text{S}_{\text{N}}2$)
Kolbe	Phenoxide $\rightarrow$ salicylic acid	CO_2 , 400 K, 4-7 atm
Reimer-Tiemann	Phenol $\rightarrow$ salicylaldehyde	CHCl_3 , aq. NaOH , 340 K
Rosenmund	$\text{RCOCl} \rightarrow \text{RCHO}$	H_2 , Pd-BaSO_4
Stephen	$\text{RCN} \rightarrow \text{RCHO}$	SnCl_2/HCl , then H_3O^+
Etard	Toluene $\rightarrow$ benzaldehyde	CrO_2Cl_2 , CS_2
Gattermann-Koch	Benzene $\rightarrow$ benzaldehyde	CO , HCl , $\text{AlCl}_3/\text{CuCl}$
Clemmensen / Wolff-Kishner	$\text{C=O} \rightarrow \text{CH}_2$	Zn-Hg/HCl / NH_2NH_2 , KOH
Aldol	$2 \text{RCH}_2\text{CHO} \rightarrow \beta\text{-hydroxy aldehyde}$	Dilute NaOH
Cannizzaro	2ArCHO (no $\alpha\text{-H}$) $\rightarrow$ alcohol + acid salt	Conc. NaOH
Hell-Volhard-Zelinsky	$\text{RCH}_2\text{COOH} \rightarrow \text{RCHXCOOH}$	X_2 , red P
Gabriel	$\text{R-X} \rightarrow \text{R-NH}_2$ (1° only)	Potassium phthalimide, then hydrolysis
Hofmann bromamide	$\text{RCONH}_2 \rightarrow \text{RNH}_2$ (one C less)	Br_2 , NaOH
Carbylamine	1° amine $\rightarrow$ isocyanide	CHCl_3 , alc. KOH
Fischer esterification	$\text{RCOOH} + \text{R}'\text{OH} \rightarrow \text{ester}$	Conc. H_2SO_4

Distinguishing tests

Pair	Test	Result
Ethanal vs propanone	Tollens' or Fehling's	Ethanal: silver mirror / red ppt
Pentan-2-one vs pentan-3-one	Iodoform	Pentan-2-one: yellow ppt
Benzaldehyde vs acetophenone	Tollens' (or iodoform)	Benzaldehyde: mirror; acetophenone: yellow CHI_3
Ethanal vs benzaldehyde	Fehling's	Ethanal only
Phenol vs ethanol	Neutral FeCl_3 ; or bromine water	Phenol: violet colour; white ppt
Benzoic acid vs phenol	NaHCO_3	Benzoic acid: CO_2 effervescence
Formic vs acetic acid	Tollens'	Formic acid reduces it
1° vs 3° alcohol	Lucas reagent	3°: immediate turbidity
Methylamine vs dimethylamine	Carbylamine	Methylamine: foul smell
Aniline vs benzylamine	NaNO_2/HCl , cold, then β -naphthol	Aniline: orange dye. Benzylamine: N_2 fizz
Chlorobenzene vs benzyl chloride	Warm AgNO_3 (aq. alcohol)	Benzyl chloride: white AgCl
Glucose vs sucrose; starch vs glucose	Tollens'; iodine	Glucose reduces; starch: blue-black

Mnemonic wall

Topic	Mnemonic
SN1 vs SN2	SN1: 2 steps, 1 species in rate. SN2: 1 step, 2 species. Tertiary = SN1, primary = SN2
KCN, AgCN, KNO_2 , AgNO_2	K-cyanide: Carbon attacks. K-nitrite: Oxygen attacks. Silver flips both
Elimination vs substitution	Alcoholic KOH = Alkene. Aqueous KOH = Alcohol
Grignard + carbonyl	H-1, Ald-2, Ket-3
Lucas test	Tertiary Today, Secondary Soon, Primary Pending
Dehydration of ethanol	Hot (443 K) = alkene. Cooler (413 K) = ether
Kolbe / Reimer-Tiemann	$\text{CO}_2 \rightarrow \text{COOH}$. $\text{CHCl}_3 \rightarrow \text{CHO}$
Aldehyde preparations	E S R G: Etard, Stephen, Rosenmund, Gattermann-Koch
Carbonyl to alkane	Clemmensen = acid. Wolff-Kishner = base
Aldol vs Cannizzaro	Aldol needs Alpha-H. Cannizzaro: No alpha-H
Amine preparation	Hofmann Hacks a carbon. Nitrile Adds a carbon
Basicity in water	Methyl 2-1-3, Ethyl 2-3-1, NH_3 last
Hinsberg	1° Dissolves, 2° Doesn't, 3° ignores
Aniline reactions	Protect the NH_2 : acetylate, react, hydrolyse
Diazonium	Sandmeyer = Cu(I), Gattermann = Cu powder; coupling keeps N_2
Fat-soluble vitamins	A Dog Eats Kibble (A, D, E, K)
Essential amino acids	PVT TIM HALL
Nucleic acid bases	Pure As Gold (A, G); CUT the pie (C, U, T); A-T 2 bonds, G-C 3
Polyhalogens	Chloroform + light + air = phosgene: dark, full, pinch of alcohol

Practice

Attempt without the notes first. Answers and hints are at the end of this chapter.

A. Quick-fire MCQs

- Which compound undergoes S_N1 hydrolysis fastest? (a) CH_3Cl (b) $(\text{CH}_3)_3\text{CBr}$ (c) $\text{CH}_3\text{CH}_2\text{Br}$ (d) $(\text{CH}_3)_2\text{CHCl}$
- (R)-2-Bromobutane reacts with aqueous NaOH by the S_N2 path. The product is: (a) (S)-butan-2-ol (b) (R)-butan-2-ol (c) racemic butan-2-ol (d) butan-1-ol
- The best reagent to convert an alcohol to the alkyl chloride with only gaseous by-products: (a) HCl/ZnCl_2 (b) PCl_5 (c) SOCl_2 (d) PCl_3
- Which gives a yellow precipitate with I_2/NaOH ? (a) propanal (b) propan-2-ol (c) pentan-3-one (d) benzaldehyde
- Which does **not** give the Cannizzaro reaction? (a) HCHO (b) benzaldehyde (c) ethanal (d) 2,2-dimethylpropanal
- Strongest acid: (a) CH_3COOH (b) ClCH_2COOH (c) FCH_2COOH (d) ICH_2COOH
- Most basic in aqueous solution: (a) NH_3 (b) CH_3NH_2 (c) $(\text{CH}_3)_2\text{NH}$ (d) $(\text{CH}_3)_3\text{N}$
- Propanamide with Br_2/NaOH gives: (a) propan-1-amine (b) ethanamine (c) methanamine (d) propan-2-amine
- The carbylamine test is given by: (a) aniline (b) N-methylaniline (c) triethylamine (d) dimethylamine
- Benzene diazonium chloride + H_3PO_2 gives: (a) phenol (b) benzene (c) chlorobenzene (d) aniline
- Which is a reducing sugar? (a) sucrose (b) maltose (c) starch (d) cellulose
- Which is **not** a fat-soluble vitamin? (a) A (b) D (c) C (d) K
- Anisole + HI gives: (a) phenol + CH_3I (b) iodobenzene + CH_3OH (c) phenol + CH_3OH (d) no reaction
- Sodium ethoxide + tert-butyl bromide mainly gives: (a) tert-butyl ethyl ether (b) 2-methylpropene (c) ethanol (d) 2-methylpropan-2-ol
- Turbidity appears immediately with Lucas reagent for: (a) butan-1-ol (b) butan-2-ol (c) 2-methylpropan-2-ol (d) 2-methylpropan-1-ol

B. Reason it out (2-3 lines each)

- Why is chlorobenzene much less reactive than chloroethane towards nucleophilic substitution?
- Why is o-nitrophenol steam volatile but p-nitrophenol is not?
- Why is phenol more acidic than ethanol?
- Why are aldehydes more reactive than ketones in nucleophilic addition?
- Why does a carboxylic acid boil higher than an alcohol of similar molar mass?
- Why is aniline a weaker base than methylamine?
- Why can the Gabriel synthesis not be used to prepare aniline?
- Why does aniline not undergo Friedel-Crafts reaction?
- Why is sucrose a non-reducing sugar?
- Why does boiling an egg not break its peptide bonds?
- Why is chloroform stored in dark, completely filled bottles?

C. Conversions (write reagents for each step)

#	Conversion	#	Conversion
1	Propene → propan-1-ol	7	Ethanal → but-2-enal
2	Benzene → acetophenone	8	Benzoic acid → benzaldehyde
3	Toluene → benzaldehyde	9	Phenol → salicylic acid
4	Aniline → chlorobenzene	10	Bromoethane → propan-1-amine
5	Ethanamide → methanamine	11	Propanone → propene
6	Benzene → aniline		

D. Identify and explain

- An organic compound A (C_3H_6O) gives an orange precipitate with 2,4-DNP, no silver mirror, and a yellow precipitate with $I_2/NaOH$. Name A and write the iodoform reaction.
- Arrange in decreasing acid strength: phenol, ethanol, acetic acid, p-nitrophenol.
- Arrange in increasing order of boiling point: butan-1-ol, butanal, butane, diethyl ether (as nearly equal mass, think of H-bonding).
- Arrange by basic strength (aqueous): aniline, p-nitroaniline, p-toluidine, NH_3 .
- How will you separate a mixture of o- and p-nitrophenol?

Answer key

MCQs: 1-b, 2-a, 3-c, 4-b, 5-c, 6-c, 7-c, 8-b, 9-a, 10-b, 11-b, 12-c, 13-a, 14-b, 15-c.

Reason it out (key words):

- **1.** Resonance gives C-Cl partial double bond; sp^2 carbon; unstable phenyl cation; π cloud repels Nu.
- **2.** Ortho: intramolecular H-bond, so no association. Para: intermolecular H-bonding.
- **3.** Phenoxide is resonance stabilised; ethoxide is destabilised by +I of ethyl.
- **4.** Less steric hindrance and only one electron-donating alkyl group.
- **5.** Acids form stable hydrogen-bonded dimers.
- **6.** Aniline's lone pair is delocalised into the ring; methylamine's is pushed forward by +I.
- **7.** Aryl halides do not undergo nucleophilic substitution with potassium phthalimide.
- **8.** $-NH_2$ forms a salt-like adduct with $AlCl_3$, creating a strongly deactivating group on N.
- **9.** Both anomeric carbons (C1 of glucose, C2 of fructose) are tied up in the glycosidic bond; no free carbonyl.
- **10.** Denaturation changes secondary/tertiary structure only; the primary sequence is untouched.
- **11.** To prevent oxidation to poisonous phosgene by air and light.

Conversions (reagent route):

- 1: B_2H_6 ; then $H_2O_2/NaOH$. 2: CH_3COCl , anhy. $AlCl_3$. 3: CrO_2Cl_2/CS_2 ; then H_3O^+ . 4: $NaNO_2/HCl$ (273-278 K); $CuCl/HCl$.
- 5: $Br_2/NaOH$ (Hofmann). 6: HNO_3/H_2SO_4 ; then Sn/HCl . 7: dilute $NaOH$; then heat. 8: $SOCl_2$; then H_2 , $Pd-BaSO_4$.
- 9: $NaOH$; CO_2 (400 K, 4-7 atm); H^+ . 10: KCN ; then $LiAlH_4$ (or H_2/Ni). 11: $NaBH_4$; then conc. H_2SO_4 , 443 K.

Part D: A = propanone (CH_3COCH_3): $CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow CHI_3 \downarrow + CH_3COONa + 3NaI + 3H_2O$.

Acid strength: acetic acid > p-nitrophenol > phenol > ethanol. **Boiling point (increasing):** butane < diethyl ether < butanal < butan-1-ol.

Basic strength: NH_3 > p-toluidine > aniline > p-nitroaniline (aromatic amines are all weaker than NH_3 ; donor groups help, acceptor groups hurt). **Separation:** steam distillation; o-nitrophenol is steam volatile and distils over.