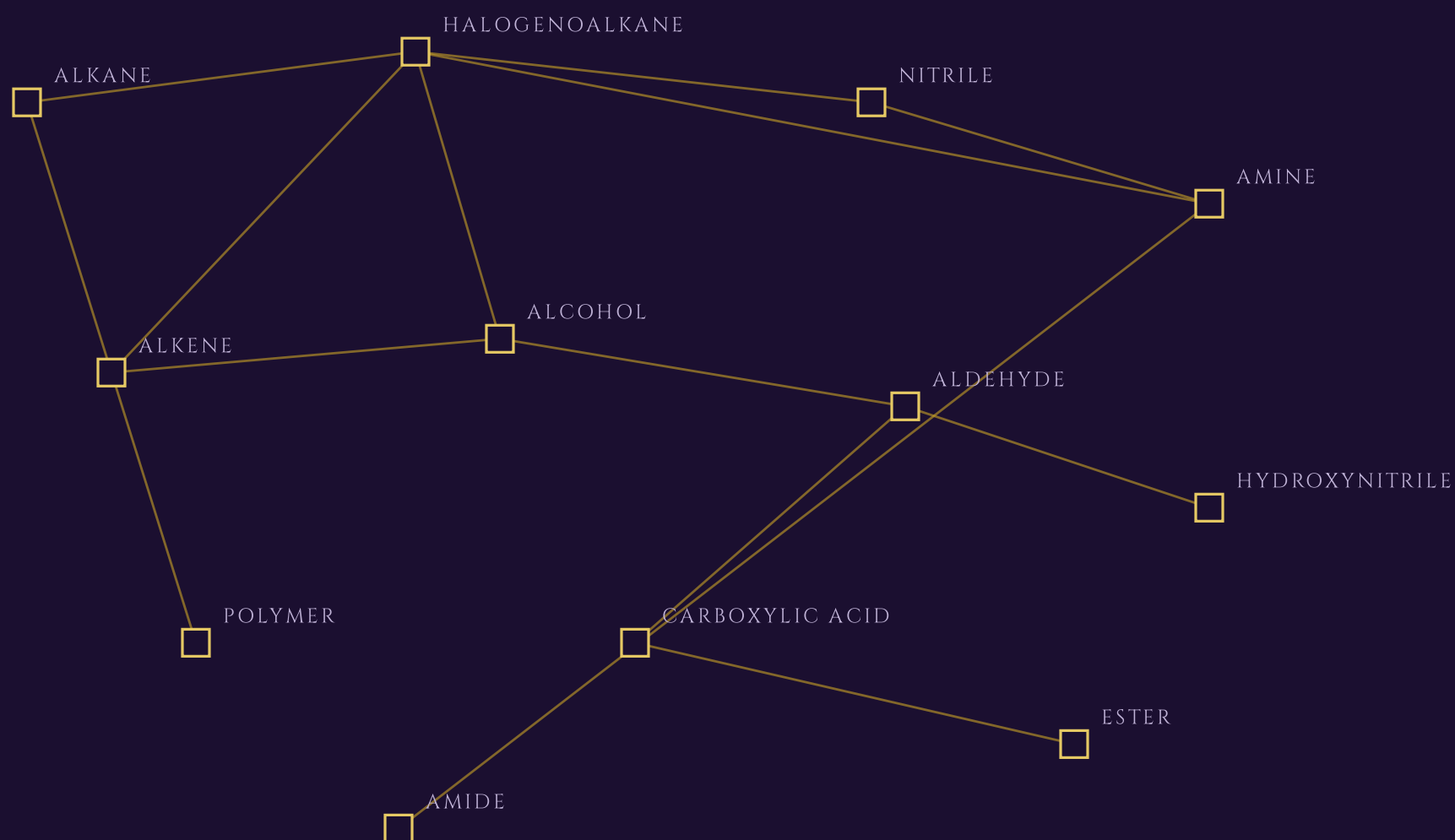


AQA A-LEVEL CHEMISTRY · 7405

The Organic *Synthesis Map*



The functional-group conversions of AQA organic chemistry, with reagents, conditions and mechanism. Then six routes to practise.

SWIPE →

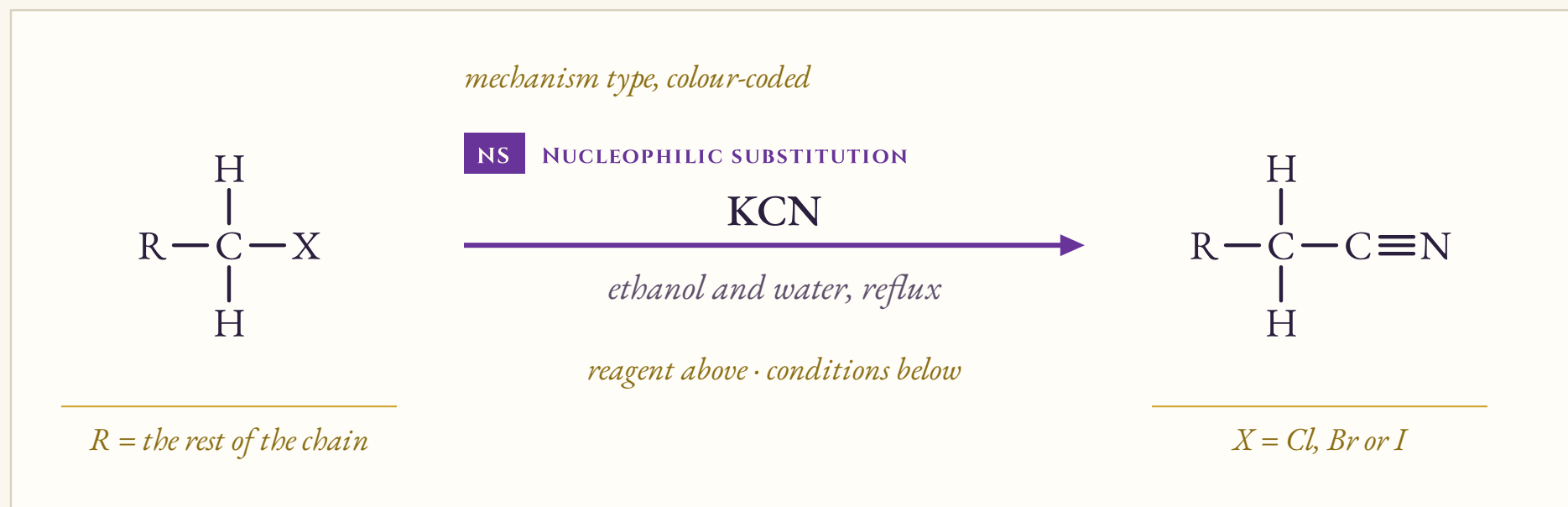


DEMOSTHENES

Free to save and share

Reading the map

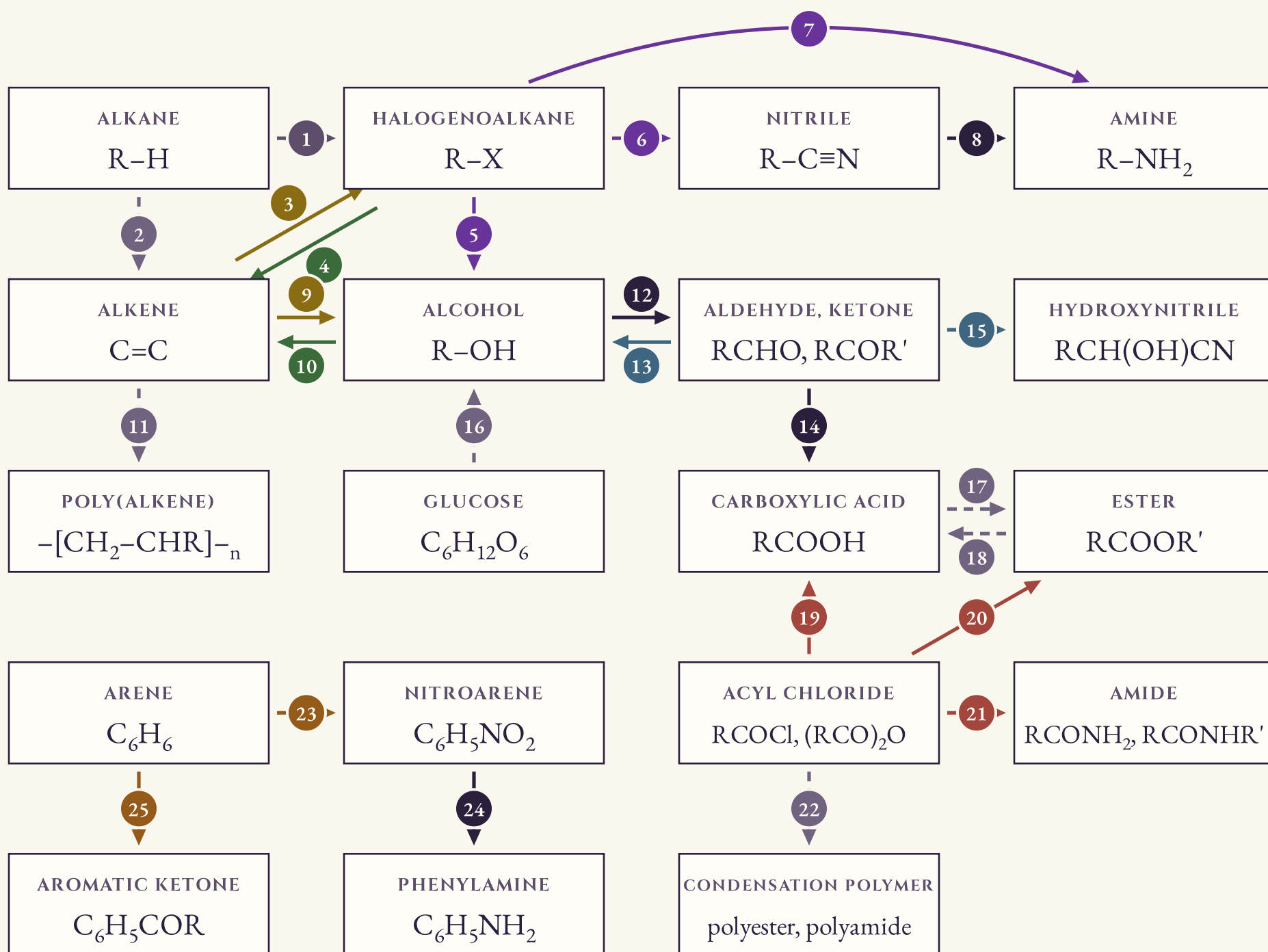
Each reaction is one row: what you start with, what you add and under what conditions, the mechanism, and what you get.



THE MECHANISM KEY

FR	Free-radical substitution	Halogen radicals, made by UV light, replace H on an alkane: initiation, propagation, termination.
NS	Nucleophilic substitution	A lone pair attacks the δ^+ carbon of C–X; the halide ion leaves.
E	Elimination	A base removes H^+ next to C–X, so C=C forms; or an acid catalyst protonates an alcohol's OH, water leaves and H^+ is lost.
EA	Electrophilic addition	The C=C electrons attack an electrophile; a carbocation forms, then a nucleophile adds.
NA	Nucleophilic addition	A nucleophile (CN^- or H^-) attacks the δ^+ carbon of C=O; the O^- is then protonated.
AE	Nucleophilic addition–elimination	A nucleophile adds to C=O of an acyl chloride; C=O reforms and Cl^- leaves, then H^+ is lost.
ES	Electrophilic substitution	The delocalised ring attacks an electrophile; H^+ is lost and the ring is restored.
OX	Oxidation	[O] from acidified potassium dichromate(VI), Tollens' reagent or Fehling's solution.
RED	Reduction	[H] from NaBH_4 , LiAlH_4 , H_2 with Ni, or Sn with conc. HCl.
POLY	Polymerisation	Addition (from C=C, no other product) or condensation (losing water or HCl at each link).
—	No mechanism required	AQA asks for reagents and conditions only: esterification, hydrolysis, cracking, fermentation.

Everything, on one page

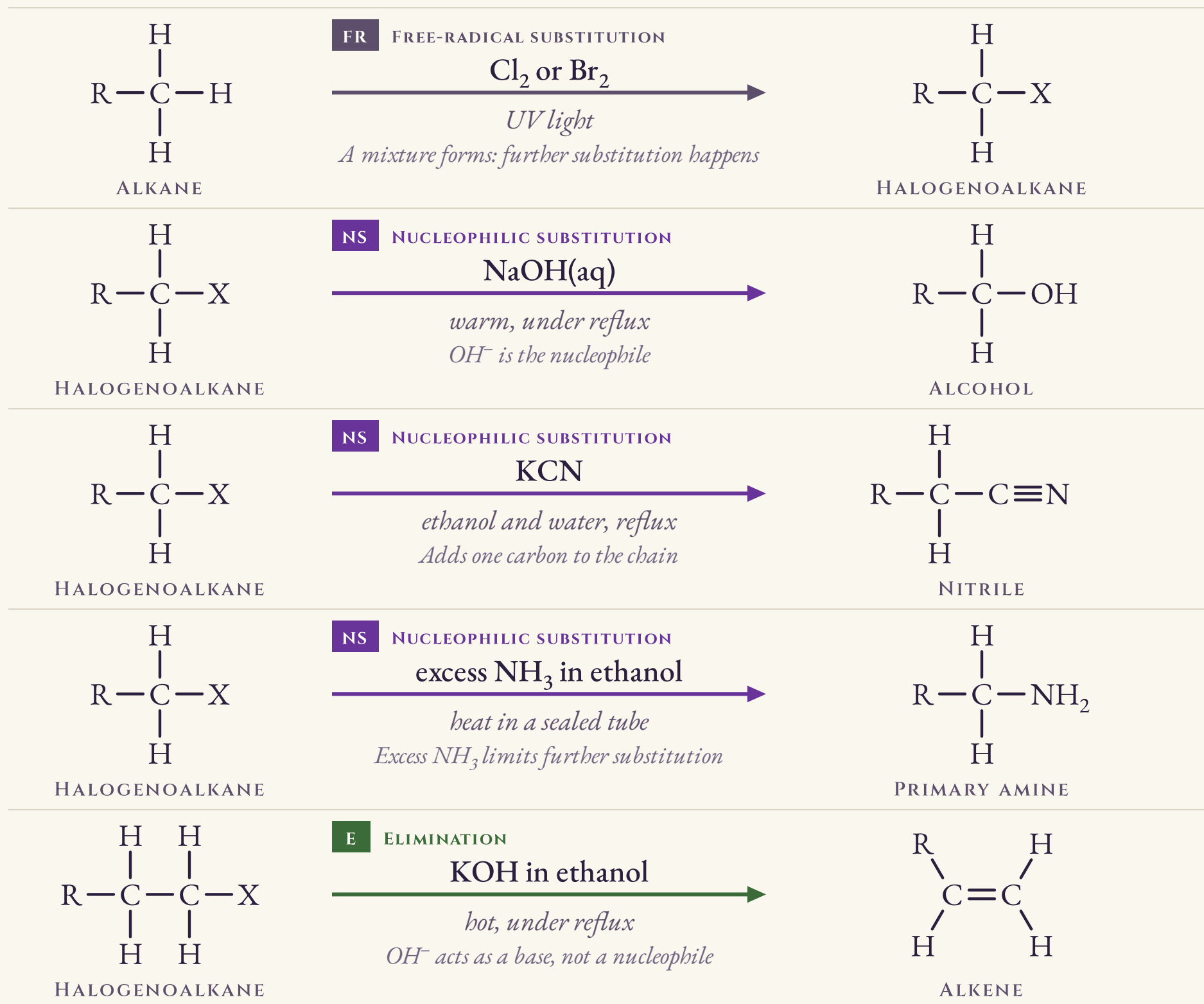


- 1 Cl_2 or Br_2 , UV light
- 2 cracking: thermal, or zeolite catalyst
- 3 HBr or Br_2 , room temperature
- 4 KOH in ethanol, hot
- 5 $NaOH(aq)$, warm
- 6 KCN in ethanol/water, reflux
- 7 excess NH_3 in ethanol, heat, sealed
- 8 $LiAlH_4$, or H_2 with Ni
- 9 steam, H_3PO_4 , $300^\circ C$, 60 atm
- 10 conc. H_2SO_4 or H_3PO_4 , heat
- 11 addition polymerisation
- 12 $K_2Cr_2O_7/H_2SO_4$: 1° distil, 2° reflux
- 13 $NaBH_4$ (reduction)

- 14 aldehyde: $K_2Cr_2O_7/H_2SO_4$, reflux
- 15 KCN , then dilute acid
- 16 yeast, $35^\circ C$, no air
- 17 alcohol, conc. H_2SO_4 , heat
- 18 dilute acid or $NaOH(aq)$, reflux
- 19 water (anhydride gives 2 $RCOOH$)
- 20 an alcohol
- 21 NH_3 or a primary amine
- 22 diacyl chloride + diol or diamine
- 23 conc. HNO_3 + conc. H_2SO_4 , $50^\circ C$
- 24 Sn , conc. HCl , then $NaOH$
- 25 $RCOCl$, $AlCl_3$

The halogenoalkane hub

The polar C-X bond makes its carbon δ^+ : nucleophiles attack it, and bases pull off a neighbouring H^+ .

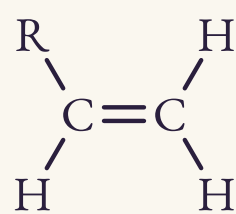


EXAM TRAPS

- C-I reacts fastest: its bond enthalpy is lowest. Bond strength, not bond polarity, decides the rate.
- Same OH^- , different outcome: aqueous and warm gives substitution; ethanolic and hot gives elimination.

Adding across C=C

The C=C bond is a region of high electron density, so electrophiles add to it.



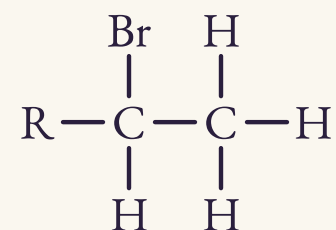
ALKENE

EA ELECTROPHILIC ADDITION

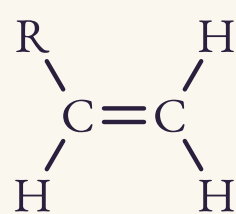
HBr

room temperature

Major product via the more stable carbocation



MAJOR PRODUCT



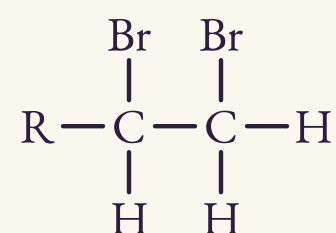
ALKENE

EA ELECTROPHILIC ADDITION

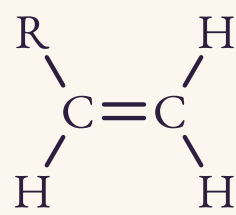
Br₂

room temperature

Test: orange bromine water turns colourless



DIBROMOALKANE



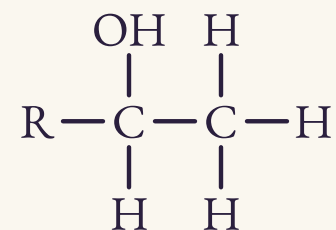
ALKENE

EA ELECTROPHILIC ADDITION

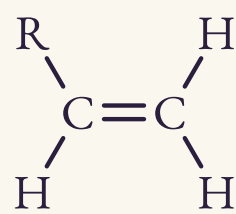
steam, H₃PO₄ catalyst

300 °C, 60 atm

Industrial hydration



ALCOHOL (MAJOR)



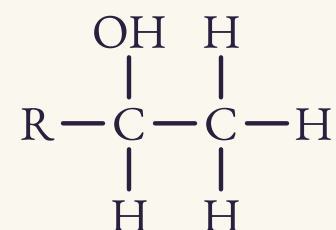
ALKENE

EA ELECTROPHILIC ADDITION

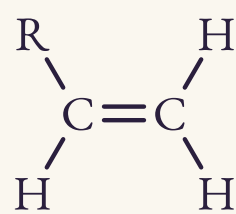
cold conc. H₂SO₄

then add water and warm

EA gives an alkyl hydrogensulfate; water hydrolyses it



ALCOHOL (MAJOR)

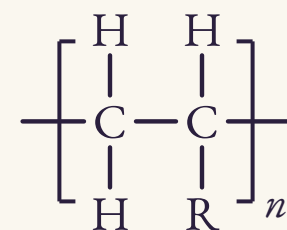


MONOMER

POLY POLYMERISATION

addition polymerisation

Saturated and unreactive: not biodegradable



POLY(ALKENE)

EXAM TRAPS

- Stability: tertiary > secondary > primary carbocation, so the electrophile's H bonds to the carbon that already has more H.
- Poly(ethene) is not an alkene: it has no C=C left. Draw brackets through the extension bonds, with n outside.

Making and oxidising alcohols

Acidified potassium dichromate(VI) is the oxidising agent: orange $\text{Cr}_2\text{O}_7^{2-}$ turns green Cr^{3+} .

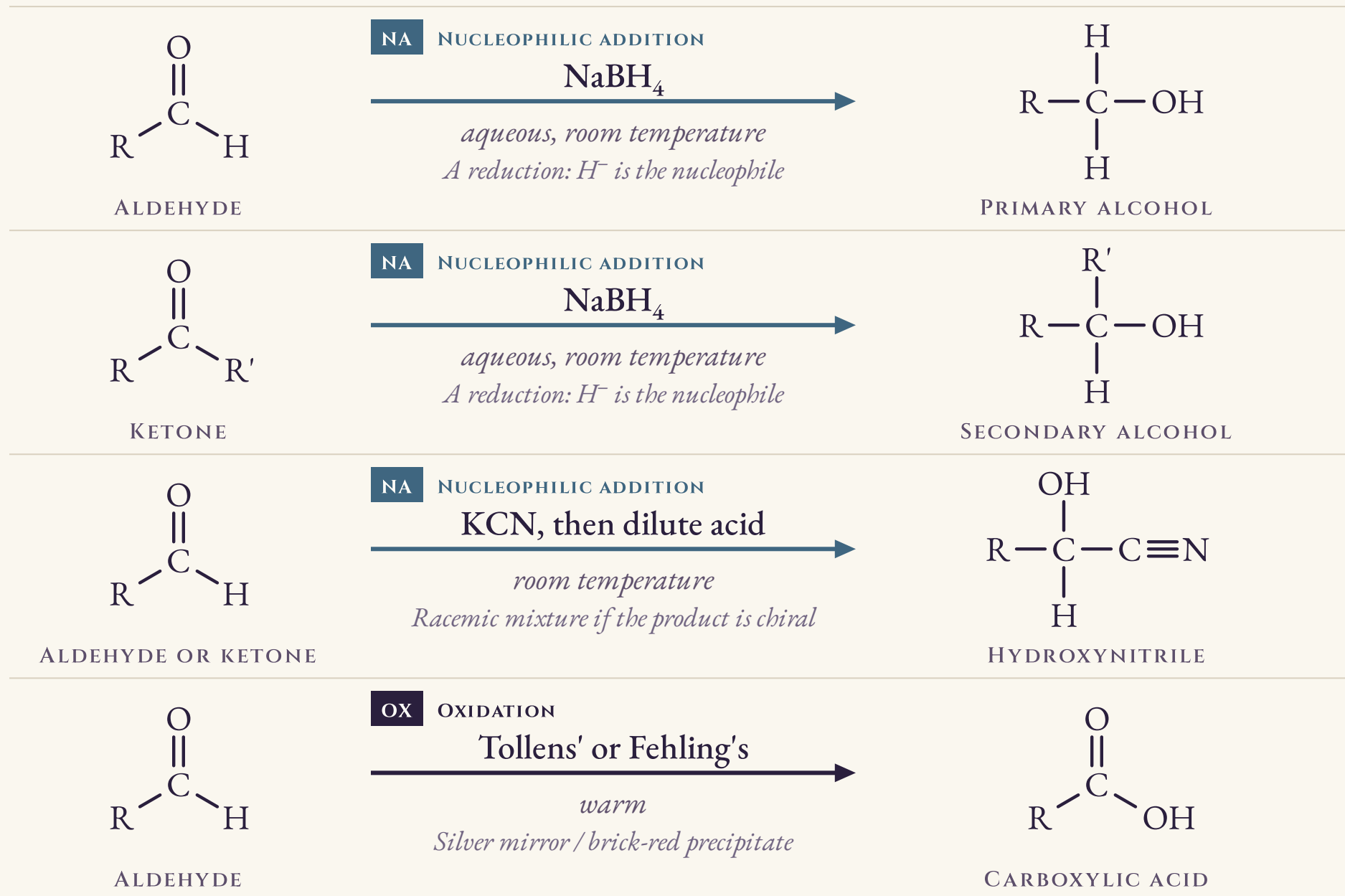
$\text{C}_6\text{H}_{12}\text{O}_6$	— NO MECHANISM REQUIRED ----- yeast -----> 35 °C, anaerobic Fermentation; CO_2 is the other product	$2 \text{CH}_3\text{CH}_2\text{OH}$ + 2CO_2
GLUCOSE		ETHANOL
$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	OX OXIDATION $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4$ -----> excess alcohol; distil off at once The aldehyde boils lower, so it escapes	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{H} \end{array}$
PRIMARY ALCOHOL		ALDEHYDE
$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	OX OXIDATION excess $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4$ -----> heat under reflux Reflux returns the aldehyde to be oxidised	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{OH} \end{array}$
PRIMARY ALCOHOL		CARBOXYLIC ACID
$\begin{array}{c} \text{R}' \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	OX OXIDATION $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4$ -----> heat under reflux Tertiary alcohols are not oxidised	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{R}' \end{array}$
SECONDARY ALCOHOL		KETONE
$\begin{array}{cc} \text{H} & \text{H} \\ & \\ \text{R}-\text{C} & -\text{C}-\text{OH} \\ & \\ \text{H} & \text{H} \end{array}$	E ELIMINATION conc. H_2SO_4 or H_3PO_4 -----> heat Acid-catalysed dehydration	$\begin{array}{cc} \text{R} & \text{H} \\ & \backslash \quad / \\ & \text{C} = \text{C} \\ & / \quad \backslash \\ \text{H} & \text{H} \end{array}$
ALCOHOL		ALKENE

EXAM TRAPS

- Why distil for the aldehyde: it has no O–H, so no hydrogen bonding, and boils below the alcohol and the acid.
- Dehydrating an unsymmetrical alcohol can give more than one alkene, including E and Z isomers.

The carbonyl group

$C=O$ is polar: its δ^+ carbon is attacked by nucleophiles, and the flat group can be attacked from either face.



EXAM TRAPS

- KCN, not HCN: HCN is a toxic gas. CN^- attacks the carbon, then H^+ from the acid protonates the O^- .
- Planar $\text{C}=\text{O}$ is attacked equally from both faces, so a chiral product forms as a racemate: no optical activity.
- Ketones give no silver mirror and no red precipitate: they are not oxidised by these mild reagents.

Acids, esters and fats

Carboxylic acids are weak acids; with alcohols they form esters, which can be split again by hydrolysis.

$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$ CARBOXYLIC ACID	— NO MECHANISM REQUIRED alcohol, conc. H_2SO_4 -----> heat <i>Reversible; esters are used as flavourings and solvents</i>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{R}' \end{array}$ ESTER
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$ CARBOXYLIC ACID	— NO MECHANISM REQUIRED $\text{NaHCO}_3(\text{aq})$ -----> room temperature <i>Effervescence: the test for COOH</i>	$\text{RCOO}^-\text{Na}^+ + \text{CO}_2 + \text{H}_2\text{O}$ CARBOXYLATE SALT
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{R}' \end{array}$ ESTER	— NO MECHANISM REQUIRED dilute acid, or $\text{NaOH}(\text{aq})$ -----> heat under reflux <i>Acid: reversible. NaOH: goes to completion</i>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$ ACID (OR ITS SALT)
$\begin{array}{l} \text{CH}_2-\text{OCOR} \\ \text{CH}-\text{OCOR} \\ \text{CH}_2-\text{OCOR} \end{array}$ FAT OR OIL	— NO MECHANISM REQUIRED $\text{NaOH}(\text{aq})$ -----> heat under reflux <i>Glycerol is propane-1,2,3-triol</i>	$3 \text{RCOO}^-\text{Na}^+ + \text{glycerol}$ SOAP
$\begin{array}{l} \text{CH}_2-\text{OCOR} \\ \text{CH}-\text{OCOR} \\ \text{CH}_2-\text{OCOR} \end{array}$ VEGETABLE OIL	— NO MECHANISM REQUIRED methanol -----> KOH catalyst <i>A mixture of methyl esters</i>	$3 \text{RCOOCH}_3 + \text{glycerol}$ BIODIESEL

EXAM TRAPS

- Name esters alcohol-part first: $\text{CH}_3\text{COOCH}_2\text{CH}_3$ is ethyl ethanoate, made from ethanol and ethanoic acid.
- Alkaline hydrolysis gives the carboxylate salt; add a strong acid to get the free carboxylic acid.

Acylation

Acyl chlorides acylate water, alcohols, ammonia and amines: quickly, at room temperature, and irreversibly.

$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{Cl} \end{array}$ ACYL CHLORIDE	AE NUCLEOPHILIC ADDITION–ELIMINATION water room temperature <i>Misty fumes of HCl</i>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OH} \end{array}$ CARBOXYLIC ACID
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{Cl} \end{array}$ ACYL CHLORIDE	AE NUCLEOPHILIC ADDITION–ELIMINATION an alcohol room temperature <i>Complete, unlike esterification of the acid</i>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{R}' \end{array}$ ESTER
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{Cl} \end{array}$ ACYL CHLORIDE	AE NUCLEOPHILIC ADDITION–ELIMINATION NH₃ room temperature <i>A second NH₃ takes the HCl, as NH₄Cl</i>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}_2 \end{array}$ PRIMARY AMIDE
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{Cl} \end{array}$ ACYL CHLORIDE	AE NUCLEOPHILIC ADDITION–ELIMINATION a primary amine room temperature <i>The amine's N lone pair attacks</i>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{NH}-\text{R}' \end{array}$ N-SUBSTITUTED AMIDE
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}-\text{C}-\text{O}-\text{C}-\text{R} \end{array}$ ACID ANHYDRIDE	AE NUCLEOPHILIC ADDITION–ELIMINATION an alcohol warm <i>Gives RCOOH, not HCl; aspirin is made this way (with a phenol –OH)</i>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{R}' \end{array}$ ESTER

EXAM TRAPS

- Mechanism: the lone pair adds to the δ^+ C of C=O; C=O reforms, Cl^- leaves, and H^+ is lost from the attacking atom.
- Anhydrides react more slowly and give no corrosive HCl, and they are cheaper: so industry prefers them.

Nitrogen in, nitrogen on

The lone pair on nitrogen makes amines bases and nucleophiles.

$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{X} \\ \\ \text{H} \end{array}$ HALOGENOALKANE	NS NUCLEOPHILIC SUBSTITUTION excess NH_3 in ethanol heat in a sealed tube <i>Same carbon count as the halogenoalkane</i>	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{NH}_2 \\ \\ \text{H} \end{array}$ PRIMARY AMINE
$\text{R}-\text{C}\equiv\text{N}$ NITRILE	RED REDUCTION LiAlH_4, or H_2 with Ni dry ether; or H_2, Ni, heat <i>Only RCH_2NH_2; the extra carbon came from CN^- earlier</i>	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{NH}_2 \\ \\ \text{H} \end{array}$ PRIMARY AMINE
$\begin{array}{c} \text{H} \\ \diagup \\ \text{R}-\text{N} \\ \diagdown \\ \text{H} \end{array}$ AMINE	NS NUCLEOPHILIC SUBSTITUTION excess halogenoalkane via 2° and 3° amines <i>Quaternary salts are cationic surfactants</i>	$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{N}-\text{R}^+ \\ \\ \text{R} \end{array} \quad \text{X}^-$ QUATERNARY SALT
$\begin{array}{c} \text{H} \\ \diagup \\ \text{R}'-\text{N} \\ \diagdown \\ \text{H} \end{array}$ PRIMARY AMINE	AE NUCLEOPHILIC ADDITION-ELIMINATION acyl chloride (or anhydride) room temperature <i>The amine is the nucleophile</i>	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{NH}-\text{R}' \end{array}$ N-SUBSTITUTED AMIDE

BASE STRENGTH

Primary aliphatic amine

alkyl groups push electron density onto N

> Ammonia

the reference point

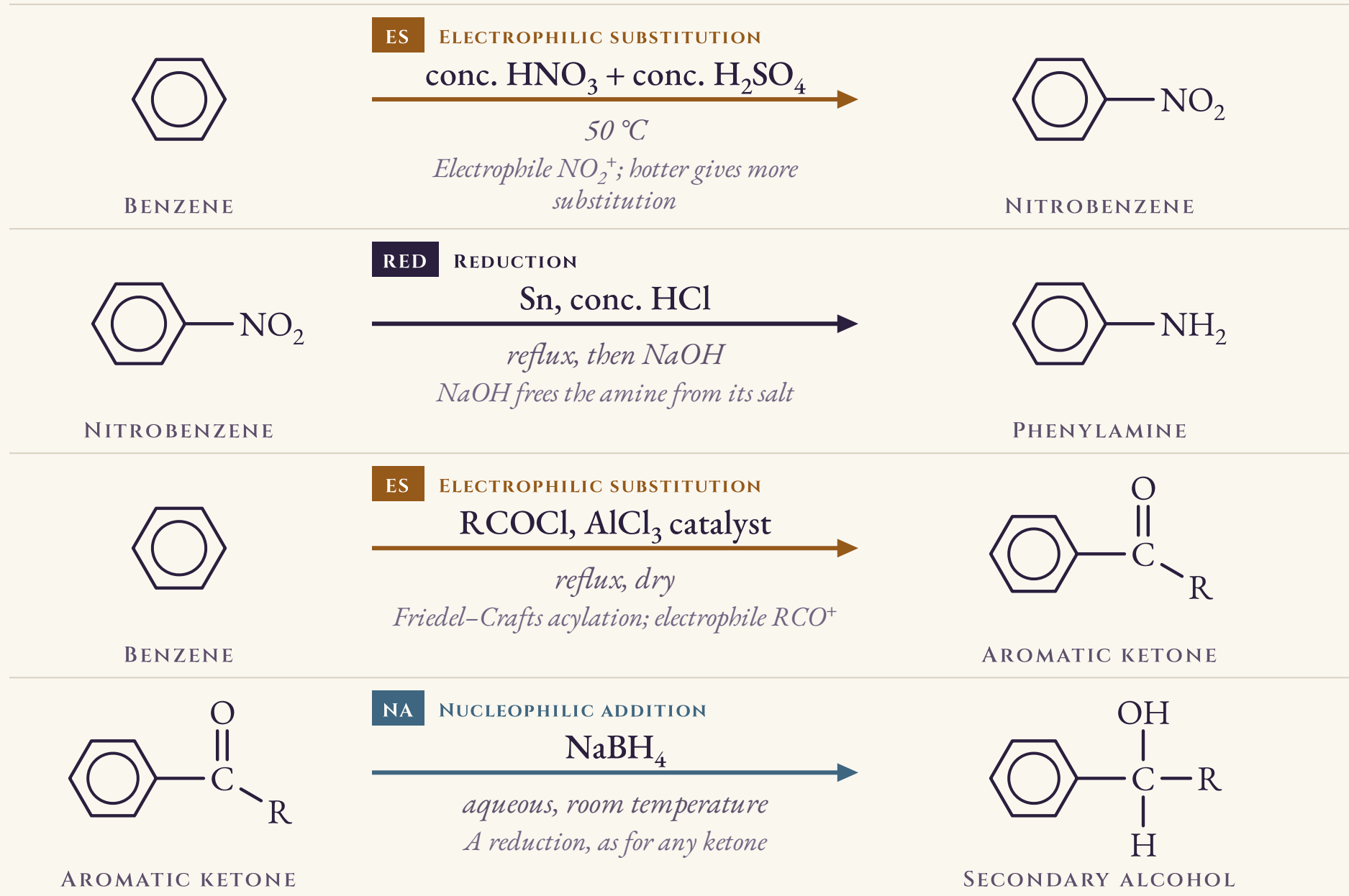
> Phenylamine

N lone pair delocalised into the ring

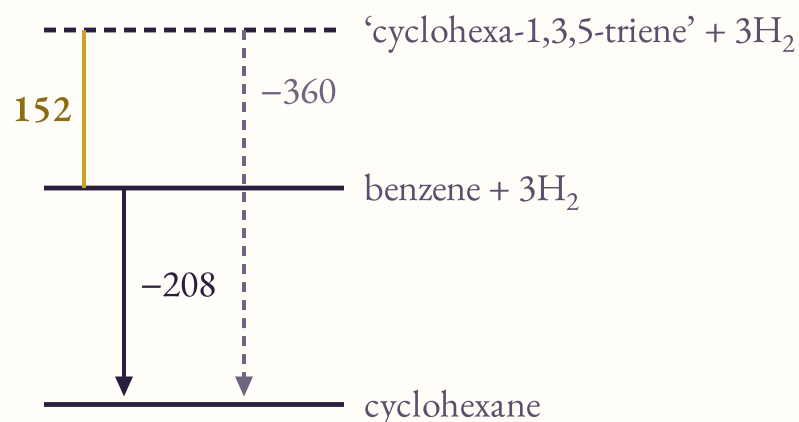
A base accepts H^+ with the lone pair on nitrogen: the more available the pair, the stronger the base.

Keeping the ring

The delocalised ring attacks strong electrophiles; one H^+ is lost and the ring is restored.



WHY SUBSTITUTION, NOT ADDITION?



Hydrogenating cyclohexene releases 120 kJ mol⁻¹, so three C=C should release 360. Benzene releases only 208: it is 152 kJ mol⁻¹ more stable, because its π electrons are delocalised. Substitution keeps that ring; addition would lose it.

Addition and condensation

Addition polymers join through C=C with no other product; condensation polymers lose a small molecule at every link.

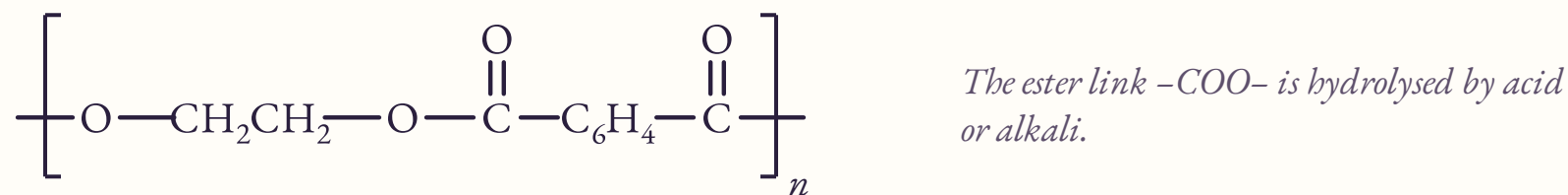
ADDITION · FROM ALKENES



POLYESTER · DIOL + DICARBOXYLIC ACID



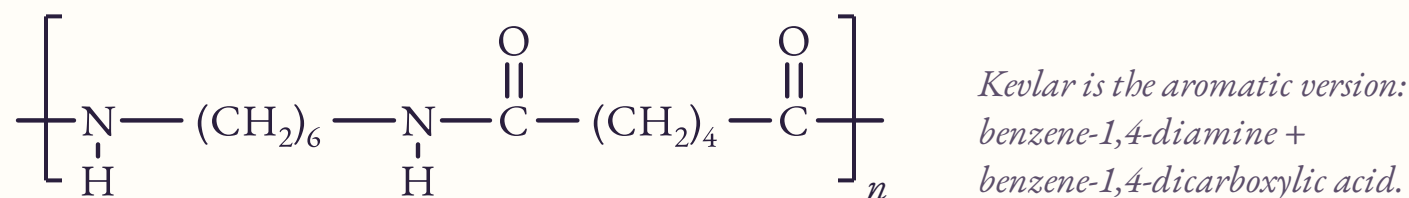
ethane-1,2-diol + benzene-1,4-dicarboxylic acid → PET, losing H₂O



POLYAMIDE · DIAMINE + DICARBOXYLIC ACID



hexane-1,6-diamine + hexanedioic acid → nylon-6,6, losing H₂O



EXAM TRAPS

- A diacyl chloride can replace the dicarboxylic acid: then HCl, not H₂O, is lost at each link.
- Proteins are polyamides of amino acids, joined by –CONH– peptide links; 6 mol dm^{–3} HCl and reflux hydrolyses them.
- Polyesters and polyamides can be hydrolysed, so they biodegrade; poly(alkenes) cannot.

Six routes to plan

For each, give every intermediate, and the reagents and conditions for every step.

Answers overleaf.

01**2 STEPS****Ethanol****Ethyl ethanoate**

Ethanol is the only organic starting material.

02**3 STEPS****Propene****2-Methylpropan-1-amine**

The chain gains a carbon.

03**3 STEPS****Benzene****N-Phenylethanamide**

Nitrogen goes onto the ring first.

04**2 STEPS****Propan-1-ol****Propan-2-ol**

Move the OH along the chain.

05**2 STEPS****Benzene****1-Phenylethanol**

Build the side chain, then reduce it.

06**2 STEPS****Bromoethane****Propan-1-amine**

Three carbons from two.

The six routes



1 excess $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, reflux · 2 $\text{CH}_3\text{CH}_2\text{OH}$, conc. H_2SO_4 , heat

Distilling would stop at ethanal; reflux with excess oxidant gives the acid.



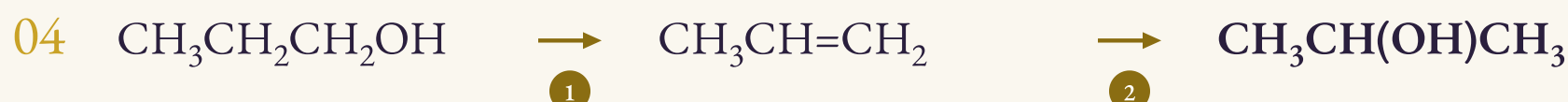
1 HBr · 2 KCN , ethanol/water, reflux · 3 LiAlH_4 , or H_2/Ni

HBr gives the 2-bromo product (secondary carbocation), so CN goes onto carbon 2.



1 conc. HNO_3 + conc. H_2SO_4 , 50 °C · 2 Sn , conc. HCl , then NaOH · 3 CH_3COCl (or ethanoic anhydride)

NaOH releases phenylamine from the salt formed in HCl.



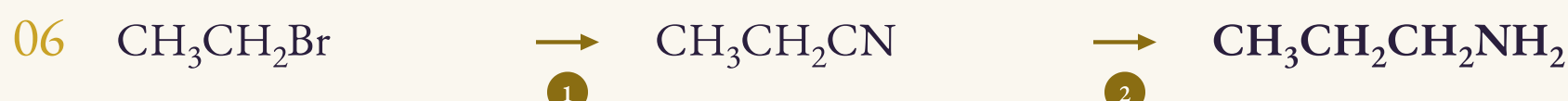
1 conc. H_2SO_4 , heat · 2 steam, H_3PO_4 , 300 °C, 60 atm

Hydration goes mainly via the secondary carbocation, so the major product has OH on carbon 2.



1 CH_3COCl , AlCl_3 · 2 NaBH_4

H^- attacks the planar $\text{C}=\text{O}$ from both faces: a racemic product.



1 KCN , ethanol/water, reflux · 2 LiAlH_4 , or H_2/Ni

NH_3 directly would give ethylamine (ethanamine): one carbon short.

NOW PRACTISE IT

A map is learned *by using it.*

Demosthenes is an A-level revision app for Maths,
Further Maths, Biology, Chemistry and Physics.

Exam-style questions across the course, optional AI
marking against each question's mark scheme, and
timed papers.

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DEMOSTHENES