9701 CHEMISTRY · TOPICS 21 & 35 · AS + A LEVEL

Organic Synthesis — Reagent Map

01 · HOW TO PLAN A ROUTE

1 Count the carbons in start and target. Same number? Then no chain step is needed. One more? Go through a **nitrile**.

2 Identify the functional group change and pick the reagent from the map below.

3 Work **backwards** from the target when the forward route is not obvious, and always quote reagent **and** conditions for each step.

02 · FROM AN ALKENE

To	Reagent and conditions
alkane	H_2, Ni, 150 °C
halogenoalkane	HBr, room temp
dihalide	Br_2, room temp
alcohol	steam, H_3PO_4, 300 °C, 60 atm
diol	cold dilute acidified $KMnO_4$
polymer	high pressure or catalyst

03 · FROM A HALOGENOALKANE

To	Reagent and conditions
alcohol	NaOH(aq), warm
alkene	KOH in ethanol, hot
nitrile (+1 C)	KCN in ethanol, reflux
amine	excess NH_3 in ethanol, heat

04 · FROM AN ALCOHOL

To	Reagent and conditions
aldehyde	$K_2Cr_2O_7$ / H^+, **distil off**
carboxylic acid	$K_2Cr_2O_7$ / H^+, reflux
ketone (from 2°)	$K_2Cr_2O_7$ / H^+, reflux
alkene	conc. H_2SO_4, 170 °C
halogenoalkane	PCl_5, or HCl / $ZnCl_2$
ester	carboxylic acid, conc. H_2SO_4, reflux

05 · FROM A CARBONYL

To	Reagent and conditions
alcohol	$NaBH_4$ or $LiAlH_4$
carboxylic acid	$K_2Cr_2O_7$ / H^+, reflux (aldehyde only)
hydroxynitrile (+1 C)	NaCN with dilute acid

06 · FROM AN ACID OR NITRILE

Change	Reagent and conditions
acid → alcohol	$LiAlH_4$ in dry ether
acid → acyl chloride	PCl_5
acid → ester	alcohol, conc. H_2SO_4, reflux
nitrile → acid	dilute HCl, reflux
nitrile → amine	$LiAlH_4$, or H_2 / Ni

07 · AROMATIC ROUTES A2

Change	Reagent and conditions
benzene → nitrobenzene	conc. HNO_3 / conc. H_2SO_4, 55 °C
nitrobenzene → phenylamine	Sn / conc. HCl, then NaOH
benzene → alkylbenzene	RCl / $AlCl_3$
methylbenzene → benzoic acid	hot alkaline $KMnO_4$, then H^+

08 · CHANGING THE CHAIN LENGTH

Add one carbon: halogenoalkane + KCN, or carbonyl + HCN. Both give a nitrile group that can then become –COOH or $–CH_2NH_2$.

Shorten a chain: vigorous oxidation of an alkene, or oxidation of an alkyl side chain on a ring. These are the only routes the syllabus expects.

09 · WORKED EXAMPLE — ALKENE TO KETONE

Convert propene into propanone.

Same carbon count, so no nitrile is needed.

1 · HBr, room temperature → 2-bromopropane
2 · NaOH(aq), warm → propan-2-ol
3 · $K_2Cr_2O_7$ / H^+, reflux → propanone

Markovnikov puts the group on carbon 2, so the alcohol is secondary and the product is a ketone. Propanoic acid cannot be made from propene at this level — start from propan-1-ol instead.

10 · WORKED EXAMPLE — CHAIN LENGTHENING

Convert ethanol into propanoic acid.

Three carbons from two, so a nitrile step is required.

1 · PCl_5 (or HCl / $ZnCl_2$) → chloroethane
2 · KCN in ethanol, reflux → propanenitrile
3 · dilute HCl, reflux → propanoic acid

11 · PURIFICATION AND YIELD

Liquids: distillation for a volatile product, or a separating funnel followed by drying with anhydrous $CaCl_2$ or $MgSO_4$.

Solids: recrystallise from a suitable solvent, filter under reduced pressure, dry, then check purity by melting point — a sharp value at the literature figure means pure.

12 · TESTS THAT IDENTIFY A GROUP

Group	Test and result
C=C	Br_2(aq) decolourised
–OH	PCl_5 → steamy HCl fumes
C=O	2,4-DNPH → orange ppt
–CHO	Tollens' → silver mirror
–COOH	Na_2CO_3 → fizzing
$CH_3CO–$ or $CH_3CH(OH)–$	I_2 / NaOH → yellow ppt
halogenoalkane	NaOH then HNO_3 and $AgNO_3$ → ppt

13 · WORKED EXAMPLE — THREE STEPS

Convert propan-1-ol into 1-aminobutane.

Four carbons from three → one nitrile step.

1 · PCl_5 → 1-chloropropane
2 · KCN in ethanol, reflux → butanenitrile
3 · $LiAlH_4$ in dry ether → 1-aminobutane

Reacting the chloropropane with ammonia instead would give propylamine — one carbon short.

MARKS LOST HERE

— Giving a reagent without its conditions, or the wrong solvent for substitution against elimination.

— Ignoring the carbon count and proposing a route that cannot change it.

— Choosing an order that puts a directing group on the ring too early.

— Using reflux where the product must be distilled off, so the aldehyde is over-oxidised.