

Cambridge AS & A Level · Chemistry 9701 · Notes

Organic synthesis A2

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What you need to know

The learning outcomes are the same three as AS organic synthesis, but now **every reaction in the syllabus** can be used, including arenes, phenol, acyl chlorides, amines, amides, diazonium salts and amino acids. You should be able to:

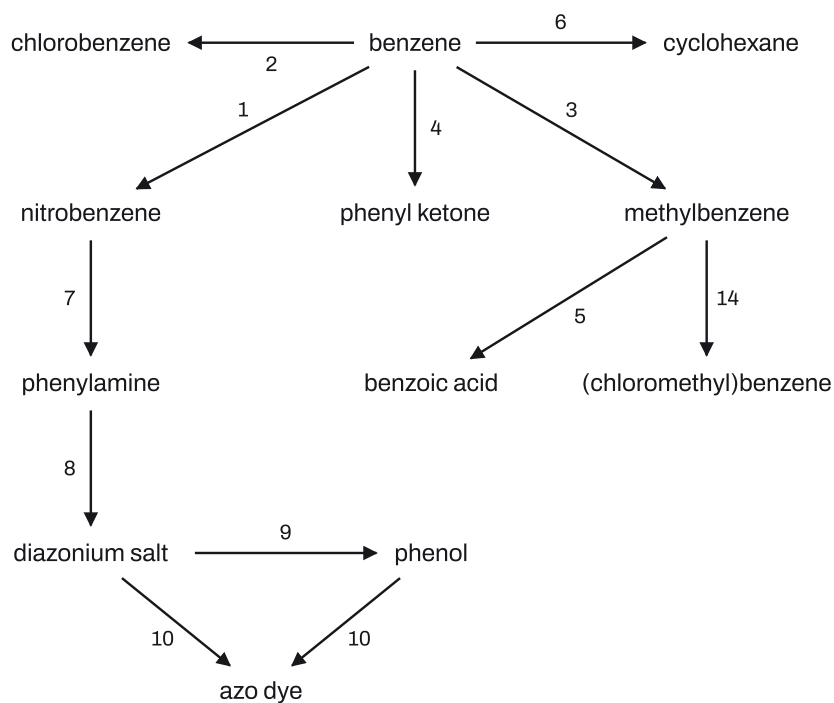
1. **Take a molecule with several functional groups and:**
 - (a) **identify its functional groups** from the reactions it does (for example, a phenol from its reaction with bromine water, a carboxylic acid from effervescence with carbonate, an aldehyde from Fehling's reagent);
 - (b) **predict its properties and reactions:** which reagents it reacts with, which groups each reagent changes, and what the products are, including acid–base properties.
2. **Devise a synthetic route** of several steps to make a target molecule, using only reactions in the syllabus, with reagents and conditions for every step and the steps in a sensible order.
3. **Analyse a route you are given:** the type of reaction and the reagents for each step, and any possible by-products.

This topic adds no new reactions. It tests whether you can **use** the reactions of the other organic topics together. The AS reactions (alkenes, halogenoalkanes, alcohols, carbonyl compounds, acids, esters, nitriles) are in "Organic synthesis" at AS; they are recapped here only where A Level questions use them.

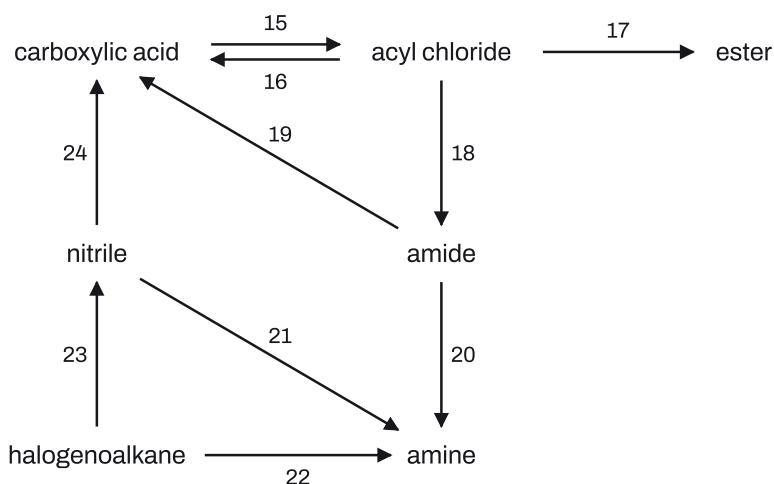
Understand it

The A Level reaction map

As at AS, each reaction turns one group into another, and a route is a path through the map. The first map is the aromatic chemistry that grows out of benzene.



The second map is the chemistry of acyl chlorides, amides and amines, joined to the AS nitrile reactions.



The numbers match this table. Nothing in it is printed in the exam.

#	Change	Reagents and conditions	Type of reaction
1	arene → nitroarene	concentrated HNO_3 and concentrated H_2SO_4 , 25–60 °C	electrophilic substitution
2	arene → chloro- or bromoarene	Cl_2 with AlCl_3 , or Br_2 with AlBr_3	electrophilic substitution
3	arene → alkylarene	CH_3Cl and AlCl_3 , heat (Friedel–Crafts alkylation)	electrophilic substitution
4	arene → aryl ketone	CH_3COCl and AlCl_3 , heat (Friedel–Crafts acylation)	electrophilic substitution

#	Change	Reagents and conditions	Type of reaction
5	alkylarene → benzoic acid	hot alkaline KMnO_4 , then dilute acid (the whole side chain becomes COOH)	oxidation
6	arene → cyclohexane ring	H_2 with Pt or Ni catalyst, heat	addition (hydrogenation)
7	nitroarene → arylamine	Sn and concentrated HCl , heat, then NaOH(aq)	reduction
8	phenylamine → diazonium salt	HNO_2 (from NaNO_2 and dilute HCl), below 10°C	diazotisation
9	diazonium salt → phenol	warm with water (N_2 is given off)	substitution
10	diazonium salt + phenol → azo compound	phenol in NaOH(aq) , cold	coupling (electrophilic substitution)
11	phenol (or phenylamine) → 2,4,6-tribromo product	$\text{Br}_2(\text{aq})$, room temperature, no catalyst	electrophilic substitution
12	phenol → 2- and 4-nitrophenol	dilute HNO_3 , room temperature	electrophilic substitution
13	phenol → sodium phenoxide	NaOH(aq) , or Na (which also gives H_2)	acid–base (redox with Na)
14	methylbenzene → (chloromethyl)benzene	Cl_2 , ultraviolet light (the side chain, not the ring)	free-radical substitution
15	carboxylic acid → acyl chloride	SOCl_2 , or PCl_5 , or PCl_3 and heat	substitution
16	acyl chloride → carboxylic acid	water, room temperature	hydrolysis (addition–elimination)
17	acyl chloride → ester	an alcohol or a phenol , room temperature	addition–elimination (condensation)
18	acyl chloride → amide	NH_3 , or a primary or secondary amine, room temperature	addition–elimination (condensation)
19	amide → carboxylic acid + amine (or NH_3)	heat with aqueous acid or aqueous alkali	hydrolysis
20	amide → amine	LiAlH_4 (the C=O becomes CH_2)	reduction
21	nitrile → primary amine	LiAlH_4 , or H_2 with Ni	reduction
22	halogenoalkane → amine	NH_3 in ethanol, heat under pressure (a primary amine in place of NH_3 gives a secondary amine, and so on)	nucleophilic substitution
23	halogenoalkane → nitrile	KCN in ethanol, heat (adds one carbon)	nucleophilic substitution

#	Change	Reagents and conditions	Type of reaction
24	nitrile → carboxylic acid	dilute acid, heat under reflux	hydrolysis

Still in use from AS: oxidising alcohols and aldehydes with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (a **primary** alcohol gives an aldehyde, then a carboxylic acid; a **secondary** alcohol gives a ketone; a **tertiary** alcohol is not oxidised, so an alcohol that loses H_2 to give an aldehyde must have been primary); reducing $\text{C}=\text{O}$ with NaBH_4 or LiAlH_4 ; HCN with a KCN catalyst adding to $\text{C}=\text{O}$; esterifying with concentrated H_2SO_4 and heat; dehydrating alcohols with concentrated H_2SO_4 and heat; hot concentrated acidified KMnO_4 splitting a $\text{C}=\text{C}$ ($=\text{CH}_2$ becomes CO_2 , $=\text{CHR}$ becomes RCOOH , $=\text{CRR}'$ becomes a ketone). Two acids are oxidised further: methanoic acid (by Fehling's or Tollens' reagent, or acidified KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$) and ethanedioic acid (warm acidified KMnO_4), both to CO_2 .

Where a new group goes on a ring

A group already on a benzene ring decides where the next group goes. The syllabus lists six:

Group already on the ring	Sends the new group to
$-\text{NH}_2$, $-\text{OH}$, $-\text{R}$ (alkyl, such as $-\text{CH}_3$)	positions 2 and 4 (and 6)
$-\text{NO}_2$, $-\text{COOH}$, $-\text{COR}$	position 3 (and 5)

The first three push electron density into the ring; the last three pull it out. The groups that pull electrons out also make the ring **less** reactive, but they still **direct** to position 3: they do not "activate" it. $-\text{OH}$ and $-\text{NH}_2$ make the ring so reactive that bromine water substitutes it at room temperature, with no catalyst.

This is why the **order of steps** matters. Methylbenzene nitrates at positions 2 and 4, because $-\text{CH}_3$ directs there. Benzoic acid nitrates at position 3, because $-\text{COOH}$ directs there. So "oxidise, then nitrate" and "nitrate, then oxidise" give different isomers from the same two reagents. When a question gives the positions of two groups in the target, read off which group must already be there when the second one goes on.

Which groups each reagent touches

In a molecule with several groups, each group reacts as it would on its own. Add these to the AS "reacts with / leaves alone" list:

Reagent	Reacts with	Leaves alone
NaBH_4	aldehyde and ketone $\text{C}=\text{O}$	COOH , ester, amide, nitrile, $\text{C}=\text{C}$, benzene ring
LiAlH_4	aldehyde and ketone $\text{C}=\text{O}$, COOH , amide , nitrile	$\text{C}=\text{C}$, benzene ring
Sn and concentrated HCl	$-\text{NO}_2$ on a ring	COOH , ester, ring
H_2 with Ni or Pt , heat	$\text{C}=\text{C}$, $\text{C}\equiv\text{N}$, and the benzene ring	

Reagent	Reacts with	Leaves alone
hot alkaline KMnO_4	an alkyl side chain on a ring (to COOH), $\text{C}=\text{C}$	the ring itself, COOH , $-\text{NO}_2$
$\text{Br}_2(\text{aq})$	$\text{C}=\text{C}$ (addition); phenol and phenylamine rings (substitution)	benzene, methylbenzene, other rings
$\text{NaOH}(\text{aq})$, room temperature	COOH and phenol OH (neutralised), acyl chloride (hydrolysed)	alcohol OH , aryl $\text{C}-\text{Cl}$
$\text{NaOH}(\text{aq})$, heat	also esters, amides and halogenoalkanes (hydrolysed)	aryl $\text{C}-\text{Cl}$, alcohol OH
$\text{Na}_2\text{CO}_3(\text{aq})$	COOH only	phenol, alcohol
Na	every $\text{O}-\text{H}$: alcohol, phenol, COOH	$\text{N}-\text{H}$ of amines and amides (in these questions)
acyl chloride	alcohol OH , phenol OH , $-\text{NH}_2$ and $-\text{NH}-$ of amines	COOH , $\text{C}=\text{C}$, amide

Three kinds of $\text{C}-\text{Cl}$

A chlorine atom can sit on three kinds of carbon, and they react very differently with water or OH^- :

- **Acyl chloride**, RCOCl : hydrolysed by cold water at once. The carbon has both O and Cl pulling electrons away, so it is very $\delta+$ and easy for a nucleophile to attack.
- **Halogenoalkane** (including a side-chain $\text{C}-\text{Cl}$ such as $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$): hydrolysed by $\text{NaOH}(\text{aq})$ on heating.
- **Aryl chloride** (Cl on the ring, such as chlorobenzene): not hydrolysed under these conditions. A lone pair on the Cl overlaps with the ring's π system, which strengthens the $\text{C}-\text{Cl}$ bond.

So in a molecule with a Cl on the ring and a Cl on a side chain, only the side-chain Cl is replaced by $\text{NaOH}(\text{aq})$ or NH_3 .

Acids and bases in one molecule

"Predict properties" includes acid-base behaviour:

- **Acid strength**: alcohol $<$ water $<$ phenol $<$ carboxylic acid. Only COOH is strong enough to release CO_2 from carbonate; phenol reacts with NaOH but not with Na_2CO_3 ; alcohols react only with Na . Chlorine atoms near a COOH make it a stronger acid.
- **Base strength**: amide $\ll$ phenylamine $<$ ammonia $<$ alkylamine. An amide's nitrogen lone pair is spread over the $\text{C}=\text{O}$, so amides are almost neutral.
- **pH matters**. In acid, amine groups are protonated ($-\text{NH}_3^+$); in alkali, COOH and phenol groups lose H^+ ($-\text{COO}^-$, $-\text{O}^-$). If a question says the products are isolated at low pH, draw amines as $-\text{NH}_3^+$ and acids as $-\text{COOH}$.

Reading changes in molecular formula

Questions often give the molecular formula at each step. The difference between two formulas tells you what the reaction did:

Change in formula	Usually means
$-H_2$	alcohol $\rightarrow$ C=O (oxidation): primary gives an aldehyde, secondary a ketone
$+O$	aldehyde $\rightarrow$ COOH
$+H_2$ or $+2H$	C=O $\rightarrow$ CH(OH), or C=C $\rightarrow$ CH-CH (reduction)
$-H_2O$	dehydration to C=C, or condensation (ester, amide, a ring closing)
$+H_2O$	hydrolysis (a ring opening, if nothing splits off)
H replaced by Br, with no H added	substitution on a phenol or phenylamine ring, not addition to C=C
$+HBr$ or $+Br_2$	addition to C=C
one C fewer, with a yellow precipitate from alkaline I_2	CH_3CO- has become $-COO^-$ and CHI_3

Making and opening rings

A molecule with **two** groups that can react with each other can react **with itself**, making a ring and a small molecule. A hydroxy acid heated with concentrated H_2SO_4 can give a cyclic ester; an amino ester can give a cyclic amide and an alcohol. Going the other way, hydrolysis of a **cyclic** ester or amide opens the ring: water adds, nothing splits off, and one molecule with **both** groups (OH and COOH, or NH_2 and COOH) is formed. A Friedel-Crafts reagent with a second reactive end, used twice, can also close a ring onto benzene.

By-products

- **Inorganic:** HCl from every acyl chloride reaction and from Friedel-Crafts reactions; SO_2 and HCl from $SOCl_2$; $POCl_3$ and HCl from PCl_5 ; H_2O from nitration, from condensations and from Sn/HCl reductions; N_2 from warming a diazonium salt; NH_4Cl (or NH_3 in alkali) from hydrolysing a primary amide or a nitrile; HBr from brominating phenol.
- **Organic:** the other ring isomer (a 2-substituted product alongside the 4-substituted one); more than one substitution (dinitration if the temperature goes above 60 °C; secondary and tertiary amines when a halogenoalkane reacts with ammonia); a salt of the amine when the HCl made in an amide synthesis reacts with a second molecule of amine.

Unfamiliar reactions

Some questions describe a reaction you have not met (a new cleavage, a ring-forming addition) with one example, then ask for the product from a new molecule. Find which bonds break and which form in the example, number the atoms, and make exactly the same changes to the new molecule. Everything else is copied unchanged, and the molecular formula must match any formula given.

Key facts and formulas

"Given" means it is on the Periodic Table or in the Data Booklet in the exam. "Learn it" means you must remember it; no reagents, conditions or directing effects are printed.

Formula or fact	Status
Relative atomic masses: H 1.0, C 12.0, N 14.0, O 16.0, Cl 35.5, Br 79.9	Given
Molar volume of gas at room conditions = $24.0 \text{ dm}^3 \text{ mol}^{-1}$	Given
The 24 reactions in the table, with reagents, conditions and types (and the AS ones)	Learn it
Directing: $-\text{NH}_2$, $-\text{OH}$, $-\text{R}$ to 2, 4; $-\text{NO}_2$, $-\text{COOH}$, $-\text{COR}$ to 3	Learn it
Reducing agents: NaBH_4 only $\text{C}=\text{O}$ of aldehydes and ketones; LiAlH_4 also COOH , amides and nitriles; Sn/HCl only $-\text{NO}_2$	Learn it
$\text{ArNO}_2 + 6[\text{H}] \rightarrow \text{ArNH}_2 + 2\text{H}_2\text{O}$; $\text{RCN} + 4[\text{H}] \rightarrow \text{RCH}_2\text{NH}_2$; $\text{RCONH}_2 + 4[\text{H}] \rightarrow \text{RCH}_2\text{NH}_2 + \text{H}_2\text{O}$	Learn it
Ease of hydrolysis: acyl chloride > halogenoalkane > aryl chloride	Learn it
Acidity: alcohol < water < phenol < carboxylic acid; basicity: amide < phenylamine < NH_3 < alkylamine	Learn it
Percentage yield = $\frac{\text{actual mass}}{\text{theoretical mass}} \times 100$	Learn it

How to do it

We have tagged 22 questions on this topic from 2021, 2022, 2024 and 2025 (15 different, since some papers share questions). 16 of them mix more than one type, so the counts add up to more than 22.

Question type	Questions
Reagents and conditions for steps in a route	15
Identify intermediates and products in a route	14

Question type	Questions
Functional groups and reactions of a molecule with several groups	8
Deduce structures from a reaction scheme and test results	5
Plan the order of steps on a ring	3
Name the type of reaction in each step	3

1. Reagents and conditions for steps in a route (15 questions)

1. **Write the structure at every stage**, including any the question leaves blank (see type 2).
2. **Say what changes in each step**: which group becomes which, whether a C–C bond forms, and whether the change is on the ring or on a side chain.
3. **Find the arrow in the table** and write its reagents **and** conditions: concentrated or dilute, aqueous or in ethanol, catalyst, temperature, heat, reflux, UV light, pressure.
4. **Check the reagent leaves the rest of the molecule alone** (the "reacts with / leaves alone" table). Sn/HCl reduces —NO_2 but not COOH ; NaBH_4 cannot reduce an amide or nitrile.

Variations you will meet:

- **Two or three routes to the same product**. A primary amine RCH_2NH_2 can come from the nitrile RCN (LiAlH_4 or H_2/Ni), from the amide RCONH_2 (LiAlH_4), or from the halogenoalkane RCH_2Br (NH_3 in ethanol, heat under pressure). The amide comes from the acyl chloride and NH_3 ; the nitrile from a halogenoalkane with one carbon fewer and KCN . One reagent that works for two arrows (such as LiAlH_4 for both the amide and the nitrile) is a common answer.
- **Acyl chloride steps** are done at room temperature, with **no water or aqueous reagents**, because water would hydrolyse the acyl chloride. An ester of an alcohol can be made either from the acid (concentrated H_2SO_4 , heat) or from the acyl chloride; an ester of a **phenol** needs the acyl chloride.
- **Adding methyl groups to an amine nitrogen** (—NH_2 to $\text{—N(CH}_3)_2$): a halogenoalkane such as CH_3Br in ethanol, heated under pressure. It is a substitution, not an oxidation.
- **A ring opened, then closed a different way**: heat with dilute aqueous acid to hydrolyse a cyclic amide or ester; then concentrated H_2SO_4 and heat to make a new cyclic ester from the OH and COOH .
- **Naming a reagent** instead of drawing it: the name must be exact, including the position number of an OH (for example butan-1-ol, not butanol).

2. Identify intermediates and products in a route (14 questions)

1. **Work forwards** from the start and **backwards** from the target, one step at a time, until they meet at the missing compound.
2. **Use every clue**: the reagent (which group can it change?), the molecular formula (the formula-change table), and the number of carbons.
3. **Draw with care**. Check every carbon has four bonds and count H atoms against any formula given.

Variations you will meet:

- **Aromatic routes:** nitro → amine (Sn/HCl) → diazonium (HNO_2 , cold) → phenol (warm) or azo compound (with a phenol in alkali). A structure "similar to phenol" couples the same way, at the position para to its OH (or ortho if para is taken).
- **Side-chain oxidation:** hot alkaline KMnO_4 turns **any** alkyl group on a ring into COOH , whatever its length; the ring and $-\text{NO}_2$ are unchanged.
- **A bifunctional Friedel–Crafts reagent**, such as a chloroalkanoic acid: the AlCl_3 step joins the alkyl end to the ring; the COOH can then be turned into COCl (SOCl_2) and a second Friedel–Crafts step joins it to the same ring, closing a new ring with a ketone.
- **Hydrolysis products at a stated pH:** amide bonds split into COOH and amine; draw amines as $-\text{NH}_3^+$ if the pH is low. Ethers ($\text{CH}_3\text{O}-$) and the ring are unchanged.
- **Unfamiliar reactions:** copy the bond changes of the example exactly (see "Unfamiliar reactions").

3. Functional groups and reactions of a molecule with several groups (8 questions)

1. **Name every group precisely:** phenol (OH on a ring) not alcohol; ester; amide (N joined **directly** to the $\text{C}=\text{O}$) versus amine; ketone ($\text{C}=\text{O}$ between two carbons, even in a ring that also contains an N); nitrile (not "cyano"); arene; primary amine or phenylamine. Classify amines by the number of carbons on the N: one is primary, two is secondary, three is tertiary.
2. **Take each reagent in turn**, use the "reacts with / leaves alone" table, and change only the groups that react.
3. **Look at the ring positions** for substitution on a phenol or phenylamine: 2, 4 and 6 relative to the OH or NH_2 , skipping positions already taken.

Variations you will meet:

- **Compare acidities or basicities** within or between molecules, with reasons (electron-donating alkyl groups, electron-withdrawing $\text{C}=\text{O}$, delocalisation of a lone pair into a ring or a $\text{C}=\text{O}$).
- **Equations with sodium or NaOH:** phenol with Na gives sodium phenoxide and $\frac{1}{2}\text{H}_2$ (not H^+ , not H_2O); with NaOH it gives the phenoxide and water.
- **Reactions of a phenol:** dilute HNO_3 gives the 2- and 4-nitro isomers (draw both, each still with its OH); bromine water gives the 2,4,6-tribromo product.

4. Deduce structures from a reaction scheme and test results (5 questions)

1. **Decode each test** into a group:

Test	Positive result	Shows
Na	effervescence (H_2)	any O–H: alcohol, phenol, COOH
$\text{Na}_2\text{CO}_3(\text{aq})$	effervescence (CO_2)	COOH
2,4-DNPH	orange precipitate	aldehyde or ketone

Test	Positive result	Shows
alkaline $I_2(aq)$, warm	yellow precipitate, CHI_3	CH_3CO- or $CH_3CH(OH)-$
Fehling's or Tollens' reagent, warm	brick-red precipitate or silver mirror	aldehyde (and methanoic acid)
$Br_2(aq)$	decolourised	$C=C$ (addition); phenol or phenylamine (substitution, white precipitate)

2. **Use the molecular formulas** at each step (formula-change table). Count double-bond equivalents if it helps: a benzene ring accounts for four.
3. **Start from the smallest pieces**, such as the products of hot $KMnO_4$ splitting, and rebuild: each $C=O$ made by the splitting was one end of a $C=C$.
4. **Check every structure against every test in its row**, including the negative ones.

Variations you will meet:

- **Stereoisomerism as a clue:** a $C=C$ with two different groups on each end (cis/trans), or a chiral carbon.
- **A chain of reagents** on one compound: $SOCl_2$ turns $-COOH$ into $-COCl$; the named alcohol then gives the matching ester (propan-2-ol gives $-COOCH(CH_3)_2$); $LiAlH_4$ reduces $C=O$ and $COOH$ but not $C=C$; alkaline I_2 gives CHI_3 and the carboxylate with one carbon fewer.
- **Bromine water with an aromatic compound:** if 2 H atoms are replaced (no atoms added), the compound is a phenol with two free 2-, 4- or 6-positions.

5. Plan the order of steps on a ring (3 questions)

1. **Mark where each group is** in the target, relative to the others (2-, 3- or 4-).
2. **Ask which group directs the next one there.** A group that directs to 3 must already be on the ring when a group is to go at position 3 from it; a group that directs to 2 and 4 must be there for a 2- or 4-product.
3. **Put ring substitutions and side-chain changes in that order**, and leave the reduction of $-NO_2$ until after any oxidation with $KMnO_4$, so the new $-NH_2$ is not attacked.
4. **Explain** with the directing effect by name, for example "COOH is electron-withdrawing and directs to position 3".

For example, a 3-nitro acid needs the COOH made **first** (oxidise the methyl side chain, then nitrate). A 4-nitro acid needs the nitro group put on **while the methyl group is still there** (nitrate, then oxidise).

6. Name the type of reaction in each step (3 questions)

Use the type column of the table. The words the mark schemes expect: electrophilic substitution (on rings), nucleophilic substitution (halogenoalkanes with NH_3 , amines, CN^- , OH^-), addition-elimination or condensation (acyl chlorides with water, alcohols, phenols, amines), condensation (esterification, amide or peptide formation, a ring closing with loss of a small molecule), hydrolysis, oxidation, reduction, elimination or dehydration, nucleophilic addition (HCN to $C=O$), addition.

Variations you will meet:

- **An ester with NaOH(aq)** is hydrolysis, and any acid or phenol formed is then neutralised: two types in one step.
- **A step that joins two molecules and releases ethanol or water** (for example an amine attacking an ester group in the same molecule to form a ring) is condensation.
- **Putting a methyl on an N** is substitution; turning $-\text{CH}_3$ into COOH is oxidation; turning $\text{C}=\text{O}$ into $\text{CH}(\text{OH})$ is reduction (also nucleophilic addition).

Worked examples

The bold codes show where marks are earned, as in Cambridge mark schemes. The number is how many marks.

- **M1** method mark: for a correct method, even if the numbers slip.
- **A1** accuracy mark: for a correct answer; it needs the M mark before it.
- **B1** mark for a correct result on its own, with no method needed.

Example 1

Compound **Q** is 2-chloro-4-(chloromethyl)phenol: a benzene ring with OH at position 1, Cl at position 2 and CH_2Cl at position 4.

(a) **Q** is heated under reflux with an excess of NaOH(aq). Explain which chlorine atom is replaced, and give the structure of the organic product. **[3]**

(b) Give the structure of the organic product when **Q** reacts with ethanoyl chloride at room temperature, and name the inorganic by-product. **[2]**

(c) **Q** decolourises bromine water. Give the structure of the organic product and calculate the mass of bromine that reacts with 1.77 g of **Q**. **[3]**

(a) Only the Cl on the side chain is replaced. That C–Cl is like a halogenoalkane's and is hydrolysed by OH^- on heating. **B1** The Cl on the ring is not replaced: its lone pair overlaps with the ring's π system, strengthening the C–Cl bond. **B1**

The phenol OH is also neutralised by the excess NaOH, so the product is the sodium salt: ring with O^-Na^+ at 1, Cl at 2 and CH_2OH at 4. **B1**

(b) The phenol OH is converted into an ester: ring with OCOCH_3 at 1, Cl at 2, CH_2Cl at 4. **B1** By-product: HCl. **B1**

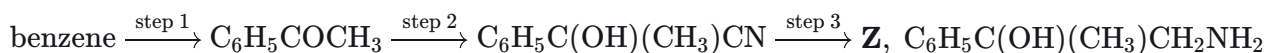
(c) OH directs to positions 2, 4 and 6. Positions 2 and 4 are already taken, so one Br goes to position 6: 2-bromo-6-chloro-4-(chloromethyl)phenol, $\text{C}_7\text{H}_5\text{BrCl}_2\text{O}$. **B1**

$M_r(\text{C}_7\text{H}_6\text{Cl}_2\text{O}) = 7(12.0) + 6(1.0) + 2(35.5) + 16.0 = 177.0$, so $n(\text{Q}) = 1.77 \div 177.0 = 0.0100 \text{ mol}$. **M1**

One Br_2 reacts per **Q** (one Br joins the ring, the other leaves as HBr): $m(\text{Br}_2) = 0.0100 \times 159.8 = 1.60 \text{ g}$. **A1**

Example 2

A chemist makes compound **Z** from benzene in three steps:



- (a) Give the reagents and conditions, and the type of reaction, for each step. **[6]**
- (b) Name the inorganic by-product of step 1. **[1]**
- (c) Explain why NaBH_4 cannot be used for step 3. **[1]**
- (d) **Z** has a chiral centre, but the **Z** made in this way does not rotate plane-polarised light. Explain why. **[2]**
- (e) Give a test that shows whether any phenylethanone is left in the product of step 3. **[1]**

(a) Step 1: CH_3COCl and AlCl_3 , heat **B1**; electrophilic substitution (Friedel–Crafts acylation). **B1**

Step 2: HCN with a KCN catalyst **B1**; nucleophilic addition. **B1**

Step 3: LiAlH_4 **B1**; reduction. **B1** The $\text{C}\equiv\text{N}$ becomes CH_2NH_2 : $\text{C}_9\text{H}_9\text{NO} + 4[\text{H}] \rightarrow \text{C}_9\text{H}_{13}\text{NO}$.

(b) HCl : $\text{C}_6\text{H}_6 + \text{CH}_3\text{COCl} \rightarrow \text{C}_6\text{H}_5\text{COCH}_3 + \text{HCl}$. **B1**

(c) NaBH_4 reduces only aldehyde and ketone $\text{C}=\text{O}$ groups; it does not reduce a nitrile. **B1**

(d) In step 2 the $\text{C}=\text{O}$ carbon is planar, so CN^- attacks from either side with equal chance. **M1** Equal amounts of the two enantiomers form (a racemic mixture), and their rotations cancel. **A1**

(e) Add 2,4-DNPH: an orange precipitate shows a ketone is still present (**Z** has no $\text{C}=\text{O}$). **B1** (Alkaline I_2 also works: a yellow precipitate from the $\text{CH}_3\text{CO}-$ group.)

Example 3

Phenyl propanoate, $\text{CH}_3\text{CH}_2\text{COOC}_6\text{H}_5$, is to be made using benzene and propan-1-ol as the only organic starting materials.

- (a) Describe a synthesis. For each step give the reagents and conditions and the organic product. **[8]**
- (b) Explain why propanoic acid and phenol are not heated with concentrated sulfuric acid for the last step. **[1]**
- (c) 5.00 g of phenol gives 6.40 g of phenyl propanoate. Calculate the percentage yield. **[2]**

Plan. The ester splits into a phenol part and a propanoyl part. An ester of a phenol is made from an **acyl chloride**, so the propanoyl part must be propanoyl chloride. Working back: phenol comes from a diazonium salt, which comes from phenylamine, which comes from nitrobenzene; propanoyl chloride comes from propanoic acid, which comes from propan-1-ol.

(a) From benzene:

1. Concentrated HNO_3 and concentrated H_2SO_4 , 25–60 °C, gives nitrobenzene. **B1**
2. Sn and concentrated HCl, heat, then NaOH(aq), gives phenylamine. **B1**
3. NaNO_2 and dilute HCl, below 10 °C, gives benzenediazonium chloride. **B1**
4. Warm with water, gives phenol (and N_2). **B1**

From propan-1-ol:

5. Acidified $\text{K}_2\text{Cr}_2\text{O}_7$, heat under reflux, gives propanoic acid. **B1**
6. SOCl_2 (or PCl_5) gives propanoyl chloride, $\text{CH}_3\text{CH}_2\text{COCl}$. **B1**

Then:

7. Propanoyl chloride and phenol at room temperature give phenyl propanoate and HCl. **B1 B1**

(b) The O–H oxygen of phenol is a poor nucleophile, because its lone pair is delocalised into the ring, so it reacts far too slowly with a carboxylic acid. The acyl chloride's carbon is much more $\delta+$ and reacts quickly. **B1**

(c) $M_r(\text{C}_6\text{H}_6\text{O}) = 94.0$ and $M_r(\text{C}_9\text{H}_{10}\text{O}_2) = 9(12.0) + 10(1.0) + 2(16.0) = 150.0$. **M1**

Theoretical mass = $\frac{5.00}{94.0} \times 150.0 = 7.98$ g, so the yield is $\frac{6.40}{7.98} \times 100 = 80.2\%$. **A1**

Common mistakes

- **Leaving out a condition.** Examiners repeatedly report "concentrated" missing from Sn and HCl, AlCl_3 missing from a Friedel–Crafts step, and "heat" missing from KMnO_4 oxidations. Learn each reagent with its conditions as one unit.
- **Calling Sn a catalyst.** Tin is a reagent in the reduction of $-\text{NO}_2$; it is used up.
- **Aqueous reagents with an acyl chloride.** NaOH(aq) or any aqueous solution hydrolyses RCOCl back to the acid, so it cannot be the reagent for making an ester or amide from it.
- **NaNO_3 or HNO_3 for diazotisation.** It is NaNO_2 (nitrite) and dilute HCl, below 10 °C.
- **Wrong reducing agent.** Sn/HCl and NaBH_4 do not reduce amides or nitriles; use LiAlH_4 (or H_2/Ni for a nitrile). LiAlH_4 does not reduce $\text{C}=\text{C}$.
- **Nitrating in the wrong order.** Nitrating methylbenzene and then oxidising gives the 2- or 4-nitro acid, not the 3-isomer. When explaining, name the directing effect; COOH directs to 3 but does not "activate" position 3.
- **Structures that do not fit the formula.** Carbons with three or five bonds are common. SOCl_2 gives $-\text{COCl}$, not $-\text{COOCl}$; the iodoform precipitate is CHI_3 ; an ester from propan-2-ol has $-\text{OCH}(\text{CH}_3)_2$, not a propyl chain. Count atoms against the given formula.
- **Missing that bromine water substituted a ring.** If two H atoms have been swapped for Br and nothing added, the compound is a phenol, not an alkene.
- **Wrong group names.** An N joined to a ring is phenylamine, not amide; "cyano" alone is not accepted for a nitrile; a phenol is not an alcohol; a ketone in a ring that also contains an N–H is still a ketone.

- **Wrong type of reaction.** Alkylating an amine is substitution, not oxidation; an intramolecular reaction that releases ethanol is condensation, not hydrolysis.
- **Forgetting protonation.** Hydrolysis in excess concentrated HCl gives $-\text{NH}_3^+$, not $-\text{NH}_2$.
- **Inexact names for reagents.** 3-methylbutan-1-ol, not 3-methylbutanol. Writing the formula avoids this.

How to get the marks

- **"Reagents and conditions":** both, with the details that change the outcome (concentrated or dilute, aqueous or in ethanol, the catalyst, the temperature, heat or reflux, UV). Each step is usually worth one mark on its own, so write something for every step.
- **"Suggest structures" or "draw":** displayed, structural or skeletal formulas are all accepted unless one is asked for; skeletal only means skeletal. Make sure the structure matches the molecular formula and the reagent.
- **"Identify"** a compound or reagent: a correct formula or an exact name.
- **"Explain" a choice of order:** name the directing effect of the group already on the ring and say which position it directs to.
- **"State the type of reaction":** use the table's words; add electrophilic or nucleophilic when asked for the mechanism.
- **Equations with [H] and [O]:** balance them and put water on the right where an O leaves ($\text{ArNO}_2 + 6[\text{H}] \rightarrow \text{ArNH}_2 + 2\text{H}_2\text{O}$). Never write $[\text{H}^+]$ or O_2 .
- **Tables of tests:** one group per test, matching the result in each column; "no visible change" for a negative result.
- **Calculations:** moles from the Data Booklet A_r values, state the ratio you use, and give 3 significant figures.

Quick check

1. Give one test that distinguishes each pair, and what each compound does: (a) chlorobenzene and (chloromethyl)benzene; (b) phenol and cyclohexanol; (c) ethanoyl chloride and ethyl ethanoate.
2. 4-hydroxyphenylethanoic acid is $\text{HOC}_6\text{H}_4\text{CH}_2\text{COOH}$. (a) Give the organic product with an excess of NaOH(aq) , and with $\text{Na}_2\text{CO}_3\text{(aq)}$. (b) Calculate the volume of hydrogen, at room conditions, given off when 1.52 g of it reacts with an excess of sodium.
3. Methylbenzene reacts with chlorine (a) with AlCl_3 and (b) in ultraviolet light. Name the organic products of each. (c) Which of these products gives an alcohol when heated with NaOH(aq) ? Name the alcohol.
4. Name the type of reaction and give the inorganic by-product: (a) $\text{CH}_3\text{CH}_2\text{COOH}$ with SOCl_2 ; (b) CH_3COCl with ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$; (c) propanamide heated with dilute HCl; (d) benzenediazonium chloride warmed with water.

Answers

- (a) Warm with AgNO_3 in ethanol: (chloromethyl)benzene gives a white precipitate of AgCl (its side-chain C-Cl is hydrolysed); chlorobenzene gives no visible change. (b) Bromine water: phenol decolourises it and gives a white precipitate (2,4,6-tribromophenol); with cyclohexanol there is no visible change. (c) Add $\text{AgNO}_3(\text{aq})$ at room temperature: ethanoyl chloride is hydrolysed at once and gives a white precipitate of AgCl ; ethyl ethanoate gives no visible change.
- (a) With excess NaOH both acidic groups react: $\text{NaOC}_6\text{H}_4\text{CH}_2\text{COONa}$. With Na_2CO_3 only the COOH reacts (a phenol is too weak an acid): $\text{HOC}_6\text{H}_4\text{CH}_2\text{COONa}$, with effervescence of CO_2 . (b)
 $M_r(\text{C}_8\text{H}_8\text{O}_3) = 152.0$, so $n = 1.52 \div 152.0 = 0.0100$ mol. Two O-H groups give one H_2 per molecule:
 $n(\text{H}_2) = 0.0100$ mol, volume = $0.0100 \times 24.0 = 0.240 \text{ dm}^3$ (240 cm^3).
- (a) Substitution on the ring: 1-chloro-2-methylbenzene and 1-chloro-4-methylbenzene (Cl on the ring, next to or opposite the CH_3). (b) Substitution on the side chain: (chloromethyl)benzene, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$. (c) Only (chloromethyl)benzene, because a Cl on the ring is not hydrolysed: it gives phenylmethanol, $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$.
- (a) Substitution; SO_2 and HCl : $\text{CH}_3\text{CH}_2\text{COOH} + \text{SOCl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{COCl} + \text{SO}_2 + \text{HCl}$. (b) Addition-elimination (condensation); HCl , which reacts with more ethylamine to give ethylammonium chloride: $\text{CH}_3\text{COCl} + 2\text{CH}_3\text{CH}_2\text{NH}_2 \rightarrow \text{CH}_3\text{CONHCH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}$. (c) Hydrolysis; ammonium chloride: $\text{CH}_3\text{CH}_2\text{CONH}_2 + \text{H}_2\text{O} + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{NH}_4\text{Cl}$. (d) Substitution (the OH replaces N_2^+); nitrogen and HCl : $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{N}_2 + \text{HCl}$.

Past questions to try

- 9701/43/M/J/22 Q7**: parts (d) and (e), reagents and conditions along a five-step route that includes an acyl chloride and a reduction.
- 9701/42/M/J/24 Q7**: a route to an azo dye, with the intermediates, reagents and a directing effect to explain.
- 9701/42/F/M/22 Q4**: part (b), a multi-step route from benzene and what happens when the order of steps changes.
- 9701/43/M/J/21 Q9**: deduce six structures from a scheme of reactions and a molecular formula.