

Hydrocarbons A2

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Read first: [An introduction to A Level organic chemistry](#), [Hydrocarbons](#)

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What you need to know

At AS, hydrocarbons meant alkanes and alkenes. At A Level the topic is **arenes**: hydrocarbons built on a benzene ring, with benzene and methylbenzene as the standard examples. There are four things to be able to do:

1. **Recall six reactions of arenes**, each with its reagent, its catalyst or conditions, and its product:
 - a halogen atom (Cl or Br) replacing a hydrogen on the ring, which needs an aluminium halide catalyst;
 - a nitro group replacing a ring hydrogen, using concentrated nitric acid mixed with concentrated sulfuric acid, kept between 25 °C and 60 °C;
 - an alkyl group joining the ring (Friedel–Crafts alkylation, taught with chloromethane, AlCl_3 and heat);
 - an acyl group, $\text{R}-\text{C}=\text{O}$, joining the ring (Friedel–Crafts acylation, taught with ethanoyl chloride, AlCl_3 and heat);
 - any alkyl side chain being oxidised all the way to $-\text{COOH}$, by heating with alkaline potassium manganate(VII) and then adding dilute acid;
 - hydrogen adding to the ring to give a cyclohexane ring (hydrogen gas, a platinum or nickel catalyst, heat).
2. **Draw the mechanism of electrophilic substitution** with curly arrows and the intermediate, using nitration and bromination as the models, and explain why the ring swaps a hydrogen for the electrophile instead of adding it: keeping the delocalised ring of electrons lowers the energy.
3. **Tell from the conditions where a halogen goes** when it reacts with an arene that has a side chain: onto the side chain, or onto the ring.
4. **Say which ring position a second group takes**. Only six groups already on the ring are asked about: $-\text{NH}_2$, $-\text{OH}$ and alkyl groups send the next group to carbons 2 and 4; $-\text{NO}_2$, $-\text{COOH}$ and $-\text{COR}$ send it to carbon 3.

The bonding in benzene (sp^2 carbons, σ bonds and the delocalised π system) belongs to the topic "An introduction to A Level organic chemistry". It is recapped here because it is asked in a quarter of the questions on arenes. The different reactivity of chlorobenzene and chloroethane belongs to halogen compounds, and the reactions of phenol to hydroxy compounds.

Understand it

Why benzene does not behave like an alkene

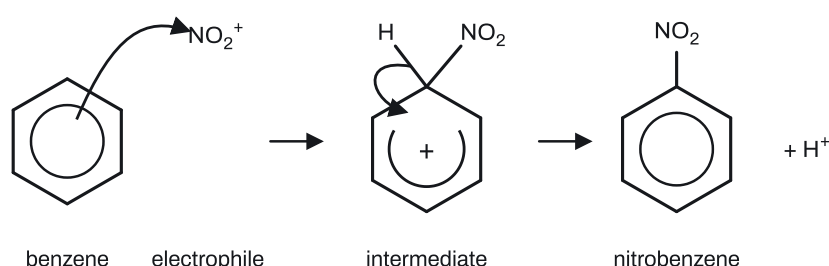
Benzene, C_6H_6 , is a flat hexagon of six sp^2 carbons with all bond angles 120° . Each carbon forms three σ bonds (head-on overlap of sp^2 orbitals with its two carbon neighbours and with the $1s$ orbital of its hydrogen). The spare p orbital on each carbon overlaps sideways with the p orbitals on **both** neighbours, above and below the ring, so the six π electrons are spread round the whole ring: a **delocalised π system**. All six C–C bonds are the same length.

That delocalisation makes benzene much more stable than a ring with three separate C=C bonds would be. It has two consequences:

- **The ring is less attractive to electrophiles than an alkene.** An alkene has two π electrons packed between two carbons; benzene's six are spread over six carbons, so the electron density at any one place is lower. Bromine water decolourises with cyclohexene but not with benzene. To make benzene react, the electrophile has to be made **stronger**, usually a positive ion formed with a catalyst.
- **Substitution, not addition.** If benzene simply added a reagent across one "double bond", the product would have lost the delocalised π system and all the stability that goes with it. Instead the ring loses an H^+ and gets its full delocalised system back. So arenes do **electrophilic substitution**: an electrophile replaces a hydrogen on the ring. Only forcing conditions (hydrogen, a metal catalyst and heat) push benzene into addition.

The mechanism of electrophilic substitution

Every ring substitution in this topic follows the same two steps, whatever the electrophile E^+ is.



1. **The ring attacks the electrophile.** A pair of π electrons from the ring forms a bond to the positive atom of E^+ . The curly arrow starts **inside the hexagon** (on the delocalised ring) and ends on that atom: on the N of NO_2^+ , the Br of Br^+ , the carbon carrying the + charge in CH_3^+ or CH_3CO^+ .
2. **The intermediate.** The carbon that has gained E is now joined to four atoms (two ring carbons, H and E), so it is sp^3 and has left the delocalised system. The other five carbons share four π electrons and the positive charge. Draw it as a **horseshoe** (a partial ring over those five carbons) with a + inside it; the sp^3 carbon sits in the gap of the horseshoe with both H and E drawn on it.

3. **The ring loses H^+** . A curly arrow goes **from the C–H bond** back into the ring. The two electrons of that bond rebuild the full delocalised π system, and H^+ leaves.

The H^+ then reacts with the ion that came from the catalyst, which gives the catalyst back.

Making the electrophile

Reaction	Reagents	Forming the electrophile	Getting the catalyst back
Chlorination	$Cl_2, AlCl_3$	$Cl_2 + AlCl_3 \rightarrow Cl^+ + AlCl_4^-$	$H^+ + AlCl_4^- \rightarrow HCl + AlCl_3$
Bromination	$Br_2, AlBr_3$ (or $FeBr_3$)	$Br_2 + AlBr_3 \rightarrow Br^+ + AlBr_4^-$	$H^+ + AlBr_4^- \rightarrow HBr + AlBr_3$
Nitration	conc. HNO_3 , conc. H_2SO_4 , 25–60 °C	$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$	$H^+ + HSO_4^- \rightarrow H_2SO_4$
Alkylation	$R-Cl, AlCl_3$, heat	$RCl + AlCl_3 \rightarrow R^+ + AlCl_4^-$	$H^+ + AlCl_4^- \rightarrow HCl + AlCl_3$
Acylation	$RCOCl, AlCl_3$, heat	$RCOCl + AlCl_3 \rightarrow RCO^+ + AlCl_4^-$	$H^+ + AlCl_4^- \rightarrow HCl + AlCl_3$

The pattern for the aluminium (or iron) halide catalysts is always the same: the catalyst accepts a halide ion from the reagent, leaving the positive electrophile. $AlCl_3$ can do this because aluminium has an empty orbital and accepts a lone pair. With a bromide reagent, use the bromide catalyst ($AlBr_3$ or $FeBr_3$), so no chlorine gets into the product. For nitration, the simpler equation $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$ is also accepted.

Above about 60 °C, nitration puts a second (and third) nitro group on the ring, which is why the temperature is kept between 25 °C and 60 °C.

Friedel–Crafts reactions make a new carbon–carbon bond to the ring. Alkylation adds a chain; acylation adds a $C=O$ group joined to the ring (a ketone such as phenylethanone, $C_6H_5COCH_3$). In acylation the ring bonds to the **C of the $C=O$** , never to the CH_3 . If the alkyl chloride would give a primary cation, such as $CH_3CH_2CH_2^+$, that cation can rearrange (an H moves along) to the secondary cation $(CH_3)_2CH^+$ before it attacks. Secondary cations are more stable because two alkyl groups push electron density towards the positive carbon (the positive inductive effect you met with Markovnikov addition at AS), so the product carries the branched group.

Oxidising the side chain

Hot alkaline $KMnO_4$ does not attack the ring, but it attacks the carbon joined to the ring. **Whatever the length of the alkyl chain, the carbon attached to the ring becomes $-COOH$** , and any further carbons in that chain leave as carbon dioxide. The reaction gives the carboxylate salt, so dilute acid is added afterwards to release

the acid.

- methylbenzene → benzoic acid: $\text{C}_6\text{H}_5\text{CH}_3 + 3[\text{O}] \rightarrow \text{C}_6\text{H}_5\text{COOH} + \text{H}_2\text{O}$
- a ring with two alkyl groups gives a ring with two $-\text{COOH}$ groups in the same positions.

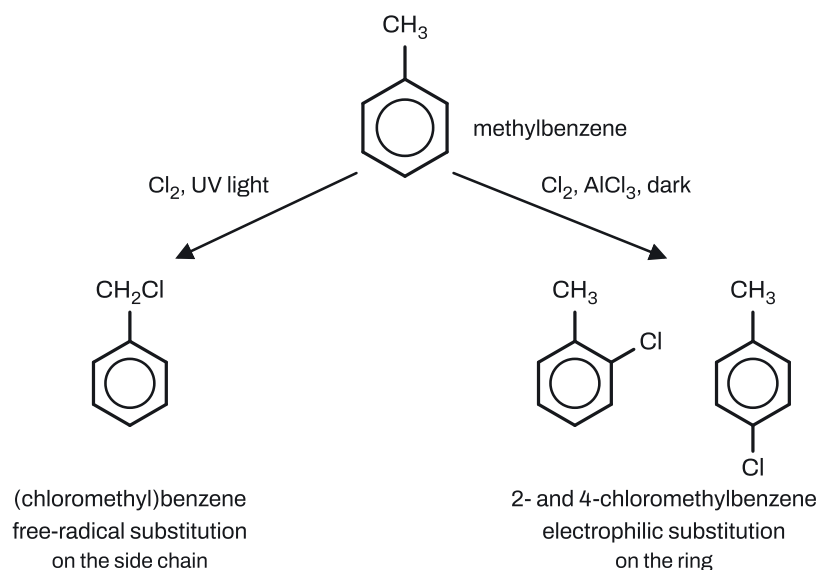
To balance, put $[\text{O}]$ on the left and CO_2 and H_2O on the right: balance C with CO_2 , then H with H_2O , and finally count the O atoms on the right to find the number of $[\text{O}]$.

Adding hydrogen to the ring

With hydrogen, a Pt or Ni catalyst and heat, each molecule of benzene adds **three** H_2 , giving cyclohexane; methylbenzene gives methylcyclohexane. All six ring carbons become sp^3 . This is an addition (reduction, or hydrogenation) reaction, and a $-\text{COOH}$ group on the ring is left alone: benzoic acid gives cyclohexanecarboxylic acid.

Side chain or ring? It depends on the conditions

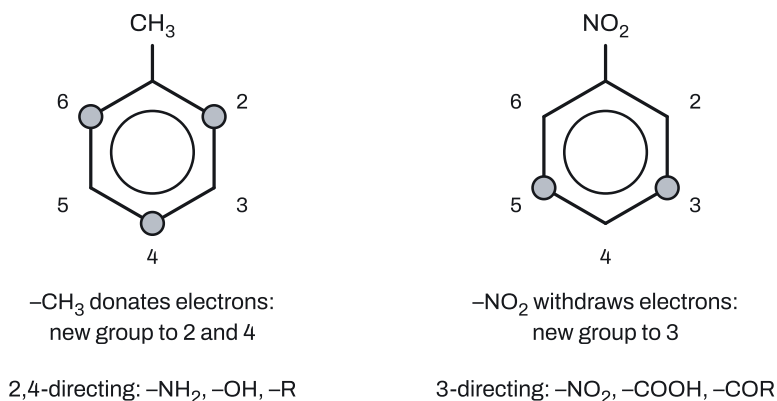
Methylbenzene has hydrogens in two very different places: on the ring and on the CH_3 .



- **Ultraviolet light, no catalyst:** the halogen splits into radicals, which take H atoms from the **side chain**. This is the free-radical substitution you met with alkanes at AS, and just like there, excess halogen replaces more of the side-chain hydrogens. The ring is untouched.
- **AlCl_3 or AlBr_3 catalyst (a "halogen carrier"), in the dark, at room temperature:** the catalyst makes X^+ , which attacks the **ring** by electrophilic substitution. The side chain is untouched. The new halogen goes to positions 2 and 4, because of the methyl group (see the next section).

Directing effects: where a second group goes

When a benzene ring already carries a group, a second group does not go on at random. The first group decides.



Group on the ring	Effect on the ring's electrons	New group goes to
–R (alkyl, such as –CH ₃ , –C ₂ H ₅)	donates (positive inductive effect)	2 and 4
–OH	donates (a lone pair on O is delocalised into the ring)	2 and 4
–NH ₂	donates (a lone pair on N is delocalised into the ring)	2 and 4
–NO ₂	withdraws	3
–COOH	withdraws (electronegative O atoms)	3
–COR	withdraws (electronegative O atom)	3

Positions are counted from the carbon carrying the first group (carbon 1). Positions 2 and 6 are equivalent, as are 3 and 5, so "2,4-directing" means the new group ends up next to or opposite the first group, and "3-directing" means one carbon further away.

Electron-donating groups also make the ring **more reactive**: phenol and phenylamine react with bromine water at room temperature, with no catalyst, and put bromine on all of positions 2, 4 and 6 at once. Electron-withdrawing groups make the ring **less reactive**: benzoic acid and nitrobenzene need harsher conditions than benzene. So for nitration the ease is phenol > methylbenzene > benzene > benzoic acid.

Order of steps in a synthesis. Directing effects decide which reaction you do first. To put two groups 1,4 on a ring, add a 2,4-director first; for 1,3, add a 3-director first. Remember that you can change a group's directing effect by reacting it: oxidising an alkyl group turns a 2,4-director into a 3-director (–COOH).

Key facts and formulas

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

Formula	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 a gas = 24.0 dm ³ mol ^{–1} at room conditions	Given

Formula	Status
Benzene: planar, 120° , six sp^2 carbons, σ bonds (head-on overlap) and a delocalised π system (sideways overlap of p orbitals)	Learn it
Halogenation: X_2 with AlX_3 (or $FeBr_3$), room temperature, dark $\rightarrow$ halogenoarene + HX	Learn it
Nitration: conc. HNO_3 + conc. H_2SO_4 , $25-60^\circ C \rightarrow$ nitroarene + H_2O	Learn it
Alkylation: $RCl + AlCl_3$, heat; acylation: $RCOCl + AlCl_3$, heat $\rightarrow$ + HCl	Learn it
Electrophiles: $X_2 + AlX_3 \rightarrow X^+ + AlX_4^-$; $RCl + AlCl_3 \rightarrow R^+ + AlCl_4^-$; $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$	Learn it
Catalyst back: $H^+ + AlX_4^- \rightarrow HX + AlX_3$	Learn it
Side-chain oxidation: hot alkaline $KMnO_4$, then dilute acid; ring carbon's chain $\rightarrow -COOH$, extra chain carbons $\rightarrow CO_2$	Learn it
Ring hydrogenation: H_2 , Pt or Ni, heat; 3 mol H_2 per benzene ring	Learn it
Side chain: X_2 in UV light (free radical); ring: X_2 with AlX_3 in the dark (electrophilic)	Learn it
2,4-directing: $-NH_2$, $-OH$, $-R$; 3-directing: $-NO_2$, $-COOH$, $-COR$	Learn it
Hybridisation: benzene-ring and $C=O$ carbons sp^2 ; carbons with four single bonds sp^3 ; $C\equiv N$ and $C\equiv C$ carbons sp	Learn it

How to do it

In the Paper 4 questions we have tagged for this topic (48 questions, 2021–2025; 35 different questions, 13 of them repeated in another variant), the types came up this often. 42 of the 48 questions mix more than one type, so the counts add up to more than 48. Almost every one is a part of a longer question built around a synthesis route from benzene or methylbenzene.

Question type	Questions
Deduce and draw products, intermediates or by-products	26
Give reagents and conditions	25
Draw the electrophilic substitution mechanism	23
Write the equation for forming the electrophile or regenerating the catalyst	20
Predict and explain directing effects	17

Question type	Questions
Describe the bonding and shape of benzene	12
Name arene compounds or draw arene isomers	9
Name the mechanism or type of reaction	8
Explain ring reactivity	8
Count sp, sp ² and sp ³ carbon atoms	6
Write a side-chain oxidation equation using [O]	6
Distinguish side-chain from ring halogenation	4

1. Deduce and draw products, intermediates or by-products (26 questions)

A route with empty boxes, or a reaction with the product missing. One mark per correct structure.

- Read the reagent** above each arrow and name the reaction it does (use the table under "Making the electrophile", plus KMnO₄ and H₂/Pt).
- Decide where on the ring the new group goes** from the group already there (directing effects). If there is no group yet, any position is the same.
- Draw only what changes**, and check against any molecular formula given: count the C, H and other atoms in your structure.

Variations you will meet:

- Molecular formula given for the box.** Work out what has been gained: +CH₂ is a methyl group from alkylation; –H + NO₂ is nitration; +O₂ and –H₂ on a methyl group means oxidation to –COOH.
- By-products.** A Friedel–Crafts alkylation can add a second alkyl group (the first one makes the ring more reactive), giving the 1,2- and 1,4-disubstituted products; a 2,4-director gives the other isomer as a minor product; a reagent with two C–Cl (or C–Br) bonds can join to two rings; side-chain chlorination in UV can go on to CHCl₂ and CCl₃.
- Hydrogenation:** the ring becomes a cyclohexane ring, drawn as a plain hexagon with no circle; side groups such as –COOH or CH₃ stay.

2. Give reagents and conditions (25 questions)

The mark usually needs the reagent **and** the catalyst or condition together; one without the other scores nothing.

Change	Reagents and conditions
ring H → Cl (or Br)	Cl ₂ and AlCl ₃ (or Br ₂ and AlBr ₃ /FeBr ₃), room temperature, dark
ring H → NO ₂	concentrated HNO ₃ and concentrated H ₂ SO ₄ , 25–60 °C
ring H → alkyl R	RCI and AlCl ₃ (or RBr and AlBr ₃ /FeBr ₃), heat

Change	Reagents and conditions
ring H $\rightarrow$ COR	RCOCl and AlCl_3 , heat
alkyl side chain $\rightarrow$ COOH	hot alkaline KMnO_4 (heat under reflux), then dilute acid
benzene ring $\rightarrow$ cyclohexane ring	H_2 and Pt or Ni, heat
side-chain H $\rightarrow$ Cl or Br	Cl_2 or Br_2 in UV light

Choose R to match the group in the product: to add an ethyl group use chloroethane; to add $\text{CH}_3\text{CH}_2\text{CO}-$ use propanoyl chloride. The other steps of a route (Sn and concentrated HCl , SOCl_2 , NaNO_2 with HCl) come from other topics.

If only the catalyst is asked for, AlCl_3 (or AlBr_3 , FeBr_3 , FeCl_3 to match the halogen) is the answer.

3. Draw the electrophilic substitution mechanism (23 questions)

Always three marks, in this order:

- M1:** a curly arrow from **inside the hexagon** (the circle) to the **positive atom** of the electrophile. For CH_3CO^+ that is the C of the $\text{C}=\text{O}$; for $(\text{CH}_3)_2\text{CH}^+$ it is the middle carbon; for NO_2^+ it is the N.
- M2:** the intermediate: a horseshoe over **five** carbons with **+** inside it, and on the sixth carbon (in the gap) both the H and the new group. The **+** goes inside the horseshoe, not on the sp^3 carbon, the H or the new group.
- M3:** a curly arrow from the **C–H bond** (starting on the bond, not on the H) into the ring, **and** H^+ shown as a product.

Variations you will meet:

- An unfamiliar electrophile** (such as SOBr^+ , $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2^+$ or ClCH_2CO^+). Find the atom carrying the **+** charge; the arrow goes to it and the new bond forms to it. Everything else in the electrophile comes along unchanged.
- A substituted ring.** Put the new group at the position the existing group directs to (2 or 4, or 3), and keep the existing group on its carbon in both the intermediate and the product.
- "Where is this pair of electrons before and after the step?"** Step 1: before, in the delocalised π system; after, in the new C–E bond. Step 2: before, in the C–H bond; after, back in the delocalised π system.

4. Write the equation for forming the electrophile or regenerating the catalyst (20 questions)

One mark, charges required. Use the patterns in the table under "Making the electrophile":

- halogen or halide reagent + aluminium (or iron) halide $\rightarrow$ positive ion + AlX_4^- (or FeX_4^-);
- nitration: $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + 2\text{HSO}_4^- + \text{H}_3\text{O}^+$;
- regeneration: $\text{H}^+ + \text{AlX}_4^- \rightarrow \text{HX} + \text{AlX}_3$.

For an unusual reagent, take the halogen off the carbon it is bonded to and give that carbon the + charge: $\text{ClCH}_2\text{CH}_2\text{Cl} + \text{AlCl}_3 \rightarrow \text{ClCH}_2\text{CH}_2^+ + \text{AlCl}_4^-$. The **overall** equation has no catalyst in it: for example $\text{C}_6\text{H}_6 + \text{Br}_2 \rightarrow \text{C}_6\text{H}_5\text{Br} + \text{HBr}$.

5. Predict and explain directing effects (17 questions)

1. **Name the group already on the ring** and classify it: electron-donating ($-\text{R}$, $-\text{OH}$, $-\text{NH}_2$) or electron-withdrawing ($-\text{NO}_2$, $-\text{COOH}$, $-\text{COR}$).
2. **State the position(s)**: 2 and 4 (and 6) for donors, 3 (and 5) for withdrawers.
3. **Give both parts** in the answer: the position **and** the reason (electron-donating or electron-withdrawing).

Variations you will meet:

- **Draw the major product(s)** of a substitution on a substituted ring.
- **"Explain why very little of one isomer forms"**: the existing group directs to other positions (for example an alkyl group is 2,4-directing, so the 3-isomer is minor), with the reason.
- **Change the route to get a different isomer**. Swap the order of two steps so that the group on the ring when the new group arrives directs it where you want, and say which group directs where. For example, a methyl group that will later be oxidised directs to 2 and 4 while it is still a methyl group, but to 3 once it has become $-\text{COOH}$, so oxidising before or after the substitution gives different isomers (Example 2 uses the same idea with an acyl group).

6. Describe the bonding and shape of benzene (12 questions)

Usually "any two, any four, all six" points for up to three marks. Write each as a short bullet:

1. planar hexagonal ring, bond angles 120° ;
2. every carbon sp^2 hybridised;
3. C–C σ bonds from head-on overlap of sp^2 orbitals;
4. C–H σ bonds from head-on overlap of a carbon sp^2 orbital with a hydrogen 1s orbital;
5. π bonding from sideways overlap of the p orbitals (one per carbon), above and below the ring;
6. the π electrons are delocalised over all six carbons.

Variation: pyridine or pyrazine (a ring with one or two N in place of CH). Each N is also sp^2 , gives one electron to the delocalised π system from its p orbital, and keeps a lone pair in an sp^2 orbital in the plane of the ring (which is why pyrazine can bond to metal ions).

7. Name arene compounds or draw arene isomers (9 questions)

1. **Find the parent:** $-\text{COOH}$ on the ring $\rightarrow$ benzoic acid; $-\text{NH}_2 \rightarrow$ phenylamine; $-\text{OH} \rightarrow$ phenol; only groups such as alkyl, NO_2 or halogens $\rightarrow$ benzene.
2. **Number the ring** from the parent group's carbon (carbon 1), going round the way that gives the lowest numbers.

3. **Prefixes in alphabetical order**, with di- and tri- for repeats: 3-ethylbenzoic acid; 1,4-dimethylbenzene; 2,4-dinitrophenylamine.

For isomers of a formula such as C_9H_{12} with a benzene ring, work through systematically: one chain (C_3 : propyl or 1-methylethyl), two chains (ethyl + methyl at 1,2, 1,3 and 1,4), three methyls (1,2,3, 1,2,4 and 1,3,5).

8. Name the mechanism or type of reaction (8 questions)

- ring halogenation, nitration, alkylation, acylation → **electrophilic substitution**;
- side-chain halogenation in UV → **free-radical substitution**;
- $KMnO_4$ on a side chain → **oxidation**;
- H_2/Pt on the ring → **addition**, also called **reduction** or **hydrogenation**.

Write the whole name: "substitution" alone does not score. A related question asks what the electrophile is and which atom replaces which: in chlorination, Cl^+ is the electrophile and a Cl atom replaces an H atom on the ring.

9. Explain ring reactivity (8 questions)

- Why substitution, not addition**: addition would destroy the delocalised π system; substitution keeps it, and delocalisation makes the ring more stable (lower in energy).
- Why a catalyst is needed**: the π electrons are spread over six carbons, so the ring cannot polarise a neutral Br_2 or Cl_2 enough; the catalyst makes a positive ion that the ring can attack.
- Why one ring reacts more easily than another**: an electron-donating group (a lone pair on O or N delocalised into the ring, or an alkyl group's positive inductive effect) **increases the electron density** of the ring, so it attracts and polarises electrophiles more; an electron-withdrawing group lowers it.
- Which end of an unsymmetrical reagent bonds to the ring**: the less electronegative end is δ^+ and becomes the electrophile. In $I-Cl$, iodine is less electronegative, so iodobenzene forms.
- Carbocation rearrangement** in alkylation: a primary cation becomes a secondary (or tertiary) one because more alkyl groups mean a greater positive inductive effect, which spreads the charge and makes the cation more stable.
- Why a strained C_6H_6 isomer is unstable**: small rings with bond angles far from 109.5° or 120° have ring strain, and have no aromatic delocalisation.

10. Count sp , sp^2 and sp^3 carbon atoms (6 questions)

- Go through every carbon.
- sp^2 : benzene-ring carbons, $C=C$ carbons and $C=O$ carbons (three regions of electron density).
- sp^3 : carbons with four single bonds, including side-chain CH_3 , CH_2 and CH .
- sp : carbons in $C\equiv N$ or $C\equiv C$.

In the intermediate of electrophilic substitution, the carbon holding both H and E is sp^3 and the other five ring carbons are sp^2 . A hydrogenated ring has six sp^3 carbons.

11. Write a side-chain oxidation equation using [O] (6 questions)

1. Write the reactant and the acid product: each alkyl side chain becomes one -COOH .
2. **C**: any carbons lost from the chains appear as CO_2 .
3. **H**: the hydrogens left over appear as H_2O .
4. **O**: count all O atoms on the right; that many [O] on the left.

For example, propylbenzene: $\text{C}_9\text{H}_{12} \rightarrow \text{benzoic acid } \text{C}_7\text{H}_6\text{O}_2 + 2\text{CO}_2$; H: $12 - 6 = 6$, so $3\text{H}_2\text{O}$; O: $2 + 4 + 3 = 9$, so $9[\text{O}]$ (this is Example 3).

Variation: partial oxidation of a CH_3 group to -CHO needs $2[\text{O}]$: $\text{RCH}_3 + 2[\text{O}] \rightarrow \text{RCHO} + \text{H}_2\text{O}$.

12. Distinguish side-chain from ring halogenation (4 questions)

1. **UV light and no catalyst** $\rightarrow$ the halogen replaces an H on the **side chain** (free-radical substitution): methylbenzene gives $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$.
2. AlCl_3 (**or** AlBr_3 , FeBr_3), **dark, room temperature** $\rightarrow$ the halogen replaces an H on the **ring** (electrophilic substitution), at positions 2 and 4 of methylbenzene.
3. Match each structure to its conditions; if the formula shows two or three halogens on the side chain, excess halogen in UV was used.

Worked examples

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

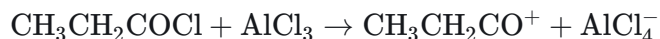
- **M1** method mark: for a correct method, even if the numbers slip.
- **A1** accuracy mark: for a correct answer; it needs the M mark before it.
- **B1** mark for a correct result on its own, with no method needed.

Example 1

Benzene reacts with propanoyl chloride, $\text{CH}_3\text{CH}_2\text{COCl}$, to form 1-phenylpropan-1-one, $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$.

- (a) Name the catalyst needed and write an equation to show how it forms the electrophile. **[2]**
- (b) Describe the mechanism of the reaction of benzene with this electrophile, stating what each curly arrow shows and describing the intermediate. **[3]**
- (c) Write an equation to show how the catalyst is regenerated. **[1]**
- (d) 7.80 g of benzene gave 10.05 g of 1-phenylpropan-1-one. Calculate the percentage yield. **[2]**

(a) Aluminium chloride, AlCl_3 (the mixture is heated). **B1**



B1, charges needed.

(b) A curly arrow from the delocalised ring (inside the hexagon) to the carbon of the $\text{C}=\text{O}$ group, the carbon carrying the + charge. **M1** The intermediate: the carbon now joined to the COCH_2CH_3 group also carries its H and is sp^3 ; the other five carbons are shown as a horseshoe with + inside. **M1** A curly arrow from the $\text{C}-\text{H}$ bond into the ring, with H^+ as the other product. **M1**

(c) $\text{H}^+ + \text{AlCl}_4^- \rightarrow \text{HCl} + \text{AlCl}_3$ **B1**

(d) $M_r(\text{C}_6\text{H}_6) = 78.0$, so $7.80 \div 78.0 = 0.100$ mol of benzene, which could give 0.100 mol of product. **M1**
 $M_r(\text{C}_9\text{H}_{10}\text{O}) = 9(12.0) + 10(1.0) + 16.0 = 134.0$, so the maximum mass is $0.100 \times 134.0 = 13.4$ g.
Percentage yield = $10.05 \div 13.4 \times 100 = 75.0\%$. **A1**

Example 2

A chemist needs two isomers, 1-(4-methylphenyl)propan-1-one and 1-(3-methylphenyl)propan-1-one. Both are made from benzene in two steps, using chloromethane with AlCl_3 in one step and propanoyl chloride with AlCl_3 in the other.

(a) Draw the structures of the two isomers. **[2]**

(b) For each isomer, state which step must come first. Explain your answers. **[3]**

(c) The route that alkylates first also gives a third isomer as a minor product. Name it and explain why it forms. **[2]**

(a) Both are a benzene ring carrying CH_3 and COCH_2CH_3 (joined through the C of the $\text{C}=\text{O}$). In the 4-isomer the two groups are on opposite carbons of the ring; in the 3-isomer there is one ring carbon between them. **B1**
B1

(b) For the **4-isomer**, alkylate first: benzene $\rightarrow$ methylbenzene with $\text{CH}_3\text{Cl}/\text{AlCl}_3$, then acylate. **M1** The methyl group is electron-donating, so it directs the acyl group to positions 2 and 4. **A1** For the **3-isomer**, acylate first: benzene $\rightarrow$ 1-phenylpropan-1-one, then alkylate. The COCH_2CH_3 group (a $-\text{COR}$ group) is electron-withdrawing, so it directs the methyl group to position 3. **A1**

(c) 1-(2-methylphenyl)propan-1-one. **B1** The methyl group is electron-donating and 2,4-directing, so it sends the acyl group to position 2 as well as to position 4. **B1**

Example 3

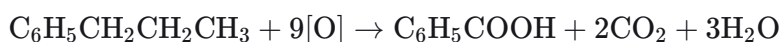
Propylbenzene, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3$, is used in three separate experiments.

(a) It is heated under reflux with alkaline KMnO_4 and then acidified. Name the organic product and write an equation for the reaction, using $[\text{O}]$ for an oxygen atom from the oxidising agent. **[3]**

(b) It reacts with chlorine under two different sets of conditions. Give the conditions that put chlorine (i) on the side chain and (ii) on the ring, name each mechanism, and give one possible monochlorinated product for each. [4]

(c) 6.00 g of propylbenzene is completely hydrogenated using a nickel catalyst. Name the product, calculate the volume of hydrogen used at room conditions, and state the number of sp^3 carbon atoms in the product. [4]

(a) Benzoic acid, C_6H_5COOH . **B1** The carbon joined to the ring becomes $-COOH$ and the other two chain carbons leave as CO_2 :



B1 for the correct products, **B1** for the balancing (H: $12 = 6 + 6$; O: $9 = 2 + 4 + 3$).

(b)(i) Ultraviolet light, no catalyst: **free-radical substitution**. **B1** For example $C_6H_5CHClCH_2CH_3$ (any side-chain H can be replaced). **B1**

(ii) $AlCl_3$ catalyst, room temperature, in the dark: **electrophilic substitution**. **B1** The propyl group is 2,4-directing, so for example 1-chloro-4-propylbenzene, $ClC_6H_4CH_2CH_2CH_3$ with Cl opposite the chain. **B1**

(c) Propylcyclohexane, C_9H_{18} . **B1** $M_r(C_9H_{12}) = 9(12.0) + 12(1.0) = 120.0$, so $6.00 \div 120.0 = 0.0500$ mol. One ring adds 3 H_2 : $3 \times 0.0500 = 0.150$ mol. **M1** Volume = $0.150 \times 24.0 = 3.60 \text{ dm}^3$. **A1** Every carbon in propylcyclohexane has four single bonds, so all **9** are sp^3 . **B1**

Common mistakes

- **Curly arrow starting in the wrong place.** The first arrow must start inside the hexagon (on the delocalised ring), not on a single carbon or outside the ring, and it must end on the atom of the electrophile carrying the + charge (the C of CH_3CO^+ , not its CH_3 ; the middle C of $(CH_3)_2CH^+$).
- **A wrong intermediate.** Examiners report this every year: the horseshoe must not include the sp^3 carbon, the + must be inside the horseshoe (not on the sp^3 carbon, the H or the new group), and the sp^3 carbon must show both H and E.
- **Second arrow starting on the H.** It starts on the C–H bond and goes into the ring; and H^+ must be shown.
- **Acyl group joined through the wrong atom.** In acylation the ring bonds to the carbon of the $C=O$, not to the far end of the group.
- **Reagent without the catalyst or condition.** " HNO_3 and H_2SO_4 " misses the mark without "concentrated"; nitration also needs the 25–60 °C range. Side-chain oxidation needs **hot** (or heat under reflux) alkaline $KMnO_4$, and then acid.
- **Mixing up side-chain and ring conditions.** UV light gives side-chain substitution; $AlCl_3$ in the dark gives ring substitution. Using UV and $AlCl_3$ together, or calling the side-chain reaction electrophilic, loses marks.
- **Direction without reason (or reason without direction).** " $-NO_2$ is 3-directing" and "because it is electron-withdrawing" are both needed. Don't say an electron-withdrawing group "activates positions 3 and 5".

- **Replacing the group already on the ring.** Nitrating benzoic acid does not give nitrobenzene; the new group goes onto a free ring position and the old group stays.
- **Wrong route order.** Putting a 3-director on first and then expecting a 1,4-product (or the reverse). Check the directing effect of the group that is on the ring **at the moment** each new group arrives.
- **Oxidising a longer chain to the wrong acid.** An ethyl or propyl side chain still gives benzoic acid, not phenylethanoic or phenylpropanoic acid; the extra carbons go to CO_2 .
- **Benzene bonding without σ bonds or without "sideways".** Say how both kinds of bond form: σ by head-on overlap of sp^2 orbitals, π by sideways overlap of p orbitals. Label p orbitals if you draw them.
- **Carbocation stability explained by the halogenoalkane.** In a rearrangement it is the secondary **carbocation** that is more stable, because of the greater positive inductive effect of its alkyl groups, not "the secondary halogenoalkane".

How to get the marks

- **"Give the reagents and conditions":** name the reagent, the catalyst and any condition (concentrated, temperature range, heat, UV, dark). Formulas or names both score, but don't mix a correct name with a wrong formula.
- **"Complete the mechanism":** three marks for three separate things (first arrow, intermediate, second arrow with H^+). Draw arrows precisely: tails where the electrons are, heads where they go.
- **"Write an equation for the formation of the electrophile":** include the charges on the electrophile and on AlCl_4^- (or FeBr_4^- , HSO_4^-).
- **"Explain" a directing effect:** position **and** electron-donating or electron-withdrawing. For the lone-pair groups ($-\text{OH}$, $-\text{NH}_2$), say the lone pair is delocalised into the ring.
- **"Describe the bonding":** write at least four separate bullet points; mark schemes give one mark for every two correct points.
- **"Suggest"** means the situation is unfamiliar (a new electrophile, a new ring): apply the same pattern and it will score.
- **Equations with [O]:** one mark for the right species (product acid, CO_2 , H_2O), one for balancing. Check C, H and O separately.
- **Structures:** draw the benzene ring as a hexagon with a circle (or Kekulé structure) and make it clear which atom of each group is joined to the ring (for example $-\text{COOH}$ joined through C, $-\text{NO}_2$ through N).
- **Calculations:** use the A_r values from the Periodic Table and 24.0 dm^3 for one mole of gas at room conditions; give answers to 3 significant figures.

Quick check

1. Give the reagents and conditions for each change, and name the type of reaction: (a) benzene to cyclohexane; (b) benzene to bromobenzene; (c) methylbenzene to benzoic acid.

2. Draw or name the major product(s) of mononitration of (a) ethylbenzene, (b) nitrobenzene and (c) phenylethanone, $\text{C}_6\text{H}_5\text{COCH}_3$. For each, say whether the group already on the ring is electron-donating or electron-withdrawing.
3. 1,4-dimethylbenzene is reacted with bromine (a) in ultraviolet light and (b) with an AlBr_3 catalyst in the dark. Name one monobrominated product for each, and explain why (b) gives only one ring-substituted product.
4. 1,3,5-triethylbenzene, $\text{C}_{12}\text{H}_{18}$, is heated with alkaline KMnO_4 and then acidified. Name the product and write a balanced equation using $[\text{O}]$.
5. When methylbenzene is nitrated at position 4, how many sp^2 and how many sp^3 carbon atoms does the intermediate contain? Explain why the intermediate then loses H^+ rather than adding a nucleophile.

Answers

1. (a) H_2 with a Pt or Ni catalyst, heat: addition (hydrogenation, reduction). (b) Br_2 with AlBr_3 (or FeBr_3), room temperature: electrophilic substitution. (c) Hot alkaline KMnO_4 under reflux, then dilute acid: oxidation.
2. (a) Ethyl is electron-donating, so 2,4-directing: 1-ethyl-2-nitrobenzene and 1-ethyl-4-nitrobenzene. (b) NO_2 is electron-withdrawing, so 3-directing: 1,3-dinitrobenzene. (c) COCH_3 is a $-\text{COR}$ group, electron-withdrawing, so 3-directing: 1-(3-nitrophenyl)ethanone.
3. (a) Side chain (free-radical substitution): 1-(bromomethyl)-4-methylbenzene, $\text{BrCH}_2\text{C}_6\text{H}_4\text{CH}_3$. (b) Ring (electrophilic substitution): 2-bromo-1,4-dimethylbenzene. By symmetry the four free ring carbons are all equivalent: each is next to one methyl group and one carbon further from the other. So whichever one is substituted, the product is the same.
4. Benzene-1,3,5-tricarboxylic acid, $\text{C}_6\text{H}_3(\text{COOH})_3 = \text{C}_9\text{H}_6\text{O}_6$. Each ethyl group loses one carbon as CO_2 : $\text{C}_{12}\text{H}_{18} + 18[\text{O}] \rightarrow \text{C}_9\text{H}_6\text{O}_6 + 3\text{CO}_2 + 6\text{H}_2\text{O}$ (H: $18 = 6 + 12$; O: $18 = 6 + 6 + 6$).
5. Five sp^2 carbons (the five in the horseshoe) and two sp^3 carbons (the ring carbon holding H and NO_2 , and the CH_3 carbon). Losing H^+ lets the C–H bond's electrons rebuild the delocalised π system, which is much more stable; adding a nucleophile would leave the ring without it.

Past questions to try

- **9701/42/O/N/23 Q7:** part (c), chlorinating methylbenzene on the ring and on the side chain, and the conditions for each.
- **9701/42/M/J/22 Q6:** the mechanism, regenerating H_2SO_4 , the major products and the relative ease of nitration.
- **9701/42/M/J/23 Q5:** three reactions of methylbenzene, why no addition happens, and a mechanism with an unfamiliar electrophile.
- **9701/42/O/N/24 Q7:** where each electron pair goes in the chlorination mechanism, and counting hybridised carbons in the intermediate.