Hydrocarbons (A Level)

The reactions of arenes, including halogenation, nitration, Friedel–Crafts alkylation and acylation, side-chain oxidation and hydrogenation, the mechanism of electrophilic substitution, and the directing effects of substituents.

30.1 Arenes

Arenes such as benzene and methylbenzene (toluene) react mainly by **electrophilic substitution**, because the delocalised π electrons attract electrophiles, but the ring is not destroyed.

Reactions

Reaction	Reagents and conditions	Product
Halogenation	Cl_2 or Br_2 with $AlCl_3$ or $AlBr_3$ (or $FeBr_3$) catalyst, room temperature	chlorobenzene or bromobenzene
Nitration	concentrated HNO_3 and concentrated H_2SO_4, **25–60 °C**	nitrobenzene
Friedel–Crafts alkylation	CH_3Cl and $AlCl_3$, heat	methylbenzene
Friedel–Crafts acylation	CH_3COCl and $AlCl_3$, heat	phenylethanone
Side-chain oxidation	hot alkaline $KMnO_4$, then dilute acid	benzoic acid
Hydrogenation	H_2, Pt or Ni catalyst, heat	cyclohexane

Examples: $C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$; $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$. Keep the temperature of nitration below about 60 °C, or a dinitro compound forms. The side-chain oxidation converts **any alkyl side-chain** (such as methyl or ethyl) to $-COOH$ on the ring, whatever its length, as long as the carbon next to the ring has a hydrogen.

Methylbenzene **halogenation depends on conditions**: with Cl_2 and $AlCl_3$ (no light) the ring is substituted (2- and 4-chloromethylbenzene); with Cl_2 in **UV light** (or at the boil) the **side-chain** is substituted by a free-radical mechanism, giving (chloromethyl)benzene, $C_6H_5CH_2Cl$.

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Mechanism of electrophilic substitution

1. **Generating the electrophile.** For nitration: $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$ (the electrophile is the **nitronium ion**, NO_2^+). For bromination: $Br_2 + AlBr_3 \rightarrow Br^+ + AlBr_4^-$ (the catalyst polarises the halogen; it is regenerated at the end). For Friedel–Crafts: $CH_3Cl + AlCl_3 \rightarrow CH_3^+ + AlCl_4^-$.
2. **Attack:** a pair of π electrons from the ring forms a bond to the electrophile, giving a **positively charged intermediate** in which the delocalisation is partly broken (arrow from the ring to E^+).
3. **Loss of H^+:** the C–H bond pair returns to restore the delocalised ring (arrow from the C–H bond into the ring); H^+ reacts with AlX_4^- to regenerate the catalyst and HX.

Substitution wins over addition because the product keeps the **stable delocalised ring** (aromatic stabilisation), whereas addition would destroy it.

Directing effects

A substituent already on the ring directs where the next group goes.

Substituent	Effect on the ring	Directs to
$-NH_2$, $-OH$, $-R$ (alkyl)	electron-donating, **activating**	**2- and 4-** (and 6-) positions
$-NO_2$, $-COOH$, $-COR$	electron-withdrawing, **deactivating**	**3-** position

For example nitration of methylbenzene gives 2- and 4-nitromethylbenzene; nitration of nitrobenzene gives 1,3-dinitrobenzene (slowly, with harsher conditions); bromination of benzoic acid gives 3-bromobenzoic acid.

> **TRY IT**
>
> Methylbenzene is converted to 3-nitrobenzoic acid by a two-step route. Which should come first: oxidation or nitration?

The $-CH_3$ group directs to 2 and 4, so **oxidise first** to benzoic acid ($-COOH$ directs to 3), then nitrate with concentrated HNO_3/H_2SO_4 to get 3-nitrobenzoic acid.

Why benzene does not behave like three alkenes

Benzene's pi system is continuous around the ring and stabilises its structure. An electrophile can attract a ring electron pair, but formation of the first bond temporarily interrupts delocalisation and carries an energetic cost. Loss of a proton then restores the aromatic system. This explains both the need for

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stronger electrophilic conditions than an ordinary alkene and the preference for substitution rather than permanent addition.

An observation such as no rapid bromine-water decolourisation distinguishes benzene from a simple alkene under ordinary test conditions. It does not mean benzene cannot react with bromine under any conditions; a halogen carrier generates a much stronger electrophilic interaction. Reagents and conditions are therefore part of the reaction's identity.

Constructing a nitration mechanism

First identify NO_2^+ as the electrophile, not NO_3^- or neutral NO_2. Concentrated sulfuric acid helps generate it from nitric acid. Draw a curly arrow from the ring's pi system to nitrogen of the electrophile. In the intermediate, the attacked carbon is bonded to both its original H and the new nitro group, and the ring carries a positive charge with disrupted aromaticity.

A base removes that proton and the C–H bond pair returns into the ring. The final product has one fewer ring H and an added NO_2 group; it does not keep both H and nitro at that carbon in an aromatic product. Sulfuric acid is regenerated in the overall catalytic process.

Worked atom count: $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$. One ring H is substituted. An equation giving $C_6H_6NO_2$ as the neutral final product has not accounted for proton loss and aromaticity restoration.

> **TRY IT**
>
> Where does the arrow start in the first ring-attack step, and why is a second step necessary?

Answer: It begins at a ring electron pair, not at the electrophile. Proton loss returns the C–H pair to the ring and restores delocalisation; attack alone leaves a non-aromatic positive intermediate.

Catalysts and the different electrophiles

Halogen carriers accept an electron pair and polarise the X–X bond. Simplified equations sometimes write a free Br^+ or alkyl cation; these represent the effective electrophile and should not imply an isolated free ion necessarily accumulates in solution. Friedel–Crafts acylation uses an acyl electrophile and creates a carbon–carbon bond to the ring through its carbonyl carbon.

Worked comparison: benzene plus $CH_3Cl/AlCl_3$ introduces methyl and gives methylbenzene. Benzene plus $CH_3COCl/AlCl_3$ introduces ethanoyl and gives $C_6H_5COCH_3$, phenylethanone. The latter has eight carbons and a ketone group; it is not an ester because no oxygen lies between phenyl and carbonyl carbon.

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Ring versus side-chain reactions

For methylbenzene, halogen carrier conditions favour ring substitution, while UV conditions allow radical substitution at the side chain. Distinguish $ClC_6H_4CH_3$ from $C_6H_5CH_2Cl$. Their atoms may be the same overall, but the chlorine attachment changes hydrolysis behaviour and subsequent synthesis.

Worked route: methylbenzene under UV chlorination can form phenylmethyl chloride, which has chlorine on an sp^3 side-chain carbon and can undergo nucleophilic substitution. Ring chlorination gives chloromethylbenzene positional isomers with C–Cl directly on the aromatic ring, much less susceptible to ordinary hydrolysis. The word "chloro" alone is insufficient to specify which product was made.

> **TRY IT**
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> Why must a side chain have a hydrogen on the carbon next to the ring for the usual oxidation-to-benzoic-acid route?

Answer: The ordinary benzylic oxidation requires that benzylic C–H site. A fully substituted benzylic carbon lacking H does not follow the same simple oxidation rule. Do not predict benzoic acid from every possible alkylbenzene without checking this condition.

Directing effects control route order

An activating substituent usually increases electron density and makes electrophilic attack easier. A deactivating substituent reduces it. Direction and rate effects are related but not identical: a group can direct to 2/4 positions while deactivating overall, so do not infer activity from position alone in unfamiliar examples.

For the listed syllabus groups, methyl/OH/NH_2 favour 2/4 substitution, while NO_2/COOH/acyl groups favour 3. In a monosubstituted benzene, positions 2 and 6 are equivalent by symmetry, as are 3 and 5. Identify equivalent drawings before counting products. With two substituents already present, consider both directing influences and any supplied information rather than promising a unique product automatically.

Worked route: to favour 3-nitrobenzoic acid from methylbenzene, oxidise methyl to COOH first, then nitrate. Nitrating first favours 2- and 4-nitro products, and subsequent side-chain oxidation preserves their ring positions. Oxidation changes a substituent's chemistry but does not move a nitro group around the ring.

> **TRY IT**
>
> A ring has COOH at position 1. Which positions are equivalent for a second substituent, and which position does COOH favour in ordinary electrophilic substitution?

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Answer: 2/6 are equivalent and 3/5 are equivalent. COOH favours substitution at 3 relative to itself; the two equivalent meta positions do not count as different constitutional products in this monosubstituted starting ring.

Chapter check: specify ring or side-chain reaction, draw the electrophile and proton-loss step, count carbons in Friedel–Crafts products, and plan route order using directing groups.

References and further reading

Scope follows section 30 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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