

Hydrocarbons

A-Level Chemistry

Arenes

Arenes are aromatic hydrocarbons, built on the **benzene** ring. The delocalised ring of electrons is stable and electron-rich, so benzene mostly reacts by **electrophilic substitution** – keeping the ring – rather than by addition.



Naphthalene, used in mothballs, is a simple arene – two benzene rings fused together

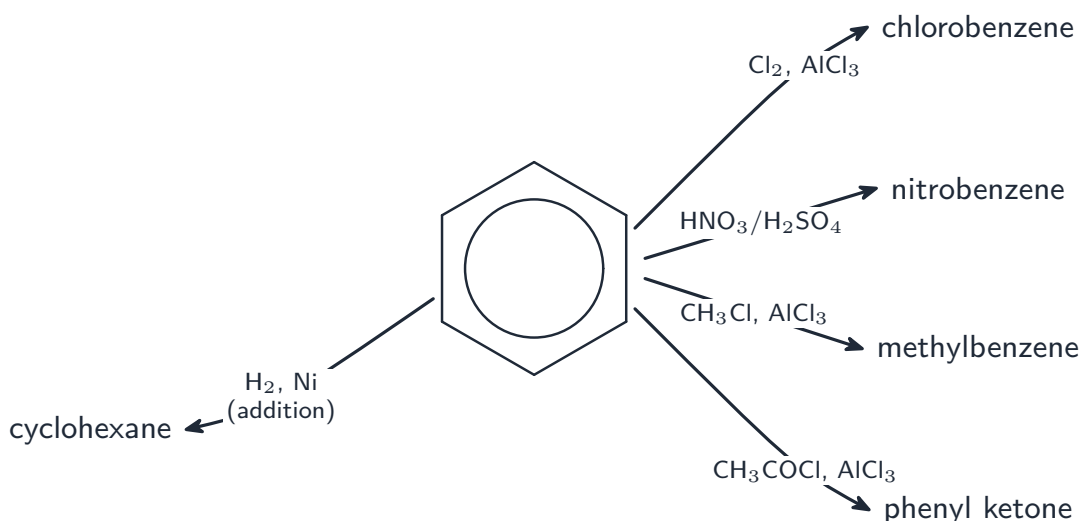
■ Reactions of benzene and methylbenzene

Reaction	Reagents and conditions	Product
halogenation	Cl_2 or Br_2 , with AlCl_3 or AlBr_3 as a catalyst	a halogenoarene (aryl halide)
nitration	concentrated HNO_3 + concentrated H_2SO_4 , 25–60 °C	nitrobenzene
Friedel–Crafts alkylation	CH_3Cl + AlCl_3 , heat	methylbenzene (adds an alkyl group)
Friedel–Crafts acylation	CH_3COCl + AlCl_3 , heat	a phenyl ketone (adds an acyl group)
side-chain oxidation	hot alkaline KMnO_4 , then dilute acid	benzoic acid
hydrogenation	H_2 , Pt/Ni catalyst, heat	cyclohexane

alkylation
adds an alkyl group
(CH_3Cl + AlCl_3)

acylation
adds an acyl group
(CH_3COCl + AlCl_3)

Friedel–Crafts: alkylation adds an alkyl group, acylation an acyl group



Benzene keeps its stable ring, reacting mostly by electrophilic substitution (and by addition only with hydrogen)

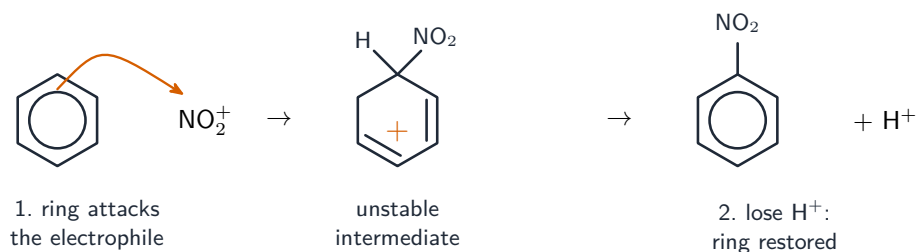
In the side-chain oxidation, the whole **side-chain** (such as the $-\text{CH}_3$ on methylbenzene) is turned into a $-\text{COOH}$ group, giving benzoic acid. In the hydrogenation, three molecules of H_2 add to the **benzene ring** to make a saturated cyclohexane ring.

■ The mechanism: electrophilic substitution

Take nitration as the example. The acid mix makes the electrophile NO_2^+ . Then:

1. the delocalised electrons of the ring form a bond to the electrophile, giving an unstable intermediate.
2. an H^+ is lost from that carbon, which restores the stable ring.

Substitution wins over addition because the **delocalisation** (aromatic stabilisation) of the ring is kept. Addition would destroy this stable system, so it is not favoured.

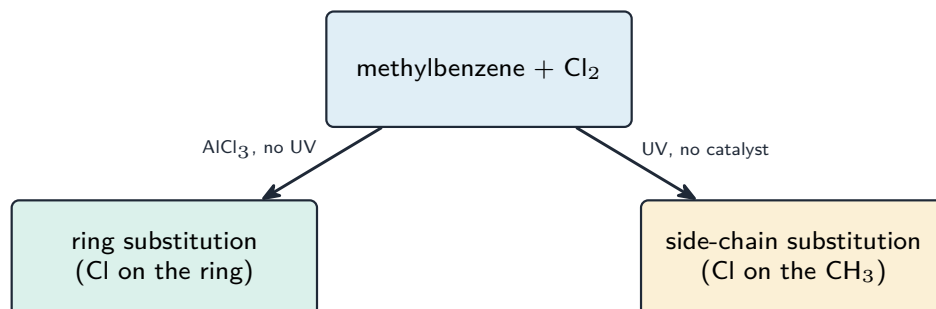


Electrophilic substitution (nitration): the ring attacks the electrophile NO_2^+ to give an unstable intermediate, then loses H^+ to restore the ring

■ Side-chain or ring?

Where a halogen reacts depends on the conditions:

- with a halogen-carrier catalyst (such as AlCl_3) and **no** UV light $\rightarrow$ substitution in the **ring**.
- with UV light and **no** catalyst $\rightarrow$ free-radical substitution in the **side-chain**.

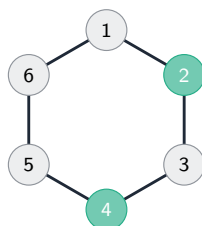


The conditions decide: a halogen carrier (AlCl_3) substitutes the ring; UV light substitutes the side-chain

■ Directing effects

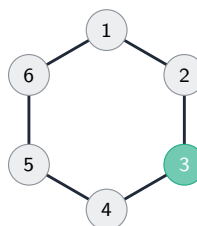
A group already on the ring decides where the next group goes – its **directing effect** :

$-\text{NH}_2$, $-\text{OH}$, $-\text{R}$



direct to **2 and 4**

$-\text{NO}_2$, $-\text{COOH}$, $-\text{COR}$



direct to **3**

A group already on the ring directs the next one: $-\text{NH}_2/-\text{OH}/-\text{R}$ send it to positions 2 and 4; $-\text{NO}_2/-\text{COOH}/-\text{COR}$ send it to position 3

Group already present	Directs the new group to
$-\text{NH}_2$, $-\text{OH}$, $-\text{R}$	positions 2 and 4
$-\text{NO}_2$, $-\text{COOH}$, $-\text{COR}$	position 3

Worked example. Methylbenzene and nitrobenzene are each nitrated. Predict where the new NO_2 group goes, and which compound reacts faster. Look at the group **already on the ring**. In methylbenzene the $-\text{CH}_3$ is an alkyl group: it directs the new group to positions **2 and 4**, and it **releases** electrons into the ring, making the ring more attractive to an electrophile - so methylbenzene nitrates **faster** than benzene. In nitrobenzene the $-\text{NO}_2$ directs to position **3**, and it **withdraws** electrons from the ring - so nitrobenzene nitrates **more slowly** than benzene. The group already present controls **both** the position **and** the rate, and the two always travel together: 2,4-directors activate the ring, 3-directors deactivate it.

Exam tips

- Benzene undergoes **electrophilic substitution**, not addition, because addition would destroy the stable delocalised ring.
- Learn **nitration** (concentrated $\text{HNO}_3/\text{H}_2\text{SO}_4$, $50 - 60\text{ }^\circ\text{C}$) and **halogenation** (halogen + AlCl_3) with the electrophile-generating step.
- Compare reactivity: benzene resists addition far more than an alkene because of delocalisation.