Hydrocarbons

A-Level Chemistry

Arenes

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

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

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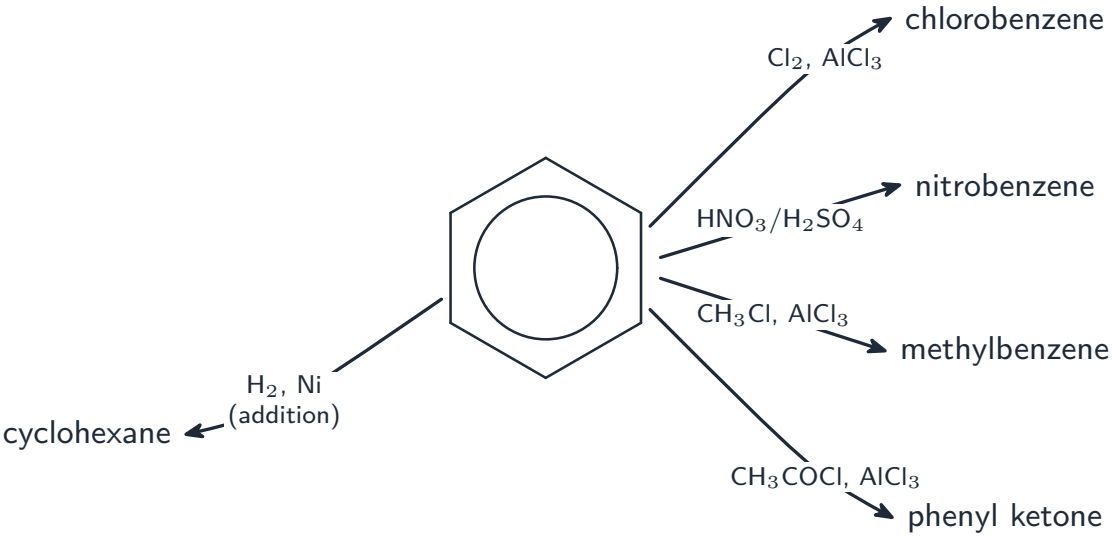
Reactions of benzene and methylbenzene

Reaction	Reagents and conditions	Product
halogenation	Cl_2 or Br_2, with $AlCl_3$ or $AlBr_3$ as a **catalyst** 催化剂	a **halogenoarene** 卤代芳烃 (aryl halide)
nitration 硝化	concentrated HNO_3 + concentrated H_2SO_4, 25–60 °C	nitrobenzene
Friedel–Crafts alkylation 傅克烷基化	CH_3Cl + $AlCl_3$, heat	methylbenzene (adds an alkyl group)
Friedel–Crafts acylation 傅克酰基化	CH_3COCl + $AlCl_3$, heat	a phenyl ketone (adds an acyl group)
side-chain oxidation	hot alkaline $KMnO_4$, then dilute acid	**benzoic acid** 苯甲酸
hydrogenation 氢化	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)

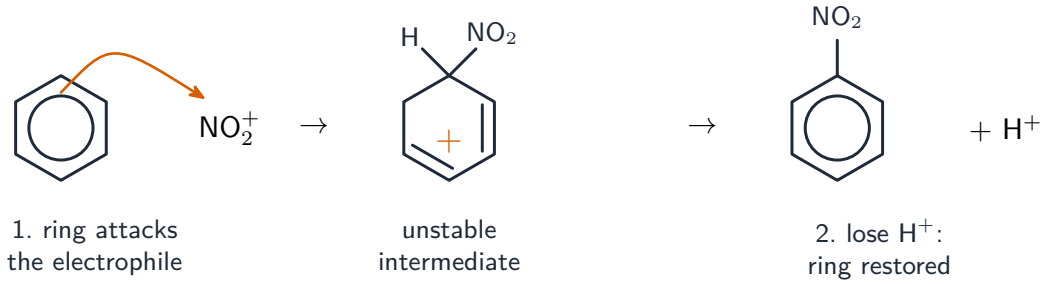
In the side-chain oxidation, the whole **side-chain** 侧链 (such as the $-CH_3$ on methylbenzene) is turned into a $-COOH$ group, giving benzoic acid. In the hydrogenation, three molecules of H_2 add to the **benzene ring** 苯环 to make a saturated cyclohexane ring.

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** 离域 (aromatic stabilisation) of the ring is kept. Addition would destroy this stable system, so it is not favoured.

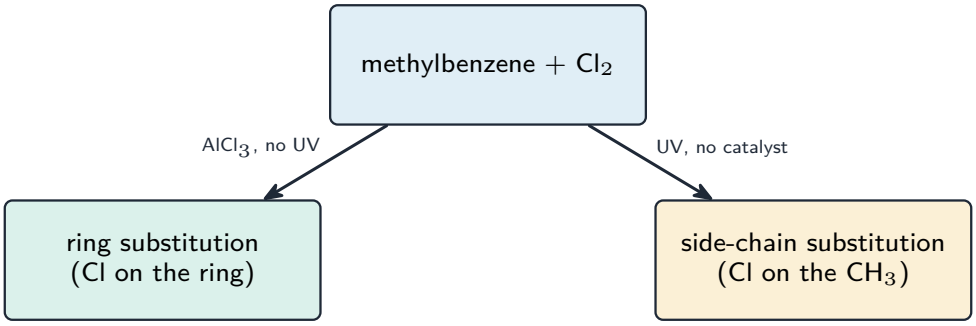


Electrophilic substitution (nitration): the ring attacks the electrophile NO_2^+ to give an unstable intermediate, then loses H^+ to restore the ring

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 → substitution in the **ring**.
- with UV light and **no** catalyst → free-radical substitution in the **side-chain**.

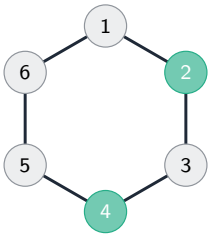


The conditions decide: a halogen carrier (AlCl) substitutes the ring; UV light substitutes the side-chain

Directing effects

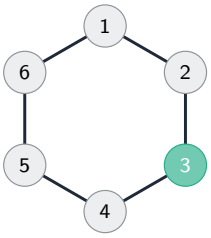
A group already on the ring decides where the next group goes —its **directing effect** 定位效应:

$-NH_2$, $-OH$, $-R$



direct to **2 and 4**

$-NO_2$, $-COOH$, $-COR$



direct to **3**

A group already on the ring directs the next one: $-NH_2$/$-OH$/$-R$ send it to positions 2 and 4; $-NO_2$/$-COOH$/$-COR$ send it to position 3

Group already present	Directs the new group to
$-NH_2$, $-OH$, $-R$	positions 2 and 4
$-NO_2$, $-COOH$, $-COR$	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 $-CH_3$ 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 $-NO_2$ 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 HNO_3/H_2SO_4, $50-60\,^{\circ}C$) and **halogenation** (halogen + $AlCl_3$) with the electrophile-generating step.
- Compare reactivity: benzene resists addition far more than an alkene because of delocalisation.