Hydrocarbons

A-Level Chemistry

Arenes

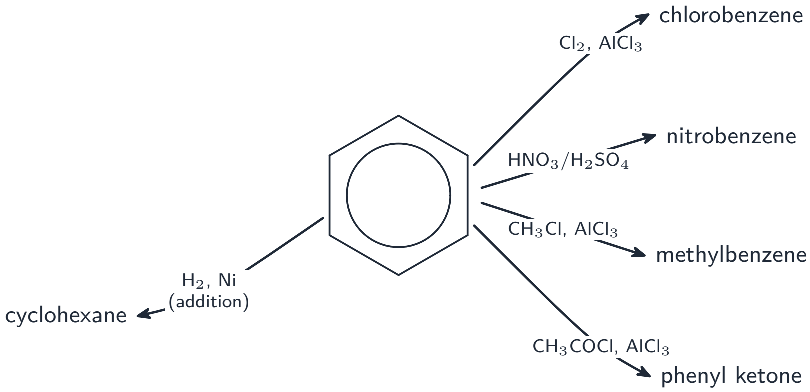
Arenes 芳烃 are aromatic hydrocarbons, built on the **benzene** 苯 ring. The delocalised ring of electrons is stable and electron-rich, so benzene mostly reacts by **electrophilic substitution** 亲电取代—keeping the ring —rather than by addition.

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

Image: Wiki Farazi, CC0 (commons.wikimedia.org)

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



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

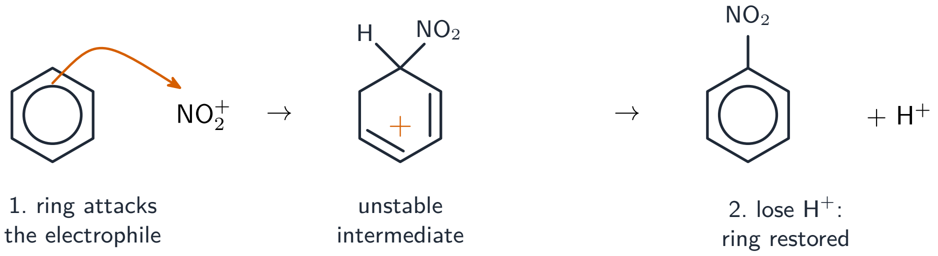
In the side-chain oxidation, the whole **side-chain** 侧链 (such as the –CH_3 on methylbenzene) is turned into a –COOH group, giving benzoic acid. In the hydrogenation, three molecules of H_2 add to the **benzene ring** 苯环 to make a saturated cyclohexane ring.

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

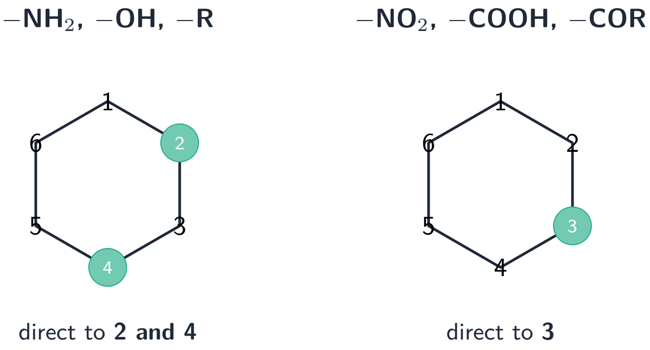
Side-chain or ring?

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**.

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