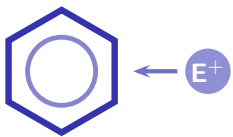
Arenes

A-Level Chemistry ▪ Topic 30

A-Level Chemistry



What we will cover

1. Reactions of benzene
2. Electrophilic substitution
3. Ring or side-chain?
4. Directing effects

naphthalene is an arene

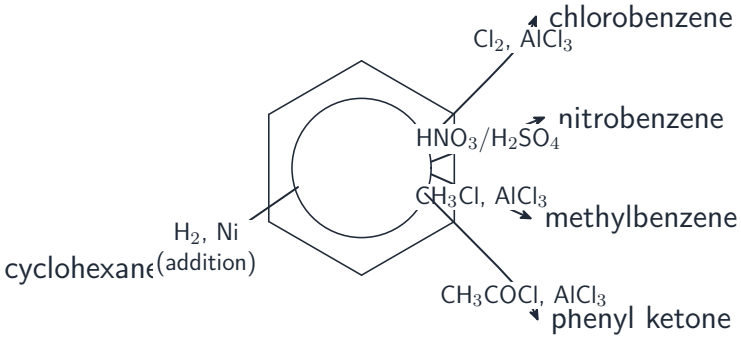
1 Benzene reactions

Reactions of benzene

Arenes 芳烃 keep their stable ring, reacting by **electrophilic substitution** 亲电取代:

- halogenation ($AlCl_3$); **nitration** 硝化
- **Friedel–Crafts** 傅克反应 alkyl/acyl
- side-chain oxidation $\rightarrow$ benzoic acid

Reactions of benzene, in detail



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

Four more reactions of the benzene ring

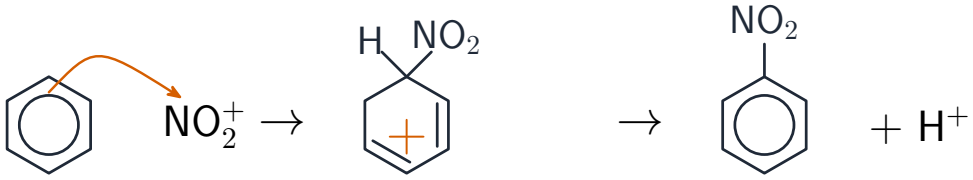
Halogenation	Cl_2 or Br_2 with $AlCl_3$ or $AlBr_3$ as **catalyst** 催化剂 gives a **halogenoarene** 卤代芳烃 (an aryl halide).
Friedel–Crafts alkylation	**Friedel–Crafts alkylation** 傅克烷基化: $CH_3Cl + AlCl_3$, heat – adds an alkyl group, giving methylbenzene.
Friedel–Crafts acylation	**Friedel–Crafts acylation** 傅克酰基化: $CH_3COCl + AlCl_3$, heat – adds an acyl group, giving a phenyl ketone.
Hydrogenation	**Hydrogenation** 氢化: H_2 with a Pt or Ni catalyst and heat destroys the **benzene ring** 苯环 entirely, giving cyclohexane.

The first three substitute *into* the ring and keep the delocalised system; only hydrogenation destroys it – which is why it needs the harshest conditions.

Electrophilic substitution

Nitration: the acid mix makes NO_2^+; the ring attacks it, then loses H^+.

> Substitution wins over addition because it keeps the stable **delocalised** 离域 ring.



1. ring attacks the electrophile

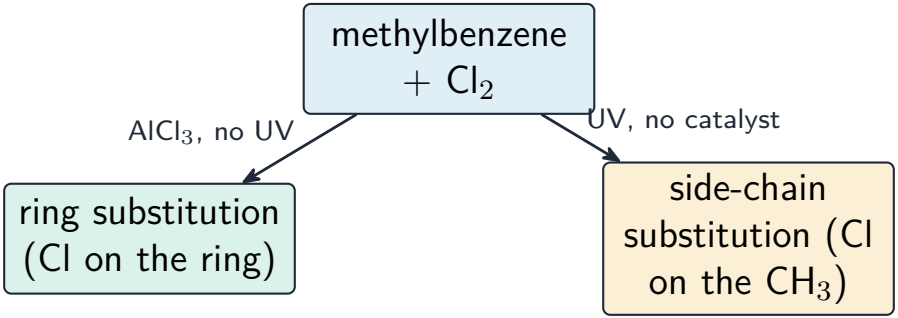
unstable intermediate

2. lose H^+: ring restored

Ring or side-chain?

The conditions decide:

- **$AlCl_3$** 卤素载体, no UV → substitution in the ring
- UV, no catalyst → free-radical substitution in the side-chain

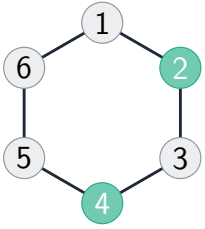


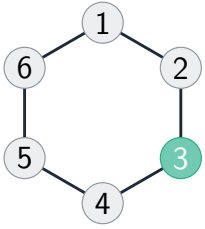
Directing effects

A group already on the ring directs the next one (its **directing effect** 定位效应):

- $-NH_2$, $-OH$, $-R$ → positions 2 & 4
- $-NO_2$, $-COOH$, $-COR$ → position 3

$-NH_2$, $-OH$, $-R$ $-NO_2$, $-COOH$, $-COR$





Reactions of benzene and methylbenzene

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

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.

2 Recap

Worked example – nitrating benzene

Give the reagents, conditions and electrophile for the nitration of benzene.

- Reagents: concentrated HNO_3 with concentrated H_2SO_4 catalyst, at $55°C$.
- H_2SO_4 protonates the HNO_3, which loses water:
- $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$
- The electrophile is the nitronium ion NO_2^+; product nitrobenzene.
- Substitution, not addition – the delocalised π system is restored.

Benzene substitutes (keeping its delocalisation) where an alkene adds. Above $55°C$ you also get dinitrobenzene.

Topic 30 – key takeaways

1 Reactions

nitration, halogenation, Friedel–Crafts

2 Mechanism

electrophilic substitution keeps the ring

3 Conditions

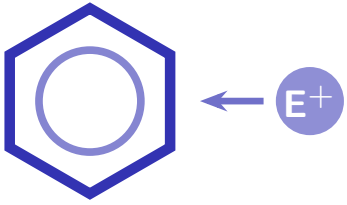
$AlCl_3$ ring vs UV side-chain

4 Directing

NH_2/OH/R to 2,4; NO_2/COOH to 3

Check yourself

1. What electrophile does nitration use?
2. Why does benzene substitute rather than add?
3. What conditions give side-chain substitution?
4. Where does an $-OH$ group direct the next substituent?



Answers **1.** NO_2^+ **2.** to keep the stable delocalised ring **3.** UV light, no catalyst **4.** positions 2 and 4