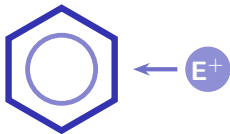


Arenes

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



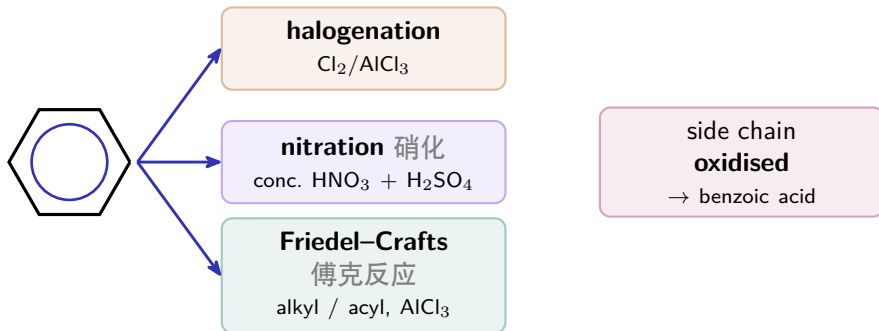
naphthalene is an arene

1

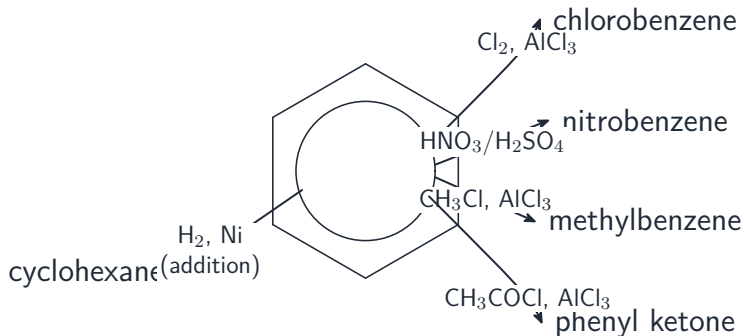
Benzene reactions

Reactions of benzene

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



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: $\text{CH}_3\text{Cl} + \text{AlCl}_3$, heat – adds an **alkyl** group, giving methylbenzene.

Friedel–Crafts acylation

Friedel–Crafts acylation 傅克酰基化: $\text{CH}_3\text{COCl} + \text{AlCl}_3$, heat – adds an **acyl** group, giving a phenyl ketone.

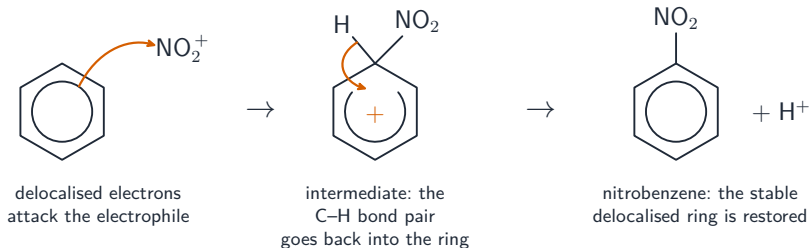
Hydrogenation

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

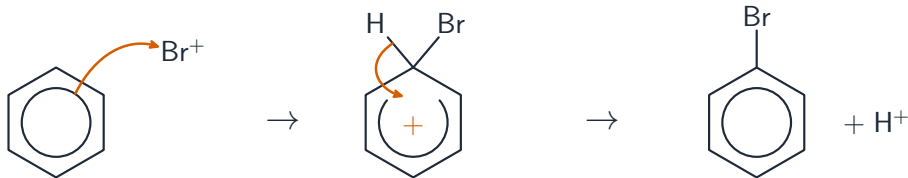
Nitration



The acid mix makes NO_2^+ ; the ring attacks it, then loses H^+ . Substitution, not addition: it **keeps** the stable **delocalised** 离域 ring.

Electrophilic substitution: bromination

Bromination electrophile: $\text{Br}_2 + \text{AlBr}_3 \longrightarrow \text{Br}^+ + \text{AlBr}_4^-$



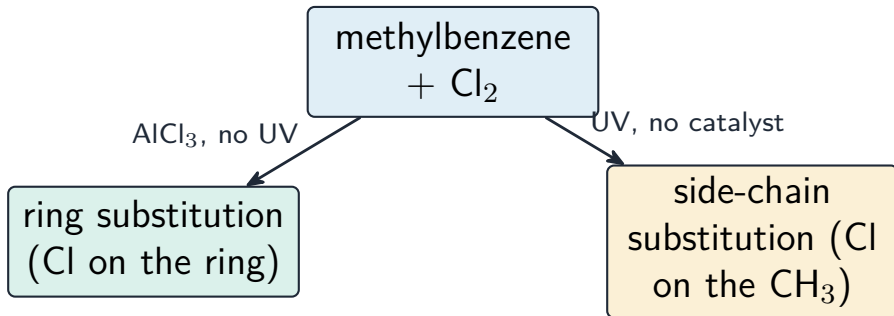
catalyst regenerated: $\text{H}^+ + \text{AlBr}_4^- \longrightarrow \text{HBr} + \text{AlBr}_3$

Same mechanism, different electrophile: the **halogen carrier** AlBr_3 makes Br^+ and is regenerated at the end.

Ring or side-chain?

The conditions decide:

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

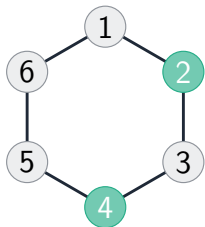
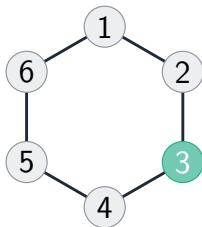


Directing effects

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

- $-\text{NH}_2$, $-\text{OH}$, $-\text{R}$ → positions 2 & 4
- $-\text{NO}_2$, $-\text{COOH}$, $-\text{COR}$ → position 3

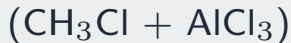
$-\text{NH}_2$, $-\text{OH}$, $-\text{R}$, $-\text{NO}_2$, $-\text{COOH}$, $-\text{COR}$



Reactions of benzene and methylbenzene

alkylation

adds an alkyl group



acylation

adds an acyl group



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 $\text{HNO}_3/\text{H}_2\text{SO}_4$, $50 - 60\text{ }^\circ\text{C}$) and **halogenation** (halogen + AlCl_3) with the electrophile-generating step.
- Compare reactivity: benzene resists addition far more than an alkene because of delocalisation.

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:
- $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-$
- 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

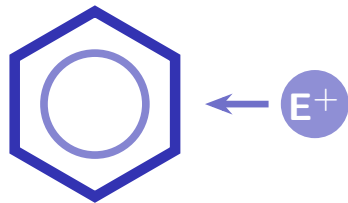
4

Directing

$\text{NH}_2/\text{OH}/\text{R}$ 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