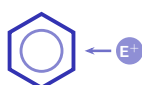


Arenes

A-Level Chemistry • Topic 30

A-Level Chemistry



Arenes

What we will cover

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



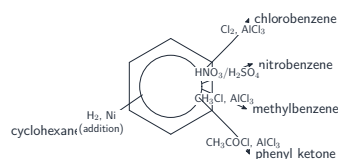
naphthalene is an arene

1 Benzene reactions

Arenes

↳ 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

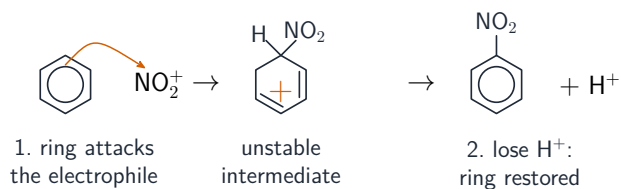
Arenes

↳ Benzene reactions

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.



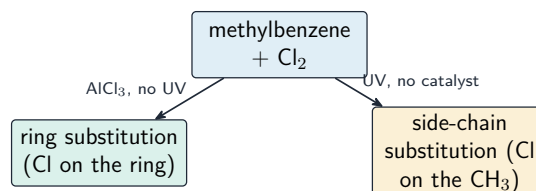
Arenes

↳ Benzene reactions

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**

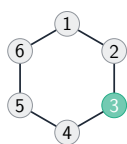
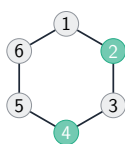


Directing effects

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

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



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

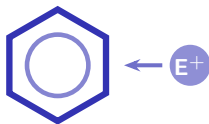
AlCl_3 ring vs UV side-chain

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 $-\text{OH}$ 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