# 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



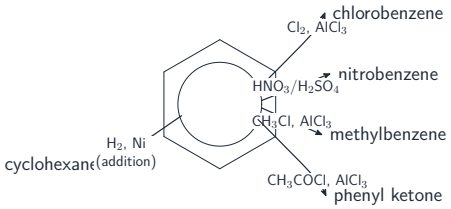
## Reactions of benzene

**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 → 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

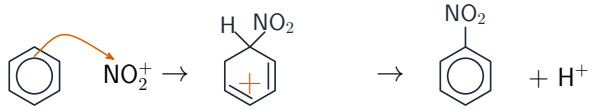
| | |
|---|---|
| **Halogenation** | $Cl_2$ or $Br_2$ with $AlCl_3$ or $AlBr_3$ as **catalyst** 催化剂 gives a **halogenoarene** 卤代芳烃 (an aryl halide). |
| **Friedel–Crafts alkylation** | **Friedel–Crafts alkylation** 傅克烷基化: $CH_3Cl + AlCl_3$, heat – adds an alkyl group, giving methylbenzene. |
| **Friedel–Crafts 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.



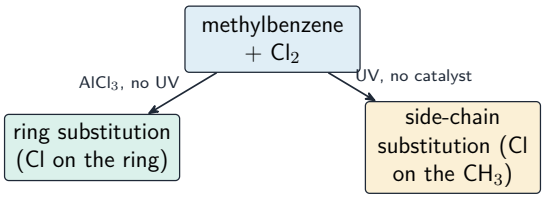

1. ring attacks the electrophile
unstable intermediate
2. lose $H^+$: ring restored



## 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



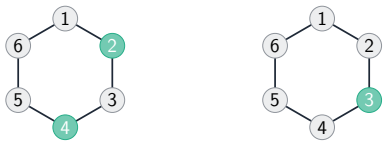



## Directing effects

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** | **acylation** |
|---|---|
| adds an alkyl group ($CH_3Cl + AlCl_3$) | 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 $HNO_3/H_2SO_4$, $50-60$ °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 $\pi$ system is restored.

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



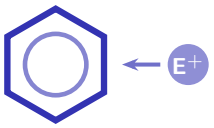
## Topic 30 – key takeaways

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