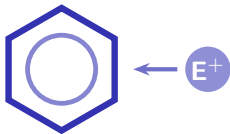


Arenes

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

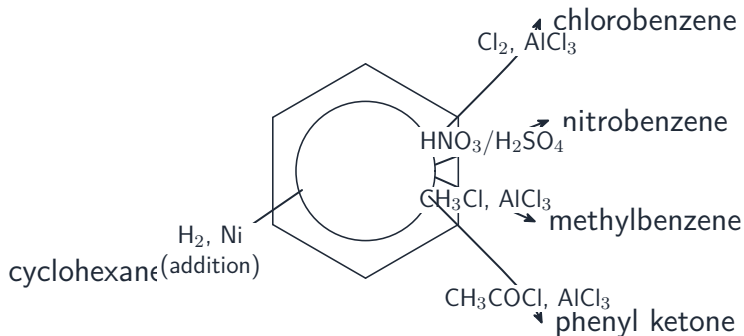


Reactions of benzene

Arenes keep their stable ring, reacting by **electrophilic substitution** :

- halogenation (AlCl_3); **nitration**
- **Friedel–Crafts** 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** gives a **halogenoarene** (an aryl halide).

Friedel–Crafts alkylation

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

Friedel–Crafts acylation

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

Hydrogenation

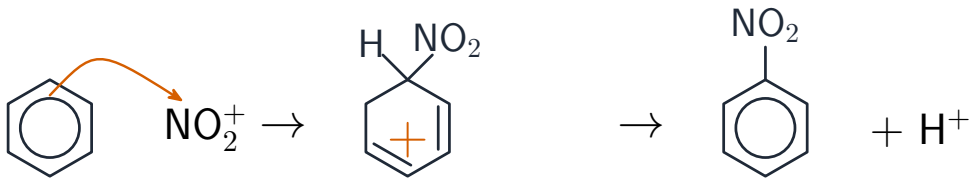
Hydrogenation : H_2 with a Pt or Ni catalyst and heat destroys the **benzene ring** entirely, giving cyclohexane.

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** ring.



1. ring attacks
the electrophile

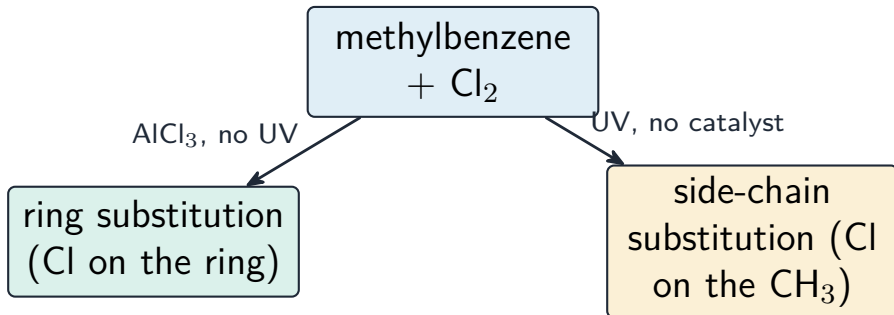
unstable
intermediate

2. lose H^+ :
ring restored

Ring or side-chain?

The conditions decide:

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

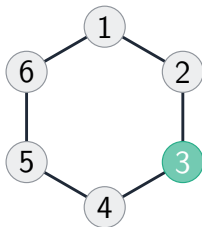
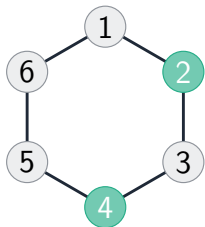


Directing effects

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

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

$-\text{NH}_2$, $-\text{OH}$, $-\text{R}$ NO_2 , $-\text{COOH}$, $-\text{COR}$



Reactions of benzene and methylbenzene

alkylation

adds an alkyl group
($\text{CH}_3\text{Cl} + \text{AlCl}_3$)

acylation

adds an acyl group
($\text{CH}_3\text{COCl} + \text{AlCl}_3$)

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



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

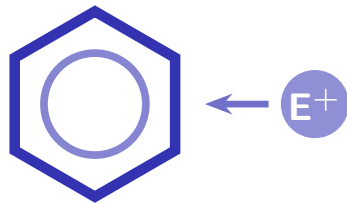
4

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