Exercise walk-through

Arenes ▪ 30.1

eXercise

You must be able to

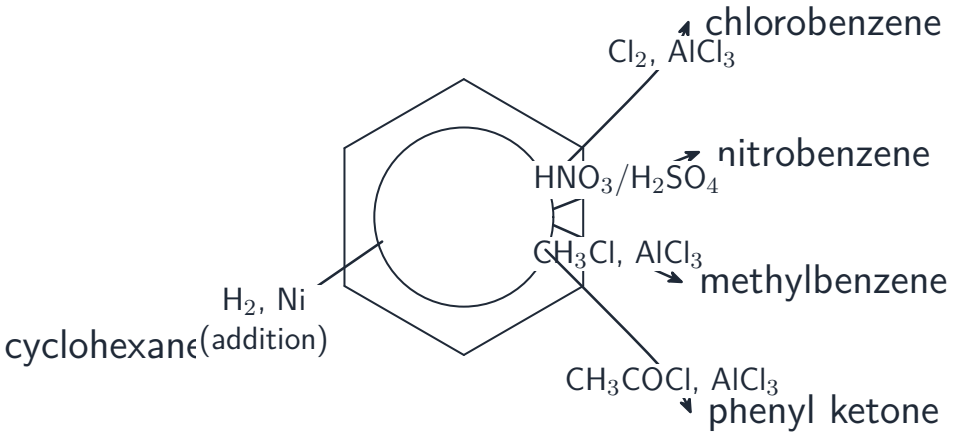
- give the reagents, conditions and products for benzene's reactions (halogenation, nitration, Friedel–Crafts, oxidation, hydrogenation)
- describe the electrophilic substitution mechanism (e.g. nitration)
- explain why benzene substitutes rather than adds
- predict where a second group goes from directing effects

Method — Reactions and mechanism

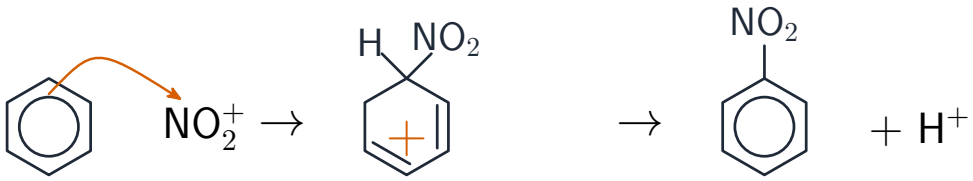
- **nitration:** conc. HNO_3 + conc. H_2SO_4, 25–60 °C $\rightarrow$ nitrobenzene.
- **Friedel–Crafts:** RCl (or RCOCl) + $AlCl_3$, heat $\rightarrow$ alkyl/acyl benzene.
- **side-chain oxidation:** hot alkaline $KMnO_4$ then acid $\rightarrow$ benzoic acid.

Why substitution, not addition? Substitution keeps the stable delocalised ring; addition would destroy it.

Method — Reactions and mechanism



Method — Reactions and mechanism



1. ring attacks the electrophile

unstable intermediate

2. lose H^+: ring restored

Practice 2.1 ▪ 2 marks

Give the reagents and conditions for the **nitration** of benzene.

Solution 2.1

Method: Reactions and mechanism

Worked steps

concentrated nitric acid and concentrated sulfuric acid M1; 25–60 °C / warm A1.

Practice 2.2 ▪ 1 mark

Name the electrophile formed in the nitration of benzene.

Solution 2.2

Method: Reactions and mechanism

Worked steps

NO_2^+ (the nitryl/nitronium cation) B1.

Exam-style 3.1 ▪ 1 mark

Benzene reacts with CH_3COCl and $AlCl_3$. This is an example of:

A Friedel–Crafts acylation

B nitration

C side-chain oxidation

D hydrogenation

Solution 3.1

Method: Reactions and mechanism

A Friedel–Crafts acylation ✓

B nitration

C side-chain oxidation

D hydrogenation

Worked steps

A. $\mathrm{RCOCl} + \mathrm{AlCl_3}$ adds an acyl group — Friedel–Crafts acylation.

Exam-style 3.2 ▪ 1 mark

Methylbenzene is treated with Cl_2 in **UV light with no catalyst**. Substitution occurs at the:

A ring, at positions 2 and 4

B ring, at position 3

C side-chain ($–CH_3$)

D both ring and side-chain equally

Solution 3.2

Method: Reactions and mechanism

A ring, at positions 2 and 4

B ring, at position 3

C side-chain (–CH_3) ✓

D both ring and side-chain equally

Worked steps

C. UV light with no catalyst gives free-radical substitution in the side-chain.

Exam-style 3.3 ▪ 4 marks

Describe the mechanism of the nitration of benzene. Include the formation of the electrophile and use curly arrows in words.

Solution 3.3

Method: Reactions and mechanism

Worked steps

the acid mixture makes the electrophile NO_2^+ (M1); the delocalised ring electrons form a bond to NO_2^+, giving a positively charged intermediate (M1); the C–H bond breaks and H^+ is lost (M1); this restores the delocalised ring, giving nitrobenzene (A1).

Exam-style 3.4 ▪ 2 marks

Nitrobenzene already carries a –NO_2 group. Predict and explain the position a second nitro group will take.

Solution 3.4

Method: Reactions and mechanism

Worked steps

–NO_2 directs the next group to **position 3** M1; because –NO_2 is an electron-withdrawing (deactivating) group that directs to the 3-position A1.