

30.1 Arenes

Name: _____ Class: _____ Date: _____

Total: 11 marks

Objective

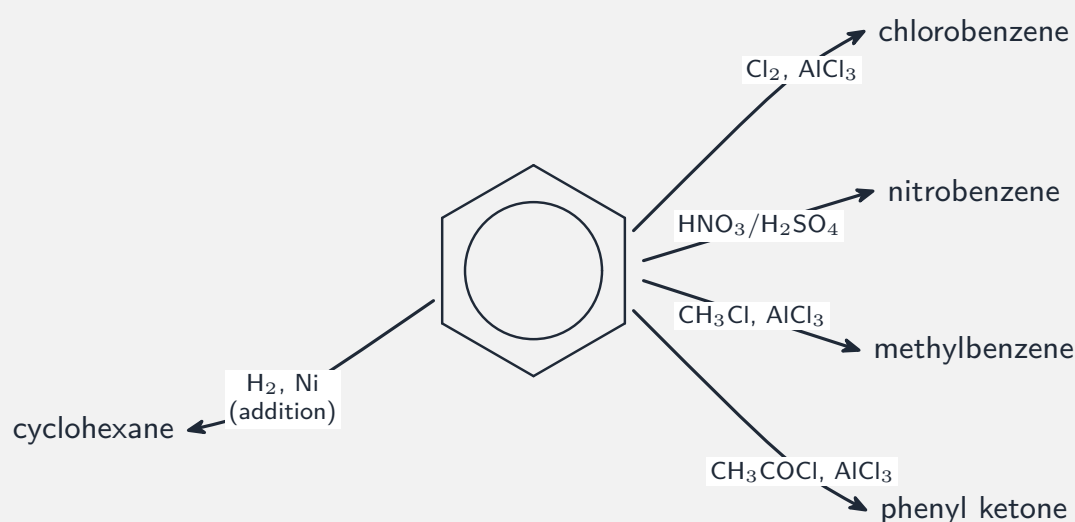
Build the skills to answer exam questions on **arenes** 芳烃—the reactions of benzene and methylbenzene, the **electrophilic substitution** 亲电取代 mechanism, side-chain vs ring substitution, and **directing effects** 定位效应.

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

1 Worked examples

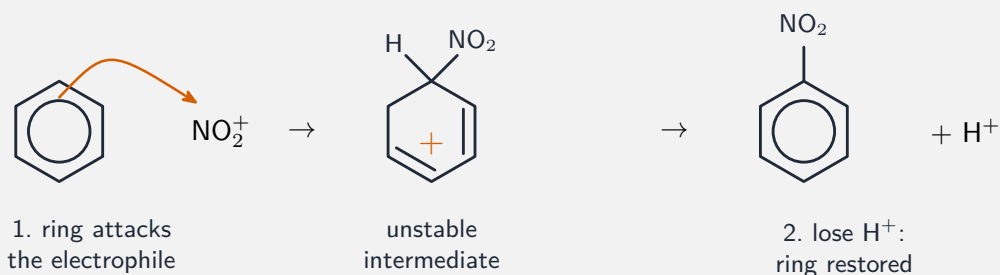
■ Reactions and mechanism



Benzene keeps its stable ring, reacting mostly by electrophilic substitution (addition only with H)

- **nitration:** conc. HNO_3 + conc. H_2SO_4 , 25–60 °C → 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.



Electrophilic substitution: the ring attacks the electrophile, then loses H to restore the stable ring

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

2 Practice

2.1 Give the reagents and conditions for the **nitration** of benzene. [2]

2.2 Name the electrophile formed in the nitration of benzene. [1]

3 Exam-style questions

3.1 Benzene reacts with CH_3COCl and AlCl_3 . This is an example of: [1]

- **A** Friedel–Crafts acylation
- **B** nitration
- **C** side-chain oxidation
- **D** hydrogenation

3.2 Methylbenzene is treated with Cl_2 in **UV light with no catalyst**. Substitution occurs at the: [1]

- **A** ring, at positions 2 and 4
- **B** ring, at position 3

- **C** side-chain ($-\text{CH}_3$)
 - **D** both ring and side-chain equally
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3.3 Describe the mechanism of the nitration of benzene. Include the formation of the electrophile and use curly arrows in words. [4]

3.4 Nitrobenzene already carries a $-\text{NO}_2$ group. Predict and explain the position a second nitro group will take. [2]

4 Go further

You are now ready for the real exam questions on this subtopic. Open the **30.1 Arenes** past-paper sheet in the Library, or try these in **Practice mode**:

- 9701/41 N25 —Q8 (arenes)
- 9701/42 N25 —Q9 (arenes)
- 9701/44 N25 —Q5 (arenes)

Solutions

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

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

3.1 A. $\text{RCOCl} + \text{AlCl}_3$ adds an acyl group —Friedel–Crafts acylation.

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

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

3.4 $-\text{NO}_2$ directs the next group to **position 3**; because $-\text{NO}_2$ is an electron-withdrawing (deactivating) group that directs to the 3-position.