A-LEVEL CHEMISTRY • EXERCISE SHEET

30.1 Arenes

Name: _____ Class: _____ Date: _____ **Total: 11 marks**

KEY WORDS electrophilic substitution 亲电取代 • arene 芳烃 • nitration 硝化 • friedel–crafts acylation 傅克酰基化 • benzene 苯

Objective

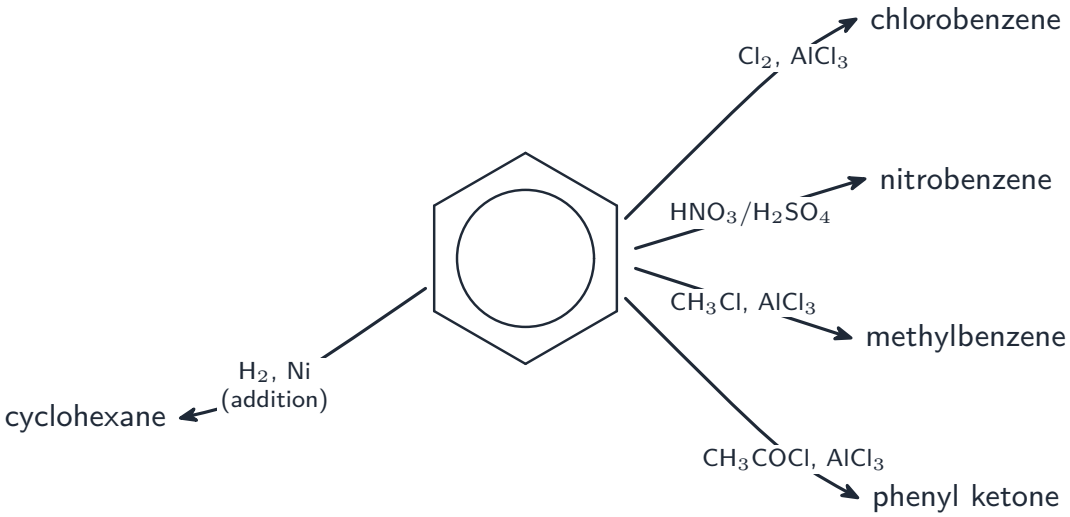
Build the skills to answer exam questions on **arenes** 芳烃 — the reactions of benzene and methylbenzene, the **electrophilic substitution** 亲电取代 mechanism, side-chain vs ring substitution, and **directing effects** 定位效应.

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

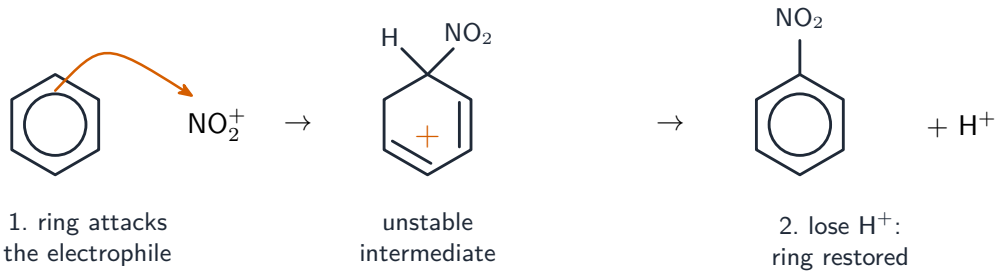
1 Worked examples

■ Reactions and mechanism



Benzene keeps its stable ring, reacting mostly by electrophilic substitution (addition only with H_2)

- **nitration:** conc. HNO_3 + conc. H_2SO_4, 25–60 °C → nitrobenzene.
- **Friedel–Crafts:** RCl (or RCOCl) + $AlCl_3$, heat → alkyl/acyl benzene.
- **side-chain oxidation:** hot alkaline $KMnO_4$ then acid → 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 ($–CH_3$)
- **D** both ring and side-chain equally

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 $–NO_2$ group. Predict and explain the position a second nitro group will take. [2]

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. $RCOCl + AlCl_3$ 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 $–NO_2$ directs the next group to **position 3**; because $–NO_2$ is an electron-withdrawing (deactivating) group that directs to the 3-position.