A-LEVEL CHEMISTRY • EXERCISE SHEET

30.1 Arenes

Name: _____ Class: _____ Date: _____ **Total: 30 marks**

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

Objective

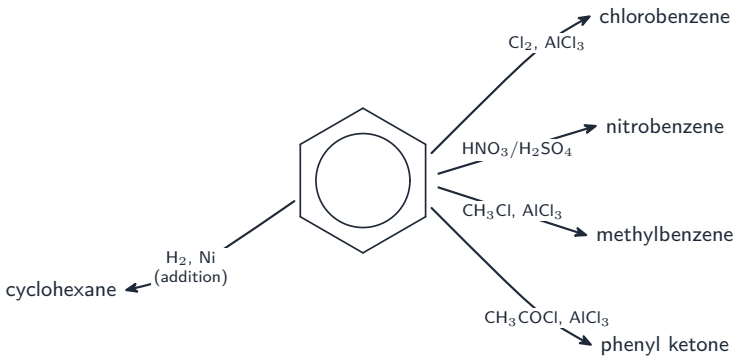
Build the skills to answer exam questions on **arenes** 芳烃 — the reactions of benzene and methylbenzene, the **electrophilic substitution** 亲电取代 mechanism, side-chain vs ring substitution, and **directing effects** 定位效应.

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

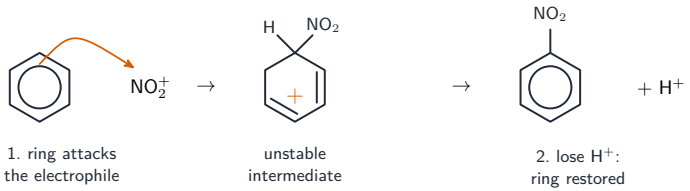
1 Worked examples

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.

Benzene: the reagents table, and why it substitutes

Benzene's delocalised π system is **stable**, so it does not undergo addition like an alkene, which would destroy the delocalisation. Instead it undergoes **electrophilic substitution** 亲电取代: an electrophile attacks the ring, and a hydrogen is lost, so the delocalised system survives.

Reaction	Reagents	Conditions	Product
nitration	conc. HNO_3 + conc. H_2SO_4	55 °C	nitrobenzene
halogenation	Cl_2 or Br_2 + $AlCl_3$ / $FeBr_3$	room temperature, anhydrous	chloro- or bromobenzene
Friedel–Crafts alkylation	RCl + $AlCl_3$	reflux, anhydrous	alkylbenzene
Friedel–Crafts acylation	RCOCl + $AlCl_3$	reflux, anhydrous	phenyl ketone
hydrogenation	H_2, Ni catalyst	150 °C, high pressure	cyclohexane

The mechanism, written the way it earns marks (nitration):

1. **Generate the electrophile:** $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$. The nitronium ion NO_2^+ is the electrophile.
2. **Attack:** a curly arrow from **inside the ring** to the nitrogen of NO_2^+, forming the unstable intermediate drawn with a **horseshoe** (a broken delocalised ring) and a + inside it.
3. **Lose H^+:** a curly arrow from the C–H bond back into the ring, restoring the delocalisation, and H^+ is released.
4. **Regenerate the catalyst:** $H^+ + HSO_4^- \rightarrow H_2SO_4$.

The horseshoe intermediate and the arrow **from the ring, not from a double bond**, are the two marks candidates most often lose.

Methylbenzene differs in two ways. The methyl group is **electron-releasing**, so it activates the ring and directs substitution to the **2- and 4- (ortho/para)** positions, and the reaction is faster than benzene's. The side chain can also be **oxidised** by hot alkaline $KMnO_4$ followed by acid, giving benzoic acid — a reaction the ring itself never undergoes.

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]

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

2.4 State why benzene undergoes substitution rather than addition. [2]

2.5 Name the product when methylbenzene is refluxed with alkaline $KMnO_4$ and then acidified. [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]

3.5 Benzene is converted to nitrobenzene and then, in a separate route, to a phenyl ketone.

(a) Give the equation showing how the electrophile for nitration is generated. [2]

(b) Draw the mechanism for the nitration of benzene, showing the curly arrows, the intermediate and the loss of H^+. [4]

(c) Explain why the intermediate is drawn with a horseshoe rather than with three double bonds. [2]

(d) Suggest the reagents and conditions needed to convert benzene into phenylethanone, $C_6H_5COCH_3$, and name the type of reaction. [3]

(e) Methylbenzene reacts faster than benzene and gives mainly the 2- and 4- products. Explain both observations. [3]

Solutions

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

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

2.3 Concentrated nitric acid and concentrated sulfuric acid; a temperature of about 55 °C.

2.4 The ring's delocalised π electrons make it unusually stable; addition would destroy that delocalisation, so substitution, which restores it, is preferred.

2.5 Benzoic acid.

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.

3.5 (a) $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$.
(b) Curly arrow from **inside the ring** to the nitrogen of NO_2^+; intermediate drawn with a horseshoe and a + inside it, with the NO_2 and H on the same carbon; curly arrow from the C–H bond into the ring; H^+ released and the delocalised ring restored.
(c) The delocalised system is broken but not destroyed — four π electrons remain delocalised over five carbons; a horseshoe shows that partial delocalisation, which three localised double bonds would not.
(d) Ethanoyl chloride, CH_3COCl, with an $AlCl_3$ catalyst; reflux under anhydrous conditions; Friedel–Crafts acylation.
(e) The methyl group is electron-releasing, so it increases the electron density of the ring and makes it more attractive to an electrophile, hence the faster reaction; the electron density is increased most at the 2- and 4- positions, so substitution occurs mainly there.