

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

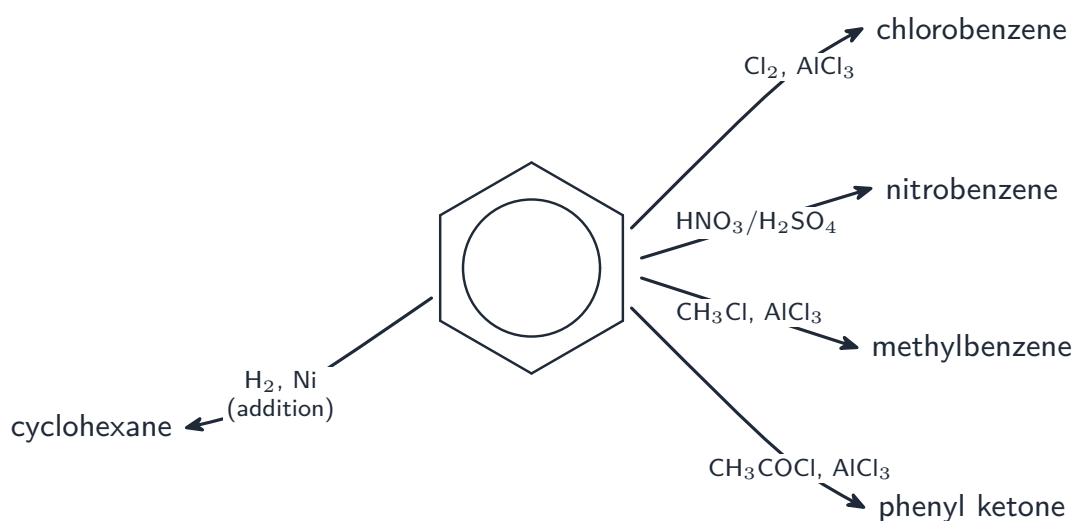
Build the skills to answer exam questions on **arenes** 芳烃 — the reactions of benzene and methylbenzene, the **electrophilic substitution** 亲电取代 mechanism, side-chain vs ring substitution, and **directing effects** 定位效应.

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

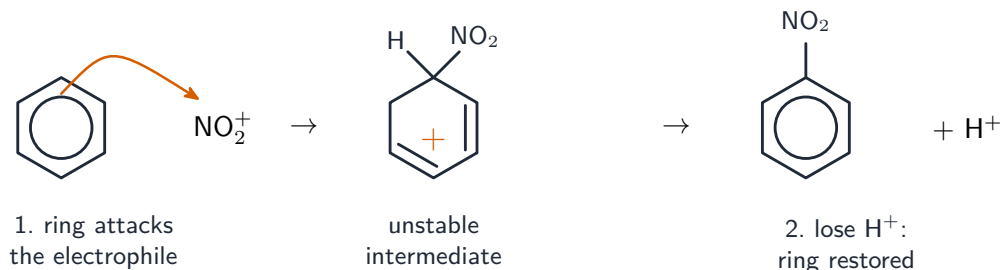
1 Worked examples

■ 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 $\rightarrow$ 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.



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:** $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-$. 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:** $\text{H}^+ + \text{HSO}_4^- \rightarrow \text{H}_2\text{SO}_4$.

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	B
C	D

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	B
C	D

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

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]

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, $\text{C}_6\text{H}_5\text{COCH}_3$, 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]
