31.1 Halogen compounds (halogenoarenes)

Name: _____ Class: _____ Date: _____ **Total: 27 marks**

KEY WORDS halogenoarene 卤代芳烃 • halogenoalkane 卤代烷 • catalyst 催化剂 • lone pair 孤对电子 • arene 芳烃

Objective

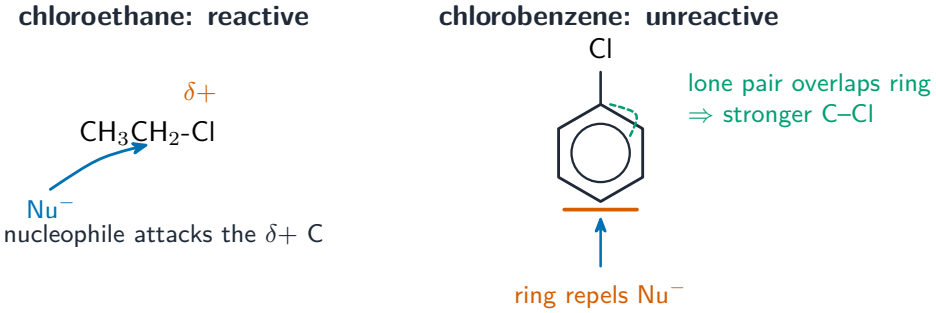
Build the skills to answer exam questions on **halogenoarenes** 卤代芳烃 — how they are made, and why they are far less reactive than **halogenoalkanes** 卤代烷 towards nucleophilic substitution.

You must be able to:

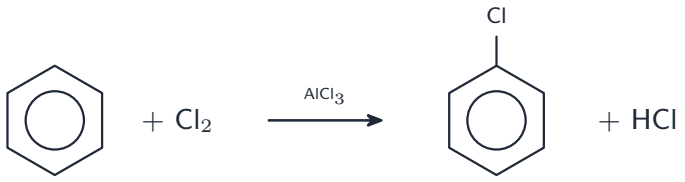
- give the reagents and conditions to make a halogenoarene from an arene
- explain why a halogenoarene resists nucleophilic substitution
- contrast its reactivity with a halogenoalkane

1 Worked examples

■ Reactivity compared



Chloroethane reacts (a nucleophile attacks the δ+ carbon); chlorobenzene does not — the Cl lone pair strengthens the C–Cl bond and the ring repels nucleophiles



Making a halogenoarene by substitution

- **make it:** arene + Cl_2/Br_2 with $AlCl_3/AlBr_3$ catalyst → halogenoarene (electrophilic substitution).
- **chlorobenzene is unreactive** because: (1) a Cl lone pair overlaps the ring, giving the C–Cl bond partial double-bond character → shorter, stronger, harder to break; (2) the electron-rich ring repels nucleophiles.

■ Why a halogenoarene barely reacts

In a **halogenoalkane** the C–X bond is polar and the halogen leaves readily, so nucleophilic substitution is easy. In a **halogenoarene** 卤代芳烃, where the halogen is attached **directly to a benzene ring**, substitution is extremely slow. Two reasons, and the exam wants both:

1. **The C–Cl bond has partial double-bond character.** A lone pair on the chlorine **overlaps with the delocalised π system** of the ring, so electron density is shared into the bond. It is therefore **shorter and stronger** than a normal C–Cl bond and much harder to break.
2. **The ring repels the nucleophile.** The delocalised π electrons above and below the ring create a region of high electron density, which repels an approaching lone pair.

The comparison the question always makes: chlorobutane is hydrolysed by warm aqueous NaOH, giving a precipitate with silver nitrate within minutes; chlorobenzene under the same conditions gives **no precipitate**, because no chloride ion is released. That contrast is the standard experimental evidence.

△ **Being attached to the ring changes the direction too.** A halogen on the ring is a **2,4-directing** group in further substitution, even though it deactivates the ring overall — a combination worth remembering because it looks contradictory.

Making them: chlorobenzene comes from benzene with Cl_2 and an $AlCl_3$ catalyst, anhydrous, at room temperature — electrophilic substitution, not addition, because addition would destroy the delocalisation.

Worked example. Explain why chlorobenzene gives no precipitate with aqueous silver nitrate after warming with NaOH, while 1-chlorobutane does within minutes.

1. In 1-chlorobutane the C–Cl bond is a normal polar single bond; the hydroxide attacks the $\delta+$ carbon and chloride ions are released, which give a white precipitate of AgCl.

2. In chlorobenzene a chlorine lone pair overlaps the ring's π system, giving the C–Cl bond partial double-bond character: it is shorter and stronger.
3. The ring's π electron density also repels the incoming hydroxide.
4. So no chloride is released, and no precipitate forms.

2 Practice

2.1 Give the reagent and catalyst used to make chlorobenzene from benzene. [2]

2.2 State the type of reaction by which a halogenoalkane reacts with OH^-. [1]

2.3 Give the reagents and conditions for making chlorobenzene from benzene. [2]

2.4 Explain why the C–Cl bond in chlorobenzene is stronger than in chloroethane. [2]

2.5 State what is observed when chlorobenzene is warmed with aqueous sodium hydroxide and then acidified silver nitrate is added. [1]

3 Exam-style questions

3.1 Chlorobenzene is much less reactive than chloroethane towards OH^- because: [1]

A	B
C	D

A the C–Cl bond in chlorobenzene is weaker
B a chlorine lone pair overlaps the ring, strengthening the C–Cl bond
C chlorobenzene has no C–Cl bond
D the ring attracts nucleophiles

3.2 Which compound reacts fastest with warm aqueous NaOH? [1]

A chlorobenzene
B chloroethane
C 2,4,6-trichlorophenol
D they react at the same rate

3.3 Explain, in terms of bonding, why chlorobenzene does **not** undergo nucleophilic substitution under normal conditions. Give **two** reasons. [3]

3.4 Methylbenzene reacts with Cl_2 and $AlCl_3$. State the **two** organic products and explain why these positions are favoured. [2]

3.5 A student warms separate samples of 1-chlorobutane and chlorobenzene with aqueous sodium hydroxide, then acidifies each and adds aqueous silver nitrate.

(a) State what the student observes with each sample. [2]

(b) Explain, in terms of the C–Cl bond, why chlorobenzene behaves differently. [3]

(c) Give a second reason, in terms of the benzene ring, why nucleophilic attack on chlorobenzene is difficult. [2]

(d) Write the equation and name the mechanism for the hydrolysis of 1-chlorobutane. [3]

(e) Chlorine is described as deactivating but 2,4-directing. Explain what this means for a further substitution on chlorobenzene. [2]