A-LEVEL CHEMISTRY • EXERCISE SHEET

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

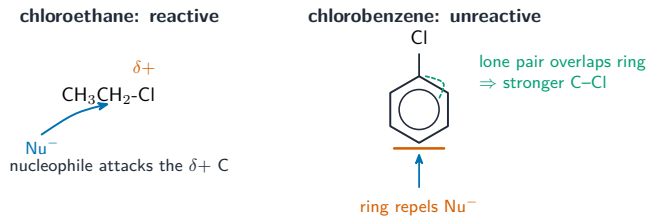
Build the skills to answer exam questions on **halogenoarenes** 卤代芳烃 — how they are made, and why they are far less reactive than **halogenoalkanes** 卤代烷 towards nucleophilic substitution.

You must be able to:

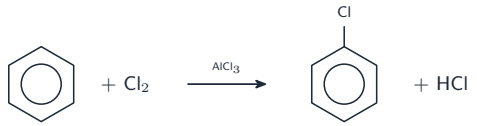
- give the reagents and conditions to make a halogenoarene from an arene
- explain why a halogenoarene resists nucleophilic substitution
- contrast its reactivity with a halogenoalkane

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 δ+ 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** 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]

Solutions

2.1 chlorine, Cl_2; with an $AlCl_3$ (aluminium chloride) catalyst.

2.2 nucleophilic substitution.

2.3 Chlorine with an aluminium chloride catalyst; anhydrous conditions at room temperature.

2.4 A lone pair on the chlorine overlaps with the delocalised π system of the ring, giving the bond partial double-bond character so it is shorter and stronger.

2.5 No precipitate is formed.

3.1 B. A Cl lone pair overlaps the delocalised ring, giving partial double-bond character and a stronger C–Cl bond.

3.2 B. Chloroethane (a halogenoalkane) reacts fastest; the aryl C–Cl bonds resist substitution.

3.3 a lone pair on chlorine overlaps the delocalised ring, giving the C–Cl bond partial double-bond character so it is shorter and stronger / harder to break; and the electron-rich ring repels the approaching nucleophile.

3.4 2-chloromethylbenzene and 4-chloromethylbenzene; the $-CH_3$ group directs the chlorine to positions 2 and 4.

3.5 (a) 1-chlorobutane gives a white precipitate of silver chloride; chlorobenzene gives no precipitate.
(b) In chlorobenzene a lone pair on the chlorine overlaps with the ring's delocalised π system; the C–Cl bond therefore has partial double-bond character and is shorter and stronger; it is not broken under these conditions, so no chloride ion is released.
(c) The delocalised π electrons lie above and below the ring, giving a region of high electron density which repels the approaching hydroxide ion.
(d) $CH_3CH_2CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2CH_2OH + Cl^-$; nucleophilic substitution.
(e) Deactivating means the ring reacts more slowly than benzene, because chlorine withdraws electron density inductively; 2,4-directing means that when substitution does occur, the new group enters mainly at the positions next to and opposite the chlorine.