

31.1 Halogen compounds (halogenoarenes)

Name: _____ Class: _____ Date: _____

Total: 10 marks

KEY WORDS halogenoarene 卤代芳烃 • halogenoalkane 卤代烷 • arene 芳烃 • lone pair 孤对电子
• nucleophile 亲核试剂

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.

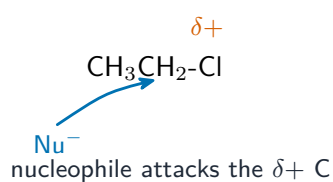
You must be able to:

- 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

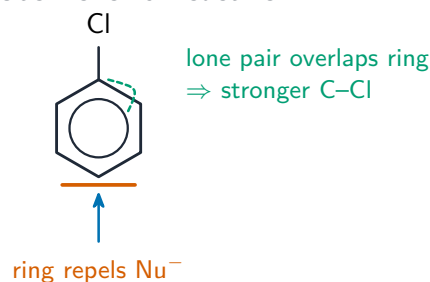
1 Worked examples

■ Reactivity compared

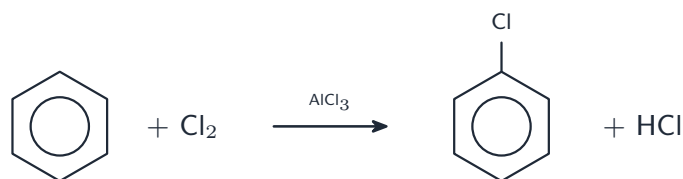
chloroethane: reactive



chlorobenzene: unreactive



Chloroethane reacts (a nucleophile attacks the $\delta+$ 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 + Cl₂/Br₂ with AlCl₃/AlBr₃ 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.

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]

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]

Solutions

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

2.2 nucleophilic substitution.

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 $-\text{CH}_3$ group directs the chlorine to positions 2 and 4.