

Exercise walk-through

Halogen compounds ■ 31.1

eXercise

You must be able to

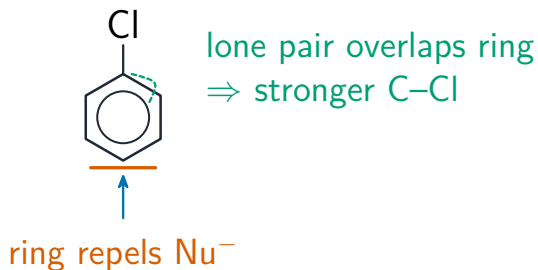
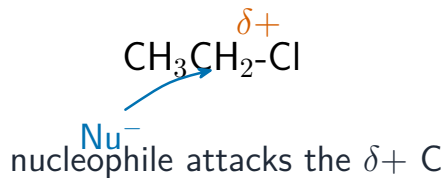
- give the reagents and conditions to make a halogenoarene from an arene
- explain why a halogenoarene resists nucleophilic substitution
- contrast its reactivity with a halogenoalkane

Method — Reactivity compared

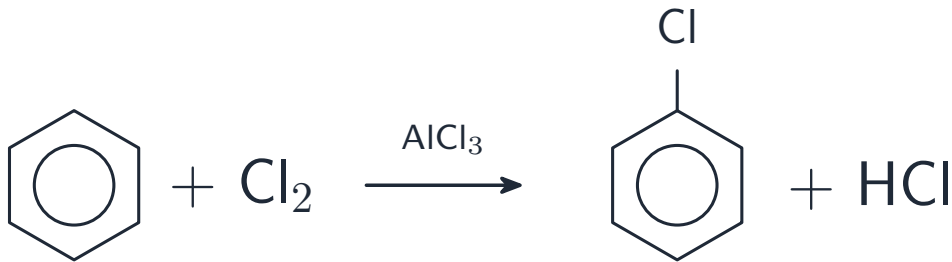
Chloroethane reacts (a nucleophile attacks the $\delta+$ carbon); chlorobenzene does not — the Cl lone pair strengthens the C–Cl bond and the ring repels nucleophiles

- **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.

chloroethane: reactive **chlorobenzene: unreactive**



Method — Reactivity compared



Making a halogenoarene by substitution

Practice 2.1 ■ 2 marks

Give the reagent and catalyst used to make chlorobenzene from benzene.

Solution 2.1

Method: Reactivity compared

Worked steps

chlorine, Cl_2 **M1**; with an AlCl_3 (aluminium chloride) catalyst **A1**.

Practice 2.2 ■ 1 mark

State the type of reaction by which a halogenoalkane reacts with OH^- .

Solution 2.2

Method: Reactivity compared

Worked steps

nucleophilic substitution **B1**.

Exam-style 3.1 ■ 1 mark

Chlorobenzene is much less reactive than chloroethane towards OH^- because:

- 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

Solution 3.1

Method: Reactivity compared

- 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

Worked steps

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

Exam-style 3.2 ■ 1 mark

Which compound reacts fastest with warm aqueous NaOH?

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

Solution 3.2

Method: Reactivity compared

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



Worked steps

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

Exam-style 3.3 ■ 3 marks

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

Solution 3.3

Method: Reactivity compared

Worked steps

a lone pair on chlorine overlaps the delocalised ring **M1**, giving the C–Cl bond partial double-bond character so it is shorter and stronger / harder to break **M1**; and the electron-rich ring repels the approaching nucleophile **A1**.

Exam-style 3.4 ■ 2 marks

Methylbenzene reacts with Cl_2 and AlCl_3 . State the **two** organic products and explain why these positions are favoured.

Solution 3.4

Method: Reactivity compared

Worked steps

2-chloromethylbenzene and 4-chloromethylbenzene **M1**; the $-\text{CH}_3$ group directs the chlorine to positions 2 and 4 **A1**.