

Halogenoarenes

A-Level Chemistry 9701 · Topic 31 revision notes

Everything from the 1 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

1. Halogenoarenes

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1 Halogenoarenes

Syllabus 31.1

A **halogenoarene** has a halogen atom bonded directly to a benzene ring. Chlorobenzene is made by **electrophilic substitution**: benzene and Cl_2 with an anhydrous **halogen carrier** (AlCl_3 or FeCl_3) at room temperature; methylbenzene gives a mixture of 2- and 4-chloromethylbenzene. Chlorobenzene is **much less reactive** towards nucleophiles than chloroethane. A **lone pair on chlorine overlaps with the delocalised π system**, giving the C-Cl bond partial double-bond character, so it is **shorter and stronger** (about 0.170 nm against 0.177 nm), and the electron-rich ring **repels** an approaching nucleophile. So chlorobenzene gives **no reaction** with NaOH(aq) on warming and **no precipitate** with ethanolic AgNO_3 , but its ring still undergoes electrophilic substitution at the 2- and 4-positions.

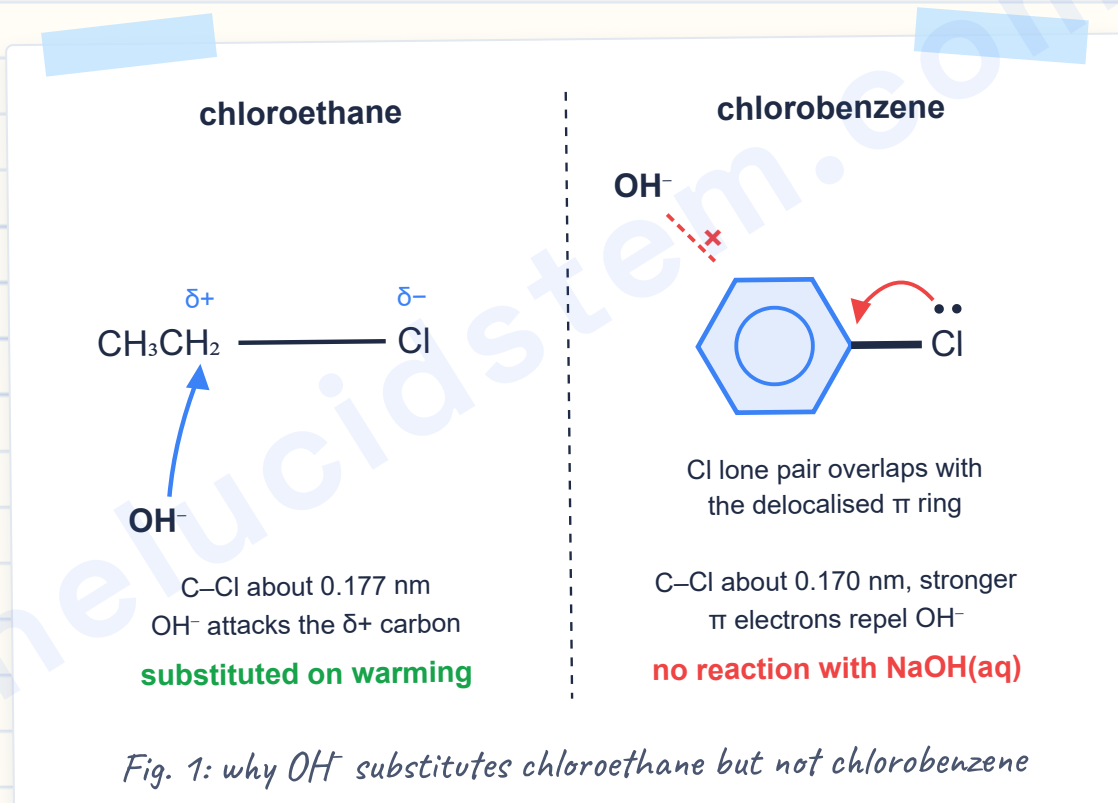


Fig. 1: why OH^- substitutes chloroethane but not chlorobenzene

Carrier for the ring, UV for the side chain.

- ✓ **$\text{Cl}_2 + \text{AlCl}_3$** : chlorine on the ring (2- and 4- on methylbenzene).
- ✓ **Stronger C-Cl**: lone pair overlaps with the π ring.
- ✓ **Ring repels nucleophiles**: no NaOH(aq) reaction, no AgCl .
- ✓ **Ring still reacts**: electrophilic substitution, 2,4-directing.

Watch out!

Do not write a halogen carrier for side-chain chlorination: AlCl_3 puts Cl on the **ring**; UV light puts it on the **CH_3** . Chlorobenzene is unreactive because the C-Cl bond is **stronger** (lone pair delocalised into the ring), not because Cl is less electronegative, and the ring **repels** nucleophiles. Never say chlorobenzene gives a white precipitate with AgNO_3 . When asked for the products of ring substitution on chlorobenzene, give **both** the 2- and 4-isomers.