Cambridge (CIE) A Level Chemistry

Your notes

Halogen Compounds

Contents

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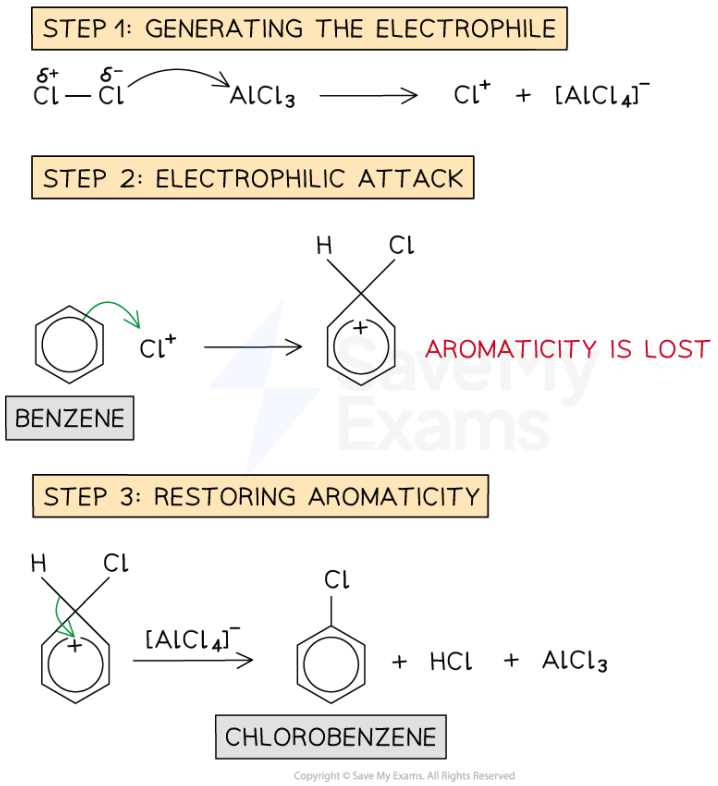
Production of Halogenoarenes

- **Halogenoarenes** are arenes which are bonded to **halogen** atoms
- They can be prepared from **substitution reactions** of arenes with chlorine or bromine in the presence of an anhydrous catalyst

Substitution of benzene to form halogenoarenes

- Chlorine gas is bubbled into benzene at room temperature and in the presence of an anhydrous $AlCl_3$ catalyst to form **chlorobenzene**
- The $AlCl_3$ catalyst is also called a **halogen carrier** and is required to generate the **electrophile** (Cl^+)
- This electrophile **attacks** the electron-rich benzene ring in the **first stage** of the reaction which **disrupts** the delocalised π system in the ring
- To restore the **aromatic stabilization,** a hydrogen atom is removed in the **second stage** of the electrophilic substitution reaction to form chlorobenzene
- When this happens, the delocalised π system of the ring is **restored**
- The same reaction occurs with benzene and bromine in the presence of an $AlBr_3$ catalyst to form **bromobenzene**

Formation of chlorobenzene



Halogenoarenes can be formed from the electrophilic substitution reaction of arenes with halogens

Substitution of methylbenzene to form halogenoarenes

- The **electrophilic substitution** of **methylbenzene** with halogens results in the formation of multiple halogenoarenes as products
- This is because the methyl group (which is an **alkyl** group) in methylbenzene is **electron-donating** and pushes **electron density** into the benzene ring
- This makes the benzene ring **more reactive** towards electrophilic substitution reactions
- The methyl group is said to be 2,4-directing and as a result, the **2** and **4 positions** are **activated**
- Electrophilic substitution of methylbenzene with chlorine and anhydrous $AlCl_3$ catalyst, therefore, gives **2-chloromethylbenzene** and **4-chloromethylbenzene**
- The reaction mechanism is **the same** as the substitution mechanism of benzene

Chlorination of methylbenzene

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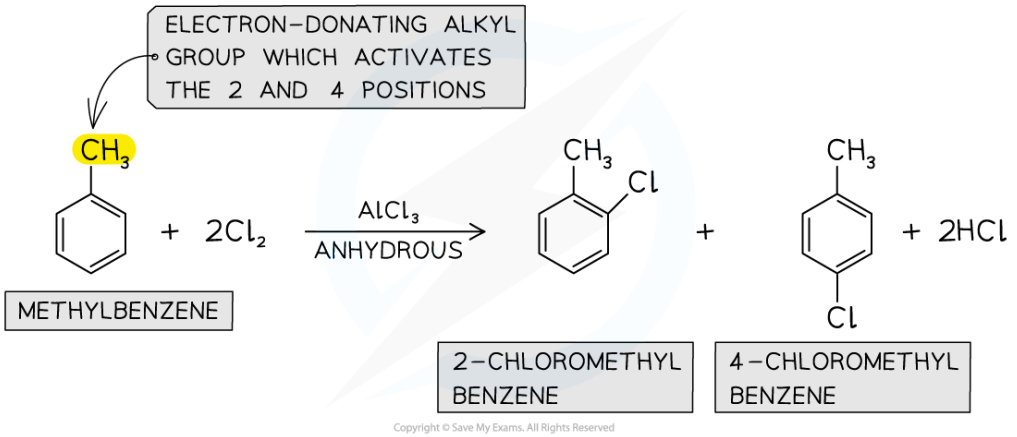

The methyl group on methylbenzene directs the incoming halogen on the 2 and 4 position

- In the presence of **excess** chlorine, substitution on the **6 position** will also occur

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Difference in Reactivity of Halogenoalkanes & Halogenoarenes

- **Halogenoarenes** are very **unreactive** compared to **halogenoalkanes**
- The difference in reactivity between the two compounds is because of the carbon-halogen bond strengths

Halogenoalkanes

- The halogenoalkane **chloroethane** can take part in **nucleophilic substitution** reactions
- A **nucleophile**, such as a hydroxide (OH^-) ion, will attack the **slightly positive carbon** atom
- A covalent bond is formed between that carbon atom and the nucleophile which causes the carbon-halogen bond to break
- Overall, the halogen is replaced by the nucleophile

Nucleophilic substitution of halogenoalkanes

Halogenoalkanes readily undergo nucleophilic substitution reactions due to the difference in electronegativity between the carbon and halogen

Halogenoarenes

- Halogenoarenes, such as chlorobenzene, **do not** readily undergo **nucleophilic substitution** reactions
  - Only under extremely **harsh** conditions, such as temperatures of 200 °C and a pressure of 200 atmospheres, will the chlorine in chlorobenzene get replaced by a nucleophile such as a hydroxide (OH^-) ion
- This is because the carbon-chlorine bond is **very strong** and cannot be easily broken
  - One of the lone pairs of electrons on the chlorine will **interact** with the π system of the ring
  - This causes the carbon-chlorine bond to have a **partial double-bond character,** which **strengthens** the bond

How the carbon-chlorine bond affects the π system

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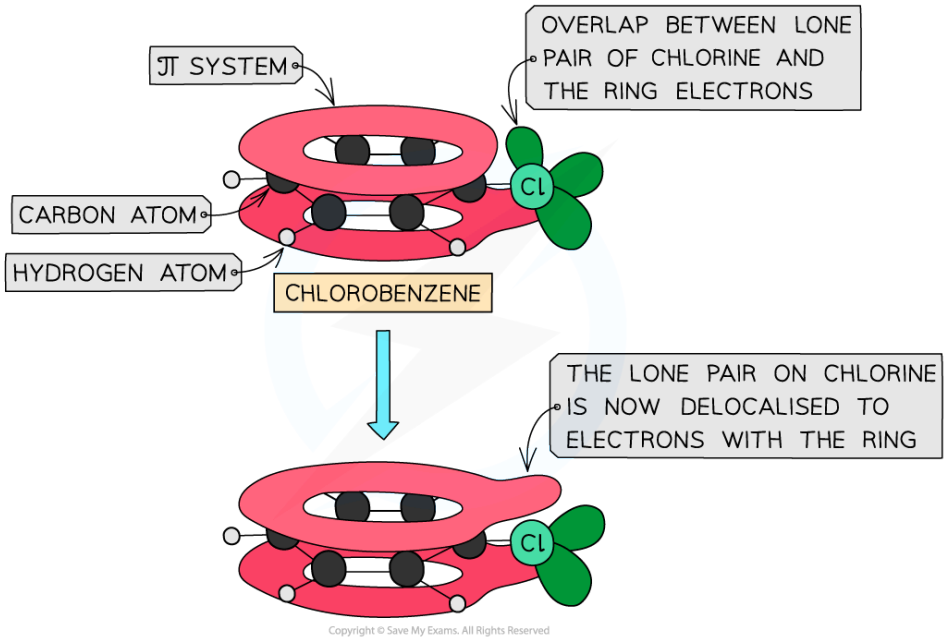

The carbon-chlorine bond is very strong, as it has partial double-bond character

- Therefore, the **unreactivity** of halogenoarenes can be explained by the **delocalisation** of a lone pair on the halogen over the benzene
- This causes additional **stabilisation** of the system and **strengthens** the carbon-halogen bond, which affects the reactions that halogenoarenes will undergo
- It gets **harder** to break the carbon-halogen bond in halogenoarenes, which decreases reactivity