CIE A Level Chemistry

Your notes

30.1 Arenes

Contents

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Reactions of Arenes

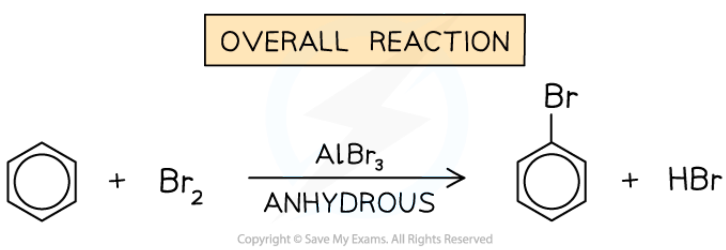
Reactions of Arenes

- Arenes are very stable compounds due to the **delocalisation of π electrons** in the ring
  - This is because the negative charge is spread out over the molecule instead of being confined to a small area
- During chemical reactions such as **substitution reactions**, this delocalised ring is maintained
  - **Addition reactions** however, **disrupt** the **aromatic stabilisation**
- Benzene undergoes a wide range of reactions including combustion - (complete and incomplete) and the following reactions:
  - Halogenation
  - Nitration
  - Friedel-Craft's alkylation
  - Friedel-Craft's acylation
  - Complete Oxidation
  - Hydrogenation

Halogenation

- **Halogenation** reactions are examples of **electrophilic substitution** reactions
- Arenes undergo **substitution** reactions with chlorine (Cl_2) and bromine (Br_2) in the presence of anhydrous $AlCl_3$ or $AlBr_3$ **catalyst** respectively to form **halogenoarenes** (**aryl halides**)
  - The chlorine or bromine acts as an **electrophile** and replaces a hydrogen atom on the benzene ring
  - The catalyst is required for the reaction to take place, due to the stability of the benzene structure

Halogenation of benzene



Arenes undergo substitution reactions with halogens to form aryl halides

- **Alkylarenes** such as methylbenzene undergo halogenation on the 2 or 4 positions
- This is due to the **electron-donating** alkyl groups which activate these positions
  - Phenol (C_6H_5OH) and phenylamine ($C_6H_5NH_2$) are also activated in the 2 and 4 positions
- The halogenation of alkylarenes, therefore, results in the formation of **two products**

Halogenation of alkylarenes

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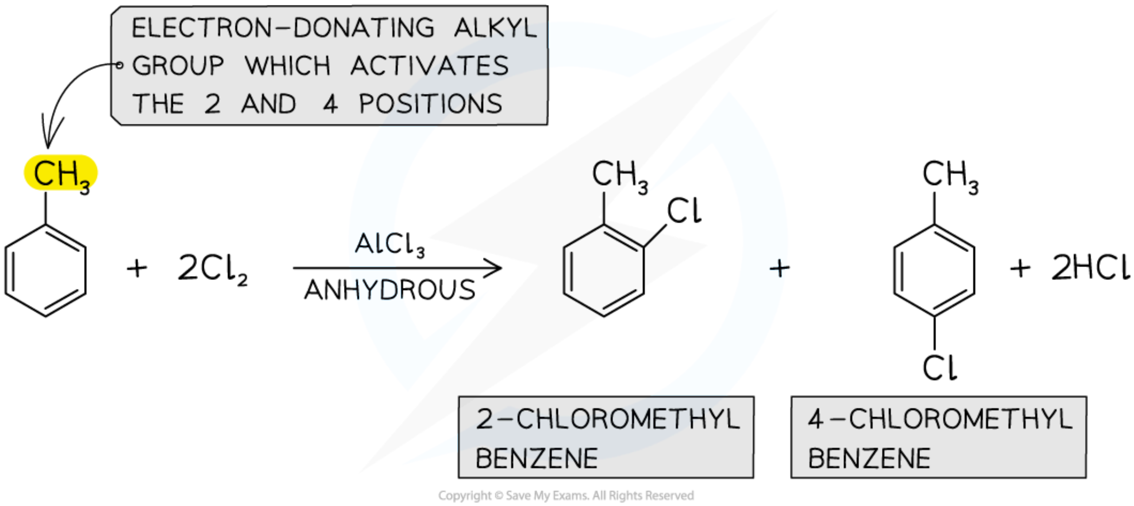
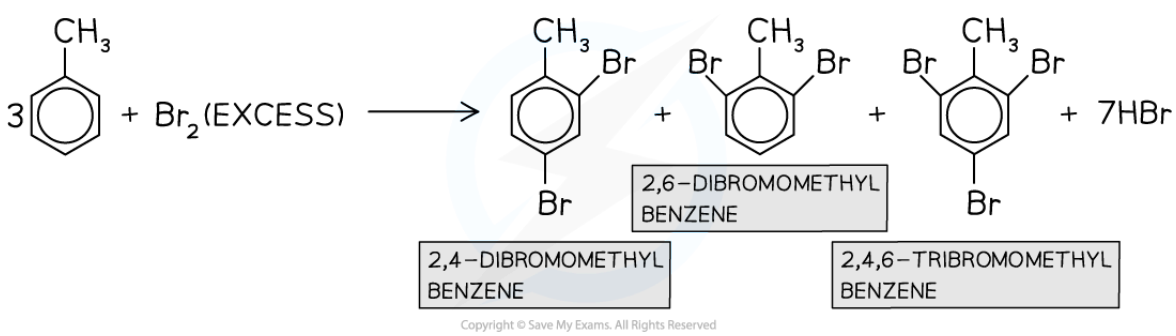


Alkylarenes are substituted on the 2 or 4 position

- **Multiple substitutions** occur when **excess** halogen is used

Halogenation of alkylarenes using an excess of halogen

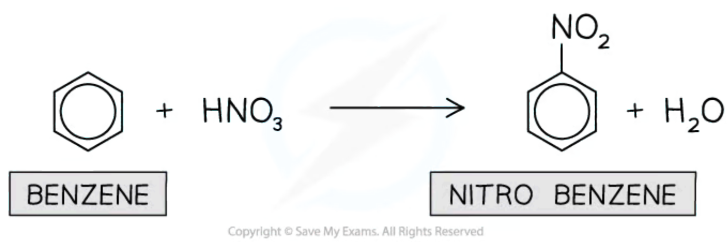


In the presence of excess halogen, multiple substitutions occur

Nitration

- Another example of a substitution reaction is the **nitration** of arenes
- In these reactions, a nitro (-NO_2) group replaces a hydrogen atom on the arene
- The benzene is reacted with a mixture of concentrated nitric acid (HNO_3) and concentrated sulfuric acid (H_2SO_4) at a temperature between 25 and 60 °C

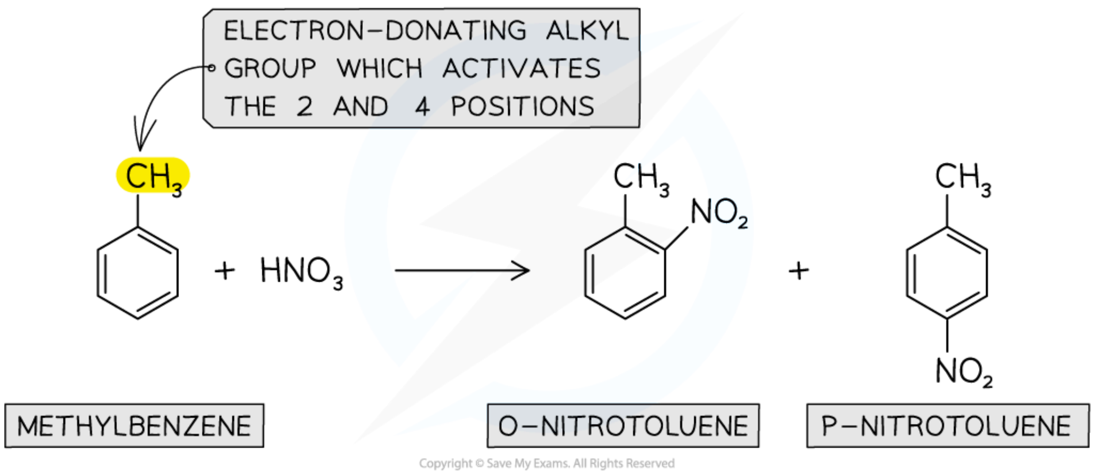
Nitration of benzene



During nitration, a hydrogen atom is replaced by an NO_2 group

- Again, due to the **electron-donating** alkyl groups in alkylarenes, nitration of methylbenzene will occur on the 2 and 4 position

Nitration of alkylarenes

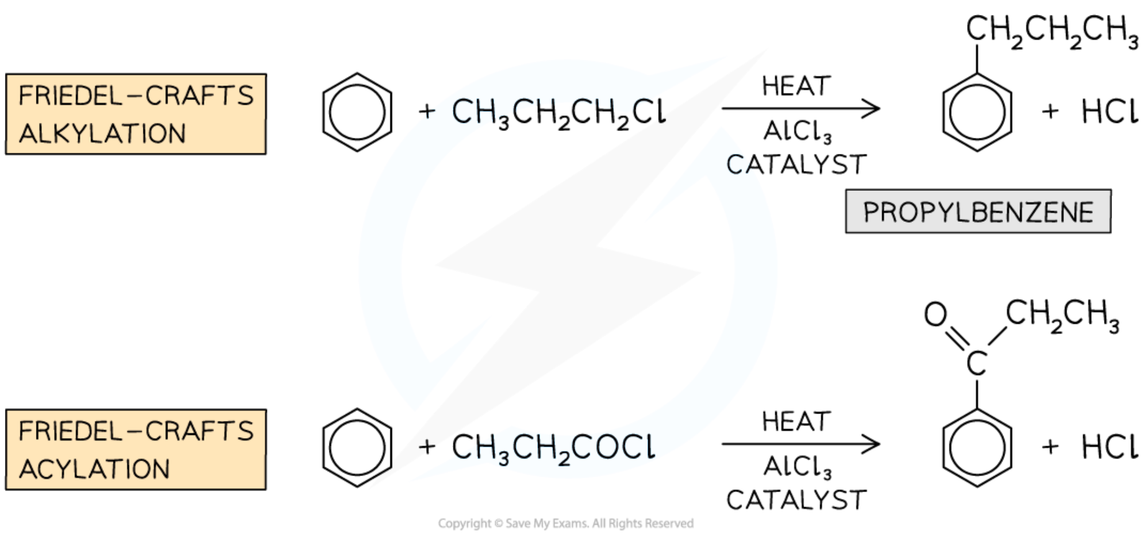


Alkylarenes are nitrated on the 2 or 4 position

Friedel-Crafts reactions

- Friedel-Crafts reactions are also **electrophilic substitution** reactions
- Due to the aromatic stabilisation in arenes, they are often **unreactive**
- To use arenes as **starting materials** for the synthesis of other organic compounds, their structure, therefore, needs to be changed to turn them into more reactive compounds
- Friedel-Crafts reactions can be used to substitute a hydrogen atom in the benzene ring for an **alkyl group** (Friedel-Crafts alkylation) or an **acyl group** (Friedel-Crafts acylation)
- Like any other electrophilic substitution reaction, the Friedel-Crafts reactions consist of three steps:
    1. Generating the electrophile
    2. Electrophilic attack on the benzene ring
    3. Regenerating aromaticity of the benzene ring

Examples of Friedel-Crafts alkylation and acylation reactions



During alkylation, an alkyl / R group is substituted on the benzene ring and during acylation, an acyl / RCO group is substituted on the benzene ring

Friedel-Crafts alkylation

- In this type of Friedel-Crafts reaction, an **alkyl chain** is substituted into the benzene ring
- The benzene ring is reacted with a chloroalkane in the presence of an $AlCl_3$ catalyst
- An example of an alkylation reaction is the reaction of benzene with chloropropane ($CH_3CH_2CH_2Cl$) to form propylbenzene

Example of a Friedel-Crafts alkylation reaction

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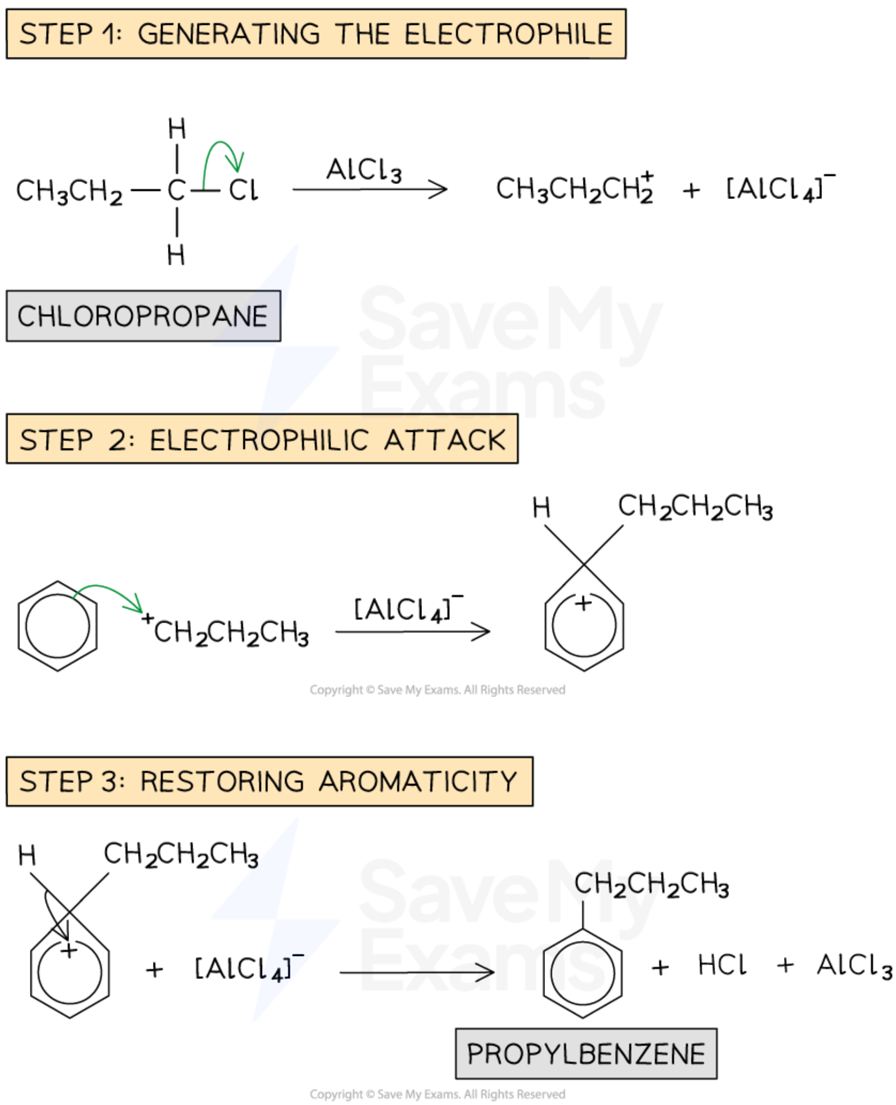

Alkylation reactions of benzene follow the 3 steps of electrophile generation, electrophilic attack and regeneration of aromaticity

Friedel-Crafts acylation

- In the Friedel-Crafts acylation reaction, an **acyl group** is substituted into the benzene ring
  - An acyl group is an alkyl group containing a carbonyl, C=O group
- The benzene ring is reacted with an acyl chloride in the presence of an $AlCl_3$ catalyst
- An example of an acylation reaction is the reaction of methylbenzene with propanoyl chloride to form an acyl benzene
  - Note that the acyl group substitutes on the 4 position due to the $-CH_3$ group on the benzene

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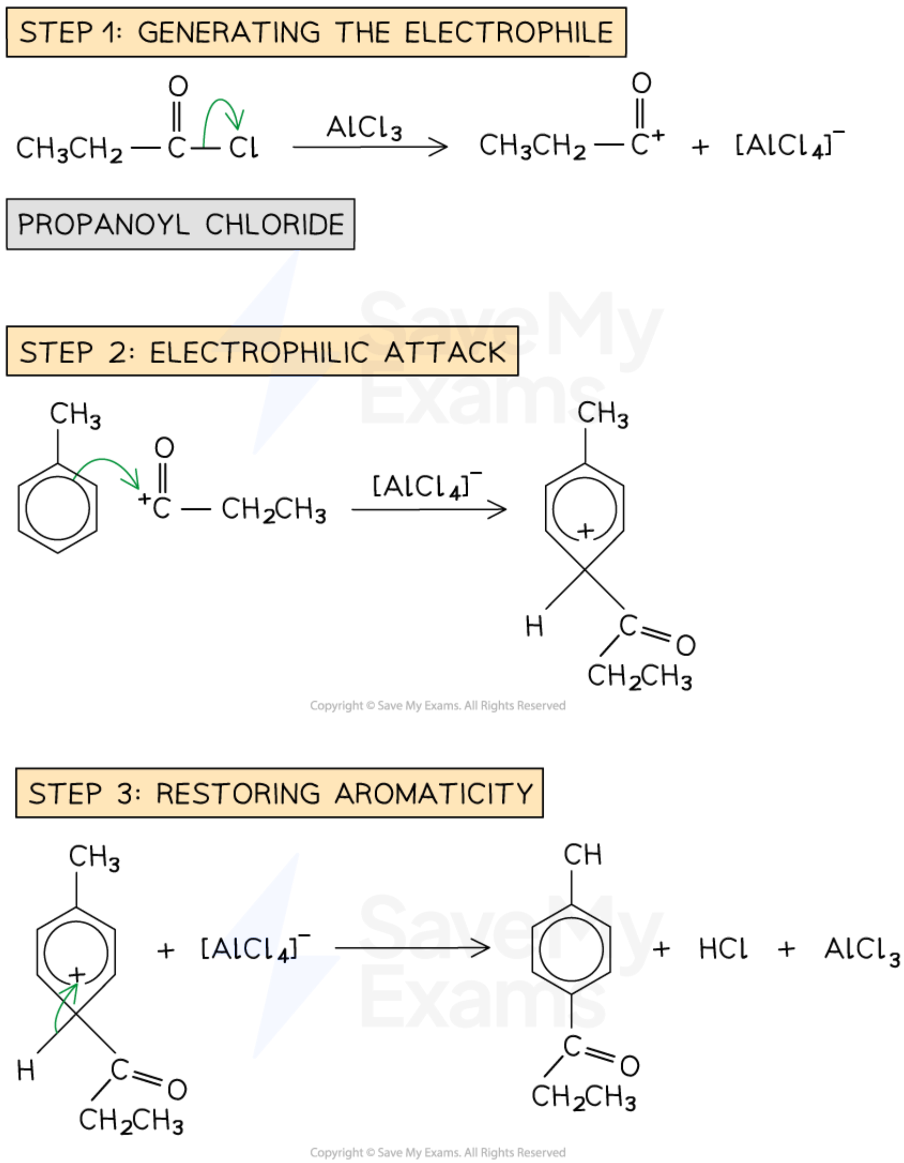
Example of a Friedel-Crafts acylation reaction



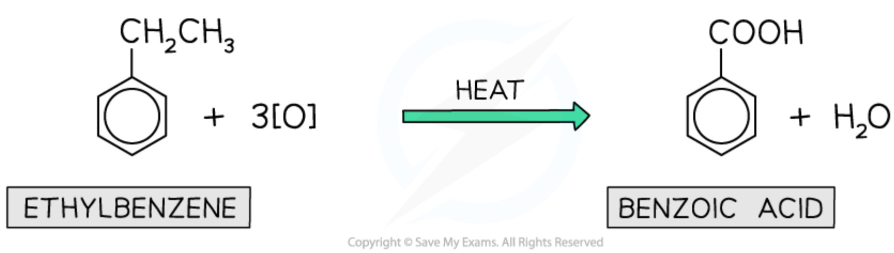
Acylation reactions of benzene follow the same 3 steps of electrophile generation, electrophilic attack and regeneration of aromaticity

Complete oxidation

- Normally, alkanes are not **oxidised** by **oxidising agents** such as potassium manganate(VII) ($KMnO_4$)
- However, the presence of the benzene ring in **alkyl arenes** affects the properties of the alkyl side-chain
- The alkyl side-chains in alkyl arenes are **oxidised** to **carboxylic acids** when **refluxed** with **alkaline potassium manganate(VII)** and then **acidified** with **dilute sulfuric acid** (H_2SO_4)

- For example, the complete oxidation of **ethylbenzene** forms **benzoic acid**

Oxidation of alkylarenes

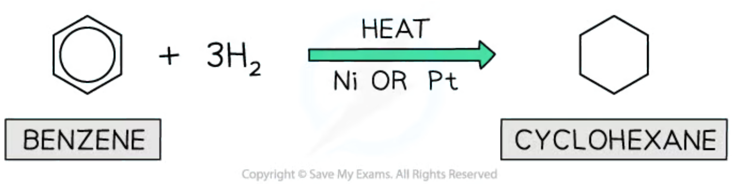


The complete oxidation of alkyl side chains in arenes gives a carboxylic acid

Hydrogenation

- The hydrogenation of benzene is an **addition reaction**
- Benzene is **heated** with **hydrogen gas** and a **nickel** or **platinum catalyst** to form **cyclohexane**

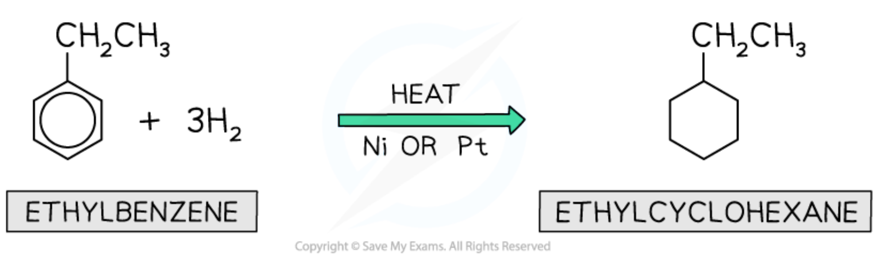
Hydrogenation of benzene



Hydrogenation of benzene results in a loss of aromaticity

- The same reaction occurs when **ethylbenzene** undergoes hydrogenation to form **cycloethylbenzene**

Hydrogenation of methylbenzene



Hydrogenation of alkylarenes also results in a loss of aromaticity

Summary of Reactions of Arenes Table

Reaction	Conditions	Products

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Halogenation	Cl_2 with an $AlCl_3$ catalyst Br_2 with an $AlBr_3$ catalyst	Aryl halide
Nitration	A mixture of concentrated H_2SO_4 and concentrated HNO_3 Temperature between 25 °C and 60 °C	Nitroarene
Friedel-Crafts alkylation	Halogenoalkane and anhydrous $AlCl_3$ catalyst	Alkylbenzene
Freidel-Crafts acylation	Acyl chloride and anhydrous $AlCl_3$ catalyst	Acylbenzene
Complete oxidation	Hot, alkaline $KMnO_4$ and then dilute acid	Benzoic acid
Hydrogenation	Heating with hydrogen and Pt / Ni catalyst	Cyclohexane

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Electrophilic Substitution of Arenes

Electrophilic Substitution of Arenes

- The **electrophilic substitution** reaction in arenes consists of **three steps**:
  1. Generation of an **electrophile**
  2. **Electrophilic attack**
  3. Regenerating **aromaticity**

Generation of an electrophile

- The **delocalised π system** is extremely stable and is a region of **high electron density**
- Consequently, the first step of an electrophilic substitution reaction involves the generation of an electrophile
  - The electrophile can be a positive ion or the positive end of a polar molecule
- There are numerous electrophiles which can react with benzene:

Table of electrophiles commonly used with benzene

Reaction type	Electrophile*
halogenation	X^+, e.g. Cl^+
nitration	NO_2^+
Friedel-Craft's alkylation	R^+
Friedel-Craft's acylation	$R\text{-}C{=}O^+$

- Typically electrophiles cannot simply be added to the reaction mixture
  - The electrophile is produced **in situ**, by adding appropriate reagents* to the reaction mixture

Electrophilic attack

- A pair of electrons from the benzene ring is donated to the electrophile to form a **covalent bond**
- This disrupts the aromaticity in the ring as there are now only four π electrons and there is a **positive charge** spread over the five carbon atoms

Regenerating aromaticity

- In the **final step** of electrophilic substitution, the aromaticity of the benzene ring system is restored
- This happens by **heterolytic cleavage** of the C-H bond
  - This means that the electrons in this bond go into the benzene π bonding system

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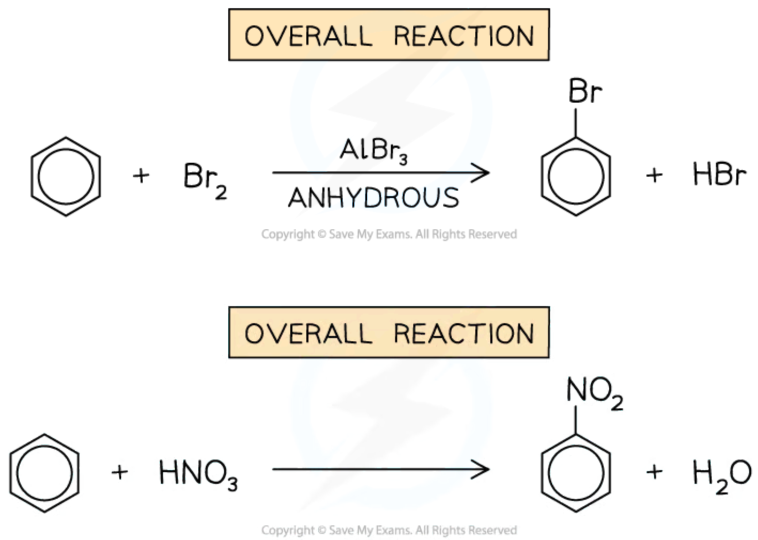
Electrophilic substitution mechanism

- The **halogenation** and **nitration** of arenes are both examples of **electrophilic substitution reactions**
  - A hydrogen atom is replaced by a halogen atom or a nitro (-NO_2) group

Bromination and nitration of benzene

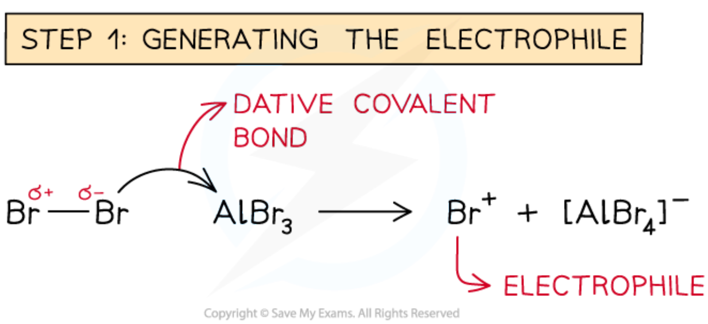


During bromination, a hydrogen atom is substituted by a bromine atom and during nitration, a hydrogen atom is substituted by a nitro group

Step 1: Generating the Br^+ and NO_2^+ electrophiles

- For the **halogenation** reaction:
  - This is achieved by reacting the halogen with a **halogen carrier**
  - The halogen molecules form a **dative bond** with the halogen carrier by donating a lone pair of electrons from one of its halogen atoms into an empty 3p orbital of the halogen carrier

Step 1 of the halogenation of arenes



During bromination, an $AlBr_3$ halogen carrier catalyst is used and during chlorination an $AlCl_3$ halogen carrier catalyst is used

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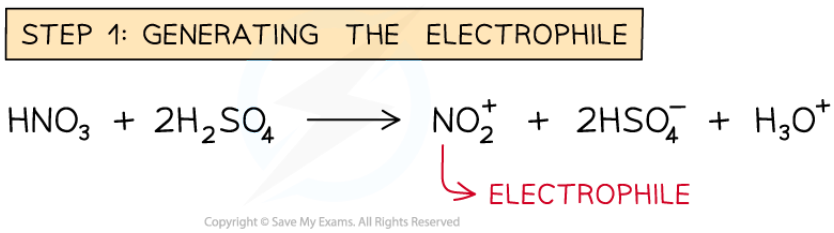
- For the **nitration** reaction:
  - The electrophile **NO_2^+ ion** is generated by reacting it with concentrated **nitric acid** (HNO_3) and **concentrated sulfuric acid** (H_2SO_4)

Step 1 of the nitration of arenes

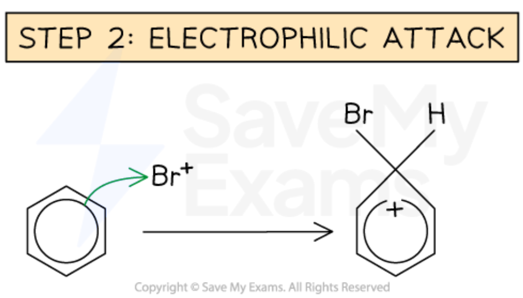


During nitration, concentrated nitric acid and concentrated sulfuric acid react to form the NO_2^+ electrophile

Step 2: Electrophilic attack by the Br^+ and NO_2^+ electrophiles

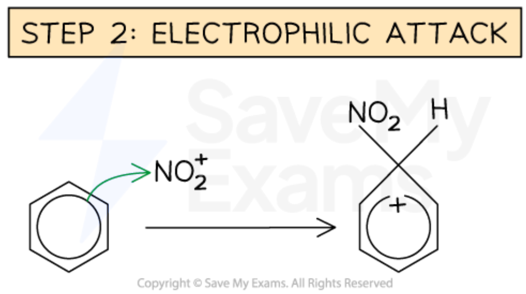
- Once the electrophile has been generated, it will carry out an **electrophilic attack** on the benzene ring
  - The nitrating mixture of HNO_3 and H_2SO_4 is **refluxed** with the arene at 25 - 60 °C
- A pair of electrons from the benzene ring is donated to the electrophile to form a **covalent bond**
  - This disrupts the aromaticity in the ring as there are now only four π electrons and there is a **positive charge** spread over the five carbon atoms

Step 2 of the halogenation of arenes



A pair of electrons from the benzene ring is donated to the Br^+ electrophile to form a covalent bond causing a loss in aromaticity

Step 2 of the nitration of arenes

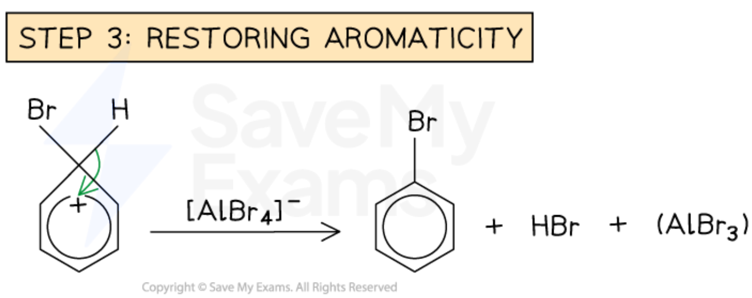


A pair of electrons from the benzene ring is donated to the NO_2^+ electrophile to form a covalent bond causing a loss in aromaticity

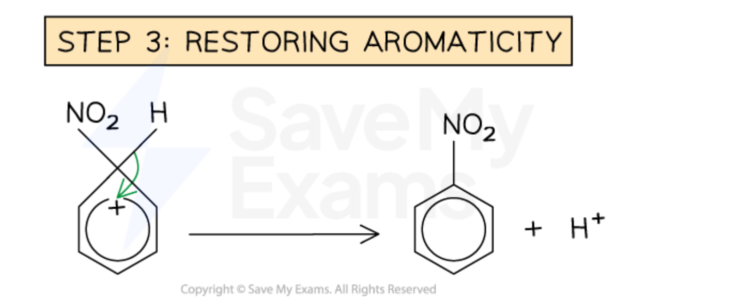
Step 3: Regenerating / restoring aromaticity

- In the **final step** of the reaction, this aromaticity is restored by **heterolytic cleavage** of the C-H bond
  - This means that the bonding pair of electrons goes into the benzene π bonding system

Step 3 of the halogenation of arenes



Step 3 of the nitration of arenes



In both reactions, the C–H bond of the substituted carbon atom breaks and the electrons go back into the benzene π bonding system, restoring aromaticity

Addition reactions of arenes

- The **delocalisation of electrons** (also called **aromatic stabilisation)** in arenes is the main reason why arenes predominantly undergo **substitution** reactions over **addition** reactions
- In substitution reactions, the **aromaticity** is restored by **heterolytic cleavage** of the C-H bond
- In addition reactions, on the other hand, the aromaticity is **not restored** and is in some cases **completely lost**
    - The **hydrogenation** of arenes is an example of an addition reaction during which the aromatic stabilisation of the arene is completely lost
    - The cyclohexane formed is **energetically less stable** than the benzene

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Location of Halogenation on Arenes

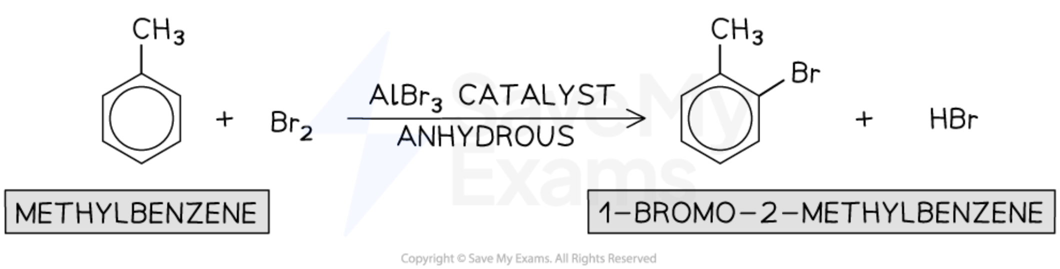
Halogenation in Arenes

- Arenes will undergo s**ubstitution reactions** with halogens to form aryl halides
  - This reaction is also called a **halogenation** reaction
- Depending on the reaction conditions, halogenation can occur:
  - In the aromatic ring
  - In the side chain

Halogenation in the aromatic ring

- Halogenation of alkylarenes **in the aromatic ring** will occur when a halogen and anhydrous halogen carrier catalyst (such as $AlBr_3$ or $AlCl_3$) is used

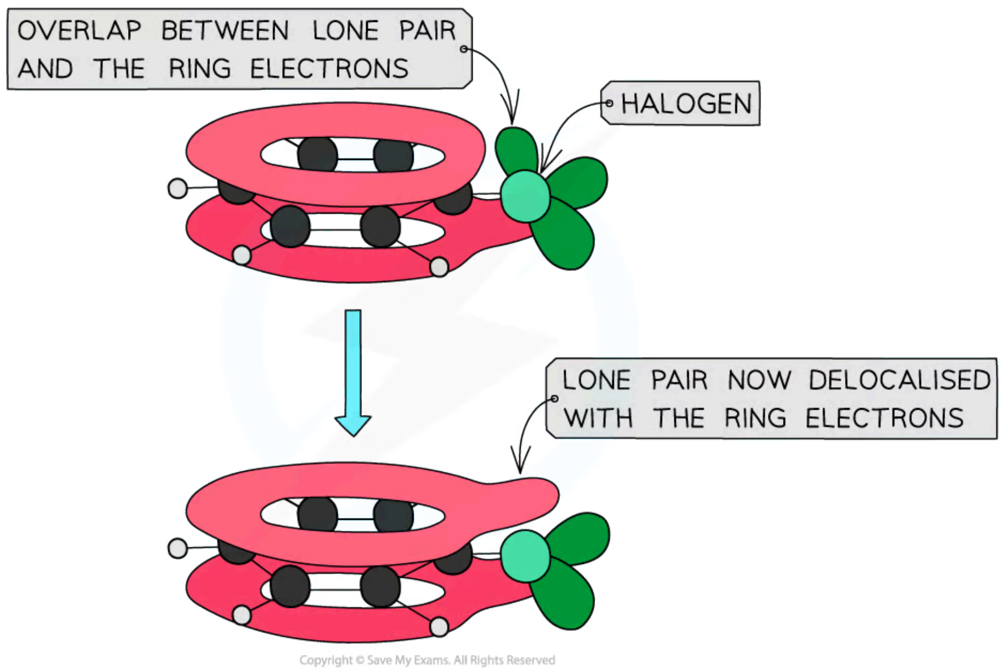
Halogenation of alkylarenes in the aromatic ring



A halogen carrier catalyst is used to generate the electrophile for the halogenation of alkylarenes

- Aryl halides are **less reactive** than **halogenoalkanes** as the **carbon-halogen** bond in aryl halides is **stronger**
- This is due to the partial overlap of the lone pairs on the halogen atom with the π system in the benzene ring
- The carbon-halogen bond, therefore, has a **partial double bond character**

The lack of reactivity in alkylarenes / aryl halides

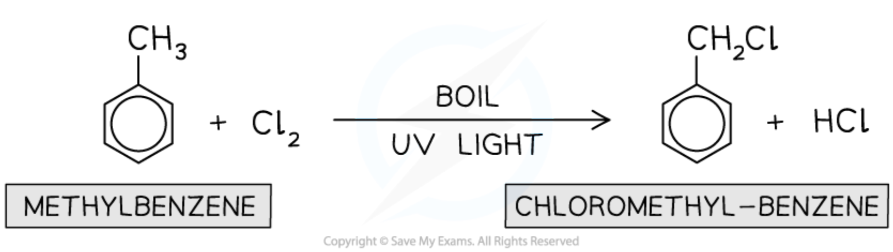


Aryl halides are unreactive due to the partial double bond character of the carbon-halogen bond

Halogenation in the side chain

- Halogenation of alkylarenes **in the side chain** will occur when the halogen is passed into **boiling alkylarene i**n the presence of **ultraviolet** (UV) **light**
  - This is a **free-radical substitution** reaction

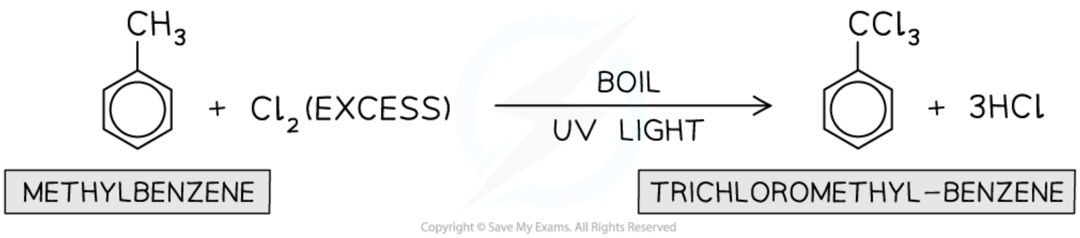
Halogenation of an alkylarene side chain



Halogenation of alkylarenes in the side chain is an example of a free-radical substitution reaction

- If **excess** halogen is used, all hydrogen atoms on the alkyl side-chain will be substituted by the halogen atoms

Halogenation of an alkylarene side chain using excess halogen



In excess halogen, all hydrogen atoms on the alkyl side-chain will be replaced

- **Note** that no substitution into the benzene ring occurs under these conditions

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Directing Effects of Substituents on Arenes

The Directing Effects of Substituents on Arenes

- Arenes readily undergo **electrophilic substitution** of one of their hydrogen atoms with another species
- **Substituents** that are already present on the arenes can affect where the substitution of the hydrogen atom on the arene takes place
  - These groups are said to **direct** substitution reactions to different **ring positions**

Electron-withdrawing & electron-donating groups

- The substituents on the arenes can either be **electron-withdrawing** or **electron-donating groups**
- Electron-withdrawing substituents **remove** electron density **from** the π system in the benzene ring making it **less reactive**
  - These groups **deactivate** attack by electrophiles and **direct** the incoming electrophile to attack the 3 and/or 5 positions
  - For example, the nitro group in nitrobenzene is an electron-withdrawing group
    - Upon bromination of nitrobenzene, the bromine electrophile will be directed to the 3 and/or 5 position
    - The products are 3-bromonitrobenzene and 5-bromonitrobenzene
- Electron-donating substituents **donate** electron density **into** the π system of the benzene ring making it **more reactive**
  - These groups **activate** attack by electrophiles and **direct** the incoming electrophile to attack the 2, 4 and/or 6 positions
  - For example, the methyl group in methylbenzene is an electron-donating group
    - Upon bromination of methylbenzene, the bromine electrophile will be directed to the 2 and/or 4 position
    - The products are 2-bromomethylbenzene and 4-bromomethylbenzene

Electron-withdrawing & electron-donating substituents table

	Substituents	Activated positions
Electron withdrawing	$-NO_2$ $-COOH$ $-COR$	3 and / or 5
Electron donating	$-R$ $-OH$ $-NH_2$	2, 4 and / or 6