Edexcel International A Level (IAL) Chemistry

Your notes

Organic Chemistry: Arenes

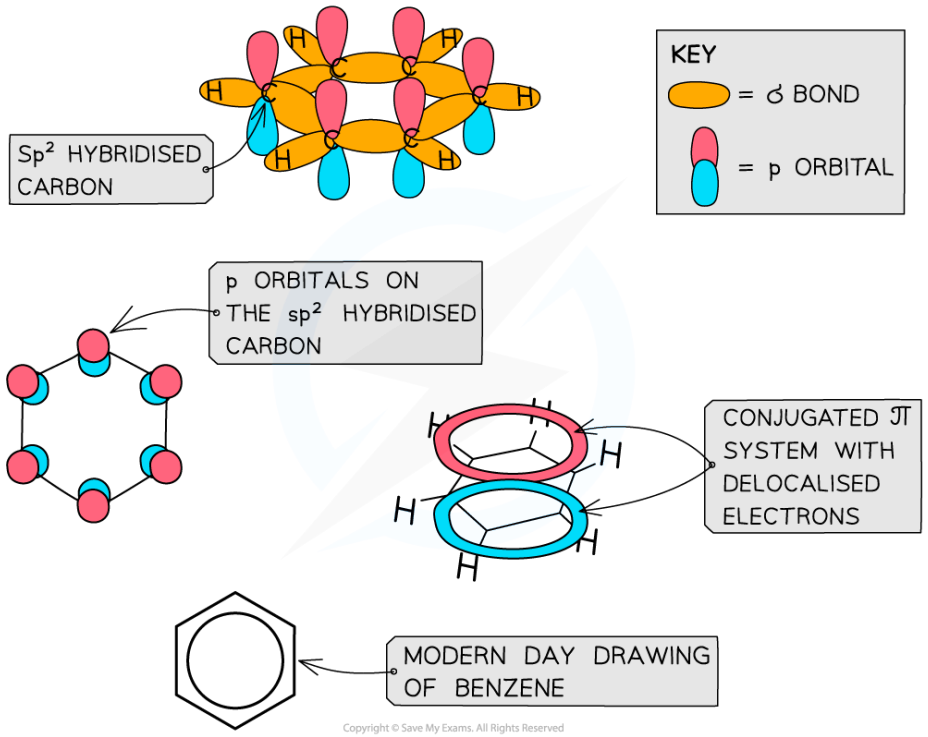
Contents

Your notes

Benzene – Structure & Stability

Structure of Benzene

- The structure of benzene was determined many years ago, by a chemist called Kekule
- The structure consists of 6 carbon atoms in a hexagonal ring, with alternating single and double carbon-carbon bonds
  - This suggests that benzene should react in the same way that an unsaturated alkene does
  - However, this is not the case



Like other aromatic compounds, benzene has a planar structure due to the sp^2 hybridisation of carbon atoms and the conjugated π system in the ring

- Each carbon atom in the ring forms three σ bonds using the sp^2 orbitals
- The remaining **p orbitals** overlap laterally with p orbitals of neighbouring carbon atoms to form a π system
- This extensive sideways overlap of p orbitals results in the electrons being delocalised and able to freely spread over the entire ring causing a π system
  - The π system is made up of two ring-shaped clouds of electron density - one above the plane and one below it

- Benzene and other aromatic compounds are **regular** and **planar** compounds with bond angles of 120 °
- The delocalisation of electrons means that all of the carbon-carbon bonds in these compounds are identical and have both **single** and **double bond** character
- The bonds all being the same length is evidence for the delocalised ring structure of benzene

Your notes

Evidence for delocalisation

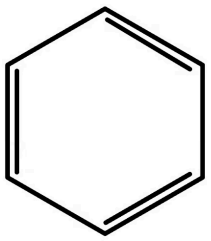
- This evidence of the bonding in benzene is provided by data from:
  - Enthalpy changes of hydrogenation
  - Carbon-carbon bond lengths from X-ray diffraction
  - Saturation tests
  - Infrared spectroscopy

Enthalpy changes of hydrogenation

- Hydrogenation of cyclohexene
  - Each molecule has one C=C double bond
  - The enthalpy change for the reaction of cyclohexene is -120 kJ mol^{-1}

$$C_6H_{10} + H_2 \rightarrow C_6H_{12} \quad \Delta H^{\ominus} = -120 \text{ kJ mol}^{-1}$$

- Hydrogenation of benzene
  - The Kekulé structure of benzene as cyclohexa-1,3,5–triene has three double C=C bonds:



- It would be expected that the enthalpy change for the hydrogenation of this structure would be three times the enthalpy change for the one C=C bond in cyclohexene

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12} \quad \Delta H^{\ominus} = 3 \times -120 \text{ kJ mol}^{-1} = -360 \text{ kJ mol}^{-1}$$

- When benzene is reacted with hydrogen, the enthalpy change obtained is actually far less exothermic, $\Delta H^{\ominus} = -208 \text{ kJ mol}^{-1}$

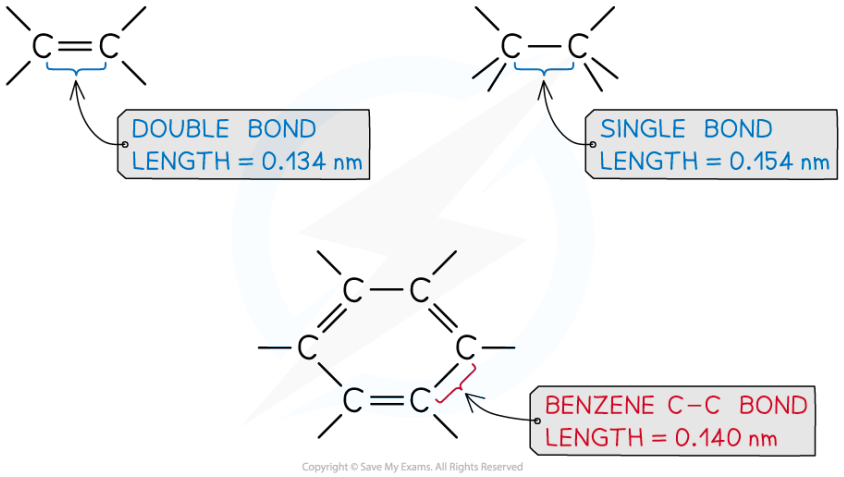
Carbon–carbon bond lengths

- Cyclohexene contains two different carbon-carbon bonds

- The single carbon-carbon bond (C-C) has a bond length of 154 pm
- The double carbon-carbon bond (C=C) has a bond length of 134 pm

Your notes

- The Kekulé structure of benzene as cyclohexa-1,3,5-triene has three single C-C and three double C=C bonds
  - It would be expected that benzene would have an equal mixture of bonds with lengths of 134pm and 154 pm



- All of the carbon-carbon bond lengths are 140 pm suggesting that they are all the same and also intermediate of the single C-C and double C=C bonds

Saturation tests

- Cyclohexene will decolourise bromine water as an electrophilic addition reaction takes place
- The Kekulé structure of benzene as cyclohexa-1,3,5-triene has three double C=C bonds
  - It would, therefore, be expected that benzene would easily decolourise bromine water
- Benzene does not decolourise bromine water suggesting that there are no double C=C bonds

Infrared spectroscopy

- Cyclohexene shows a peak at around 1650 cm^{-1} for the double C=C bond within its structure
- The Kekulé structure of benzene as cyclohexa-1,3,5-triene has three double C=C bonds
  - It would, therefore, be expected to also show a peak at around 1650 cm^{-1} for the double C=C bonds
- Benzene does not show a peak at around 1650 cm^{-1} for the double C=C bonds, instead, peaks are seen at around 1450, 1500 and 1580 cm^{-1} which are characteristic of double C=C bonds in arenes

Bromination Resistance

Your notes

- Alkenes tend to undergo bromination easily which can be observed in cyclohexene

$$C_6H_{10} + Br_2 \rightarrow C_6H_{10}Br_2$$

- As the π bond contains localised electrons, it produces an area of high electron density allowing it to repel the electron in the bromine molecule
- Therefore a dipole is introduced making one bromine atom δ+ and one δ- bromine atom
- The δ+ bromine is attracted to the π bond in the cyclohexene
- This then leaves a carbocation in the intermediate molecule which the negative bromide ion is attracted to, hence forming 1,2-dibromocyclohexane by electrophilic addition
- In benzene, there are no localised areas of high electron density, preventing it from being able to polarise the bromine moelcule
- In order for benzene to undergo electrophilic substitution with bromine, a halogen carrier must be present in the reaction e.g. $AlBr_3$

Your notes

Benzene – Reactions

Reaction with oxygen

- Hydrocarbons will burn in air or oxygen to produce carbon dioxide and water providing sufficient oxygen is available
- Benzene will also follow this pattern

$$2C_6H_6\,(l) + 15O_2\,(g) \rightarrow 12CO_2\,(g) + 6H_2O\,(g)$$

- Given that a large volume of oxygen is required for this reaction, incomplete combustion could occur
  - Therefore unreacted benzene may remain
- This would lead to a smokey yellow flame as there would be insufficient oxygen available

Halogenation

- The nature of benzene is different to other unsaturated compounds such as alkenes and halogenation via electrophilic addition is not possible
- Therefore aromatic compounds will react with halogens in the presence of a **metal halide carrier**
  - iron(III) bromide
  - aluminium chloride
- The reaction of the metal halide carrier acts as a catalyst and creates the electrophile, X^+ (where X represents a halogen atom)
- At the end of the reaction it is regenerated

$$AlCl_3 + Cl_2 \rightarrow AlCl_4^- + Cl^+$$

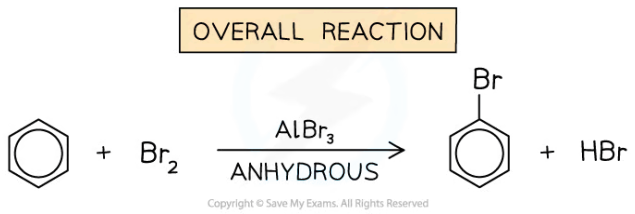
$$FeBr_3 + Br_2 \rightarrow FeBr_4^- + Br^+$$

- The overall equation for halogenation is

$$C_6H_6 + X_2 \rightarrow C_6H_5X + HX$$

Or with Br_2 in the presence of a $AlBr_3$

$$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$$



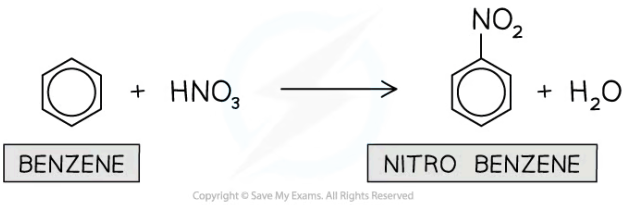
Bromination of benzene

- Remember that one hydrogen atom on the benzene ring has been substituted for one halogen atom, therefore HX will be a product

Your notes

Nitration

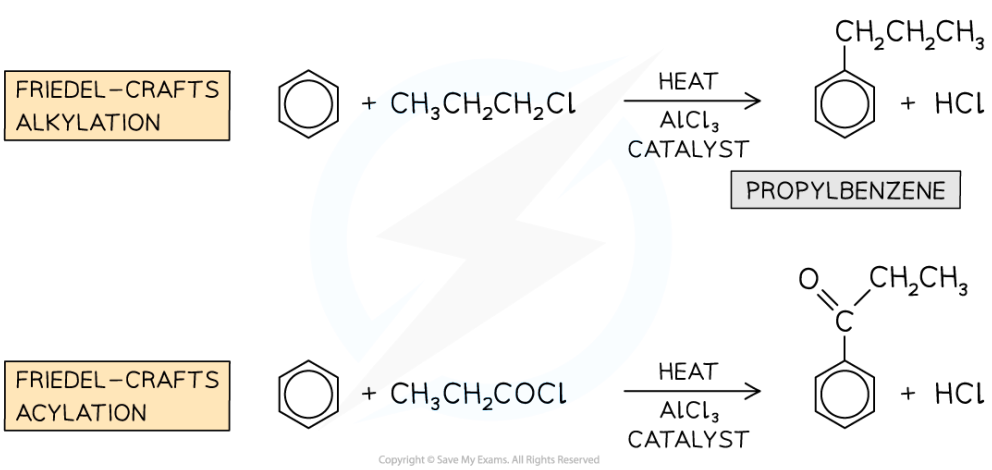
- Another example of a substitution reaction is the **nitration** of arenes
- In these reactions, a nitro (-NO_2) group replaces a hydrogen atom on the arene
- The benzene is reacted with a mixture of concentrated nitric acid (HNO_3) and concentrated sulfuric acid (H_2SO_4) at a temperature between 25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



Nitration of benzene

Friedel-Crafts Reactions

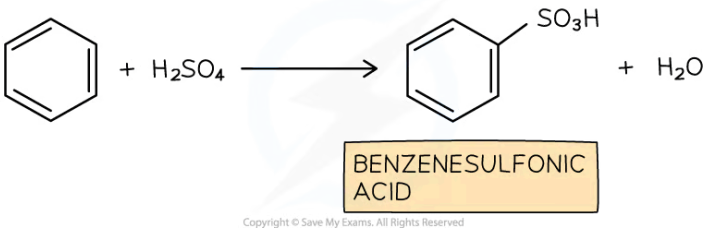
- Friedel-Crafts reactions are also substitution reactions
- Due to the aromatic stabilisation in arenes, they are often **unreactive**
- To use arenes as **starting materials** for the synthesis of other organic compounds, their structure, therefore, needs to be changed to turn them into more reactive 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:
  - Generating the electrophile
  - Electrophilic attack on the benzene ring
  - Regenerating aromaticity of the benzene ring



Examples of Friedel-Crafts alkylation and acylation reactions

Sulfonation

- Another example of a substitution reaction is the **sulfonation** of arenes
- In these reactions, a sulfonyl group ($-SO_3H$) replaces a hydrogen atom on the arene
- The benzene is warmed with a fuming sulfuric acid at a temperature of 40 °C for around 30 minutes
  - The fuming sulfuric acid is made by dissolving sulfur trioxide in concentrated sulfuric acid



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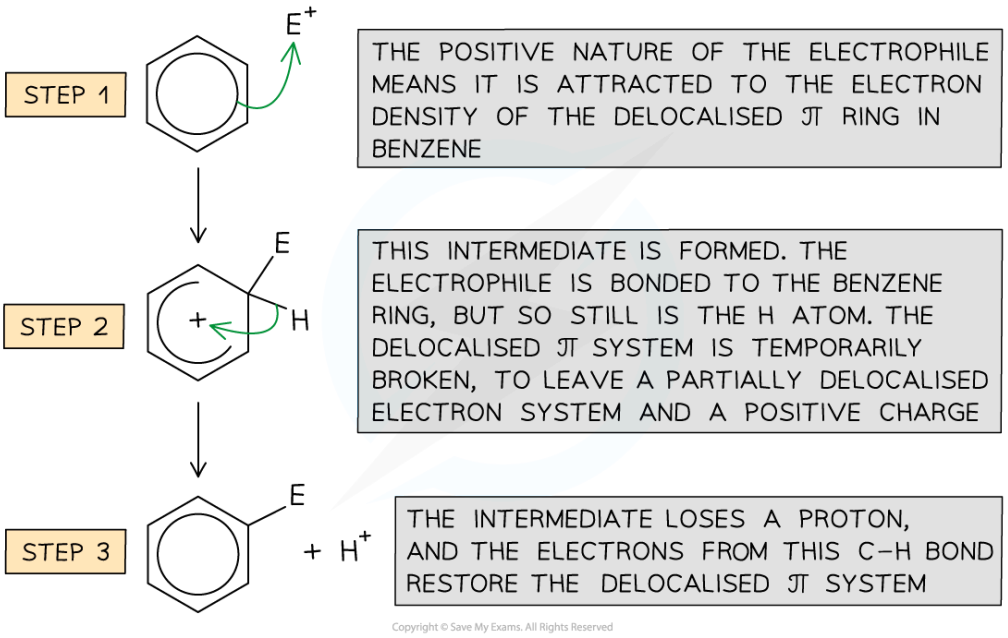
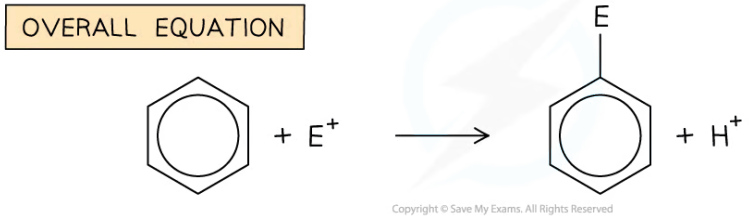
Benzene - Electrophilic Substitution

- The main reactions which benzene will undergo include the replacement of one of the 6 hydrogen atoms from the benzene ring
  - This is different to the reactions of unsaturated alkenes, which involve the double bond breaking and the electrophile atoms 'adding on' to the carbon atoms
- These reactions are called electrophilic substitution reactions
  - This is where at least one of the H atoms of benzene are substituted by the electrophile
- You must be able to provide the mechanisms for specific examples of the electrophilic substitution of benzene

General Electrophilic Substitution Mechanism:





- The delocalised π system is extremely stable and is a region of high electron density

- Electrophilic substitution reactions involve an electrophile, which is either a positive ion or the positive end of a polar molecule
- There are numerous electrophiles which can react with benzene
  - However, they usually cannot simply be added to the reaction mixture to then react with benzene
  - The electrophile has to be produced in situ, by adding appropriate reagents to the reaction mixture
- The **electrophilic substitution** reaction in arenes consists of **steps**:
  - Generation of an **electrophile**
  - **Electrophilic attack**
  - Regenerating **aromaticity**

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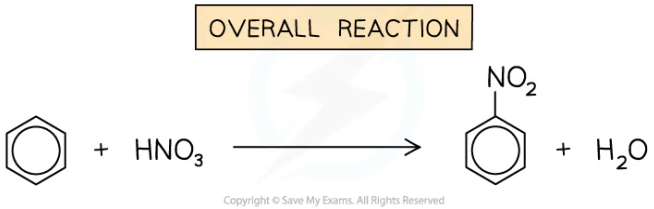
Nitration of benzene mechanism

- One hydrogen atom is substituted by a nitro group - NO_2
- The overall reaction is:

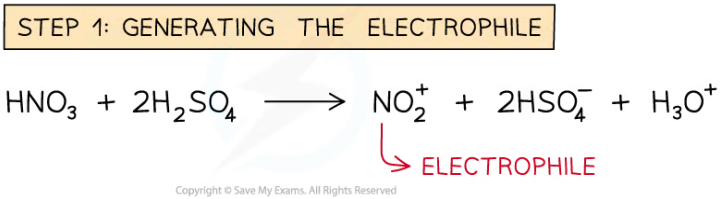


$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

- The reaction is conducted under reflux at 55 °C or 60 °C

Step 1: Electrophile generation

- The electrophile **NO_2^+** ion is generated by reacting **concentrated** nitric acid (HNO_3) and **concentrated** sulfuric acid (H_2SO_4)
- The equation for the generation of the electrophile is:



Examiner Tips and Tricks

There are 2 accepted equations for the formation of the eletrophile:

$$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$$

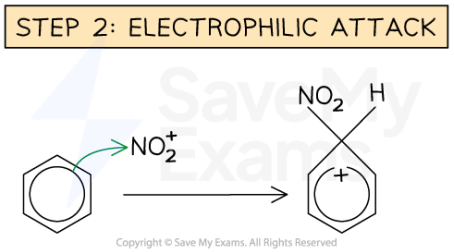
OR

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

Your notes

Step 2: 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



A pair of electrons from the benzene ring is donated to the nitronium ion electrophile forming a covalent bond and a loss in aromaticity

Examiner Tips and Tricks

Examiners are looking for very specific points in an electrophilic substitution mechanism:

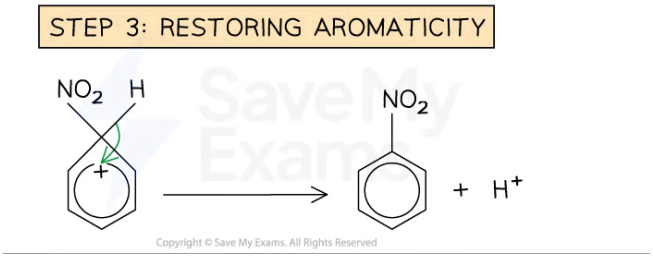
1. The initial arrow:
   - The curly arrow must start from on or within the circle/hexagon of the benzene ring and point to the NO_2^+ electrophile.
   - Do not forget to draw the + charge on the electrophile.
2. The horseshoe shape:
   - The intermediate must be drawn with a 'horseshoe' (an incomplete circle) that faces the tetrahedral carbon, which is the carbon atom attached to the H and NO_2 group.
3. Horseshoe size:
   - The horseshoe must be large enough to cover at least 3 carbon atoms.
   - Ideally it should cover the 5 carbon atoms that have not been substituted.
4. The charge:

- The positive charge (+) must be drawn inside the horseshoe

Your notes

Step 3: Regenerating / restoring aromaticity

- 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



Examiner Tips and Tricks

The curly arrow must start from the C–H bond and point to anywhere within the ring to show the reforming of the delocalised structure

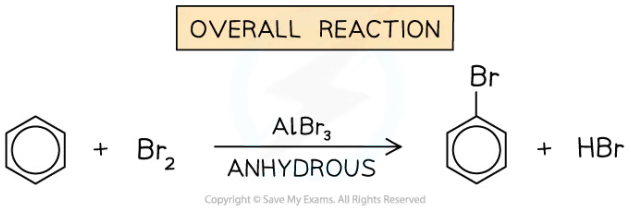
Step 4: Regenerating the catalyst

- The H^+ ion (released in Step 3) reacts to reform the original catalyst:

$$H^+ + HSO_4^- \rightarrow H_2SO_4$$

Halogenation of benzene mechanism

- One hydrogen atom is substituted by a halogen atom
- For bromine, the overall reaction is:

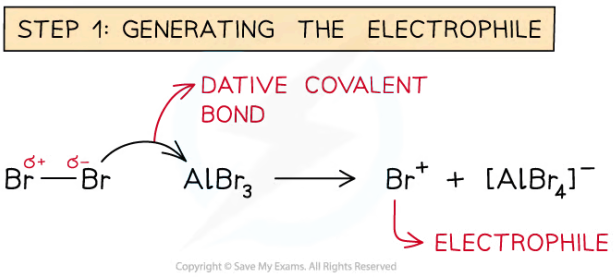


$$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$$

- The reaction is conducted using a halogen carrier catalyst and requires heat / heating under reflux

Step 1: Electrophile generation

- The electrophile **X^+** ion is generated by reacting the halogen with a **halogen carrier**
- The common halogen carriers are:
  - $AlBr_3$
  - $AlCl_3$
  - $FeCl_3$ (or iron and bromine, which react to form $FeBr_3$)
- 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



Your notes

Examiner Tips and Tricks

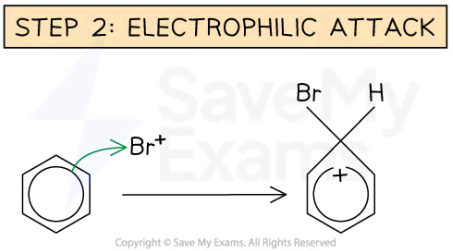
The halogen carrier used must correspond to the halogen that is involved in the substitution reaction:

$$Br\text{-}Br + AlBr_3 \rightarrow Br^+ + [AlBr_4]^-$$

$$Cl\text{-}Cl + FeCl_3 \rightarrow Cl^+ + [FeCl_4]^-$$

Step 2: 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



A pair of electrons from the benzene ring is donated to the bromine ion electrophile forming a covalent bond and a loss in aromaticity

Your notes

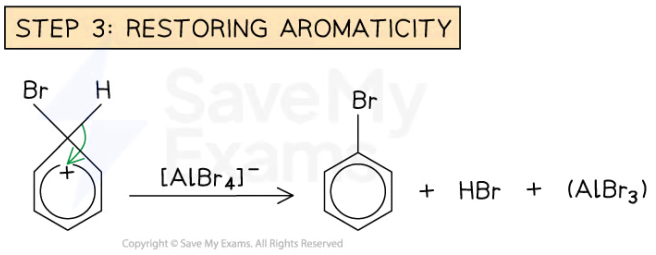
Examiner Tips and Tricks

Examiners are looking for similar specific points to the nitration mechanism:

1. The initial arrow:
    - The curly arrow must start from on or within the circle/hexagon of the benzene ring and point to the Br^+ or Cl^+ electrophile.
    - Do not forget to draw the + charge on the electrophile.
2. The horseshoe shape:
    - The intermediate must be drawn with a 'horseshoe' (an incomplete circle) that faces the tetrahedral carbon, which is the carbon atom attached to the H and halogen atom.
3. Horseshoe size:
    - The horseshoe must be large enough to cover at least 3 carbon atoms.
    - Ideally it should cover the 5 carbon atoms that have not been substituted.
4. The charge:
    - The positive charge (+) must be drawn inside the horseshoe

Step 3: Regenerating / restoring aromaticity

- 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 4: Regenerating the catalyst

- The H^+ ion (released in Step 3) reacts to reform the original catalyst:

$$H^+ + [AlBr_4]^- \rightarrow HBr + AlBr_3$$

Friedel-Crafts acylation of benzene mechanism

- One hydrogen atom on the benzene ring is substituted by an acyl group (e.g., an ethanoyl group, $-COCH_3$).
- For the reaction with ethanoyl chloride, the overall reaction is:

$$C_6H_6 + CH_3COCl \rightarrow C_6H_5COCH_3 + HCl$$

- The reaction is conducted using an anhydrous aluminium chloride ($AlCl_3$) catalyst and requires heating under reflux

Your notes

Step 1: Electrophile generation

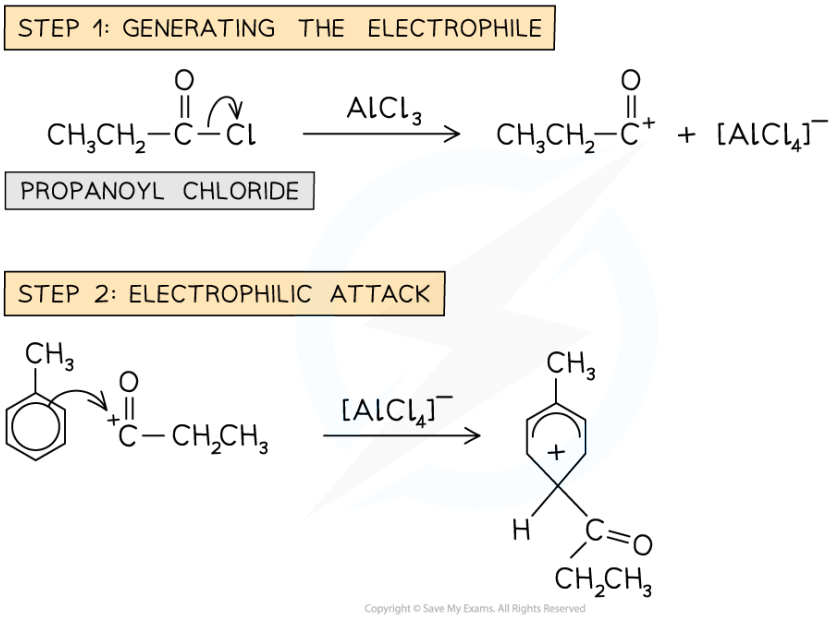
The electrophile is an acylium ion (e.g., CH_3CO^+).

It is generated by reacting the acyl chloride with the halogen carrier catalyst, which accepts a lone pair of electrons from the chlorine atom.

The equation for the generation of the electrophile is:

$$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + [AlCl_4]^-$$

- 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



Step 2: 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.

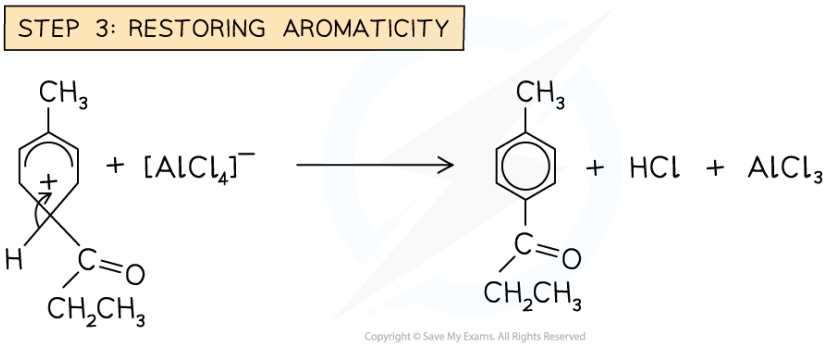
Examiner Tips and Tricks

Examiners are looking for similar specific points to the nitration mechanism:

1. The initial arrow:
    - The curly arrow must start from on or within the circle/hexagon of the benzene ring and point to the positively charged carbon atom of the CH_3CO^+ electrophile.
    - Do not forget to draw the + charge on the electrophile.
2. The horseshoe shape:
    - The intermediate must be drawn with a 'horseshoe' (an incomplete circle) that faces the tetrahedral carbon, which is the carbon atom attached to the H and acyl group.
3. Horseshoe size:
    - The horseshoe must be large enough to cover at least 3 carbon atoms.
    - Ideally it should cover the 5 carbon atoms that have not been substituted.
4. The charge:
    - The positive charge (+) must be drawn inside the horseshoe

Step 3: Regenerating / restoring aromaticity

- 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 4: Regenerating the catalyst

- The H+ ion (released in Step 3) reacts with the complex ion to reform the original catalyst and produce hydrogen chloride gas:

$$H^+ + [AlCl_4]^- \rightarrow HCl + AlCl_3$$

Your notes

Your notes

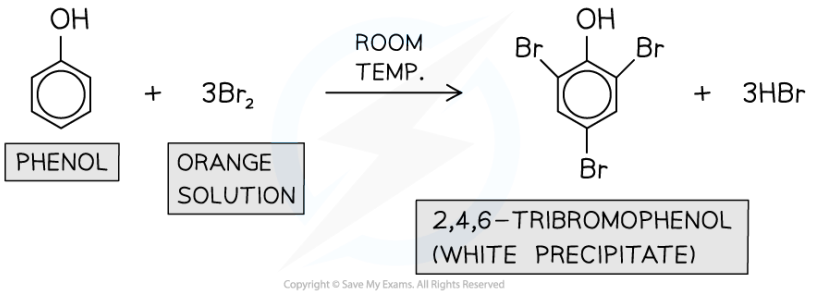
Phenol Bromination

Reactions of the aromatic ring in phenols

- Phenols react more readily with electrophiles compared to benzene
- This is because one of the lone pairs of electrons on the oxygen atom in -OH overlaps with the π bonding system
- This **increases the electron density** of the benzene ring making it more susceptible to electrophilic attack
- The -OH group in phenols is activating and directs incoming electrophiles to the **2, 4, and 6 positions**

Bromination

- Phenols also undergo electrophilic substitution reactions when reacted with bromine water at room temperature
- Phenol **decolourises** the **orange** bromine solution to form a **white precipitate** of 2,4,6–tribromophenol
- This is also known as the **bromination of phenol**



Phenols undergo bromination when reacted with bromine water at room temperature