

# Edexcel IAL Chemistry A-level

## Topic 18: Organic Chemistry – Arenes

Detailed notes

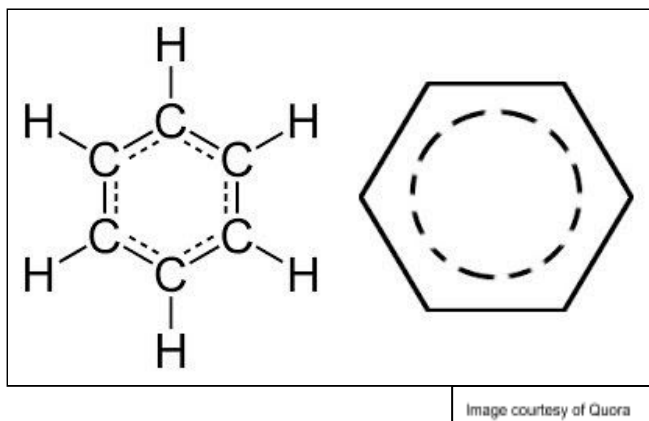
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## Bonding in Aromatic Compounds

Arenes are aromatic compounds that **contain a benzene ring as part of their structure**. They have **high melting points** due to the high stability of the delocalised benzene ring, but **low boiling points** as they are **non-polar** molecules and generally **cannot be dissolved** in water. Benzene is an **arene** consisting of a ring of **six carbon atoms** with **six hydrogen atoms**. This structure means benzene has a ring of **delocalised electrons**:

*Example: Displayed and skeletal formula of benzene*



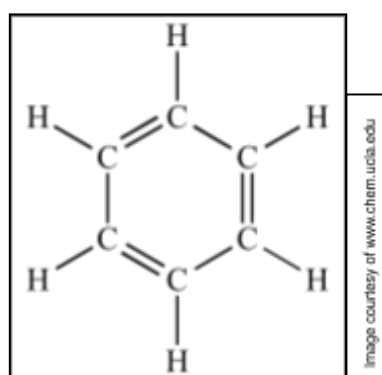
The outer electron from the **p-orbital** of each carbon atom is **delocalised** into the centre to form the central ring. This overlap of electrons results in the formation of  **$\pi$ -bonds**.

The delocalised ring structure makes benzene **very stable** compared to other molecules of a similar size.

## Evidence for Benzene's structure

When benzene was first discovered its structure was unknown. It was predicted from empirical measurements that it had a structure similar to that of **cyclohexatriene**, with three double bonds and three single bonds. However, chemical evidence and experiments suggested benzene actually had the structure given above.

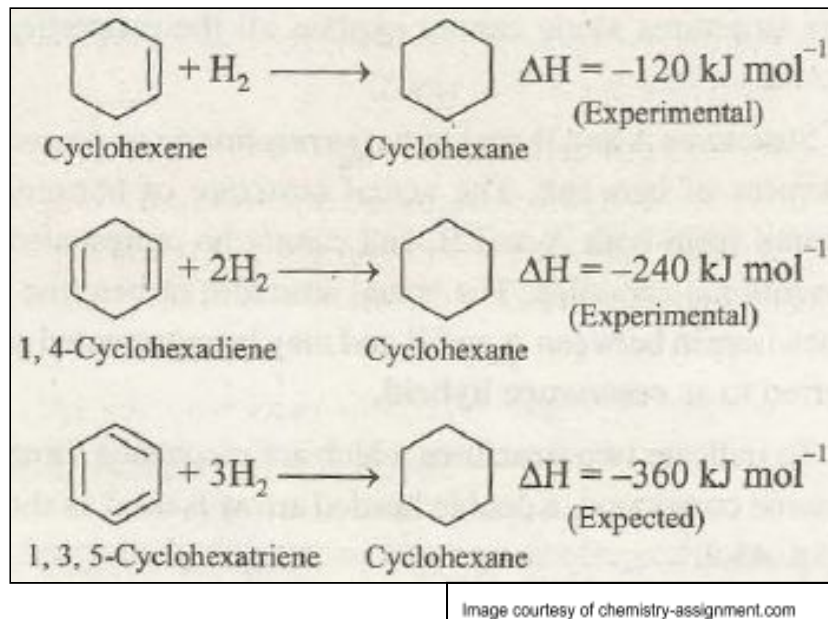
*Example: Displayed formula of cyclohexatriene*



## Thermochemical - Cyclohexatriene vs. Benzene

Based on the structure of cyclohexatriene, the enthalpy change of hydrogenation for benzene was **predicted to be  $-360 \text{ kJ mol}^{-1}$** , three times the enthalpy change of cyclohexene.

*Example:*



It was later discovered that the enthalpy change of hydrogenation of benzene was **actually  $-208 \text{ kJ mol}^{-1}$** , leading to the conclusion that its **structure** was **different** to that of **cyclohexatriene**. The enthalpy change of hydrogenation was **less negative than expected** (less exothermic), indicating that benzene is more stable than the suggested cyclohexatriene structure predicts.

## X-ray Diffraction and Infrared Data

X-ray diffraction experiments have shown that **all** the bond lengths between carbon atoms in benzene are **the same**. If the cyclohexatriene structure was correct, three of the bond lengths would be the length of a **single** carbon bond and three would be the length of a **double** carbon bond. In reality, each bond in the benzene ring has an **intermediate length** in between that of a double and single bond.

The cyclohexatriene structure also did not explain **infrared data** collected from benzene molecules.

## Reactions of Benzene

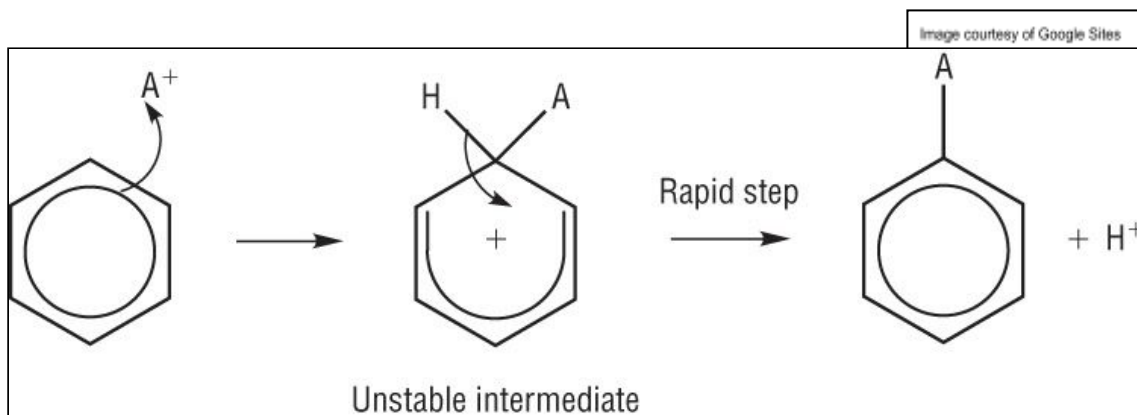
Benzene is resistant to **electrophilic addition** reactions, such as bromination, which other compounds with carbon-carbon double bonds, such as **alkenes**, readily undergo. Benzene does not undergo electrophilic addition since this would involve breaking up the **stable** delocalised ring of electrons.



## Electrophilic Substitution

The delocalised ring in benzene is an **area of high electron density**, making it susceptible to attack from **electrophiles**. In an electrophilic substitution mechanism, electrophiles attack the electron ring, **partially destroying** it, before it is then restored to form the aromatic product. This mechanism allows **aromatic amines** and **nitrobenzene** to be produced from benzene.

### Mechanism - general electrophilic substitution mechanism

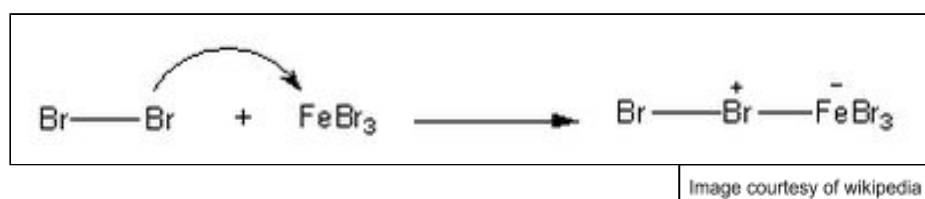


*The electrophile is shown as A<sup>+</sup>.*

## Halogenation

Halogenation is a type of **electrophilic substitution reaction** in which benzene will react with halogens in the presence of a **catalyst**, such as iron(III) bromide (FeBr<sub>3</sub>). The catalyst is required to generate the electrophile, which then reacts as shown above.

*Example: The iron(III) bromide polarises the bromine molecule. This makes it easier for the bromine bond to break so that the bromine atom can act as an electrophile.*

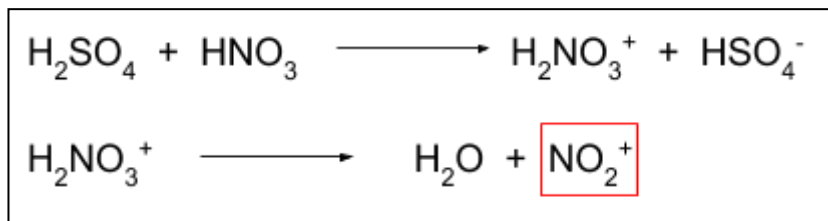


## Nitration

Nitration is a form of electrophilic substitution, where the electrophile is an **NO<sub>2</sub><sup>+</sup> ion**. This is a **reactive intermediate**, produced in the reaction of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) with concentrated nitric acid (HNO<sub>3</sub>). Sulfuric acid behaves as a **catalyst** since it is not used up in the reaction.

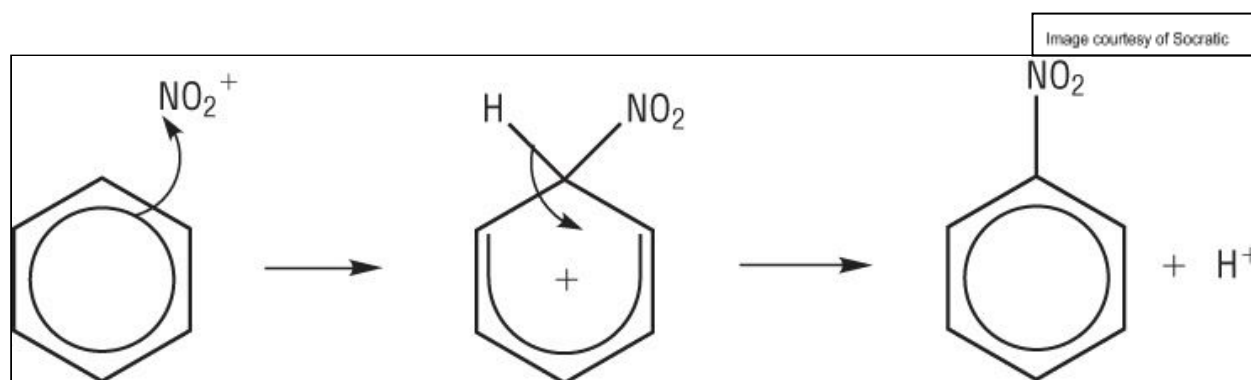
*Example: Formation of the electrophile*





When heated with benzene, these reagents lead to the **substitution of the  $\text{NO}_2^+$  electrophile** onto the benzene ring, **replacing a hydrogen** atom. The hydrogen ion released reacts with the  $\text{HSO}_4^-$  (produced above) to **reproduce** the sulfuric acid **catalyst**.

### Mechanism

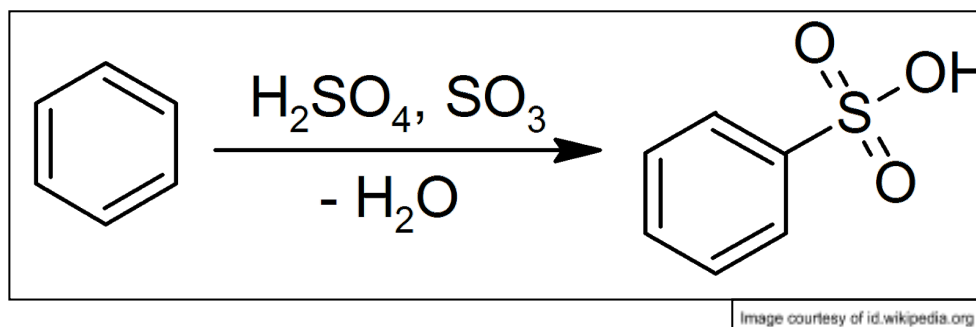


This reaction shows the **mono-substitution** of a single  $\text{NO}_2^+$  electrophile, which takes place when the reaction temperature is  **$55^\circ\text{C}$** . At temperatures greater than this, multiple substitutions can occur on the benzene ring. It is vital that only one substitution occurs for the production of **aromatic amines**.

### Sulfonation

When **sulfur trioxide** and **fuming sulfuric acid** are added to benzene, **benzenesulfonic acid** is produced via an electrophilic substitution mechanism.

*Example:*



### Friedel-Crafts Acylation

The delocalised electron ring in benzene can also act as a **nucleophile**, leading to the **attack on acyl chlorides**. This reaction is known as **Friedel-Crafts acylation**.



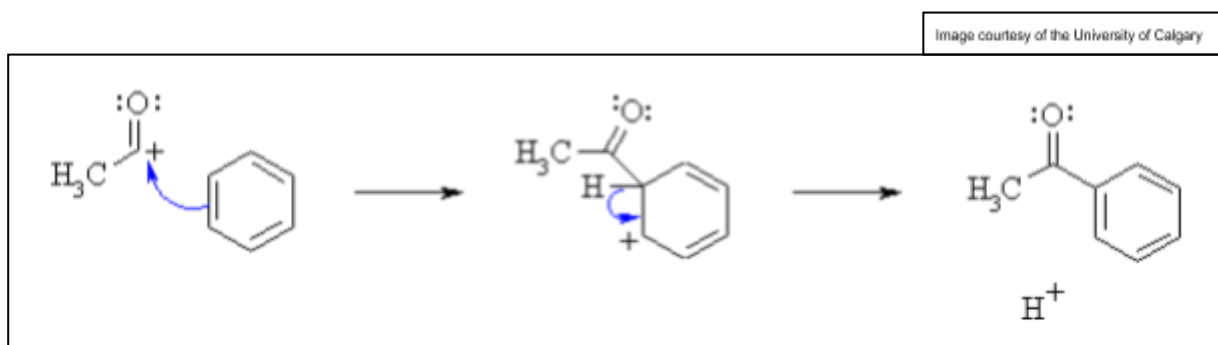
In order for the reaction to take place, a **reactive intermediate** must be produced from a reaction between the acyl chloride and an **aluminium chloride catalyst**.

*Example: Formation of the reactive intermediate*



This reactive intermediate is then attacked by the benzene ring.

### Mechanism



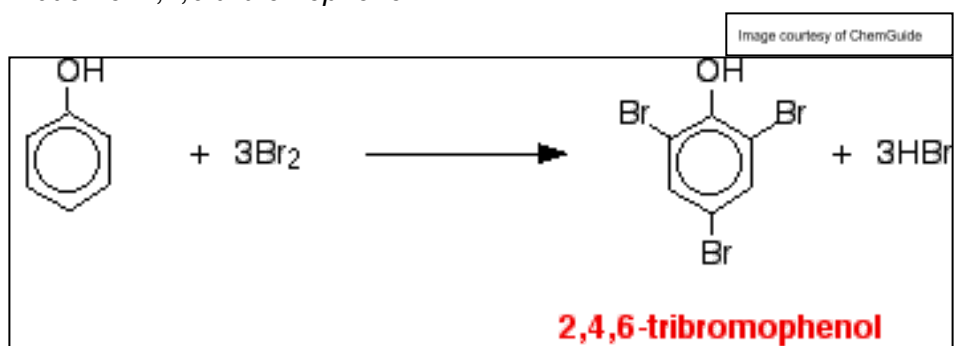
At the end of the reaction, the **H<sup>+</sup> ion** removed from the ring reacts with the **AlCl<sub>4</sub><sup>-</sup> ion** to reform the aluminium chloride, indicating it to be a **catalyst**.

The product of this reaction is a **phenylketone**. In this case, the benzene group is called a **phenyl group**. These molecules are commonly used in the industrial production of dyes, pharmaceuticals and even explosives.

### Bromine Water

Phenol, produced in electrophilic substitution reactions with benzene, can react with bromine water via **multiple substitutions** to produce 2,4,6-tribromophenol which forms as a **white precipitate** with a distinct smell of antiseptic. This reaction decolourises bromine water.

*Example: Formation of 2,4,6-tribromophenol*



Benzene cannot react with bromine water. The increased reactivity of phenol is due to the **lone pair of electrons on the oxygen atom**, which is delocalised into the benzene ring structure. This increases the **electron density** of the ring, making it less stable and thus **more susceptible to attack** from electrophiles.

### Combustion

Benzene reacts with oxygen to produce carbon dioxide and water. This reaction produces a **smoky flame** due to the high carbon-content of benzene.

