CAIE Chemistry A-level

30: Hydrocarbons

(A-level only)

Notes

Arenes

Arenes are aromatic hydrocarbons.

Substitution

Aromatic hydrocarbons, such as benzene, are able to undergo **electrophilic substitution**. Benzene's **delocalised electron system** makes it a very **stable** molecule. Benzene is highly **attractive to electrophiles** because of the high electron density in the benzene ring. Electrophiles can be a positive ion or a positive end of a polar molecule. When the reaction takes place, the delocalised electron system remains in the compound and one of the **hydrogen atoms swaps places with the electrophile**. Various different types of substitution reactions can take place:

Substitution with Chlorine

The reaction of benzene with chlorine requires an **aluminium chloride catalyst**.

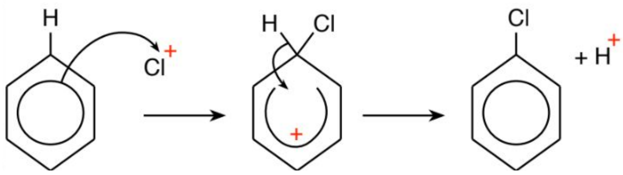
$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$

The mechanism for the electrophilic substitution reaction:

Stage 1: The aluminium chloride catalyst generates the electrophile from chlorine.

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

Stage 2: The electrophile reacts with the benzene molecule.



Stage 3: The hydrogen ion reacts with the $AlCl_4^-$, reforming the $AlCl_3$ catalyst.

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

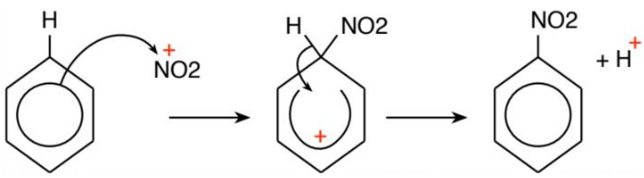
Substitution - Nitration

The reaction of benzene to form nitrobenzene requires a mixture of **concentrated nitric acid and concentrated sulfuric acid to generate the electrophile**.

Stage 1: The electrophile is generated from concentrated nitric acid and concentrated sulfuric acid.

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

Stage 2: The NO_2^+ electrophile reacts with the benzene molecule in electrophilic substitution.



Stage 3: The hydrogen ion reacts with the HSO_4^-, reforming the H_2SO_4 catalyst.

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

Acylation

Acylation of benzene involves the **substitution of an acyl group**. This reaction takes place when benzene is reacted with **ethanoyl chloride** in the presence of an **aluminium chloride catalyst.**

Stage 1: The electrophile is generated from ethanoyl chloride and aluminium chloride.

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

Stage 2: The CH_3CO^+ electrophile reacts with the benzene molecule.

$$CH_3CO^+ + C_6H_6 \rightarrow C_6H_5COCH_3 + H^+$$

Stage 3: The aluminium chloride catalyst is regenerated.

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

Alkylation

Alkylation of benzene involves the **substitution of an alkyl group**. The reaction occurs in the same way as the acylation reaction takes place above. It requires a **halogenoalkane** as a reactant as they contain a **polar bond** between the carbon and halogen.

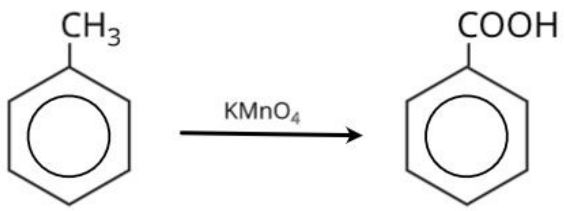
Stage 1: $CH_3Cl + AlCl_3 \rightarrow AlCl_4^- + CH_3^+$

Stage 2: $CH_3^+ + C_6H_6 \rightarrow C_6H_5CH_3 + H^+$

Stage 3: $H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

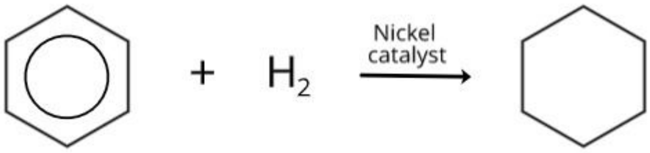
Complete Oxidation of Side Chains

If an alkyl group is attached to benzene, it can be easily oxidised to form benzoic acid. They can be oxidised using the oxidising agent, **potassium manganate(VII)**.



Hydrogenation

Hydrogenation takes place when **hydrogen atoms are added all around the benzene ring**, removing the delocalised electron system. A **cycloalkane** is formed as the product. The reaction is carried out with hydrogen, in the presence of a **nickel catalyst**. A temperature around **150°C** is required.

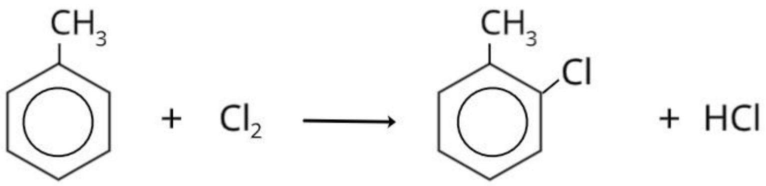


Halogenation

When a halogen reacts with methylbenzene, two possible reactions can take place depending on the conditions. The halogen can bond to the benzene ring or the methyl group.

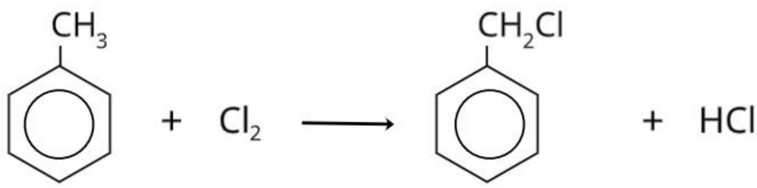
Substitution in the benzene ring

This reaction happens in the presence of **aluminium chloride** and in the **absence of UV light.**



Substitution in the methyl group

This reaction happens in the **presence of UV light**, without a catalyst.



The reaction can **continue to undergo substitution** so that all the hydrogen atoms in the methyl group are replaced by chlorine atoms, forming $C_6H_5CCl_3$.