FACTFILE:
GCE CHEMISTRY

4.10 AROMATIC CHEMISTRY

Rewarding Learning

Learning Outcomes

Students should be able to:

4.10.1 explain the structure of the benzene molecule with reference to delocalised π electrons; and

4.10.2 explain the reactivities of benzene and alkenes related to the relative stabilities of the π electron systems, for example the resistance of benzene to addition of bromine compared with an alkene;

4.10.3 explain the mechanisms of the monobromination, mononitration, alkylation and acylation of benzene including equations for the formation of the electrophile;

4.10.4 recall the names of the electrophiles for bromination and nitration of benzene; and

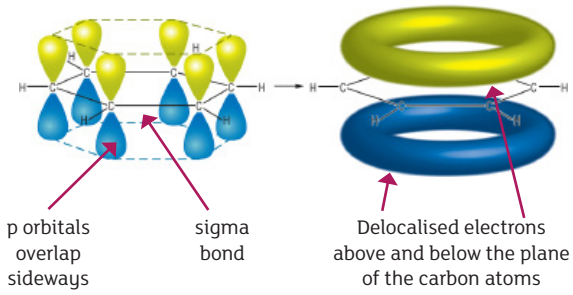
4.10.5 prepare methyl 3-nitrobenzoate from methyl benzoate to illustrate nitration of the benzene ring

Structure of benzene

Delocalisation (arenes) - the π electrons are spread over several atoms.

Today's accepted structure for benzene C_6H_6 is of a delocalised model which has the following features.

- It is a **planar hexagonal** molecule of six carbon atoms with bond angles of 120°
- All **carbon-carbon bond lengths are intermediate in length** between that of a single C-C and a double C=C.
- Each carbon uses three of its outer electrons to form 3 sigma bonds to two other carbon atoms, and one hydrogen atom. This leaves each carbon atom with one electron in a p orbital. The p orbitals overlap sideways and the 6 p electrons **delocalise** and give regions of electron density above and below the ring. It is this **delocalised ring of π electrons** which give benzene its stability.



Before delocalisation | After delocalisation

A circle is used to represent the ring of delocalised electrons 

Delocalisation (arenes) means that the π electrons are spread over several atoms.

Comparison of the reactions of benzene and alkenes

Alkenes react readily with bromine in an addition reaction, as the double bond breaks.

Benzene is resistant to addition reactions as the electrons from the delocalised system would need to bond to the atom or groups being added, disrupting the delocalised ring and causing the molecule to lose its stability.

Instead benzene undergoes substitution reactions, where one or more of the hydrogen atoms is replaced by another atom or group. The organic product formed retains the delocalised ring of electrons and hence the stability of the benzene ring.

Monobromination, mononitration, alkylation and acylation of benzene

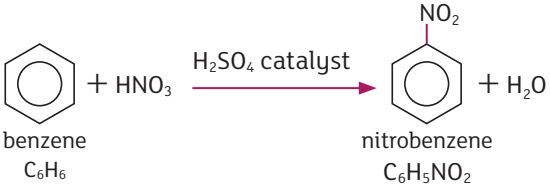
The mechanism for these reactions is electrophilic substitution. The region of high electron density above and below the plane of the molecule results in benzene being attacked by electrophiles

An electrophile is an ion or molecule that attacks regions of high electron density.

A substitution reaction is where one atom or group is replaced by a different atom or group

Mononitration

In mononitration of benzene a nitro group (NO_2) replaces one of the hydrogen atoms.

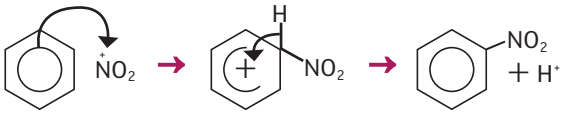


condition: concentrated sulfuric acid and concentrated nitric acid (nitrating mixture).

The overall equation for the generation of the electrophile $\mathbf{NO_2^+}$ (nitronium ion) is

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

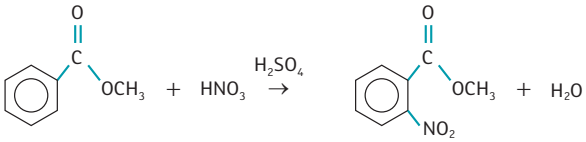
The mechanism for mononitration is shown below:



The concentrated sulfuric acid acts as a catalyst in the reaction as it is regenerated in the last step when H^+ ion is released in the mechanism and combines with HSO_4^- to reform sulfuric acid.

Preparation of Methyl 3–Nitrobenzoate

Nitrobenzene is not prepared in the laboratory due to the high toxicity of benzene. To illustrate nitration in the laboratory methyl benzoate, an ester of low toxicity is used.

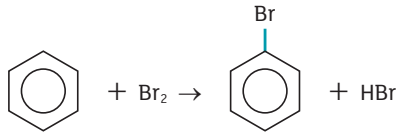


- Place methyl benzoate in a conical flask.
- Add concentrated sulfuric acid to dissolve the methyl benzoate.
- Cool the mixture in ice.
- Prepare the nitrating mixture of concentrated sulfuric acid and concentrated nitric acid.
- Cool the nitrating mixture in ice.
- Add the nitrating mixture dropwise to the solution of methyl benzoate.
- Keep the temperature below 10°C. (this prevents multiple nitrations)
- Allow to stand at room temperature for 10 minutes.

- Pour the mixture over crushed ice.
- Filter off the solid.
- Wash with cold water
- Recrystallise.
- Filter off the cream solid and dry

Monobromination

$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$

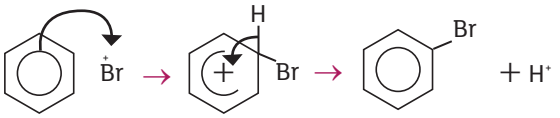


Condition: room temp, catalyst of iron or iron(III) bromide; the iron is converted to $FeBr_3$ by the reaction:

$2Fe + 3Br_2 \rightarrow 2FeBr_3$

The required electrophile is the **bromonium** ion Br^+ and is formed by the reaction of bromine and the catalyst:

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

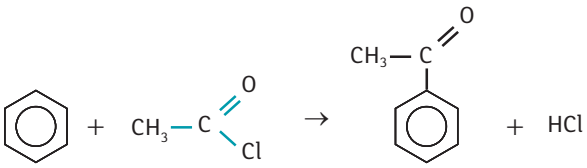


The catalyst is regenerated

$\mathbf{H^+ + FeBr_4^- \rightarrow FeBr_3 + HBr}$

Acylation

Acylation reactions occur when acyl chlorides react with benzene in the presence of an aluminium chloride catalyst to form an aromatic ketone. This



C_6H_6 + CH_3COCl (ethanoyl chloride) → phenylethanone (a ketone) + HCl

is an electrophilic substitution reaction in which an acyl group is attached to the ring.
Condition: catalyst of aluminium chloride, anhydrous conditions to prevent hydrolysis of the catalyst.

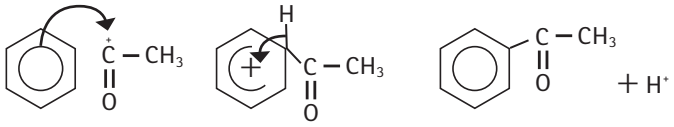
The electrophile is:

$CH_3 - \overset{+}{C} = O$

It is formed by reaction between the ethanoyl chloride and the aluminium chloride catalyst. The **equation for the formation of the electrophile** is

$CH_3COCl + AlCl_3 \rightarrow CH_3\overset{+}{C}O + AlCl_4^-$

The mechanism for acylation is shown below:



The catalyst is regenerated

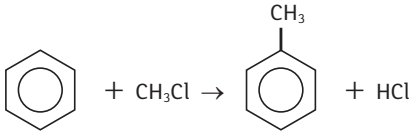
$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

Alkylation

Benzene reacts with a halogenoalkane in the presence of an aluminium chloride catalyst to form an alkyl benzene.

$C_6H_6 + CH_3Cl \rightarrow C_6H_5CH_3 + HCl$

or



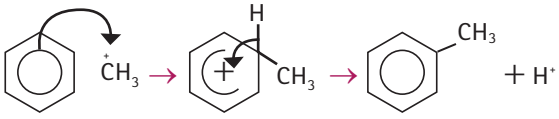
methylbenzene

Condition: catalyst of aluminium chloride, anhydrous conditions to prevent hydrolysis of the catalyst

The electrophile is the **carbocation** ion. It is formed by reaction between the halogenoalkane and the aluminium chloride catalyst. The **equation for the formation of the electrophile** is

$CH_3Cl + AlCl_3 \rightarrow \overset{+}{C}H_3 + AlCl_4^-$

The mechanism for alkylation is shown below:
The catalyst is regenerated



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

Revision Questions

1 How many p orbitals are involved in the delocalised π electrons of a benzene molecule?

A 2

B 3

C 6

D 12 [1]

2 Benzene and chloroethane react together in the presence of a

a) Name the catalyst.

..... [2]

b) Write an equation for the formation of the electrophile in this reaction.

..... [2]

c) Write an equation for the reaction of benzene and chloroethane and name the organic product.

..... [2]

d) Outline the mechanism for the reaction of benzene and chloroethane.

..... [3]

3 a) Benzene is more resistant than alkenes to reaction with bromine.

(i) What type of reaction do alkenes undergo with bromine?

..... [1]

(ii) Name a catalyst required for the reaction of benzene with bromine.

..... [1]

(iii) Draw a flow scheme to show the mechanism for the catalysed reaction of benzene with bromine.

[1]

(iv) Name the mechanism for the reaction of benzene with bromine.

..... [1]

b) Toluene, $C_6H_5CH_3$, can be nitrated in a similar way to benzene to form 2,4,6-trinitrotoluene.

(i) Suggest the structure of 2,4,6-trinitrotoluene.

[1]

(ii) Name the reagents used and write the equation for the formation of the nitronium ion.

Reagents: .....

Equation: ..... [2]

4 What is the total number of isomers of dichlorobenzene, $C_6H_4Cl_2$?

A 2

B 3

C 4

D 5 [1]