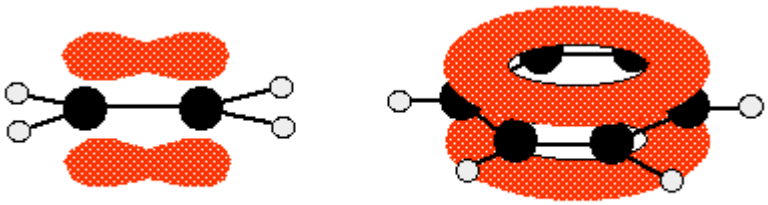
ELECTROPHILIC SUBSTITUTION

1. The diagrams show simplified orbital models of ethene and benzene:

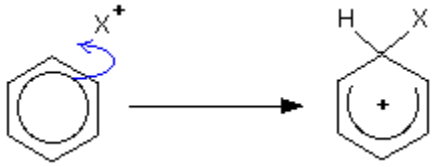


ethene benzene

a) Both molecules are attacked by electrophiles. What is an electrophile, and why are both of these molecules attacked by them?

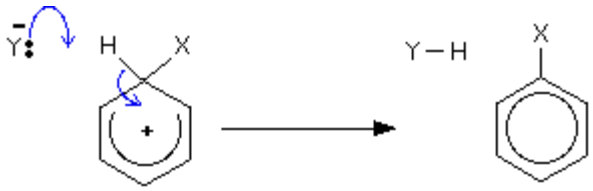
b) Ethene undergoes addition reactions whereas benzene normally undergoes substitution reactions. Explain why benzene doesn't normally undergo addition reactions.

c) A common first stage of the substitution of an atom or group X onto a benzene ring involves this process:



Explain what is happening.

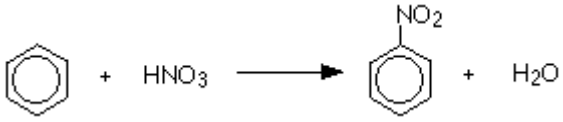
d) The second stage involves this reaction, involving a second ion, Y^-:



Explain what is happening this time.

e) Why are these electrophilic substitution reactions of benzene relatively slow?

2. The nitration of benzene involves this overall reaction involving benzene and concentrated nitric acid:



a) State the conditions for the reaction.

b) The electrophile in this case is the nitronium ion, NO_2^+. Write an equation showing its formation.

c) Give the mechanism for the reaction. There is no need to comment on it.

Chemguide – questions

Everybody studying electrophilic substitution is likely to have met the nitration of benzene, but other parts of the Chemguide material on this topic may not be required by your syllabus. If a question looks completely unfamiliar to you leave it out.

3. Friedel-Crafts alkylation and acylation reactions are very similar both in terms of the conditions for the reactions and the mechanisms. Both are used to substitute carbon-containing groups onto a benzene ring. Alkylation substitutes an alkyl group, and acylation substitutes an acyl group.

   a) Draw the structures for the final products of reactions substituting a group containing two carbon atoms during

   (i) alkylation;

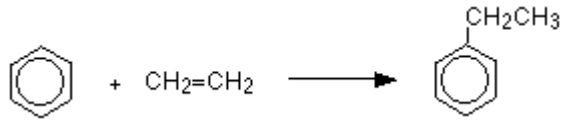
   (ii) acylation.

   b) Name the catalyst used during both alkylation and acylation.

   c) Write the equation showing the formation of the electrophile during the reaction between benzene and chloroethane, CH_3CH_2Cl, in the presence of the catalyst you have named.

   d) Give the rest of the mechanism for this reaction.

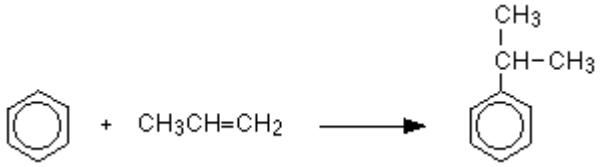
4. Ethylbenzene is manufactured using a reaction between ethene and benzene in the presence of HCl and aluminium chloride, $AlCl_3$, as catalysts.



   a) The electrophile in this case would have to be the ion $CH_3CH_2^+$. Explain how this is formed from an interaction between ethene, HCl and aluminium chloride.

   b) Give the rest of the mechanism for this reaction.

   The reaction between benzene and propene under the same conditions gives the overall reaction



   c) Draw the structure of the electrophile in this instance.

   d) Explain why that is formed rather than $CH_3CH_2CH_2^+$.

   e) Give the rest of the mechanism for this reaction.

5. Chlorine reacts with benzene in the presence of an aluminium chloride catalyst to make chlorobenzene.

a) Describe the mechanism for this reaction, making it clear how a neutral molecule like chlorine becomes an electrophile.

b) Iron can also be used as a "catalyst". Explain why that is essentially similar to using aluminium chloride. Why have I put inverted commas around the word catalyst?

6. Benzene reacts with concentrated sulphuric acid (slowly) or fuming sulphuric acid (more quickly) to form benzenesulphonic acid.

The electrophile is sulphur trioxide.

a) Explain the source of the sulphur trioxide if you are using

(i) concentrated sulphuric acid;

(ii) fuming sulphuric acid.

b) Explain why sulphur trioxide is an electrophile.

c) Give the full mechanism for the reaction.

7. This question is about substitution in methylbenzene and nitrobenzene.

a) The methyl group in methylbenzene is 2,4-directing. Explain what this means with the help of simple diagrams using nitration as an example.

b) Write the equation for the formation of the electrophile from the nitrating mixture of concentrated nitric and sulphuric acids.

c) Give the first stage of the mechanisms (showing the reaction of the nitronium ion with the ring to produce the intermediate positive ions) for the nitration of methylbenzene leading to

(i) 2-nitrobenzene;

(ii) 4-nitrobenzene.

d) The nitro group in nitrobenzene is 3-directing. Write the first stage of the mechanism (to produce the intermediate positive ion) for the further nitration of nitrobenzene to give 1,3-dinitrobenzene.

e) In the presence of UV light, chlorine substitutes into the methyl group of methylbenzene, and not into the ring. What conditions are necessary for ring substitution?

f) Ring substitution leads to a mixture of 2-chloromethylbenzene and 4-chloromethylbenzene. Write the full mechanism for the formation of 4-chloromethylbenzene.