

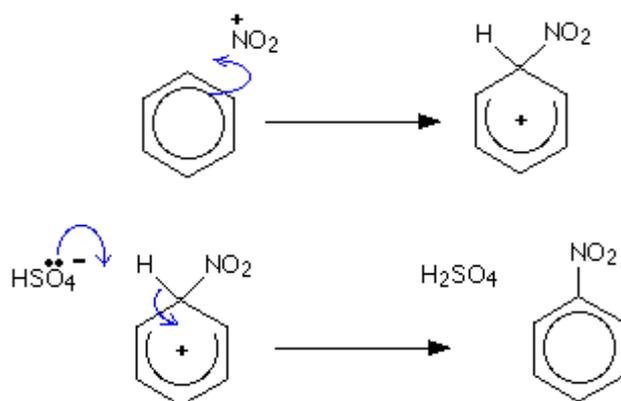
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ELECTROPHILIC SUBSTITUTION

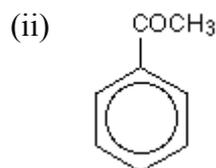
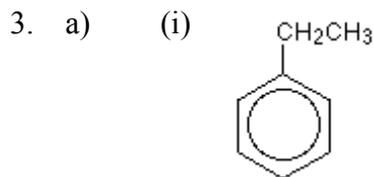
1. a) An electrophile is a species (a positive ion or the slightly positive end of a polar molecule) which is attracted to electron-rich areas of other molecules. Both ethene and benzene are attractive for electrophiles because of the exposed pi bonds.
- b) The pi system in benzene is delocalised over the entire ring, and this makes the molecule more energetically stable than it would otherwise be. If benzene undergoes addition reactions, some of the delocalised electrons would be used to form bonds to whatever was being added. That permanently breaks the complete delocalisation and this costs energy.
- c) Two electrons involved in the delocalisation move to form a bond with the electrophile X^+ which then joins to the nearest carbon atom. In the process the delocalisation is temporarily broken and now only covers a part of the ring. The positive charge is spread over the remaining delocalised part of the ring.
- d) A lone pair on a negative ion, Y^- , in the reaction mixture moves to form a bond with the hydrogen atom attached to the same carbon as the X. In the process, the two electrons in the carbon-hydrogen bond are forced down to fill the temporary gap in the delocalised ring electrons. A new molecule HY is formed.
- e) It needs quite a lot of energy to break the delocalisation on the ring and form the intermediate ion. That means that the activation energy for the overall reaction is high, and so relatively few collisions will have enough energy for the reaction to proceed.
2. a) Benzene is treated with a mixture of concentrated nitric and sulphuric acids keeping the temperature below 50°C .



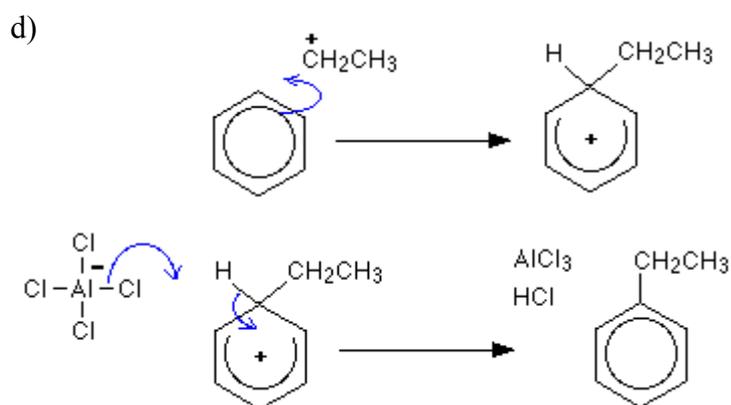
c)



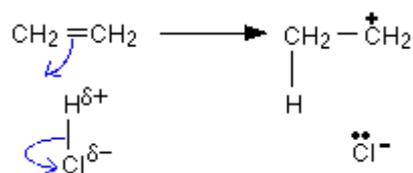
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b) aluminium chloride

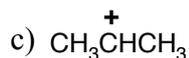


4. a) The HCl starts to react with the ethene as it does in an electrophilic addition reaction:



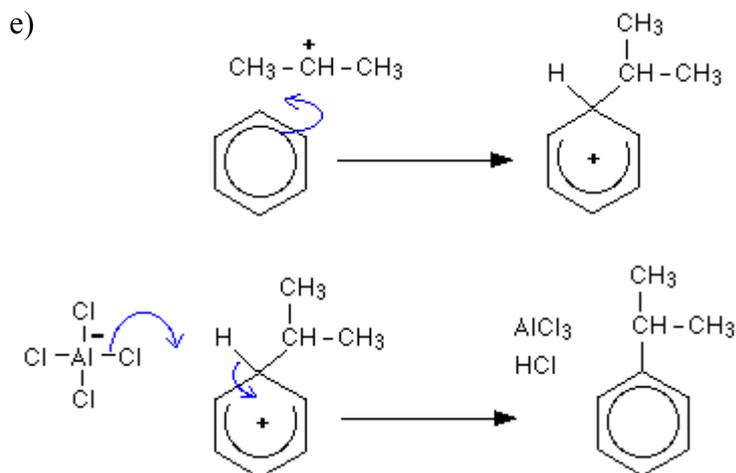
The chloride ion immediately reacts with AlCl_3 to make the ion AlCl_4^- , leaving the CH_3CH_2^+ ion to be used as the electrophile.

b) See 3(d) above.

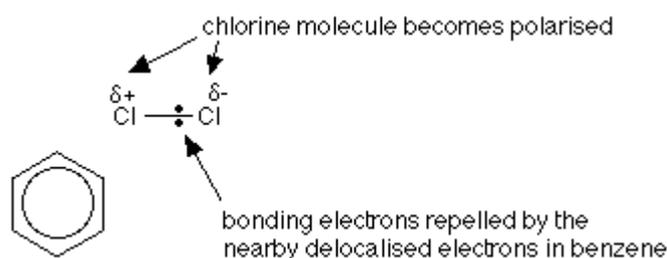


d) $\text{CH}_3\text{CH}_2\text{CH}_2^+$ is a primary carbocation (carbonium ion) which isn't as stable as the ion in (c) which is secondary.

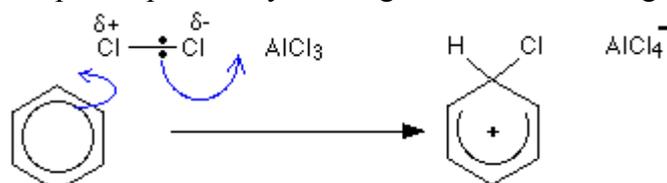
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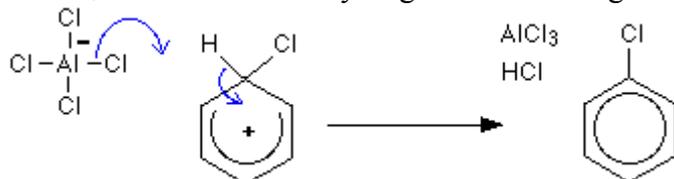
5. a) As chlorine approaches benzene, the electrons in the chlorine-chlorine bond are repelled towards the far chlorine, and an induced dipole is formed.



The aluminium chloride helps this process by forming a bond with the slightly negative chlorine:



Finally, the AlCl_4^- ion removes the hydrogen from the ring:



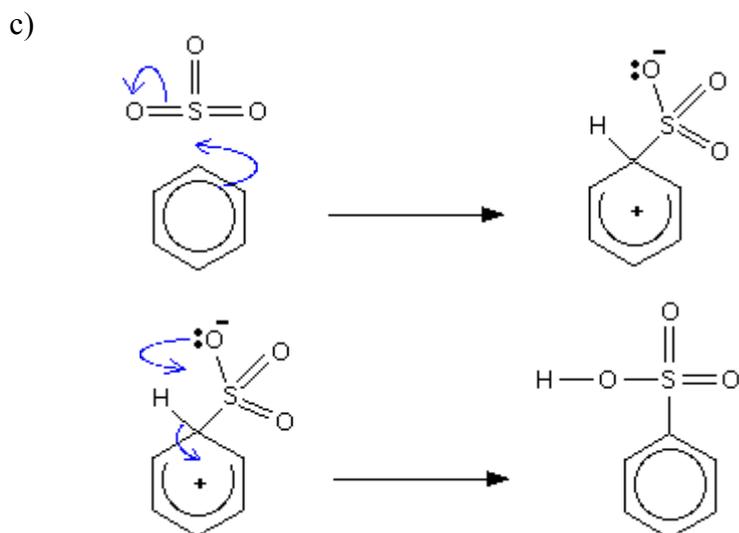
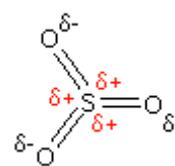
- b) The iron reacts with chlorine to form iron(III) chloride, FeCl_3 , which behaves exactly like the aluminium chloride in this reaction. The actual catalyst is the iron(III) chloride, not the iron. The iron isn't recovered unchanged from the reaction.

6. a) (i) concentrated sulphuric acid: $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2\text{O} + \text{SO}_3$

(ii) fuming sulphuric acid, $\text{H}_2\text{S}_2\text{O}_7$: This can be thought of as a solution of sulphur trioxide in concentrated sulphuric acid.

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b) Sulphur is more electronegative than oxygen, and the three oxygen atoms pull electrons away from the sulphur leaving it fairly positive.

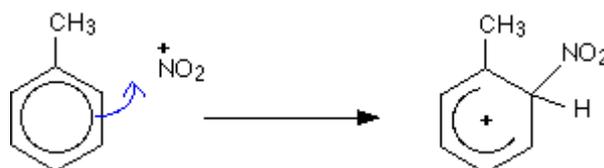


7. a) A 2,4-directing group attached to a benzene ring causes any new substitution to go into the 2- and 4- positions on the ring relative to the existing group. So when you substitute a nitro group into methylbenzene, you get mainly 2-nitromethylbenzene and 4-nitromethylbenzene, and very little of the 3- isomer.

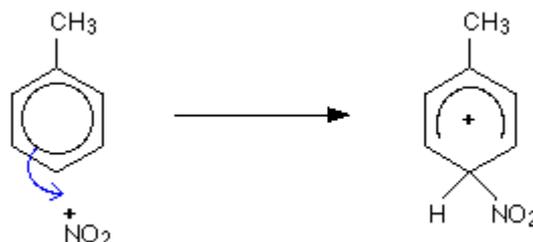


c)

(i) 2-nitrobenzene:

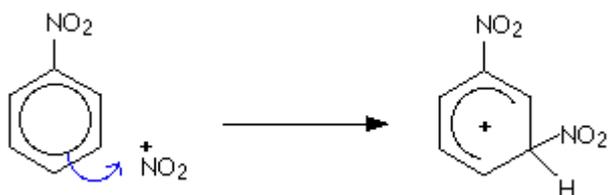


(ii) 4-nitrobenzene:



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d)



(I have only asked about the first stage of these mechanisms in the last two questions to make sure that you can draw the partial delocalisation on the ring properly. You should, of course, also know how the hydrogen is removed from the ring.)

e) An aluminium chloride (or iron) catalyst, and the absence of UV light.

f)

