Aromatic chemistry

AQA 7405 · A level

Show your working where needed. Check the worked answers when you finish.

Name _____ Date _____

1. Benzene bonding

Describe the overlap of p orbitals in benzene. State how many electrons are delocalised and where the resulting electron density lies.

2. Measure the bonds

Diffraction gives six equal C-C bond lengths for benzene, each 139 pm. A typical C-C bond is 154 pm and a typical C=C bond is 134 pm. Explain which model the measurements support.

3. Use hydrogenation data

Hydrogenation of cyclohexene to cyclohexane gives −119 kJ mol^{-1}. Hydrogenation of benzene to cyclohexane gives −206 kJ mol^{-1}. Estimate the extra stability of benzene using the isolated-double-bond model.

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4. Two ways a ring could react

Benzene can undergo electrophilic substitution. Compare the bonding in its substitution product with the bonding that would result from simple addition across two ring carbons.

5. Make the electrophile

Write an equation for the formation of the electrophile when concentrated nitric acid and concentrated sulfuric acid are used to nitrate benzene. Identify the electrophile.

6. The reaction of benzene with NO_2^+

Draw the mechanism for benzene reacting with NO_2^+. Include the ring intermediate and the step giving the organic product.

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7. Interpret a bromine test

Benzene and cyclohexene are treated separately with bromine water without a halogen carrier. Predict the result for each and explain the difference.

8. Friedel-Crafts acylation

Explain how the catalyst is regenerated.

9. Extra challenge · Correct an acylation mechanism

Benzene reacts with propanoyl chloride in the presence of $AlCl_3$. A diagram shows the ring donating to the ethyl carbon and the product retaining two groups on a saturated ring.

Draw the correct mechanism from electrophile formation to the organic product. Write the equation that regenerates the catalyst.

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Worked answers

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1. Benzene bonding

Six parallel p orbitals overlap sideways around the planar ring. The six electrons are delocalised in regions above and below the plane of the ring.

2. Measure the bonds

All six bonds have the same length, intermediate between the two reference lengths. This supports delocalised bonding across the ring. A model of alternating localised single and double bonds predicts two bond lengths.

3. Use hydrogenation data

Three isolated double bonds would give an estimated $3 \times (-119) = -357$ kJ mol^{-1}.

Benzene gives out 151 kJ mol^{-1} less energy on reaching the same product. Its enthalpy is about 151 kJ mol^{-1} lower than the model predicts.

4. Two ways a ring could react

Loss of H^+ from the attacked carbon in substitution restores the delocalised π system.

Simple addition leaves two newly bonded groups on the ring and disrupts the continuous ring of overlapping p orbitals. The product loses the extra stability of aromatic delocalisation.

5. Make the electrophile

$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$. The nitronium ion, NO_2^+, is the electrophile.

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Worked answers

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6. The reaction of benzene with NO_2^+

Draw a curly arrow from the delocalised ring to N in NO_2^+. On the attacked carbon show both H and NO_2. Put the gap in the horseshoe at that carbon and the positive charge inside the ring away from it.

Draw a curly arrow from that C-H bond back into the ring. Loss of H^+ restores the delocalised ring and gives nitrobenzene.

7. Interpret a bromine test

Cyclohexene decolourises bromine water. The localised π bond has a high electron density and reacts readily with bromine.

Benzene does not decolourise the bromine water in this test. Its π electrons are spread around the ring, and simple addition would destroy aromatic delocalisation.

8. Friedel-Crafts acylation

CH_3CO^+ is the electrophile. $C_6H_6 + CH_3COCl \rightarrow C_6H_5COCH_3 + HCl$.

$AlCl_3$ accepts chloride to form $AlCl_4^-$ when the electrophile is generated. $AlCl_4^-$ combines with H^+ to give HCl and regenerate $AlCl_3$.

9. Extra challenge · Correct an acylation mechanism

$CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2CO^+ + AlCl_4^-$. The ring donates to the positively charged acyl carbon. Draw H and $-COCH_2CH_3$ on the attacked carbon, the interrupted ring and the positive charge on the ring intermediate.

The C-H bond electrons restore the aromatic ring as H^+ leaves, giving $C_6H_5C(=O)CH_2CH_3$. $AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$.

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