Aromatic chemistry

OCR A H432 · 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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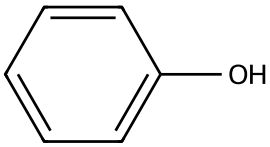
7. Compare two observations

Compound A is shown. A gives a white precipitate when shaken with bromine water under the usual test conditions. Benzene gives no such precipitate in the same test. Name A and the precipitate, then explain the different reactivity.

A 

8. Compare two carbon sources

Benzene reacts separately with chloroethane and ethanoyl chloride. Name a suitable halogen carrier. Give both structures and identify which carbon of each reagent bonds to the ring.

9. Extra challenge · Choose the order of substitution

Start with benzene and make 1-bromo-3-nitrobenzene in two substitutions. Choose the order, give the two sets of reagents or conditions and explain the position of the second group.

Draw the ring mechanism for the second reaction using Br^+ as the electrophile.

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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. Compare two observations

A is phenol. The white precipitate is 2,4,6-tribromophenol.

One of the oxygen lone pairs overlaps with the ring π system. This increases ring electron density, so the ring attracts an electrophile more strongly.

8. Compare two carbon sources

$AlCl_3$ is suitable. Chloroethane yields ethylbenzene, $C_6H_5CH_2CH_3$, by bonding through its CH_2Cl carbon. Ethanoyl chloride yields $C_6H_5COCH_3$ by bonding through its carbonyl carbon.

9. Extra challenge · Choose the order of substitution

Nitrate benzene first with concentrated HNO_3 and concentrated H_2SO_4 to give nitrobenzene. Use bromine with a halogen carrier, such as $FeBr_3$, for the next step. NO_2 directs substitution to position 3 or the equivalent position 5.

The ring π electrons attack Br^+. The attacked carbon temporarily carries both H and Br, with an interrupted π system and positive charge on the intermediate. The C-H bond electrons then re-form the delocalised ring, giving 1-bromo-3-nitrobenzene.

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