

5.3.1 Use benzene evidence and select substitution conditions

Name: _____ Class: _____ Date: _____

Total: 18 marks

KEY WORDS evidence • conditions

Objective

Use benzene evidence and select substitution conditions. All questions and marking guidance are original.

1 Key knowledge and worked examples

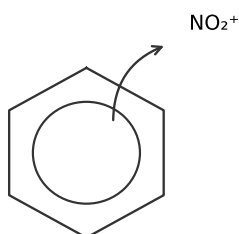
Benzene has equal C–C lengths and a delocalised ring. Addition would destroy that system. Electrophilic substitution replaces H then restores delocalisation. Phenol reacts with bromine water more readily because oxygen's lone pair increases ring electron density.

■ Worked method

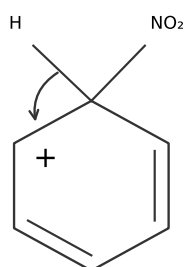
If three isolated C=C bonds predict hydrogenation -360 kJ mol^{-1} but benzene gives -208 , benzene is 152 kJ mol^{-1} more stable than that hypothetical localised model. Nitration uses concentrated $\text{HNO}_3/\text{H}_2\text{SO}_4$. $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$ generates the electrophile. A ring electron pair attacks NO_2^+ ; loss of H^+ restores the ring.

Nitration mechanism after NO_2^+ generation; curly arrows show electron pairs

1 Ring electron pair attacks

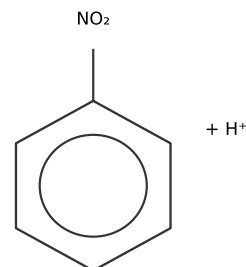


2 Positive intermediate



C–H bond pair restores ring

3 Nitrobenzene + H^+



2 Practice

2.1 Give two pieces of evidence against three separate ordinary C=C bonds in benzene. [2]

2.2 Calculate stabilisation relative to the hypothetical model if one C=C hydrogenation is -118 kJ mol^{-1} and benzene is -206 kJ mol^{-1} . [3]

2.3 State benzene bromination conditions and compare phenol with bromine water. [3]

3 Exam-style questions

3.1 Write the nitrating-electrophile generation equation and name the electrophile. Explain how substitution retains the aromatic system overall. [4]

3.2 Give reagents for making ethylbenzene and phenylethanone from benzene. Identify which is Friedel–Crafts acylation. [3]

3.3 A student predicts benzene will rapidly decolourise bromine water because it has six π electrons. Explain the error, and state sulfonation conditions. [3]

Solutions

Original marking guidance: M1 method, A1 accuracy, B1 explanation.

2.1 Equal intermediate C–C bond lengths; hydrogenation less exothermic than three isolated double bonds predict. Accept appropriate IR evidence in place of either.

2.2 Three-bond prediction = $3(-118) = -354 \text{ kJ mol}^{-1}$. Difference = 148 kJ mol^{-1} , benzene lower in starting enthalpy/more stable.

2.3 Benzene needs a halogen carrier such as FeBr_3 . Phenol reacts without that catalyst, making white 2,4,6-tribromophenol and decolourising bromine water.

3.1 $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}$. NO_2^+ is nitronium. Ring attack temporarily breaks delocalisation; loss of H^+ restores it.

3.2 Ethylbenzene: chloroethane/anhydrous AlCl_3 . Phenylethanone: ethanoyl chloride/anhydrous AlCl_3 , the acylation reaction.

3.3 Its electrons are delocalised and addition would lose stabilisation, so it resists the usual bromine-water addition test. Sulfonation uses fuming sulfuric acid.