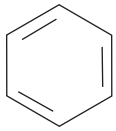
1 Benzene is sometimes represented as Structure **X**, shown below, called a Kekulé structure after the chemist who suggested it.



Structure **X**

(a) What structural feature of benzene shows that Structure **X** is not an accurate representation?

(1)

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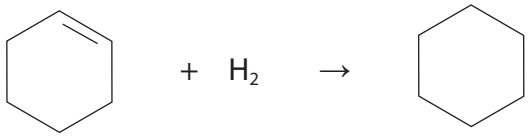
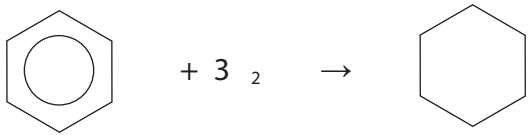
(b) The enthalpy changes for the formation of cyclohexane from cyclohexene and from the actual structure of benzene are given below.



$\Delta H = -118$ kJ mol^{-1}



$\Delta H = -205$ kJ mol^{-1}

(i) Use the necessary data to estimate the enthalpy change for the theoretical conversion of Structure **X** to cyclohexane.

(1)

(ii) On the enthalpy level diagram below, draw labelled horizontal lines to show the relative enthalpies of the actual structure of benzene, Structure **X** and cyclohexane. Add an arrow to show the enthalpy change from Structure **X** to benzene and calculate the value of this enthalpy change in kJ mol^{-1}. Write this value next to your arrow.

(2)

*(iii) Explain the difference in the arrangement of the electrons between benzene and Structure **X**.

(2)

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(c) Benzene reacts with bromine in the presence of a catalyst of iron(III) bromide.

Write a mechanism for the reaction of benzene with bromine to form bromobenzene. Include an equation to show the involvement of the catalyst.

(4)

(d) (i) State **two** observations which would be made when phenol reacts with bromine water.

(2)

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(ii) Write the equation for this reaction showing the structure of the organic product.

(2)

*(iii) Explain why phenol can react with either bromine or with bromine water without a catalyst.

(2)

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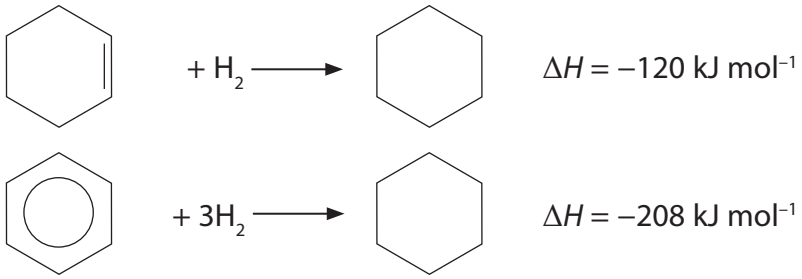
(Total for Question = 16 marks)

2 (a) Equations for the catalytic hydrogenation of cyclohexene and of benzene are shown below.



(i) What is the type of reaction in both of these hydrogenations?

(1)

*(ii) The enthalpy of hydrogenation of benzene might be expected to be −360 kJ mol^{-1}. Explain why this is **not** the actual value.

(2)

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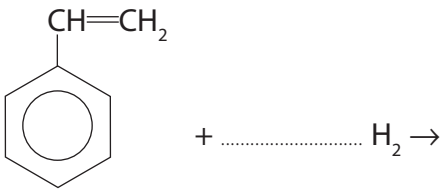
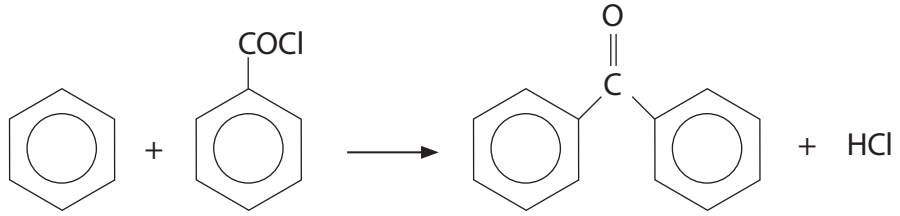
(iii) Complete the following equation for the total hydrogenation of phenylethene. Suggest a value for the enthalpy change of this reaction.

(3)



ΔH = ... kJ mol^{-1}

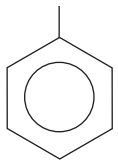
(b) The compound benzophenone is used as a sunscreen. It can be prepared from benzene, in the presence of aluminium chloride by the following reaction.



benzene + compound **A** benzophenone

(i) Complete the diagram below by showing the **displayed** formula of the –COCl group in compound **A**.

(1)



(ii) Classify the type and mechanism of the reaction between benzene and compound **A**.

(1)

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(iii) Give the names of the two chemists associated with the type of reaction described in (b)(ii).

(1)

..... and .....

(iv) Give the mechanism for the reaction between benzene and compound **A** in the presence of an aluminium chloride catalyst.

Start by showing the equation for the generation of the species which then attacks the benzene ring.

(4)

Equation to show generation of species attacking the benzene ring:

Rest of the mechanism:

(v) Suggest the essential property of a substance that will be used as a sunscreen.

(1)

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(c) (i) The identity of a sample of benzophenone can be confirmed by recording its infrared and proton nmr spectra.

Identify **two** different bonds that would produce an absorption in the infrared spectrum of benzophenone. Use the Data Booklet to suggest the wavenumber of each of these absorptions.

(4)

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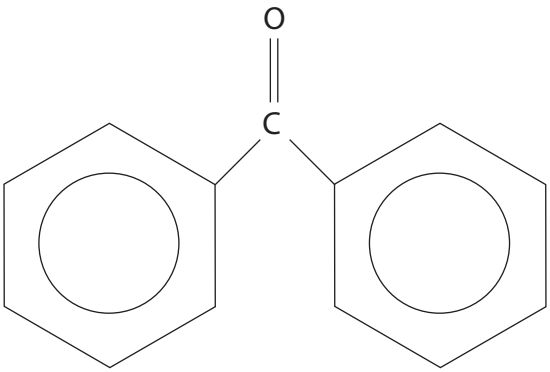
(ii) In benzophenone there are three different hydrogen environments, X, Y and Z, that produce signals in the ratio 2:2:1 respectively in the proton nmr spectrum.

Identify, **on the structure drawn below**, the positions of all the hydrogen atoms in each environment, labelling the different environments **X**, **Y** and **Z**.

(2)

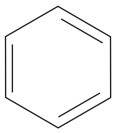


benzophenone

(Total for Question = 20 marks)

3 This question is about benzene and its compounds.

(a) A Kekulé structure of benzene suggests the molecule consists of alternate double and single carbon to carbon bonds.



The standard enthalpy change of hydrogenation of a carbon to carbon double bond is 120 kJ mol ^{1}.

(i) Calculate the standard enthalpy change of hydrogenation of benzene for the Kekulé structure.

(1)

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*(ii) The actual standard enthalpy change of hydrogenation of benzene is 208 kJ mol ^{1}.

Use this information and your answer to (i), to calculate the difference in stability of benzene and the Kekulé structure.

What does this tell us about the bonding in benzene?

Explain how this influences the type of chemical reactions that benzene undergoes.

(4)

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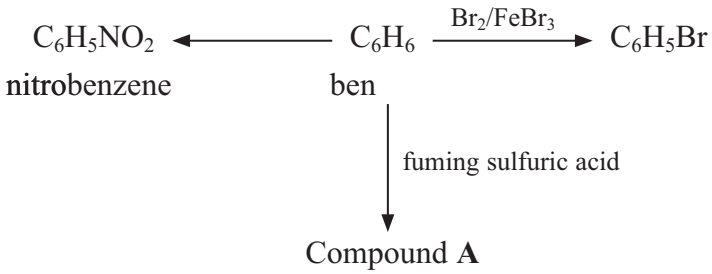
(b) The flow chart shows some typical reactions of benzene.



(i) Identify the two chemicals needed to make nitrobenzene from benzene.

(2)

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(ii) Classify the type of reagent required in all three reactions.

(1)

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(iii) Show, with appropriate diagrams, the mechanism for the reaction of benzene with bromine, in the presence of iron(III) bromide, to form bromobenzene. Include the formation of the ion attacking the benzene molecule.

(4)

(iv) Give the structural formula and the name for compound **A**.

(2)

Name.....

(c) (i) Explain why phenol, C_6H_5OH, and methoxybenzene, $C_6H_5OCH_3$, are much more reactive than benzene with bromine.

(3)

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(ii) Write the equation for the reaction between phenol and bromine water. State symbols are **not** required.

(2)

(d) Diphenylmethane, $(C_6H_5)_2CH_2$, is often added to soap to create the pleasant smell of geraniums. It can be made from benzene and one other reagent, using a suitable catalyst.

Identify the other starting material and the catalyst by name or formula.

(2)

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(Total for Question 21 marks)