PEARSON EDEXCEL IAL CHEMISTRY · YCH11

CHEMISTRY



EXAM QUESTION PACK

UNIT 5: ARENES

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Q1.

Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

How many σ bonds and π bonds are there in a molecule of benzene?

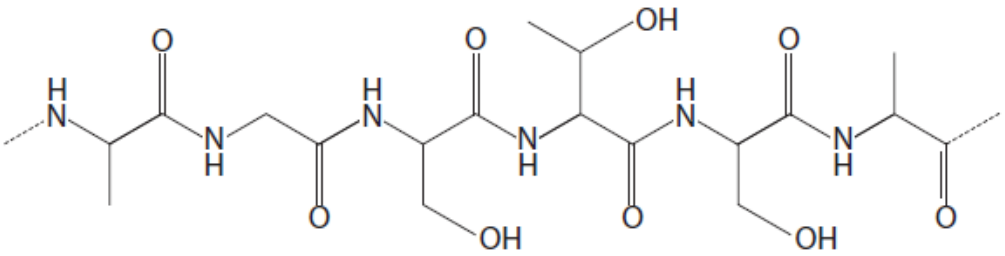
	σ bonds	π bonds
☒ **A**	6	3
☒ **B**	6	6
☒ **C**	12	3
☒ **D**	12	6

(Total for question = 1 mark)

Q2.

Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

Part of the structure of a protein is shown.



How many **different** amino acids were used to form this part of the structure?

☒ **A** 3

☒ **B** 4

☒ **C** 5

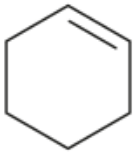
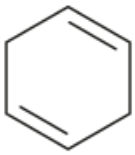
☒ **D** 6

(Total for question = 1 mark)

Q3.

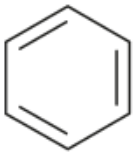
This question is about benzene and some related compounds.

(a) Some standard enthalpies of combustion are shown.

Compound	Structure	Standard enthalpy of combustion, $\Delta_c H^\ominus$ / kJ mol^{-1}
cyclohexene		–3752
cyclohexa-1,4-diene		–3584
benzene		–3267

(i) Using the standard enthalpies of combustion of cyclohexene and cyclohexa-1,4-diene, calculate a value for the enthalpy of combustion of the theoretical compound 'cyclohexa-1,3,5-triene'.

(2)



cyclohexa-1,3,5-triene

(ii) Explain the difference between the enthalpy of combustion of 'cyclohexa-1,3,5-triene' calculated in (a)(i) and the enthalpy of combustion of benzene given in the table.

(3)

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(b) Bromine reacts with cyclohexene to form 1,2-dibromocyclohexane, and with benzene to form bromobenzene.

Compare and contrast these reactions, considering the type and mechanism of each reaction and the conditions required.

You are **not** required to draw the mechanisms of the reactions.

(4)

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(c) Bromine also reacts with phenol.

(i) Identify, by name or formula, the organic product when phenol reacts with **excess** bromine.

(1)

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(ii) Explain why bromine reacts much faster with phenol than with benzene.

(2)

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(Total for question = 12 marks)

Q4.

Answer the question with a cross in the box you think is correct ☒ . If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒ .

The reaction of ethene with bromine occurs under normal laboratory conditions but the reaction of benzene with bromine to form bromobenzene requires heat and the presence of a catalyst.

The best explanation for the difference in reactivity is that the delocalised electrons in benzene

☐ **A** repel electrophiles

☐ **B** result in a kinetic barrier to intermediate formation

☐ **C** result in benzene having an endothermic enthalpy of formation

☐ **D** make benzene thermodynamically stable with respect to the formation of bromobenzene

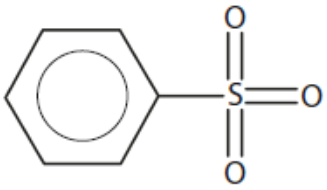
(Total for question = 1 mark)

Q5.

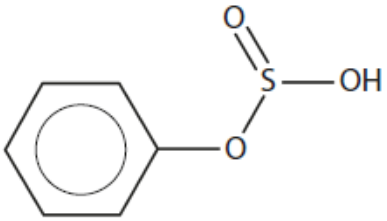
Answer the question with a cross in the box you think is correct ☒ . If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒ .

What is the product when benzene reacts with fuming sulfuric acid?

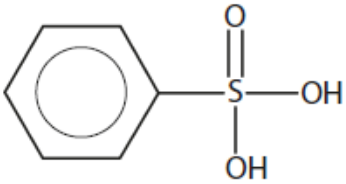
☒ **A**



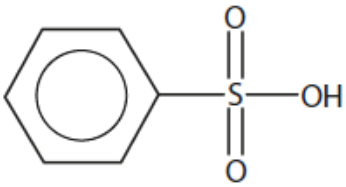
☒ **B**



☒ **C**



☒ **D**



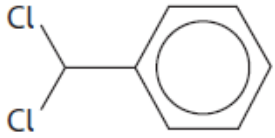
(Total for question = 1 mark)

Q6.

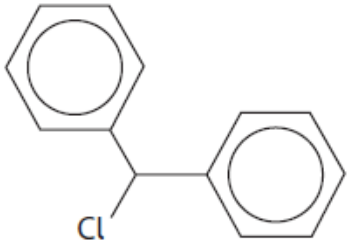
Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

Which of these could **not** be formed when excess benzene is heated with trichloromethane, $CHCl_3$, in the presence of an aluminium chloride catalyst?

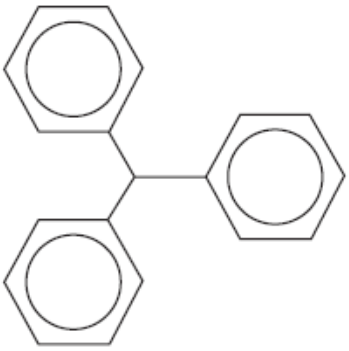
☒ **A**



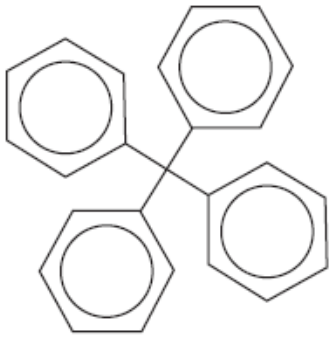
☒ **B**



☒ **C**



☒ **D**

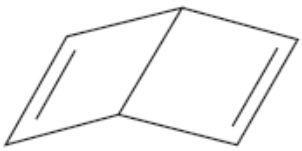
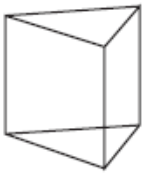


(Total for question = 1 mark)

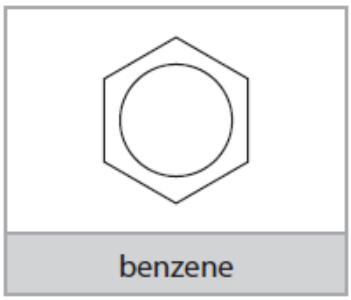
Q7.

This question is about benzene, C_6H_6, a colourless liquid first isolated in 1825, and some related compounds.

Three C_6H_6 structures proposed in the 1860s are shown.

		
Kekulé structure	Dewar structure	Ladenburg structure

The delocalised model for the structure of benzene has been accepted since the 1930s following the study of its X-ray diffraction pattern and the understanding of electron delocalisation in bonding theory.



benzene

The Dewar and Ladenburg structures have since been isolated as stable compounds but there is no compound with the Kekulé structure.

(a) Describe a **chemical** test, including the result, that could distinguish the Dewar structure from benzene.

(2)

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(b) State **one** similarity and **one** difference you would expect in the **low** resolution proton NMR spectrum of the Ladenburg structure and that of benzene.

You **must** include data from the Data Booklet to support your answer.

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(c) Explain how X-ray diffraction shows that benzene has a delocalised structure and **not** a Kekulé structure.

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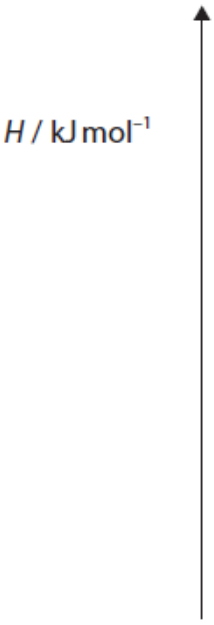
(d) The Ladenburg and Dewar structures both isomerise to benzene.

The enthalpy changes are –376 kJ mol^{-1} and –297 kJ mol^{-1} respectively.

(i) Draw a **labelled** enthalpy level diagram showing the relative thermodynamic stability of the Ladenburg structure, the Dewar structure and benzene.

Include the enthalpy change values in kJ mol^{-1}.
Your diagram does **not** need to be to scale.

(2)



(ii) Give a possible reason why the isomerisation of the Dewar structure to benzene has a lower activation energy than that of the Ladenburg structure to benzene.

(1)

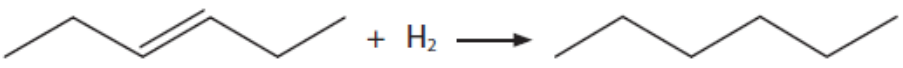
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(e) The enthalpy change of hydrogenation of hex-3-ene is –118 kJ mol^{-1}.



The table shows the enthalpy changes of hydrogenation of two further alkenes containing six carbon atoms.

Alkene	Enthalpy change of hydrogenation / kJ mol^{-1}
 *E*-hexa-1,4-diene	–236
 *E*-hexa-1,3-diene	–214

Use your knowledge of benzene thermochemistry to suggest explanations for **both** of these enthalpy changes of hydrogenation in relation to the value for hex-3-ene.

(2)

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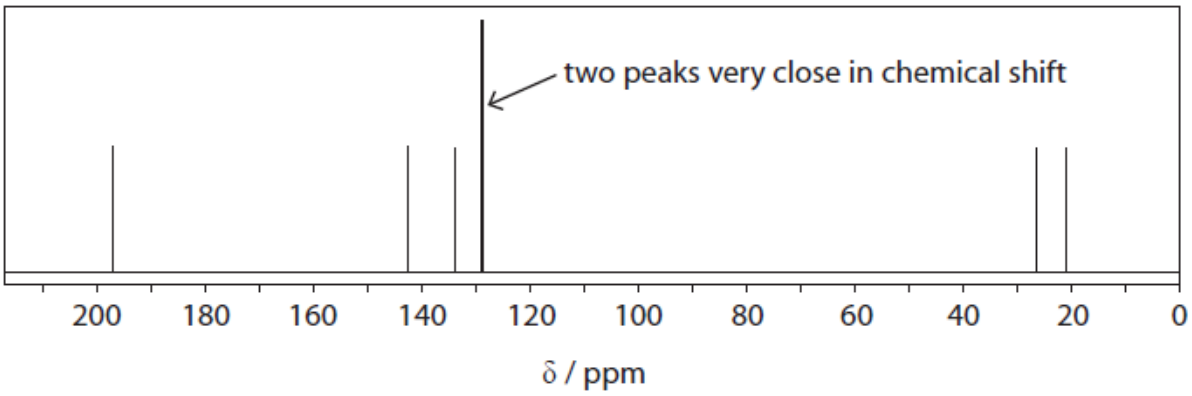
(f) Methylbenzene, $C_6H_5CH_3$, reacts with ethanoyl chloride, CH_3COCl, in the presence of the catalyst aluminium chloride, $AlCl_3$, to form a mixture of organic products with the formula $CH_3COC_6H_4CH_3$.

$$C_6H_5CH_3 + CH_3COCl \rightarrow CH_3COC_6H_4CH_3 + HCl$$

(i) Draw the **skeletal** formulae of **three** different arenes with the formula $CH_3COC_6H_4CH_3$.

(2)

(ii) The ^{13}C NMR spectrum of **one** of these arenes, compound **X**, is shown.



Identify compound **X**.
Use the number of peaks on the ^{13}C NMR spectrum to justify your answer.

(2)

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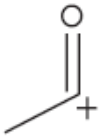
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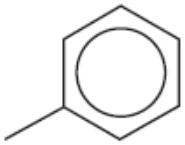
(iii) Complete the diagram, including curly arrows, to show the mechanism for the formation of compound **X** in this reaction.

Include an equation for the regeneration of the catalyst.

(4)

$$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$$





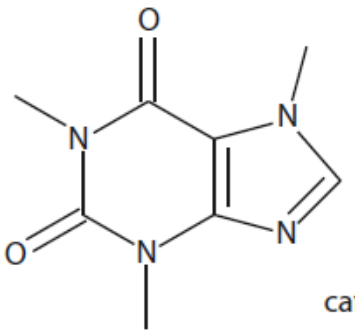
(Total for question = 19 marks)

Q8.

Coffee Chemistry

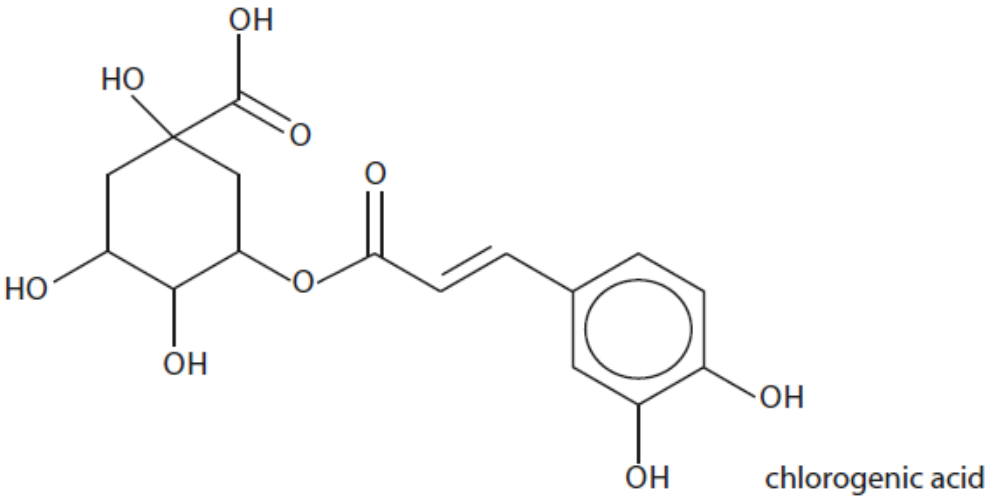
There are over a thousand chemical compounds in coffee and their physiological effects are the subject of considerable speculation and research. The verdict on coffee is contradictory: some of the compounds have been identified as toxic and even carcinogenic but others are antioxidants associated with cancer prevention. Recent research has identified compounds in coffee that might be used in the treatment of prostate cancer.

By far the best known compound in coffee is caffeine, the most widely consumed psychoactive drug in the world. In small amounts it is a stimulant but doses in excess of 10 g per day are toxic. Caffeine contains amide and amine groups.



caffeine

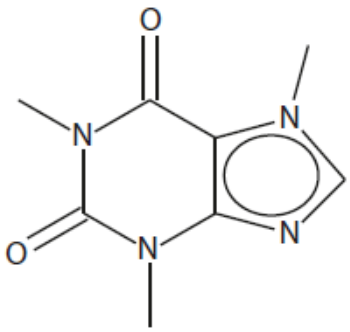
Chlorogenic acid is responsible for the acidic taste of coffee. It is an antioxidant and has also been shown to slightly decrease blood pressure.



chlorogenic acid

Caffeic acid, quinic acid and acetoin are also present in coffee.

(a) Another way of drawing the structure of caffeine is shown.



(i) The bonding represented by this diagram of caffeine differs from that given in the passage.

Explain what this diagram indicates about the bonding in caffeine, stating the effect on the structure of caffeine.

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(ii) Suggest why caffeine is a much weaker base than a primary amine such as ethylamine, even though the right-hand ring has two amine groups.

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(b) A 200 cm^3 cup of coffee contains approximately 85 mg of caffeine.

(i) Calculate the concentration, in mol dm^{-3}, of caffeine in this cup of coffee.
Give your answer to an appropriate number of significant figures.

(4)

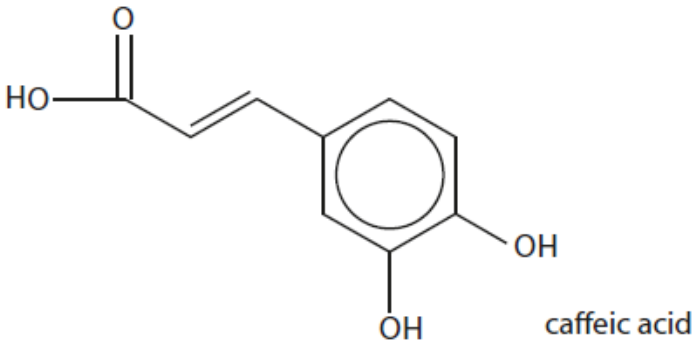
(ii) The removal of caffeine from the body is a first order reaction with a half-life of between three and seven hours for an adult.

An adult drinks coffee containing a total of 160 mg of caffeine.

Calculate to the nearest hour the **minimum** time needed for the amount of caffeine in their body to drop to 20 mg.

(2)

(c) Chlorogenic acid is an ester of caffeic acid, a compound that is present in all plants.



caffeic acid

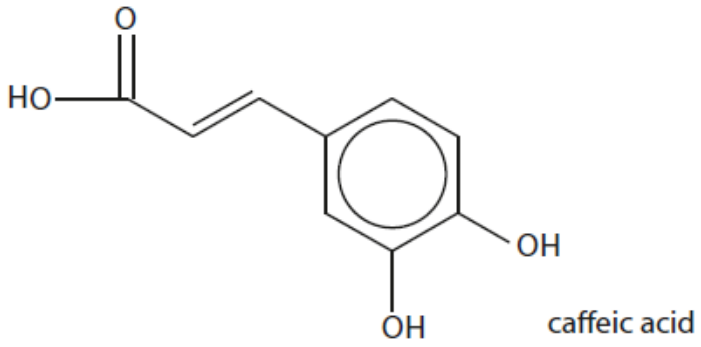
(i) A student suggested that caffeic acid could be synthesised by an electrophilic substitution of 1,2-dihydroxybenzene.

Draw the mechanism of this electrophilic substitution, including the formation of a suitable electrophile.

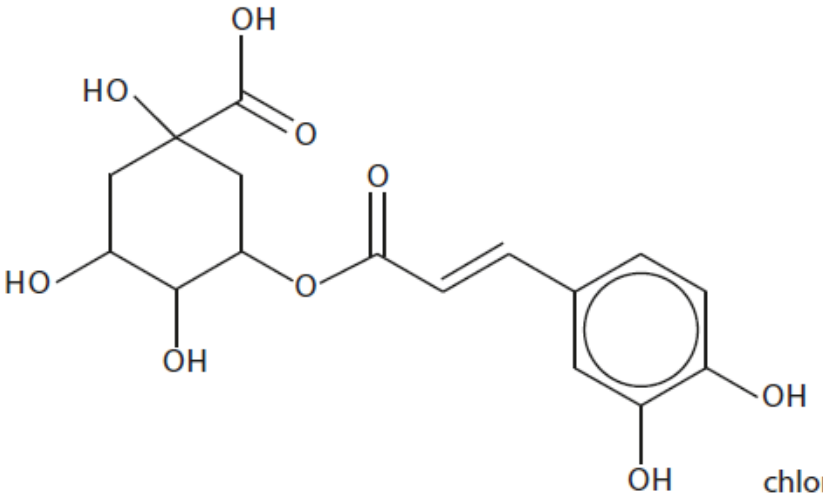
(5)

(ii) Deduce the structure of quinic acid which combines with caffeic acid to form chlorogenic acid.

(1)



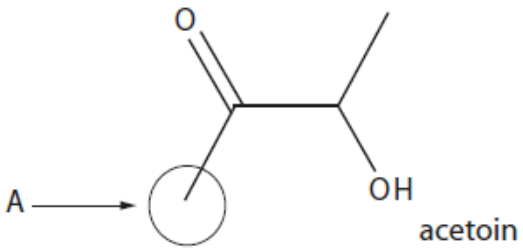
caffeic acid



chlorogenic acid

quinic acid

(d) The structure of acetoin is shown with one of the proton environments labelled.



acetoin

(i) Identify the other proton environments of acetoin on the structure and label them B, C etc.

(1)

(ii) Complete the table to show the splitting pattern in the high resolution proton NMR spectrum of acetoin.

(2)

Proton environment	Splitting pattern
A	

(Total for question = 20 marks)

Q9.

A compound, **Q**, is a pale yellow liquid that is the main constituent of cinnamon oil. **Q** contains the elements carbon, hydrogen and oxygen only.

(a) Complete combustion of 6.02 g of **Q** produces 18.07 g of carbon dioxide and 3.30 g of water.

Determine the empirical formula of **Q**.

(4)

(b) Tests on samples of **Q** show that it

- burns in air with a very sooty flame

- forms an orange precipitate with Brady's reagent (2,4-dinitrophenylhydrazine solution)
- forms a silver precipitate with Tollens' reagent
- decolourises bromine water
- exists as a pair of geometric isomers.

Deduce a structure for **Q**, explaining how each piece of information supports your answer.

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(Total for question = 10 marks)

Q10.

* Delocalised electron systems are important in determining the chemical properties of some compounds.

Compare and contrast the chemical reactions of bromine with benzene and cyclohexene, and with benzene and phenol, by considering the effects of delocalised electrons.

Detailed descriptions of the bonds or of the reaction mechanisms involved are **not** required.

(Total for question = 6 marks)

Q11.

Answer the question with a cross in the box you think is correct ☒ . If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒ .

The delocalised electrons in benzene result from the overlap of

☒ **A** s orbitals to form σ bonds

☒ **B** s orbitals to form π bonds

☒ **C** p orbitals to form σ bonds

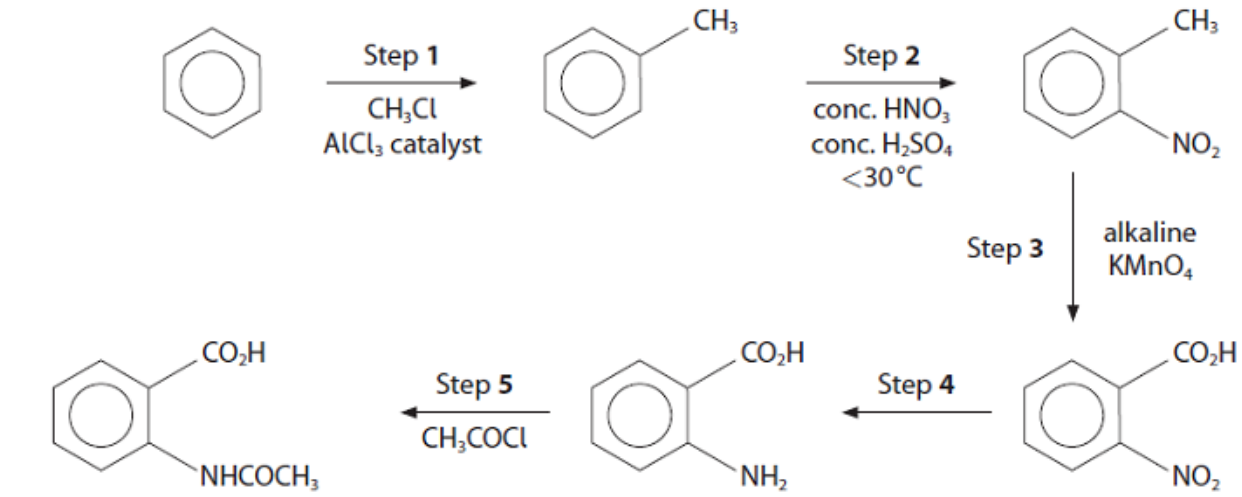
☒ **D** p orbitals to form π bonds

(Total for question = 1 mark)

Q12.

This question is about 2-ethanoylaminobenzoic acid.
Crystals of this compound emit flashes of light when crushed.

2-ethanoylaminobenzoic acid can be synthesised using benzene as a starting material.

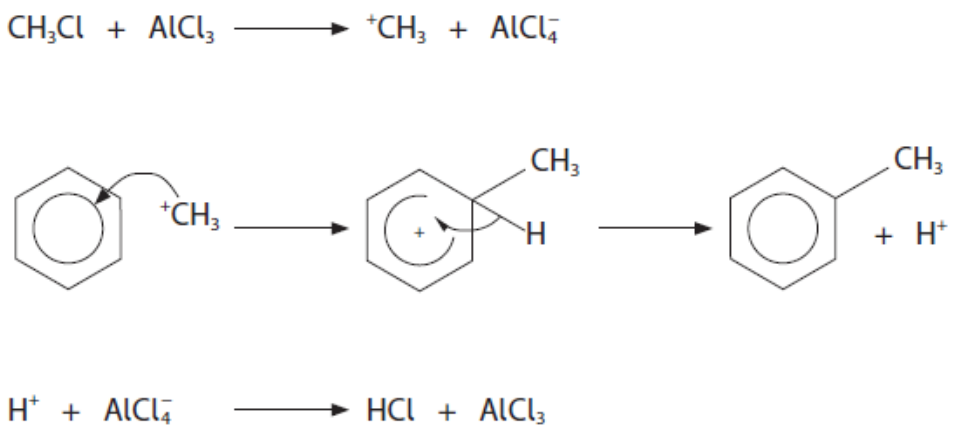


2-ethanoylaminobenzoic acid

compound **A**

(a) A student proposed a mechanism for Step **1**.

(a) A student proposed a mechanism for Step 1.



(i) Identify **two** errors in the mechanism by circling them.

(2)

(ii) State how the errors identified in (a)(i) should be corrected. Justify your answer in terms of the structures involved.

(2)

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(b) Give a reason why it is important to keep the temperature below 30 °C in Step **2**.

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(c) State the type of reaction in Step **3**.

(1)

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(d) Identify, by name or formula, the reagents needed for Step **4**.

(1)

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(e) Explain how the structures of ethanoyl chloride, CH_3COCl, and compound **A** enable them to react forming 2-ethanoylaminobenzoic acid in Step **5**.

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(f) Calculate the volume of benzene required to form 5.92 g of 2-ethanoylaminobenzoic acid, assuming the overall yield for the synthesis is 28.2 %.

Give your answer to an appropriate number of significant figures.

[Density of benzene = 0.879 g cm^{-3}]

(4)

(Total for question = 14 marks)

Q13.

Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

Benzene reacts with fuming sulfuric acid to form benzenesulfonic acid.

Fuming sulfuric acid is

(1)

☒ **A** sulfuric acid with a concentration of 98 %

☒ **B** pure sulfuric acid

☒ **C** concentrated sulfuric acid containing dissolved sulfur dioxide

☒ **D** concentrated sulfuric acid containing dissolved sulfur trioxide

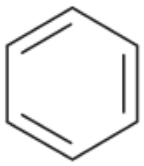
(Total for question = 1 mark)

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Q14.

Answer the question with a cross in the box you think is correct ☒ . If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒ .

Benzene is sometimes represented by a Kekulé structure.



Kekulé structure of benzene

If this were the **only** structure of benzene, what would be the total number of isomers of dichlorobenzene?

☒ **A** two

☒ **B** three

☒ **C** four

☒ **D** five

(Total for question = 1 mark)

Q15.

Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

Which organic compound reacts with a Grignard reagent to give a product that forms a secondary alcohol on hydrolysis?

☒ **A** carbon dioxide

☒ **B** ethanal

☒ **C** methanal

☒ **D** propanone

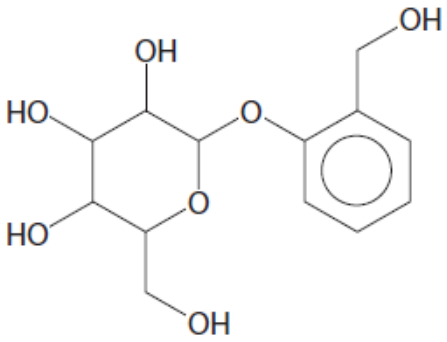
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(Total for question = 1 mark)

Q16.

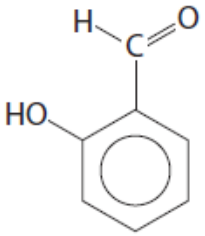
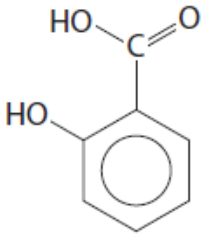
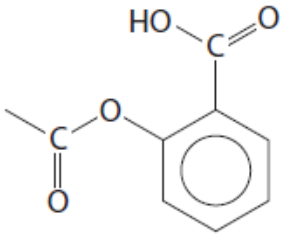
Chemicals from Plants

Plants are a rich source of useful chemicals, although their applications have often pre-dated the identification of the active compound. One of the best known examples of this is the use of willow bark extracts to reduce pain and fevers, a practice that is at least two thousand years old. The active compound in willow bark is salicin.



salicin

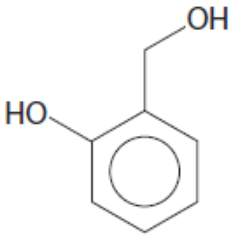
In the body, salicin is changed into salicylaldehyde and then salicylic acid. Salicylic acid may in turn be converted into 2-acetoxybenzenecarboxylic acid, a compound which is better known as aspirin, one of the most widely used medications in the world.

		
salicylaldehyde	salicylic acid	2-acetoxybenzenecarboxylic acid

(a) Calculate the percentage composition by mass of the elements in salicin.

(4)

(b) The first stage in the breakdown of salicin results in the formation of salicyl alcohol.



salicyl alcohol

Salicyl alcohol is readily oxidised in the laboratory to form salicylic acid.

(i) State the reagents and conditions needed for this oxidation.

(2)

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(ii) The boiling temperature of salicylaldehyde is 197 °C.

Suggest why this makes it very difficult to obtain salicylaldehyde by oxidising salicyl alcohol.

(2)

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(c) Aromatic aldehydes such as salicylaldehyde may be prepared in the laboratory by electrophilic substitution.

For example, benzaldehyde may be obtained by reacting benzene with a mixture of carbon monoxide and hydrogen chloride in the presence of aluminium chloride.
The mixture of carbon monoxide and hydrogen chloride reacts like methanoyl chloride.

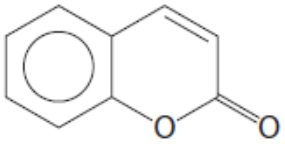
(i) Write an equation for the formation of the electrophile from methanoyl chloride. Use displayed formulae.

(1)

(ii) Draw the mechanism of the formation of benzaldehyde from benzene using the electrophile from (c)(i).

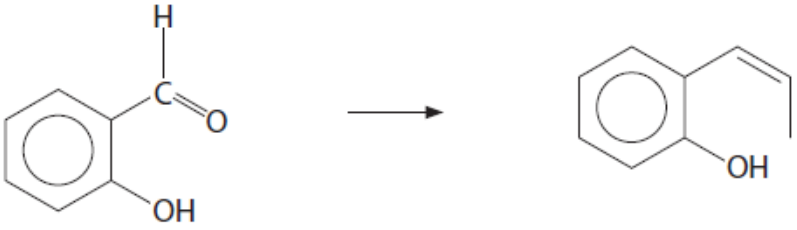
(3)

(d) Salicylaldehyde may be used in the synthesis of coumarin, a compound which occurs in many plants. Coumarin is in turn used to prepare warfarin, a compound prescribed to reduce blood clotting.



coumarin

One suggested synthesis of coumarin from salicylaldehyde involves the formation of an intermediate compound, **F**.

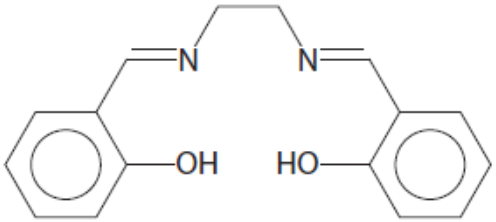


salicylaldehyde compound **F**

Devise a synthesis of **F** using salicylaldehyde and bromoethane as the **only** organic starting materials.
Include any other reagents and intermediate compounds, and give essential reaction conditions.

(4)

(e) Salicylaldehyde combines with 1,2-diaminoethane in a condensation reaction to form salen ligand.



salen ligand

Salen ligand reacts with many metal ions to form very stable complexes which are useful catalysts.

(i) Draw a diagram of the complex that **one** salen ligand forms with a Ni^{2+} ion, showing the type of bonding involved.

(2)

(ii) Explain why the salen ligand complex of the Ni^{2+} ion is much more stable than the aqua complex of the same ion.

(2)

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(Total for question = 20 marks)

Q17.

Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

What is the molar mass, in g mol^{-1}, of the organic product when phenol reacts with **excess** bromine water?

☐ **A** 156.9

☒ **B** 172.9

☒ **C** 330.7

☒ **D** 488.5

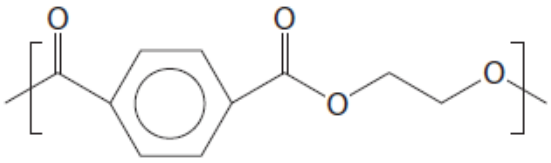
(Total for question = 1 mark)

Q18.

Answer the questions with a cross in the boxes you think are correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

This question is about polymers.

(a) A repeat unit of the polymer PET has the structure shown.



What is the percentage by mass of carbon in the repeat unit?

(1)

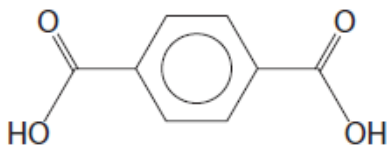
☒ **A** 57.1 %

☒ **B** 62.5 %

☒ **C** 65.2 %

☒ **D** 66.7 %

(b) One of the monomers used to make PET is benzene-1,4-dicarboxylic acid.



How many peaks are there in the 13C NMR spectrum of benzene-1,4-dicarboxylic acid?

(1)

☒ **A** 2

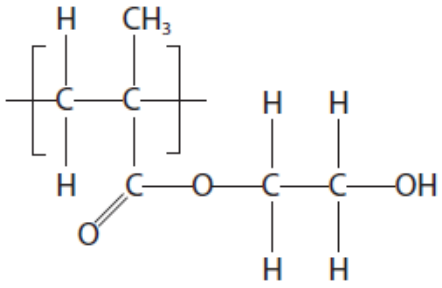
☒

B 3

☒ **C** 4

☒ **D** 6

(c) The repeat unit of another polymer has the structure shown.



This polymer is formed from

(1)

☒ **A** a single type of monomer by an addition reaction

☒ **B** a single type of monomer by a condensation reaction

☒ **C** two different types of monomer by an addition reaction

☒ **D** two different types of monomer by a condensation reaction

Use this space for rough working. Anything you write in this space will gain no credit.

(Total for question = 3 marks)

Q19.

Answer the question with a cross in the box you think is correct ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

Which is correct for the reaction of bromine with phenol when compared with benzene?

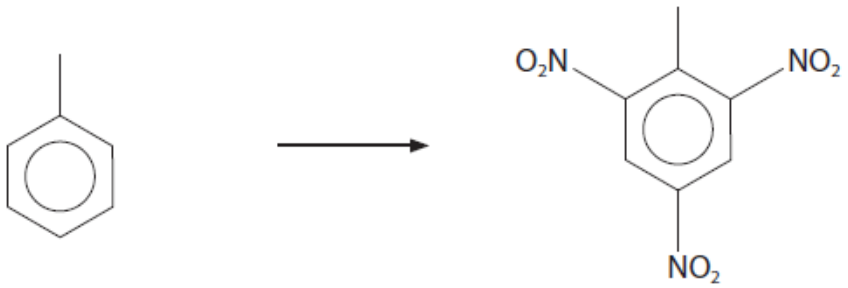
		Reactivity of phenol	Electron density of the ring in phenol
☒	**A**	more reactive	higher electron density
☒	**B**	more reactive	lower electron density
☒	**C**	less reactive	higher electron density
☒	**D**	less reactive	lower electron density

(Total for question = 1 mark)

Q20.

For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

Methylbenzene reacts with a mixture of concentrated nitric acid and concentrated sulfuric acid to form
2,4,6-trinitromethylbenzene.



(a) What is the number of peaks in the ^{13}C NMR spectrum of methylbenzene?

(1)

☒ **A** seven

☒ **B** six

☒ **C** five

☒ **D** four

(b) What type of reaction takes place?

(1)

☒ **A** nucleophilic addition

☒ **B** nucleophilic substitution

☒ **C** electrophilic addition

☒ **D** electrophilic substitution

(c) Which expression shows the mass in grams of 2,4,6-trinitromethylbenzene formed from 10 g of methylbenzene if the yield of the reaction is 85 %?

[M_r values: methylbenzene = 92 2,4,6-trinitromethylbenzene = 227]

(1)

☒ **A** (10 × 85 × 227) ÷ (92 × 100)

☒ **B** (10 × 100 × 227) ÷ (92 × 85)

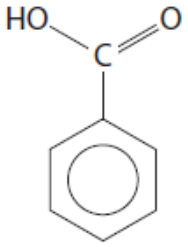
☒ **C** (10 × 100 × 227) ÷ (92 × 115)

☒ **D** (10 × 115 × 227) ÷ (92 × 100)

(Total for question = 3 marks)

Q21.

Benzoic acid is a white crystalline solid with the structure shown.



It is found in many plants as it is an important building block for the biosynthesis of a variety of compounds, such as plant hormones and attractants for pollinators.

The role of benzoic acid in the chemical industry is also widespread and approximately 500 000 tonnes are produced annually. It is used in the synthesis of many compounds, including medicines, dyes and insect repellents.

Such synthetic dyes are often classified as aryl azo dyes. These dyes have a range of vivid colours and a wide range of uses in many industries, including food and textiles. Their synthesis involves the formation of a diazonium ion. This ion then reacts with a phenol in a coupling reaction, to form the dye. The relative simplicity of the reactions involved and ready availability of starting materials make azo dyes cheap to produce.

Salts of benzoic acid, such as calcium benzoate and sodium benzoate, are used in the food

industry as preservatives.

(a) Devise a reaction scheme to produce benzoic acid from benzene, via bromobenzene and then a Grignard reagent.

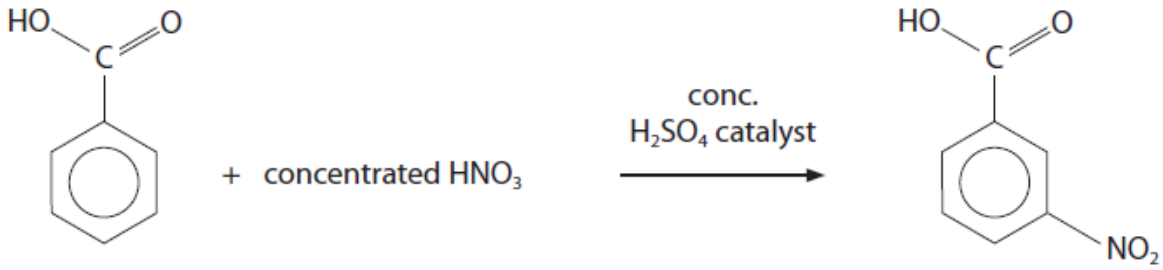
Include the reagents and essential conditions for each step and give the name or structure of each of the intermediate compounds.

Details of practical procedures and reaction mechanisms are **not** required.

(6)

(b) Benzoic acid can be used in the synthesis of azo dyes.

(i) In Step **1**, benzoic acid reacts with concentrated nitric acid to form 3-nitrobenzoic acid.



benzoic acid

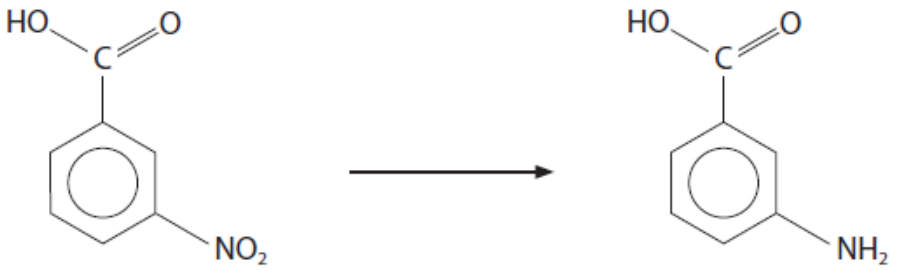
3-nitrobenzoic acid

Draw the mechanism for the reaction, using appropriate curly arrows.

Include equations showing the role of the catalyst and how it is regenerated.

(5)

(ii) In Step **2**, the 3-nitrobenzoic acid reacts to form 3-aminobenzoic acid.



3-nitrobenzoic acid

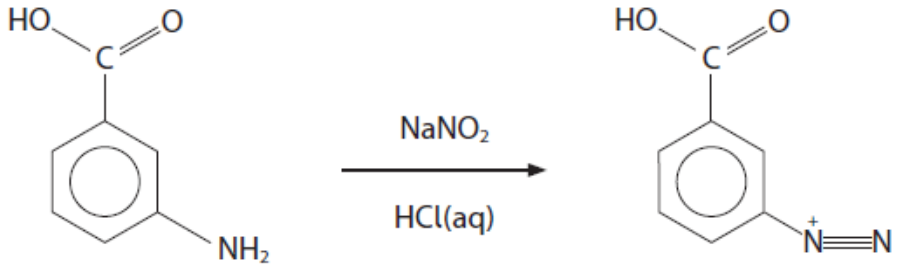
3-aminobenzoic acid

State the reagents required for this reaction.

(1)

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(iii) In Step **3**, the 3-aminobenzoic acid reacts with sodium nitrite and dilute hydrochloric acid, forming a diazonium ion.



3-aminobenzoic acid diazonium ion

State a temperature at which this reaction should take place, giving **one** reason for your answer.

(2)

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(iv) Draw the structure of the azo dye formed when the diazonium ion reacts with phenol.

(1)

(c) Hydrated calcium benzoate is used as a preservative in soft drinks. It has the formula $Ca(C_6H_5COO)_2 \bullet xH_2O$.

2.60 g of hydrated calcium benzoate was dissolved in deionised water. Excess lead(II) nitrate solution was added, forming a precipitate of lead(II) benzoate, $Pb(C_6H_5COO)_2(s)$. This precipitate was removed and dried. The mass of the dry solid was 3.89 g.

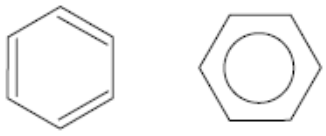
Calculate the molar mass of hydrated calcium benzoate and hence deduce the value of x.

(6)

(Total for question = 21 marks)

Q22.

Benzene can be represented by either a cyclic triene or with a delocalised ring of electrons.



*(a) Discuss the evidence, including one example from each of spectroscopy, thermochemistry and the type of reaction normally undergone, that supports the view that the better representation of benzene is with a delocalised ring of electrons.

(6)

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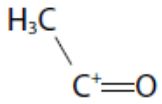
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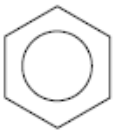
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(b) Benzene can be converted into phenylethanone by a Friedel-Crafts acylation.

(i) Complete the diagram, including curly arrows, to show the mechanism for this reaction.

(4)





(ii) Write an equation to show how the species, CH_3CO^+, could be generated.

(1)

(c) Explain why phenol reacts with bromine more readily than benzene reacts with bromine.

(2)

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(d) Benzene can be converted into nitrobenzene.

(i) Complete the flow diagram showing this conversion.

(2)



(ii) Calculate the percentage yield if 0.642 g of nitrobenzene was made from 0.936 g of benzene.

Give your answer to an appropriate number of significant figures.

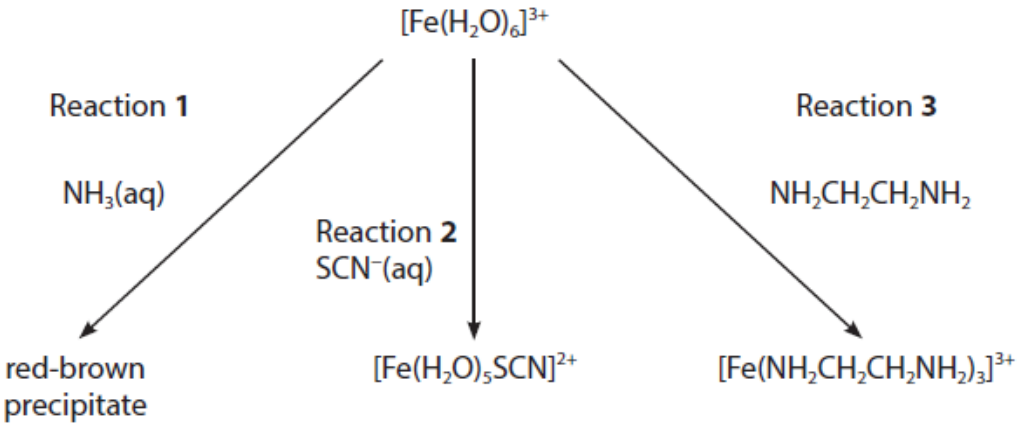
(3)

(Total for question = 18 marks)

Q23.

This question is about transition metals and their compounds.

(a) Three reactions were carried out on a solution containing $[Fe(H_2O)_6]^{3+}$ ions.



(i) Complete the equation for Reaction **1**. State symbols are not required.

(2)

$[Fe(H_2O)_6]^{3+}$ + ... NH_3 →

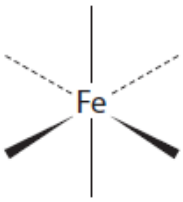
(ii) State the type of reaction occurring in Reaction **2**.

(1)

.....

(iii) Complete the diagram to show the structure of the complex ion formed in Reaction **3**, showing **all** of the atoms.

(2)



(b) Vanadium can exist in the oxidation states +2, +3, +4 and +5.

(i) Complete the table to show the colours of the ions that each of these oxidation states has in aqueous solution.

(2)

Oxidation state of vanadium	Colour of the ions in aqueous solution
+2	mauve
+3	
+4	
+5	

(ii) Two vanadium species exist in equilibrium in an aqueous solution.

$$VO_3^-(aq) + H_2O(l) \rightleftharpoons VO_2^+(aq) + 2OH^-(aq)$$

Deduce whether or not this is a redox reaction.

Justify your answer in terms of oxidation numbers.

(1)

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(iii) Predict the oxidising agent that could convert vanadium(II) ions to vanadium(III) ions and then vanadium(IV) ions, but **not** to vanadium(V) ions, under standard conditions.

Only use data from the tables shown.

Include equations and $E^{\ominus}_{cell}$ values for the two reactions that occur.

(5)

Vanadium systems

Electrode system	$E^{\ominus}$ / V
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	−0.26
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00

Oxidising agents

Electrode system	$E^{\ominus}$ / V
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+0.15
$NO_3^-(aq) + 2H^+(aq) + e^- \rightleftharpoons NO_2(g) + H_2O(l)$	+0.80
$\frac{1}{2}Br_2(aq) + e^- \rightleftharpoons Br^-(aq)$	+1.09

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*(c) Transition metals, their compounds and their ions can act as heterogeneous and homogeneous catalysts.

Compare and contrast these two types of catalytic behaviour.

Include one specific example from transition metal chemistry of each of these types of catalyst and a reaction
in which it is used.

(6)

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(Total for question = 19 marks)

Mark Scheme

Q1.

Question number	Answer	Mark
	The only correct answer is C (12 (σ bonds) 3 (π bonds)) ***A*** *is incorrect because this does not include the C−H bonds* ***B*** *is incorrect because this does not include the C−H bonds and counts all the C−C bonds asboth σ bonds and πbonds* ***D*** *is incorrect because this counts all the C−C bonds as both σ bonds and π bonds*	**(1)**

Q2.

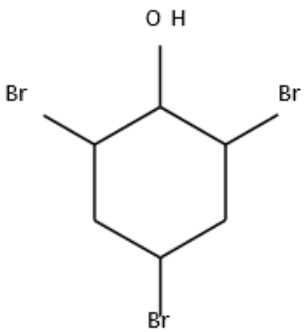
Question number	Answer	Mark
	The only correct answer is B (4) ***A*** *is incorrect because the 1st and 6th amino acids are the same, the 2nd is different, the 3rd and 5th are the same and the 4th is different* ***C*** *is incorrect because the 1st and 6th amino acids are the same, the 2nd is different, the 3rd and 5th are the same and the 4th is different* ***D*** *is incorrect because the 1st and 6th amino acids are the same, the 2nd is different, the 3rd and 5th are the same and the 4th is different*	**(1)**

Q3.

Q	Answer	Additional guidance	Mark
(a)(i)	• calculation of the difference between the enthalpies of combustion of cyclohexene and cyclohexa-1,4-diene (1) • subtraction of the calculated difference from the enthalpy of combustion of cyclohexa-1,4-diene to give the enthalpy of combustion of cyclohexa-1,3,5-triene (1)	Example of calculation $-3752 - (-3584) = -168$ (kJ mol^{-1}) Ignore sign of 168 $-3584 - (-168) = -3416$ (kJ mol^{-1}) TE on numerical errors in M1 Correct answer with some working scores (2)	**2**

Q	Answer	Additional guidance	Mark
(a)(ii)	An explanation that makes reference to • calculation of the difference between the enthalpies of combustion of benzene and cyclohexa-1,3,5-triene (1) • benzene **more** stable than cyclohexa-1,3,5-triene by 149 (kJ mol^{-1}) (1) • (benzene **more** stable) because the π electrons in benzene are delocalised (1)	$-3416 - (-3267) = -149$ (kJ mol^{-1}) TE on value calculated in (a)(i) Ignore omission of negative sign Allow enthalpy of combustion of benzene less negative / less exothermic /lower than that of cyclohexa-1,3,5-triene **and** so benzene is more stable If M1 is scored Allow just 'benzene **more** stable than cyclohexa-1,3,5-triene' Allow reverse arguments Do not award M2 if the enthalpy of combustion of benzene is more negative than that calculated for cyclohexa-1,3,5-triene Allow benzene has delocalisation energy / resonance stability /bonds delocalised standalone mark	**3**

Q	Answer	Additional guidance	Mark
(b)	An answer that makes reference to **four** of the following: Similarities • **both** reactions involve electrophilic attack(1) • **both** reactions form a carbocation (1) Differences • reaction with benzene is substitution (because the stable benzene ring is retained / restored)(1) • reaction with cyclohexene is addition (because σ bonds stronger than π bonds)(1) • reaction with benzene requires a catalyst (and heat) **and** whereas reaction with cyclohexene occurs under normal laboratory conditions (1)	This may be shown using a **labelled** diagram Accept 2 C—H and 1 C—C stronger than C=C and Br—Br Allow cyclohexene reaction does not require catalyst / heat Allow cyclohexene reacts with bromine water Do not award if conditions are incorrect e.g. cyclohexene reaction requires heat	4

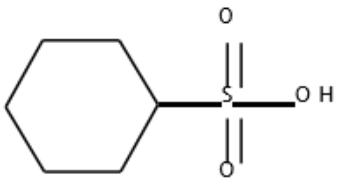
Q	Answer	Additional guidance	Mark
(c)(i)	• 2,4,6-tribromophenol OR  	If name and formula are given both must be correct Accept Kekulé structure Allow Correct structure and tribromophenol Ignore punctuation errors in the name such as omission of commas or hyphen and inclusion of spaces	1

Q	Answer	Additional guidance	Mark
(c)(ii)	An explanation that makes reference to • lone pair of electrons on the oxygen (1) • overlap / interact with the π electrons of the ring **and** increasing its electron density / becomes more susceptible to electrophilic attack (1)	Allow lone pair of electrons on the OH Allow (lone pair) donated to the π electrons of the ring Ignore increasing the reactivity of the ring Ignore reference to phenol being a nucleophile	2
			(Total for Question = 12 marks)

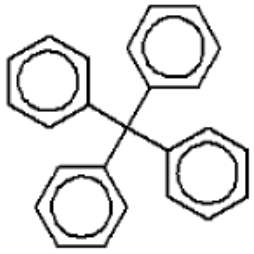
Q4.

Question number	Answer	Mark
	The only correct answer is B (result in a kinetic barrier to intermediate formation) ***A*** *is incorrect because the delocalised electrons attract electrophiles* ***C*** *is incorrect because both ethene and benzene have endothermic enthalpies of formation and this is not a factor in their reactivity* ***D*** *is incorrect because catalysts have no effect on the thermodynamics of a reaction*	(1)

Q5.

Q	Answer	Mark
	The only correct answer is D  ***A*** *is not correct because the substituent is SO_3H* ***B*** *is not correct because the substituent is SO_3H with a C—S bond* ***C*** *is not correct because the substituent is SO_3H*	**1**

Q6.

Question number	Answer	Mark
	The only correct answer is D () ***A*** *is incorrect because this product is formed by the substitution of one chlorine atom in $CHCl_3$* ***B*** *is incorrect because this product is formed by the substitution of two chlorine atoms in $CHCl_3$* ***C*** *is incorrect because this product is formed by the substitution of all three chlorine atoms in $CHCl_3$*	**1**

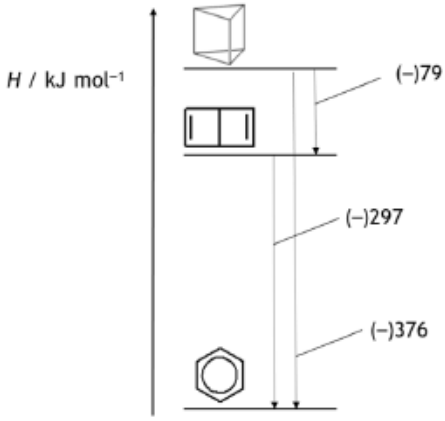
Q7.

Question Number	Answer	Additional guidance	Mark
(a)	• suitable test: bromine water/Br_2(aq) (1) • result of test: decolourises (from orange) with Dewar structure (and no change with benzene) (1)	Allow bromine / Br_2((l)) / Br_2 in organic solvent Do not award Br/Br^- Accept potassium manganate((VII))/$KMnO_4$ **and** acidified/ named acid/H^+ Do not award hydrogenation Do not award combustion Allow does not decolourise with benzene Allow brown/orange/yellow for colour of bromine water Allow red/brown/orange for colour of bromine Allow pink/purple for colour of potassium manganate((VII)) Ignore colour fades for decolourises Ignore reference to addition/substitution Do not award any reference to decolourisation/reaction with benzene	2

Question Number	Answer	Additional guidance	Mark
(b)	• similarity: (both compounds have) one (NMR) peak (1) • difference: expected chemical shift values (1)	Ignore any reference to IR and/or ^{13}C NMR Allow (both compounds have) one proton environment Ignore just same number of peaks Ignore references to relative peak area/integration/splitting Do not award any other number of peaks chemical shift for benzene within range of 6.4 to 8.4 ppm (actual value is 7.3 ppm) **and** chemical shift for Ladenburg structure within range of 0 to 2.3 ppm (actual value is 2.3 ppm) Allow any range or value within the above ranges Ignore just benzene would have a higher chemical shift than Ladenburg structure or reverse argument Do not award additional incorrect chemical shifts	2

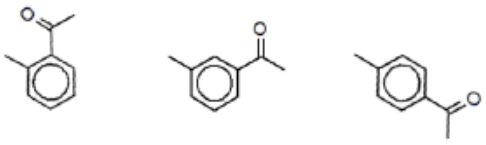
Question Number	Answer	Additional guidance	Mark
(c)	An explanation that makes reference to the following points: • showed that all C–C bonds are the same length in benzene (1) • in Kekulé structure the C=C bonds would be shorter than the C–C bonds (or reverse argument) (1)	Ignore any reference to: C–H bonds bond strength/bond angle delocalised electrons Dewar/Ladenburg structures Allow showed benzene is a regular hexagon Allow showed benzene contains only one type of carbon-carbon bond Allow benzene bond lengths are in between C=C and C–C Ignore just benzene has no C=C bonds Do not award benzene bond lengths are longer than C–C/ shorter than C=C Allow Kekulé structure would have shown two different lengths/types of carbon-carbon bond Allow Kekulé structure would have alternating carbon-carbon bond lengths Ignore just Kekulé has C=C bonds Do not award C–C bonds would be shorter than the C=C bonds If no other mark awarded, just bond lengths equal in benzene but different in Kekulé scores (1)	2

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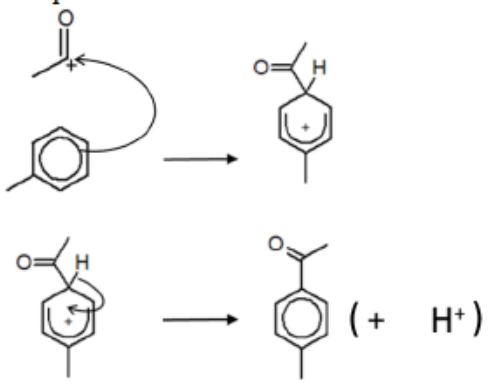
Question Number	Answer	Additional guidance	Mark
(d)(i)	A diagram showing: • correct relative stabilities (1) • two or three numerical differences in enthalpy with appropriate arrows (1)	Example of diagram:  Allow names for structures If three values and arrows are given they must all be correct to score M2 Allow slight imprecision in start and end of arrows in M2 Ignore any x-axis label Do not award double headed arrows in M2 Do not award incorrect sign in M2	2

Question Number	Answer	Additional guidance	Mark
(d)(ii)	An answer that makes reference to the following: • pi bonds are weaker/more reactive/require less energy to break (than sigma bonds) **or** fewer bonds must break to convert the Dewar structure to benzene	Ignore just Dewar structure has pi/double bonds/is unsaturated Ignore just Dewar structure has weaker bonds Do not award C=C/double bonds weaker/require less energy to break (than C–C/single bonds) Accept reverse argument Allow any specified numbers to indicate fewer bonds must break Ignore fewer new bonds must form Ignore Dewar structure is more similar to benzene Ignore carbon atoms already in a ring/hexagon Ignore any reference to intermolecular forces Do not award (higher) ring strain in Ladenburg Do not award smaller difference in enthalpy Do not award Ladenburg structure more stable	1

Question Number	Answer	Additional guidance	Mark
(e)	An explanation that makes reference to the following points: ***E*-hexa-1,4-diene** • twice the hydrogenation enthalpy (of hex-3-ene) as two (isolated) C=C bonds (1) ***E*-hexa-1,3-diene** • less exothermic/more stable (by 22 kJ mol^{-1} than *E*-hexa-1,4-diene **and** as some delocalisation of pi-bond(s) (1)	Allow double bond for C=C throughout Accept −118 × 2 (=−236) as two C=C bonds Allow twice the hydrogenation enthalpy as no delocalisation of pi-bond(s) Accept less negative Allow more positive Allow some delocalisation of double bond(s) Allow double bonds/p-orbitals are conjugated Allow double bonds/p-orbitals are close enough to overlap Ignore just C=C are close Ignore just delocalisation of electrons Ignore electron density more spread out Ignore resonance stabilised	2

Question Number	Answer	Additional guidance	Mark
(f)(i)	• skeletal formula of any one isomer (1) • skeletal formulae of second and third isomers (1)	Example of correct skeletal formulae:  (1,2-isomer) (1,3-isomer) (1,4-isomer) Allow Kekulé benzene ring Allow structural/displayed CH_3 and CH_3CO groups If no other mark awarded, 1,2-, 1,3- and 1,4-isomers with incorrect side chain/cyclohexane ring scores (1)	2

Question Number	Answer	Additional guidance	Mark
(f)(ii)	• (identification of **X** as) 1,4-isomer (1) • (7 peaks consistent with) 7 carbon environments (1)	Allow any form of identification, including (f)(i) annotation Allow just '1,4' or 'para' **M2 dependent on a structure containing 7 carbon environments** Accept 1,2-isomer and/or 1,3-isomer have 9 carbon environments/would have 9 peaks Allow (4 arene peaks consistent with) 4 arene carbon environments Allow 1,2-isomer and/or 1,3-isomer have 6 arene carbon environments/would have 6 arene peaks	**2**

Question Number	Answer	Additional guidance	Mark
(f)(iii)	A mechanism including: • curly arrow from on or within circle to C^+ of CH_3CO^+ (1) • structure of intermediate ion (1) • curly arrow from C–H bond to within ring **and** correct product (1) • balanced equation for regeneration of catalyst (1)	Example of mechanism:  Allow Kekulé benzene ring 'Horseshoe' facing tetrahedral carbon and covering at least three carbons with some part of positive sign within 'horseshoe' Allow methyl at 1,2- or 1,3-positions Ignore missing methyl substituent Do not award dotted/dashed C–H/C–C bonds unless 3D structure Allow 1,2- or 1,3-product from corresponding intermediate Do not award missing methyl substituent $AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$	**4**

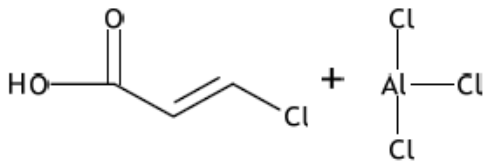
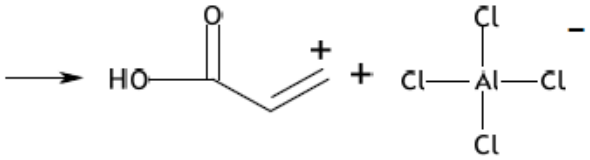
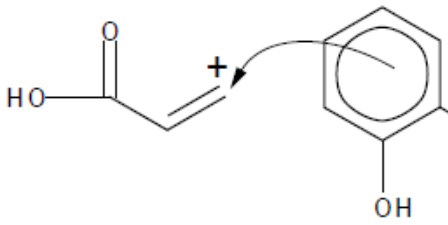
Q8.

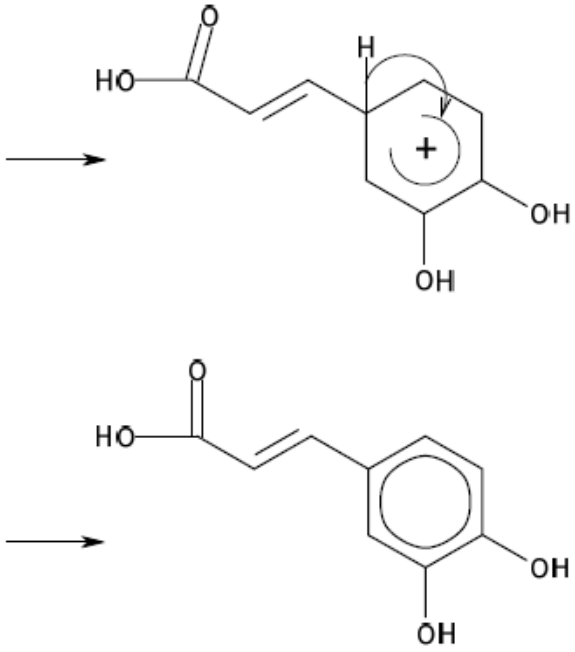
Question number	Answer	Additional guidance	Mark
(a)(i)	An explanation that makes reference to the following points • (π) electron system (in the right-hand ring) is delocalised (1) M2 and M3 scored from any **two** of • the delocalisation involves the lone-pair(s) in the nitrogen (atom(s)) and the π electrons of the double bonds (1) • (the right-hand ring) will undergo substitution reactions rather than addition reactions (1) • caffeine has stabilisation / delocalisation energy (1) • all the C—N bonds (in the 5-membered ring) will be the same (length)(1)	Allow aromatic ring Ignore just 'form aπ bond' Do not award just it is a benzene ring Allow just 'the delocalisation involves the lone-pair(s) in the nitrogen (atom(s)) Allow electrophilic substitution (rather than addition) Ignore electrophilic reaction Allow caffeine / (delocalised) ring is more stable Allow all the bonds will be the same length Ignore C=C bonds will be the same length	(3)

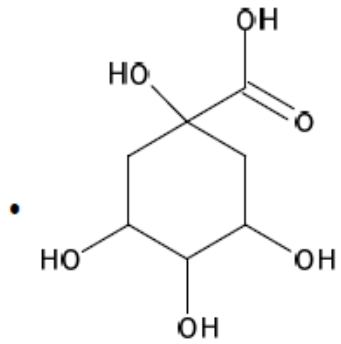
Question number	Answer	Additional guidance	Mark
(a)(ii)	An explanation that makes reference to the following points • Description of basicity (1) • Effect of delocalisation(1)	 Either lone pair donation Or proton acceptor Nitrogen lone pair incorporated in delocalised system / overlaps with the π (electron) ring **and** reduces electron density / lone pair availability Do not award overlap with the benzene ring Ignore references to the amide even if incorrect. If no other mark is scored the positive inductive effect of alkyl groups increases availability of the lone pair in a primary amine scores (1)	(2)

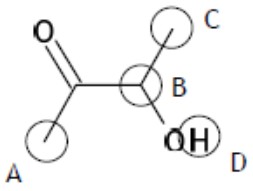
Question number	Answer	Additional guidance	Mark
(b)(i)	• determination of M_r (from molecular formula) (1) • calculation of amount of caffeine (1) • calculation of concentration of caffeine (1) • final answer to 1 or 2 SF (1)	Example of calculation $(C_8H_{10}N_4O_2)$ M_r = 194 $\frac{85}{1000 \times 194}$ (= 4.3814×10^{-4}/ 0.00043814) (mol) $= \frac{1000 \times 85}{200 \times 1000 \times 194} / \frac{1000 \times 0.00043814}{200}$ = 2.1907×10^{-3}/ 0.0021907 (mol dm^{-3}) = 2×10^{-3} /2.2×10^{-3} / 0.002 /0.0022(mol dm^{-3}) Do not award > 2 SF TE at each stage correct answer with no working scores (1)	(4)

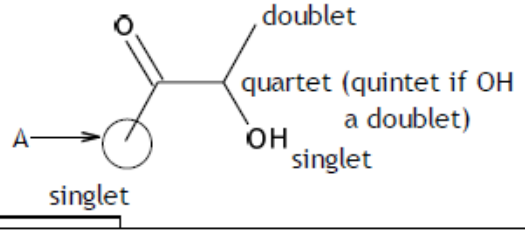
Question number	Answer	Additional guidance	Mark
(b)(ii)	• calculation of number of half-lives (1) • applies half-lives to three hours (1)	Example of calculation $\frac{20}{160} = \frac{1}{8} = \left(\frac{1}{2}\right)^n$ n = 3 or 160 → 80 → 40 → 20 (3 half lives) time = 3 x 3 = 9 hours TE on number of half lives calculated correct answer with some working scores (2)	(2)

Question number	Answer	Additional guidance	Mark
(c)(i)	A mechanism showing the following • structure of 3-chloropropenoic acid (1) • structure of the electrophile **and** balanced equation involving $AlCl_3$ and $AlCl_4^-$ (1) • curly arrow from on or within the circle to the positively charged carbon (1) **Allow any electrophile for M3, M4 and M5**	M1 and M2 are for the electrophile formation M3, M4 and M5 are for the electrophilic substitution Example of mechanism  Allow Br or I for Cl and Fe for Al Penalise errors in structure of 3-chloropropenoic acid / electrophile in M1 or M2 only   Allow curly arrow from anywhere in the hexagon Allow dotted horseshoe	(5)

Question number	Answer	Additional guidance	Mark
(c)(i) cont	• intermediate structure including charge with horseshoe covering at least 3 carbon atoms **and** facing the tetrahedral carbon **and** with some part of the positive charge within the horseshoe (1) • curly arrow from C—H bond to anywhere in the benzene ring reforming delocalised structure with phenol groups in the 3 and 4 positions (1)	 penalise incorrect position / omission of the phenol groups at final marking point. Ignore omission of H^+ in final step correct Kekulé structures score full marks Ignore structure of substituents apart from the position of the OH groups in final structure	

Question number	Answer	Additional guidance	Mark
(c)(ii)	•  	or displayed structure Allow COOH and CO_2H Ignore all connectivity errors to 'OH' Only penalise O–H–C	(1)

Question number	Answer	Additional guidance	Mark
(d)(i)	• 	Allow any labelling sequence Do not award any other labelling	(1)

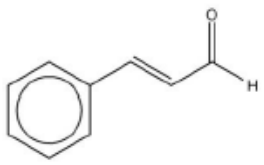
Question number	Answer	Additional guidance	Mark
(d)(ii)	<table><tr><th>Proton environment (labelled as in (i))</th><th>Splitting pattern</th></tr><tr><td>A</td><td>singlet</td></tr><tr><td>B</td><td>quartet</td></tr><tr><td>C</td><td>doublet</td></tr><tr><td>D</td><td>singlet</td></tr></table> OR 	all four correct (2) three correct (1) Allow non-standard terms such as 'two splits' or just '2' for doublet If D (OH proton) is given as a doublet, allow B as a quartet **or** as a quintet Ignore carbonyl carbon labelled as a proton environment	(2)

Q9.

<table>
<tr><th>Question Number</th><th>Acceptable Answers</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr><td>(a)</td><td>• calculation of mass of C and H (1)
• calculation of mass of oxygen (1)
• calculation of moles of C, H and O (1)
• calculation of ratio and deduction of empirical formula (1)</td><td>Example of calculation
<table><tr><td>Element</td><td>C</td><td>H</td><td>O</td></tr><tr><td>Mass (g)</td><td>18.07 x (12÷44) = 4.9282</td><td>3.30 x (2÷18) = 0.36667</td><td>6.02 – (4.9282+0.36667) =0.72513</td></tr><tr><td>Moles (mol)</td><td>4.9282 ÷12 =0.41068</td><td>0.36667÷1 = 0.3667</td><td>0.72513 ÷ 16 = 0.045320</td></tr><tr><td>Ratio</td><td>0.41068÷0.045320 = 9.06</td><td>0.36667÷0.045320 = 8.09</td><td>0.045320÷0.045320 = 1</td></tr></table>
C_9H_8O

Allow TE throughout
Ignore minor rounding errors in M1-M3</td><td>(4)</td></tr>
</table>

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Question Number	Acceptable Answers	Additional Guidance	Mark
(b)	An explanation that makes reference to the following points: • correct structure of Q shown (1) • sooty flame indicates benzene ring / arene / phenyl group / high C : H ratio / aromatic (1) • orange precipitate with 2,4-dinitrophenylhydrazine indicates carbonyl group / C=O / aldehyde **or** ketone (1) • silver precipitate with Tollens' reagent indicates aldehyde (1) • decolourises bromine water indicates C=C bond / alkene (functional group) / unsaturated (1) • exists as a pair of geometric isomers indicates only 1 hydrogen atom on each carbon of the C=C bond / each carbon of the C=C has two different groups attached (1)	e.g  Accept cis structure Accept skeletal structure without terminal hydrogen Accept hybrid structures e.g. partially displayed Ignore 'it is an alkene' Ignore references to phenol Do not award benzene Allow 'cannot have -CH=CH$_2$ group' Allow '2 different groups on each side of the C=C bond'	(6)

Q10.

<table>
<tr><th>Question number</th><th>Answer</th><th>Additional guidance</th><th>Mark</th></tr>
<tr>
<td>*</td>
<td>
This question assesses the student's ability to show a coherent and logically structured answer with linkages and fully sustained reasoning.
Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning.

The following table shows how the marks should be awarded for indicative content.
<table>
<tr><th>Number of indicative marking points seen in answer</th><th>Number of marks awarded for indicative marking points</th></tr>
<tr><td>6</td><td>4</td></tr>
<tr><td>5-4</td><td>3</td></tr>
<tr><td>3-2</td><td>2</td></tr>
<tr><td>1</td><td>1</td></tr>
<tr><td>0</td><td>0</td></tr>
</table>

The following table shows how the marks should be awarded for structure and lines of reasoning
<table>
<tr><th></th><th>Number of marks awarded for structure of answer and sustained lines of reasoning</th></tr>
<tr><td>Answer shows a coherent logical structure with linkages and fully sustained lines of reasoning demonstrated throughout</td><td>2</td></tr>
<tr><td>Answer is partially structured with some linkages and lines of reasoning</td><td>1</td></tr>
<tr><td>Answer has no linkages between points and is unstructured</td><td>0</td></tr>
</table>
</td>
<td>
Guidance on how the mark scheme should be applied.

The mark for indicative content should be added to the mark for lines of reasoning. For example, a response with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning).

If there were no linkages between the points, then the same indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages).

In general it would be expected that 5 or 6 indicative points would get 2 reasoning marks, and 3 or 4 indicative points would get 1 mark for reasoning, and 0, 1 or 2 indicative points would score zero marks for reasoning.

If there is incorrect chemistry, deduct mark(s) from the reasoning.

If no reasoning mark(s) awarded do not deduct mark(s).

Comment: Look for the indicative marking points first, then consider the mark for the structure of the answer and sustained line of reasoning
</td>
<td>6</td>
</tr>
</table>

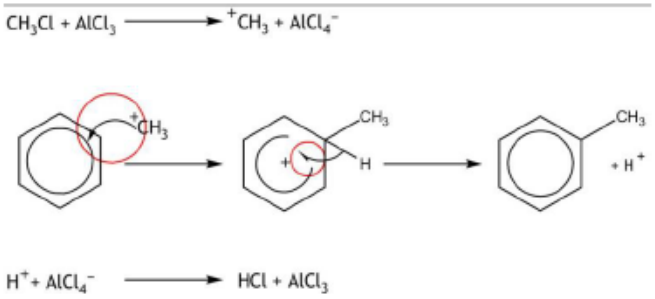
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Question number	Answer	Additional guidance	Mark
continued	**Indicative content** **IP1** (the π electrons of) both benzene and cyclohexene attract / react with electrophiles (similarity) **IP2** delocalised (π) **electron** ring in benzene is (very)stable **IP3** so benzene undergoes (electrophilic) substitution whereas cyclohexene undergoes (electrophilic) addition **IP4** both benzene and phenol undergo (electrophilic) substitution (similarity) **IP5** the lone pair of electrons on the oxygen in phenol interacts with / overlaps the delocalised (π)electron system of the benzene ring **IP6** phenol reacts (with electrophiles) much faster / under much milder conditions / does not require a catalyst / has a lower activation energy / E_a	Accept structures for names throughout Do not penalise unbalanced / incomplete / incorrect equations If name and formula given both must be correct Allow both benzene and cyclohexene form carbocation (intermediates) Do not award nucleophilic reactions Allow delocalised (π) **electrons** make benzene stable If neither IP1 or IP2 given, allow an IP for benzene has delocalised **electrons** but cyclohexene does not. Allow benzene forms bromobenzene **and** cyclohexene forms 1,2-dibromocyclohexane. Do not award nucleophilic reactions Allow benzene forms bromobenzene **and** phenol forms 2,4,6-tribromophenol Allow the lone pair of electrons on the oxygen in phenol increases the electron density of the (benzene) ring Accept benzene requires a halogen carrier / catalyst Allow $AlBr_3$ / $AlCl_3$ / $FeBr_3$ / Fe & Br_2 Ignore just 'bromine reacts more easily with phenol than with benzene' / 'phenol is more susceptible to electrophilic attack'	6

Q11.

Question number	Answer	Mark
	The only correct answer is D ((the overlap of) p orbitals to form π bonds) ***A*** *is incorrect because the σ bonds are not delocalised* ***B*** *is incorrect because s orbitals do not form π bonds* ***C*** *is incorrect because the σ bonds are not delocalised*	(1)

Q12.

Question Number	Acceptable Answers	Additional Guidance	Mark
(a)(i)	An answer that makes reference to the following points: • circle around arrow from $^{+}CH_3$ to ring (wrong direction) (1) • circle around arrow from bond attached to H, to partial ring (single-headed arrow) (1)		(2)

Question Number	Acceptable Answers	Additional Guidance	Mark
(a)(ii)	An answer that makes reference to the following points: • arrow should move from ring / arrow is going the wrong way **and** ring is electron-rich / as ring cannot accept electrons / as $^{+}CH_3$ does not have a lone pair (of electrons) / as $^{+}CH_3$ needs to gain electrons / as $^{+}CH_3$ is an electrophile (1) • arrow (from C-H bond) should be double-headed **and** as both electrons in the bond pair move (to complete the ring) / as moving a single electron would not complete the ring / as moving a single electrons would form (free) radicals (1)	If no other credit awarded, then 1 mark can be given for both corrections correctly identified	(2)

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)	An answer that makes reference to one of the following points: • to prevent further substitutions (of nitro groups)	Allow methylbenzene is (more) reactive (than benzene) **and** because a methyl group is electron releasing Allow ring in methylbenzene is (more) electron-rich (than benzene) Allow forms dinitrobenzene / trinitrobenzene Ignore further reactions / forms other products	(1)

Question Number	Acceptable Answers	Additional Guidance	Mark
(c)	An answer that makes reference to the following point: • oxidation	Allow oxidation and reduction / oxidation and redox Ignore references to redox	(1)

Question Number	Acceptable Answers	Additional Guidance	Mark
(d)	An answer that makes reference to the following point: • Sn **and** (concentrated) HCl	Accept correct names Allow Zn as alternative to Sn Ignore references to concentration or state of HCl Ignore any references to heat / temperature Ignore addition of NaOH after reaction with Sn and HCl	(1)

Question Number	Acceptable Answers	Additional Guidance	Mark
(e)	An explanation that makes reference to three of the following points: • (carbonyl) carbon is electron-deficient / has a partial positive charge • nitrogen (on NH_2 group) has a lone pair (of electrons) • which move to (carbonyl) carbon (to form bond) / which form a bond with the (carbonyl) carbon • Cl is a good leaving group / bond to Cl breaks / C-Cl bond pair moves to Cl	Allow M1, M2 and M3 on a clearly annotated diagram Ignore references to delocalisation Ignore references to nucleophilic substitution / nucleophilic additionelimination	(3)

Question Number	Acceptable Answers	Additional Guidance	Mark
(f)	• calculation of moles of 2-ethanoylaminobenzoic acid (1) • calculation of moles of benzene required, taking into account the overall percentage yield (1) • calculation of mass of benzene (1) • calculation of volume of benzene to 1/2/3 SF (1)	<u>Example of calculation</u> 5.92 ÷ 179 = 0.033073 (mol) / 3.3073 x 10^{-2} 0.033073 × (100 ÷ 28.2) = 0.11728 (mol) 0.11728 × 78 = 9.1477 (g) 9.1477 ÷ 0.879 = 10.407 = 10.4 / 10 cm^3 Ignore absence of units but do not award incorrect units. Marks 2 – 4 can be in any order Allow TE throughout Answer of 10 cm^3 with no working scores M4 only Correct answer with some working scores 4	(4)

Q13.

Question number	Answer	Mark
	The only correct answer is D(concentrated sulfuric acid containing dissolved sulfur trioxide) ***A*** *is incorrect because fuming sulfuric acid contains dissolved* sulfur trioxide ***B*** *is incorrect because fuming sulfuric acid contains dissolved* sulfur trioxide ***C*** *is incorrect because fuming sulfuric acid contains dissolved* sulfur trioxide	(1)

Q14.

Q	Answer	Mark
	The only correct answer is C(four) ***A*** *is not correct because this omits two isomers* ***B*** *is not correct because in the Kekulé structure1,2-dichlorobenzene has two isomers, one with the carbon atoms carrying the chlorines joined by a single bond and the other with them joined by a double bond* ***D*** *is not correct because this overlooks the fact that the 1,3 and 1,5 structures are identical*	**1**

Q15.

Question number	Answer	Mark
	The only correct answer is B (ethanal) ***A*** *is incorrect because carbon dioxide produces a carboxylic acid* ***C*** *is incorrect because methanal produces a primary alcohol* ***D*** *is incorrect because propanone produces a tertiary alcohol*	(1)

Q16.

Question number	Answer	Additional guidance	Mark
(a)	• working out molecular formula (1) • calculation of molar mass (1) • calculation of percentage by mass of one element (1) • calculation of percentage by mass of other elements (1)	Example of calculation $C_{13}H_{18}O_7$ (Accept numbers of C, H and O indicated in calculation) 286 % by mass of carbon = 100 x 13 x 12 ÷ 286 = 54.545 % by mass of hydrogen = 100 x 18 x 1 ÷ 286 = 6.294 and % by mass of oxygen = 100 x 7 x 16 ÷ 286 or % by mass of oxygen = 100 – (54.545 + 6.2937) = 39.161 TE at each stage Ignore SF except 1 SF	4

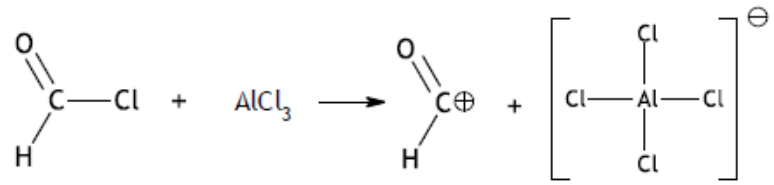
Some common incorrect answers (score (3))

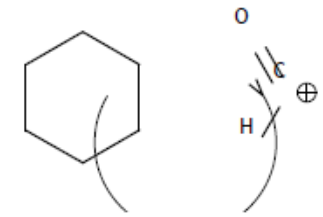
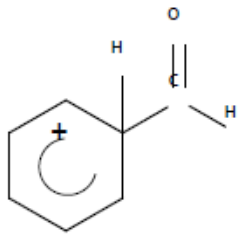
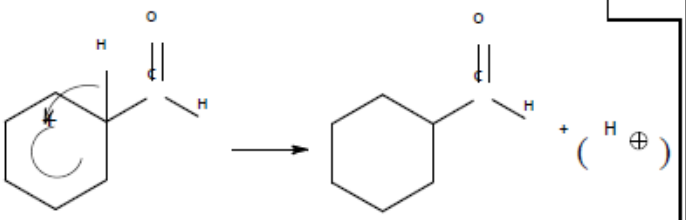
Formula	M_r	%C	%H	%O
$C_{13}H_{10}O_7$	278	56.12	3.60	40.29
$C_{13}H_{11}O_7$	279	55.91	3.94	40.14
$C_{13}H_{13}O_7$	281	55.52	4.63	39.86
$C_{13}H_{17}O_7$	285	54.74	5.96	39.30
$C_{13}H_{20}O_7$	288	54.17	6.94	38.89
$C_{13}H_{23}O_7$	291	53.61	7.90	38.49
$C_{13}H_{24}O_7$	292	53.42	8.22	38.36

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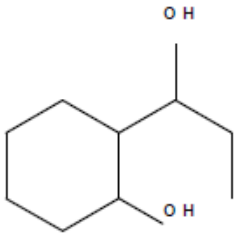
Question number	Answer	Additional guidance	Mark
(b)(i)	An answer that makes reference to the following • a suitable oxidising agent (1) • sulfuric acid / H_2SO_4 **and** (heat under) reflux (1)	Standalone marks sodium dichromate(VI) / $Na_2Cr_2O_7$ / potassium dichromate(VI) / $K_2Cr_2O_7$ Allow dichromate(VI) / $Cr_2O_7^{2-}$ Ignore omission of oxidation state but, if given, oxidation state must be correct Allow acid / acidified / H^+ / H_3O^+ Ignore concentration of the acid Do not award other acids Do not award other solvents / reagents If name and formula are given both must be correct.	**2**

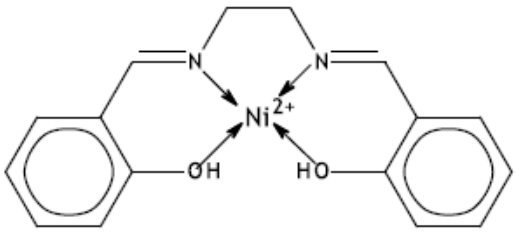
Question number	Answer	Additional guidance	Mark
(b)(ii)	An answer that makes reference to the following • salicylaldehyde needs to be distilled / separated (from the reaction mixture to prevent its further oxidation) (1) EITHER • (because) at high temperatures salicylaldehyde will be oxidised (to salicylic acid / carboxylic acid) (1) OR • (because) its high boiling temperature means that salicylaldehyde cannot be easily be separated as the other components of the mixture have lower / similar boiling temperatures (1)	 Allow salicylaldehyde is more easily oxidised than salicyl alcohol Allow oxidation of salicylaldehyde is fast Allow salicylaldehyde is hard to separate from the mixture If no other mark is scored, salicylaldehyde / salicyl alcohol will be oxidised to salicylic acid / carboxylic acid scores (1)	**2**

Question number	Answer	Additional guidance	Mark
(c)(i)	• equation showing formation of electrophile	Example of equation  Allow Structural formulae Allow $CO + HCl + AlCl_3 \rightarrow HCO^+ + AlCl_4^-$ Allow $CO + HCl \xrightarrow{AlCl_3} HCO^+ + Cl^-$ Ignore $CO + HCl \longrightarrow HCO^+ + Cl^-$	1

Question number	Answer	Additional guidance	Mark
(c)(ii)	A mechanism showing the following • curly arrow from on or within the circle to the positively charged carbon (1) • intermediate structure including charge with horseshoe covering at least 3 carbon atoms **and** facing the tetrahedral carbon **and** with some part of the positive charge within the horseshoe (1) • curly arrow from C—H bond to anywhere in the benzene ring reforming delocalised structure and giving benzaldehyde (1) Ignore use of $AlCl_4^-$ in mechanism	Example of mechanism  Allow curly arrow from anywhere in the hexagon Allow arrow to positive charge provided the charge is on the C atom TE on **any** correct electrophile formed in (c)(i)   Allow TE on any electrophile from (c)(i) Correct Kekule mechanism scores (3) Ignore connectivity of undisplayed CHO in M2 and M3	3

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Question number	Answer	Additional guidance	Mark
(d)	An answer that makes reference to the following points: • reagent and conditions for the formation of the Grignard reagent (1) • identification of Grignard reagent (1) • addition product of reaction between salicylaldehyde and Grignard reagent (1) • identification of a suitable dehydrating reagent (1)	Penalise use of Cl or I in Grignard once only Reaction of bromoethane with magnesium (powder) in (dry) ether (under reflux) Ignore heat CH_3CH_2MgBr / ethyl magnesium bromide  Ignore reference to hydrolysis of the Grignard intermediate (conc) phosphoric((V)) acid / H_3PO_4 / (conc) sulfuric acid / H_2SO_4 Do not award dilute acids Allow conversion of OH to halogen using a suitable reagent (e.g. PCl_5) **and** Dehydrohalogenation using alcoholic KOH / NaOH	4

Question number	Answer	Additional guidance	Mark
(e)(i)	A diagram showing • nickel(II) ion coordinated to the two oxygen and two nitrogen atoms of the salen ligand (1) • at least one **dative** covalent bond from an oxygen or a nitrogen to the nickel (II) ion in any structure involving one salen ligand (1)	Example of diagram  Accept charge shown over whole structure Ignore omission of C=N double bond Allow 'dative /coordinate (covalent) bond' stated provided complex structure is involves a salen ligand and at least one O—Ni^{2+} or N—Ni^{2+} bond is shown Penalise incorrect connectivity of OH with Ni^{2+} only in M2. If two OH groups are shown, both must be correctly connected to the Ni^{2+}	2

Question number	Answer	Additional guidance	Mark
(e)(ii)	An answer that makes reference to the following points: • converting the aqua complex to the salen ligand complex results in an increase in the number of particles (in solution) (1) • (thus) the entropy of the system increases / ΔS_{system} is positive (1)	Standalone marks Allow 'molecules' for 'particles' Accept ΔS_{system} increases Ignore just 'entropy increases' If no other mark is scored balanced equation (1)	2

Q17.

Question number	Answer	Mark
	The only correct answer is C (330.7) ***A*** *is incorrect because this is the molar mass of bromobenzene* ***B*** *is incorrect because this is the molar mass of the monosubstituted product* ***D*** *is incorrect because this is the molar mass of the fully substituted product*	1

Q18.

Question Number	Correct Answer	Mark
(a)	**The only correct answer is B** (62.5 %) ***A*** *is incorrect because the two carbonyl carbon atoms have not been included* ***C*** *is incorrect because the hydrogen atoms have not been included* ***D*** *is incorrect because two additional carbon atoms have been included*	(1)

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Question Number	Correct Answer	Mark
(b)	**The only correct answer is B** (3) ***A*** *is incorrect because the carbons in the benzene ring are not all in the same environment* ***C*** *is incorrect because there are only 2 different carbon environments in the benzene ring* ***D*** *is incorrect because there are only 2 different carbon environments in the benzene ring*	(1)

Question Number	Correct Answer	Mark
(c)	**The only correct answer is A** (a single type of monomer by an addition reaction) ***B*** *is incorrect because the polymer is not formed by a condensation reaction* ***C*** *is incorrect because the polymer is not formed by two different types of monomer* ***D*** *is incorrect because the polymer is not formed by two different types of monomer or a condensation reaction*	(1)

Q19.

Question Number	Correct Answer	Mark
	The only correct answer is A (more reactive and higher electron density) ***B*** *is incorrect because phenol has a higher electron density* ***C*** *is incorrect because phenol is not less reactive* ***D*** *is incorrect because phenol is not less reactive and has a higher electron density*	(1)

Q20.

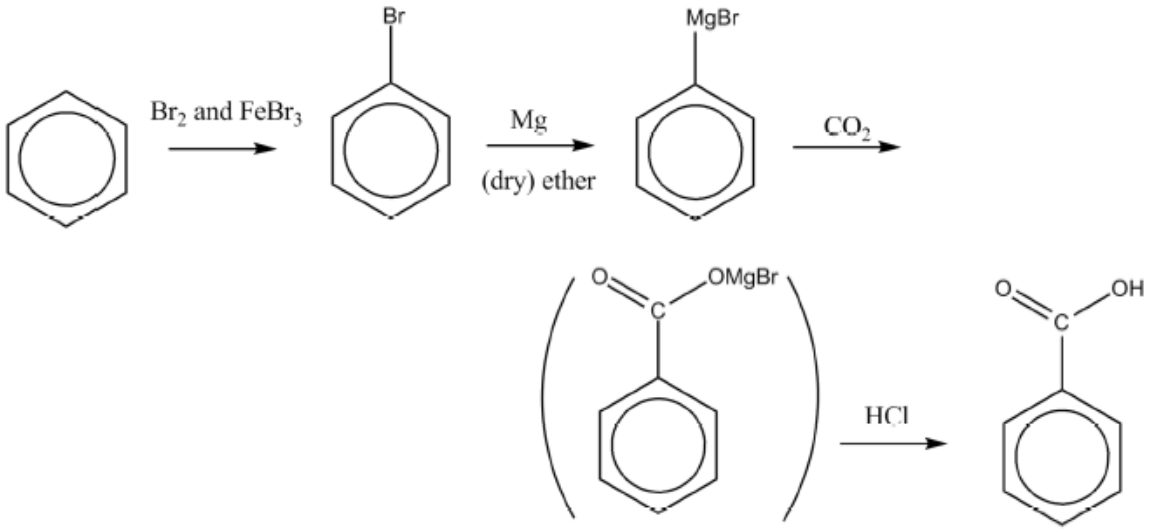
Question Number	Correct Answer	Mark
(a)	**The only correct answer is C** (five) ***A*** *is incorrect because it assumes all the carbon atoms are in a different environment* ***B*** *is incorrect because it assumes only two of the benzene ring carbon atoms are in the same environment* ***D*** *is incorrect because it assumes the carbon atoms at position 1 and position 4 of the ring are in the same environment*	**(1)**

Question Number	Correct Answer	Mark
(b)	**The only correct answer is D** (electrophilic substitution) ***A*** *is incorrect because the nitrating mixture produces an electrophile, NO_2^+, and addition does not occur due to stability of ring system* ***B*** *is incorrect because the nitrating mixture produces an electrophile, NO_2^+,* ***C*** *is incorrect because addition does not occur due to stability of ring system*	**(1)**

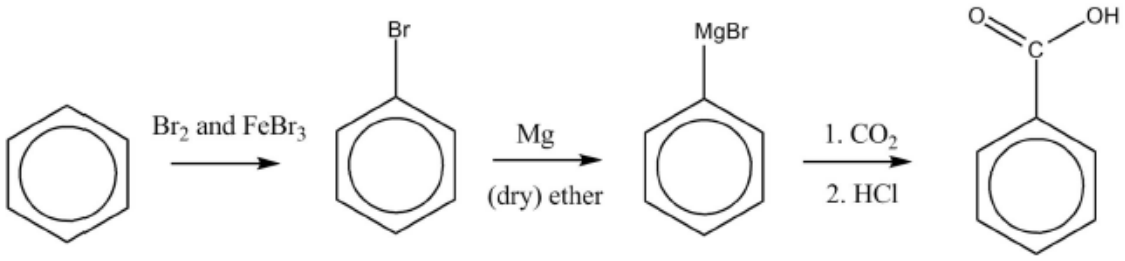
Question Number	Correct Answer	Mark
(c)	**The only correct answer is A** ((10 x 85 x 227) ÷ (92 x 100)) ***B*** *is incorrect because the scaling factor for the yield is incorrect* ***C*** *is incorrect because the scaling factor for the yield is incorrect* ***D*** *is incorrect because the scaling factor for the yield is incorrect*	**(1)**

Q21.

Question Number	Acceptable Answers	Additional Guidance	Mark
(a)	An answer that makes reference to the following points: • reaction of benzene with Br_2 and $FeBr_3$ / $AlBr_3$ **(1)** • reaction of bromobenzene with Mg **(1)** • in (dry) ether **(1)** • structure of Grignard reagent **(1)** • reaction of Grignard reagent with CO_2 / **(1)** • (hydrolysis of acid salt) with dilute HCl **(1)** Alternative route for M5 and M6 • reaction of Grignard reagent with HCHO **(1)** • (hydrolysis of acid salt) with dilute HCl **and** oxidation (of primary alcohol) with acidified $Cr_2O_7^{2-}$ **(1)**	See below for reaction scheme Ignore references to heating / refluxing throughout Allow Fe & Br_2 Allow other halogens and halides Allow aluminium halide M5 and M6 with CO_2 can be shown in the same part of the process providing it it's clear that each step is separate e.g. by labelling (see example below) Allow any dilute acid / H^+ Ignore structure of salt Ignore H_2O	**(6)**

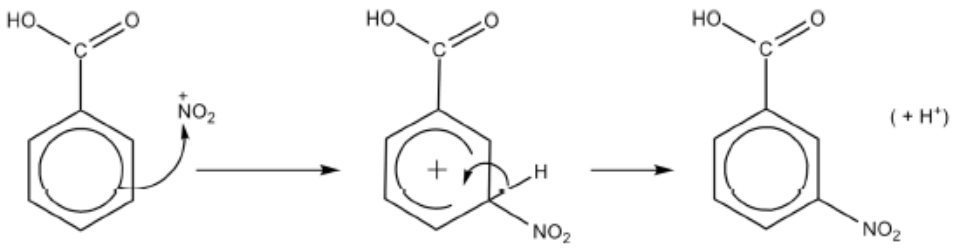


Allow CO_2 and HCl as parts 1 and 2 of the final step if clearly labelled e.g.



Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(i)	An answer that makes reference to the following points: • equation to show formation of electrophile **(1)**	$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$ Or $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$ Or $HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$ and $H_2NO_3^+ \rightarrow NO_2^+ + H_2O$ Do not award $H_3SO_5^-$ in M1 but allow as potential TE in M5	**(5)**
	• curly arrow from anywhere on the central ring to positive **nitrogen** **(1)**	Allow curly arrow from anywhere **within** the hexagon	
	• structure of intermediate **(1)**	Horseshoe facing the tetrahedral carbon and covering at least three carbon atoms. Some part of the positive charge in the horseshoe Do not award dotted lines unless clearly part of a 3D structure	
	• curly arrow from C-H bond to reform the ring **(1)**	Do not award M4 if substitution position is incorrect	
	• equation showing regeneration of catalyst **(1)**	$HSO_4^- + H^+ \rightarrow H_2SO_4$ Allow M5 as part of mechanism, with curly arrow from oxygen of HSO_4^- to H on benzene ring	

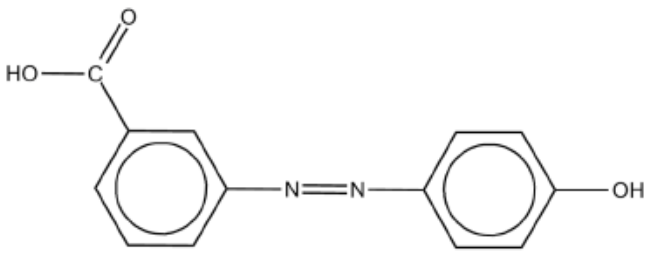
Example of mechanism for bi



Ignore postion of '+' in NO_2^+
No TE from incorrect species from equation in M1 to M2
Use of benzene can score M1, M2, M3 and M5

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(ii)	• Sn and (concentrated) HCl / tin and (concentrated) hydrochloric acid	Allow Fe for Sn Do not award other acids e.g. sulfuric acid Do not award $LiAlH_4$ Do not award Sn is a catalyst Do not award dilute HCl Do not award 'followed by NaOH' Ignore heating / reflux / stated temperatures	**(1)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(iii)	An explanation that makes reference to the following points: • any temperature between 0°C and 10°C , inclusive **(1)** • to prevent formation of by-products / phenol (compounds) **(1)**	Mark independently Allow just 'less than 10°C' / 'below 5°C' Allow to prevent decomposition of HNO_2 / to prevent decomposition of diazonium ion/ diazonium ion is unstable / to prevent weak C-N bond breaking / prevent formation of (stable) nitrogen Allow reaction is too slow at temperatures below 0°C / low temperatures Do not award decomposition of $NaNO_2$ / nitro group	**(2)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)(iv)		Ignore additional products Ignore connectivity of -OH group Do not award if OH or COOH are at incorrect positions on ring Do not award carboxylate ion Do not award $-N_2-$ in between two rings Do not award N≡N	**(1)**

Question Number	Acceptable Answers	Additional Guidance	Mark
(c)	• calculation of molar mass of $Pb(C_6H_5COO)_2$ **(1)** • calculation of amount of $Pb(C_6H_5COO)_2$ **(1)** • deduction of amount of $Ca(C_6H_5COO)_2.xH_2O$ **(1)** • calculation of M_r of $Ca(C_6H_5COO)_2.xH_2O$ **(1)** • calculation of mass of water in M_r **(1)** • calculation of amount of water and hence x **(1)** **Alternative route for M4-M6** • calculation of mass of $Ca(C_6H_5COO)_2$ **(1)** • calculation of mass of water in hydrated sample **(1)** • calculation of amount of water and hence x **(1)**	Example of calculation 449.2 can be subsumed within M2 3.89 / 449.2 = 8.65984 x 10^{-3} (mol) 1:1 so 8.65984 x 10^{-3} (mol) M3 can be subsumed in M4 2.60 / 8.65984 x 10^{-3} = 300.24 300.24 – (40.1 + (14x12) + (1x10) + (4x16) = 18.14 18.14 ÷18 = 1, so x = 1 Allow TE throughout Correct value for x with no working scores M6 only 8.65984 x 10^{-3} x 282.1 = 2.44 g 2.60 – 2.44 = 0.16 g 0.16 ÷18 = 0.000889, so x = 1 Ignore SF except 1 SF for M1-M5	**(6)**

Q22.

<table>
<tr><th>Question number</th><th>Answer</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr><td>(a)</td><td>This question assesses the student's ability to show a coherent and logically structured answer with linkages and fully sustained reasoning.

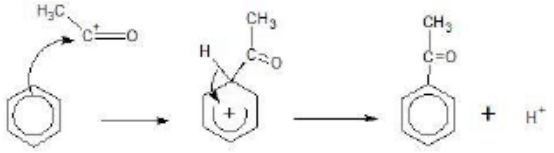
Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning.

The following table shows how the marks should be awarded for indicative content.
<table><tr><th>Number of indicative marking points seen in answer</th><th>Number of marks awarded for indicative marking points</th></tr><tr><td>6</td><td>4</td></tr><tr><td>5-4</td><td>3</td></tr><tr><td>3-2</td><td>2</td></tr><tr><td>1</td><td>1</td></tr><tr><td>0</td><td>0</td></tr></table>
The following table shows how the marks should be awarded for structure and lines of reasoning.
<table><tr><th></th><th>Number of marks awarded for structure of answer and sustained lines of reasoning</th></tr><tr><td>Answer shows a coherent logical</td><td>2</td></tr></table></td><td>Guidance on how the mark scheme should
be applied.
The mark for indicative content should be added to the mark for lines of reasoning. For example, a response with four indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning).
If there were no linkages between the points, then the same indicative marking points would yield an overall score of 3 marks
(3 marks for indicative content and zero marks for linkages).

If there is any incorrect chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded, do not deduct mark(s).</td><td>6</td></tr>
</table>

	structure with linkages and fully sustained lines of reasoning demonstrated throughout			
	Answer is partially structured with some linkages and lines of reasoning	1		
	Answer has no linkages between points and is unstructured	0		
	Indicative content: Spectroscopy: (IP 1 and 2) either X-ray diffraction • all C-C bond lengths in benzene are equal • but if it was a cyclic triene then they would alternate in 'short' and 'long' lengths or which is consistent with equivalent C-C bonds with a delocalised ring of electrons or (infrared spectroscopy) • benzene has peaks at 1600, 1580, 1500, 1450 (cm^{-1}) for an aromatic C=C		Ignore references to equal/120° bond angles Allow for one indicative point The infrared spectrum for benzene has a peak for an aromatic C=C at a different	

	• alkene C=C has a peak at 1669 - 1645 (cm^{-1}).	wavenumber/absorption/frequency to an alkene C=C	
	Thermochemistry: (IP 3 and 4) • enthalpy of hydrogenation is less exothermic than expected for a cyclic triene or enthalpy of combustion data	Allow benzene is more stable by ~150 kJ mol^{-1}	
	• which is consistent with the delocalisation stability of the ring from the ring of electrons	Stated enthalpies (of hydrogenation) −205 to −210 kJ mol^{-1} for benzene and −360 kJ mol^{-1} for 3 (localised C=C) double bonds	
	Type of reaction: (IP 5 and 6) • benzene undergoes substitution reactions • alkenes undergo addition reactions/decolourise bromine water.	Allow di-substitution There are only 3 isomers of di-substituted compounds (not 4) or some di-substituted compounds are the same, e.g. 1,2 and 1,6	

Question number	Answer	Additional guidance	Marks
(b)(i)	An answer that makes reference to the following points: • electron pair movement from ring to electrophile (1) • formula of intermediate ion (1) • movement of electron pair to reinstate delocalised ring (1) • formulae of products. (1)	Allow arrow that starts from anywhere from within the hexagon 'Horseshoe' to cover at least three carbon atoms and facing the tetrahedral carbon with some part of the positive sign to be inside the 'horseshoe'. Exemplar mechanism:  Do not award dotted bonds unless clearly part of a 3-D structure	4

Question number	Answer	Additional guidance	Marks
(b)(ii)	• $CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$	Accept use of $FeCl_3/Fe + 3Cl_2$	1

Question number	Answer	Additional guidance	Marks
(c)	An explanation that make reference to the following points: • lone pair of electrons on the oxygen atom increases the electron density of the ring (1) • more susceptible to attack by electrophiles. (1)		2

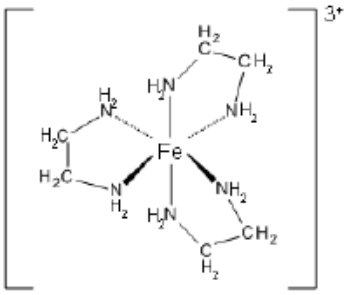
Question number	Answer	Additional guidance	Marks
(d)(i)	• (reactant) (conc) HNO_3 (1) • (catalyst) (conc) H_2SO_4 (1)	Ignore name Allow name Penalise reference to dilute acid once only	2

Question number	Answer	Additional guidance	Marks
(d)(ii)	• calculation of molar masses (1) • number of moles of benzene and maximum mass of nitrobenzene (1) • percentage yield of nitrobenzene to 2/3 SF (1)	Example of calculation: M_r of benzene = 78 **and** M_r of nitrobenzene = 123 n(0.936 ÷ 78=) 0.012 (mol) m(0.012 × 123=) 1.476 (g) % = ((0.642 ÷ 1.476) × 100= 43.4959) = 43.5/43% Do not award 44%	3

Q23.

Question number	Answer	Additional guidance	Mark
(a)(i)	• correct formula of iron(III) hydroxide (1) • rest of equation correct, conditional on correct precipitate (1)	Examples of equation: $[Fe(H_2O)_6]^{3+} + 3NH_3 \rightarrow Fe(OH)_3 + 3H_2O + 3NH_4^+$ or $[Fe(H_2O)_6]^{3+} + 3NH_3 \rightarrow Fe(OH)_3(H_2O)_3 + 3NH_4^+$ Allow $Fe(H_2O)_3(OH)_3$ Ignore state symbols, even if incorrect Ignore square brackets around iron(III) hydroxide formulae	(2)

Question number	Answer	Additional guidance	Mark
(a)(ii)	• ligand exchange / ligand substitution / ligand displacement	Allow ligand replacement Do not award ligand change / change in co-ordination number / redox / deprotonation in addition to correct answer	(1)

Question number	Answer	Additional guidance	Mark
(a)(iii)	• 6 bonds between N in diamines and Fe (1) • rest of diagram correct (1)	Example of diagram:  Allow NH_2– Fe on left of structure Conditional on 6 N-Fe bonds Allow C_2H for CH_2, H_2N for NH_2 etc Allow displayed / skeletal formulae for ligands Ignore bond lengths and bond angles Ignore missing brackets and charge / 3+ on Fe Ignore lone pairs on N / arrows added to bonds unless pointing towards the nitrogen atoms Do not award two nitrogens from the molecule bonded at 180° to Fe ion	(2)

Question number	Answer	Additional guidance	Mark
(b)(i)	• any 2 colours (1) • third colour (1)	Example of table: Oxidation state of vanadium / Colour of aqueous solution +3 / green +4 / blue +5 / yellow or colourless Ignore any further description of colour e.g. pale yellow Do not award combined colours e.g. blue/green	(2)

Question number	Answer	Additional guidance	Mark
(b)(ii)	• it is not a redox reaction because the oxidation number of vanadium is (+)5 in both species	Allow the oxidation number of vanadium remains the same if one oxidation number given - this may be shown by the equation Ignore 'there are no electrons in the equation' Ignore just 'the oxidation number of vanadium does not change' Do not award reference to any atom oxidised or reduced Do not award vanadium oxidation number is (+)5 in both species so it is a redox reaction	(1)

Question number	Answer	Additional guidance	Mark
(b)(iii)	An answer that makes reference to the following points: • equation for oxidation of V^{2+} to V^{3+} **(1)** • $E^{\ominus}_{cell}$ for oxidation of V^{2+} to V^{3+} **(1)** • equation for oxidation of V^{3+} to VO^{2+} **(1)** • $E^{\ominus}_{cell}$ for oxidation of V^{3+} to VO^{2+} **(1)** • VO^{2+} is not oxidised to VO_2^+ / any further as $E^{\ominus}_{cell}$ is −0.2 (V) / negative **(1)**	Examples of equations: Allow multiples Ignore state symbols even if incorrect Ignore uncancelled H^+ / H_2O Penalise uncancelled electrons once only $NO_3^- + 2H^+ + V^{2+} \rightarrow NO_2 + H_2O + V^{3+}$ Allow $Cu^{2+} + V^{2+} \rightarrow Cu^+ + V^{3+}$ Allow $\frac{1}{2}Br_2 + V^{2+} \rightarrow Br^- + V^{3+}$ $E^{\ominus}_{cell}$ = (+)1.06 (V) TE on Cu^{2+} / Br_2 chosen as oxidising agent With Cu^{2+} $E^{\ominus}_{cell}$ = (+)0.41(0) (V) With Br_2 $E^{\ominus}_{cell}$ = (+)1.35 (V) $NO_3^- + V^{3+} \rightarrow NO_2 + VO^{2+}$ Allow $\frac{1}{2}Br_2 + V^{3+} + H_2O \rightarrow Br^- + VO^{2+} + 2H^+$ $E^{\ominus}_{cell}$ = (+)0.46 (V) With Br_2 $E^{\ominus}_{cell}$ = (+)0.75 (V) Allow this shown in an equation	**(5)**

Question number	Answer	Additional guidance	Mark
(c)	This question assesses the student's ability to show a coherent and logically structured answer with linkages and fully sustained reasoning. Marks are awarded for indicative content and for how the answer is structured and shows lines of reasoning. The following table shows how the marks should be awarded for indicative content. **Number of indicative marking points seen in answer / Number of marks awarded for indicative marking points** 6 / 4 5-4 / 3 3-2 / 2 1 / 1 0 / 0	Guidance on how the mark scheme should be applied. The mark for indicative content should be added to the mark for lines of reasoning. For example, a response with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some linkages and lines of reasoning). If there were no linkages between the points, then the same indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages).	**(6)**

The following table shows how the marks should be awarded for structure and lines of reasoning

	Number of marks awarded for structure of answer and sustained lines of reasoning
Answer shows a coherent logical structure with linkages and fully sustained lines of reasoning demonstrated throughout	2
Answer is partially structured with some linkages and lines of reasoning	1
Answer has no linkages between points and is unstructured	0

Comment: Look for the indicative marking points first, then consider the mark for the structure of the answer and sustained line of reasoning.

In general it would be expected that 5 or 6 indicative points would get 2 reasoning marks, and 3 or 4 indicative points would get 1 mark for reasoning, and 0, 1 or 2 indicative points would score zero marks for reasoning.

If there is any incorrect chemistry, deduct mark(s) from the reasoning. If no reasoning mark(s) awarded do not deduct mark(s).
e.g. iron catalysing formation of ammonia from nitrogen and hydrogen but naming it the Contact Process / incorrect formula e.g. for persulfate ions

Allow correct formulae for names

Do not award examples that are not transition metals, ions or compounds

Indicative content

- **IP1 Comparison - Activation energy**
  both catalysts increase the rate of reaction by providing an alternative route / mechanism with a lower activation energy

  Allow this shown on a Maxwell-Boltzmann distribution / reaction profile diagram

- **IP2 Phase**
  a heterogeneous catalyst is in a different phase from the reactants **and** a homogeneous catalyst is in the same phase as the reactants / all solutions / gases

  Allow (physical) state for phase
  Allow heterogeneous catalysts are easy to separate from the reaction mixture / reactants / products **and** homogeneous catalysts are difficult to separate from the reaction mixture / reactants / products

- **IP3 Example of heterogeneous**
  example of a heterogeneous catalyst **and** reaction it catalyses e.g. iron and Haber Process, nickel and hydrogenation of alkenes, platinum in a catalytic converter / with CO and NO

- **IP4 Example of homogeneous**
  example of a homogeneous catalyst **and** reaction it catalyses e.g. iron(II) / iron(III) ions and reaction between iodide ions and persulfate ions

- **IP5 Mechanism of heterogeneous**
  reactant molecules are adsorbed onto the catalyst surface, the bonds are weakened, reaction takes place then the product molecules are desorbed

  Allow e.g. reactant molecules bind to active sites for adsorbed /
  particles react for bonds weakened /
  product molecules leave for desorbed
  Allow vanadium(V) oxide reduced to vanadium(IV) and oxidised back to vanadium(V) for the Contact Process

	• **IP6 Mechanism of homogeneous** the transition metal ion is oxidised / reduced to a different oxidation state then changes back to the original oxidation state	Allow this shown in equations, even if unbalanced Allow donate / receive electrons for oxidised / reduced	