PEARSON EDEXCEL IAL CHEMISTRY · YCH11

CHEMISTRY



EXAM QUESTION PACK

UNIT 5: ORGANIC SYNTHESIS

SCORE	PERCENTAGE
/206	%

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Q1.

This question is about the investigation of an organic compound **X**.
X is a liquid at room temperature and pressure, which turns damp red litmus paper blue.

(a) (i) Name the functional group present in **X**.

(1)

.....

(ii) When 0.493 g of **X** was vaporised, 157 cm^3 of dry air was displaced, measured at 15°C and 103 000 Pa.

Calculate the molar mass of **X**, using the ideal gas equation.
You **must** show your working.

(4)

(b) **X** reacted vigorously with ethanoyl chloride forming steamy fumes and a white solid **Y**.

(i) Identify the steamy fumes, by name or formula.

(1)

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(ii) Suggest the functional group present in **Y**.

(1)

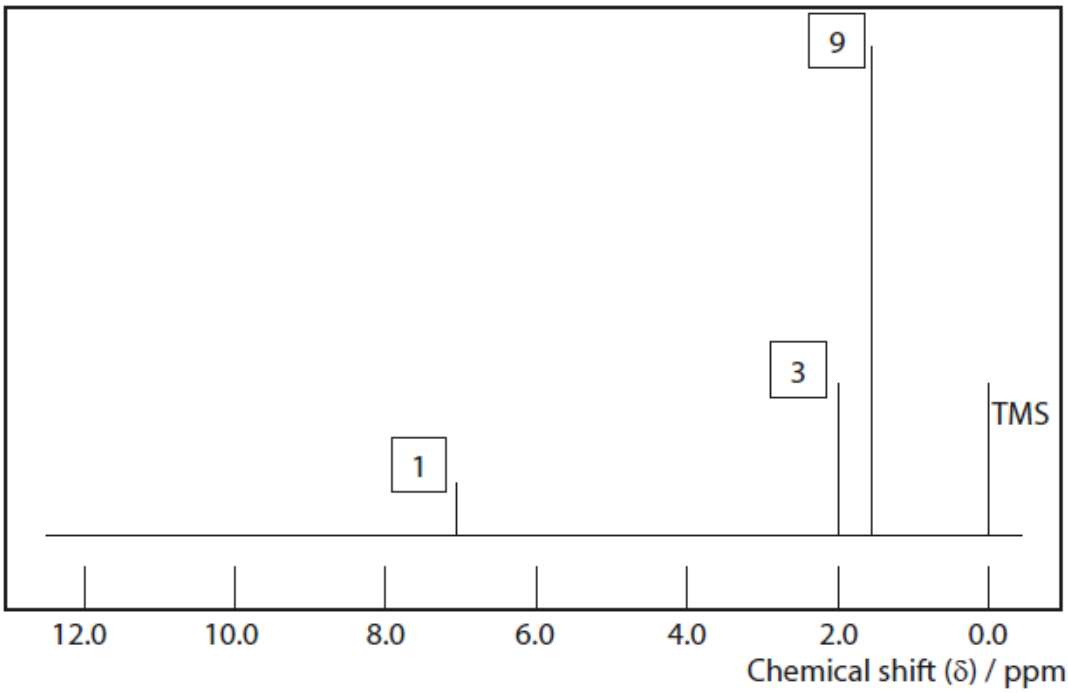
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(iii) Analysis of **Y** showed that its composition by mass was 62.6 % carbon; 11.3 % hydrogen; 12.2 % nitrogen; 13.9 % oxygen.

Determine the empirical formula of **Y**. You **must** show your working.

(3)

*(c) A simplified **high** resolution proton NMR spectrum of **Y** is shown.
The relative peak areas are given near each peak.



Deduce the structure of **Y**, using the NMR spectrum and the other information in the question.

(6)

(d) Draw the structure of compound **X**.

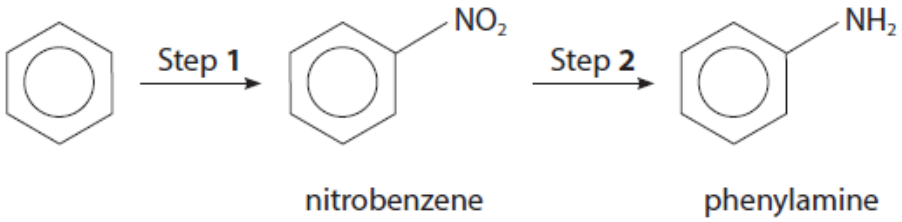
(1)

(Total for question = 17 marks)

Q2.

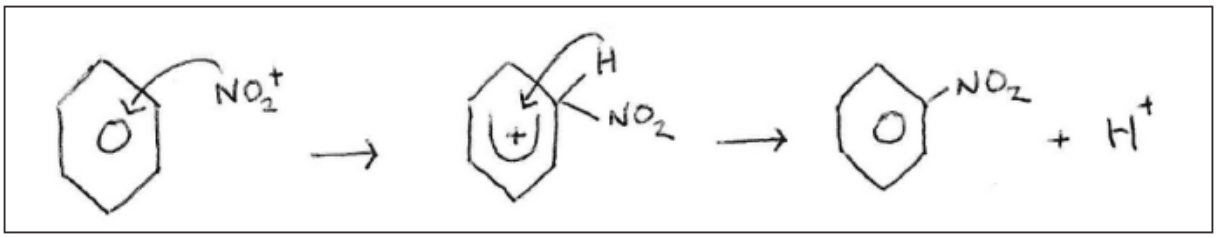
This question is about aromatic amines and amino acids.

(a) A synthesis of phenylamine is shown.



(i) Benzene is converted into nitrobenzene in Step 1 using a mixture of concentrated nitric acid and concentrated
sulfuric acid. The electrophile is NO_2^+.

A student drew a mechanism for the reaction.



Describe the three changes needed to correct this student's mechanism.

(3)

Change 1

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Change 2

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Change 3

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(ii) Give the reagents for Step **2**.

(1)

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(b) Phenylamine is a base.

(i) Explain why phenylamine is a weaker base than ammonia.

(3)

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(ii) State what is **seen** when a few drops of an aqueous solution of phenylamine are added to an aqueous solution containing Cu^{2+} ions.

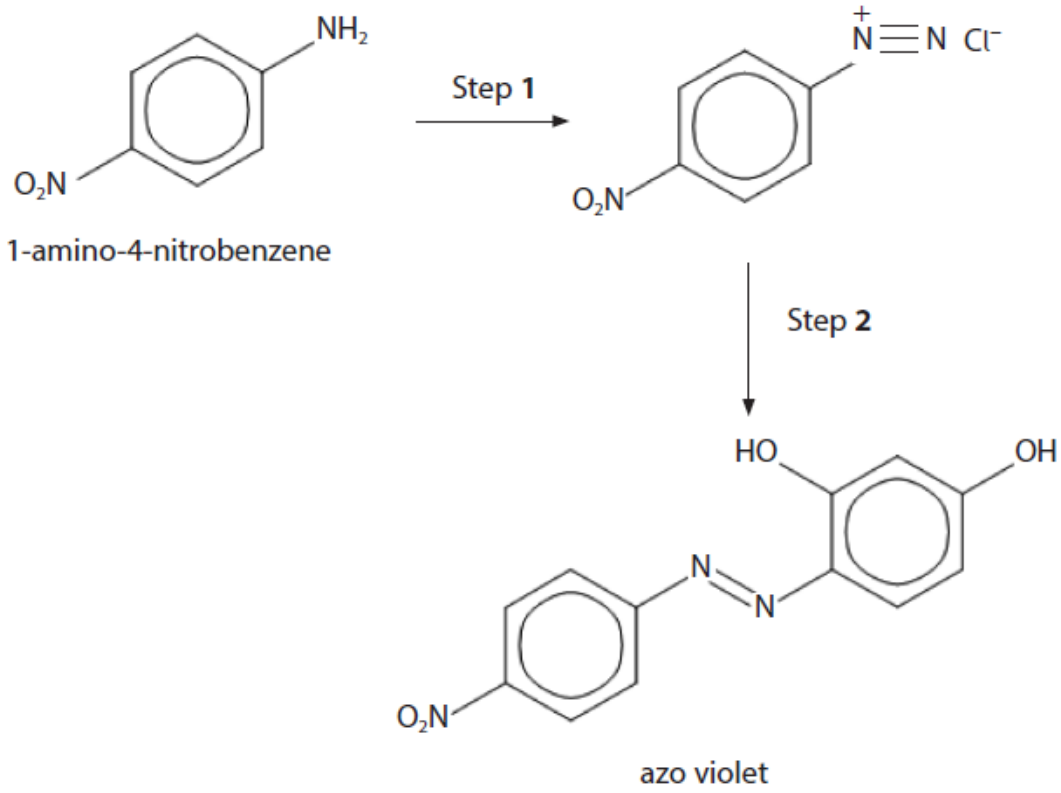
(1)

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(c) Azo violet is used as a dye and an indicator.

A synthesis of azo violet from 1-amino-4-nitrobenzene is shown.



(i) Give the reagents and condition for Step **1**.

(2)

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(ii) Deduce the structure of the organic compound needed to produce azo violet in Step **2**.

(1)

(iii) Give a reason why azo violet exists as geometric isomers.

(1)

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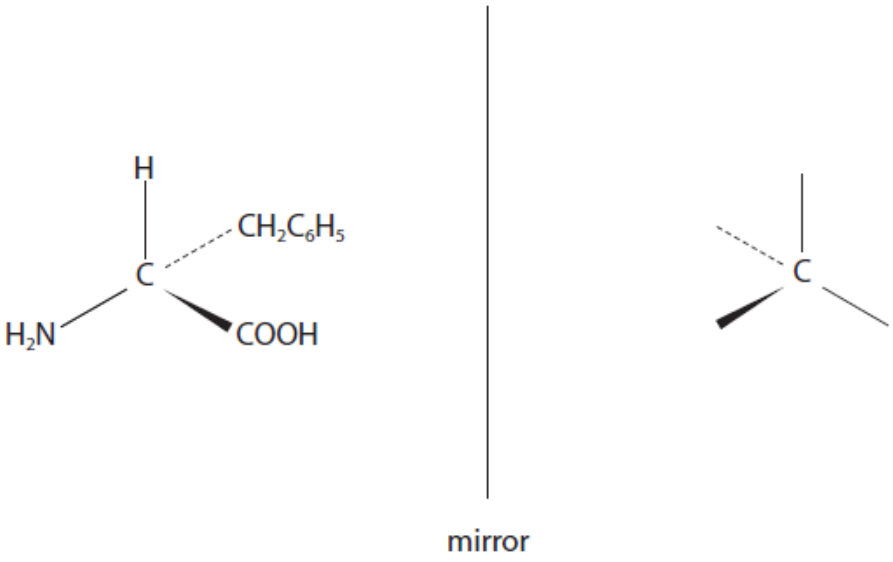
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(d) Phenylalanine is an amino acid that exists as optical isomers.

The structure of one of the optical isomers is shown.

Complete the diagram to show the other optical isomer of phenylalanine.

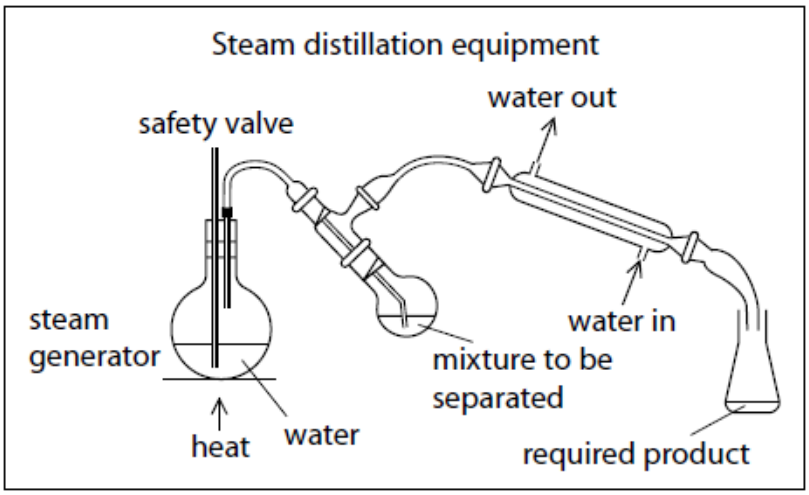
(1)



(Total for question = 13 marks)

Q3.

Steam distillation is a technique used during some organic preparations to separate the product from the reaction mixture.



What benefit is gained from the use of steam distillation compared to other methods of distillation?

(1)

☒ **A** a pure distillate is produced

☒ **B** high distillation temperatures are required

☒ **C** it works well for molecules miscible with water

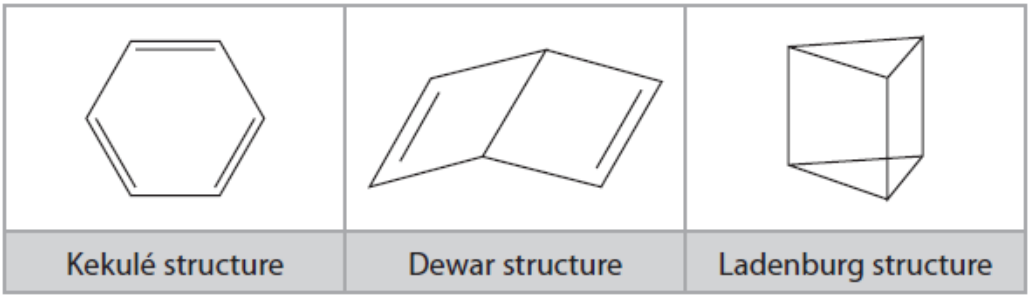
☒ **D** it avoids the decomposition of the organic molecule when it distils

(Total for question = 1 mark)

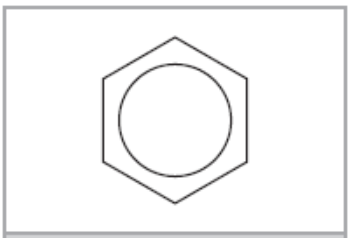
Q4.

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.



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.

(2)

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

(2)

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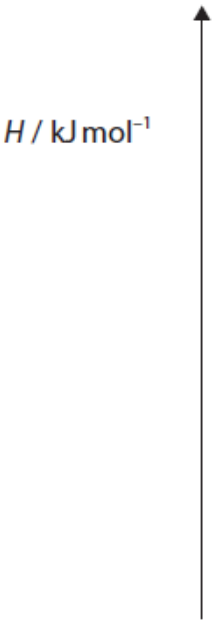
(d) The Ladenburg and Dewar structures both isomerise to benzene.

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)

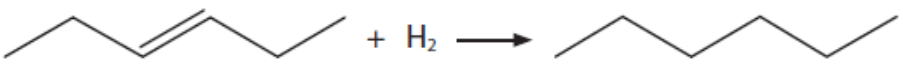
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(e) The enthalpy change of hydrogenation of hex-3-ene is –118 kJ mol^{-1}.



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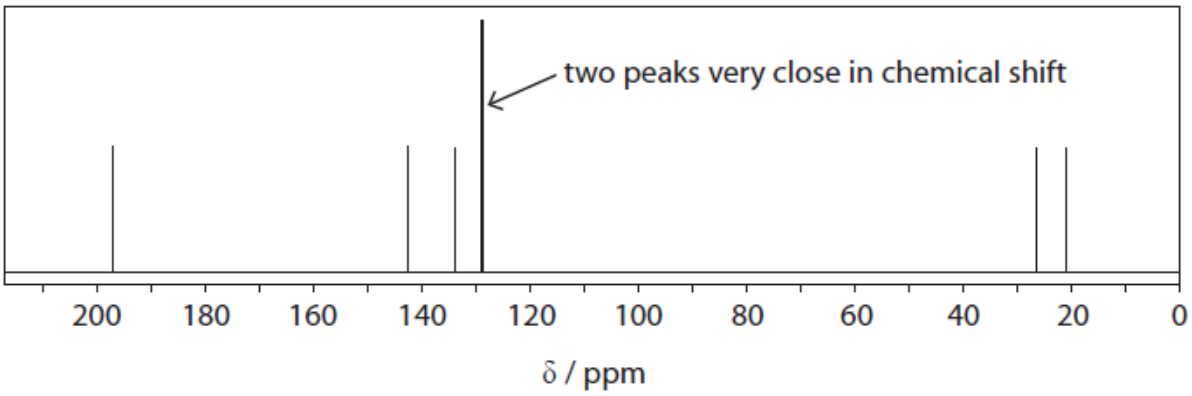
(f) Methylbenzene, $C_6H_5CH_3$, reacts with ethanoyl chloride, CH_3COCl, in the presence of the catalyst aluminium chloride, $AlCl_3$, to form a mixture of organic products with the formula $CH_3COC_6H_4CH_3$.

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

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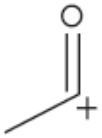
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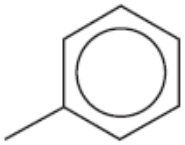
(iii) Complete the diagram, including curly arrows, to show the mechanism for the formation of compound **X** in this reaction.

Include an equation for the regeneration of the catalyst.

(4)

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



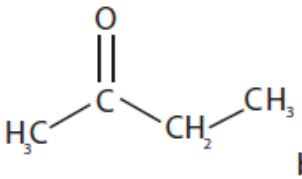


(Total for question = 19 marks)

Q5.

Ketones are useful starting compounds in organic synthesis.

This question is about butanone.



butanone

(a) The mass spectrum of butanone has significant peaks at $m / z = 43$ and at $m / z = 57$.

(i) Give the structures of the species responsible for these two peaks.

(2)

(ii) Give the structure of **one** other species that you would expect to produce a peak at a different m / z value in the mass spectrum of butanone.

(1)

(b) Devise a reaction scheme to prepare propan-1-ol from butanone, using no more than **four** steps.

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

(4)

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(c) Devise a reaction scheme to prepare 2-methylbut-2-ene from butanone, using no more than **four** steps.

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

(5)

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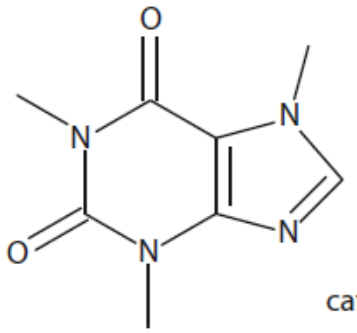
(Total for question = 12 marks)

Q6.

Coffee Chemistry

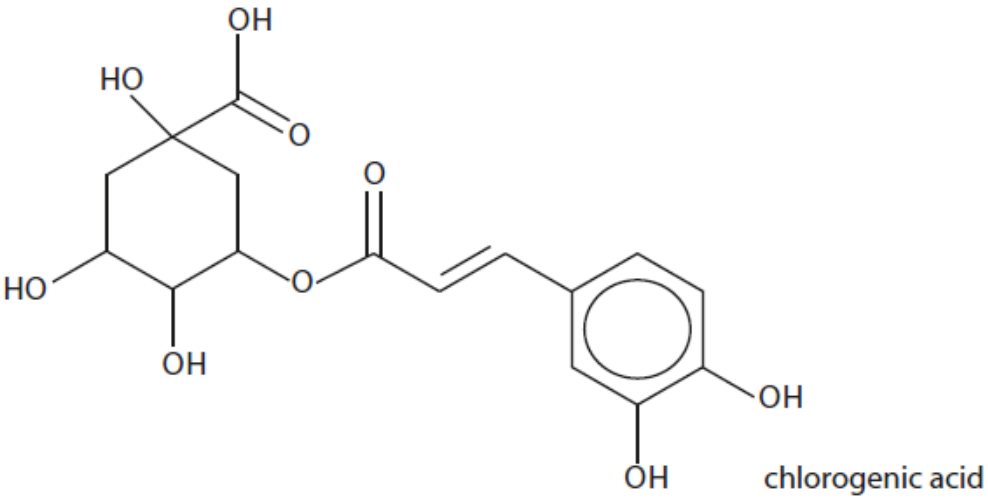
There are over a thousand chemical compounds in coffee and their physiological effects are the subject of considerable speculation and research. The verdict on coffee is contradictory: some of the compounds have been identified as toxic and even carcinogenic but others are antioxidants associated with 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

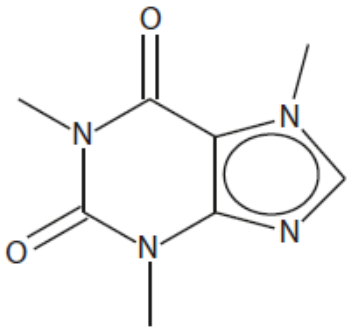
Chlorogenic acid is responsible for the acidic taste of coffee. It is an antioxidant and has also been shown to slightly decrease blood pressure.



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.

(3)

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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.

(2)

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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)

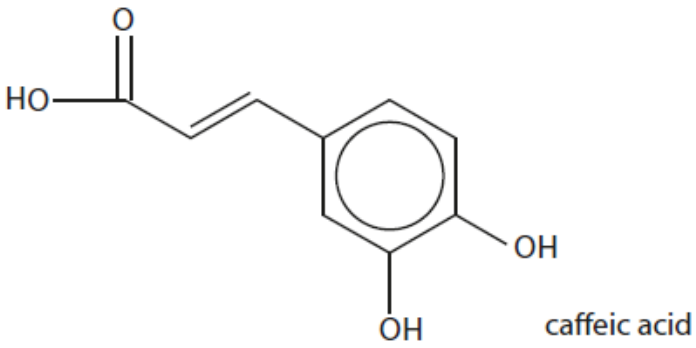
(ii) The removal of caffeine from the body is a first order reaction with a half-life of between three and seven hours for an adult.

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

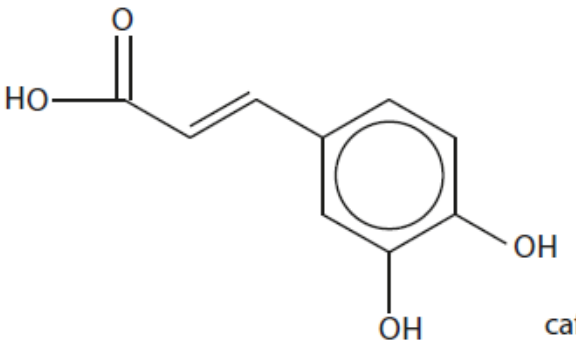
(i) A student suggested that caffeic acid could be synthesised by an electrophilic substitution of 1,2-dihydroxybenzene.

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

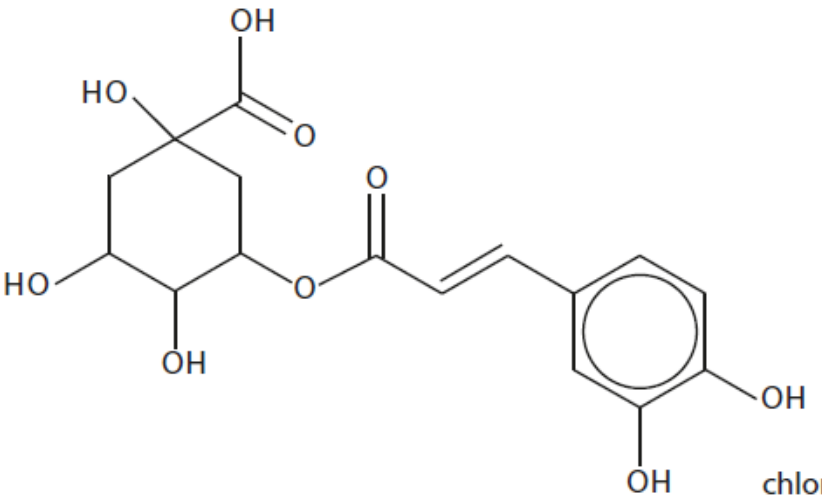
(5)

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

(1)



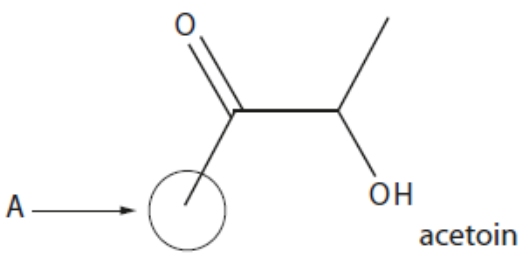
caffeic acid



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)

Q7.

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.

(6)

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(Total for question = 10 marks)

Q8.

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 ☒.

A solution contains 19.6 g dm^{-3} of chromium(III) sulfate, $Cr_2(SO_4)_3$.

[Molar mass $Cr_2(SO_4)_3$ = 392 g mol^{-1}]

☒ **A** 0.05

☒ **B** 0.10

☒ **C** 0.15

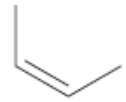
☒ **D** 0.25

(Total for question = 1 mark)

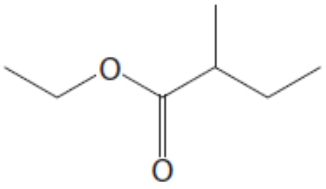
Q9.

The ester ethyl 2-methylbutanoate is found in wild berries such as bilberries.

Devise a synthesis to convert but-2-ene into ethyl 2-methylbutanoate in **four** steps.



but-2-ene



ethyl 2-methylbutanoate

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

Details of practical procedures are not required.

(Total for question = 6 marks)

Q10.

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 melting temperature is determined for impure crystals of an organic compound. When compared with a data book value for the pure compound, the measured melting temperature

☒ **A** will be the same as the true value

☒ **B** will be higher than the true value

☒ **C** will be lower than the true value

☒ **D** could be higher or lower than the true value

(Total for question = 1 mark)

Q11.

A compound **Q** contains the elements carbon, hydrogen and oxygen only.

(a) Combustion analysis of 4.91 g of **Q** produces 14.6 g of carbon dioxide and 3.58 g of water.

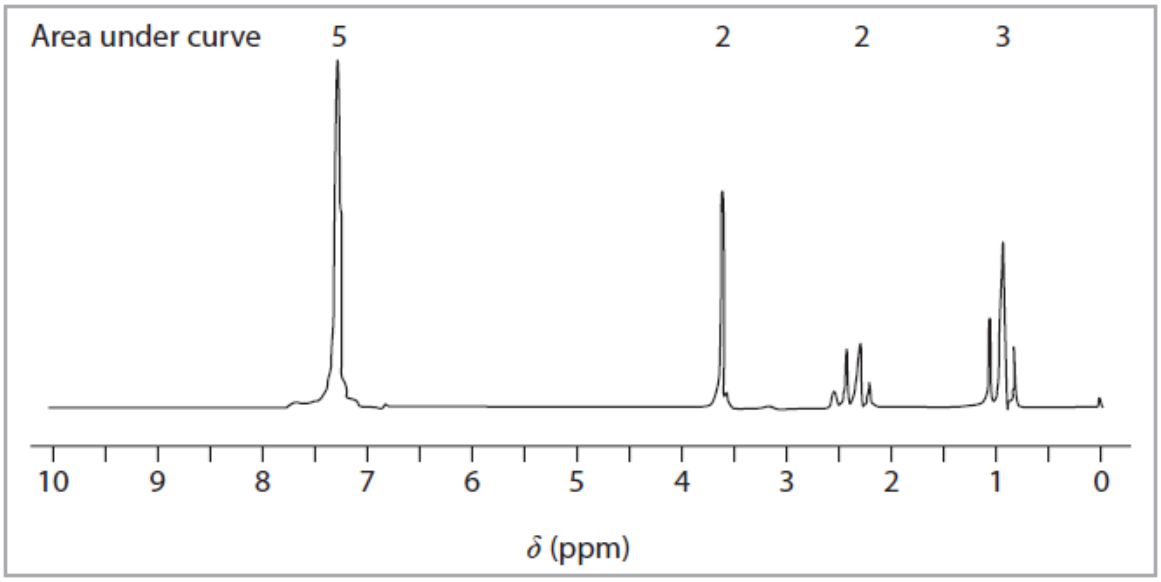
Show that the molecular formula of **Q** is $C_{10}H_{12}O$.

You **must** show all your working.

[M_r of **Q** = 148]

(4)

(b) The high resolution proton NMR spectrum of **Q** is shown.



Deduce the structure of **Q**. Justify your answer by considering the relative peak areas, the chemical shifts and the splitting patterns.

You will find it helpful to refer to page 8 of the Data Booklet.

The peak at 3.6 ppm is due to a proton environment on a carbon bonded to the benzene ring. The peak is not where it might be expected from the general values in the Data Booklet.

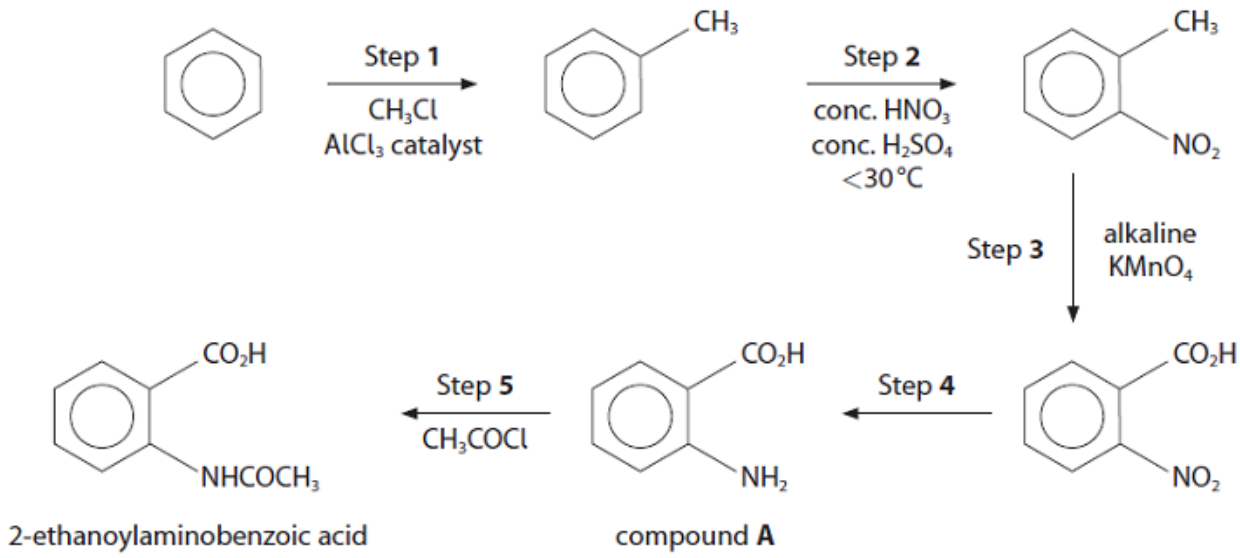
(7)

(Total for question = 11 marks)

Q12.

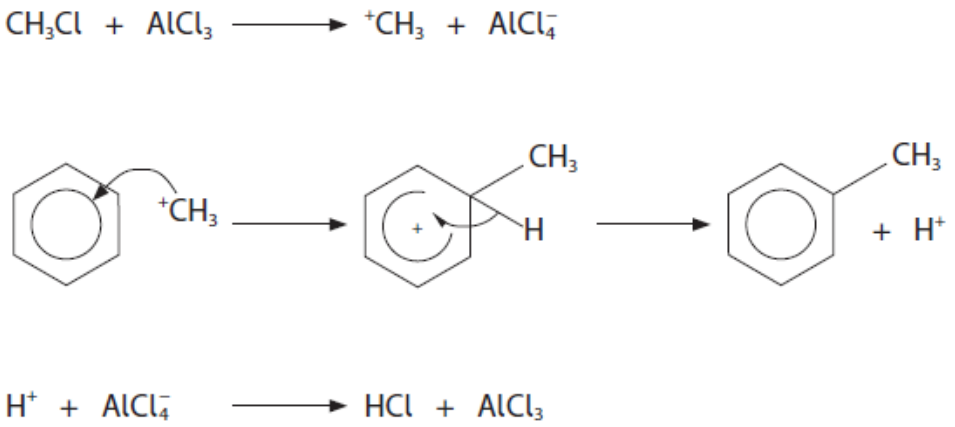
This question is about 2-ethanoylaminobenzoic acid.
Crystals of this compound emit flashes of light when crushed.

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



(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**.

(1)

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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**.

(3)

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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.

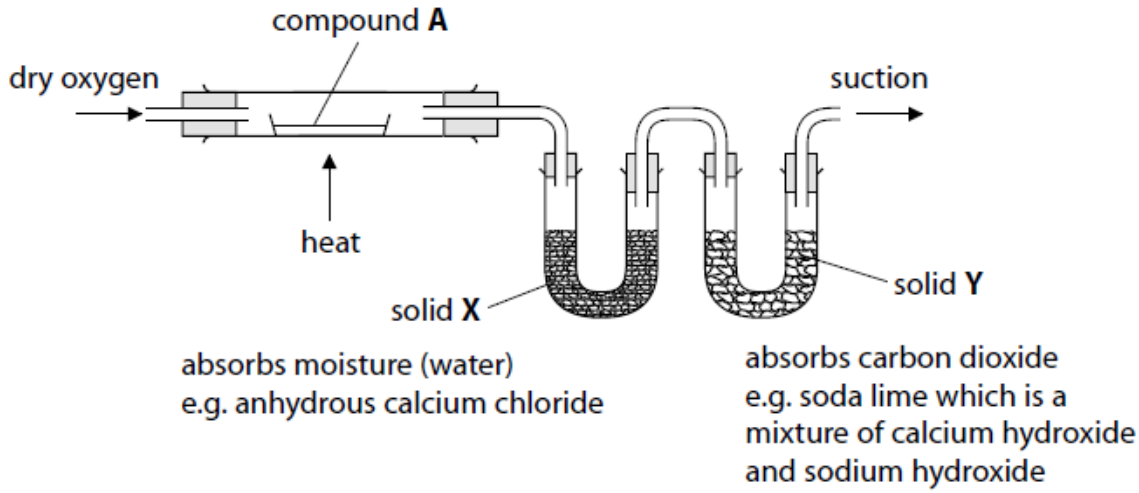
Butan-2-ol is a secondary alcohol with four carbon atoms.

(a) Devise a reaction scheme to form butan-2-ol from iodoethane, C_2H_5I, as the only organic compound.

Give reagents, conditions and equations for each of the steps.

(8)

(b) A 1.850 g sample of an organic substance, compound A, that is thought to be butan-2-ol is tested by combustion analysis using the apparatus shown.



(i) Calculate the mass increase of solid X and solid Y that would result if compound A is butan-2-ol.

(4)

(ii) Predict a substance which would give the same mass increase in solids X and Y from combustion analysis as butan-2-ol.

Give a reason for your prediction.

(2)

.....

.....

.....

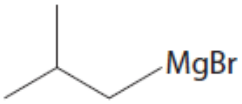
.....

(Total for question = 14 marks)

Q14.

Answers the question 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 a Grignard reagent, 2-methylpropylmagnesium bromide.



This Grignard reagent can be prepared by refluxing 1-bromo-2-methylpropane with magnesium in a flask containing a dry solvent and anti-bumping granules.

(a) Which solvent is used in this preparation?

(1)

☒ **A** ethanol

☒ **B** ether

☒ **C** pentane

☒ **D** propanone

(b) Why are anti-bumping granules added to the flask?

(1)

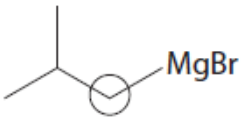
☒ **A** to lower the boiling temperature of the solvent

☒ **B** to prevent the solvent evaporating

☒ **C** because the solvent is highly flammable

☒ **D** to ensure the solvent boils smoothly

(c) The structure of 2-methylpropylmagnesium bromide is shown.



Which statement best describes the circled carbon atom?

(1)

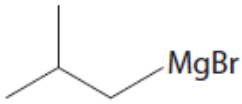
☒ **A** positive and electrophilic

☒ **B** positive and nucleophilic

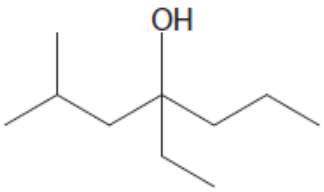
☒ **C** negative and electrophilic

☒ **D** negative and nucleophilic

(d) Which compound reacts with 2-methylpropylmagnesium bromide to form 4-ethyl-2-methylheptan-4-ol?



2-methylpropylmagnesium bromide



4-ethyl-2-methylheptan-4-ol

(1)

☒ **A** hexan-3-one

☒ **B** hexan-2-one

☒ **C** hexan-3-ol

☒ **D** hexan-2-ol

(Total for question = 4 marks)

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 ☒.

Grignard reagents react with

☒ **A** water giving primary alcohols

☒ **B** all aldehydes giving secondary alcohols

☒ **C** ketones giving secondary or tertiary alcohols

☒ **D** carbon dioxide giving carboxylic acids

(Total for question = 1 mark)

Q16.

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 ☒ .

In the **high** resolution proton NMR spectrum of propan-2-ol, $CH_3CHOHCH_3$ there are

☒ **A** one singlet, one doublet and a heptet

☒ **B** one singlet, two doublets and a heptet

☒ **C** two singlets and two triplets

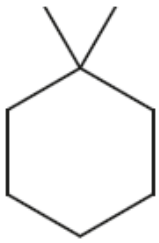
☒ **D** three singlets and a quartet

(Total for question = 1 mark)

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 ☒ .

The structure of a hydrocarbon is shown.



How many peaks will there be in the ^{13}C NMR spectrum of this compound?

☒ **A** four

☒ **B** five

☒ **C** seven

☒ **D** eight

(Total for question = 1 mark)

Q18.

Using excess oxygen, 25 cm^3 of a gaseous hydrocarbon C_xH_y was burned completely.

After cooling to room temperature the total gas volume was measured and found to be 75 cm^3 less than the total gas volume before the mixture was ignited.

When the product gases were shaken with potassium hydroxide solution, the total gas volume decreased by a further 100 cm^3.

All gas volumes were measured at room temperature and pressure.

A general equation for the combustion of a hydrocarbon is

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow xCO_2 + \left(\frac{y}{2}\right) H_2O$$

(a) Determine the molecular formula of C_xH_y. You **must** show your working.

(3)

(b) When C_xH_y was added to a little bromine water and the mixture shaken, the bromine water remained yellow.

Suggest **two** possible structures for C_xH_y .

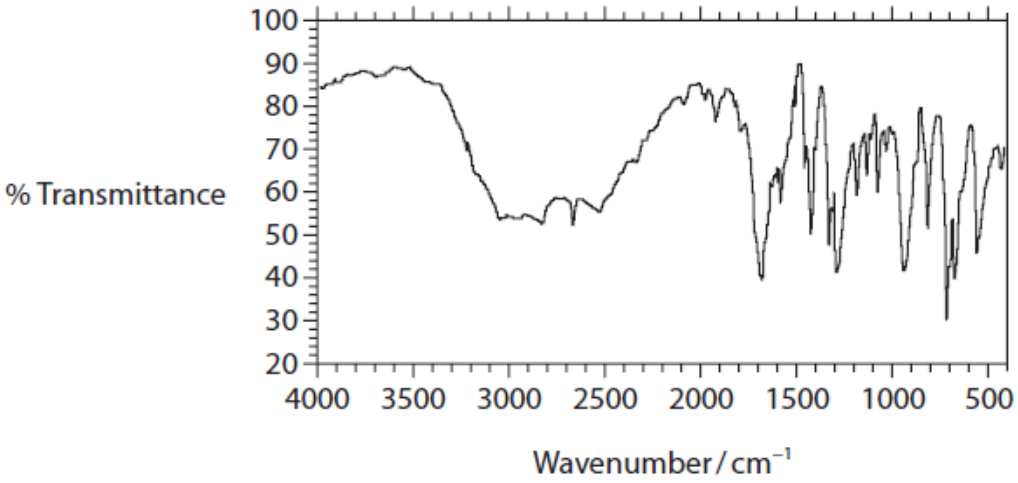
(2)

(Total for question = 5 marks)

Q19.

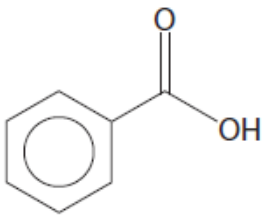
For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

The infrared spectrum of a compound **X** is shown.

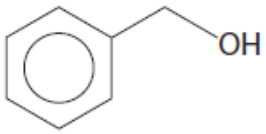


Which could be compound **X**?

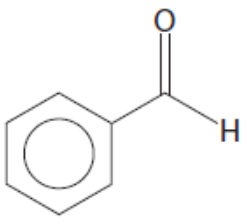
☒ **A**



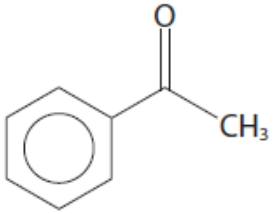
☒ **B**



☒ **C**



☒ **D**

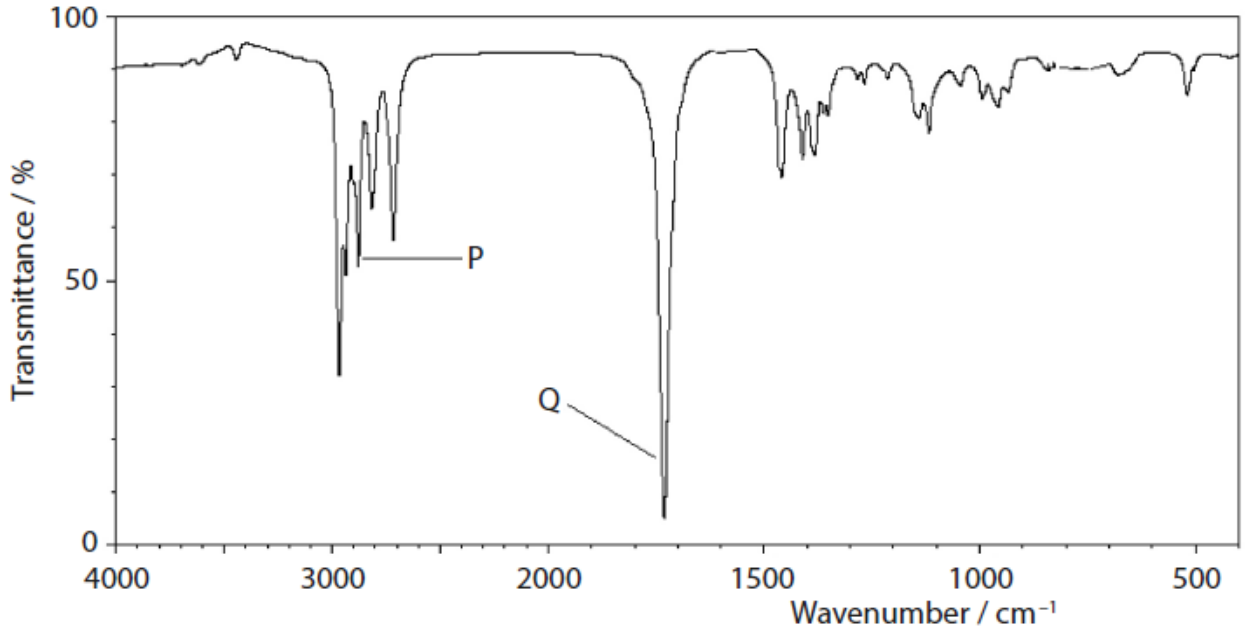


(Total for question = 1 mark)

Q20.

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 ☒ .

An aliphatic organic compound has the infrared spectrum shown.



What are the bond stretches responsible for the peaks **P** and **Q** in the spectrum?

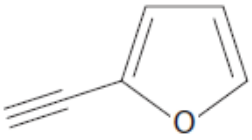
	P	Q
☒ **A**	O—H carboxylic acid	C═O carboxylic acid
☒ **B**	O—H carboxylic acid	C═O aldehyde
☒ **C**	C—H aldehyde	C═O carboxylic acid
☒ **D**	C—H aldehyde	C═O aldehyde

(Total for question = 1 mark)

Q21.

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 ☒.

The mass spectrum of the compound shown is obtained using a high resolution mass spectrometer.



What is the mass to charge ratio, *m* / *z*, of the molecular ion of this compound?

[A_r values: H = 1.0078 C = 12.0000 O = 15.9949]

☒ **A** 92.0261

☒ **B** 92.0312

☒ **C** 93.0339

☒ **D** 93.0390

(Total for question = 1 mark)

Q22.

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 electronic configuration of the atoms of an element is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$.

What is the maximum oxidation number shown in compounds of this element?

☒ **A** +1

☒ **B** +5

☒ **C** +6

☒ **D** +7

(Total for question = 1 mark)

Q23.

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 ☒ .

When a sample of a hydrocarbon is burned completely in oxygen, 2.64 g of carbon dioxide and 0.81 g of water are formed.

Which of these could be the **molecular** formula of the hydrocarbon?

☒ **A** C_2H_3

☒ **B** C_4H_3

☒ **C** C_4H_6

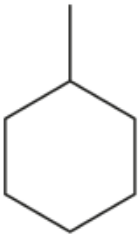
☒ **D** $C_{12}H_9$

(Total for question = 1 mark)

Q24.

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 peaks are there in the carbon-13 (^{13}C) NMR spectrum of methylcyclohexane?



methylcyclohexane

☒ **A** one

☒ **B** three

☒ **C** five

☒ **D** seven

(Total for question = 1 mark)

Q25.

What is the number of peaks in a ^{13}C NMR spectrum of 1,4-dimethylbenzene?



(1)

☒ **A** 3

☒ **B** 4

☒ **C** 7

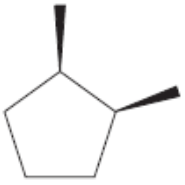
☒ **D** 8

(Total for question = 1 mark)

Q26.

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 structure of a hydrocarbon is shown.



How many peaks will there be in the ^{13}C NMR spectrum of this compound?

☒ **A** four

☒ **B** five

☒ **C** six

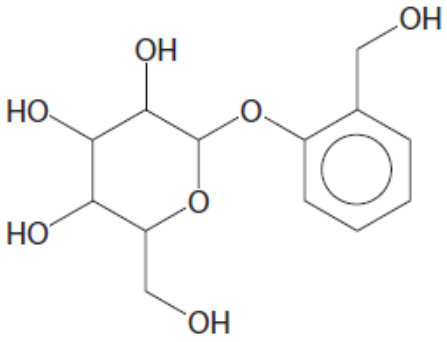
☒ **D** seven

(Total for question = 1 mark)

Q27.

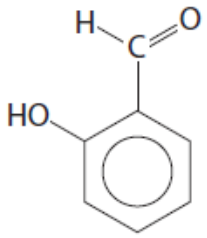
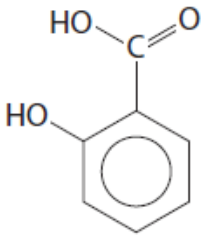
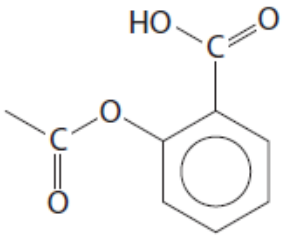
Chemicals from Plants

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

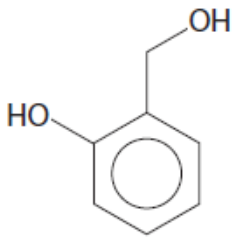
In the body, salicin is changed into salicylaldehyde and then salicylic acid. Salicylic acid may in turn be converted into 2-acetoxybenzenecarboxylic acid, a compound which is better known as aspirin, one of the most widely used medications in the world.

		
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)

.....

.....

.....

.....

(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.

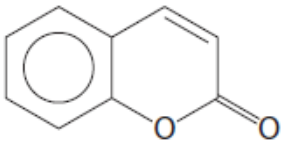
(i) Write an equation for the formation of the electrophile from methanoyl chloride. Use displayed formulae.

(1)

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

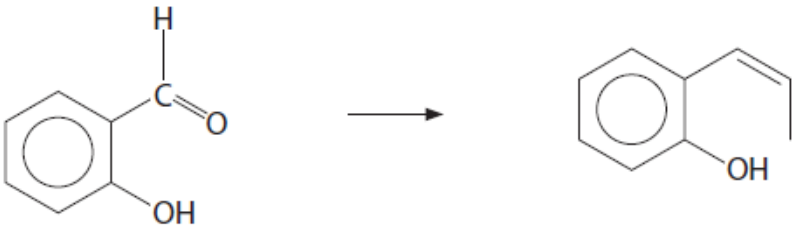
(3)

(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**.

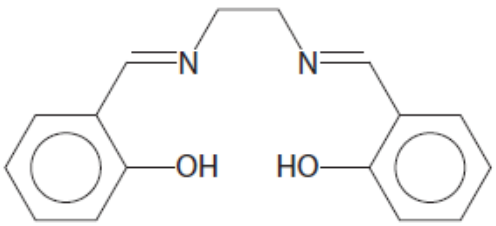


salicylaldehyde compound **F**

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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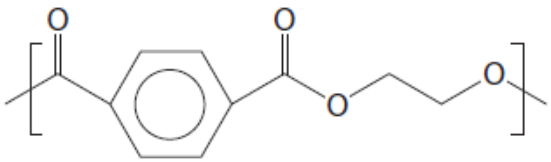
(Total for question = 20 marks)

Q28.

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)

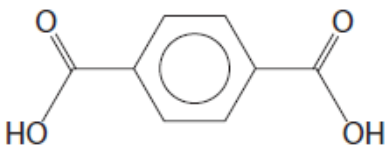
☒ **A** 57.1 %

☒ **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)

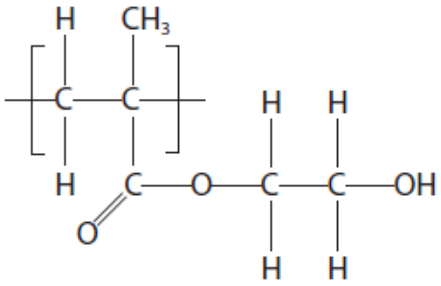
☒ **A** 2

☒ **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

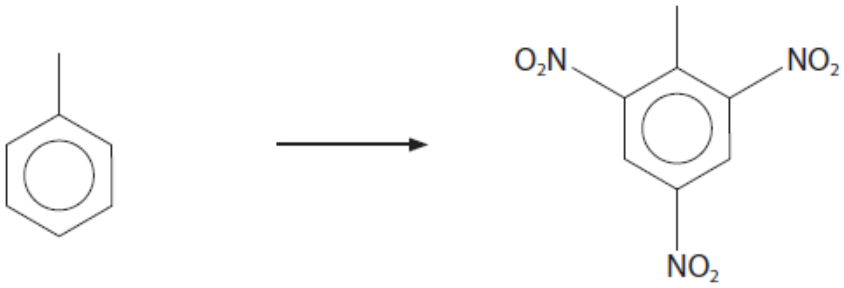
Use this space for rough working. Anything you write in this space will gain no credit.

(Total for question = 3 marks)

Q29.

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)

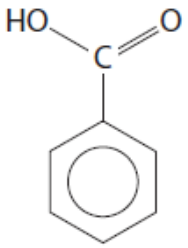
☒ **C** (10 × 100 × 227) ÷ (92 × 115)

☒ **D** (10 × 115 × 227) ÷ (92 × 100)

(Total for question = 3 marks)

Q30.

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.

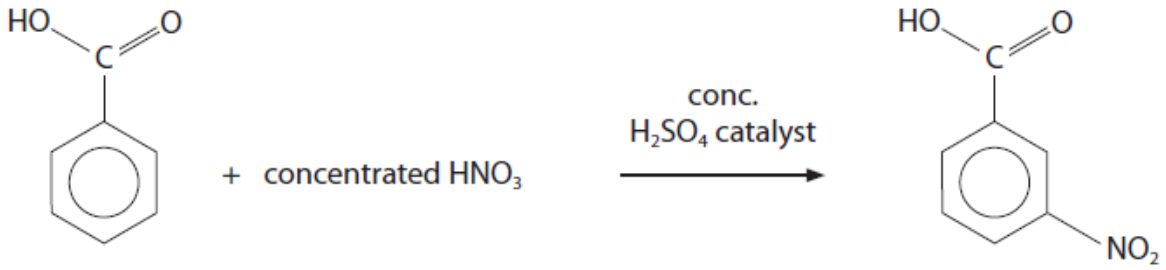
Include the reagents and essential conditions for each step and give the name or structure of each of the intermediate compounds.

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

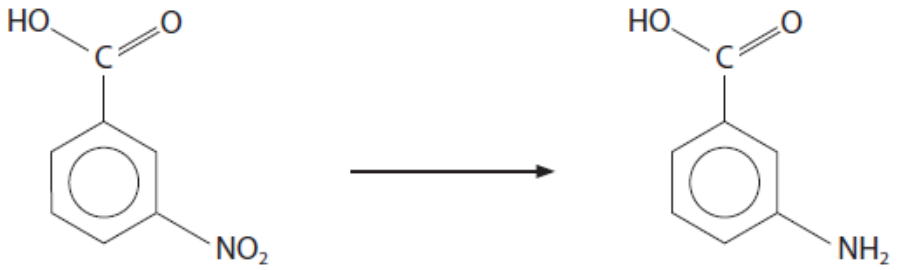
3-nitrobenzoic acid

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.



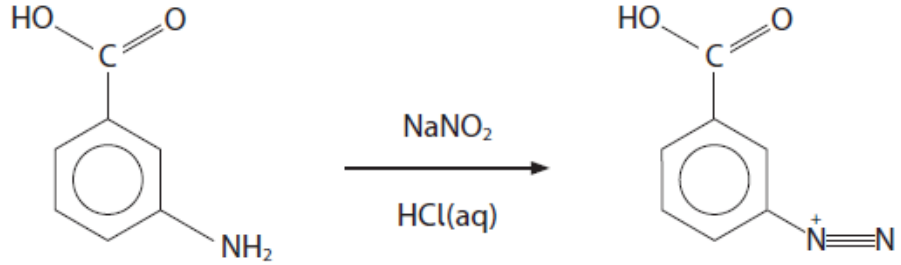
3-nitrobenzoic acid 3-aminobenzoic acid

State the reagents required for this reaction.

(1)

.....

(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)

.....

.....

.....

.....

.....

(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)

Mark Scheme

Q1.

Q	Answer	Additional guidance	Mark
(a)(i)	• Amine	Allow amino Ignore classification such as 'tertiary' Ignore NH_2 Do not award ammine	1

Q	Answer	Additional guidance	Mark
(a)(ii)	Method 1 • rewrite the Ideal Gas Equation in terms of mass and molar mass(1) • change the subject of the equation (1) • change volume to m^3 **and** temperature to K(1) • calculation of molar mass (1)	Example of calculation $PV = \frac{mRT}{M_r}$ $M_r = mRT/PV$ 157 cm^3 = 1.57 x 10^{-4} / 0.000157 m^3 Allow conversion to kPa & vol to dm^3 15°C = 288 K $M_r = \frac{0.493 \times 8.31 \times 288}{103000 \times 1.57 \times 10^{-4}}$ = 72.963 = 73.0 / 73 (g mol^{-1})	4

	• Method 2 • Change subject of equation (1) • change volume to m^3 **and** temperature to K (1) • evaluate n (1) • calculation of molar mass (1)	$n = PV/RT$ 157 cm^3 = 1.57 x 10^{-4} / 0.000157 m^3 Allow conversion to kPa & vol to dm^3 n = 103000 x 1.57 x 10^{-4} / 8.31 x 288 =6.7568 x 10^{-3} M_r = 0.493 / 6.7568 x 10^{-3} = 72.963 = 73 (g mol^{-1}) Ignore just 'g' do not award 72.9 (g mol^{-1}) if rounded from 72.963 Correct answer with some working scores (4) Correct answer with no working scores zero Ignore premature rounding if final answer correct otherwise allow rounding to at least 3SF Ignore SF except 1 SF in final answer	

Q	Answer	Additional guidance	Mark
(b)(i)	• hydrogen chloride / HCl	Allow hydrochloric acid / HCl(aq)	**1**

Q	Answer	Additional guidance	Mark
(b)(ii)	• N-substituted amide / -CONHR	Accept amide / acid amide / -$CONH_2$ / -CONH- If name and formula are given, both must be correct	**1**

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<table>
<tr><th>Q</th><th>Answer</th><th>Additional guidance</th><th>Mark</th></tr>
<tr><td>(b)(iii)</td><td>• conversion of percentages by mass into moles (1)
• evaluation of moles and division by the smallest value to give a ratio (1)
• conversion of ratio into an empirical formula (1)</td><td>Example of calculation
<table><tr><td></td><td>C</td><td>H</td><td>N</td><td>O</td></tr><tr><td>%</td><td>62.6</td><td>11.3</td><td>12.2</td><td>13.9</td></tr><tr><td>mol</td><td>62.6/12 (=5.2167)</td><td>11.3/1 (=11.3)</td><td>12.2/14 (= 0.8714)</td><td>13.9/16 =0.86875</td></tr><tr><td>Ratio</td><td>6.00</td><td>13.01</td><td>1.00</td><td>1.00</td></tr></table>$C_6H_{13}NO$
Correct answer with no working scores (1)

Ignore SF except 1 SF in mol calculation</td><td>3</td></tr>
</table>

<table>
<tr><th>Q</th><th>Answer</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr><td>(c)</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.

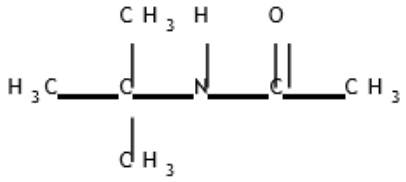
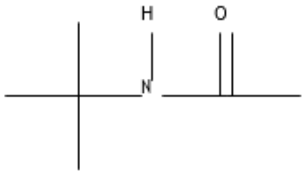
The mark for indicative content should be added to the mark for lines of reasoning.
For example, a response with five indicative marking points that is partially structured with some linkages and lines of reasoning scores 4 marks (3 marks for indicative content and 1 mark for partial structure and some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

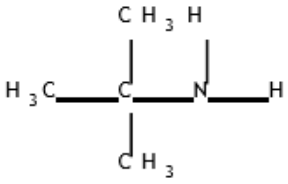
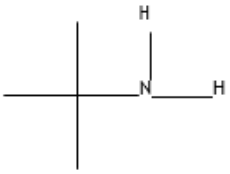
If there were no linkages between the points, then the same indicative marking points would yield an overall score of 3 marks (3 marks for indicative content and no marks for linkages).

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 0 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).

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></td></tr>
</table>

Q	Answer	Additional guidance	Mark
(c) cont	Indicative points • **IP1** three peaks indicates three proton environments • **IP2** no splitting shows no proton environment is adjacent to another • **IP3** chemical shift = 7 (ppm) indicates N—**H** proton • **IP4** nine protons in one environment and no coupling indicates $(CH_3)_3C$— • **IP5** chemical shift = 2 (ppm) indicates CH_3C=O protons • **IP6** structure is 	Marks may be awarded for **IP**s annotated on the NMR or on the structure Allow three types of proton / hydrogen Allow 'peaks have one split' Accept CH_3C=O indicated by amide responsible for the peak at 2 (ppm) Allow CH_3C=O indicated by use of ethanoyl chloride Allow displayed, structural or skeletal formulae or any combination of these e.g. 	6

Q	Answer	Additional guidance	Mark
(d)		Allow displayed, structural or skeletal formulae or any combination of these e.g.  Allow TE on the amide in 19(c)providing **X** is shown as an amine	1
		(Total for Question = 17 marks)	

Q2.

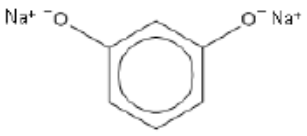
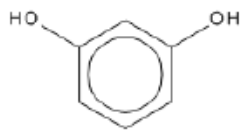
Question number	Answer	Additional guidance	Mark
(a)(i)	An answer that makes reference to the following points: • the curly arrow should go (from the benzene ring/ π bond / delocalised electrons / inside the hexagon and) towards the nitrogen / NO_2^+ **(1)** • the open end of the 'horseshoe' should be pointing towards the tetrahedral carbon / carbon with 4 bonds **(1)** • the curly arrow should start from the (C-H) bond **(1)**	Allow the changes in any order Allow the changes shown in diagrams / amended diagrams in the question Penalise any additional incorrect changes Allow first arrow must be reversed Ignore just 'the curly arrow is incorrect' Ignore just 'the curly arrow should not start from the hydrogen atom' / ' the curly arrow is incorrect' Ignore use of ion / molecule for hydrogen atom	**(3)**

Question number	Answer	Additional guidance	Mark
(a)(ii)	• tin **and** (concentrated) hydrochloric acid / (concentrated) HCl((aq))	Allow just 'HCl' for hydrochloric acid Allow iron **and** (concentrated) hydrochloric acid / (concentrated) HCl((aq)) Ignore addition of sodium hydroxide / NaOH / alkali added **after** the acid Ignore mention of heat / catalyst Do not award dilute acid / sulfuric acid / nitric acid	**(1)**

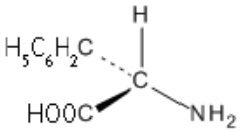
Question Number	Answer		Additional guidance	Mark
(b)(i)	An explanation that makes reference to the following points:			**(3)**
	• the lone pair (of electrons) on the nitrogen atom	**(1)**	Allow pair of electrons for lone pair Allow lone pair on the amine / NH_2 group	
	• overlaps with π cloud / delocalised electrons / delocalised system **or** interacts with (benzene) ring / delocalised electrons / delocalised system	**(1)**	Allow increases the electron density in the (benzene) ring / feeds into the delocalised electrons **or** decreases the electron density on the nitrogen atom	
	• so the nitrogen atom is less able to accept a hydrogen ion / H^+ / proton	**(1)**	Allow the lone pair (of electrons) is less available to accept a hydrogen ion / H^+ / proton Allow nitrogen is less able to donate electrons to a hydrogen ion / H^+ / proton Allow lone pair is less available to form a dative bond with an acid Allow phenylamine for nitrogen Allow ammonia is more able to accept a hydrogen ion / H^+ / proton	

Question Number	Answer	Additional guidance	Mark
(b)(ii)	A description that makes reference to the following point: • a (pale) blue precipitate forms	Allow any shade of blue Ignore reference to precipitate dissolving Ignore original colour of solution Do not award any other colours with blue e.g. blue-green	(1)

Question number	Answer	Additional guidance	Mark
(c)(i)	• sodium nitrite / sodium nitrate(III) / $NaNO_2$ **and** hydrochloric acid / HCl (1) • at 5˚C / between 0 and 10˚C (1)	Allow nitrous acid / HNO_2 / HONO **and** hydrochloric acid / HCl Ignore concentration of acid Do not award sodium nitrate / $NaNO_3$ / nitric ((V)) acid / HNO_3 Stand alone mark Allow any temperature or range of temperatures within the range 0 and 10˚C / less than any temperature within that range Allow ice-bath	(2)

Question number	Answer	Additional guidance	Mark
(c)(ii)	• correct structure	<u>Examples of structure:</u>  or  Allow ONa with no charges Allow O^- Do not award bond between O and Na i.e. O-Na / OH-C / additional atoms bonded to benzene	(1)

Question number	Answer	Additional guidance	Mark
(c)(iii)	• there is restricted rotation around N=N / the nitrogen bridge / the azo bridge / nitrogen π bond (and the lone pair of electrons on nitrogen)	Allow no rotation around N=N / the double bond Ignore just 'two different groups on N atoms' Do not award the molecule does not rotate Do not award restricted / no rotation around C=C	(1)

Question number	Answer	Additional guidance	Mark
(d)	• other optical isomer	Example of optical isomer:  The groups must be joined in the correct bonds around the central carbon atom but ignore the connectivity of the groups Allow the mirror images of the symbols Allow subscripts the other side of the symbols e.g. $_5H_6C_2HC$	(1)

Q3.

Question number	Answer	Mark
	D it avoids the decomposition of the organic molecule when it distils	1

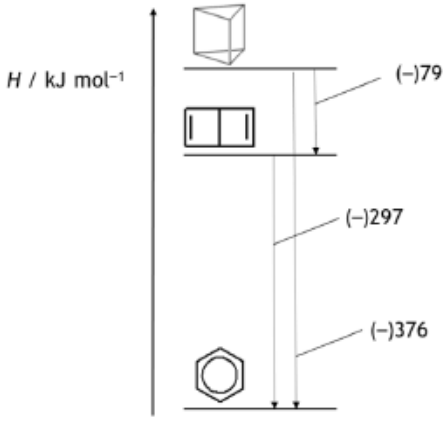
Q4.

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

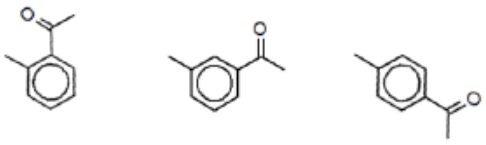
Question Number	Answer	Additional guidance	Mark
(c)	An explanation that makes reference to the following points: • showed that all C–C bonds are the same length in benzene (1) • in Kekulé structure the C=C bonds would be shorter than the C–C bonds (or reverse argument) (1)	Ignore any reference to: C–H 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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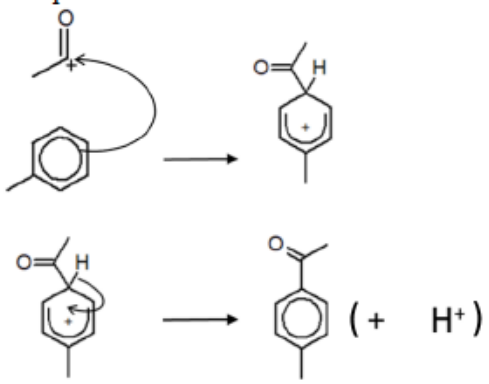
Question Number	Answer	Additional guidance	Mark
(d)(i)	A diagram showing: • correct relative stabilities (1) • two or three numerical differences in enthalpy with appropriate arrows (1)	Example of diagram:  Allow names for structures If three values and arrows are given they must all be correct to score 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

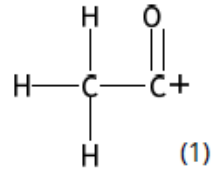
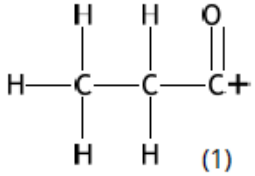
Question Number	Answer	Additional guidance	Mark
(e)	An explanation that makes reference to the following points: ***E*-hexa-1,4-diene** • twice the hydrogenation enthalpy (of hex-3-ene) as two (isolated) C=C bonds (1) ***E*-hexa-1,3-diene** • less exothermic/more stable (by 22 kJ mol^{-1} than *E*-hexa-1,4-diene **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**

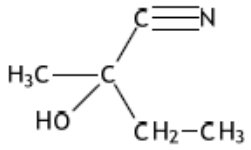
Question Number	Answer	Additional guidance	Mark
(f)(iii)	A mechanism including: • curly arrow from on or within circle to C^+ of CH_3CO^+ (1) • structure of intermediate ion (1) • curly arrow from C–H bond to within ring **and** correct product (1) • balanced equation for regeneration of catalyst (1)	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**

Q5.

Question number	Answer	Additional guidance	Mark
(a)(i)	•  (1) •  (1)	Penalise omission of the positive charge or use of negative charges once only in 20(a)(i) and (ii) Penalise use of **just** molecular formulae once only in 20(a)(i) and (ii) Allow the positive charge anywhere on a structure or outside brackets covering a structure Allow structural formulae e.g. CH_3CO^+ Allow $C_2H_5CO^+$ Allow $CH_3COCH_2^+$ Ignore *m/z* values even if incorrect	(2)

Question number	Answer	Additional guidance	Mark
(a)(ii)	• reasonable species	Allow only CH_3^+, $CH_3CH_2^+$, $C_2H_5^+$, $CH_3COCH_2CH_3^+$ Ignore *m/z* values even if incorrect Do not award species with *m/z* = 43 or 57	(1)

Question number	Answer	Additional guidance	Mark
(b)	An answer that makes reference to the following points: • reaction of butanone with iodine in sodium hydroxide / NaOH (1) • to form sodium propanoate (1) • add dilute sulfuric acid / H_2SO_4 **and** to form propanoic acid / CH_3CH_2COOH (and distil off) (1) • (reflux propanoic acid with) lithium tetrahydridoaluminate(III) / $LiAlH_4$/ lithium aluminium hydride in dry ether (to give propan-1-ol) (1)	Score correct compounds / reagents even if preceding chemistry is incorrect) Allow unbalanced equations and reaction schemes Accept potassium hydroxide Allow alkali / alkaline / OH^- Accept $CH_3CH_2COO^-Na^+$ / CH_3CH_2COONa Allow propanoate (ion) Accept any identified strong acid. Ignore H^+ Allow 'lithal' Allow the use of $LiAlH_4$ in dry ether on propanoic acid or propanal (however these are obtained) to give propan-1-ol	(4)

Question number	Answer	Additional guidance	Mark
(c)	An answer that makes reference to the following points: • identification of a suitable halogenoalkane (1) • reaction with magnesium (powder) in dry ether (1) • to form the Grignard reagent CH_3MgBr / methyl magnesium bromide (1) • formation of 2-methylbutan-2-ol by reacting the Grignard reagent with butanone (1)  • reaction with concentrated phosphoric acid or concentrated sulfuric acid (to give 2-methylbut-2-ene (and some 2-methylbut-1-ene)) (1)	Allow names or formulae for reagents and intermediates. Score correct compounds and reagents even if preceding chemistry is incorrect) Equations need not balance CH_3Br Allow Cl or I, Ignore X for halogen Allow the use of dry ether with or without Mg in this reaction or halogen given for M1 Ignore just 2-methylbutan-2-ol If Grignard reagent not used (i.e. M1, M2, M3 & M4 not scored, reaction of butanone with HCN / KCN / CN^- to form 2-hydroxy-2-methylbutanenitrile scores (1) [ignore reaction conditions] Allow pass alcohol (vapour) over heated alumina / Al_2O_3 Allow correct reaction to form halogenoalkane **and** dehydrohalogenation with OH^- in ethanol Allow 1 mark for the dehydration of **any** alcohol by any of these reactions	(5)

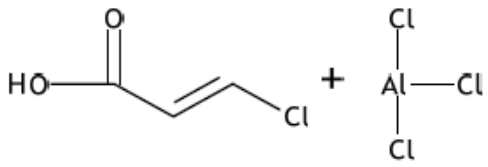
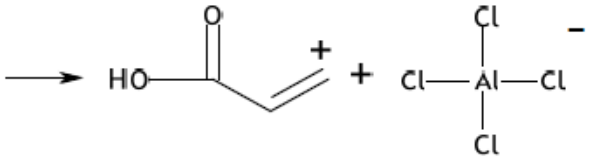
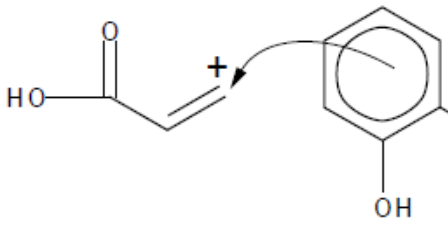
Q6.

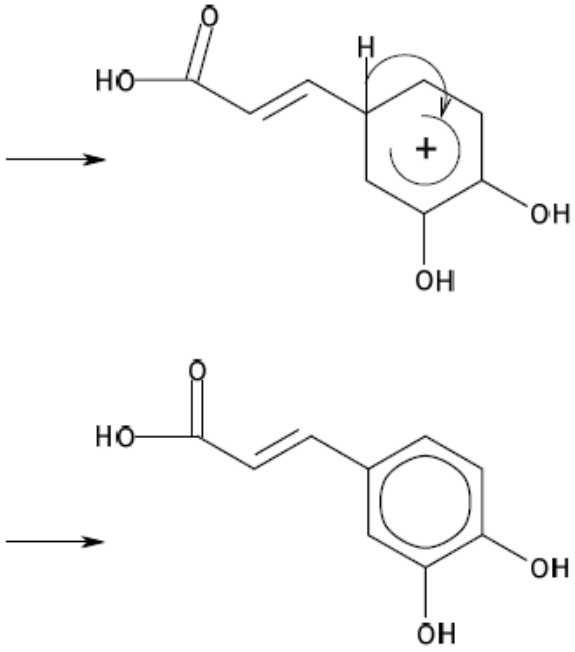
Question number	Answer	Additional guidance	Mark
(a)(i)	An explanation that makes reference to the following points • (π) electron system (in the right-hand ring) is delocalised (1) M2 and M3 scored from any **two** of • the delocalisation involves the lone-pair(s) in the nitrogen (atom(s)) and the π 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)

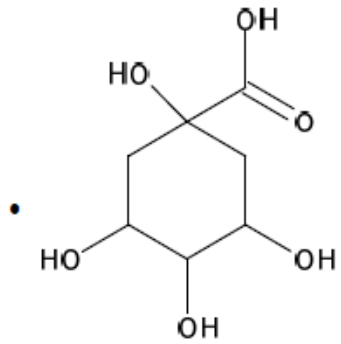
Question number	Answer	Additional guidance	Mark
(a)(ii)	An explanation that makes reference to the following points • Description of basicity (1) • Effect of delocalisation(1)	 Either lone pair donation Or proton acceptor Nitrogen lone pair incorporated in delocalised system / overlaps with the π (electron) 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)

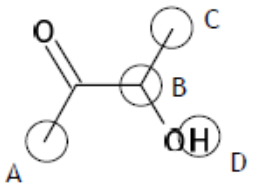
Question number	Answer	Additional guidance	Mark
(b)(i)	• determination of M_r (from molecular formula) (1) • calculation of amount of caffeine (1) • calculation of concentration of caffeine (1) • final answer to 1 or 2 SF (1)	Example of calculation $(C_8H_{10}N_4O_2)$ M_r = 194 $\frac{85}{1000 \times 194}$ (= 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)

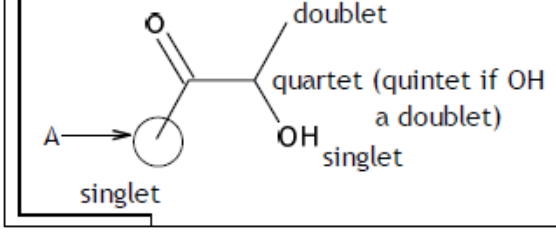
Question number	Answer	Additional guidance	Mark
(b)(ii)	• calculation of number of half-lives (1) • applies half-lives to three hours (1)	Example of calculation $\frac{20}{160} = \frac{1}{8} = \left(\frac{1}{2}\right)^n$ n = 3 or 160 → 80 → 40 → 20 (3 half lives) time = 3 x 3 = 9 hours TE on number of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

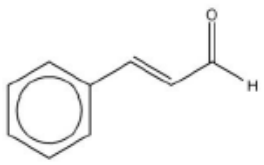
Question number	Answer	Additional guidance	Mark
(d)(ii)	<table><tr><th>Proton environment (labelled as in (i))</th><th>Splitting pattern</th></tr><tr><td>A</td><td>singlet</td></tr><tr><td>B</td><td>quartet</td></tr><tr><td>C</td><td>doublet</td></tr><tr><td>D</td><td>singlet</td></tr></table> OR 	all 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)

Q7.

<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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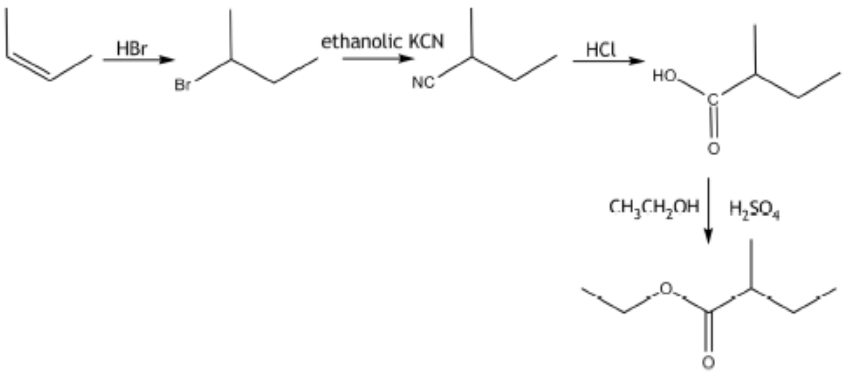
Question Number	Acceptable Answers	Additional Guidance	Mark
(b)	An explanation that makes reference to the following points: • correct structure of Q shown (1)	e.g  Accept cis structure Accept skeletal structure without terminal hydrogen Accept hybrid structures e.g. partially displayed Ignore 'it is an alkene'	(6)
	• 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)	Ignore references to phenol Do not award benzene	
	• 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)	Allow 'cannot have -CH=CH$_2$ group' Allow '2 different groups on each side of the C=C bond'	

Q8.

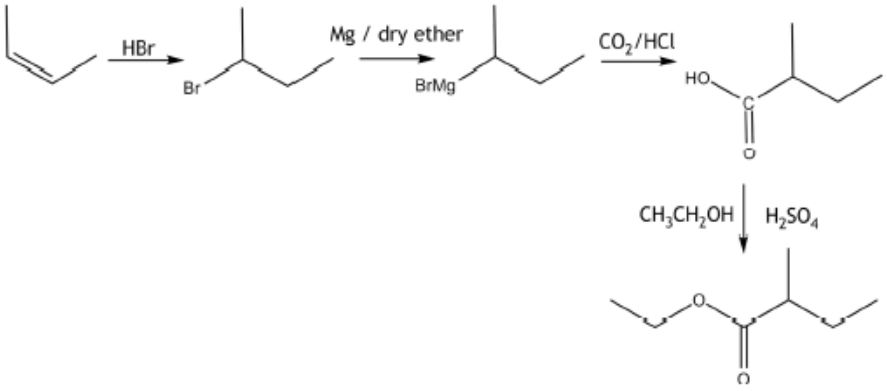
Question number	Answer	Mark
	The only correct answer is C (0.15 (mol dm^{-3})) ***A*** *is incorrect because this is the concentration with respect to* $Cr_2(SO_4)_3$ ***B*** *is incorrect because this is the concentration with respect to chromium ions* ***D*** *is incorrect because this is the total concentration of all ions*	(1)

Q9.

Question Number	Acceptable Answers	Additional Guidance	Mark
	An answer that makes reference to the following points: • formation of 2-bromobutane using HBr **(1)** • use of ethanolic KCN / alcoholic KCN / KCN(eth) **(1)** • formation of 2-methylbutanenitrile **(1)** • using HCl(aq) **(1)** • formation of 2-methylbutanoic acid **(1)** • formation of ethyl 2-methylbutanoate using ethanol and sulfuric acid **(1)** **OR** • formation of 2-bromobutane using HBr **(1)** • using magnesium in (dry) ether **(1)** • formation of sec-butyl magnesium bromide **(1)** • using CO_2 and HCl(aq) **(1)** • formation of 2-methylbutanoic acid **(1)** • formation of ethyl 2-methylbutanoate using ethanol and sulfuric acid **(1)**	See below Allow HCl and 2-chlorobutane Must be in context of attempted reaction with a haloalkane Allow CN^- / Ignore HCN Accept any strong mineral acid Allow H^+ Allow any strong mineral acid Allow H^+ Do not award just 'acid' Must be in context of attempted reaction with a haloalkane Allow H^+ / acid work up Do not award just 'acid' Accept any strong mineral acid Allow any strong mineral acid Allow H^+ Do not award just 'acid'	**(6)**



OR



Note - the reaction of the Grignard with CO_2 and HCl can be shown as two separate steps. If this is the case ignore the structure of any intermediate species

Q10.

Question number	Answer	Mark
	The only correct answer is C (will be lower than the true value) ***A*** *is incorrect because using a sample that is impure would cause the value to be lower* ***B*** *is incorrect because using a sample that is impure would cause the value to be lower* ***D*** *is incorrect because using a sample that is impure would cause the value to be lower*	1

Q11.

<table>
<tr><th>Question Number</th><th>Answer</th><th>Additional Guidance</th><th>Mark</th></tr>
<tr><td>(a)</td><td>

- calculation of mass of carbon **(1)**
- calculation of mass of hydrogen and oxygen **(1)**
- calculation of moles of carbon, hydrogen and oxygen **(1)**
- calculation of ratio **(1)**

alternative method

M1 moles of Q = 4.91 ÷ 148 = 0.0332 (mol)
M2 moles of CO_2 = 14.6 ÷ 44 = 0.332 (mol) **and** moles of H_2O = 3.58 ÷ 18 = 0.199 (mol)
M3 calculation of the ratio 10 : 12

M4 show that O = 1

(10 x 12) + (12 x 1) + (16 x number of oxygen atoms) = 148 , so O = 1

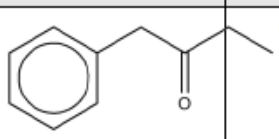
</td><td>

Example of calculation

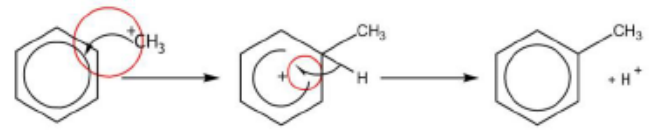
<table>
<tr><td></td><td>C</td><td>H</td><td>O</td></tr>
<tr><td>mass =</td><td>14.6 x (12÷44) = 3.982 (g)</td><td>3.58 x (2÷18) = 0.398 (g)</td><td>4.91 – (3.982+0.398) =0.53 (g)</td></tr>
<tr><td>Moles =</td><td>= 3.982 ÷12 = 0.332 (mol)</td><td>= 0.398 ÷ 1 = 0.398 (mol)</td><td>0.53 ÷ 16 0.0331 (mol)</td></tr>
<tr><td>Ratio</td><td>10</td><td>12</td><td>1</td></tr>
<tr><td>Formula =</td><td colspan="3">$C_{10}H_{12}O$</td></tr>
</table>

Allow TE from M1 to M3

</td><td>**(4)**</td></tr>
</table>

Question Number	Acceptable Answers	Additional Guidance	Mark
(b)	An explanation that makes reference to the following points: **structure** • correct structure **(1)** **chemical shifts -** allow any three from four • 4 peaks / chemical shifts means 4 (different) hydrogen environments **(1)** • peak at 7.5 ppm is due (hydrogen atoms on) benzene ring **(1)** • peak at 2.3 ppm is due **H**-C-C=O / ketone / C=O **(1)** • peak at 1.0 ppm is due to **H**-C-C / alkyl group / methyl group / alkane **(1)**	 Allow chemical environment Ignore references to peak at 3.6 ppm Do not award aldehyde If no reference to neighbouring hydrogens in M4, M5 or M6 allow 1 mark for idea that a quartet-triplet pattern is due to CH_2CH_3	**(7)**
	splitting patterns - allow any two from three • peak at 2.3 ppm is a quartet as there are 3 hydrogens on neighbouring carbon / it is bonded to a CH_3 group **(1)** **Or** • peak at 1.0 ppm is a triplet as there are 2 hydrogens on neighbouring carbon / bonded to a CH_2 **(1)** **Or** • peak at 3.6 ppm is a singlet as there are no hydrogens on neighbouring carbon **(1)** **area under curve** • (area of 5 for peak at 7.5 ppm) shows the benzene ring has (only) 1 side group / is C_6H_5 **(1)**	Ignore references to splitting of peak at 7.5 ppm Allow benzene has 5 H (atoms) DNA if more than 1 side group on structure	

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)**	$CH_3Cl + AlCl_3 \longrightarrow {}^{+}CH_3 + AlCl_4^-$  $H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$	**(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)	Example of calculation 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	Additional guidance	Marks
(a)	An answer that makes reference to the following points: • react iodoethane with **aqueous** hydroxide ions (1) • $C_2H_5I + OH^- \rightarrow C_2H_5OH + I^-$ (1) • oxidation of C_2H_5OH with acidified dichromate(VI) under **distillation** conditions (1) • $C_2H_5OH + [O] \rightarrow CH_3CHO + H_2O$ (1) • react iodoethane with magnesium (in **ethoxyethane)** (1) • $C_2H_5I + Mg \rightarrow C_2H_5MgI$ (1) • reaction of ethylmagnesium iodide with ethanal to form butan-2-ol (1) • $C_2H_5MgI + CH_3CHO + H_2O \rightarrow C_2H_5CH(OH)CH_3 + Mg(OH)I$ (1)	Accept displayed/skeletal formulae Accept aqueous sodium hydroxide/ potassium hydroxide $C_2H_5I + NaOH \rightarrow C_2H_5OH + NaI$ Accept reference to sodium/ potassium dichromate(VI) Allow this to be shown as two separate equations	8

Question number	Answer	Additional guidance	Marks
(b)(i)	• calculation of number of moles of butan-2-ol (1) • calculation of number of moles of carbon dioxide and water (1) • calculation of carbon dioxide mass/mass increase of solid X (1) • calculation of mass of water/mass increase of solid Y (1)	Example of calculation: n=(1.850 ÷ 74 =) 0.025 (mol) $n(CO_2) = 4 \times 0.025 = 0.100$ (mol) and $n(H_2O) = 5 \times 0.025 = 0.125$ (mol) $m(CO_2) = 0.100 \times 44 = 4.40$ (g) $m(H_2O) = 0.125 \times 18 = 2.25$ (g)	4

Question number	Answer	Additional guidance	Marks
(b)(ii)	Prediction: • suitable example by name or formula. (1) Reason: • the same molecular formula as butan-2-ol / is an isomer of butan-2-ol. (1)	Allow structural /displayed / skeletal formula. Any molecule with the molecular formula $C_4H_{10}O$ Do not award just '$C_4H_{10}O$'	2

Q14.

Question Number	Correct Answer	Mark
(a)	**The only correct answer is B** (ether) *A is incorrect because it would protonate the Grignard reagent* *C is incorrect because it is non-polar* *D is incorrect because it would react with the Grignard reagent to form a tertiary alcohol*	(1)

Question Number	Correct Answer	Mark
(b)	**The only correct answer is D** (to ensure the solvent boils smoothly) *A is incorrect because the anti-bumping granules will not change the boiling temperature* *B is incorrect because this is the role of the condenser* *C is incorrect because the anti-bumping granules will not affect the flammability of the solvent*	(1)

Question Number	Correct Answer	Mark
(c)	**The only correct answer is D** (negative and nucleophilic) *A is incorrect because the carbon atom is not positive or electrophilic* *B is incorrect because the carbon atom is not positive* *C is incorrect because the carbon atom is not electrophilic*	(1)

Question Number	Correct Answer	Mark
(d)	**The only correct answer is A** (hexan-3-one) *B is incorrect because the product would be 2,4-dimethyloctan-4-ol* *C is incorrect because hexan-3-ol does not have a carbonyl bond* *D is incorrect because hexan-2-ol does not have a carbonyl bond*	(1)

Q15.

Question number	Answer	Mark
	The only correct answer is D (carbon dioxide giving carboxylic acids) ***A*** *is incorrect because Grignard reagents react with water giving alkanes* ***B*** *is incorrect because Grignard reagents react with methanal giving primary alcohols* ***C*** *is incorrect because Grignard reagents react with ketones giving tertiary alcohols only*	1

Q16.

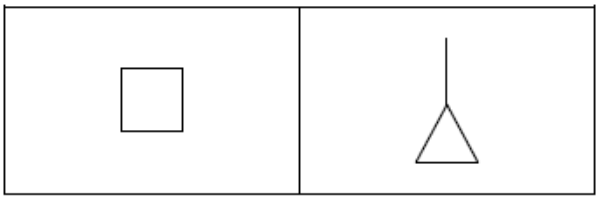
Q	Answer	Mark
	The only correct answer is A(one singlet, one doublet and a heptet) ***B*** *is not correct because this ignores the fact that the proton environments on C1 and C3 are the same* ***C*** *is not correct because this is the number of protons in each environment, not the splitting pattern* ***D*** *is not correct because this ignores all the splitting except the effect of one methyl on the C2 proton*	1

Q17.

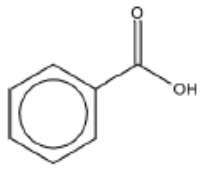
Question number	Answer	Mark
	The only correct answer is B (five) ***A*** *is incorrect because the carbon with the two methyl groups attached has been omitted* ***C*** *is incorrect because the carbon with the two methyl groups attached has been omitted and the symmetry of the structure has been ignored* ***D*** *is incorrect because the symmetry of the structure has been ignored*	(1)

Q18.

Question number	Answer	Additional guidance	Mark
(a)	• identification of correct algebraic equation for x **and** solves equation to obtain x (1) • identification of correct algebraic equation for x and y (1) • solves equation to obtain y and gives formula of the hydrocarbon (1)	Example of calculation {from the equation 1 mol of C_xH_y gives x mol of CO_2 so 25 mol will give 25x mol CO_2 and 25 cm^3 will give 25x cm^3CO_2 . Hence} 25x = 100 **and** x = 4 Allow just x = 4 with no working {change in volume is} (25 + 25(x+y/4) − 25x = 75 25y/4 = 50 therefore y = 8 **and** C_4H_8 correct formula with no working scores (1)	(3)

Question number	Answer	Additional guidance	Mark
(b)	• structure of cyclobutane (1) • structure of methylcyclopropane(1)	Examples of structures  or displayed / semi-displayed structures Ignore names even if incorrect TE on 22(a) for cycloalkanes only If (a) is an alkane with C>3 2 correct isomers scores 1 mark	(2)

Q19.

Question Number	Correct Answer	Mark
	The only correct answer is A  ***B*** *is incorrect because the structure has no C=O group* ***C*** *is incorrect because the structure has no O-H group* ***D*** *is incorrect because the structure has no O-H group*	**(1)**

Q20.

Q	Answer	Mark
	The only correct answer is D(P is due to C—H aldehydeand Q is due to C=O aldehyde) ***A*** *is not correct because P is too sharp to be an OH stretch and Q is outside the region of 1725-1700 cm^{-1} for a carboxylic acid C=O stretch* ***B*** *is not correct because P is too sharp to be an OH stretch* ***C*** *is not correct because Q is outside the region of 1725-1700 cm^{-1} for a carboxylic acid C=O stretch*	**1**

Q21.

Question Number	Correct Answer	Mark
	The only correct answer is A (92.0261) ***B*** *is incorrect because it uses O = 16* ***C*** *is incorrect because it has 5 hydrogens in the structure instead of 4* ***D*** *is incorrect because it has 5 hydrogens in the structure instead of 4 and uses O = 16*	**(1)**

Q22.

Question number	Answer	Mark
	The only correct answer is C (+6) **A** *is incorrect because the maximum oxidation state occurs when all the 3d and 4s electrons are used in bonding* **B** *is incorrect because the maximum oxidation state occurs when all the 3d and 4s electrons are used in bonding* **D** *is incorrect because the maximum oxidation state occurs when all the 3d and 4s electrons are used in bonding*	(1)

Q23.

Question number	Answer	Mark
	The only correct answer is C (C_4H_6) **A** *is incorrect because C_2H_3 cannot be a molecular formula* **B** *is incorrect because this formula is obtained without doubling the moles of water to give the moles of hydrogen* **D** *is incorrect because the moles of water has been halved instead of doubled*	(1)

Q24.

Q	Answer	Mark
	The only correct answer is C(five) **A** *is not correct because the C atoms in methylcyclohexane are not all equivalent* **B** *is not correct because there are five types of C atom in methylcyclohexane not three* **D** *is not correct because the C atoms in methylcyclohexane are not all different*	**1**

Q25.

Question number	Answer	Mark
	A 3	1

Q26.

Question number	Answer	Mark
	The only correct answer is A(four) ***B*** *is incorrect because onlythe ring carbon atomshave been considered and symmetry has been ignored* ***C*** *is incorrect because the ring symmetry has been ignored* ***D*** *is incorrect because this is just the total number of carbon atoms*	**(1)**

Q27.

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

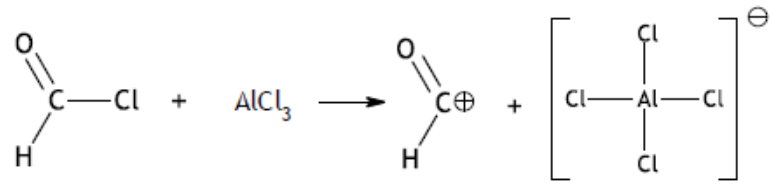
Some common incorrect answers (score (3))

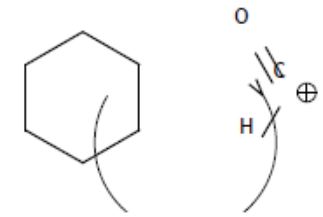
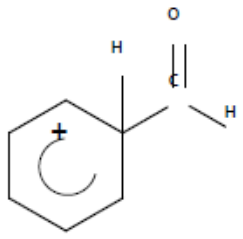
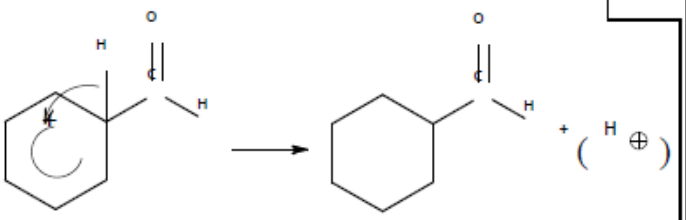
Formula	M_r	%C	%H	%O
$C_{13}H_{10}O_7$	278	56.12	3.60	40.29
$C_{13}H_{11}O_7$	279	55.91	3.94	40.14
$C_{13}H_{13}O_7$	281	55.52	4.63	39.86
$C_{13}H_{17}O_7$	285	54.74	5.96	39.30
$C_{13}H_{20}O_7$	288	54.17	6.94	38.89
$C_{13}H_{23}O_7$	291	53.61	7.90	38.49
$C_{13}H_{24}O_7$	292	53.42	8.22	38.36

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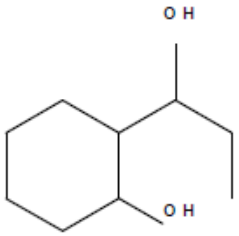
Question number	Answer	Additional guidance	Mark
(b)(i)	An answer that makes reference to the following • a suitable oxidising agent (1) • sulfuric acid / H_2SO_4 **and** (heat under) reflux (1)	Standalone marks sodium dichromate(VI) / $Na_2Cr_2O_7$ / potassium dichromate(VI) / $K_2Cr_2O_7$ Allow dichromate(VI) / $Cr_2O_7^{2-}$ 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**

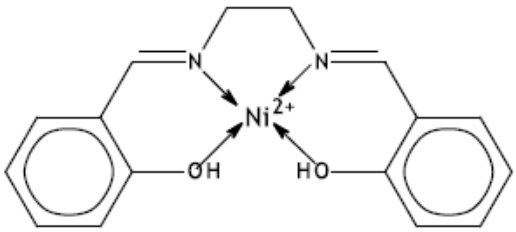
Question number	Answer	Additional guidance	Mark
(b)(ii)	An answer that makes reference to the following • salicylaldehyde needs to be distilled / separated (from the reaction mixture to prevent its further oxidation) (1) EITHER • (because) at high temperatures salicylaldehyde will be oxidised (to salicylic 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

Q28.

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)

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)

Q29.

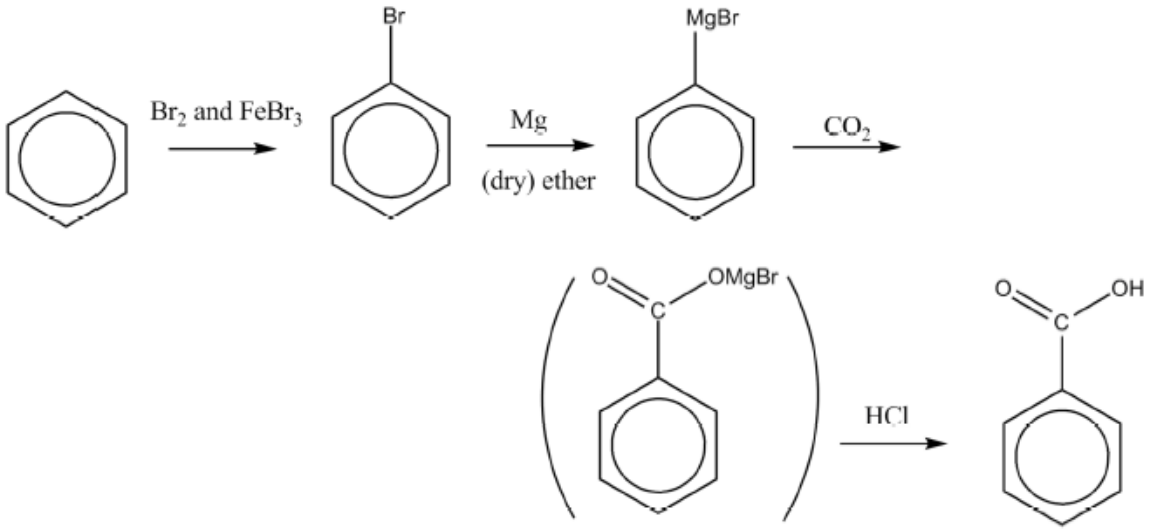
Question Number	Correct Answer	Mark
(a)	**The only correct answer is C** (five) ***A*** *is incorrect because it assumes all the carbon atoms are in a different environment* ***B*** *is incorrect because it assumes only two of the benzene ring carbon atoms are in the same environment* ***D*** *is incorrect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

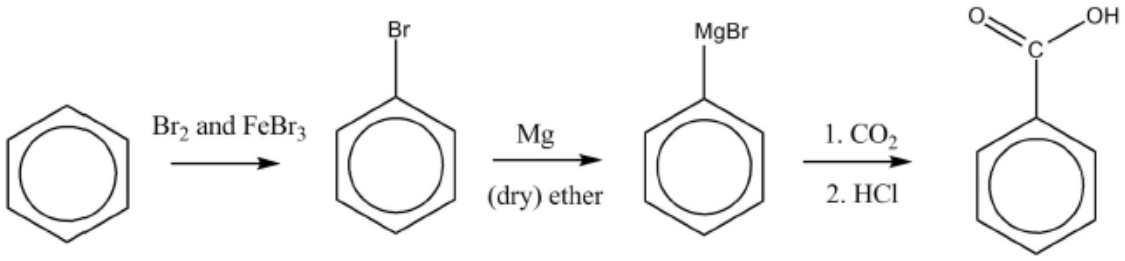
Question Number	Correct Answer	Mark
(c)	**The only correct answer is A** ((10 x 85 x 227) ÷ (92 x 100)) ***B*** *is incorrect because the scaling factor for the yield is incorrect* ***C*** *is incorrect because the scaling factor for the yield is incorrect* ***D*** *is incorrect because the scaling factor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

Q30.

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)**

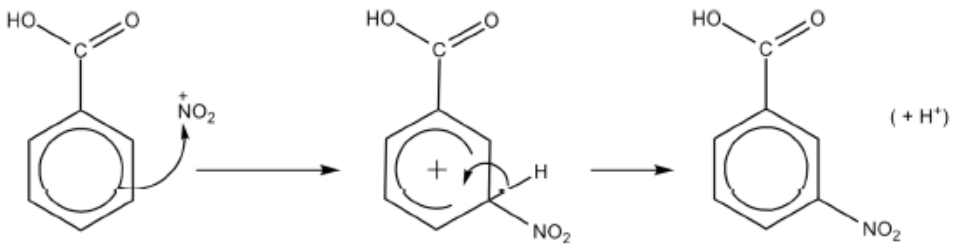


Allow CO_2 and HCl as parts 1 and 2 of the final step if clearly labelled e.g.



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	

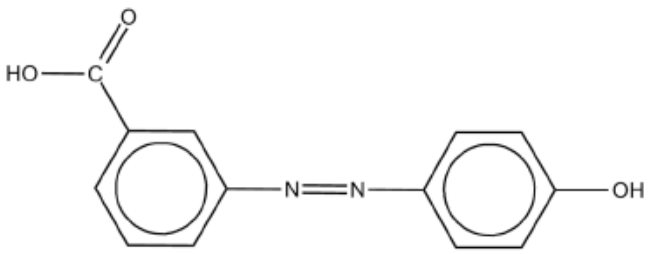
Example of mechanism for bi



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 $3.89 / 449.2 = 8.65984 \times 10^{-3}$ (mol) 1:1 so 8.65984×10^{-3} (mol) M3 can be subsumed in M4 $2.60 / 8.65984 \times 10^{-3} = 300.24$ 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 $8.65984 \times 10^{-3} \times 282.1 = 2.44$ 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)**