A' Level Chemistry

Year 2

Unit 20: NMR

Summer Examination Revision Pack

The questions in this pack should be attempted **AFTER** completing all other revision.

Grade Accelerator

Recall Definitions
Drawing Diagrams
Using Equations
Drawing Graphs

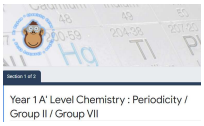
Quizlet

Quizlet Classes

Flashcard Based
Games
Tests & Quizzes
Keyword Spell Checker

Condensed Notes

Keywords & Definitions
Key Concepts
Application
Key Skills



Online Forms

Take Time to Answer
Use Paper & Calculator
Work It Out
Review Missed Marks

Use the 3 Wave Process when completing these revision packs.

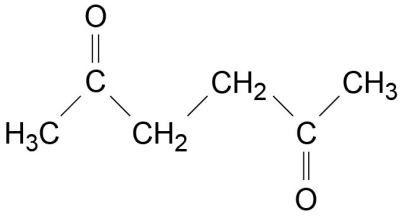
1. Complete the questions without assistance
(Can't answer a question? Leave it and move on)
2. Use your notes to fill any gaps after step 1
3. Use the mark scheme to fill in any remaining gaps.

1. Having gaps after step 1 is normal, that's why we are doing revision!
2. If your notes don't help during step 2, they are not good enough!
(Change your note taking method and try to understand the problem)
3. If you don't understand why the mark scheme answer is correct, **see Andy.**

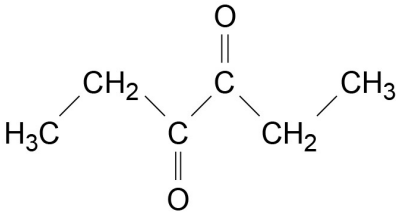
If you struggle with the questions in the pack, **STOP!** and complete some more revision.

If you come to a complete dead-end, **STOP!** and speak to **Andy** asap.

1 0 . 4 Isomers **R** and **S** are shown.



R



S

Although the ^{13}C spectra of **R** and **S** both show the same number of peaks, the spectra can be used to distinguish between the isomers.

Justify this statement using Table **C** from the Data Booklet.

Give the number of peaks for each isomer.

[3 marks]

Justification

Number of peaks

1 0 . 5 Although the ^{1}H spectra of **R** and **S** both show the same number of peaks, the spectra can be used to distinguish between the isomers.

Justify this statement using the splitting patterns of the peaks.

Give the number of peaks for each isomer.

[3 marks]

Justification

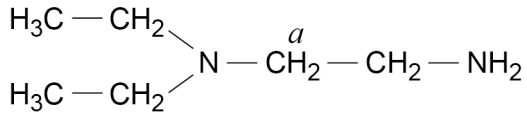
Number of peaks

10.4	**R** has 4 C next to C=O **S** has 2 C next to C=O in range δ = 20-50 **R** has two peaks and **S** only one peak in this range Or **R** has more peaks (allowed if no numbers given) **OR** **S** has a -C(H_2)-C(H_3) **R** does not **S** has one peak in range δ = 5-40 **R** does not ***/*** lowest peak for **S** is lower than lowest for **R** (Both have) three peaks	M1 M2 M1 M2 M3	M1 for structural point M2 for resulting peak in spectra

10.5	**R** Both singlets **S** has triplet and a quartet OR **R** CH_3/peak at 2.1-2.6 is a singlet **S** CH_3/peak at 0.7-1.2 is a triplet OR **R** CH_2/peak at 2.1-2.6 is a singlet **S** CH_2/peak at 2.1-2.6 is a quartet (Both have) two peaks	M1 M2 M1 M2 M1 M2 M3	

1 1 There are several isomers with the molecular formula $C_6H_{16}N_2$

1 1 . 1 One isomer is shown.



Give the number of peaks in the ^{13}C NMR spectrum of this isomer.

State and explain the splitting pattern of the peak for the hydrogens labelled *a* in its ^{1}H NMR spectrum.

[3 marks]

Number of ^{13}C peaks _____

Splitting pattern _____

Explanation _____

_____

_____

_____

1 1 . 2 Draw the structure of the isomer of $C_6H_{16}N_2$ used to make nylon 6,6

[1 mark]

Question 11 continues on the next page

1 1 . 3 Draw the structure of the isomer of $C_6H_{16}N_2$ that contains two **primary** amine groups and has only two peaks in its ^{13}C NMR spectrum.

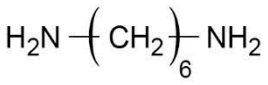
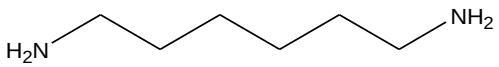
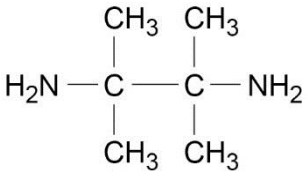
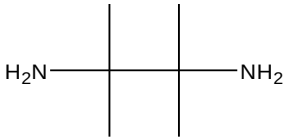
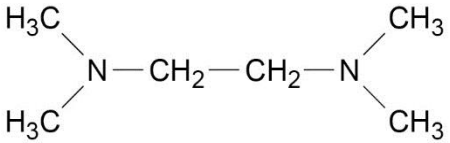
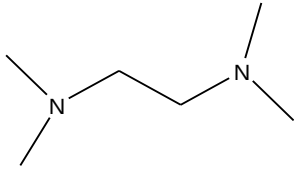
[1 mark]

1 1 . 4 Draw the structure of the isomer of $C_6H_{16}N_2$ that contains two **tertiary** amine groups and has only two peaks in its ^{13}C NMR spectrum.

[1 mark]

END OF QUESTIONS

6

Question	Answers	Mark	Additional Comments/Guidance
11.1	4 peaks Triplet Two H on adjacent C	1 1 1	 M3 dependent on correct M2
11.2	 or 	1	Not $-C_6H_{12}-$
11.3	 or 	1	
11.4	 or 	1	Not $-C_2H_4-$

Total		6	

Do not write outside the box

0 6 This question is about isomers.

0 6 . 1 Give a reagent and observations for a test-tube reaction to distinguish between 2-methylbutan-1-ol and 2-methylbutan-2-ol.

[3 marks]

Reagent _____

_____

Observation with 2-methylbutan-1-ol _____

_____

_____

Observation with 2-methylbutan-2-ol _____

_____

_____

0 6 . 2 Compounds **A** and **B** both have the molecular formula $C_4H_8Br_2$
A has a singlet, a triplet and a quartet in its ^1H NMR spectrum.
B has only two singlets in its ^1H NMR spectrum.

Draw a structure for each of **A** and **B**.

[2 marks]

A **B**

Question 6 continues on the next page

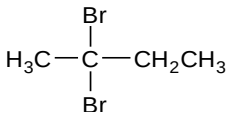
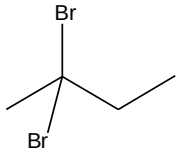
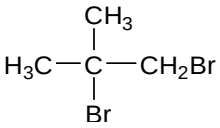
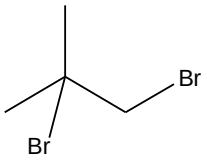
Do not write outside the box

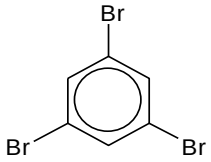
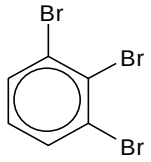
0 6 . 3 Compounds **C** and **D** both have the molecular formula $C_6H_3Br_3$
C has two peaks in its ^{13}C NMR spectrum.
D has four peaks in its ^{13}C NMR spectrum.

Draw a structure for each of **C** and **D**

[2 marks]

C **D**

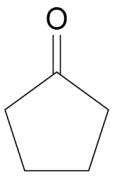
Question	Answers	Additional Comments/Guidelines	Mark
06.1	**Must be a single test-tube reaction** **M1** Reagent: acidified potassium dichromate ***OR*** $K_2Cr_2O_7/H_2SO_4$ ***OR*** $K_2Cr_2O_7/H^+$ ***OR*** acidified $K_2Cr_2O_7$ **M2** ….-1-ol (orange to) <u>green</u> solution ***OR*** goes <u>green</u> **M3** ….-2-ol no (visible/observed) reaction/change or NVR or stays orange **OR** **M1** Reagent**:** acidified potassium manganate(VII) or $KMnO_4/H_2SO_4$ ***OR*** $KMnO_4/H^+$ ***OR*** acidified $KMnO_4$ **M2**….-1-ol (purple to) <u>colourless</u> solution **OR** goes <u>colourless</u> **M3**….-2-ol no (visible/observed) reaction/change or stays purple	If incorrect reagent then no marks For acidified potassium dichromate: if "dichromate" or "(potassium) dichromate(IV)" or incorrect formula or no acid, penalise **M1** but mark on - ignore dichromate described as "yellow" or "red". For acidified potassium manganate(VII): If "manganate" or "(potassium manganate(IV)" or incorrect formula or no acid, penalise **M1** but mark on Credit alkaline / neutral $KMnO_4$ for possible full marks but **M2** gives <u>brown precipitate</u> or solution goes <u>green</u>	1 1 1
06.2	**A**  **OR** 	**B**  **OR** 	2

06.3	**C**  	**D**  	Allow Kekulé structures Penalise missing aromatic ring each time	2

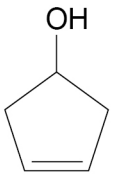
Do not write outside the box

0 7 Isomers **X** and **Y** have the molecular formula C_5H_8O

Isomer **X**



Isomer **Y**



0 7 . 1 Give the IUPAC name for isomer **X**.

[1 mark]

0 7 . 2 Explain how and why isomers **X** and **Y** can be distinguished by comparing **each** of their

- boiling points
- ^{13}C NMR spectra
- infrared spectra.

Use data from Tables **A** and **C** in the Data Booklet in your answer.

[6 marks]

Do not write outside the box

7

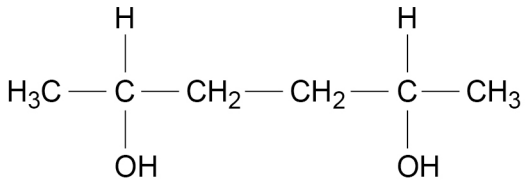
Turn over ►

Question	Answers		Additional Comments/Guidelines	Mark
G 07.1	Cyclopentanone		Allow cyclopentan -1-one but no other numbers Ignore spaces, commas and hyphens	1
07.2	This question is marked using Levels of Response. Refer to the Mark Scheme Instructions for Examiners for guidance.		**Indicative Chemistry content** **Stage 1**: boiling points 1a) **Y** has a higher bp 1b) **Y** has H-bonds between molecules and **X** has dip-dip imf 1c) More energy required to overcome H-bonds Mention of covalent bond breaking loses 1c **Stage 2**: ^{13}C NMR 2a) Both have 3 peaks/absorptions in their ^{13}C NMR 2b) **X** has peaks at 20-50 **OR** 190-220ppm 2c) **Y** has peaks at 50-90 **OR** 90-150ppm (Ignore peaks at 5-40ppm - present in both) **Stage 3**: ir 3a) **X** has a peak (for C=O) at 1680-1750 cm^{-1} 3b) **Y** has peak (for O–H) at 3230-3550 cm^{-1} **OR** peak (for C=C) at 1620-1680 cm^{-1} 3c) They would have different fingerprint regions (below 1500 cm^{-1})	**6**
	Level 3 5-6 marks	**All stages are covered and each stage is generally correct and virtually complete.** Answer is well structured with no repetition or irrelevant points. Accurate and clear expression of ideas with no errors in use of technical terms.		
	Level 2 3-4 marks	**All stages are covered but stage(s) may be incomplete or may contain inaccuracies OR two stages are covered and are generally correct and virtually complete**. Answer shows some attempt at structure Ideas are expressed with reasonable clarity with, perhaps, some repetition or some irrelevant points. Some minor errors in use of technical terms		
	Level 1 1-2 marks	**Two stages are covered but stage(s) may be incomplete or may contain inaccuracies OR only one stage is covered but is generally correct and virtually complete.** Answer includes isolated statements and these are presented in a logical order. Answer may contain valid points which are not clearly linked. Errors in the use of technical terms.		
	0 mark	Insufficient correct chemistry to gain a mark.		

.

Do not write outside the box

1 0 . 3 Compounds with molecular formula $C_6H_{14}O_2$ also have a relative molecular mass of 118 to the nearest whole number. These include the diol shown.



Deduce the number of peaks in the ^1H NMR spectrum of this diol.

[1 mark]

1 0 . 4 Draw the structure of a different diol also with molecular formula $C_6H_{14}O_2$ that has a ^1H NMR spectrum that consists of two singlet peaks.

[1 mark]

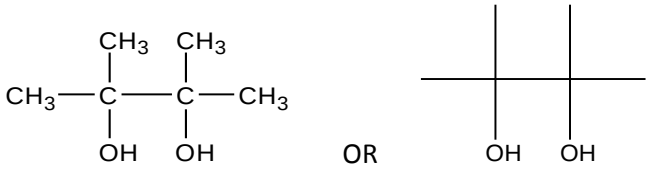
1 0 . 5 The dicarboxylic acid in question **10.1** and the isomers of $C_6H_{14}O_2$ in Questions **10.3** and **10.4** all have a relative molecular mass of 118

State why the dicarboxylic acid can be distinguished from the two diols by high resolution mass spectrometry using electrospray ionisation.

[1 mark]

10

Turn over for the next question

Question	Answers	Additional Comments/Guidelines	Mark
G 10.3	4 or four		1
10.4	 OR		1
10.5	The precise (relative molecular) masses are <u>different</u> or wtte	Allow M_r are different to 2 or more or several dp Ignore different molecular formula Ignore accuracy Penalise fragments	1

Do not write outside the box

0 7 This question is about NMR spectroscopy.

0 7 . 1 A compound is usually mixed with $Si(CH_3)_4$ and either CCl_4 or $CDCl_3$ before recording the compound's ^1H NMR spectrum.

State why $Si(CH_3)_4$, CCl_4 and $CDCl_3$ are used in ^1H NMR spectroscopy.

Explain how their properties make them suitable for use in ^1H NMR spectroscopy.

[6 marks]

Do not write outside the box

Question 7 continues on the next page

Do not write outside the box

0 7 . 2 Deduce the splitting pattern for each of the peaks given by the H atoms labelled ***x***, ***y*** and ***z*** in the ^{1}H NMR spectrum of the compound shown.

$$\underset{x}{CH_3}\underset{y}{CHCl}COCH(\underset{z}{CH_3})_2$$

[3 marks]

x _____

y _____

z _____

0 7 . 3 Suggest why it is difficult to use **Table B** in the Data Booklet to predict the chemical shift (δ value) for the peak given by the H atom labelled ***y***.

[1 mark]

_____

_____

_____

_____

0 7 . 4 Two isomers of $CH_3CHClCOCH(CH_3)_2$ each have two singlet peaks only in their ^{1}H NMR spectra.
In both spectra the integration ratio for the two peaks is 2:9

Deduce the structures of these two isomers.

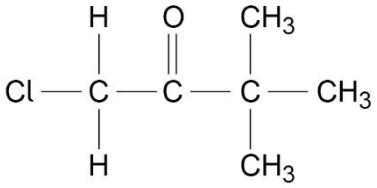
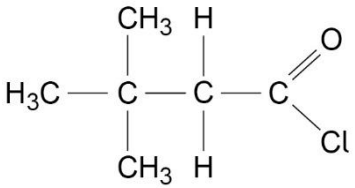
[2 marks]

Isomer 1

Isomer 2

12

<table>
<tr><th>Question</th><th colspan="2">Answers</th><th>Additional Comments/Guidelines</th><th>Mark</th></tr>
<tr><td rowspan="5">07.1</td><td colspan="2">This question is marked using Levels of Response. Refer to the Mark Scheme Instructions for Examiners for guidance.</td><td rowspan="5">Indicative Chemistry content
Stage 1:
1a $CDCl_3$ or CCl_4 solvent
1b TMS as reference / calibration / standard / peak at 0 (ppm)
1c Inert (so unlikely to react with the sample allow if inert tied to either TMS or $CDCl_3$ or CCl_4)
Stage 2 CCl_4 or $CDCl_3$ as solvent:
2a (Both) have no H (atoms so give no signals in spectrum) tied to either $CDCl_3$ or CCl_4
2b CCl_4 non polar (- good solvent for non-polar organic molecules)
2c $CDCl_3$ polar covalent molecule (– good solvent for polar organic compounds)
Stage 3 TMS as reference:
3a (Lots (12) of equivalent H to) give one signal / single environment
3b Signal in an area away from other typical H signals / peak upfield from others
OR
(Low electronegativity of Si shifts) signal right
3c Easy to remove / volatile / low bp</td><td rowspan="5">6</td></tr>
<tr><td>Level 3
5-6 marks</td><td>All stages are covered and each stage is generally correct and virtually complete.
Answer is communicated coherently and shows a logical progression from Stage 1 to Stages 2 and 3.</td></tr>
<tr><td>Level 2
3-4 marks</td><td>All stages are covered but stage(s) may be incomplete or may contain inaccuracies
OR two stages are covered and are generally correct and virtually complete.
Answer is communicated mainly coherently and shows a logical progression from Stage 1 to Stages 2 and 3.</td></tr>
<tr><td>Level 1
1-2 marks</td><td>Two stages are covered but stage(s) may be incomplete or may contain inaccuracies OR only one stage is covered but is generally correct and virtually complete.
Answer includes isolated statements but these are not presented in a logical order.</td></tr>
<tr><td>0 mark</td><td>Insufficient correct chemistry to gain a mark.</td></tr>
</table>

07.2	**M1** *x* – doublet **M2** *y* – quartet **M3** *z* – doublet	Allow similar words eg double, quadruplet Allow numbers Allow diagrams with correct numbers of lines	1 1 1
07.3	H attached to both C-Cl and adjacent to C=O so doesn't fit with data in table B		1
07.4	**M1**  **M2** 	Allow abbreviated structural formulae	1 1

Do not write outside the box

0 6 This question is about isomers with the molecular formula $C_5H_{10}O$

0 6 . 1 Draw the skeletal formula of a branched chain aldehyde with molecular formula $C_5H_{10}O$ that is optically active.

[1 mark]

0 6 . 2 Describe how you distinguish between separate samples of the two enantiomers of the branched chain aldehyde $C_5H_{10}O$

[2 marks]

0 6 . 3 Draw the *E* and *Z* forms of a structural isomer of $C_5H_{10}O$ that shows **both** optical and geometric isomerism.

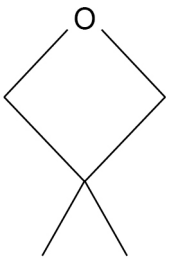
[2 marks]

E isomer	*Z* isomer

Question 6 continues on the next page

0 6 . 4 Isomer J is cyclic and has an ether functional group (C–O–C)
Isomer J has only three peaks in its ^{13}C NMR spectrum.

Isomer J



Draw **two** other cyclic isomers of $C_5H_{10}O$ that have an ether functional group and only three peaks in their ^{13}C NMR spectra.

[2 marks]

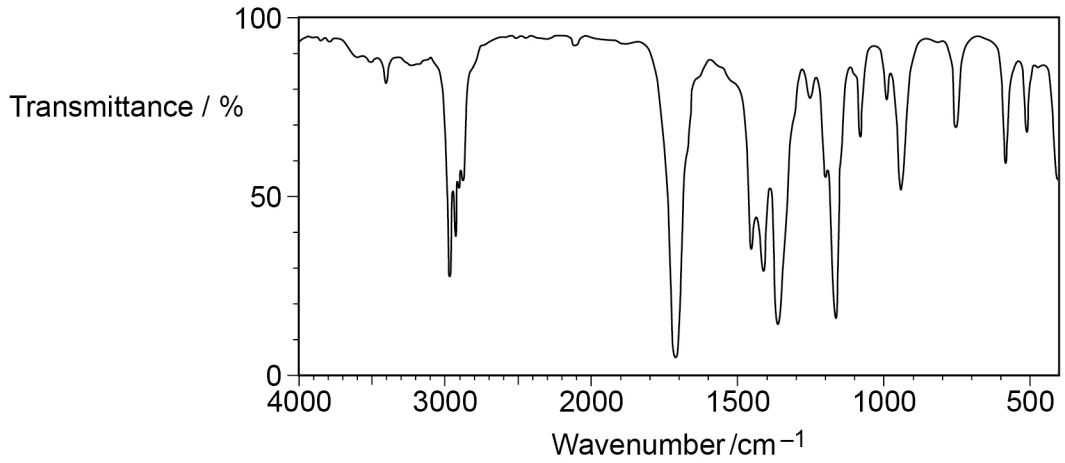
7

Do not write outside the box

0 7 This question is about spectroscopy.

0 7 . 1 Compound **K** has molecular formula C_4H_8O
Figure 5 shows the infrared spectrum of **K**.

Figure 5



Which functional group does **K** contain?

Tick (✓) **one** box.

[1 mark]

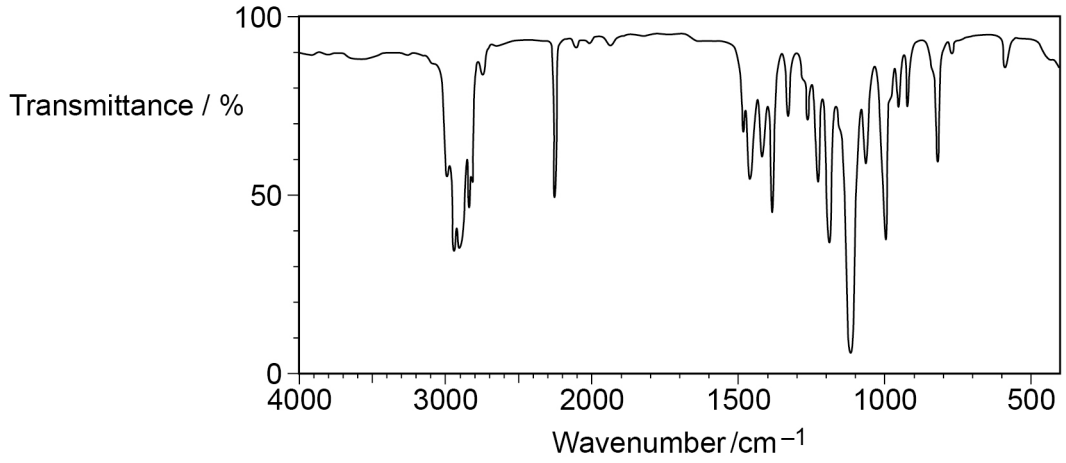
Functional Group				
alcohol	alkene	amine	carbonyl	nitrile

Question 7 continues on the next page

Do not write outside the box

0 7 . 2 Compound **L** has molecular formula C_4H_7NO
Figure 6 shows the infrared spectrum of **L**.

Figure 6



L reacts with H_2 in the presence of a nickel catalyst to give compound **M**.

Suggest **three** ways in which the infrared spectrum of **M** is different from the infrared spectrum of **L**.

[3 marks]

1 _____

_____

2 _____

_____

3 _____

_____

Do not write outside the box

0 7 . 3 **Figure 7** shows the ^{1}H NMR spectrum of **Q**, C_3H_7ClO

Figure 7

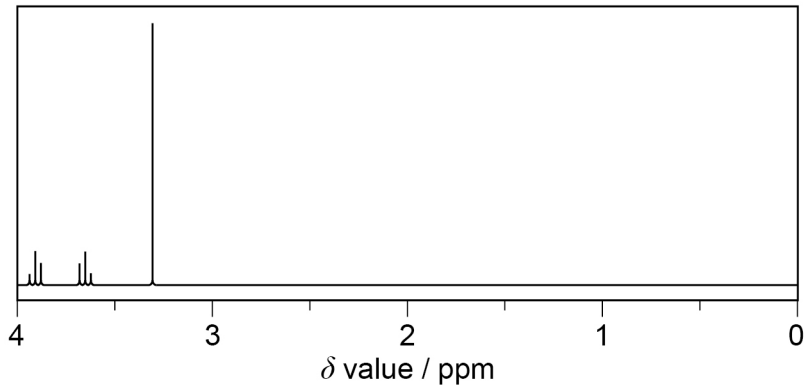


Table 4 shows the chemical shifts (δ values) and integration values for each peak.

Table 4

δ value / ppm	3.95	3.65	3.35
Integration value	0.6	0.6	0.9

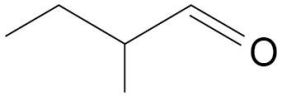
Deduce the structure of **Q**.

Explain your answer.

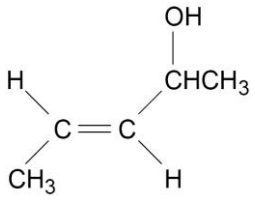
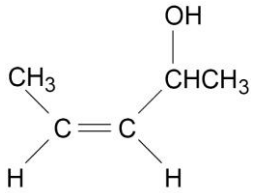
[5 marks]

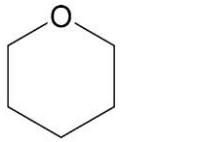
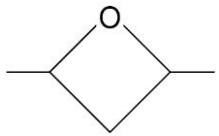
9

Turn over ►

Question	Answers	Additional Comments/Guidelines	Mark
06.1			1

Question	Answers	Additional Comments/Guidelines	Mark
06.2	Use Plane polarised light rotates (the plane of) in opposite directions		M1 M2

Question	Answers	Additional Comments/Guidelines	Mark
06.3	 	Must be E isomer Must be Z isomer Allow 1 mark out of 2 for 2 correct structures but shown in the wrong boxes	M1 M2

Question	Answers	Additional Comments/Guidelines	Mark
06.4	 		M1 M2

Question	Answers	Additional Comments/Guidelines	Mark
07.1	Tick in carbonyl box only		1

Question	Answers	Additional Comments/Guidelines	Mark
07.2	Peak at 2220-2260 cm^{-1} (for C≡N) disappears Peak at 3300-3500 cm^{-1} (for N-H) appears Fingerprint region different	If both C≡N disappears and N-H appears without wavenumbers scores 1	M1 M2 M3

Question	Answers	Additional Comments/Guidelines	Mark
07.3	Integration ratio 2:2:3 Peak at 3.95 triplet (integration 2) $Cl\text{-}CH_2$ next to CH_2 Peak at 3.65 triplet (integration 2) $O\text{-}CH_2$ next to CH_2 Peak at 3.35 singlet (integration 3) $O\text{-}CH_3$ no adjacent H Structure $CH_3\text{-}O\text{-}CH_2CH_2Cl$	If no link between delta value and oxygen and chlorine, then can award 1 mark for correct explanation of splitting of all 3 peaks If no explanation of splitting, then can award 1 mark for 3 correct links between delta value and oxygen and chlorine	M1 M2 M3 M4 M5

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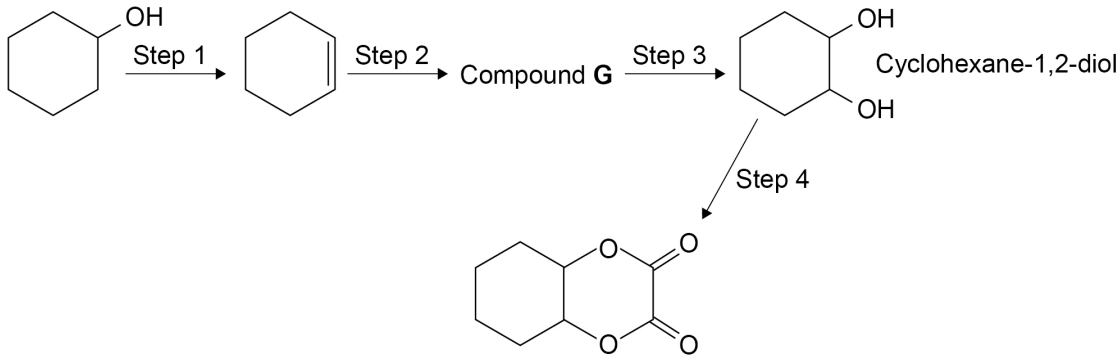
0 8 This question is about making a diester from cyclohexanol.



0 8 . 1 State the type of reaction in step **1**.

Give the name of the reagent needed for step **1**.

[2 marks]

Type of reaction _____

Reagent _____

0 8 . 2 State the reagents needed and give equations for step **2** and step **3**.

Show the structure of Compound **G** in your equations.

[4 marks]

Step 2 reagent _____

Step 2 equation

_____

Step 3 reagent _____

Step 3 equation

_____

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0 8 . 3 Cyclohexane-1,2-diol reacts with ethanedioyl dichloride.

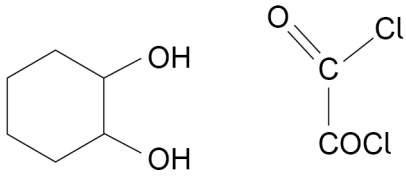
Give the name of the mechanism for this reaction.

Complete the mechanism to show the formation of **one** ester link in the first step of this reaction.

[5 marks]

Mechanism name _____

Mechanism



0 8 . 4 Suggest why chemists usually aim to design production methods
- with fewer steps
- with a high percentage atom economy.

[2 marks]

Fewer steps _____

_____

_____

High percentage atom economy _____

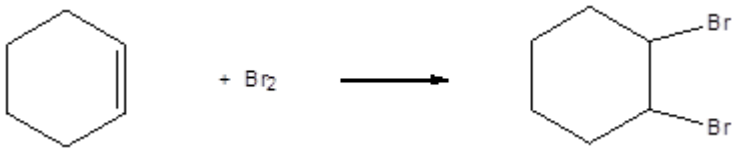
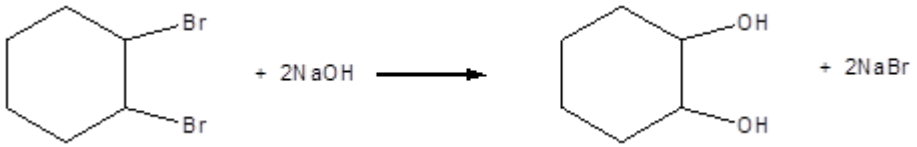
_____

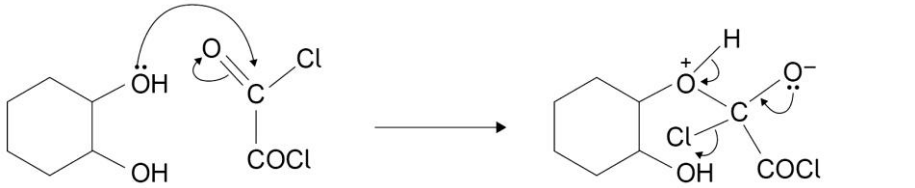
_____

13

Turn over ►

Question	Answers	Additional Comments/Guidelines	Mark
08.1	Dehydration Conc H_2SO_4	Allow (acid catalysed) Elimination Allow Conc H_3PO_4	M1 M2

Question	Answers	Additional Comments/Guidelines	Mark
08.2	Br_2  NaOH  	Allow bromine (water) Allow Cl_2 or I_2 Allow O_2 if epoxide route used allow conseq equation to H_2, H_2O, HBr, HCl. HI and H_2SO_4 An epoxide is a feasible alternative that could score here and consequentially M3 and M4 **Or** KOH or other suitable strong alkali Allow this equation with molecular formulae	M1 M2 M3 M4

Question	Answers	Additional Comments/Guidelines	Mark
08.3	**M1** (nucleophilic)addition-elimination  **M2** curly arrow from lp on O to C **M3** curly arrow from double bond to O **M4** for structure of intermediate **M5** for 3 curly arrows	Note lone pair required for M5	1 M2 M3 M4 M5

Question	Answers	Additional Comments/Guidelines	Mark
08.4	Less energy used **OR** Better yield Less waste **OR** Less pollution	**OR** reduces practical losses, simpler plant, **OR** maximises the use of raw materials in the process into useful products, saves resources	M1 M2

0 6 This question is about compound **X** with the empirical formula C_2H_4O

Figure 2 shows the infrared spectrum of **X**.

Figure 3 shows the ^{13}C NMR spectrum of **X**.

The ^{1}H NMR spectrum of **X** shows four peaks with different chemical shift values. **Table 3** gives data for these peaks.

Figure 2

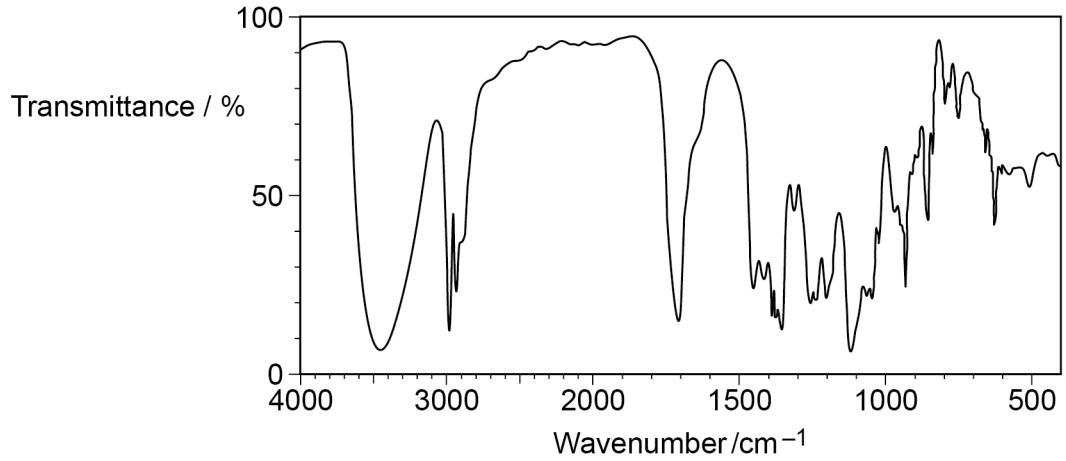


Figure 3

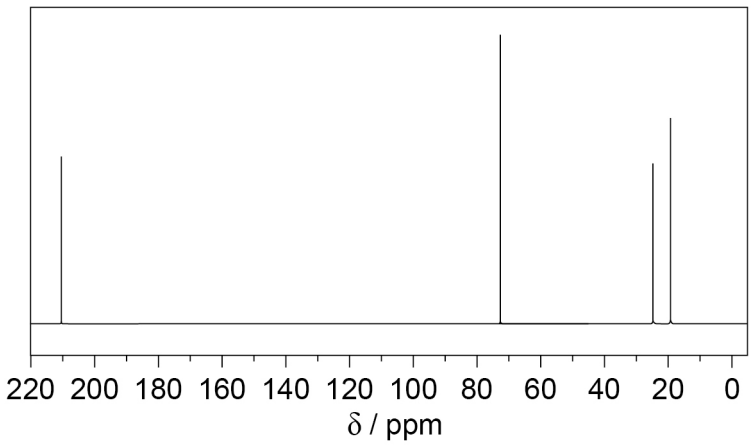


Table 3

Chemical shift δ / ppm	3.9	3.7	2.1	1.2
Splitting pattern	quartet	singlet	singlet	doublet
Integration value	1	1	3	3

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Show how information from **Figure 2**, **Figure 3** and **Table 3** can be used to deduce the structure of compound **X**.

[6 marks]

The answer space for this question continues on the next page

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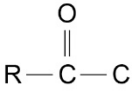
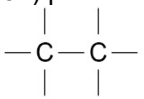
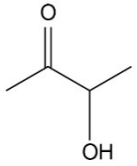
6

<table>
<tr><th>Question</th><th colspan="2">Answers</th><th>Additional Comments/Guidelines</th><th>Mark</th></tr>
<tr><td rowspan="4">06.1</td><td colspan="2">This question is marked using Levels of Response. Refer to the Mark Scheme Instructions for Examiners for guidance.</td><td rowspan="4">Indicative Chemistry content
Stage 1: infrared
1a) (broad peak) at 3400 cm^{-1} (any value from 3230-3550) indicates <u>OH in alcohols</u>
1b) peak at 1720 cm^{-1} (any value from 1680-1750) indicates C=O
Stage 2: ^{1}H nmr
2a) peak at 3.9 ppm integration 1 so 1 H-C-O AND quartet so adjacent to CH_3 (stated or shown)
2b) peak at 3.7 ppm integration 1 so HO-C-(stated or shown)
2c) peak at 2.1 ppm integration 3 so H$_3$C-C=O AND singlet so no adjacent H (stated or shown)
2d) peak at 1.2 ppm integration 3 so H$_3$C- AND doublet so adjacent to CH (stated or shown)
2e) sum of integration values = 8 Hence $C_4H_8O_2$
Stage 3: ^{13}C nmr
3a) peak at 210 ppm C=O <u>aldehydes or ketones</u>
3b) peak at 75 ppm C–O (alcohols, ethers or esters)
3c) peak at 25 ppm
 
3d) peak at 20 ppm
 
3e) structure
  </td><td rowspan="4">6

(3 x AO1, 3 x AO3)</td></tr>
<tr><td>Level 3
5-6 marks</td><td>All stages are covered and each stage is generally correct and virtually complete.
Answer is communicated coherently and shows a logical progression from Stage 1 to Stages 2 and 3
Covers at least 1 point for stage 1, 3 for stage 2 and 3 for stage 3.</td></tr>
<tr><td>Level 2
3-4 marks</td><td>All stages are covered but stage(s) may be incomplete or may contain inaccuracies
Covers at least 1 point for stage 1 stage 2 and stage 3.
OR
two stages are covered and are generally correct and virtually complete.
Covers at least 1 point for stage 1, and 3 for stage 2 or stage 3 OR 3 for stage 2 and 3 for stage 3
Answer is communicated mainly coherently and shows a logical progression from Stage 1 to Stages 2 and 3.</td></tr>
<tr><td>Level 1
1-2 marks</td><td>Two stages are covered but stage(s) may be incomplete or may contain inaccuracies OR only one stage is covered but is generally correct and virtually complete.
Answer includes isolated statements but these are not presented in a logical order.</td></tr>
<tr><td></td><td>0 mark</td><td>Insufficient correct chemistry to gain a mark</td></tr>
</table>