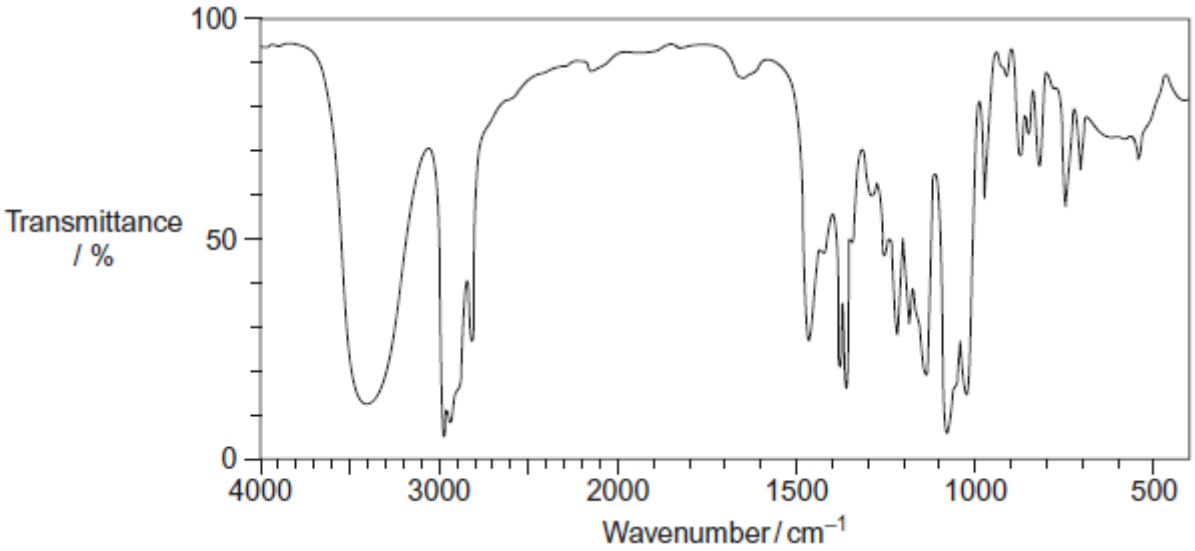
**Q1.** Compound **R** contains 61.0% carbon and 11.9% hydrogen by mass. The remainder is oxygen. The mass spectrum of **R** contains a molecular ion peak at $m/z$ = 118.

(a) Use these data to show that the molecular formula of **R** is $C_6H_{14}O_2$.

**(3)**

(b) The infrared spectrum of **R** ($C_6H_{14}O_2$) is shown below.




The proton n.m.r. spectrum of **R** contains five peaks. The chemical shift values, integration ratios and splitting patterns of these peaks are given in the table.

| **Chemical shift/ppm** | 3.8 | 3.2 | 3.1 | 1.4 | 1.1 |
|---|---|---|---|---|---|
| **Integration ratio** | 2 | 3 | 1 | 2 | 6 |
| **Splitting patterns** | triplet | singlet | singlet | triplet | singlet |

When **R** is warmed with acidified potassium dichromate(VI) a green solution is formed.

Use **Table A** and **Table B** on the data sheet and all of the data provided in the question to deduce the structure of **R**.

In your answer, explain how you have used the data provided in the question.

**(9)**

**(Total 12 marks)**

**Q2.** Butan-2-ol can be oxidised by acidified potassium dichromate(VI) to form butanone as shown by the following equation.

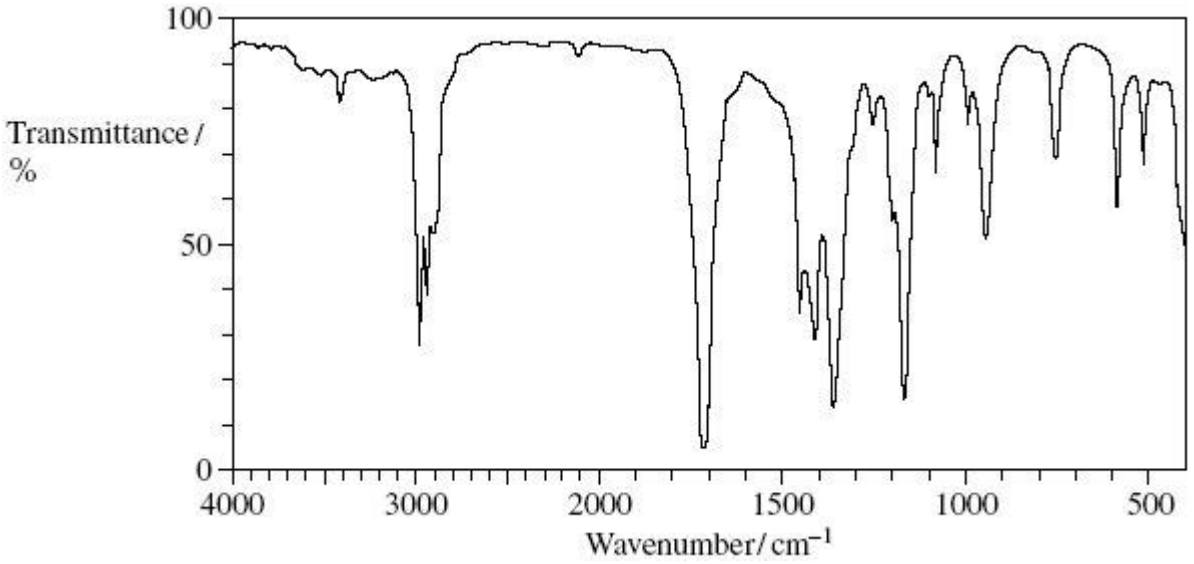
$$CH_3CH_2CH(OH)CH_3 + [O] \rightarrow CH_3CH_2COCH_3 + H_2O$$

(a) State the class of alcohol to which butan-2-ol belongs.

_____

**(1)**

(b) The infrared spectrum shown below is either that of butan-2-ol or that of butanone.




Identify the compound to which this infrared spectrum refers.

Explain your answer.

You may find it helpful to refer to the table of infrared absorption data on the back of the Periodic Table (**Table 1**).

Identity of the compound _____

Explanation _____

_____

_____

**(3)**

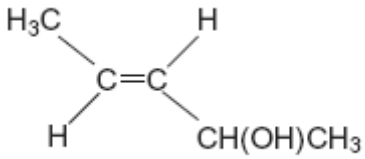
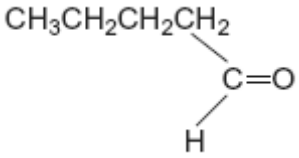
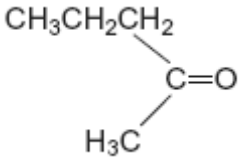
(c) Draw the displayed formula of the alcohol $C_4H_9OH$ which is resistant to oxidation by acidified potassium dichromate(VI).

_____

**(1)**

**(Total 5 marks)**

**Q3.** The table below shows the structures of three isomers with the molecular formula $C_5H_{10}O$

| | |
|---|---|
| Isomer **1**  | (*E*)-pent-3-en-2-ol |
| Isomer **2**  | pentanal |
| Isomer **3**  | |

(a) Complete the table by naming Isomer **3**.

**(1)**

(b) State the type of structural isomerism shown by these three isomers.

_____

**(1)**

(c) The compound (*Z*)-pent-3-en-2-ol is a stereoisomer of (*E*)-pent-3-en-2-ol.

(i) Draw the structure of (*Z*)-pent-3-en-2-ol.

**(1)**

(ii) Identify the feature of the double bond in (*E*)-pent-3-en-2-ol and that in (*Z*)-pent-3-en-2-ol that causes these two compounds to be stereoisomers.

_____

**(1)**

(d) A chemical test can be used to distinguish between separate samples of Isomer **2** and Isomer **3**.
Identify a suitable reagent for the test.
State what you would observe with Isomer **2** and with Isomer **3**.

Test reagent _____

Observation with Isomer **2** _____

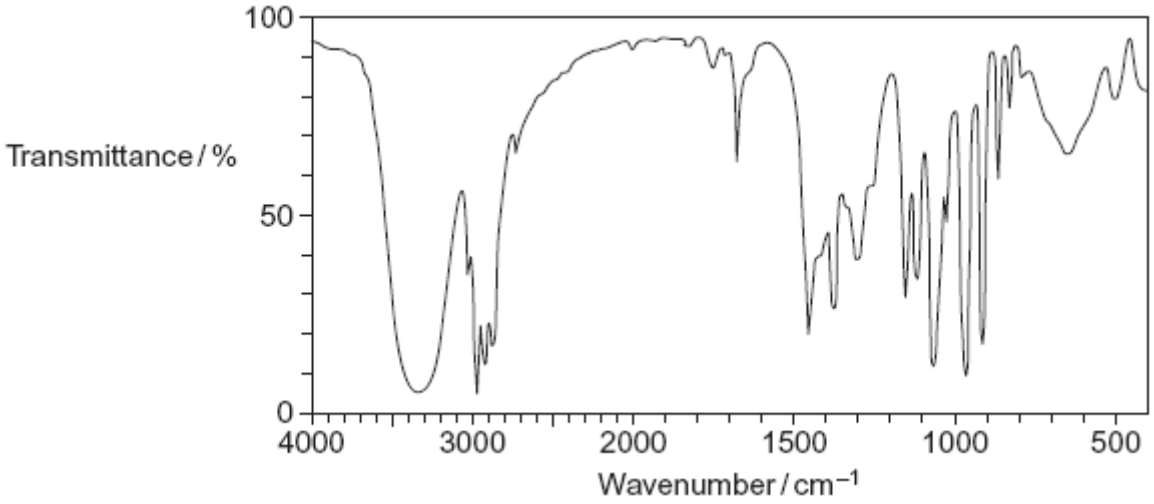
_____

Observation with Isomer **3** _____

_____

**(3)**

(e) The following is the infrared spectrum of one of the isomers **1**, **2** or **3**.




(i) Deduce which of the isomers (**1**, **2** or **3**) would give this infrared spectrum. You may find it helpful to refer to **Table 1** on the Data Sheet.

_____

**(1)**

(ii) Identify two features of the infrared spectrum that support your deduction.
In each case, identify the functional group responsible.

Feature 1 and functional group _____

_____

_____

Feature 2 and functional group _____

_____

_____

**(2)**

**(Total 10 marks)**

## Q1.

(a) Method 1

M1 %O = 27.1

$$\frac{61.0}{12.0} \qquad \frac{11.9}{1.0} \qquad \frac{27.1}{16.0}$$

$$= 5.08 \qquad = 11.9 \qquad = 1.69$$

M2 3 7 1

M3 $C_3H_7O$ = 59 which is half of $M_r$ so MF = 2EF

**OR**

Method 2

M1 61% of 118 = 72.0 and 11.9% of 118 = 14.0

M2 72 + 14 = 86 so oxygen = 32 out of 118

OR 27.1% of 118 = 32.0

M3

$$\frac{72.0}{12.0} \qquad \frac{14.0}{1.0} \qquad \frac{32.0}{16.0}$$

$$= 6 \qquad = 14 \qquad = 2$$

*Method 3*

*Alternative using given molecular formula*

M1 $C = \frac{12 \times 6}{118} \times 100 = 61.0\%$

M2 $H = \frac{14 \times 1}{118} \times 100 = 11.9\%$

M3 $O = \frac{16 \times 2}{118} \times 100 = 27.1\%$

**3**

(b) For this question, marks can be awarded either for a description of how the structure is derived or from the given structure itself. The maximum mark to be awarded is nine from the ten marks listed.

Marks fall into three sections:

- Infrared evidence : two marks are available for use of the infrared evidence, (M1 and M10)
- Chemical evidence: one mark is available for use of the chemical evidence (M2)

- N.m.r. evidence: six marks are available for use of the n.m.r. evidence (M3 – M8 inclusive)

plus one mark (M9) for a completely correct structure.

**Suggested procedure for marking**

First look at the infrared spectrum: marks M1 and M10 may be scored there or in the written answer.

Then look for use of the acidified potassium dichromate(VI) evidence, (M2).

Then look at the final structure: this may lead to the award of marks M3 to M9 as shown on the structures below.

Beware contradictions, e.g. using the chemical evidence they may state that **R** is a primary or secondary alcohol but then draw a tertiary alcohol. This will lose M2 but may score M3.

The written 'evidence' frequently simply contains extracts from the Table **B** on the Data Sheet and, if only this is given, is unlikely to score many marks.

Described

*Or drawn*

M1 Infared peak/absorbance at 3400 ($cm^{-1}$) = O-H alcohol
(reference to ir spectrum needed)

*Note: please check the spectrum*

*If peak at 3000 (cm-1) is identified as acid then cannot score M1 (contradiction)*

M10 **Either** no peak between 1680-1750 ($cm^{-1}$) so no C=O or not aldehyde/acid **OR** peak at 1000-1300 ($cm^{-1}$) so C–O present

*Apply list principle to IR analysis for M10*

M2 (Acidified potassium dichromate(VI) turns green) so primary alcohol or secondary alcohol or not tertiary alcohol

*Ignore aldehyde here*

*Lose M2 if just tertiary alcohol in structure*

M3 δ = 3.1 singlet or integration = 1 is O-H

*Award M3 if structure has 1 O-H group only (can be primary, secondary or tertiary)*

*Lose M3 if more than one OH group shown*

M4 two triplets at 1.4 & 3.8 = $–CH_2–CH_2–$

*Allow $–CH_2–CH_2–CH_2–$*

M5 δ = 3.8 means $CH_2$ attached to O (in ether NOT ester)

*Allow $O–CH_2–CH_2–CH_2–C$*

δ = 1.4 means $CH_2$ attached to C (but not to C=O)

M6 δ = 1.1 (singlet) integration 6 = 2 × equivalent $CH_3$ on same C

*$–C(CH_3)_2–$*

M7 δ = 1.1 singlet so no H attached to $–C(CH_3)_2$-

*$R–C(CH_3)_2–R$*

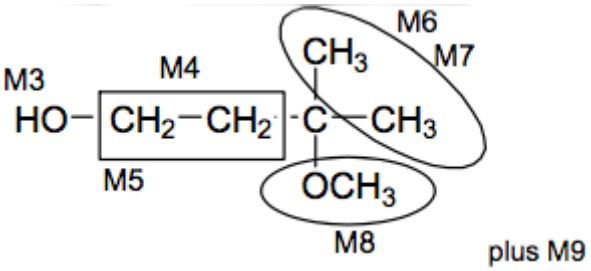
M8 δ = 3.2 singlet integration 3 = $-OCH_3$

*$–OCH_3$*

M9 For completely correct

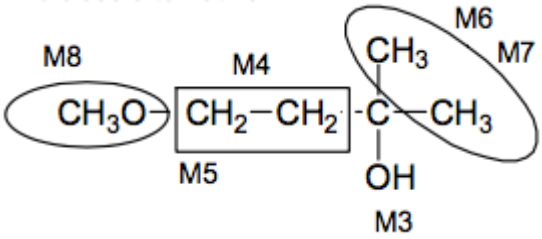
*If no structure given then Max 8*

R is




plus M9

This close alternative




*would not score M9, but could score up to 8 marks*

**[12]**

## Q2.

(a) Secondary ***OR*** 2° (alcohol);

**1**

(b) Spectrum is for **butanone (or formula) or butan-2-one**

*The explanation marks depend on correctly identifying butanone.*

If butanone is correctly identified, award any two from

- (Strong) absorption / peak at approximately 1700 ($cm^{-1}$) / 1710 ($cm^{-1}$) / in the range 1680 – 1750 ($cm^{-1}$) This needs to be stated.
- (Characteristic) absorption / peak for C=O (may be shown on the spectrum in the correct place).
- No absorption / peak in range 3230 to 3550 $cm^{-1}$.

**1**

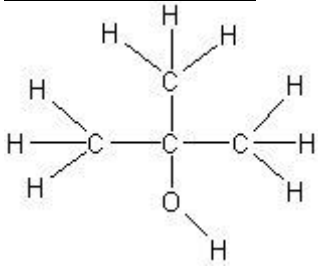
- No absorption / peak for an OH group.

*Look at the spectrum to see if anything is written on it that might gain credit.*
*Allow the words "dip" OR "spike" OR "low transmittance" as*

*alternatives for absorption.*

**2**

(c) Displayed structure for 2-methylpropan-2-ol



*Must have **all bonds** drawn out but ignore the bond angles*

**1**

**[5]**

## Q3.

(a) Pentan-2-one

*ONLY but ignore absence of hyphens*

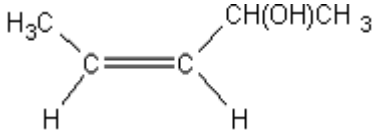
**1**

(b) Functional group (isomerism)

*Both words needed*

**1**

(c) (i)



*Award credit provided it is obvious that the candidate is drawing the Z / cis isomer*

*The group needs to be $CHOHCH_3$ but do not penalise poor C–C bonds or absence of brackets around OH*

*Trigonal planar structure not essential*

**1**

(ii) Restricted rotation (about the C=C)

OR

No (free) rotation (about the C=C)

**1**

(d)

| | |
|---|---|
| **M1** Tollens' (reagent)<br><br>*(Credit ammoniacal silver nitrate OR a description of making Tollens')*<br><br>*(Do not credit $Ag^+$, $AgNO_3$ or $[Ag(NH_3)_2^+]$ or "the silver mirror test" on their own, but mark M2 and M3)* | **M1** Fehling's (solution) / Benedict's<br><br>*(Penalise $Cu^{2+}(aq)$ or $CuSO_4$ but mark M2 and M3)* |

| | |
|---|---|
| **M2** <u>silver mirror</u><br>OR <u>black solid or black precipitate</u> | **M2** <u>Red solid/precipitate</u><br>*(Credit <u>orange</u> or <u>brown solid</u>)* |
| **M3** (stays) colourless<br>OR<br>no (observed) change / no reaction | **M3** (stays) blue<br>OR<br>no (observed) change / no reaction |

*If **M1** is blank CE = 0, for the clip*

*Check the partial reagents listed and if M1 has a <u>totally incorrect</u> reagent, CE = 0 for the clip*

*Allow the following alternatives*

***M1** (acidified) potassium dichromate(VI) (solution); mark on from incomplete formulae or incorrect oxidation state*

***M2** (turns) green*

*M3 (stays) orange / no (observed) change / no reaction*

*OR*

***M1** (acidified) potassium manganate(VII) (solution); mark on from incomplete formulae or incorrect oxidation state*

***M2** (turns) colourless*

***M3** (stays) purple / no (observed) change / no reaction*

*In all cases for **M3***

*Ignore "nothing (happens)"*

*Ignore "no observation"*

**3**

(e) (i) **Spectrum is for Isomer 1**

or named or correctly identified

*The explanation marks in (e)(ii) depend on correctly identifying Isomer 1.*

*The identification should be unambiguous but candidates should not be penalised for an imperfect or incomplete name. They may say "the alcohol" or the "alkene" or the "E isomer"*

**1**

(ii) **If Isomer 1 is correctly identified, award <u>any two</u> from**

- (Strong / broad) absorption / peak in the range **<u>3230 to 3550</u>** $cm^{-1}$ or specified value <u>in this range</u> or **<u>marked correctly</u>** on spectrum **<u>and</u>** (characteristic absorption / peak for) <u>OH</u> group /**<u>alcohol</u>** group

- No absorption / peak in range **<u>1680 to 1750</u>** $cm^{-1}$ or absence <u>marked correctly</u> on spectrum **<u>and</u>** (No absorption / peak for a) **<u>C=O</u>** group / **<u>carbonyl</u>** group / **<u>carbon-oxygen double bond</u>**

- Absorption / peak in the range **1620 to 1680** $cm^{-1}$
  or specified value in this range or marked correctly
  on spectrum
  **and**

  (characteristic absorption / peak for) **C=C** group
  / **alkene** / **carbon-carbon double bond**

  *If 6(e)(i) is incorrect or blank, CE=0*

  *Allow the words ''dip'' OR ''spike'' OR ''trough'' OR ''low transmittance'' as alternatives for absorption.*

  *Ignore reference to other absorptions e.g. C-H, C-O*

**2**

**[10]**