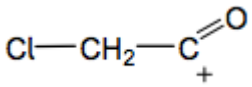
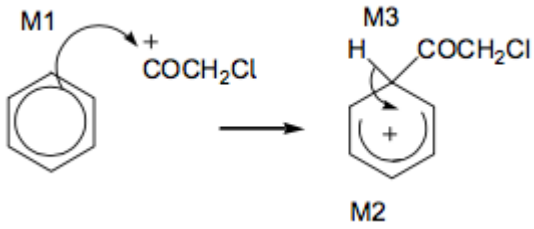
1 (a) (i) 

Allow $[ClCH_2CO]^+$

1

(ii) 

M1 for arrow from inside hexagon to C or + on C on correct electrophile

M2 for structure of intermediate

- *Horseshoe centred on C1;*
- *+ in intermediate not too close to C1 (allow on or "below" a line from C2 to C6)*

M3 for Arrow from bond to H into ring

- *Allow M3 arrow independent of M2 structure*
- *+ on H in intermediate loses M2 not M3*
- *Ignore Cl- removing H^+*

1
1
1

(b) Reagent

Water

(Aqueous) silver nitrate

NaOH followed by acidified silver nitrate

(Water +) named indicator

Named alcohol

Na_2CO_3 or $NaHCO_3$

Ammonia

1

P

No reaction

No reaction (or slow formation of ppt)

No reaction (or slow formation of ppt)

No colour change

NVC

NVC

No reaction

Do NOT award

No observation

1

Q

Steamy /misty/ white fumes

White precipitate (immediately formed)

White precipitate (immediately formed)

Indicator turns to correct acid colour

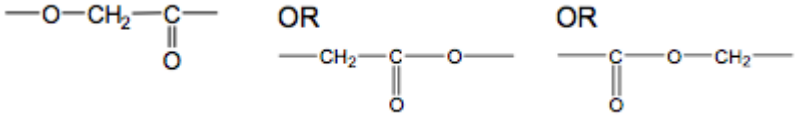
Fruity or sweet smell or misty fumes

Fizzing or effervescence (not just gas produced)

White smoke

1

(c) (i)



One unit only

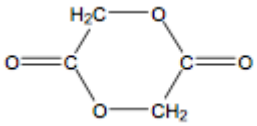
Must have trailing bonds

Ignore n and brackets

allow —O—CH_2—CO—

1

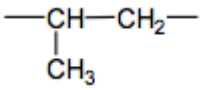
(i)



Allow CO for C=O

1

(d) (i)



One unit only

Must have trailing bonds

Ignore n and brackets

1

(ii) PGA sutures react/dissolve/break down/are biodegradable/ are hydrolysed / attacked by water or nucleophiles /no need to remove

OR Polypropene not biodegradeable/ not hydrolysed / not attacked by water/nucleophiles

1

(Ester links have) <u>polar bonds</u>

polypropene contains <u>non-polar bonds</u>

ignore intermolecular forces

1

[12]

2 (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 $–C(CH_3)_2-$

$R–C(CH_3)_2–R$

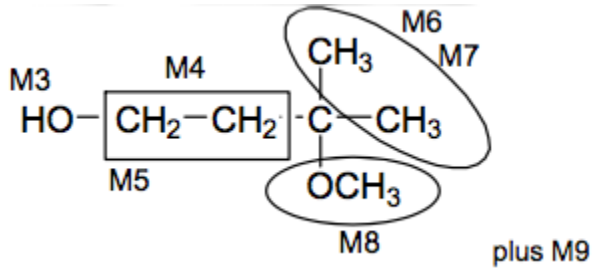
M8 δ = 3.2 singlet integration 3 = $-OCH_3$

$–OCH_3$

M9 For completely correct

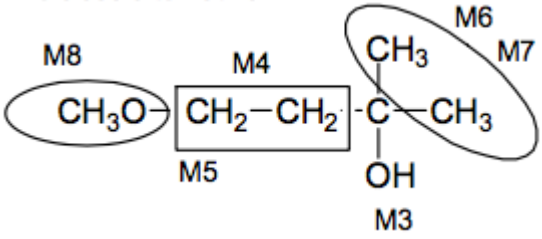
If no structure given then Max 8

R is



plus M9

This close alternative



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

[12]

3

IR

Extended response

Absorption at 3360 cm^{-1} shows OH alcohol present

Deduction of correct structure without explanation scores maximum of 4 marks as this does not show a clear, coherent line of reasoning.

M1 1

NMR

There are 4 peaks which indicates 4 different environments of hydrogen

Maximum of 6 marks if no structure given OR if coherent logic not displayed in the explanations of how two of OH, CH_3 and CH_2CH_3 are identified.

M2 1

The integration ratio = 1.6 : 0.4 : 1.2 : 2.4

The simplest whole number ratio is 4 : 1 : 3 : 6

M3 1

The singlet (integ 1) must be caused by H in OH alcohol

M4 1

The singlet (integ 3) must be due to a CH_3 group with no adjacent H

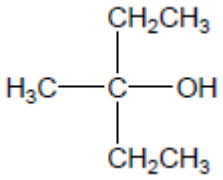
M5 1

Quartet + triplet suggest CH_2CH_3 group

M6 1

Integration 4 and integration 6 indicates two equivalent CH_2CH_3 groups

M7 1



M8 1

[8]

4 (a) Reagent

Acidified
$K_2Cr_2O_7$

Acidified
$KMnO_4$

I_2 / NaOH

Named
RCOOH with HCl or H_2SO_4

Named
RCOCl

Allow names including potassium permanganate

Wrong or no reagent CE = 0

1

P (ketone)
no reaction
no reaction
Yellow ppt
no reaction
no reaction

Penalise incorrect formulae or incomplete reagent, such as $K_2Cr_2O_7$ or acidified dichromate, but mark on.

1

S (2° alcohol)
(orange to) green
(purple to) colourless
no reaction
fruity or sweet smell
Misty fumes

Allow no change or nvc but penalise nothing or no observation

If 2 reagents added sequentially or 2 different reagents used for P and S then CE = 0

1

(b) Tollens'
silver mirror / solid

1

Fehling's / Benedicts
red ppt

1

(c) **G**

P

If not P then no marks for clip

1

5 OR five

1

(d) $C_4H_{12}Si$

Must be molecular formula

Wrong substance CE = 0 for clip

1

Any **two** from

- One or single peak OR all (four) carbon atoms are equivalent or one environment

1

- upfield from others or far away from others or far to right
- non toxic OR inert
- low boiling point or volatile or easy removed from sample

Ignore and don't credit single peak linked to 12 equivalent H or has a peak at δ = 0

but use list principle for wrong statements

1
1

(e) Figure 1 is **R**

*If not **R** cannot score M2*

M1

1

90−150 (ppm) or value in range is (two peaks for) C = C / alkene

M2

1

Figure 2 is **T**

*If not **T** cannot score M4 or M5*

M3

1

50-90 (ppm) or value in range is C—O or alcohol or ether

M4

1

two peaks (so not S which would have only one)

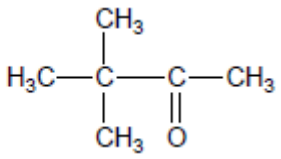
M5

1

(f)

U

$C_6H_{12}O_6$

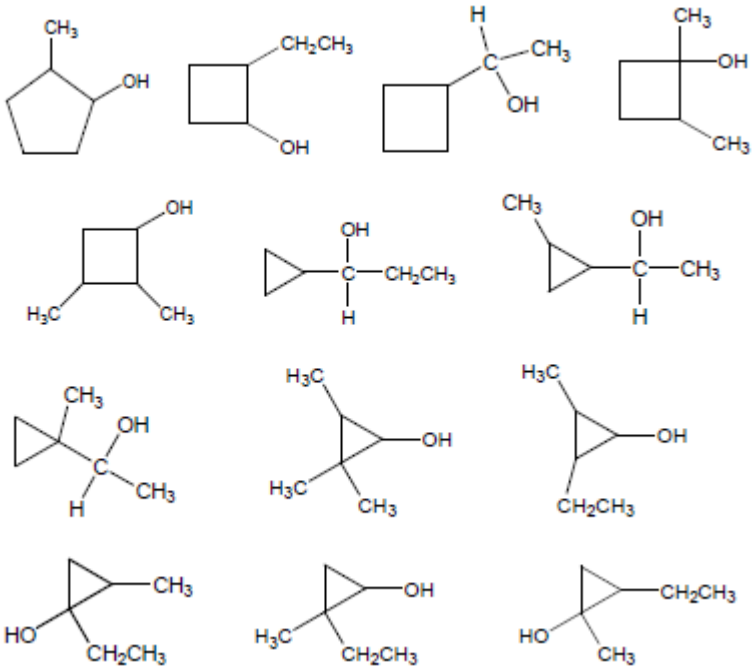


1

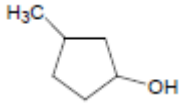
Answers include

V

$C_6H_{12}O_6$



*Not allow **S***



*because **V** must be an isomer of **S***

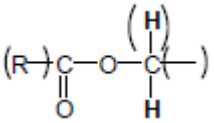
[17]

5 (a) M1 Ester **1**

If Ester 2, can score M3 only.

1

M2 peak at δ = 4.1 due to



When marking M2 and M3, check any annotation of structures in the stem at the top of the page.

1

M3 (δ = 4.1 peak is) quartet as <u>adjacent / next to / attached to CH_3</u>

1

M4 Other spectrum quartet at δ = 2.1-2.6 (or value in this range)

1

(b) M1 Quaternary (alkyl) ammonium salt / bromide

1

M2 CH_3Br or bromomethane

Penalise contradictory formula and name.

1

M3 Excess (CH_3Br or bromomethane)

Mention of acid eg H_2SO_4 OR alkali eg NaOH loses both M2 and M3.

1

M4 Nucleophilic substitution

Can only score M3 if reagent correct.

Ignore alcohol or ethanol (conditions) or Temp.

1

(c)

	Bromine (penalise Br but mark on)	Acidified $KMnO_4$ (Penalise missing acid but mark on)

Wrong reagent = no marks.

If bromine colour stated it must be red, yellow, orange, brown or any combination, penalise wrong starting colour.

1

Benzene	no reaction / colour remains / no (visible) change	no reaction / colour remains / no (visible) change

Ignore 'clear', 'nothing'.

Allow colour fades slowly.

Allow 'nvc' for no visible change.

1

cyclohexene	(Bromine) decolourised	(Acidified $KMnO_4$) decolourised

1

[11]

6 Identification of acid by suitable method eg named indicator, named carbonate, specified reactive metal

Ignore any reference to the smell of the ester.

1

with expected results

Do not allow the use of any instrumental method eg i.r. or n.m.r.; must be a chemical test.

1

Identification of alcohol by suitable method eg oxidation by acidified potassium dichromate(VI)

1

with expected results

1

[4]

7 (a) **If 2 stage test for one compound, award no marks for that compound, eg no mark for ROH or RX to alkene then Br_2 test. If reagent is wrong or missing, no mark for that test; if wrong but close/incomplete, lose reagent mark but can award for correct observation. In each test, penalise each example of wrong chemistry, eg $AgClr_2$**

propan-1-ol

acidified
potassium
dichromate

sodium

Named acid + conc H_2SO_4

named acyl chloride

PCl_5

M1

1

(orange) turns green

effervescence

Sweet smell

Sweet smell /misty fumes

Misty fumes

M2

1

propanal

add Tollens or Fehlings / Benedicts

acidified
potassium
dichromate

Bradys or 2,4-dnph

if dichromate used for alcohol cannot be used for aldehyde

M3

1

Tollens: silver mirror or Fehlings/ Benedicts: red ppt

(orange) turns green

Yellow or orange ppt

M4

1

propanoic acid

Named carbonate/ hydrogencarbonate

water and UI (paper)

Named alcohol + conc H_2SO_4

sodium or magnesium

PCl_5

if sodium used for alcohol cannot be used for acid

M5

1

effervescence

orange/red

Sweet smell

effervescence

Misty fumes

if PCl_5 used for alcohol cannot be used for acid

M6

1

1-chloro propane

NaOH then acidified $AgNO_3$

$AgNO_3$

If acidification missed after NaOH,
no mark here but allow mark for observation

M7

1

white ppt

white ppt

M8

1

(b) oxidation (of alcohol by oxygen in air)

M1

1

absorption at <u>1680 -1750</u> (due to C=O)

Must refer to the spectrum

M2

1

comparison of polarity of molecules or correct imf statement:
propanone is less polar OR propan-2-ol is more polar
OR propanone has dipole-dipole forces
OR propan-2-ol has hydrogen bonding

M3

1

about attraction to stationary phase or solubility in moving phase
Propan-2-ol has greater affinity for stationary phase or vice versa
OR propanone is more soluble in solvent/moving phase or vice versa

M4

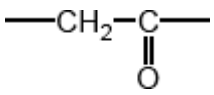
1

[12]

8 (a) <u>OH alcohols</u>

1

(b) (i) 2.6



Ignore any group on RHS

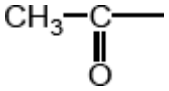
*Must clearly indicate relevant **two** H on a C next to C=O*

On LHS, penalise H or CH or CH_2 or CH_3

Ignore missing trailing bonds or attached R groups

1

(ii) 2.2



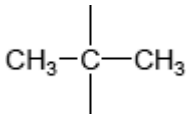
Ignore all groups on RHS

*Must clearly indicate relevant **three** H on C next to C=O*

Ignore missing trailing bonds or attached R group

1

(iii) 1.2



Or in words: two <u>equivalent</u> CH_3 groups

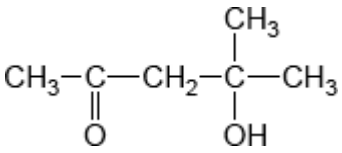
Must clearly indicate two <u>equivalent</u> methyl groups.

Penalise attached H

Ignore missing trailing bonds or attached R groups

1

(iv)



1

[5]

9 (a) (i) Green

Ignore shades of green.

1

(ii) <u>Excess</u> acidified potassium dichromate(VI)

1

Reflux (for some time)

1

In the diagram credit should be given for

- a vertical condenser

  Lose M3 and M4 for a distillation apparatus.

1

- an apparatus which would clearly work

  Do not allow this mark for a flask drawn on its own.

  Penalise diagrams where the apparatus is sealed.

1

(iii) Distillation

1

Immediately (the reagents are mixed)

1

(b) Keep away from naked flames

Allow heat with water-bath or heating mantle.

If a list is given ignore eye protection, otherwise lose this mark.

1

(c) (i) Tollens' or Fehling's reagents

*Incorrect reagent(s) loses **both** marks.*

Accept mis-spellings if meaning is clear.

1

Silver mirror / red ppt. formed

Accept 'blue to red' but not 'red' alone.

1

(ii) Sodium carbonate (solution) / Group II metal

Allow indicator solutions with appropriate colours.

Accept any named carbonate or hydrogen carbonate.

1

Effervescence / evolves a gas

Accept 'fizzes'.

1

(d) Propanoic acid

If this mark is lost allow one mark if there is reference to stronger intermolecular forces in the named compound.

Lose M1 and M3.

1

Contains hydrogen bonding

1

Some comparison with other compounds explaining that the intermolecular forces are stronger in propanoic acid

1

[15]