## Mark schemes

**1**

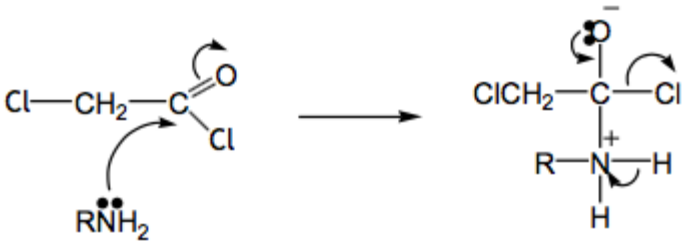
(a) (i) (2-)chloroethan (-1-) oyl chloride

*2 not required but penalise 1- or other numbers at start. Ignore 1 in ethanoyl*

*Ignore hyphens, commas, spaces*

**1**

(ii)




*M1 for arrow from lp on N to C*

*(or to space half way between N and C)*

*If full amine drawn, ignore slips except in –$NH_2$*

*M2 for arrow from C=O bond to O*

*Not score M2 as an independent first step, but can allow M1 for attack on C+ produced*

*If Cl lost at this stage, Max 1 for M1*

*M3 for structure of ion including 2 charges*

*M4 for 3 arrows and lp on O*

*- may be scored in two steps*

*Ignore use of $RNH_2$ to remove H+ in M4, but penalise use of $Cl^-$*

**4**

(b) Nucleophilic substitution

*Allow minor spelling errors e.g. nucleophyllic*

**1**

(c) 9

**1**

(d) $M_r$ = 234(.0)

*9.4 scores 2 marks*

**1**

% H = 9.4(0)

*M2* = $\frac{22}{M1} \times 100$

*If $M_r$ = 234 not shown, can score M1 if their answer × 234 = their no of H*

**1**

(e) Tertiary amine OR $3^o$ amine OR $III^o$ amine

*Ignore N- substituted*

**1**

(f) (i) If ***a*** given: CE=0, can only score if answer given is **b**

M1 lp on $N^b$ or on **b**

M2 alkyl groups donate electron density or positive inductive effect or electron donating groups attached

M3 (lp on $N^b$) more available or protonated amine stabilised or better lp donor/$H^+$ acceptor

Ignore reference to nucleophiles

*NOTE – there is NO mark for **b** alone*

*Alternatives*

*M1 lp on $N^a$ or on **a***

*M2 lp or electrons (on $N^a$) <u>delocalised</u> into ring /towards O in C=O*

*M3 (lp on $N^a$) less available (to bond to $H^+$/accept proton)*

**1**
**1**
**1**

(ii) Salt is ionic

*Independent marks*

**1**

(More) soluble (in blood/body fluids/water)

**1**

**[15]**

**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 $–C(CH_3)_2-$

*$R–C(CH_3)_2–R$*

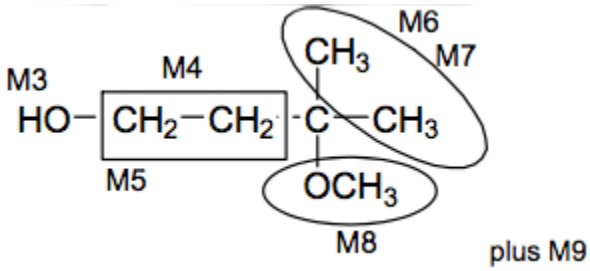
M8 δ = 3.2 singlet integration 3 = $-OCH_3$

*$–OCH_3$*

M9 For completely correct

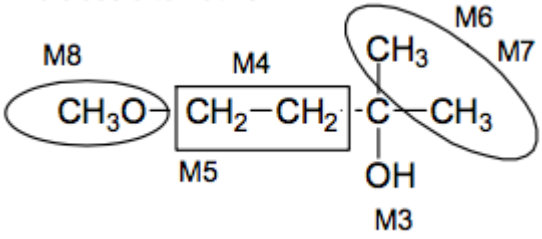
*If no structure given then Max 8*

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

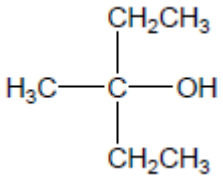
**M5** 1

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** C

**[1]**

**5** (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

- <u>One or single</u> 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)

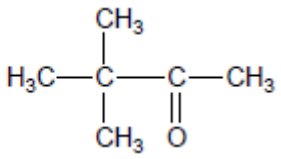
M5

**1**

(f)

**U**

$C_6H_{12}O_6$

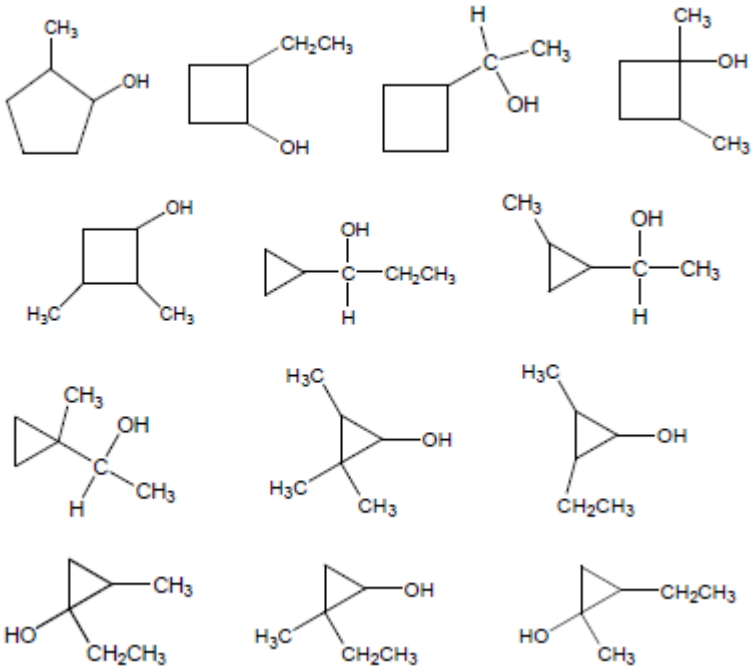


1

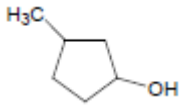
Answers include

**V**

$C_6H_{12}O_6$



*Not allow **S***



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

**[17]**

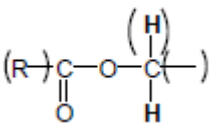
**6** 6 / six

**[1]**

**7** (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<br><br>(penalise Br but mark on) | Acidified $KMnO_4$<br><br>(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]**

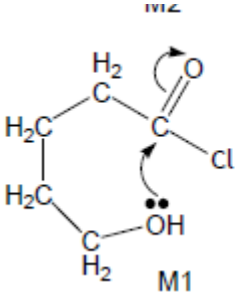
**8**

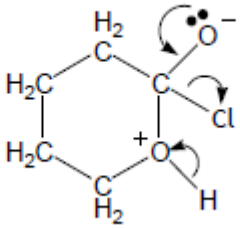
(a) (i) (nucleophilic) addition-elimination

*Not electrophilic addition-elimination*

*Ignore esterification*

**1**



M4 for 3 arrows and lp

M3 for structure

- *If wrong nucleophile used or O–H broken in first step, can only score M2.*
- *M2 not allowed independent of M1, but allow M1 for correct attack on C+*
- *+ rather than δ+ on C=O loses M2.*
- *If Cl lost with C=O breaking lose M2.*
- *M3 for correct structure <u>with charges</u> but lone pair on O is part of M4.*
- *Only allow M4 after correct / very close M3.*
- *Ignore HCl shown as a product.*

**4**

*a* 20-50 (ppm) or single value or range entirely within this range

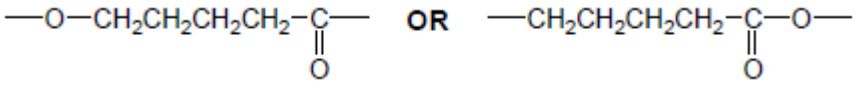
*If values not specified as a or b then assume first is a.*

**1**

*b* 50-90 (ppm) or single value or range entirely within this range

**1**

(ii)

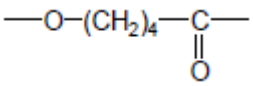



*Must have trailing bonds, but ignore n.*

**1**

**OR** –$OCH_2CH_2CH_2CH_2CO$– **OR** –$CH_2CH_2CH_2CH_2COO$–

*Allow*



*but not* - $C_4H_8$-

one unit only

Condensation

**1**

(b)

| | Tollens' | Fehling's / Benedicts | Acidified potassium dichromate |
|---|---|---|---|

*Penalise wrong formula for Tollens or missing acid with potassium dichromate but mark on.*

**1**

| | | | |
|---|---|---|---|
| **J** | No reaction / no (visible) change / no silver mirror | No reaction / no (visible) change / stays blue / no red ppt | No reaction / no (visible) change / stays orange / does not turn green |

*Ignore 'clear', 'nothing'.*

*Penalise wrong starting colour for dichromate.*

**1**

| | | | |
|---|---|---|---|
| **K** | Silver <u>mirror</u> / grey <u>ppt</u> | Red <u>ppt</u><br><br>(allow brick red or red-orange) | (orange) turns green |

**1**

**J** Two (peaks)

*Allow trough, peak, spike.*

**1**

**K** Four (peaks)

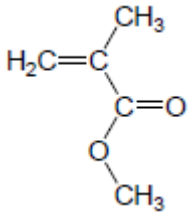
*Ignore details of splitting.*

*If values not specified as J or K then assume first is J.*

**1**

(c) If all the structures are unlabelled, assume that the first drawn ester is L, the second ester is M; the first drawn acid is N, the second P. The cyclic compound should be obvious.

**L**
ester




**OR** $H_2C=C(CH_3)COOCH_3$

***All $C_5H_8O_2$ L to P must have C=C.***

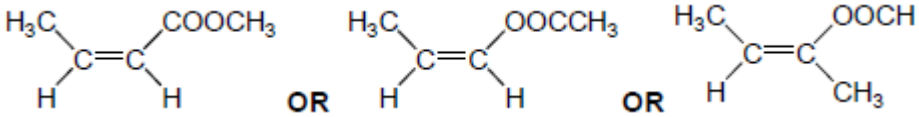
*Allow $CH_3$–.*

*Allow $-CO_2CH_3$ etc.*

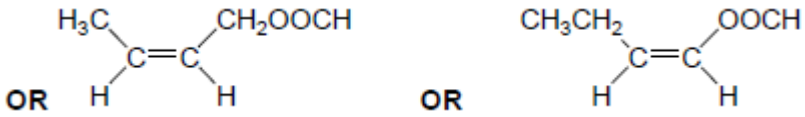
*Allow $CH_2C(CH_3)COOCH_3$.*

**1**

**M**

ester 


$CH_3CH=CHCOOCH_3$ $CH_3CH=CHOOCCH_3$ $CH_3CH=C(CH_3)OOCH$




$CH_3CH=CHCH_2OOCH$ $CH_3CH_2CH=CHOOCH$

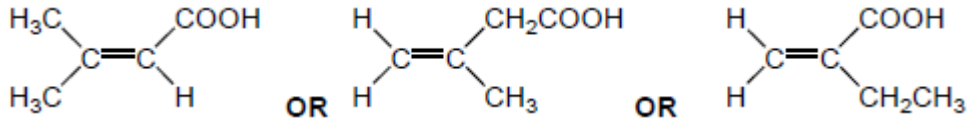
*Allow either E–Z isomer.*

*Allow $CH_3$- or $C_2H_5$- but not $CH_2CH_3$-.*

*Allow $CH_3CHCHCOOCH_3$ etc.*

**1**

**N**

acid 

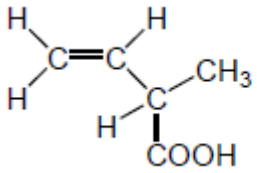

$(CH_3)_2C=CHCOOH$ $H_2C=C(CH_3)CH_2COOH$ $H_2C=C(COOH)CH_2CH_3$

*Allow $CH_3$- or $C_2H_5$- but not $CH_2CH_3$-.*

*Allow $-CO_2H$.*

*Not cyclic isomers.*

*Not the optically active isomer.*

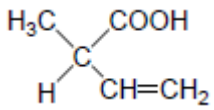


which is P anyway

*Allow $(CH_3)_2CCHCOOH$ etc.*

**1**

**P**

acid 

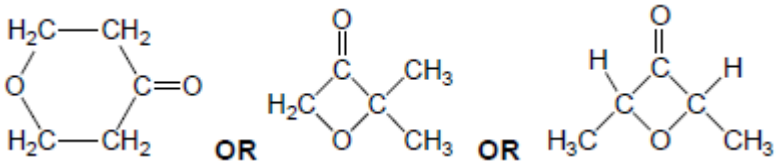

*Allow $-CO_2H$.*

$CH_3CH(COOH)CH=CH_2$

*Allow $CH_3CH(CO_2H)CHCH_2$ or $CH_3CH(CO_2H)C_2H_3$.*

**1**

**Q**




*Not cyclic esters.*

1

**[19]**