AQA A-LEVEL CHEMISTRY · 7405

CHEMISTRY



MARK SCHEME

3.3.15 NMR SPECTROSCOPY

SCORE	PERCENTAGE
/327	%

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Q1.

(a) 4 peaks

1

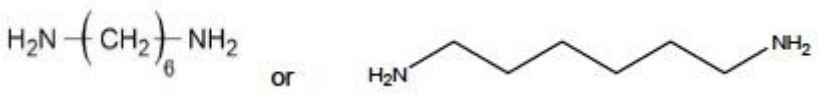
Triplet

1

Two H on adjacent C

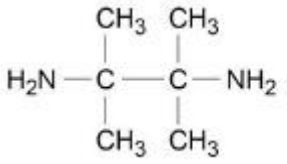
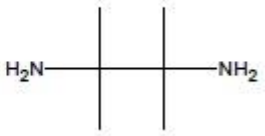
M3 dependent on correct M2

1

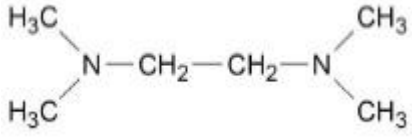
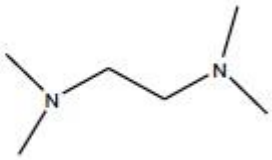
(b)  or

Not –C_6H_{12}–

1

(c)  or 

1

(d)  or 

Not –C_2H_4–

1

[6]

Q2.

C

[1]

Q3.

(a) Z-2-methylpent-2-en (-1-) oic acid

Ignore missing hyphens or extra commas, spaces, hyphens

1

(b) $C_6H_{10}O_2 + 7½\ O_2 \rightarrow 6CO_2 + 5H_2O$

Allow multiple

M1

Volume of CO_2 formed = 180 cm^3

If incorrect volume:155 gives 125mg / 335 gives 270mg could score M1,M3,M4 – max 3

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If incorrect volume from AE then penalise M2 and mark on
(Final answer is 0.806 × their volume)

M2

Mol carbon dioxide = pV/RT = $\frac{105000 \times (180 \times 10^{-6})}{8.31 \times 298}$

$= 7.632 \times 10^{-3}$

If unit error in p, V or T lose M3 and M5
If incorrect rearrangement lose M3 and M5
If both errors seen then no further marks

M3

Mol **P**, $C_6H_{10}O_2$ used $= 7.632 \times 10^{-3} / 6 = 1.272 \times 10^{-3}$
M3 divided by 6 If wrong no further marks

M4

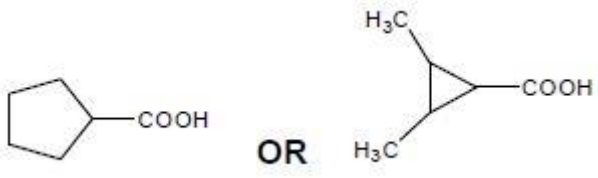
Mass **P** used $= 1.272 \times 10^{-3} \times 114(.0)$ g

$= 145$ mg

Mark for answer (allow ans to 2 sf)
Check chemical equation before awarding final mark

M5

(c)



Mark independently
Apply the list principle

M1

Fig 4: IR OH (acid) peak (2500-3000cm^{-1}) present
Ignore C=O signal at 1750 cm^{-1}

M2

Fig 5: ^{13}C NMR 4 peaks so 4 (non-equivalent) environments
Or Peak at 160-185 (show C=O) in (esters or) acids
Or Peak at 40-50 (show R-CO-CH) presence of carbonyl

M3

Both M2 & M3 can be awarded on the spectra
Allow correct Fig 4 answers in Fig 5 and converse

(d) **R** has 4 C next to C=O **S** has 2 C next to C=O
M1 for structural point

M1

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)
M2 for resulting peak in spectra

M2

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OR

S has a -C(H_2)-C(H_3) **R** does not

M1

S has one peak in range δ = 5-40 **R** does not
/ lowest peak for **S** is lower than lowest for **R**

M2

(Both have) three peaks

M3

(e) **R** Both singlets

M1

S has triplet and a quartet

M2

OR

R CH_3/peak at 2.1-2.6 is a singlet

M1

S CH_3/peak at 0.7-1.2 is a triplet

M2

OR

R CH_2/peak at 2.1-2.6 is a singlet

M1

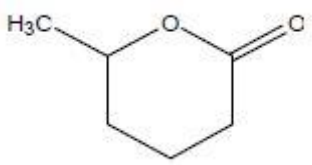
S CH_2/peak at 2.1-2.6 is a quartet

M2

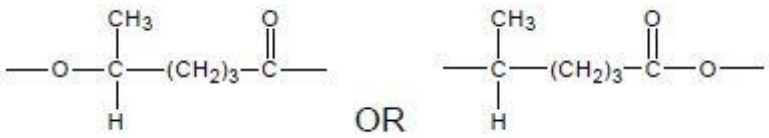
(Both have) two peaks

M3

(f)



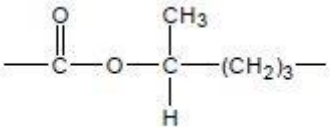
1



Must have trailing bonds

Ignore brackets and n

1



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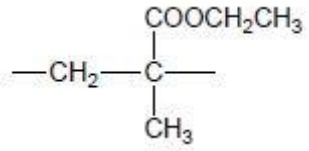
OR

condensation

Ignore esterification

1

(g)



Must have trailing bonds

Ignore brackets and n

M1

Strong / non-polar C-C bonds (in the chain)

M2

cannot be attacked by nucleophiles / acids / cannot be hydrolysed.

M3

OR

Only polar ester group

M2

Can be attacked by nucleophiles / acids / can be hydrolysed

M3

M3 dependent on correct or close M2

Allow 1 mark for in (polar) ester link in side chain/not in main chain therefore polymer chain not broken

[21]

Q4.

D

[1]

Q5.

(a)



1×AO1

1

(b) **S**

1

R

1

Q

1

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(c) (Isomer **T**)

signals due to OH (alcohol) at 3230−3350 and C=O at 1680−1750

1

OH and C=O (functional groups) separated in molecule.

Allow not a carboxylic acid.

1

(Isomer U)

(only) signal for OH (alcohol) at 3230−3350

1

2 × OH groups present / diol / OH & cyclo(ether) structure.

Allow OH but not C=O.

1

(Isomer V)

signals due to OH (acid) at 2500−3000 (and C=O at 1680−1750)

carboxylic acid group / −COOH present.

1
1

(d) 2:2:2:3:3

Any order.

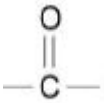
1

(e) (The quartet at δ=3.5 is for a CH_2 group) next to −**O**−**CH_2** **OR** shifted significantly downfield by electronegative O

1

(is a quartet) because of an adjacent CH_3 group / couple with 3 adjacent protons

1

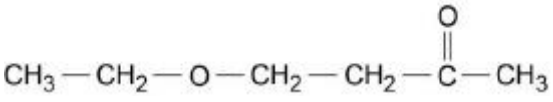
(singlet at δ=2.2 is for a CH_3 group) attached to  C**H_3** **OR** shifted downfield by electronegative C=O

1

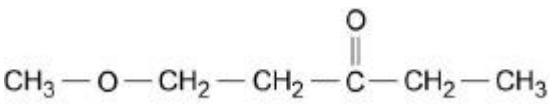
(is a singlet) because there are no adjacent protons / no coupling.

1

(f)



Allow 1 mark for:



2

[17]

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Q6.

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

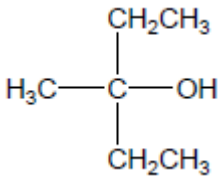
M5 1

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]

Q7.

C

[1]

Q8.

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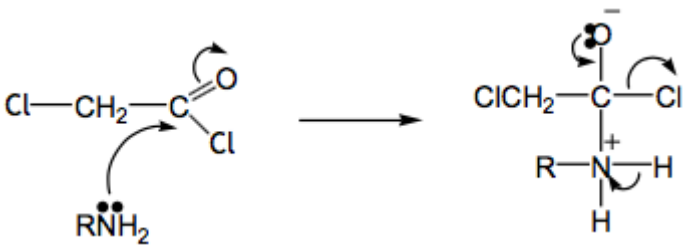
(a) (i) (2-)chloroethan (-1-) oyl chloride

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° amine OR III° 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**

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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]

Q9.

(a) Method 1

M1 %O = 27.1

$\frac{61.0}{12.0}$	$\frac{11.9}{1.0}$	$\frac{27.1}{16.0}$
= 5.08	= 11.9	= 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

$\frac{72.0}{12.0}$	$\frac{14.0}{1.0}$	$\frac{32.0}{16.0}$
= 6	= 14	= 2

M3

Method 3

Alternative using given molecular formula

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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

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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 $–C(CH_3)_2-$

$R–C(CH_3)_2–R$

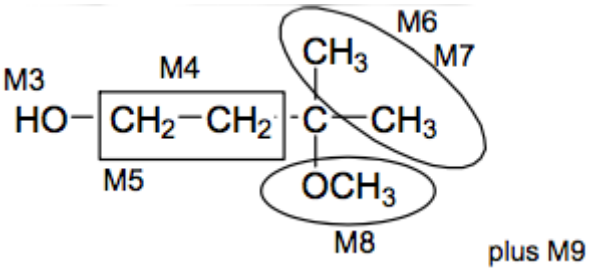
M8 δ = 3.2 singlet integration 3 = $-OCH_3$

$–OCH_3$

M9 For completely correct

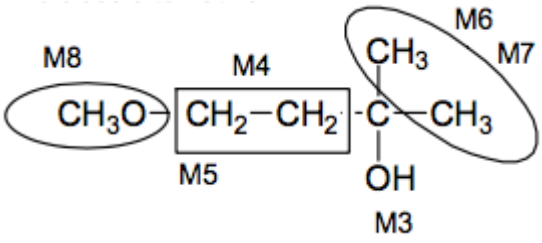
If no structure given then Max 8

R is



plus M9

This close alternative



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

[12]

Q10.

(a) Reagent

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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 <u>nothing or no observation</u>

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

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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

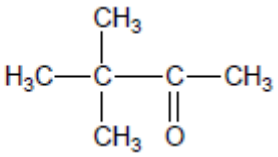
two peaks (so not S which would have only one)

M5
1

(f)

U

$C_6H_{12}O_6$



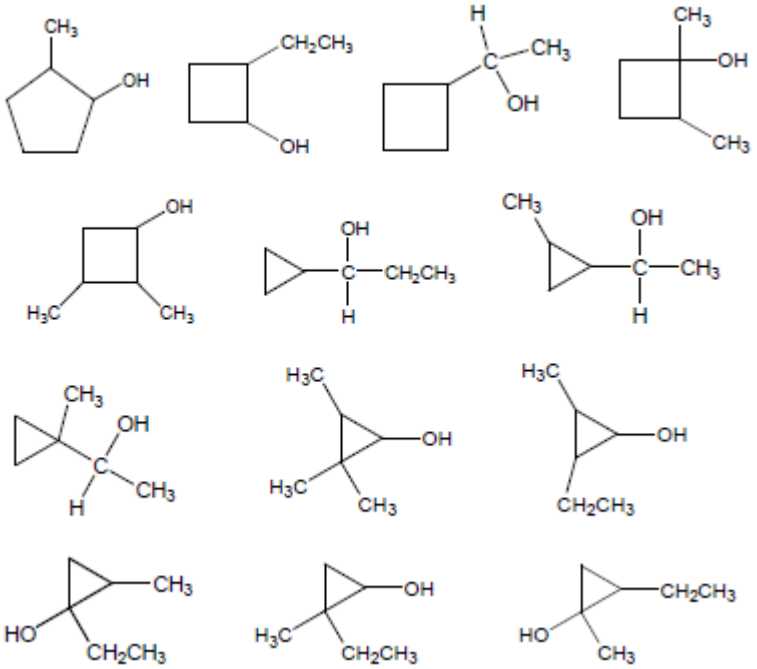
1

Answers include

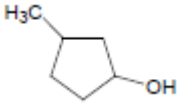
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V

$C_6H_{12}O_6$



*Not allow **S***



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

[17]

Q11.

6 / six

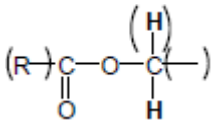
[1]

Q12.

(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 <u>Quaternary</u> (alkyl) <u>ammonium salt / bromide</u>

1

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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]

Q13.

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

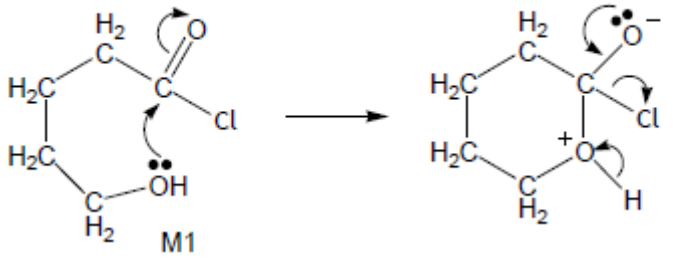
Not electrophilic addition-elimination

Ignore esterification

1

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M2



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

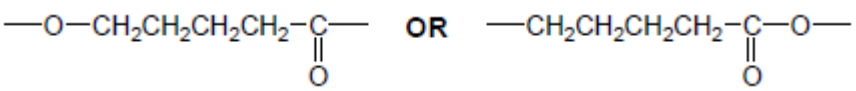
If values not specified as a or b then assume first is a.

1

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

1

(ii)

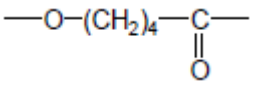


Must have trailing bonds, but ignore n.

1

OR –OCH₂CH₂CH₂CH₂CO– **OR** –CH₂CH₂CH₂CH₂COO–

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.

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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> (allow brick red or red-orange)	(orange) turns green

1

J Two (peaks)

Allow trough, peak, spike.

1

K Four (peaks)

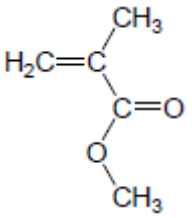
Ignore details of splitting.

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.

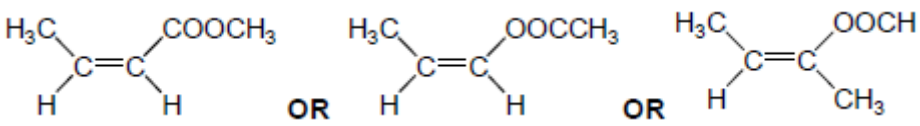
Allow CH_3-.

Allow $-CO_2CH_3$ etc.

Allow $CH_2C(CH_3)COOCH_3$.

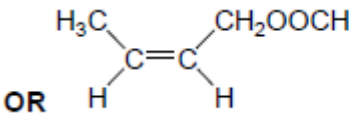
1

M
ester

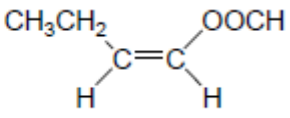


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$CH_3CH=CHCOOCH_3$ $CH_3CH=CHOOCCH_3$ $CH_3CH=C(CH_3)OOCH$



OR



OR

$CH_3CH=CHCH_2OOCH$ $CH_3CH_2CH=CHOOCH$

Allow either E–Z isomer.

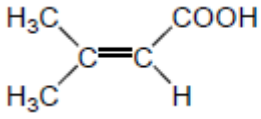
Allow CH_3- or C_2H_5- but not CH_2CH_3-.

Allow $CH_3CHCHCOOCH_3$ etc.

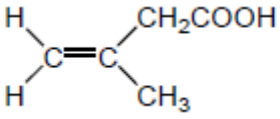
1

N

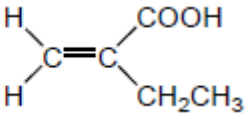
acid



OR



OR



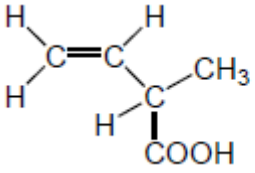
$(CH_3)_2C=CHCOOH$ $H_2C=C(CH_3)CH_2COOH$ $H_2C=C(COOH)CH_2CH_3$

Allow CH_3- or C_2H_5- but not CH_2CH_3-.

Allow $-CO_2H$.

Not cyclic isomers.

Not the optically active isomer.



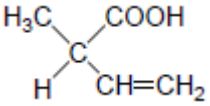
which is P anyway

Allow $(CH_3)_2CCHCOOH$ etc.

1

P

acid



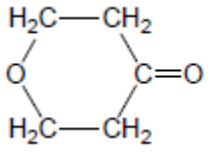
Allow $-CO_2H$.

$CH_3CH(COOH)CH=CH_2$

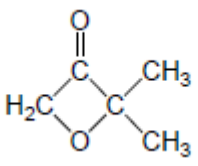
Allow $CH_3CH(CO_2H)CHCH_2$ or $CH_3CH(CO_2H)C_2H_3$.

1

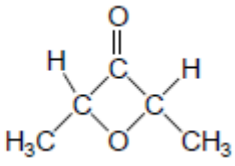
Q



OR



OR



Not cyclic esters.

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1

[19]

Q14.

(a) (i) $CDCl_3$ or CD_2Cl_2 or C_6D_6 or CCl_4

Not D_2O Allow CD_3Cl

1

(ii) 4 **or four**

1

(iii) Triplet or 3 or three

1

(iv) 1,4-dichloro-2,2-dimethylbutane

Do not penalise different or missing punctuation or extra spaces.

Spelling must be exact and order of letters and numbers as here.

1

(b) (i) 3 or three

1

(ii) 190-220 (cm^{-1})

Allow a single number within the range.

***OR** a smaller range entirely within this range.*

1

(iii) hexan**e**-2,5-dione

Do not penalise different or missing punctuation or extra spaces.

Spelling must be exact and order of letters and numbers as here.

NB so must have middle e

1

[7]

Q15.

(a) (i) Single / one (intense) peak / signal ***OR** all H or all C in same environment **OR** 12 equiv H or 4 equiv C*

Do not allow non-toxic or inert (both given in Q)

Any 2 from three

Ignore peak at zero

OR

Upfield / to the right of (all) other peaks ***OR** well away from others **OR** doesn't interfere with other peaks*

Ignore cheap

Ignore non-polar

OR

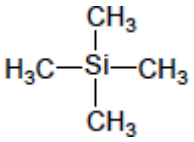
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Low bp ***OR*** *volatile* ***OR*** *can easily be removed*

Ignore mention of solubility

2

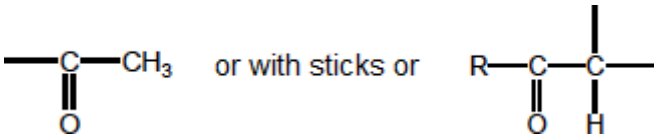
(ii)



Allow $Si(CH_3)_4$

1

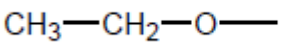
(b) (i)



Ignore any group joined on other side of CO
Ignore missing trailing bond
Ignore charges

1

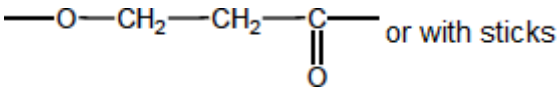
(ii)



Ignore any group joined on other side of −O−
Ignore missing trailing bond
Ignore charges as if MS fragment

1

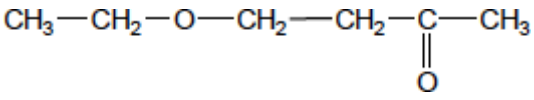
(iii)



Ignore missing trailing bonds
Ignore charges as if MS fragment

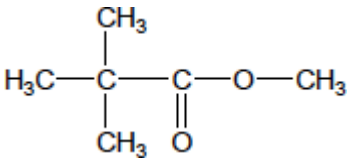
1

(iv)



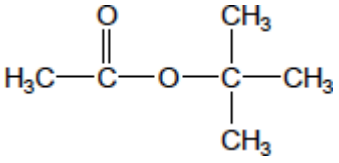
1

(c) (i) Check structure has 6 carbons



Allow $(CH_3)_3CCOOCH_3$ or $(CH_3)_3CCO_2CH_3$

1

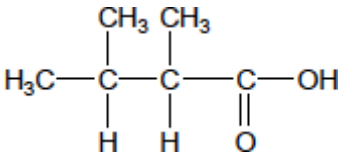


Allow $CH_3COOC(CH_3)_3$ or $CH_3CO_2C(CH_3)_3$

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1

(ii) Check structure has 6 carbons

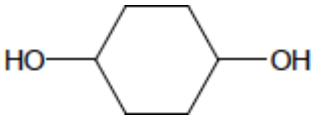


Allow $(CH_3)_2CHCH(CH_3)COOH$ or $(CH_3)_2CHCH(CH_3)CO_2H$

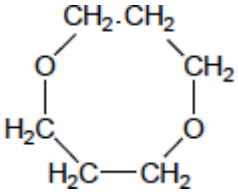
Penalise C_3H_7

1

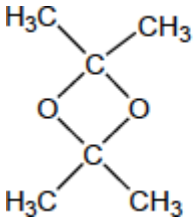
(iii) Check structure has 6 carbons



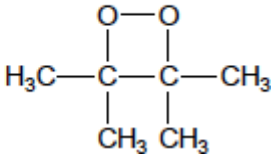
OR



Allow



OR

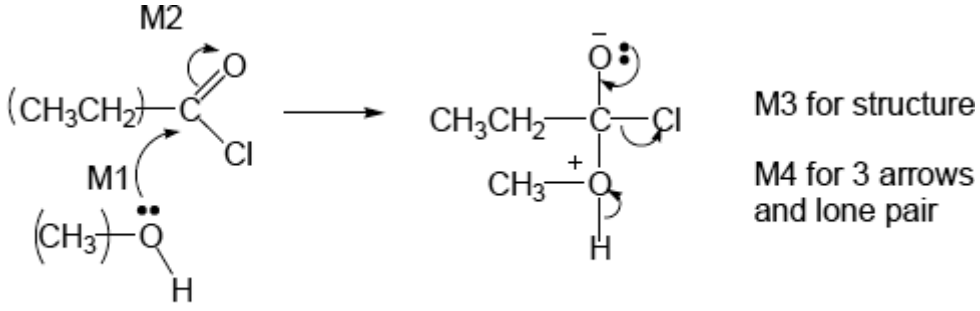


1

[11]

Q16.

(a)



methyl propanoate (**NO** mark for name of mechanism)

- *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, max1 for M1*
- *M3 for correct structure <u>with charges</u> but lp on O*

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is part of M4

- *only allow M4 after correct/very close M3*
- *ignore Cl^- removing H^+*

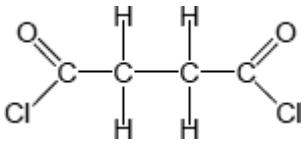
4

(b) (i) pentan<u>e</u>-<u>1,5</u>-diol

Second 'e' and numbers needed

Allow <u>1,5</u>-pentan<u>e</u>diol but this is not IUPAC name

(ii)



Must show ALL bonds

1

(iii) All three marks are independent

M1 (base or alkaline) Hydrolysis (allow close spelling)

1

Allow (nucleophilic) addition-elimination or saponification

M2 <u>δ+ C</u> in polyester

1

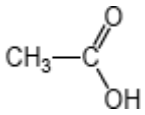
M3 reacts with OH^- or hydroxide ion

1

Not reacts with NaOH

1

(c) (i)



Allow CH_3COOH or CH_3CO_2H

1

(ii) (nucleophilic) <u>addition-elimination</u>

Both addition and elimination needed and in that order

OR

(nucleophilic) addition followed by elimination

*Do **not** allow electrophilic addition-elimination / esterification*

Ignore acylation

1

(iii) any **two** from: ethanoic anhydride is

- less corrosive
- less vulnerable to hydrolysis
- less dangerous to use,
- less violent/exothermic/vigorous reaction OR more controllable rxn

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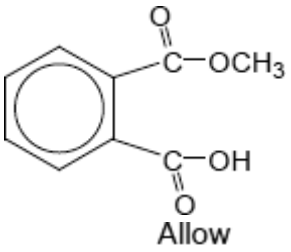
- does not produce toxic/corrosive/harmful fumes (of HCl) OR does not produce HCl
- less volatile

NOT *COST*

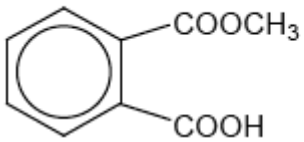
List principle beyond two answers

2

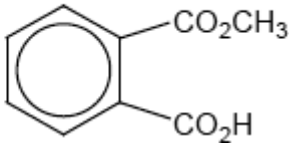
(d)



Allow



or



1

(e) (i) ester

*Do **not** allow ether*

Ignore functional group/linkage/bond

1

(ii) 12 or twelve (peaks)

1

(iii) 160 – 185

Allow a number or range within these limits

Penalize extra ranges given

Ignore units

1

(f) (i)

sulfuric acid	sodium hydroxide	✓
hydrochloric acid	ammonia	X or blank
ethanoic acid	potassium hydroxide	✓
nitric acid	methylamine	X or blank

4 correct scores 2

3 correct scores 1

2 or 1 correct scores 0

2

(ii) <u>Pink to colourless</u>

Allow 'red' OR 'purple' OR 'magenta' instead of 'pink'

*Do **not** allow 'clear' instead of 'colourless'*

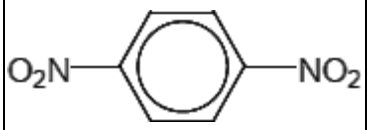
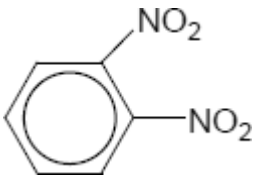
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1

[21]

Q17.

(a)

F	G
	

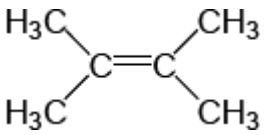
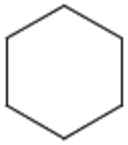
Penalize $–O_2N$ once

Penalise missing circle once

Don't penalise attempt at bonding in NO_2

1

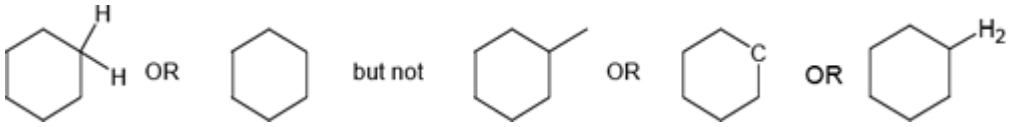
(b)

H	J
	

*If **both H** and **J** correct but reversed, award one mark*

1

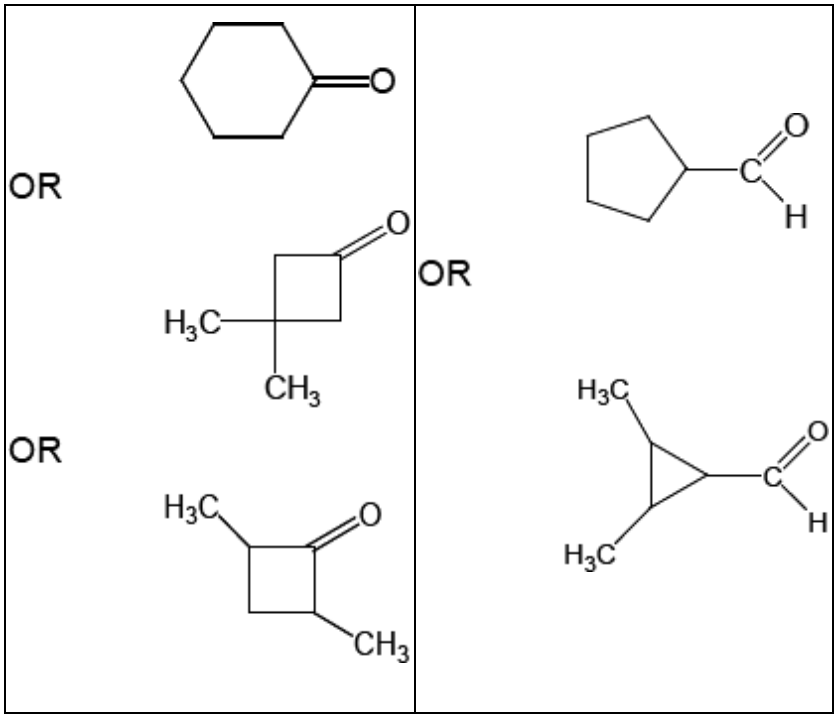
A carbon in saturated ring structures should be shown as



(c)

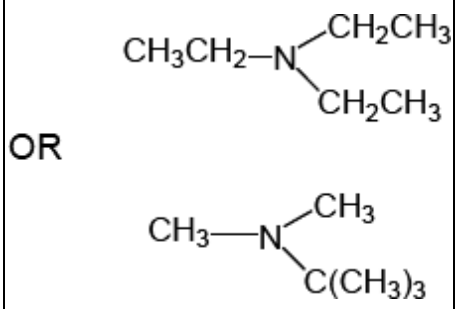
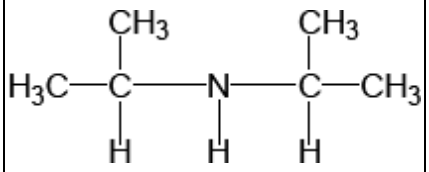
K	L

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1

(d)

M	N
	

Allow C_2H_5 but
NOT allow C_4H_9 or C_3H_7

1
1

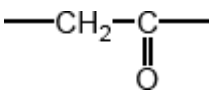
[8]

Q18.

(a) OH alcohols

1

(b) (i) 2.6



Ignore any group on RHS
*Must clearly indicate relevant **two** H on a C next to C=O*

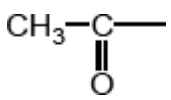
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On LHS, penalise H or CH or CH_2 or CH_3

Ignore missing trailing bonds or attached R groups

1

(ii) 2.2



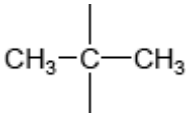
Ignore all groups on RHS

*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

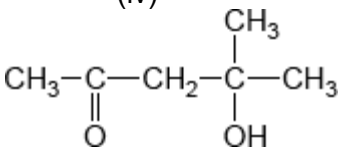
Must clearly indicate two <u>equivalent</u> methyl groups.

Penalise attached H

Ignore missing trailing bonds or attached R groups

1

(iv)



1

[5]

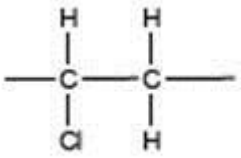
Q19.

(a) <u>Benzene-1,2-dicarboxylic acid</u>

Allow 1,2-benzenedicarboxylic acid

1

(b)



Must show all bonds including trailing bonds

Ignore n

1

(c) (i) 2 C_2H_5OH

NB Two ethanols

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1

H_2O

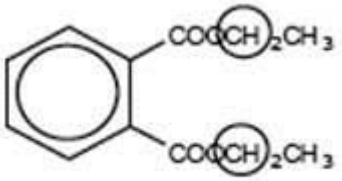
but only one water

1

(ii) 6 or six

1

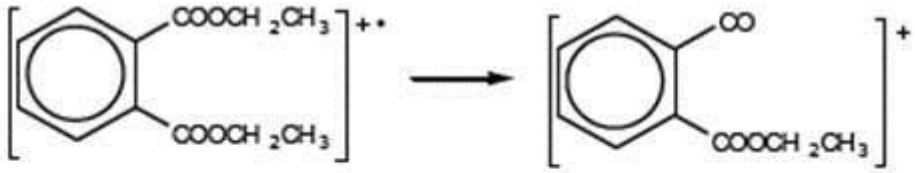
(iii)

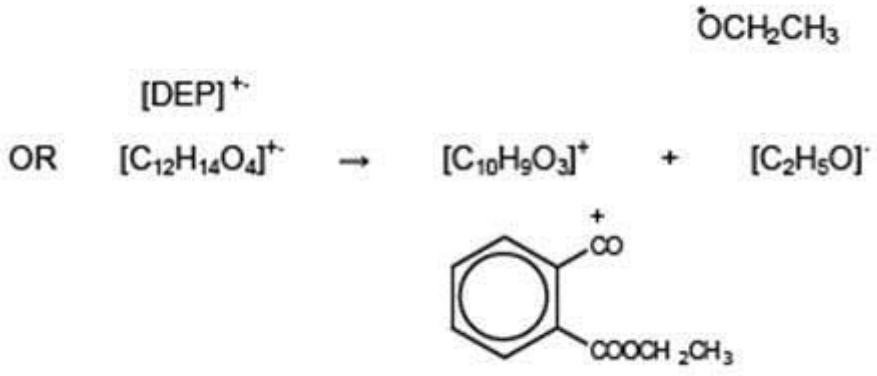


Ignore overlap with O to the left or H to the right, but must only include this one carbon. either or allow both (as they are identical)

1

(d)





Allow + on C or O in

1

Dot must be on O in radical

1

(e) (i) Rate = k[DEP]

Must have brackets but can be ( )

1

(ii) Any **two** of

- experiment repeated/continued <u>over a long period</u>
- repeated by independent body/other scientists/avoiding bias

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- investigate breakdown products
- results made public

Not just repetition

Ignore animal testing

2 max

[11]

Q20.

(a) (i) Single reagent

If wrong single reagent, CE = zero

Incomplete single reagent (e.g. carbonate) or wrong formula (e.g.$NaCO_3$) loses reagent mark, but mark on

For "no reaction" allow "nothing"

Different reagents

If different tests on E and F; both reagents and any follow on chemistry must be correct for first (reagent) mark.
Reagent must react: i.e. not allow Tollens on G (ketone) – no reaction.
Second and third marks are for correct observations.
i.e. for different tests on E and F, if one reagent is correct and one wrong, can score max 1 for correct observation with correct reagent.

PCl_5 PCl_3

$SOCl_2$

1

E ester

Na_2CO_3/$NaHCO_3$ named carbonate

metal e.g.Mg

no reaction

no reaction

named indicator

no effect

No reaction

1

F acid

Na_2CO_3/$NaHCO_3$ named carbonate

Effervescence or CO_2

metal e.g.Mg

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Effervescence or H_2

named indicator

acid colour
fumes

1

(ii) Single reagent

If wrong single reagent, CE = zero
Incomplete single reagent (e.g. carbonate) or wrong formula (e.g.$NaCO_3$) loses reagent mark, but mark on
For "no reaction" allow "nothing"

Different reagents

If different tests on E and F; **both** reagents and any follow on chemistry must be correct for first (reagent) mark.
Reagent must react: i.e. not allow Tollens on G (ketone) – no reaction.
Second and third marks are for correct observations.

1

i.e. for different tests on E and F, if one reagent is correct and one wrong, can score max 1 for correct observation with correct reagent.

G ketone

$AgNO_3$

no reaction

Na_2CO_3/$NaHCO_3$ named carbonate

water

no reaction

named indicator

no effect

Named alcohol

no reaction

Named amine or ammonia

no reaction

1

H Acyl chloride

$AgNO_3$

(white) ppt

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Na_2CO_3/$NaHCO_3$ named carbonate

Effervescence or CO_2 or fumes or exothermic

water

fumes

named indicator

acid colour

Named alcohol

Smell or fumes

Named amine or ammonia

fumes

1

Allow iodoform test or Brady's reagent (2,4,dnph) test (both positive for G)

(iii) Single reagent

If wrong single reagent, CE = zero
Incomplete single reagent (e.g. carbonate) or wrong formula (e.g.$NaCO_3$) loses reagent mark, but mark on

For "no reaction" allow "nothing"

Different reagents

If different tests on E and F; **both** reagents and any follow on chemistry must be correct for first (reagent) mark.

Reagent must react: i.e. not allow Tollens on G (ketone) – no reaction.

Second and third marks are for correct observations.

i.e. for different tests on E and F, if one reagent is correct and one wrong, can score max 1 for correct observation with correct reagent.

1

J Primary alcohol

$K_2Cr_2O_7$/ H^+

goes green

$KMnO_4$/ H^+

decolourised / goes brown

Lucas test ($ZnCl_2$/HCl)

Penalise missing H^+ but mark on

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1

K Tertiary alcohol

$K_2Cr_2O_7$/ H^+

No reaction

$KMnO_4$/ H^+

no reaction

Lucas test ($ZnCl_2$/HCl)

Rapid cloudiness

1

If uses subsequent tests e.g. Tollens/Fehlings, test must be on product of oxidation

(b) (i) 3,3-dimethylbutan-1-ol

Allow 3,3-dimethyl-1-butanol

1

4

1

Triplet on three

1

(ii) 2-methylpentan-2-ol

Allow 2-methyl-2-pentanol

1

5

1

Singlet or one or no splitting

1

[15]

Q21.

(a) chromatography (allow GLC TLC GC HPLC)

allow any qualification

1

(b) 5

1

Allow 320(.0) or 322(.0)

1

(c) Use of excess air/oxygen or high temperature (over 800 °C) or remove chlorine-containing compounds before incineration

1

(d) (i) $Si(CH_3)_4$ allow SiC_4H_{12}

allow displayed formula and do not penalise sticks

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1

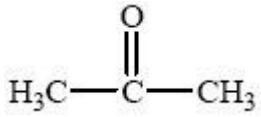
(ii) 3

1

[6]

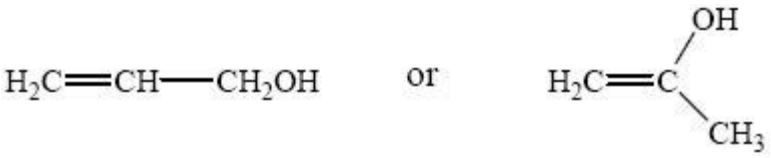
Q22.

(a) A



allow CH_3COCH_3

1

B 

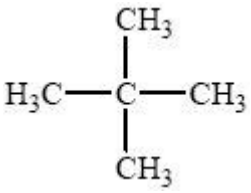
must show C=C

Penalise sticks once per pair

1

(b) C $CH_3CH_2CH_2CH_2CH_3$

1

D 

NOT cyclopentane which is only C_5H_{10}

Penalise sticks once per pair

1

(c) E $CH_3CH_2COOCH_3$

Allow $C_2H_5CO_2CH_3$

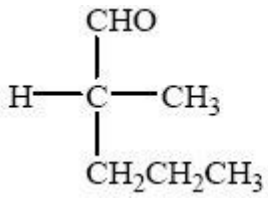
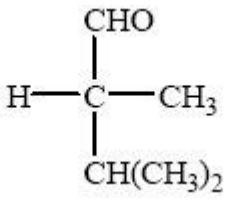
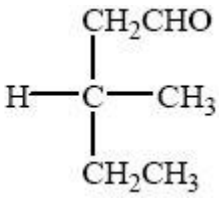
1

F $CH_3COOCH_2CH_3$

Allow $CH_3CO_2CH_2CH_3$ or $CH_3CO_2C_2H_5$

Penalise sticks once per pair

1

(d) G  ***OR***  ***OR*** 

allow C_3H_7

C_3H_7

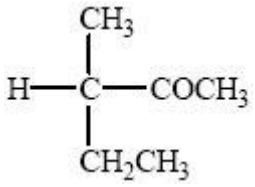
allow

allow C_2H_5

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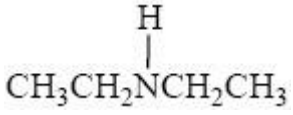
not C_5H_{11} nor C_4H_9
Penalise sticks once per pair

1

H 

allow C_2H_5

1

(e) I 

allow C_2H_5

1

J 

NOT C_3H_7
Penalise sticks once per pair

1

[10]

Q23.

(a) GLC or distillation

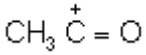
1

(b) C=O

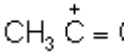
1

(c) (i) Cl has two isotopes

1

(ii) 

1

$C_4H_7ClO^{+\cdot} \rightarrow$  + $C_2H_4Cl^{\cdot}$

1

(d) (i) e.g. $CDCl_3$ or CCl_4

1

(ii) $Si(CH_3)_4$

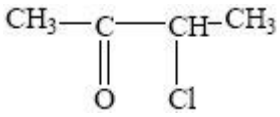
1

(e) 0 and 3

1

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(f)



1

(g) $CH_3CH_2CH_2COCl$ or $(CH_3)_2CHCOCl$

1

[10]

Q24.

(a) (i) There are three pairs of equivalent carbon atoms

1

(ii) 75ppm

1

(b) (i) 4

1

(ii) 2

1

(c) Each structure can represent a pair of cis/Z and trans/E isomers
OR
Optical isomers

1

[5]

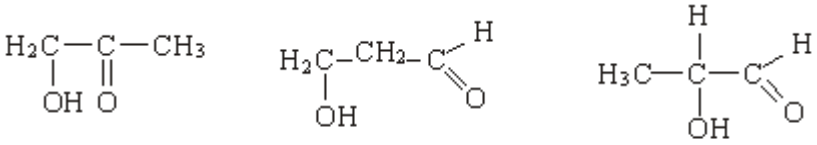
Q25.

(a) **X** (O–H) (alcohols)
penalise acid or missing "alcohol"

1

Y C=O
allow carbonyl

1

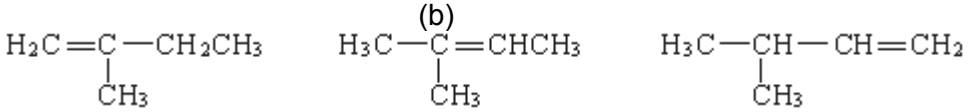


A

NOT acid

4

(b)



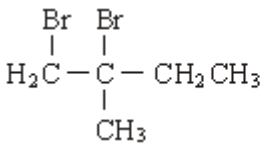
Allow conseq dibromocompounds following incorrect unbranched alkenes

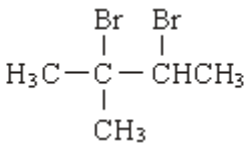
NOT allow dibromocompound consequent on a duplicate alkene

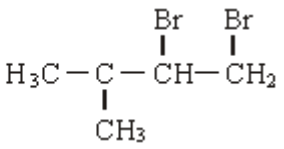
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NOT allow monobromocompounds if HBr added

3







3

6:3:1 either next to correct structure or to none

1

Allow a mark for identifying correct dibromocompound with three peaks even if integration ratio is wrong

1

if 6:3:1 missing or wrong, no marks for splitting

Only award a mark for splitting if it is clear which integration number it refers to

6 singlet or drawn

1

3 doublet or drawn

1

1 quartet/quadruplet or drawn

1

(max 10 marks)

[16]

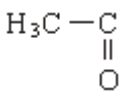
Q26.

B

[1]

Q27.

(a) (i)



or $RCOCH_3$;

(or description in words)
(ignore trailing bonds)

1

(ii) H_3C—O or $ROCH_3$;

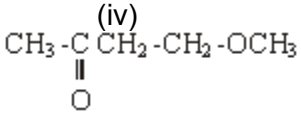
(allow 1 if both (i) and (ii) give CH_3- or H_3C– only)

1

(iii) CH_2CH_2 or two <u>adjacent</u> methylene groups;

1

(iv)



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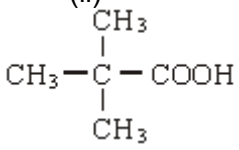
OR

$CH_3COCH_2CH_2OCH_3$;

1

(b) (i) OH <u>in acids</u> or (carboxylic) acid present

(ii)



(c)

reagent	$K_2Cr_2O_7$ /H^+	$KMnO_4$ /H^+
Y	no reaction	no reaction
Z	orange to green or turns green	purple to colourless or turns colourless

5

[9]

Q28.

D

[1]

Q29.

(a) **A** any C_5 alkene

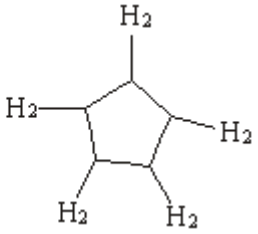
1

B



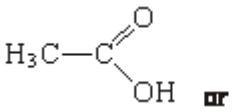
etc

penalise

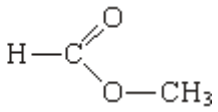


1

(b) **C**



or

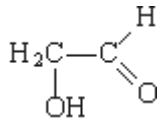


or CH_3COOH or $HCOOCH_3$

1

D

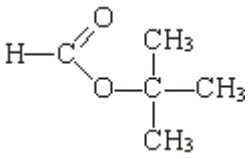
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or $HOCH_2CHO$

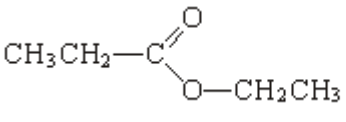
1

(c) **E**



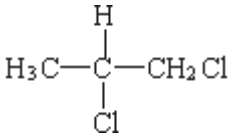
1

F



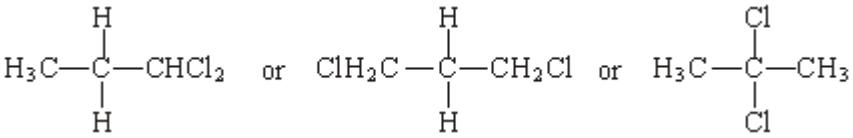
1

(d) **G**



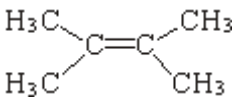
1

H



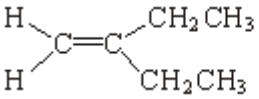
1

(e) **I**



1

J



NOT hex-3-ene

1

[10]

Q30.

(a) Pentan-2-one

1

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(b) (i) 1680 – 1750 (cm^{-1})

1

(ii) 3230 – 3550 or 1000 – 1300 (cm^{-1})

1

(iii) 4

1

(c)

Reagent	$K_2Cr_2O_7/H^+$	$KMnO_4/H^+$	Na	CH_3COOH/H_2SO_4
with **C**	no reaction	no reaction	no reaction	no reaction
with **D**	goes green	goes colourless	effervescence	smell

1 1 1

(penalise incomplete reagent e.g. $K_2Cr_2O_7$ or $Cr_2O_7^{2-}/H^+$ then mark on)

(d)

Reagent	Tollens	Fehlings or Benedicts
with **E**	silver (mirror)	red ppt or goes red *(not red solution)*

1 1

[9]

Q31.

(a) (i)

Reagent	Tollens	Fehlings or Benedicts	$K_2Cr_2O_7/H^+$ or acidified	$KMnO_4/H^+$	$I_2/NaOH$
Propanal	silver (mirror)	red ppt or goes red *(not red solution)*	goes green	goes colourless	No reaction
Propanone	no reaction	no reaction	no reaction	no reaction	Yellow (ppt)

(penalise incomplete reagent e.g. $K_2Cr_2O_7$ or $Cr_2O_7^{2-}/H^+$ then mark on)

3

(ii) propanal 3 peaks

ignore splitting even if wrong

1

propanone 1 peak

1

(b) **X** is CH_3CH_2COOH or propanoic acid if both name and formula given, both must be correct,

but

1

Y is $CH_3CH(OH)CH_3$ or propan-2-ol allow propanol with correct formula

1

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Mark the type of reaction and reagent/condition independently.
The reagent must be correct or close to score condition

Step 1 Oxidation

$K_2Cr_2O_7/H^+$ or other oxidation methods as above
allow $Cr_2O_7^{2-}H^+$ if penalised above (ecf)
reflux (not Tollens/Fehlings) or heat or warm

1

Step 2

reduction or nucleophilic addition	reduction or nucleophilic addition	reduction or hydrogenation
$NaBH_4$	$LiAlH_4$	H_2
in (m)ethanol or water or ether or dry	ether or dry	Ni / Pt etc

1 1 1

Step 3 esterification or (nucleophilic) addition-elimination or condensation

1

(conc) H_2SO_4 or HCl

1

warm (allow without acid reagent if **X** and **Y** given as reagents)

1

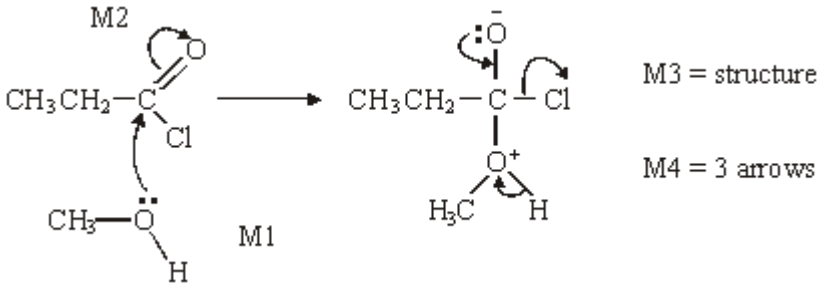
or reflux or heat

1

[15]

Q32.

X is methyl propanoate



1

M1 for arrow and lone pair,

4

M2 for arrow
addition-elimination

1

Spectrum 2
if thinks Spectrum 1 = X can only score for structure of Y

1

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Y is $CH_3COOCH_2CH_3$

1

The two marks for explanation are awarded for discussing one or more of the four peaks (not those for the CH_3 of the ethyl groups)
for stated δ values the integration or the splitting should be related to the structure: e.g. structure of **X** shows that
at δ 3.7 – 4.1 **(1)** spectrum of **X** should have integration 3 / singlet **(1)**

or

at δ 2.1 – 2.6 **(1)** spectrum of **X** should have integration 2 / quartet **(1)**

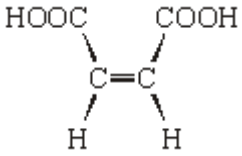
Spectrum 2 has these
[OR Spectrum 1 has
at 3.7 – 4.1 **(1)** quartet / integration 2 **(1)** so not **X**
at 2.1 – 2.6 **(1)** singlet / integration 3 **(1)** so not **X**]

2

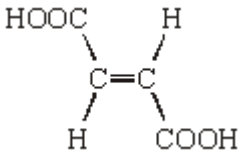
[10]

Q33.

(a)



1



1

NB The bonds shown in the structure must be correct

Isomerism: E-Z isomerism

If written answer is correct, ignore incorrect labelling of structures.
If no written answer, allow correctly labelled structures.

1

Both COOH groups must be on the same side/ close together/ cis

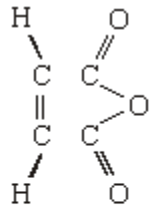
1

No rotation about C=C axis

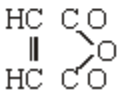
1

Structure

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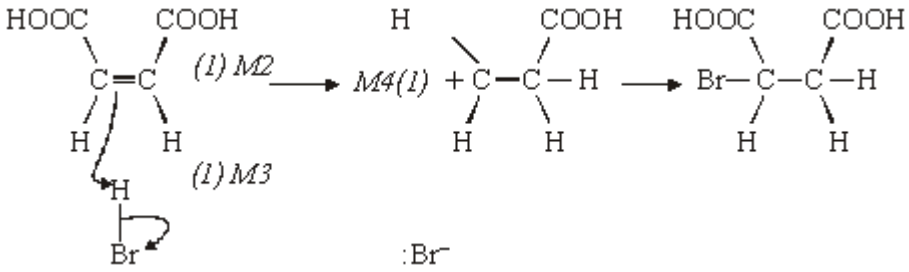


Allow



1

(b) Br_2 / HBr / H_2SO_4 / H^+ / Br^+ / NO_2^+ (*Mark M1*)



NB If electrophile H^+ / Br^+ / NO_2^+ allow M1, M2 and M4
If the acid is incorrect, M2 and M3 can still be scored
Allow M4 consequentially if repeat error from part (a)

4

(c) e.g. $2NaOH + HO_2CCHCHCO_2H \rightarrow NaO_2CCHCHCO_2Na + 2H_2O$

Both H replaced

1

Balanced for atoms and charges

1

NB Allow ionic equations and
$2NaOH + C_4H_4O_4 \rightarrow C_4H_2O_4Na_2 + 2H_2O$
Allow one if structure incorrect but molecular formula correct
Allow one for a correct equation showing one H replaced

(d) *M1* Two peaks

1

M2 No splitting or singlets

1

M3 (Two) non-equivalent protons or two proton environments

1

M4 No adjacent protons

1

M5 Same area under the two peaks or same relative intensity

1

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NB Doublet could score M1 and M3 or M5 (Max 2)

More than two peaks CE = 0

Apply the "list principle" to incorrect answers if more than 3 given

Max 3

[15]

Q34.

C

[1]

Q35.

D

[1]

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Q1.

(a) This part was answered well and over half of the students, 56.6%, gained full marks. The third 'explanation' mark was the one least frequently awarded. An explanation was required that referred to the number of adjacent hydrogens, not just a generic statement that the *n*+1 rule applies.

(b) This was the most familiar of the three isomers required and was correctly answered by 55.3% of students. The most common errors seen were cyclic or aromatic structures or those with an incorrect number of carbon atoms in the chain. A disappointing proportion of students (17.5%) made no attempt to answer the question.

(c) Although this isomer was found to be the most difficult of the three, 32% of the students answered correctly. Others suggested cyclic structures that contained two primary amine groups and produced only two ^{13}C NMR peaks, but sadly contained too few hydrogen atoms to be isomers of $C_6H_{16}N_2$. As with the previous part, there were many students, 15.6%, who did not attempt to answer this question.

(d) This isomer was drawn correctly by just over 40% of the students, but the question was also not attempted by 20.7%.

Q2.

59.5% of students were successful here. B was the commonest incorrect response – possibly due to students failing to appreciate that carbons 2,3,5 and 6 are all equivalent.

Q3.

(a) The full IUPAC name of isomer P includes the letter *Z* to indicate its stereochemistry. Only 10% of students answered this difficult question correctly.

(b) This extended response question was a good discriminator. An appreciable number of students failed to write an equation and, of those who did, many students forgot that **P** contains two oxygen atoms so used too much oxygen in their answer. It was expected that the volume of oxygen used (180 cm^3) would be deduced directly, and the amount of oxygen in moles calculated from this. Some answers contained calculation of the amount in moles of gas at the start and at the end and subtraction at this later stage. The main errors were in rearranging $pV = nRT$, in failing to convert the volume units to m^3, and then, most commonly, failing to divide the amount of oxygen by 6 to obtain the amount in moles of **P**. Sadly a number of students got this far but then gave their answer in g rather than mg.

(c) The identity of **Q** discriminated well. Many students were not able to relate an aspect of its structure to a peak / signal. In the evidence from Figure 2, many students failed to state that the infrared absorption between 2500 and 3000 cm^{-1} showed the presence of an O−H bond **in an acid**. In the ^{13}C NMR evidence, many students thought that the structure was an aldehyde/ketone having been careless in reading the value of the chemical shift on the x-axis.

(d) Few students gained full marks here. Although the number of peaks was deduced correctly, few gave a correct comparison of the spectra of **R** and **S**. The symmetry of each compound was not always noted, so the number of peaks given was double the correct value.

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(e) Again, the fact that the two CH_2 groups were identical, and would therefore produce a singlet, was missed by most students who predicted a triplet in the spectrum of R. The triplet and quartet for S were usually predicted correctly but full marks were obtained by relatively few students. Over 5% of students made no attempt at the question.

(f) The two structures were found difficult, particularly that of **T**, and the polyester repeating unit was often shown as a double unit. The type of polymerisation, however, was well known.

(g) The question was not attempted by 7% of the students. Of those who did answer, only the best scored all three marks. Many answers were vague and missed the required comparison of the position of the ester group. Large numbers either only gained the first mark or alternatively did not score, because their repeating unit was incorrect.

Q8.

The IUPAC name in part (a)(i) proved harder than expected with answers including 1-chloro or ethyl. The mechanism in part (a)(ii) was well known with over half of students gaining full marks. There was a wide range of answers to part (d) with both the number of hydrogens and the overall M_r proving harder than expected, but, even so, nearly half of all students scored both marks. Many students knew (e) was tertiary but some thought it was an amide rather than an amine.

Part (f)(i) was generally well done and in the correct responses there was a fairly even distribution between those describing why b is a stronger base or why a is a weaker base. Part (f)(ii) proved more difficult and only the best students scored any marks. The term salt was given in the question and so just that link was not credited. Few stated that the ionic character of the salt would make it more water-soluble than lidocaine itself.

Q9.

Part (a) proved straightforward and most students gained full marks. A number lost the final mark because they did not explain why the empirical formula was half of the molecular formula.

Part (b) proved a challenging question which required a logical approach. It was pleasing to see many excellent answers and nearly a quarter of students scored seven or more marks. In the infrared analysis some students did not include the full name of O-H (alcohol) for the peak at 3400 cm^{-1} whilst some described the adjacent C-H absorption as OH (acid) and lost the first mark.

The outcome of the potassium dichromate(VI) test was not always fully explained and some of those who correctly stated that compound **R** was a primary or secondary alcohol but not a tertiary, then contradicted themselves in their final structure by drawing a tertiary alcohol.

When analysing the nmr data, many simply restated the information on the data sheet without using the integration data and then struggled to ‘do the jigsaw’ at the end and come up with a structure that fitted everything.

Most students did draw a structure for **R** as required although some only included analysis of the separate peaks and not the overall structure. A few students who drew several suggested structures were penalised if they failed to cross out the extras to leave just one answer.

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Q10.

Part (a) was answered well. "A simple test-tube reaction" was required so students lost the marks if they suggested that two reagents were added sequentially or two different reagents were used for **P** and **S**. The most common test used was acidified potassium dichromate(VI). A few students gave the observations the wrong way round.

The answer to part (b) was usually given correctly although a number gave acidified potassium dichromate(VI) again even though this also react with **S**. Part (c) was found to be more difficult. In part (d), most students gained at least two marks out of three. Tetramethylsilane was well known but often given as a structural formula or even as a displayed formula when the molecular formula was required. A few students referred to the proton nmr spectrum rather than the ^{13}C.

There were some good, well explained answers to part (e). The spectrum in Figure 1 was usually identified as **R**, but the spectrum in Figure 2 was less well answered as **T**. The data sheet was used well, but the terms ester and ether from the table on the sheet were sometimes muddled.
Students who were unable to state correctly which isomer produced each spectrum could not access the explanation marks. Isomer **S** was the most common incorrect answer for Figure 2. Better students appreciated that the spectrum of **T** would show two C-O peaks in the region 50-90 ppm but **S** would only have one of these and then used the two peaks in this region of the spectrum to confirm their choice.

In part (f), compound **U** was often correct. There are many cyclic alcohols of $C_6H_{12}O$ which exist as optical isomers and most were seen and gained credit. Common incorrect answers were **S** itself and the optically inactive 1-methylcyclopentan-1-ol and cyclohexanol.

Q11.

This question caused few problems.

Q12.

Although many students scored well in part (a), answers were often badly expressed and very wordy. Most students gained M3 for explaining that the quartet was due to the CH_2 group being next to a CH_3 group and this mark was allowed even if the wrong ester was given. The question instructed students to use Table B on the Data Sheet, and it was only by doing this that M2 and M4 could be accessed and earned. Parts (b) and (c) proved very straightforward, although the full name “quaternary ammonium salt” was only given by a minority of students. A significant number of students who identified the correct reagent in part (c) either had the results reversed, or discussed cyclohexane and benzene in their answer, thinking that benzene would react with bromine.

Q13.

The nucleophilic addition-elimination mechanism in part (a)(i) presented a real challenge to many students, who were confused by the cyclic nature of the product, failed to identify the correct nucleophile and suggested either separate nucleophiles such as H_2O, CH_3OH and OH^- or alternatively loss of the proton from the OH group before nucleophilic attack. Most students gave the correct range for the carbon atom labelled **b**, but often the range for the carbon atom labelled **a** was given as 160–185 as for a carbonyl carbon. In part (a)(ii), the repeating unit for the polyester was answered well although some students gave twice the repeating unit.

The distinguishing test in part (b) was well done, although a significant number of students

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thought that substance **K** was an acid and wrongly suggested $NaHCO_3$ or Na_2CO_3 to distinguish between the compounds. It was common for students to fail to see the symmetry of **J** and so to predict, incorrectly, three peaks in its proton n.m.r. spectrum. Five peaks was a common incorrect answer for **K**, suggesting that students had misread the question and given the ^{13}C n.m.r. result.

Part (c) of this question proved to be very challenging and fewer than 10% of students scored full marks. Isomer **Q** was found particularly difficult where many students omitted one of the O atoms from their suggested structure. Other common errors included missing the double bond in **L**, giving the structure of **P** as the structure of **N** (which suggests a failure to recognise that optical isomerism is a form of stereoisomerism) or writing an unbranched carbon chain for the acid **N**. Answers to part (c) were often very badly presented, with a great deal of crossing out, duplication of answers and poor labelling of structures.

Q14.

In part (a)(i), tetramethylsilane was a common incorrect answer. The rest of the question was answered well apart from part (b)(iii) where the name of the ketone was found more difficult.

Q15.

Only 21% of students gained both marks in part (a)(i). A surprising number repeated inert or non-toxic despite these properties being stated in the question.

Students found part (b) hard. Many failed to use all three pieces of information in each case and an appreciable number thought the compound was an ester.

Part (c)(i) was well done but (c)(ii) proved to be very difficult. Many gave structures with 5 or 7 C atoms. In part(c)(iii), many suggested structures that contained benzene rings and some contained no O atoms while others contained N atoms.

Q16.

In part (a), the mechanism was frequently correct and well presented, but some students lost a mark by writing a minus charge on the oxygen of methanol. Methyl ethanoate was a common wrong name for the product ester.

There were few correct answers to part (b)(i); IUPAC nomenclature requires an ‘e’ before the numbers. Many correctly identified the diacyl chloride in part (b)(ii) but some failed to give its displayed formula. Although hydrolysis was often correctly identified, part (b)(iii) proved to be difficult, with many offering the breaking of peptide bonds as an explanation and very few identifying attack by the hydroxide ion on the electron deficient carbon as a contributory factor. Part (c)(i) was very well done although a few lost the mark by drawing incomplete structures, notably by omitting the oxygen in the OH of the acid group so giving an aldehyde.

Despite the question in part (c)(iii) stating ‘other than cost’, many students still gave the answer that the anhydride is cheaper. Another common wrong answer was to describe the loss of chlorine rather than hydrogen chloride. Part (d) was correctly answered by half of the students; some of the others lost the mark by careless omission of an oxygen atom and so drew a ketone rather than an ester.

Only the weakest students failed to answer parts (e)(i) and (e)(iii) correctly, but only the top 20% were able to deduce the number of ^{13}C peaks correctly in part (e)(ii).

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Q17.

Part (a) was answered correctly by over half of the students. Careless representation of the C–NO_2 bond lost some students a mark from otherwise correct structures.

The remaining parts were found harder. In part (b), benzene was often given as an incorrect structure for **J**. Missing hydrogen atoms and non–cyclic compounds often lost students marks in part (c), especially for substance **L**.

Students struggled with part (d) and an appreciable number omitted this part completely. Although **M** was identified more frequently than **N**, students demonstrated, as in previous examinations, their lack of understanding of the structures of secondary and tertiary amines.

Q18.

Part (a) was fairly well answered although many lost this mark as they did not specify that the O–H group was in an alcohol. However, students found parts (b)(i) to (b)(iii) quite challenging, often having difficulty expressing their answers clearly if they tried to describe the grouping present in words. Many ignored the integration value and simply copied directly from the Data Sheet. Occasionally, students who had failed to score in parts (b)(i) to (b)(iii) gained the mark for the overall structure in part (b)(iv) while others ignored the information from part (a) that compound **X** contained an alcohol group.

Q19.

There were very few correct answers to part (a), but part (b) was well answered, although some misread the question here and tried to use benzene-1,2-dicarboxylic acid or tetrachloroethene.

Part (c)(i) was quite well done although many wrong answers included CH_2CH_3OH for ethanol or two moles of water.

In part (d), many candidates missed the +. from the molecular ion or put the . on the radical in the wrong place. Several of those who chose to write a formula for the benzene ring in DEP, rather than use the structure given, lost the mark if they gave C_6H_6 rather than C_6H_4 in the formula for the molecular ion and fragment ion.

A surprising number of candidates wrote a chemical equation or included [H_2O] in the rate equation in part (e)(i). Not many candidates scored both marks in part (e)(ii), with many simply referring to more repeats.

Q20.

Part (a) was often interpreted badly, leading to fewer correct answers than usual for this type of question. Candidates often unnecessarily performed two separate tests or chose to do a follow-up test when a single test would have distinguished between the two substances. This created greater opportunity for chemical errors to arise. Many candidates failed to recognise F as an acid and K as a tertiary alcohol.

Although there were many correct answers in part (b), others were poorly expressed. Use of hydroxy rather than ol in the names and omission of di- in part (b)(i) were common mistakes.

Q21.

Apart from part (b), this proved to be a relatively easy question with most candidates

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scoring well. In part (b), as a “stretch and challenge” exercise, the candidates were expected to deduce that there are five possible combinations of the 35 and 37 isotopes of chlorine and hence five molecular ion peaks for TCDD. If it is assumed that all of the chlorine atoms in the compound are the more abundant Cl-35 isotope, the value for its M_r is 320. Statistically, however, with four chlorine atoms present in the molecule, there is a greater likelihood that one of these chlorines will be a Cl-37 so the answer m/z of 322 was also accepted.

Q22.

This question differentiated well and the five sections were found progressively harder by candidates. Over two-thirds scored both marks in part (a) but only a fifth gave both amines correctly in part (e). In part (b) a common wrong answer for **D** was cyclopentane. This clearly has only one ^{1}H peak, but its molecular formula is C_5H_{10} and not C_5H_{12} In part (e) candidates showed a lack of understanding of the structure of secondary amines and many drew NH_2 groups on a central carbon atom of butane.

Q25.

In part (a) most candidates were able to identify the absorption labelled X as due to the presence of the alcohol O–H bond and that labelled Y as due to the presence of the C=O bond. Yet many then drew a carboxylic acid or even an ester as a possible structure. An appreciable number failed to label one of their structures as A. Better candidates scored highly here.

Part (b) discriminated well. Better candidates were able to score (almost) full marks but weak candidates struggled to score more than a few marks. Many had difficulty with the structure of the three branched-chain C5 alkenes; unbranched alkenes were commonly given as were duplicates of a previous answer.

Only the better candidates were able to identify which dibromoalkane gave only three n.m.r. peaks and only the most able were able to deduce correctly the integration ratio and the splitting pattern of the three peaks.

Q27.

Better candidates answered part (a) well, but weaker candidates were unable answer part (a)(iii) correctly and many gave an ester as the suggested structure of **W**. The difference between the wavenumbers of the absorptions of the O—H bond in alcohols and in carboxylic acids was noted by most. However, despite the information given that the proton n.m.r. spectrum had only two peaks, the unbranched pentanoic acid was more common than the correct answer in part (b)(ii). Surprisingly, there were many weak answers to part (c). Tollens' or Fehling's tests were often given despite both structure being ketones.

Q29.

Parts (a) and (d) were the least discriminating, but only the most able were able to identify both **E** and **J** correctly.

In part (b), most were able to identify **C** correctly as either ethanoic acid or methyl methanoate, but many suggested that **D** was ethanoic acid, despite the wavenumber given for the O-H infra-red absorption being that for O-H in alcohols not that for O-H in acids.

Most found **F** easy to deduce, but several forgot that both compounds were esters and

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suggested dimethylpropanoic acid for **E.**

In part (d), **G** was better answered than H and in part (e), more were able to deduce the structure of I correctly than that of **J**.

Q30.

Compound **C** was named correctly by the more able, but the requirement for the number 2 was not appreciated by the weaker candidates. Part (b) was answered well by most, although some did not distinguish between the O-H absorption in alcohols such as compound **D** and the O-H absorption in carboxylic acids. A surprising number of candidates gave the answer 5 in part (c) rather than the expected 4. Answers to part (d) were disappointing even from otherwise good candidates. It seemed that as soon as the ketone **C** was seen, then tests using Fehlings or Tollens' solutions were suggested, without the candidates noticing that **D** was an alcohol and not an aldehyde. Those who chose a correct test usually scored well. Answers to part (e) were better.

Q31.

Part (a) was answered well. Most candidates were able to describe a correct chemical test to distinguish between the aldehyde, propanal, and the ketone, propanone. However, many thought that propanone had two peaks in its proton n.m.r. spectrum.

In part (b), better candidates had no difficulty in identifying propanoic acid as **X** and propan-2-ol as **Y** and in giving correct descriptions of oxidation in Step 1, reduction in Step 2 and esterification in Step 3. Weaker candidates lost marks for incorrect reagents or for wrong or missing conditions in the reactions.

Q32.

Many candidates were able to name ester **X** correctly but fewer could give the correct name for the mechanism involved in the formation of **X** from an acid chloride and an alcohol. Too many candidates also forgot that the mechanism initially involves addition in which the C=O bond becomes C-O and then, subsequently, the C=O bond is reformed in the second step which involves elimination. Better candidates were able to state that Spectrum 2 was that of ester **X**, but many did not explain their deduction clearly. Both spectra contain a peak in the δ range 3.7 - 4.1 which could apply to an ester, and this statement alone was insufficient. It was necessary to state that for **X**, the absorption in this region must be a singlet or have an integration value 3. Despite the statement in the question that **Y** was "an isomeric ester", many suggestions for the structure of **Y** were not those of esters.

Q33.

Relatively few candidates scored high marks in part (a). Most candidates knew the type of isomerism shown by butenedioic acid and were able to draw correct structures of the two isomers. Only the best candidates then went on to deduce which isomer would readily form an anhydride and drew its structure correctly.

Many candidates identified a correct electrophile in part (b) and outlined an accurate mechanism but lost marks when their structures were inaccurately drawn. Sadly, a significant number of weaker candidates scored no marks in part (b) as their answers incorrectly referred to an attack by a nucleophile.

Although the structure of butenedioic acid was given in the question, a number candidates lost marks when they gave an incorrect structure in their answer to part (c). Others failed

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to recognise the acid-base nature of the reaction and gave equations for addition or substitution reactions. One mark was lost by candidates who reacted the acid with one, rather than two, moles of NaOH.

Part (d) was generally well done and many candidates deduced correctly that there were just two different proton environments. Many, however, lost one mark when they stated incorrectly that the two peaks would be doublets.

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