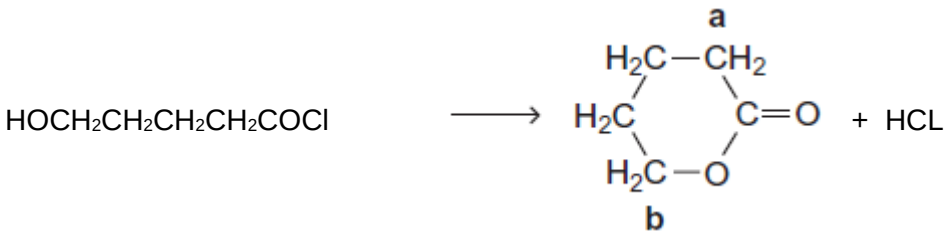
Q23.

This question is about some isomers of $C_5H_8O_2$

(a) Compound **H** is a cyclic ester that can be prepared as shown.

On the structure of **H**, two of the carbon atoms are labelled.



H

(i) Name and outline a mechanism for this reaction.

Use **Table C** on the Data Sheet to give the ^{13}C n.m.r. δ value for the carbon atom labelled **a** and the δ value for the carbon atom labelled **b**.

(7)

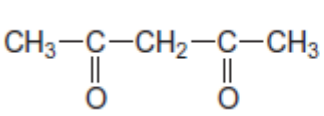
(ii) $HOCH_2CH_2CH_2CH_2COCl$ can also react to form a polyester in a mechanism similar to that in part (i).

Draw the repeating unit of the polyester and name the type of polymerisation involved.

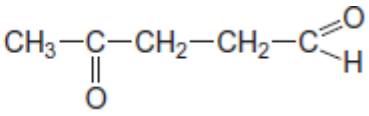
(2)

(b) State how you could distinguish between compounds **J** and **K** by a simple test-tube reaction.

State how you could distinguish between **J** and **K** by giving the number of peaks in the ^1H n.m.r. spectrum of each compound.



J



K

(5)

(c) Draw the structure of each of the following isomers of $C_5H_8O_2$
Label each structure you draw with the correct letter **L**, **M**, **N**, **P** or **Q**.

L is methyl 2-methylpropenoate.

M is an ester that shows E-Z stereoisomerism.

N is a carboxylic acid with a branched carbon chain and does **not** show stereoisomerism.

P is an optically active carboxylic acid.

Q is a cyclic compound that contains a ketone group and has only two peaks in its ^{1}H n.m.r. spectrum.

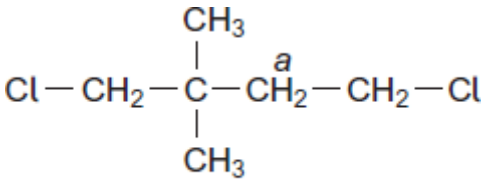
(5)

(Total 19 marks)

Q24.

N.m.r. spectroscopy can be used to study the structures of organic compounds.

(a) Compound **J** was studied using ^{1}H n.m.r. spectroscopy.



J

(i) Identify a solvent in which **J** can be dissolved before obtaining its ^{1}H n.m.r. spectrum.

_____

(1)

(ii) Give the number of peaks in the ^{1}H n.m.r. spectrum of **J**.

_____

(1)

(iii) Give the splitting pattern of the protons labelled *a*.

_____

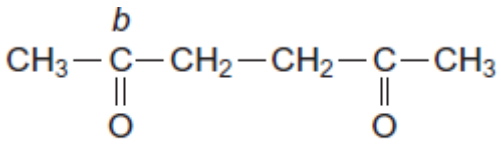
(1)

(iv) Give the IUPAC name of **J**.

_____

(1)

(b) Compound **K** was studied using ^{13}C n.m.r. spectroscopy.



K

(i) Give the number of peaks in the ^{13}C n.m.r. spectrum of **K**.

_____

(1)

(ii) Use **Table 3** on the Data Sheet to suggest a δ value of the peak for the carbon labelled *b*.

_____

(1)

(iii) Give the IUPAC name of **K**.

_____

(1)

(Total 7 marks)

Q25.

This question concerns isomers of $C_6H_{12}O_2$ and how they can be distinguished using n.m.r. spectroscopy.

(a) The non-toxic, inert substance TMS is used as a standard in recording both ^1H and ^{13}C n.m.r. spectra.

(i) Give **two** other reasons why TMS is used as a standard in recording n.m.r. spectra.

Reason 1 _____

_____

Reason 2 _____

_____

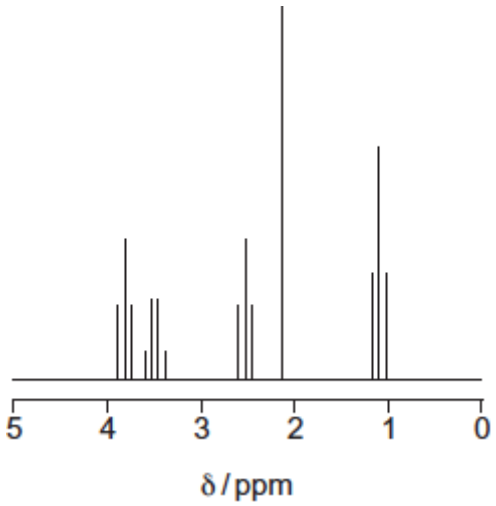
(2)

(ii) Give the structural formula of TMS.

(1)

(b) The proton n.m.r. spectrum of compound **P** ($C_6H_{12}O_2$) is represented in **Figure 1**.

Figure 1



The integration trace gave information about the five peaks as shown in **Figure 2**.

Figure 2

δ / ppm	3.8	3.5	2.6	2.2	1.2
Integration ratio	2	2	2	3	3

(i) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peak at δ 2.2.

(1)

(ii) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peaks at δ 3.5 and 1.2.

(1)

(iii) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peaks at δ 3.8 and 2.6.

(1)

(iv) Deduce the structure of **P**.

(1)

(c) These questions are about different isomers of **P** ($C_6H_{12}O_2$).

(i) Draw the structures of the two esters that both have only two peaks in their proton n.m.r. spectra. These peaks both have an integration ratio of 3:1.

Ester 1

Ester 2

(2)

(ii) Draw the structure of an optically active carboxylic acid with five peaks in its ^{13}C n.m.r. spectrum.

(1)

(iii) Draw the structure of a cyclic compound that has only two peaks in its ^{13}C n.m.r. spectrum and has no absorption for C = O in its infrared spectrum.

(1)
(Total 11 marks)

Q26.

Acyl chlorides and acid anhydrides are important compounds in organic synthesis.

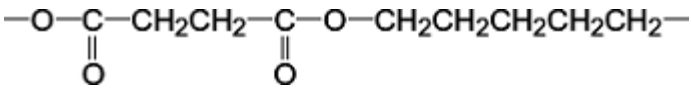
(a) Outline a mechanism for the reaction of CH_3CH_2COCl with CH_3OH and name the organic product formed.

Mechanism

Name of organic product _____

(5)

(b) A polyester was produced by reacting a diol with a diacyl chloride. The repeating unit of the polymer is shown below.



(i) Name the diol used.

_____

(1)

(ii) Draw the displayed formula of the diacyl chloride used.

(1)

(iii) A shirt was made from this polyester. A student wearing the shirt accidentally splashed aqueous sodium hydroxide on a sleeve. Holes later appeared in the sleeve where the sodium hydroxide had been.

Name the type of reaction that occurred between the polyester and the aqueous sodium hydroxide. Explain why the aqueous sodium hydroxide reacted with the polyester.

Type of reaction _____

Explanation _____

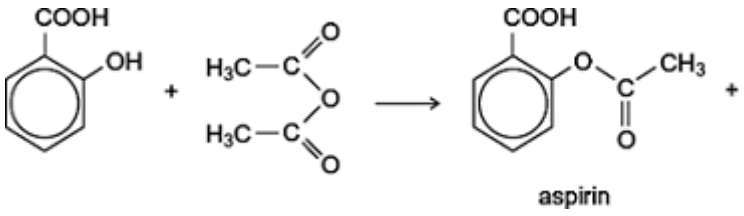
_____

_____

_____

(3)

(c) (i) Complete the following equation for the preparation of aspirin using ethanoic anhydride by writing the structural formula of the missing product.



(1)

(ii) Suggest a name for the mechanism for the reaction in part (c)(i).

_____

(1)

(iii) Give **two** industrial advantages, other than cost, of using ethanoic anhydride rather than ethanoyl chloride in the production of aspirin.

Advantage 1 _____

_____

_____

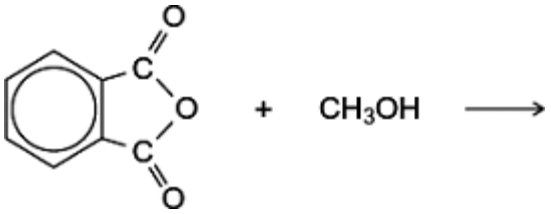
Advantage 2 _____

_____

_____

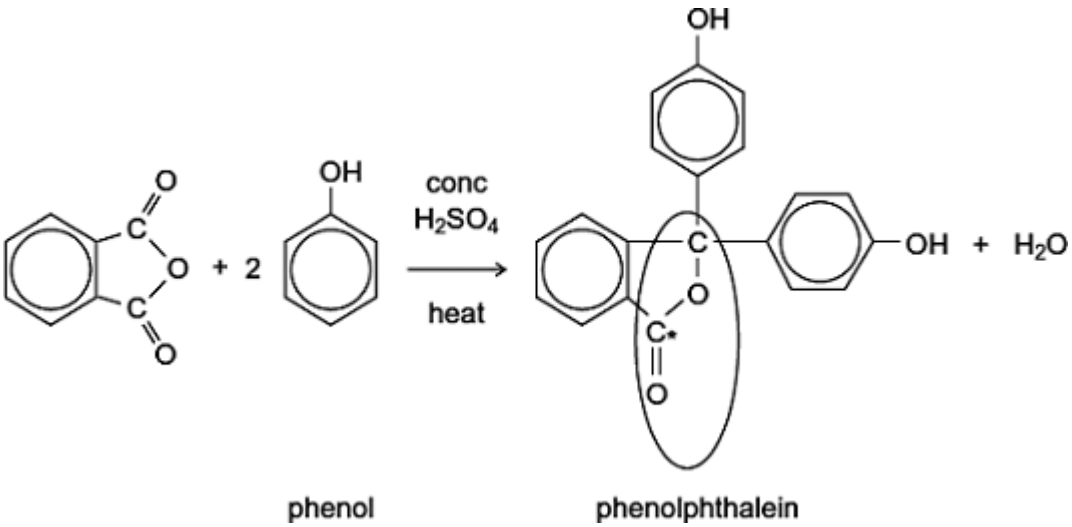
(2)

(d) Complete the following equation for the reaction of one molecule of benzene-1,2-dicarboxylic anhydride (phthalic anhydride) with one molecule of methanol by drawing the structural formula of the single product



(1)

(e) The indicator phenolphthalein is synthesised by reacting phthalic anhydride with phenol as shown in the following equation.



(i) Name the functional group ringed in the structure of phenolphthalein.

_____

(1)

(ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of phenolphthalein.

_____

(1)

(iii) One of the carbon atoms in the structure of phenolphthalein shown above is labelled with an asterisk (*).
Use **Table 3** on the Data Sheet to suggest a range of δ values for the peak due to this carbon atom in the ^{13}C n.m.r. spectrum of phenolphthalein.

_____

(1)

(f) Phenolphthalein can be used as an indicator in some acid–alkali titrations.
The pH range for phenolphthalein is 8.3 – 10.0

(i) For **each** acid.alkali combination in the table below, put a tick (✓) in the box if phenolphthalein could be used as an indicator.

Acid	**Alkali**	**Tick box (✓)**
sulfuric acid	sodium hydroxide	
hydrochloric acid	ammonia	
ethanoic acid	potassium hydroxide	
nitric acid	methylamine	

(2)

(ii) In a titration, nitric acid is added from a burette to a solution of sodium hydroxide containing a few drops of phenolphthalein indicator.
Give the colour **change** at the end-point.

_____

(1)

(Total 21 marks)

Q27.

When the molecular formula of a compound is known, spectroscopic and other analytical techniques can be used to distinguish between possible structural isomers.

Draw **one** possible structure for each of the compounds described in parts (a) to (d).

(a) Compounds **F** and **G** have the molecular formula $C_6H_4N_2O_4$ and both are dinitrobenzenes.
F has two peaks in its ^{13}C n.m.r. spectrum.
G has three peaks in its ^{13}C n.m.r. spectrum.

F **G**

(2)

(b) Compounds **H** and **J** have the molecular formula C_6H_{12}.
Both have only one peak in their ^{1}H n.m.r. spectra.
H reacts with aqueous bromine but **J** does not.

H **J**

(2)

(c) **K** and **L** are cyclic compounds with the molecular formula $C_6H_{10}O$.
Both have four peaks in their ^{13}C n.m.r. spectra.
K is a ketone and **L** is an aldehyde.

K **L**

(2)

(d) Compounds **M** and **N** have the molecular formula $C_6H_{15}N$.
M is a tertiary amine with only two peaks in its ^1H n.m.r. spectrum.
N is a secondary amine with only three peaks in its ^1H n.m.r. spectrum.

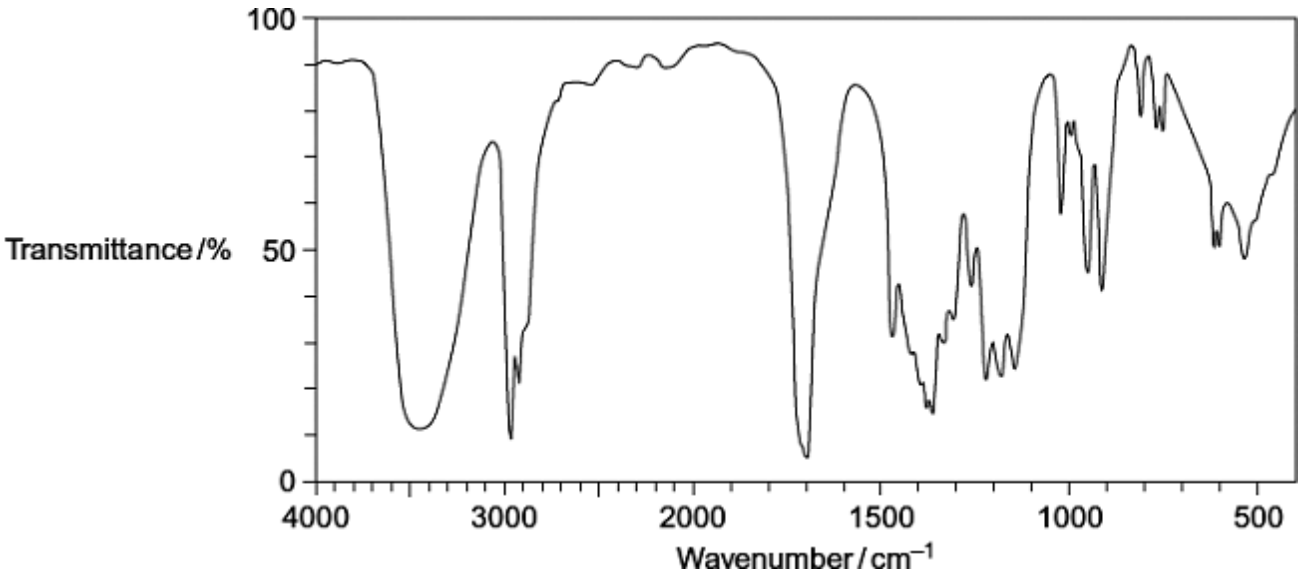
M **N**

(2)
(Total 8 marks)

Q28.

Compound **X** ($C_6H_{12}O_2$) was analysed by infrared spectroscopy and by proton nuclear magnetic resonance spectroscopy.

(a) The infrared spectrum of **X** is shown below.
Use **Table 1** on the Data Sheet to help you answer the question.



Identify the functional group that causes the absorption at 3450cm^{-1} in the spectrum.

_____

(1)

(b) The proton n.m.r. spectrum of **X** consists of 4 singlet peaks.

The table below gives the chemical shift for each of these peaks, together with their integration values.

δ /ppm	1.2	2.2	2.6	3.8
Integration value	6	3	2	1

Use **Table 2** on the Data Sheet to help you answer the following questions.

Use the chemical shift and the integration data to show what can be deduced about the structure of **X** from the presence of the following in its proton n.m.r. spectrum.

(i) The peak at δ = 2.6

(1)

(ii) The peak at δ = 2.2

(1)

(iii) The peak at δ = 1.2

(1)

(iv) Deduce the structure of **X** ($C_6H_{12}O_2$)

(1)

(Total 5 marks)

Mark Scheme

Q23.

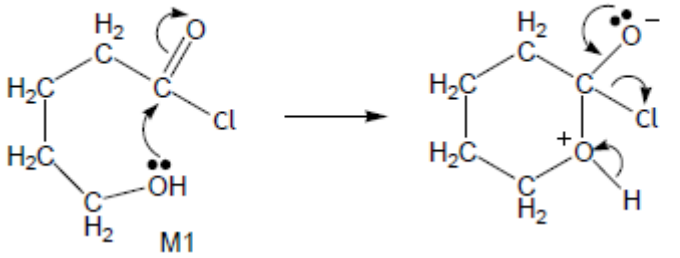
(a) (i) (nucleophilic) addition-elimination

Not electrophilic addition-elimination

Ignore esterification

1

M2



M4 for 3 arrows and lp

M1

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

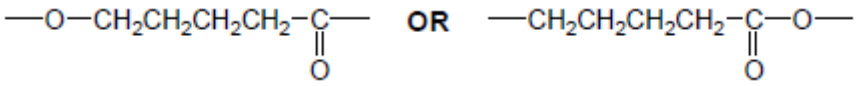
If values not specified as a or b then assume first is a.

1

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

1

(ii)



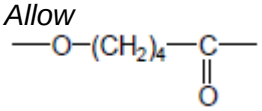
OR

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

1

J Two (peaks)

Allow trough, peak, spike.

1

K Four (peaks)

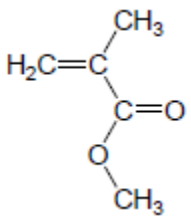
Ignore details of splitting.

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–.

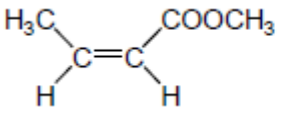
Allow -CO_2CH_3 etc.

Allow $CH_2C(CH_3)COOCH_3$.

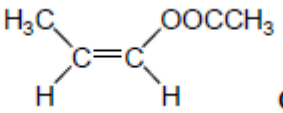
1

M

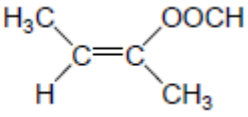
ester



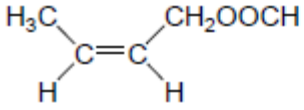
OR



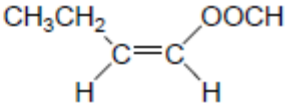
OR



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



OR



OR

$CH_3CH=CHCH_2OOCH$ $CH_3CH_2CH=CHOOCH$

Allow either E–Z isomer.

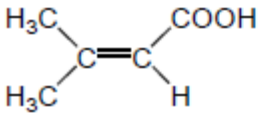
Allow CH_3– or C_2H_5– but not CH_2CH_3–.

Allow $CH_3CHCHCOOCH_3$ etc.

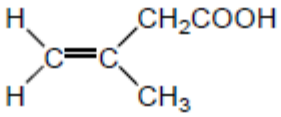
1

N

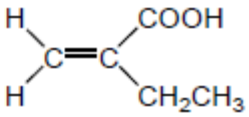
acid



OR



OR



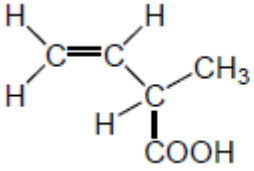
$(CH_3)_2C=CHCOOH$ $H_2C=C(CH_3)CH_2COOH$ $H_2C=C(COOH)CH_2CH_3$

Allow CH_3– or C_2H_5– but not CH_2CH_3–.

Allow –CO_2H.

Not cyclic isomers.

Not the optically active isomer.



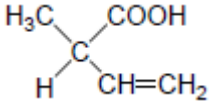
which is P anyway

Allow $(CH_3)_2CCHCOOH$ etc.

1

P

acid



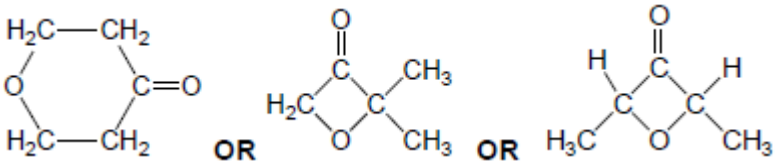
Allow –CO_2H.

$CH_3CH(COOH)CH=CH_2$

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

1

Q



Not cyclic esters.

1

[19]

Q24.

(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]

Q25.

(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

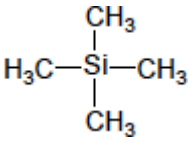
OR

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

Ignore mention of solubility

2

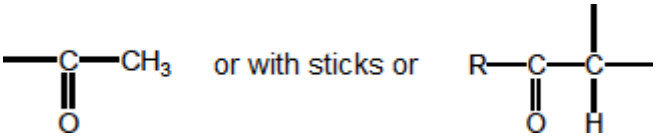
(ii)



Allow $Si(CH_3)_4$

1

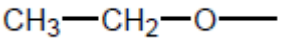
(b) (i)



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

1

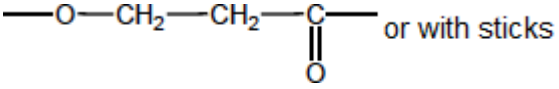
(ii)



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

1

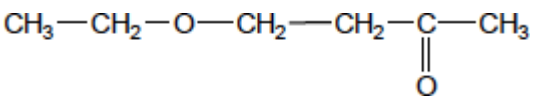
(iii)



Ignore missing trailing bonds
Ignore charges as if MS fragment

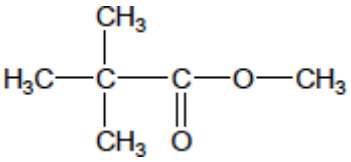
1

(iv)



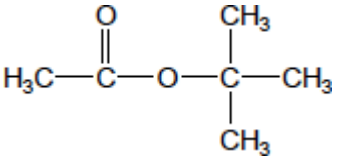
1

(c) (i) Check structure has 6 carbons



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

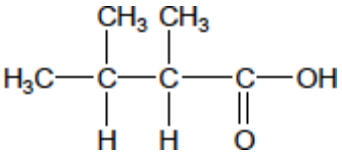
1



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

1

(ii) Check structure has 6 carbons

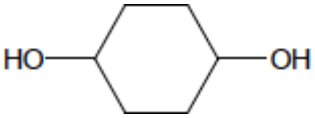


Allow $(CH_3)_2CHCH(CH_3)COOH$ or $(CH_3)_2CHCH(CH_3)CO_2H$

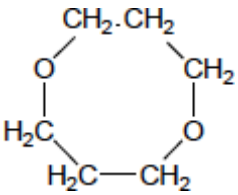
Penalise C_3H_7

1

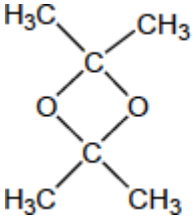
(iii) Check structure has 6 carbons



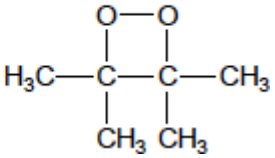
OR



Allow



OR

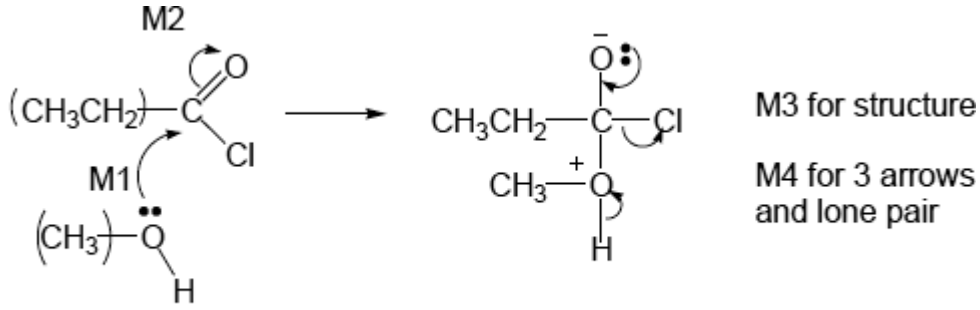


1

[11]

Q26.

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

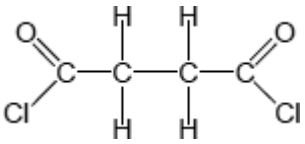
4

(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

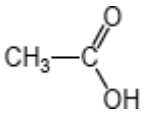
M3 reacts with OH^- or hydroxide ion

1

Not reacts with NaOH

1

(c) (i)



Allow CH_3COOH or CH_3CO_2H

1

(ii) (nucleophilic) addition-elimination

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

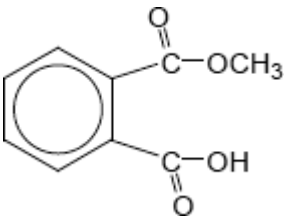
- less corrosive
- less vulnerable to hydrolysis
- less dangerous to use,
- less violent/exothermic/vigorous reaction OR more controllable rxn
- does not produce toxic/corrosive/harmful fumes (of HCl) OR does not produce HCl
- less volatile

***NOT** COST*

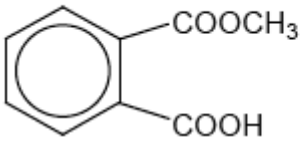
List principle beyond two answers

2

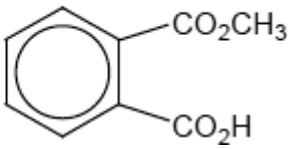
(d)



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) Pink to colourless

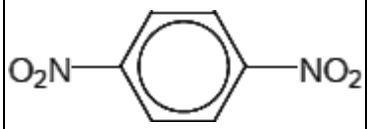
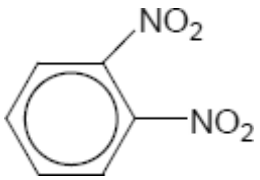
Allow 'red' OR 'purple' OR 'magenta' instead of 'pink'
*Do **not** allow 'clear' instead of 'colourless'*

1

[21]

Q27.

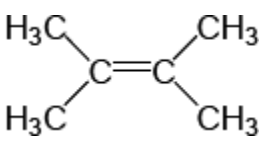
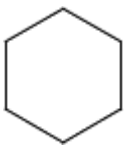
(a)

F	G
	

Penalize $-O_2N$ once
Penalise missing circle once
Don't penalise attempt at bonding in NO_2

1

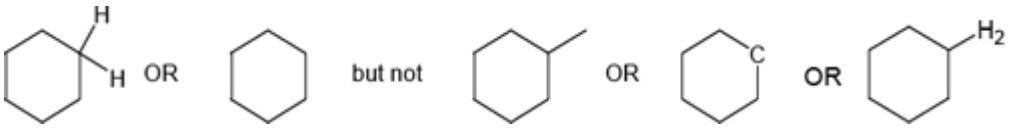
(b)

H	J
	

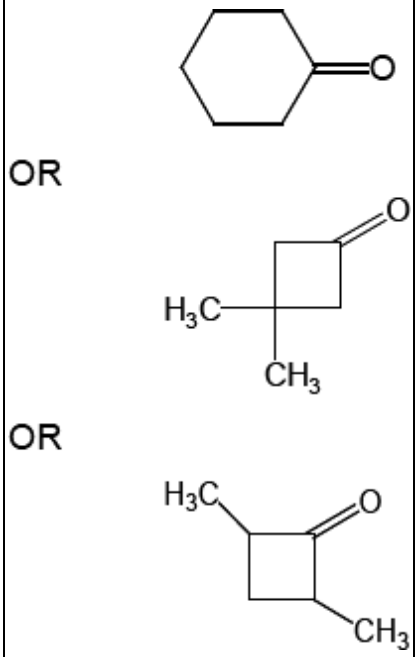
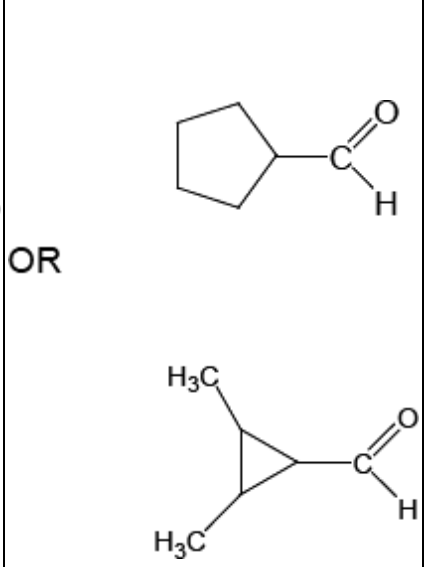
*If **both H** and **J** correct but reversed, award one mark*

1

A carbon in saturated ring structures should be shown as

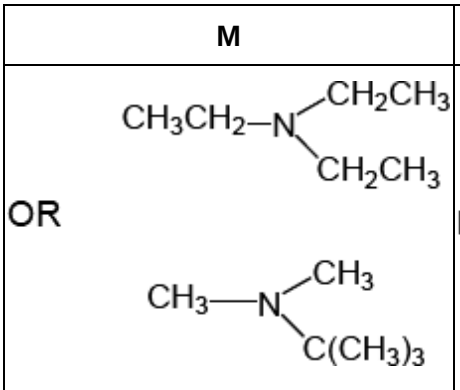
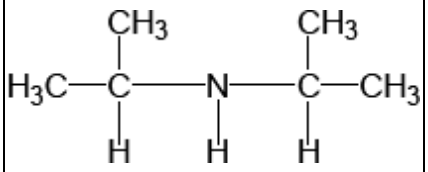


(c)

K	L
	

1

(d)

M	N
	

Allow C_2H_5 but
NOT allow C_4H_9 or C_3H_7

1
1

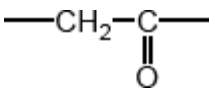
[8]

Q28.

(a) OH alcohols

1

(b) (i) 2.6



Ignore any group on RHS

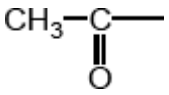
*Must clearly indicate relevant **two** H on a C next to C=O*

On LHS, penalise H or CH or CH_2 or CH_3

Ignore missing trailing bonds or attached R groups

1

(ii) 2.2



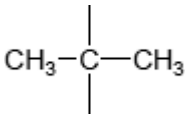
Ignore all groups on RHS

*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 equivalent CH_3 groups

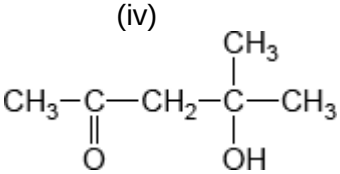
Must clearly indicate two equivalent methyl groups.

Penalise attached H

Ignore missing trailing bonds or attached R groups

1

(iv)



1

[5]