

1 Butanone is reduced in a two-step reaction using NaBH_4 followed by dilute hydrochloric acid.

(a) Write an overall equation for the reduction of butanone using $[\text{H}]$ to represent the reductant.

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(1)

(b) By considering the mechanism of the reaction, explain why the product has **no** effect on plane polarised light.

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(6)
(Total 7 marks)

2 Which compound forms optically active compounds on reduction?

A $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{CHCH}_3$

B $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$

C CH_3COCH_3

D $\text{CH}_3\text{CH}_2\text{COCH}_3$

(Total 1 mark)

3

The carbonyl compound $\text{CH}_3\text{CH}_2\text{CHO}$ reacts very slowly with HCN

(a) Name and outline a mechanism for the reaction of $\text{CH}_3\text{CH}_2\text{CHO}$ with HCN

Name of mechanism

Mechanism

(5)

(b) The reaction in part (a) produces a pair of enantiomers.

(i) Draw the structure of each enantiomer to show how they are related to each other.

(2)

(ii) State and explain how you could distinguish between the two enantiomers.

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(2)

(c) Give the IUPAC name of the product of the reaction in part (a).

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(1)

(d) In practice, KCN rather than HCN is added to the carbonyl compound.

Given that K_a for HCN = $4.0 \times 10^{-10} \text{ mol dm}^{-3}$, suggest why the reaction with HCN is very slow.

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(2)

(e) Acrylic fibres are used as a substitute for wool. Acrylics are copolymers of acrylonitrile with other compounds.

Acrylonitrile is the common name for the following compound.



(i) Acrylonitrile can be formed from propene.

Write an equation for the reaction of propene with ammonia and oxygen to form acrylonitrile and one other product.

.....

(1)

(ii) The term copolymer is used to describe the product obtained when two or more different monomers form a polymer.

Draw the repeating unit of the acrylic copolymer that contains 75% acrylonitrile monomer and 25% chloroethene monomer.

(1)

(iii) Name the type of polymerisation involved in part (ii)

.....

(1)

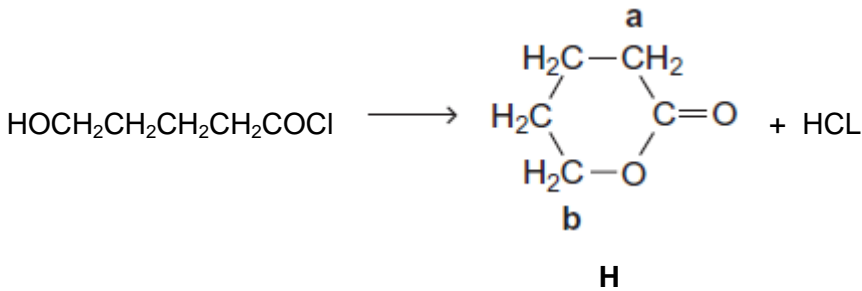
(Total 15 marks)

4

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.



(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**.

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(7)

- (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.

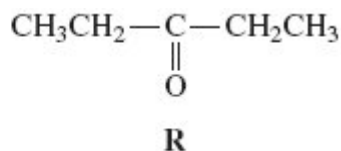
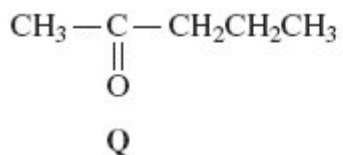
P is an optically active carboxylic acid.

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

(5)
(Total 19 marks)

5

Two isomeric ketones are shown below.



- (a) Name and outline a mechanism for the reaction of compound **Q** with HCN and name the product formed.

Name of mechanism

Mechanism

Name of product

(6)

(b) Some students were asked to suggest methods to distinguish between isomers **Q** and **R**.

One student suggested testing the optical activity of the products formed when **Q** and **R** were reacted separately with HCN.

By considering the optical activity of these products formed from **Q** and **R**, explain why this method would **not** distinguish between **Q** and **R**.

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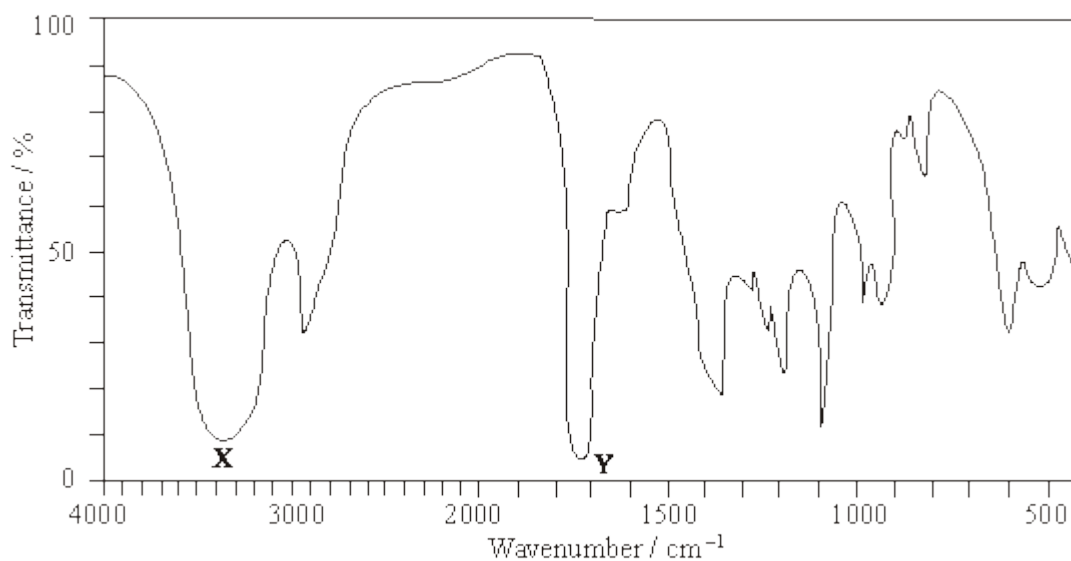
.....

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(3)
(Total 9 marks)

6

(a) The infra-red spectrum of compound **A**, $C_3H_6O_2$, is shown below.



Identify the functional groups which cause the absorptions labelled **X** and **Y**.

Using this information draw the structures of the three possible structural isomers for **A**.

Label as **A** the structure which represents a pair of optical isomers.

(6)

(b) Draw the structures of the three **branched-chain** alkenes with molecular formula C_5H_{10}

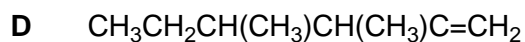
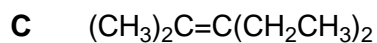
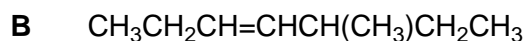
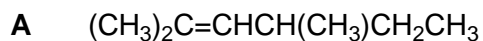
Draw the structures of the three dibromoalkanes, $C_5H_{10}Br_2$, formed when these three alkenes react with bromine.

One of these dibromoalkanes has only three peaks in its proton n.m.r. spectrum. Deduce the integration ratio and the splitting patterns of these three peaks.

(10)
(Total 16 marks)

7

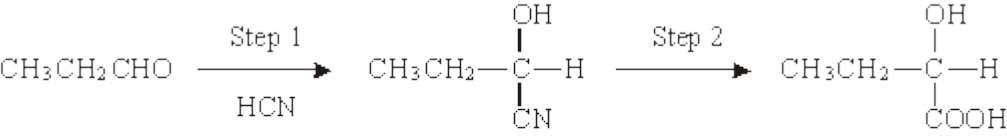
Which one of the following can exhibit both geometrical and optical isomerism?



(Total 1 mark)

8

Consider the reaction sequence shown below.



propanal

Q

(a) Name and outline a mechanism for the reaction in Step 1.

Name of mechanism

Mechanism

(5)

- (b) (i) Name compound **Q** formed in Step 2.

.....

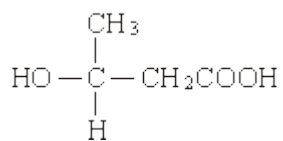
- (ii) Two stereoisomers are formed by the dehydration of **Q**. Give the structures of these two isomers and name the type of stereoisomerism shown.

Structures of isomers

Type of stereoisomerism

(4)

- (c) An isomer of **Q** which has the structure shown below is polymerised to form the biodegradable polymer known as PHB.



- (i) Draw the repeating unit of the polymer PHB.

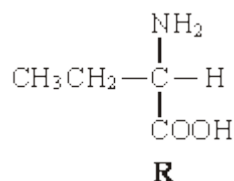
- (ii) Suggest a reason why the polymer is biodegradable.

.....

.....

(2)

(d) The amino acid **R** is shown below.



- (i) Draw the structure of the zwitterion formed by **R**.
- (ii) Draw the structure of the major organic product formed when an excess of **R** is reacted with bromomethane.
- (iii) Name the mechanism of the reaction which results in the formation of the product given in part (ii).

.....

(3)
(Total 14 marks)

9 Which one of the following reactions will produce an organic compound that has optical isomers?

- A** dehydration of butan-2-ol by heating with concentrated sulphuric acid
- B** reduction of pentan-3-one by warming with NaBH_4
- C** addition of Br_2 to 3-bromopropene
- D** reduction of 2,3-dimethylpent-2-ene with H_2 in the presence of a nickel catalyst

(Total 1 mark)

10

Each of the parts (a) to (e) below concerns a different pair of isomers.

Draw one possible structure for each of the species **A** to **J**, using Table 2 on the Data Sheet where appropriate.

- (a) Compounds **A** and **B** have the molecular formula C_5H_{10}
A decolourises bromine water but **B** does not.

A **B**

(2)

- (b) Compounds **C** and **D** have the molecular formula $C_2H_4O_2$

Each has an absorption in its infra-red spectrum at about 1700 cm^{-1} but only **D** has a broad absorption at 3350 cm^{-1}

C **D**

(2)

- (c) Compounds **E** and **F** are esters with the molecular formula $C_5H_{10}O_2$

The proton n.m.r. spectrum of **E** consists of two singlets only whereas that of **F** consists of two quartets and two triplets.

E **F**

(2)

- (d) Compounds **G** and **H** have the molecular formula $C_3H_6C_{12}$. **G** shows optical activity but **H** does not.

G H

(2)

- (e) Compounds **I** and **J** have the molecular formula C_6H_{12}

Each has an absorption in its infra-red spectrum at about 1650 cm^{-1} and neither shows geometrical isomerism. The proton n.m.r. spectrum of **I** consists of a singlet only whereas that of **J** consists of a singlet, a triplet and a quartet.

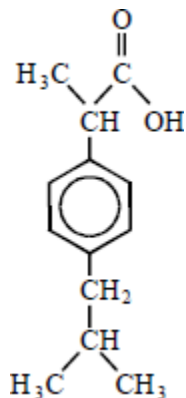
I J

(2)

(Total 10 marks)

11

Ibuprofen is a drug used as an alternative to aspirin for the relief of pain, fever and inflammation. The structure of ibuprofen is shown below.



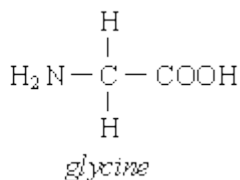
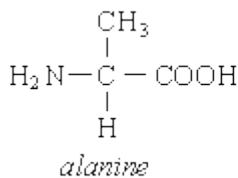
Which one of the following statements is **not** correct?

- A It has optical isomers.
- B It liberates carbon dioxide with sodium carbonate solution.
- D It undergoes esterification with ethanol.
- D It undergoes oxidation with acidified potassium dichromate(VI).

(Total 1 mark)

12

The structures of the amino acids *alanine* and *glycine* are shown below.



- (a) Give the systematic name for *alanine*.

.....

(1)

- (b) *Alanine* exists as a pair of stereoisomers.

- (i) Explain the meaning of the term *stereoisomers*.

.....

(ii) State how you could distinguish between the stereoisomers.

.....
.....
.....

(4)

(c) Give the structural formula of the species formed by *glycine* at pH 14.

(1)

(d) When two amino acids react together, a dipeptide is formed. Give the structural formulae of the **two** dipeptides which are formed when *alanine* and *glycine* react together.

Dipeptide 1

Dipeptide 2

(2)

- (e) Give the structural formula of the organic compound formed when *glycine* reacts with methanol in the presence of a small amount of concentrated sulphuric acid.

(1)
(Total 9 marks)

13

Which one of the following statements about but-2-enal, $\text{CH}_3\text{CH}=\text{CHCHO}$, is **not** true?

- A It has stereoisomers.
- B It shows a strong absorption in the infra-red at about 1700 cm^{-1} .
- C It will turn an acidified solution of potassium dichromate(VI) green.
- D It can be dehydrated by concentrated sulphuric acid.

(Total 1 mark)

14

(a) **P**, **Q** and **R** have the molecular formula C_6H_{12}

All three are branched-chain molecules and none is cyclic.

P can represent a pair of optical isomers.

Q can represent a pair of geometrical isomers.

R can represent another pair of geometrical isomers different from **Q**.

Draw one possible structure for one of the isomers of each of **P**, **Q** and **R**.

Structure of **P**

Structure of **Q**

Structure of **R**

(3)

(b) Butanone reacts with reagent **S** to form compound **T** which exists as a racemic mixture. Dehydration of **T** forms **U**, C_5H_7N , which can represent a pair of geometrical isomers.

(i) State the meaning of the term *racemic mixture* and suggest why such a mixture is formed in this reaction.

Racemic mixture

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Explanation.....

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- (ii) Identify reagent **S**, and draw a structural formula for each of **T** and **U**.

Reagent **S**

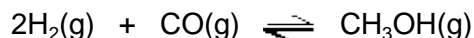
Compound **T**

Compound **U**

(6)
(Total 9 marks)

15

Hydrogen and carbon monoxide were mixed in a 2:1 mole ratio. The mixture was allowed to reach equilibrium according to the following equation at a fixed temperature and a total pressure of 1.75×10^4 kPa.



- (a) The equilibrium mixture contained 0.430 mol of carbon monoxide and 0.0850 mol of methanol.

- (i) Calculate the number of moles of hydrogen present in the equilibrium mixture.

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- (ii) Hence calculate the mole fraction of hydrogen in the equilibrium mixture.

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.....

.....

- (iii) Calculate the partial pressure of hydrogen in the equilibrium mixture.

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.....

(5)

(b) In a different mixture of the three gases at equilibrium, the partial pressure of carbon monoxide was 7550 kPa, the partial pressure of hydrogen was 12300 kPa and the partial pressure of methanol was 2710 kPa.

(i) Write an expression for the equilibrium constant, K_p , for this reaction.

.....

(ii) Calculate the value of the equilibrium constant, K_p , for the reaction under these conditions and state its units.

K_p

.....

Units

(3)

(c) Two isomeric esters **E** and **F** formed from methanol have the molecular formula $C_6H_{12}O_2$

Isomer **E** has only 2 singlet peaks in its proton n.m.r. spectrum.

Isomer **F** is optically active.

Draw the structures of these two isomers.

Isomer E

Isomer F

(2)
(Total 10 marks)

16

On reduction, a racemate can be formed by

- A $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$
- B $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$
- C $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$
- D $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CHO}$

(Total 1 mark)

17

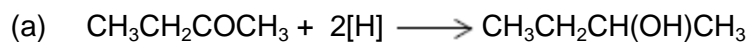
Which one of the following reaction mixtures would give a product capable of exhibiting optical isomerism?

- A $\text{CH}_3\text{CH}=\text{CH}_2$ + HBr
- B $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ + NaOH
- C $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ + H_2SO_4
- D $\text{CH}_3\text{CH}_2\text{CHO}$ + HCN

(Total 1 mark)

Mark schemes

1



1

- (b) This question is marked using levels of response. Refer to the Mark Scheme Instructions for Examiners for guidance on how to mark this question.

All stages are covered and the explanation of each stage is generally correct and virtually complete.

Answer is communicated coherently and shows a logical progression from stage 1 to stage 2 then stage 3.

Level 3
5 – 6 marks

All stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies OR two stages are covered and the explanations are generally correct and virtually complete.

Answer is mainly coherent and shows progression from stage 1 to stage 3.

Level 2
3 – 4 marks

Two stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies, OR only one stage is covered but the explanation is generally correct and virtually complete.

Answer includes isolated statements but these are not presented in a logical order or show confused reasoning.

Level 1
1 – 2 marks

Insufficient correct chemistry to gain a mark.

Level 0
0 marks

Indicative Chemistry content

Stage 1: Formation of product

- Nucleophilic attack
- Planar carbonyl group
- H⁻ attacks from either side (stated or drawn)

Stage 2: Nature of product

- Product of step 1 shown
- This exists in two chiral forms (stated or drawn)
- Equal amounts of each enantiomer / racemic mixture formed

Stage 3: Optical activity

- Optical isomers / enantiomers rotate the plane of polarised light equally in
- With a racemic / equal mixture the effects cancel

6

[7]

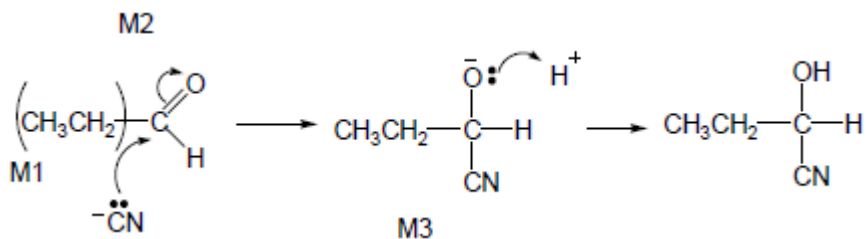
2 D

[1]

3 (a) Nucleophilic addition

1

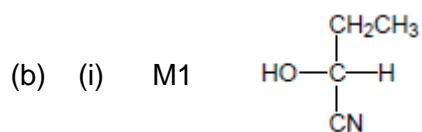
M4 for lp, arrow and H+



Allow C₂H₅- for CH₃CH₂-

- M1 and M4 include lone pair and curly arrow.
- Allow: CN⁻ but arrow must start at lone pair on C.
- M2 not allowed independent of M1, but allow M1 for correct attack on C⁺.
- + rather than δ⁺ on C=O loses M2.
- Penalise incorrect partial charges.
- M3 is for correct structure including minus sign but lone pair is part of M4.
- Penalise extra curly arrows in M4.

4



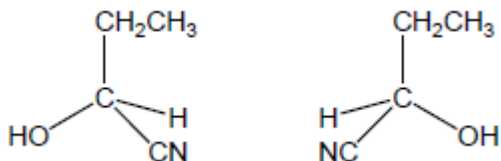
M1 for correct structure of product of part (a).

Allow C₂H₅- for CH₃CH₂-.

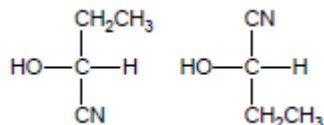
Penalise wrongly bonded, OH or CN or CH₂CH₃ once only in clip.

1

M2

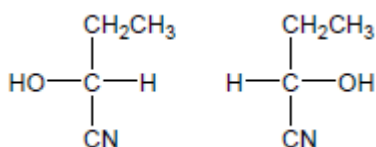


M2 cannot be gained by simply swapping two or more groups with no attempt to show a mirror image., e.g. do not allow M2 for



because these do not show the enantiomers as mirror images.

Students must show an attempt at mirror images, eg allow

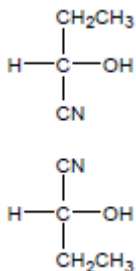


ie vertical groups same and horizontal swapped as if there was a mirror between them

No mirror need be shown

Do not penalize wedge bond when wedge comes into contact with both C & N

However these two could score M2 if placed as below as if with a "mirror" horizontally between them.



1

- (ii) M1 (Plane) polarized light
M2 *only scores following correct M1*

1

M2 Rotated in opposite directions (equally) (only allow if M1 correct or close)

Not just in different directions but allow one rotates light to the left and one to the right.

Not molecules rotate.

1

- (c) 2-hydroxybutane(-1-)nitrile

1

- (d) Weak acid / (acid) only slightly / partially dissociated / ionised
Ignore rate of dissociation.

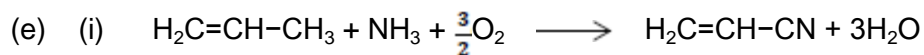
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[CN⁻] very low

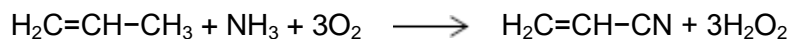
Allow (very) few cyanide ions.

Mark independently.

1



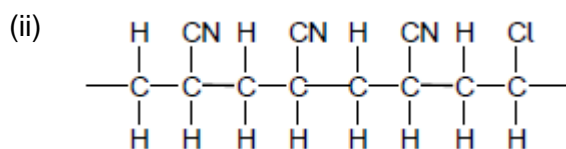
OR



OR doubled.

Allow C₃H₆ and CH₂CHCN or C₃H₃N on this occasion only.

1

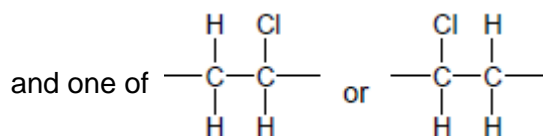
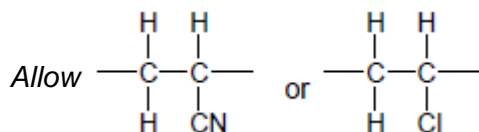
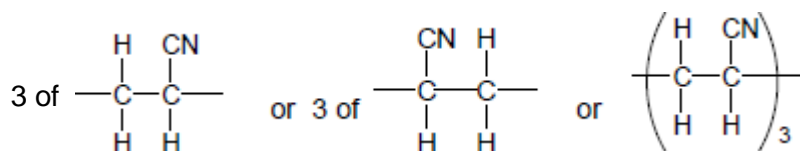


Ignore n.

Must show trailing bonds.

Do not penalise C–NC bond here on this occasion.

Must contain, in any order,



Allow –CH₂CH(CN)CH₂CHCl– etc.

1

- (iii) Addition (polymerization)

Allow self-addition.

Do not allow additional.

1

[15]

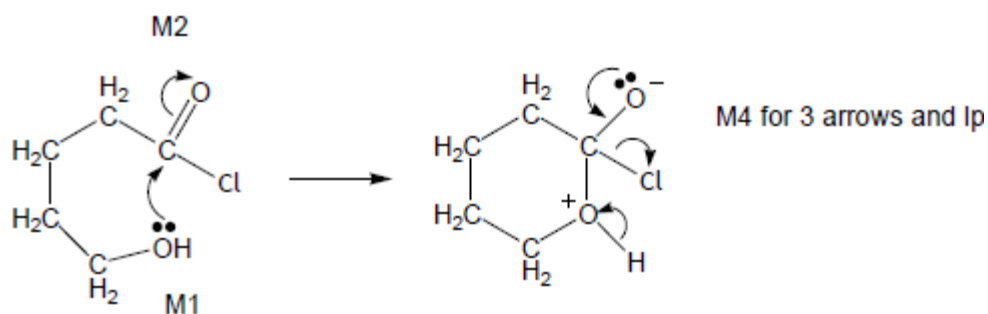
4

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

Not electrophilic addition-elimination

Ignore esterification

1



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 with charges but lone pair on O is part of M4.*
- *Only allow M4 after correct / very close M3.*
- *Ignore HCl shown as a product.*

4

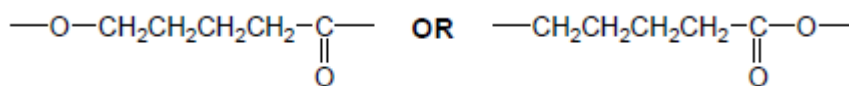
a 20-50 (ppm) or single value or range entirely within this range
If values not specified as a or b then assume first is a.

1

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

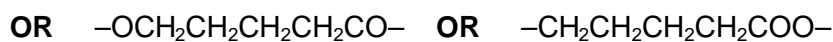
1

(ii)

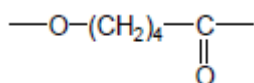


Must have trailing bonds, but ignore n.

1



Allow



but not $\text{—C}_4\text{H}_8\text{—}$

one unit only

Condensation

1

(b)

	Tollens'	Fehling's / Benedict's	Acidified potassium dichromate
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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
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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
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1

J Two (peaks)

Allow trough, peak, spike.

1

K Four (peaks)

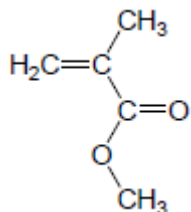
Ignore details of splitting.

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 $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COOCH}_3$

All $\text{C}_5\text{H}_8\text{O}_2$ L to P must have $\text{C}=\text{C}$.

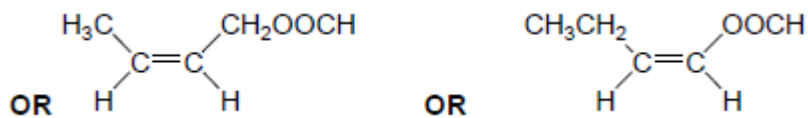
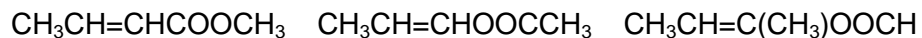
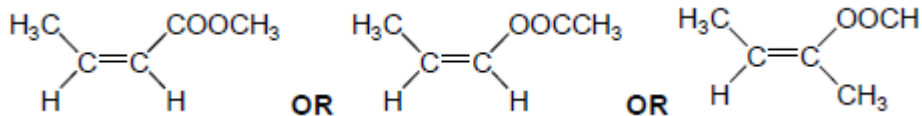
Allow CH_3^- .

Allow $-\text{CO}_2\text{CH}_3$ etc.

Allow $\text{CH}_2\text{C}(\text{CH}_3)\text{COOCH}_3$.

1

M
ester



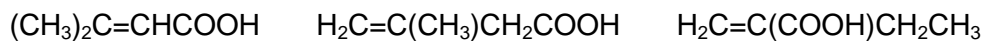
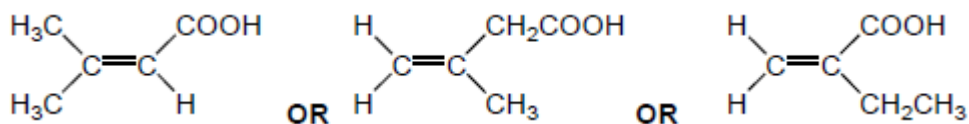
Allow either *E-Z* isomer.

Allow CH_3- or C_2H_5- but not CH_2CH_3- .

Allow $\text{CH}_3\text{CHCHCOOCH}_3$ etc.

1

N
acid

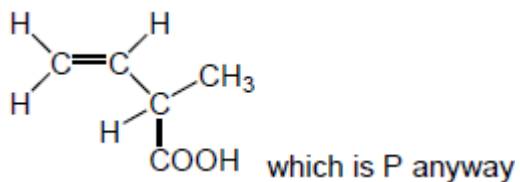


Allow CH_3- or C_2H_5- but not CH_2CH_3- .

Allow $-\text{CO}_2\text{H}$.

Not cyclic isomers.

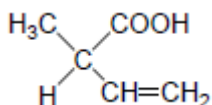
Not the optically active isomer.



Allow $(\text{CH}_3)_2\text{CCHCOOH}$ etc.

1

P
acid



Allow $-\text{CO}_2\text{H}$.

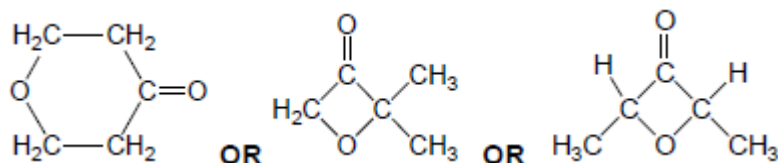


Allow $\text{CH}_3\text{CH}(\text{CO}_2\text{H})\text{CHCH}_2$ or

$\text{CH}_3\text{CH}(\text{CO}_2\text{H})\text{C}_2\text{H}_5$.

1

Q



Not cyclic esters.

1

[19]

5

(a) nucleophilic addition

1



Attack by HCN loses M1 and M2
M2 not allowed independent of M1, but
allow M1 for correct attack on C+
+C=O loses M2
M2 only allowed if correct carbon attacked
allow minus charge on N i.e. :CN⁻

4

M3 for completely correct structure not including lp

allow C₃H₇ in M3

M4 for lp and arrow

allow without –

1

2-hydroxy-2-methylpentan(e)nitrile

allow 2-hydroxy-2-methylpentanonitrile

(b) Product from **Q** is a racemic mixture/equal amounts of enantiomers

if no reference to products then no marks;

1

racemic mixture is inactive or inactive explained

not **Q** is optically active or has a chiral centre etc

1

Product from **R** is inactive (molecule) or has no chiral centre

1

[9]

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)

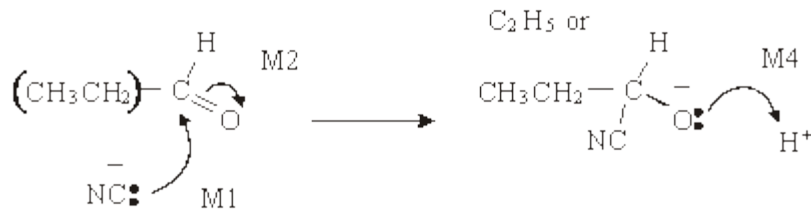
[16]

7

[1]

8

(a) nucleophilic addition;



1

M3 structure;

(be lenient on position of charge on CN-)

(M2 not allowed independent of M1,

but allow M1 for correct attack on C+

if M2 show as independent first.)

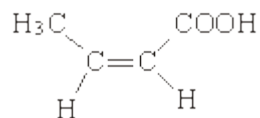
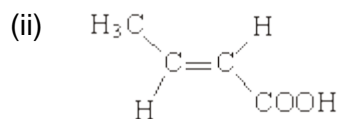
(+on C of C=O loses M2 but ignore $\delta+$ if correct)

(M4 for arrow and lone pair (only allow for correct M3 or close))

4

(b) (i) 2-hydroxybutanoic acid

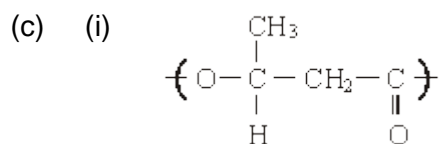
1



1

geometric(al) or cis-trans

1



(one unit only) (ignore brackets or n) (trailing bonds are needed)

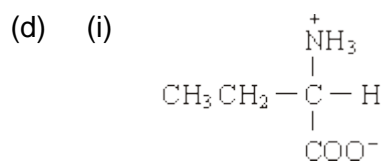
1

(ii) can be hydrolysed

OR

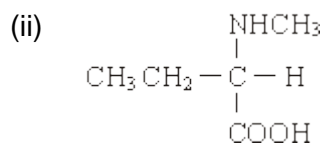
can be reacted with/attacked by acid/base/nucleophiles/H₂O/OH⁻;

1



(allow -NH₃⁺)

1



(or zwitterions product)

1

(iii) nucleophilic substitution;

1

[14]

9

[1]

10

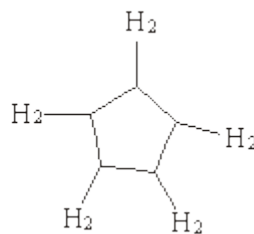
(a) A any C₅ alkene

1

B

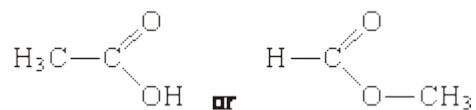


penalise



1

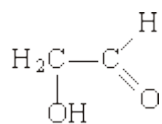
(b) C



or CH₃COOH or HCOOCH₃

1

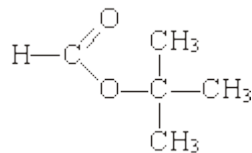
D



or HOCH₂CHO

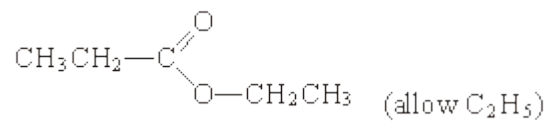
1

(c) E



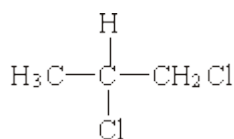
1

F



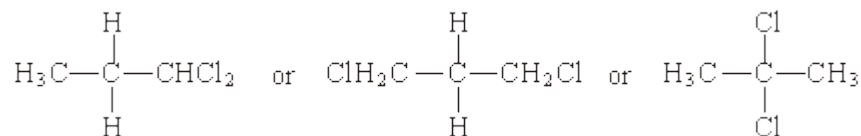
1

(d) **G**



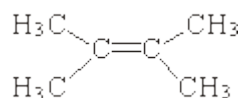
1

H



1

(e) **I**



1

J



1

[10]

11

[1]

12

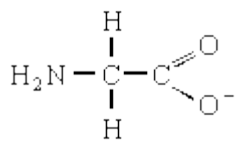
(a) 2-amino(e) propanoic acid (1)

1

(b) (i) molecules with same structure / structural formula (1)
but with bonds (**atoms or groups**) arranged differently in
space (3D) (1)

(ii) Plane polarised light (1)
Rotated (equally) in opposite directions (1)

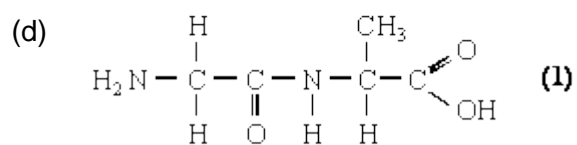
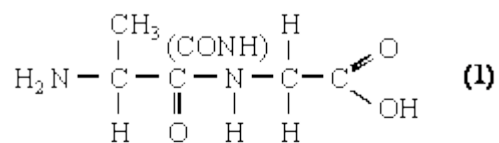
4



allow $\text{H}_2\text{NCH}_2\text{COO}^-$

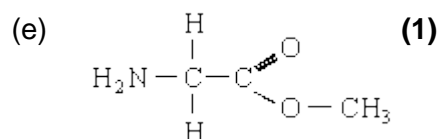
Penalise NH_2^- and OH^- once per paper
but CH_3^- is allowed

1



Not anhydrides; not repeating units

2



or $\text{H}_2\text{NCH}_2\text{COOCH}_3$

1

[9]

D
13

[1]

(iii) $pp = \text{mole fract}^n \times \text{total P (1)}$
 $= 0.625 \times 1.75 \times 10^4$
 $= 1.09 \times 10^4 \text{ (kPa) (1)}$
or 1.1(0)
Ignore units
Conseq on (ii)

5

(b) (i) $K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{H}_2}^2 \times P_{\text{CO}}} \text{ (1)}$

Penalise []

(ii) $K_p = \frac{2710}{(12300)^2 \times (7550)} = 2.37 \text{ (2.4)} \times 10^{-9} \text{ (1)}$

OR 2.37×10^{-15}

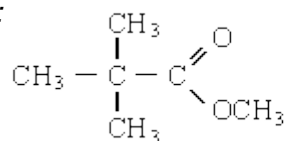
Units: kPa⁻² (1)

or Pa⁻²

not conseq to wrong K_p expression

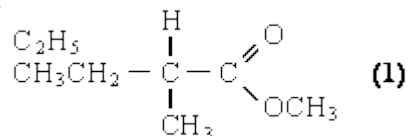
3

(c) *Isomer E:*



allow
(1) $(\text{CH}_3)_3\text{CCOOCH}_3$
or
 $(\text{CH}_3)_3\text{CCO}_2\text{CH}_3$

Isomer F:



2

[10]

B
16

[1]

D
17

[1]