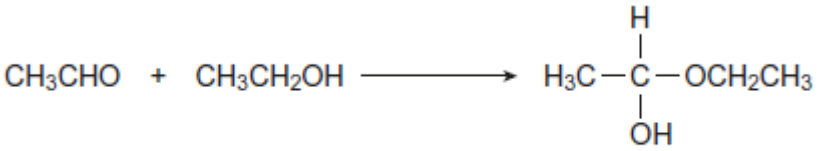
Q11.

Hemiacetals and acetals are compounds formed by the reaction of aldehydes with alcohols, such as the reaction of ethanal with ethanol.



a hemiacetal

(a) (i) Use your knowledge of carbonyl mechanisms to suggest the name of the mechanism of this reaction.

_____

(1)

(ii) Outline how an ethanol molecule reacts with an ethanal molecule in the first step of this mechanism. Include two curly arrows to show the movement of electron pairs.

(2)

(b) The reaction produces a racemic mixture of chiral molecules.

(i) Explain the meaning of the term racemic mixture.

_____

_____

(1)

(ii) State the relationship between two chiral molecules with the same structural formula.

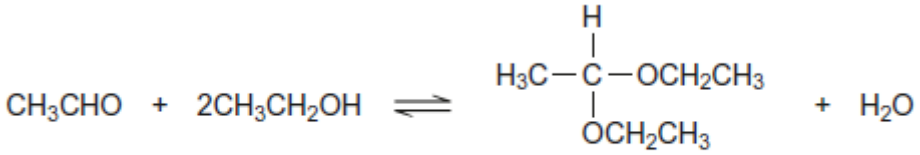
_____

_____

(1)

(c) In the presence of an acid catalyst such as dry hydrogen chloride, ethanal reacts with an excess of ethanol to form an acetal.

The overall reaction of ethanal with an excess of ethanol forms an equilibrium mixture as shown. All reactants and products are liquids.



an acetal

A mixture of 0.75 mol of ethanal and 5.00 mol of ethanol was left to reach equilibrium in the presence of dry hydrogen chloride at a given temperature. The equilibrium mixture contained 0.42 mol of the acetal.

(i) Calculate the amount, in moles, of ethanal and of ethanol in this equilibrium mixture.

Amount of ethanal _____ mol

Amount of ethanol _____ mol

Space for working _____

_____

_____

_____

(2)

(ii) In a different experiment using the same reaction as in part **(c)**, an equilibrium mixture was established at a given temperature.
This mixture contained 0.58 mol of ethanal, 3.76 mol of ethanol, 0.37 mol of the acetal and 0.65 mol of water in a total volume of 310 cm^3.

Write an expression for the equilibrium constant K_c for this reaction.
Calculate a value for K_c at this temperature. Give units with your answer.

K_c _____

_____

Calculation _____

_____

_____

_____

_____

(4)

(d) Draw the structure of the acetal ($C_4H_8O_2$) formed by the reaction of ethanal with ethane-1,2-diol.

(1)

(Total 12 marks)

Q12.

The carbonyl compound CH_3CH_2CHO reacts very slowly with HCN

(a) Name and outline a mechanism for the reaction of CH_3CH_2CHO 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.

_____

_____

_____

_____

(2)

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

_____

(1)

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

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

_____

_____

_____

_____

(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.

$$H_2C = CH - C \equiv N$$

(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)

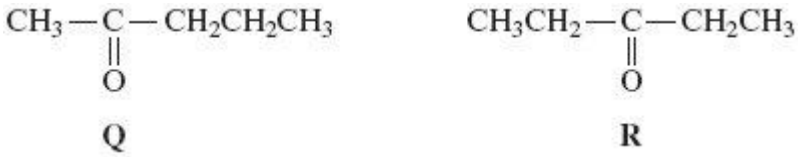
_____

(1)

(Total 15 marks)

Q13.

Two isomeric ketones are shown below.



Q R

(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**.

_____

_____

_____

_____

_____

(3)

(Total 9 marks)

Q14.

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

A $(CH_3)_2C=CHCH(CH_3)CH_2CH_3$

B $CH_3CH_2CH=CHCH(CH_3)CH_2CH_3$

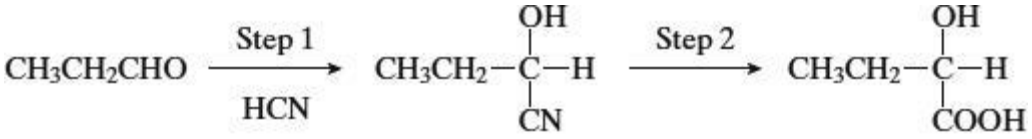
C $(CH_3)_2C=C(CH_2CH_3)_2$

D $CH_3CH_2CH(CH_3)CH(CH_3)C=CH_2$

(Total 1 mark)

Q15.

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.

_____

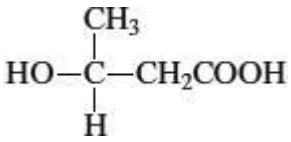
(ii) Two stereoisomers are formed by the dehydration of **Q**. Give the structures of these two isomers and name the type of stereoisomerism shown.

Structures of isomers

Type of stereoisomerism _____

(4)

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



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

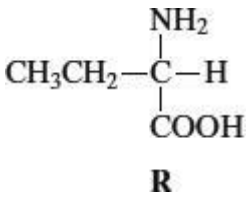
(ii) Suggest a reason why the polymer is biodegradeable.

_____

_____

(2)

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



R

(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)

Q16.

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)

Q17.

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 $C_3H_6Cl_2$ **G** shows optical activity but **H** does not.

G **H**

(2)

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

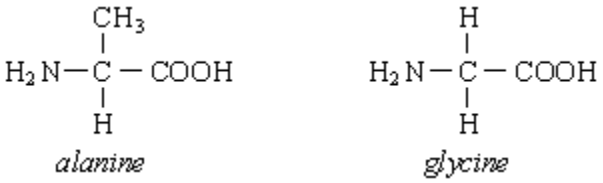
Each has an absorption in its infra-red spectrum at about 1650 cm^{-1} and neither shows geometrical isomerism. The proton n.m.r. spectrum of **I** consists of a singlet only whereas that of **J** consists of a singlet, a triplet and a quartet.

I **J**

(2)
(Total 10 marks)

Q18.

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)

Q19.

(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 _____

_____

Explanation _____

_____

_____

(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)

Q20.

On reduction, a racemate can be formed by

A $CH_3CH_2CH_2CH_2CHO$

B $CH_3CH_2CH_2COCH_3$

C $CH_3CH_2COCH_2CH_3$

D $CH_3CH=CHCH_2CHO$

(Total 1 mark)

Q21.

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

A $CH_3CH=CH_2$ + HBr

B $CH_3CH_2CH_2Br$ + NaOH

C $CH_3CH_2CH_2OH$ + H_2SO_4

D CH_3CH_2 CHO + HCN

(Total 1 mark)

Mark Scheme

Q11.

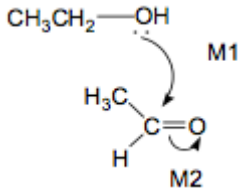
(a) (i) Nucleophilic addition

Any extra loses the mark

Allow minor spelling errors e.g. nucleophyllic

1

(ii)



M1 for arrow from lone pair on oxygen in ethanol to C of C=O (or to space half way between O and C)

M2 for arrow from C=O bond to oxygen in ethanal

Do not allow M2 as first step without nucleophilic attack, but can allow M1 for attack on C+ produced

+ rather than δ+ on C=O loses M2

Ignore any further steps

Mark independently

1
1

(b) (i) Equal mixture of enantiomers/optical isomers OWTTE

1

(ii) (Non-superimposable) mirror images

Ignore rotates light in opposite directions

Ignore stereoisomers

1

(c) (i) Ethan**al** 0.33

1

Ethan**ol** 4.16

Allow 4.2 for ethanol

1

(ii) $K_c = \dfrac{[acetal][H_2O]}{[CH_3CHO][CH_3CH_2OH]^2}$ or with names

$\dfrac{(0.37/0.31)(0.65/0.31)}{(0.58/0.31)(3.76/0.31)^2}$ **OR** $\dfrac{(0.37)(0.65)}{(0.58)(3.76)^2} \times 0.31$

Ignore slips in acetal structure or formula $C_6H_{14}O_2$

If K_c wrong, allow M4 only for units conseq to their K_c

If volume omitted (gives 2.93×10^{-2}) may only score M1 and M4

If volume used = 310 cm^3 allow M2 then award M3 for 9.08 – 9.23 only and M4 for mol^{-1} cm^3 only

Treat error in converting 310 cm³ to dm³ as AE

M1
M2

9.1×10^{-3}

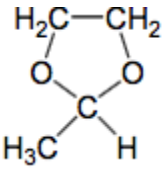
Allow range 9.08×10^{-3} – 9.23×10^{-3}

M3

$mol^{-1}dm^3$

Not $moles^{-1}dm^3$

M4

(d) 

1

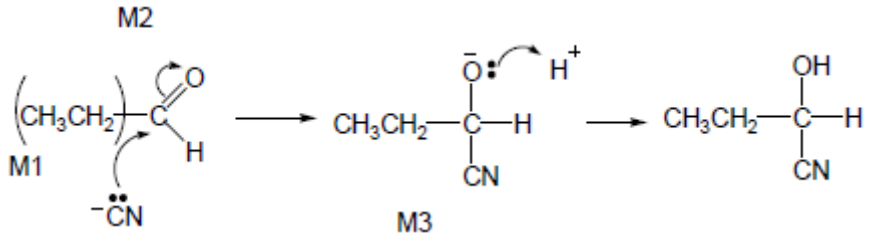
[12]

Q12.

(a) Nucleophilic addition

1

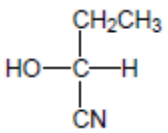
M4 for lp, arrow and H+



Allow C_2H_{5-} for CH_3CH_{2-}

- *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

(b) (i) M1 

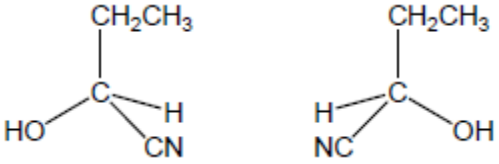
M1 for correct structure of product of part (a).

Allow C_2H_{5-} for CH_3CH_{2-}.

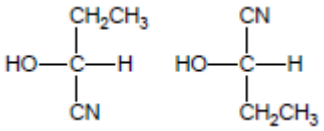
Penalise wrongly bonded, OH or CN or CH_2CH_3 once only in clip.

1

M2

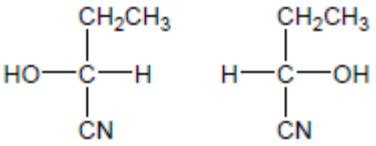


M2 cannot be gained by simply swapping two or more groups with no attempt to show a mirror image., e.g. do not allow M2 for



because these do not <u>show</u> the enantiomers as mirror images.

Students must <u>show</u> an attempt at mirror images, eg allow

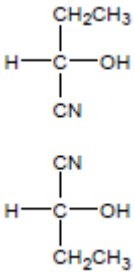


ie vertical groups same and horizontal swapped as if there was a mirror between them

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) <u>polarized light</u>

M2 only scores following correct M1

1

M2 <u>Rotated</u> in <u>opposite</u> directions (equally) (only allow if M1 correct close)
or

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.

1

$[CN^-]$ very low

Allow (very) few cyanide ions.

Mark independently.

1

(e) (i) $H_2C{=}CH{-}CH_3 + NH_3 + \frac{3}{2}O_2 \longrightarrow H_2C{=}CH{-}CN + 3H_2O$

OR

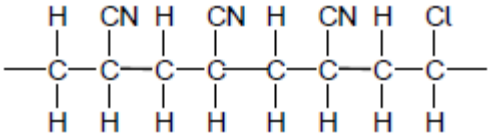
$H_2C{=}CH{-}CH_3 + NH_3 + 3O_2 \longrightarrow H_2C{=}CH{-}CN + 3H_2O_2$

OR doubled.

Allow C_3H_6 and CH_2CHCN or C_3H_3N on this occasion only.

1

(ii)

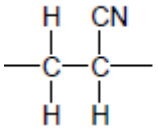
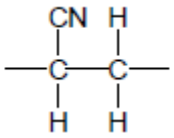
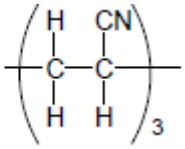


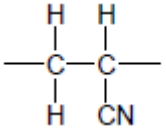
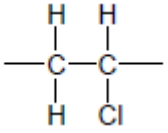
Ignore n.

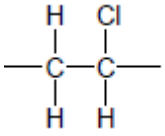
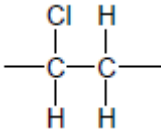
Must show trailing bonds.

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

Must contain, in any order,

3 of  or 3 of  or 

Allow  or 

and one of  or 

Allow –$CH_2CH(CN)CH_2CHCl$– etc.

1

(iii) Addition (polymerization)

Allow self-addition.

Do not allow additional.

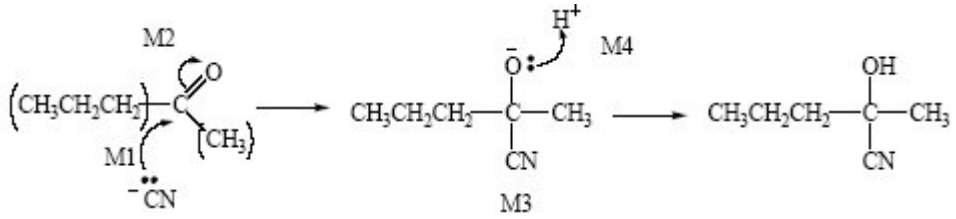
1

[15]

Q13.

(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 C_3H_7 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]

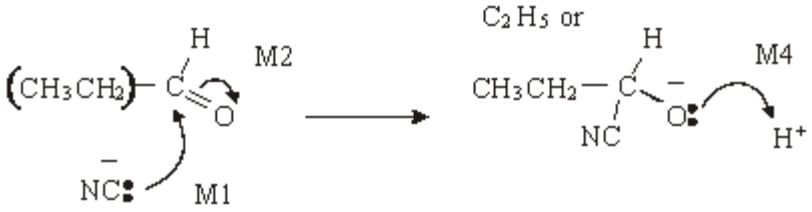
Q14.

B

[1]

Q15.

(a) necleophilic addition;



1

M3 structure;

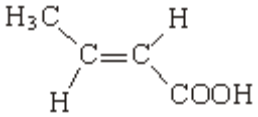
(be lenient on position of charge on CN–)
(M2 not allowed independent of M1,
but allow M1 for correct attack on C+
if M2 show as independent first.)
(+on C of C=O loses M2 but ignore δ+ if correct)
(M4 for arrow and lone pair (only allow for correct M3 or close))

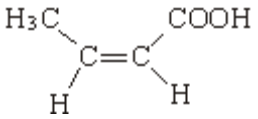
4

(b) (i) 2-hydroxybutanoic acid

1

(ii)



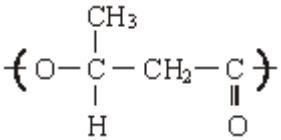


1

geometric(al) or cis-trans

1

(c) (i)



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

1

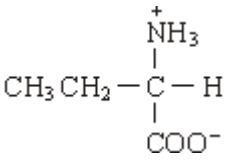
(ii) can be hydrolysed

OR

can be reacted with/attacked by acid/base/nucleophiles/H_2O/OH^-;

1

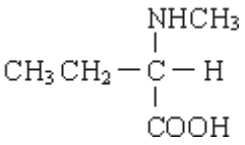
(d) (i)



(allow –NH_3^+)

1

(ii)



(or zwitterions product)

1

(iii) nucleophilic substitution;

1

[14]

Q16.

D

[1]

Q17.

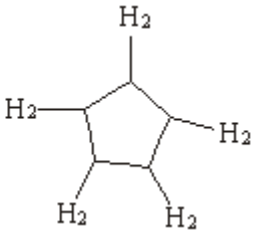
(a) **A** any C_5 alkene

1

B

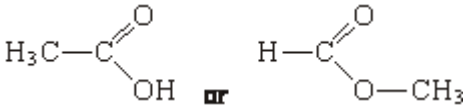
etc

penalise



1

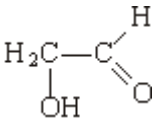
(b) **C**



or CH_3COOH or $HCOOCH_3$

1

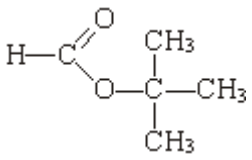
D



or $HOCH_2CHO$

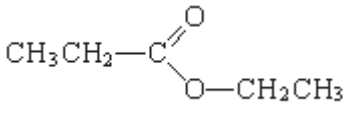
1

(c) **E**



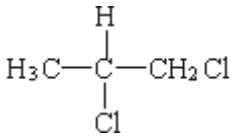
1

F



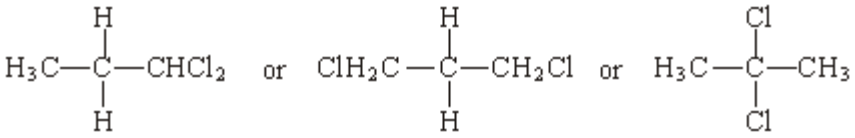
1

(d) **G**



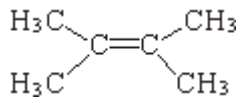
1

H



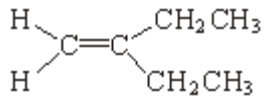
1

(e) **I**



1

J



NOT hex-3-ene

1

[10]

Q18.

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

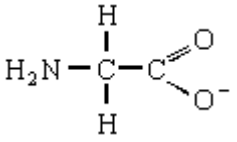
1

(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)**

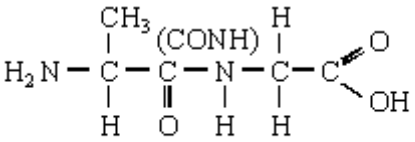
4

(c)  **(1)**

allow $H_2NCH_2COO^-$

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

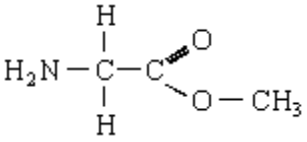
1

 **(1)**

(d)

Not anhydrides; not repeating units

2



(e) **(1)**

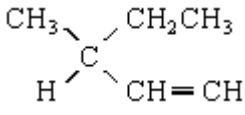
or $H_2NCH_2COOCH_3$

1

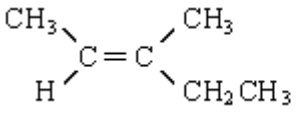
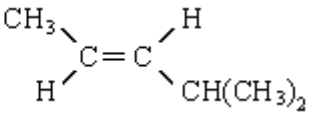
[9]

Q19.

(a) *Structure of* **P**:

 (1)

Structures of **Q** and **R**:

 and 

NOT C_3H_7

(1) **(1)**

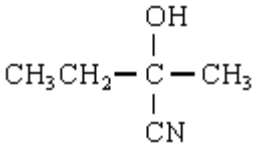
Q and R in any order

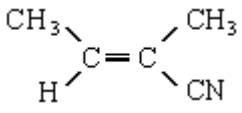
3

(b) (i) *Racemic mixture*: <u>equal</u> mixture of optical isomers / enantiomers
OR in explanation

Explanation: planar (>C=O) **(1)**
attack from either side is equally likely **(1)**

(ii) *Reagent **S***: HCN or (KCN / HCl **or** H_2SO_4) **(1)**

*Compound **T***:  **(1)**

*Compound **U***:  **(1)**

6

[9]

Q20.

B

[1]

Q21.

D

[1]