

**Question 1: N/A**

**Question 2: N/A**

**Question 3: N/A**

4 This question is about acylium ions,  $[\text{RCO}]^+$

4 (a) The acylium ion  $\text{H}_3\text{C}-\overset{+}{\text{C}}=\text{O}$  is formed in a mass spectrometer by fragmentation of the molecular ion of methyl ethanoate.

Write an equation for this fragmentation.

Include in your answer a displayed formula for the radical formed.

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(2 marks)

4 (b) The acylium ion  $\text{H}_3\text{C}-\overset{+}{\text{C}}=\text{O}$  can also be formed from ethanoyl chloride. The ion reacts with benzene to form  $\text{C}_6\text{H}_5\text{COCH}_3$

4 (b) (i) Write an equation to show the formation of this acylium ion by the reaction of ethanoyl chloride with **one** other substance.

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(2 marks)

4 (b) (ii) Name and outline a mechanism for the reaction of benzene with this acylium ion.

Name of mechanism .....

Mechanism

(4 marks)

4 (b) (iii) Ethanoic anhydride also reacts with benzene to form  $\text{C}_6\text{H}_5\text{COCH}_3$

Write an equation for this reaction.

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(1 mark)

- 5** Lactic acid,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ , is formed in the human body during metabolism and exercise. This acid is also formed by the fermentation of carbohydrates such as sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

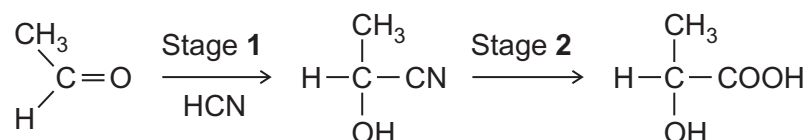
- 5 (a) (i)** Give the IUPAC name for lactic acid.

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(1 mark)

- 5 (a) (ii)** Write an equation for the formation of lactic acid from sucrose and water.

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(1 mark)

- 5 (b)** A molecule of lactic acid contains an asymmetric carbon atom.  
The lactic acid in the body occurs as a single enantiomer.  
A racemic mixture (racemate) of lactic acid can be formed in the following two-stage synthesis.



- 5 (b) (i)** Name and outline a mechanism for Stage 1.

Name of mechanism .....

Mechanism

(5 marks)

**5 (b) (ii)** Give the meaning of the term *racemic mixture* (*racemate*).

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(1 mark)

**5 (b) (iii)** Explain how you could distinguish between a racemic mixture (racemate) of lactic acid and one of the enantiomers of lactic acid.

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(2 marks)

**5 (c)** A mixture of lactic acid and its salt sodium lactate is used as an acidity regulator in some foods. An acidity regulator makes sure that there is little variation in the pH of food.

**5 (c) (i)** Write an equation for the reaction of lactic acid with sodium hydroxide.

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(1 mark)

**5 (c) (ii)** The acid dissociation constant  $K_a$  for lactic acid has the value  $1.38 \times 10^{-4} \text{ mol dm}^{-3}$  at 298 K.

Calculate the pH of an equimolar solution of lactic acid and sodium lactate.

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(2 marks)

**Question 5 continues on the next page**

**Turn over ►**

- 5 (c) (iii) Suggest an alternative name for the term *acidity regulator*.  
Explain how a mixture of lactic acid and sodium lactate can act as a regulator when natural processes increase the acidity in some foods.

Name .....

Explanation .....

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(3 marks)

(Extra space) .....

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- 5 (d) The cup shown is made from PLA, poly(lactic acid).  
PLA is the condensation polymer formed from lactic acid.

The polymer is described as 100% biodegradable and 100% compostable.

Compostable material breaks down slowly in contact with the moist air in a garden bin. This produces compost that can be used to improve soil.

The manufacturers stress that PLA cups differ from traditional plastic cups that are neither biodegradable nor compostable.



- 5 (d) (i) Draw a section of PLA that shows **two** repeating units.

(2 marks)

5 (d) (ii) Name the type of condensation polymer in PLA.

.....  
(1 mark)

5 (d) (iii) An intermediate in the production of PLA is a cyclic compound ( $C_6H_8O_4$ ) that is formed from two PLA molecules.

Draw the structure of this cyclic compound.

(1 mark)

5 (d) (iv) Traditional non-biodegradable plastic cups can be made from poly(phenylethene), commonly known as *polystyrene*.

Draw the repeating unit of poly(phenylethene).

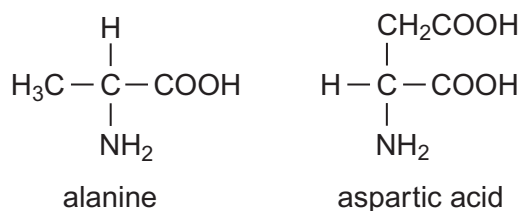
(1 mark)

5 (d) (v) The manufacturers of PLA claim that the material will break down to compost in just 12 weeks.

Suggest **one** reason why PLA in landfill may take longer than 12 weeks to break down.

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(1 mark)

- 6** Alanine and aspartic acid are naturally occurring amino acids.



- 6 (a)** Draw the structure of the zwitterion formed by alanine.

(1 mark)

- 6 (b)** Draw the structure of the compound formed when alanine reacts with methanol in the presence of a small amount of concentrated sulfuric acid.

(1 mark)

- 6 (c)** Draw the structure of the species formed by aspartic acid at high pH.

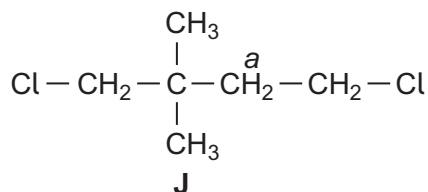
(1 mark)

- 6 (d)** Draw the structure of a dipeptide formed by two aspartic acid molecules.

(1 mark)

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

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



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

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(1 mark)

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

.....  
(1 mark)

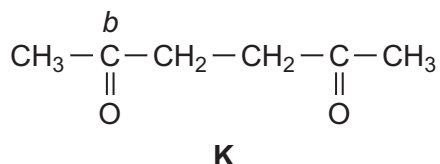
7 (a) (iii) Give the splitting pattern of the protons labelled *a*.

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(1 mark)

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

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(1 mark)

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



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

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(1 mark)

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

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(1 mark)

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

.....  
(1 mark)

**Section B**

Answer **all** questions in the spaces provided.

**8** This question is about the primary amine  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$

**8 (a)** The amine  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  reacts with  $\text{CH}_3\text{COCl}$

Name and outline a mechanism for this reaction.

Give the IUPAC name of the organic product.

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(6 marks)

**8 (b)** Isomers of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  include another primary amine, a secondary amine and a tertiary amine.

**8 (b) (i)** Draw the structures of these **three** isomers.  
Label each structure as primary, secondary or tertiary.

(3 marks)

**8 (b) (ii)** Use **Table 1** on the Data Sheet to explain how you could use infrared spectra in the range outside the fingerprint region to distinguish between the secondary amine and the tertiary amine.

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(2 marks)

**Question 8 continues on the next page**

**Turn over ►**

**8 (c)** The amine  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  can be prepared by two different routes.

Route **A** is a two-stage process and starts from  $\text{CH}_3\text{CH}_2\text{Br}$

Route **B** is a one-stage process and starts from  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$

**8 (c) (i)** Identify the intermediate compound in Route **A**.

Give the reagents and conditions for both stages in Route **A** and the single stage in Route **B**.

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(7 marks)

**8 (c) (ii)** Give **one** disadvantage of Route **A** and **one** disadvantage of Route **B**.

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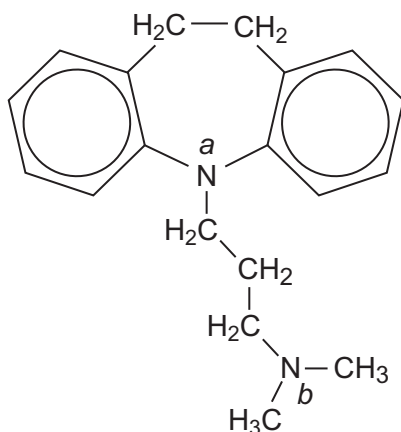
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(2 marks)

- 9 Imipramine has been prescribed as an antidepressant. The structure of imipramine is shown below.



- 9 (a) The medicine is usually supplied as a salt. The salt is formed when one mole of imipramine reacts with one mole of hydrochloric acid.

Suggest why the nitrogen atom labelled *b* is more likely to be protonated than the nitrogen atom labelled *a* when the salt is formed.

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(3 marks)

- 9 (b) Deduce the molecular formula of imipramine and give the number of peaks in its  $^{13}\text{C}$  n.m.r. spectrum.

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(2 marks)

**10** The amide or peptide link is found in synthetic polyamides and also in naturally-occurring proteins.

- (a) (i)** Draw the repeating unit of the polyamide formed by the reaction of propanedioic acid with hexane-1,6-diamine.

(2 marks)

- (a) (ii)** In terms of the intermolecular forces between the polymer chains, explain why polyamides can be made into fibres suitable for use in sewing and weaving, whereas polyalkenes usually produce fibres that are too weak for this purpose.

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(3 marks)

(Extra space) .....

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- 10 (b) (i)** Name and outline a mechanism for the reaction of  $\text{CH}_3\text{CH}_2\text{COCl}$  with  $\text{CH}_3\text{NH}_2$

Name of mechanism.....

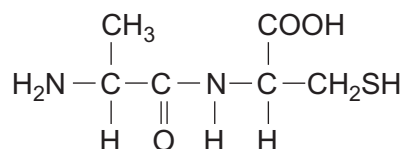
Mechanism

(5 marks)

- (b) (ii)** Give the name of the product containing an amide linkage that is formed in the reaction in part **4 (b) (i)**.

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(1 mark)

- (c)** The dipeptide shown below is formed from two different amino acids.

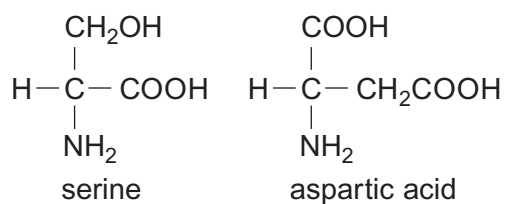


Draw the structure of the alternative dipeptide that could be formed by these two amino acids.

(1 mark)

Turn over ►

- 10 (d)** The amino acids serine and aspartic acid are shown below.



- (d) (i)** Give the IUPAC name of serine.

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(1 mark)

- (d) (ii)** Draw the structure of the species formed when aspartic acid reacts with aqueous sodium hydroxide.

(1 mark)

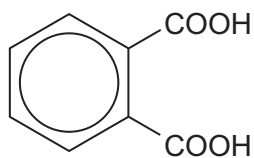
- (d) (iii)** Draw the structure of the species formed when serine reacts with dilute hydrochloric acid.

(1 mark)

- (d) (iv)** Draw the structure of the species formed when serine reacts with an excess of bromomethane.

(1 mark)

- 11** Items softened with plasticisers have become an essential part of our modern society.
- Compound **S**, shown below, is commonly known as phthalic acid.
- Esters of phthalic acid are called phthalates and are used as plasticisers to soften polymers such as PVC, poly(chloroethene).

**S**

- (a)** Give the IUPAC name for phthalic acid.

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(1 mark)

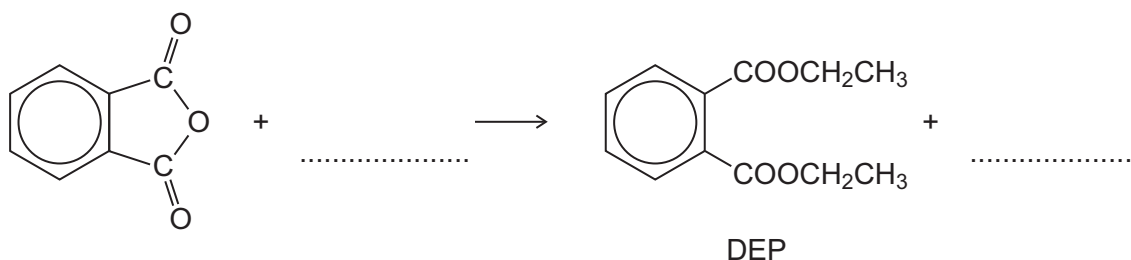
- (b)** Draw the displayed formula of the repeating unit of poly(chloroethene).

(1 mark)

Turn over ►

**11 (c)** The ester diethyl phthalate (DEP) is used in food packaging and in cosmetics.

**(c) (i)** Complete the following equation showing the formation of DEP from phthalic anhydride.



(2 marks)

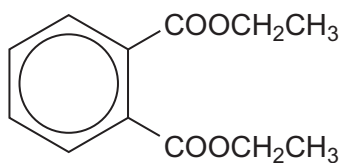
**(c) (ii)** Deduce the number of peaks in the  $^{13}\text{C}$  n.m.r. spectrum of DEP.

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(1 mark)

**(c) (iii)** One of the peaks in the  $^{13}\text{C}$  n.m.r. spectrum of DEP is at  $\delta = 62$  ppm.  
**Table 3** on the Data Sheet can be used to identify a type of carbon atom responsible for this peak.

Draw a circle around **one** carbon atom of this type in the structure below.



(1 mark)

**(d)** The mass spectrum of DEP includes major peaks at  $m/z = 222$  (the molecular ion) and at  $m/z = 177$

Write an equation to show the fragmentation of the molecular ion to form the fragment that causes the peak at  $m/z = 177$

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(2 marks)

- 11 (e)** Because of their many uses, phthalates have been tested for possible adverse effects to humans and to the environment.

The European Council for Plasticisers and Intermediates is an organisation that represents the manufacturers of plasticisers.

The text below is taken from a document written by the organisation.

‘Research demonstrates that phthalates, at current and foreseeable exposure levels, do not pose a risk to human health or to the environment. Experimental evidence shows that phthalates are readily biodegradable and do not persist for long in the environment.’

- (e) (i)** Hydrolysis of DEP in an excess of water was found to follow first order kinetics. Write a rate equation for this hydrolysis reaction using DEP to represent the ester.

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(1 mark)

- (e) (ii)** Suggest what needs to be done so that the public could feel confident that the research quoted above is reliable.

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(2 marks)

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