Answer **all** the questions.

1 A chemist was investigating the reactions of benzene, phenol and cyclohexene with bromine. She found that they all reacted with bromine but under different conditions.

(a) The chemist found that when benzene reacts with bromine, a halogen carrier is required as a catalyst.

Write an equation for this reaction.
You do **not** need to show the halogen carrier in your equation.

[1]

(b) The chemist also found that when phenol or cyclohexene reacts with bromine, a halogen carrier is **not** required.

(i) The chemist observed that bromine decolourises when it reacts with phenol.

What other observation would she have made?

Draw the structure of the organic product formed.

Observation .....

Organic product:

[2]

(ii) Cyclohexene also decolourises bromine.

Name the organic product formed.

1

..... **[1]**

(iii) Explain the relative resistance to bromination of benzene compared to phenol and compared to cyclohexene.

In your answer, you should use appropriate technical terms, spelt correctly.

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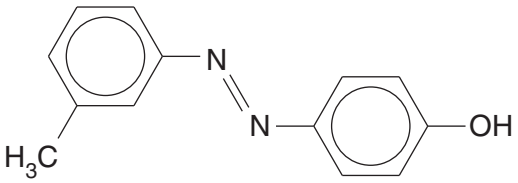
..... **[5]**

(c) Compound **A**, shown below, is being considered as an azo dye by a chemical company. A chemist planned a two-stage synthesis of compound **A** starting from an aromatic amine.



compound A

The aromatic amine is first converted into a diazonium ion.

- Draw the displayed formula of the aromatic amine **and** of the diazonium ion.
- State the reagents and conditions for each stage in the synthesis of compound **A** from an aromatic amine.

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..... **[5]**

[Total: 14]

2 Hydroxyethanal, $HOCH_2CHO$, is sometimes referred to as the 'first sugar' as it is the simplest possible molecule that contains both an aldehyde group and an alcohol group.

A biochemist investigated some redox reactions of hydroxyethanal and found that several different products were produced.

(a) The biochemist reacted hydroxyethanal with Tollens' reagent.

(i) State what the biochemist would see when hydroxyethanal reacts with Tollens' reagent.

..... **[1]**

(ii) Write the structural formula of the organic product formed when hydroxyethanal reacts with Tollens' reagent.

[1]

(b) The biochemist also reacted hydroxyethanal with acidified dichromate by heating under reflux.

Write an equation for this oxidation.

Use **[O]** to represent the oxidising agent.

[2]

(c) The biochemist then reduced hydroxyethanal using aqueous $NaBH_4$.

(i) Write the structural formula of the organic product.

..... **[1]**

(ii) Outline the mechanism for this reduction.

Use curly arrows and show any relevant dipoles.

[4]

[Total: 9]

3 α-Amino acids are found in human sweat. A student had read that chromatography could be used to separate and identify the amino acids present in human sweat.

(a) The student used Thin-Layer Chromatography (TLC) to separate the α-amino acids in a sample of human sweat and discovered that three different α-amino acids were present.

(i) Name the process by which TLC separates α-amino acids.

..... **[1]**

(ii) The chromatogram was treated to show the positions of the separated α-amino acids.

Explain how the student could analyse the chromatogram to identify the three α-amino acids that were present.

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..... **[2]**

(iii) Several α-amino acids have structures that are very similar.

Suggest why this could cause problems when using TLC to analyse mixtures of α-amino acids.

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..... **[1]**

(b) Some of the α-amino acids found in human sweat are shown in the table below.

α-amino acid	**R group**
glycine	H
leucine	$CH_2CH(CH_3)_2$
isoleucine	$CH(CH_3)CH_2CH_3$
alanine	CH_3
valine	$CH(CH_3)_2$
lysine	$(CH_2)_4NH_2$
glutamic acid	$(CH_2)_2COOH$

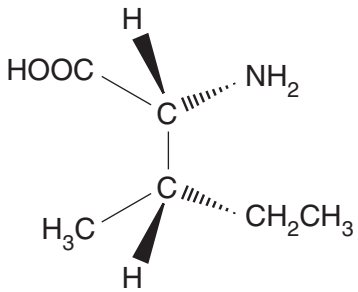
Table 1

(i) State the general formula of an α-amino acid.

[1]

(ii) There are four stereoisomers of isoleucine.

One of the stereoisomers is shown below.



Draw 3D diagrams for the other **three** stereoisomers of isoleucine.

[3]

α-amino acid	**R group**
glycine	H
leucine	$CH_2CH(CH_3)_2$
isoleucine	$CH(CH_3)CH_2CH_3$
alanine	CH_3
valine	$CH(CH_3)_2$
lysine	$(CH_2)_4NH_2$
glutamic acid	$(CH_2)_2COOH$

Table 1

(c) α-Amino acids form different ions at different pH values. Zwitterions are formed when the pH is equal to the isoelectric point of the α-amino acid.

The isoelectric points of three α-amino acids are given below:

alanine, pH = 6.0 **glutamic acid, pH = 3.2** **lysine, pH = 9.7**

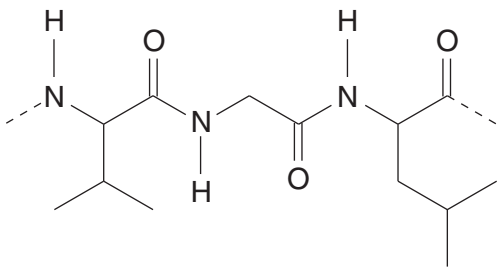
Draw the structures of the ions formed by these α-amino acids at the pH values below. Refer to **Table 1** above.

alanine at pH = 6.0	**glutamic acid at pH = 10**	**lysine at pH = 2.0**

[3]

(d) α-Amino acids can react to form polypeptides.

A short section of a polypeptide is shown below.

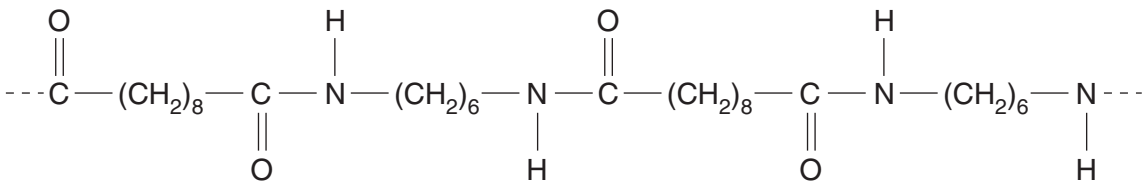


Name the α-amino acid sequence in this section of the polypeptide. Refer to **Table 1**.

..... **[1]**

(e) Synthetic polyamides, such as nylon, contain the same link as polypeptides. Nylon is the general name for a family of polyamides.

A short section of a nylon polymer is shown below.



Draw the structures of **two** monomers that could be used to make this nylon.

[2]

[Total: 14]

4 An industrial chemist discovered five bottles of different chemicals (three esters and two carboxylic acids) that were all labelled $C_5H_{10}O_2$.

The different chemicals had the structural formulae below.

$CH_3CH_2COOCH_2CH_3$ $(CH_3)_3CCOOH$ $CH_3COOCH(CH_3)_2$

$(CH_3)_2CHCH_2COOH$ $(CH_3)_2CHCOOCH_3$

(a) The chemist used both infrared and ^{13}C NMR spectroscopy to identify the two carboxylic acids and to distinguish between them.

How do both types of spectra allow the carboxylic acids to be identified and distinguished?

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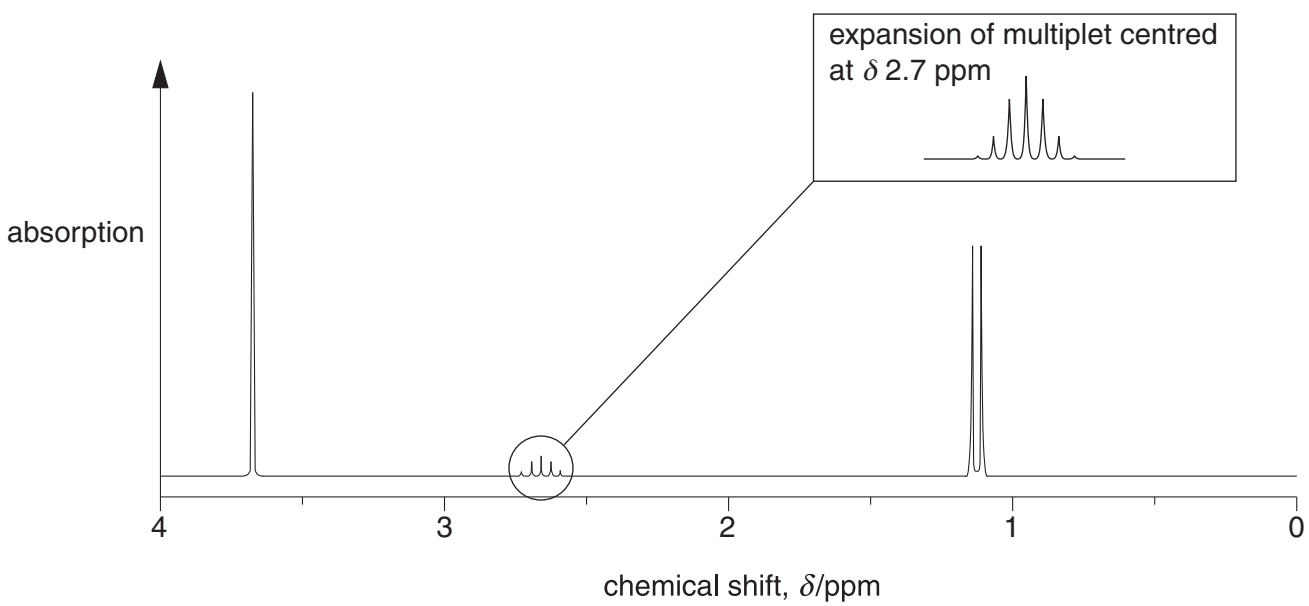
..... **[3]**

(b) The chemist analysed one of the esters by ^1H NMR spectroscopy. The spectrum is shown below.



Analyse the splitting patterns and the chemical shift values to identify the ester.

Give your reasoning.

In your answer, you should use appropriate technical terms, spelt correctly.

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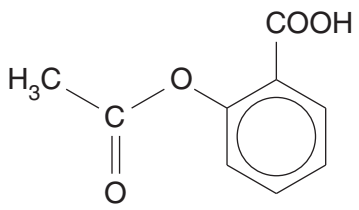
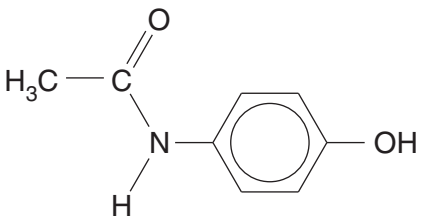
..... **[6]**

[Total: 9]

5 Aspirin and paracetamol are commonly available painkillers.



aspirin



paracetamol

Aspirin and paracetamol can be prepared using ethanoic anhydride, $(CH_3CO)_2O$.

Some examples of the reactions of ethanoic anhydride are shown below.

reaction 1 $(CH_3CO)_2O + CH_3OH \rightarrow CH_3COOCH_3 + CH_3COOH$

reaction 2 $(CH_3CO)_2O + CH_3NH_2 \rightarrow CH_3CONHCH_3 + CH_3COOH$

reaction 3 $(CH_3CO)_2O + C_6H_5OH \rightarrow CH_3COOC_6H_5 + CH_3COOH$

(a) Draw the structure of a compound that could react with ethanoic anhydride to form aspirin.

[1]

(b) Ethanoic anhydride can react with 4-aminophenol to produce paracetamol.

(i) Write an equation, showing structural formulae, for this formation of paracetamol.

[2]

(ii) An impurity with molecular formula $C_{10}H_{11}NO_3$ is also formed.

Draw the structure of this impurity.

[1]

(iii) Explain why it is necessary for pharmaceutical companies to ensure that drugs and medicines are pure.

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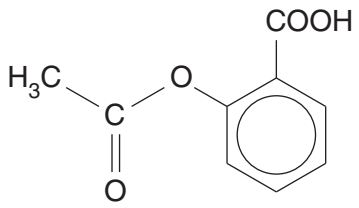
..... **[1]**

(c) Name the functional groups in aspirin and in paracetamol.

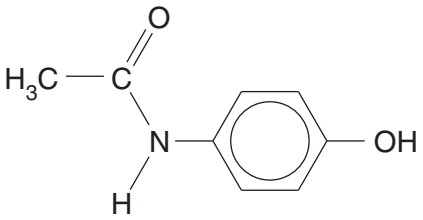
aspirin .....

paracetamol ..... **[2]**

(d) A student carried out some reactions with samples of aspirin and paracetamol in the laboratory. Their structures are repeated below.



aspirin



paracetamol

The student tried to react each of the reagents **A**, **B** and **C** with aspirin and paracetamol.

- Reagent **A** reacted with aspirin **and** with paracetamol.
- Reagent **B** reacted **only** with aspirin.
- Reagent **C** reacted **only** with paracetamol.

Suggest possible identities of reagents **A**, **B** and **C** and the organic products that would be formed.

(i) Reagent **A**: .....

Organic product with aspirin:

Organic product with paracetamol:

[3]

(ii) Reagent **B**: .....

Organic product with aspirin:

[2]

(iii) Reagent **C**: .....

Organic product with paracetamol:

[2]

[Total: 14]

END OF QUESTION PAPER