OXFORD CAMBRIDGE AND RSA EXAMINATIONS
A2 GCE

F324/01

CHEMISTRY A

Rings, Polymers and Analysis

MONDAY 14 JANUARY 2013: Afternoon
DURATION: 1 hour 15 minutes
plus your additional time allowance

MODIFIED ENLARGED 18pt

Candidate forename		Candidate surname	

Centre number						Candidate number				

Candidates answer on the Question Paper.

OCR SUPPLIED MATERIALS:

Data Sheet for Chemistry A (inserted)
Insert for question 2(b)

OTHER MATERIALS REQUIRED:

Scientific calculator

READ INSTRUCTIONS OVERLEAF

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INSTRUCTIONS TO CANDIDATES

- **The Inserts will be found in the centre of this document.**
- **Write your name, centre number and candidate number in the boxes on the first page. Please write clearly and in capital letters.**
- **Use black ink. HB pencil may be used for graphs and diagrams only.**
- **Answer ALL the questions.**
- **Read each question carefully. Make sure you know what you have to do before starting your answer.**
- **Write your answer to each question in the space provided. If additional space is required, you should use the lined pages at the end of this booklet. The question number(s) must be clearly shown.**

INFORMATION FOR CANDIDATES

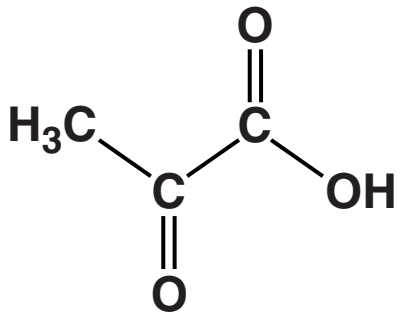
- **The number of marks is given in brackets [ ] at the end of each question or part question.**
-  **Where you see this icon you will be awarded marks for the quality of written communication in your answer.**

  This means for example you should:

  - **ensure that text is legible and that spelling, punctuation and grammar are accurate so that meaning is clear;**
  - **organise information clearly and coherently, using specialist vocabulary when appropriate.**
- **You may use a scientific calculator.**
- **A copy of the Data Sheet for Chemistry A is provided as an Insert with this Question Paper.**
- **You are advised to show all the steps in any calculations.**
- **The total number of marks for this paper is 60.**

Answer ALL the questions.

1 Pyruvic acid, shown below, is an organic compound that has a smell similar to ethanoic acid. It is extremely soluble in water.



PYRUVIC ACID

(a) Explain why pyruvic acid is soluble in water.

Use a labelled diagram to support your answer.

_____

_____

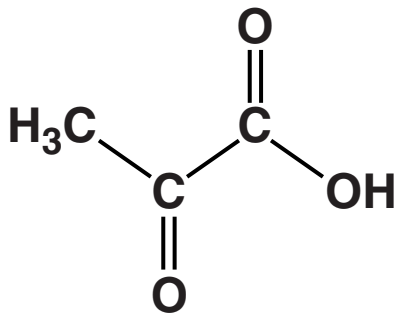
_____ **[2]**

(b) Pyruvic acid can be prepared in the laboratory by reacting propane-1,2-diol with excess acidified potassium dichromate(VI). The reaction mixture is heated under reflux.

Write an equation for this oxidation.

Use [O] to represent the oxidising agent and show structural formulae for organic compounds.

[2]



PYRUVIC ACID

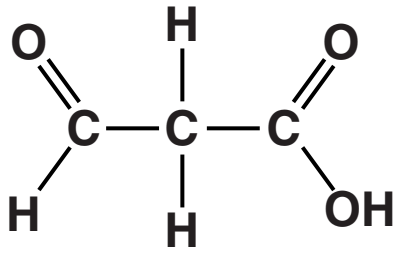
(c) Pyruvic acid can also be reduced by $NaBH_4$ to form $CH_3CH(OH)COOH$.

Outline the mechanism for this reduction.

Use curly arrows and show relevant dipoles.

[4]

(d) Compound A, shown below, is a structural isomer of pyruvic acid.



COMPOUND A

Describe a chemical test that could be carried out in a laboratory to distinguish between samples of pyruvic acid and compound A.

Your answer should include reagents, observations, the type of reaction and the organic product formed.

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

_____

_____

_____

_____

_____

_____ **[3]**

(e) Compound B is an organic compound used to make some cosmetics.

Compound B contains C, H and O only. Elemental analysis shows that B has the percentage composition by mass: C, 55.81%; H, 7.02%; O, 37.17%.

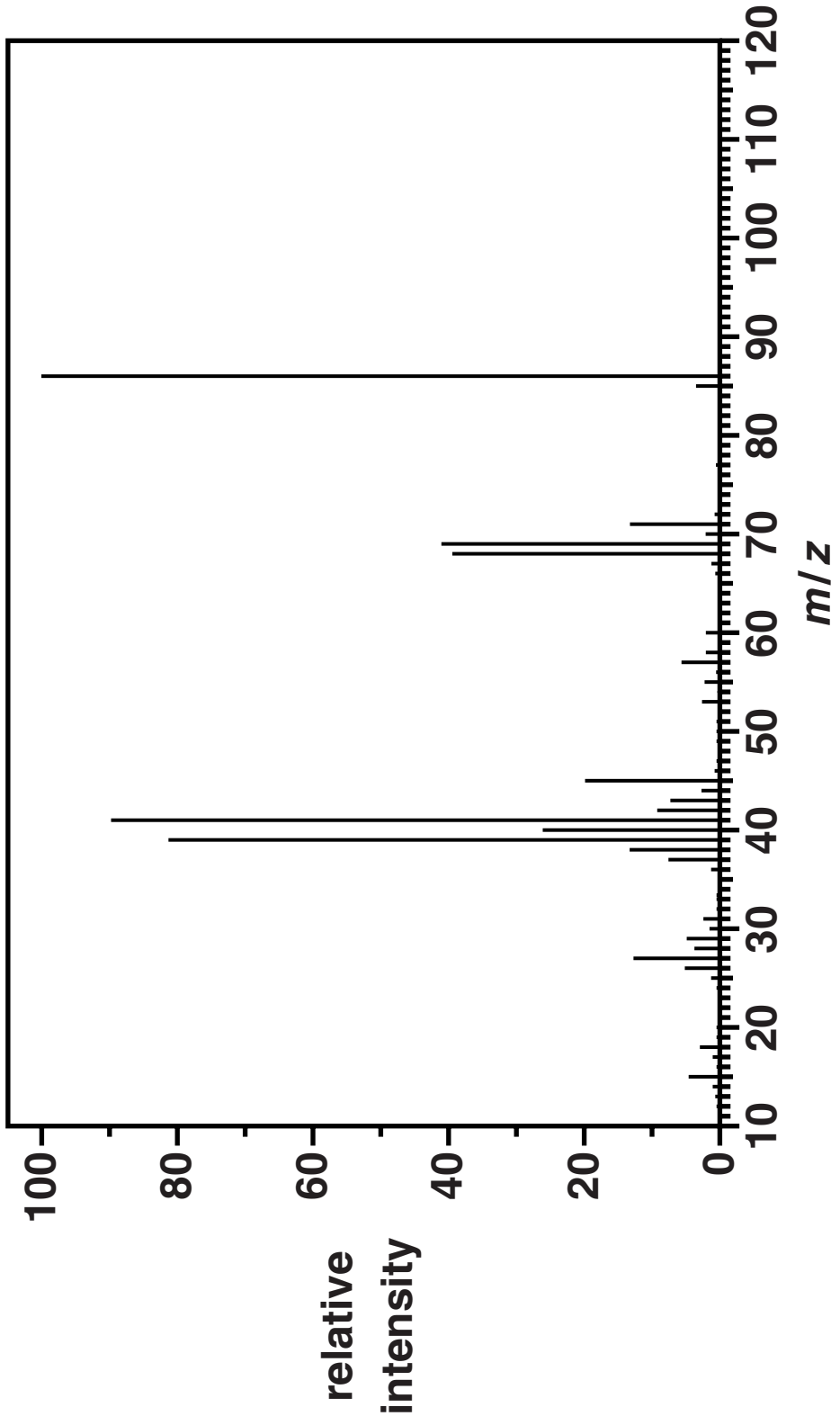
The mass spectrum of compound B is shown opposite.

(i) Determine the MOLECULAR formula of compound B.

Show all of your working.

molecular formula of compound B =

_____ **[2]**


relative intensity
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
110
120
m/z

(ii) Compound B is an *E*-stereoisomer.

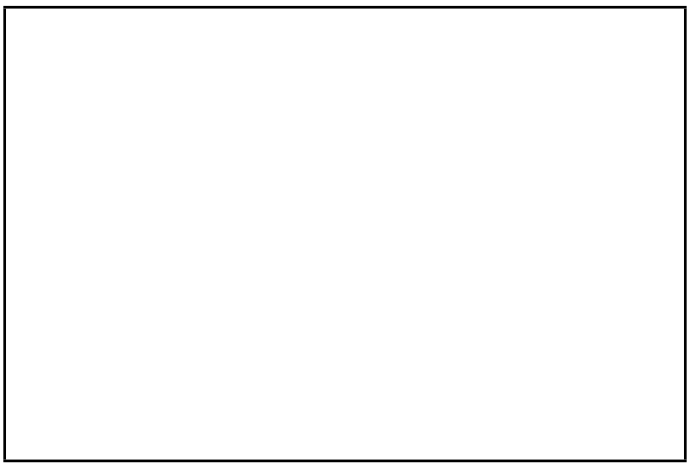
Compound B effervesces with aqueous Na_2CO_3 to form organic compound C.

Compound B decolourises Br_2 to form compound D.

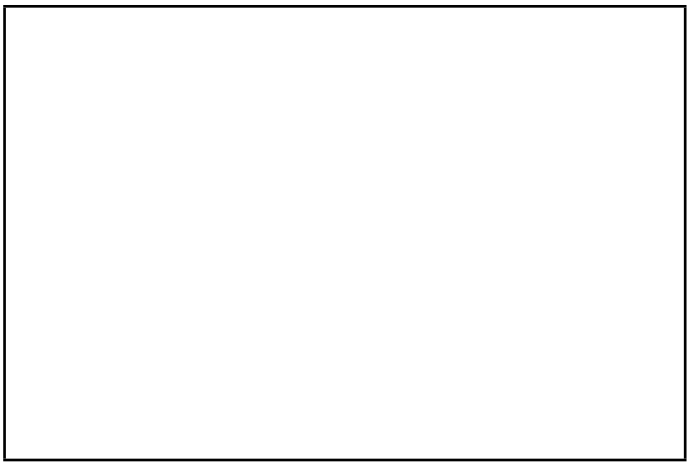
Compound B polymerises to form polymer E.

In the boxes opposite:

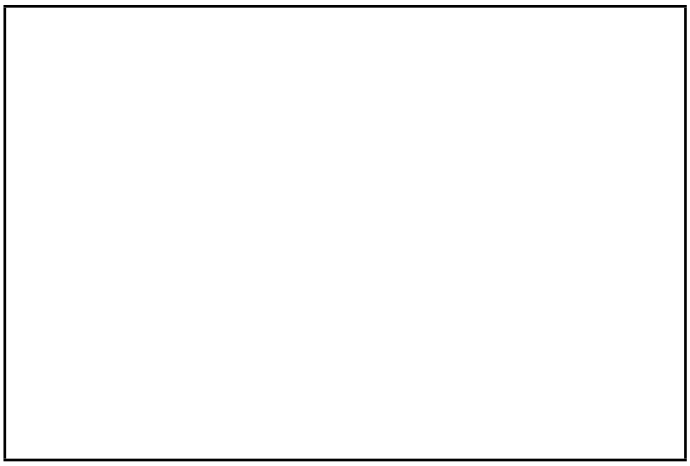
- **draw structures for compounds B, C and D.**
- **draw ONE repeat unit for polymer E.**



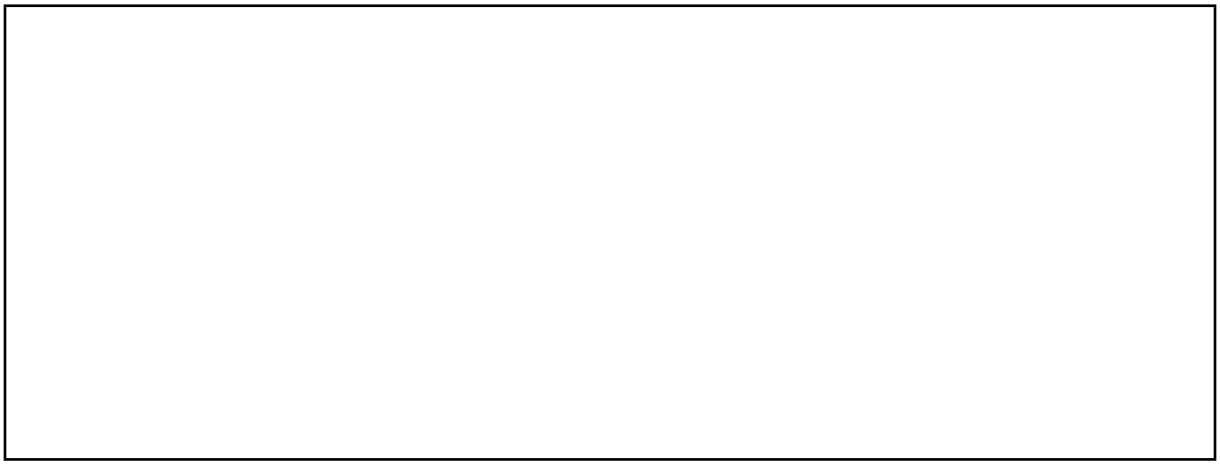
COMPOUND B



COMPOUND C



COMPOUND D

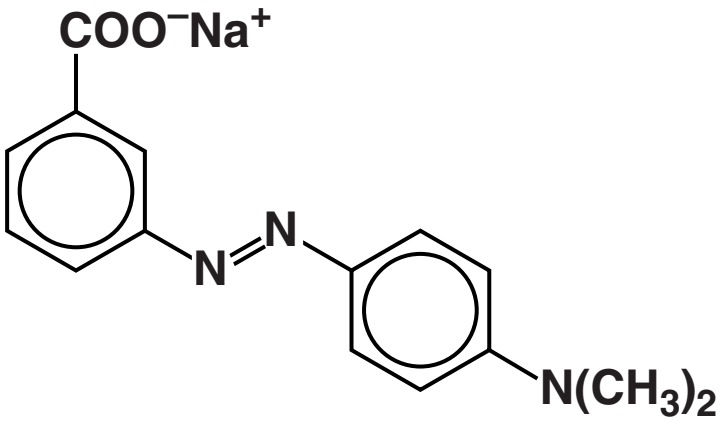


ONE REPEAT UNIT OF POLYMER E

[4]

[TOTAL: 17]

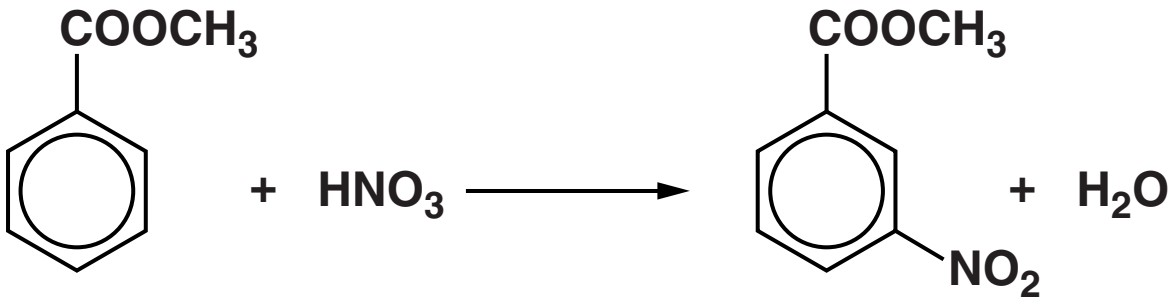
2 A chemist is developing a new azo dye. The structure of this dye is shown below.



AZO DYE

(a) In the first stage of the synthesis of this dye, methyl 3-nitrobenzoate is formed.

In this stage, methyl benzoate is nitrated by concentrated nitric acid, in the presence of concentrated sulfuric acid as a catalyst.



METHYL BENZOATE

METHYL 3-NITROBENZOATE

(i) Outline the mechanism for this nitration of methyl benzoate.

Show how H_2SO_4 behaves as a catalyst.

[5]

(ii) State the name for this type of mechanism.

_____ **[1]**

(b) Methyl 3-nitrobenzoate can be converted into the azo dye in a multi-step synthesis.

The multi-step synthesis is shown in the flowchart on the insert.

(i) In the flowchart on the insert, draw the structure of the organic product of REACTION 1. [1]

(ii) Suggest the reagents for REACTION 1, and the reagents and conditions for REACTIONS 2 and 4.

REACTION 1 _____

_____

REACTION 2 _____

_____

_____

REACTION 4 _____

_____

[4]

(iii) The reactions of aromatic amines with bromine and with diazonium ions are similar to those of phenol with bromine and with diazonium ions.

In REACTION 3, suggest why *N*,*N*-dimethylphenylamine reacts with the diazonium ion, but benzene would NOT react.

Explain your answer.

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

_____

_____

_____

_____

_____

_____

_____

_____

_____

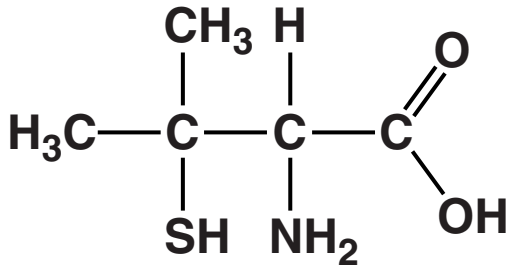
_____

_____ **[3]**

[TOTAL: 14]

3 Penicillamine is an α-amino acid that is used as a drug to treat rheumatoid arthritis.

The structure of penicillamine is shown below.



PENICILLAMINE

(a) Explain why penicillamine is described as an α-amino acid.

_____

_____ **[1]**

(b) Penicillamine exists as a zwitterion in aqueous solution.

(i) Draw the structure of this zwitterion.

[1]

(ii) Dilute aqueous acid is added to an aqueous solution of penicillamine.

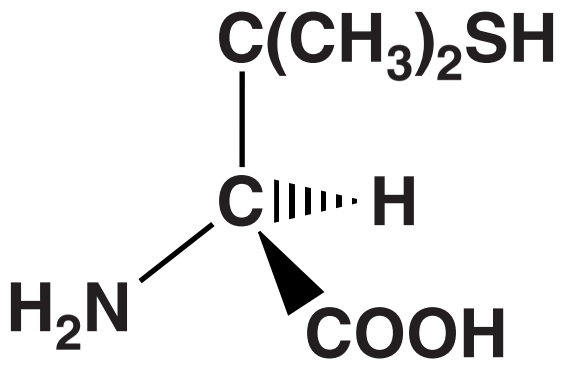
Draw the structure of the ion that forms.

[1]

(c) Penicillamine exists as optical isomers. Only one isomer is pharmacologically active. Its 3-D structure is shown opposite.

In the box opposite, draw a 3-D diagram to show the structure of the other optical isomer of penicillamine.

19



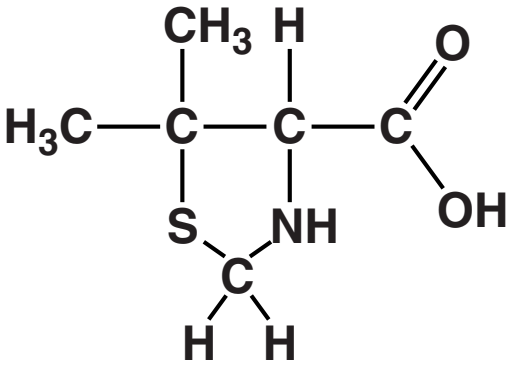
PHARMACOLOGICALLY ACTIVE
ISOMER OF PENICILLAMINE

[1]

(d) The –SH (thiol) group shows similar chemical properties to –OH.

(i) The –SH and $–NH_2$ groups in penicillamine react with halogenoalkanes by nucleophilic substitution.

Penicillamine reacts with a dihalogenoalkane to form the compound shown below.



Suggest the formula of a dihalogenoalkane that will react with penicillamine to form this compound.

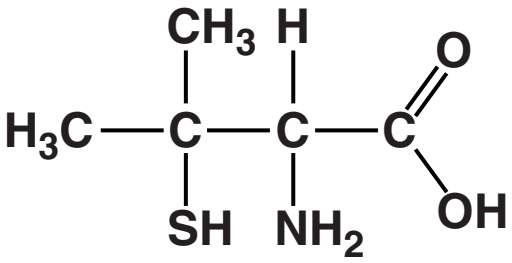
_____ **[1]**

(ii) Penicillamine is able to undergo condensation polymerisation to form polypeptide chains.

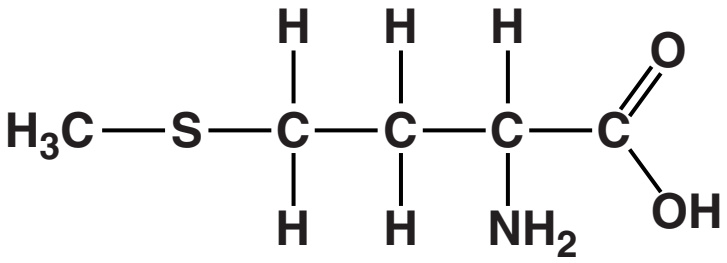
Draw TWO repeat units of a polypeptide chain of penicillamine.

[2]

(e) Penicillamine is a structural isomer of methionine, which is also an α-amino acid.



PENICILLAMINE



METHIONINE

NMR spectroscopy can be used to distinguish samples of the two isomers.

(i) Predict the number of peaks in the ^{13}C NMR spectrum of EACH of these α-amino acids.

penicillamine _____

methionine _____ **[2]**

(ii) A ^{1}H NMR spectrum of PENICILLAMINE showed five peaks.

A solution of penicillamine was shaken with a few drops of D_2O and a second ^{1}H NMR spectrum was run. The second ^{1}H NMR spectrum is shown opposite.

- **Identify the THREE types of protons in penicillamine responsible for the peaks that disappeared in the second ^{1}H NMR spectrum.**

- **Explain why these peaks were NOT seen in the second spectrum.**

_____

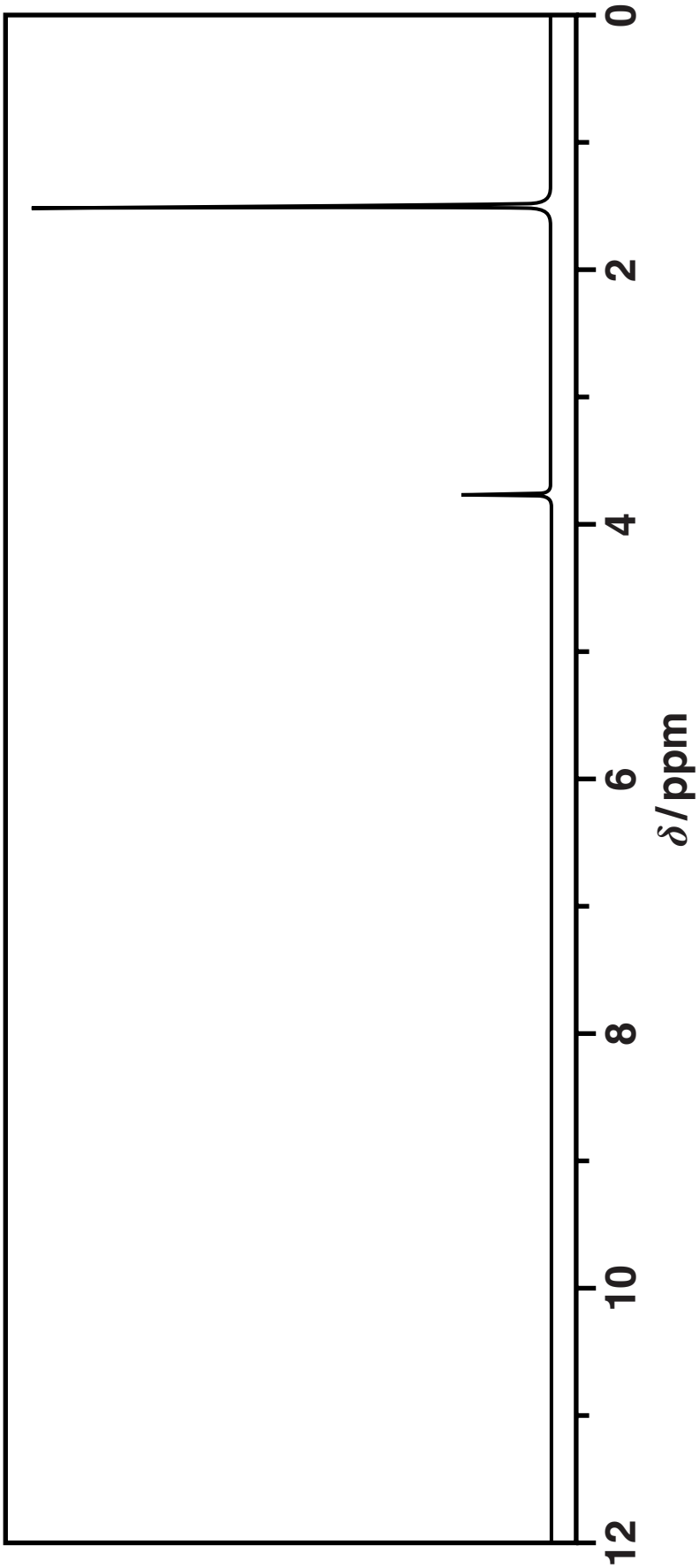
_____

_____

_____

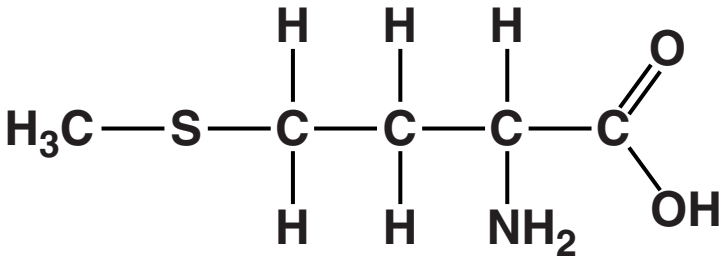
_____

_____ **[2]**


0
2
4
6
8
10
12
δ/ppm

(iii) **^{1}H NMR spectroscopy can be used to distinguish between penicillamine and methionine.**

Complete the table opposite to predict the ^{1}H NMR spectrum of METHIONINE, which is shown below. The actual chemical shifts for three types of proton in methionine have been added for you.



METHIONINE

25

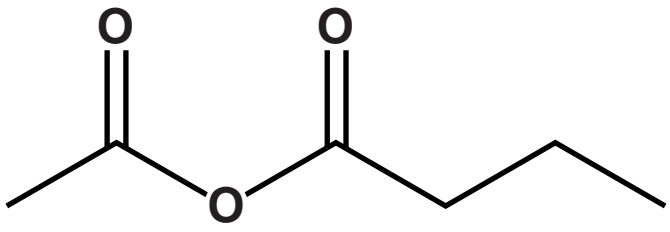
^{1}H NMR SPECTRUM FOR METHIONINE			
TYPE OF PROTON(S)	**CHEMICAL SHIFT, δ/ppm**	**SPLITTING PATTERN**	**RELATIVE PEAK AREA**
$N\underline{H}_2$	4.5	Singlet	2
$\underline{H}_3C—S—$	2.1		
$—S—C\underline{H}_2—$	2.4		

[5]

[TOTAL: 16]

4 Acid anhydrides are organic compounds that can be reacted with alcohols to form esters and carboxylic acids.

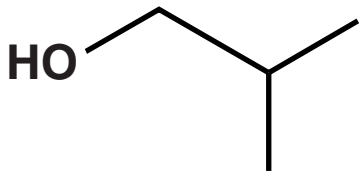
Compound F, shown below, is an acid anhydride used in the perfume industry as a starting material in the production of esters.



COMPOUND F

Compound F is a 'mixed' acid anhydride, formed from two different carboxylic acids.

(a) A chemist reacts compound F with an alcohol, G.



ALCOHOL G

(i) Name alcohol G.

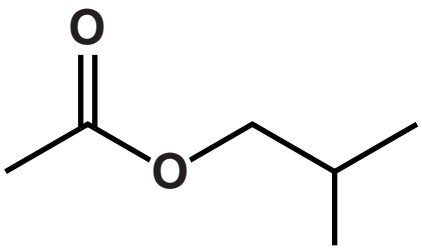
_____ **[1]**

(ii) The reaction between F and G forms a mixture of four organic compounds.

Two of the compounds are esters, and two are carboxylic acids.

One of the esters is shown below.

Draw the structures of the other three organic compounds formed.



[3]

(b) After the reaction in part (a), the chemist wished to analyse the mixture by separating the compounds using gas chromatography (GC), and measuring their retention times.

(i) State what is meant by retention time.

_____

_____ **[1]**

(ii) What are the possible limitations of this analysis by GC?

_____

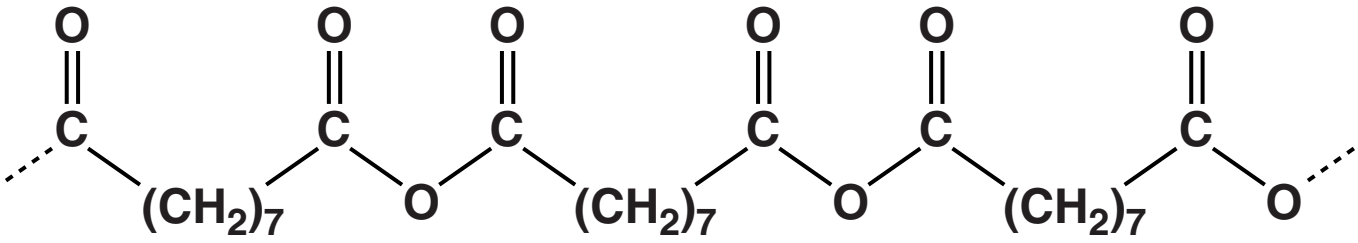
_____

_____ **[1]**

(c) Polyanhydrides are condensation polymers that have been recently developed for use in the pharmaceutical industry.

The polyanhydride, PAPA, is used to form a protective coating around some anti-cancer drugs.

A section of the polymer chain of PAPA is shown below.



(i) IN THE DIAGRAM ABOVE, draw a box around a repeat unit of PAPA. [1]

(ii) The PAPA coating is degradable and breaks down to form the dicarboxylic acid $HOOC(CH_2)_7COOH$.

Name the type of reaction that occurs when PAPA degrades.

_____ **[1]**

(iii) PAPA-coated tablets can be stored for a long time in blister packets. Scientists can detect whether PAPA has degraded using infrared (IR) spectroscopy.

Outline how IR spectroscopy could be used to determine if PAPA has degraded.

Include in your answer the wavenumber range of any characteristic absorptions that would be seen.

_____

_____

_____

_____

_____ **[2]**

(iv) **The dicarboxylic acid, $HOOC(CH_2)_7COOH$, can react with benzene-1,3-diol to form a condensation polymer.**

Draw ONE repeat unit of this condensation polymer.

[3]

[TOTAL: 13]

END OF QUESTION PAPER

ADDITIONAL ANSWER SPACE

If additional space is required, you should use the following lined page(s). The question number(s) must be clearly shown in the margins.

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