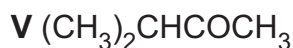
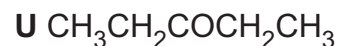
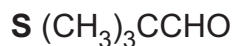
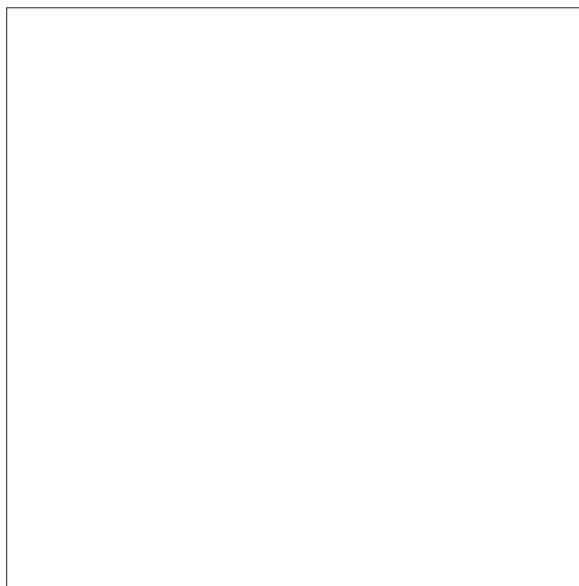
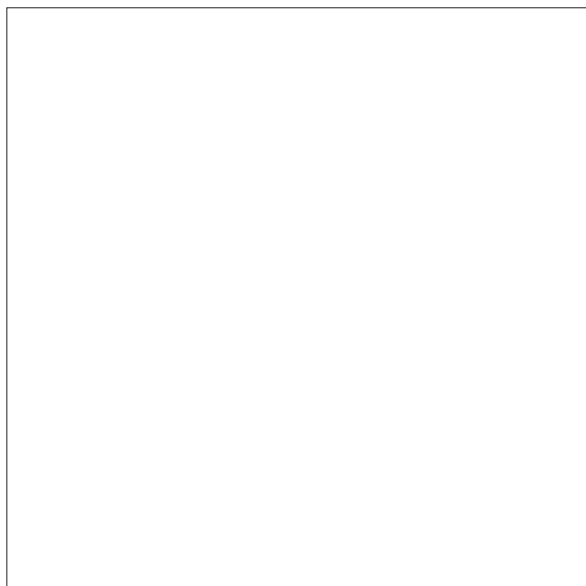


- 7 **P, Q, R, S, T, U, and V** are the seven structural isomers with molecular formula $C_5H_{10}O$ that have a carbonyl group.



- (a) Only one of these seven compounds has stereoisomers.

Draw three-dimensional diagrams of the **two** stereoisomers of this compound.



[2]

- (b) **P, Q, R, S, T, U, and V** are treated separately with alkaline $I_2(aq)$ and the product mixture is acidified.

- (i) Identify the **two** compounds that give a positive result with alkaline $I_2(aq)$.

..... and [1]

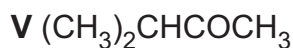
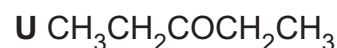
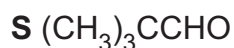
- (ii) Describe the observations when **one** of the compounds you have identified in (b)(i) is treated with alkaline $I_2(aq)$ and give the structural formulae of the **two** carbon-containing products of this reaction.

observations

two carbon-containing products

and

[2]



(c) The proton (^1H) NMR spectra of **P**, **Q**, **R**, **S**, **T**, **U**, and **V** are compared.

(i) Identify the only compound that gives a spectrum with two singlets and no other peaks.

..... [1]

Fig. 7.1 shows the spectrum obtained from one of the compounds.

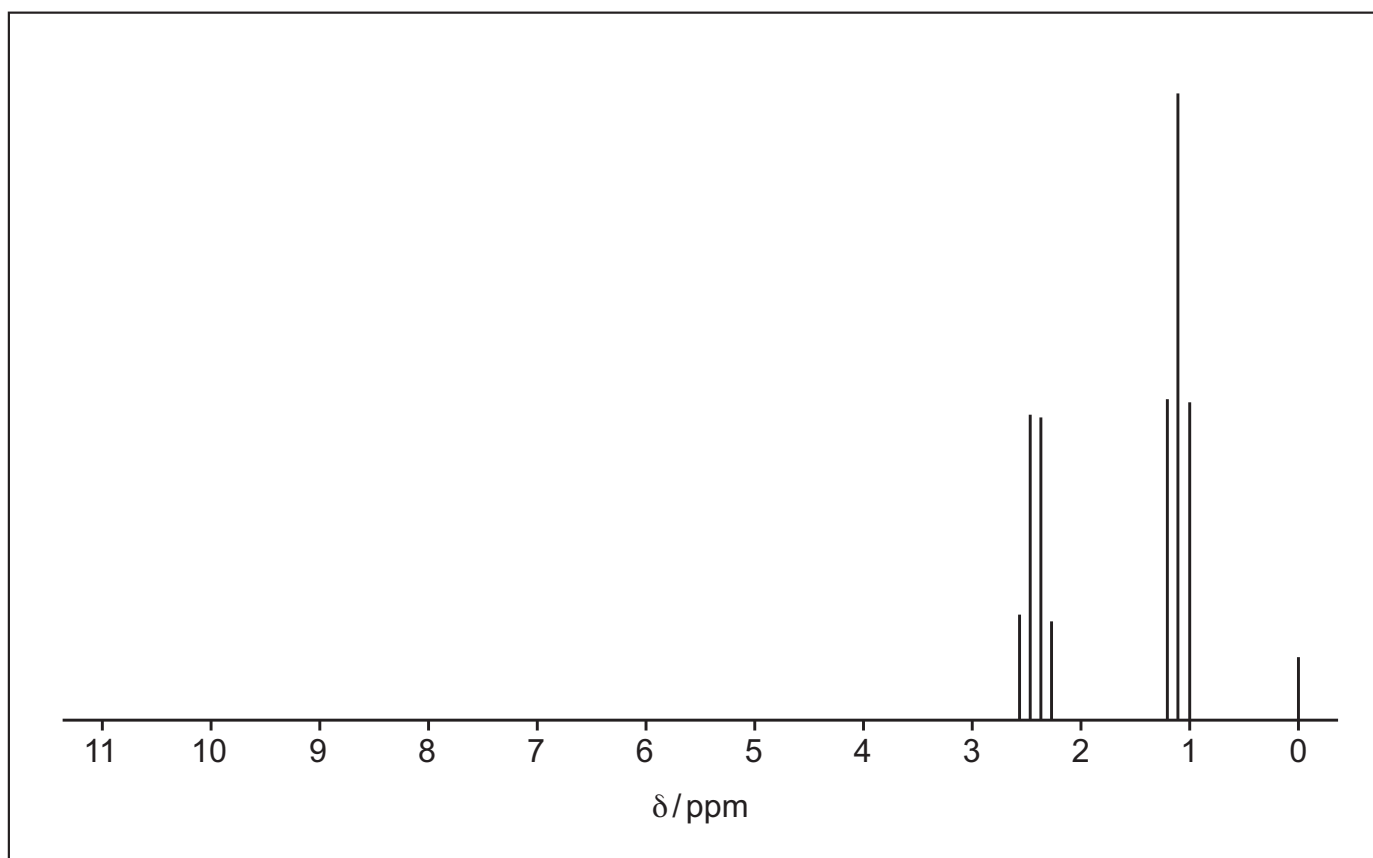


Fig. 7.1

(ii) Identify the compound that gives this spectrum.

..... [1]

(iii) Name the splitting pattern of the peak at $\delta = 1.1$ in Fig. 7.1.

Give the reason for this splitting.

name

reason [1]

(iv) Identify the substance that gives the small peak at $\delta = 0$ in Fig. 7.1.

(2)

..... [1]

(d) The carbon-13 NMR spectra of **R**, **S**, **T** and **U** are compared.

Complete Table 7.1 to state the number of peaks in the spectrum of each compound.

Table 7.1

	compound	number of peaks
R	$(\text{CH}_3)_2\text{CHCH}_2\text{CHO}$	
S	$(\text{CH}_3)_3\text{CCHO}$	
T	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_3$	
U	$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$	

[2]

[Total: 11]

6 (a) Thin-layer and gas/liquid chromatography can be used to separate mixtures into their individual components.

(i) Define the following terms used in chromatography.

R_f value

.....

retention time

.....

[2]

(ii) Each type of chromatography makes use of a stationary phase and a mobile phase.

Complete Table 6.1 with a description of each of these.

Table 6.1

	stationary phase	mobile phase
thin-layer chromatography	X	
gas/liquid chromatography		X

[1]

(b) A mixture of two substances **A** and **B** is analysed by thin-layer chromatography.

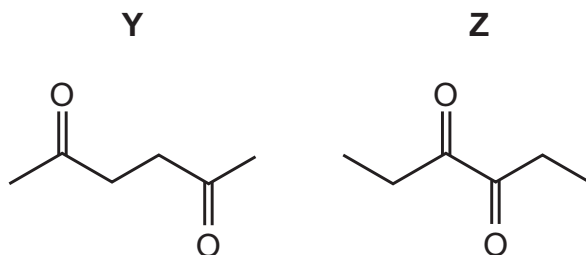
The R_f value of substance **A** is larger than that of substance **B**.

Suggest why substance **A** has a larger R_f value.

.....

..... [1]

(c) The two isomeric compounds **Y** and **Z** are analysed by proton (^1H) NMR spectroscopy.



(i) Complete Table 6.2 to predict the number of peaks observed in the proton (^1H) NMR spectra for **Y** and **Z**.

Table 6.2

compound	number of peaks observed
Y	
Z	

[1]

(ii) Name **all** the different splitting patterns observed in the proton (^1H) NMR spectra for **Y** and **Z**.

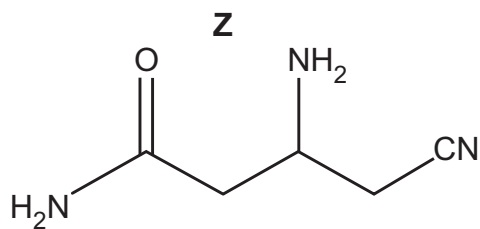
Y

Z

[2]

[Total: 7]

6 (a) Compound **Z** is used in organic synthesis.



Complete Table 6.1 to show the number of sp , sp^2 and sp^3 hybridised carbon atoms present in one molecule of **Z**.

Table 6.1

type of hybridisation	sp	sp^2	sp^3
number of carbon atoms			

[1]

(b) **Z** can undergo different reactions, as shown in Fig. 6.1.

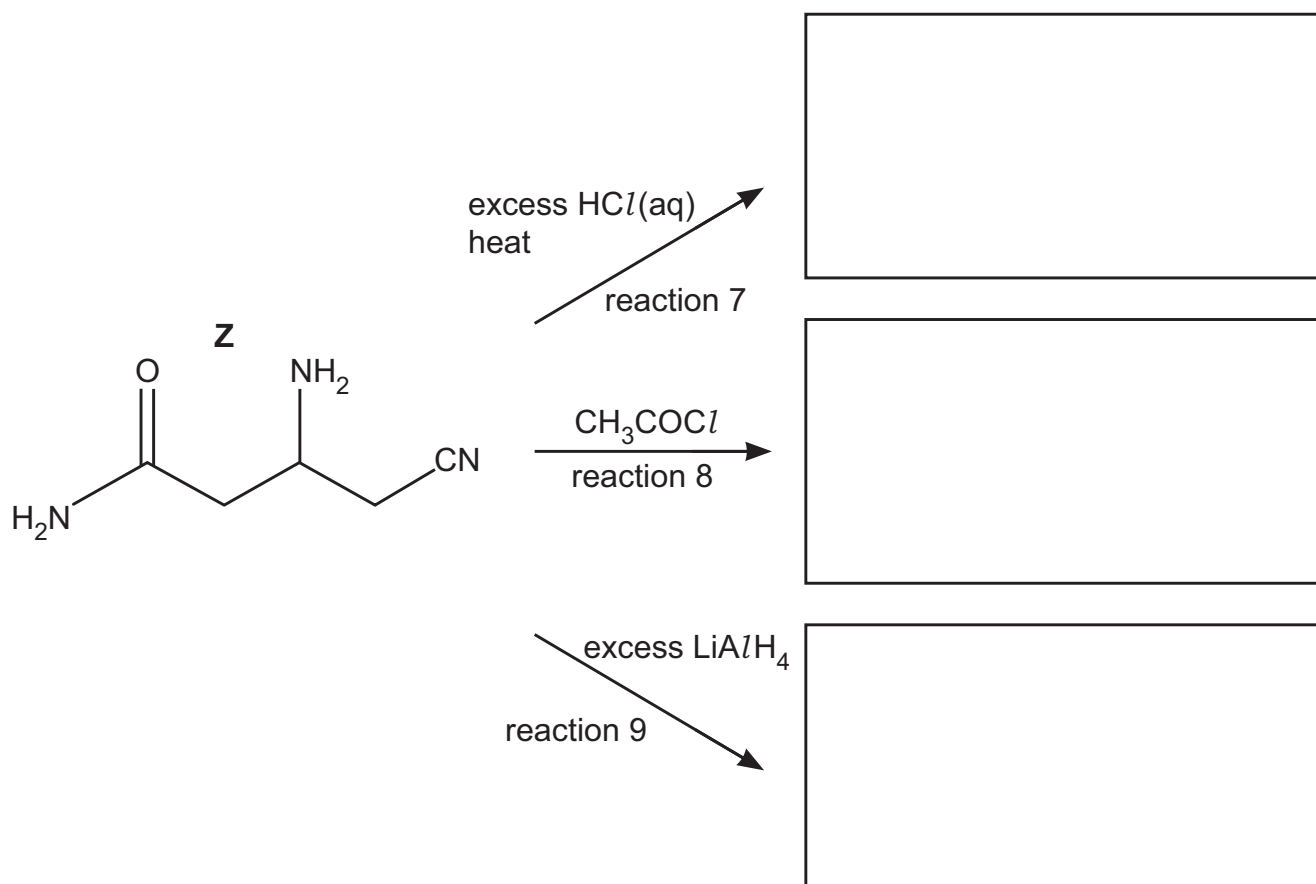


Fig. 6.1

(i) Name the **two** types of reaction occurring in reaction 7 in Fig. 6.1.

..... and [1]

(ii) Draw the structures of the organic products of reactions 7, 8 and 9 in Fig. 6.1.

[4]

(c) Compound **Z** is dissolved in D₂O and analysed by carbon-13 NMR and proton (¹H) NMR spectroscopy.

(i) Predict the number of peaks in the carbon-13 NMR spectrum of **Z**.

..... [1]

(ii) The proton (¹H) NMR spectrum of **Z** in D₂O gives three peaks for the proton environments, labelled **a**, **b** and **c**, as shown on Fig. 6.2.

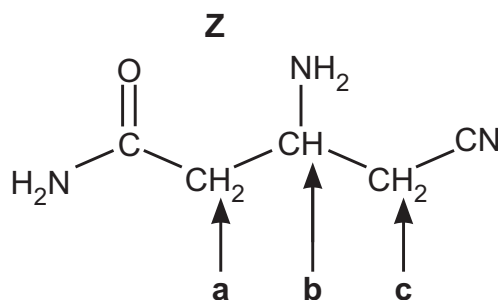


Fig. 6.2

Complete Table 6.2 for the proton (¹H) NMR spectrum of **Z** in D₂O.

Table 6.2

proton environment	a	b	c
name of splitting pattern			
chemical shift range, δ /ppm			

[2]

Table 6.3

environment of proton	example	chemical shift range, δ /ppm
alkane	$-\text{CH}_3$, $-\text{CH}_2-$, $>\text{CH}-$	0.9–1.7
alkyl next to C=O	$\text{CH}_3-\text{C}=\text{O}$, $-\text{CH}_2-\text{C}=\text{O}$, $>\text{CH}-\text{C}=\text{O}$	2.2–3.0
alkyl next to nitrile	$-\text{CH}_2-\text{CN}$	2.0–3.0
alkyl next to electronegative atom	CH_3-O , $-\text{CH}_2-\text{O}$, $-\text{CH}_2-\text{N}$	3.2–4.0
attached to alkene	$=\text{CHR}$	4.5–6.0
alkyl amine	$\text{R}-\text{NH}-$	1.0–5.0
amide	RCONHR	5.0–12.0

[Total: 9]

- 8 (a) Describe the difference in reactivity between ethanoyl chloride and chlorobenzene with water.

Explain your answer.

.....

.....

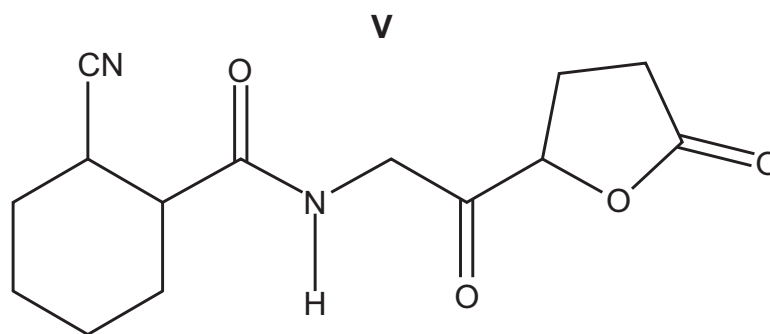
.....

.....

.....

..... [2]

- (b) The structure of compound **V** is shown.



- (i) Name all the functional groups in **V**.

.....

.....

..... [2]

- (ii) Deduce the number of possible optical isomers for **V**.

..... [1]

- (iii) Suggest **one** reason, other than better biological activity and lower dosage required, why it is beneficial to synthesise a single optical isomer of **V** for use as a drug.

.....

.....

..... [1]

(c) A sample of **V** is hydrolysed with an excess of hot aqueous alkali.

The products are isolated from the reaction mixture at pH 12.

Draw the structures of the **two** organic products of the **complete** alkaline hydrolysis of **V** in Fig. 8.1.

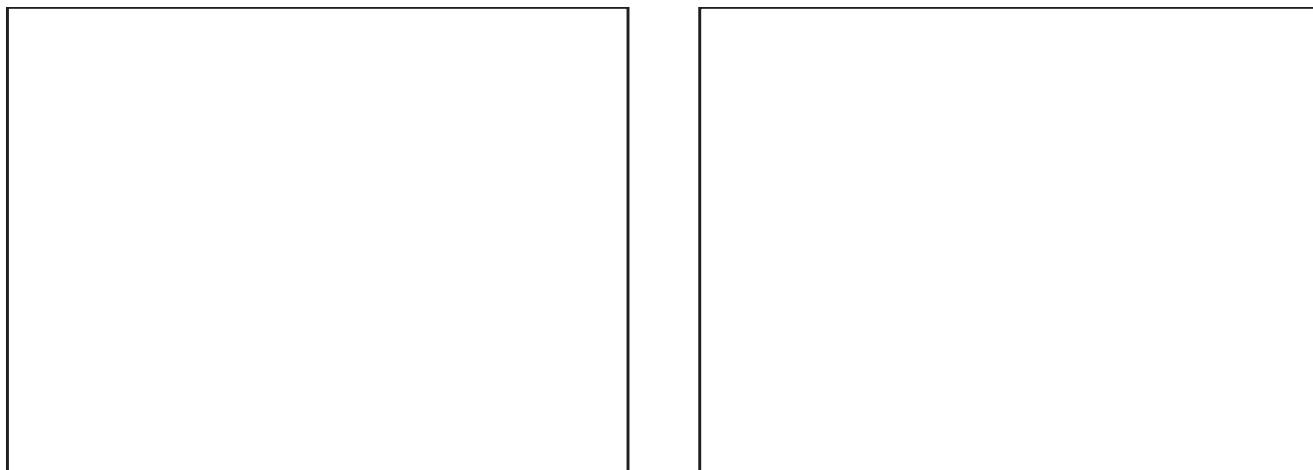


Fig. 8.1

[3]

- (d) A polypeptide formed from four amino acids, **A**, **B**, **C** and **D**, is completely hydrolysed and then analysed by gas–liquid chromatography.

The chromatogram produced is shown in Fig. 8.2.

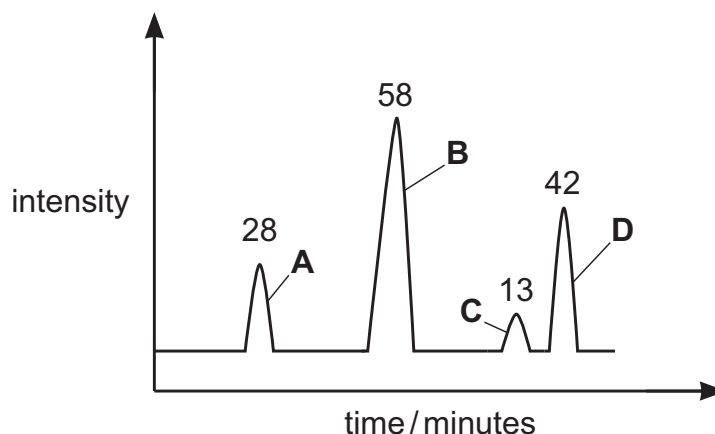


Fig. 8.2

The number above each peak represents the area under the peak.

The area under each peak is proportional to the mass of the respective amino acid in the mixture.

- (i) Calculate the percentage by mass of amino acid **A** in the original mixture.

percentage by mass of amino acid **A** = [1]

- (ii) The retention time for amino acid **D** is the longest.

Explain why **D** has a longer retention time than the **other** amino acids **A**, **B** and **C**.

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

[Total: 11]

Important values, constants and standards

molar gas constant	$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^4 \text{ C mol}^{-1}$
Avogadro constant	$L = 6.02 \times 10^{23} \text{ mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19} \text{ C}$
molar volume of gas	$V_m = 22.4 \text{ dm}^3 \text{ mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (4.18 J g ⁻¹ K ⁻¹)

