Q1. Which one of the following does **not** have a singlet peak in its proton n.m.r. spectrum?

A butyl methanoate

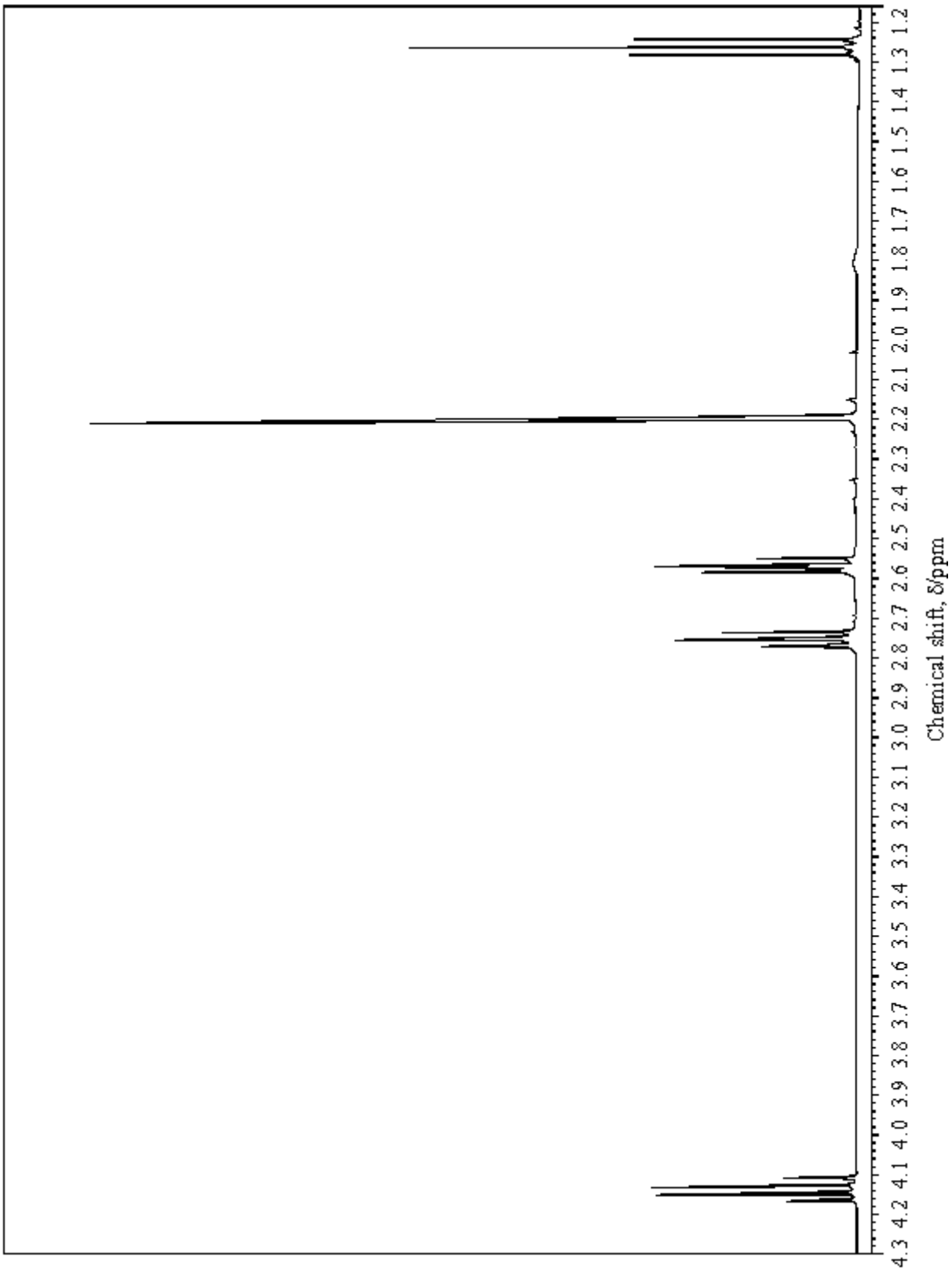
B propyl ethanoate

C ethyl propanoate

C methyl butanoate

(Total 1 mark)

Q2. The proton n.m.r. spectrum of compound **X** is shown below.



Compound **X**, $C_7H_{12}O_3$, contains both a ketone and an ester functional group. The measured integration trace for the peaks in the n.m.r. spectrum of **X** gives the ratio shown in the table below.

Chemical shift, δ/ppm	4.13	2.76	2.57	2.20	1.26
Integration ratio	0.8	0.8	0.8	1.2	1.2

Refer to the spectrum, the information given above and the data below the Periodic Table provided to answer the following questions.

(a) How many different types of proton are present in compound **X**?

.....

(1)

(b) What is the whole-number ratio of each type of proton in compound **X**?

.....

(1)

(c) Draw the part of the structure of **X** which can be deduced from the presence of the peak at δ2.20.

.....

(1)

(d) The peaks at δ4.13 and δ1.26 arise from the presence of an alkyl group. Identify the group and explain the splitting pattern.

Alkyl group .....

Explanation .....

.....

.....

(3)

(e) Draw the part of the structure of **X** which can be deduced from the splitting of the peaks at δ2.76 and δ2.57.

.....

(1)

(f) Deduce the structure of compound **X**.

.....

(2)
(Total 9 marks)

Q3. The three compounds $CH_3CH_2CH_2CH_2OH$, $(CH_3)_3COH$ and $CH_3CH_2CH_2CHO$ can be distinguished by use of the following three reagents

1. potassium dichromate(VI) acidified with dilute sulphuric acid
2. Tollens' reagent
3. ethanoic acid, together with a small amount of concentrated sulphuric acid.

(a) Identify which of these three organic compounds would reduce acidified potassium dichromate(VI). Give the structures of the organic products formed. Write a half-equation for the reduction of dichromate(VI) ions in acidic solution.

(6)

(b) Identify which one of these three organic compounds would reduce Tollens' reagent. Give the structure of the organic product formed. Write a half-equation for the reduction of Tollens' reagent.

(3)

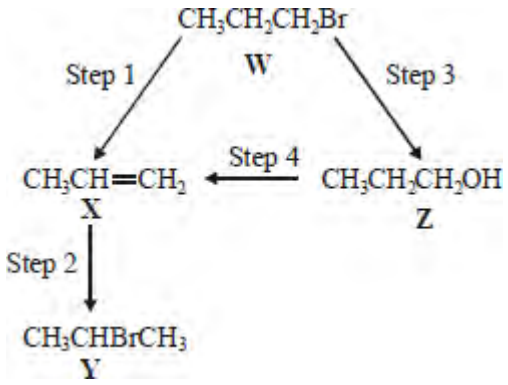
(c) Identify which of these three organic compounds would react with ethanoic acid in the presence of concentrated sulphuric acid. In each case, give the structure of the organic product formed.

(4)

(d) State the number of peaks in the proton n.m.r. spectra of $CH_3CH_2CH_2CH_2OH$ and of $(CH_3)_3COH$. (Analysis of peak splitting is not required.)

(2)
(Total 15 marks)

Q4. For this question refer to the reaction scheme below.



Which one of the following statements is **not** correct?

A **W** and **Y** are structural isomers.

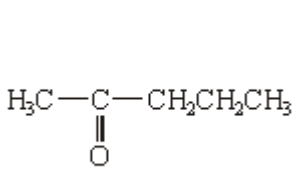
B **Z** is a primary alcohol.

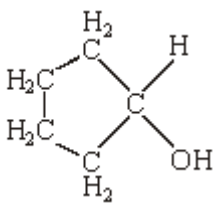
C **Y** gives two peaks in its proton n.m.r. spectrum.

C **X** has geometrical isomers.

(Total 1 mark)

Q5. Compounds **C** and **D**, shown below, are isomers of $C_5H_{10}O$





C **D**

(a) Name compound **C**.

.....

(1)

(b) Use **Table 2** on the Data Sheet to help you to answer this question.

(i) Suggest the wavenumber of an absorption which is present in the infra-red spectrum of **C** but not in that of **D**.

.....

(ii) Suggest the wavenumber of an absorption which is present in the infra-red spectrum of **D** but not in that of **C**.

.....

(2)

(c) Deduce the number of peaks in the proton n.m.r. spectrum of **C**.

.....

(1)

(d) Identify a reagent that you could use to distinguish between **C** and **D**. For each of **C** and **D**, state what you would observe when the compound is treated with this reagent.

Reagent .....

Observation with **C** .....

Observation with **D** .....

(3)

(e) Compound **E**, $CH_3CH_2CH_2CH_2CHO$, is also an isomer of $C_5H_{10}O$

Identify a reagent which will react with **E** but not with **C** or **D**. State what you would observe when **E** is treated with this reagent.

Reagent .....

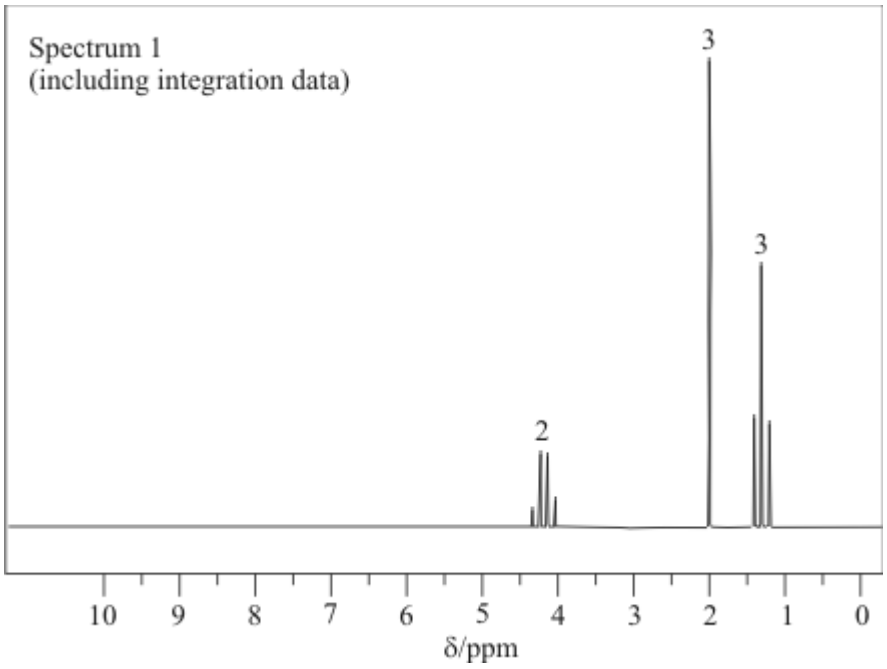
Observation with **E** .....

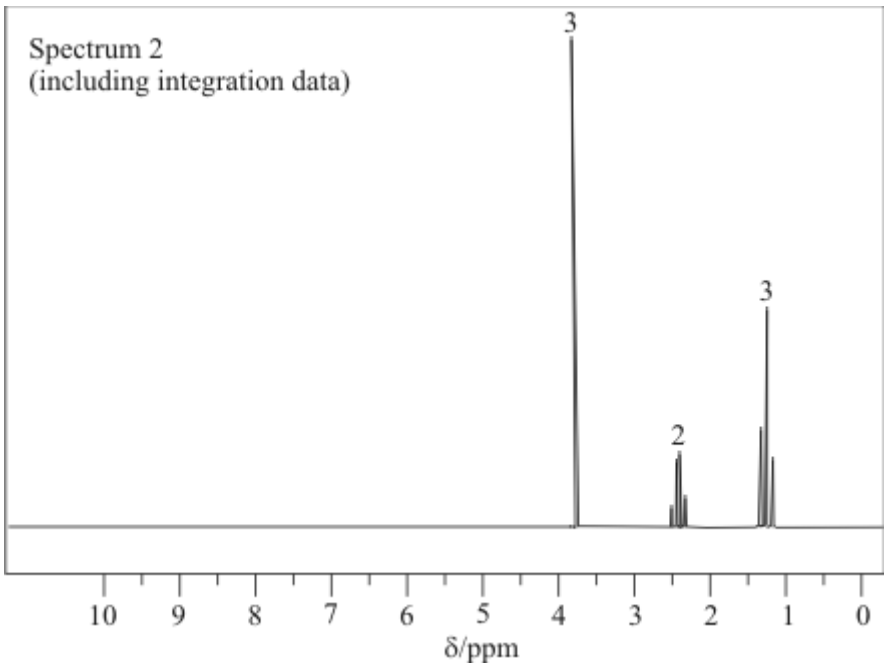
(2)
(Total 9 marks)

Q6. (a) Ester **X**, $CH_3CH_2COOCH_3$, can be produced by the reaction between propanoyl chloride and methanol. Name **X** and outline a mechanism for this reaction. Name the mechanism involved.

(6)

(b) The proton n.m.r. spectrum of **X** is shown below together with that of an isomeric ester, **Y**. Deduce which of Spectrum 1 and Spectrum 2 is that obtained from **X**. Use **Table 1** on the Data Sheet and the integration data on the spectra to help you to explain your deduction. Suggest a structure for **Y**.





(4)
(Total 10 marks)

Q7. Butenedioic acid, HOOCCH=CHCOOH, occurs as two stereoisomers. One of the isomers readily forms the acid anhydride $C_4H_2O_3$ when warmed.

(a) Draw the structures of the two isomers of butenedioic acid and name the type of isomerism shown.
Use the structures of the two isomeric acids to suggest why only one of them readily forms an acid anhydride when warmed. Draw the structure of the acid anhydride formed.

(6)

(b) Identify one electrophile which will react with butenedioic acid and outline a mechanism for this reaction.

(4)

(c) Write an equation for a reaction which occurs when butenedioic acid is treated with an excess of aqueous sodium hydroxide.

(2)

(d) Describe and explain the appearance of the proton n.m.r. spectrum of butenedioic acid.

(3)
(Total 15 marks)