MEGA LECTURE

A LEVEL CHEMISTRY

TOPIC 20 – CHROMATOGRAPHY AND SPECTROSCOPY

ASSESSED HOMEWORK

Answer all questions

Max 80 marks

Name ……
Mark ……../80 ……..% Grade ……

1. (a) A chemist discovered four unlabelled bottles of liquid, each of which contained a different pure organic compound. The compounds were known to be propan-1-ol, propanal, propanoic acid and 1-chloropropane.

Describe four **different** test-tube reactions, one for each compound, that could be used to identify the four organic compounds.
Your answer should include the name of the organic compound, the reagent(s) used and the expected observation for each test.

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(8)

(b) A fifth bottle was discovered labelled propan-2-ol. The chemist showed, using infrared spectroscopy, that the propan-2-ol was contaminated with propanone.

The chemist separated the two compounds using column chromatography. The column contained silica gel, a polar stationary phase.

The contaminated propan-2-ol was dissolved in hexane and poured into the column.
Pure hexane was added slowly to the top of the column. Samples of the eluent (the solution leaving the bottom of the column) were collected.

- Suggest the chemical process that would cause a sample of propan-2-ol to become contaminated with propanone.
- State how the infrared spectrum showed the presence of propanone.
- Suggest why propanone was present in samples of the eluent collected first (those with shorter retention times), whereas samples containing propan-2-ol were collected later.

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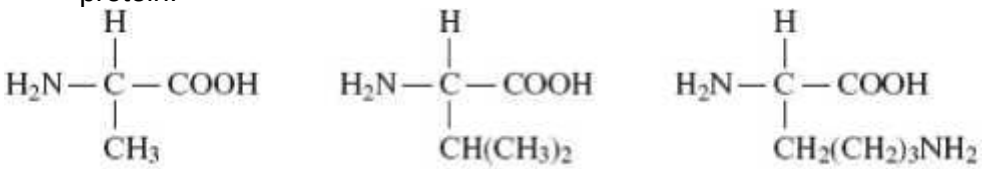
(4)
(Total 12 marks)

2. The three amino acids shown below were obtained by hydrolysis of a protein.



alanine valine lysine

(a) (i) Draw the zwitterion of alanine.

(1)

(ii) Draw the species formed when valine is dissolved in an alkaline solution.

(1)

(iii) Draw the species formed by lysine at low pH.

(1)

(b) Draw the two dipeptides formed by the reaction of alanine with valine.

(2)

(c) Name a suitable method by which the mixture of amino acids formed by hydrolysis of the protein can be separated.

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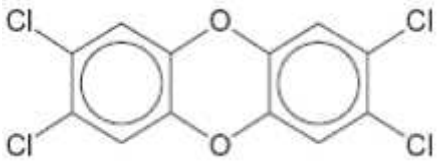
(1)
(Total 6 marks)

3. In 2008, some food products containing pork were withdrawn from sale because tests showed that they contained amounts of compounds called dioxins many times greater than the recommended safe levels.
Dioxins can be formed during the combustion of chlorine-containing compounds in waste incinerators. Dioxins are very unreactive compounds and can therefore remain in the environment and enter the food chain.
Many dioxins are polychlorinated compounds such as tetrachlorodibenzodioxin (TCDD) shown below.



In a study of the properties of dioxins, TCDD and other similar compounds were synthesised. The mixture of chlorinated compounds was then separated before each compound was identified by mass spectrometry.

(a) Fractional distillation is **not** a suitable method to separate the mixture of chlorinated compounds before identification by mass spectrometry. Suggest how the mixture could be separated.

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(1)

(b) The molecular formula of TCDD is $C_{12}H_4O_2Cl_4$

Chlorine exists as two isotopes ^{35}Cl (75%) and ^{37}Cl (25%).
Deduce the number of molecular ion peaks in the mass spectrum of TCDD and calculate the *m/z* value of the most abundant molecular ion peak.

Number of molecular ion
peaks .....

.....
.....

m/z value of the most abundant molecular ion peak .....

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.....

(2)

(c) Suggest **one** operating condition in an incinerator that would minimise the formation of dioxins.

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(1)

(d) TCDD can also be analysed using ^{13}C n.m.r.

(i) Give the formula of the compound used as the standard when recording a ^{13}C spectrum.

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.....

(1)

(ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of TCDD.

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(1)
(Total 6 marks)

4. This question concerns four isomers, **W**, **X**, **Y** and **Z**, with the molecular formula $C_5H_{10}O_2$

(a) The proton n.m.r. spectrum of **W** shows 4 peaks.
The table below gives the chemical shifts, δ values, for each of these peaks, together with their splitting patterns and integration values.

δ/ppm	2.18	2.59	3.33	3.64
Splitting pattern	singlet	triplet	singlet	triplet
Integration value	3	2	3	2

State what can be deduced about the structure of **W** from the presence of the following in its n.m.r. spectrum.

(i) The singlet peak at δ = 2.18

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.....

(ii) The singlet peak at δ = 3.33

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.....

(iii) Two triplet peaks.

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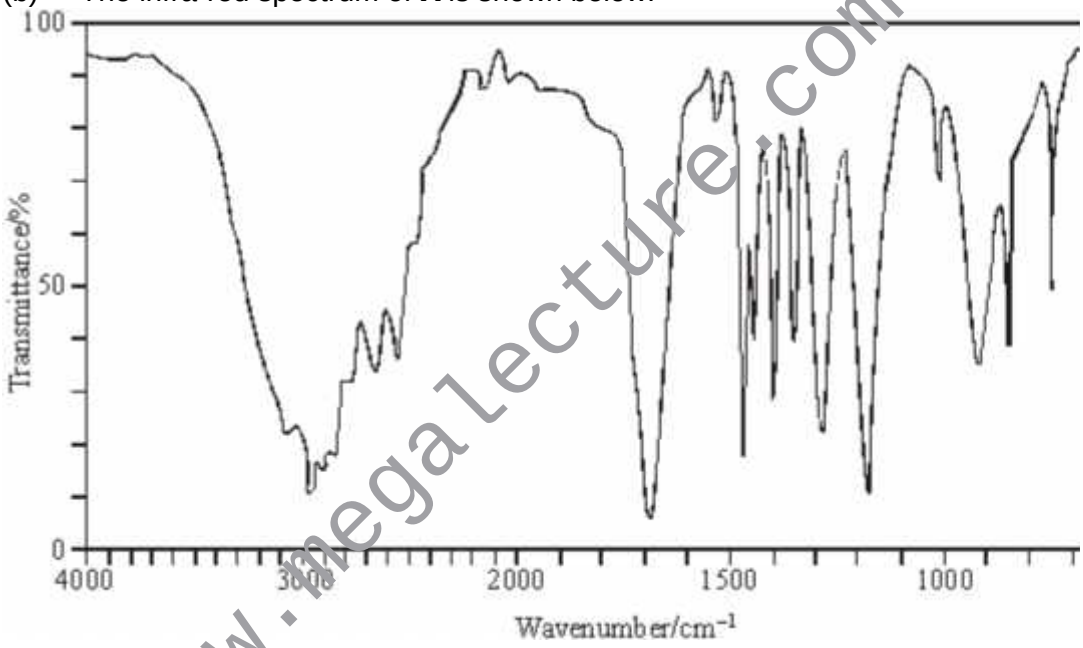
.....

(iv) Hence, deduce the structure of **W**.

(4)

(b) The infra-red spectrum of **X** is shown below.



(i) What can be deduced from the broad absorption centred on 3000 cm^{-1} in the infra-red spectrum of **X**?

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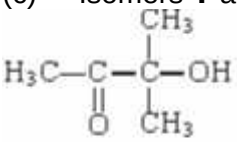
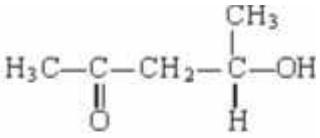
(ii) Given that the proton n.m.r. spectrum of **X** contains only two peaks with the integration ratio 9:1, deduce the structure of **X**.

(2)

(c) Isomers **Y** and **Z** have the structures shown below.



Y



Z

Identify the two reagents you could use in a simple chemical test to distinguish between **Y** and **Z**. State what you would observe when each of **Y** and **Z** is tested with a mixture of these two reagents.

Reagents .....
.....

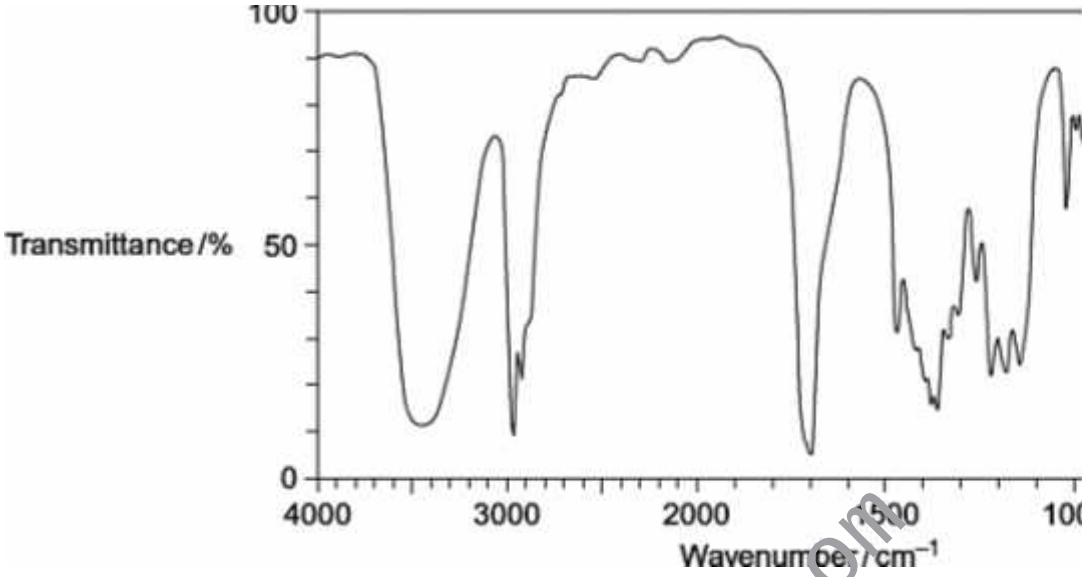
Observation with
Y .....

Observation with
Z .....

(3)
(Total 9 marks)

5. Compound **X** ($C_6H_{12}O_2$) was analysed by infrared spectroscopy and by proton nuclear magnetic resonance spectroscopy.

(a) The infrared spectrum of **X** is shown below.
Use **Table 1** on the Data Sheet to help you answer the question.



Identify the functional group that causes the absorption at 3450cm^{-1} in the spectrum.

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(1)

(b) The proton n.m.r. spectrum of **X** consists of 4 singlet peaks.

The table below gives the chemical shift for each of these peaks, together with their integration values.

δ /ppm	1.2	2.2	2.6	3.8
Integration value	6	3	2	1

Use **Table 2** on the Data Sheet to help you answer the following questions.

Use the chemical shift and the integration data to show what can be deduced about the structure of **X** from the presence of the following in its proton n.m.r. spectrum.

(i) The peak at δ = 2.6

.....
.....

(1)

(ii) The peak at δ = 2.2

.....
.....

(1)

(iii) The peak at δ = 1.2

.....
.....

(1)

(iv) Deduce the structure of **X** ($C_6H_{12}O_2$)

(1)
(Total 5 marks)

6. This question concerns isomers of $C_6H_{12}O_2$ and how they can be distinguished using n.m.r. spectroscopy.

(a) The non-toxic, inert substance TMS is used as a standard in recording both ^{1}H and ^{13}C n.m.r. spectra.

(i) Give **two** other reasons why TMS is used as a standard in recording n.m.r. spectra.

Reason
1 .....
...

.....
.....

Reason
2 .....
...

.....
.....

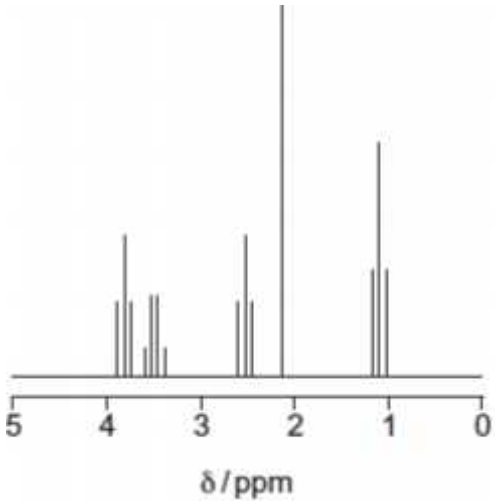
(2)

(ii) Give the structural formula of TMS.

(1)

(b) The proton n.m.r. spectrum of compound **P** ($C_6H_{12}O_2$) is represented in **Figure 1**.

Figure 1



The integration trace gave information about the five peaks as shown in **Figure 2**.

Figure 2

δ / ppm	3.8	3.5	2.6	2.2	1.2
Integration ratio	2	2	2	3	3

(i) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peak at δ 2.2.

(1)

(ii) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peaks at δ 3.5 and 1.2.

(1)

(iii) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peaks at δ 3.8 and 2.6.

(1)

(iv) Deduce the structure of **P**.

(1)

(c) These questions are about different isomers of **P** ($C_6H_{12}O_2$).

(i) Draw the structures of the two esters that both have only two peaks in their proton n.m.r. spectra. These peaks both have an integration ratio of 3:1.

Ester 1

Ester 2

(2)

(ii) Draw the structure of an optically active carboxylic acid with five peaks in its ^{13}C n.m.r. spectrum.

(1)

(iii) Draw the structure of a cyclic compound that has only two peaks in its ^{13}C n.m.r. spectrum and has no absorption for C = O in its infrared spectrum.

(1)
(Total 11 marks)

7. Organic chemists use a variety of methods to identify unknown compounds. When the molecular formula of a compound is known, spectroscopic and other analytical techniques are used to distinguish between possible structural isomers. Use your knowledge of such techniques to identify the compounds described below.

Use the three tables of spectral data on the Data Sheet where appropriate.

Each part below concerns a different pair of structural isomers.
Draw **one** possible structure for each of the compounds **A** to **J**, described below.

(a) Compounds **A** and **B** have the molecular formula C_3H_6O
A has an absorption at 1715 cm^{-1} in its infrared spectrum and has only one peak in its ^1H n.m.r. spectrum.
B has absorptions at 3300 cm^{-1} and at 1645 cm^{-1} in its infrared spectrum and does **not** show *E*–*Z* isomerism.

A **B**

(2)

(b) Compounds **C** and **D** have the molecular formula C_5H_{12}
In their ^1H n.m.r. spectra, **C** has three peaks and **D** has only one.

C **D**

(2)

(c) Compounds **E** and **F** are both esters with the molecular formula $C_4H_8O_2$
In their ^1H n.m.r. spectra, **E** has a quartet at δ = 2.3 ppm and **F** has a quartet at δ = 4.1 ppm.

E **F**

(2)

(d) Compounds **G** and **H** have the molecular formula $C_6H_{12}O$
Each exists as a pair of optical isomers and each has an absorption at about 1700 cm^{-1} in its infrared spectrum. **G** forms a silver mirror with Tollens' reagent but **H** does not.

G **H**

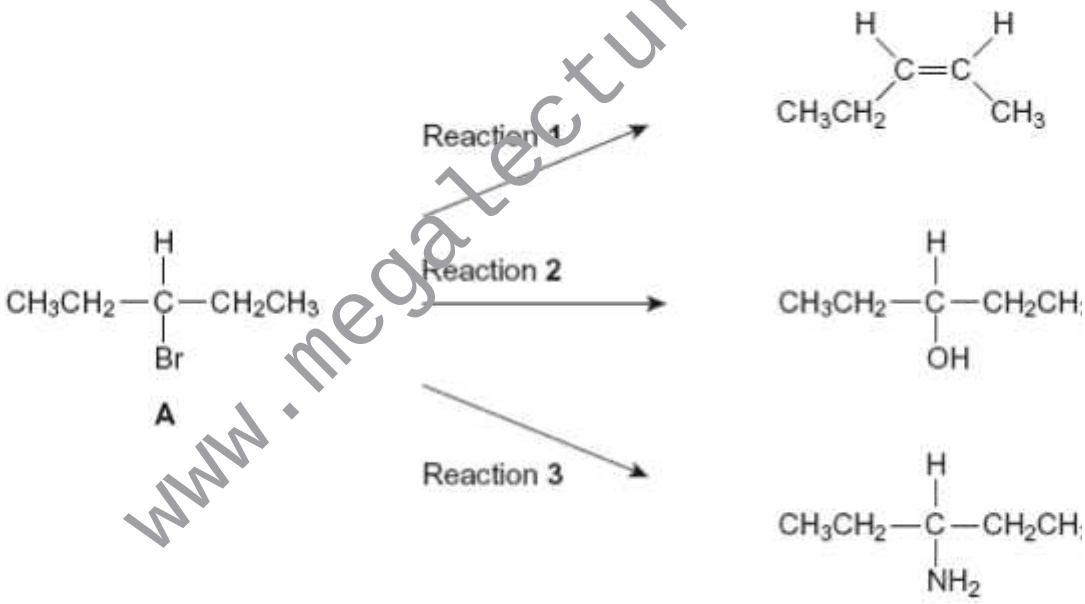
(2)

(e) Compounds **I** and **J** have the molecular formula $C_4H_{11}N$ and both are secondary amines. In their ^{13}C n.m.r. spectra, **I** has two peaks and **J** has three.

I **J**

(2)
(Total 10 marks)

8. Haloalkanes are useful compounds in synthesis.
Consider the three reactions of the haloalkane **A** shown below.



(a) (i) Draw a **branched-chain** isomer of **A** that exists as optical isomers.

(1)

(ii) Name the type of mechanism in Reaction **1**.

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(1)

(iii) Give the full IUPAC name of compound **B**.

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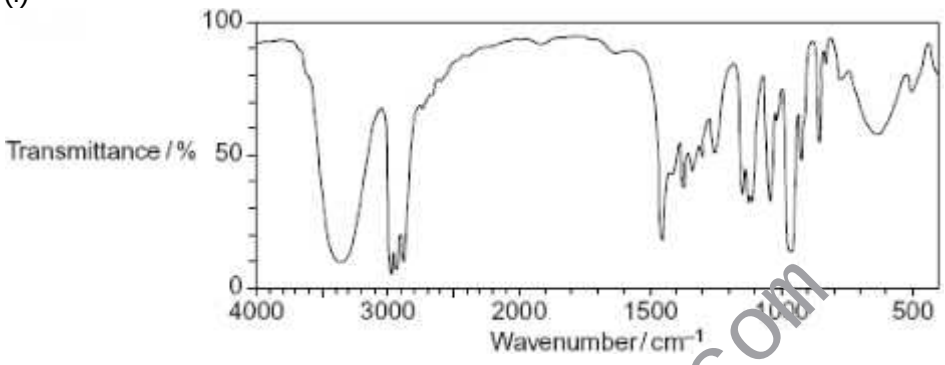
.....

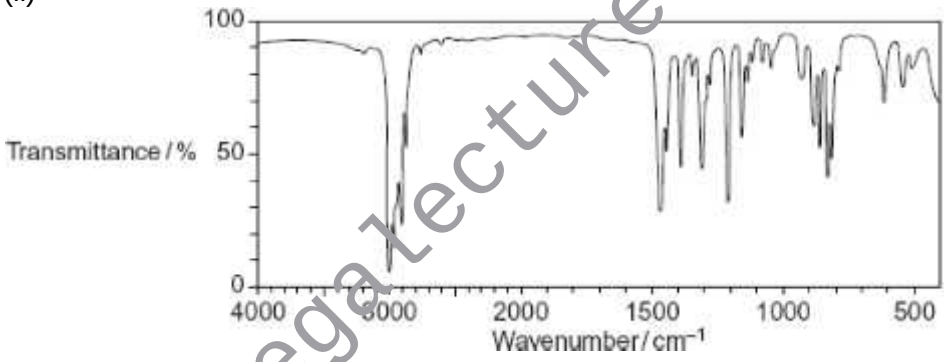
(1)

(b) The infrared spectra shown below are those of the four compounds, **A**, **B**, **C** and **D**.
Using **Table 1** on the Data Sheet, write the correct letter in the box next to each spectrum.

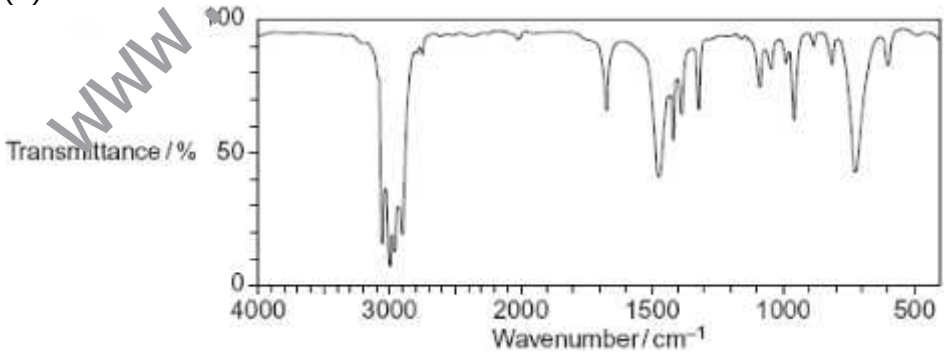
(i)



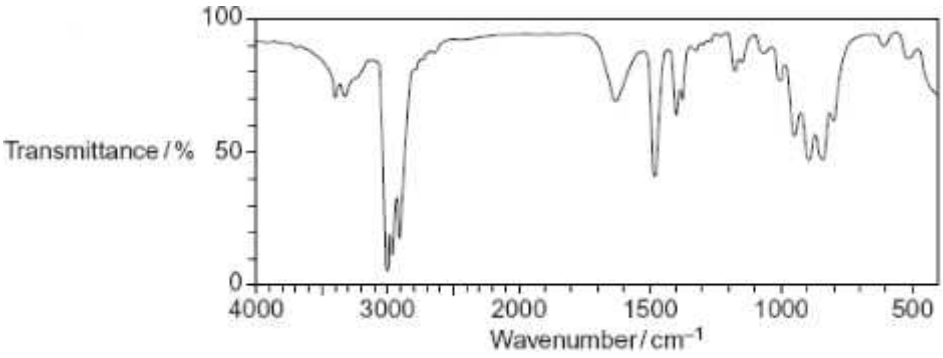
(ii)



(iii)



(iv)



(4)

(c) Draw the repeating unit of the polymer formed by **B** and name the type of polymerisation involved.

Repeating unit

Type of polymerisation .....

(2)

(d) (i) Outline a mechanism for Reaction **3**.

(4)

(ii) State the conditions used in Reaction **3** to form the maximum amount of the primary amine, **D**.

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(1)

(iii) Draw the structure of the secondary amine formed as a by-product in Reaction **3**.

(1)

(e) **D** is a primary amine which has three peaks in its ^{13}C n.m.r. spectrum.

(i) An isomer of **D** is also a primary amine and also has three peaks in its ^{13}C n.m.r. spectrum. Draw the structure of this isomer of **D**.

(1)

(ii) Another isomer of **D** is a tertiary amine. Its ^1H n.m.r. spectrum has three peaks. One of the peaks is a doublet. Draw the structure of this isomer of **D**.

(1)
(Total 17 marks)

9. Propene reacts with hydrogen bromide to form a mixture of saturated organic products. The proton n.m.r. spectrum of the major organic product has

A 3 peaks with relative intensities 3 : 2 : 2

B 2 peaks with relative intensities 3 : 4

C 3 peaks with relative intensities 3 : 1 : 3

D 2 peaks with relative intensities 6 : 1

(Total 1 mark)

10. Which one of the following has a singlet peak in its proton n.m.r. spectrum?

A ethyl propanoate

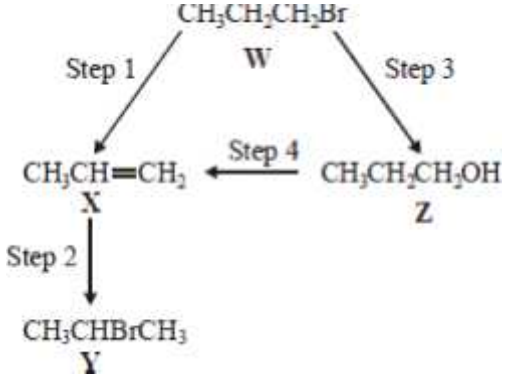
B propyl methanoate

C hexan-3-one

D 2-chlorobutane

(Total 1 mark)

11. 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)

12. 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)