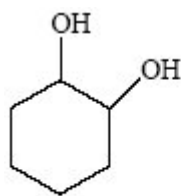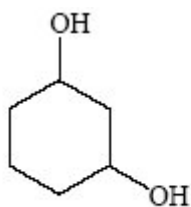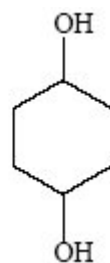**Q1.**    Three cyclic alcohols, cyclohexan–1,2-diol, cyclohexan–1,3-diol and cyclohexan–1,4-diol were compared using $^{13}C$ n.m.r. spectroscopy.
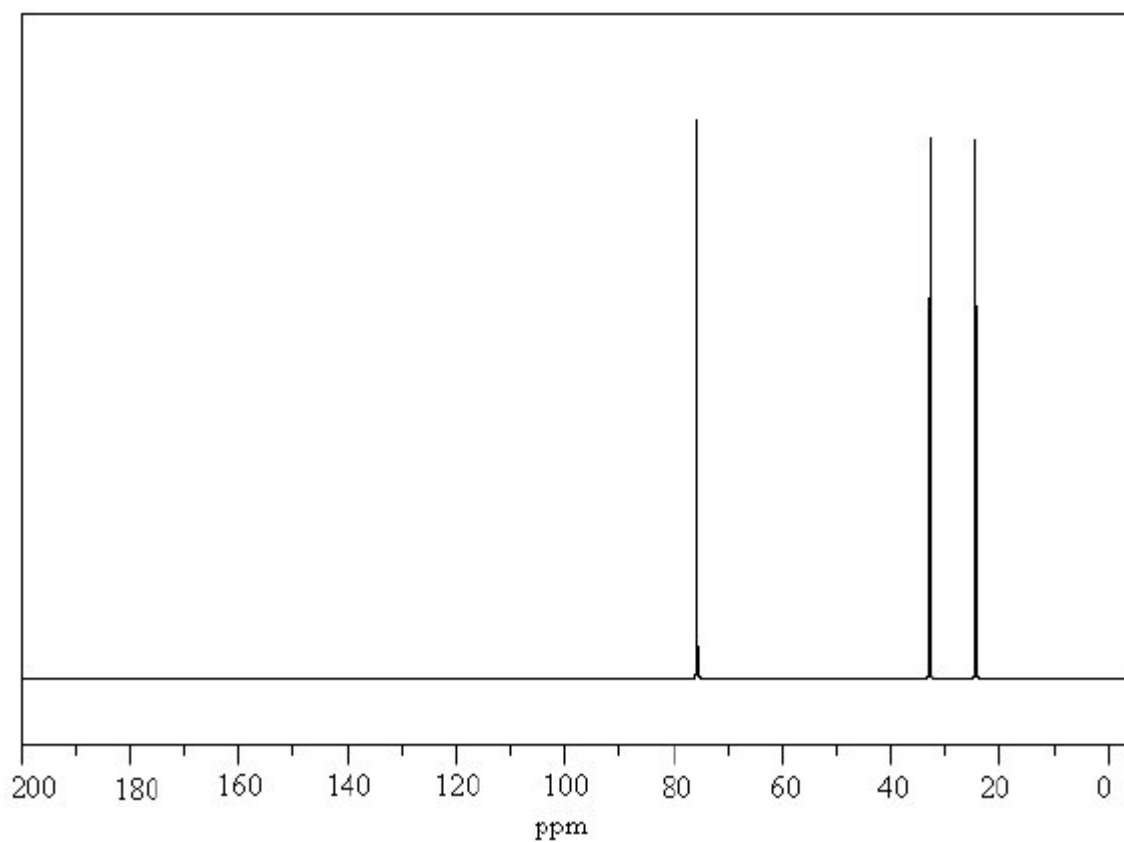


    cyclohexan-1,2-diol    cyclohexan-1,3-diol    cyclohexan-1,4-diol

The $^{13}C$ n.m.r. spectrum of cyclohexan-1,2-diol is shown below.



(a)    (i)    Explain why there are three peaks.

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(ii) Proton n.m.r. chemical shift data is shown in Table 1 on the reverse of the Periodic Table. Chemical shift values for $^{13}C$ vary similarly with chemical environment.

Suggest the δ value of the peak in the spectrum above which corresponds to the absorption for carbon atom 1 in cyclohexan-1,2-diol.

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(b) (i) Predict the number of peaks in the $^{13}C$ n.m.r. spectrum of cyclohexan-1,3-diol.

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(ii) Predict the number of peaks in the $^{13}C$ n.m.r. spectrum of cyclohexan-1,4-diol.

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(c) Suggest why the structures drawn above represents several stereoisomers.

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**(Total 5 marks)**

**Q2.** (a) Describe how propanal, $CH_3CH_2CHO$, and propanone, $CH_3COCH_3$, can be distinguished using

(i) a chemical test and

(ii) the number of peaks in their proton n.m.r. spectra.

**(5)**

(b)    Compound **Z** can be produced by the reaction of compound **X** with compound **Y** as
       shown in the synthesis outlined below.

$$CH_3CH_2CHO \xrightarrow{\text{Step 1}} X$$

$$CH_3COCH_3 \xrightarrow{\text{Step 2}} Y$$

$$\xrightarrow{\text{Step 3}} CH_3CH_2 - C \overset{O}{\underset{O-C-H}{\diagdown}} \overset{CH_3}{\underset{CH_3}{}}$$

**Z**
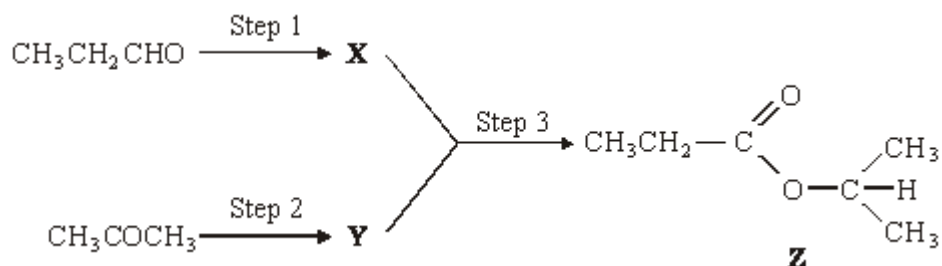
Identify compounds **X** and **Y**.
For each of the three steps in the synthesis, name the type of reaction involved and
give reagents and conditions. Equations are **not** required.

**(10)**
**(Total 15 marks)**

**Q3.**    Each of the parts (a) to (e) below concerns a different pair of isomers.

Draw one possible structure for each of the species **A** to **J**, using Table 2 on the Data
Sheet where appropriate.

(a)    Compounds **A** and **B** have the molecular formula $C_5H_{10}$
       **A** decolourises bromine water but **B** does not.

       **A**      **B**

**(2)**

(b)    Compounds **C** and **D** have the molecular formula $C_2H_4O_2$

Each has an absorption in its infra-red spectrum at about 1700 cm$^{-1}$ but only **D** has a broad absorption at 3350 cm$^{-1}$

**C**      **D**

**(2)**

(c)     Compounds **E** and **F** are esters with the molecular formula $C_5H_{10}O_2$

The proton n.m.r. spectrum of **E** consists of two singlets only whereas that of **F** consists of two quartets and two triplets.

**E**      **F**

**(2)**

(d)     Compounds **G** and **H** have the molecular formula $C_3H_6Cl_2$ **G** shows optical activity but **H** does not.
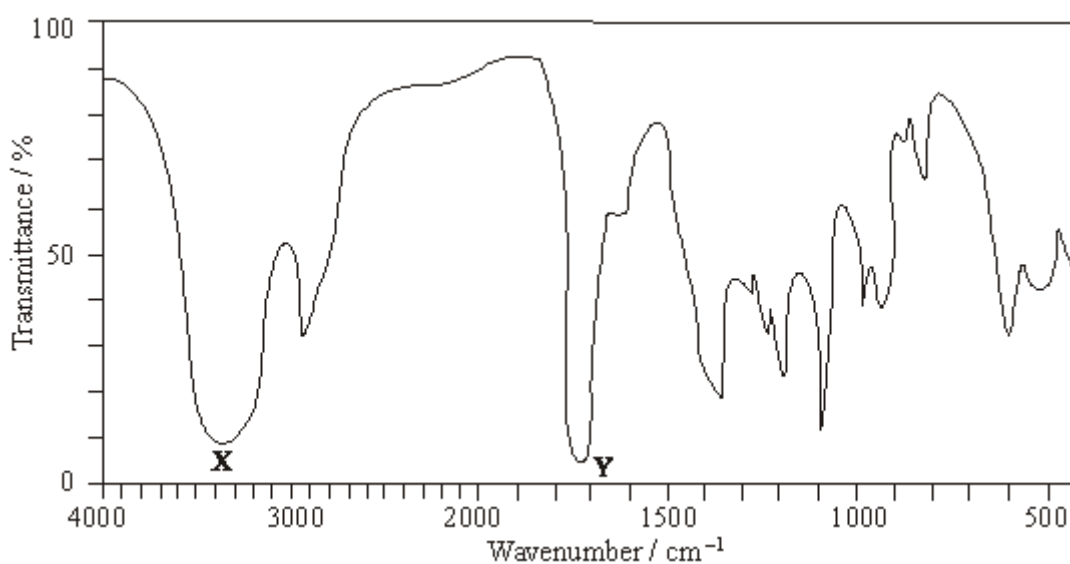
**G**      **H**

**(2)**

(e)     Compounds **I** and **J** have the molecular formula $C_6H_{12}$

Each has an absorption in its infra-red spectrum at about 1650 cm$^{-1}$ and neither shows geometrical isomerism. The proton n.m.r. spectrum of **I** consists of a singlet only whereas that of **J** consists of a singlet, a triplet and a quartet.

I        J

(2)
(Total 10 marks)

**Q4.**     (a)     The infra-red spectrum of compound **A**, $C_3H_6O_2$, is shown below.



Identify the functional groups which cause the absorptions labelled **X** and **Y**.

Using this information draw the structures of the three possible structural isomers for **A**.

Label as **A** the structure which represents a pair of optical isomers.

**(6)**

(b)     Draw the structures of the three **branched-chain** alkenes with molecular formula $C_5H_{10}$

Page 6

Draw the structures of the three dibromoalkanes, $C_5H_{10}Br_2$, formed when these three alkenes react with bromine.

One of these dibromoalkanes has only three peaks in its proton n.m.r. spectrum. Deduce the integration ratio and the splitting patterns of these three peaks.

**(10)**
**(Total 16 marks)**

**Q5.** Which one of the following pairs reacts to form an organic product with only 2 singlets in its proton n.m.r. spectrum?

**A**  ethene and bromine

**B**  propan-2-ol and acidified potassium dichromate(VI)

**C**  ethanol and concentrated sulphuric acid

**D**  epoxyethane and water in the presence of dilute sulphuric acid

**(Total 1 mark)**

**Q6.**  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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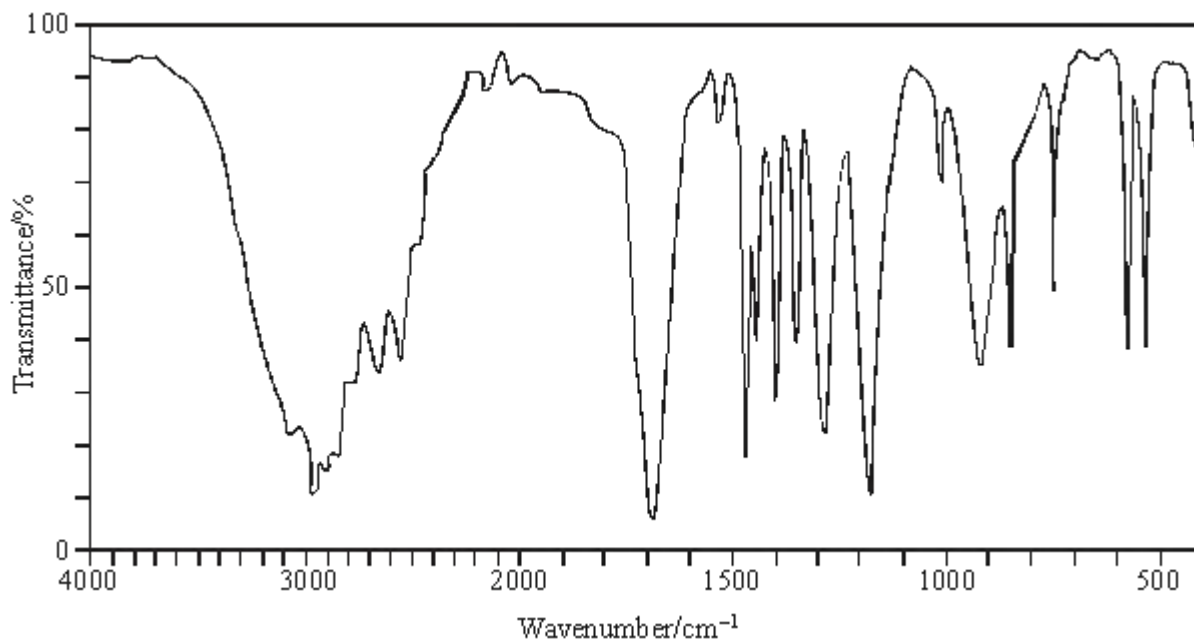


(iv)    Hence, deduce the structure of **W**.

**(4)**



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

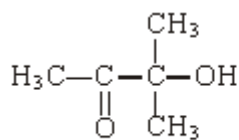(i) What can be deduced from the broad absorption centred on 3000 cm⁻¹ in the infra-red spectrum of **X**?

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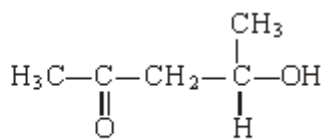
(ii) Given that the proton n.m.r. spectrum of **X** contains only two peaks with the integration ratio 9:1, deduce the structure of **X**.

**(2)**

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



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)**

**Q7.** Which one of the following pairs of reagents reacts to form an organic product that shows only 2 peaks in its proton n.m.r. spectrum?

    **A**      butan-2-ol and acidified potassium dichromate(VI)

    **B**      ethanoyl chloride and methanol

    **C**      propanoic acid and ethanol in the presence of concentrated sulphuric acid

    **D**      ethene and hydrogen in the presence of nickel

**(Total 1 mark)**