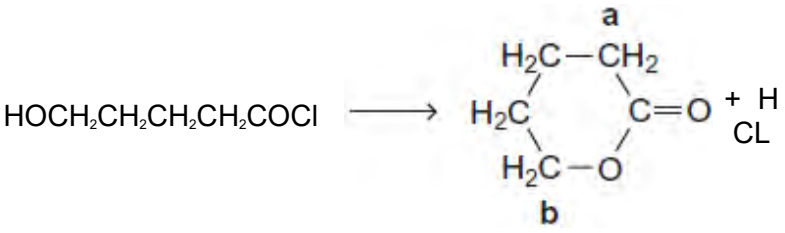
Q1. This question is about some isomers of $C_5H_8O_2$

(a) Compound **H** is a cyclic ester that can be prepared as shown.

On the structure of **H**, two of the carbon atoms are labelled.



H

(i) Name and outline a mechanism for this reaction.

Use **Table C** on the Data Sheet to give the ^{13}C n.m.r. δ value for the carbon atom labelled **a** and the δ value for the carbon atom labelled **b**.

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(7)

(ii) $HOCH_2CH_2CH_2CH_2COCl$ can also react to form a polyester in a mechanism similar to that in part (i).

Draw the repeating unit of the polyester and name the type of polymerisation involved.

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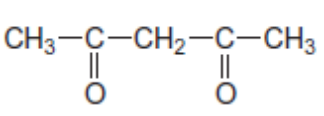
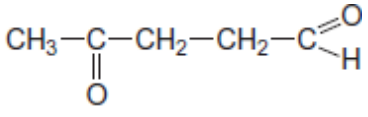
(2)

(b) State how you could distinguish between compounds **J** and **K** by a simple test-tube reaction.

State how you could distinguish between **J** and **K** by giving the number of peaks in the ^1H n.m.r. spectrum of each compound.



J



K

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(5)

(c) Draw the structure of each of the following isomers of $C_5H_8O_2$
Label each structure you draw with the correct letter **L**, **M**, **N**, **P** or **Q**.

L is methyl 2-methylpropenoate.

M is an ester that shows E-Z stereoisomerism.

N is a carboxylic acid with a branched carbon chain and does **not** show stereoisomerism.

P is an optically active carboxylic acid.

Q is a cyclic compound that contains a ketone group and has only two peaks in its ^{1}H n.m.r. spectrum.

(5)
(Total 19 marks)

Q2. When the molecular formula of a compound is known, spectroscopic and other analytical techniques can be used to distinguish between possible structural isomers.

Draw **one** possible structure for each of the compounds described in parts (a) to (d).

(a) Compounds **F** and **G** have the molecular formula $C_6H_4N_2O_4$ and both are dinitrobenzenes.
F has two peaks in its ^{13}C n.m.r. spectrum.
G has three peaks in its ^{13}C n.m.r. spectrum.

FG

(2)

(b) Compounds **H** and **J** have the molecular formula C_6H_{12}.
Both have only one peak in their ^{1}H n.m.r. spectra.

H reacts with aqueous bromine but **J** does not.

HJ

(2)

(c) **K** and **L** are cyclic compounds with the molecular formula $C_6H_{10}O$.
Both have four peaks in their ^{13}C n.m.r. spectra.
K is a ketone and **L** is an aldehyde.

KL

(2)

(d) Compounds **M** and **N** have the molecular formula $C_6H_{15}N$.
M is a tertiary amine with only two peaks in its ^{1}H n.m.r. spectrum.
N is a secondary amine with only three peaks in its ^{1}H n.m.r. spectrum.

MN

(2)
(Total 8 marks)

Q3. Acyl chlorides and acid anhydrides are important compounds in organic synthesis.

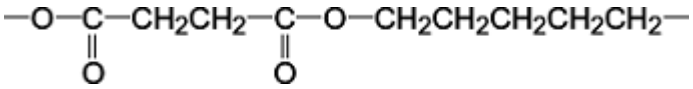
(a) Outline a mechanism for the reaction of CH_3CH_2COCl with CH_3OH and name the organic product formed.

Mechanism

Name of organic product .....

(5)

(b) A polyester was produced by reacting a diol with a diacyl chloride. The repeating unit of the polymer is shown below.



(i) Name the diol used.

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(1)

(ii) Draw the displayed formula of the diacyl chloride used.

(1)

(iii) A shirt was made from this polyester. A student wearing the shirt accidentally splashed aqueous sodium hydroxide on a sleeve. Holes later appeared in the sleeve where the sodium hydroxide had been.

Name the type of reaction that occurred between the polyester and the aqueous sodium hydroxide. Explain why the aqueous sodium hydroxide reacted with the polyester.

Type of reaction .....

Explanation .....

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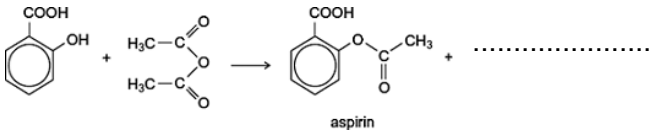
(3)

(c) (i) Complete the following equation for the preparation of aspirin using ethanoic anhydride by writing the structural formula of the missing product.



aspirin

(1)

(ii) Suggest a name for the mechanism for the reaction in part (c)(i).

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(1)

(iii) Give **two** industrial advantages, other than cost, of using ethanoic anhydride rather than ethanoyl chloride in the production of aspirin.

Advantage 1 .....

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Advantage 2 .....

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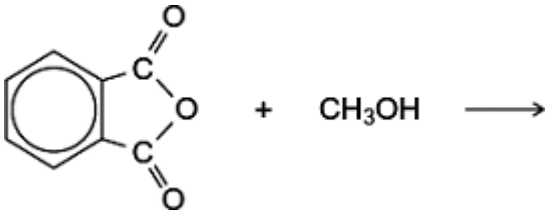
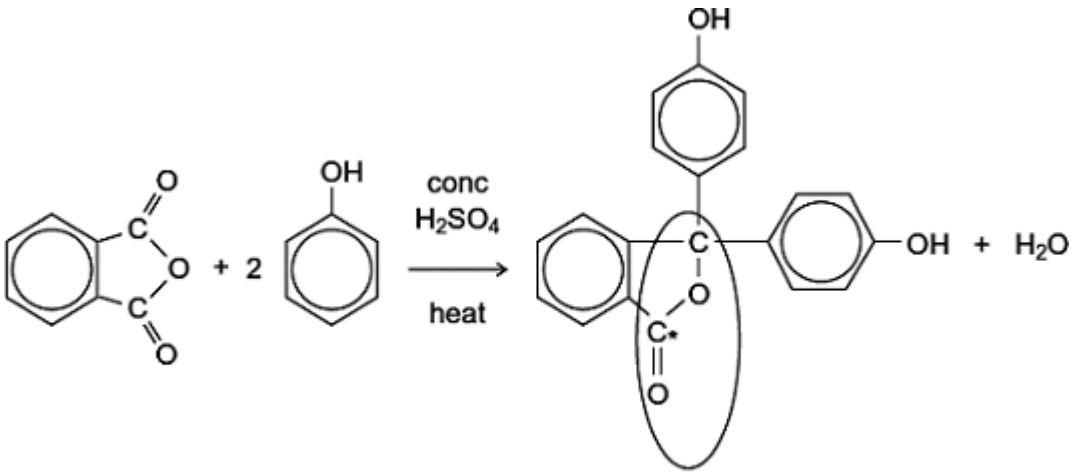
(2)

(d) Complete the following equation for the reaction of one molecule of benzene-1,2-dicarboxylic anhydride (phthalic anhydride) with one molecule of methanol by drawing the structural formula of the single product



(1)

(e) The indicator phenolphthalein is synthesised by reacting phthalic anhydride with phenol as shown in the following equation.



(i) Name the functional group ringed in the structure of phenolphthalein.

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(1)

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

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(1)

(iii) One of the carbon atoms in the structure of phenolphthalein shown above is labelled with an asterisk (*).
Use **Table 3** on the Data Sheet to suggest a range of δ values for the peak due to this carbon atom in the ^{13}C n.m.r. spectrum of phenolphthalein.

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(1)

(f) Phenolphthalein can be used as an indicator in some acid–alkali titrations.
The pH range for phenolphthalein is 8.3 – 10.0

(i) For **each** acid.alkali combination in the table below, put a tick (✓) in the box if phenolphthalein could be used as an indicator.

Acid	**Alkali**	**Tick box (✓)**
sulfuric acid	sodium hydroxide	
hydrochloric acid	ammonia	
ethanoic acid	potassium hydroxide	
nitric acid	methylamine	

(2)

(ii) In a titration, nitric acid is added from a burette to a solution of sodium hydroxide containing a few drops of phenolphthalein indicator.
Give the colour **change** at the end-point.

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(1)
(Total 21 marks)

Q4. 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 .....

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Reason 2 .....

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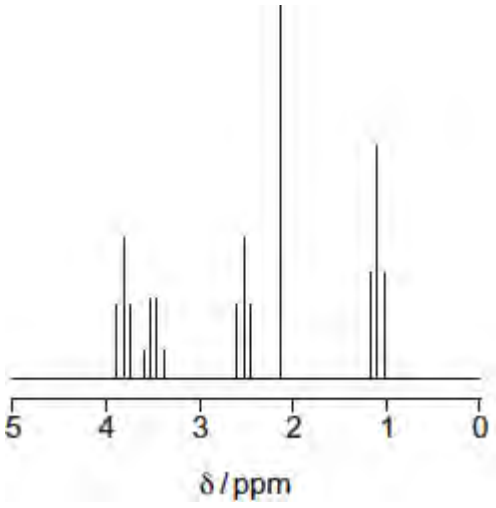
(2)

(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)