

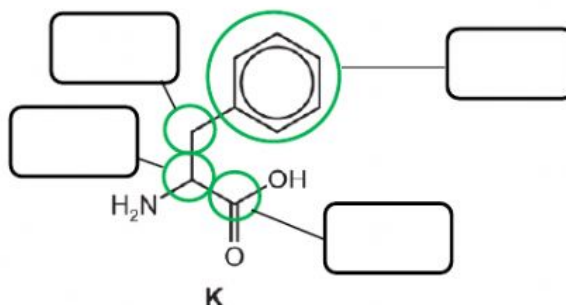
Name: _____

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¹³C NMR Spectroscopy

- 1 Use the *Data Booklet* to help you answer this question.

The carbon-13 NMR spectrum of **K** was recorded.



- (i) State how many different carbon environments are present in **K**.

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- (ii) The chemical shifts, δ , due to two of the carbon atoms x and y present in **K** are given in the table.

carbon atom	δ /ppm
x	130
y	170

On the structure of **K**, label two carbon atoms which could correspond to x and y.

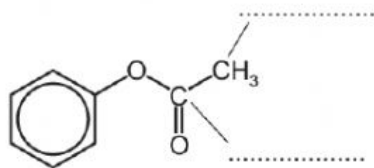
- 2 Sample bottles of each of the isomers phenyl ethanoate and methyl benzoate have lost their labels and so have been named isomer **A** and isomer **B**.

The carbon-13 NMR spectra of isomers **A** and **B** contain the following peaks.

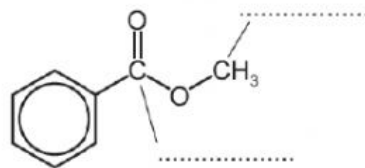
isomer A	isomer B
δ 52	δ 26
δ 128	δ 122
δ 129	δ 126
δ 130	δ 129
δ 133	δ 151
δ 167	δ 169

The identity of the compound responsible for each spectrum can be deduced by studying the chemical shifts (δ) of the peaks in the spectra.

Use the *Data Booklet* to assign the correct peaks to the labelled carbon atoms in the structures of the isomers below. Write each value next to the relevant carbon atom and hence deduce the identity of each isomer.



phenyl ethanoate is isomer

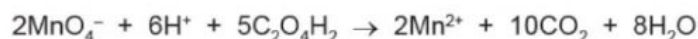


methyl benzoate is isomer

- 3 (a) Ethanedioic acid, $\text{C}_2\text{O}_4\text{H}_2$, occurs in many vegetables. The amount that occurs in spinach can be estimated as follows.

- 40.0g of spinach leaves are crushed and mixed with distilled water, using a mortar and pestle.
- The mixture is filtered, and the leaves are washed with a little more water.
- The combined filtrate and washings are made up to 100.0 cm^3 with water.
- A 25.0 cm^3 portion of the resulting solution is added to a conical flask, along with an excess of dilute sulfuric acid.
- The acidified solution is warmed, and then titrated with $0.0200\text{ mol dm}^{-3}\text{ KMnO}_4$.

The equation for the reaction between ethanedioic acid and acidified manganate(VII) ions is shown.



In the titration, 15.20 cm^3 of KMnO_4 was required to reach the end-point.

Calculate the percentage by mass of ethanedioic acid in the spinach leaves (round off to 2 decimal place) and do the working on page 20 of the analytical notes.

Percentage by mass of ethanedioic acid =%

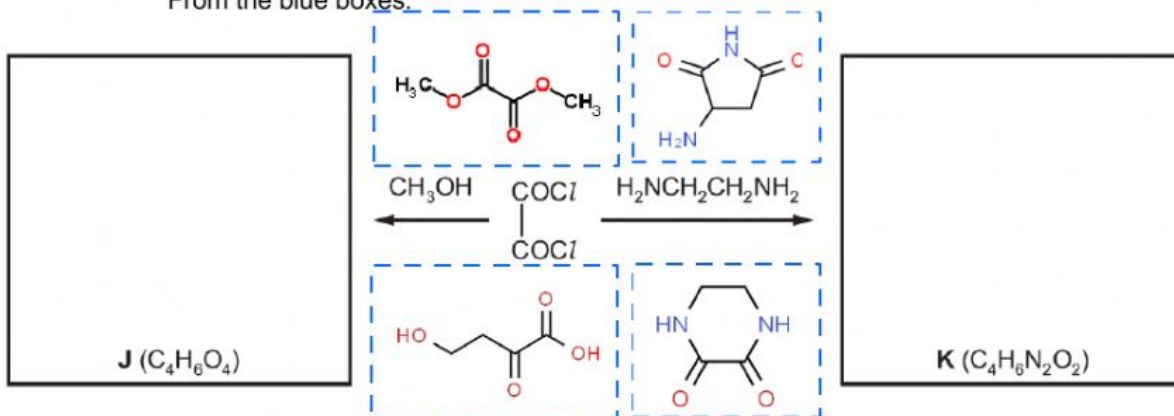
- (b) Ethanedioic acid can be converted into ethanedioyl chloride:



- (i) State a suitable reagent for this reaction.

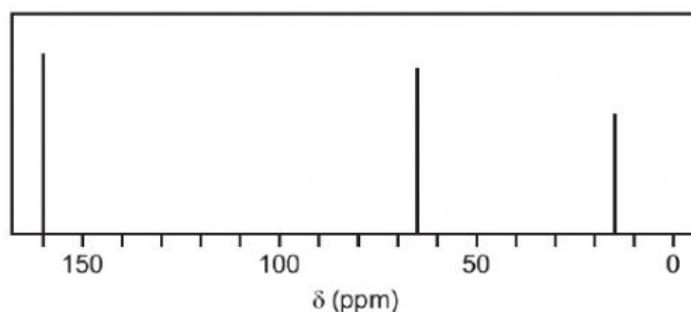
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- (ii) For the reactions of ethanedioyl chloride below, select the correct structures of J and K From the blue boxes.

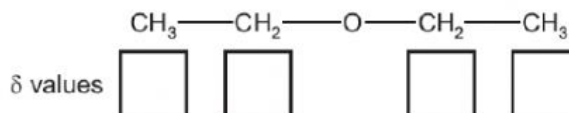


- (c) When ethanedioyl chloride is reacted with silver ethanedioate, $\text{AgO}_2\text{CCO}_2\text{Ag}$, in ethoxyethane at -30°C , an oxide of carbon, L, is formed. The molecule of L has no overall dipole and has molecular formula C_4O_6 .

The carbon-13 NMR spectrum of a solution of L in ethoxyethane, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, is shown below.



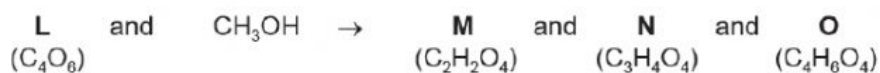
- (i) Use the *Data Booklet* to state in the boxes below the δ values for the peaks in the spectrum which are due to the carbon atoms in ethoxyethane.



- (ii) From the ^{13}C NMR spectrum given, explain what the spectrum indicates about the of structure L.

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(d) When pure **L** is reacted with an excess of CH_3OH , a mixture of three compounds is formed.

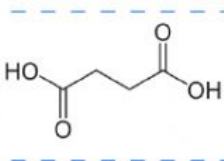
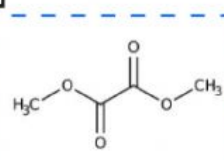
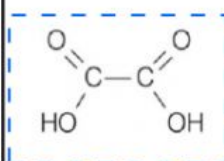
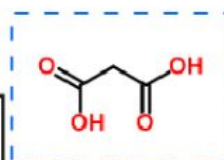
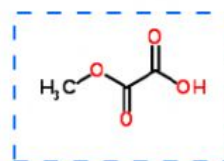
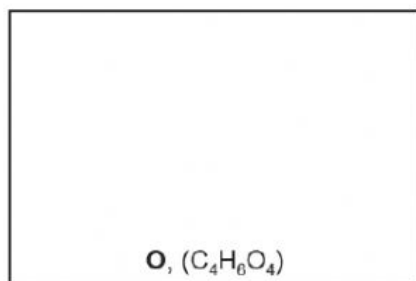
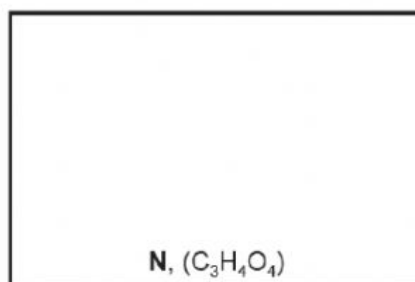
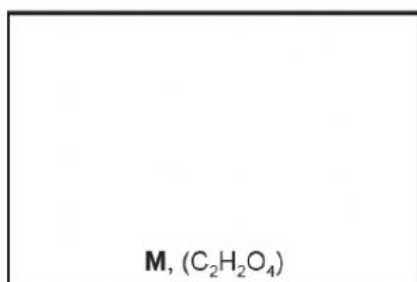


M is formed as one of the products when either **N** or **O** is heated with aqueous acid.

The table gives information of the peaks recorded in the carbon-13 NMR spectra of **M**, **N** and **O**.

compound	peaks recorded in carbon-13 NMR spectrum
M	δ 162
N	δ 53 δ 160 δ 162
O	δ 53 δ 160

(i) Drag and drop the correct structures of **M**, **N** and **O**.



(ii) Select the correct structures of **L** that fits all the data given in (c) and (d).

