

Organic Synthesis

Question Paper 2

Level	International A Level
Subject	Chemistry
Exam Board	Edexcel
Topic	Transition Metals & Organic Nitrogen Chemistry
Sub Topic	Organic Synthesis
Booklet	Question Paper 2

Time Allowed:	68 minutes
Score:	/56
Percentage:	/100

Grade Boundaries:

A*	A	B	C	D	E	U
>85%	'77.5%	70%	62.5%	57.5%	45%	<45%

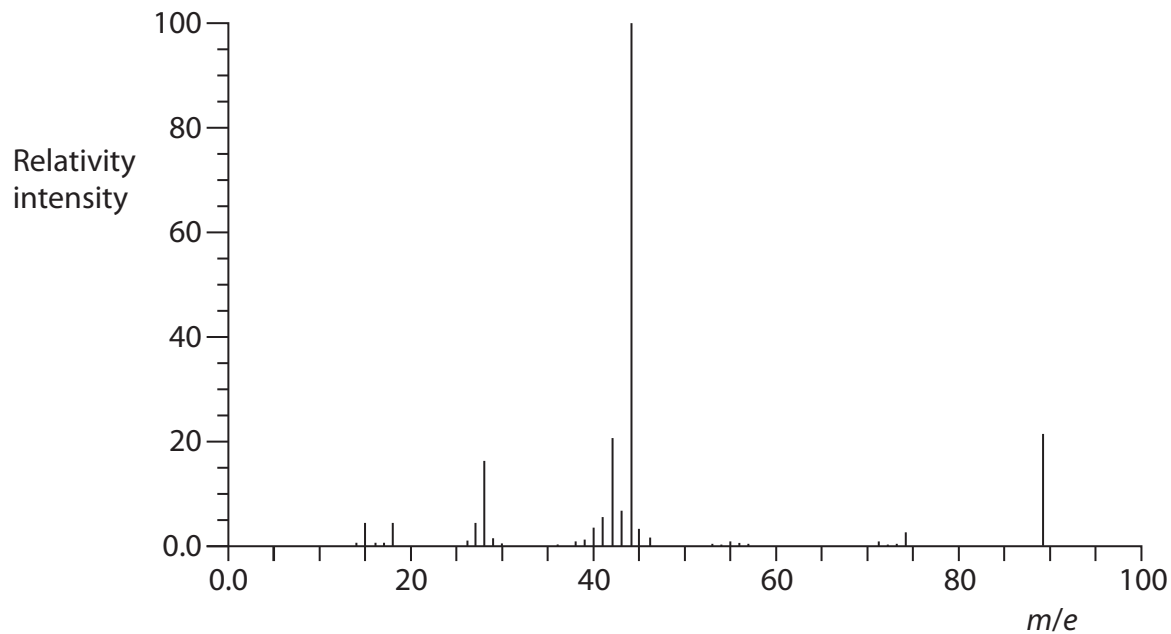
- 1 Compound **P** is a white crystalline solid with the following percentage composition by mass.

Element	% composition by mass
carbon	40.44
hydrogen	7.87
oxygen	35.96
nitrogen	15.73

- (a) Calculate the empirical formula of **P**. You **must** show your working.

(3)

(b) The mass spectrum of **P** is shown below.



(i) Label the molecular ion on the mass spectrum using the symbol M^+ .

(1)

(ii) Deduce the molecular formula of **P**.

(1)

(c) **P** was dissolved in sodium carbonate solution and, on heating, a colourless gas, which turned lime water cloudy, was very slowly evolved. When an aqueous solution of **P** was mixed with an aqueous solution of copper(II) sulfate, the blue colour of the copper(II) sulfate solution darkened.

(i) Use the results of these two experiments to deduce the functional groups that are present in **P**. Explain your answers.

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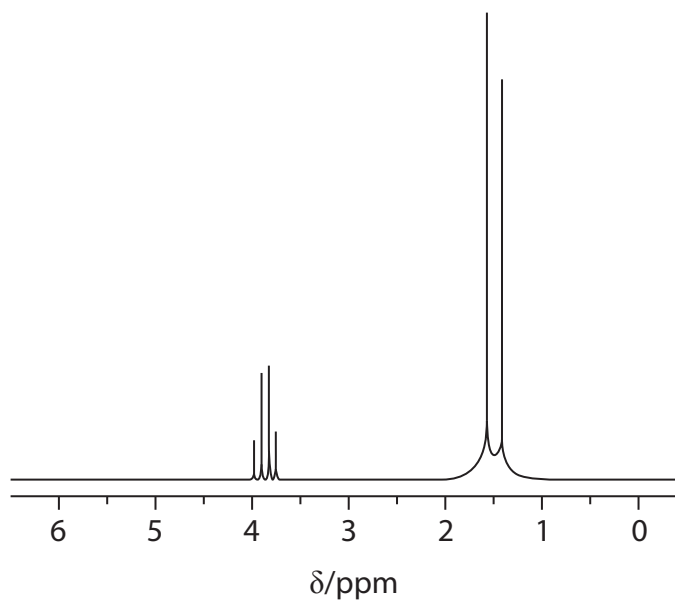
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(ii) There are several compounds which have the formula you have deduced in (b)(ii) and contain the two functional groups you have identified in (c)(i).

Draw the structural or displayed formulae of **two** of these compounds.

(2)

(iii) The nuclear magnetic resonance spectrum of compound **P** is shown below.



This part of the spectrum only shows the peaks due to the hydrogen atoms which are attached directly to carbon atoms.

Use this spectrum to deduce the structure of **P**. Justify your answer.

(2)

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(d) Explain why **P** is a solid at room temperature and pressure.

(1)

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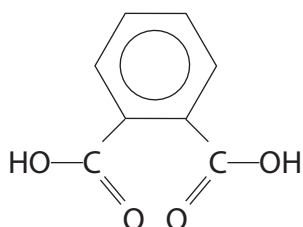
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(Total for Question 1 = 14 marks)

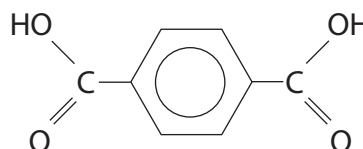
2

Phthalates

The benzene dicarboxylic acids and their esters are important industrial compounds. The structures of two of these acids are shown below.

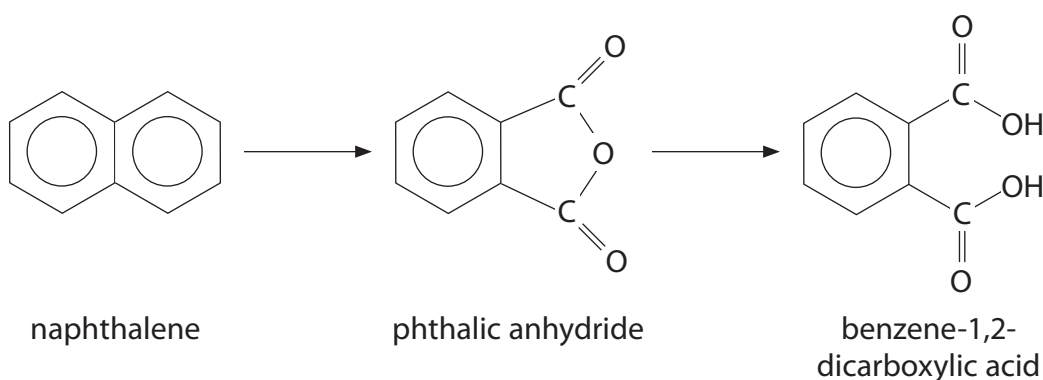


benzene-1,2-dicarboxylic acid



benzene-1,4-dicarboxylic acid

Benzene-1,2-dicarboxylic acid is manufactured by the catalytic oxidation of naphthalene to phthalic anhydride which is then hydrolysed. This reaction sequence is summarised below.



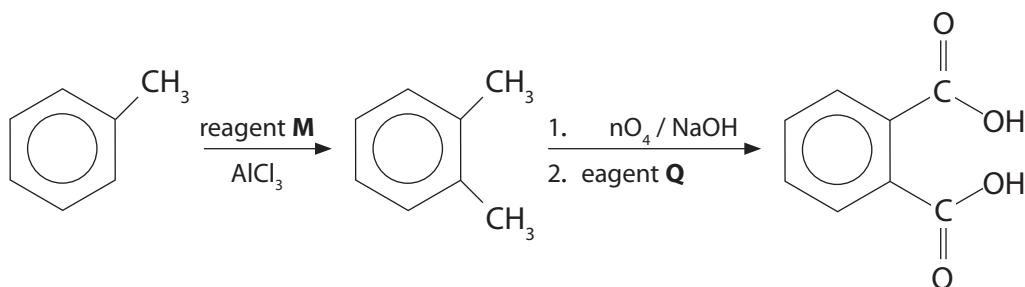
The use of naphthalene as a source of these compounds gave rise to the common names, phthalic acid for benzene-1,2-dicarboxylic acid and terephthalic acid for benzene-1,4-dicarboxylic acid.

The alkyl esters derived from benzene-1,2-dicarboxylic acid are known as phthalates.

Phthalates are used as plasticisers to increase the flexibility of many common plastics. However, some phthalates are known to be endocrine disruptors and recent studies have raised concerns about their role in the fall in human fertility rates. Because phthalates are used in making plastic drinks bottles and leach readily out of the structure, they are easily ingested.

The polyester *Terylene* is derived from benzene-1,4-dicarboxylic acid and ethane-1,2-diol.

- (a) One method of preparing benzene dicarboxylic acids in the laboratory is from methylbenzene in the sequence shown below.



- (i) Identify reagent **M**, by name or formula.

(1)

- (ii) Write the equation for the reaction between **M** and AlCl_3 to form an electrophile.

(1)

(iii) Give the mechanism for the reaction of methylbenzene with your electrophile in (a)(ii).

(3)

(iv) Suggest why methylbenzene reacts faster than benzene in this type of reaction.

(2)

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(v) In the second step of the synthesis, the potassium manganate(VII) is an oxidizing agent.

Suggest the identity of reagent **Q**, which is added when oxidation is complete.

(1)

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(b) In the oxidation of naphthalene to phthalic anhydride, the catalyst is vanadium(V) oxide. With fresh catalyst, the reaction occurs at 360 °C but, over time, the temperature must be slowly increased as the catalyst activity decreases.

(i) State the property which gives transition metal compounds, such as vanadium(V) oxide, catalytic properties.

(1)

(ii) Suggest why the catalyst activity decreases over time.

(1)

(c) The simplest phthalate of benzene-1,2-dicarboxylic acid is its dimethyl ester (1,2-dimethyl benzene-1,2-dicarboxylate).

(i) Draw the structure of this phthalate.

(1)

- (ii) Suggest and explain what can be deduced about the interactions between the phthalate and the plastic from the fact that phthalates are readily leached from plastic bottles.

(2)

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- *(iii) Suggest how a plasticiser works.

(2)

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- (d) One way of making *Terylene* is by converting benzene-1,4-dicarboxylic acid into the di-acyl chloride and then reacting it with ethane-1,2-diol.

- (i) Suggest a reagent that could be used to convert benzene-1,4-dicarboxylic acid into the di-acyl chloride.

(1)

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- (ii) Suggest an advantage of using the di-acyl chloride rather than the dicarboxylic acid to make the polyester.

(1)

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(iii) Draw the structure of the polyester, *Terylene*, showing two repeat units.

(2)

(iv) In practice, the manufacture of *Terylene* involves a process called ester exchange in which ethane-1,2-diol reacts with the dimethyl ester of benzene-1,4-dicarboxylic acid.

What would be the by-product of this reaction?

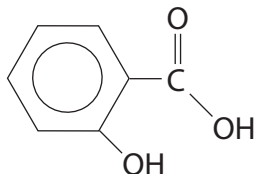
(1)

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(Total for Question 2 = 20 marks)

- 3 This question is about the naturally occurring substance, 2-hydroxybenzoic acid, which can be extracted from the bark of willow trees.



- (a) Give the molecular formula of 2-hydroxybenzoic acid. (1)

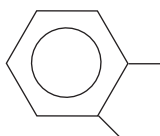
- (b) The presence of the carboxylic acid group in 2-hydroxybenzoic acid is shown by the fact that it neutralizes sodium carbonate solution.

Write the equation for this neutralization. State symbols are not required.

(2)

- (c) The 2-hydroxybenzoic acid forms a hydrogen bond within the molecule.

- (i) Complete the formula below to show this hydrogen bonding by displaying all the remaining atoms and bonds. (1)



- *(ii) Will the melting temperature of 4-hydroxybenzoic acid be higher or lower than that of 2-hydroxybenzoic acid? Justify your answer. (2)

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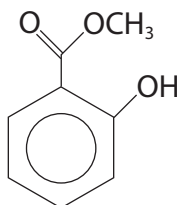
(d) Phenol and 2-hydroxybenzoic acid react with excess bromine water in a similar way.

Suggest the structural formula and name of the organic product formed when excess bromine water reacts with 2-hydroxybenzoic acid.

(2)

Name

(e) The main chemical present in oil of wintergreen is methyl 2-hydroxybenzoate which is a liquid at room temperature.



(i) Give the chemicals and conditions needed to prepare methyl 2-hydroxybenzoate from 2-hydroxybenzoic acid in a **single** step reaction.

(2)

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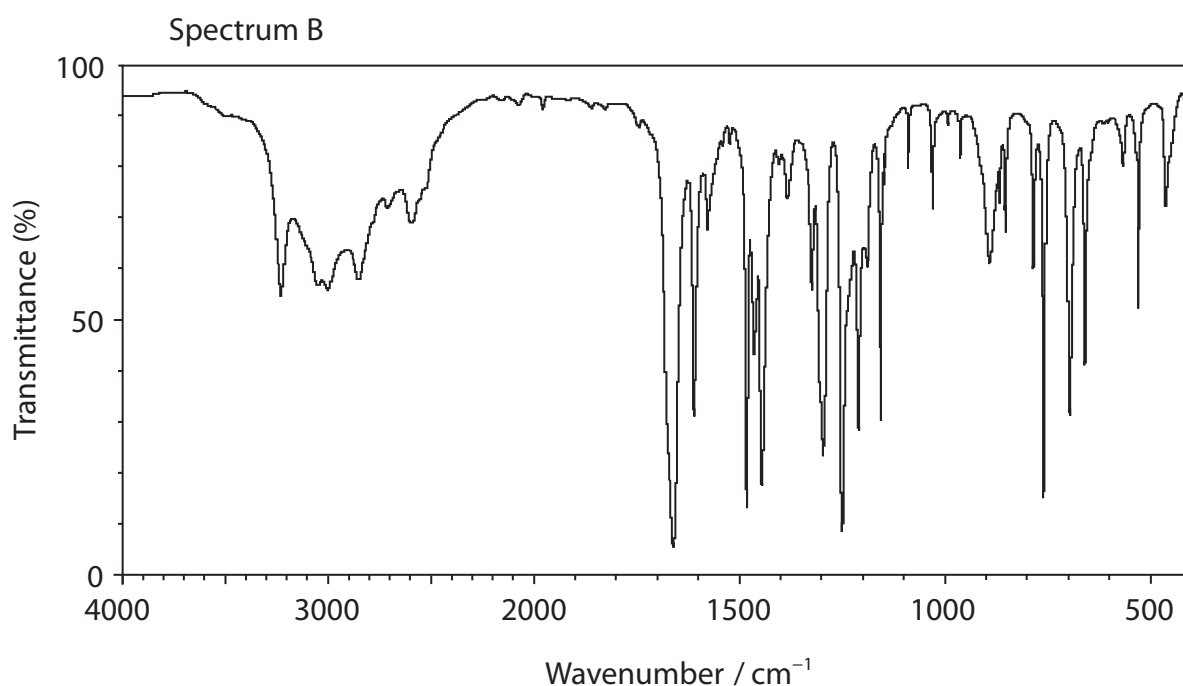
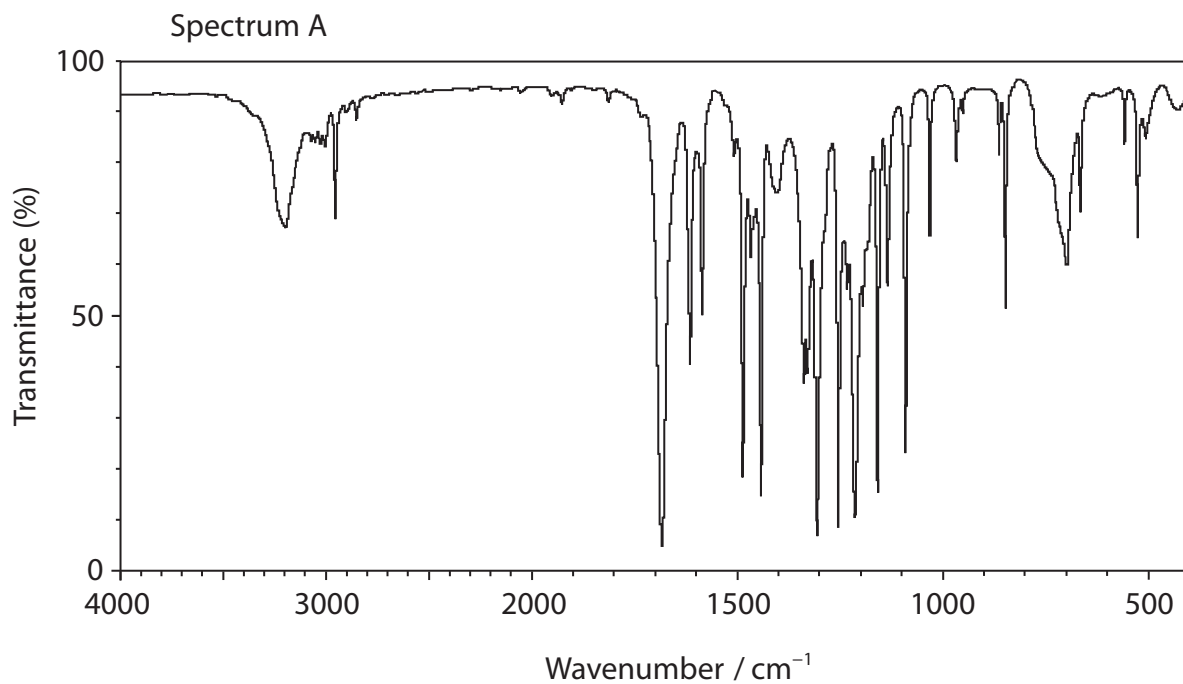
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- (v) The identity of methyl 2-hydroxybenzoate can be confirmed by infrared spectroscopy.

Which of the infrared spectra below is given by methyl 2-hydroxybenzoate and which by 2-hydroxybenzoic acid?

Justify your answer by identifying the bond responsible for a distinguishing absorption. Give the wavenumber range for this absorption.

(2)



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(vi) Calculate the **volume** of methyl 2-hydroxybenzoate produced from 9.00 g of 2-hydroxybenzoic acid, assuming the yield for this reaction is 60%, and the other reagents are present in excess.

DATA

Molar mass of 2-hydroxybenzoic acid = 138 g mol^{-1}

Molar mass of methyl 2-hydroxybenzoate = 152 g mol^{-1}

Density of methyl 2-hydroxybenzoate = 1.174 g cm^{-3}

(3)