

Arenes/Benzene Chemistry

Question Paper 1

Level	International A Level
Subject	Chemistry
Exam Board	Edexcel
Topic	Transition Metals & Organic Nitrogen Chemistry
Sub Topic	Arenes/Benzene Chemistry
Booklet	Question Paper 1

Time Allowed: **68 minutes**

Score: **/56**

Percentage: **/100**

Grade Boundaries:

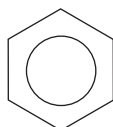
A*	A	B	C	D	E	U
>85%	'77.5%	70%	62.5%	57.5%	45%	<45%

1 If the temperature of the nitration of benzene is allowed to rise too high, dinitration and trinitration can occur. This is evidence that the

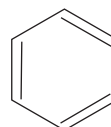
- A nitro group is electron withdrawing.
- B nitro group is electron donating.
- C delocalisation energy of nitrobenzene is greater than that of benzene.
- D delocalisation energy of nitrobenzene is less than that of benzene.

(Total for Question 1 = 1 mark)

2 The benzene molecule may be represented in two ways:



structure I



structure II

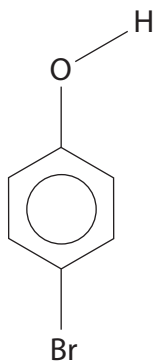
Which of the following does **not** provide evidence that **structure I** is the better representation of benzene?

- A Infrared spectroscopy
- B High performance liquid chromatography
- C Thermochemistry
- D X-ray diffraction

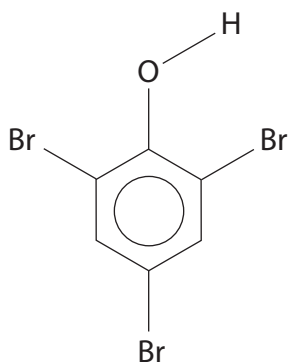
(Total for Question 2 = 1 mark)

3 When phenol, C_6H_5OH , reacts with excess bromine water, the organic product is

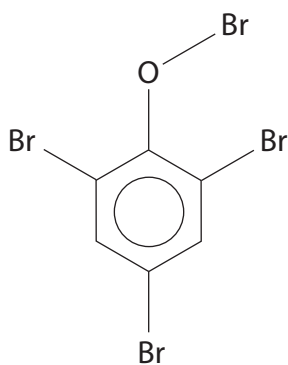
A



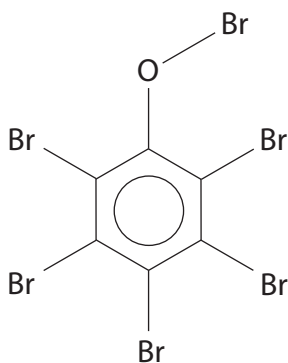
B



C



D



(Total for Question 3 = 1 mark)

4 Aromatic amines may be converted into benzenediazonium ions. What are the most suitable reagents and conditions for this reaction?

	Reagent 1	Reagent 2	Temperature / °C
<input type="checkbox"/> A	NaNO ₂	sulfuric acid	+55
<input type="checkbox"/> B	NaNO ₃	hydrochloric acid	+5
<input type="checkbox"/> C	NaNO ₂	hydrochloric acid	+5
<input type="checkbox"/> D	NaNO ₃	sulfuric acid	+55

(Total for Question 4 = 1 mark)

5 All the bond angles in the benzene molecule are 120°. Which of the following provides the best evidence for this?

- A Valence shell electron pair repulsion theory
- B X-ray diffraction
- C High resolution nuclear magnetic resonance
- D Infrared spectroscopy

(Total for Question 5 = 1 mark)

6 Benzene burns with a very smoky flame. This is evidence for the extent to which the benzene molecule is

- A delocalised.
- B stabilised.
- C unsaturated.
- D activated.

(Total for Question 6 = 1 mark)

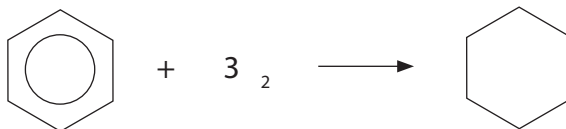
- 7 When bromine water is added to benzene, no reaction occurs. However, when bromine water is added to an aqueous solution of phenol, a white precipitate with an antiseptic smell is formed. What is the explanation for this difference?
- A Bromine is a powerful electrophile.
 - B The benzene ring in phenol is activated.
 - C The reaction of phenol with bromine is similar to the iodoform reaction.
 - D The OH group in phenol is much more acidic than that in ethanol.

(Total for Question 7 = 1 mark)

- 8 The reaction between hydrogen and benzene is normally very slow but it speeds up in the presence of finely divided nickel. The nickel
- A acts as a homogeneous catalyst by acting as an electron pair acceptor in the formation of an electrophile.
 - B acts as a homogeneous catalyst by acting as an electron pair donor in the formation of an electrophile.
 - C acts as a heterogeneous catalyst by providing active sites on which the reaction occurs.
 - D reacts with the hydrogen to form nickel(II) hydride which then reacts with the benzene.

(Total for Question 8 = 1 mark)

9 When the enthalpy change for the hydrogenation of benzene to cyclohexane



is compared to the calculated enthalpy change for the hydrogenation of the theoretical compound cyclohexa-1,3,5-triene to cyclohexane, benzene is calculated to have a stabilization energy of 150 kJ mol^{-1} . This means that

- A the enthalpy change for the hydrogenation of benzene is $+150 \text{ kJ mol}^{-1}$.
- B the enthalpy change for the hydrogenation of benzene is -150 kJ mol^{-1} .
- C the enthalpy change for the conversion of benzene to cyclohexa-1,3,5-triene is $+150 \text{ kJ mol}^{-1}$.
- D the enthalpy change for the conversion of benzene to cyclohexa-1,3,5-triene is -150 kJ mol^{-1} .

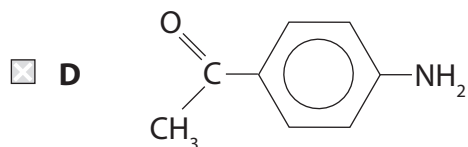
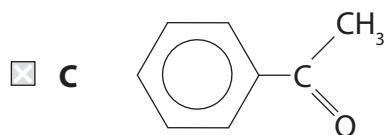
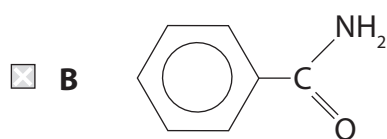
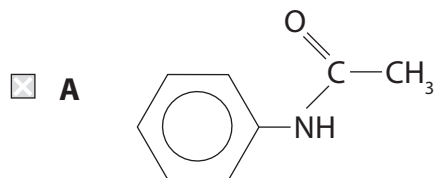
(Total for Question 9 = 1 mark)

10 Nitrobenzene is prepared by heating benzene and a mixture of concentrated nitric and sulfuric acids under reflux at 55°C . If the temperature rises above 55°C , the yield of nitrobenzene is reduced. This is because, at temperatures above 55°C , the

- A benzene evaporates.
- B nitrating mixture decomposes.
- C nitrobenzene reacts to form benzenesulfonic acid.
- D nitrobenzene reacts to form dinitrobenzene.

(Total for Question 10 = 1 mark)

11 When ethanoyl chloride is added to phenylamine at room temperature, the main organic product of the reaction is



(Total for Question 11 = 1 mark)

12 The carbon-carbon bonds in benzene are all the same length. The best evidence for this comes from

- A high resolution proton nmr spectroscopy.
- B X-ray diffraction.
- C mass spectrometry.
- D bomb calorimetry.

(Total for Question 12 = 1 mark)

- 13** Benzene reacts very slowly with chlorine but the reaction speeds up when finely divided iron is added. This is because
- A** the chlorine molecule donates an electron pair to the iron producing an electrophile.
 - B** the iron reacts with chlorine to form iron(III) chloride which then acts as an electrophile in its reaction with benzene.
 - C** the iron reacts with chlorine to form iron(III) chloride which then acts as an electron pair acceptor.
 - D** iron is a transition metal and acts as a heterogeneous catalyst in the reaction.

(Total for Question 13 = 1 mark)

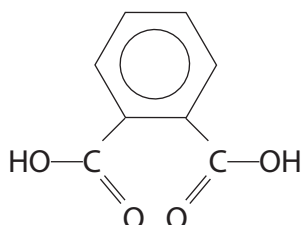
- 14** It is calculated that, as a result of delocalization, benzene has a stabilization energy of 150 kJ mol^{-1} . This means that
- A** the enthalpy change for the conversion of benzene to cyclohexa-1,3,5-triene would be $+150 \text{ kJ mol}^{-1}$.
 - B** the enthalpy change for the conversion of cyclohexa-1,3,5-triene to benzene would be $+150 \text{ kJ mol}^{-1}$.
 - C** the enthalpy change for the conversion of cyclohexane to benzene is $+150 \text{ kJ mol}^{-1}$.
 - D** the enthalpy change for the conversion of benzene to cyclohexane is $+150 \text{ kJ mol}^{-1}$.

(Total for Question 14 = 1 mark)

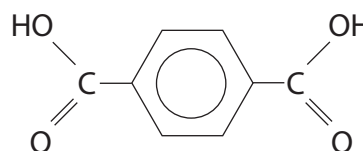
15

Phthalates

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

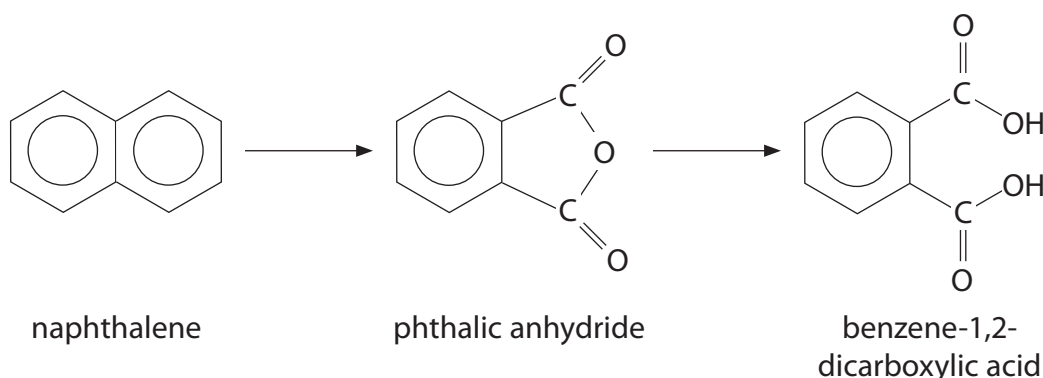


benzene-1,2-dicarboxylic acid



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.



naphthalene

phthalic anhydride

benzene-1,2-dicarboxylic acid

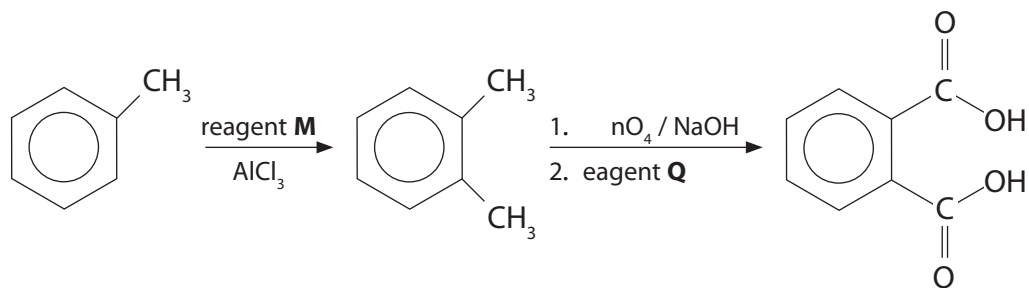
The use of naphthalene as a source of these compounds gave rise to the common names, phthalic acid for benzene-1,2-dicarboxylic acid and terephthalic acid for benzene-1,4-dicarboxylic acid.

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)

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

(1)

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(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?

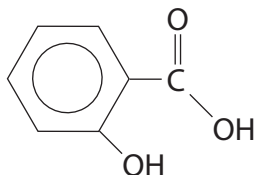
(1)

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(Total for Question 15 = 20 marks)

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



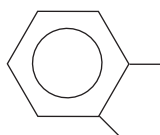
(a) Give the molecular formula of 2-hydroxybenzoic acid. (1)

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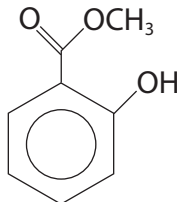
(d) Phenol and 2-hydroxybenzoic acid react with excess bromine water in a similar way.

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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- * (ii) Because methyl 2-hydroxybenzoate is sparingly soluble in water, it is extracted from the reaction mixture using ethyl ethanoate.

Explain why methyl 2-hydroxybenzoate is sparingly soluble in water.

(3)

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- (iii) The solution of methyl 2-hydroxybenzoate in ethyl ethanoate is washed and then dried.

Suggest the chemicals needed for these steps.

Justify your suggestions.

(3)

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- (iv) State how methyl 2-hydroxybenzoate is separated from ethyl ethanoate.

(1)

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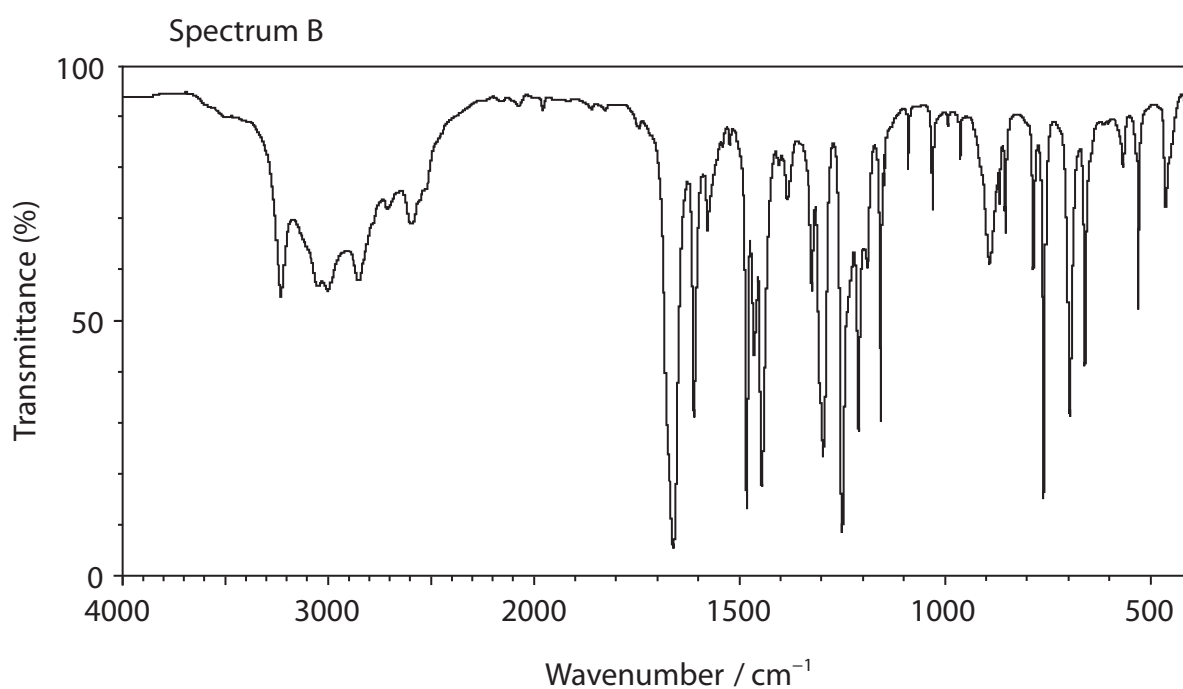
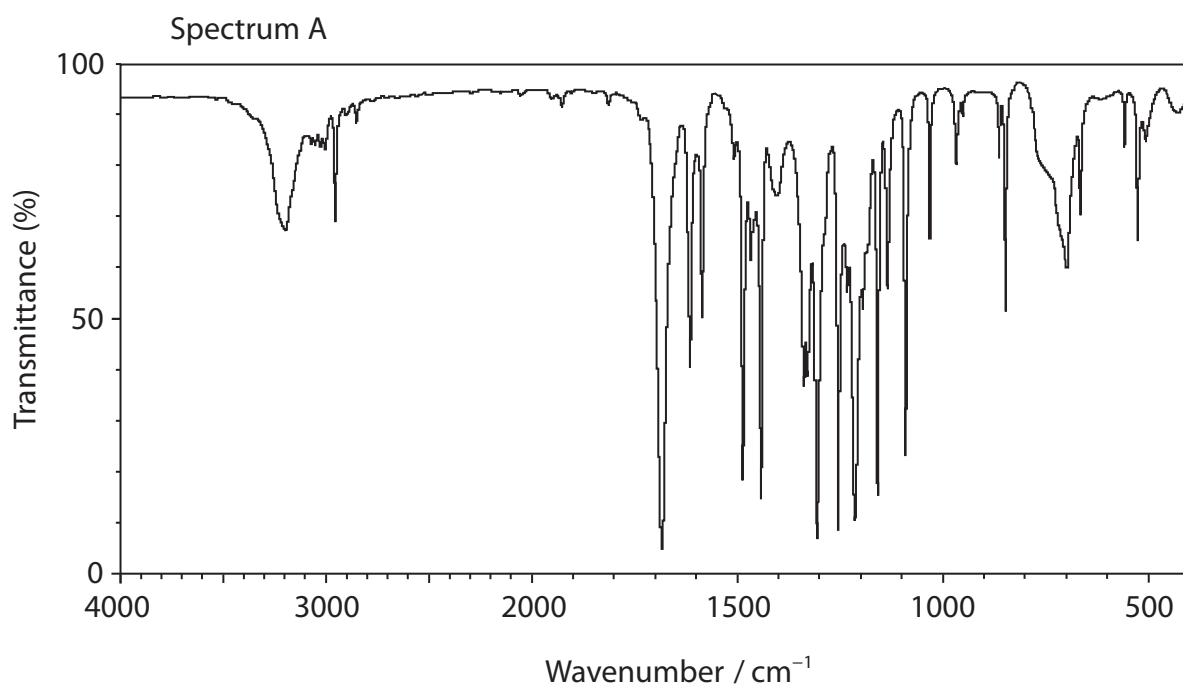
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- (v) The identity of methyl 2-hydroxybenzoate can be confirmed by infrared spectroscopy.

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)