Arenes/Benzene Chemistry

Question Paper 2

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

Time Allowed: **68 minutes**

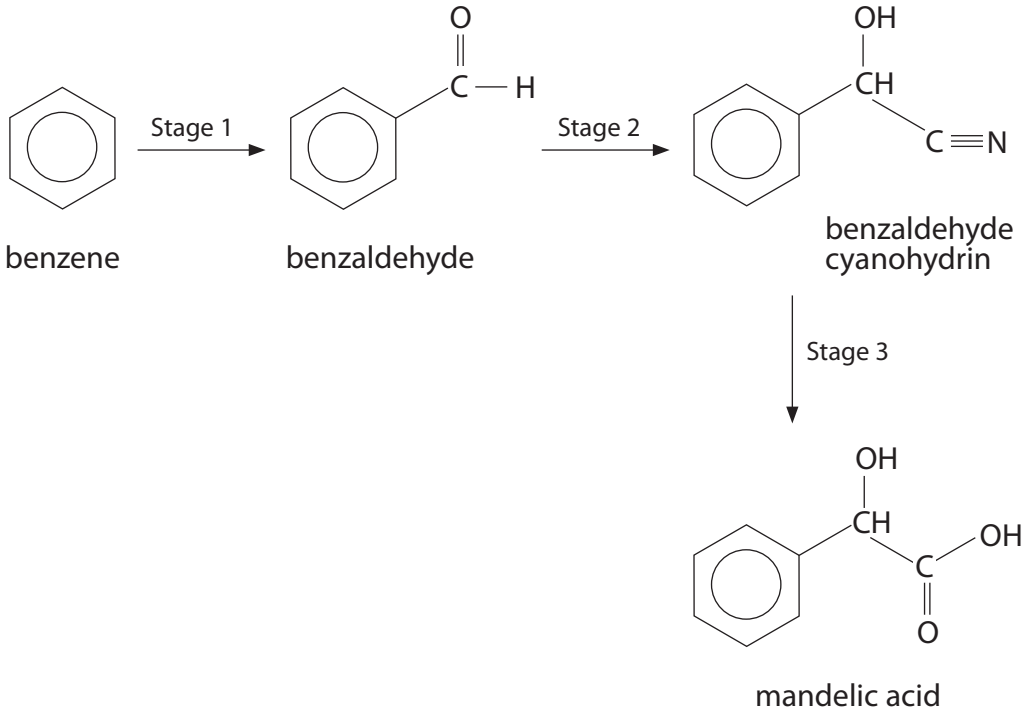
Score: **/56**

Percentage: **/100**

Grade Boundaries:

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

1 Mandelic acid, 2-hydroxy-2-phenylethanoic acid, has a long history of medical use as an antibiotic and as a component of some cosmetic face creams. It was first obtained from an extract of bitter almonds and 'Mandel' is the German word for almond. Mandelic acid can be synthesized from benzene in the sequence shown below.



(a) (i) Use your knowledge of electrophilic substitution to suggest the identity of the electrophile in Stage 1 of the synthesis.

(1)

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(ii) Write the mechanism for the electrophilic substitution in Stage 1, using the electrophile that you have given in (a)(i).

(3)

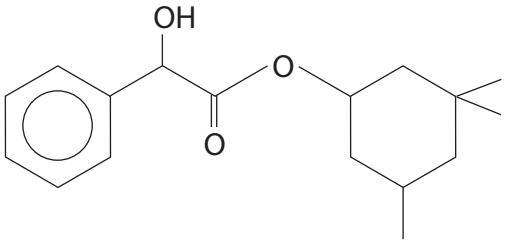
(iii) State the reagents and conditions required for Stage 2. You may assume that the reaction is carried out at a suitable temperature.

(2)

(iv) State the reagent (or reagents) required for Stage 3.

(1)

(b) Cyclandelate is a vasodilator (causes blood vessels to dilate) used in the treatment of arteriosclerosis (hardening of artery walls). The structure of cyclandelate is shown below.



(i) Suggest a single stage synthesis of cyclandelate from mandelic acid. Draw the skeletal formula of the organic compound that would be required and state any essential reagents and conditions.

(3)

(ii) Suggest a disadvantage of using the synthesis that you have suggested in (b)(i) for the large scale manufacture of cyclandelate.

(1)

(iii) An alternative **two** stage synthesis of cyclandelate was proposed. This involved reacting mandelic acid with phosphorus(V) chloride. Explain why this suggestion is unsatisfactory.

(1)

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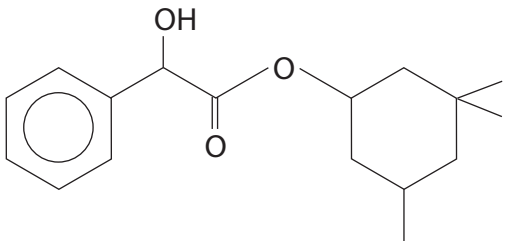
(c) Cyclandelate has **three** asymmetric carbon atoms.

(i) cle these three asymmetric carbon atoms on the structure below.

(2)



(ii) Explain the possible problem that the presence of asymmetric carbon atoms might cause with the medical applications of cyclandelate.

(2)

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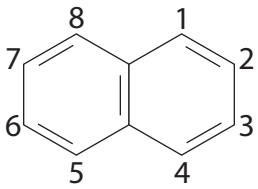
(Total for Question 1 = 16 marks)

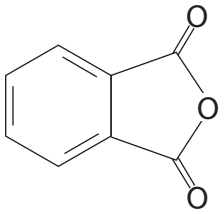
2 Naphthalene is a white solid traditionally used in mothballs and is extracted from coal tar. It is an arene which can be represented by the formula below.



Although it is an aromatic compound, naphthalene has carbon to carbon bonds of different lengths.

Like benzene, naphthalene undergoes electrophilic substitution. Substitution usually occurs at one of the carbons 1, 4, 5 or 8 and naphthalene reacts under milder conditions than benzene.

Oxidation of naphthalene, using oxygen gas with vanadium(V) oxide catalyst at about 650 K, produces phthalic anhydride:



(a) State which physical method would be used to determine the lengths of the carbon to carbon bonds in naphthalene.

(1)

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(b) Use your knowledge of benzene to draw an alternative way of representing the structure of naphthalene. Explain what this structure represents and how it arises.

(3)

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(c) Naphthalene is nitrated using a mixture of concentrated nitric and sulfuric acids. Write a mechanism for this reaction. Include one or more equations to show how the electrophile is formed.

(4)

(d) 1.28 g of naphthalene is completely burned in oxygen.

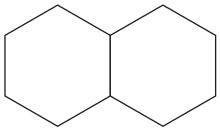
Write the equation for the combustion of naphthalene. State symbols are not required.

Calculate the volume of carbon dioxide produced, measured at room temperature and pressure.

1 mol of a gas occupies 24.0 dm^3 at room temperature and pressure.

(3)

(e) Suggest the reagent and appropriate conditions for the synthesis of decalin from naphthalene.



Decalin

(2)

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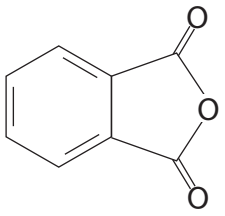
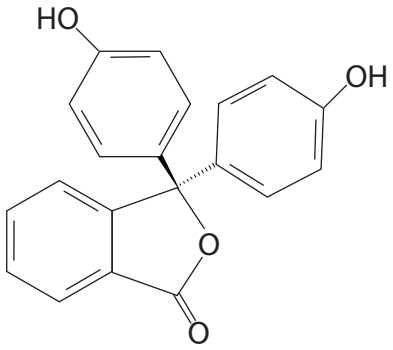
(f) When phenol is heated with phthalic anhydride in the presence of the catalyst concentrated sulfuric acid, the indicator phenolphthalein is formed.



Phthalic anhydride



Phenolphthalein

(i) When phenol reacts with phthalic anhydride to form phenolphthalein, state the inorganic product of the reaction.

(1)

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(ii) When phenolphthalein is colourless it can be represented as H_2In.

At very low pH, H_3In^+ is formed which is orange.

Between pH 9 and 12, In^{2-} is formed which has the familiar pink colour.

By referring to the structure of phenolphthalein given above, suggest how these two ions are formed.

(2)

$H_3 In^+$ .....

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In^{2-} .....

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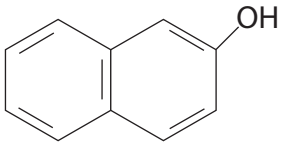
(g) Coal tar also contains 2-naphthol.



2-naphthol and phenol react with phenylamine in a similar way to form dyes.

Suggest a synthesis of a chemical dye starting with 2-naphthol and phenylamine.

You should include chemicals and conditions for your reactions.

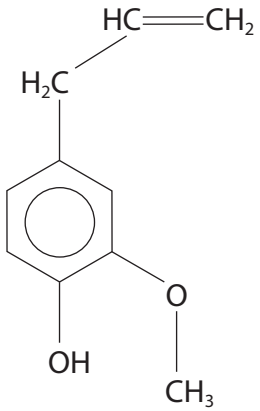
Suggest the structural formula of your dye.

(4)

(Total for Question 2 = 20 marks)

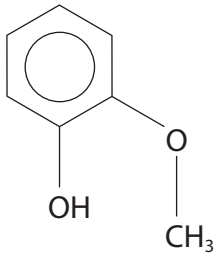
3 **Oil of cloves**

Oil of cloves is a traditional remedy for toothache; it is a topical treatment, which means that it is applied externally. The main active ingredient of oil of cloves is eugenol, which also gives cloves their characteristic smell. The structure of eugenol is shown below.



eugenol

(a) A student suggested that eugenol could be prepared by an electrophilic substitution of 2-methoxyphenol, which is produced in the gut of desert locusts. This compound is one of the main components of the pheromones that cause locust swarming. The structure of 2-methoxyphenol is shown below.



2-methoxyphenol

(i) Use your knowledge of electrophilic substitution reactions to suggest the structure of an electrophile that might be used in this reaction.

(1)

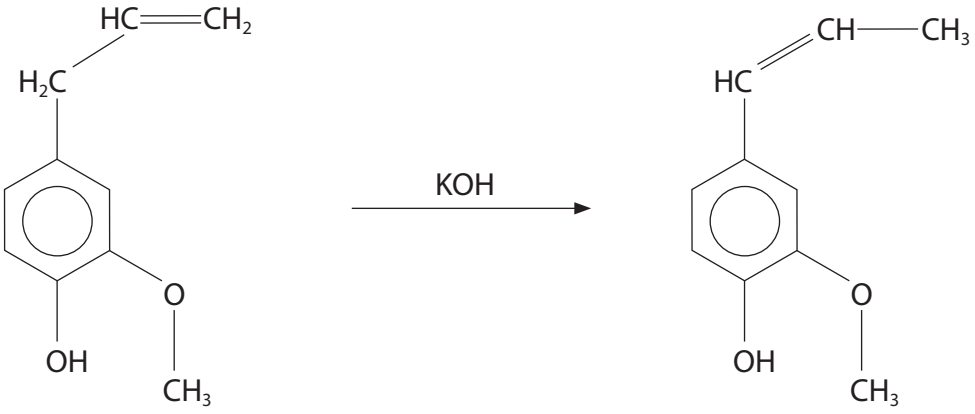
(ii) Suggest an organic compound that could be used to produce the electrophile that you have given in (a)(i).

(1)

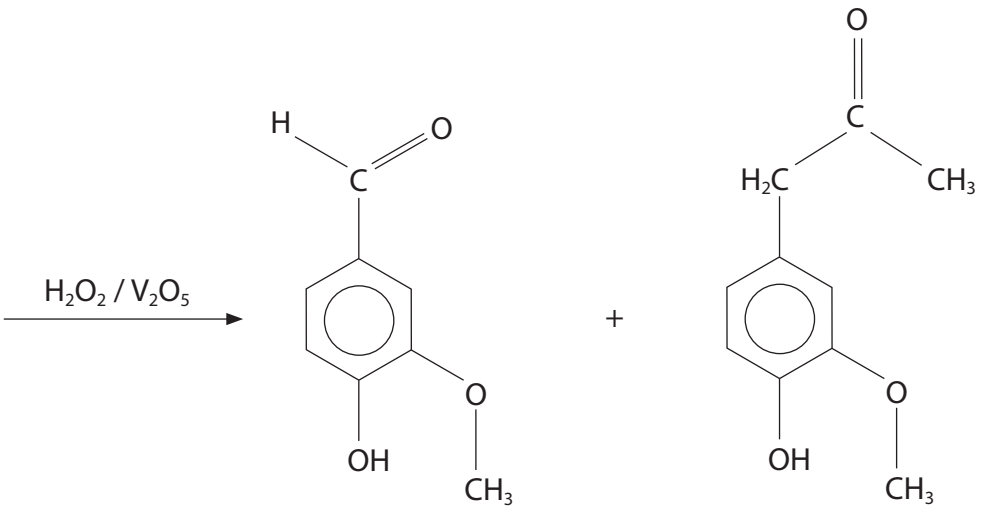
(iii) Write the mechanism for the electrophilic substitution to prepare eugenol from 2-methoxyphenol, using the electrophile that you have given in (a)(i).

(3)

(b) Eugenol has been used in the manufacture of vanillin, the compound responsible for the flavour of vanilla. The process involves the conversion of eugenol to its isomer isoeugenol, which is then oxidized by hydrogen peroxide with a vanadium(V) oxide catalyst.



eugenol isoeugenol



vanillin methyl vanillyl ketone

(i) Isoeugenol exists as two stereoisomers, whereas eugenol has just one structure. State the type of stereoisomerism shown by isoeugenol and explain why it can show this type of stereoisomerism, whereas eugenol does not.

(2)

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*(ii) Discuss whether or not high resolution proton nmr spectroscopy could be used to distinguish between eugenol and a single isomer of isoeugenol.

You should consider the numbers of peaks in the spectra, their splitting patterns and the areas under the peaks. You are **not** expected to suggest chemical shift values.

(4)

(iii) Suggest, in outline, a mechanism by which vanadium(V) oxide acts as a catalyst for the reaction between hydrogen peroxide and isoeugenol to form vanillin. You are **not** expected to give equations for the mechanism.

(2)

(iv) A student suggested that the infrared spectroscopy data on page 5 of the Data Booklet could be used to show whether the purified vanillin contains a trace of methyl vanillyl ketone.

Explain the basis of this idea and suggest why it may not work in practice.

(2)

(c) The Zeisel method for determining the purity of vanillin involves estimating the percentage by mass of methoxy group (CH_3O) in the sample and comparing this with the percentage in pure vanillin.

In a sequence of reactions, each methoxy group produces iodine which is estimated by titration with a sodium thiosulfate solution of known concentration. The Zeisel sequence is

Step 1 $ROCH_3 + HI \rightarrow ROH + CH_3I$

Step 2 $CH_3I + Br_2 \rightarrow CH_3Br + IBr$

Step 3 $IBr + 3H_2O + 2Br_2 \rightarrow HIO_3 + 5HBr$

Step 4 $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

Step 5 $I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$

(i) Deduce the number of moles of thiosulfate ions that are equivalent to one mole of methoxy group. Explain your answer.

(2)

(ii) A sample of vanillin was found to have 20.09% by mass of methoxy group. Calculate the percentage purity of the vanillin.

(3)

(Total for Question 3 = 20 marks)