

**ADVANCED GCE
CHEMISTRY**

Chains, Rings and Spectroscopy

TUESDAY 29 JANUARY 2008

2814/01

Afternoon

Time: 1 hour 30 minutes

Additional materials: Scientific calculator
Data Sheet for Chemistry (Inserted)



Candidate
Forename

Candidate
Surname

Centre
Number

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Candidate
Number

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INSTRUCTIONS TO CANDIDATES

- Write your name in capital letters, your Centre Number and Candidate Number in the boxes above.
- Use blue or black ink. Pencil may be used for graphs and diagrams only.
- Read each question carefully and make sure that you know what you have to do before starting your answer.
- Answer **all** the questions.
- Do **not** write in the bar codes.
- Do **not** write outside the box bordering each page.
- Write your answer to each question in the space provided.

INFORMATION FOR CANDIDATES

- The number of marks for each question is given in brackets [] at the end of each question or part question.
- The total number of marks for this paper is **90**.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- A copy of the *Data Sheet for Chemistry* is provided as an insert with this question paper.
- You are advised to show all the steps in any calculations.

FOR EXAMINER'S USE

Qu.	Max	Mark
1	11	
2	12	
3	9	
4	13	
5	9	
6	13	
7	9	
8	14	
TOTAL	90	

This document consists of **19** printed pages, **1** blank page and a *Data Sheet for Chemistry*.

Answer **all** the questions.

- 1 The table below gives information about some carbonyl compounds.

name	structural formula	boiling point / °C	melting point of the 2,4-dinitrophenylhydrazine derivative / °C
butanal	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	74	123
.....	$(\text{CH}_3)_2\text{CHCHO}$	64	187
butanone	$\text{CH}_3\text{COCH}_2\text{CH}_3$	80	117
pentanal	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$		98
methylbutanone	$(\text{CH}_3)_2\text{CHCOCH}_3$	94	120
pentan-2-one	102	143
pentan-3-one	102	156
hexanal	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$	131	104

- (a) In the table above, complete the missing name and structural formulae. [2]

- (b) Predict the boiling point of pentanal.

.....[1]

- (c) (i) State what you would observe when a carbonyl compound reacts with 2,4-dinitrophenylhydrazine.

.....[1]

- (ii) State why the melting points of the derivatives are more useful in the identification of carbonyl compounds than the boiling points of the carbonyl compounds. Use the data in the table to justify your answer.

.....

.....

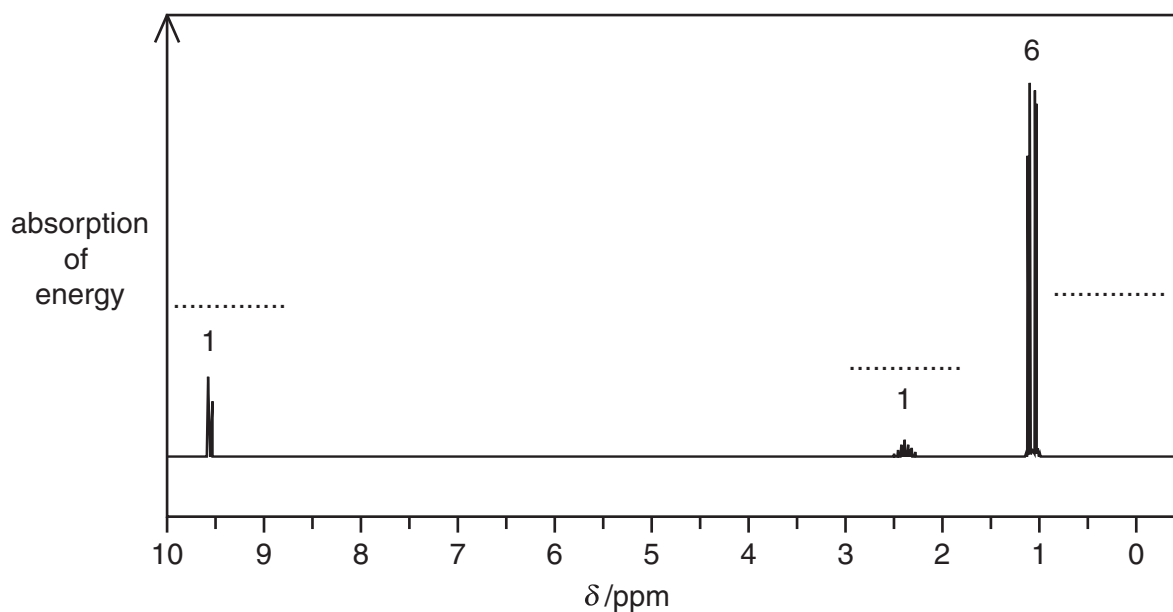
.....[1]

- (d) Carbonyl compounds can also be analysed by mass spectrometry.

State the m/e value of the molecular ion peak you would expect to find on the mass spectrum of butanal.

.....[1]

(e) The n.m.r. spectrum of one of the carbonyl compounds in the table is shown below.



(i) What do the relative peak areas on the spectrum represent?

.....
[1]

(ii) The peaks at $\delta = 1.0$ and 9.5 ppm are both doublets.
 What does this information tell you about the structure?

.....

[1]

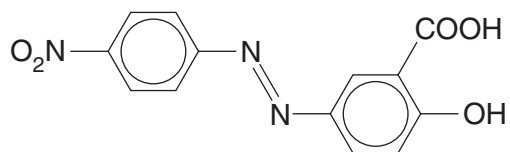
(iii) Draw the displayed formula of the compound.

[1]

(iv) Label the spectrum to show which atoms on your structure are responsible for each peak on the spectrum. [2]

[Total: 11]

- 2 Mordant Orange 1 is an azo-dye with the structure shown below.



Mordant Orange 1

- (a) Draw a circle around the azo group that identifies this molecule as an azo-dye. [1]
- (b) Describe how Mordant Orange 1 can be made starting from 4-nitrophenylamine and another suitable organic reagent.

Include in your answer:

- the structure of 4-nitrophenylamine, the intermediate diazonium ion and the other organic reagent;
- essential reagents and conditions for each stage.

.....

.....

.....

.....[6]

- (c) Mordant Orange 1 is yellow in acidic conditions, but changes to a red colour in the presence of strong bases, such as aqueous sodium hydroxide.

Draw the structure of Mordant Orange 1 after reaction with excess aqueous sodium hydroxide.

[2]

- (d) The colour of the dye can also be changed by reducing the nitro group.

- (i) State suitable reagents to reduce a nitro group.

.....
.....[1]

- (ii) Write an equation for the reduction of Mordant Orange 1. Use [H] to represent the reducing agent.

You may simplify the structure of Mordant Orange 1 to $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{R}$

[2]

[Total: 12]

3 Glutamic acid is an amino acid, $\text{H}_2\text{NCH}(\text{CH}_2\text{CH}_2\text{COOH})\text{COOH}$.

(a) Glutamic acid has two stereoisomers.

Explain how these stereoisomers arise. Illustrate your answer with suitable diagrams.

.....

.....

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.....

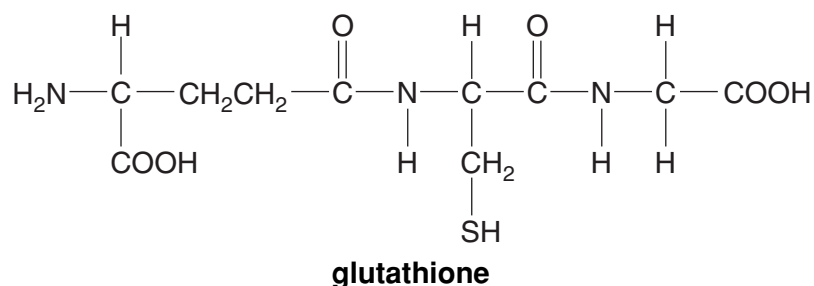
[3]

(b) Complete the table to show the structure of glutamic acid that would exist in an aqueous solution at each pH value shown.

pH 1	pH 3
	$ \begin{array}{c} \text{H} \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2\text{CH}_2\text{COOH} \\ \\ \text{COO}^- \end{array} $
	pH 12

[2]

- (c) Glutathione is a naturally occurring molecule made from glutamic acid and two other amino acids. The structure of glutathione is shown below.



- (i) Show the structures of the other **two** amino acids used to make glutathione.

[2]

- (ii) State the type of reaction that takes place when glutathione is made from its three constituent amino acids.

.....[1]

- (iii) Glutathione can be hydrolysed by enzymes. Describe one **other** way that this reaction can be carried out in the laboratory.

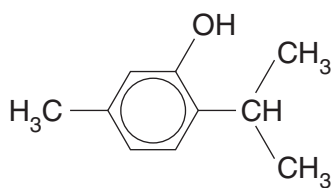
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.....[1]

[Total: 9]

- 4 Thymol is a phenol that is used in mouthwashes.



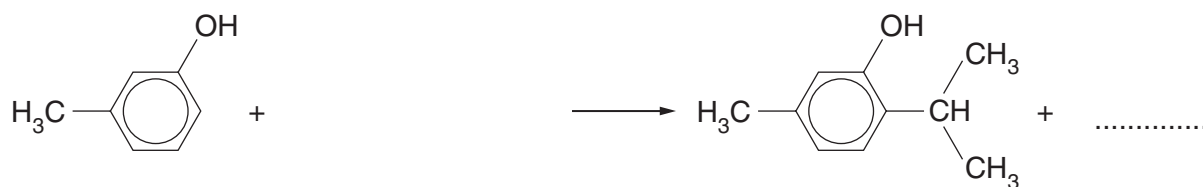
thymol

- (a) Suggest why phenols are often used in mouthwashes.

.....[1]

- (b) Thymol can be manufactured from 3-methylphenol by a Friedel–Crafts reaction.

- (i) Complete the equation for this reaction below.



[2]

- (ii) State a suitable catalyst for this reaction.

.....[1]

- (c) In a typical mouthwash, the concentration of thymol is $3.0 \times 10^{-3} \text{ mol dm}^{-3}$.

Calculate the mass of thymol that would be contained in a bottle containing 400 cm^3 of mouthwash. Show all your working clearly.

mass of thymol =g [3]

- (d) Esters of thymol are used in some cosmetics.

An ester can be obtained by reacting thymol with ethanoyl chloride.

- (i) Draw the displayed formula of ethanoyl chloride.

[1]

- (ii) Ethanoyl chloride can be made from ethanoic acid.
State a suitable reagent and write a balanced equation for this reaction.

reagent

equation

[2]

- (iii) Draw the structure of the ester formed from thymol and ethanoyl chloride.

[1]

- (iv) State how you would expect the infra-red spectrum of the thymol ester to differ from the spectrum of thymol.

.....

.....

.....[2]

[Total: 13]

5 Poly(propene) is used in the manufacture of ropes.

(a) Write a balanced equation for the formation of poly(propene) from propene.

[1]

(b) The strength of the rope can be improved by using the stereochemical form of poly(propene) which is described as isotactic.

Describe and explain with the aid of suitably labelled 3-D diagrams the **three** different stereochemical forms of poly(propene).

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.....[4]

- (c) Ropes can also be made from polymers such as Terylene.

Terylene is made from benzene-1,4-dicarboxylic acid and ethane-1,2-diol.

- (i) Draw the structures of the two monomers used to make Terylene.

[2]

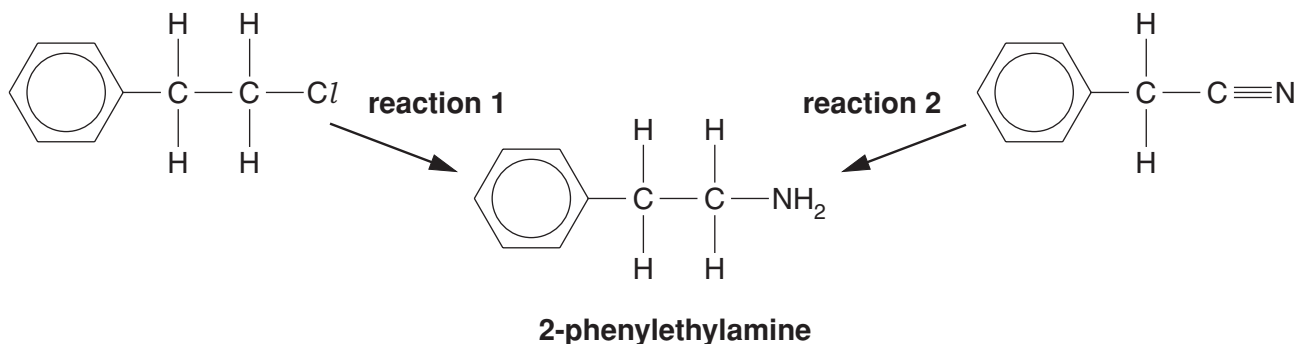
- (ii) Draw the structure of a section of Terylene, showing one repeat unit.

[2]

[Total: 9]

6 2-Phenylethylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_2$, is a compound that is found in chocolate.

(a) 2-Phenylethylamine can be synthesised by the two reactions shown below.



(i) State the reagent for **reaction 1**.

.....[1]

(ii) What type of reaction is **reaction 1**?

.....[1]

(iii) State the reagent for **reaction 2**.

.....[1]

(iv) What type of reaction is **reaction 2**?

.....[1]

(b) 2-Phenylethylamine can be converted into $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NHCOCH}_3$ by reaction with a suitable reagent.

Write a balanced equation for the reaction.

[2]

- Explain these two statements.

[6]

[Total: 13]

- 7 (a) In this question, one mark is available for the quality of use and organisation of scientific terms.

Describe the bonding in benzene.

Illustrate your answer with a suitable diagram.

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.....[4]

Quality of Written Communication [1]

(b) Benzene reacts with reagent **A** to produce a hydrocarbon, **B**, containing 90.57% carbon by mass. The relative molecular mass of **B** is between 100 and 150.

- Deduce the empirical formula of **B**.
- Suggest a possible structure for **B**.
- Suggest the identity of reagent **A**.

Show all your working.

[4]

[Total: 9]

8 There are many isomers with the molecular formula $C_6H_{12}O_2$.

(a) Ester **C**, $CH_3CH_2CH_2COOC_2H_5$, is used in the manufacture of a variety of foods and drinks. When heated, ester **C** can be hydrolysed by aqueous hydrochloric acid or aqueous sodium hydroxide.

(i) State the name of this ester.

.....[1]

(ii) Write a balanced equation for the hydrolysis of ester **C** with aqueous hydrochloric acid.

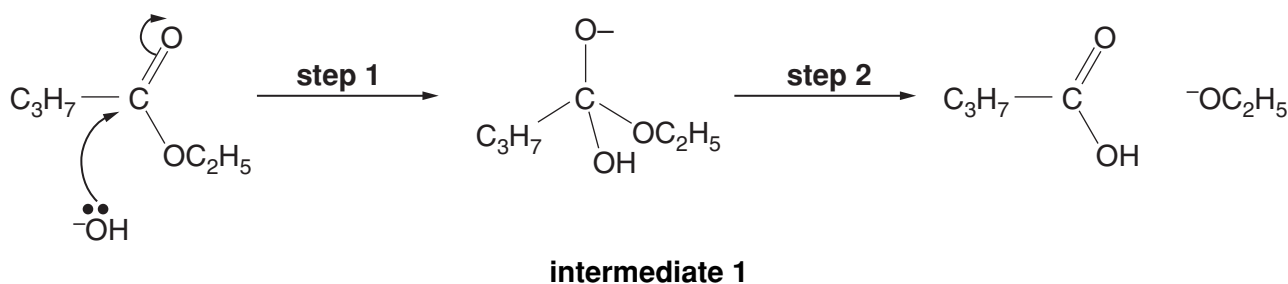
.....[1]

(iii) The hydrolysis of ester **C** is carried out with aqueous sodium hydroxide. Identify the products.

.....

.....[1]

(b) Part of the mechanism for the reaction of ester **C** with aqueous sodium hydroxide is shown below.



(i) Add curly arrows to **intermediate 1** to show how the products of **step 2** are formed. [2]

(ii) State what the curly arrows represent.

.....

.....[1]

(iii) Why is the OH^- ion acting as a nucleophile?

.....

.....[1]

- (c) The structural isomers **D**, **E** and **F** are all carboxylic acids with the molecular formula $C_6H_{12}O_2$.

Each structural isomer has one chiral carbon atom.

Draw the structural formulae of the structural isomers **D**, **E** and **F**.

[3]

TURN OVER FOR QUESTION 8(d) AND (e)

- (d) Compound **G** is another carboxylic acid with the molecular formula $C_6H_{12}O_2$.

In its n.m.r. spectrum, isomer **G** has three singlet peaks.

Draw the structural formula of isomer **G**.

[1]

- (e) Cyclohexane-1,4-diol has the molecular formula $C_6H_{12}O_2$.

- (i) Draw the skeletal formula of cyclohexane-1,4-diol.

[1]

- (ii) Predict the number of peaks, and the relative peak areas, that would be observed in the n.m.r. spectrum of cyclohexane-1,4-diol.

.....
.....
.....[2]

[Total: 14]

END OF QUESTION PAPER

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