

**ADVANCED GCE****CHEMISTRY**

Chains, Rings and Spectroscopy

2814/01

Candidates answer on the question paper

OCR Supplied Materials:

- *Data Sheet for Chemistry* (inserted)

Other Materials Required:

- Scientific calculator

Wednesday 28 January 2009**Afternoon****Duration:** 1 hour 30 minutes

Candidate Forename		Candidate Surname	
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Centre Number						Candidate Number				
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INSTRUCTIONS TO CANDIDATES

- Write your name clearly in capital letters, your Centre Number and Candidate Number in the boxes above.
- Use 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.
- Write your answer to each question in the space provided, however additional paper may be used if necessary.

INFORMATION FOR CANDIDATES

- The number of marks 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.
- This document consists of **16** pages. Any blank pages are indicated.

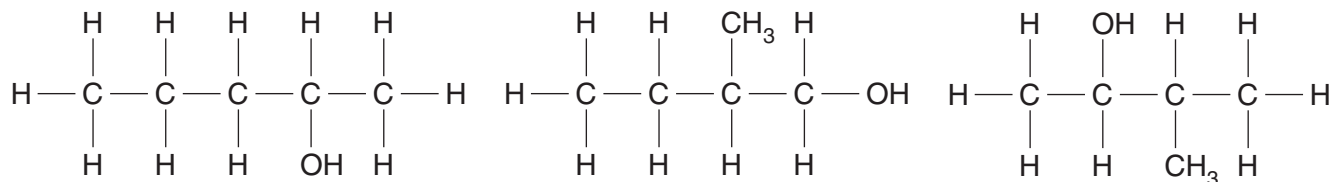
FOR EXAMINER'S USE

Qu.	Max	Mark
1	11	
2	11	
3	15	
4	17	
5	11	
6	9	
7	16	
TOTAL	90	

Answer **all** the questions.

1 There are eight alcohols with the molecular formula $C_5H_{12}O$.

(a) Three of these alcohols contain chiral centres. Their structures are shown below.

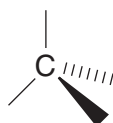


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3-methylbutan-2-ol

- (i)** Write the names of the two other alcohols in the spaces above. **[2]**
- (ii)** Complete the structure below to show the 3-D arrangement of groups around the chiral centre in 3-methylbutan-2-ol.



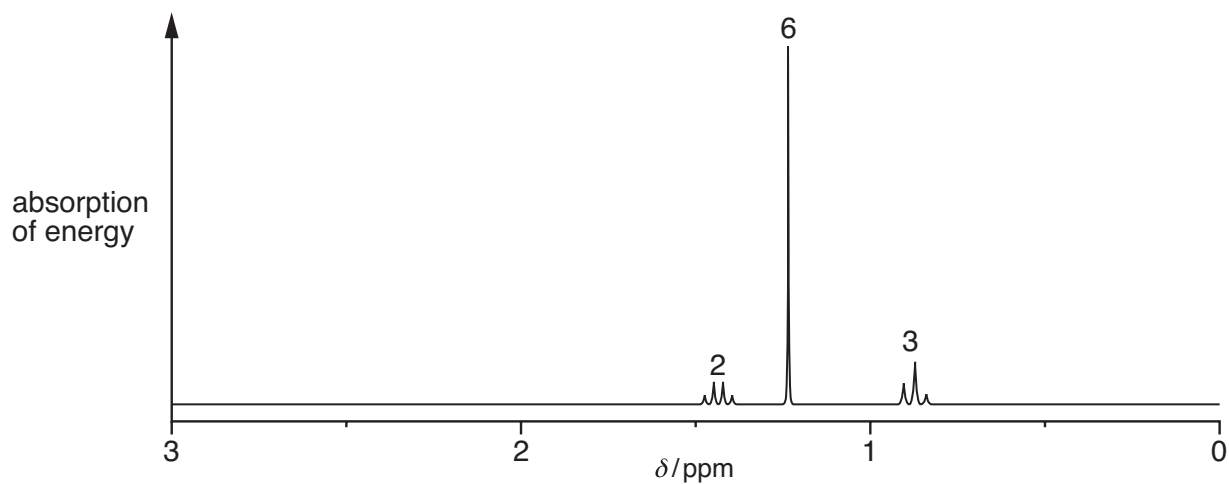
[1]

- (b)** Only one of the chiral alcohols above can be made from a carbonyl compound that is also chiral.

Deduce the structure of the carbonyl compound.

[2]

- (c) The section of the n.m.r. spectrum, in D_2O , of another alcohol with the molecular formula $C_5H_{12}O$ is shown below.



- (i) Complete the table below to help you identify the protons responsible for each peak.

δ / ppm	relative peak area	splitting pattern	number of H on the adjacent C	type of proton
0.9	3	triplet		R-CH ₃
1.2	6			
1.4	2			

[3]

- (ii) Deduce the structure of this alcohol.

[1]

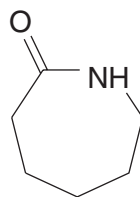
- (iii) Explain how the n.m.r. spectrum would differ from the one above if it was re-run **without** D_2O .

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..... [2]

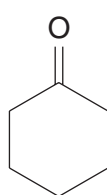
[Total: 11]

- 2 Caprolactam is a cyclic amide used in the manufacture of one type of nylon. Over 4 million tonnes of caprolactam are produced annually worldwide.

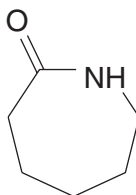
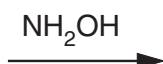


caprolactam

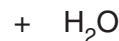
- (a) Caprolactam can be synthesised from cyclohexanone using NH_2OH .



cyclohexanone



caprolactam



- (i) Describe a simple chemical test to show that cyclohexanone contains a carbonyl group.

.....

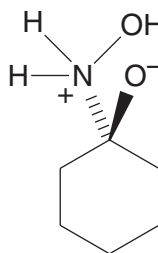
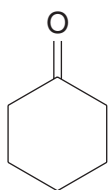
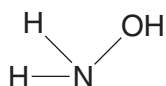
 [1]

- (ii) Describe a simple chemical test to show that cyclohexanone is **not** an aldehyde.

.....

 [2]

- (iii) The reaction of NH_2OH with cyclohexanone begins with a nucleophilic addition mechanism. Complete the first part of this mechanism by adding relevant dipoles, lone pairs and curly arrows to the reactants. [3]



cyclohexanone

intermediate

- (iv) The synthesis of caprolactam from cyclohexanone is very efficient and can be achieved with a 99% yield of product.

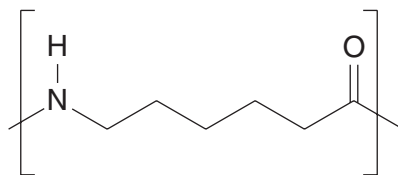
Calculate the mass of cyclohexanone needed to produce one tonne of caprolactam.

$$1 \text{ tonne} = 1.0 \times 10^6 \text{ g} \quad M_r \text{ cyclohexanone} = 98$$

mass of cyclohexanone = tonnes [3]

- (b) Caprolactam is polymerised to produce the polyamide, nylon-6.

The repeat unit of nylon-6 is shown below.

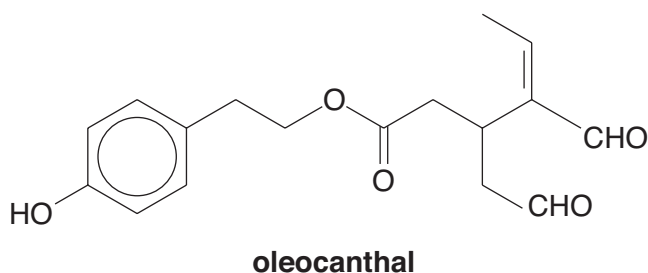


Draw the structure of a monomer, other than caprolactam, that could be polymerised to give nylon-6.

[2]

[Total: 11]

- 3 Oleocanthal, $C_{17}H_{20}O_5$, is a natural compound found in olive oil. A formula of oleocanthal is shown below.



- (a) Oleocanthal has stereoisomers.

(i) What is meant by the term *stereoisomers*?

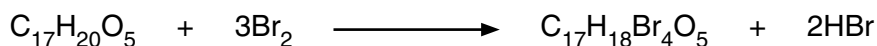
.....

 [1]

(ii) Draw a circle around each part of the structure above that can give rise to stereoisomerism. [2]

- (b) Oleocanthal reacts with a number of common laboratory reagents.

(i) Oleocanthal reacts with aqueous bromine by both substitution and addition. The equation for the reaction is shown below.

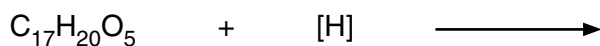


Name the functional groups on oleocanthal that react with bromine by:

substitution
 addition [2]

(ii) Oleocanthal can be reduced using $NaBH_4$.

Complete the equation for this reaction.



[1]

- (iii) Oleocanthal reacts with hot aqueous sodium hydroxide.

Draw structures to show the **two** organic products formed in this reaction.

[3]

- (c) The structure of oleocanthal, $C_{17}H_{20}O_5$, was determined using spectroscopy.

- (i) Deduce the m/e value of the molecular ion peak in the mass spectrum of oleocanthal.

..... [1]

- (ii) Identify the wavenumber ranges of **three** absorptions you would expect to see on the infrared spectrum of oleocanthal. For each range, state the bond responsible.

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..... [3]

- (d) Oleocanthal has shown pharmacological activity as an anti-inflammatory drug. Chemists have attempted to synthesise oleocanthal in the laboratory.

The product from this synthesis had a lower pharmacological activity than oleocanthal extracted from olive oil. Suggest why.

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..... [2]

[Total: 15]

Turn over

4 Organic bases are used widely in the manufacture of drugs and other chemicals.

(a) Ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$, can be made from ethanenitrile, $\text{CH}_3\text{C}\equiv\text{N}$.

(i) Name a suitable reagent you could use to carry out this reaction in the laboratory.

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

(ii) State the type of reaction occurring.

..... [1]

(b) Organic bases such as ethylamine can be neutralised by acids to form salts.

Give the formula of the salt formed when ethylamine is neutralised by:

(i) dilute hydrochloric acid,

[1]

(ii) dilute ethanoic acid.

[1]

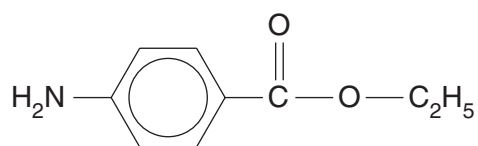
(c) In this question, one mark is available for the quality and use of technical terms.

Explain the relative basicities of ethylamine and phenylamine.

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..... [4]

Quality of Written Communication [1]

(d) Benzocaine is a local anaesthetic with the structure shown below.



benzocaine

Benzocaine can be synthesised from **4-nitrobenzoic acid** in **two** stages.

Write an equation for the reaction in each stage, and state any essential reagents and conditions.

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..... [6]

(e) A sample of benzocaine was warmed in dilute hydrochloric acid for an hour.

Draw the structures of the **two** organic products formed in these acidic conditions.

[2]

[Total: 17]

- 5 Most plastic toys are made from polymers such as atactic poly(phenylethene), $(\text{C}_6\text{H}_5\text{CHCH}_2)_n$, which is coloured with a non-toxic dye.

(a) (i) State the type of polymerisation reaction used to make poly(phenylethene).

..... [1]

(ii) Write a balanced equation for the reaction using displayed formulae.

[2]

(iii) Complete the 3-D structure to show a short length of atactic poly(phenylethene).



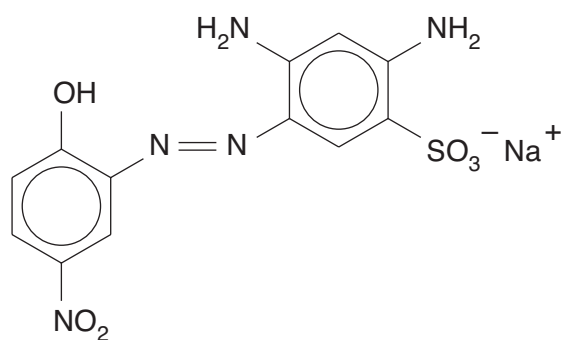
[2]

(iv) State how the structure of an *isotactic* polymer would differ from an atactic polymer.

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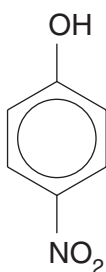
 [1]

(b) The structure of a dye called solochrome brown is shown below.



solochrome brown

Outline how this compound can be made in **two** stages from a suitable amine and the phenol shown below.



In your answer:

- draw the structure of the amine;
- the product formed after the first stage;
- identify the essential reagents and conditions for each stage.

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..... [5]

[Total: 11]

Turn over

- 6 Acyl chlorides such as ethanoyl chloride and benzoyl chloride are widely used in organic synthesis.

(a) (i) Draw a displayed formula to show the structure of benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$.

[1]

(ii) Write an equation to show how you can make benzoyl chloride from benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$.

[2]

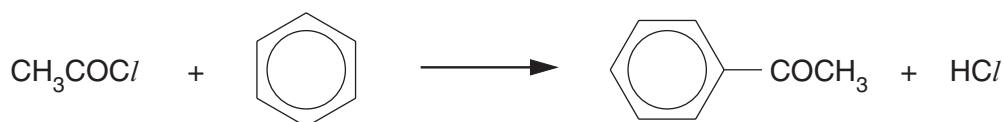
(b) Benzoyl chloride is used in the synthesis of esters and amides.

Write equations using suitable examples to illustrate the formation of an ester and the formation of an amide using benzoyl chloride.

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 [4]

(c) Ethanoyl chloride reacts with benzene in a similar way to the reaction of a halogenoalkane with benzene.



(i) Suggest a suitable catalyst for this reaction.

..... [1]

(ii) Suggest the name of the mechanism of this reaction.

..... [1]

[Total: 9]

13
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Include the type of reaction occurring and an equation for each reaction in your answer.

..... [8]

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(b) Under certain conditions, benzene and bromine can react to give an aromatic compound that contains 30.5% carbon, 1.7% hydrogen and 67.8% bromine by mass.

- (i) Use this information to deduce the empirical formula of the compound.
Show your working.

[2]

- (ii) The compound has a relative molecular mass of 235.8.

Deduce the molecular formula of the aromatic compound and suggest **three** possible structures.

molecular formula

[3]

- (c) Under very different conditions, benzene will react with excess bromine in an addition reaction. A halogenocycloalkane with the empirical formula CHBr is the only product.

Suggest the structure of this compound and write an equation for its formation from benzene.

[2]

[Total: 16]

END OF QUESTION PAPER

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