

**ADVANCED GCE
CHEMISTRY**

Chains, Rings and Spectroscopy

TUESDAY 23 JANUARY 2007

2814/01

Morning

Time: 1 hour 30 minutes

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



Candidate
Name

Centre
Number

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Candidate
Number

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INSTRUCTIONS TO CANDIDATES

- Write your name, Centre number and Candidate number in the boxes above.
- Answer **all** the questions.
- Use blue or black ink. Pencil may be used for graphs and diagrams only.
- Read each question carefully and make sure you know what you have to do before starting your answer.
- Do **not** write in the bar code.
- Do **not** write outside the box bordering each page.
- **WRITE YOUR ANSWER TO EACH QUESTION IN THE SPACE PROVIDED. ANSWERS WRITTEN ELSEWHERE WILL NOT BE MARKED.**

INFORMATION FOR CANDIDATES

- The number of marks for each question is given in brackets [] at the end of each question or part question.
- 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.

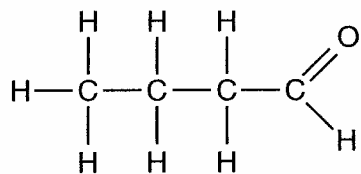
FOR EXAMINER'S USE

Qu.	Max.	Mark
1	15	
2	7	
3	14	
4	14	
5	8	
6	12	
7	7	
8	13	
TOTAL	90	

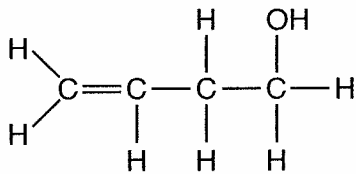
This document consists of **15** printed pages, **1** blank page and a *Data Sheet for Chemistry*.

Answer **all** the questions.

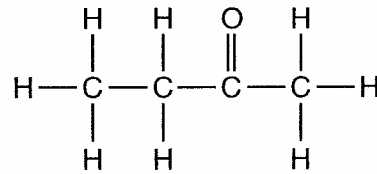
- 1 An unknown colourless liquid with molecular formula C_4H_8O was thought to be one of butanal, but-3-en-1-ol, or butanone.



butanal



but-3-en-1-ol



butanone

- (a) State a simple chemical test that would positively identify:

- (i) **butanal only;**

reagent

observation.....

organic product [3]

- (ii) **but-3-en-1-ol only.**

reagent

observation.....

type of reaction..... [3]

- (b) Butanal and butanone both react with 2,4-dinitrophenylhydrazine to produce mixtures containing orange precipitates.

Outline how the mixtures containing these orange precipitates can be used to distinguish between butanal and butanone.

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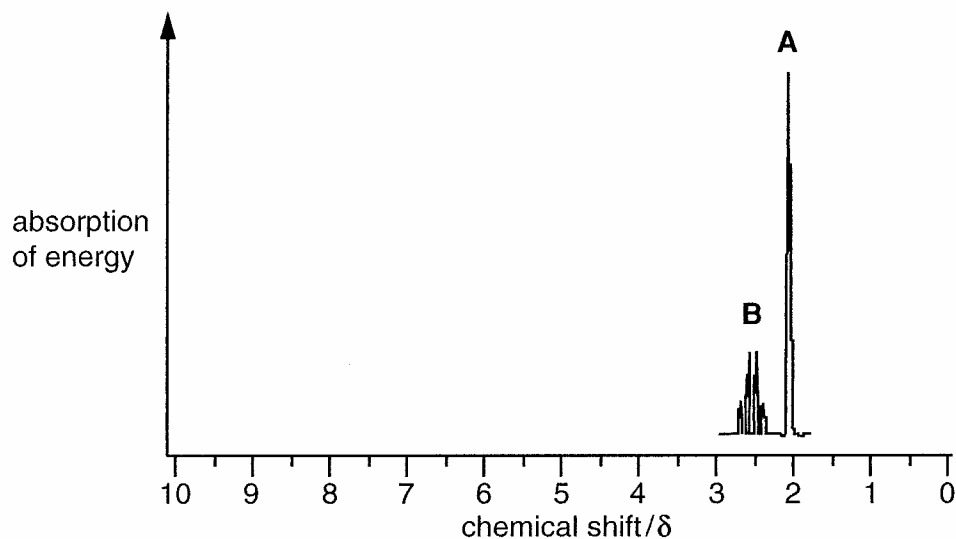
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..... [3]

(c) Unknown compounds are often identified by n.m.r. spectroscopy.

Part of the n.m.r. spectrum of **butanone** is shown on the axes below.



(i) State which part of the butanone molecule is responsible for peak **A** at $\delta = 2.1$.
Explain your reasoning.

.....

 [2]

(ii) Explain why peak **B** is split into a quartet.

.....
 [1]

(iii) Predict the remainder of the n.m.r. spectrum of butanone by sketching it on the axes above. [2]

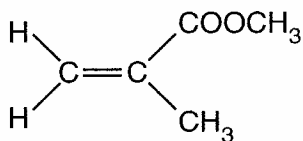
(iv) Write the relative peak area above each of the peaks on the completed spectrum of butanone.

[1]

[Total: 15]

[Turn over

- 3 *Perspex* is a tough transparent polymer made from methyl 2-methylpropenoate.



methyl 2-methylpropenoate

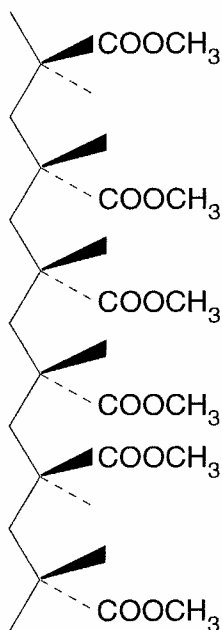
- (a) State the type of polymerisation used to form *Perspex* from methyl 2-methylpropenoate.

..... [1]

- (b) *Perspex* is typically about 30% atactic and 70% syndiotactic.

A section of atactic *Perspex* is shown on the left below.

atactic



syndiotactic



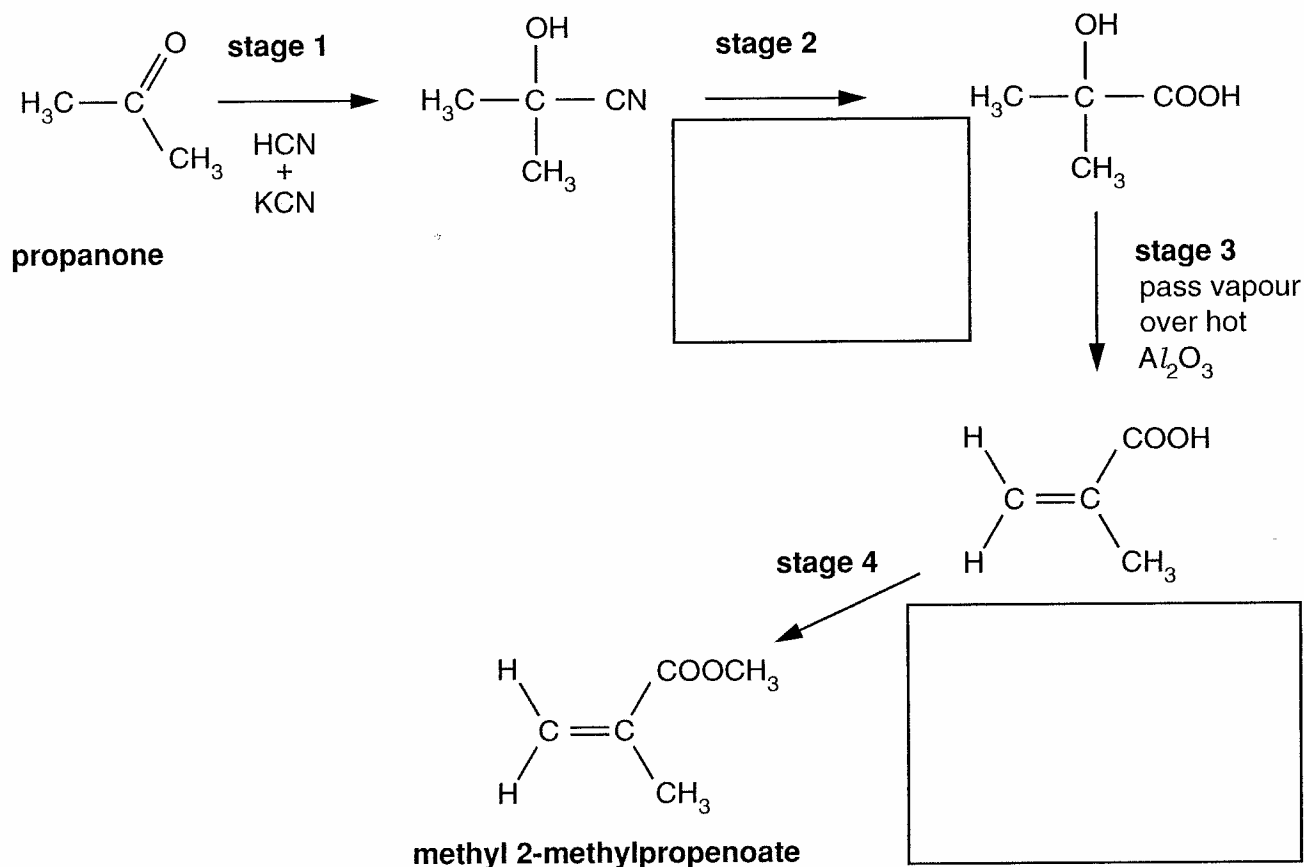
- (i) Complete the diagram on the right to show a section of syndiotactic *Perspex*. [1]
- (ii) State the name of one **other** possible 3-D arrangement of the side groups in polymers such as *Perspex*. Explain how this arrangement differs from atactic and syndiotactic.

.....

.....

..... [2]

(c) Methyl 2-methylpropenoate can be manufactured from propanone. The diagram below shows a synthesis of methyl 2-methylpropenoate from propanone in four stages.



(i) Identify reagents and conditions that could be used to carry out **stage 2** and **stage 4** by filling in the boxes above. [4]

(ii) State why reactions, such as **stage 1**, are particularly useful in organic synthesis. [1]

..... [1]

(d) (i) State the name of the mechanism occurring in **stage 1**. [1]

..... [1]

(ii) Show this mechanism below. Include curly arrows, relevant lone pairs and the structure of the intermediate.

[4]

[Total: 14]

[Turn over

- 4 The method below can be used to make phenylamine from nitrobenzene in the laboratory.

3.69 g of nitrobenzene and 8 g of tin (an excess) were placed into a flask. The flask was fitted with a reflux condenser. Concentrated hydrochloric acid was then added dropwise to the flask.

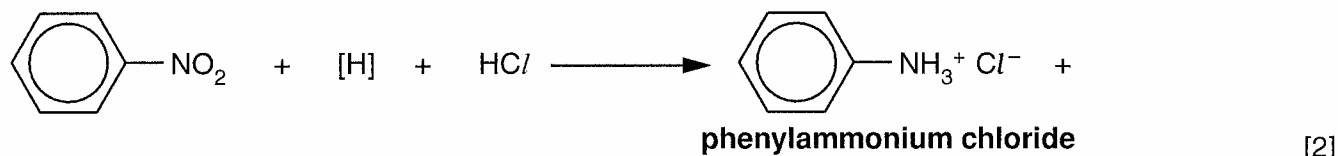
The mixture was heated for 30 minutes to complete the reaction.

Once the mixture had cooled, concentrated sodium hydroxide solution was added until the mixture was alkaline.

Purification gave a 72.1% yield of phenylamine.

- (a) Reaction of nitrobenzene with the tin and hydrochloric acid produces phenylammonium chloride as the organic product.

- (i) Complete the equation for this reaction.



- (ii) State what the symbol [H] in the equation represents.

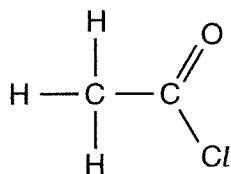
..... [1]

- (b) When the sodium hydroxide was added, the phenylammonium chloride was converted to phenylamine.

Write an equation for this reaction.

[2]

- 5 Ethanoyl chloride, CH_3COCl , is widely used in organic synthesis.



ethanoyl chloride

- (a) Write an equation to show how ethanoyl chloride can be made from ethanoic acid.

[2]

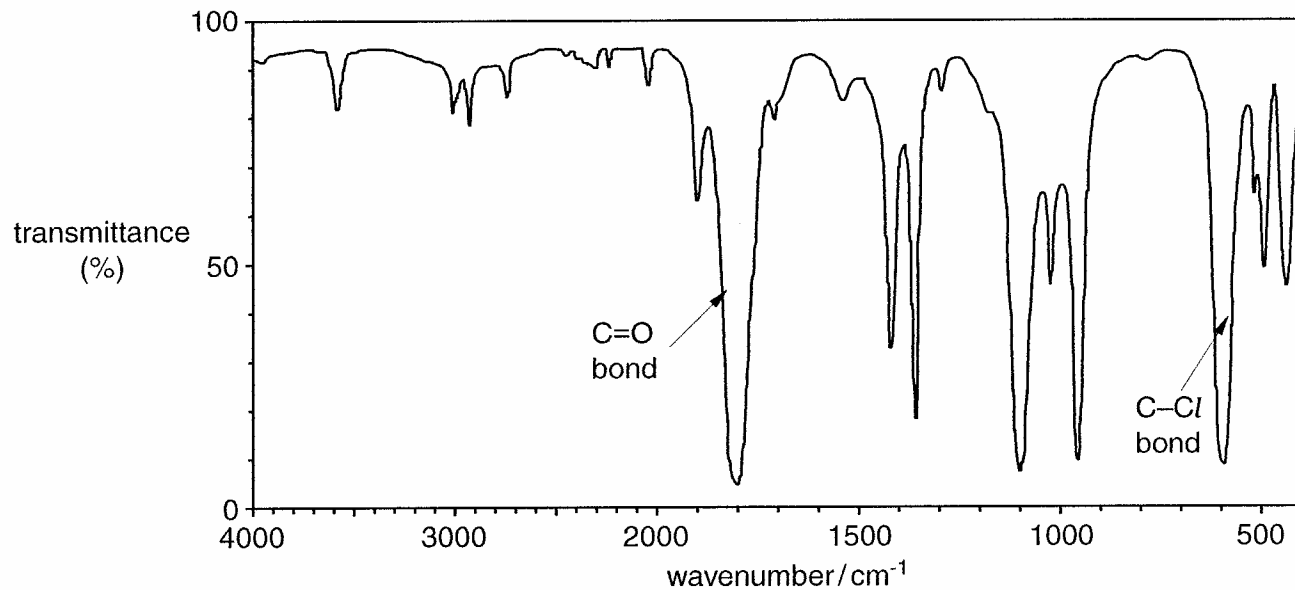
- (b) Supplies of ethanoyl chloride must be kept completely dry as they are readily hydrolysed by water to form ethanoic acid.

Write an equation for the hydrolysis of ethanoyl chloride by water.

[1]

- (c) Infra-red spectroscopy can be used to detect whether a sample of ethanoyl chloride has been hydrolysed.

The infra-red spectrum of ethanoyl chloride is shown below. The absorptions due to the $\text{C}=\text{O}$ and $\text{C}-\text{Cl}$ bonds are labelled.



Describe how you would expect the infra-red spectrum of **ethanoic acid** to differ from the spectrum of ethanoyl chloride.

Explain your answer by referring to the wavenumber ranges of any peaks you would expect to be present for ethanoic acid.

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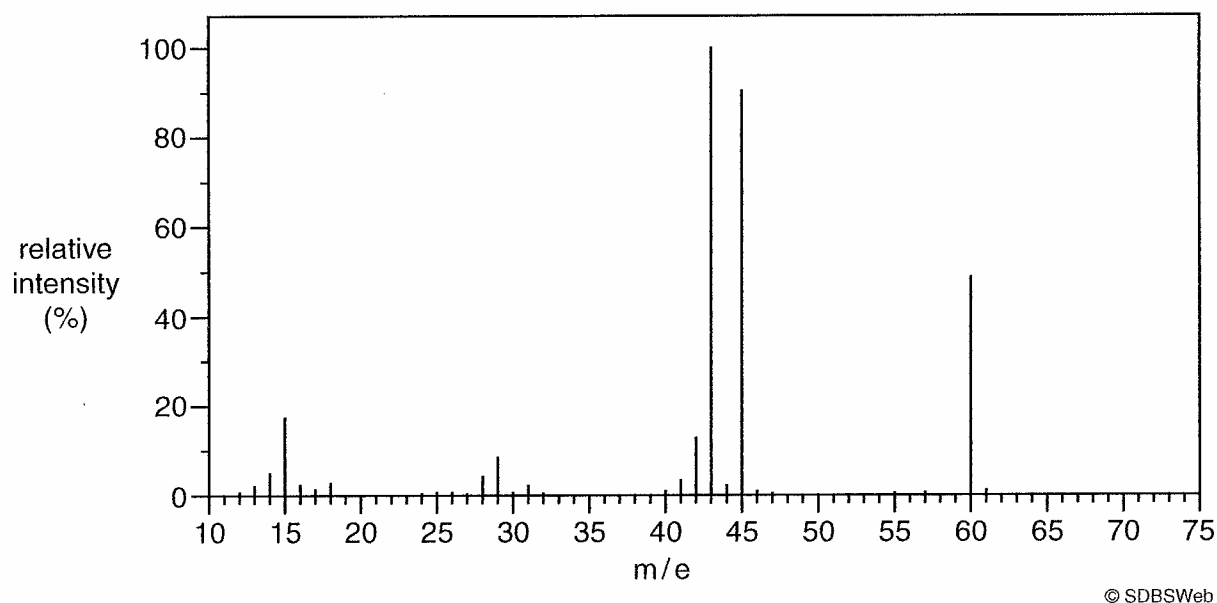
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..... [3]

(d) Ethanoyl chloride and ethanoic acid can also be identified using their mass spectra.

The mass spectrum of **one** of these two compounds is shown below.



State whether this spectrum is of ethanoyl chloride or ethanoic acid. Explain your reasoning.

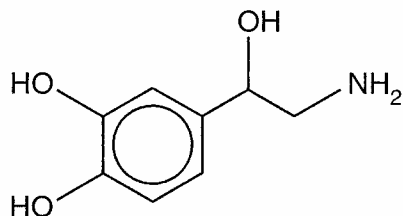
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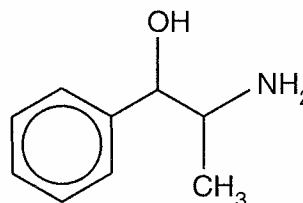
..... [2]

[Total: 8]

- 6 Noradrenaline is produced naturally by nerve cells in the brain. Compound **P** is a synthetic compound that has been widely used as an appetite suppressant. It is thought to be effective because it is similar to noradrenaline.



noradrenaline



compound P

- (a) (i) Suggest a reagent that could be used in a test to distinguish compound **P** from noradrenaline.

..... [1]

- (ii) Draw a ring round the functional group responsible for the positive result in the test you have chosen. [1]

- (iii) State the expected observation for the positive result in the test you have chosen.

..... [1]

- (b) Both these compounds have stereoisomers due to the presence of chiral centres.

- (i) Identify the chiral centres in each molecule by labelling them clearly with asterisks (*) on the structures above. [2]

- (ii) State the type of stereoisomerism caused by the presence of chiral centres.

..... [1]

- (iii) Using **noradrenaline** as an example, explain how a chiral centre gives rise to the stereoisomers. Illustrate your answer with a suitable diagram of the stereoisomers.

.....

[3]

(c) Explain why a pharmaceutical company may produce an appetite suppressant containing only one stereoisomer of compound P, rather than a mixture of the stereoisomers.

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..... [3]

[Total: 12]

7 In this question, one mark is available for the quality of spelling, punctuation and grammar.

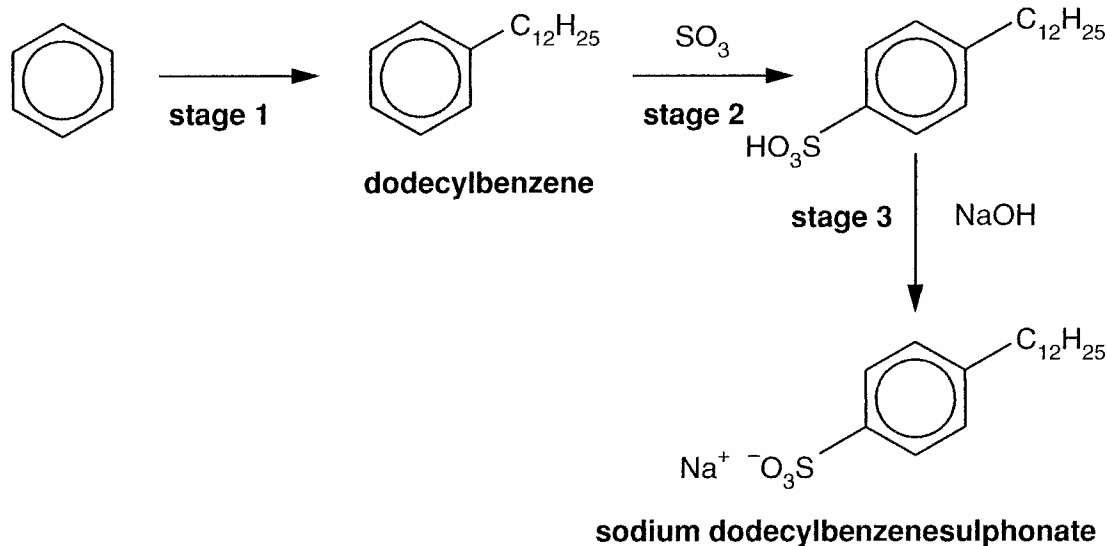
Describe with the aid of suitable diagrams the bonding and structure of a benzene molecule. [6]

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Quality of Written Communication [1]

[Total: 7]

- 8 Sodium dodecylbenzenesulphonate is the active ingredient in many detergents and shampoos. This salt can be manufactured from benzene in three stages.



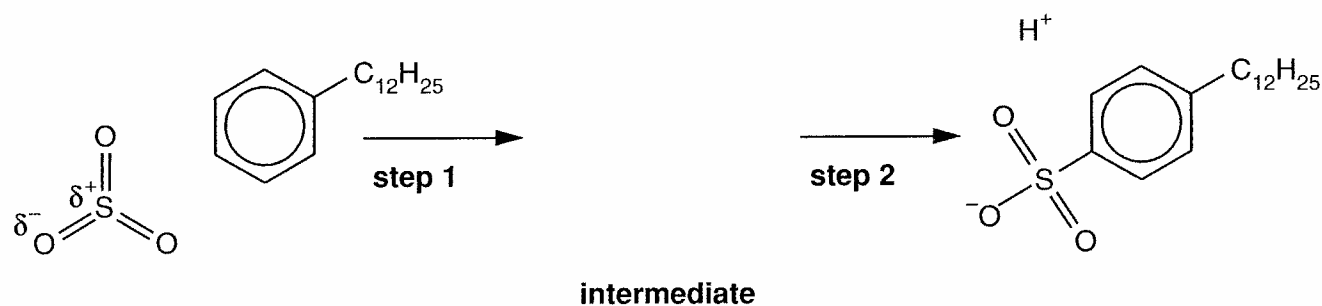
- (a) In **stage 1**, benzene is converted to dodecylbenzene by a Friedel-Crafts reaction.
- (i) Suggest reagents and conditions that could be used to form dodecylbenzene from benzene.
-
- [2]
- (ii) Write an equation for this reaction.
- [1]
- (iii) State why this reaction is described as a *substitution* reaction.

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..... [1]

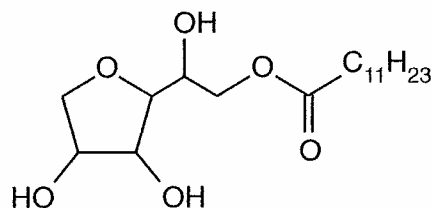
(b) In **stage 2** of the synthesis, dodecylbenzene is reacted with sulphur trioxide, SO_3 .

It is thought that the SO_3 reacts with the benzene by electrophilic substitution. Part of the mechanism is shown below.



Complete the mechanism by:

- (i) drawing the structure of the intermediate [2]
 - (ii) adding curly arrows to show the movement of electron pairs in **steps 1** and **2**. [3]
- (c) The demand for 'natural' shampoos and detergents has led to the development of more biodegradable detergents such as sorbitan monolaurate, which is made from plants.



sorbitan monolaurate

- (i) Suggest a type of reaction that could break down sorbitan monolaurate when it is washed into drains and rivers.

Explain your answer and state the type of organic products formed.

.....

 [3]

- (ii) Suggest **one other** reason why detergents such as sorbitan monolaurate are regarded as 'environmentally friendly'.

.....
 [1]

[Total: 13]