

Advance	d GCE		
CHEMIS	STRY		2814
Chains, I	Rings and Spectroscopy		
Friday	21 JANUARY 2005	Morning	1 hour 30 minutes
Additional n Data Sh	answer on the question paper. naterials: <i>neet for Chemistry</i> c calculator		

OXFORD CAMBRIDGE AND RSA EXAMINATIONS

Candidate Name	Centre Number	Candidate Number

TIME 1 hour 30 minutes

INSTRUCTIONS TO CANDIDATES

- Write your name in the space above.
- Write your Centre number and Candidate number in the boxes above.
- Answer all the questions.
- Write your answers in the spaces provided on the question paper.
- Read each question carefully and make sure you know what you have to do before starting your answer.

INFORMATION FOR CANDIDATES

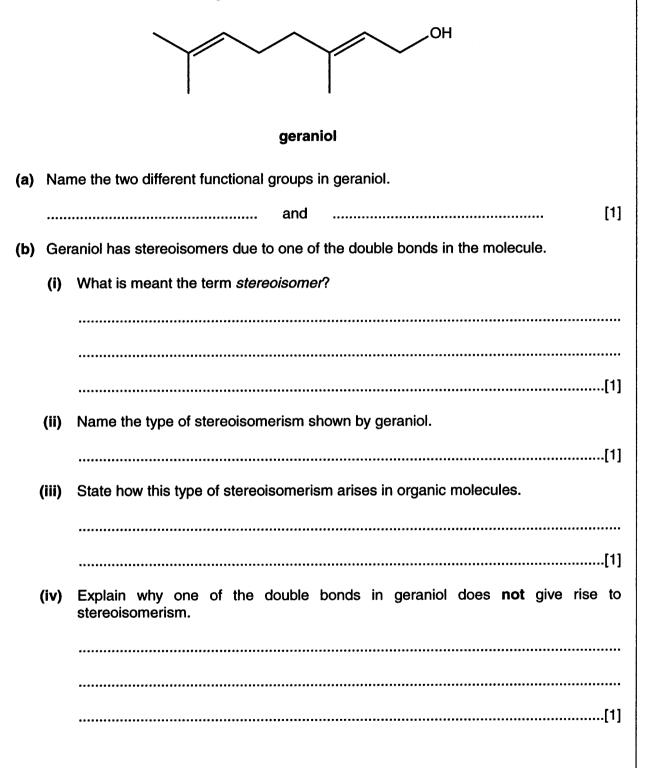
- The number of marks is given in brackets [] at the end of each question or part question.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- You may use the Data Sheet for Chemistry.
- You are advised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

FOR EXAMINER'S USE		
Qu.	Max.	Mark
1	20	
2	17	
3	13	
4	16	
5	10	
6	14	
TOTAL	90	

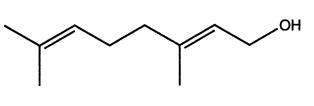
This question paper consists of 15 printed pages and 1 blank page.

Answer all the questions.

1 Geraniol, C₉H₁₅CH₂OH, is a naturally occurring compound that contributes to the smell of roses. The skeletal formula of geraniol is shown below.

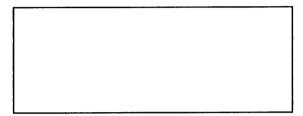






geraniol

- (c) Mild oxidation of geraniol gives an aldehyde Y.
 - (i) Draw the skeletal formula of aldehyde Y below.



aldehyde Y

[2]

[2]

(ii) Complete the equation for the oxidation of geraniol to aldehyde Y.

$$C_9H_{15}CH_2OH$$
 + [O] \rightarrow

(d) Reaction of geraniol with ethanoic acid can be used to make ester Z, which is used in chewing gum and desserts.

(i) Suggest why esters are used in the manufacture of foods.

.....[1]

.....

(ii) State the conditions needed to make ester **Z** from geraniol and ethanoic acid.

.....[2]

(iii) Complete the equation for the formation of ester Z.

+ $C_9H_{15}CH_2OH \rightarrow$

[3]

- For Examiner's Use
- (e) Infra-red spectroscopy can be used to distinguish between geraniol, aldehyde Y and ester Z.

Describe how the infra-red spectra of these three compounds differ. Identify the wavenumber ranges at which you would expect to find the characteristic absorptions for each of the three compounds.

 ••••••	

[5]

[Total: 20]

For Examiner's Use

- 2 The nitration of benzene is a very important industrial reaction.
 - (a) Name two types of commercially important material whose manufacture involves the nitration of benzene.

.....[2]

- (b) State the conditions required for the nitration of benzene using nitric acid and sulphuric acid.
 -[2]
- (c) Write a balanced equation for the nitration of benzene.

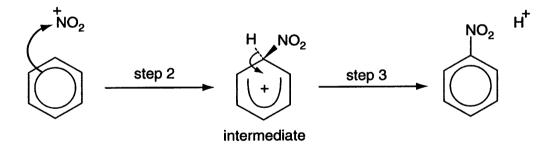
[2]

(d) The mechanism for the reaction is given below.

Step 1: formation of the electrophile, NO_2^+ , from HNO_3 and H_2SO_4

 $HNO_3 + H_2SO_4 \rightarrow H_2O + NO_2^+ + HSO_4^-$

Steps 2 and 3: substitution of NO₂⁺ into the benzene ring



Step 4: protonation of the HSO_4^-

 H^+ + $HSO_4^- \rightarrow H_2SO_4$

(i) Explain what a curly arrow 💛 represents in this type of mechanism.

.....[2]

.....

		7	For Examiner's
	(ii)	State why the NO_2^+ is described as an electrophile in this mechanism.	Use
		[1]	
	(iii)	State why this mechanism is described as substitution.	
		[1]	
	(iv)	How does the mechanism show that the sulphuric acid is acting as a catalyst?	
		[1]	
(e)		his question, one mark is available for the quality of spelling, punctuation and nmar.	
		benzene ring and the ring in the intermediate formed after step 2 have different ctures shown below. Both structures have π -bonds.	
		\mathbf{X}	
		benzene ring ring in the intermediate	
		uce how many electrons are involved in the π -bonding in each structure and cribe how their arrangements are different.	
	•••••		
	•••••		
	•••••		
	•••••		
		[5]	
		Quality of Written Communication [1]	

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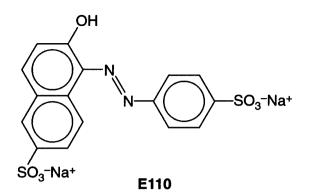
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8	For Examiner's
E110 is a yellow colouring agent that is commonly added to a variety of foods.	Use
E110 contains an azo dye made from an amine and a phenol.	
(a) Describe how you would prepare a sample of an azo dye in the laboratory from an amine, a phenol and any other necessary reagents.	
Include in your answer	
essential reagents and conditions for each stage	
 names of any functional groups formed during the process. 	
[7]	

•

3

(b) The structure of E110 is shown below.



- (i) On the structure above, draw a circle around the functional group that identifies this molecule as an azo dye. [1]
- (ii) Deduce how many carbon and hydrogen atoms are in a molecule of E110.

..... carbon atoms and hydrogen atoms. [2]

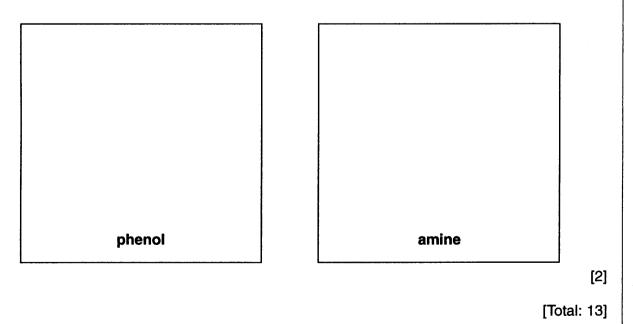
(c) The solubility of E110 in water can be improved by converting the phenolic –OH group into a charged –O⁻ group.

Suggest a suitable reagent that will convert the -OH group in E110 into an $-O^-$ group.

.....[1]

(d) In the boxes below, draw the structures of a phenol and an amine that could be used to make E110 by the method in part (a).

Assume that the SO_3^- Na⁺ groups do not change during the process.



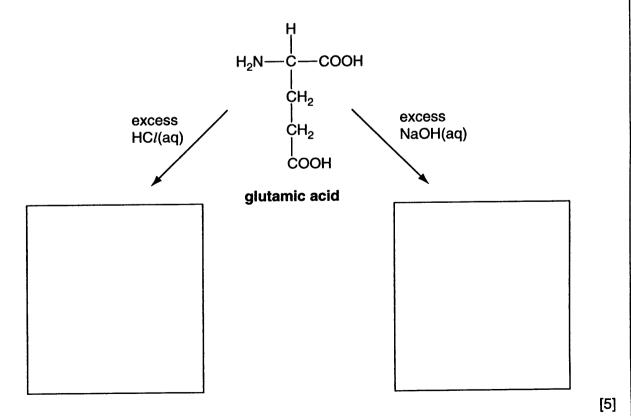
For 10 Examiner's Use Glutamic acid and glycine are both α -amino acids that occur widely in living organisms. Their structures are shown below. н -соон H₂N-H₂N--COOH С ĊH₂ ĊH₂ COOH glycine glutamic acid (a) (i) State the general formula for an α -amino acid.[1] Explain how glutamic acid and glycine both fit the general formula given in part (i) (ii)

.....[2]

(b) Amino acids react with both acids and alkalis.

4

Draw structures below to show how the glutamic acid molecule is changed in the presence of excess acid and alkali.



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For Examiner's Use

Glutamic acid exists as two optical isomers, but glycine does not.

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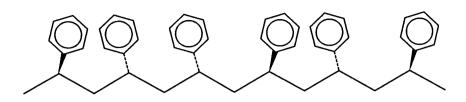
Explain what structural feature causes optical isomerism in organic molecules. Include appropriate diagrams and use these two amino acids to illustrate your answer.

Quality of Written Communication [1]

[Total: 16]

5 Poly(phenylethene) is one of the most versatile and successful polymers.

The 3-D skeletal formula of a section of atactic poly(phenylethene) is shown in Fig 5.1 below.





- (a) (i) State the type of polymerisation used to make poly(phenylethene).
 - (ii) Draw a skeletal or displayed formula to show the monomer used to make poly(phenylethene).

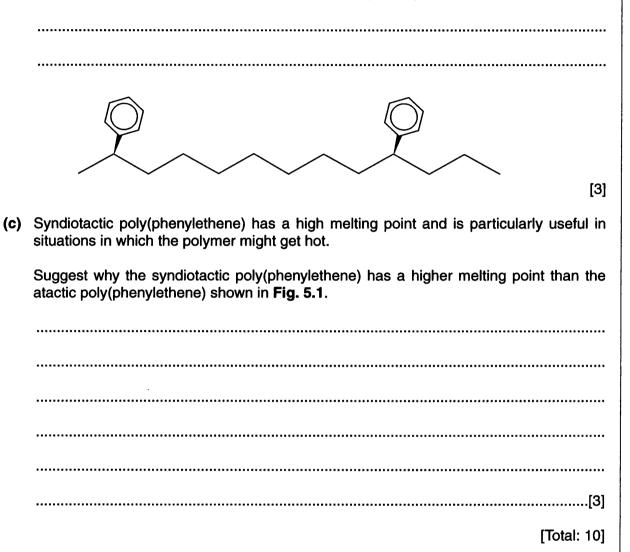
[1]

(iii) Outline how the polymer is formed from the monomer molecules. (You do **not** need to give any details of the catalyst or conditions involved.)

 (b) Poly(phenylethene) can also be made with a *syndiotactic* arrangement of its side chains.

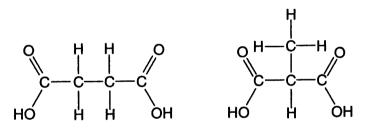
13

Explain what is meant by the term *syndiotactic*. Illustrate your answer by completing the 3-D skeletal formula of a section of syndiotactic poly(phenylethene) below.



- For 14 Examiner's Use Forest fires release a large number of organic compounds into the atmosphere. These include alcohols and carboxylic acids. An environmental chemist is trying to identify one of these compounds in a sample of air. The unknown compound **X** is thought to be a carboxylic acid with empirical formula $C_{2}H_{3}O_{2}$. (a) Mass spectrometry is used to help deduce the molecular formula of compound X. Describe how the mass spectrum of compound X is used to determine its relative **(i)** molecular mass.[2] (ii) The relative molecular mass of compound X is shown to be 118. Explain how this relative molecular mass and the empirical formula are used to deduce that the molecular formula of compound X is $C_4H_6O_4$. Show any working.[2]
- (b) The two dicarboxylic acids with molecular formula $C_4H_6O_4$ are shown below.

6



N.m.r. spectroscopy is used to deduce which of these is the unknown compound.

The environmental chemist obtains an n.m.r. spectrum of compound X and then adds some D₂O and obtains a second n.m.r. spectrum.

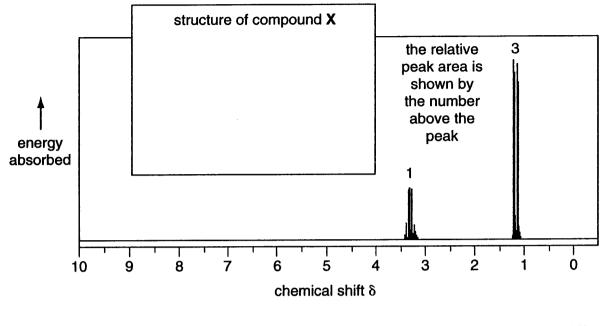
(i) What difference would you expect between these two n.m.r. spectra?

.....[1]

1

For Examiner's Use

(ii) The n.m.r. spectrum of compound X in D₂O is shown below.



15

Use this spectrum to identify which of the two carboxylic acids is compound X.

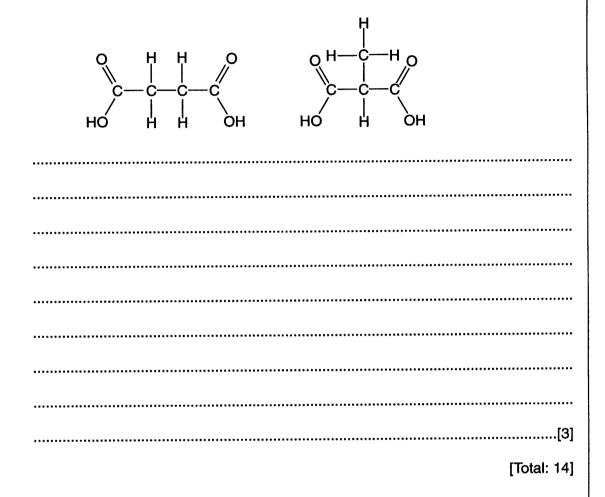
- Draw the correct structure in the box above the spectrum.
- Use labels to show which protons on the structure are responsible for each peak on the spectrum.
- Explain your reasoning by referring to the relative peak areas and the spin-spin splitting patterns of the peaks.

TURN OVER FOR Q6 PART (b)(iii)

(iii) Predict the number of peaks and any spin-spin splitting expected on the n.m.r. spectrum of a solution in D_2O of the **other** acid with formula $C_4H_6O_4$.

Explain your reasoning.

(The two possible structures of compound **X** are shown again below.)



END OF QUESTION PAPER

Copyright Acknowledgements:

Q.6(b)(ii) n.m.r. spectrum adapted from http://www.aist.go.jp./RIODB/SDBS (11/10/03) © SPECTRAL DATA BASE SERVICE (SDBS).

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