OCR
RECOGNISING ACHIEVEMENT

OXFORD CAMBRIDGE AND RSA EXAMINATIONS

Advanced GCE

CHEMISTRY 2814

Chains, Rings and Spectroscopy

Wednesday **19 JUNE 2002** Afternoon 1 hour 30 minutes

Candidates answer on the question paper
Additional materials.
Data Sheet for Chemistry
Scientific calculator

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 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	10	
2	11	
3	10	
4	6	
5	14	
6	15	
7	12	
8	12	
TOTAL	90	

This question paper consists of 12 printed pages.

Registered Charity Number 1066969
[Turn over

1 A ketone **A** has the molecular formula C_3H_6O.

(a) Name **A** and draw its structure to show clearly its functional group.

name .....

structure:

[2]

(b) Ketone **A** can be **reduced** to an alcohol, **B**.

(i) Name **B** and draw its structure.

name .....

structure:

[2]

(ii) State a suitable reagent for this reduction.

..... [1]

(iii) Write a balanced equation for the reduction of **A** to **B**. You may use the symbol [H] in this redox reaction to represent the reducing agent.

..... [1]

(c) Describe a chemical method to detect the presence of a carbonyl group in a compound such as **A**. Explain how you would use the product from this chemical method to identify **A**.

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..... [4]

[Total : 10]

2 The reaction of benzene with bromine requires a halogen carrier but the reaction of phenol with bromine does not.

(a) **(i)** Write the equation for the reaction of benzene with bromine.

..... [2]

(ii) State a substance that will act as the halogen carrier for this reaction.

..... [1]

(b) The reaction of phenol with excess bromine gives the organic product **C**.

(i) Draw the structure of **C**.

[2]

(ii) Cold aqueous NaOH is added to compound **C**. Using structural formulae, predict the equation for the reaction that takes place.

[2]

(iii) Explain why the reaction of phenol with bromine does **not** require a halogen carrier.

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..... [3]

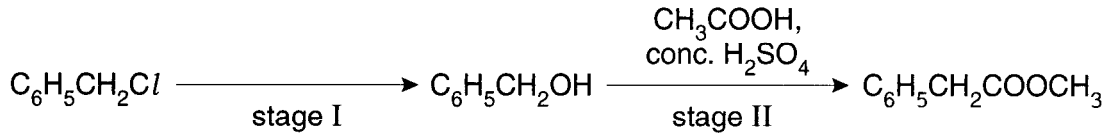
(iv) State a general use for halogenated phenols.

..... [1]

[Total : 11]

[Turn over

3 A commercial synthesis of the ester **G** is shown below.



E **F** **G**

(a) Stage I:

(i) Suggest a suitable reagent.

..... [1]

(ii) State the type of reaction occurring.

..... [2]

(iii) Write the equation for this reaction.

..... [1]

(b) Stage II:

(i) Draw the displayed formula for the ester **G**.

[1]

(ii) Write the equation.

..... [1]

(iii) Suggest a general use for esters such as **G**.

..... [1]

(iv) **G** can also be made directly from **E** by reaction with $CH_3COO^-Na^+$. Suggest a possible mechanism for this reaction.

[3]

[Total : 10]

4 Describe the synthesis of a diazonium salt from phenylamine. Explain why diazonium salts are important.

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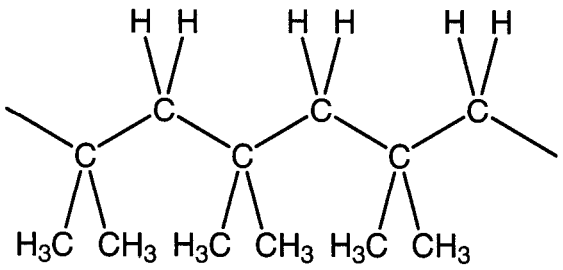
..... [6]

[Total : 6]

[Turn over

5 **(a)** A section of a polymer has the structure shown below.



(i) Circle a repeat unit of this polymer on the diagram above. [1]

(ii) Deduce the empirical formula of this polymer.

..... [1]

(iii) Draw a structure for a monomer from which this polymer could be made. Your structure should show any multiple bonds.

[1]

(b) Proteins are natural polymers made from α-amino acids, such as glycine, H_2NCH_2COOH.

(i) Name the functional group made during amino acid polymerisation and draw its displayed formula.

name of functional group .....

displayed formula of functional group:

[2]

(ii) Name this type of polymerisation reaction.

..... [1]

(iii) Draw a displayed and a skeletal formula for the dipeptide **H**, $C_4H_8N_2O_3$, made from glycine, H_2NCH_2COOH.

displayed formula of **H**

skeletal formula of **H**

[2]

(iv) A student made 1.10 g of dipeptide **H** starting from 1.40 g of glycine.

Calculate the percentage yield obtained. Give your answer to 3 significant figures.

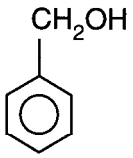
Percentage yield ..... % [4]

(v) When glycine is treated with hydrochloric acid a compound **J**, $C_2H_6Cl NO_2$, is formed. Draw a structure for compound **J**.

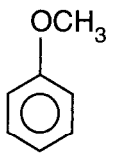
[2]

[Total : 14]

6 Compounds **K** and **L** are structural isomers.



K



L

(a) **(i)** What is the molecular formula of these isomers?

..... [1]

(ii) Calculate the mass:charge ratio, m/e, you expect for the molecular ion peak in the mass spectrum of **K**, showing your working.

Answer ..... [1]

(iii) A sample of **L** is sent for analysis to determine its percentage by mass of carbon and hydrogen. Calculate the expected results.

%C

%H

[2]

(b) Explain how infra-red spectra would allow you to distinguish between samples of **K** and **L**.

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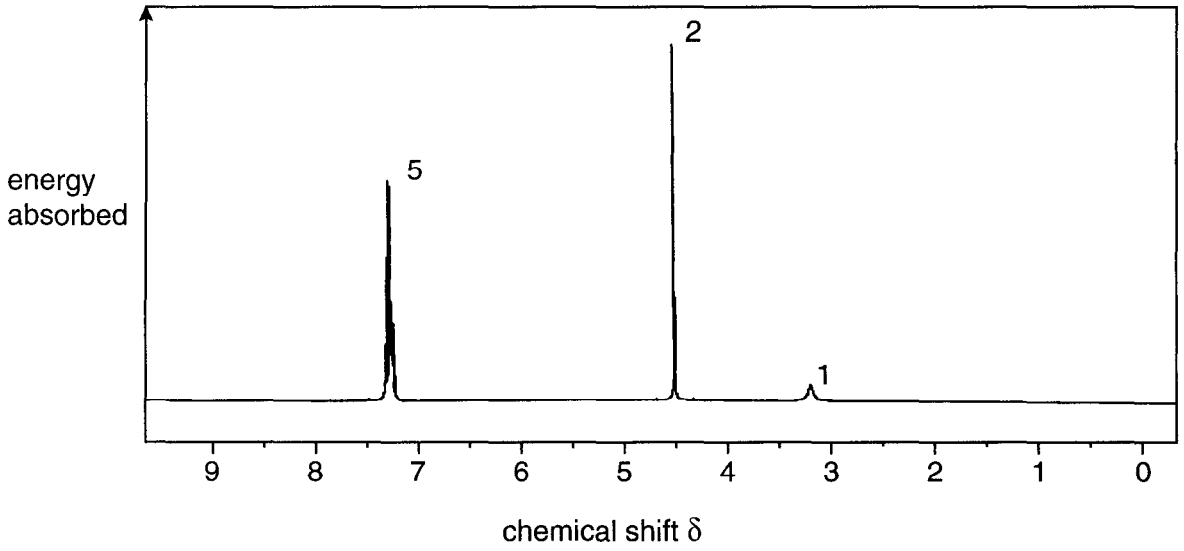
..... [3]

(c) **(i)** Compound **K** gives the n.m.r. spectrum below. Identify which of the protons are responsible for each peak. Explain your reasoning.



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..... [3]

(ii) A sample of **K** is shaken with D_2O and the spectrum is re-run. Describe how the spectrum is changed.

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..... [1]

(iii) Suggest possible δ values for the peaks in the n.m.r. spectrum of compound **L**. For each peak, give the number of protons responsible.

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..... [4]

[Total : 15]

7 Complete the reaction schemes below. Draw the structural formula of an appropriate organic compound, or give a suitable reagent, in each of the boxes provided.

(a) CH_3CH_2CHO —(Tollen's reagent (ammoniacal $AgNO_3$))→ [ ] [1]

(b) C_6H_6 —(conc. H_2SO_4 and conc. HNO_3)→ [ ] [1]

(c) C_6H_6 —([ ] and [ ])→ $C_6H_5CH_3$ [2]

(d) $C_6H_5NO_2$ —(Sn and conc. HCl, heat)→ [ ] [1]

(e) [ ] —(aqueous NaOH, heat)→ $CH_3COO^-Na^+ + C_2H_5OH$ [1]

(f) **(i)** CH_3COCH_3 —(HCN and KCN)→ [ ] [1]

(ii) Describe the mechanism for the reaction in **(f)(i)** above. State the name for this type of mechanism.

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..... [5]

[Total : 12]

8 *In this question, two marks are available for the quality of written communication.*

Explain the different types of isomerism encountered in organic chemistry.

Outline the importance of stereoisomerism in the synthesis and use of compounds as pharmaceuticals.

In your answer use diagrams of suitable examples to illustrate both structural isomerism and stereoisomerism.

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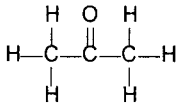
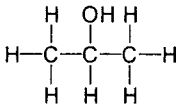
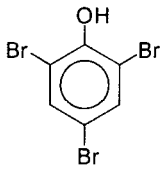
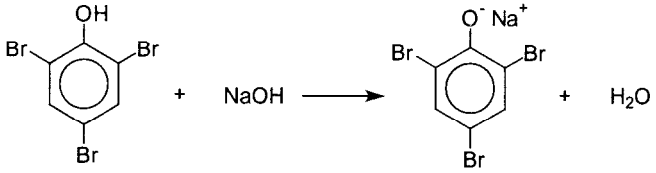
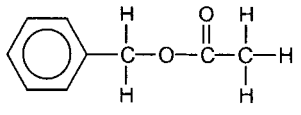
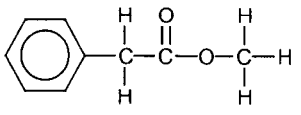
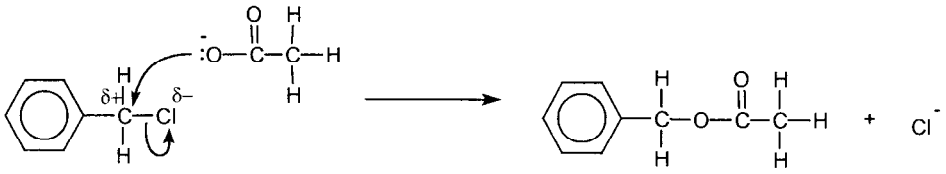
[10]

Quality of Written Communication [2]

[Total : 12]

Qu.	Expected answers:	Marks
1 (a)	propanone ✓  ✓	[2]
(b) (i)	propan-2-ol ✓  ✓	[2]
(ii)	$NaBH_4$ ✓	[1]
(iii)	$C_3H_6O + 2[H] \longrightarrow C_3H_8O / C_3H_7OH$ ✓	[1]
(c)	2,4-dinitrophenylhydrazine ✓ yellow / orange/red … crystals /solid / ppt. etc ✓ (re)crystallise / purify ✓ measure melting point/m.p. (of product) ✓ compare with known compounds ✓ **ANY 4** out of **5**	**max [4]**
		[Total: 10]

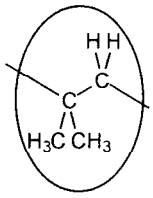
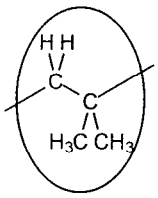
Qu.	Expected answers:	Marks
2 (a) (i)	$C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$ organic product ✓ rest of the equation also correct ✓	[2]
(ii)	$FeBr_3$ / $AlBr_3$ / iron(III)bromide / aluminium bromide	[1]
(b) (i)	 ✓✓	[2]
(ii)	 organic product ✓(allow ecf from (i) but must be a ring with OH) rest of the equation also correct ✓	[2]
(iii)	(benzene) ring is activated ✓ lone pair on oxygen is delocalised / interacts with the π electrons ✓ more (π) electron density (around ring) ✓ attracts bromine / electrophiles more / polarises Br_2 molecule more ✓ ***ANY* 3** marks from **4**	max [3]
(iv)	antiseptics / disinfectants	[1]
		[Total: 11]

Qu.	Expected answers:	Marks
3 (a) (i)	$NaOH$ / KOH / OH^- / H_2O ✓	[1]
(ii)	nucleophilic ✓ substitution ✓	[2]
(iii)	$C_6H_5CH_2Cl + NaOH \longrightarrow C_6H_5CH_2OH + NaCl$ ✓ / $OH^- \longrightarrow Cl^-$ if water in (i), then: $H_2O \longrightarrow HCl$	[1]
(b) (i)	allow either  or  ✓	[1]
(ii)	$C_6H_5CH_2OH + CH_3COOH \longrightarrow CH_3COOCH_2C_6H_5 + H_2O$ ✓ allow $C_6H_5CH_2COOCH_3$ as the ester	[1]
(iii)	perfumes / flavourings / solvents ✓	[1]
(iv)	suggested mechanisms could be S_N1 or S_N2 type (such as the example shown below)  look for diagram or words describing: nucleophilic ✓ substitution / ester + Cl^- as products ✓ dipole on C-Cl bond ✓ curly arrow from COO^- to C ✓ curly arrow from bond to Cl ✓ **ANY 3** out of **5** (allow anything reasonable producing $C_6H_5CH_2COOCH_3$)	max [3]
		[Total: 10]

Qu.	Expected answers:	Marks
4	(at a temperature) < 10° ✓ ***ESSENTIAL*** mark	[1]
	(reagent is) nitrous acid / HNO_2 ✓ (made by) sodium nitrite / $NaNO_2$ … ✓ … (with) hydrochloric acid / HCl ✓ … (to give diazonium salt with formula) eg $C_6H_5N_2^+$ / $C_6H_5N_2Cl$ / $C_6H_5N^+{\equiv}N\ Cl$ ✓	
	balanced equation - e.g. $C_6H_5NH_2 + HNO_2 + H^+ \longrightarrow C_6H_5N_2^+ + 2H_2O$ ✓	
	(any of the other marks above may be awarded if they appear in an equation)	max [4]
	MAX 4 from these 5	
	(used to form) dyes / colourings / coloured compounds ✓ ***ESSENTIAL*** mark	[1]
		[Total: 6]

Qu.	Expected answers:	Marks

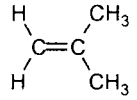
5 (a) (i)

/ ✓ **[1]**

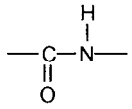
(ii) CH_2 ✓ **[1]**

(iii)



✓ **[1]**

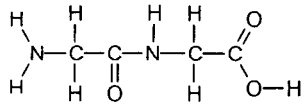
(b) (i) peptide / amide ✓ **[1]**



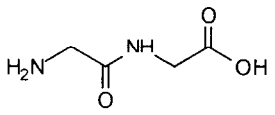
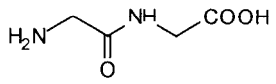
✓ **[1]**

(ii) condensation ✓ **[1]**

(iii)



✓ **[1]**

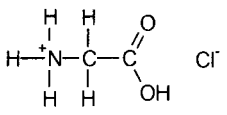
/ ✓ **[1]**

5 (b) (iv) M_r glycine, $C_2H_5NO_2$ = **75**.(0) ✓
M_r $C_4H_8N_2O_3$ = **132**.(0) ✓ **[2]**

use of 2:1 ratio to give **0.009333**mol of dipeptide ***H*** expected / ecf ✓ (or use of 2:1 ratio to give mass ratio of **150:132** / ecf) **[1]**

answer in the range **89.2** - **89.4** with 3 sf / ecf ✓(correct answer gets all **4** marks) (answer in the range **44.6** - **44.7** (no 2.1) with 3 sf gets **3** marks overall) **[1]**

(v)

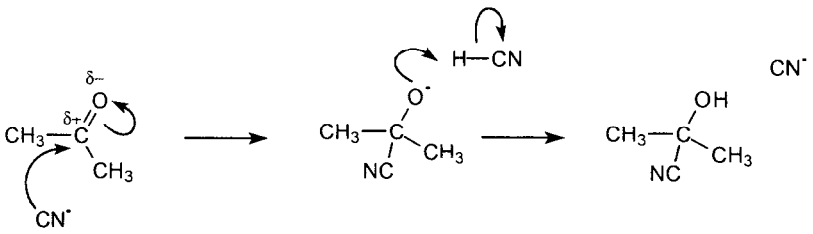


$H_3N^+CH_2COOH$ Cl^-/
NH_3^+ group ✓
rest of the molecule and Cl^- ✓ **[2]**

[Total: 14]

Qu.	Expected answers:	Marks
6 (a) (i)	C_7H_8O ✓	[1]
(ii)	M_r = 108 so m/e of molecular ion = **108** / ecf from **(i)** ✓	[1]
(iii)	%C = (84.0)/(108) x 100% = **77.8%** ✓ %H = (8.0)/(108) x 100% = **7.4%** ✓ / ecf from **(i)** or **(ii)**	[2]
(b)	***K*** has OH group ✓ ***K*** has peak at 3230 - 3550 cm^{-1} ✓ (ignore reference to any other bonds) ***L*** does not have OH group / peak at 3230 - 3550 cm^{-1} ✓	[3]
(c) (i)	peak at δ = 7.3ppm / with area 5, is due to the benzene ring (protons) ✓ peak at δ = 4.5ppm / with area 2, is due to the $-CH_2-$ (protons) ✓ peak at δ = 3.2ppm / with area 1, is due to the OH (proton) ✓	[3]
(ii)	peak at δ = 3.2ppm / with area 1 disappears / ecf from *(i)* ✓	[1]
(iii)	expect peak at δ = 7.1-7.7 ppm ✓ 5 protons responsible / area = 5 ✓ expect peak at δ = 3.3-4.3ppm ✓ 3 protons responsible / area = 3 ✓	[4]
		[Total: 15]

Qu.		Expected answers:	Marks
7	(a)	CH_3CH_2COOH ✓	[1]
	(b)	$C_6H_5NO_2$ ✓	[1]
	(c)	CH_3Cl / CH_3Br ✓ $AlCl_3$ / $FeCl_3$ / $FeBr_3$ etc ✓	[2]
	(d)	$C_6H_5NH_3^+$ / $C_6H_5NH_2$ ✓	[1]
	(e)	$CH_3COOC_2H_5$ ✓	[1]
	(f) (i)	$(CH_3)_2C(OH)CN$ etc ✓	[1]
	(ii)	nucleophilic ✓ addition ✓	



Look for the following in a diagram as above or description: (dipoles **not** required)

CN^-/nucleophile attacks (δ)+ carbonyl C / curly arrow from CN^- to carbonyl C ✓
(curly arrow) breaking C=O ✓
correct structure of the intermediate ✓
curly arrow from O^- to HCN / H_2O ✓

***ANY* 5** out of the **6** marks above **max [5]**

(curly arrows must be clearly from and to the correct bond / atom to gain the mark)

[Total: 12]

Qu.	Expected answers:	Marks
8	(**structural** isomerism is) same molecular formula, different structural formulae ✓ two correct structures of suitable example ✓ **stereoisomerism** (is same structural) formula /order of bonds, different spatial arrangements of the atoms ✓ (**cis-trans** / **geometric** isomerism is due to) non-rotation around a C=C double bond ✓ two correct structures of suitable example ✓ (**optical** isomerism is when) molecules are non-superimposable mirror images / asymmetric / contain a chiral centre ✓ (or polymers may be isotactic, atactic or syndiotactic) carbon atom is attached to four distinguishable / different groups / atoms /(or shown in diagram) ✓ (or polymer side chain on the same, random or alternate sides) two correct 3-d structures of suitable example ✓ **8 points on isomerism (3 MAX for optical isomerism / polymers)** (synthesis of only one stereoisomer of a **pharmaceutical** is good because . .) ... only one of the two stereoisomers may be active /the two isomers may have different activity in the body ✓ ... a smaller dose needed /saves cost of materials/separation ✓ (ora) ... the other may have (harmful) side effects ✓ good example of stereospecific drug e.g Thalidomide / Dopa / Ibuprofen ✓ **4 points on chiral synthesis** **Quality of Written Communication** the answer is coherent, and at least **two** of the specialist terms: **structural**, **cis-trans/geometric** and **optical isomerism** are assigned correctly ✓ the text contains at least two legible sentences with reasonably accurate spelling, punctuation and grammar ✓	**max [10]** **[2]** **[Total: 12]**