

OXFORD CAMBRIDGE AND RSA EXAMINATIONS

Advanced GCE

**CHEMISTRY**

**2814**

Chains, Rings and Spectroscopy

Thursday

**23 JUNE 2005**

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												
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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

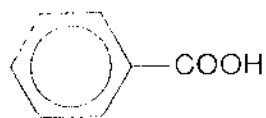
- The number of marks is given in brackets [ ] at the end of each question or part question.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- You may use the *Data Sheet for Chemistry*.
- You are advised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

FOR EXAMINER'S USE		
Qn.	Max.	Mark
1	10	
2	15	
3	13	
4	15	
5	20	
6	17	
<b>TOTAL</b>	<b>90</b>	

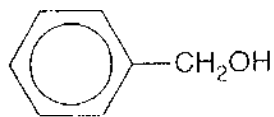
This question paper consists of 16 printed pages.

Answer all the questions.

- 1 A student decided to investigate the reactivity of the  $-OH$  group in the three organic compounds shown below.



benzoic acid



phenylmethanol



4-methylphenol

- (a) Benzoic acid reacts with aqueous sodium hydroxide.



- (i) Complete the equation above. [2]
- (ii) State which, if any, of the other two compounds above would react with aqueous sodium hydroxide. Explain your answer.

.....

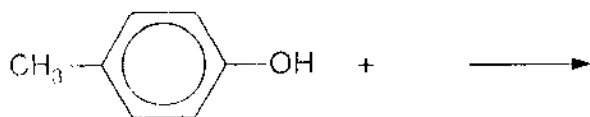
.....

..... [2]

- (b) All three compounds react with sodium metal, giving off a gas.

- (i) Identify the gas given off in this reaction. [1]
- .....

- (ii) Complete and balance the equation for the reaction of 4-methylphenol with sodium.



[2]

(c) Benzoic acid and phenylmethanol will react with each other in the presence of a suitable catalyst.

(i) State a suitable catalyst for this reaction.

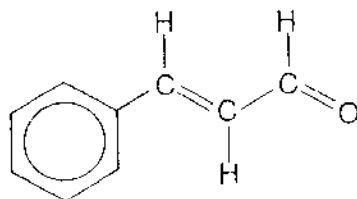
.....[1]

(ii) Draw the displayed formula of the organic product.

[2]

[Total: 10]

- 2 Cinnamaldehyde is the compound that gives cinnamon its distinctive flavour.



cinnamaldehyde

- (a) Draw the skeletal formula of cinnamaldehyde.

[1]

- (b) Cinnamaldehyde shows *cis-trans* isomerism.

- (i) Explain how *cis-trans* isomerism arises in cinnamaldehyde.

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

- (ii) State and explain whether cinnamaldehyde is a *cis* or a *trans* isomer.

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

- (iii) Draw a skeletal or displayed formula to show the structure of the other *cis-trans* isomer of cinnamaldehyde.

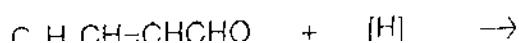
[1]

- (c) Cinnamaldehyde can be reduced using sodium borohydride,  $\text{NaBH}_4$ .

- (i) State which functional group reacts with the sodium borohydride.

..... [1]

- (ii) Complete and balance the equation for this reaction.

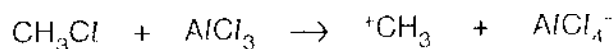




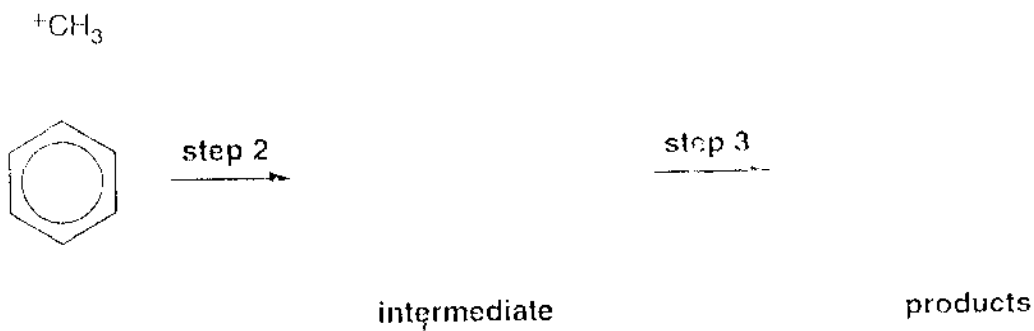
- 3 Benzene reacts with  $\text{CH}_3\text{Cl}$  to form methylbenzene  $\text{C}_6\text{H}_5\text{CH}_3$ . This is an electrophilic substitution reaction.

A possible mechanism for this reaction is shown below.

Step 1: the electrophile  $^+\text{CH}_3$  is formed from  $\text{CH}_3\text{Cl}$  and the catalyst,  $\text{AlCl}_3$



Steps 2 and 3: substitution of  $^+\text{CH}_3$  into the benzene ring



Step 4: the catalyst,  $\text{AlCl}_3$ , is regenerated

- (a) (i) Complete **steps 2 and 3** of the mechanism above. Show the relevant curly arrows and the charges on any ions. [4]

- (ii) State why  $^+\text{CH}_3$  is described as an electrophile in this mechanism.

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

- (iii) Suggest an equation to show how the catalyst,  $\text{AlCl}_3$ , is regenerated in **step 4**.

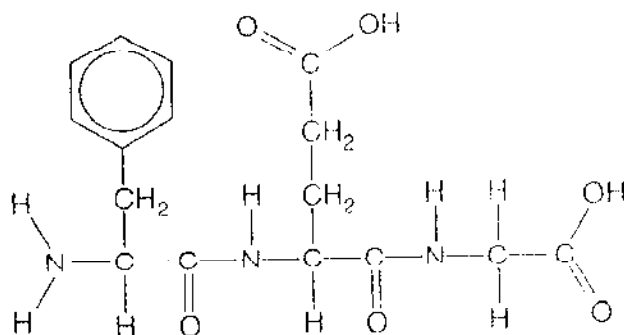
[1]

- (b) Write an overall equation for this reaction.

[2]



- 4 Compound **A** is currently being tested as a possible anti-allergic drug.



compound **A**

- (a) Compound **A** can be hydrolysed to form three organic products.

(i) Name a suitable reagent and conditions for the hydrolysis of compound **A**.

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

(ii) The three organic products all belong to the same class of compound. State the general name for this class of organic compound.

..... [1]

(iii) Draw the structure of **one** of the organic products from the hydrolysis of **A** using the reagent you have given in (a)(i) above.

[2]

(iv) Explain what is meant by the term *hydrolysis*. Use this reaction to illustrate your answer.

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

(b) Compound **A** can exist as a number of stereoisomers, but only one of them is pharmacologically active as the anti-allergic drug.

(i) Explain what causes stereoisomerism in compounds such as **A**.

.....  
.....  
.....  
.....  
.....  
.....  
.....  
.....  
.....  
.....[3]

(ii) Explain why there are **four** different stereoisomers of compound **A**.

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

(iii) Suggest how a drug company could synthesise compound **A** so that the drug contains only the pharmacologically active stereoisomer.

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

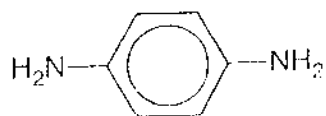
(iv) Sometimes it is difficult to manufacture a drug containing only the one pharmacologically active stereoisomer.

Describe **two** possible disadvantages of producing a drug containing a mixture of several stereoisomers.

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

[Total: 15]

- 5 1,4-Diaminobenzene is used in the manufacture of a variety of materials including dyes and polymers.



**1,4-diaminobenzene**

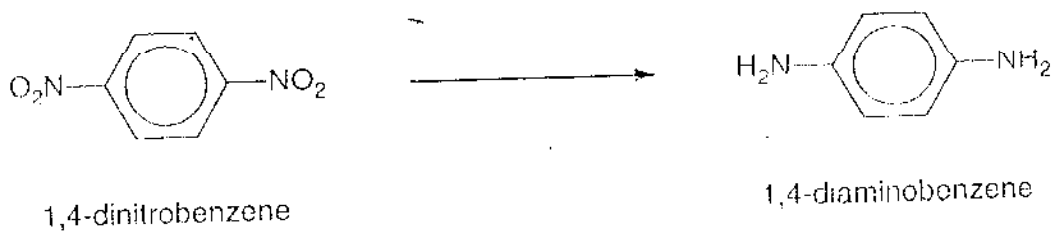
- (a) Explain what is meant by the term *1,4-diamino* in the name of this compound.

.....

.....

..... [2]

- (b) 1,4-diaminobenzene can be manufactured from 1,4-dinitrobenzene.



- (i) What type of reaction is this?

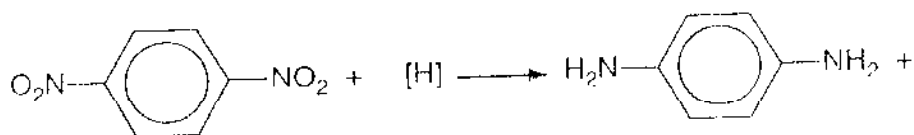
..... [1]

- (ii) State reagents and conditions that could be used to carry out this reaction.

.....

..... [2]

- (iii) Complete and balance the equation below for this reaction.



[2]

(c) 1,4-Diaminobenzene is used to make permanent black dye for hair.

1,4-Diaminobenzene can irritate the skin because it is basic. Therefore, it is sometimes neutralised with **excess** hydrochloric acid to give the salt.

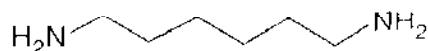
(i) Explain how the amino groups in a primary amine such as 1,4-diaminobenzene allow the molecule to act as a base.

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

(ii) Draw the structure of the salt formed in this reaction.

[2]

(iii) State whether you would expect hexane-1,6-diamine to be a stronger or weaker base than 1,4-diaminobenzene. Explain your reasoning.



hexane-1,6-diamine

.....  
.....  
.....  
.....  
.....[3]

(c) Kevlar is a very tough polymer made from 1,4-diaminobenzene and benzene-1,4-dicarboxylic acid.

(i) State a use for Kevlar.

.....[1]

(ii) Describe the polymerisation reaction that forms Kevlar. Include in your answer:

- an explanation of the type of polymerisation involved
- an equation for the reaction
- a repeat unit to show the structure of Kevlar.

.....  
.....  
.....  
.....  
.....  
.....  
.....  
.....  
.....  
.....[5]

[Total: 20]








# Mark Scheme 2814



## June 2005

2  
1

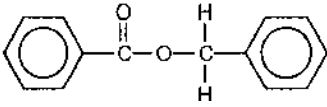
1 (a)(i) balanced equation to give  COO ✓ + H<sub>2</sub>O ✓ allow C<sub>7</sub>H<sub>5</sub>O<sub>2</sub><sup>-</sup> [2]

(ii) 4-methylphenol reacts (phenylmethanol does not) ✓  
 ... because phenols are (more) acidic / donate H<sup>+</sup> more easily AW ✓ [2]

(b)(i) H<sub>2</sub> / hydrogen [1]

(ii)  + 2 Na → 2  + H<sub>2</sub>  
 phenoxide/sodium phenoxide structure / formula ✓ allow C<sub>7</sub>H<sub>7</sub>ONa  
but NOT -NaO  
or O-Na  
 rest the equation also correct and balanced ✓ [2]

(c) (i) H<sup>+</sup> / acid / named strong acid eg H<sub>2</sub>SO<sub>4</sub> / HCl [1]

(ii)   
 displayed ester group ✓  
 rest of the ester ✓ [2]

[Total: 10]



(b) *C=C double bond does not rotate* ✓  
*two different groups on each carbon (of the C=C) AW* ✓ *NOT on "each side" of the C=C* [ 2 ]

i. *trans because H / groups are on opposite sides AW* ✓ [ 1 ]

ii. *any formula that shows the H on the same side - eg*



(c) (i) *aldehyde / C=O / carbonyl* ✓ [ 1 ]

(ii)  $C_6H_5CHCHCHO + 2[H] \rightarrow C_6H_5CHCHCH_2OH$  ✓ *allow C<sub>9</sub>H<sub>10</sub>O* [ 1 ]

(d) *method*

*silver nitrate* ✓

*ammonia / ammoniacal* ✓

*warm / heat* ✓

*silver (mirror) / brown ppt forms* ✓

*explanation*

*silver ions reduced /  $Ag^+ + e^- \rightarrow Ag$*  ✓

*aldehyde oxidised to a carboxylic acid* ✓

*correct structure - eg C<sub>6</sub>H<sub>5</sub>CHCHCOO / COOH* ✓

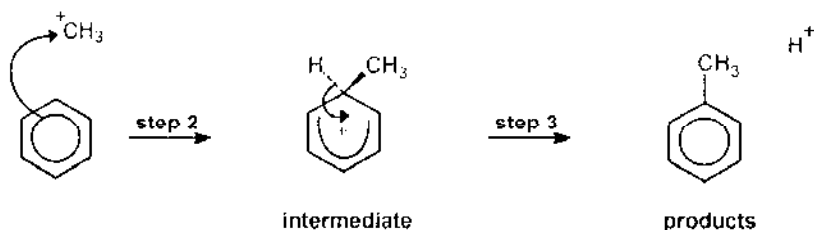
*quality of written communication*

*mark for correct spelling, punctuation and grammar in at least two*

*sentences* ✓ [ 8 ]

[Total: 15]

3 (a) (i)



curly arrow from  $\pi$ -bond towards the carbon of  $\text{CH}_3^+$  ✓

**intermediate**

structure of the intermediate ✓

curly arrow from C-H bond ✓

**products**

structure of methylbenzene and  $\text{H}^+$  shown ✓

intermediate must have the "+" within the delocalised area

allow HCl as product if Cl is shown with the intermediate

[4]

(ii) accepts an electron pair ✓

NOT a "lone" pair

[1]

(iii)  $\text{H} + \text{AlCl}_4 \longrightarrow \text{AlCl}_3 + \text{HCl}$

[1]

$\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \longrightarrow \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl}$

products ✓

rest of the equation also correct ✓

[2]

(b) (i) (benzene) ring is activated ✓

lone pair from oxygen is delocalised / interacts with the  $\pi$  electrons around the ring / AW or diagram ✓

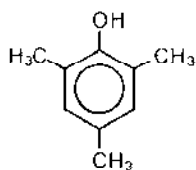
ignore references to the inductive effect

greater electron density (around the ring) ✓

attracts  $\text{CH}_3^+$  / electrophiles more easily ✓

[4]

(ii)



[1]

[Total: 13]

- 4 (a) (i) water / evidence of a solution in water - eg  
(aq), 'dil', '6M' or 'conc' for HCl ✓

NOT conc HNO<sub>3</sub>  
or conc H<sub>2</sub>SO<sub>4</sub>

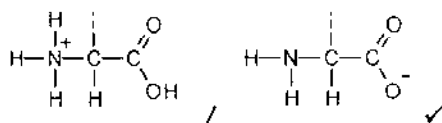
a named strong acid or alkali (heated under) reflux /  
a suitable enzyme at around 37°C ✓

[2]

- (ii) amino acids ✓

[1]

- (iii) correct structure for one of the amino acids ✓  
correct ionic form for reagent used in a(i) - eg



[2]

- (iv) reaction with water to split/break down the compound ✓

peptide bond in the compound is broken / diagram to show AW ✓

[2]

- (b) (i) a carbon with four different groups attached ✓

a chiral carbon / centre ✓

different spatial / 3-D arrangement (of the groups) ✓

(stereo)isomers / mirror images are non-superimposable / molecules  
are asymmetric ✓

ANY 3 out of 4 marks

[3]

- (ii) contains 2 chiral centres ✓

each can have 2 (stereo)isomers / 2x2 possibilities AW ✓

[2]

- (iii) use naturally occurring / enantiomerically pure amino acids

OR

use a stereospecific catalyst / enzyme / micro-organisms

OR

separate the mixture using a suitable method ✓

[1]

- (iv) higher doses are required ✓

the drug / other stereoisomers may have (harmful) side-effects ✓

[2]

[Total: 15]

5 (a) (i) Diamino

two/2 amine groups ✓

1, 4

their position on the ring / numbering of carbons  
around ring (or shown on a diagram) ✓

[2]

(b) (i) reduction / redox ✓

[1]

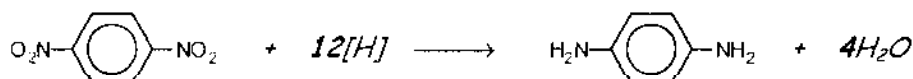
(ii) tin and HCl ✓

conc acid under reflux ✓

or H<sub>2</sub> gas +

Ni/Pd catalyst [2]

(iii)

H<sub>2</sub>O as product ✓

and the equation balanced ✓

[2]

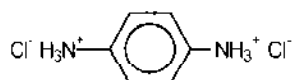
(c) (i) accepts H<sup>+</sup> using the lone pair (on N) ✓

which is donated/forms a (dative) covalent bond ✓

either mark can be  
obtained with a good  
diagram

[2]

(ii)



correct structure with charges shown ✓✓

one mark for either: just one neutralised,

both neutralised, but without Cl<sup>-</sup>,

both neutralised, but no charges shown

[2]

(iii) hexane-1,6-diamine is a stronger base because:

electrons move towards the N (due to the inductive effect)

(in hexane-1,6-diamine) ✓

the lone pair from N is (partially) delocalised around the ring (in  
diaminobenzene) ✓

so the electron pair is more easily donated /

H<sup>+</sup> more easily accepted (in hexane-1,6 diamine) ora ✓

[3]

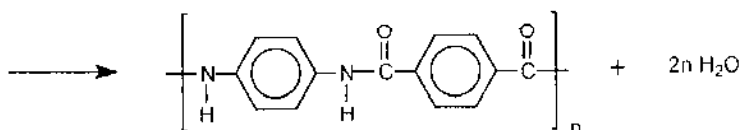
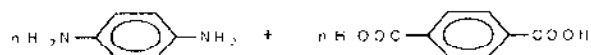
question 5 continued over

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question 5 continued

- (d) (i) eg fire resistant / bullet proof clothing /  
cycle tyres / tennis rackets ✓ allow any use where a tough  
flexible material is needed [1]

- (ii) condensation (polymerisation) ✓



structure of benzene-1,4-dicarboxylic acid ✓

amide /peptide bond displayed ✓

repeat unit of correct polymer indicated ✓

formula of water shown as the product in an equation ✓

[5]

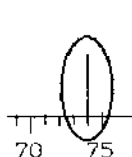
[Total: 20]

6 (a) *Molecular ion peak circled* ✓

*Compound X has  $M_r = 74$*  ✓

*Empirical formula has  $M_r = (36 + 6 + 32) = 74$*

*∴ (so must be the same as the molecular formula)* ✓



[3]

(b) (i) *compound X is not an aldehyde or ketone / not a carbonyl compound* ✓

[1]

(ii) *compound X does not contain a C=C double bond / is not an alkene / is not a phenol* ✓

[1]

(c) *structure 1 ethyl methanoate* ✓  
*structure 3 propanoic acid* ✓

[2]

(d) *presence or absence of relevant peaks (in the context of any of the structures) ...*

*peak at  $\sim 1750 / 1680-1750(\text{cm}^{-1})$  for C=O* ✓

*peak at  $\sim 1250 / 1000-1300(\text{cm}^{-1})$  for C-O* ✓

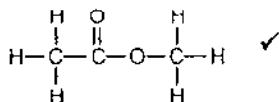
*no peak at  $2500 - 3300(\text{cm}^{-1})$*  ✓

*structures possible or ruled out ...*

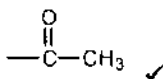
*structure 3 is ruled out / can only be structure 1 or 2* ✓

[4]

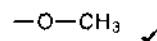
(e) *correct structure:*



*reasoning: peak at  $\sim 2 / 2.0-2.9(\text{ppm})$  is due to*



*peak at  $\sim 3.7 / 3.3-4.3(\text{ppm})$  is due to*



*relative peak area is 1:1/equal as both groups have the same number of protons* ✓ **AW**

*peak(s) not split as there are no protons on the neighbouring carbons* ✓

*allow max 1 as ecf from the wrong structure for valid reasoning from the  $\delta$  value*

*quality of written communication*

*for use and correct organisation of at least two of the scientific terms: ppm, environment, methyl, proton, adjacent, singlet (doublet etc)* ✓

[6]

[Total: 17]