

OXFORD CAMBRIDGE AND RSA EXAMINATIONS

Advanced GCE

CHEMISTRY

Chains, Rings and Spectroscopy

2814

Wednesday

18 JUNE 2003

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										
	<table border="1" style="display: inline-table; border-collapse: collapse;"> <tr> <td style="width: 20px; height: 20px;"></td> <td style="width: 20px; height: 20px;"></td> <td style="width: 20px; height: 20px;"></td> <td style="width: 20px; height: 20px;"></td> <td style="width: 20px; height: 20px;"></td> </tr> </table>						<table border="1" style="display: inline-table; border-collapse: collapse;"> <tr> <td style="width: 20px; height: 20px;"></td> <td style="width: 20px; height: 20px;"></td> <td style="width: 20px; height: 20px;"></td> <td style="width: 20px; height: 20px;"></td> <td style="width: 20px; height: 20px;"></td> </tr> </table>					

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	12	
2	12	
3	12	
4	8	
5	12	
6	10	
7	9	
8	10	
9	5	
TOTAL	90	

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

Answer **all** the questions.

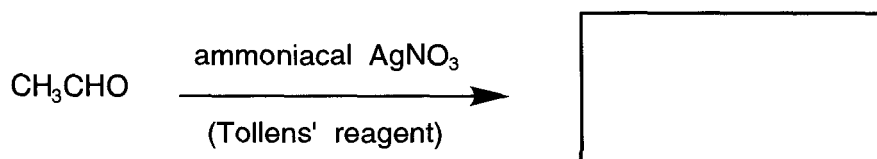
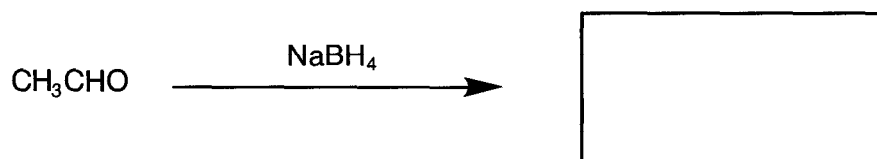
- 1 (a) (i) Name the compound CH_3CHO .

.....[1]

- (ii) Name the functional group of CH_3CHO .

.....[1]

- (iii) Draw structural formulae for the **organic** products of the reactions below.



[2]

- (b) (i) Describe what is meant by *nucleophilic addition*. Use the mechanism of the reaction of CH_3CHO with HCN in the presence of KCN in your answer.

.....

[5]

(ii) Explain why this reaction is not normally carried out in a school or college laboratory.

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

(iii) Will the product consist of optical isomers or not? Explain your answer.

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

[Total: 12]

2 Compound **A**, $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$, can be made by heating benzene with 2-chloropropane in the presence of a catalyst.

(a) (i) Draw the structural formula of 2-chloropropane.

[1]

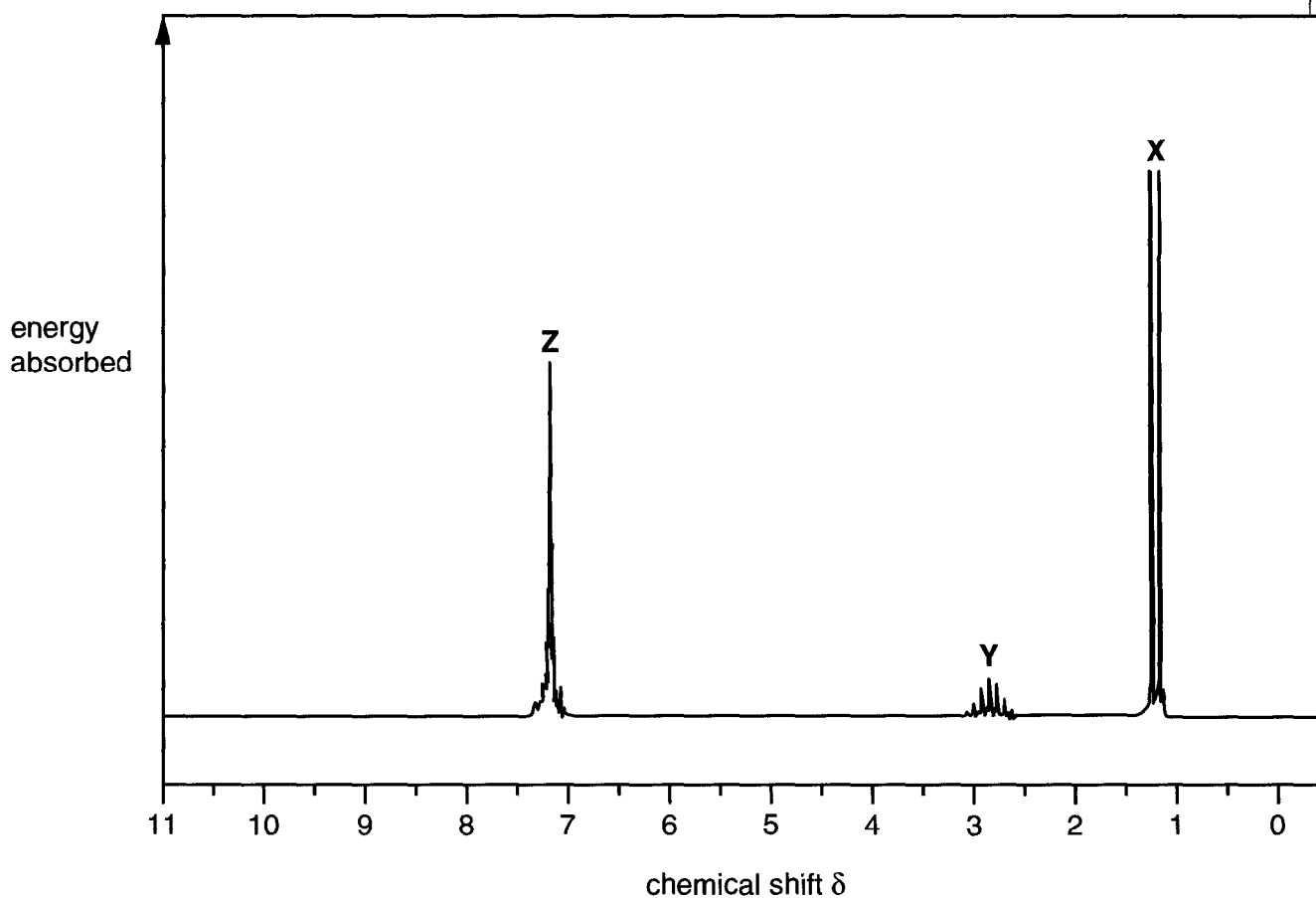
(ii) Write the equation for the synthesis of **A**.

[1]

(iii) Suggest the **type** of catalyst required.

[1]

(b) The n.m.r. spectrum of **A**, $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$, is shown below.



- (i) Suggest the identity of the protons responsible for the groups of peaks **X**, **Y**, and **Z**. For each group of peaks, explain your reasoning in terms of the chemical shift value.

X

.....

Y

.....

Z

.....[6]

- (ii) Explain why peak **X** is split into a doublet.

.....

.....

..... [2]

- (iii) Suggest a reason why peak **Y** is split into many lines.

.....

.....

.....[1]

[Total: 12]

- 3 Analysis of some samples of soy sauce recently showed the presence of the potentially harmful chemical 3-chloropropane-1,2-diol.
This could be formed from soya oil during the hydrolysis of soya.

(a) (i) Draw a displayed formula for 3-chloropropane-1,2-diol.

[2]

(ii) Does your displayed formula contain a chiral centre? Explain your answer.

.....

.....[1]

(b) In this question, one mark is available for the quality of written communication.

Explain how **two** spectroscopic techniques could be used to confirm the presence of an OH group in an organic compound such as 3-chloropropane-1,2-diol or ethanol.

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[5]

Quality of Written Communication [1]

(c) Soya is a useful source of protein for vegetarians.
Soya protein can be hydrolysed in the laboratory.

(i) State the reagent used.

.....[1]

(ii) Draw a displayed formula for the functional group which is hydrolysed in the protein.

[1]

(iii) State the class of organic compounds produced by hydrolysis of proteins.

.....[1]

[Total: 12]

4 In aqueous solution, some organic compounds are bases and some are acids; others are neither.

(a) Identify an organic compound that acts as an acid in water, and give an equation to show this behaviour.

name or formula

equation[2]

(b) Phenylamine, $C_6H_5NH_2$, acts as a base in water.

(i) Give an equation to show this behaviour.

.....[1]

(ii) Explain why phenylamine is a weaker base than ethylamine, $C_2H_5NH_2$.

.....

.....

.....

.....

.....

.....

.....

.....

.....[3]

(c) Identify an organic compound which can act both as an acid and as a base. Explain your answer.

name or formula

explanation

.....

.....

.....[2]

[Total: 8]

7 Diazonium salts are important reactive intermediates. They are made from aromatic amines, which themselves are usually made from aromatic nitro-compounds.

(a) (i) State the reagents required for the preparation of phenylamine from nitrobenzene.

.....[2]

(ii) A student obtained 6.80g phenylamine starting from 10.0g nitrobenzene. Calculate the percentage yield of phenylamine. Give your answer to three significant figures.

answer[4]

(b) State the reagents and conditions needed to make a diazonium salt from phenylamine.

reagents

.....

.....

conditions

.....[3]

[Total: 9]

8 There are two major types of polymerisation: addition polymerisation and condensation polymerisation.

(a) (i) Propene undergoes addition polymerisation.

Give a balanced equation for this polymerisation, using structural formulae.

[2]

(ii) Explain the differences between **addition** polymerisation and **condensation** polymerisation.

.....

.....

.....

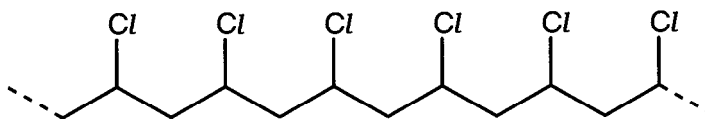
.....

.....

.....[2]

(b) Polymer **G** is also formed by addition polymerisation.

a section of
polymer **G**

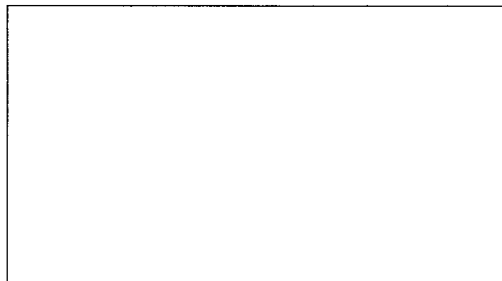


Deduce the structure of a monomer from which **G** could be made.

[1]

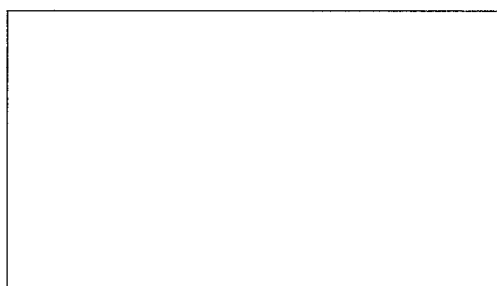
9 From the information given, draw the structural formula for each organic compound.

- (a) This compound is made by reaction of benzene with concentrated nitric acid in the presence of concentrated sulphuric acid.



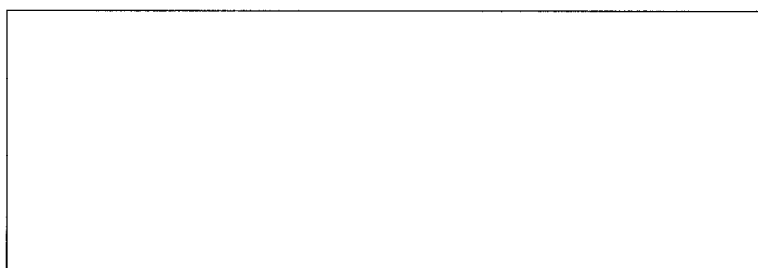
[1]

- (b) These two compounds react together in the presence of concentrated sulphuric acid to make methyl ethanoate, $\text{CH}_3\text{COOCH}_3$.



[2]

- (c) These two different compounds can be made by reaction of $\text{C}_6\text{H}_5\text{CH}(\text{NH}_2)\text{COOH}$ with $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$.



[2]

[Total: 5]

Acknowledgement

SDBS Web http://www.aist.go.jp/RIODB/SDBS/21_06_02

OCR has made every effort to trace the copyright holders of items used in this Question paper, but if we have inadvertently overlooked any, we apologise

2814 Chains, Rings and Spectroscopy

June 2003

Mark Scheme

The following annotations may be used when marking:

X	=	incorrect response (errors may also be underlined)
^	=	omission mark
bod	=	benefit of the doubt (where professional judgement has been used)
ecf	=	error carried forward (in consequential marking)
con	=	contradiction (in cases where candidates contradict themselves in the same response)
sf	=	error in the number of significant figures

Abbreviations, annotations and conventions used in the Mark Scheme:

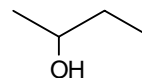
/	=	alternative and acceptable answers for the same marking point
;	=	separates marking points
NOT	=	answers not worthy of credit
()	=	words which are not essential to gain credit
___ (underlining)	=	key words which <u>must</u> be used
ecf	=	allow error carried forward in consequential marking
AW	=	alternative wording
ora	=	or reverse argument

Marking structures in organic chemistry

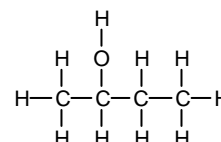
When a structure is asked for, there must be sufficient detail using conventional carbon skeleton and functional group formulae (e.g. CH₃, C₂H₅, OH, COOH, COOCH₃) to unambiguously define the arrangement of the atoms. (E.g. C₃H₇ would not be sufficient).

If not specified by the question, this may be given as either:

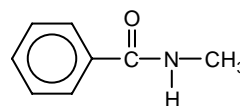
- a **structural formula** – e.g. CH₃CH(OH)C₂H₅,



- a **skeletal formula** – e.g. ,



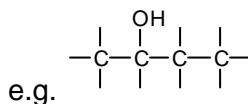
- a **displayed formula** – e.g.



or as a hybrid of these – e.g.

The following errors should be penalised – although each one only loses a maximum of one mark on the paper:

- clearly connecting a functional group by the wrong atom
- showing only 'sticks' instead of hydrogen atoms –



Benzene rings may be represented as



as well as



in any of the types of formula above.

1 (a) (i) ethanal ✓ [1]

(ii) aldehyde / carbonyl ✓ [1]

(iii) $\text{CH}_3\text{CH}_2\text{OH}$ / $\text{C}_2\text{H}_5\text{OH}$ ✓
 CH_3COO^- / CH_3COOAg / CH_3COOH ✓ [2]

allow displayed formulae, but
 penalise poor connections to the
 OH, sticks etc

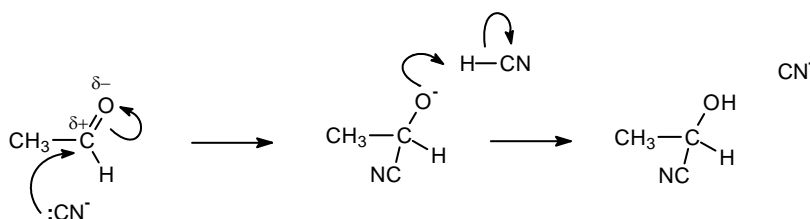
(b) (i) (nucleophile/ CN^-) is an electron/lone pair donor ✓ **ESSENTIAL MARK**

then look for the following points:

in the diagram ...

or a written alternative ...

CN^-	the nucleophile is CN^-	✓
curly arrow clearly starts from a lone pair drawn on the C	the electron/lone pair is donated from the C of the CN^-	✓
curly arrow towards $\text{C}^{\delta+}$ and breaking $\text{C}=\text{O}$	(nucleophile/ CN^-) is attracted to an electron deficient carbon	✓
correct structure of the intermediate	(nucleophile/ CN^-) forms a covalent/dative bond (to the carbon)	✓
correct structure of the product	HCN is added	✓



ANY 4 out of 5 [5]

(ii) HCN / KCN / CN^- is toxic / AW **NOT** dangerous or explosive [1]

(iii) Yes, because ...
 (the product) has a chiral centre/carbon ✓
 four different groups around the carbon ✓
 assymmetric ✓
 cannot be superimposed on its mirror image ✓ allow ecf from b(i)

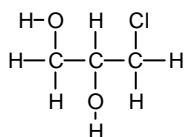
ANY 2 out of 4 [2]

[Total: 12]

- 2 (a) (i) $\text{CH}_3\text{CHClCH}_3$ ✓ allow any formula that is unambiguously 2-chloropropane [1]
- (ii) $\text{CH}_3\text{CHClCH}_3 + \text{C}_6\text{H}_6 \longrightarrow \text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2 + \text{HCl}$ ✓ [1]
- (iii) halogen carrier ✓ [1]
- (b) (i) **peaks identified**
- peak X – CH_3 (protons) ✓
 - peak Y – CH (proton) ✓
 - peak Z – benzene ring (protons) ✓
- 3 identification marks
- reasoning from δ value** ... for each, either:
- quotes a δ value for the peak **and** refers explicitly to the Data Sheet /or
 - quotes the relevant functional group in the Data Sheet (eg R- CH_3 for X) /or
 - quotes exactly the relevant Data Sheet range, ie (0.7–1.6 for X)
(2.3 – 2.7 for Y)
(7.1 – 7.7 for Z) ✓✓✓
- 3 reasoning marks
- ignore any attempts to reason from the splitting here, but look out for credit to parts (ii) and (iii) if not given below
- (ii) 1 proton / CH/ 'n' = 1 (using the n+1 rule) ✓ [6]
- on the neighbouring/adjacent carbon ✓ [2]
- (iii) the CH_3 protons are all equivalent/in the same (chemical) environment / there are six protons adjacent to the CH ✓ [1]

[Total: 12]

3 (a) (i)



the correct compound ✓

shown as a correctly displayed formula ✓

[2]

(ii) yes, because there are four different groups around the central carbon ✓
(or ecf on the structure given in (i)) **AW**

allow asymmetric / non-super-imposable on its mirror image

[1]

(b) infra-red/i.r. (spectroscopy) ✓
peak/absorption at 3230 - 3550 (cm⁻¹) ✓

n.m.r. (spectroscopy) ✓
peak at 3.5–5.5 (ppm) ... ✓
... which disappears in D₂O ✓

Quality of Written Communication

mark for good organisation / a logical response and technical terms, using at least **two** of the following words:

infra-red, nuclear magnetic resonance, spectroscopy, wavenumber, cm⁻¹, chemical shift, ppm) ✓

[6]

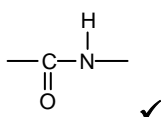
(c) (i) dil/conc/(aq) HCl
or dil/(aq) H₂SO₄ /H⁺/acid
or dil/conc/(aq) OH⁻/alkali/NaOH etc ✓

if a formula given, there must be some indication that it is aqueous

allow an enzyme as long as aq

[1]

(ii)



✓

[1]

(iii) amino acids ✓

allow peptides

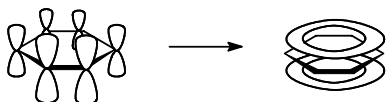
[1]

[Total: 12]

- 4 (a) carboxylic acid / phenol / amino acid / named example or correct formula ✓
- equation to give the correct negative ion ✓
eg $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$
/ $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$
- (b) (i) $\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$ ✓
- (ii) (base, phenylamine, ethylamine) accepts H^+ ✓
/ donates lone pair
- (uses the) lone pair on the nitrogen ✓
- the lone pair (in phenylamine) is delocalised
/interacts with the delocalised/ π electrons in the ring
or
inductive effect pulls electrons (from the nitrogen)
- ora ✓
- (c) amino acid / $\text{RCH}(\text{NH}_2)\text{COOH}$
/ named example or correct formula ✓
- contains both carboxylic acid/ COOH and basic amine/ NH_2 groups ✓
- NOT** 'HX' or any inorganic acid
- allow ecf on the formula or an inorganic acid from above as long as donation of H^+ shown [2]
- do not penalise a correct equation using H^+ or another acid [1]
- allow **AW** throughout
(or shown on a diagram)
- It must be clear which way the electrons are going" [3]
- do not allow non-organic acids for the first mark, but give ecf on good explanation
- allow any explanation describing acidity and basicity eg "can donate and accept H^+ ") [2]

[Total: 8]

5 (a) planar molecule (or shown in diagram) ... ✓



p-orbitals (or shown in diagram) ✓
... overlap (or shown in a diagram) ✓

(p-orbital overlap forms) π -bonds ✓
electrons are delocalised ✓
C-C bonds are all the same length ✓

ANY 5 out of 6

Quality of Written Communication

mark for spelling, punctuation and grammar. Look for at least two sentences with legible text, accurate spelling, grammar and punctuation, so the meaning is clear ✓

[6]

(b) (i) $C_6H_5CHBrCH_2Br$ ✓

[1]

(ii) phenylethene has a double bond ✓

benzene (π) electrons are:
spread out / delocalised / lower electron density
✓ **ora** for 2 marks

then either ...
so the bromine molecule gets less polarised / needs the catalyst to help polarise it ... ✓

and the bromine/electrophile is less strongly attracted (to the π electrons) ✓

ora and AW for 2 marks

or ...
(delocalised (π) electrons make) benzene stable ... ✓

so more energy is needed (to overcome it) / higher E_a / it is not easily disrupted ✓

ora and AW for 2 marks

TOTAL 2 + 2 marks

[4]

(c) (to make) poly(phenylethene) / polymers / plastics /
a named use of poly(phenylethene) ✓
eg packaging, insulation, toys, moulded casings etc

[1]

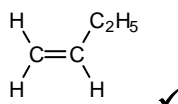
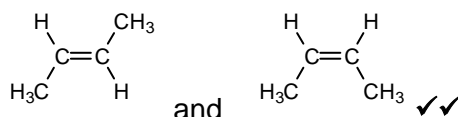
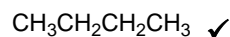
[Total: 12]

6 (a) 184

[1]

(b) (i) identification of the compounds ...

any type of formula that unambiguously identifies the compound – eg

B**C****D and E****F**

5 marks

reasoning ...

H can be taken from either carbon 1 or carbon 3 \checkmark **AW**

D and E are cis-trans/geometric (isomers) \checkmark

double bond does not rotate \checkmark

explanation why but-2-ene gives cis/trans isomers or why but-1-ene doesn't \checkmark

ANY 3 out of **4** marks

[8]

(ii) addition / hydrogenation / reduction \checkmark

[1]

[Total: 10]

7 (a) (i) tin/iron ✓

hydrochloric acid / HCl ✓

allow LiAlH₄ ✓ anyhydrous/ether ✓

[2]

(ii) M_r of C₆H₅NO₂ = 123(.0) ✓

M_r of C₆H₅NH₂ = 93(.0) ✓

(use of correct M_r s get 2 marks)

theoretical mass of C₆H₅NH₂ = 7.56(g) /ecf

/ moles of C₆H₅NH₂ = 0.08(13) /ecf ✓

answer in the range 89.8-90.0(%) /ecf 3 sf ✓

(correct answer gets 2 more marks)

answer in the range 87-92% due to
rounding errors and/or with sig figs ≠
3 gets 3 marks max

[4]

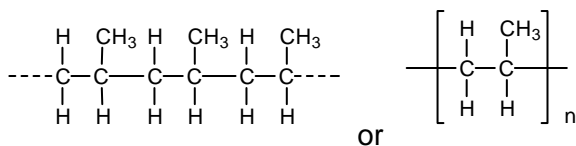
(b) sodium nitrite + (hydrochloric) acid
/ nitrous acid / HNO₂ ✓✓

< 10°C ✓

[3]

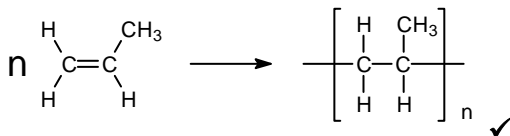
[Total: 9]

8 (a) (i) a correct structure for poly(propene), eg



bonds must extend outside any brackets ✓

equation showing 'n' monomers



[2]

(ii) addition:

monomer has C=C double bond / is an alkene / double bond breaks/ no (other) substance lost ✓

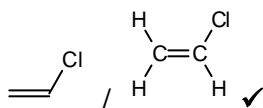
NOT just "monomer has a double bond"

condensation:

water / small molecule lost ✓

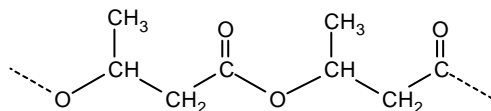
[2]

(b)



[1]

(c) (i)



at least one correct ester link ✓
rest of the structure and repeat also correct ✓

allow a break in the repeat at any point

[2]

(ii) H reacts with NaOH / poly(propene) does not ✓

H is an ester / is polar ... ✓
will be hydrolysed by NaOH ✓
poly(propene) is non-polar ✓

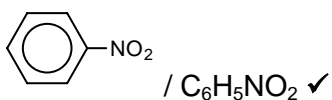
"hydrolysed by NaOH" gets the reacts with NaOH mark as well

ANY 3 out of 4 marks;

[3]

[Total: 10]

9 (a)



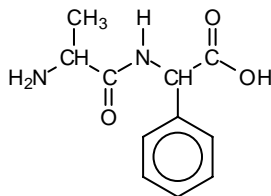
allow poly-nitrated benzene in any positions

[1]

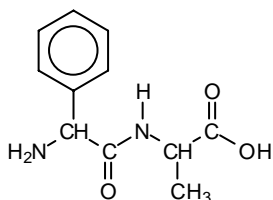
(b) CH₃COOH ✓CH₃OH ✓

[2]

(c) two structures made by joining the amino acids



either way round – eg



peptide bond in one structure ✓

two dipeptides with R groups swapped ✓

allow H₂O ✓ and one correct dipeptide ✓ as an alternative answer

[2]

[Total: 5]