OCR
RECOGNISING ACHIEVEMENT

OXFORD CAMBRIDGE AND RSA EXAMINATIONS
Advanced GCE

CHEMISTRY 2814

Chains, Rings and Spectroscopy

Thursday **24 JANUARY 2002** Morning 1 hour 30 minutes

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

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 are advised to show all the steps in any calculations.
- You may use a scientific calculator.
- You may use the *Data Sheet for Chemistry*.

FOR EXAMINER'S USE		
Qu.	Max.	Mark
1	14	
2	11	
3	12	
4	17	
5	11	
6	14	
7	11	
TOTAL	90	

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

Registered Charity Number. 1066969

Answer **all** the questions.

1 Benzene can be nitrated to form nitrobenzene, $C_6H_5NO_2$.

(a) Draw the structural formula for **benzene** and give its empirical formula.

structure:

empirical formula ..... [2]

(b) State the reagents needed for the nitration of benzene.

..... [2]

(c) An electrophile is formed during the nitration of benzene.

(i) What is the formula of this electrophile?

..... [1]

(ii) Write an equation for the production of the electrophile.

..... [1]

(iii) Use curly arrows to show the mechanism for the nitration of benzene.

[4]

(d) 10.0 g of benzene was nitrated to give 13.3 g of nitrobenzene. Calculate the percentage yield, giving your answer to three significant figures.

[4]

[Total : 14]

2 Amines are commonly occurring compounds. Ethylamine, $C_2H_5NH_2$, is a primary amine responsible for the smell of decaying fish.

(a) Explain the meaning of the term *primary amine*.

.....

..... [1]

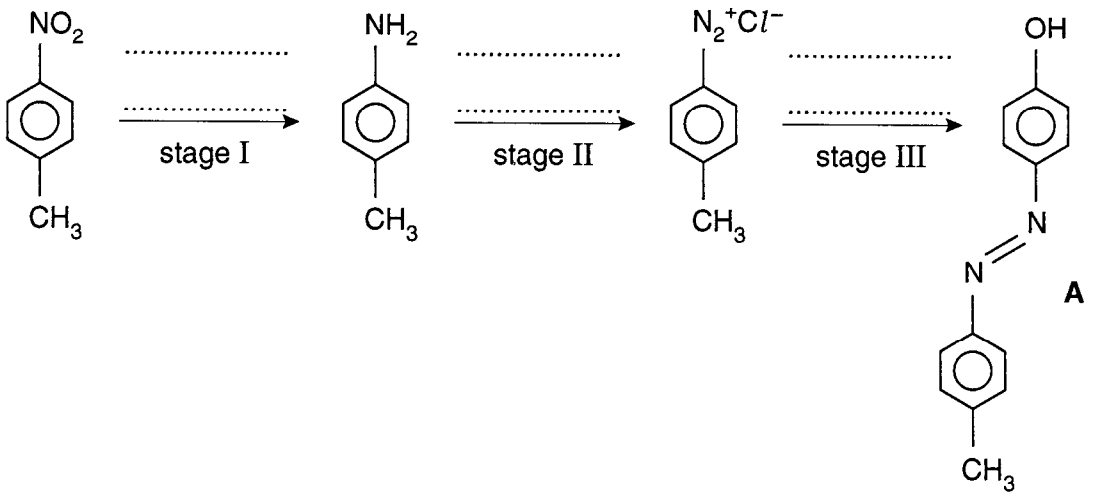
(b) Ethylamine and phenylamine are bases.

Write an equation to show ethylamine acting as a base.

..... [2]

(c) Aromatic amines such as phenylamine are intermediates in the synthesis of many other compounds such as **A** below.

(i) Complete the scheme by writing the reagents on the lines provided.



[5]

(ii) Write the equations for stages I and III.

stage I

stage III [2]

(iii) State a general use for compounds such as **A**.

..... [1]

[Total : 11]

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Question 3 starts on page 6

3 **(a)** Esters are well known as compounds providing the flavour in many fruits and the scent of some flowers. The ester $CH_3(CH_2)_2COOCH_3$ contributes to the aroma of apples.

(i) Name the ester $CH_3(CH_2)_2COOCH_3$.

..... [1]

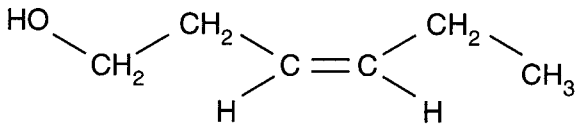
(ii) State the reagents and conditions for the hydrolysis of this ester in the laboratory.

.....

.....

..... [3]

(b) Leaf alcohol, **B**, is a stereoisomer that can form when insects eat leaves.



B

(i) Draw the skeletal formula of **B**.

[1]

(ii) Draw the geometric isomer of **B**.

[1]

(iii) Draw a structure for the ester expected when **B** reacts with ethanoic acid in the presence of an acid catalyst. Show **all** the bonds in the ester group.

[2]

(c) A chemist analysed a sample of **B** and determined its M_r value

(i) Deduce the M_r value that the chemist would expect for leaf alcohol.

expected M_r ..... [1]

(ii) What technique could the chemist have used to determined the M_r for leaf alcohol?

..... [1]

(iii) A chemist reacted **B** to form a product **C** with an M_r 18 units less than that of **B**.

Suggest a structrure for **C** and deduce the type of reaction that took place.

structure of ***C***

type of reaction ..... [2]

[Total : 12]

4 Propene is in the 'top 20' most heavily used chemical feedstocks in the U.S.A. It is used for the manufacture of polymers such as poly(propene).

(a) Suggest, with a reason, the names of **two** other alkenes you might expect to find in the 'top 20' feedstocks.

.....

.....

.....

..... [3]

(b) Explain why there are three different stereochemical forms of poly(propene). These forms are described as atactic, isotactic and syndiotactic. Illustrate your answer with diagrams.

(In this question, 1 mark is available for the quality of written communication.)

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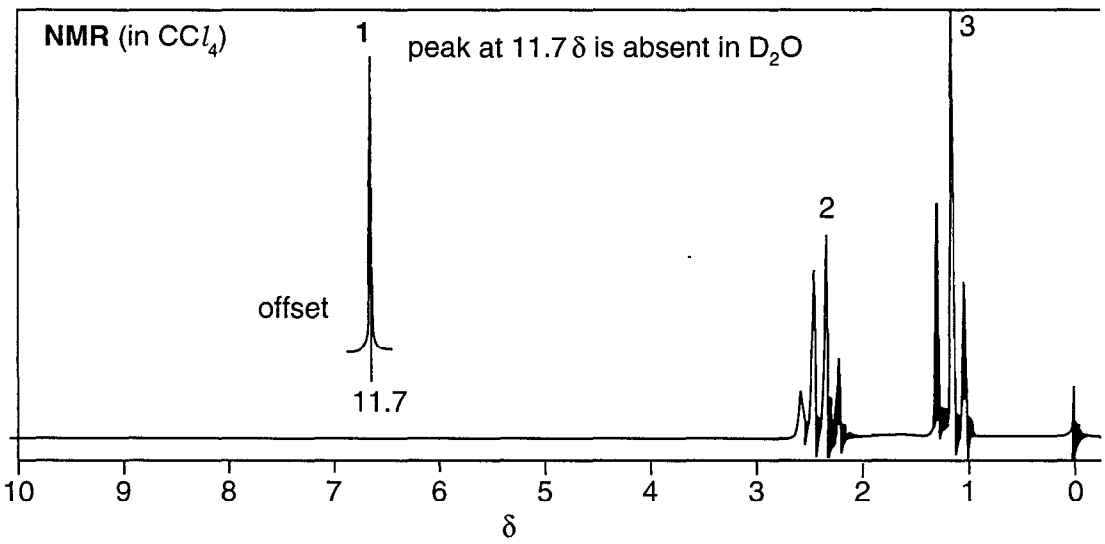
[7]

(c) Propanoic acid, CH_3CH_2COOH, can be synthesised from propene. The nmr spectrum of propanoic acid is shown below.



(i) Use the *Data Sheet* to explain the chemical shifts and splitting patterns shown by each peak in this nmr spectrum.

.....

.....

.....

.....

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.....

.....

..... [6]

(ii) Explain why the peak at 11.7 δ disappears on addition of D_2O.

..... [1]

[Total : 17]

5 A diagram of a section of nylon-6,6 is shown below.

$$—CO(CH_2)_4CONH(CH_2)_6NHCO(CH_2)_4CONH(CH_2)_6NH—$$

(a) Identify the monomer(s) from which nylon-6,6 is obtained.

.....

..... [2]

(b) State and explain the type of polymerisation reaction which gives nylon-6,6.

.....

.....

..... [2]

(c) Proteins and polypeptides are polymers which have been described as being similar to nylon-6,6.

Suggest with the aid of diagrams and equations.

- **one** structural similarity
- **one** chemical similarity
- **one** important difference

(In this question, 1 mark is available for the quality of written communication.)

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..... [7]

[Total : 11]

6 Like esters, carbonyl compounds can contribute to the smell of plants and food. The carbonyl compounds **D** and **E** are structural isomers.

D CH_3COCH_3 **E** CH_3CH_2CHO

(a) Name compounds **D** and **E**.

(i) **D** .....

(ii) **E** .....
[2]

(b) State the reagents you would use and the observations you would make for a simple chemical test

(i) in which **D** and **E** behave in the same way;

reagent(s) .....

observation ..... [2]

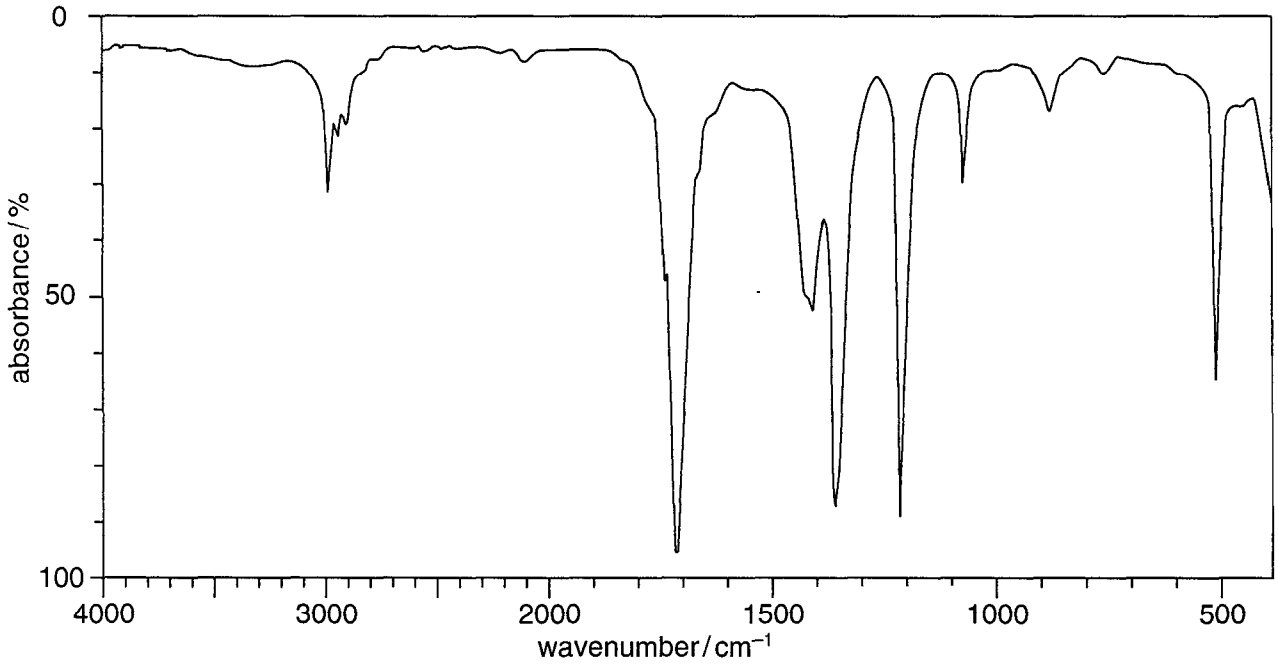
(ii) which can be used to distinguish between **D** and **E**.

reagent(s) .....

observation for **D** .....

observation for **E** ..... [3]

(c) The infrared spectrum of **D** is shown below.



(i) On the spectrum above, mark with a cross the absorption peak that identifies the functional group. Explain how you made your choice. (Use the *Data Sheet* provided to answer this question.)

.....

.....

..... [2]

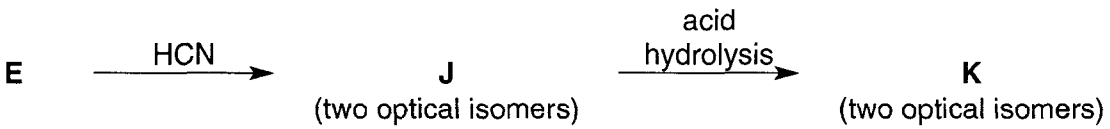
(ii) Reduction of compound **D** with $NaBH_4$ produces a compound with the molecular formula C_3H_8O.

How would the infrared spectrum of this product be different from that of **D**?

.....

..... [2]

(d) Compound **K** can be synthesised in two steps from compound **E**, CH_3CH_2CHO. The sythetic steps are shown below.



(i) Draw the structural formula of **J**.

[1]

(ii) Draw three-dimensional structures to show clearly the **two** optical isomers of **K**.

[2]

[Total : 14]

7 The α-amino acid glycine, H_2NCH_2COOH, is used as a poultry feed additive and in the fertiliser industry. There are twenty naturally occurring α-amino acids.

(a) Draw the general formula for an α-amino acid.

[1]

(b) In the crystalline state, glycine contains zwitterions.

(i) Draw the structure of the zwitterion of glycine.

[1]

(ii) Explain how this zwitterion arises.

.....

.....

.....

.....

..... [2]

(iii) Crystals of glycine melt between 230 and 235°C. Explain why the melting point of glycine is higher than that of hydroxyethanoic acid, $HOCH_2COOH$ (m.p. 75–80 °C).

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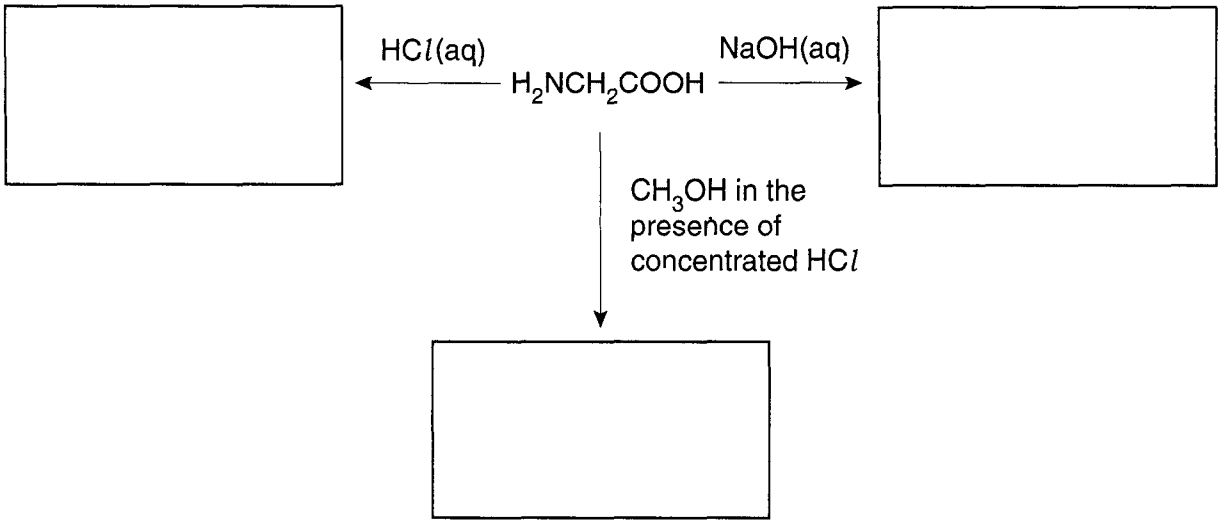
..... [3]

(c) In the boxes below, draw suggested structures for the organic products obtained from glycine.



[4]

[Total : 11]

RECOGNISING ACHIEVEMENT

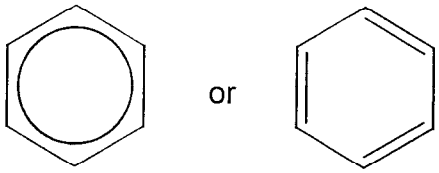
Subject: Chains, Rings & Spectroscopy
Code: 2814

Session: January
Year: 2002

Final Mark Scheme

MAXIMUM MARK	90

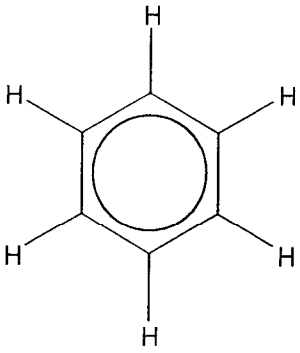
1 **(a)** structure. **[2]**

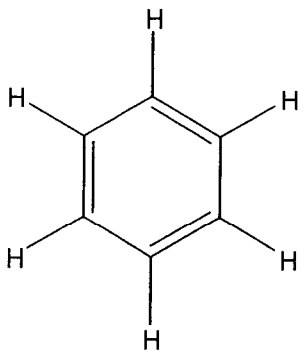


or

✓

accept





empirical formula: CH ✓ **NOT** C_6H_6 or $(CH)_6$

(b) HNO_3 ✓ **[2]**
H_2SO_4 ✓
accept words or formulae
NOT <u>dilute</u> acids – penalise dilute ONCE only; so dil H_2SO_4 + dil HNO_3 gets (1)
NOT correct words with wrong formula eg nitric acid HNO_2
NOT wrong words with correct formula eg nitrous acid, HNO_3
ignore state symbols
mark any wrong answers and subtract from correct answers to min of 0

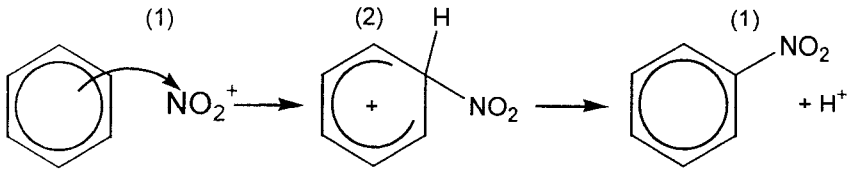
(c) (i) NO_2^+ ✓ **[1]**
NOT NO^{2+}

(ii) $HNO_3 + H^+ \rightleftharpoons H_2O + NO_2^+$ ✓ **[1]**
$HNO_3^+ \rightleftharpoons H_2O + NO_2^+$
or
$HNO_3 + 2H^+ \rightleftharpoons H_3O^+ + NO_2^+$
or
$2\ H_2SO_4 + HNO_3 \rightleftharpoons H_3O^+ + 2HSO_4^- + NO_2^+$
or
$HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O$

equation must balance; $\rightleftharpoons$ not essential

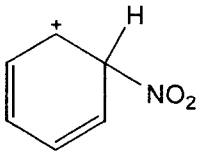
NOT $HNO_3 \rightleftharpoons NO_2^+ + HO^-$

(iii) electrophilic attack by NO_2^+ ✓ **[4]**
correct structure of cationic intermediate ✓ ✓
correct structure of product **and** H^+ ✓
(Kekulé structures accepted)
e g



arrow required, doesn't matter where it comes from but must be in **correct direction**

be careful with position of horseshoe and of +



both products required or $PhNO_2$ and arrow for loss of H^+
NOT H_2SO_4 as product unless HSO_4^- given as base to remove H^+

(d) M_r C_6H_6 = 78 ✓
M_r $C_6H_5NO_2$ = 123 ✓ **[4]**

all correct working ✓
allow e.c.f from wrong M_r
e g

moles $C_6H_6 = \frac{10}{78} = 0.128$

100% yield = 0.128 x 123 = 15.77g

%yield = $\frac{13.3}{15.77}$ x 100 = **84.3%** ✓ (answer) must have 3 sig figs

accept any answer in the range 84.2 → 84.5 as 'correct'
Correct answer on its own = 4 marks

Total = 14

2 **(a)** Only one C substituent on N ✓ **[1]**
or two H substituents on N
or RNH_2 as a general structure
NOT attached to a C only attached to one other carbon ie RCH_2NH_2
NOT NH_2 is on the first/end carbon

(b) $C_2H_5NH_2 + H^+ \rightleftharpoons C_2H_5N^+H_3$ balanced eq ✓ **[2]**
structure ✓ (+ is essential)
any acid OR water accept in equation
or
$C_2H_5NH_2 + HCl \rightleftharpoons C_2H_5N^+H_3\ Cl^-$
($\rightleftharpoons$ not essential)

(c) **(i)** Stage I: **[5]**
H_2 + catalyst, or H_2 + specified metal catalyst e.g. Ni, Pd, Pt; or metal ✓ **NOT** acid catalyst

or Sn/HCl } words or formula
or Fe/HCl }
or Na in ethanol or liq. NH_3

Stage II:
$NaNO_2$ ✓, an acid e.g. HCl ✓
or HNO_2 ✓✓
HNO_3 / HCl gets (1)
NOT just HCl only; not eg $HCl + H_2SO_4$

Stage III:
Phenol ✓, (aq) NaOH or base or alkali ✓

(ii) Stage I: **[2]**
$C_7H_7NO_2 + 3H_2 \rightarrow C_7H_9N + 2H_2O$ ✓
or 6[H]/6H

Stage III:
$C_7H_7N_2^+Cl^- + C_6H_5ONa \rightarrow C_{13}H_{12}N_2O + NaCl$ ✓
or without the Cl^- or without the Na^+ or without both
or $C_7H_7N_2^+Cl^- + C_6H_5ONa + NaOH \rightarrow C_{13}H_{12}N_2O + NaCl + H_2O$

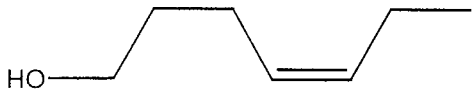
Both equations MUST be balanced
ecf· if no base in Stage III then allow phenol giving HCl and product in equation

(iii) Dyes ✓ **[1]**
allow indicators, pharmaceuticals

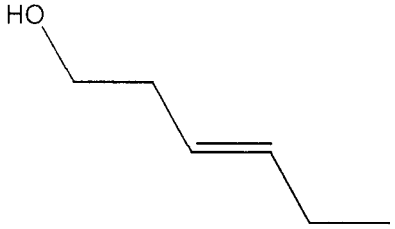
Total = 11

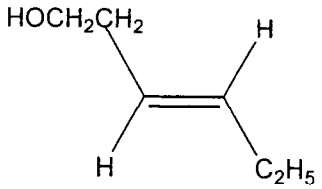
3 **(a)** **(i)** Methyl butanoate ✓ **[1]**

(ii) Warm / hot / boil / reflux ✓
water or aqueous or dilute✓
NaOH / KOH / HCl / H_2SO_4 ✓ } words or formulae
acid/alkali/base H^+ / OH^-
or any strong acid, **NOT** HNO_3 **[3]**

(b) **(i)** 

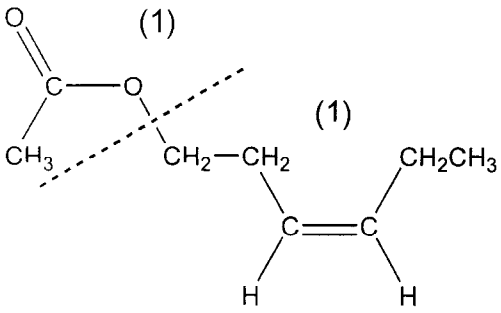
ONLY ✓ **[1]**

(ii) 

or 

✓ **[1]**

not necessarily skeletal, but MUST show the C=C stereochemistry
(right angles not penalised)

(iii) 

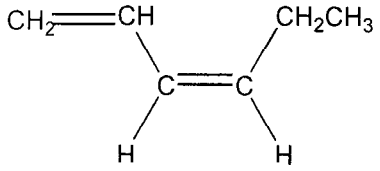
[2]

correct left of O-C bond✓
correct right of O-C bond✓
must show bonding in ester and alkene;
structure with CH_3COO... gets (1) only if rest is correct;
structure with trans double bond gets (1) if rest is correct

(c) **(i)** M_r B: $C_6H_{12}O$ 72 + 12 + 16 = 100 ✓ **[1]**

(ii) Mass spectroscopy / spectrometer / spec / spectrum ✓ **[1]**

(iii) Structure of C: **[2]**



✓

or any other correct drawing of hexa-1,3-diene C_6H_{10}
or any hydrocarbon of M_r 82 correctly drawn

Type of reaction:
dehydration ✓
or loss of water or elimination
NOT condensation

Total = 12

4 (a) **Two** of ethene, chloroethene, phenylethene or any alkene monomer ✓✓ **[3]**

One reason eg all polymer monomers ✓ not benzene
NOT for cracking or fuels

(b) Diagram with correct structure of poly(propene), not necessarily 3-D (1) **[7]**
Polymer has chiral centres (1) ESSENTIAL MARK
can have. all methyls same chirality / 'side' of chain (1)
methyls alternating chirality / 'side' (1)
all methyls random chirality / 'side' (1)

same = isotactic, alt = syndiotactic, random = atactic
all 3 names correctly assigned (1)

(6) available for chemistry, of which
at least (1) must be for a diagram ✓

QWC. At least two coherent sentences with reasonable spelling and punctuation. Show as QWC x or ✓ (1)

MAX = 7

(c) **(i)** For each signal. (1) for identification and (1) for reason. **[6]**
δ 11 7· H of –OH or -COOH; one H: ✓
because it exchanges with D_2O/labile proton
or singlet because it has no ✓
H atoms on an adjacent atom
or data table 11.0 – 11.7

δ 2 4 2H of $–CH_2–$ ✓
quartet because it has 3 H atoms on the adjacent carbon
(n+1) = 4 lines ✓
or data table 2.0 – 2.9 CHC=0

δ 1 1. 3H of $CH_3–$ ✓
triplet because it has 2 H atoms on the adjacent carbon
(n+1) = 3 lines ✓
or data table 0.7 – 1 6 $CH_3–R$

(ii) It is due to OH and the proton can **exchange/swap/substitute** **[1]**
(1) with the D in D_2O ✓
or D replaces H
NOT just reacts with water

Total = 17

5 **(a)** $HOOC(CH_2)_4COOH$ ✓ } words or formula [2]
$H_2N(CH_2)_6NH_2$ ✓ }
(or any pair of monomers that would work)

(b) condensation polymerisation ✓ [2]
small molecule / H_2O is eliminated ✓

(c) **max of 6 marks from:** [7]

- structural similarity

e.g peptide/amide link (1)

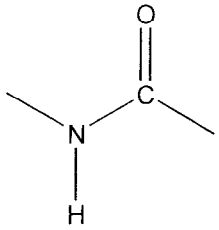


diagram (1)

both form H-bonds between molecules (1) picture of H-bond (1)
or can be in second bullet point

- chemical similarity

e.g. both condensation polymers (1)
$\sim NH_2 + HOOC\sim \rightarrow \sim NHCO\sim + H_2O$ equation (1)
both are hydrolysed (1) back to monomers (1)

- differences

e.g.
protein can be water-soluble, nylon not (1)
protein biodegradable, nylon not (1)
nylon regular, protein irregular (1)
nylon one or two monomers, protein many (1)
proteins are made from amino acids (1) which can be chiral (1)
proteins are natural and nylon is synthetic (owtte) (1)

At least one mark from each bullet point and not more than three from each bullet point. MAX = 6
Plus
Quality of written communication ✓
Correct reference to **two** chemical terms e.g. condensation, peptide, biodegradeable.
Show as QWC x or ✓

Total = 11

6 **(a)** **(i)** propanone ✓ **[1]**
accept acetone or propan-2-one

(ii) propanal ✓ **[1]**
accept propanaldehyde but **not** ethanal

(b) **(i)** *reagent(s):* e.g. 2,4-dinitrophenylhydrazine ✓ **[2]**
in words or formula

observation: e.g. orange / red / yellow precipitate / crystals ✓

no mark for observation if no reagent given

(ii) *reagent(s):* e.g. ammoniacal $AgNO_3$ ✓ or Ag_2O or Ag^+ or Tollens **[3]**
*observation for **D**:* No change ✓
*observation for **E**:* silver (mirror) ✓ grey ppte

or similarly for another **chemical** test that works e.g. acid dichromate, Fehlings or CHI_3 test

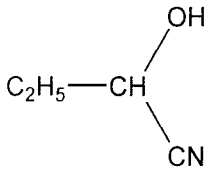
(c) **(i)** Marked cross at $\nu \sim 1700$ ✓ **[2]**
D has carbonyl group or ketone or C=O ✓

(ii) e g Reduction $CH_3COCH_3 \rightarrow CH_3CHOHCH_3$ (1) **[2]**
(or product is an alcohol)

new (broad) peak at ~3230 – 3550 cm^{-1} (1)
loss of peak at ~ 1700 cm^{-1} (1)

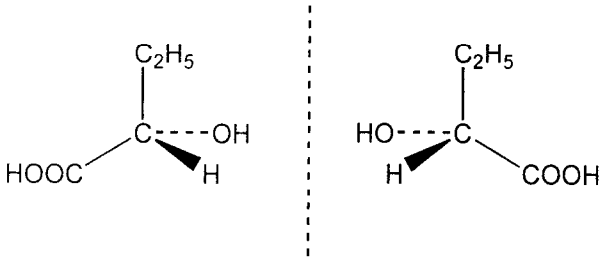
any two good points ✓ ✓

(d) **(i)** **[1]**



✓ allow $C_2H_5CH(OH)CN$

(ii) e g



✓✓

with at least one bond shown out of plane of paper
(1) for correct structure of K, but poor 3-D diagrams
(1) for correct 3-D structures of J
watch out for –CN instead of -COOH
allow ecf from (i) e.g. $-CH_3$ instead of $-C_2H_5$
allow correct 3-D diagrams of amide as hydrolysis product instead of acid

Total = 14

7 (a) $RCH(NH_2)COOH$ or $RCH(NH_3^+)COO^-$ ✓ **[1]**

(b) (i) $H_3N^+CH_2COO^-$ ✓ **[1]**
accept $NH_3^+CH_2COO^-$

(ii) COOH is acidic / loses H^+ ✓ **[2]**
NH_2 is basic / has a lone pair / gains H^+ ✓(not H transfer)

(iii) High m.p. means strong **intermolecular** / between molecules **[3]**
(1) forces in the solid glycine; ✓

coulombic (ion/ion) forces (1) in zwitterion are strong; ✓

any comment on why hydroxyethanoic acid is lower ✓
e g H-bonding (1) holds crystal together

(c) $H_3N^+CH_2COOH$✓←glycine→$H_2NCH_2COO^-$✓ or H_2NCH_2COONa **[4]**
↓
$H_2NCH_2COOCH_3$ ✓
or $H_3N^+CH_2COOCH_3$

any correct balancing ion ✓

Total = 11