

**OXFORD CAMBRIDGE AND RSA EXAMINATIONS**

**Advanced GCE**

**CHEMISTRY**

**2814**

Chains, Rings and Spectroscopy

Friday

**24 JANUARY 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> <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 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	11	
2	13	
3	12	
4	11	
5	13	
6	13	
7	8	
8	9	
<b>TOTAL</b>	<b>90</b>	

**This question paper consists of 16 printed pages.**

Answer **all** the questions.

1 Benzene, methylbenzene and phenol are used in the chemical and pharmaceutical industry as starting materials for making more complex aromatic compounds.

(a) Methylbenzene can also be made in the laboratory from benzene and chloromethane.

(i) Draw the structural formula of methylbenzene.

[1]

(ii) Give the equation for the preparation of methylbenzene from benzene.

[1]

(iii) Identify, by name or formula, a suitable catalyst for this reaction.

.....[1]

(iv) Methylbenzene is more reactive than benzene.

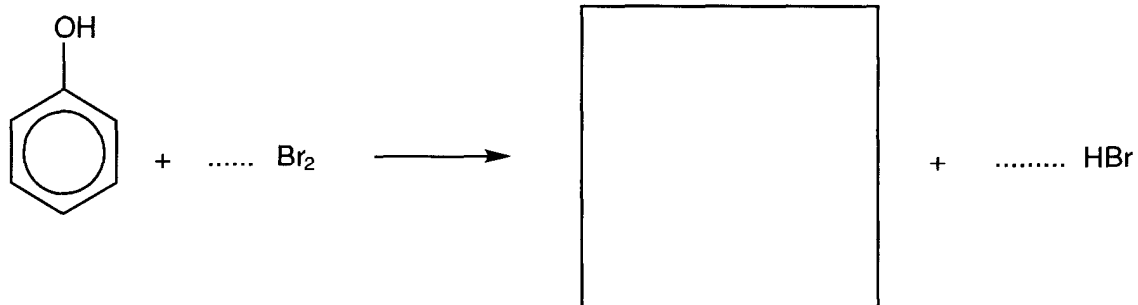
Name and draw the structural formula of an **organic** product which might be formed from the reaction of methylbenzene with chloromethane in the presence of the catalyst.

structural formula

name .....[2]

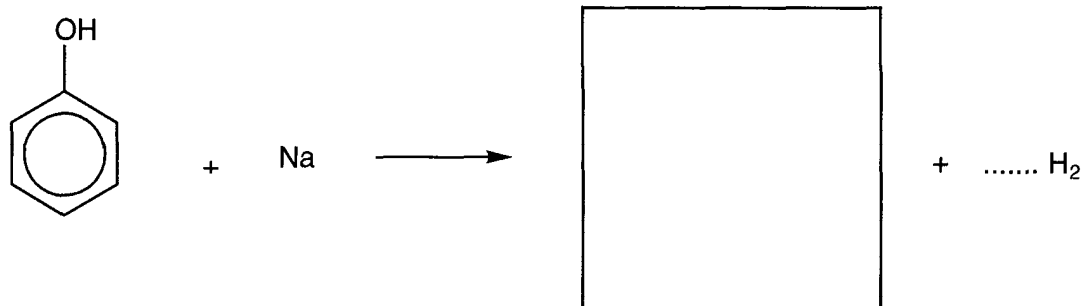
(b) Complete and balance the following equations for the reactions of phenol, giving structural formulae for the organic compounds in the boxes provided.

(i)



[3]

(ii)



[2]

(c) State a general use for phenols. ....[1]

[Total: 11]

2 Glycine is an amino acid obtained from natural proteins by digestion. The structure of glycine is  $\text{CH}_2(\text{NH}_2)\text{COOH}$ .

(a) State **in words** the three dimensional shape adopted by the **bonds** in a molecule of glycine

(i) around the nitrogen atom,

.....[1]

(ii) around the carbon atom of the  $\text{CH}_2$  group,

.....[1]

(iii) around the carbon atom of the  $\text{COOH}$  group.

.....[1]

(b) Amino acids react both with acids and with bases. Draw the structure you expect for glycine

(i) in acidic solution,

[1]

(ii) in alkaline solution.

[1]

(c) Proteins can also be converted into amino acids in the laboratory.

(i) State the reagents and conditions required.

.....[2]

(ii) State the type of reaction taking place.

.....[1]

(d) Alanine,  $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ , is another amino acid obtained from proteins. Alanine has a chiral centre but glycine does not.

(i) What is meant by the term *chiral centre*?

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

(ii) Draw the two stereoisomers of alanine.

[2]

(iii) Would you expect the alanine isolated from a protein to be:

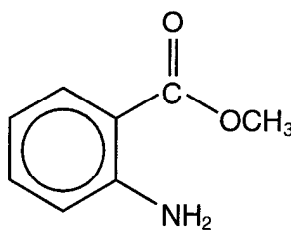
- either** only one stereoisomer .....
- or** a 1:1 mixture of both stereoisomers .....
- or** unequal amounts of the two stereoisomers? .....

Tick one answer and explain your choice.

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

[Total: 13]

- 3 Many organic compounds are used to add flavour to food and drink. Compound **A** has been used to add grape flavour to soft drinks.

**A**

- (a) Apart from the benzene ring, name the **two** functional groups in **A**.

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

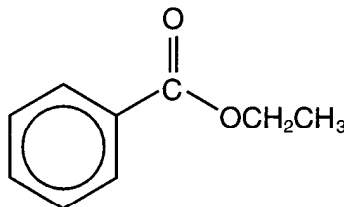
- (b) (i) Deduce the molecular formula of **A**.

..... [1]

- (ii) A 330 cm<sup>3</sup> can of soft drink contains 0.100 g **A**.  
 Calculate the concentration, in mol dm<sup>-3</sup>, of **A**.

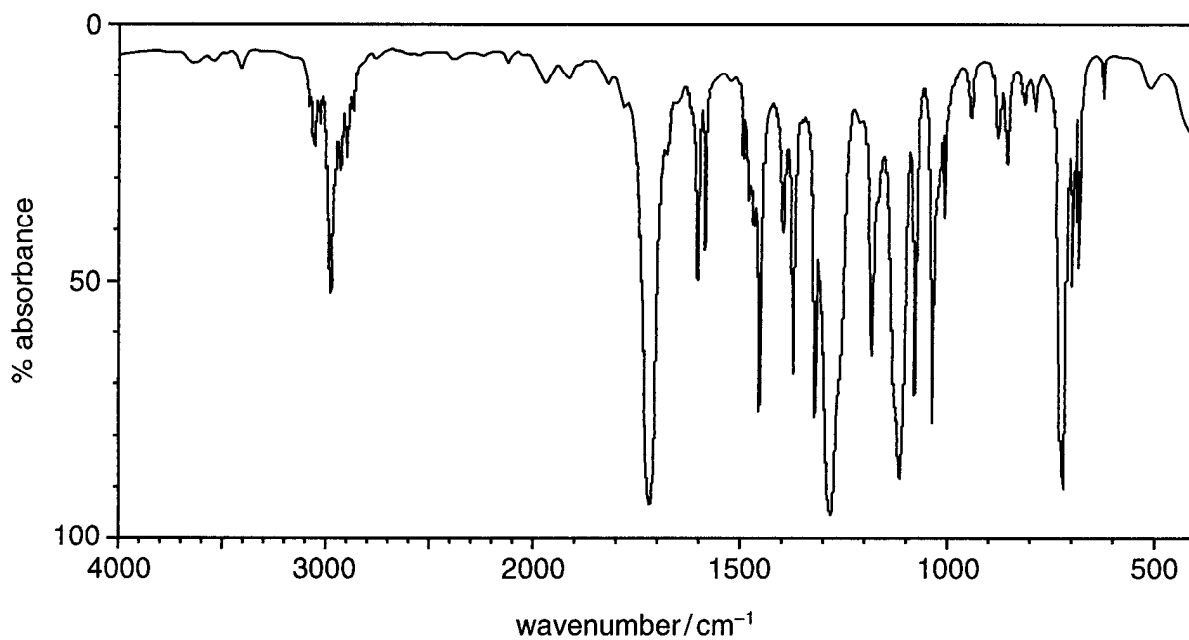
concentration ..... mol dm<sup>-3</sup> [2]

- (c) Compound **B** is similar to **A** and also has a fruity odour.

**B**



- (ii) The infra-red spectrum of **B** is shown below. Mark with a cross the **major** absorption peak which is characteristic of the  $-\text{COOCH}_2\text{CH}_3$  group.



[1]

[Total: 12]

- 4 The nitration of an aromatic compound is the first stage in the synthesis of many commercially important compounds.

- (a) (i) Describe the mechanism of the nitration of benzene. Include the reagents and overall equation in your answer, and show how the electrophile is generated.

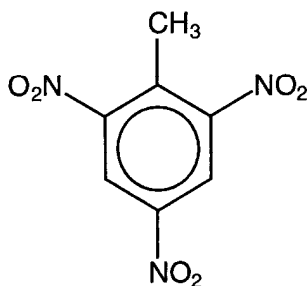
[6]



(ii) Explain why this is classified as an *electrophilic substitution* reaction.

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

(b) Compound **C** is an aromatic nitro compound.



**C**

Predict the chemical shifts of the peaks in the n.m.r. spectrum of **C**.

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

[Total: 11]

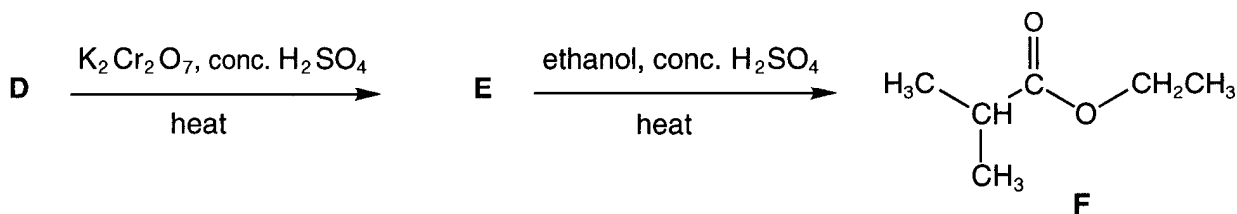
5 Compounds with the formula  $C_4H_9OH$  are alcohols.

(a) Draw formulae to show the four structural isomers of alcohols with the molecular formula  $C_4H_{10}O$ .

[4]

(b) One of the isomers in (a), compound **D**, reacts with  $K_2Cr_2O_7$  in the presence of  $H_2SO_4$ , to give **E**.

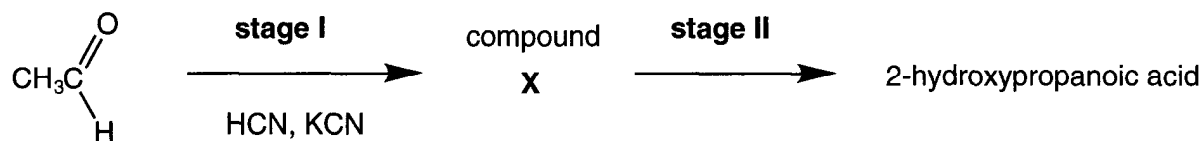
When **E** is heated with ethanol in the presence of concentrated  $H_2SO_4$ , compound **F** is formed.





- 6 2-Hydroxypropanoic acid (lactic acid) is present in milk. It can also be made in two stages from ethanal.

The laboratory synthesis of 2-hydroxypropanoic acid is outlined below.



- (a) (i) Give the mechanism for **stage I**.

[4]

- (ii) Describe the second stage of the synthesis by suggesting a suitable reagent and stating the type of reaction involved.

reagent: .....

type of reaction: .....

[2]

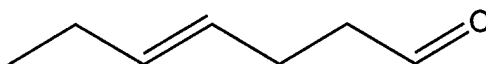
- (iii) Draw the structure of 2-hydroxypropanoic acid.

[1]

- (b) 2-Hydroxypropanoic acid was dissolved in  $D_2O$  and an n.m.r. spectrum of the solution was taken. Predict, with reasons, the **splitting patterns** observed in this spectrum.

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

- (c) Hept-4-enal, **H**, is also present in milk.

**H**

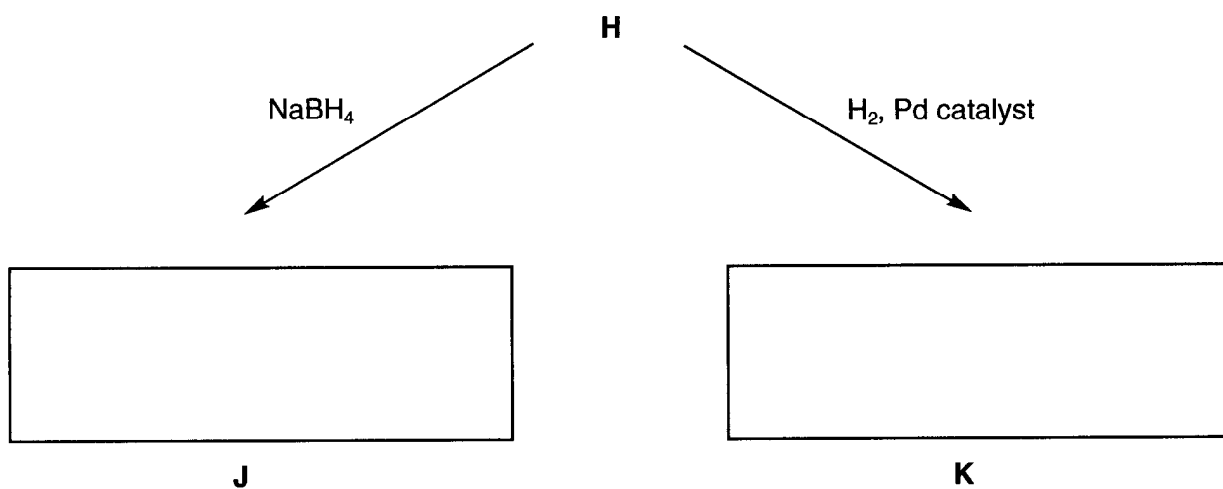
- (i) Deduce the molecular formula of **H**.

.....[1]

- (ii) Draw the skeletal formula of a stereoisomer of **H**.

[1]

- (iii) **J** and **K** can be made from **H**.  
 Draw skeletal formulae for **J** and **K** in the boxes provided.

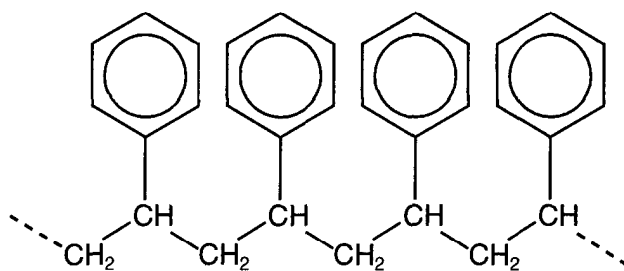


[2]

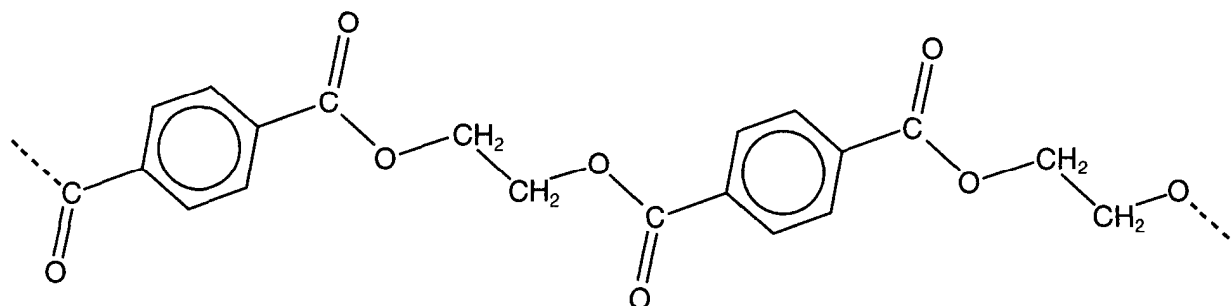
[Total: 13]

- 7 Polymers can be made either from a single monomer or from more than one monomer. Two polymers, **L** and **M**, are shown below.

Polymer  
**L**



Polymer  
**M**



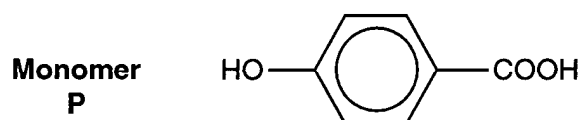
- (a) Deduce the structures of the monomers from which **L** and **M** could be obtained.

For **L**:

For **M**:

[3]

- (b) Polymer **N** can be made from the monomer **P** only, shown below.



Suggest a structure for polymer **N**, showing three repeat units.

[2]

- (c) Polymers **M** and **N** are made by the same type of polymerisation.  
Name this type of polymerisation and describe its characteristic features.

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

- (d) State a major use for polymers such as **M**.

.....[1]

[Total: 8]







RECOGNISING ACHIEVEMENT

**2814 Chains, Rings and Spectroscopy**

**January 2003**

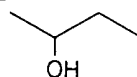
**Mark Scheme**

### Marking structures in organic chemistry

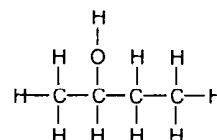
When a structure is asked for, there must be sufficient detail using conventional carbon skeleton and functional group formulae (e.g.  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{OH}$ ,  $\text{COOH}$ ,  $\text{COOCH}_3$ ) to unambiguously define the arrangement of the atoms. (E.g.  $\text{C}_3\text{H}_7$  would not be sufficient)

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

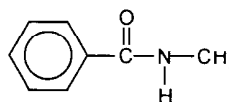
- a **structural formula** – e.g.  $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_5$ ,



- a **skeletal formula** – e.g.



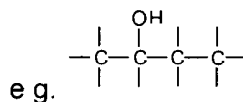
- a **displayed formula** – e.g.



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

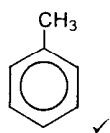


in any

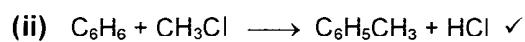
of the types of formula above

<sup>1</sup> Note that in organic chemistry a candidate may identify a compound by name and formula. If one of these is wrong then the mark is not awarded as this is a contradictory answer.

1 (a) (i)



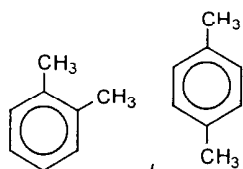
[1]



[1]

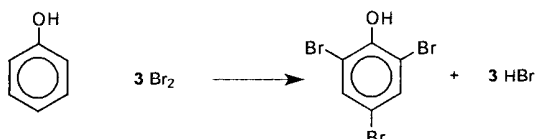
(iii) iron / aluminium chloride / iron(III)chloride etc  
Fe / AlCl<sub>3</sub> / FeCl<sub>3</sub> ✓

[1]

(iv) any polymethylated benzene ring ✓  
egname ✓ eg 1,2-dimethylbenzene/  
1,4-dimethylbenzene

[2]

(b) (i)

brominated phenol ✓ 2,4,6 substituted ✓  
balancing ✓

[3]

(ii)

phenoxide ✓  
balancing ✓

[2]

(c)

any general use that contains phenols - eg  
antiseptics / disinfectants / dyes / plastics / pharmaceuticals / pesticides/explosives ✓

[1]

[Total: 11]

- 2 (a) (i) (trigonal) pyramidal ✓ [1]
- (ii) tetrahedral ✓ [1]
- (iii) trigonal (planar) ✓ [1]
- (b) (i)  $\text{H}_3\text{N}^+\text{CH}_2\text{COOH}$  ✓ [1]
- (ii)  $\text{NH}_2\text{CH}_2\text{COO}^-$  ✓ [1]
- (c) (i)  $\text{H}^+$  / acid /  $\text{HCl}$  /  $\text{H}_2\text{SO}_4$  /  $\text{OH}^-$  / alkali ✓  
/heat / reflux ✓  
(or use of an enzyme at 37°ish) [2]
- (ii) hydrolysis ✓ [1]
- (d) (i) carbon with four different / distinguishable groups attached ✓  
(or carbon / part of the molecule / atom which is assymetric / non-superimposable on its mirror image) [1]
- (ii)
- 
- one structure of alanine with at least one 3-d bond ✓  
two optical isomers / reflections of a 3-d structure ✓ [2]
- (iii) one stereoisomer ✓  
natural / from a living system / made by enzymes etc ✓ [2]

[Total: 13]

3 (a) ester ✓  
(primary) amine ✓ [2]

(b) (i)  $C_8H_9NO_2$  ✓ [1]

(ii)  $M_r$  of A = 151 (or ecf from (i)) ✓

moles A =  $0.100g/151 = 0.000662$

conc A =  $0.000662/0.330dm^3$

= **0.002 / 0.0020** (ecf from a wrong  $M_r$ ) ✓

[2]

(c) (i) **peaks identified**

peak X – benzene ring protons ✓

peak Y –  $CH_2$  protons ✓

peak Z –  $CH_3$  protons ✓

3 identification marks

**reasoning from  $\delta$  value** . . . for each, either.

- quotes the relevant functional group in the Data Sheet (eg  $-O-CH_2-R$ ) /or
- quotes the relevant Data Sheet range (eg 3.3–4.3) / or
- from first principles using the expected deshielding to assign the peaks

✓✓✓

**reasoning from the splitting pattern** .

Y peak is a quadruplet/1:3:3:1 etc

this is due to 3 neighbours / adjacent to a  $CH_3$  ✓

Z peak is a triplet / 1:2:1 etc

this is due to 2 neighbours / adjacent to a  $CH_2$  ✓

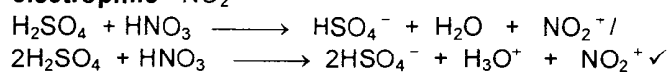
**ANY 3 out of 5 reasoning marks** [6]

(ii) peak at  $1700cm^{-1}$  and/or at  $1280cm^{-1}$  marked ✓ [1]

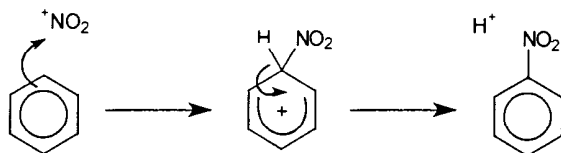
**[Total: 12]**

4 (a) (i) reagents conc  $\text{H}_2\text{SO}_4 + \text{HNO}_3$  ✓

electrophile  $\text{NO}_2^+$  ✓

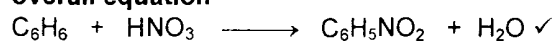


mechanism



curly arrow from benzene  $\pi$ -bond to electrophile ✓  
 correct intermediate (ecf on electrophile formula) ✓  
 curly arrow from C-H bond to  $\pi$ -bond and  $\text{H}^+$  formed ✓

overall equation



ANY 6 out of 7 [6]

(ii)  $\text{NO}_2^+$  accepts an electron pair ✓  
 H is replaced / substituted by  $\text{NO}_2$  ✓

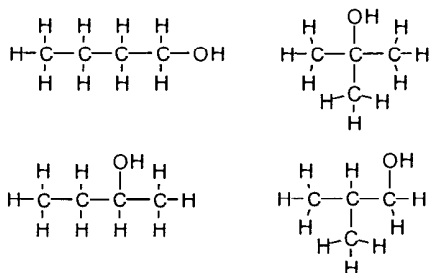
[2]

(b) two peaks ✓  
 peak at/between 2.3-2.7 ✓  
 peak at/between 7.1-7.7 ✓

[3]

[Total: 11]

5 (a)



any unambiguous type of formula ✓✓✓✓

[4]

- (b) (i) butan-1-ol gives butanal /butanoic acid / an aldehyde / a carboxylic acid  
 butan-2-ol gives butanone / a ketone  
 2-methylpropan-2-ol gives no reaction ✓✓✓

3 marks for the alcohol reactions

D is methylpropan-1-ol ✓

E is methylpropanoic acid ✓✓

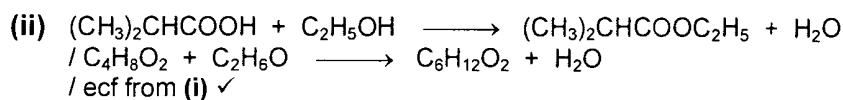
(where any carboxylic acid for E gets the first mark)

3 marks for identifying D and E

**Quality of Written Communication**

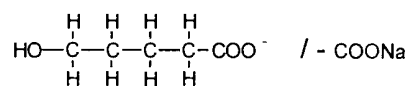
information is organised clearly and coherently using at least **two** specialist terms not mentioned in the question (eg correct names of compounds, primary, secondary, aldehyde, ketone, oxidised etc ) ✓

[6]



[1]

(c)



where

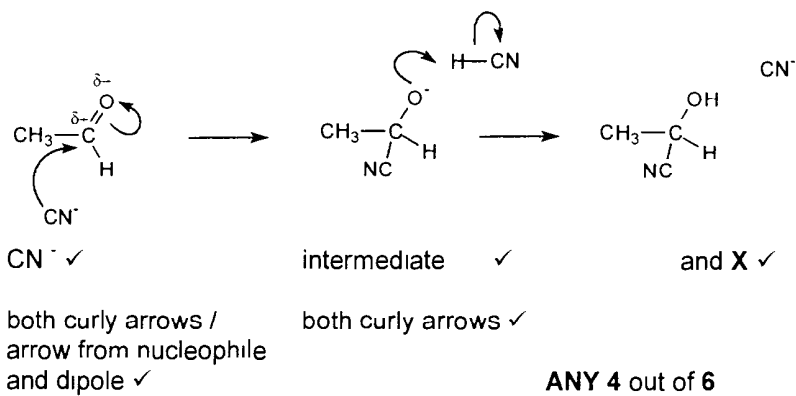
-OH ✓

-COO<sup>-</sup> / COO<sup>-</sup> Na<sup>+</sup> / COONa ✓

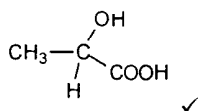
2]

[Total: 13]

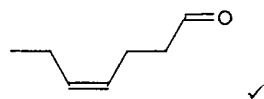
6 (a) (i) nucleophilic addition ✓

(ii) HCl / H<sub>2</sub>SO<sub>4</sub> / H<sup>+</sup> / acid ✓  
hydrolysis ✓**[ 2 ]**

(iii)

**[ 1 ]**(b) 1 doublet and 1 quadruplet / 1 3 3 1 and 1.1 ✓  
correct reason for at least one peak ✓  
(eg 1,3 3,1 due to 3 neighbours / next to CH<sub>3</sub> / use of n+1 rule)**[ 2 ]**(c) (i) C<sub>7</sub>H<sub>12</sub>O ✓**[ 1 ]**

(ii)

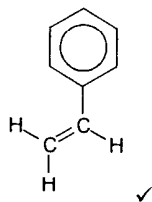
**[ 1 ]**

(iii)

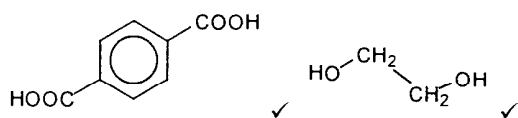
**[ 2 ]****[Total: 13]**



7 (a) L:

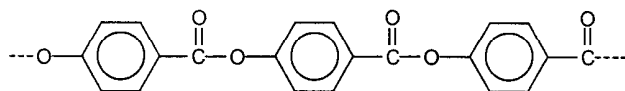


M:



[3]

(b)



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

[2]

(c)

condensation ✓  
 loss of water / small molecule ✓

[2]

(d)

fibres / clothing / bottles etc ✓

[1]

[Total: 8]

**8 to detect the presence of C=O ...**

2,4-dinitrophenylhydrazine / 2,4-DNPH ✓  
red/orange/yellow ppt/solid/crystals ✓

or

IR spectrum ✓  
has peak at 1680-1750 cm<sup>-1</sup> ✓

2 marks

**to confirm it is a ketone not an aldehyde ...**

Tollens' reagent / (acidified) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> ✓  
aldehyde: silver mirror / green colour ✓  
ketone: no silver mirror / no green colour ✓

or

NMR spectrum ✓  
aldehyde: peak at 9.5-10 ✓  
ketone: no peak at 9.5-10 ✓

3 marks

**a chemical method to identify the ketone ...**

use the product / solid / ppt from 2,4-DNPH / 2,4-dinitrophenylhydrazine ✓  
(re)crystallise / purify (the product) ✓  
measure the melting point ✓  
compare with known compounds / data book ✓

4 marks

**ANY 8 marks out of 9 [8]**

**Quality of Written Communication**

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

[1]

**[Total: 9]**