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| Centre Number | Candidate Number |
| Surname | MARK SCHEME |
| Other Names | |
| Candidate Signature | |

| For Examiner's Use | |
|---|---|
| Examiner's Initials | |
| Question | Mark |
| 1 | |
| 2 | |
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| 8 | |
| TOTAL | |

AQA

General Certificate of Education
Advanced Level Examination
June 2014

# Chemistry CHEM4

## Unit 4 Kinetics, Equilibria and Organic Chemistry

Monday 9 June 2014 1.30 pm to 3.15 pm

**For this paper you must have:**
- the Periodic Table/Data Sheet provided as an insert (enclosed)
- a ruler with millimetre measurements
- a calculator.

**Time allowed**
- 1 hour 45 minutes

**Instructions**
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

**Information**
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- You are expected to use a calculator where appropriate.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  - use good English
  - organise information clearly
  - use scientific terminology accurately.

**Advice**
- You are advised to spend about 70 minutes on **Section A** and about 35 minutes on **Section B**.

## Section A

Answer **all** questions in the spaces provided.

**1** This question is about the gaseous equilibrium between compounds **E**, **F** and **G** as shown in the equation.

$$\mathbf{E}(g) + 2\mathbf{F}(g) \rightleftharpoons 2\mathbf{G}(g) \qquad \Delta H = -50 \text{ kJ mol}^{-1}$$

**1 (a)** A 2.0 mol sample of **E** was heated in a sealed container with a 1.0 mol sample of **F**. Equilibrium was established at a given temperature and the equilibrium mixture formed contained 0.80 mol of **G**.

Calculate the amount, in moles, of **E** and of **F** in this equilibrium mixture.

**[2 marks]**

Moles of **E** $2.0 - (0.8/2) = 1.6$

Moles of **F** $1.0 - 0.8 = 0.2$

**1 (b)** Write an expression for the equilibrium constant $K_c$ for this equilibrium.
State the units of $K_c$

**[2 marks]**

Expression $K_c = \dfrac{[G]^2}{[E][F]^2}$ * Products over reactants - remember to take into account moles!

Units .....

**1 (c)** A different mixture of **E** and **F** reached equilibrium at temperature $T_1$ in a container of volume 1.50 $dm^3$. This equilibrium mixture contained 2.50 mol of **E**, 1.20 mol of **F** and 0.85 mol of **G**.

Calculate a value of $K_c$ for the equilibrium at temperature $T_1$

**[2 marks]**

$K_c = \frac{[G]^2}{[E][F]^2}$ $K_c = \frac{(0.85)^2/1.5}{(2.50)/1.5 \times (1.20)^2/1.5)}$

$K_c = \frac{0.4816}{1.6 \times 0.96}$ $K_c = 0.31\ mol^{-1}dm^3$

* Don't forget your units!

**1 (d)** The mixture in Question **1 (c)** was allowed to reach equilibrium at temperature $T_1$ in a different container of volume 3.00 $dm^3$.

State whether the amount of **G** in the equilibrium mixture will increase, decrease or stay the same. Explain your answer.

**[3 marks]**

Effect on the amount of **G** Decrease

Explanation As reactants and products are gaseous, an increase in volume decreases pressure. As pressure decreases this causes equilibrium to shift to LHS (side with more moles) to counteract the drop in pressure.

* Always answer in terms of equilibrium position.

**1 (e)** The mixture in Question **1 (c)** was allowed to reach equilibrium at temperature $T_2$ in the original container of volume 1.50 $dm^3$.

The value of $K_c$ for the equilibrium was found to have increased.

State and explain which of $T_1$ or $T_2$ is the higher temperature.

**[3 marks]**

Higher temperature $T_1$

Explanation Because forward reaction is exothermic, to get a higher $K_c$ value $T_2$ must be lower as equilibrium shifted to RHS.

* If $K_c$ value has increased the more products made.

12

**2** This question is about alkalis and carboxylic acids.

In this question, all data are quoted at 25 °C.

**2 (a)** Carboxylic acids are weak acids.

State the meaning of the term **weak** as applied to carboxylic acids.

**[1 mark]**

partial dissociation.

**2 (b)** Write an equation for the reaction of propanoic acid with sodium carbonate.

**[1 mark]**

$2CH_3CH_2COOH + Na_2CO_3 \rightarrow 2CH_3CH_2COONa + CO_2 + H_2O$

**2 (c)** Calculate the pH of a 0.0120 mol $dm^{-3}$ solution of calcium hydroxide.
The ionic product of water $K_w = 1.00 \times 10^{-14}$ $mol^2$ $dm^{-6}$.
Give your answer to 2 decimal places.

**[3 marks]**

$K_w = [H^+][OH^-]$ $Ca(OH)_2 \rightarrow \therefore 2 \times 0.0120 = 0.0240$

$1 \times 10^{-14} = [H^+][0.0240]$ $\frac{1 \times 10^{-14}}{0.0240} = [H^+] = 4.16 \times 10^{-13}$

$-\log(4.16 \times 10^{-13}) = 12.38$

**[Extra space]**

* Do not forget $Ca(OH)_2$ produces 2 $OH^-$ so id is conc. $\times 2$!

**2 (d)** The value of the acid dissociation constant $K_a$ for benzenecarboxylic acid ($C_6H_5COOH$) is $6.31 \times 10^{-5}$ mol dm$^{-3}$.

**2 (d) (i)** Write an expression for the acid dissociation constant $K_a$ for benzenecarboxylic acid.

**[1 mark]**

$K_a = \frac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]}$

**2 (d) (ii)** Calculate the pH of a 0.0120 mol dm$^{-3}$ solution of benzenecarboxylic acid. Give your answer to 2 decimal places.

**[3 marks]**

$K_a = \frac{[H^+]^2}{[C_6H_5COOH]}$ $\quad 6.31 \times 10^{-5} = \frac{[H^+]^2}{0.0120}$

$\sqrt{6.31 \times 10^{-5} \times 0.0120} = H^+ \quad H^+ = 8.7017 \times 10^{-4}$

$-\log(8.7017 \times 10^{-4}) = 3.06$

* In these cases you use the assumption that $C_6H_5COO^- = H^+$ so $(H^+)^2$.

[Extra space]

**Question 2 continues on the next page**

**2 (d) (iii)** A buffer solution with a pH of 4.00 is made using benzenecarboxylic acid and sodium benzenecarboxylate.

Calculate the mass of sodium benzenecarboxylate ($M_r$ = 144.0) that should be dissolved in 1.00 $dm^3$ of a 0.0120 mol $dm^{-3}$ solution of benzenecarboxylic acid to produce a buffer solution with a pH of 4.00

The value of the acid dissociation constant $K_a$ for benzenecarboxylic acid ($C_6H_5COOH$) is $6.31 \times 10^{-5}$ mol $dm^{-3}$.

**[5 marks]**

$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$ $\quad K_a = \frac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]}$

$C_6H_5COONa \rightleftharpoons C_6H_5COO^- + Na^+$

$\therefore H^+ = 10^{-4.00} = 1 \times 10^{-4}$ $\quad 6.31 \times 10^{-5} = \frac{C_6H_5COO^- \times 1 \times 10^{-4}}{0.0120}$

$\frac{6.31 \times 10^{-5} \times 0.0120}{1 \times 10^{-4}} = C_6H_5COO^-$ $\quad C_6H_5COO^- = 7.572 \times 10^{-3}$

Mr of $C_6H_5COONa$

$7.572 \times 10^{-3} \times 144 = 1.09\,g$

**[Extra space]**

* Remember the exact assumptions.
* weak acids we assume NO dissociation.
* salts we assume full dissociation.
* Conc x Mr = mass!

2 (e) Two solutions, one with a pH of 4.00 and the other with a pH of 9.00, were left open to the air.

The pH of the pH 9.00 solution changed more than that of the other solution.

Suggest what substance might be present in the air to cause the pH to change.
Explain how and why the pH of the pH 9.00 solution changes.

**[3 marks]**

Substance present in air ..... $CO_2$ .....

Explanation ..... $CO_2$ is an acidic gas so it will cause pH .....

to fall. .....

* $CO_2$ in water creates carbonic acid. .....

.....

.....

.....

17

**Turn over for the next question**

**3 (a)** **Table 1** shows the results of three experiments to investigate the rate of reaction between compounds **A** and **B** dissolved in a given solvent.
All three experiments were carried out at the same temperature.

**Table 1**

| | Experiment 1 | Experiment 2 | Experiment 3 |
|---|---|---|---|
| **Initial concentration of A / mol dm$^{-3}$** | $1.60 \times 10^{-2}$ | $2.40 \times 10^{-2}$ | $3.60 \times 10^{-2}$ |
| **Initial concentration of B / mol dm$^{-3}$** | $4.20 \times 10^{-2}$ | $6.30 \times 10^{-2}$ | $6.30 \times 10^{-2}$ |
| **Initial rate / mol dm$^{-3}$ s$^{-1}$** | $8.00 \times 10^{-5}$ | $1.80 \times 10^{-4}$ | $4.05 \times 10^{-4}$ |

**3 (a) (i)** Deduce the order of reaction with respect to **A**.
Tick (✓) **one** box.

**[1 mark]**

| Order of reaction with respect to A | Tick (✓) |
|---|---|
| 0 | |
| 1 | |
| 2 | ✓ |

$2.4\times10^{-2} \rightarrow 3.60\times10^{-2} = \times 1.5$
$1.80\times10^{-4} \rightarrow 4.05\times10^{-4} = 1.5^2$

**3 (a) (ii)** Deduce the order of reaction with respect to **B**.
Tick (✓) **one** box.

**[1 mark]**

| Order of reaction with respect to B | Tick (✓) |
|---|---|
| 0 | ✓ |
| 1 | |
| 2 | |

If $8.00\times10^{-5} \times 1.5^2 = 1.8\times10^{-4}$
then B must be zero order.

**3 (b)** The reaction between two different compounds, **C** and **D**, is studied at a given temperature.
The rate equation for the reaction is found to be

$$\text{rate} = k[\mathbf{C}][\mathbf{D}]^2$$

**3 (b) (i)** When the initial concentration of **C** is $4.55 \times 10^{-2}$ mol dm$^{-3}$ and the initial concentration of **D** is $1.70 \times 10^{-2}$ mol dm$^{-3}$, the initial rate of reaction is $6.64 \times 10^{-5}$ mol dm$^{-3}$ s$^{-1}$.

Calculate the value of the rate constant at this temperature and deduce its units.

**[3 marks]**

Calculation $\text{rate} = k[C][D]^2$ $\dfrac{\text{rate}}{[C][D]^2} = k$

$\dfrac{6.64\times10^{-5}}{(4.55\times10^{-2})\times(1.70\times10^{-2})^2} = k$ $k = 5.05$

Units of rate constant $\dfrac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol dm}^{-3}\times\text{mol dm}^{-3}\times\text{mol dm}^{-3}} = \text{mol}^{-2}\text{ dm}^6\text{ s}^{-1}$

**3 (b) (ii)** The experiment in Question **3 (b) (i)** is repeated at the same temperature but after the addition of extra solvent so that the total volume of the mixture is doubled.

Deduce the new initial rate of reaction.

**[1 mark]**

$5.05 \times 0.02275 \times 7.225\times10^{-5} = 8.3\times10^{-6}$

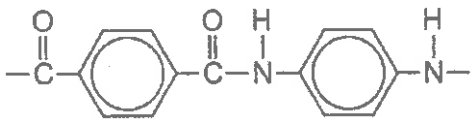
↓ $k$ from b i) ↓ $\dfrac{4.55\times10^{-2}}{2}$ ↓ $\left(\dfrac{1.7\times10^{-2}}{2}\right)^2$

* as volume is doubled the conc is halved.

6

**Turn over for the next question**

4 Kevlar is a polymer used in protective clothing.
The repeating unit within the polymer chains of Kevlar is shown.



**4 (a)** Name the strongest type of interaction between polymer chains of Kevlar.

**[1 mark]**

Hydrogen bonding

* we have oxygen and nitrogen with l.p. and δ+ H.

**4 (b)** One of the monomers used in the synthesis of Kevlar is

An industrial synthesis of this monomer uses the following two-stage process starting from compound **X**.

Stage **1**

**X**

Stage **2**

**4 (b) (i)** Suggest why the reaction of ammonia with **X** in Stage **1** might be considered unexpected.

**[2 marks]**

Ammonia is a nucleophile and benzene repels nucleophiles.

* Benzene usually reacts with electrophiles!

**4 (b) (ii)** Suggest a combination of reagents for the reaction in Stage **2**.

**[1 mark]**

Sn/HCl

**4 (b) (iii)** Compound **X** can be produced by nitration of chlorobenzene.

Give the combination of reagents for this nitration of chlorobenzene.
Write an equation or equations to show the formation of a reactive intermediate from these reagents.

**[3 marks]**

Reagents Conc. $HNO_3$ and conc. $H_2SO_4$

Equation(s) $HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + H_2O + HSO_4^-$

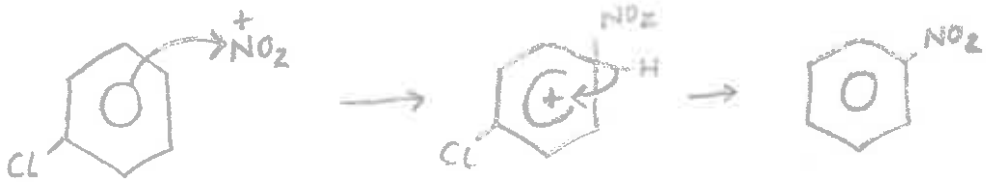
* Remember this!

**4 (b) (iv)** Name and outline a mechanism for the formation of **X** from chlorobenzene and the reactive intermediate in Question **4 (b) (iii)**.

**[4 marks]**

Name of mechanism Electrophilic Substitution

Mechanism




* Curly arrows show electron transfer so show where the electrons are going!

**Turn over for the next question**

11

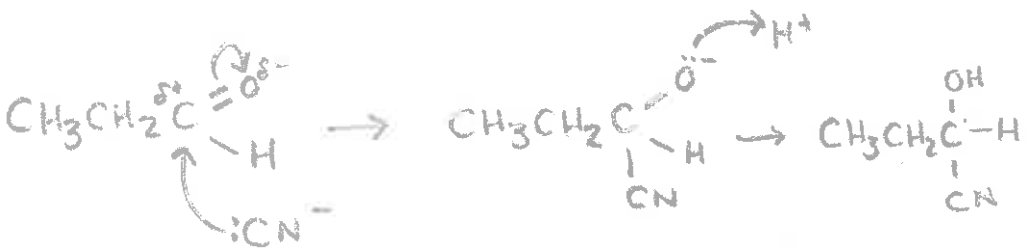
**5** The carbonyl compound $CH_3CH_2CHO$ reacts very slowly with HCN

**5 (a)** Name and outline a mechanism for the reaction of $CH_3CH_2CHO$ with HCN

**[5 marks]**

Name of mechanism ...Nucleophilic Addition...

Mechanism

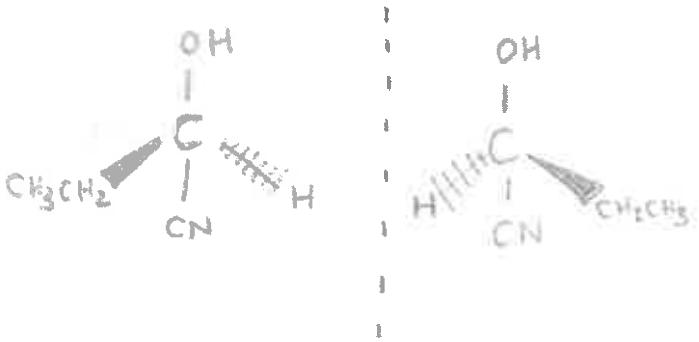


* Classic nucleophilic addition reaction - Learn this!

**5 (b)** The reaction in Question **5 (a)** produces a pair of enantiomers.

**5 (b) (i)** Draw the structure of each enantiomer to show how they are related to each other.

**[2 marks]**



* This has happened as the carbon has four different groups surrounding it, it is chiral.

* Any decent attempt at a pair of mirror images would gain the marks - don't overcomplicate wedged bonds.

**5 (b) (ii)** State and explain how you could distinguish between the two enantiomers. **[2 marks]**

use plane polarised light. Each enantiomer rotates in opposite directions.

**5 (c)** Give the IUPAC name of the product of the reaction in Question **5 (a)**. **[1 mark]**

2-hydroxybutanenitrile

**5 (d)** In practice, KCN rather than HCN is added to the carbonyl compound.

Given that $K_a$ for HCN = $4.0 \times 10^{-10}$ mol dm$^{-3}$, suggest why the reaction with HCN is very slow. **[2 marks]**

HCN is a weak acid therefore concentration of $CN^-$ ions is very low.

* if you see a Ka value, you know it's a weak acid → therefore partial dissociation.

**Question 5 continues on the next page**

**5 (e)** Acrylic fibres are used as a substitute for wool. Acrylics are copolymers of acrylonitrile with other compounds.

Acrylonitrile is the common name for the following compound.

$$H_2C=CH-C\equiv N$$

**5 (e) (i)** Acrylonitrile can be formed from propene.

Write an equation for the reaction of propene with ammonia and oxygen to form acrylonitrile and one other product.

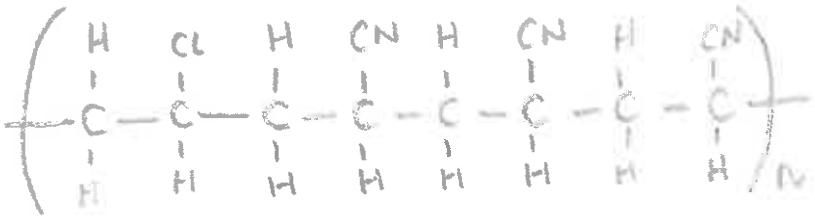
**[1 mark]**

$CH_2CHCH_3 + NH_3 + \frac{3}{2}O_2 \longrightarrow CH_2CHCN + 3H_2O$

**5 (e) (ii)** The term copolymer is used to describe the product obtained when two or more different monomers form a polymer.

Draw the repeating unit of the acrylic copolymer that contains 75% acrylonitrile monomer and 25% chloroethene monomer.

**[1 mark]**



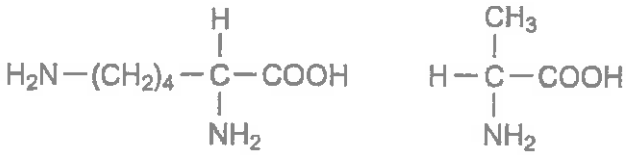
**5 (e) (iii)** Name the type of polymerisation involved in Question **5 (e) (ii)**.

**[1 mark]**

Addition polymerisation

15

**6** Lysine and alanine are two amino acids.



lysine



alanine

**6 (a)** Give the IUPAC name of lysine.

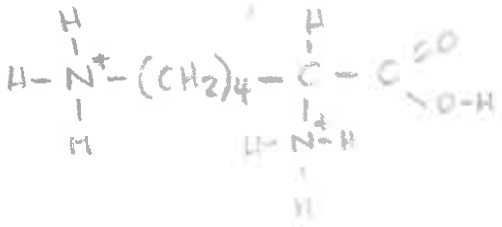
**[1 mark]**

2,6-diaminohexanoic acid.

**6 (b)** Draw structures to show the product formed in each case when lysine reacts with

**6 (b) (i)** an excess of aqueous HCl

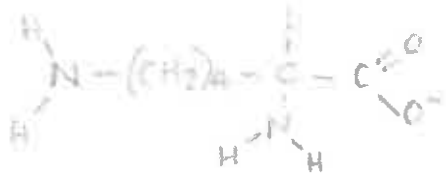
**[1 mark]**



* In acidic conditions the $NH_2$ group gains a $H^+$ ion. Don't forget there are two!

**6 (b) (ii)** an excess of aqueous NaOH

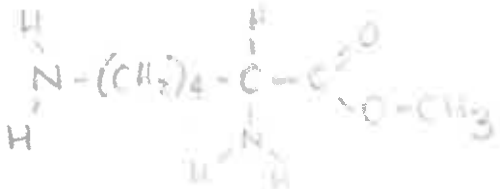
**[1 mark]**



* In alkaline conditions the COOH group loses its $H^+$ group.

**6 (b) (iii)** methanol in the presence of a small amount of concentrated $H_2SO_4$

**[1 mark]**

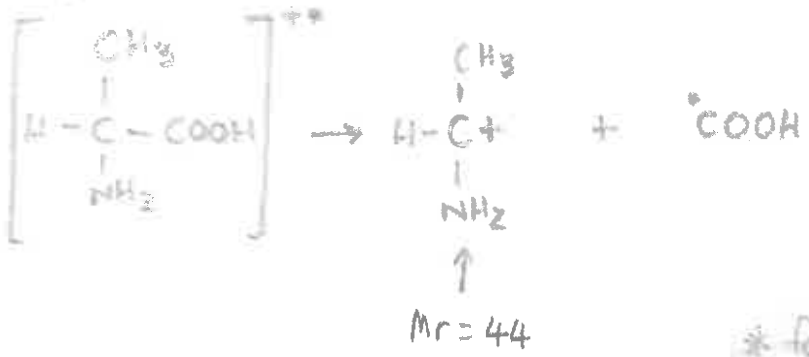


* Esterification!! Alcohol + carboxylic acid.

**6 (c)** The mass spectrum of alanine gives a major peak at $m/z = 44$

Write an equation for the fragmentation of the molecular ion of alanine to give an ion that produces this peak.
In your answer, draw the displayed formula for this fragment ion.

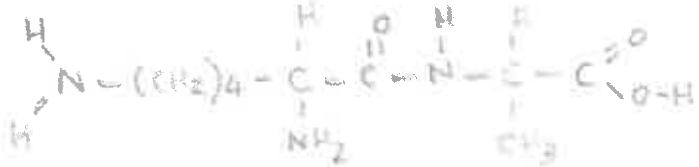
**[2 marks]**

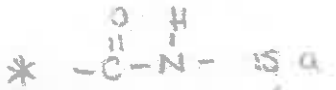



* for it to give a peak in a mass spectrometer then it must be a +ve ion!

**6 (d)** Draw a dipeptide formed from one molecule of lysine and one molecule of alanine.

**[1 mark]**






* is a peptide bond (or amide linkage).

**6 (e)** The dipeptide in Question **6 (d)** is hydrolysed in acid conditions and the mixture produced is analysed by column chromatography. The column is packed with a resin which acts as a polar stationary phase.

Suggest why lysine leaves the column after alanine.

**[2 marks]**

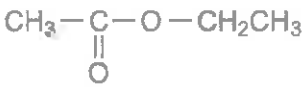
In acidic conditions lysine has two positive charges verses alanine which has one. This means it has a greater affinity for the stationary phase.

9

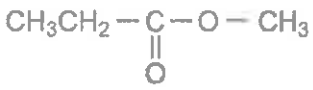
## Section B

Answer **all** questions in the spaces provided.

**7 (a)** **Ester 1** and **Ester 2** were studied by $^1$H n.m.r. spectroscopy.

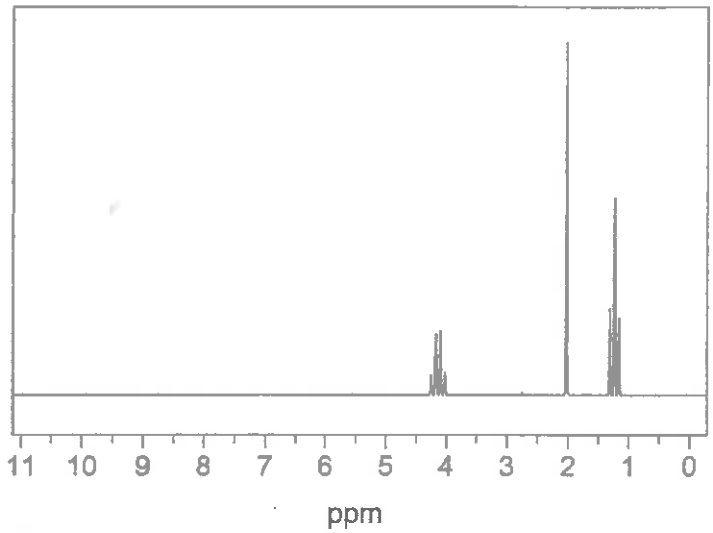


**Ester 1**



**Ester 2**

One of the two esters produced this spectrum.




Deduce which of the two esters produced the spectrum shown. In your answer, explain the position and splitting of the quartet peak at δ = 4.1 ppm in the spectrum.

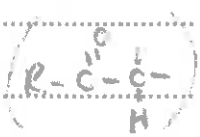
Predict the δ value of the quartet peak in the spectrum of the other ester.

Use **Table B** on the Data Sheet.

**[4 marks]**

Ester 1

peak at 4.1 is due to  It is a quartet which tells us that it is next to a $CH_3$ group.

Ester 2's quartet peak would be at 2.1-2.6 

**7 (b)** Cetrimide is used as an antiseptic.

$[CH_3(CH_2)_{15}N(CH_3)_3]^+ Br^-$

cetrimide

Name this type of compound.

Give the reagent that must be added to $CH_3(CH_2)_{15}NH_2$ to make cetrimide and state the reaction conditions.

Name the type of mechanism involved in this reaction.

**[4 marks]**

Centrimide is a quaternary ammonium salt.
You need to add $CH_3Br$ (bromoethane), in excess.
Mechanism would be Nucleophilic Substitution.

* This question gives you the overall answer and wants you to work backwards. Just remember it's an amine which is getting multiple substitutions.

**7 (c)** Give a reagent that could be used in a test-tube reaction to distinguish between benzene and cyclohexene.
Describe what you would see when the reagent is added to each compound and the test tube is shaken.

**[3 marks]**

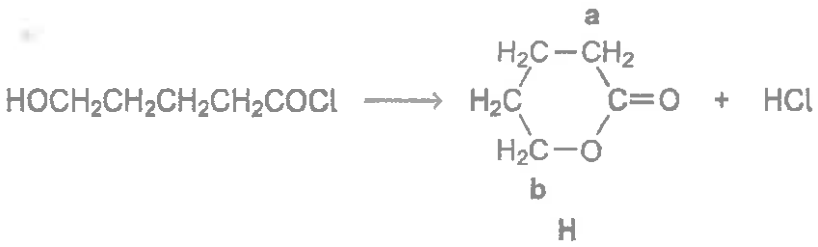
I would add bromine water to each. In Benzene the bromine would stay Red/orange but in cyclohexene it would decolarise.

11

8 This question is about some isomers of $C_5H_8O_2$

8 (a) Compound **H** is a cyclic ester that can be prepared as shown.

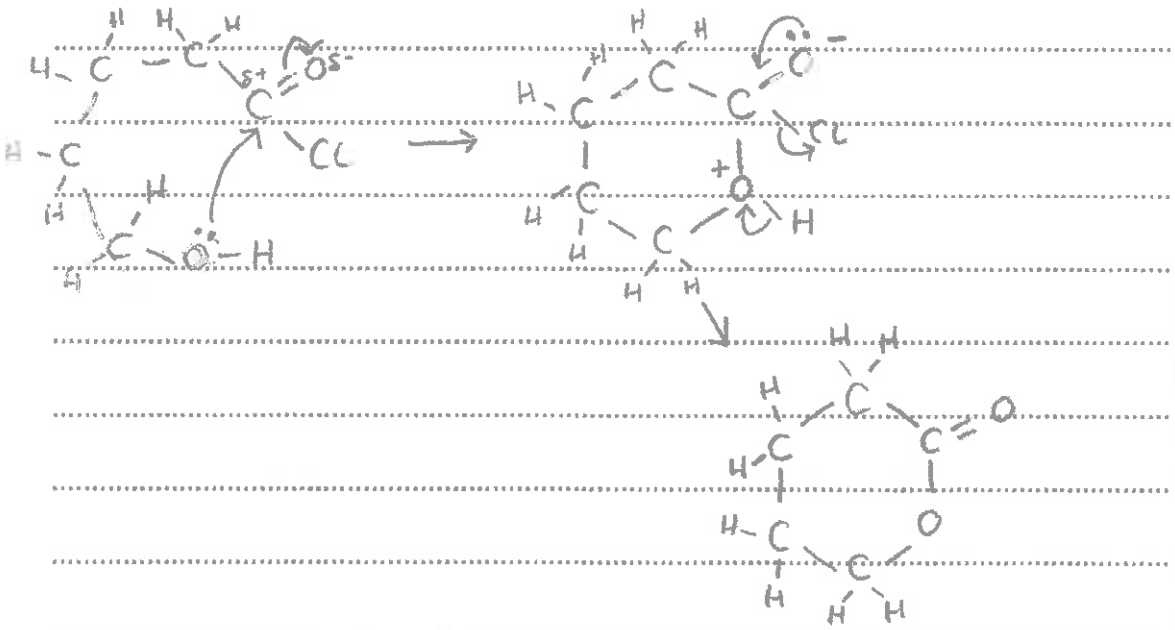
On the structure of **H**, two of the carbon atoms are labelled.




8 (a) (i) Name and outline a mechanism for this reaction.

Use **Table C** on the Data Sheet to give the $^{13}C$ n.m.r. δ value for the carbon atom labelled **a** and the δ value for the carbon atom labelled **b**.

**[7 marks]**

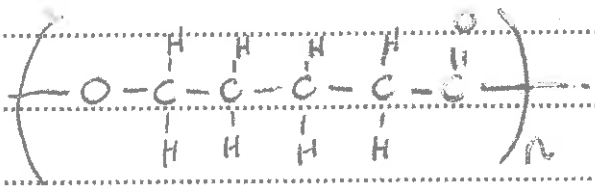


* this may look complicated but its just esterification again. this time with an alcohol and acyl chloride but on the same molecule to create a ring structure.

**8 (a) (ii)** $HOCH_2CH_2CH_2CH_2COCl$ can also react to form a polyester in a mechanism similar to that in Question **8 (a) (i)**.

Draw the repeating unit of the polyester and name the type of polymerisation involved.

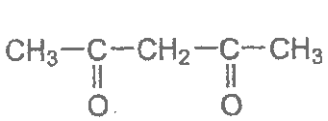
**[2 marks]**



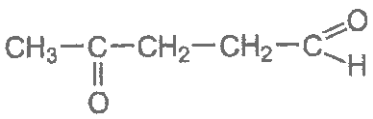
**8 (b)** State how you could distinguish between compounds **J** and **K** by a simple test-tube reaction.

State how you could distinguish between **J** and **K** by giving the number of peaks in the $^1H$ n.m.r. spectrum of each compound.

**[5 marks]**



**J**



**K**

Add Tollens reagents (Ammonical Silver Nitrate).

J would give no visible change

K would form a silver mirror.

* You could have used fehlings or acidified potassium dichromate.

J would give two peaks

K would give four peaks.

* Look at the number of different environments!

**Question 8 continues on the next page**

8 (c) Draw the structure of each of the following isomers of $C_5H_8O_2$
Label each structure you draw with the correct letter **L**, **M**, **N**, **P** or **Q**.

**L** is methyl 2-methylpropenoate.

**M** is an ester that shows E-Z stereoisomerism.

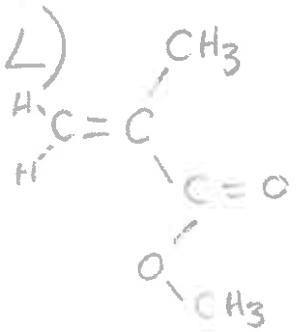
**N** is a carboxylic acid with a branched carbon chain and does **not** show stereoisomerism.

**P** is an optically active carboxylic acid.

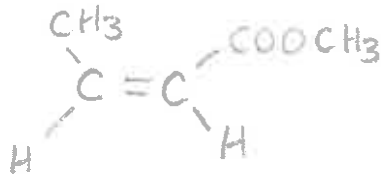
**Q** is a cyclic compound that contains a ketone group and has only two peaks in its $^1H$ n.m.r. spectrum.

**[5 marks]**

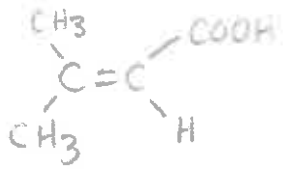
L)



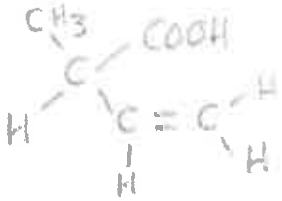
M)



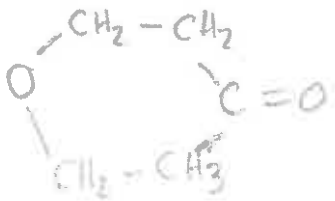
N)



P)



Q)



* only tip here is to read each description very carefully - such as for N which says does NOT show stereoisomerism and P which IS optically active so has a chiral carbon!

19

**END OF QUESTIONS**