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

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

General Certificate of Education
Advanced Level Examination
June 2010

# Chemistry CHEM4

## Unit 4 Kinetics, Equilibria and Organic Chemistry

**Thursday 17 June 2010 1.30 pm to 3.15 pm**

**For this paper you must have:**
- the Periodic Table/Data Sheet, provided as an insert (enclosed)
- 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.
- 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 accurate scientific terminology.

**Advice**
- You are advised to spend about 75 minutes on **Section A** and about 30 minutes on **Section B**.

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**DO NOT WRITE ON THIS PAGE**
**ANSWER IN THE SPACES PROVIDED**

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## Section A

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

**1** A reaction mechanism is a series of steps by which an overall reaction may proceed. The reactions occurring in these steps may be deduced from a study of reaction rates. Experimental evidence about initial rates leads to a rate equation. A mechanism is then proposed which agrees with this rate equation.

Ethanal dimerises in dilute alkaline solution to form compound **X** as shown in the following equation.

$$2CH_3CHO \longrightarrow \underset{\mathbf{X}}{CH_3CH(OH)CH_2CHO}$$

A chemist studied the kinetics of the reaction at 298 K and then proposed the following rate equation.

$$\text{Rate} = k[CH_3CHO][OH^-]$$

**1 (a)** Give the IUPAC name of compound **X**.

.....

*(1 mark)*

**1 (b)** The initial rate of the reaction at 298 K was found to be $2.2 \times 10^{-3}$ mol dm$^{-3}$ s$^{-1}$ when the initial concentration of ethanal was 0.10 mol dm$^{-3}$ and the initial concentration of sodium hydroxide was 0.020 mol dm$^{-3}$.
Calculate a value for the rate constant at this temperature and give its units.

Calculation .....

.....

.....

Units .....

*(3 marks)*

**1 (c)** The sample of **X** produced consists of a racemic mixture (racemate). Explain how this racemic mixture is formed.

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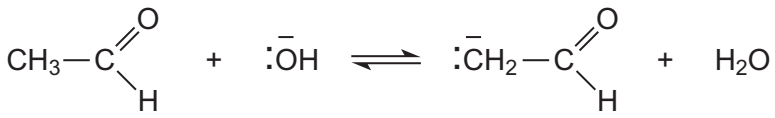
*(2 marks)*

**Question 1 continues on the next page**

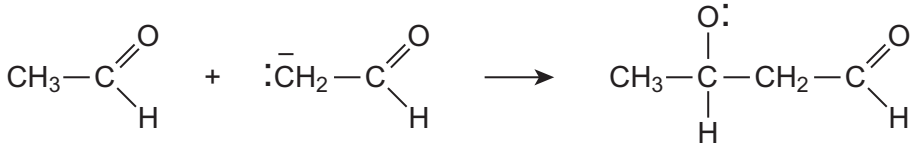
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**1 (d)** A three-step mechanism has been proposed for this reaction according to the following equations.

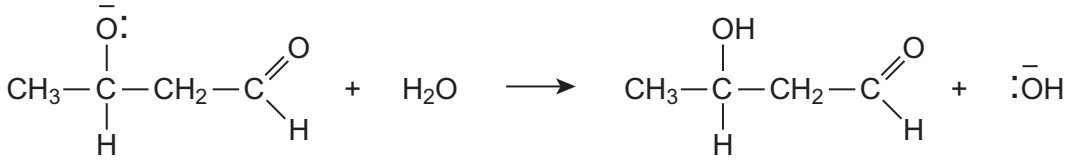
Step **1**



Step **2**



Step **3**



**1 (d) (i)** Using the rate equation, predict which of the three steps is the rate-determining step. Explain your answer.

Rate-determining step .....

Explanation .....

.....

*(2 marks)*

**1 (d) (ii)** Deduce the role of ethanal in Step **1**.

.....

*(1 mark)*

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**1 (d) (iii)** Use your knowledge of reaction mechanisms to deduce the type of reaction occurring in Step **2**.

.....

*(1 mark)*

**1 (d) (iv)** In the space below draw out the mechanism of Step **2** showing the relevant curly arrows.

*(2 marks)*

**1 (e)** In a similar three-step mechanism, one molecule of **X** reacts further with one molecule of ethanal. The product is a trimer containing six carbon atoms.

Deduce the structure of this trimer.

*(1 mark)*

**13**

Do not write outside the box

**2** The reaction of methane with steam produces hydrogen for use in many industrial processes. Under certain conditions the following reaction occurs.

$$CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g) \qquad \Delta H^{\ominus} = +165\ kJ\,mol^{-1}$$

**2 (a)** Initially, 1.0 mol of methane and 2.0 mol of steam were placed in a flask and heated with a catalyst until equilibrium was established. The equilibrium mixture contained 0.25 mol of carbon dioxide.

**2 (a) (i)** Calculate the amounts, in moles, of methane, steam and hydrogen in the equilibrium mixture.

Moles of methane .....

Moles of steam .....

Moles of hydrogen .....

*(3 marks)*

**2 (a) (ii)** The volume of the flask was 5.0 $dm^3$. Calculate the concentration, in mol $dm^{-3}$, of methane in the equilibrium mixture.

.....

.....

*(1 mark)*

**2 (b)** The table below shows the equilibrium concentration of each gas in a different equilibrium mixture in the same flask and at temperature *T*.

| gas | $CH_4(g)$ | $H_2O(g)$ | $CO_2(g)$ | $H_2(g)$ |
|---|---|---|---|---|
| concentration / mol $dm^{-3}$ | 0.10 | 0.48 | 0.15 | 0.25 |

**2 (b) (i)** Write an expression for the equilibrium constant, $K_c$, for this reaction.

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.....

.....

*(1 mark)*

Do not write outside the box

**2 (b) (ii)** Calculate a value for $K_c$ at temperature $T$ and give its units.

Calculation .....

.....

.....

.....

Units of $K_c$ .....

*(3 marks)*

**2 (c)** The mixture in part (b) was placed in a flask of volume greater than 5.0 $dm^3$ and allowed to reach equilibrium at temperature $T$.
State and explain the effect on the amount of hydrogen.

Effect on amount of hydrogen .....

Explanation .....

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*(3 marks)*

**2 (d)** Explain why the amount of hydrogen decreases when the mixture in part **(b)** reaches equilibrium at a lower temperature.

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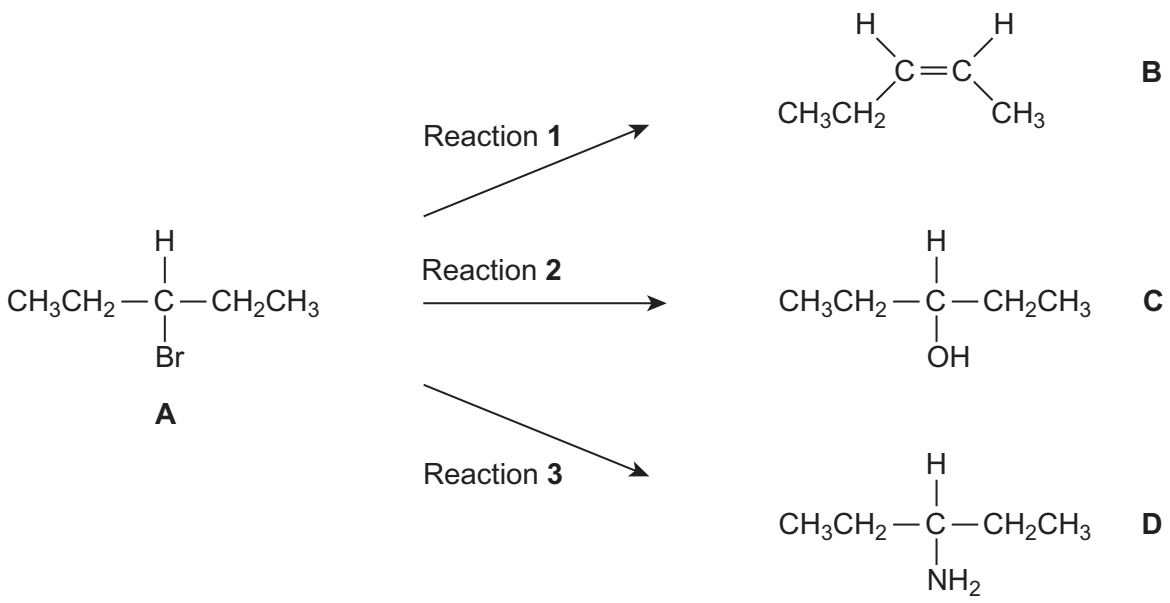
*(2 marks)*

13

**Turn over for the next question**

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**3** Haloalkanes are useful compounds in synthesis.
Consider the three reactions of the haloalkane **A** shown below.




**3 (a) (i)** Draw a **branched-chain** isomer of **A** that exists as optical isomers.

*(1 mark)*

**3 (a) (ii)** Name the type of mechanism in Reaction **1**.

.....

*(1 mark)*

**3 (a) (iii)** Give the full IUPAC name of compound **B**.

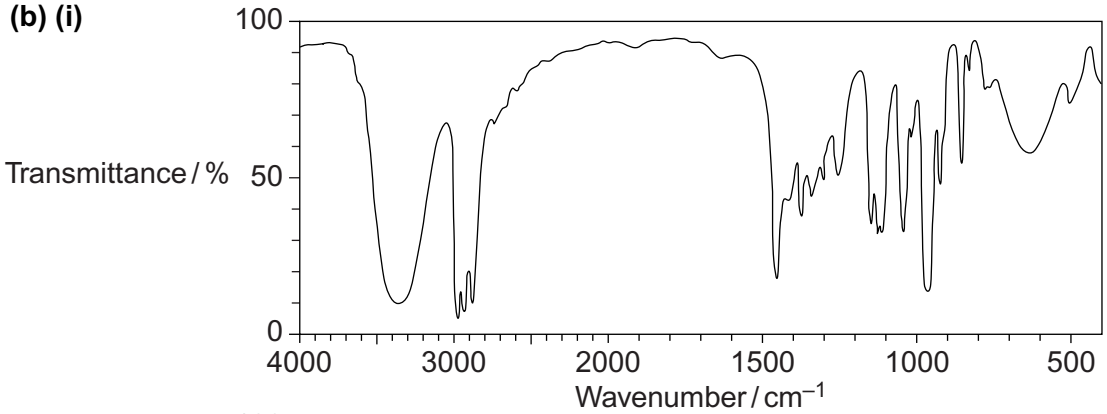
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*(1 mark)*

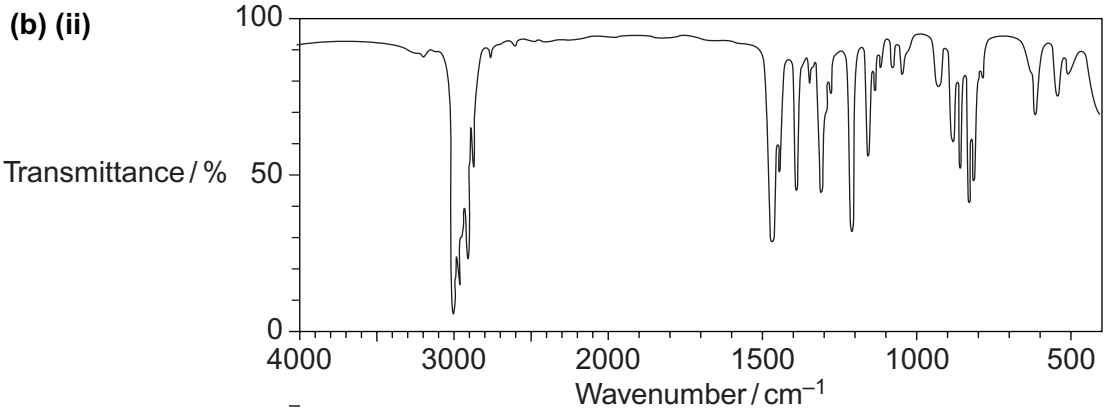
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**3 (b)** The infrared spectra shown below are those of the four compounds, **A**, **B**, **C** and **D**. Using **Table 1** on the Data Sheet, write the correct letter in the box next to each spectrum.

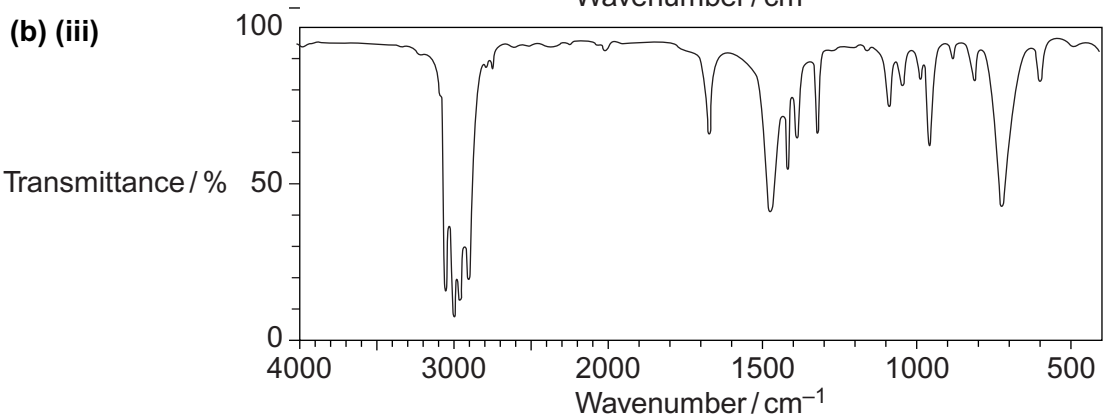
**3 (b) (i)**



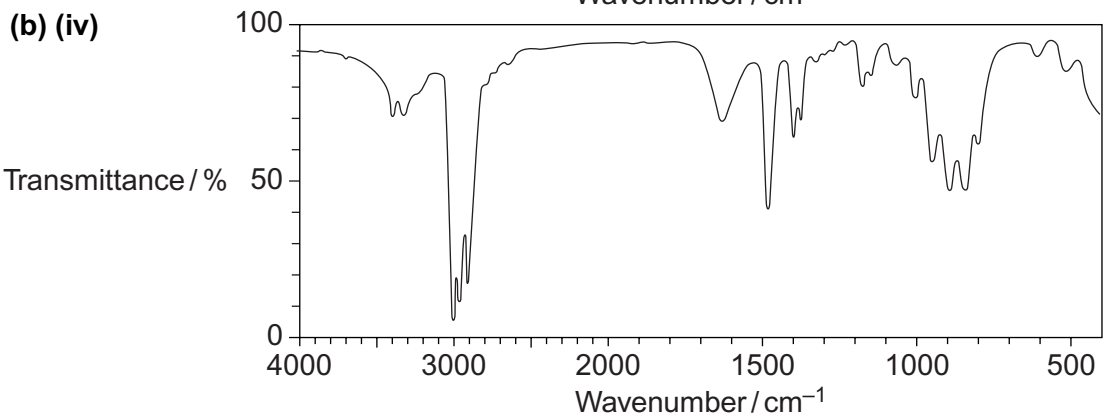

**3 (b) (ii)**




**3 (b) (iii)**




**3 (b) (iv)**




*(4 marks)*

**Question 3 continues on the next page**

**Turn over ▶**

*Do not write outside the box*

**3 (c)** Draw the repeating unit of the polymer formed by **B** and name the type of polymerisation involved.

Repeating unit

Type of polymerisation .....

*(2 marks)*

**3 (d) (i)** Outline a mechanism for Reaction **3**.

*(4 marks)*

**3 (d) (ii)** State the conditions used in Reaction **3** to form the maximum amount of the primary amine, **D**.

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*(1 mark)*

*Do not write outside the box*

**3 (d) (iii)** Draw the structure of the secondary amine formed as a by-product in Reaction **3**.

*(1 mark)*

**3 (e)** **D** is a primary amine which has three peaks in its $^{13}C$ n.m.r. spectrum.

**3 (e) (i)** An isomer of **D** is also a primary amine and also has three peaks in its $^{13}C$ n.m.r. spectrum. Draw the structure of this isomer of **D**.

*(1 mark)*

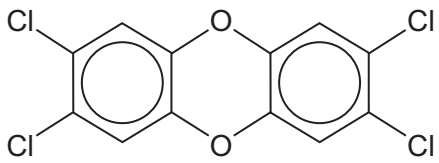
**3 (e) (ii)** Another isomer of **D** is a tertiary amine. Its $^{1}H$ n.m.r. spectrum has three peaks. One of the peaks is a doublet. Draw the structure of this isomer of **D**.

*(1 mark)*

**17**

Do not write outside the box

**4** In 2008, some food products containing pork were withdrawn from sale because tests showed that they contained amounts of compounds called dioxins many times greater than the recommended safe levels.
Dioxins can be formed during the combustion of chlorine-containing compounds in waste incinerators. Dioxins are very unreactive compounds and can therefore remain in the environment and enter the food chain.
Many dioxins are polychlorinated compounds such as tetrachlorodibenzodioxin (TCDD) shown below.




In a study of the properties of dioxins, TCDD and other similar compounds were synthesised. The mixture of chlorinated compounds was then separated before each compound was identified by mass spectrometry.

**4 (a)** Fractional distillation is **not** a suitable method to separate the mixture of chlorinated compounds before identification by mass spectrometry.
Suggest how the mixture could be separated.

.....

*(1 mark)*

**4 (b)** The molecular formula of TCDD is $C_{12}H_4O_2Cl_4$
Chlorine exists as two isotopes $^{35}Cl$ (75%) and $^{37}Cl$ (25%).
Deduce the number of molecular ion peaks in the mass spectrum of TCDD and calculate the *m*/*z* value of the most abundant molecular ion peak.

Number of molecular ion peaks .....

.....

*m*/*z* value of the most abundant molecular ion peak .....

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*(2 marks)*

**4 (c)** Suggest **one** operating condition in an incinerator that would minimise the formation of dioxins.

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*(1 mark)*

Do not write outside the box

**4 (d)** TCDD can also be analysed using $^{13}C$ n.m.r.

**4 (d) (i)** Give the formula of the compound used as the standard when recording a $^{13}C$ spectrum.

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*(1 mark)*

**4 (d) (ii)** Deduce the number of peaks in the $^{13}C$ n.m.r. spectrum of TCDD.

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*(1 mark)*

6

**Turn over for the next question**

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**5** In this question, give all values of pH to two decimal places.

Calculating the pH of aqueous solutions can involve the use of equilibrium constants such as $K_w$ and $K_a$

$K_w$ is the ionic product of water. The value of $K_w$ is $5.48 \times 10^{-14}\,mol^2\,dm^{-6}$ at 50 °C.

**5 (a) (i)** Write an expression for pH.

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*(1 mark)*

**5 (a) (ii)** Write an expression for $K_w$

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*(1 mark)*

**5 (b) (i)** Calculate the pH of pure water at 50 °C.

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*(2 marks)*

**5 (b) (ii)** Suggest why this pure water is **not** acidic.

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*(1 mark)*

**5 (b) (iii)** Calculate the pH of $0.140\,mol\,dm^{-3}$ aqueous sodium hydroxide at 50 °C.

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*(3 marks)*

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**5 (c)** Calculate the pH of the solution formed when 25.0 $cm^3$ of 0.150 mol $dm^{-3}$ aqueous sulfuric acid are added to 30.0 $cm^3$ of 0.200 mol $dm^{-3}$ aqueous potassium hydroxide at 25 °C. Assume that the sulfuric acid is fully dissociated.

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*(6 marks)*

**5 (d) (i)** Write an expression for the acid dissociation constant, $K_a$, for ethanoic acid.

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*(1 mark)*

**5 (d) (ii)** The value of $K_a$ for ethanoic acid is $1.74 \times 10^{-5}$ mol $dm^{-3}$ at 25 °C.
Calculate the pH of a 0.136 mol $dm^{-3}$ aqueous solution of ethanoic acid at this temperature.

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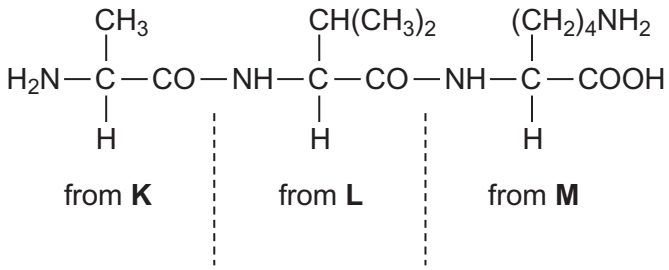
*(3 marks)*

18

**Turn over ▶**

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**6 (a)** Consider the tripeptide shown below that is formed from three amino acids, **K**, **L** and **M**.




**6 (a) (i)** Name the process by which the tripeptide is split into three amino acids.

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*(1 mark)*

**6 (a) (ii)** Give the IUPAC name for the amino acid **K**.

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*(1 mark)*

**6 (a) (iii)** Draw the structure of the zwitterion of amino acid **L**.

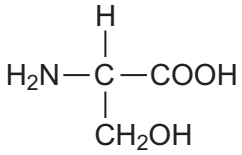
*(1 mark)*

**6 (a) (iv)** Draw the structure of the species formed by amino acid **M** at low pH.

*(1 mark)*

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**6 (b)** Consider the amino acid serine.



**6 (b) (i)** Draw the structure of the product formed when serine reacts with an excess of $CH_3Br$

*(1 mark)*

**6 (b) (ii)** Draw the structure of the dipeptide formed by two molecules of serine.

*(1 mark)*

6

**Turn over for the next question**

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## Section B

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

**7** Esters have many important commercial uses such as solvents and artificial flavourings in foods.

Esters can be prepared in several ways including the reactions of alcohols with carboxylic acids, acid anhydrides, acyl chlorides and other esters.

**7 (a)** Ethyl butanoate is used as a pineapple flavouring in sweets and cakes.

Write an equation for the preparation of ethyl butanoate from an acid and an alcohol.

Give a catalyst used for the reaction.

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*(4 marks)*

Do not write outside the box

**7 (b)** Butyl ethanoate is used as a solvent in the pharmaceutical industry.

Write an equation for the preparation of butyl ethanoate from an acid anhydride and an alcohol.

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*(3 marks)*

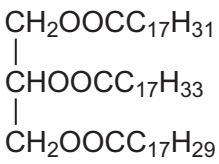
**7 (c)** Name and outline a mechanism for the reaction of $CH_3COCl$ with $CH_3OH$ to form an ester.

*(5 marks)*

**Question 7 continues on the next page**

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**7 (d)** The ester shown below occurs in vegetable oils. Write an equation to show the formation of biodiesel from this ester.



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*(3 marks)*

Do not write outside the box

**7 (e)** Draw the repeating unit of the polyester Terylene that is made from benzene-1,4-dicarboxylic acid and ethane-1,2-diol.

Although Terylene is biodegradeable, it is preferable to recycle objects made from Terylene.

Give **one** advantage and **one** disadvantage of recycling objects made from Terylene.

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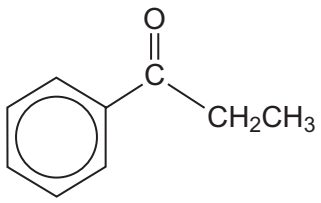
*(4 marks)*

19

**Turn over for the next question**

*Do not write outside the box*

**8** Consider compound **P** shown below that is formed by the reaction of benzene with an electrophile.




**P**

**8 (a)** Give the **two** substances that react together to form the electrophile and write an equation to show the formation of this electrophile.

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*(3 marks)*

**8 (b)** Outline a mechanism for the reaction of this electrophile with benzene to form **P**.

*(3 marks)*

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**8 (c)** Compound **Q** is an isomer of **P** that shows optical isomerism. **Q** forms a silver mirror when added to a suitable reagent.

Identify this reagent and suggest a structure for **Q**.

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*(2 marks)*

8

**END OF QUESTIONS**

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