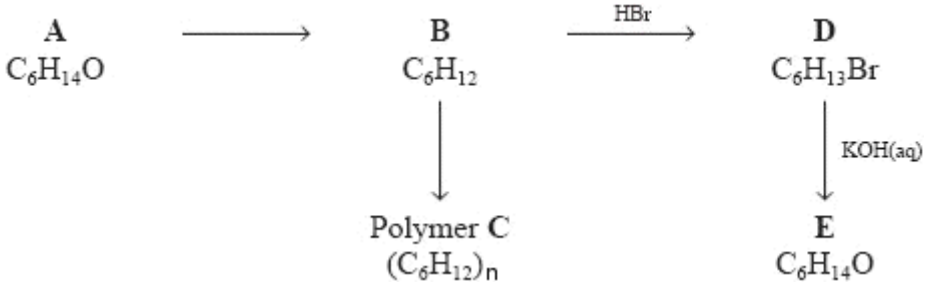
**1. The quality of written communication will be assessed in this question. To gain full marks you must explain your ideas clearly using equations and diagrams where appropriate.**

This question is about the reaction sequence shown below




(a) Compound **A** has the composition, by mass, 70.5% carbon, 13.7% hydrogen and 15.8% oxygen. Show that this percentage composition is consistent with the molecular formula $C_6H_{14}O$.

**(2)**

(b) Deduce the displayed formula for **A** showing how you used each of the following pieces of information.

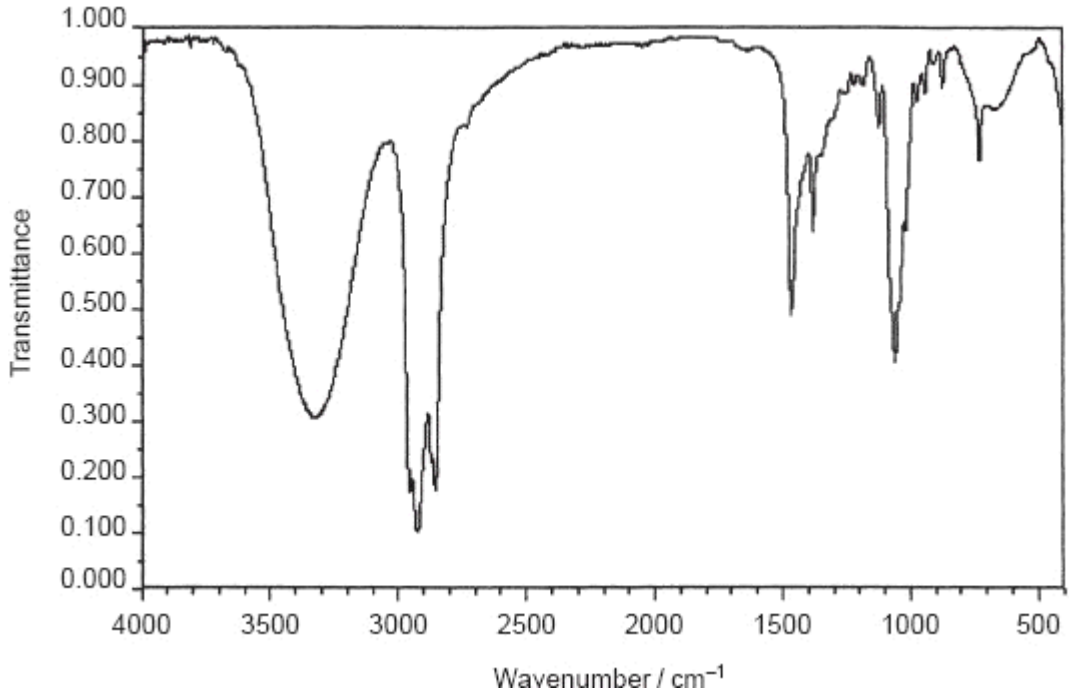
1 Infra-red spectrum.

2 Mass spectrum.

3 On dehydration, only a single isomer **B** can be formed.

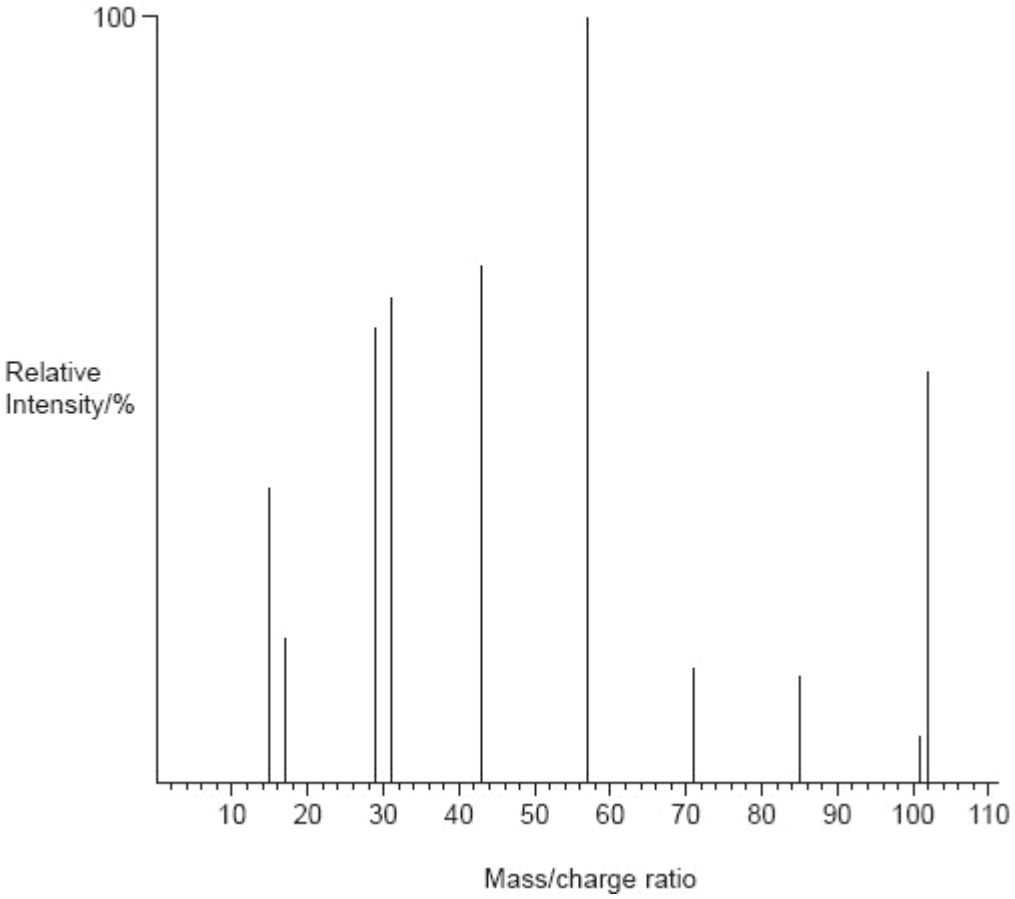
**(6)**

1 Infra-red spectrum of **A**.



2 A simplified mass spectrum of **A**.

2 A simplified mass spectrum of **A**.




(c) By drawing part of the chain formed from two monomer units, show the structural formula of the polymer **C**.

**(1)**

(d) Both compounds **D** and **E** are chiral and compound **E** is an isomer of compound **A**.

(i) Draw diagrams to show the two optical isomers of compound **D** and suggest how they could be distinguished.

.....

.....

**(2)**

(ii) Give the systematic name for compound **E**.

.....

**(1)**

(e) Would you expect the conversion of compound **D** to compound **E** to be a first or second order reaction? Justify your answer.

…….....

…….....

…….....

…….....

**(2)**

(f) Name the THREE oxidation products obtainable from compounds **A** and **E**.

…….....

…….....

…….....

**(2)**

**(Total 16 marks)**

**2.** Which of the following isomers of $C_4H_{10}O$ has a chiral centre?

**A** Butan-1-ol

**B** Butan-2-ol

**C** 2-methylpropan-1-ol

**D** 2-methylpropan-2-ol

**(Total 1 mark)**

**3.** Methanoic acid and ethanol react together to form ethyl methanoate, $HCOOC_2H_5$, and water. This reaction is reversible and can be allowed to reach equilibrium.

$$HCOOH(l) + C_2H_5OH(l) \rightleftharpoons HCOOC_2H_5\ (l) + H_2O(l) \qquad \Delta H = +45\ kJ\ mol^{-1}$$

(a) Draw the **full** structural formula of ethyl methanoate, showing all bonds.

**(1)**

(b) What type of organic compound is ethyl methanoate?

.....

**(1)**

(c) In an experiment, 3.00 mol methanoic acid, HCOOH, and 6.25 mol ethanol, $C_2H_5OH$, were mixed together. A small quantity of catalyst was added. The mixture was left for several days in a water bath to reach equilibrium at constant temperature.

(i) Complete the table.

| Number of moles in the reaction mixture | | | | |
|---|---|---|---|---|
| | HCOOH | $C_2H_5OH$ | $HCOOC_2H_5$ | $H_2O$ |
| at start of experiment | 3.00 | 6.25 | 0.00 | 0.00 |
| at equilibrium | 0.50 | | | |

**(2)**

(ii) Write an expression for the equilibrium constant, $K_c$, for the reaction.

**(1)**

(iii) Calculate $K_c$ for the reaction at the temperature of the experiment. The total volume of the equilibrium mixture was 485 $cm^3$.

**(2)**

(iv) State and explain whether $K_c$ for this reaction has units.

.....

.....

**(1)**

(d) (i) The temperature of this equilibrium mixture is **lowered**.

Explain the effect of this on the value of the equilibrium constant and **hence** on the yield of ethyl methanoate.

.....

.....

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.....

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**(4)**

(ii) A student added more catalyst to the mixture.

State, giving a reason, what would happen to the composition of the equilibrium mixture.

.....

.....

**(1)**

**(Total 13 marks)**

**4.** The substance **R** is chiefly responsible for the smell of ripe raspberries.

(a) Analysis of **R** showed that it contained 73.2% carbon, 7.3% hydrogen and 19.5% oxygen by mass.

The molar mass of **R** is 164 g $mol^{-1}$. Calculate the empirical formula **and** the molecular formula of **R**.

**(2)**

(b) The following tests were carried out on samples of **R**. For each test and its result, state what can be deduced about the structure of **R**.

(i) **R** burnt with a very sooty flame.

.....

**(1)**

(ii) **R** reacted with sodium to give off hydrogen gas.

.....

**(1)**

(iii) **R** produced a slightly acidic solution in water, but did **not** react with sodium carbonate solution.

.....

**(1)**

(iv) **R** gave an orange precipitate with Brady's reagent (2,4-dinitrophenylhydrazine).

.....

**(1)**

(v) **R** did **not** react when warmed with Benedict's solution.

.....

**(1)**

(vi) A solution of **R** rotated the plane of plane-polarised light.

.....

**(1)**

(vii) The infra-red spectrum of **R** had an absorption at 830 $cm^{-1}$.

.....

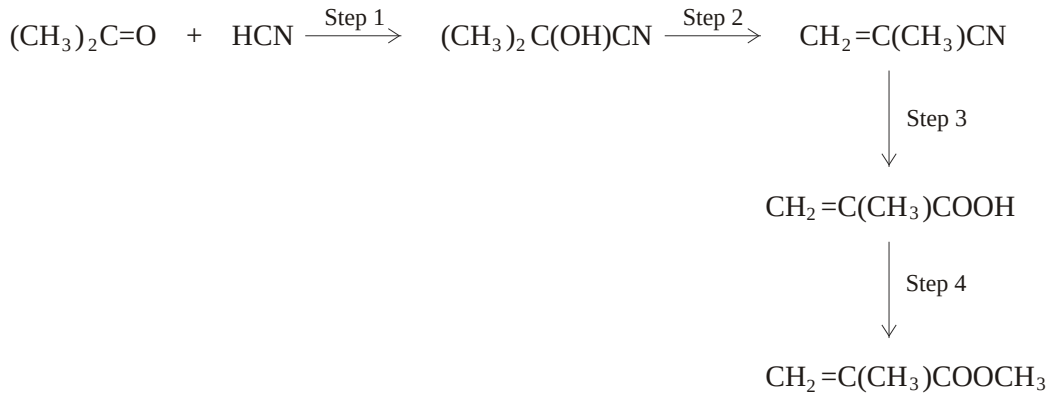
.....

**(2)**

(c) Deduce a displayed formula for **R**.

**(1)**
**(Total 11 marks)**

**5.** Consider the reaction scheme below, which shows how the compound methyl methacrylate, $CH_2=C(CH_3)COOCH_3$, is prepared industrially from propanone.




(a) (i) State the type of reaction which occurs in **Step 2**.

.....

**(1)**

(ii) Name the reagent in **Step 2**.

.....

**(1)**

(iii) State the type of reaction which occurs in **Step 3**.

.....

**(1)**

(iv) State the type of reaction which occurs in **Step 4**

.....

**(1)**

(v) Give then organic reagent required for **Step 4**.

.....

**(1)**

(b) (i) Give the mechanism for the reaction in **Step 1** between the hydrogen cyanide and propanone.

**(4)**

(ii) The reaction in (b)(i) is carried out at a carefully controlled pH. Given that hydrogen cyanide is a weak acid, suggest why this reaction occurs more slowly at both high and low concentrations of hydrogen ions.

High $H^+$ concentration

.....

.....

Low $H^+$ concentration

.....

.....

**(2)**

(c) Methyl methacrylate polymerises in a homolytic addition reaction to form the industrially important plastic, Perspex.

(i) Identify the type of species that initiates this polymerisation.

.....

**(1)**

(ii) Draw a sufficient length of the Perspex polymer chain to make its structure clear.

**(2)**

(iii) Suggest why it is **not** possible to quote an exact value for the molar mass of Perspex, but only an average value.

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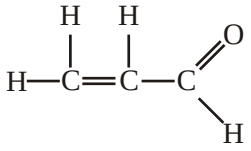
.....

**(1)**

**(Total 15 marks)**

**6.** The structural formula of the compound propenal is shown below.




In this question, assume that the functional groups in the molecule behave independently.

(a) (i) State what is observed when propenal reacts with 2,4-dinitrophenylhydrazine.

.....

**(1)**

(ii) Give the structural formula of the compound formed in the reaction in (a)(i).

**(2)**

(b) Explain why propenal has three peaks in its low-resolution n.m.r. spectrum. Suggest the relative areas under these peaks.

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**(3)**

(c) Propenal reacts with hydrogen cyanide as shown by the following equation

$$CH_2{=}CHCHO + HCN \longrightarrow CH_2{=}CHCH(OH)CN$$

(i) Write the mechanism for the reaction.

**(4)**

(ii) Name the type of mechanism involved in this reaction.

.....

**(1)**

(d) Propenal reacts with hydrogen bromide as shown by the following equation

$$CH_2{=}CHCHO + HBr \longrightarrow CH_3CHBrCHO$$

(i) Write the mechanism for the reaction.

**(3)**

(ii) Name the type of mechanism involved in this reaction.

.....

**(1)**

(e) The C═O and C═C bonds have the same electronic structure but their reactions occur by different mechanisms. Explain why this is so.

.....

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.....

**(3)**
**(Total 18 marks)**

**7.** (a) The table below shows the acid dissociation constants, $K_a$, of three carboxylic acids.

| Acid | Structural formula | $K_a$/ mol dm$^{-3}$ |
|---|---|---|
| Chloroethanoic | $CH_2ClCO_2H$ | $1.3 \times 10^{-3}$ |
| Dichloroethanoic | $CHCl_2CO_2H$ | $5.0 \times 10^{-2}$ |
| Trichloroethanoic | $CCl_3CO_2H$ | $2.3 \times 10^{-1}$ |

(i) Write an expression for the acid dissociation constant, $K_a$, of chloroethanoic acid.

**(1)**

(ii) Calculate the pH of a 0.0010 mol $dm^{-3}$ solution of chloroethanoic acid, making the usual assumptions.

**(3)**

(iii) Which acid would have the lowest pH at a concentration of 0.0010 mol $dm^{-3}$? Use both the data and the structure of the acids to justify your answer. No further calculation is required.

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**(2)**

(b) Chloroethanoic acid, $CH_2ClCO_2H$, reacts with methanol, $CH_3OH$, in the presence of a sulphuric acid catalyst.

(i) Draw the **displayed** formula and give the name of the **organic** product formed.

Displayed Formula

Name .....

**(3)**

(ii) What name is given to the functional group formed in this organic product?

.....

**(1)**

(iii) What type of reagent is methanol in this reaction? Explain why it is able to behave in this way and describe how it attacks the chloroethanoic acid.
You may find it helpful to draw a diagram.

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**(3)**

(iv) How would you convert the organic product of the reaction between chloroethanoic acid and methanol back into the original compounds?

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.....

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**(2)**
**(Total 15 marks)**

**8.** This question is about propanal, $CH_3CH_2CHO$, propanone, $CH_3COCH_3$, and propanoic acid, $CH_3CH_2CO_2H$.

(a) Explain why all three compounds are soluble in water.

.....

.....

**(1)**

(b) Propanal and propanone contain the carbonyl group.

State a chemical test for the presence of this group. Give the result of a positive test.

Test .....

Result .....

**(2)**

(c) Propanal can be distinguished from propanone by its oxidation to propanoic acid.

(i) Name an oxidising agent you would use.

.....

.....

**(1)**

(ii) State the colour change you would observe during the oxidation.

From ..... to .....

**(1)**

(iii) State how propanone can be distinguished from propanal using infra-red spectra.

You are not expected to give actual absorption values, but you should indicate the bonds in the molecules which would give rise to the distinguishing absorptions.

.....

.....

**(1)**

(d) A useful test for carboxylic acids is that they will neutralise sodium carbonate solution.

Write a balanced equation, including state symbols, for the neutralisation of sodium carbonate solution by propanoic acid.

**(2)**

(e) Give the names of TWO other inorganic chemicals that could be used to make sodium propanoate from propanoic acid.

.....

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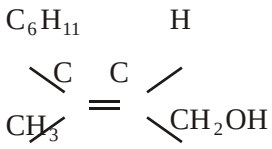
**(2)**
**(Total 10 marks)**

**9.** Geraniol is a fragrance obtained from rose petals. Its formula is

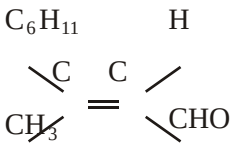


(a) Explain why geraniol exhibits geometric isomerism.

.....

**(2)**

(b) Geraniol can be oxidised to citral, which is the main ingredient of lemon grass oil. Citral's formula can be written as:



Identify the reagents and suggest conditions necessary for the preparation of citral from geraniol.

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**(3)**

(c) State what you would **see** when citral reacts with:

(i) bromine dissolved in water;

.....

**(1)**

(ii) a solution of 2,4-dinitrophenylhydrazine;

.....

**(1)**

(iii) Fehling's solution.

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**(1)**

**(Total 8 marks)**

**10.** Iodine and propanone react together in the presence of dilute hydrochloric acid according to the equation:

$$CH_3COCH_3 + I_2 \xrightarrow{H^+(aq)} CH_3COCH_2I + HI$$

The rate of reaction can be measured by recording the decrease in the concentration of the iodine.

The results of four experiments are given below:

| **Experiment** | **initial $[CH_3COCH_3]$ /mol dm$^{-3}$** | **initial $[I_2]$ /mol dm$^{-3}$** | **initial $[H^+]$ /mol dm$^{-3}$** | **Rate /mol dm$^{-3}$ s$^{-1}$** |
|---|---|---|---|---|
| **1** | 0.40 | 0.0040 | 0.40 | $1.5 \times 10^{-5}$ |
| **2** | 0.80 | 0.0040 | 0.40 | $3.0 \times 10^{-5}$ |
| **3** | 0.40 | 0.0020 | 0.40 | $1.5 \times 10^{-5}$ |
| **4** | 0.80 | 0.0020 | 0.80 | $6.0 \times 10^{-5}$ |

(a) (i) State the order of the reaction with respect to $CH_3COCH_3$, $I_2$ and $H^+$. Justify your answer.

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**(4)**

(ii) Give the value of the overall order of the reaction.

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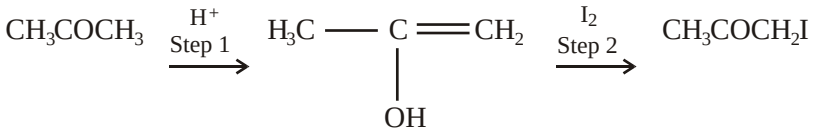
**(1)**

(b) Write the rate equation for the reaction.
Calculate the value of the rate constant and give its units.

**(3)**

(c) A suggested mechanism for the reaction is shown below:




Use your answers to (a)(i) to compare the relative rates of the two steps.
Explain your reasoning.

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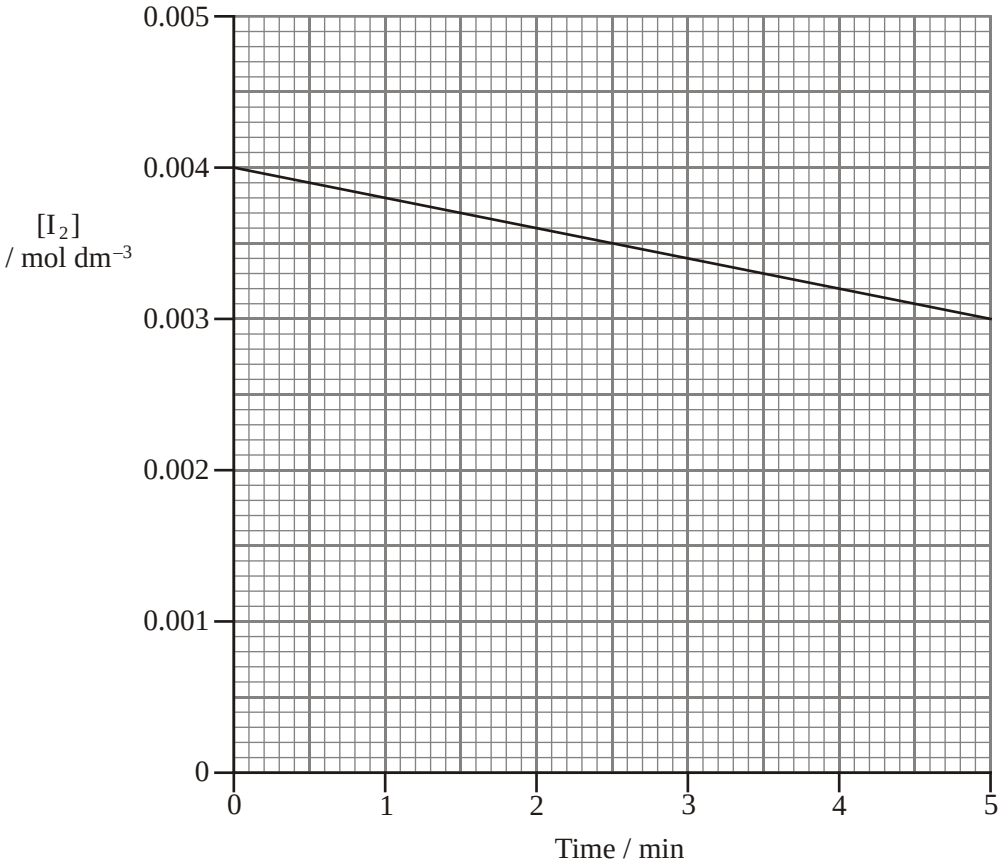
**(2)**

(d) The graph below represents the change in concentration of iodine in Experiment 1 over a 5 minute period.




Add labelled lines to represent Experiment 2 and Experiment 3.

**(3)**

(e) (i) Propanone can also react with iodine to form a pale yellow precipitate of tri-iodomethane. What other reagent is needed for this reaction?

.....

**(1)**

(ii) Propanone reacts with lithium tetrahydridoaluminate, $LiAlH_4$, in dry ether. Suggest which reagent needs to be added to liberate the final organic product. Draw the **full** structural formula of this product.

**(2)**

(f) State and explain how the n.m.r. spectra of propanone and propanal would differ.

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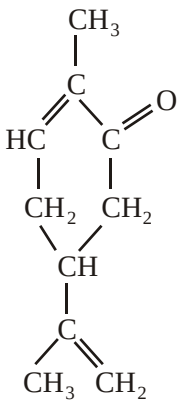
**(2)**

**(Total 18 marks)**

**11.** Carvone is an essential oil found as two enantiomers in nature; one enantiomer is found in caraway seed oil, the other in spearmint oil. The structural formula is:




(a) (i) **On the formula above,** show with an asterisk (*) the chiral centre in carvone.

**(1)**

(ii) Each of the enantiomers of carvone is optically active. State how such activity is detected.

.....

**(1)**

(b) Give a test and the observed result to show that carvone is a carbonyl compound and a further test to show it is not an aldehyde.

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.....

.....

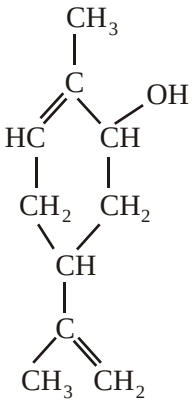
**(4)**

(c) In a particular preparation carvone was reduced with hydrogen and a platinum catalyst; 2.70 g of carvone reacted with 864 $cm^3$ of hydrogen. Calculate the reacting mole ratio of carvone to hydrogen and hence give, with reasons, the structural formula of the reduction product.

(The molar mass of carvone is 150 g $mol^{-1}$; 1 mol of gas occupies 24 $dm^3$ under the conditions of the experiment.)

**(5)**

(d) A different reducing agent, lithium tetrahydridoaluminate(III), $LiAlH_4$, gives compound **Z** from carvone. **Z** has the structure




(i) State the conditions used for reduction using $LiAlH_4$.

.....

**(2)**

(ii) Suggest why $LiAlH_4$ reduces the C==O bond but not the C==C bond.

.....

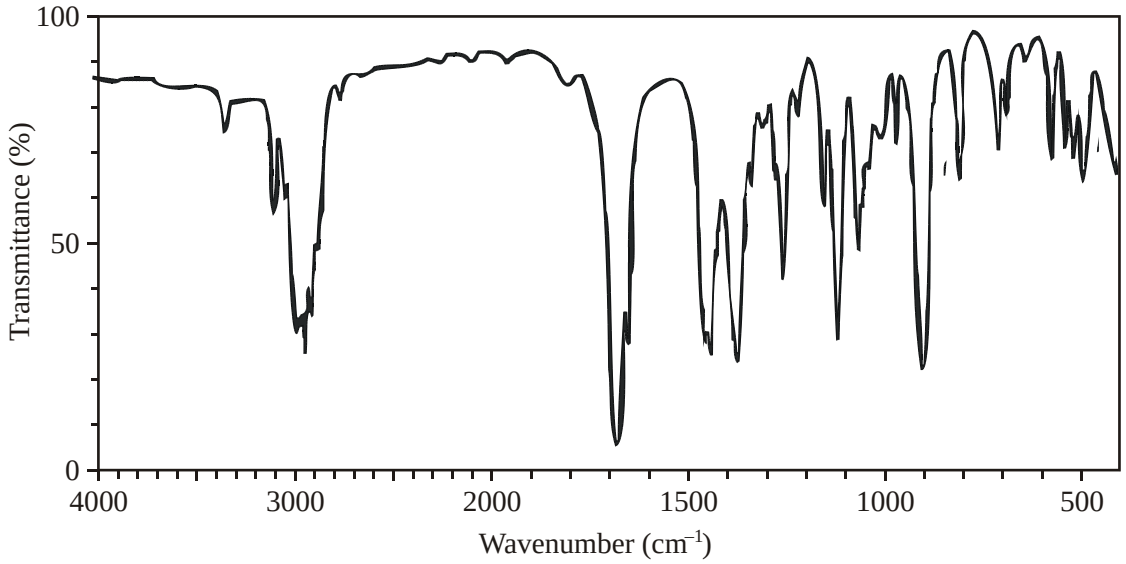
.....

.....

**(2)**

(iii) The infra-red spectra of carvone and of **Z,** together with a table of absorption frequencies for specified bonds are shown below.

**Infra-red spectrum of carvone**




**Infra-red spectrum of Z**

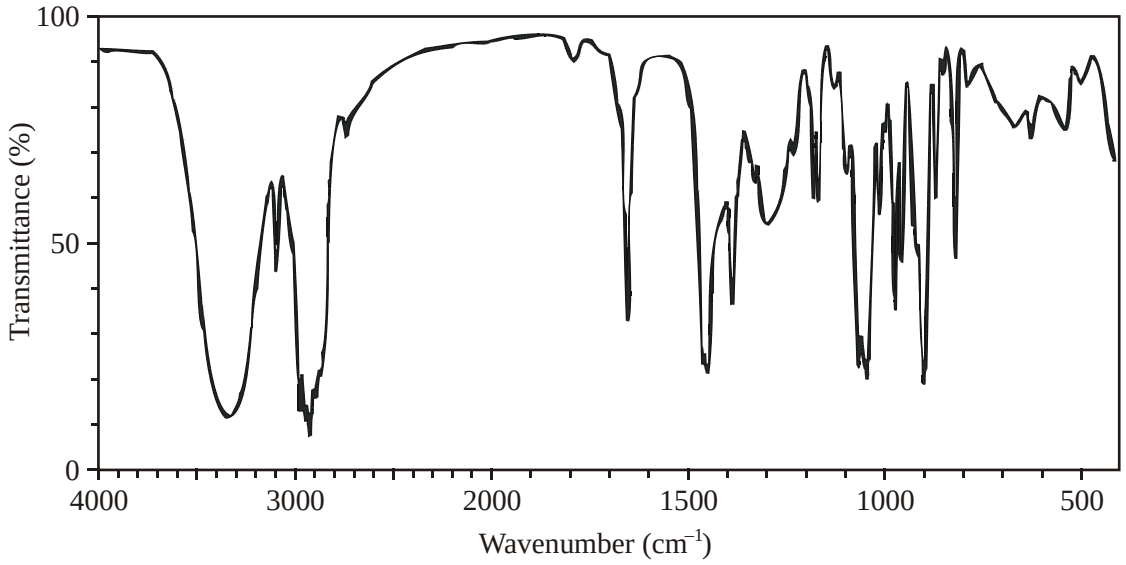


**Table of infra-red absorption frequencies for specified bonds**

| Bond | Assignment | | Wavenumbers /$cm^{-1}$ |
|---|---|---|---|
| C—H | alkanes | | 2850–2950 |
| | | alkenes, arenes | 3000–3100 |
| C==O | aldehydes, ketones, esters, carboxylic acids | | 1681–1750 |
| O—H | free | | 3580–3670 |
| | | hydrogen bonded in alcohols or phenols | 3230–3550 |
| | | Hydrogen bonded in carboxylic acids | 2500–3300 |

Use evidence from the spectra to show that carvone has been reduced.

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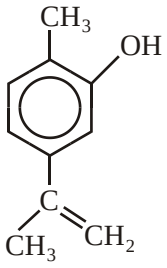
**(3)**

(e) **Z,** which is an alcohol, could be converted into the phenol




Phenols and alcohols have some reactions in common and some that are different.
Name a reagent that reacts with phenols and with alcohols in a different manner.
Write equations for any reactions that occur between your chosen reagent and phenol and ethanol. If there is no reaction with one or other hydroxy compound you must say so.

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.....

.....

**(3)**

**(Total 21 marks)**

**12.** This question is about butanal, $CH_3CH_2CH_2CHO$, and several related compounds.

(a) What would you **see** when Brady's reagent is added to a sample of butanal?

.....

**(1)**

(b) **F**, **G** and **H** are three isomers of butanal which are each tested with sodium, Benedict's reagent and Brady's reagent. The results are shown in the table below.

Key: ✓ = positive result
✗ = negative result

| | Sodium | Benedict's reagent | Brady's reagent |
|---|---|---|---|
| **F** | ✗ | ✓ | ✓ |
| **G** | ✗ | ✗ | ✓ |
| **H** | ✓ | ✗ | ✗ |

Suggest structural formulae for **F**, **G** and **H**.

**F**

**G**

**H**

**(3)**

(c) An ester with the formula, $CH_3CH_2CH_2CO_2CH_2CH_3$, is heated under reflux with aqueous sodium hydroxide.

(i) Give ONE advantage of "heating under reflux", rather than simply boiling the two liquids together in a beaker.

.....

.....

.....

**(1)**

(ii) Name the **ester**.

.....

**(1)**

(iii) Name the TWO **products** of this reaction.

.....

**(2)**

(iv) What type of reaction is taking place?

.....

**(1)**

**(Total 9 marks)**

**13.** This question is about compounds with the molecular formula $C_4H_8O$.

(a) (i) Draw the displayed formulae of TWO isomers, **A** and **B**, which are both aldehydes. Give their systematic names.

**A** **B**

Name ..... .....

**(4)**

(ii) Suggest an instrumental method by which these isomers, **A** and **B**, could be distinguished.

Outline how the results would differ.

.....

.....

.....

**(2)**

(b) Substance **C**, butanone, is another isomer of $C_4H_8O$.

(i) Name a reagent which results in the same observation when it reacts with all three isomers, **A, B** and **C**.

Reagent .....

.....

Observation .....

.....

.....

**(2)**

(ii) Name a reagent where the resulting observation for **C** would be different from that for **A** and **B.**

Reagent .....

.....

Observation with **C** .....

.....

.....

Observation with **A** and **B** .....

.....

.....

**(3)**

(c) (i) Suggest structural formulae for TWO more isomers of $C_4H_8O$, **D** and **E**, which are cyclic and react with sodium to give off hydrogen.

**D** **E**

**(2)**

(ii) Both **A** and **B** can be oxidised to carboxylic acids. These acids will then react with either of the isomers **D** or **E** in the presence of a strong acid as a catalyst.

What is the name given to the products of this type of reaction?

.....

**(1)**

(iii) For one of the carboxylic acids formed from **A** or **B** and one of the isomers **D** or **E**, draw a displayed formula of the product formed when they react together.

**(2)**
**(Total 16 marks)**

**14.** (a) Propanoic acid, $CH_3CH_2COOH$, can be prepared from carbon dioxide and an organic reagent.

Name this organic reagent and state the conditions for the preparation.

Reagent .....

Conditions .....

.....

**(3)**

(b) Describe what you would **see** and write the equations for the reactions of propanoic acid with:

(i) a solution of sodium carbonate

Observation .....

Equation .....

**(2)**

(ii) solid phosphorus pentachloride.

Observation .....

Equation .....

**(2)**

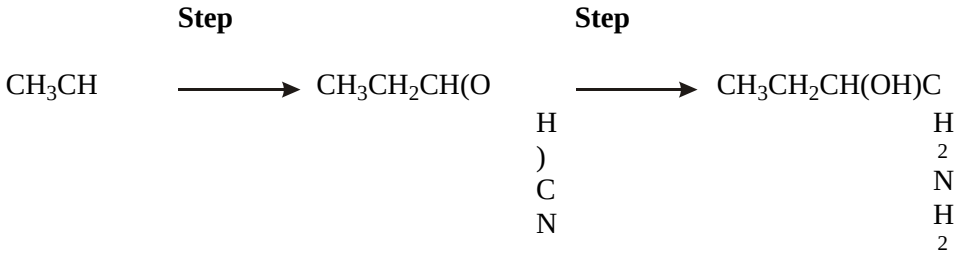
(c) Propanoic acid can also be prepared from propanal, $CH_3CH_2CHO$. State the reagents for this conversion.

Reagents .....

**(2)**

(d) 1-aminobutan-2-ol, $CH_3CH_2CH(OH)CH_2NH_2$, is an active ingredient in some deodorant sprays.

It can be prepared from propanal by the following two-step process.




(i) For **Step 1**

State the reagents and conditions.

.....

.....

Name the type of reaction.

.....

**(3)**

(ii) For **Step 2**

State the reagents and conditions.

.....

.....

Name the type of reaction.

.....

**(3)**

(e) Write the structural formula of the organic product formed when 1-aminobutan-2-ol reacts with:

(i) ethanoyl chloride, $CH_3COCl$

**(2)**

(ii) hydrochloric acid.

**(1)**

(f) 1-aminobutan-2-ol exists as two isomers with the same structural formula.

Identify the type of isomerism and draw the TWO isomers, showing clearly the difference between them.

Type of isomerism .....

**(3)**
**(Total 21 marks)**

**15.** Two compounds, **X** and **Y**, are isomers with the formula $C_4H_8O$. They can be prepared from different alcohols, each containing four carbon atoms.

Both compounds produce a yellow precipitate with Brady's reagent (2,4-dinitrophenylhydrazine).

When the compounds are warmed with Benedict's solution, **X** forms a red-brown precipitate but **Y** does not change.

When **X** is oxidised it produces $CH_3CH_2CH_2CO_2H$.

(a) Draw displayed formulae for **X** and **Y**.

| | Formula |
|---|---|
| **X** | |
| **Y** | |

**(2)**

(b) Name compound **Y**.

.....

**(1)**

(c) Compound **Y** mixes readily with water. Suggest a reason for this.

.....

.....

**(1)**

(d) (i) Draw the structural formula of an alcohol which could be used to prepare a sample of **Y**.

**(1)**

(ii) What reagents would you use to prepare **Y** from the alcohol?

.....

**(1)**

(e) (i) The infra-red spectra of **X** and **Y** were compared with the infra-red spectrum of ethanol.

The spectra of **X** and **Y** contain an absorption peak which is not present in the spectrum of ethanol.

Identify the bond in **X** and **Y** which causes this peak.

.....

**(1)**

(ii) The spectrum of ethanol contains a broad peak which does not occur in the spectra of **X** or **Y**. Suggest which bond causes this peak and why the peak is broad.

.....

.....

**(2)**

**(Total 9 marks)**

**16.** (a) Propan-1ol, $C_2H_5CH_2OH$ can be oxidised to propanoic acid, $C_2H_5COOH$.

(i) State the names of the reagents necessary for this conversion.

.....

.....

**(2)**

(ii) 5.67 of propan-1-o1 was oxidised in a reaction with a 64% yield. Calculate the mass of propanoic acid produced.

**(3)**

(b) Propanoic acid is a weak acid. It ionises according to the equation:

$$C_2H_5COOH(aq)+H_2O(l) \rightleftharpoons C_2H_5COO^-(aq) + H_3O^+(aq) \quad \Delta H^{\ominus} = +6\text{kJ mol}^{-1}$$

(i) State and explain the effect on the position of this equilibrium of:

an increase in temperature;

.....

.....

**(2)**

an addition of solid sodium propanoate.

.....

.....

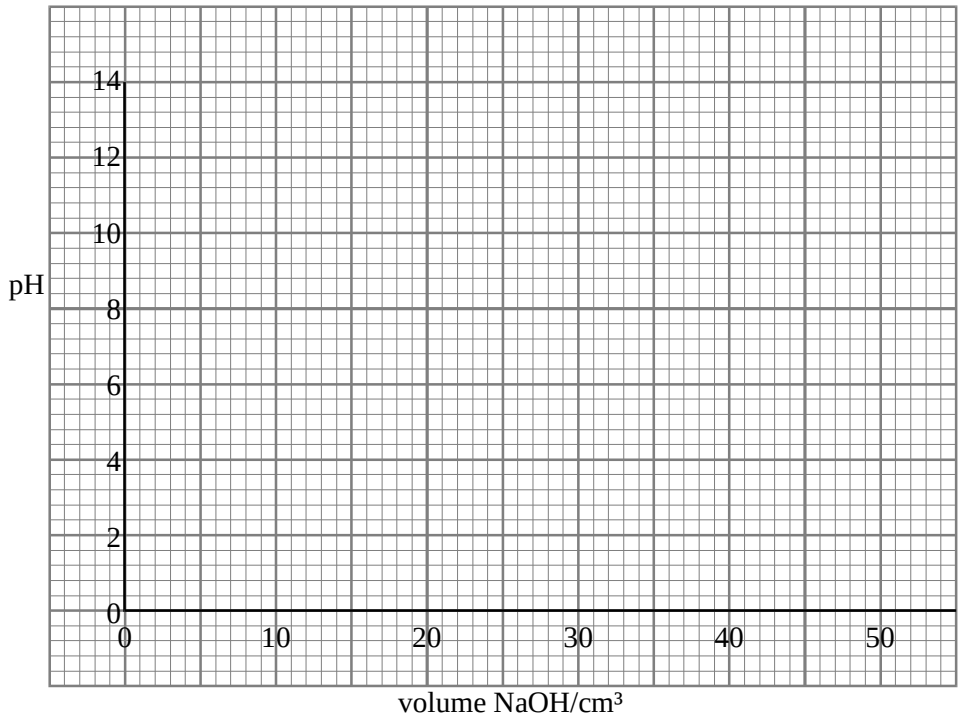
**(2)**

(ii) How does the addition of sodium propanoate affect the pH of the solution of propanoic acid?

.....

**(1)**

(c) (i) Sketch, with reasonable accuracy, how the pH changes during the titration of $25cm^3$ of a weak acid, such as propanoic acid, with sodium hydroxide solution of the same concentration.



(ii) The table contains some data about three indicators.

| Indicator | $pK_{ind}$ | Acid colour | Alkaline colour |
|---|---|---|---|
| Bromophenol blue | 4.0 | yellow | blue |
| Bromothymol blue | 7.0 | yellow | blue |
| Thymol blue | 8.9 | yellow | blue |

State which of these indicators would be best for this titration. Give a reason for your choice.

Indicator .....

Reason .....

.....

**(2)**

(d) The standard enthalpy change of neutralisation of some acids with sodium hydroxide is tabulated below:

| Acid | $\Delta H^{\ominus}$/kJ mol$^{-1}$ |
|---|---|
| Propanoic acid, $C_2H_5COOH$ | –51 |
| Hydrocyanic acid, HCN | –12 |
| Hydrochloric acid, HCl | –57 |
| Nitric acid, $HNO_3$ | –57 |

(i) Why are the values for the enthalpy change of neutralisation of the two strong acids the same?

.....

.....

**(1)**

(ii) Why is the enthalpy change of neutralisation of hydrocyanic acid so much less than that of hydrochloric acid?

.....

.....

**(2)**
**(Total 19 marks)**

**17.** This question concerns the compounds linked by the reaction scheme

$C_4H_8O \rightarrow C_4H_{10}O \rightarrow C_4H_9Br \rightarrow C_4H_8$

**A** **B** **C** **D**

**A** reacts with 2,4-dinitrophenylhydrazine to give a solid **E** which, when recrystallised, has a melting temperature of 126°C. The melting temperatures of some 2,4-dinitrophenylhydrazine derivatives are listed below:

| Compound | Melting temperature of 2,4-dinitrophenylhydrazine derivatives/°C |
|---|---|
| propanone | 126 |
| butanone | 116 |
| propanal | 155 |
| methyl propanal | 187 |
| butanal | 126 |

The infra red spectrum of **A** has a peak at 1720 $cm^{-1}$, but none at about 3500$cm^{-1}$ or 1650$cm^{-1}$. The spectrum of **B** has a very broad peak at 3500$cm^{-1}$, but none at about 1720$cm^{-1}$ or 1650$cm^{-1}$.

Some typical infra red absorption wavenumbers are shown in the table below:

| Bond | Wavenumber/$cm^{-1}$ |
|---|---|
| O–H | 3600 to 3300 |
| C–O | 1200 to 1150 |
| C=C | 1680 to 1620 |
| C=O | 1750 to 1680 |

(a) (i) Why must solid **E** be recrystallised before its melting temperature is measured?

.....

**(1)**

(ii) What bond in **A** is responsible for the peak at 1720cm$^{-1}$?

.....

**(1)**

(iii) Why is the peak at 3500cm$^{-1}$ in the spectrum of **B** very broad?

.....

.....

**(2)**

(iv) Draw the structural formula of **A** and **B**.

**A**

**B**

**(2)**

(b) (i) Name the reagent and the solvent used for the conversion of **C** to **D**.

.....

.....

**(2)**

(ii) Draw the structural formula of **D**.

**(1)**

(iii) Draw the structural formula of the major product of the addition of HBr to **D**.

**(1)**

(iv) Suggest why the reaction in (iii) does not produce **C** as the major product.

.....

.....

**(1)**
**(Total 11 marks)**

**18.** Butan-1-ol, a primary alcohol, can be oxidised to form the aldehyde, butanal.

(a) Give the name or formula of an oxidising agent used in this reaction and of the other reagent required.

Oxidising Agent

.....

Other Reagent

.....

**(2)**

(b) A possible by-product of this reaction is butanoic acid, $CH_3CH_2CH_2CO_2H$, which is classified as a weak acid.

Explain what is meant by a **weak acid**.

Acid .....

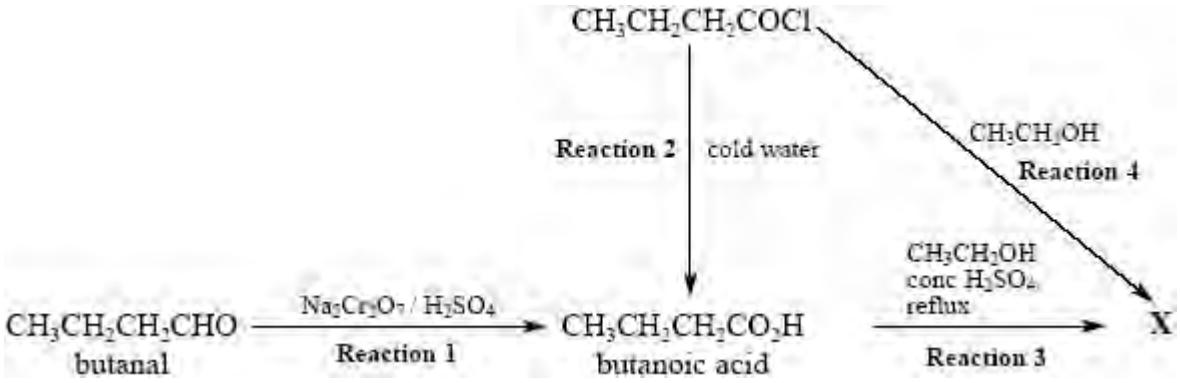
.....

Weak .....

.....

**(2)**
**(Total 4 marks)**

**19.** Study the reaction scheme below, then answer the questions that follow.




(a) (i) Butanal contains a carbonyl group. State a chemical test for a carbonyl group and describe the result of the test.

Test .....

Result .....

**(2)**

(ii) An isomer of butanal also possesses a carbonyl group, but cannot be oxidised by acidified sodium dichromate(VI). Give the **structural** formula of this isomer and its name.

Structural formula .....

Name .....

**(2)**

(iii) Another isomer of butanal contains a carbonyl group and **can** be oxidised by acidified sodium dichromate(VI). Draw the **displayed** formula of this isomer.

**(1)**

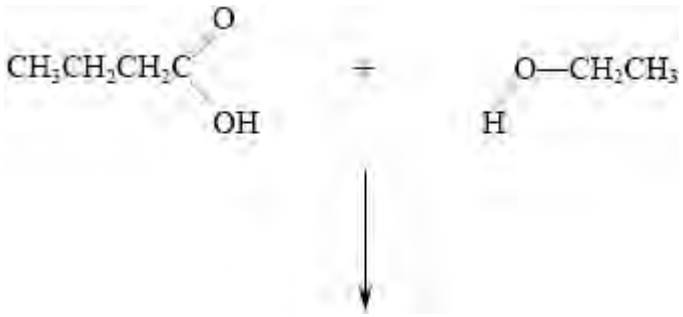
(b) Compound **X** is a colourless liquid that smells of pineapples.

(i) To what class of compounds does **X** belong?

.....

**(1)**

(ii) Ethanol, $C_2H_5OH$, reacts with butanoic acid to form compound **X**. Complete the diagram below to show the structural formula of **X** and the other product.




**(1)**

(iii) Give the name of compound **X**.

.....

**(1)**

(iv) What type of attacking species is ethanol in this reaction?

.....

**(1)**

(c) Describe what you would expect to **see** during **Reaction 2**.

.....

.....

.....

**(1)**

(d) Explain why **Reaction 4** is far more vigorous than **Reaction 3**.

.....

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.....

.....

**(2)**

**(Total 12 marks)**

**20.** Dichloroethanoic acid reacts with pent-1-ene as shown by the following equation:

$$CHCl_2CO_2H(l) + C_5H_{10}(l) \rightleftharpoons CHCl_2CO_2C_5H_{11}(l)$$

(a) Give the name of the product of this reaction and also the name for the new functional group it contains.

.....

.....

**(2)**

(b) In an experiment to determine the equilibrium constant, 1.00 mol of dichloroethanoic acid was mixed with 2.30 mol of pent-1-ene. The total volume remained at 300 $cm^3$ throughout. When equilibrium had been reached, it was found that 0.40 mol of dichloroethanoic acid was left.

(i) List the steps in the experiment you would carry out to determine the concentration of dichloroethanoic acid present at equilibrium.

.....

.....

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**(4)**

(ii) Give the expression for the equilibrium constant, $K_c$, for this reaction.

**(1)**

(iii) Complete the table for the number of moles and concentrations at equilibrium.

| Substance | Number of moles at start | Number of moles at equilibrium | Concentration at equilibrium /mol $dm^{-3}$ |
|---|---|---|---|
| $CHCl_2COOH$ | 1.00 | 0.40 | 1.33 |
| $C_5H_{10}$ | 2.30 | | |
| $CHCl_2COOC_5H_{11}$ | 0 | | |

**(3)**

(iv) Calculate the value of $K_c$, and give its units.

**(3)**
**(Total 13 marks)**

**21.** This question concerns the reactions of some compounds of nitrogen.

(a) The ammonium ion reacts with water and behaves as an acid.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

(i) Identify the TWO conjugate acid-base pairs in the spaces provided.

acid 1 ..... base 1 .....

acid 2 ..... base 2 .....

**(1)**

(ii) Write the expression for the acid dissociation constant, $K_a$, of the ammonium ion.

**(1)**

(iii) A solution of ammonium chloride has a pH of 5.00 at 25°C.
$K_a$ for the ammonium ion is $5.62 \times 10^{-10}$ mol dm$^{-3}$ at 25°C.

Calculate the concentration of this solution. State any assumptions you have made.

**(4)**

(iv) Use the following table and your answer from part (iii) to suggest a suitable indicator for the titration of ammonia solution with hydrochloric acid. Justify your answer.

| **Indicator** | **p$K_{In}$** |
|---|---|
| thymol blue | 1.7 |
| methyl red | 5.1 |
| phenolphthalein | 9.3 |

.....

.....

**(2)**

(b) Hydrogen cyanide is a weak acid in aqueous solution.

Write an equation to show why aqueous solutions of cyanide ions are alkaline.

.....

**(1)**

(c) Hydrogen cyanide reacts with propanal as follows:

$$CH_3CH_2CHO + HCN \rightarrow CH_3CH_2CH(OH)CN$$

Propanal is reacted with a solution of potassium cyanide, KCN, containing a little dilute sulphuric acid.

(i) What **type** of reaction is this?

.....

**(1)**

(ii) Give the mechanism for the reaction.

**(3)**

(iii) It is important that the pH is neither too acidic nor too alkaline if a good yield of the product is to be obtained. Explain why this is so.

.....

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.....

.....

**(2)**

(d) In an investigation of the kinetics of the nucleophilic substitution reaction between 1-chloropropane and potassium cyanide in aqueous ethanolic solution, the reaction was found to be first order with respect to 1-chloropropane and first order with respect to cyanide ions.

(i) Give the rate equation for the reaction.

.....

**(1)**

(ii) Write a mechanism for the reaction that is consistent with this rate equation.

**(3)**
**(Total 19 marks)**

**22.** This question is about the pineapple flavouring used in sweets. It is an ester with the formula $C_3H_7COOCH_3$, which can be broken down into butanoic acid and methanol when mixed with hydrochloric acid.

The following equilibrium is set up:

$$C_3H_7COOCH_3(l) + H_2O(l) \rightleftharpoons C_3H_7COOH(l) + CH_3OH(l)$$

(a) Give the name of this ester.

.....

**(1)**

(b) Why does the ester have a comparatively low boiling point compared to the other three substances in the equation?

.....

.....

.....

**(1)**

(c) What is the name given to this type of reaction?

.....

**(1)**

(d) Suggest the reasons why manufacturers choose to use the chemically manufactured pineapple flavouring rather than the natural product and why consumers might prefer to choose the natural product.

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.....

**(4)**

(e) In an experiment, 10.2 g (0.10 mol) of the ester was mixed with 18 $cm^3$ of 1.0 mol $dm^{-3}$ hydrochloric acid and left until equilibrium had been reached. The hydrochloric acid acts as a catalyst and contains 18 g (1 mol) of water. At equilibrium, 4.4 g of butanoic acid was found to be present.

Molar mass of butanoic acid = 88 g; assume the total volume at equilibrium is 30 $cm^3$.

Give the expression for the equilibrium constant, $K_c$, for this equilibrium and calculate its value. Explain why it has no units.

.....

.....

.....

**(5)**
**(Total 12 marks)**

**23.** This question concerns the following compounds containing four carbon atoms.

**A** Butanoic acid, $CH_3CH_2CH_2COOH$

**B** Butanone, $CH_3COCH_2CH_3$

**C** Propyl methanoate, $HCOOCH_2CH_2CH_3$

**D** Butanoyl chloride, $CH_3CH_2CH_2COCl$

Select, from A to D, the compound that

(a) can be made by the oxidation of a primary alcohol.

**A**

**B**

**C**

**D**

**(1)**

(b) would be expected to react most rapidly with ethanol.

**A**

**B**

**C**

**D**

**(1)**

(c) would have 4 different chemical shifts in its nmr spectrum and a broad absorption between 2500–3300 $cm^{-1}$ in its infrared spectrum.

**A**

**B**

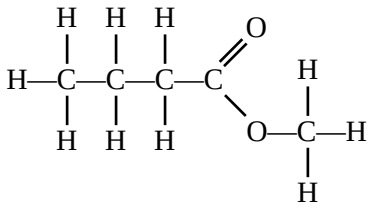
**C**

**D**

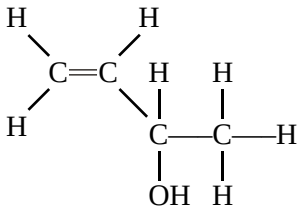
**(1)**
**(Total 3 marks)**

**24.** Consider the following compounds.

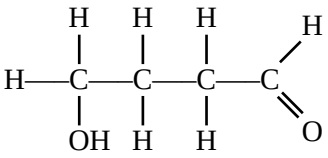
**Compound X**



**Compound Y**



**Compound Z**



(a) Name the functional groups present in the three compounds **X**, **Y** and **Z**.

| Compound | Functional groups present |
|---|---|
| **X** | |
| **Y** | |
| **Z** | |

**(3)**

(b) Compounds **X**, **Y** and **Z** are heated separately with alkaline ammoniacal silver nitrate solution.

Draw the full structural formula, showing all bonds, of any **organic product** formed.

If a reaction does **not** occur, write **'no reaction'**.

**Product from X**

**Product from Y**

**Product from Z**

**(3)**

(c) Draw the formulae of the organic products formed by the reaction of

(i) **X**, $CH_3CH_2CH_2COOCH_3$, with aqueous sodium hydroxide solution.

**(2)**

(ii) **Z**, $CH_2(OH)CH_2CH_2CHO$, with hydrogen cyanide.

**(1)**
**(Total 9 marks)**

**25.** (a) Name the homologous series to which the compound $CH_3CH_2CHO$ belongs.

.....

**(1)**

(b) Describe what you would **see** if a sample of $CH_3CH_2CHO$ was warmed with Benedict's solution.

.....

.....

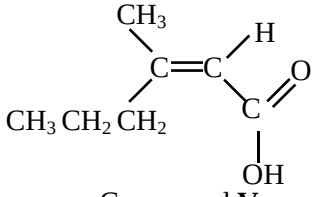
.....

.....

.....

**(2)**
**(Total 3 marks)**

**26.** Compound **V**, the structure of which is shown below, is found in human sweat.




Compound **V**

(a) Compound **V** contains two functional groups.

Identify both functional groups and state a chemical test for each. The result of each test should also be included in your answer.

One functional group in **V** .....

Test and result .....

.....

.....

The other functional group in **V** .....

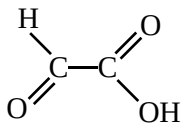
Test and result .....

.....

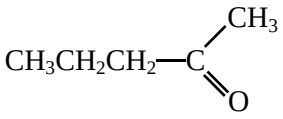
.....

**(4)**

(b) Compound **V** can be converted into two carbonyl compounds **W** and **X**, shown below.



**W**



**X**

(i) Which of the compounds **W** or **X** would react when warmed with Fehling's solution to give a red precipitate? Justify your answer.

.....

.....

**(1)**

(ii) Compound **W** can be reduced in two steps to compound **Y** of molecular formula $C_2H_6O_2$.

Identify **Y**.

.....

**(1)**

(iii) Compound **W** can be oxidised to compound **Z** of molecular formula $C_2H_2O_4$.

Identify **Z**.

.....

**(1)**

(c) The compounds **Y** and **Z** react together under suitable conditions to form a polymer.

(i) Draw the structural formula of the repeating unit for the polymer formed.

**(2)**

(ii) What type of polymerisation reaction occurs between compounds **Y** and **Z**?

.....

**(1)**

**(Total 10 marks)**

**27.** (a) Draw the displayed formula of a branched chain ketone containing **five** carbon atoms.

**(2)**

(b) Give the systematic name for this ketone.

.....

**(1)**

(c) What is the **molecular** formula of the alcohol this ketone could be made from?

.....

**(1)**

(d) An alcohol can be converted into a ketone by oxidation with sodium dichromate(VI) and sulphuric acid.

Explain why refluxing the mixture first, rather than immediately distilling the product over from the beginning, results in a higher yield of the ketone.

.....

.....

.....

.....

**(1)**

**(Total 5 marks)**