UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Level

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| CANDIDATE NAME | | | | | | | | | |
| CENTRE NUMBER | | | | | | CANDIDATE NUMBER | | | | |

*7179008534*

**CHEMISTRY** **9701/42**

Paper 4 Structured Questions **May/June 2012**

**2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your Centre number, candidate number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

**Section A**
Answer **all** questions.

**Section B**
Answer **all** questions.

You may lose marks if you do not show your working or if you do not use appropriate units.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

| For Examiner's Use | |
|---|---|
| 1 | |
| 2 | |
| 3 | |
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| 7 | |
| 8 | |
| Total | |

This document consists of **17** printed pages and **3** blank pages.


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## Section A

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

**1 (a) (i)** What is meant by the term *enthalpy change of hydration*, $\Delta H^{\ominus}_{hyd}$?

.....

.....

**(ii)** Write an equation that represents the $\Delta H^{\ominus}_{hyd}$ of the $Mg^{2+}$ ion.

.....

**(iii)** Suggest a reason why $\Delta H^{\ominus}_{hyd}$ of the $Mg^{2+}$ ion is greater than $\Delta H^{\ominus}_{hyd}$ of the $Ca^{2+}$ ion.

.....

.....

**(iv)** Suggest why it is impossible to determine the enthalpy change of hydration of the oxide ion, $O^{2-}$.

.....

.....

[5]

**(b)** The enthalpy change of solution for $MgCl_2$, $\Delta H^{\ominus}_{sol}(MgCl_2(s))$, is represented by the following equation.

$$MgCl_2(s) + aq \rightarrow Mg^{2+}(aq) + 2Cl^{-}(aq)$$

Describe the simple apparatus you could use, and the measurements you would make, in order to determine a value for $\Delta H^{\ominus}_{sol}(MgCl_2(s))$ in the laboratory.

.....

.....

.....

.....

.....

..... [4]

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**(c)** The table below lists data relevant to the formation of $MgCl_2(aq)$.

| enthalpy change | value / kJ mol$^{-1}$ |
|---|---|
| $\Delta H_f^{\ominus}(MgCl_2(s))$ | –641 |
| $\Delta H_f^{\ominus}(MgCl_2(aq))$ | –801 |
| lattice energy of $MgCl_2(s)$ | –2526 |
| $\Delta H_{hyd}^{\ominus}(Mg^{2+}(g))$ | –1890 |

By constructing relevant thermochemical cycles, use the above data to calculate a value for

**(i)** $\Delta H_{sol}^{\ominus}(MgCl_2(s))$,

$\Delta H_{sol}^{\ominus}$ = ..... kJ mol$^{-1}$

**(ii)** $\Delta H_{hyd}^{\ominus}(Cl^-(g))$.

$\Delta H_{hyd}^{\ominus}$ = ..... kJ mol$^{-1}$
[3]

**(d)** Describe and explain how the solubility of magnesium sulfate compares to that of barium sulfate.

.....

.....

.....

.....

..... [4]

[Total: 16]

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**[Turn over**

**2** Carbon monoxide, CO, occurs in the exhaust gases of internal combustion engines.

**(a) (i)** Suggest a dot-and-cross diagram for CO.

**(ii)** Suggest **one** reason why CO is produced in addition to $CO_2$ in some internal combustion engines.

.....

.....

**(iii)** Carbon monoxide can be removed from the exhaust gases by a catalytic converter. Write an equation for a reaction that occurs in a catalytic converter that removes CO.

.....

[3]

**(b)** The standard enthalpy change of formation, $\Delta H_f^{\ominus}$, of CO is $-111\ kJ\ mol^{-1}$, and that of $CO_2$ is $-394\ kJ\ mol^{-1}$.
Calculate the standard enthalpy change of the following reaction.

$$C(s) + CO_2(g) \rightarrow 2CO(g)$$

$\Delta H^{\ominus}$ = ..... $kJ\ mol^{-1}$

[2]

**(c)** Carbon monoxide reacts with a ruthenium(II) chloride complex according to the equation

$$[Ru(H_2O)_2Cl_4]^{2-} + CO \rightarrow [Ru(H_2O)(CO)Cl_4]^{2-} + H_2O.$$

**(i)** Describe the *type of reaction* that is occurring here.

.....

**(ii)** During the reaction, the colour of the solution changes from deep blue to green.
Explain the origin of colour in transition element complexes, and why different complexes often have different colours.

.....

.....

.....

.....

.....

.....

.....

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The following table shows how the initial rate of this reaction varies with different concentrations of reactants.

| $[[Ru(H_2O)_2Cl_4]^{2-}]$ / mol dm$^{-3}$ | [CO] / mol dm$^{-3}$ | rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|
| $1.1 \times 10^{-2}$ | $1.7 \times 10^{-3}$ | $1.6 \times 10^{-7}$ |
| $1.6 \times 10^{-2}$ | $3.6 \times 10^{-3}$ | $2.3 \times 10^{-7}$ |
| $2.2 \times 10^{-2}$ | $2.7 \times 10^{-3}$ | $3.2 \times 10^{-7}$ |

**(iii)** Use these data to determine the order of reaction with respect to each reagent, and write the rate equation for the reaction.

.....

.....

.....

.....

.....

.....

There are three possible mechanisms for this reaction, which are described below.

mechanism 1 $[Ru(H_2O)_2Cl_4]^{2-} + CO \xrightarrow{\text{slow}} [Ru(H_2O)(CO)Cl_4]^{2-} + H_2O$

mechanism 2 $[Ru(H_2O)_2Cl_4]^{2-} \xrightarrow{\text{slow}} [Ru(H_2O)Cl_4]^{2-} + H_2O$

$[Ru(H_2O)Cl_4]^{2-} + CO \xrightarrow{\text{fast}} [Ru(H_2O)(CO)Cl_4]^{2-}$

mechanism 3 $[Ru(H_2O)_2Cl_4]^{2-} + CO \xrightarrow{\text{slow}} [Ru(H_2O)_2(CO)Cl_4]^{2-}$

$[Ru(H_2O)_2(CO)Cl_4]^{2-} \xrightarrow{\text{fast}} [Ru(H_2O)(CO)Cl_4]^{2-} + H_2O$

**(iv)** Deduce which of these three mechanisms is consistent with the rate equation you suggested in part **(iii)**. Explain your answer.

.....

.....

.....

[10]

[Total: 15]

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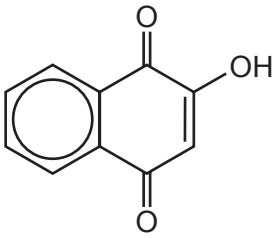
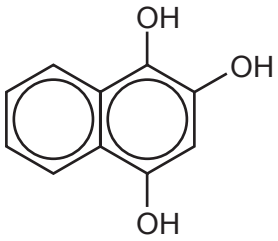
**3** Lawsone is the dye that is extracted from the henna plant, *Lawsonia inermis*. Although its natural colour is yellow, lawsone reacts with the proteins in hair and skin to produce the characteristic brown henna colour.

Lawsone can readily be reduced to 1,2,4-trihydroxynaphthalene, compound **A**.




+ $2H^+$ + $2e^-$ $\rightleftharpoons$




$E^\ominus = +0.36\,V$

lawsone

1,2,4-trihydroxynaphthalene, **A**

**(a) (i)** Name **three** functional groups in lawsone.

.....

.....

**(ii)** Describe a reaction (reagent with conditions) that you could use to distinguish lawsone from compound **A**.
Describe the observations you would make with **both** compounds.

.....

.....

.....

.....

**(iii)** Suggest a reagent that could be used to convert lawsone into compound **A** in the laboratory.

.....

.....

**(iv)** Draw the structural formula of the compound formed when lawsone is reacted with $Br_2(aq)$.

[6]

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**(b)** Compound **A** can be oxidised to lawsone by acidified $K_2Cr_2O_7$.

**(i)** Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for this reaction.

.....

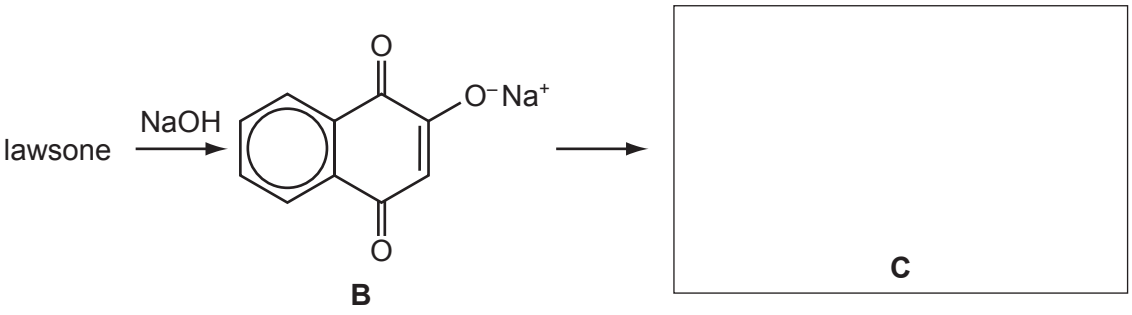
**(ii)** Construct an equation for this reaction. Use the molecular formulae of lawsone, $C_{10}H_6O_3$, and compound **A**, $C_{10}H_8O_3$, in your equation.

.....

**(iii)** When 20.0 $cm^3$ of a solution of compound **A** was acidified and titrated with 0.0500 mol $dm^{-3}$ $K_2Cr_2O_7$, 7.50 $cm^3$ of the $K_2Cr_2O_7$ solution was needed to reach the end-point.
Calculate [**A**] in the solution.

[**A**] = ..... mol $dm^{-3}$
[5]

**(c)** When lawsone is reacted with NaOH(aq), compound **B** is produced.

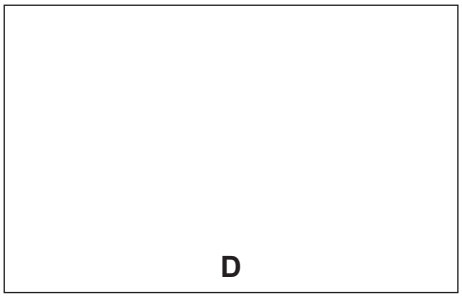



Reacting **B** with ethanoyl chloride, $CH_3COCl$, produces compound **C**, with the molecular formula $C_{12}H_8O_4$.

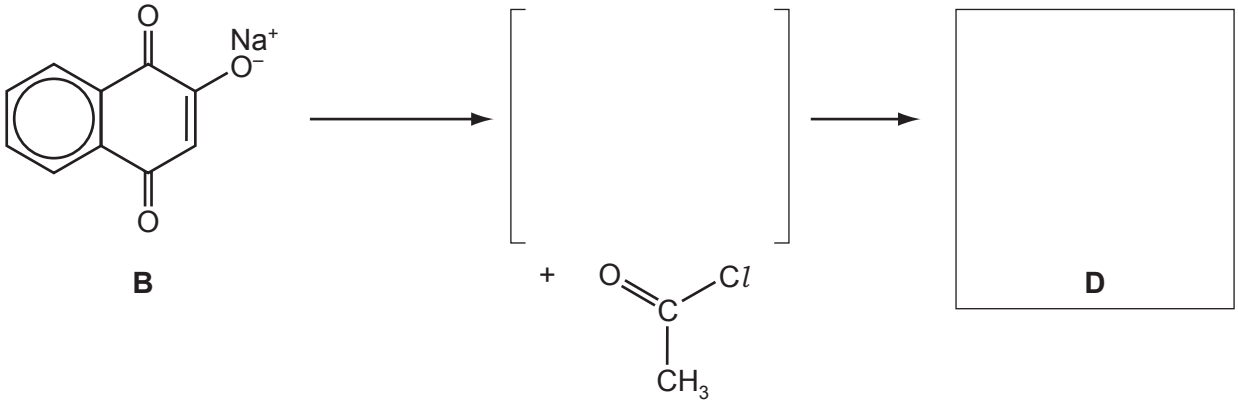
**(i)** Suggest the identity of compound **C**, and draw its structure in the box above.

Another compound, **D**, in addition to **C**, is produced in the above reaction. **D** is an isomer of **C** which contains the same functional groups as **C**, but in different positions.

**(ii)** Suggest a possible structure for **D**.




**(iii)** Suggest a mechanism for the formation of **D** from **B** and ethanoyl chloride by drawing relevant structures and curly arrows in the following scheme.




[3]

[Total: 14]

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**4** **(a)** Describe and explain the trend in the volatilities of the halogens $Cl_2$, $Br_2$ and $I_2$.

.....

.....

.....

..... [3]

**(b)** For each of the following pairs of compounds, predict which compound has the higher boiling point, and explain the reasons behind your choice.
Use diagrams in your answers where appropriate.

**(i)** $H_2O$ and $H_2S$

**(ii)** $CH_3-CH_2-CH_3$ and $CH_3-O-CH_3$

[4]

**(c)** Briefly explain the shape of the $SF_6$ molecule, drawing a diagram to illustrate your answer.

[2]

[Total: 9]

For Examiner's Use

**5** **(a)** Describe and explain how the acidities of $CHCl_2CO_2H$ and $CH_2ClCO_2H$ compare to each other, and to the acidity of ethanoic acid.

.....

.....

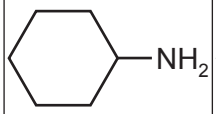
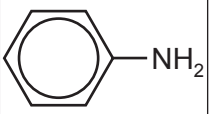
.....

.....

.....

[3]

**(b)** For each of the following pairs of compounds, suggest one chemical test (reagents and conditions) that would distinguish between them.
State the observations you would make with each compound, writing 'none' if appropriate.

| first compound | second compound | test (reagents and conditions) | observation with first compound | observation with second compound |
|---|---|---|---|---|
|  |  | | | |
| $CH_3CH_2COCl$ | $CH_3COCH_2Cl$ | | | |
| $CH_3CH_2CHO$ | $CH_3COCH_3$ | | | |

[7]

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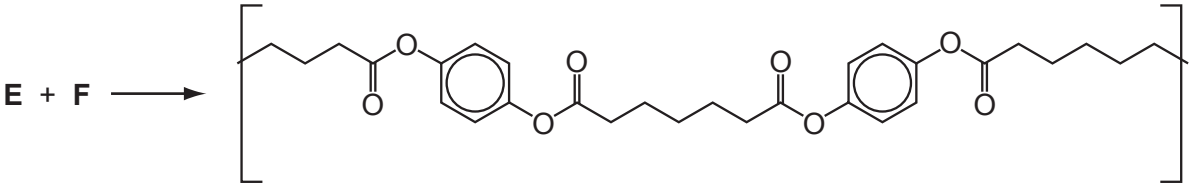
**(c)** The following diagram shows a section (not a repeat unit) of a polymer, **G**, that can be made from the two monomers **E** and **F**.




polymer **G**

**(i)** What *type of polymerisation* made this polymer?

.....

**(ii)** Draw the structures of the two monomers **E** and **F**.

**E**

**F**

**(iii)** Suggest the conditions needed to make polymer **G** from **E** and **F** in the laboratory.

.....

.....

.....

**(iv)** One of the monomers, **E** or **F**, could be changed to make a more rigid polymer of a similar chemical type to **G**.
Suggest which of your two monomers could be changed, and suggest a structure for the new monomer.

Monomer to be changed (**E** or **F**) .....

Structural formula of the new monomer

[6]

[Total: 16]

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## Section B

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

*For Examiner's Use*

**6** **(a)** The table shows the structures of four amino acids found in proteins in the human body. Complete the table by indicating the type of tertiary interaction each side-chain is most likely to have when its amino acid is present in a protein chain.

| amino acid | structure | type of interaction |
|---|---|---|
| alanine | $H_2NCH(CH_3)CO_2H$ | |
| cysteine | $H_2NCH(CH_2SH)CO_2H$ | |
| lysine | $H_2NCH((CH_2)_4NH_2)CO_2H$ | |
| serine | $H_2NCH(CH_2OH)CO_2H$ | |

[3]

**(b)** Metal ions play an important role in the biochemistry of the human body. For each of the following metal ions, outline one of the places in the body it can be found and its main role there.

iron .....

.....

.....

potassium .....

.....

.....

zinc .....

.....

.....

[3]

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**(c)** Many chemical reactions at a cellular level require energy in order to take place. This energy is largely provided by the breakdown of one particular compound.

**(i)** Write an equation showing the breakdown of this compound.

.....

**(ii)** What type of chemical reaction is this?

.....

[2]

**(d)** Cystic fibrosis is a genetic disease caused by a mutation in the DNA sequence resulting in the production of a faulty version of an important protein which acts as an ion pump in the cell membrane. This pump controls the flow of ions into and out of cells.
People with the faulty protein show two major symptoms.

- water is retained in cells in the lungs resulting in the formation of a thick, sticky mucous outside the cells;
- their sweat is very salty.

Based on the information given for people with cystic fibrosis,

**(i)** suggest which ions are involved in the ion flow,

.....

.....

**(ii)** suggest and explain what type of bonding might result in thick or sticky mucous.

.....

.....

[2]

[Total: 10]

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**7** NMR and X-ray crystallography are two important analytical techniques which can be used to study the structure and function of molecules.

**(a)** Nuclear magnetic resonance, NMR, arises because protons possess spin which generates a small magnetic moment. When an external magnetic field is applied the protons can align with or against the external field. If they are given a small amount of energy in the radio frequency range each can be 'promoted' so that their magnetic moment opposes the external field.

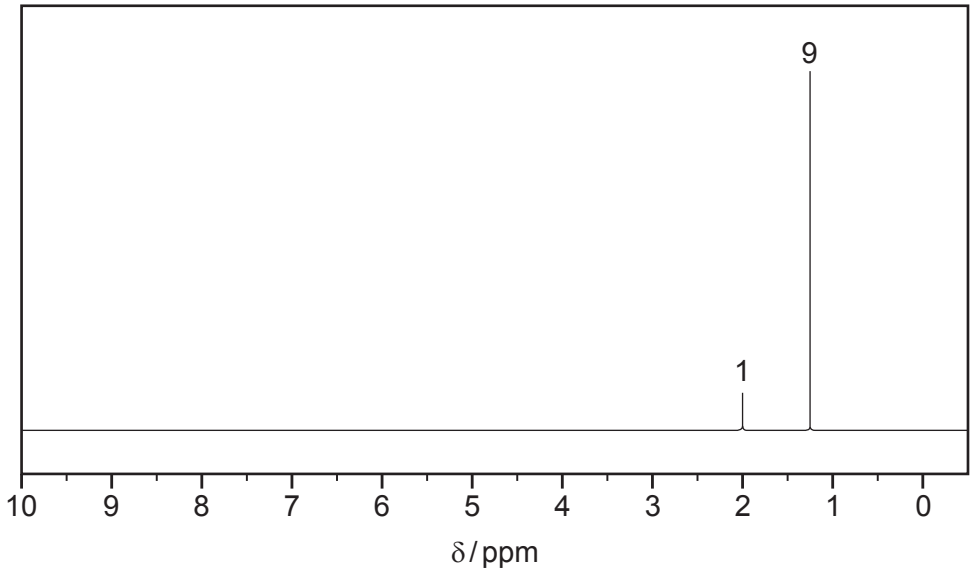
Two factors can influence the energy required for this promotion. What are they?

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

**(ii)** .....

[2]

**(b)** A compound, **J**, has the formula $C_4H_{10}O$. The NMR spectrum of **J** is shown.




**(i)** Indicate the groups responsible for each peak and hence deduce the structure of **J**.

peak at 1.26 δ ..... peak at 2.0 δ .....

structure of **J**

**(ii)** There are three other isomers of **J** containing the same functional group as **J**. Draw the structures of two of these three isomers and indicate how many different chemical shifts each would show in its NMR spectrum.

isomer 1 isomer 2

number of groups of peaks ..... number of groups of peaks .....

[6]

**(c)** X-ray crystallography can be useful in gathering information about the structure of large organic molecules, such as nucleic acids.

**(i)** Which element will show up most strongly in the X-ray crystallography of a nucleic acid? Explain your answer.

.....

.....

**(ii)** X-ray crystallography will **not** detect hydrogen atoms. Explain why this is so.

.....

.....

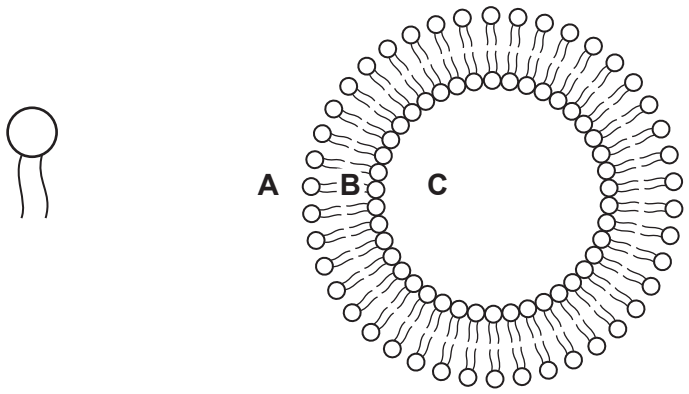
[2]

[Total: 10]

For Examiner's Use

**8** The developments in nanotechnology and drug delivery over the past 20 years have been wide-ranging.

**(a)** One of the most widespread developments for delivering a range of pharmaceutical products has been the use of liposomes. These are artificially created spheres made from phospholipids which have an ionic phosphate 'head' and two hydrocarbon 'tails'.




phospholipid liposome

Liposomes have also been used to carry pharmaceuticals such as vitamins and moisturisers used in cosmetic anti-ageing creams. Otherwise these pharmaceuticals may be oxidised or dehydrated if exposed to air.

**(i)** State in which area of the liposome, **A**, **B** or **C**, each of the following types of molecule would be carried.

**a hydrophilic moisturiser** .....

**a fat-soluble vitamin** .....

**(ii)** For one of the areas, **A**, **B** or **C**, suggest why this would **not** be an appropriate place to carry either molecule.

.....

.....

.....

[3]

**(b)** When liposomes are used to carry drugs, their main purpose is to prevent the drug molecules from being broken down on passage through the digestive system.

**(i)** Name a functional group present in drug molecules that might be broken down by acid in the stomach.

.....

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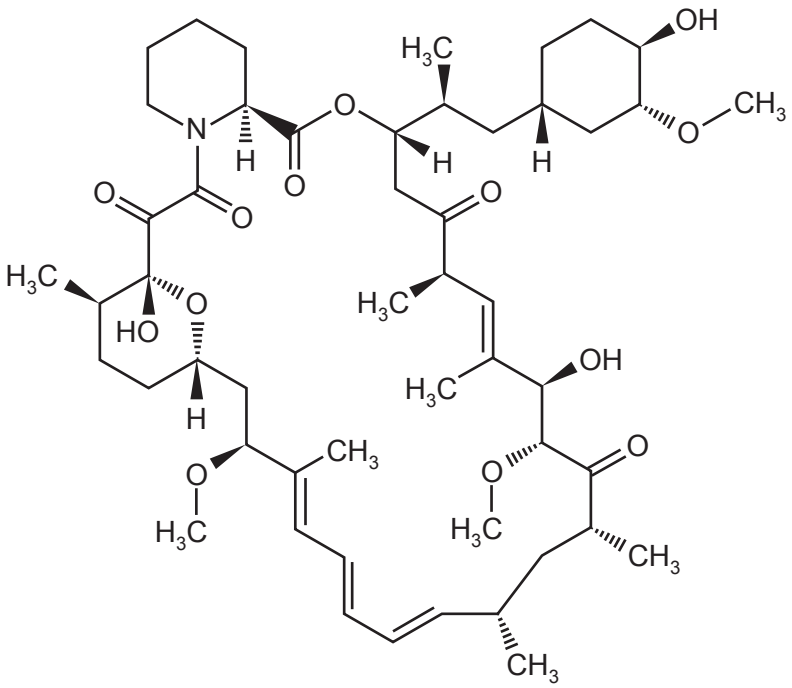
**(ii)** Name the *type of reaction* that would cause such a breakdown.

.....

**(iii)** The drug *Sirolimus* is used to suppress possible rejection by the body after kidney transplants.



*Sirolimus*

Circle **two bonds**, each in a **different** functional group that could be broken down in the digestive system.

[4]

**(c)** *Sirolimus* is not very soluble in water, greatly reducing its effectiveness when given by mouth or by injection. To increase its effectiveness when taken by mouth nano-sized crystals of the drug combined with poly(ethylene glycol) or PEG (shown below) are produced.

$$HO—(CH_2—CH_2—O)_n—H$$

**(i)** Suggest what is meant by the term *nano-sized*.

.....

**(ii)** Suggest where on the molecule of PEG the drug would be attached.

.....

**(iii)** Why would bonding the drug to a PEG molecule improve its solubility in water?

.....

[3]

[Total: 10]

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