TAMPINES MERIDIAN JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **23 September 2019**

2 hours

Candidates answer on Answer Booklet.

Additional Materials: Answer Booklet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and civics group on all your work you hand in.

Write in dark blue or black pen on both pages in the answer booklet.
You may use an HB pencil for any diagrams, graphs or rough working.
Do not use paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

A *Data Booklet* is provided.
The use of an approved scientific calculator is expected, where appropriate.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **14** printed pages.

Section A

Answer **all** the questions from this section.

1 Hydrocarbons, C_xH_y, are used extensively as sources of fuel in our modern day civilisation.

(a) 10 cm^3 of a gaseous hydrocarbon C_5H_y was allowed to burn in an excess of oxygen at 300 ºC and 1 atm. In the reaction, there was an expansion of volume by 20 cm^3.

(i) Write a balanced equation, with state symbols, for the reaction at 300 ºC and 1 atm. [2]

(ii) Determine the value of **y**. [2]

Methane, CH_4, is sometimes used in the production of hydrogen via a process known as steam reforming.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

(b) The steam reforming process is an endothermic reaction.

(i) Using data from the *Data Booklet*, calculate a value for the enthalpy change of the forward reaction. [2]

(ii) The actual value of the enthalpy change of reaction is found to be +206 kJ mol^{-1}. Suggest a reason why your calculated answer in **(i)** differs from this value. [1]

(c) At 600 K, the value of the equilibrium constant, K_p, for the steam reforming reaction is 7.20×10^{-4}.

(i) Write the K_p expression for this reaction, giving its units. [2]

(ii) Gaseous CH_4, H_2O and CO are introduced into a closed container at 600 K and their initial partial pressures are 1.20 atm, 2.10 atm and 1.80 atm respectively.

Determine the partial pressure of H_2 when equilibrium is reached.

(You may assume that the extent of the forward reaction is small.) [3]

(iii) Using information from **(b)**, suggest how the temperature of the reaction can be changed so as to increase the yield of H_2. Explain your answer. [2]

(d) Additional hydrogen can be recovered using the carbon monoxide produced in another reaction known as the water-gas shift reaction.

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

(i) Name the type of hybridisation in the carbon atom in CO. Draw the hybrid orbitals around the carbon atom. [2]

(ii) Given that the above reaction was conducted at 300 ^oC and 1 atm, calculate the volume of H_2 that can be recovered from 5 kg of CO. [3]

(iii) The volume of CO_2 collected in the water-shift reaction should be the same as that of H_2. However, the actual volume of CO_2 collected was smaller. Suggest a reason why this is so. [1]

[Total: 20]

2 Propanoic acid, CH_3CH_2COOH was initially known as propionic acid based on the Greek words, *protos*, meaning 'first' and *pion*, meaning 'fat'.

The pK_a values of CH_3CH_2COOH and $CH_3CH(Cl)COOH$ are listed below.

acid	structural formula	pK_a
1	CH_3CH_2COOH	4.9
2	$CH_3CH(Cl)COOH$	2.8
3	$CH_2(Cl)CH_2COOH$	

(a) **(i)** Explain why acid 2 has a lower pK_a than acid 1. [2]

(ii) Suggest a pK_a value for acid 3. [1]

(b) A 25.0 cm^3 solution of 0.10 mol dm^{-3} CH_3CH_2COOH was titrated against 0.20 mol dm^{-3} sodium hydroxide, NaOH.

(i) Calculate the pH of the 0.10 mol dm^{-3} CH_3CH_2COOH. [1]

(ii) Calculate the volume of NaOH required for complete neutralisation. [1]

(iii) Write a suitable equation to explain why the pH at equivalence point is greater than 7. [1]

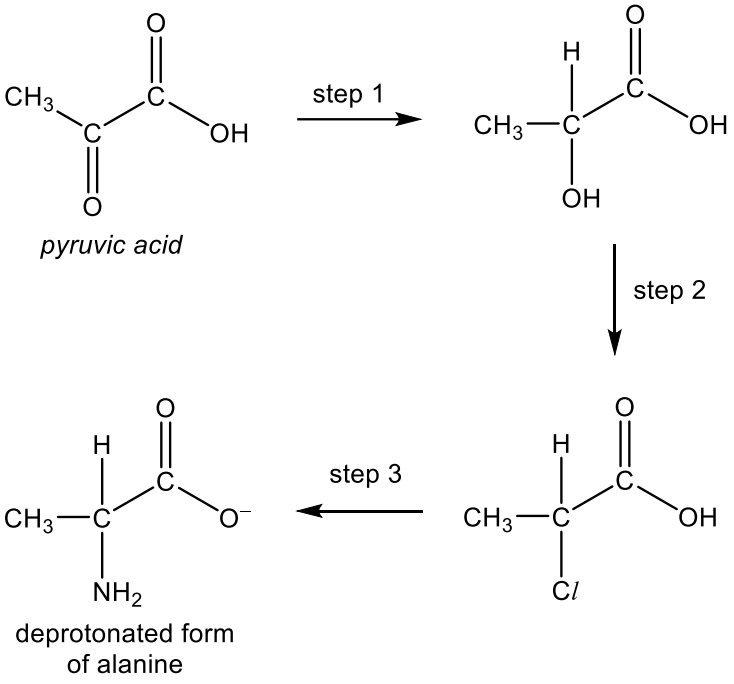
(iv) Sketch the expected titration curve for this titration given that a total volume of 25.0 cm^3 of NaOH was added. On the titration curve, indicate the initial pH value and the equivalence volume. [2]

(v) A buffer involving CH_3CH_2COOH and its salt was formed during the progress of the titration. Circle the buffer region on the sketched curve in **(iv)** and indicate the corresponding pH value and volume at the maximum buffering capacity. [2]

There are many organic compounds such as amino acids and drug molecules that are derivatives of propanoic acid.

(c) The starting material to synthesise 2-aminopropanoic acid, also known as alanine can be either *pyruvic acid* or ethanal.

(i) The proposed synthesis for the deprotonated form of alanine from *pyruvic acid* is shown below.



pyruvic acid

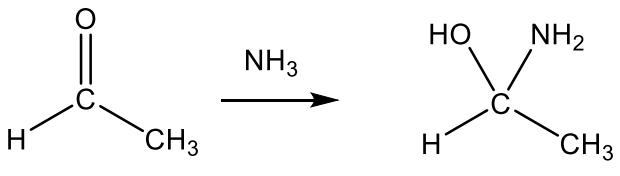
deprotonated form of alanine

Suggest the reagents and conditions for steps 1, 2 and 3. [3]

(ii) State the **two** types of reaction that had occurred in step 3 of the above proposed synthesis. [2]

(iii) Write an equation to show how the zwitterion form of *alanine* can act as a buffer when a small amount of base is added. [1]

(iv) The first step to synthesise alanine from ethanal is shown below.

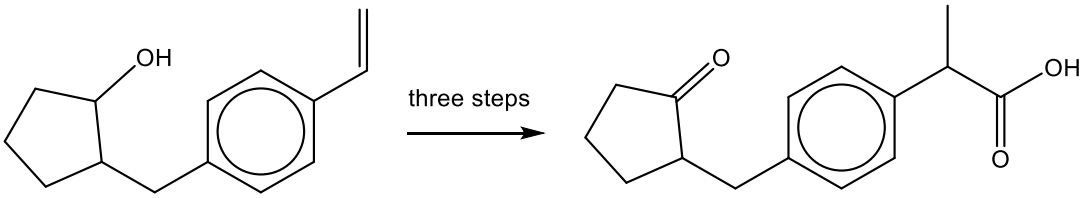


ethanal

Explain whether ammonia can be considered as a Lewis base in the context of this synthesis. [1]

(d) Non-steroidal anti-inflammatory drugs are used for the relief of pain. One example is *loxoprofen* that is considered as a propanoic acid derivative based on its chemical structure.

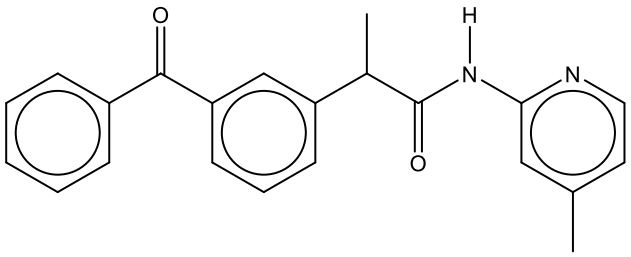
(i) Suggest a three-step synthesis of *loxoprofen* starting from compound **E**.



compound **E** *loxoprofen*

[4]

(ii) *Piketoprofen* is produced by the reaction between an acyl chloride and a suitable organic compound. Suggest the structures of the acyl chloride and the organic compound.



piketoprofen

[1]

(iii) The use of acyl chloride requires anhydrous conditions. Explain why acyl chloride undergoes hydrolysis more readily than chloroalkane. [2]

[Total: 24]

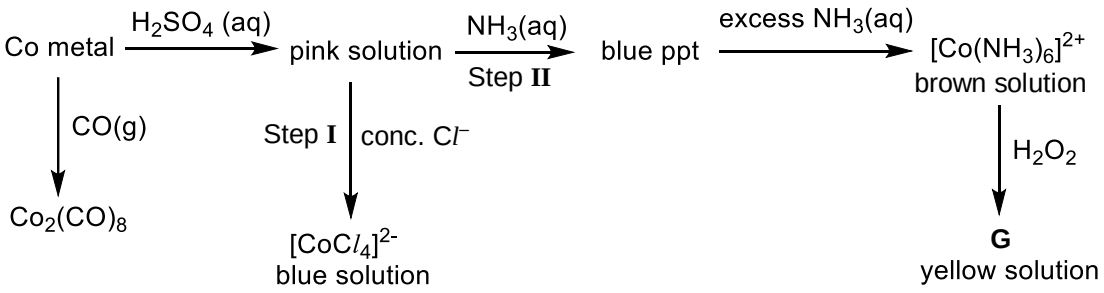
3 Cobalt is a transition element that plays an important role in hybrid electric vehicles and is also an essential part of vitamin B12. The common oxidation states of cobalt are +2 and +3.

(a) Define *transition element*. [1]

(b) Write the electronic configuration of cobalt(II) ion. [1]

(c) State one **physical** characteristic property of transition elements that is different from the main group metals. Briefly explain why transition elements exhibit this property. [2]

(d) The following sequence of reactions involving cobalt illustrates many of the characteristic properties of transition elements.

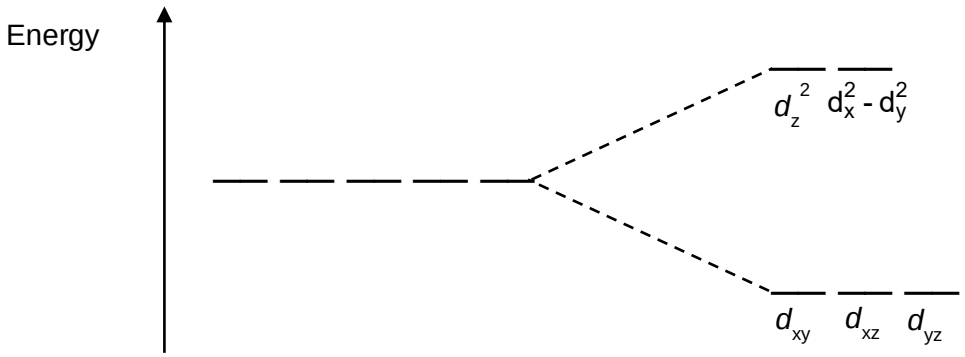


(i) State the types of reaction occurring in steps **I** and **II**. [2]

(ii) Suggest the formula of the cobalt-containing species **G**. [1]

(iii) Cobalt is said to be a d-block element.

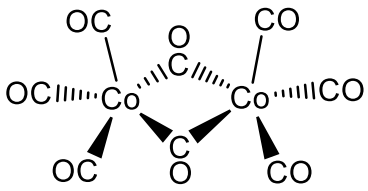
The five degenerate orbitals in the 3d subshell are split into two energy levels in the presence of ligands in an octahedral environment as shown.



Explain why the splitting occurs. [2]

(iv) Given the fact in **(iii)** that d orbitals split into 2 energy levels in the presence of ligands, explain why $[CoCl_4]^{2-}$ solution is blue. [2]

(v) Cobalt can react with carbon monoxide to form $Co_2(CO)_8$, a commonly used reagent and catalyst in organic synthesis.



Suggest the co-ordination number and the oxidation state of cobalt in the complex, $Co_2(CO)_8$. [1]

(vi) With the aid of *Data Booklet* and given that $E^{\ominus}_{[Co(NH_3)_6]^{3+}/[Co(NH_3)_6]^{2+}}$ is +0.10 V, predict the stability of an alkaline solution of $[Co(NH_3)_6]^{2+}$ when left exposed to air. [2]

(e) A radioactive form of cobalt, ^{60}Co, is used in the inspection of materials to reveal internal structure, flaws, or foreign objects.

(i) State the number of protons, neutrons and electrons present in the isotopic species, ^{60}Co. [1]

(ii) The radioactive decay of ^{60}Co produces beta (β) particles. A simplified balanced decay equation is provided below.

$$^{60}Co \rightarrow \mathbf{L} + \beta$$

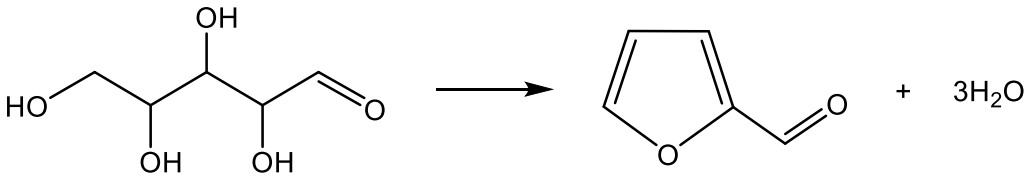
Given that β is $^{0}_{-1}e$, deduce the identity of the element **L**. [1]

[Total: 16]

Section B

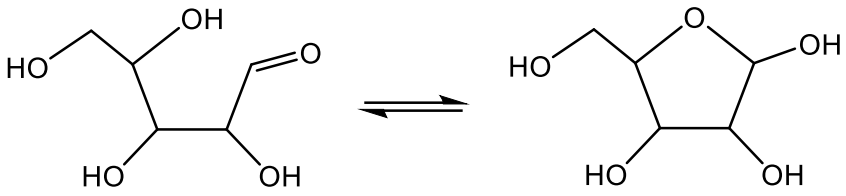
Answer **one** question from this section.

4 Furfural is an aromatic compound with all its carbon atoms lying on the same plane. Today, one of the ways to manufacture furfural is by the acid catalysed dehydration of xylose.



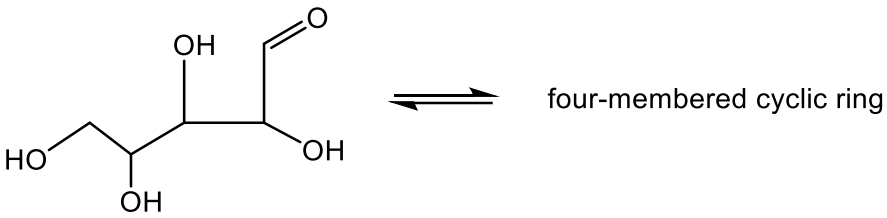
xylose furfural

(a) Xylose exists in more than one form, one of which is the non-cyclic form shown below (i.e. form 1). Form 2 is a five-membered cyclic ring produced as follows.



form 1 of xylose form 2 of xylose

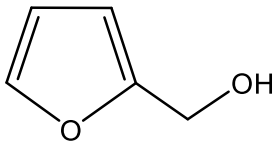
It is theoretically possible to produce a four-membered cyclic ring by following a similar pattern of reaction.



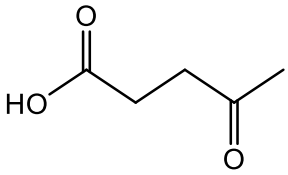
(i) Draw the structure of the theoretical four-membered cyclic ring. [1]

(ii) The four-membered cyclic ring is **not** actually produced because it is unstable. Suggest why it is unstable. [1]

(b) Furfural can be reduced into furfuryl alcohol. Furfuryl alcohol can then be used to synthesise levulinic acid.



furfuryl alcohol

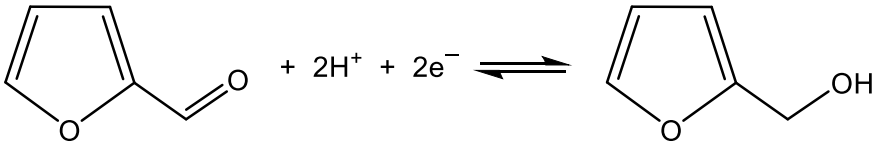


levulinic acid

(i) Using the **molecular** formulae of furfuryl alcohol and levulinic acid, write a balanced equation for the synthesis of furfuryl alcohol into levulinic acid. [2]

(ii) Using your answer in **(i)**, state the type of reaction that has taken place. [1]

(c) The standard reduction potential involving furfural, $C_5H_4O_2$ measured against the standard hydrogen electrode (S.H.E.) is shown below.

electrode reaction	$E^{\ominus}$ / V
 furfural + $2H^+$ + $2e^-$ ⇌ furfuryl alcohol	–0.80

A neutral aqueous solution of furfural is prepared. Electrolysis of this solution is performed using copper at both electrodes to increase the percentage yield of the reaction.

When 0.030 A was passed through the cell for 2.0 hours, the *actual* mass of the product formed at the cathode was found to be 0.060 g. Copper is reacted at the anode but not the cathode.

(i) Using the $E^{\ominus}$ values given above as well as that from the *Data Booklet*, deduce the products formed at the anode and the cathode.
(In your deduction, you may use name or molecular formula to represent the structures of the respective organic compounds.) [3]

(ii) Write the overall balanced equation for the reaction. [1]

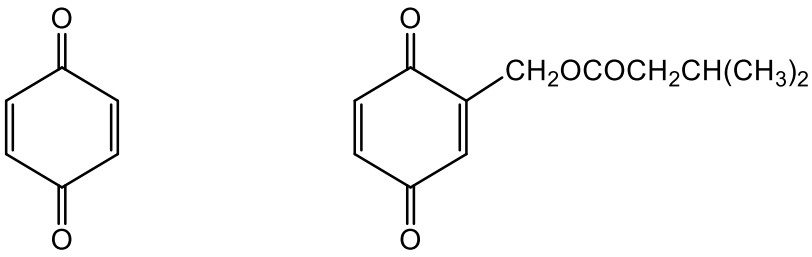
(iii) Calculate the *expected* mass of the product formed at the cathode. [2]

(iv) Calculate the percentage yield of the product formed at the cathode. [1]

(v) Besides the S.H.E., another standard electrode that can be used is the standard calomel electrode (S.C.E.). When the S.C.E. is compared against the S.H.E., the $E^{\ominus}$ of the S.C.E. is +0.24 V.

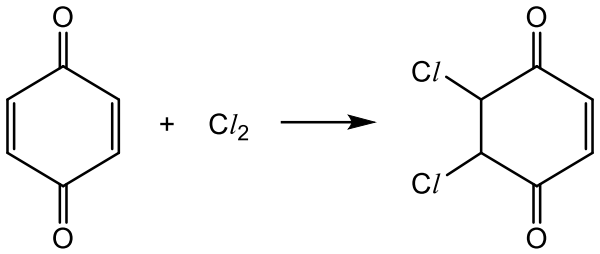
Calculate the $E^{\ominus}$ of the furfural / furfuryl alcohol half-cell when measured against the S.C.E. [1]

Another compound with all its carbon atoms lying on the same plane is paraquinone, with a characteristic irritating odour of hot plastic. One derivative of paraquinone is blattellaquinone which is a pheromone in cockroaches.



paraquinone blattellaquinone

(d) Paraquinone and limited chlorine react as follows.



Name and draw the mechanism of this reaction. [3]

(e) Draw the major products formed when **blattellaquinone** is separately reacted under suitable conditions with each of the following:

(i) hydrogen gas [1]

(ii) gaseous hydrogen bromide [1]

(iii) hot acidified potassium manganate(VII) [2]

[Total: 20]

5 This question concerns the compounds of Period 3 elements.

(a) Properties of the oxides of some Period 3 elements, **P**, **Q** and **R**, are given below.

oxide	physical state at room conditions	electrical conductivity when molten
P	gas	nil
Q	solid	high
R	solid	low

These three oxides, in no particular order, are Al_2O_3, SiO_2 and SO_3.

(i) Identify **P**, **Q** and **R**. [1]

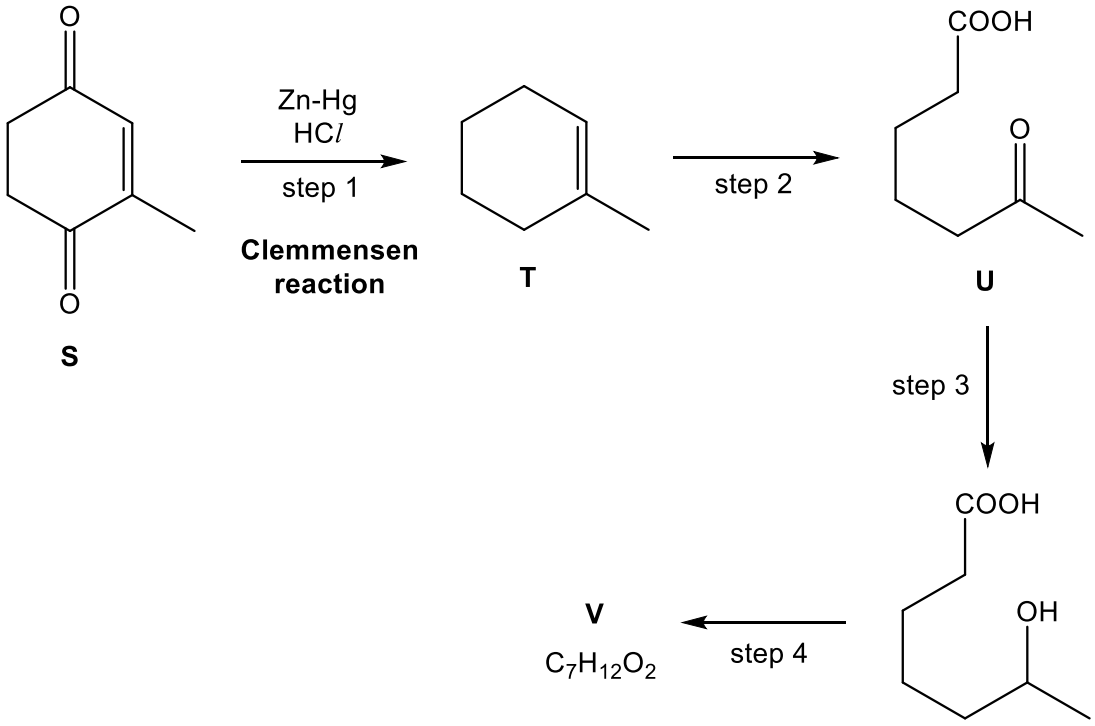
(ii) Account for your answer, in terms of their structure and bonding. [4]

(iii) Al_2O_3 is described as an amphoteric oxide.
Write two equations to show the amphoteric nature of Al_2O_3. [2]

(b) Hydrogen chloride is a colourless gas commonly used in organic synthesis.

In the Clemmensen reaction, carbonyl compounds are reduced to alkanes using zinc-mercury and hydrogen chloride dissolved in an organic solvent.

A reaction scheme involving the Clemmensen reaction is shown below.



(i) Write the balanced equation for the reduction of compound **S** to **T**. Use [H] to represent the formula of the reducing agent. [1]

(ii) Suggest a reagent which can determine if the reaction in step 3 is complete. [1]

(iii) Given that compound **V** is neutral, state the type of reaction occurring in step 4 and suggest the structure of compound **V**. [2]

(iv) Compound **U** is more soluble in water than compound **S**.

1. Suggest a reason why this is so. [1]

2. Draw a labelled diagram to show how compound **U** dissolves in water. [1]

(c) HC*l* is stable to heat while HBr and HI, can undergo thermal decomposition. At 700 K, HBr is approximately 10% decomposed but HI, is approximately 20% decomposed.

Explain these differences with reference to relevant data in the *Data Booklet* and the factors that affect them. [3]

(d) Compound **W**, $C_6H_{10}O_2$ is an ester which decolourises Br_2 in CCl_4 to form $C_6H_{10}Br_2O_2$.

Upon prolonged heating with excess acidified $KMnO_4$, 1 mol of **W** produces 1 mol of **X**, $C_4H_6O_3$ and 2 mol of CO_2.

X gives a yellow precipitate **Y** when warmed with aqueous alkaline iodine. **X** also undergoes the Clemmensen reaction to give **Z**, $C_4H_8O_2$. Both **X** and **Z** produce effervescence when reacted with aqueous sodium carbonate.

Suggest structures for the identity of **W**, **X**, **Y** and **Z**. [4]

[Total: 20]

End of Paper 3