H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY **9729/02**

Paper 2 Structured Questions **17 September 2019**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
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	**/18**
2	**/13**
3	**/14**
4	**/15**
5	**/15**
Total	**/75**

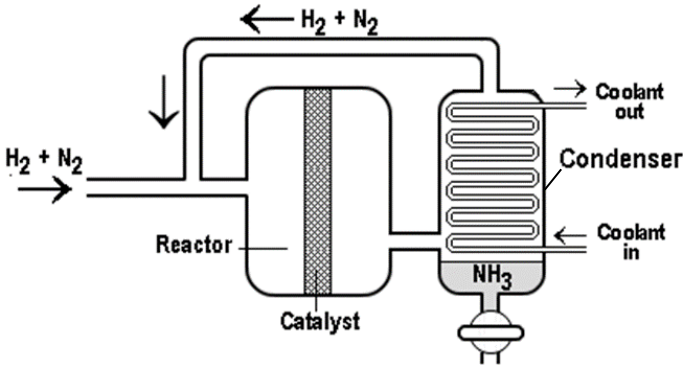
This document consists of **20** printed pages.

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

1 (a) Ammonia is one of the world's most produced inorganic chemical due to its many uses. The current method of producing ammonia is the Haber-Bosch process.

This involves reacting nitrogen and hydrogen in a recycled process as shown. Nitrogen and hydrogen are pumped into the reactor where reaction to form ammonia takes place. The output from the reactor then goes into a condenser.

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H < 0$$



(i) An optimal temperature of 500 ^{o}C is used inside the reactor. Explain why this temperature is used.

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(ii) Finely divided iron is used as catalyst inside the reactor. Outline the mode of action of the iron catalyst in this reaction.

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(iii) Using a Boltzmann diagram, explain why rate increases in the presence of catalyst.

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(iv) The condenser helps to cool the gases and in doing so, maximises the yield of ammonia. Explain in terms of structure and bonding how this is achieved.

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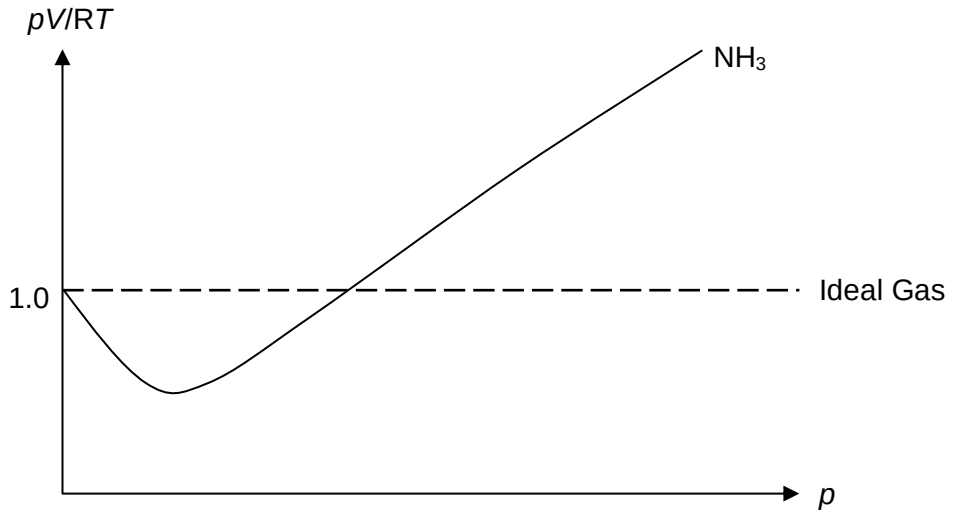
(v) Hydrazoic acid, HN_3, is a compound of nitrogen and hydrogen like ammonia.

The plots of pV/RT against p for one mole of an ideal gas and one mole of ammonia are given below.



On axes above, sketch a graph to illustrate the behaviour of one mole of hydrazoic acid. Explain your answer.

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(b) Globally, approximately 88 % of ammonia is used as fertilisers. Research is actively carried out to seek new uses for ammonia in other areas.

For example, when $NH_3(aq)$ is added to a solution of $Zn^{2+}(aq)$, a solution of $[Zn(NH_3)_4]^{2+}(aq)$ can be formed. It is then possible to design an electrochemical cell based on the following half equations.

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^\ominus = -0.76V$$

$$[Zn(NH_3)_4]^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) + 4NH_3(aq) \qquad E^\ominus = -1.04V$$

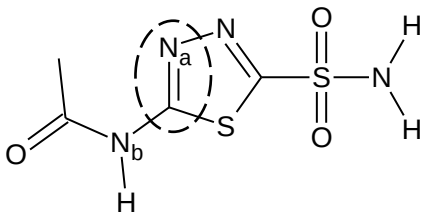
(i) Draw a fully labelled diagram of the electrochemical cell that could be set up, showing the polarity of the electrodes during discharge.

[2]

(ii) Write a balanced equation for the overall reaction that occurs during the discharging process. Hence calculate $\Delta G^\ominus$ of the electrochemical cell.

[2]

(c) Ammonia is used in the pharmaceutical industry for synthesising of drugs. An example is acetazolamide, a drug used for treating heart failure.



acetazolamide

(i) The molecule of acetazolamide contains both σ (sigma) and π (pi) bonds.

With respect to the C=N_a bond circled, draw a labelled diagram to show how orbitals overlap to form σ (sigma) and π (pi) bonds.

[1]

(ii) Suggest how the basicity of N_a might compare to that of N_b. Explain your answer with reference to your answer in (c)(i).

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[Total:18]

2 Copper has a wide range of common uses, such as electrical wiring and water piping because it is relatively inexpensive and has a high resistance to corrosion.

Copper is also an unreactive metal which does not react directly with dilute acids. Therefore, the enthalpy change of reaction, ΔH_r, for the following reaction, cannot be determined directly.

$$Cu(s) + H_2SO_4(aq) \longrightarrow CuSO_4(aq) + H_2(g) \quad \Delta H_r$$

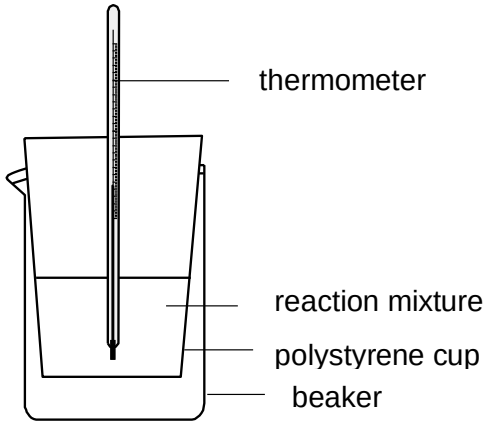
In order to determine a value for ΔH_r, you will therefore need to find the enthalpy change of reaction for two reactions that do occur. One of these reactions involve adding a reactive metal M to dilute sulfuric acid.

$$nM(s) + H_2SO_4(aq) \longrightarrow M_nSO_4(aq) + H_2(g) \quad \Delta H_1$$

The other reaction is a displacement of copper from aqueous copper(II) sulfate using metal M.

$$nM(s) + CuSO_4(aq) \longrightarrow M_nSO_4(aq) + Cu(s) \quad \Delta H_2$$

The value for the enthalpy change of the displacement reaction ΔH_2 can be determined using a graphical method by finding the maximum temperature change ΔT_{max}. The following experiment is carried out and the metal M used in this experiment can be assumed to be in excess.



Determination of ΔT_{max}

1 Weigh accurately the mass of the metal powder M.

2 Measure 50 cm^3 of 0.3 mol dm^{-3} $CuSO_4(aq)$ and pour it into the polystyrene cup.

3 Measure the temperature of $CuSO_4(aq)$ every half minute.

4 At the 3rd minute, pour the metal powder M into the polystyrene cup.

5 Record the temperature of the solution at the 4th minute and thereafter at every half minute until the 10th minute.

However, the polystyrene cup used in the experiment can also absorb heat, so a separate experiment is performed to find the heat capacity of the polystyrene cup. This process is known as the calibration of the calorimeter.

One way to do this is to use a common metal of known specific heat capacity. A piece of nickel bar can be heated to around 100 °C and then dropped into the polystyrene cup containing water. The heat capacity of the polystyrene cup can then be calculated from the known specific heat capacity of nickel.

(a) Suggest, with the aid of a labelled diagram, why copper is suitable to be used in electrical wiring.

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..... [2]

(b) (i) The $E^{\ominus}$ values of some redox reactions are shown below.

reaction	$E^{\ominus}$ / V
$Ag^{+} + e^{-} \rightleftharpoons Ag$	+0.80
$Ba^{2+} + 2e^{-} \rightleftharpoons Ba$	–2.90
$Ca^{2+} + 2e^{-} \rightleftharpoons Ca$	–2.87
$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$	+0.34
$2H^{+} + 2e^{-} \rightleftharpoons H_2$	+0.00
$Mg^{2+} + 2e^{-} \rightleftharpoons Mg$	–2.38

By considering the $E^{\ominus}$ values given, suggest the most suitable metal from the following list to be used as metal M in both reactions. Give reasons for your choice.

barium calcium magnesium silver

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..... [2]

(ii) Using the metal you have chosen in (b)(i), construct an energy cycle to show how ΔH_r can be calculated from ΔH_1 and ΔH_2.

[1]

(iii) Outline how you would determine the heat capacity of the polystyrene cup, using a nickel bar of approximately 50 g.

You should include brief details of the apparatus you would use, the procedure you would follow, and the measurements you would make.

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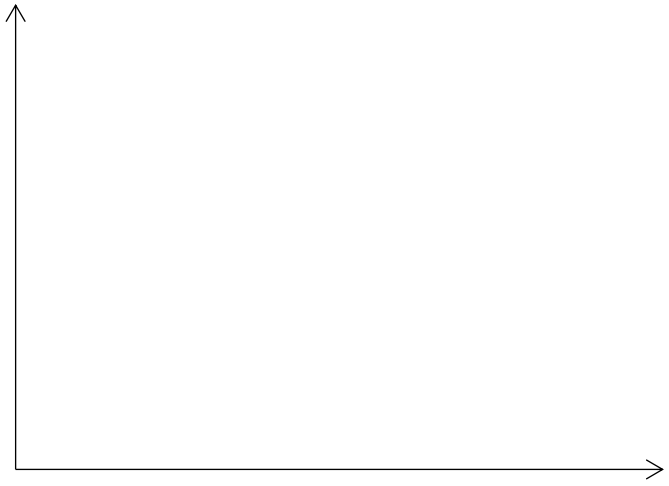
(iv) Sketch, with clearly labelled axes, the graph that you would expect to obtain in the experiment described on page 7 and show how the value of ΔT_{max} can be obtained.



[1]

(v) The heat capacity of the polystyrene cup was found to be 9.7 J K^{-1} in (b)(iii) and the value of ΔT_{max} was found to be 34.8 ^{o}C in (b)(iv).

Calculate the value of ΔH_2.

[2]

(c) Calcium is found in the same Period as copper in the Periodic Table. However, Ca has a significantly larger atomic radius than Cu.

Explain why Cu has a smaller atomic radius.

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..... [2]

[Total:13]

3 The numerical value of the solubility products of some iron containing salts at 298 K are given below.

salt	value of solubility product
iron(II) hydroxide, $Fe(OH)_2$	8.0×10^{-16}
iron(II) disulfide, FeS_2	1.3×10^{-27}
iron(III) hydroxide, $Fe(OH)_3$	4.0×10^{-38}

In this question, give each of your numerical answers to one decimal place.

(a) (i) Write an expression for the solubility product of iron(III) hydroxide, stating its units.

..... [1]

(ii) From the data above, calculate a value for the solubility of iron(III) hydroxide.

[1]

(iii) Solid $Fe(NO_3)_2$ was added to a solution containing 0.25 mol dm^{-3} of sodium disulfide and 0.40 mol dm^{-3} of sodium hydroxide at 298 K.

Calculate the concentration of disulfide ions remaining in the solution when the first trace of iron(II) hydroxide appears.

[2]

When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$ is given by the following expression.

$$\Delta G^{\ominus}_{ppt} = 2.303\ RT \log K_{sp}$$

(b) **(i)** Use the data above to calculate $\Delta G^{\ominus}_{ppt}$, in kJ mol^{-1}, for FeS_2.

[1]

(ii) The standard enthalpy change of formation of the precipitate FeS_2 is –178.0 kJ mol^{-1}. Use your answer in (b)(i) to calculate $\Delta S^{\ominus}_{ppt}$.

[2]

(iii) Explain the significance of the sign of your answer in (b)(ii).

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(c) When $FeCl_3$ is mixed with CaC_2O_4 in NH_4Cl(aq), a yellow salt, X, is formed as one of the products. X has the following composition by mass

C, 19.3 %; Fe, 14.9 %; H, 3.2 %; N, 11.2 %; O, 51.4 %

X is ionic with a formula mass of 373.8. One formula unit of X contains one type of anion and one type of cation in the ratio of 1:3.

(i) Calculate the empirical formula of X.

[1]

(ii) Suggest the formulae of each of the ions present in X.

Cation: ..... Anion: .....

[2]

(iii) Suggest the coordination number of the iron-containing ion and hence state its shape.

Coordination number: …… Shape: .....

[1]

(iv) Explain why the salt is yellow in colour.

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..... [2]

[Total: 14]

4 (a) The Contact Process produces sulfuric acid in high concentrations needed for industrial processes. V_2O_5 is the catalyst used in this process.

SO_2 is first produced by heating sulfur in oxygen. It is then oxidised to SO_3 by air.

The oxidation of SO_2 to SO_3 is reversible and exothermic.

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g) \qquad \Delta H = -197\ kJ\ mol^{-1}$$

(i) SO_2 and O_2 were mixed in a 2:1 mole ratio. Given that the partial pressure of SO_2 in the equilibrium mixture was 24 kPa and the total pressure of the flask was 104 kPa, determine the equilibrium partial pressures of O_2 and SO_3. Hence, calculate K_p, giving the units.

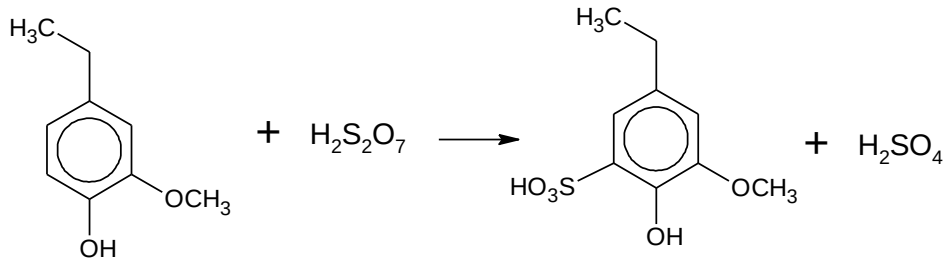
[2]

In the next step of the Contact Process, oleum and sulfuric acid are produced according to the equations below.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7\ (oleum)$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

The oleum produced can react with 4-ethylguaiacol, a key flavour component that gives robusta coffee beans the spicy and earthy notes.



4-ethylguaiacol

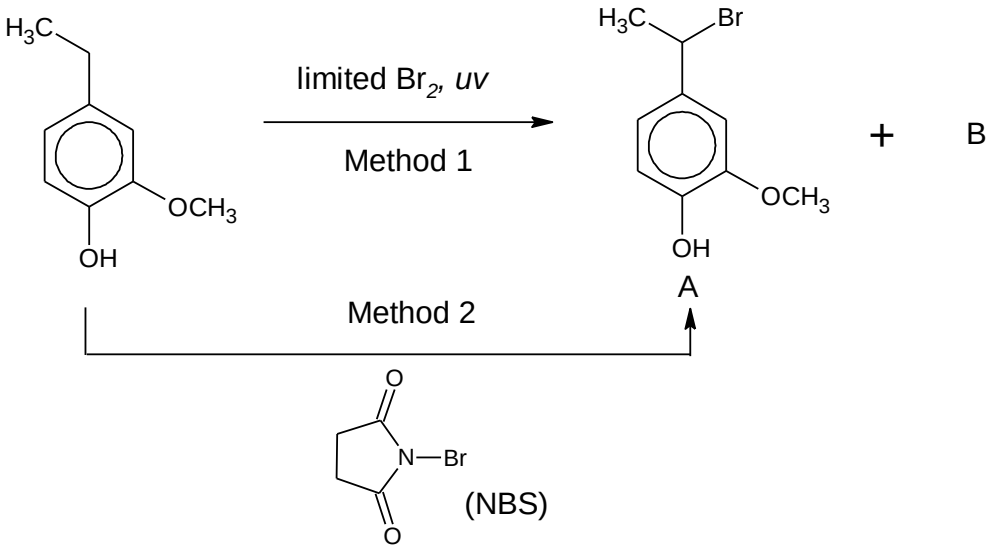
Assume that oleum ionises as shown.

$$H_2S_2O_7 \rightleftharpoons HSO_4^- + SO_3H^+$$

(ii) Propose a mechanism for this reaction of 4-ethylguaiacol, showing the structure of the intermediate, lone electron pairs, and movement of electrons pairs by using curly arrows.

[3]

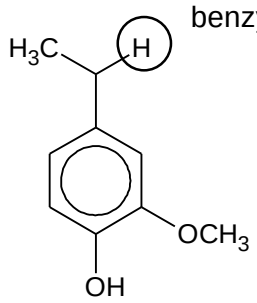
(b) 4-ethylguaiacol can undergo bromination using the following methods.



(i) Give the structure of monobrominated product B and the ratio of A to B formed in method 1, assuming that $-OCH_3$ is inert.

[2]

(ii) In method 2, the presence of n-bromosuccinimide (NBS) results in side-chain bromination occuring exclusively at the benzylic position, the yield of A is 97 % in this reaction.



The NBS bromination occurs by a radical chain pathway.

- The first step involves a bromine radical abstracting a benzylic hydrogen atom, forming a benzylic radical and HBr.
- This is followed by the benzylic radical reacting with a bromine molecule to yield the product and bromine radical.

Suggest the two-step mechanism, using curly arrows to show the movement of electrons.

[2]

(iii) The bromine molecule that reacts with the benzylic radical in the second step of the mechanism in (b)(ii) is produced by a concurrent reaction of HBr with NBS.

The reaction involves homolytic bond fissions in the molecules.

Using the reaction of HBr with NBS, explain the term, *homolytic fission* and provide a balanced equation for this reaction.

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..... [2]

(iv) Method 2 forms A as the only monobrominated product with 97 % yield where bromination occurs exclusively at the benzylic position. Explain why other products do not form in method 2.

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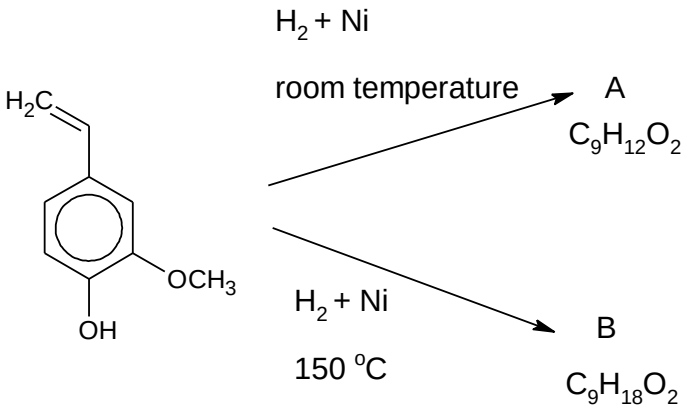
..... [1]

(c) Organic reductions commonly use nickel catalyst but not all possible functional groups can be reduced. Heating increases the catalytic ability of nickel.

The following reactions illustrate reductions using different conditions.



(i) Suggest the identities of A and B.

A	B

[2]

(ii) Explain why B only forms at very high temperature.

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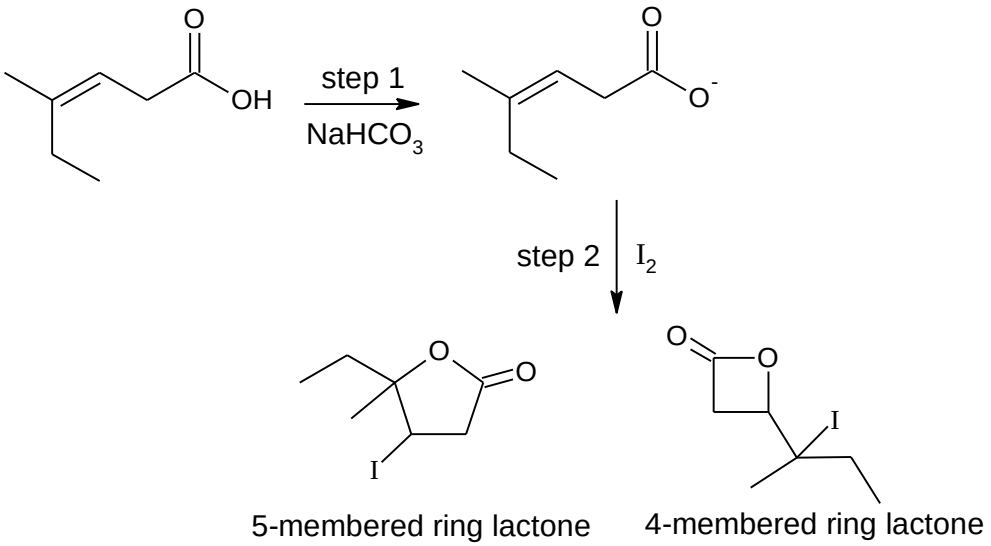
[Total: 15]

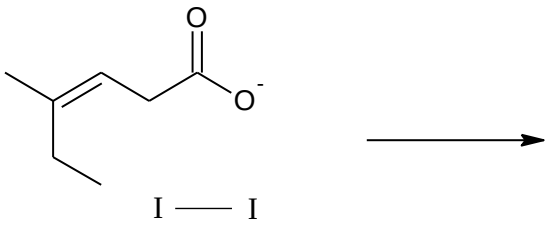
5 Lactones contain the ester functional group and are often used as flavours or fragrances. They could be synthesised using the reaction scheme given below.



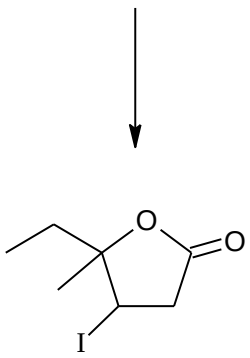
5-membered ring lactone 4-membered ring lactone

(a) (i) The reaction between the carboxylate ion and iodine in step 2 is an electrophilic addition.

Complete the diagram to suggest a mechanism to show how a 5-membered ring lactone is formed. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. Indicate the slow step of the mechanism.



intermediate



5-membered ring lactone

[2]

(ii) Explain why $NaHCO_3$ is added in step 1.

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..... [1]

(iii) Suggest two reasons for the preferential production of the 5-membered ring lactone instead of the 4-membered ring lactone.

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..... [2]

(iv) Outline a simple chemical test that could be carried out to see if any 4-membered ring lactone is produced in the reaction mixture in step 2.

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(v) With reference to the *Data Booklet*, explain why the product will be more stable when CI_2 is used in step 2.

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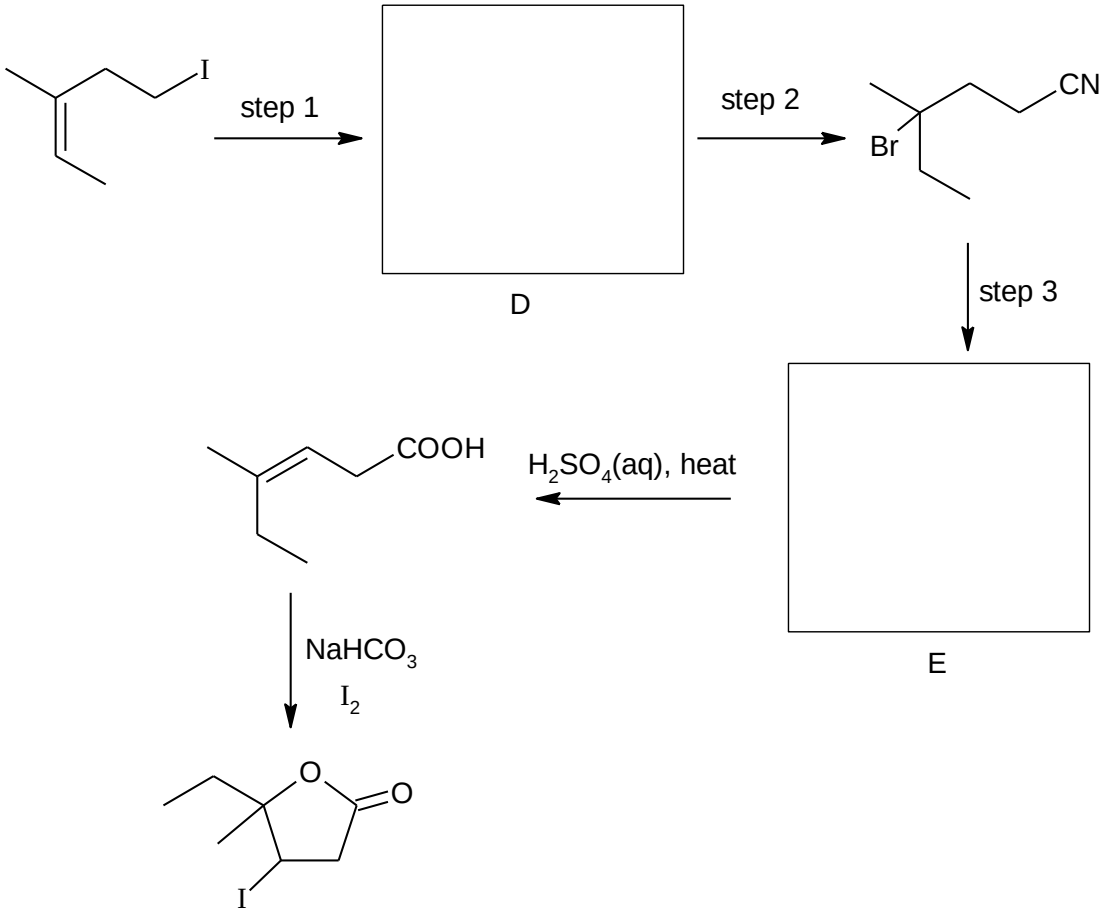
..... [1]

(b) The 5-membered ring lactone formed in step 2, exists as a mixture of stereoisomers. Draw the structures of each stereoisomer of the 5-membered ring lactone.

[2]

(c) The reaction scheme below shows how the 5-membered ring lactone could be synthesised. Suggest the reagents and conditions needed for step 1, 2 and 3. Draw the structures of D and E in the boxes.



5-membered ring lactone

step 1 .....

step 2 .....

step 3 .....

[5]

[Total: 15]