TEMASEK JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS
HIGHER 2

For Examiner's Use

CANDIDATE NAME									
CIVICS GROUP			/						
CENTER NUMBER	S					INDEX NUMBER			

CHEMISTRY
9647/02

Paper 2 Structured Questions **17th September 2013**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group and name on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.
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.

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1	/12
2	/20
3	/10
4	/15
5	/15
Total	

This document consists of **21** printed pages.

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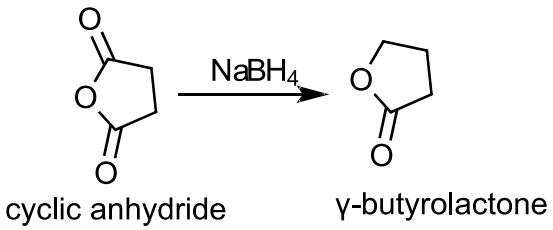
1 Planning (P)

Scientists in the 1970s have discovered that the reduction of cyclic anhydrides using sodium borohydride ($NaBH_4$) is more convenient and versatile method than lithium aluminium hydride ($LiAlH_4$). γ-butyrolactone, a pro-drug to GHB, can be synthesized from its starting cyclic anhydride using $NaBH_4$, as shown in the diagram below.



(a) A research student wishes to synthesize γ-butyrolactone to determine the enthalpy change of combustion of γ-butyrolactone. Professor Hamilton pointed out to him that the product synthesized has to be purified before further use.

This is because in the preparation of crude γ-butyrolactone, sodium borohydride was added in excess to ensure maximum yield in synthesizing γ-butyrolactone. After the reaction is complete, the excess sodium borohydride is decomposed by acidifying the reaction mixture to pH 6 or below (slowly and while stirring) using excess 6 mol dm^{-3} aqueous hydrochloric acid. Hydrogen gas is evolved during this process as the excess sodium borohydride decomposes.

The purification of crude γ-butyrolactone involves performing a liquid-liquid extraction initially using a separating funnel seen in Figure 1 below, before final purification of the product by recrystallization or distillation.

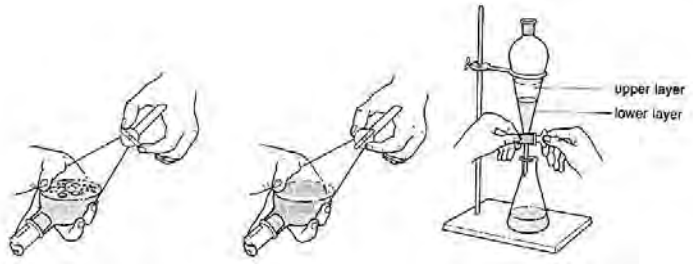


Figure 1: Liquid-liquid extraction using a separating funnel

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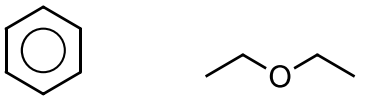
(i) Which of the following two organic solvents would be a good choice to dissolve crude γ-butyrolactone to perform a liquid-liquid extraction? Explain your answer.



benzene diethyl ether

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(ii) One common mistake when performing a liquid-liquid extraction is to mix-up the layers and hence the organic product would be lost in the discarded layer.

Using the following data in the table,

Solvent	Density (g cm^{-3})
Benzene	0.877
Diethyl ether	0.713
Water	1.000

Identify if the organic solvent identified in (i) would be the upper or lower layer? Explain your answer.

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(iii) The experimental procedures of the purification of crude γ-butyrolactone via liquid-liquid extraction is described below:

1. Dissolve the crude γ-butyrolactone in 30 cm^3 of the organic solvent.
2. Cool the flask in an ice bath and then add 20 cm^3 of 6 mol dm^{-3} hydrochloric acid dropwise, while stirring, to quench the reaction.
3. Place the reaction mixture in a separating funnel and separate the aqueous layer from the organic layer. Reject the aqueous layer.
4. Add about half its volume of **chemical reagent A.** Shake the reaction mixture in the separating funnel cautiously, releasing the pressure at intervals.
5. Transfer the organic layer into a conical flask and add some **chemical reagent B**. Filter off **chemical reagent B** and evaporate the solvent at room temperature.

State the identities of chemical reagents **A** and **B**, explaining the role each plays in the experimental procedures 4 and 5.

[5]

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Chemical reagent **A**: .....

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Chemical reagent **B**: .....

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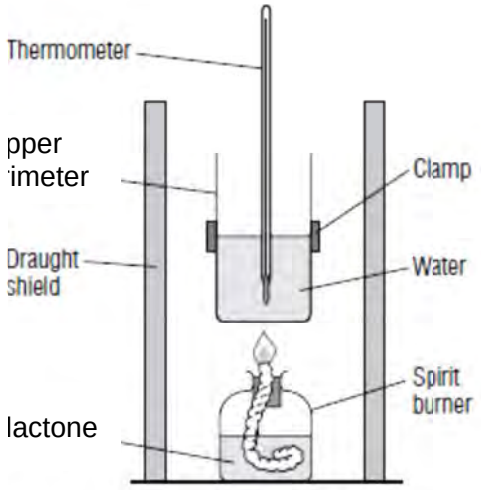
(b) The following experimental set-up can be used to design an experiment to determine the enthalpy change of combustion of γ-butyrolactone.



You are to plan a step-by-step method to determine the enthalpy change of combustion, ΔH_c, under laboratory conditions, of γ -butyrolactone. You should use the apparatus in the diagram above and any apparatus required that is normally found in a school laboratory.

Your method should cover the following points:

1. appropriate quantities to be used in the experimental procedures
2. how the raw data is to be recorded
3. how this data is to be processed to determine the enthalpy change of combustion of γ -butyrolactone

Given:

1) Specific heat capacity of copper calorimeter = 0.385 J g^{-1} K^{-1}
2) 4.2 J of heat is needed to raise the temperature of 1 cm^3 (1 g) of water by 1 ^oC.

[5]

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Experimental Procedures:

Recording of raw data:

Analysis of raw data:

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(c) Upon analysis of his raw data, the research student obtained a value less than the literature value of -2010 kJ mol^{-1}.

(i) Other than heat loss to the surrounding, suggest another reason to explain his observation, explaining your answer clearly.

[2]

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[Total: 12]

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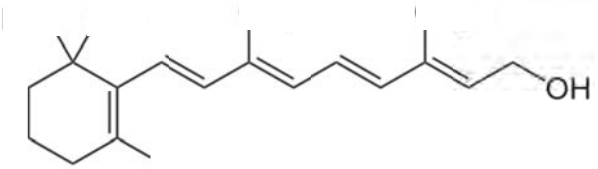
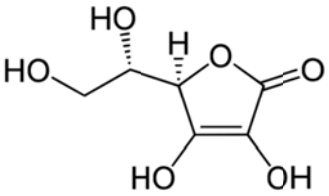
2 This question is about the applications of solubility in nutrition and pharmaceutics.

(a) Vitamins are an important part of daily nutrition. Vitamins soluble in lipids are able to be stored within the body, but water-soluble vitamins are not stored and need replacement every day. The structures of two vitamins are shown below.



Vitamin A



Vitamin C

In terms of structure and bonding, discuss whether vitamins A and C can be stored in the body or need daily replacement. You may assume lipids to be non-polar solvents.

[5]

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(b) Proteins are necessary in the human diet, as they are an important source of amino acids via digestion. Amino acids are generally soluble in water and crucial to many biological processes in the body. At varying pH, the net charge of a protein molecule is the arithmetic average of all charges, and each protein has an isoelectric point. This isoelectric point is dependent on the exact amino acid sequence and the number of acidic and basic R-groups present in it.

(i) In terms of structure and bonding, explain why amino acids are generally soluble in water.

(ii) With reference to an amino acid, explain what is meant by the term *isoelectric point*.

(iii) Proteins tend to coagulate near to or at their respective isoelectric points. For instance, in milk, casein (a type of protein) clumps together and precipitates as it reaches its isoelectric point of 4.6 and forms curd. However, proteins generally do not coagulate at extreme pH, remaining soluble and discrete. Explain this phenomenon with reference to the casein in milk at a pH of 4.6 and 1.

[6]

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(c) Calcium is best known for its role in bone health. It is common to increase calcium intake by consuming calcium supplements, which usually contain calcium carbonate extracted from oyster shells. However, calcium citrate is an increasingly common replacement for calcium carbonate, because calcium citrate does not have any reaction with stomach acid that would cause discomfort, unlike calcium carbonate.

(i) Suggest a reason why consumption of calcium carbonate causes discomfort in the stomach.

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(ii) Calcium is absorbed only in the intestines and when it is a free aqueous Ca^{2+} ion. The upper part of the small intestines has a pH of about 4 to 5 due to the presence of some stomach acid, and the pH increases throughout until about 8 to 9 at the end of the small intestines.

Deduce how the absorption of calcium will likely vary with pH.

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[3]

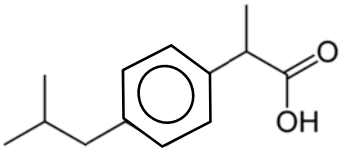
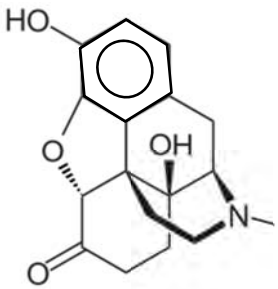
For Examiner's Use

(d) In pharmaceutics, an important aspect of a drug is how it is absorbed into the human body, which is related to its lipophilicity, i.e. its ability to dissolve in non-polar solvents such as lipids. Lipophilicity of a compound can be measured by its log*P* value, which is defined as:

$$\log P = \log_{10}\left(\frac{[\text{solute}]_{\text{octanol}}}{[\text{solute}]_{\text{water}}}\right)$$

Octanol is considered non-polar and is immiscible with water. Usually, in order to calculate log*P*, a compound (solute) is dissolved in an octanol-water mixture and shaken vigorously, after which its concentration in each layer is determined.

Ibuprofen and oxymorphone are both analgesics, i.e. painkillers. The following table contains data about these two drugs.

	ibuprofen	oxymorphone
Structure		
Relative molecular mass	206	301
Solubility in water	1 mg cm^{-3}	250 mg cm^{-3}
log*P*	?	0.98

(i) In an experiment where a mixture comprising 100 cm^3 of octanol and 100 cm^3 of water was shaken with ibuprofen, it was found that a total of 30.3 g of ibuprofen dissolved in the mixture.

Using this information and the data given above, determine the log*P* value for ibuprofen.

log*P* value of ibuprofen: .....

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(ii) Drugs meant for topical use, i.e. applied onto the skin, need to have high skin permeability. One pathway of delivery of the drug requires it to penetrate the lipid matrix beneath the skin, for which a higher degree of lipophilicity is necessary.

Using the log*P* value calculated in **(d)(i)** and the data given above, state and explain whether ibuprofen or oxymorphone is more suitable for topical use.

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(iii) Deduce how a high pH may affect the log*P* of ibuprofen.

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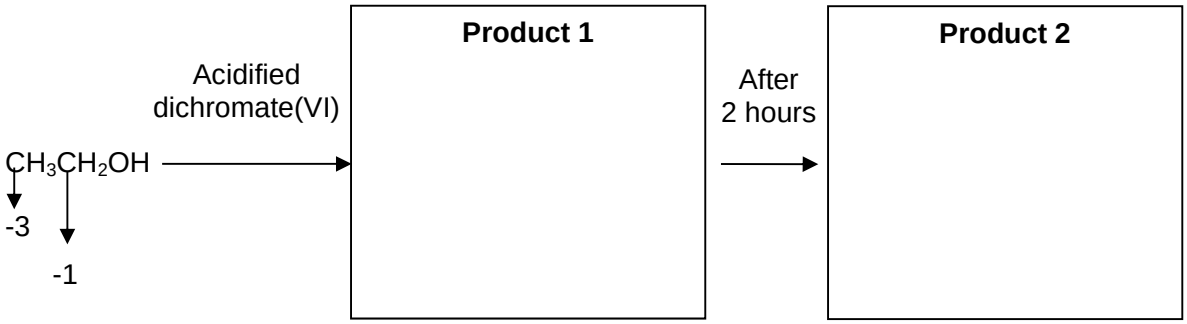
[6]

[Total: 20]

For Examiner's Use

3 (a) Use of *Data Booklet* is relevant to this question.

Ethanol undergoes oxidation with acidified dichromate(VI) under different conditions to produce different products. The oxidation state of the carbon atoms in ethanol are indicated below.



(i) Draw the structures of the possible products formed. Label the oxidation states of all the carbon atoms in your structures.

(ii) In an experiment, it was found that 0.2 mol of acidified dichromate(VI) reacted with 0.3 mol of ethanol. Using your answer in **(a)(i)**, deduce the product formed from the reaction.

(iii) Hence, construct a balanced ionic equation for the reaction in **(a)(ii)**.

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[4]

For Examiner's Use

(b) Isotopes are first founded by J. J Thompson in 1913. Variation of isotopes of carbon, nitrogen and oxygen has a wide range of application. One use is the use of isotope tracers to determine structures.

(i) Oxygen-18, ^{18}O, which is an isotope of the naturally occurring oxygen-16, ^{16}O, is one such isotope used as a tracer for organic compounds.

The table below shows the relative abundance of the oxygen isotopes.

Relative Isotopic Mass	Abundance
16	99.757
17	0.038
18	0.205

Calculate the relative atomic mass of oxygen. Leave your answers to 3 decimal places.

(ii) Would you expect the atomic radius of ^{16}O and ^{18}O to differ? .....

Explain.

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For Examiner's Use

(iii) In order to study the mechanism of organic reactions, tracer studies using isotopes can be used. ^{18}O in water can be used to understand the hydrolysis of esters.

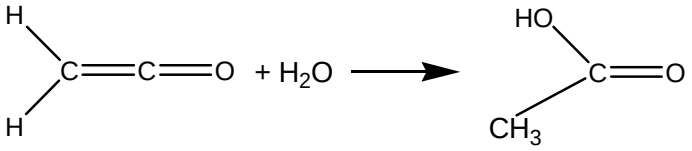
Draw the structures of the two products formed when methylpropanoate is hydrolysed with $H_2{}^{18}O$ in an acidic medium. Label the ^{18}O isotope clearly.

(iv) Draw all the possible structural isomers of esters with the same molecular formula as methylpropanoate.

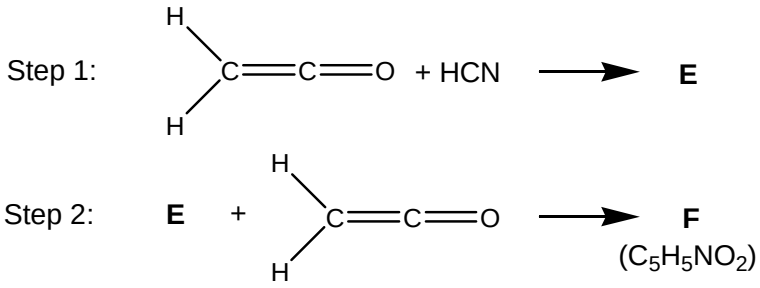
[4]

For Examiner's Use

(c) Ketene is a reactive compound that undergoes addition reaction as shown below



Compound **F** is an ester formed via a two-step process.



The first step involves an addition reaction to form the cyanohydrin intermediate.

Suggest the structure of compound **E** and **F**.

Compound **E**	Compound **F**

[2]

[Total: 10]

For Examiner's Use

4 (a) When heated in chlorine, aluminium and phosphorous form chlorides.

Describe the reactions, if any, of the chlorides with water, suggesting the pH of the resulting solution and writing equations where appropriate.

[5]

(b) There is said to be a diagonal relationship between elements of the second and third periods of the Periodic Table exemplified by beryllium and aluminium where they exhibit similar chemical properties.

Using the diagonal relationship between beryllium and aluminium, describe, with the aid of an equation, what would be observed when a few drops of water is added to solid $BeCl_2$.

[2]

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(c) Boron and silicon also show a diagonal relationship. For example, both BCl_3 and $SiCl_4$ are readily hydrolysed by water.

(i) By analogy with the reaction of $SiCl_4$, suggest a balanced equation for the hydrolysis of BCl_3.

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(ii) Explain why BCl_3 can undergo hydrolysis like $SiCl_4$. [2]

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(d) Another pair of elements that show diagonal relationship is nitrogen and sulfur. One of the most readily prepared sulfur nitrides is S_4N_4, which can be made by passing dry $NH_3(g)$ into a solution of SCl_2 in an organic solvent.

The reactants react in a ratio of 8 : 3, and sulfur and ammonium chloride are produced.

(i) Construct a balanced equation for this reaction.

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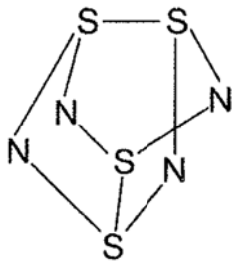
The shape of the molecule of S_4N_4 is described as follows.

* The four N atoms are in a plane.
* All the N atoms have an octet configuration.
* There are two S atoms above the plane, and two S atoms below the plane.
* All the S atoms are in equivalent environment to each other.
* The single lines represent the atom that are bonded to each other. These do not necessarily represent single bonds between those atoms.



(ii) Using the information given about the structure of S_4N_4, draw the pi bonds in the diagram above.

(iii) State the oxidation state of S in S_4N_4.

oxidation state of S in S_4N_4: .....

(iv) Construct a suitable energy cycle to calculate the average S-N bond energy in S_4N_4, using the following data.

$\Delta H_f^{\theta}(S_4N_4)$ = +460 kJ mol^{-1}
ΔH_{at}^{θ}(sulfur) = +279 kJ mol^{-1}
ΔH_{at}^{θ}(nitrogen) = +497 kJ mol^{-1}
(S-S) bond energy in S_4N_4 = +204 kJ mol^{-1}

[6]

[Total: 15]

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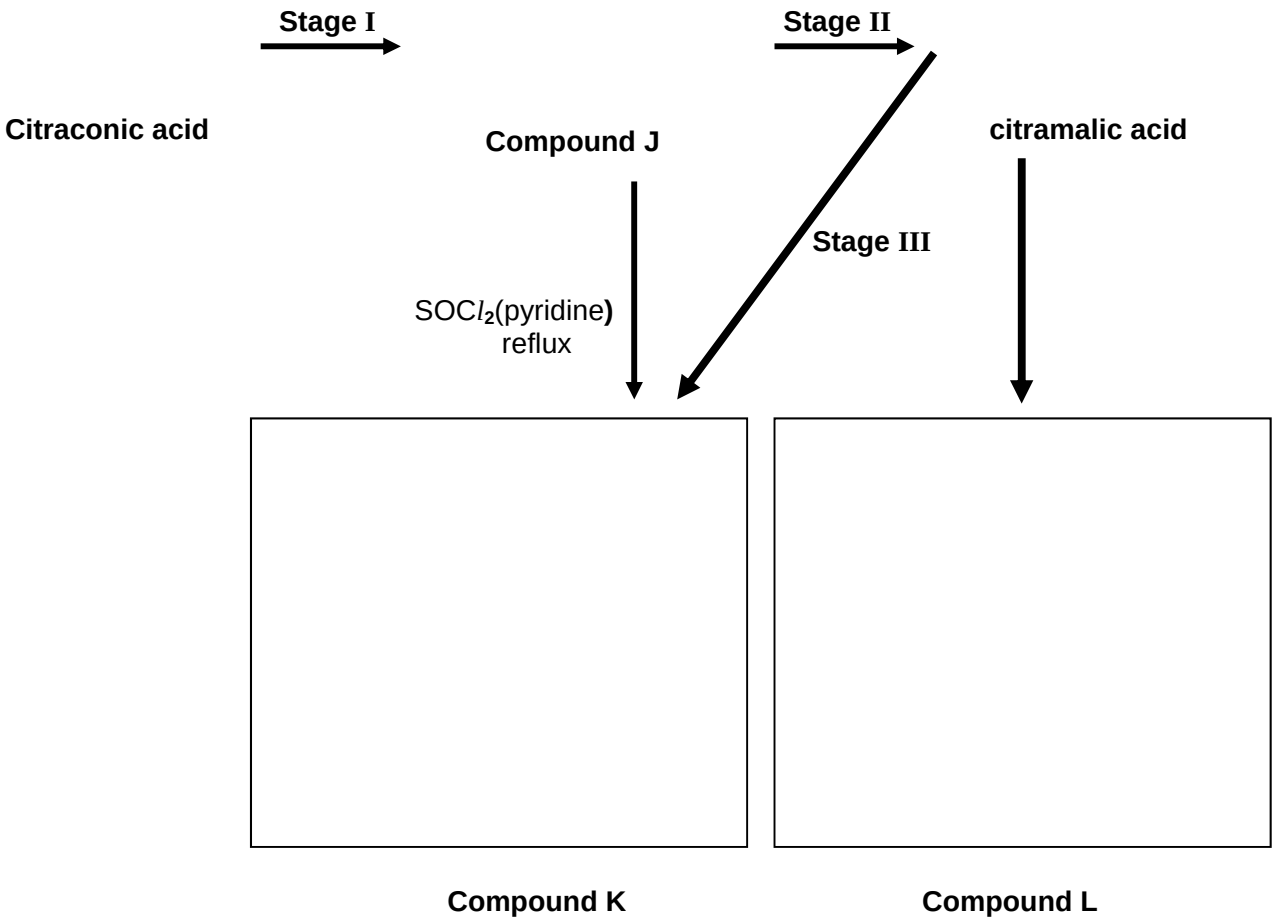
5 Citraconic acid is one of several isomeric carboxylic acids obtained from citric acid. Studies showed that citraconic acid was involved in vitamin B12 synthesis.

(a) Citraconic acid can be converted into citramalic acid by the following scheme:



(i) State the functional groups present in citramalic acid.

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(ii) State the reagents and conditions needed for Stages **I**, **II** and **III**.

	Reagents and Conditions
Stage **I**	
Stage **II**	
Stage **III**	

(iii) Draw the structures of the organic compounds **K** and **L** in the boxes in the scheme.

(iv) Name and describe the mechanism involved in Stage **II**.

(v) In view of the mechanism describe in **(iv)**, explain if the citramalic acid formed in Stage **II** is optically active.

[12]

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(b) Mesaconic acid is a stereoisomer of citraconic acid.

(i) Draw the displayed structure of mesaconic acid.

(ii) Suggest a simple test to differentiate between citraconic acid and mesaconic acid. Explain the basis of your test.

[3]

[Total: 15]

End of Paper