RIVER VALLEY HIGH SCHOOL
JC 2 PRELIMINARY EXAMINATION

CANDIDATE NAME						
CLASS	2	0	J			
CENTRE NUMBER	S					
INDEX NUMBER						

H2 CHEMISTRY

9729/03

Paper 3 Free Response

21 September 2021

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** the questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use								
Question Number	**1**	**2**	**3**	**4**	**5**	**s.f.**	**units**	**Total**
Marks	20	22	18	20	20			80

This document consists of **32** printed pages and **0** blank page.

Section A

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

1 In a 2014 paper published in the Journal of Agricultural and Food Chemistry, Hendon and Colonna-Dashwood discovered the effect of water hardness on coffee flavour. Compounds in hard water tend to attach to the flavourful elements in roasted coffee beans during brewing. Water with higher levels of magnesium will likely extract more flavour from a coffee bean.

Water described as "hard" is high in concentration of Total Dissolved Solids (TDS), specifically calcium and magnesium. The hardness of water may be reported in parts per million (ppm). The solute concentration of a dilute aqueous solution in units of mg dm^{-3} is called parts per million, or ppm.

Classification	**ppm**
Soft	0 – 17.1
Slightly hard	17.1 – 60.0
Moderately hard	60.0 – 120
Hard	120 – 180
Very hard	> 180

(a) In a sample of Singapore's tap water, the concentration of magnesium and calcium ions present are found to be 5.97×10^{-5} mol dm^{-3} and 5.49×10^{-4} mol dm^{-3} respectively. These two ions can be separated by selective precipitation with potassium hydroxide. The numerical values of solubility product of magnesium hydroxide and calcium hydroxide at 25 °C are 1.50×10^{-11} and 5.50×10^{-6} respectively.

(i) Calculate the total concentration of magnesium and calcium ions in ppm, and hence classify the hardness of water in this sample of tap water. **[2]**

(ii) Calculate the minimum pH of the solution at which the magnesium ion precipitates as magnesium hydroxide. **[2]**

(iii) The magnesium hydroxide continues to precipitate out of the solution as potassium hydroxide is being added continuously. Eventually, the concentration of the hydroxide becomes high enough to precipitate the calcium ions as well.

What is the concentration of magnesium ions when calcium ions begin to precipitate?

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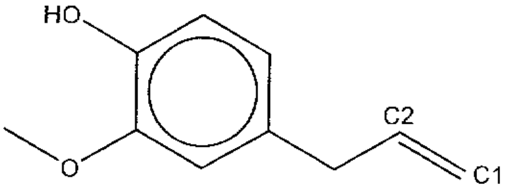
(b) A balanced extraction is a well-brewed cup of coffee that is aromatic and rich in flavours. Eugenol is a flavour note with a "woodsy" taste found in coffee, wine and whisky.



Eugenol

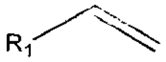
Like other alkenes, it undergoes hydrohalogenation when treated with hydrogen halides.

(i) Draw a labelled diagram showing the orbital overlap between the carbon atoms C1 and C2 and state the hybridisation involved.

Do **not** include other atoms. **[2]**

(ii) Hydrohalogenation of unsymmetrical alkenes results in a mixture of products. In such cases, the major product can be predicted using Markovnikov's rule.

Describe the mechanism of the reaction between eugenol and hydrogen chloride.

You may represent eugenol using  . **[2]**

(iii) With reference to your mechanism in **(b)(ii)**, explain why the major product is formed. **[2]**

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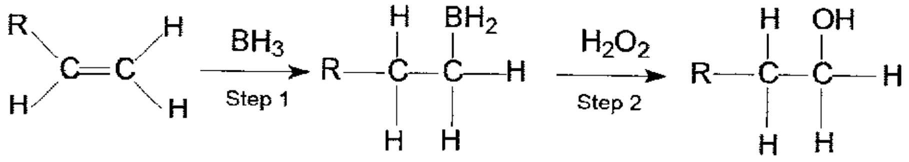
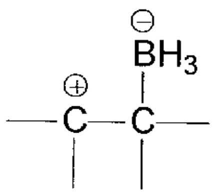
(c) Hydration of alkenes via hydroboration favours formation of the anti–Markovnikov product. The hydroboration reaction involves 2 stages: first with limited borane, BH_3, followed by treatment with alkaline hydrogen peroxide.



R = alkyl/aryl group

It is suggested that the mechanism goes through the formation of the intermediate below.



(i) The initial reaction between the alkene and borane can be considered to occur in a similar fashion as the hydrohalogenation reaction in **(b)(ii)**.

Suggest the mechanism showing the formation of the intermediate given above when eugenol reacts with borane. Indicate clearly the polarity of the B–H bond in borane by drawing δ+ and δ– on the appropriate atoms. **[2]**

(ii) By determining the change in the oxidation number of the reactive carbon, suggest the role of hydrogen peroxide in Step 2 in the reaction. **[1]**

(d) 3 bottles of halogens are labelled as X_2, Y_2 and Z_2. They are chlorine, bromine and iodine.

The table shows the results of experiments in which the halogens X_2, Y_2 and Z_2 were added to separate solutions [illegible] and Z^- ions.

	X^-(aq)	Y^-(aq)	Z^-(aq)
X_2	no reaction	no reaction	no reaction
Y_2	X_2 formed	no reaction	Z_2 formed
Z_2	X_2 formed	no reaction	no reaction

With reference to the table above, identify the halogens **X**, **Y** and **Z**. Explain your reasoning. **[2]**

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(e) A glass rod was heated in a Bunsen burner flame and placed into a jar of hydrogen chloride gas. The experiment was repeated using a jar of hydrogen iodide gas. A colour change was observed in one of the samples.

Using relevant data from *Data Booklet*, explain these observations.

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[Total: 20]

2 Nitrous acid, HNO_2, is a weak monoprotic acid. HNO_2 is unstable and decomposes readily.

It can be prepared by acidification of aqueous solutions of potassium nitrite with a mineral acid. The acidification is usually conducted at low temperatures, and the HNO_2 is consumed *in situ*.

An equilibrium exists as follows.

$$H^+(aq) + NO_2^-(aq) \rightleftharpoons HNO_2(aq),$$
$$K_c = 1.66 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$$

(a) Calculate the value of the acid dissociation constant, K_a, of HNO_2. [1]

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(b) A solution of HNO_2 was prepared by mixing equal volumes of 0.40 mol dm^{-3} HCl(aq) with 0.40 mol dm^{-3} KNO_2(aq).

Calculate the pH of this solution. **[2]**

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(c) Calculate the pH of the aqueous mixture when 10.0 cm^3 of 0.400 mol dm^{-3} $HCl(aq)$ is added to 30.0 cm^3 of 0.400 mol dm^{-3} $KNO_2(aq)$. **[2]**

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(d) Gaseous nitrous acid decomposes into nitrogen dioxide, nitric oxide, and water:

$$2HNO_2 \rightarrow NO_2 + NO + H_2O$$

(i) Draw the dot–and–cross diagram of NO_2.

Explain the difference in bond angles in H_2O and NO_2. **[2]**

(ii) Calculate the increase in pressure when 2.00 g of HNO_2 decomposes under 1 atm and 150 °C in a 1 dm^3 container. **[2]**

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(e) Similar to HNO_2, 3–chloropropanoic acid is a weak monobasic organic acid.

Compounds **E** and **F** are constitutional isomers of 3–chloropropanoic acid.

When the same amount of 3–chloropropanoic, **E** and **F**, is each added to separate portions of water of equal volume, the three solutions obtained have pH values as shown in the table below.

compound	pH of aqueous solution
3–chloropropanoic acid	2.3
E	1.9
F	1.0

Suggest structural formulae for compounds **E** and **F** and hence, account for the difference in pH values of the three solutions obtained. One of the compounds has the structure R–O–R. **[4]**

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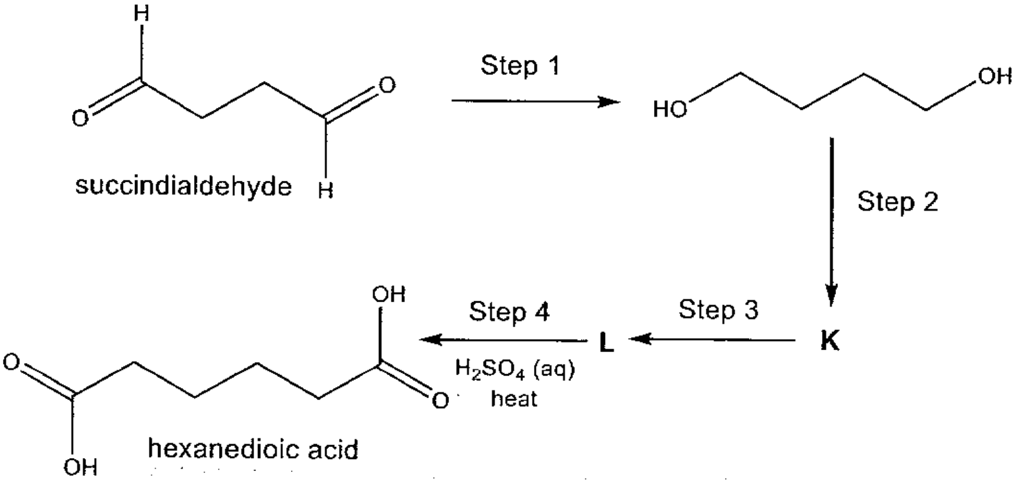
(f) Hexanedioic acid, a diprotic acid, can be synthesised from succindialdehyde by the following synthesis pathway.



(i) Suggest reagents and conditions for each of the Steps 1, 2 and 3. **[3]**

(ii) Suggest the structures for **K** and **L**. **[2]**

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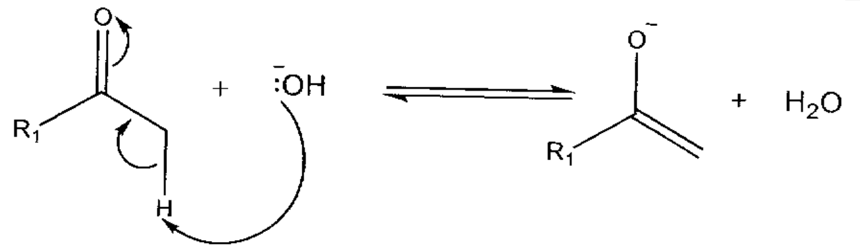
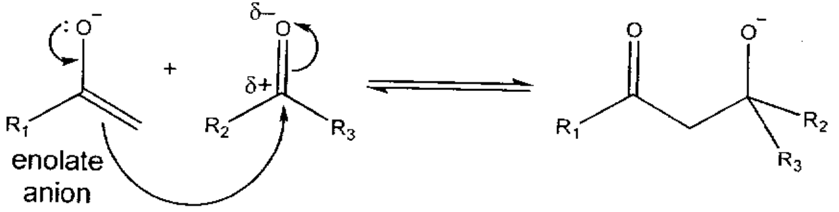
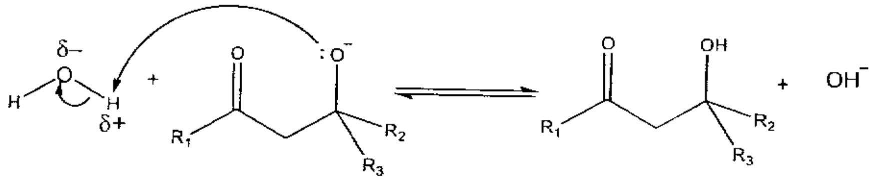
(g) Carbonyl compounds can undergo the Aldol reaction under basic conditions. The mechanism is shown below.

Step 1	
	One of the hydrogen atoms, bonded to the carbon next to the carbonyl carbon, forms a bond with a hydroxide ion via an acid–base reaction.
Step 2	
	Nucleophilic attack by enolate anion.
Step 3	
	Acid–base reaction.
R1, R2, R3 = H, alkyl or aryl	

(i) Suggest the structure of the compound formed from the Aldol reaction between 1 molecule of succindialdehyde and 1 molecule of methanal. **[1]**

(ii) Compound **M** is a compound with 8 carbon atoms and undergoes the following reactions.

- **M** gives an orange precipitate with 2,4–DNPH.
- **M** does not react with Tollens' reagent.
- **M** reacts with alkaline aqueous iodine to give a yellow precipitate and product **N**, $C_7H_5O_2^-$.
- **M** undergoes Aldol reaction to form **O**, $C_{16}H_{16}O_2$, under basic conditions.

Suggest the structures for **M**, **N** and **O**. **[3]**

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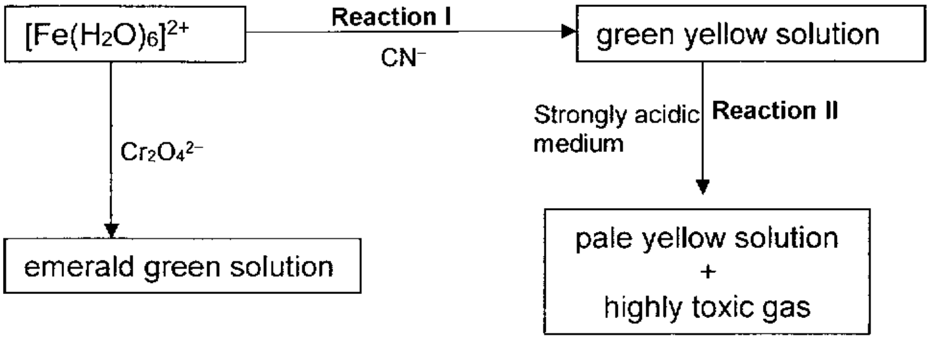
[Total: 22]

3 **(a)** The following scheme illustrates a series of reaction involving $Fe^{3+}(aq)$.



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

(ii) State the type of reaction which occurred in reaction **I** and write an equation for the reaction. **[2]**

(iii) Write an equation for reaction **II**. **[1]**

(iv) Given that $C_2O_4^{2-}$ is a bidentate ligand, draw the structural formula of the complex formed. **[1]**

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(b) Ferromanganese is an alloy added to steels to improve their mechanical properties. A 15.0 g sample of ferromanganese was dissolved in 250 cm^3 of dilute sulfuric acid to give an solution containing iron(II) sulfate and manganese(II) sulfate. 25.0 cm^3 of the resulting solution required 20.0 cm^3 of 0.0360 mol dm^{-3} of potassium manganate(VII) solution for complete reaction.

(i) By using the *Data Booklet*, construct a balanced equation for the reaction between resulting solution and potassium manganate(VII) solution. **[1]**

(ii) Calculate the percentage by mass of iron in ferromanganese. **[3]**

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(c) Neutral $FeCl_3$ remains yellow when reacted with compound **S**, $C_{11}H_{10}O_3$. **S** gives a silver mirror with silver diammine complex. However, **S** does not give a precipitate with hot alkaline Cu^{2+} solution.

S is heated with acidified $KMnO_4$ for several hours to give benzene–1,2,3–tricarboxylic acid as one of the organic products. When heated with NaOH(aq) followed by acidification, **S** forms **T**, $C_{11}H_{12}O_4$. **T** reacts with alkaline aqueous iodine to give a yellow precipitate. **S** reacts with $NaBH_4$ to give **U**, $C_{11}H_{12}O_3$.

Suggest the structures for **S**, **T** and **U**. Explain the reactions described. **[9]**

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[Total : 18]

Section B

Answer **one** question from this section.

4 **(a)** Alkaline earth metals, also known as Group 2 elements, are highly metallic and are good conductors of electricity. They have a grey-white lustre when freshly cut but tarnish readily in air.

(i) Describe and explain the trend in thermal stability of the Group 2 carbonates. **[2]**

(ii) When ozone (O_3) is passed over dry powdered BaO at `10.0 °C, barium ozonide, $Ba(O_3)_2$, is formed as a red-brown solid.

Adding water to the solid and warming to room temperature causes a reaction to occur. Oxygen gas is produced and an alkaline solution is left.

Write a balanced equation for the reaction between barium ozonide and water. **[1]**

(iii) Suggest a suitable temperature to produce calcium ozonide by passing ozone through powdered CaO. **[1]**

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(b) Ozone is usually produced by passing oxygen gas through two highly-charged electrical plates.

$$3O_2(g) \rightarrow 2O_3(g)$$

The reaction does not go to completion and a mixture of gases will be produced.

The concentration of O_3 in the mixture can be determined by its reaction with aqueous KI.

$$O_3 + 2KI + H_2O \rightarrow I_2 + O_2 + 2KOH$$

The iodine formed can be estimated by its reaction with sodium thiosulfate.

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

When 300 cm^3 of an oxygen/ozone gaseous mixture at s.t.p. was passed into an excess of aqueous KI, and the iodine formed was titrated against $Na_2S_2O_3$. 24.0 cm^3 of 0.100 mol dm^{-3} $Na_2S_2O_3$ was required to discharge the iodine colour.

(i) Suggest a suitable indicator can be used in the titration and state the colour change at end point. **[1]**

(ii) Calculate the percentage of O_3 in the gaseous mixture. **[2]**

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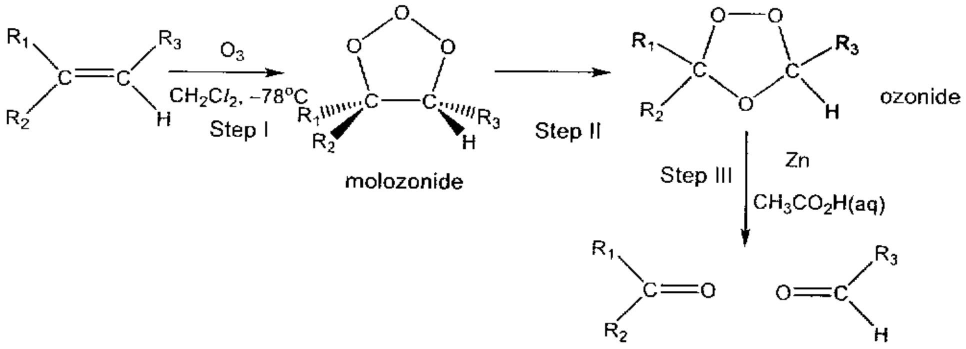
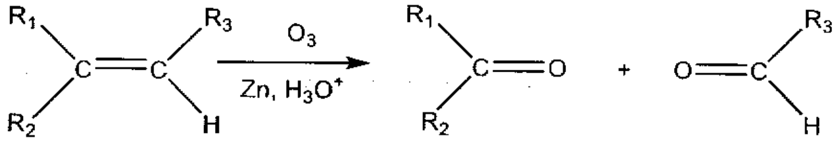
(c) Ozone adds rapidly to alkenes at low temperature to give cyclic intermediates, called molozonides. Once formed, molozonides then rapidly rearranges to form ozonides. The reaction scheme is shown below.



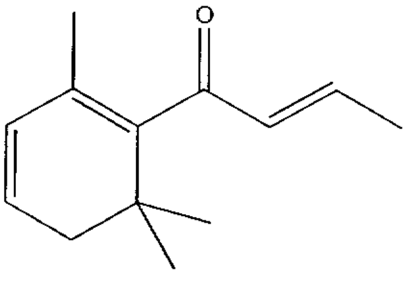
The reaction can also be expressed as



(i) State the type of reaction occurring in Step I of the reaction scheme. **[1]**

(ii) Suggest the role of zinc in the reaction scheme. **[1]**

(iii) β-Damascenone is a chemical compound found in whisky, which is an alcoholic liquor. Also known as rose ketones, β-damascenone is a key compound that contributes a floral note to whisky.



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β-damascenone

Predict the organic products formed when β-damascenone reacts with ozone as shown by the reaction scheme above.

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(d) Apart from β-damascenone, whisky contains an array of compounds that affect its taste and flavour, which include phenolic compounds, aldehydes and esters. The use of different grains, distillation process and wood used in the ageing process can also change the flavour profile.

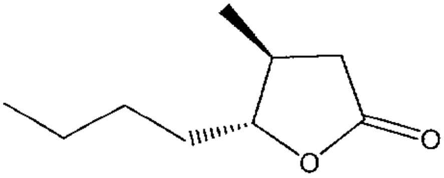
(i) Phenolic compounds in general contributes smoky flavours and bitterness in whisky. In Scotch whisky, the use of peat fires to dry the barley grains creates a class of medicinal-smelling compounds known as cresols.

Cresols exists as constitutional isomers with the formula C_7H_8O. When added to aqueous bromine, rapid decolourisation followed by the formation of a white precipitate is observed for all isomers of cresol.

Draw all the possible isomers of cresol. **[3]**

(ii) Whisky lactones, such as trans-3-methyl-4-octanolide, are responsible for the woody, spicy and coconut flavour notes.

A student wanted to synthesise an amide from this lactone.



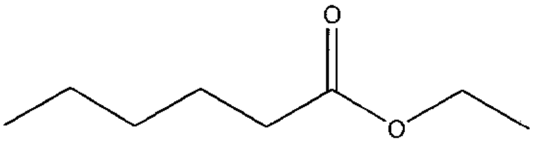
trans-3-methyl-4-octanolide

The following steps were proposed.

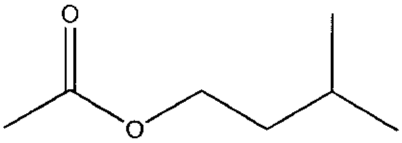
1. heat with dilute H_2SO_4
2. addition of ethylamine

Comment on the feasibility of this reaction scheme. **[2]**

(iii) Esters in whisky can also contribute fruity flavours such as ethyl hexanoate, which imparts a sweet apple flavor, and isoamyl acetate, which gives a banana aroma.



ethyl hexanoate



isoamyl acetate

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Describe a simple chemical test that can be used to distinguish ethyl hexanoate from isoamyl acetate.

State any observations you would make with each compound.

(iv) Whisky is a mixture of water, ethanol and organic compounds like whisky lactones. When the alcoholic whisky is stored for a long period of time, as the ethanol content decreases, a cloudiness can be observed in the whisky.

Suggest a reason why the cloudiness occurs. **[1]**

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[Total: 20]

5 Cyclopropane is an explosive, colourless gas that was discovered by August Freund in 1881, and was once used as a general anesthetic in clinical practice.

(a) Cyclopropane can undergo isomerisation to propene at 298 K.

$\Delta H_{\text{isomerisation}} = -33.0$ kJ mol^{-1}

Table 5.1

	ΔH / kJ mol^{-1}
standard enthalpy change of formation of $CO_2(g)$	−394
standard enthalpy change of formation of $H_2O(l)$	−286
standard enthalpy change of combustion of cyclopropane	−2091

Using the data given above and in Table 5.1, construct a suitable energy cycle and calculate the enthalpy change of formation of propene at 298 K. **[3]**

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(b) 100 cm^3 of a mixture of methane and cyclopropane was completely burnt in 300 cm^3 of oxygen and then cooled to room temperature.

The total volume of the gaseous reaction mixture decreases by 215 cm^3.

On passing the resultant gaseous mixture through potassium hydroxide, the final volume was found to be 25.0 cm^3.

What is the ratio of methane to cyclopropane in the original mixture? **[2]**

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Cyclopropane can undergo free radical substitution with chlorine, similar to an aliphatic alkane. Chlorocyclopropane is the major product formed under a certain set of conditions.

(c) **(i)** State the conditions needed to produce chlorocyclopropane as the major product. **[1]**

(ii) Describe the mechanism for this reaction. **[3]**

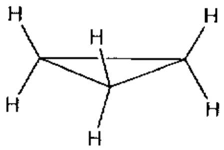
Trichlorocyclopropane, $C_3H_3Cl_3$, is one of the possible polysubstituted by-products of the reaction under a different set of conditions.

This tri-substituted cycloalkane can exist as 3 constitutional isomers, all of which exhibit stereoisomerism.

(iii) Define the term *stereoisomerism.* **[1]**

(iv) Draw the structures of the 3 isomers of trichlorocyclopropane and suggest the type of stereoisomerism associated with each of them.

Note: You may refer to the diagram of cyclopropane shown below to draw the isomers.



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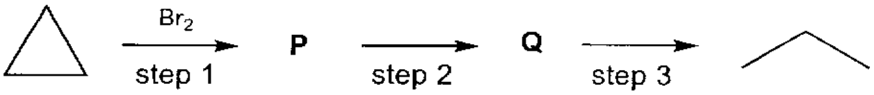
(d) However, in the absence of ultraviolet light, cyclopropane can undergo addition reactions similarly as alkenes. This leads to the opening of the ring structure.

For example,

(i) Suggest a possible reason why cyclopropane can undergo addition reactions, unlike aliphatic alkanes. **[1]**

(ii) Propane can be produced from cyclopropane in a three-step synthesis as shown below.

Suggest the reagents and conditions you would use in steps 2 and 3, and identify the intermediates **P** and **Q**.



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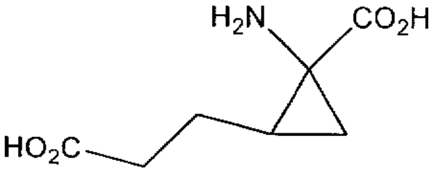
(e) A possible amino acid derivative of cyclopropane is shown below.



Draw the structure of the zwitterion formed by this amino acid derivative. **[1]**

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RIVER VALLEY HIGH SCHOOL
JC 2 PRELIMINARY EXAMINATION

CANDIDATE NAME						
CLASS	2	0	J			
CENTRE NUMBER	S					
INDEX NUMBER						

H2 CHEMISTRY

9729/03

Paper 3 Free Response

21 September 2021

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** the questions.

Section B
Answer **one** question. **Circle** the question number of the question you attempted.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use								
Question Number	**1**	**2**	**3**	**4**	**5**	**s.f.**	**units**	**Total**
Marks	20	22	18	20	20			80

This document consists of **32** printed pages and **0** blank pages.

Section A

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

1 In a 2014 paper published in the Journal of Agricultural and Food Chemistry, Hendon and Colonna-Dashwood discovered the effect of water hardness on coffee flavour. Compounds in hard water tend to attach to the flavourful elements in roasted coffee beans during brewing. Water with higher levels of magnesium will likely extract more flavour from a coffee bean.

Water described as "hard" is high in concentration of Total Dissolved Solids (TDS), specifically calcium and magnesium. The hardness of water may be reported in parts per million (ppm). The solute concentration of a dilute aqueous solution in units of mg dm^{-3} is called parts per million, or ppm.

Classification	**ppm**
Soft	0 – 17.1
Slightly hard	17.1 – 60.0
Moderately hard	60.0 – 120
Hard	120 – 180
Very hard	> 180

(a) In a sample of Singapore's tap water, the concentration of magnesium and calcium ions present are found to be 5.97×10^{-5} mol dm^{-3} and 5.49×10^{-4} mol dm^{-3} respectively. These two ions can be separated by selective precipitation with potassium hydroxide. The numerical values of solubility product of magnesium hydroxide and calcium hydroxide at 25 °C are 1.50×10^{-11} and 5.50×10^{-6} respectively.

(i) Calculate the total concentration of magnesium and calcium ions in ppm, and hence classify the hardness of water in this sample of tap water. **[2]**

$[Mg^{2+}]$ in ppm = $5.97 \times 10^{-5} \times 24.3 \times 1000$

= 1.45 ppm

$[Ca^{2+}]$ in ppm = $5.49 \times 10^{-4} \times 40.1 \times 1000$

= 22.0 ppm

Total $[Mg^{2+}]$ and $[Ca^{2+}]$ = 1.45 + 22.0 = 23.5 ppm

The sample of water is slightly hard.

(ii) Calculate the minimum pH of the solution at which the magnesium ion precipitates as magnesium hydroxide. **[2]**

Ppt is formed when IP ($Mg(OH)_2$) ≥ K_{sp} ($Mg(OH)_2$),

$(5.97 \times 10^{-5})[OH^-]^2 \geq 1.5 \times 10^{-11}$ mol^3 dm^{-9}

$[OH^-] \geq 5.01 \times 10^{-4}$ mol dm^{-3}

Minimum pH = 14 – pOH

= 14 – 3.30

= 10.7

(iii) The magnesium hydroxide continues to precipitate out of the solution as potassium hydroxide is being added continuously. Eventually, the concentration of the hydroxide becomes high enough to precipitate the calcium ions as well.

What is the concentration of magnesium ions when calcium ions begin to precipitate? **[2]**

When IP ($Ca(OH)_2$) = K_{sp} ($Ca(OH)_2$),

$(5.49 \times 10^{-4})[OH^-]^2 = 5.5 \times 10^{-6}$ mol^3 dm^{-9}

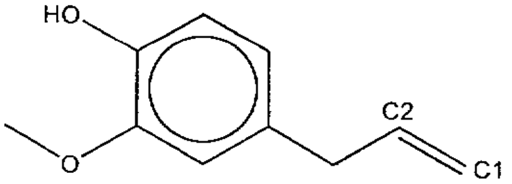
$[OH^-] = 0.100$ mol dm^{-3}

When IP ($Mg(OH)_2$) = K_{sp} ($Mg(OH)_2$),

$[Mg^{2+}](0.100)^2 = 1.5 \times 10^{-11}$ mol^3 dm^{-9}

$[Mg^{2+}] = 1.50 \times 10^{-9}$ mol dm^{-3}

(b) A balanced extraction is a well-brewed cup of coffee that is aromatic and rich in flavours. Eugenol is a flavour note with a "woodsy" taste found in coffee, wine and whisky.

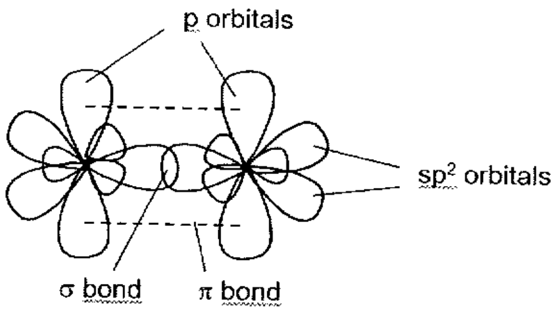


Eugenol

Like other alkenes, it undergoes hydrohalogenation when treated with hydrogen halides.

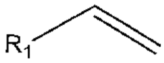
(i) Draw a labelled diagram showing the orbital overlap between the carbon atoms C1 and C2 and state the hybridisation involved.

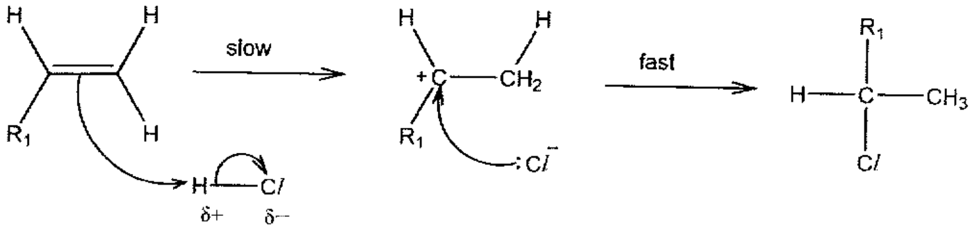
Do **not** include other atoms. **[2]**



(ii) Hydrohalogenation of unsymmetrical alkenes results in a mixture of products. In such cases, the major product can be predicted using Markovnikov's rule.

Describe the mechanism of the reaction between eugenol and hydrogen chloride.

You may represent eugenol using  . **[2]**

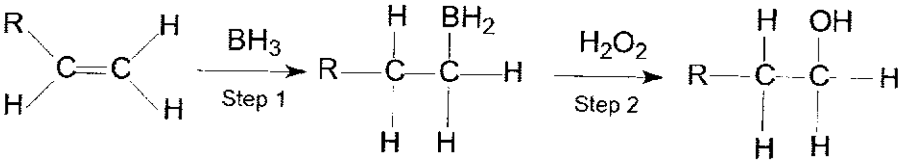


(iii) With reference to your mechanism in **(b)(ii)**, explain why the major product is formed. **[2]**

In step 1, the more stable secondary carbocation intermediate is formed instead of a primary carbocation.

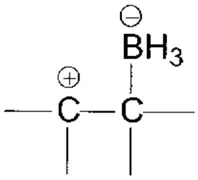
(More) alkyl groups exert an electron–donating effect, helping to reduce/ disperse the positive charge on the carbocation, stabilising it.

(c) Hydration of alkenes via hydroboration favours formation of the anti–Markovnikov product. The hydroboration reaction involves 2 stages; first with limited borane, BH_3, followed by treatment with alkaline hydrogen peroxide.



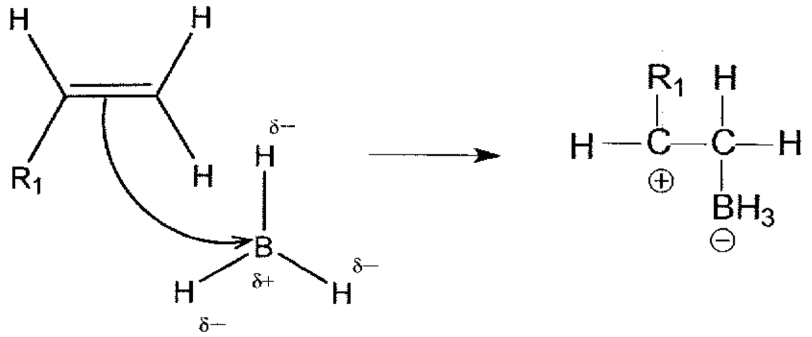
R = alkyl/aryl group

It is suggested that the mechanism goes through the formation of the intermediate below.



(i) The initial reaction between the alkene and borane can be considered to occur in a similar fashion as the hydrohalogenation reaction in **(b)(ii)**.

Suggest the mechanism showing the formation of the intermediate given above when eugenol reacts with borane. Indicate clearly the polarity of the B–H bond in borane by drawing δ+ and δ– on the appropriate atoms. **[2]**



(ii) By determining the change in the oxidation number of the reactive carbon, suggest the role of hydrogen peroxide in step 2 in the reaction. **[1]**

Oxidation number of C bonded to $-BH_2$ changes from –3 to –1.

H_2O_2 acts as an oxidising agent.

(d) 3 bottles of halogens are labelled as **X_2, Y_2 and Z_2**. They are chlorine, bromine and iodine.

The table shows the results of experiments in which the halogens **X_2**, **Y_2** and **Z_2** were added to separate solutions containing **X^-**, **Y^-** and **Z^-** ions.

	X^-(aq)	**Y^-(aq)**	**Z^-(aq)**
X_2	no reaction	no reaction	no reaction
Y_2	**X_2** formed	no reaction	**Z_2** formed
Z_2	**X_2** formed	no reaction	no reaction

[2]

With reference to the table above, identify the halogens **X, Y** and **Z.** Explain your reasoning.

Y$_2$ displaces (oxidises) both **X**$^-$ and **Z**$^-$ from solution, hence it must be the strongest oxidising agent, Cl_2 (or **Y**$^-$ is the weakest reducing agent).

X$_2$ cannot displace (oxidise) **Y**$^-$ and **Z**$^-$ from solution, hence it must be the weakest oxidising agent, I_2 (or **X**$^-$ is the strongest reducing agent). Therefore, **Z**$_2$ is Br_2.

(e) A glass rod was heated in a Bunsen burner flame and placed into a jar of hydrogen chloride gas. The experiment was repeated using a jar of hydrogen iodide gas. A colour change was observed in one of the samples.

Using relevant data from *Data Booklet*, explain these observations. **[3]**

The sample with HI will give a colour change.

Bond energy of HCl = 431 kJ mol^{-1}

Bond energy of HI = 299 kJ mol^{-1}

The thermal stability of hydrogen halides decreases down the Group due to decreasing H–X bond energy. The I atom is larger than the C*l* atom and its valence orbitals are more diffuse. This results in less effective overlap between the small H atom and the larger I atom and less energy is required to break the weaker H–I bond, forming H_2 and (violet fumes) of I_2, accounting for the colour change.

[Total: 20]

2 Nitrous acid, HNO_2, is a weak monoprotic acid. HNO_2 is unstable and decomposes readily.

It can be prepared by acidification of aqueous solutions of potassium nitrite with a mineral acid. The acidification is usually conducted at ice temperatures, and the HNO_2 is consumed *in situ*.

An equilibrium exists as follows.

$$H^+(aq) + NO_2^-(aq) \rightleftharpoons HNO_2(aq),$$
$$K_c = 1.66 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$$

(a) Calculate the value of the acid dissociation constant, K_a, of HNO_2. **[1]**

$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$

K_a
$= 1 / K_c$
$= 1 / 1.66 \times 10^3$
$= 6.02 \times 10^{-4}$ mol dm^{-3}

(b) A solution of HNO_2 was prepared by mixing equal volumes of 0.40 mol dm^{-3} HCl(aq) with 0.40 mol dm^{-3} KNO_2(aq).

Calculate the pH of this solution. **[2]**

Initial concentration of $HNO_2(aq)$ after mixing
= 0.40 / 2
= 0.20 mol dm^{-3}.

$[H^+]$
= $\sqrt{(6.02 \times 10^{-4})(0.20)}$
= 1.097×10^{-2} mol dm^{-3}

pH
= $-\lg (1.097 \times 10^{-2})$
= 1.96

(c) Calculate the pH of the aqueous mixture when 10.0 cm^3 of 0.400 mol dm^{-3} HCl (aq) is added to 30.0 cm^3 of 0.400 mol dm^{-3} KNO_2 (aq). **[2]**

$[HNO_2]$
$= \frac{10}{1000} \times 0.400 / \frac{40}{1000}$
= 0.100 mol dm^{-3}

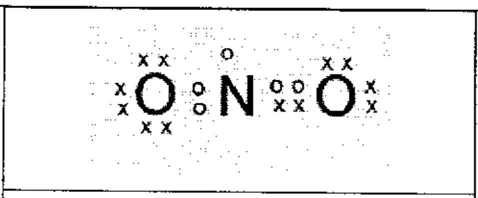
$[NO_2^-]$
$= \frac{20}{1000} \times 0.400 / \frac{40}{1000}$
= 0.200 mol dm^{-3}

Buffer calculation
$pH = pK_a + \lg\frac{[salt]}{[acid]}$
$pH = -\lg(6.02 \times 10^{-4}) + \lg(\frac{0.200}{0.100})$
pH = 3.52 [1]

(d) Gaseous nitrous acid decomposes into nitrogen dioxide, nitric oxide, and water:

$$2HNO_2 \rightarrow NO_2 + NO + H_2O$$

(i) Draw the dot–and–cross diagram of NO_2.
Explain the difference in bond angles in H_2O and NO_2. **[2]**



NO_2

In water, the H–O–H bond angle is **smaller** than the O–N–O bond angle as the **lone electron on N** in NO_2 exerts **weaker lone electron–bond pair repulsion** as compared to the **2 lone pairs of electrons on O** in H_2O.

(ii) Calculate the increase in pressure when 2.00 g of HNO_2 decomposes under 1 atm and 150 °C in a 1 dm^3 container. **[2]**

Molar mass of HNO_2 = 47.0 g mol^{-1}

Amount of $HNO_2 = \frac{2.00}{47.0} = 4.255 \times 10^{-2}$ mol

Increase in number of moles of gases

$= (3–2) \times 4.255 \times 10^{-2} \times 1/2$

$= 2.128 \times 10^{-2}$ mol

Increase in pressure

$= \frac{nRT}{V}$

$= \frac{(0.02128)(8.31)(150+273)}{0.001}$

$= 7.48 \times 10^{4}$ Pa

(e) Similar to HNO_2, 3–chloropropanoic acid is a weak monobasic organic acid.

Compounds **E** and **F** are constitutional isomers of 2–chloropropanoic acid.

When the same amount of 3–chloropropanoic, **E** and **F**, is each added to separate portions of water of equal volume, the three solutions obtained have pH values as shown in the table below.

compound	pH of aqueous solution
3–chloropropanoic acid	2.3
E	1.9
F	1.0

Suggest structural formulae for compounds **E** and **F** and hence, account for the difference in pH values of the three solutions obtained. One of the compounds has the structure of R–O–R. **[4]**

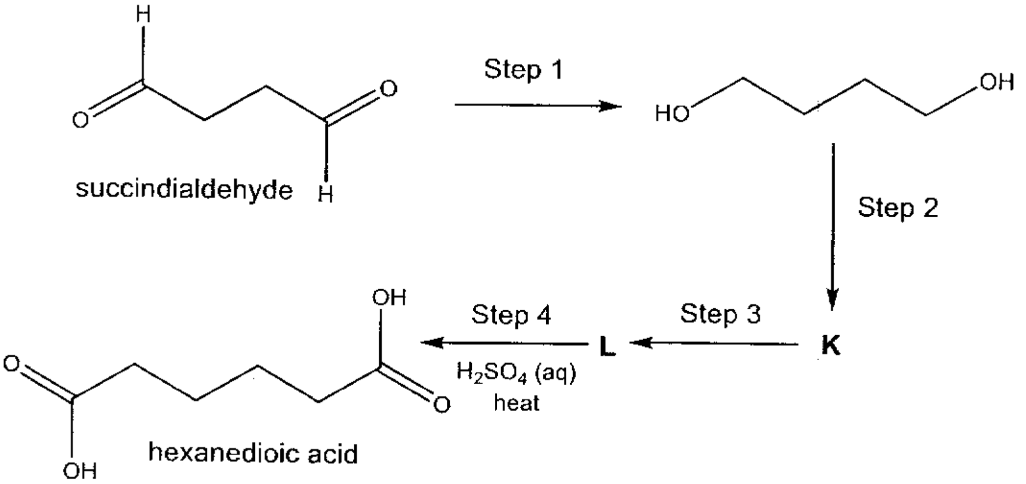
E is 2–chloropropanoic acid

F is $CH_3–O–CH_2COCl$

The aqueous solution of **E** has a lower pH than that of 3–chloropropanoic acid because **E** is **a stronger acid** than 3–chloropropanoic acid. The electron-withdrawing $–Cl$ atom is **nearer to** the $–CO_2^-$ group in $CH_2CH_2ClCO_2^-$. Thus, the negative charge in the $CH_2CH_2ClCO_2^-$ ion is **more dispersed** and this ion is **more stable** than the $CH_2ClCH_2CO_2^-$ ion.

The aqueous solution of **F** has a lower pH than that of 2-chloropropanoic acid because **F** reacts with water to produce **hydrochloric acid**, which is a **strong acid**.

(f) Hexanedioic acid, a diprotic acid, can be synthesised from succindialdehyde by the following synthesis pathway.



(i) Suggest reagents and conditions for each of the Steps 1, 2 and 3. **[3]**

Step 1: $LiAlH_4$ in dry ether

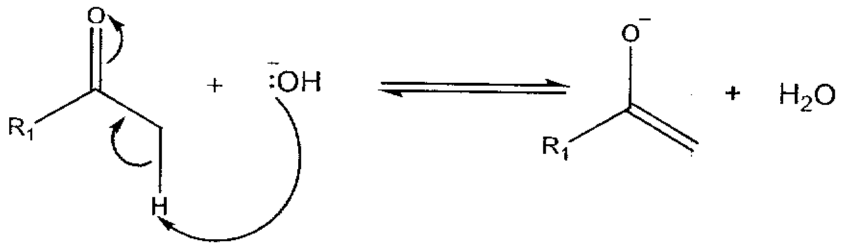
Step 2: (dry) PCl_5

Step 3: ethanolic KCN, heat under reflux

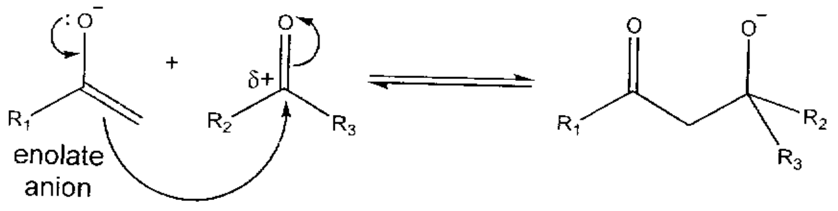
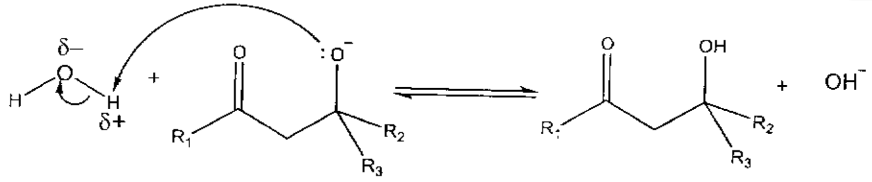
(ii) Suggest the structures for **K** and **L**. **[2]**

	
K	**L**

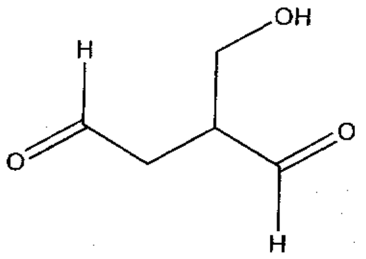
(g) Carbonyl compounds can undergo the Aldol reaction under basic conditions. The mechanism is shown below.

Step 1	
	One of the hydrogen atoms, bonded to the carbon next to the carbonyl carbon, forms a bond with a hydroxide ion via an acid–base reaction.

δ–

Step 2	
	Nucleophilic attack by enolate anion.
Step 3	
	Acid–base reaction.
R_1, R_2, R_3 = H, alkyl or aryl	

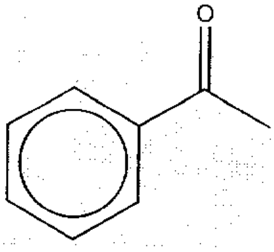
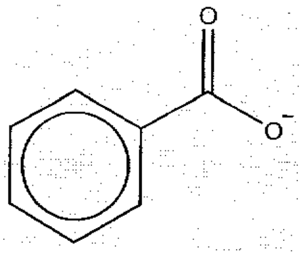
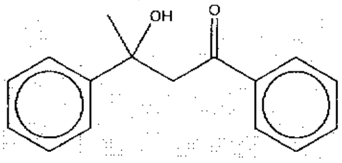
(i) Suggest the structure of the compound formed from the Aldol reaction between 1 molecule of succindialdehyde and 1 molecule of methanal. **[1]**



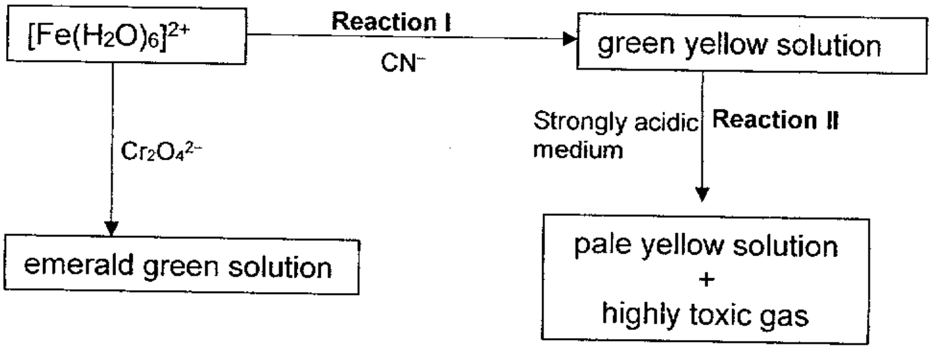
(ii) Compound **M** is a compound with 8 carbon atoms and undergoes the following reactions.

- **M** gives an orange precipitate with 2,4–DNPH.
- **M** does not react with Tollen's reagent.
- **M** reacts with alkaline aqueous iodine to give a yellow precipitate and product **N**, $C_7H_5O_2^-$.
- **M** undergoes Aldol reaction to form **O**, $C_{16}H_{16}O_2$, under basic conditions.

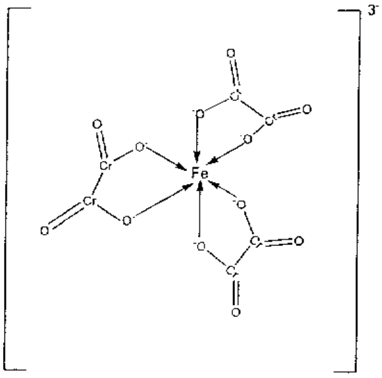
Suggest the structures for **M**, **N** and **O**. **[3]**

				
		M	**N**	**O**
		[Total: 22]		

3 **(a)** The following scheme illustrates a series of reaction involving Fe^{3+}(aq).



		(i)	Define transition element	[1]
			A transition element is a d-block element which forms at least one stable ion with a partially filled d subshell.	

		(ii)	State the type of reaction which occurred in reaction **I** and write an equation for the reaction.	**[2]**
			type of reaction : ligand exchange equation : $[Fe(H_2O)_6]^{3+} + 6CN^- \rightarrow [Fe(CN)_6]^{3-} + 6H_2O$	
		(iii)	Write an equation for reaction **II**.	**[1]**
			$[Fe(CN)_6]^{3-}\ 6H^+ + 6H_2O \rightarrow [Fe(H_2O)_6]^{3+} + 6HCN$	
		(iv)	Given that $C_2O_4^{2-}$ is a bidentate ligand, draw the structural formula of the complex formed.	**[1]**
				
	(b)	Ferromanganese is an alloy added to steels to improve their mechanical properties. A 15.0 g sample of ferromanganese was dissolved in 250 cm^3 of dilute sulfuric acid to give an solution containing iron(II) sulfate and manganese(II) sulfate. 25.0 cm^3 of the resulting solution required 20.0 cm^3 of 0.0360 mol dm^{-3} of potassium manganate(VII) solution for complete reaction.		
		(i)	By using the *Data Booklet*, construct a balanced equation for the reaction between resulting solution and potassium manganate(VII) solution.	**[1]**
			$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$	
		(ii)	Calculate the percentage by mass of iron in ferromanganese.	**[3]**
			amt of $MnO_4^- = \frac{20.0}{1000} \times 0.036 = 7.20 \times 10^{-4}$ mol amt of Fe^{2+}in 25 cm^3 = $7.20 \times 10^{-4} \times 5 = 3.60 \times 10^{-3}$ mol amt of Fe^{2+}in 250 cm^3 = $3.60 \times 10^{-3} \times \frac{250}{25} = 3.60 \times 10^{-2}$ mol mass of Fe in sample = $3.60 \times 10^{-2} \times 55.8 = 2.009$ g	

% of Fe in sample = $\frac{2.009}{15} \times 100\% = 13.4\%$

(c) Neutral $FeCl_3$ remain yellow when reacted with compound **S**, $C_{11}H_{10}O_3$. **S** gives a silver mirror with silver diammine complex. However, **S** does not give a precipitate with hot alkaline Cu^{2+} solution.

S is heated with acidified $KMnO_4$ for several hours to give benzene–1,2,3–tricarboxylic acid as the one of the organic products. When heated with NaOH(aq) followed by acidification, **S** forms **T**, $C_{11}H_{12}O_4$. **T** reacts with alkaline aqueous iodine to give yellow precipitate. **S** reacts with $NaBH_4$ to give **U**, $C_{11}H_{12}O_3$.

Suggest the structure for **S**, **T** and **U**. Explain the reactions described. **[9]**

S does not react with neutral $FeCl_3$ ⇒ phenol is not present

In **S**, the C:H ratio is 1:1 ⇒ benzene is present

S undergoes oxidation with silver diammine complex

⇒ aldehyde is present

S does not undergoes oxidation with Cu^{2+} ⇒ aromatic aldehyde is present

S undergoes oxidation with hot acidified $KMnO_4$ to give benzene-1,2,3-tricarboxylic acid as the only organic product.

⇒ substituents of benzene ring are on 1,2,3 position

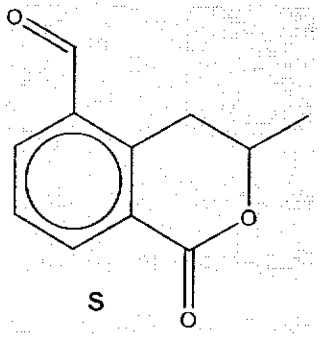
S undergoes alkaline hydrolysis to form **T**

⇒ **S** is a cyclic ester/ester bond present

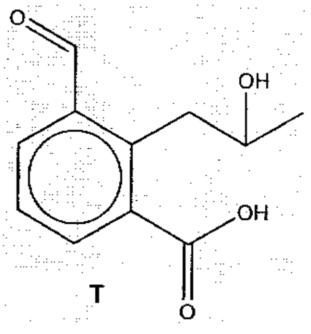
⇒ **T** contains a carboxylic acid and an alcohol

T undergoes a oxidation/ positive iodoform test ⇒ **T** has $-CH_3CH(OH)$ group

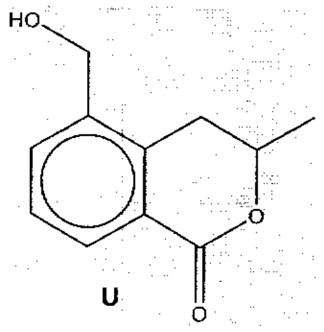
S undergoes reduction with $NaBH_4$ to for **U** ⇒ primary alcohol is formed



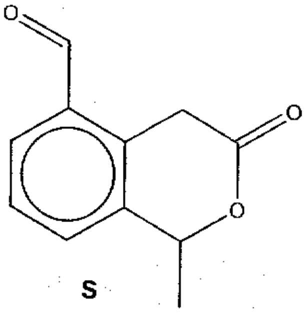
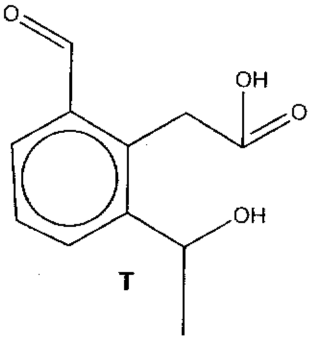
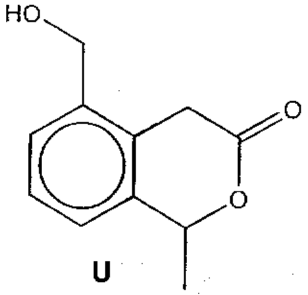
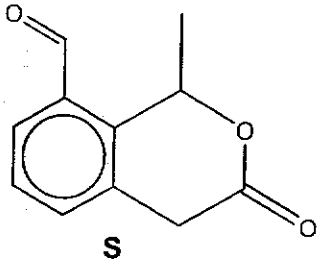
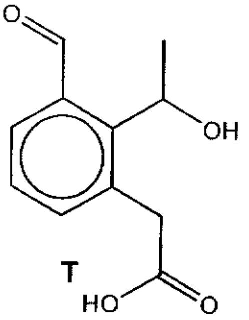
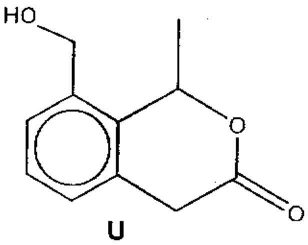
S



T



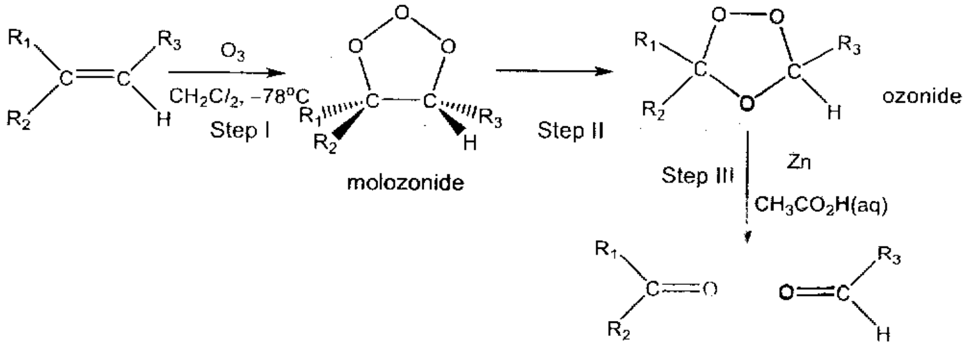
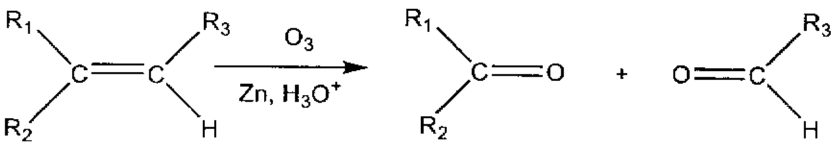
U

		 **S**	 **T**	 **U**	
		 **S**	 **T**	 **U**	
					[Total : 18]

Section B

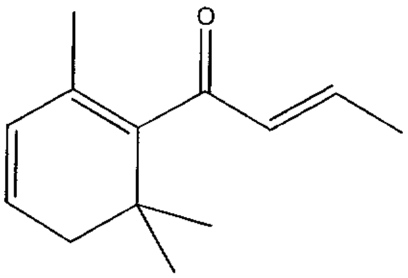
Answer **one** question from this section.

4	**(a)**	Alkaline earth metals, also known as Group 2 elements are highly metallic and are good conductors of electricity. They have a grey-white lustre when freshly cut but tarnish readily in air.		
		(i)	Describe and explain the trend in thermal stability of the Group 2 carbonates.	**[2]**
			Down the Group, the radius of the metal cation, M^{2+}, increases and its charge density decreases. As a result, the ability of M^{2+} to polarise the electron cloud of the large CO_3^{2-} anion decreases and the C–O bonds are polarised and weakened to a smaller extent. Hence thermal stability of the Group 2 carbonates increases down the Group.	
		(ii)	When ozone (O_3) is passed over dry powdered BaO at −10°C, barium ozonide, $Ba(O_3)_2$, is formed as a red-brown solid. Adding water to the solid and warming to room temperature causes a reaction to occur. Oxygen gas is produced and an alkaline solution is left. Write a balanced equation for the reaction between barium ozonide and water.	**[1]**
			$Ba(O_3)_2(s) + H_2O(l) \rightarrow Ba(OH)_2(aq) + 5/2O_2(g)$	
		(iii)	Suggest a suitable temperature to produce calcium ozonide by passing ozone through powdered CaO.	**[1]**
			Accept any temperature lower than −10°C	
	(b)	Ozone is usually produced by passing oxygen gas through two highly-charged electrical plates. $3O_2(g) \rightarrow 2O_3(g)$ The reaction does not go to completion and a mixture of gases will be produced. The concentration of O_3 in the mixture can be determined by its reaction with aqueous KI. $O_3 + 2KI + H_2O \rightarrow I_2 + O_2 + 2KOH$ The iodine formed can be estimated by its reaction with sodium thiosulfate. $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$		

		When 300 cm^3 of an oxygen/ozone gaseous mixture at s.t.p. was passed into an excess of aqueous KI, and the iodine titrated, 24.0 cm^3 of 0.100 mol dm^{-3} $Na_2S_2O_3$ was required to discharge the iodine colour.		
		(i)	Suggest a suitable indicator can be used in the titration and state the colour change at end point.	[1]
			Starch solution. Blue-black to colourless.	
		(ii)	Calculate the percentage of O_3 in the gaseous mixture.	[2]
			$I_2 \equiv 2S_2O_3^{2-}$ n_{I_2} = (0.100 × 24.0 ÷ 1000) ÷ 2 = 1.200 × 10^{-3} mol n_{O_3} = n_{I_2} = 1.200 × 10^{-3} mol total amount of gas = 300 ÷ 22700 = 0.01322 mol % of O_3 = (1.200 × 10^{-3} ÷ 0.01322) × 100% = 9.08%	
	(c)	Ozone adds rapidly to alkenes at low temperature to give cyclic intermediates, called molozonides. Once formed, molozonides then rapidly rearranges to form ozonides. The reaction scheme is shown below.  The reaction can also be expressed as  		
		(i)	State the type of reaction occurring in Step I of the reaction scheme.	[1]
			Oxidation/ Electrophilic Addition	
		(ii)	Suggest the role of zinc in the reaction scheme.	[1]

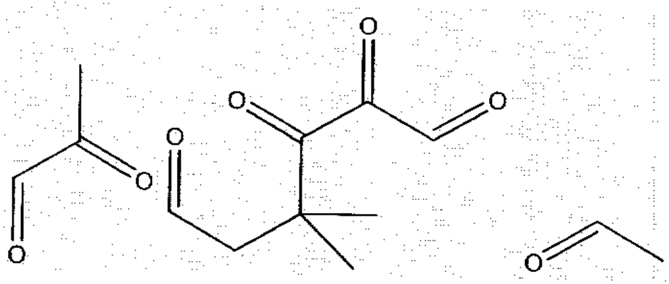
Reducing agent

(iii) β-Damascenone is a chemical compound found in whisky, which is an alcoholic liquor. Also known as rose ketones, β-damascenone is a key compound that contributes a floral note to whisky.



β-damascenone

Predict the organic products formed when β-damascenone reacts with ozone as shown by the reaction scheme above. **[3]**

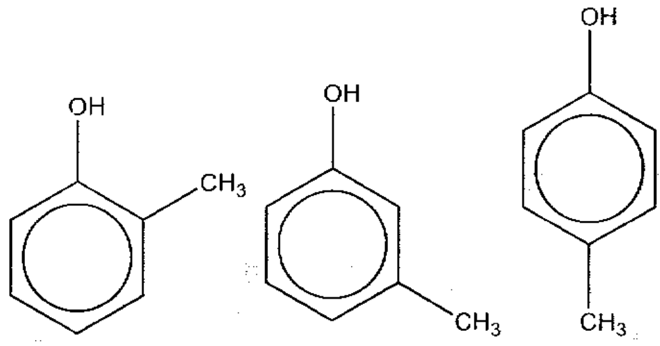
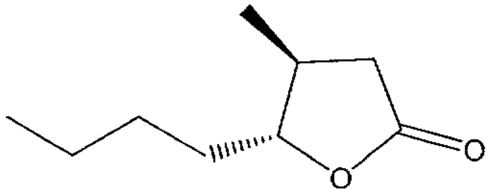
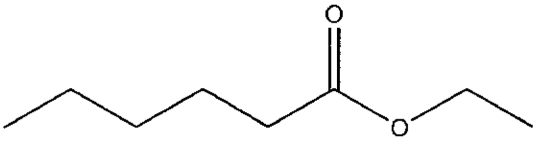
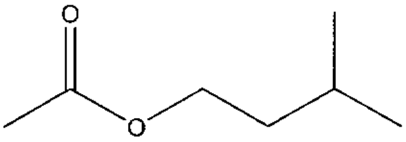


(d) Apart from β-damascenone, whisky contains an array of compounds that affect its taste and flavour, which include phenolic compounds, aldehydes and esters. The use of different grains, distillation process and wood used in the ageing process can also change the flavour profile.

(i) Phenolic compounds in general contributes smoky flavours and bitterness in whisky. In Scotch whisky, the use of peat fires to dry the barley grains creates a class of medicinal-smelling compounds known as cresols.

Cresols exists as constitutional isomers with the formula C_7H_8O. When added to aqueous bromine, rapid decolourisation followed by the formation of a white precipitate is observed for all isomers of cresol.

Draw all the possible isomers of cresol. **[3]**

				
		(ii)	Whisky lactones are responsible for the woody, spicy and coconut flavour notes. One such compound is trans-3-methyl-4-octanolide. A student wanted to synthesise an amide from this lactone.  trans-3-methyl-4-octanolide The following steps were proposed. 1. heat with dilute H_2SO_4 2. addition of ethylamine Comment on the feasibility of this reaction scheme.	**[2]**
			The reaction scheme is not feasible. The hydrolysis of ester in (1) will result in the formation of a carboxylic acid that will undergo an acid-base reaction with ethylamine rather than a condensation reaction.	
		(iii)	Esters in whisky can also contribute fruity flavours such as ethyl hexanoate, which imparts a sweet apple flavor, and isoamyl acetate, which gives a banana aroma.  ethyl hexanoate  isoamyl acetate	

Describe a simple chemical test that can be used to distinguish ethyl hexanoate from isoamyl acetate.

State any observations you would make with each compound. **[2]**

(1) Aqueous NaOH, heat

(2) Aqueous (alkaline) iodine, warm

Pale yellow ppt will be observed for ethyl hexanoate (due to formation of ethanol). No pale yellow ppt will be observed for isoamyl acetate.

(iv) Whisky is a mixture of water, ethanol and organic compounds like whisky lactones. When the alcoholic whisky is stored for a long period of time, as the ethanol content decreases, a cloudiness can be observed in the whisky.

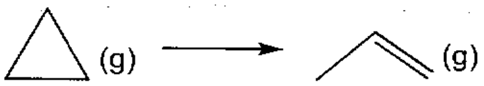
Suggest a reason why the cloudiness occurs. **[1]**

As the ethanol is evaporated, the chemical compounds can precipitate, giving rise to cloudiness.

[Total: 20]

5 Cyclopropane is an explosive, colourless gas that was discovered by August Freund in 1881, and was once used as a general anesthetic in clinical practice.

(a) Cyclopropane can undergo isomerisation to propene at 298 K.

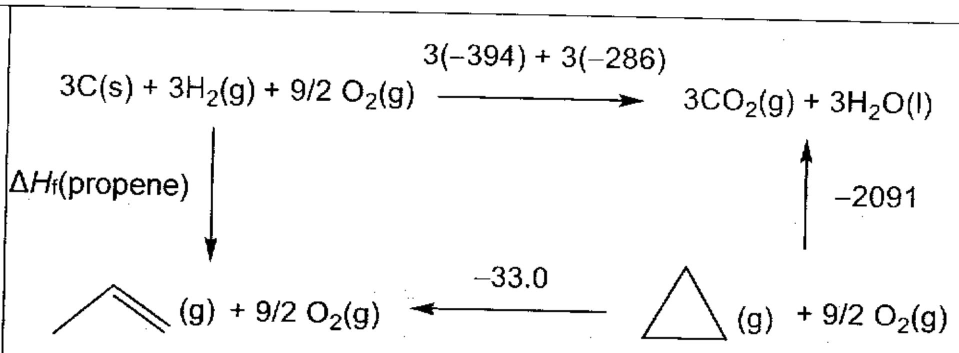


$\Delta H_{\text{isomerisation}} = -33.0 \text{ kJ mol}^{-1}$

Table 5.1

	ΔH / kJ mol^{-1}
standard enthalpy change of formation of $CO_2(g)$	−394
standard enthalpy change of formation of $H_2O(l)$	−286
standard enthalpy change of combustion of cyclopropane	−2091

Using the data given above and in Table 5.1, construct a suitable energy cycle and calculate the enthalpy change of formation of propene at 298 K. **[3]**



ΔH_f(propene)

= 3(−394) + 3(−286) − (−2091) + (−33.0) = **+18.0** kJ mol^{-1}

(b) 100 cm^3 of a mixture of methane and cyclopropane was completely burnt in 300 cm^3 of oxygen and then cooled to room temperature.

The total volume of the gaseous reaction mixture decreases by 215 cm^3.

On passing the resultant gaseous mixture through potassium hydroxide, the final volume was found to be 25 cm^3.

What is the ratio of methane to cyclopropane in the original mixture? **[2]**

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$C_3H_6(g) + 9/2O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$

Volume of resultant gaseous mixture after combustion

= 400 – 215 = 185 cm^3 (contains remaining O_2 & CO_2)

Volume of CO_2 in resultant gaseous mixture

= 185 – 25 = **160 cm^3**

Let x be the volume of CH_4 and (100 – x) be the volume of C_3H_6 in the original mixture

Volume of CO_2 = x + 3(100 – x) = 160

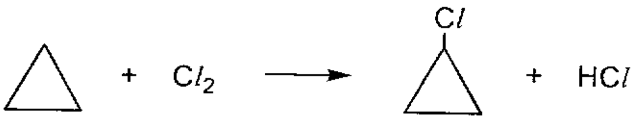
300 – 2x = 160

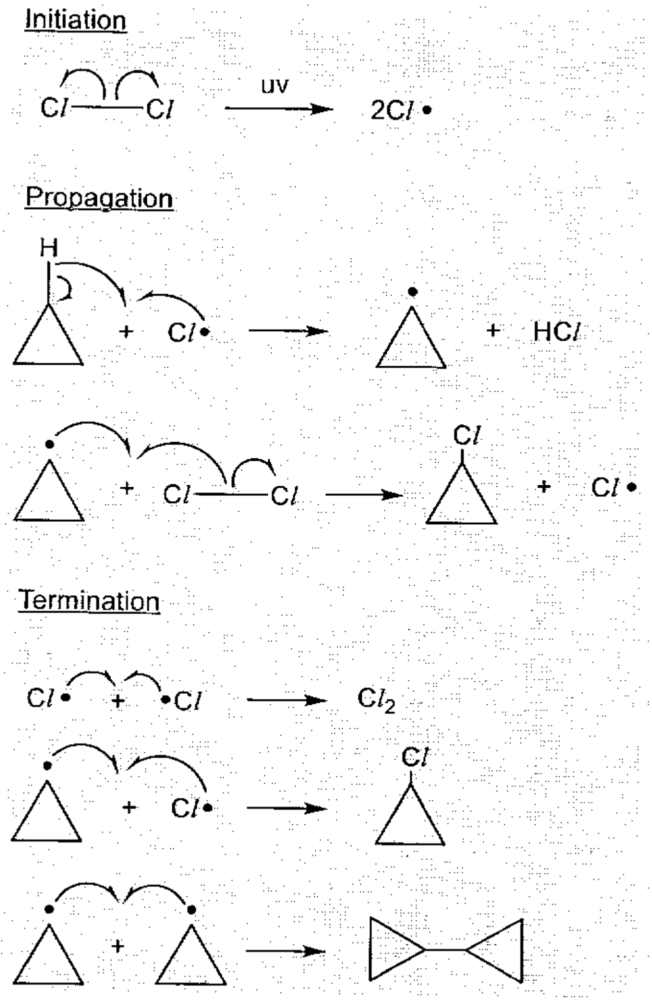
x = 70

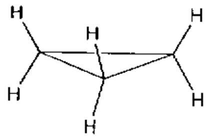
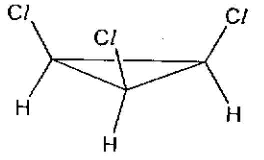
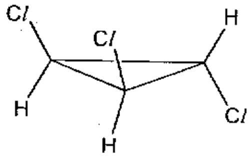
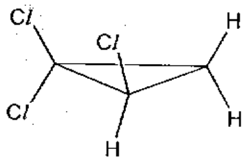
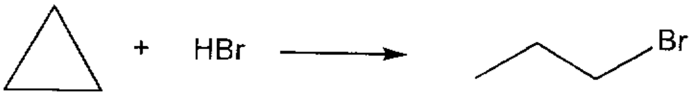
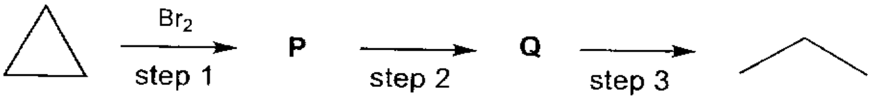
Volume of CH_4 = 70 cm^3 and volume of C_3H_6 = 30 cm^3

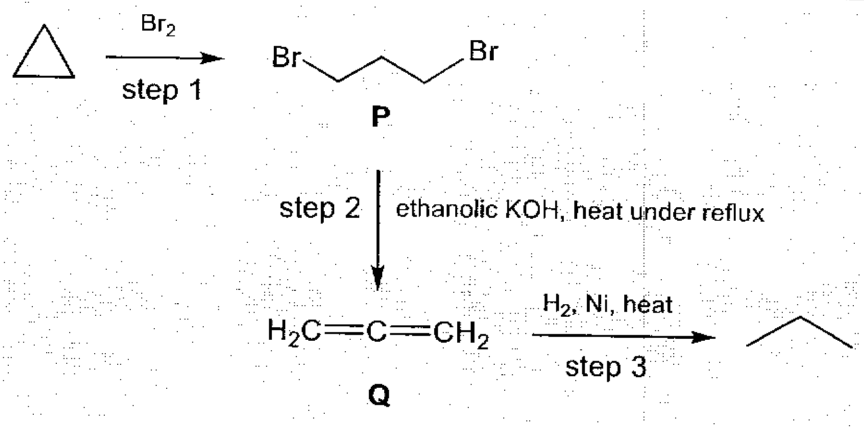
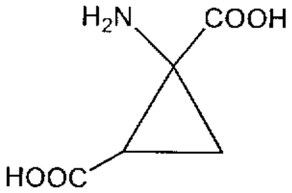
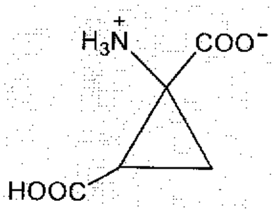
Ratio of CH_4 to C_3H_6 = **7 : 3**

Cyclopropane can undergo free radical substitution with chlorine, similar to an aliphatic alkane. Chlorocyclopropane is the major product formed under a certain set of conditions.



	(c)	(i)	State the conditions needed to produce chlorocyclopropane as the major product.	[1]
			limited Cl_2, uv, (excess cyclopropane)	
		(ii)	Describe the mechanism for this reaction.	[3]
			 	
		Trichlorocyclopropane, $C_3H_3Cl_3$, is one of the possible polysubstituted by-products of the reaction under a different set of conditions. This tri-substituted cycloalkane can exist as 3 constitutional isomers, all of which exhibit stereoisomerism.		
		(iii)	Define the term *stereoisomerism.*	[1]
			Stereoisomerism is a type of isomerism in which **molecules have the same molecular and structural formulae, but differ in the spatial arrangement of their atoms**.	
		(iv)	Draw the structures of the 3 isomers of trichlorocyclopropane and suggest the type of stereoisomerism associated with each of them.	

			Note: You may refer to the diagram of cyclopropane shown below to draw the isomers accordingly. 	**[4]**
			 cis-trans isomerism  cis-trans isomerism  enantiomerism	
	(d)		However, in the absence of uv light, cyclopropane can undergo addition reactions similarly as alkenes. This leads to the opening of the ring structure. For example, 	
		(i)	Suggest a possible reason why cyclopropane can undergo addition reactions, unlike aliphatic alkanes.	**[1]**
			Cyclopropane is highly unstable due to the **ring strain**, as the bond angles in the ring are at 60°, rather than 109.5° for sp^3 carbons.	
		(ii)	Propane can be produced from cyclopropane in a three-step synthesis as shown below. Suggest the reagents and conditions you would use for steps 2 and 3, and identify the intermediates **P** and **Q**. 	**[4]**

			
	(e)	A possible amino acid derivative of cyclopropane is shown below.  Draw the structure of the zwitterion formed by this amino acid derivative.	[1]
			
			[Total: 20]