VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 3

CANDIDATE NAME ……………………………………………………………..

CT GROUP ……………………………..

CHEMISTRY **9813/01**

Paper 1 **27 September 2021**

2 hours 30 minutes

Candidates answer on the Question Paper.

Additional Materials: Data Booklet
Insert

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, highlighters, 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** questions.

Section B
Answer **two** questions.

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

The number of marks is given in brackets [ ] at the end of each question or part question.
You are reminded of the need for clear presentation in your ans

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This document consists of **46** printed pages and **0** blank page.

Section A

Answer **all** questions in this section.

The information provided in the insert is taken from published scientific articles. Other published articles may not agree with all of this information.

You should read all the above information before you start to answer any questions and use the information it contains to answer the questions.

1 **(a)** **(i)** State two main assumptions of an ideal gas. [2]

(ii) A 2 dm^3 container half filled with water was left exposed to an atmosphere of hydrogen for a long time at 0.8 atm and 25 ºC. The resultant solution contained 6.96×10^{-4} mol dm^{-3} of dissolved H_2 according to the following equilibrium.

$$H_2(g) \rightleftharpoons H_2(aq)$$

The atmosphere in contact with this water is replaced with 1.0 atm argon and sealed. The mixture is stirred for the gas–aqueous equilibrium to be established at 25 ºC. The hydrogen dissolved in water before the replacement is distributed between the gas phase and water after the replacement.

Use equation 1.1 and the ideal gas equation to calculate the partial pressure of H_2 (in atm) in the sealed container. [3]

(iii) Explain how your answer in **(a)(ii)** will change if the temperature was increased to 50 ºC and all other conditions remained constant. [2]

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(b) **(i)** State and explain, using the change in oxidation numbers, the reaction TCE underwent with H_2. [1]

(ii) A sample of ground water contaminated with TCE was analysed. Three other chlorine-containing organic compounds were present in the sample.

Suggest the structures of these compounds. [2]

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(c) **(i)** Suggest why the bubble stripping process is continued for 30 min. [1]

(ii) To determine the concentration of H_2 (in ppm) in the headspace using gas chromatography, a calibration curve must first be prepared.

The area count (obtained from the gas chromatogram) was measured for various known concentrations of H_2 (in ppm). The data was plotted to obtain a calibration curve (**Fig. 1.2**).

(1 ppm of H_2 = 1 molecule of H_2 in 10^6 air molecules)

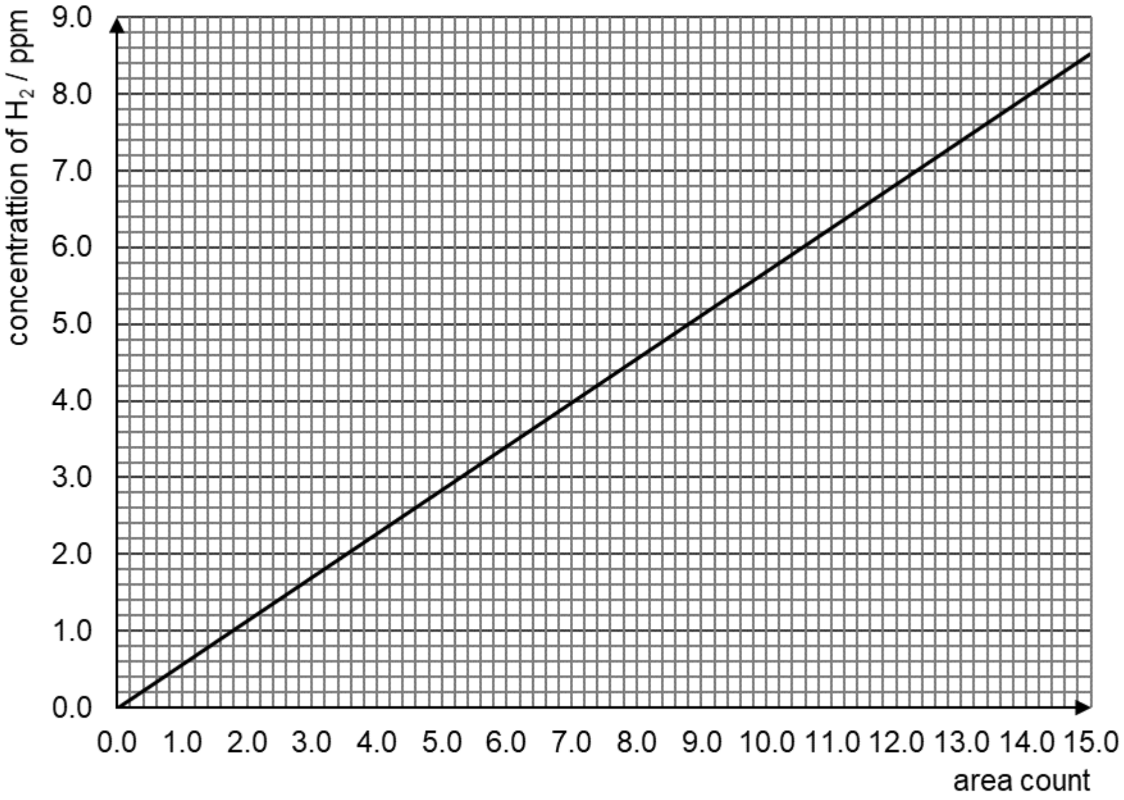

Fig. 1.2 Calibration Curve of H_2

Another sample of ground water was allowed to undergo the bubble stripping process. The gas in the headspace was analysed using gas chromatography. The gas obtained has an area count of 10.4.

Calculate the partial pressure of H_2 (in atm) in the headspace, stating any assumptions made during the calculation. [3]

(iii) Hence, use equation 1.2 to calculate the solubility of H_2 in ground water (expressed in mole fraction), S_{H2}, and comment on the likelihood of anaerobic biodegradation taking place in this sample of groundwater. (density of water under these conditions = 0.998 g cm^{-3}) [3]

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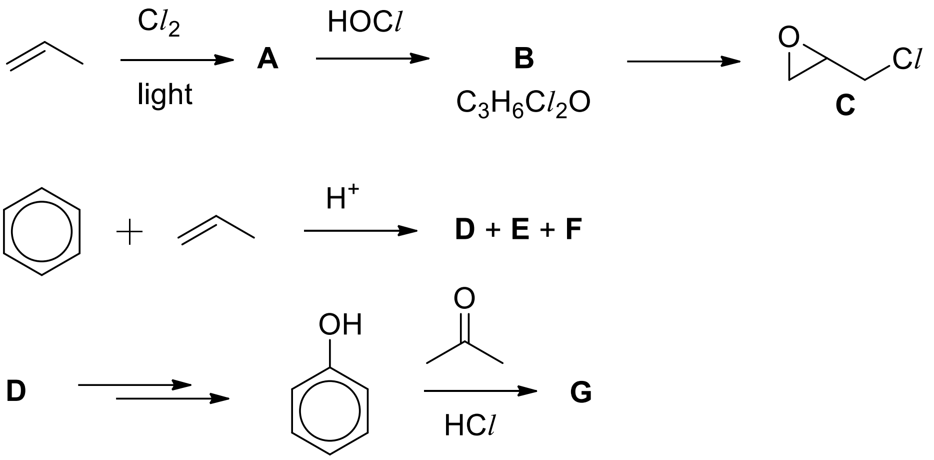
[Total: 17]

2 **(a)** The synthesis of epoxy resins is a multi-billion dollar industry worldwide. Epoxy resins are high performance adhesives synthesised from the reaction of a bis-epoxide with a diamine. The bis-epoxide is made from **G** and epichlorohydrin, **C**. **C** and **G** can be synthesised according to the schemes below.



The synthesis of epichlorohydrin **C** begins with the reaction of propene with chlorine in the presence of light.

(i) Draw the structures of **A** and **B**. [1]

(ii) Work out the ratio of the M, M+2 and M+4 peaks in the mass spectrum of **B**. [1]

(iii) Suggest a reagent for the conversion of **B** into epichlorohydrin **C**. [1]

(iv) The synthesis of **G** commences with the reaction of benzene with propene in the presence of an acid catalyst which gives **D** as the major product and **E** and **F** as minor products.

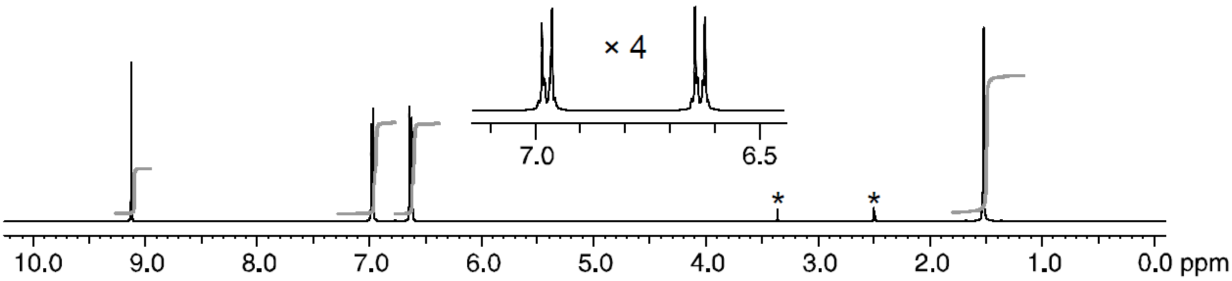
Draw the structures of **D**, **E**, and **F** from the following data:

D: Elemental composition: C 89.94 %, H 10.06 %; 6 signals in the ^{13}C NMR spectrum.
E: Elemental composition: C 88.82 %, H 11.18 %; 4 signals in the ^{13}C NMR spectrum.
F: Elemental composition: C 88.82 %, H 11.18 %; 5 signals in the ^{13}C NMR spectrum.

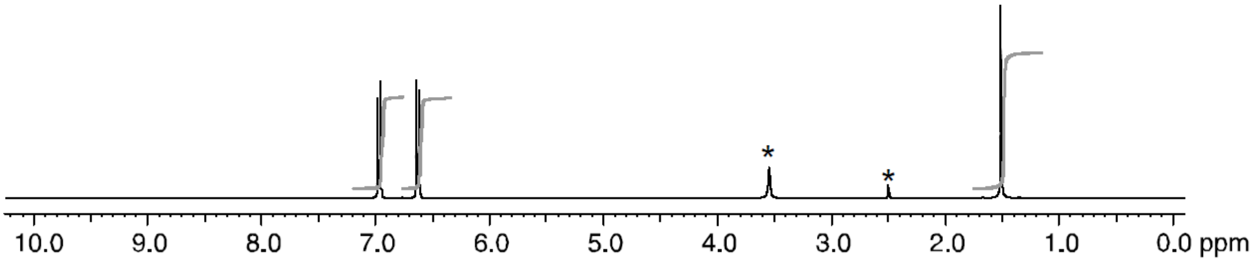
The principles of ^{13}C NMR are similar to ^{1}H NMR spectroscopy. [3]

(v) State the difference in the ^{1}H NMR spectrum of **E** and **F**. Your answer should include the chemical shift, multiplicity, number of protons and the group(s) responsible for the signal(s) being compared. [1]

(vi) Exposure of phenol and propanone to hydrochloric acid gives **G** ($C_{15}H_{16}O_2$). The ^{1}H NMR spectrum is shown below together with a four-fold expansion of the region 6.5 – 7.1 ppm. The ^{1}H NMR spectrum after the addition of a drop of D_2O, is also shown below. Peaks due to the solvent are marked with an asterisk (*).



^{1}H NMR spectrum of **G** (without addition of D_2O)



^{1}H NMR spectrum of **G** (after addition of D_2O)

Deduce the structure of **G** and explain your reasoning. [3]

(vii) Draw one mesomeric (resonance) structure of phenol which explains the formation of **G** and not the other positional isomers. [1]

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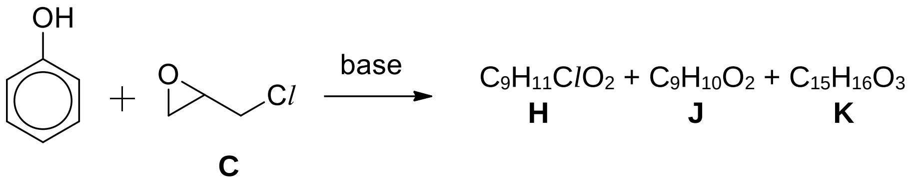
(b) Excess phenol reacts with epichlorohydrin **C** in the presence of base to give **H** which has 7 signals in its ^{13}C NMR spectrum. **J** and **K** can also be isolated. **K** is formed from **J** and **J** is formed from **H**.



$C_9H_{11}ClO_2 + C_9H_{10}O_2 + C_{15}H_{16}O_3$

Draw the structures of **H**, **J** and **K**. [3]

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(c) 2-nitrochlorobenzene can be converted to 2-nitrophenol using NaOH(aq), followed by addition of a suitable acid.

(i) Draw the mechanism of this reaction. [2]

(ii) How would you monitor the progress of this reaction using IR spectroscopy? Your answer should include the wavenumbers, the vibrational mode(s) and functional group(s) responsible for the peak(s) being monitored. [1]

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(d) Transition metals and their compounds play an important role in organic chemistry, for instance the halogenation of benzene involves use of $FeCl_3$ as a catalyst. This part of question concerns another transition metal, gold.

Many different methods have been used to determine the Avogadro constant. One method involves X-ray diffraction data through study of unit cells. The unit cell is the smallest repeating unit in a crystal structure. The unit cell of a gold crystal is found by X-ray diffraction to have the face-centred cubic unit structure (i.e. where the centre of an atom is located at each corner of a cube and in the middle of each face). The side of the unit cell is found to be 0.408 nm.

(i) Sketch the unit cell and calculate how many Au atoms the cell contains. [1]

(ii) The density of Au is 1.93×10^4 kg m^{-3}. Calculate the volume and mass of the cubic unit cell. [1]

(iii) Hence calculate the mass of a gold atom and the Avogadro constant, given that the relative atomic mass of Au is 196.97. [2]

Another method to determine the Avogadro constant was carried out by studying the vertical distribution under gravity of colloidal particles suspended in water. In one such experiment, particles with effective mass of each particle, m^* of 8.3×10^{-18} kg were suspended in a tube of water at 15 °C and allowing sufficient time to equilibrate. The mean numbers of particles per unit volume observed at four heights from the bottom of the tube were given below.

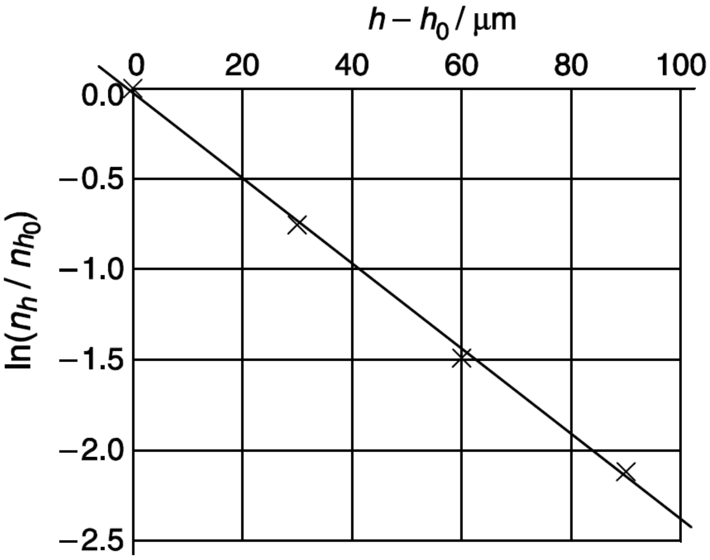
height / 10^{-6} m	5	35	65	95
mean number per unit volume	4.00	1.88	0.90	0.48

At equilibrium, the number of particles per unit volume at different heights may be modelled according to a Boltzmann distribution:

$$\frac{n_h}{n_{h_0}} = \exp\left[-\frac{E_h - E_{h_0}}{RT}\right]$$

where
n_h is the number of particles per unit volume at height h,
n_{h0} is the number of particles per unit volume at the reference height h_0,
E_h is the gravitational potential energy per mol of particles at height h relative to the particles at the bottom of the tube and $E_h = mgh$ where $g = 9.81$ m s^{-2} and m = total mass of 1 mol of particles,
R is the molar gas constant,
T is the temperature of the tube of water.

A graph of $\ln(n_h / n_{h0})$ against $(h - h_0)$, based on the data in the table above, is shown below. The reference height is taken to be 5×10^{-6} m (5 μm) from the bottom of the tube.



(iv) Derive an expression for the gradient of the graph from the formulae given above and hence determine the Avogadro constant from these data. [4]

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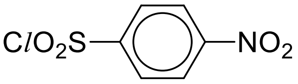
[Total: 25]

3 **(a)** **(i)** Explain the principles of UV-visible spectroscopy. [2]

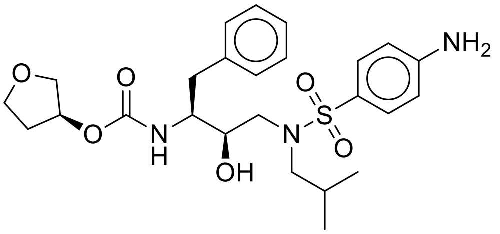
(ii) One class of anti-HIV drugs, known as *protease inhibitors*, works by blocking the active site of one of the enzymes used in assembly of the viruses within the host cell. One of the drugs is *amprenavir*.

In one of the steps for synthesis of *amprenavir*, the reagent used has the following structure.



State and explain one major difference in the UV-visible spectrum of this reagent as compared to benzene. [1]

(iii) The structure of *amprenavir* is given below. State the configuration (*R*/*S*) of all chiral carbon(s) in *amprenavir*.

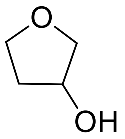


[2]

(iv) The specific optical rotation of pure *amprenavir* in methanol has been determined to be in the range +8 to +12°. A sample containing a mixture of *amprenavir* and its enantiomer is found to have an optical rotation of +2° measured under the same conditions.

Draw the structure of the enantiomer and calculate the maximum optical purity. [1]

(v) In the synthesis of *amprenavir*, the intermediate whose structure is given below has a 5-membered ring. 5-membered rings adopt an envelope conformation.



Draw two possible conformers of this intermediate. [1]

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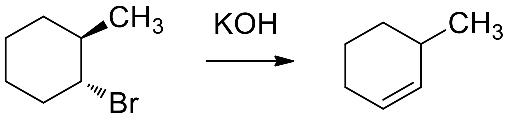
(b) 6-membered rings also adopt particular conformations and the most representative example is cyclohexane.

(i) Explain by drawing relevant conformation of the following substituted cyclohexane and drawing the mechanism, why the following non-Zaitsev alkene is formed.



[2]

(ii) Draw a structural isomer of the starting compound in **(b)(i)** that contains a cyclohexane ring and will yield the thermodynamic or kinetic alkene under different conditions. Describe what are the conditions needed to favour each of the products. [2]

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(c) Thiomolybdate ions, MoS_4^{2-}, are derived from molybdate ions, MoO_4^{2-}, by replacing oxygen atoms with sulfur atoms. In nature, thiomolybdate ions are found in such places as the deep waters of the Black Sea, where biological sulfate reduction generates H_2S. The molybdate to thiomolybdate transformation leads to rapid loss of dissolved Mo from seawater to underlying sediments, depleting the ocean in Mo, a trace element essential for life.

The following equilibria control the relative concentrations of molybdate and thiomolybdate ions in dilute aqueous solution. Their respective equilibrium constant values are also given.

$MoS_4^{2-}(aq) + H_2O(l) \rightleftharpoons MoOS_3^{2-}(aq) + H_2S(aq)$ $K_1 = 1.3 \times 10^{-5}$
$MoOS_3^{2-}(aq) + H_2O(l) \rightleftharpoons MoO_2S_2^{2-}(aq) + H_2S(aq)$ $K_2 = 1.0 \times 10^{-5}$
$MoO_2S_2^{2-}(aq) + H_2O(l) \rightleftharpoons MoO_3S^{2-}(aq) + H_2S(aq)$ $K_3 = 1.6 \times 10^{-5}$
$MoO_3S^{2-}(aq) + H_2O(l) \rightleftharpoons MoO_4^{2-}(aq) + H_2S(aq)$ $K_4 = 6.5 \times 10^{-6}$

(i) If at equilibrium the concentrations of $MoO_4^{2-}(aq)$ and $H_2S(aq)$ are equal to 1×10^{-7} mol dm^{-3} and 1×10^{-6} mol dm^{-3}, respectively, what would be the equilibrium concentration of $MoS_4^{2-}(aq)$? Consider all of the above equilibria. [1]

(ii) Solutions containing $MoO_2S_2^{2-}$, $MoOS_3^{2-}$ and MoS_4^{2-} display absorption peaks in the UV-visible spectrum at 395 and 468 nm. The other ions, as well as H_2S, absorb negligibly in this range. The molar absorptivity coefficient at these two wavelengths are given in the following table.

	ε at 468 nm dm^3 mol^{-1} cm^{-1}	ε at 395 nm dm^3 mol^{-1} cm^{-1}
MoS_4^{2-}	11870	120
$MoOS_3^{2-}$	0	9030
$MoO_2S_2^{2-}$	0	3230

A solution contains a mixture of $MoO_2S_2^{2-}$, $MoOS_3^{2-}$ and MoS_4^{2-} and no other Mo-containing species. The total concentration of all species containing Mo, i.e. $[MoO_2S_2^{2-}] + [MoOS_3^{2-}] + [MoS_4^{2-}]$ is 6.0×10^{-6} mol dm^{-3}. In a 10.0 cm absorption cell, the absorbance of the solution at 468 nm is 0.365 and that at 395 nm is 0.213. Calculate the concentrations of all three Mo-containing anions in this mixture. You do **not** need to consider the equilibria in **(c)(i)**. [2]

(iii) A solution with initial concentration of MoS_4^{2-} equal to 2.0×10^{-7} mol dm^{-3} hydrolyses in a closed system. The H_2S product accumulates until equilibrium is reached. When calculating the final equilibrium concentrations of $H_2S(aq)$, and all five Mo-containing anions (that is MoO_4^{2-}, MoO_3S^{2-}, $MoO_2S_2^{2-}$, $MoOS_3^{2-}$ and MoS_4^{2-}) ignore the possibility that H_2S might ionise to HS^- under certain pH conditions.

By using the following equations, and the equilibria in **(c)(i)**, calculate the concentrations of the above mentioned six species, giving your answers to **two** significant figures.

$[MoO_3S^{2-}] + [MoO_4^{2-}] = 2.0 \times 10^{-7}$

$[MoO_3S^{2-}] + [H_2S] = 8.0 \times 10^{-7}$ [4]

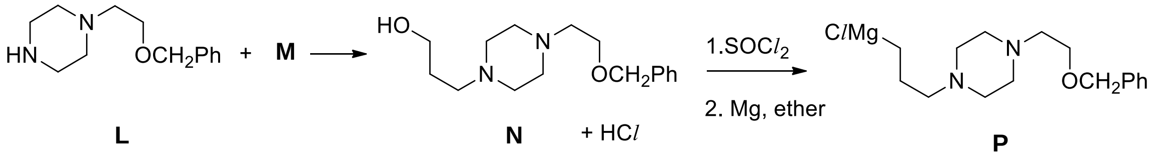
[Total: 18]

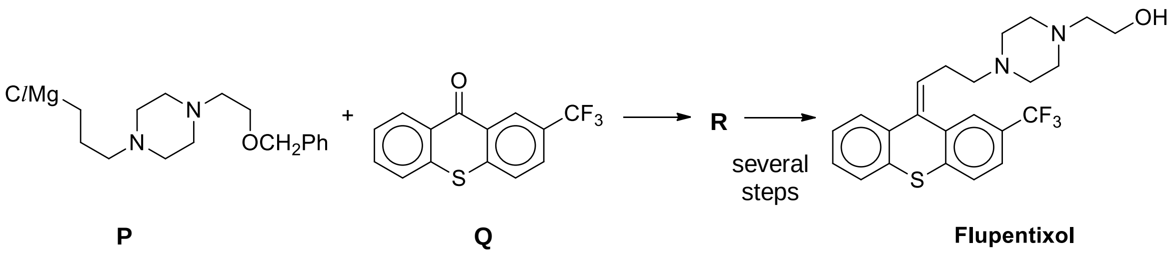
Section B

Answer **two** questions from this section.

Name: ………………………………………………………… CT group: ………………

4 **(a)** The antipsychotic drug flupentixol is prepared from the following scheme. Ph represent phenyl ring.





(i) Suggest the structural formula of an alkyl chloride **M** and describe the mechanism for the reaction with amine **L** to form **N**. [2]

(ii) **P** is a Grignard reagent with a highly polarised C-Mg bond. As the carbon atom in the C-Mg bond has a partial negative charge, it resembles a carbanion, and it reacts with electron deficient carbon centres in ketone group in **Q** to form new carbon-carbon bonds. A tertiary alcohol **R** which exist as a pair of enantiomers are formed in this case. Using the *R* and *S* convention, draw both enantiomers and assign the configuration at the chiral centres. [1]

(iii) Flupentixol exist as a pair of stereoisomers. One of them is shown in the synthesis above. Draw both isomers, identify the type of stereoisomerism and assign the configuration for both isomers. [2]

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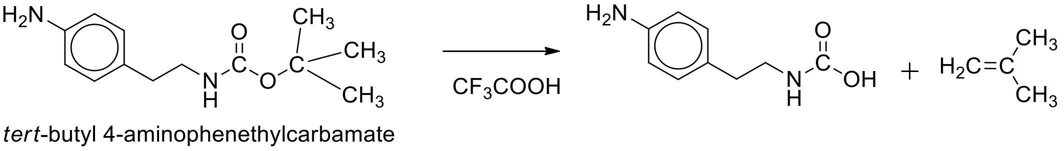
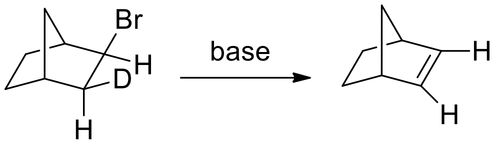
(b) **(i)** A catalyst CF_3COOH is used to react with *tert*-butyl 4-aminophenethylcarbamate to form the following products via a 3-step reaction. This reaction is important in the synthesis of proteins and herbicides.

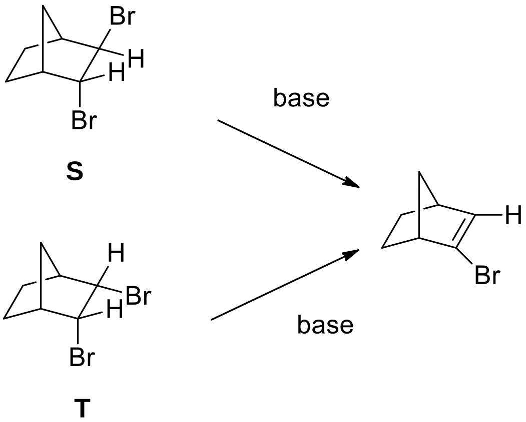


Draw a mechanism for this reaction. [3]

(ii) Although *anti* periplanar geometry is preferred for E2 elimination reaction, the following bicyclic compound can only undergo E2 elimination with *syn* periplanar geometry. This is due to the deuterium (D represents ^2H), bromine and the two carbon atoms that will form the double bond in the product to all lie in a plane which does not allow the adoption of *anti* periplanar geometry.



Based on your understanding above, identify and explain which of the isomers **S** or **T** shown below will result in a faster elimination reaction.



[2]

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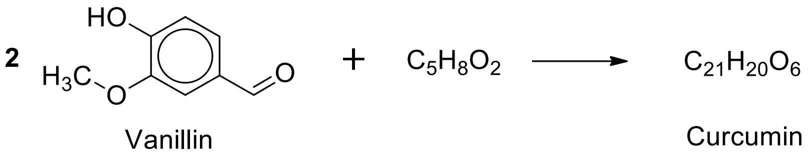
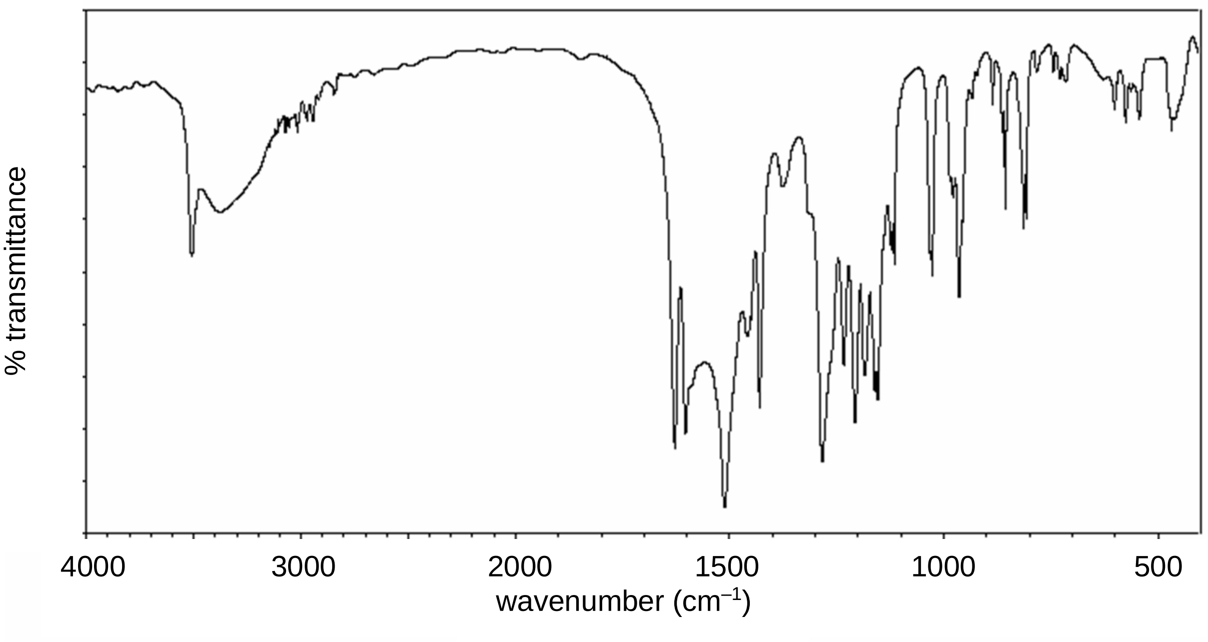
(c) Curcumin is a non-flavonoid polyphenol with the molecular formula $C_{21}H_{20}O_6$ where it is used in the treatment of inflammatory ailments, obesity and other metabolic diseases. One of the starting materials used to synthesise curcumin is vanillin, where each aldehyde group in **two** vanillin molecules undergo a condensation reaction with two methyl groups of another starting material with molecular formula $C_5H_8O_2$, containing a diketone. Curcumin has an internal plane of symmetry between two ketone groups and exist as a *trans-trans* configuration.



The ^{1}H NMR spectrum of curcumin is given below. The signal at δ 5.35 disappears in the presence of D_2O.

δ	splitting pattern	number of protons
3.97	singlet	6
4.59	singlet	2
5.35	singlet	2
6.8 - 7.2	multiplet	6
6.91	doublet	2
7.60	doublet	2

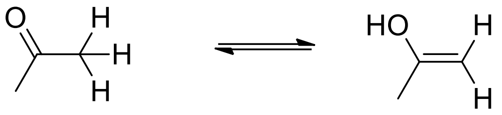
Below shows the IR spectrum of curcumin.



(i) Outline the principles of IR spectroscopy. [2]

(ii) Deduce the structural formula of curcumin. Explain your reasoning clearly. [6]

(iii) Carbonyl compounds can undergo keto – enol tautomerism. An example is shown below.



Keto Enol

Curcumin can also undergo a similar tautomerism and adopt the enol form. Draw the structural formula of the enol form of curcumin and deduce the maximum total number of stereoisomers. [2]

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5 Calcium carbide, CaC_2, is produced in large quantities around the world, mostly in the Far East. Calcium carbide has been used in a variety of ways, including as a component in self-igniting maritime distress flares.

Calcium carbide reacts with excess water to form a colourless, flammable gas, **U**. A white solid **V** is also formed which is slightly soluble in water to give a colourless alkaline solution. Gas **U** is a hydrocarbon containing 92.3% carbon by mass. The M_r of **U** is 26.

Gaseous nitrogen is passed through a bed of calcium carbide at 1000 – 1100 °C in order to start its transformation into a highly reactive ionic solid **W** and a carbon residue only. Elemental analysis reveals that **W** contains 50% calcium and 15% carbon by mass.

W reacts with water in an equimolar ratio to give an alkaline solution and an ionic intermediate **X**. The anion in **X** is obtained from an acid-base reaction between the anion in **W** and water. **X** then reacts with carbon dioxide and water in another acid-base reaction to form only calcium carbonate and a molecular solid **Y** with an M_r of 42. Based on the formula, **Y** can be represented by two different structures. However, only one of these structures is actually observed for this substance.

Y is mostly used in the production of chemical fertilizers. Its hydrolysis produces another molecular solid **Z** that can be directly used in fertilizers. On the other hand, hydrolysis of **Z** forms 2 gases, one of which has a strong characteristic odour.

(a) Determine the molecular formula of hydrocarbon **U**. [1]

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(b) Write a balanced equation for the reaction of calcium carbide with water. [1]

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(c) Deduce the formula of solid **W**. [1]

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(d) Suggest the identity of the anion in **X** and hence write an equation for the reaction between **W** and water. [1]

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(e) Deduce the molecular formula of **Y** and write an equation for the reaction with **X**, carbon dioxide and water. [2]

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(f) Write two possible structures for the molecular solid **Y** and specify the one that is actually observed, given that its IR spectrum shows an absorption band between 2220 and 2260 cm^{-1}, and that it does not possess a centre of symmetry. [2]

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(g) Hence, give the structural formula of **Z** and write an equation for its hydrolysis. [1]

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(h) Calcium carbide, CaC_2, contains the carbide anion, C_2^{2-}.

(i) Draw the molecular orbital (MO) energy level diagram for this anion and hence determine its bond order. It is given that the energy level of σ_{2p} MO is higher than π_{2p} MO. [2]

(ii) The C_2^{2-} ion can react with H^+ to form a chemical bond. Using your answer to **(h)(i)**, do you expect the shape of this acid-base adduct to be linear or bent? Explain your reasoning. [1]

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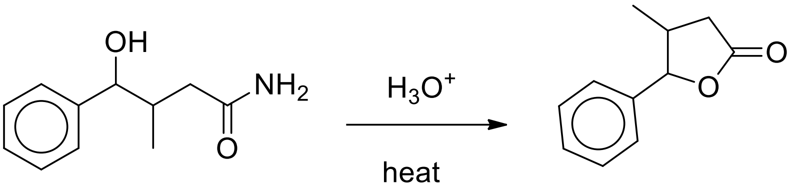
(i) Suggest a mechanism for the following reaction of **I** to form **II**.



I **II**

[3]

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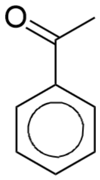
(j) **III** is a starting material that can be used to synthesise **I**.



III

By drawing resonance (mesomeric) forms of the intermediates, explain why chlorination of **III** gave 3-substitution to be the major product but not the other positional isomers. [2]

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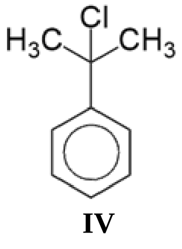
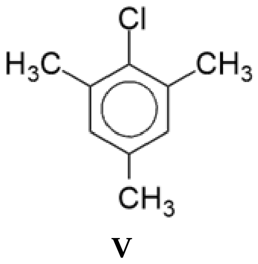
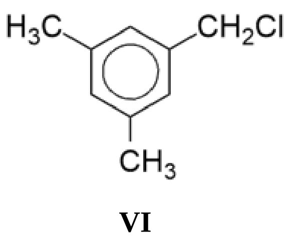
(k) Explain in detail how you would distinguish each of the following compounds **IV** to **VI** from the others using ^1H NMR spectroscopy.



IV



V



VI

[3]

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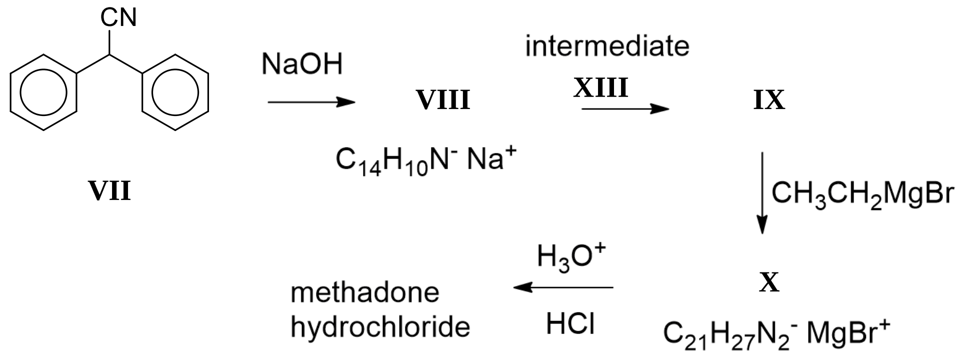
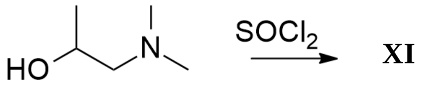
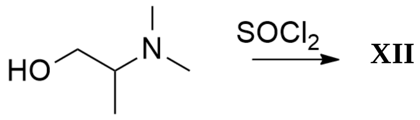
6 Methadone ($C_{21}H_{27}NO$) is an analgesic drug and is used in treating heroin addicts. It may be prepared as its hydrochloride salt by the following synthesis:



Intermediate **XIII** is a chloride salt. By treating two isomeric alcohols with $SOCl_2$ and then heating either **XI** or **XII**, the same intermediate **XIII** is formed via an intramolecular nucleophilic substitution.





$$\mathbf{XI} \xrightarrow{\text{warm}} \underset{\mathbf{XIII}}{\text{intermediate}} \xleftarrow{\text{warm}} \mathbf{XII}$$

(a) State the type of reaction that has occurred when **VII** reacted with NaOH in the first step. [1]

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(b) Deduce the structures for **XI**, **XII** and hence for the intermediate **XIII**. [2]

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(c) CH_3CH_2MgBr is a Grignard reagent with a highly polarised C-Mg bond. As the carbon atom in the C-Mg bond has a partial negative charge, it resembles a carbanion, and it reacts with electron deficient carbon centres in aldehydes, ketones, carbon dioxide etc to form new carbon-carbon bonds.

Suggest the structures for **IX** and **X**. [2]

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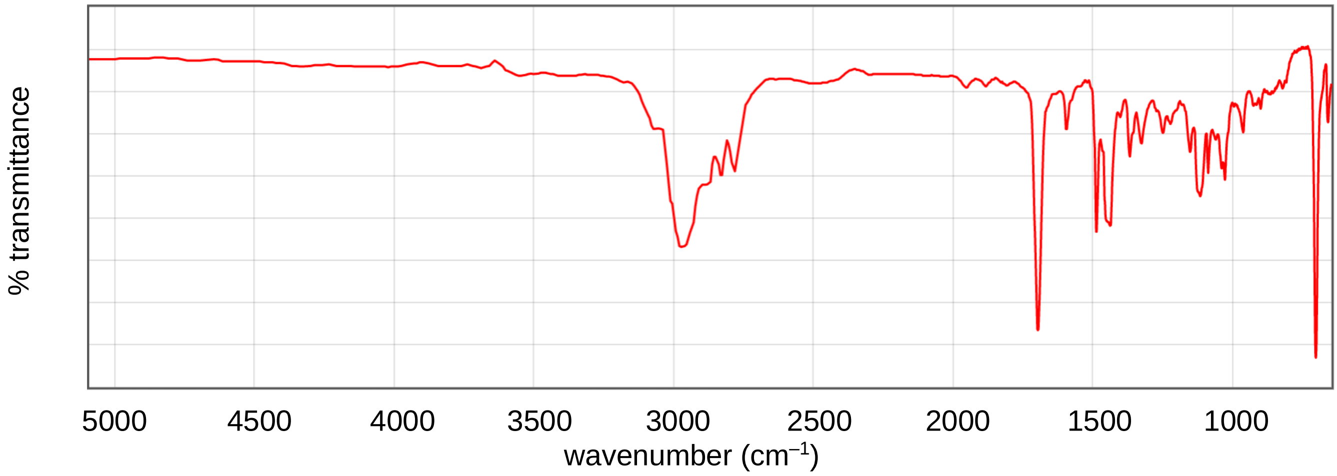
(d) The ^1H NMR spectrum of methadone shows the following signals.

δ	splitting pattern	number of protons
1.05	triplet	3
1.10	doublet	3
2.12	doublet	2
2.26	singlet	6
2.49	quartet	2
2.78	multiplet	1
7.35	multiplet	10

The IR spectrum of methadone is shown below.



Use the ^{1}H NMR and IR spectra to deduce the structure of methadone (ignore stereochemistry). Explain your reasoning. [5]

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(e) (*R*)-methadone is believed to account for most of the therapeutic effects of methadone maintenance treatment.

(i) Explain the rationale for obtaining an optically pure enantiomer of methadone as the final product. [1]

(ii) Given a racemic mixture of methadone, explain how resolution may be achieved by using (+)–tartaric acid. [1]

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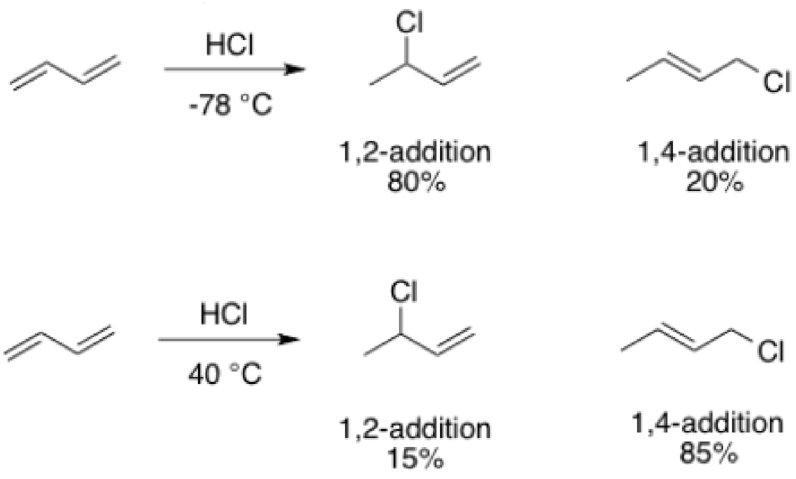
(f) **(i)** For the reaction below, identify the temperature which favours the formation of the thermodynamic product and the kinetic product respectively. Explain your reasoning.



[1]

(ii) Draw the structure of the transition state leading to the formation of the 1,4-addition product. Explain your answer. [2]

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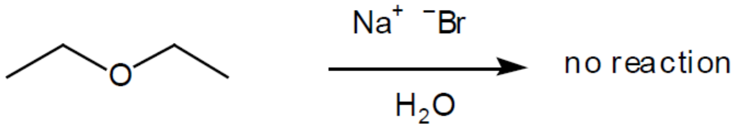
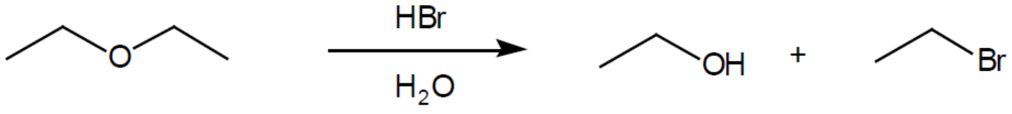
(g) Explain the following observations.

(i) Reaction **I** fails but **II** succeeds.

I



II



[2]

(ii) When (*R*)-2-bromobutane is reacted with diethylamine, $(CH_3CH_2)_2NH$, the reaction solution gradually loses optical activity. [1]

(iii) When the experiment in **(g)(ii)** is repeated with (*R*)-2-chlorobutane, it was found that the reaction solution gave a slightly higher optical activity than in **(g)(ii)**. Assume a similar mechanism occurs here as in **(g)(ii)**. [2]

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Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.