Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY 9729/03

Paper 3 Free Response **13 September 2022**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams 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.

For Examiner's Use		
Section A	Q1	/15
	Q2	/21
	Q3	/24
Section B	Q4	/20
	OR	
	Q5	/20
TOTAL		80

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

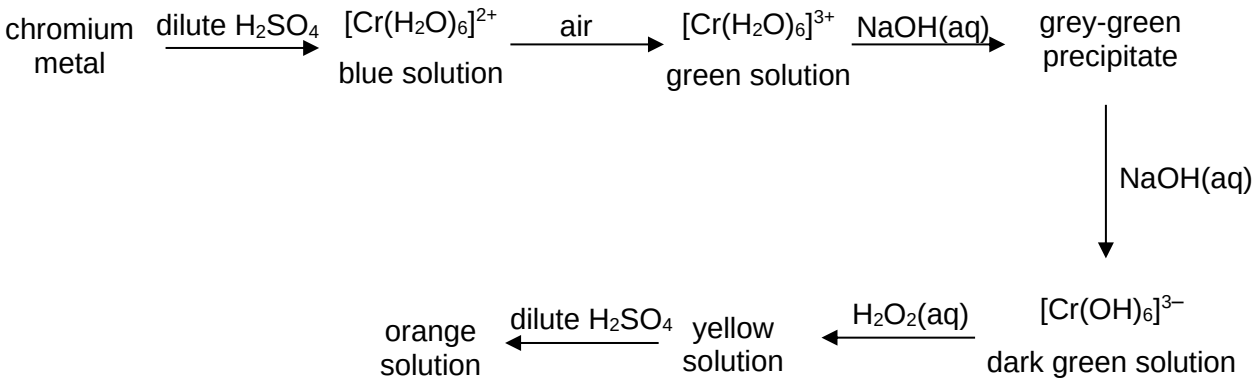
At the end of examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Section A

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

1 Chromium is a hard, steel-grey metal with a lustrous appearance. It is valued for its high corrosion resistance and hardness and is commonly used to manufacture alloys such as steel. Chromium plating is sometimes used to give a polished mirror finish to steel. Chromium compounds are also often used as pigments, known as chrome yellow.

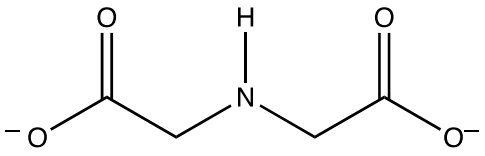
(a) The following sequence of reactions involving chromium illustrates many of the characteristics properties of transition metals.



(i) Solutions of transition metals are frequently coloured. With reference to $[Cr(H_2O)_6]^{2+}$,explain fully why it forms a blue solution. [2]

(ii) Suggest the identity of the grey-green precipitate formed in the reaction between $[Cr(H_2O)_6]^{3+}$ and aqueous sodium hydroxide.
With the aid of an equation, explain fully how it is formed. [2]

(iii) Chromium(III) ions can also react with iminodiacetate ions (tridentate ligand) to form a chelating complex ion. Draw the structure of the complex ion, showing the shape clearly. [1]



iminodiacetate ion

(iv) Identify the species present in the yellow and orange solutions.
Hence write an equation to show the formation of the species in the orange solution from that in the yellow solution. [2]

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1 **(b)** Draw a fully labelled diagram of the experimental set-up used to measure the standard electrode potential of the $Cr^{3+}(aq)/Cr(s)$ half-cell, indicating the direction of electron flow. [3]

(c) Chromium is electrolytically deposited on the cathode from a solution containing $Cr^{3+}(aq)$ using inert electrodes.

Calculate the volume of oxygen, at room temperature and pressure, produced at the anode when 1.00 kg of chromium is deposited on the cathode. [2]

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1 **(d)** Chrome yellow containing Na_2CrO_4, has been used for a long time as a yellow pigment in oil paintings.

(i) Use the standard redox potentials below to explain why the yellow colour changes when the painting is exposed to an atmosphere containing sulfur dioxide.

$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons 2H_2O + SO_2$ $\quad E^\ominus = +0.17$ V

$CrO_4^{2-} + 8H^+ + 3e^- \rightleftharpoons Cr^{3+} + 4H_2O$ $\quad E^\ominus = +1.33$ V [2]

(ii) Suggest why this colour change takes a long time. [1]

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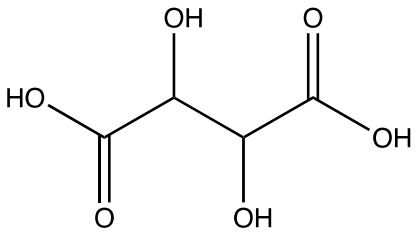
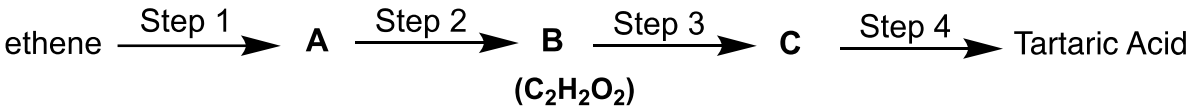
[Total: 15]

2 **(a)** Tartaric acid is a white crystalline diprotic organic acid. It can be synthesised from ethene in four steps.



Tartaric acid



($C_2H_2O_2$)

Draw the structures of the intermediates, **A**, **B** and **C**, and give the required reagents and conditions for each step of the conversion. [7]

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2 (b) Salts of tartaric acid are known as tartrates or hydrogen tartrates. One of these salts, potassium hydrogen tartrate, $KC_4H_5O_6$, is a weak monobasic acid and is sparingly soluble in water.

An experiment was conducted to determine the K_{sp} of the salt, $KC_4H_5O_6$. 1.00 g of the salt, $KC_4H_5O_6$ was dissolved in a beaker containing 100 cm^3 of water and was stirred constantly for 15 minutes at constant temperature, until a saturated solution was produced.

20.0 cm^3 of the filtered solution was titrated against 0.035 mol dm^{-3} NaOH, using phenolphthalein as an indicator. The volume of NaOH needed for the indicator to change colour is 12.50 cm^3.

(i) Calculate the initial concentration of potassium hydrogen tartrate used in the titration. [1]

(ii) Hence, calculate the K_{sp} value of potassium hydrogen tartrate. [1]

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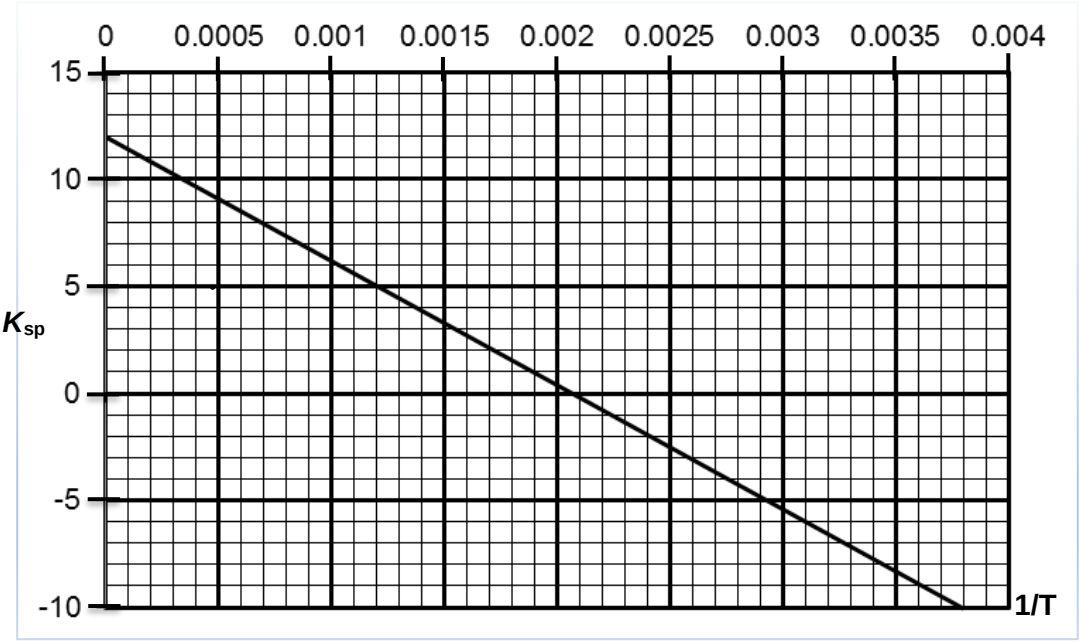
2 **(c)** The van 't Hoff equation relates equilibrium constants to enthalpy (ΔH) and entropy changes (ΔS) as follows:

$$\ln K_{sp} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

where R is the molar gas constant and T is measured is in Kelvin.
The titration in **(b)** was repeated at different temperatures and the following results were obtained.



(i) Using the information provided, calculate ΔH and ΔS for the dissolution of potassium hydrogen tartrate in water. [2]

(ii) Hence, predict the temperature at which potassium hydrogen tartrate becomes soluble in water. [1]

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2 **(d)** At 800 K, nitrogen monoxide reacts with hydrogen as shown below in an enclosed gas tank.

$$2H_2(g) + 2NO(g) \longrightarrow 2H_2O(g) + N_2(g)$$
$$\text{rate} = k(P_{H_2})(P_{NO})^2$$

On the same axes, sketch suitable graphs to illustrate clearly how the rate of reaction would vary when partial pressures of

(i) H_2
(ii) and NO

is increased respectively. [1]

2 **(e)** Nitrogen dioxide, NO_2, is an air pollutant produced from volcanic eruptions and combustion of fossil fuels in automobile engines.

(i) Draw the dot-and-cross diagram for nitrogen dioxide, NO_2, molecule stating its shape and bond angle. [2]

(ii) A 1.00 dm^3 gas cylinder is used to store 35.0 g of NO_2 at 25º C. The gas cylinder is fitted with a safety valve that will rupture when there is a great difference between the internal pressure and the atmospheric pressure.
The gas cylinder fitted with a burst disc can withstand a pressure difference of 2500 kPa.
Calculate the pressure exerted by NO_2 at 25º C in kPa. [1]

(iii) Assuming the atmospheric pressure is 101 kPa, calculate the maximum internal pressure of the gas cylinder. [1]

(iv) Hence, determine the maximum temperature that this gas cylinder can be exposed to before the burst disc ruptures. [1]

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2 **(f)** A gas tank contains a mixture of NO_2 and monoatomic gas **A** in the ratio of 4:1. At 300 K, the total pressure of the gas mixture is 100 kPa.

(i) Given that the density of the gas mixture is 1638 g m^{-3}, calculate the average relative molecular mass of the mixture to 1 decimal place. [1]

(ii) Hence, calculate the A_r of monoatomic gas **A** and suggest its identity. [2]

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[Total: 21]

3 This question is about nitrogen containing compounds.

(a) Nitrogen monoxide reacts with chlorine to form nitrosyl chloride, according to the equation:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

In an experiment, student **A** kept the amount of $Cl_2(g)$ in large excess while the initial partial pressure of NO(g) was varied at constant temperature of 550 K.

The table below shows the experimental results obtained.

time / s	P_{NO} / atm	(Rate / P_{NO}) / s^{-1}	(Rate / $(P_{NO})^2$) / (atm^{-1} s^{-1})
0	0.917	1.033×10^{-4}	1.126×10^{-4}
1000	0.827	9.312×10^{-5}	1.126×10^{-4}
2000	0.753	8.486×10^{-5}	1.127×10^{-4}
3000	0.691	7.788×10^{-5}	1.127×10^{-4}
4000	0.638	7.190×10^{-5}	1.127×10^{-4}

(i) Suggest why the amount of $Cl_2(g)$ was kept in large excess. [1]

(ii) Define the term *order of reaction*. [1]

(iii) Using the data from the table above, deduce the order of reaction with respect to NO(g). [1]

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3 (a) (iv) In another experiment, the initial partial pressure of NO(g) was 4.2 atm and it was reacted with Cl_2(g) at a constant temperature of 550 K. The partial pressure of Cl_2(g) was recorded at time intervals of 30 seconds.

The data obtained are tabulated below.

time / s	partial pressure of Cl_2(g)/ atm
0	0.78
30	0.76
60	0.72
90	0.70
120	0.66
150	0.63
180	0.59
210	0.57
240	0.54
270	0.52

time / s	partial pressure of Cl_2(g)/ atm
300	0.49
330	0.46
360	0.44
390	0.42
420	0.39
450	0.38
480	0.36
510	0.34
540	0.33
570	0.32

Using the data but without plotting of any graph, deduce the order of reaction with respect to Cl_2(g). [1]

(v) Write the rate equation for the overall reaction. Hence, calculate the rate constant, stating its units. [3]

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3 **(b)** In another reaction, $2NO_2(g) + 4CO(g) \longrightarrow N_2(g) + 4CO_2(g)$, it was found that the rate equation is rate = $k[NO_2]^2$.
A proposed mechanism for this reaction is shown.

Step 1	$NO_2(g) + NO_2(g) \longrightarrow 2NO(g) + O_2(g)$	slow
Step 2	$2NO(g) + O_2(g) + 4CO(g) \longrightarrow N_2(g) + 4CO_2(g)$	fast

Explain whether it is consistent with the established rate equation. [1]

(c) Tryptophan metabolism plays an important role in the mechanisms associated with the gut-brain axis. At least 90% of human intake of tryptophan is converted to kynurenine for further metabolism via a catalyst.

(i) Explain how the activation energy of a reaction is affected by the presence of a catalyst, and with an appropriate sketch of a Maxwell–Boltzmann distribution curve, explain how a catalyst increases the rate of reaction. [3]

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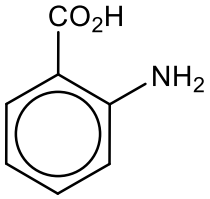
3 (c) (ii) Kynurenine has the molecular formula $C_{10}H_{12}N_2O_3$. When dissolved, an aqueous solution of kynurenine is almost neutral and maintains its pH upon addition of small amounts of aqueous sodium hydroxide or hydrochloric acid. Addition of this solution to aqueous 2,4-dinitrophenylhydrazine causes an orange precipitate to form.

Kynurenine reacts with $NaBH_4$ to form compound **L**, $C_{10}H_{14}N_2O_3$. Heating **L** with concentrated H_2SO_4 produces only **M**, $C_{10}H_{12}N_2O_2$. Heating **M** with acidified $KMnO_4$ under reflux results in the formation of compound **N**, $C_3H_5NO_4$ and anthranilic acid.

The molecular structure of anthranilic acid is as shown below.



anthranilic acid

Reaction of **N** with $LiAlH_4$ in dry ether produces compound **O**, $C_3H_9NO_2$. A solution of **O** turns litmus paper blue.

Suggest possible structures for **L, M**, **N**, **O** and kynurenine. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound. [13]

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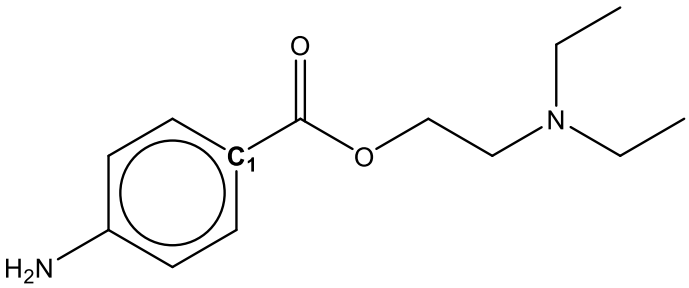
[Total: 24]

Section B

Answer **one** question from this section.

4 An anaesthetic is a drug used to induce a temporary loss of sensation or awareness. They may be classified as general anaesthetics that result in a reversible loss of consciousness, or local anaesthetics which cause a reversible loss of sensation for a limited region of the body without necessarily affecting consciousness.

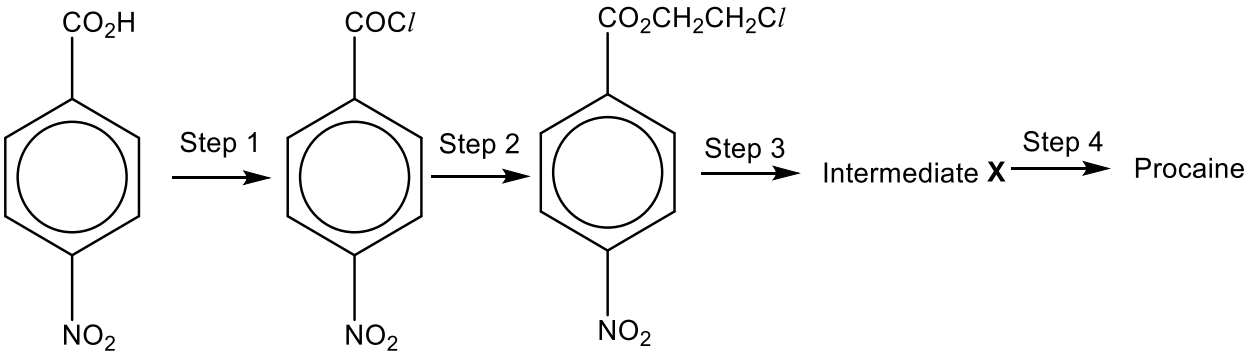
(a) Procaine, one of the first injectable local anaesthetic used during surgery has the following structure:



Procaine

(i) State the oxidation state of C_1 in Procaine. [1]

(ii) Procaine can be made by the following reaction scheme:



State the reagents and conditions used for steps 1, 2, 3 and 4. Draw the structure of intermediate **X**. [5]

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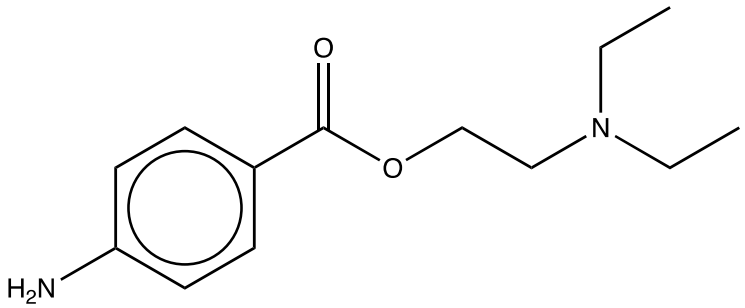
4 (a) (iii) One molecule of Procaine contains two nitrogen atoms, both of which can act as a base by accepting a proton. On the diagram below, circle the nitrogen atom which will be a stronger base. Explain your reasoning.



Procaine [2]

(iv) Procaine undergoes hydrolysis rapidly in the small intestines where the pH is about 9. Give the structural formulae of the products obtained from the hydrolysis under such conditions. [2]

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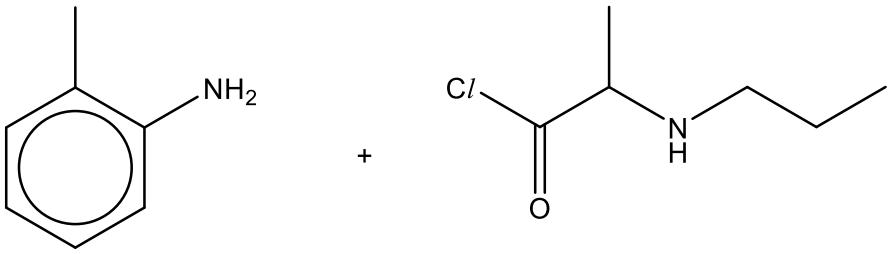
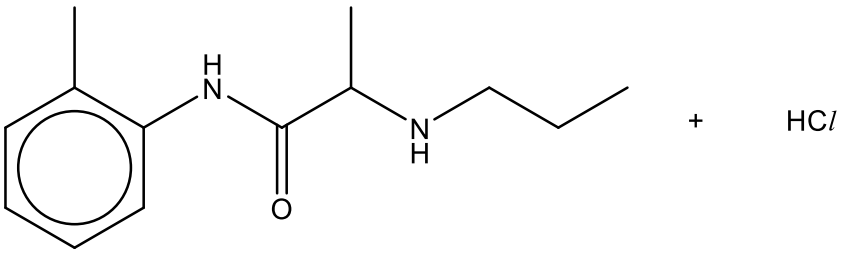
4 **(b)** Prilocaine, an amide-based local anaesthetic, is commonly used in dentistry. Prilocaine is synthesised when the following substituted acyl chloride undergoes a condensation (addition-elimination) reaction with 2-methylphenylamine.



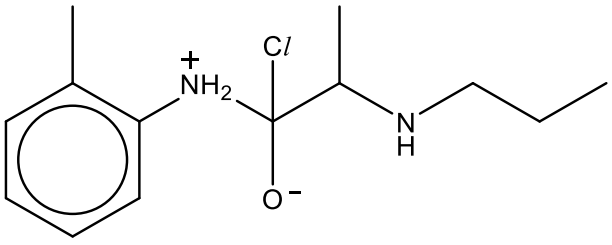
2-methylphenylamine substituted acyl chloride



Prilocaine

The reaction above takes place in three steps.

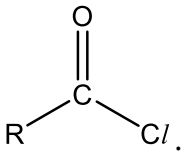
The first step involves the nucleophilic addition of 2-methylphenylamine to the substituted acyl chloride to form the following dipolar ion as an intermediate.



In the second step, the nitrogen atom on another molecule of 2-methylphenylamine acts as a base and accepts a proton from the dipolar ion intermediate.

In the final step, the C=O bond of the amide bond is restored when the chlorine atom leaves as a chloride ion.

With reference to the information provided above, suggest a three-step mechanism for the formation of Prilocaine.

You may wish to represent the substituted acyl chloride as 

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Show all partial charges and curly arrows clearly in your answer. [3]

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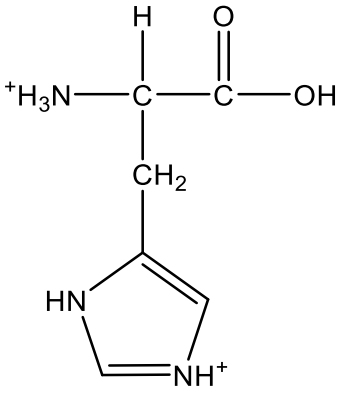
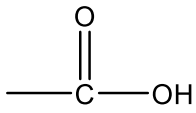
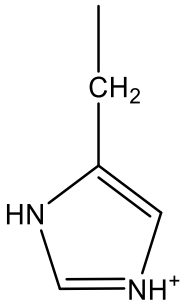
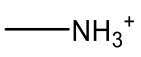
4 **(c)** Limiting the intake of certain essential nutrients, either proteins or amino acids for several days before surgery may reduce the risk of serious surgical complications such as heart attack or stroke.

Histidine is an essential amino acid utilised by the body to develop and maintain healthy tissues. The structure of the fully protonated form of histidine is given below.



Histidine

The pK_a values of the respective functional groups attached to the α-carbon in histidine are given in the following table.

functional group	pK_a value
	1.82
	6.00
	9.17

(c) **(i)** With reference to the given pK_a values, suggest the major species present in solutions of histidine with the following pH values:

- pH 4
- pH 8
- pH 12 [3]

4 (c) (ii) Histidine is also important for digestion in human body as it helps to produce gastric juices in the stomach.

A stomach juice sample is extracted from a patient to determine the concentration of histidine by titrating it with aqueous sodium hydroxide.

Draw a labelled titration curve of pH against amount of NaOH(aq) added when one mole of fully protonated histidine is titrated with NaOH(aq).

You should clearly label the following points in your titration curve.

- amounts of NaOH required at each equivalence point
- pH values at the points of maximum buffer capacity [3]

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4 (c) (iii) Histidine can be converted to histamine by an enzyme called histidine decarboxylase. The enzyme undergoes partial hydrolysis to produce the following fragments:

- ala-cys-phe
- lys-asp-asp-gly
- phe-arg-lys
- ala-cys-phe-phe-arg-lys
- asp-asp-gly

Give the sequence of the nine amino acid residues of the enzyme. [1]

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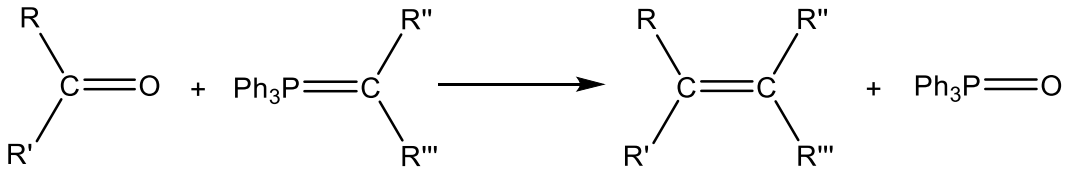
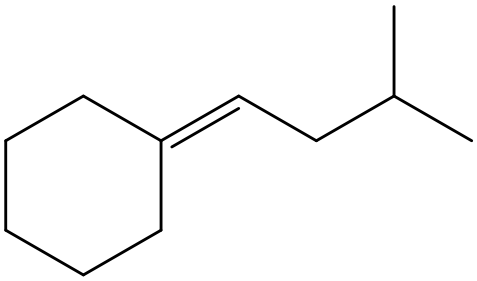
5 Wittig reaction is a very important tool in organic chemistry and is particularly useful for the synthesis of alkenes, as the double bond forms specifically at the location of the original aldehyde or ketone. The Wittig reagent used is triphenyl phosphonium ylide, $Ph_3P{=}CR''R'''$, where the phenyl group is abbreviated as 'Ph'.



phosphonium ylide

where R,R',R'',R''' = H or alkyl

(a) Draw the structures of the carbonyl compound and the specific phosphonium ylide that can be used to produce the following organic compound.



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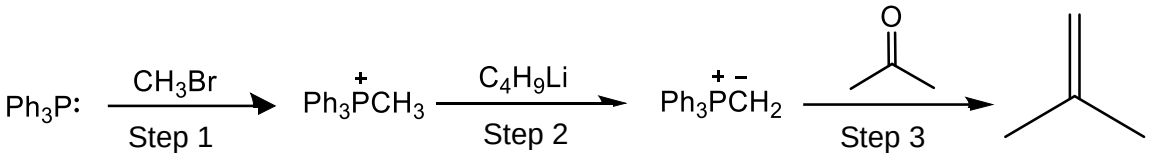
5 **(b)** The synthesis of methylpropene via the Wittig reaction is shown below.



(i) Name the type of reaction that occurs in step 1. [1]

(ii) State the role of butyl lithium, C_4H_9Li, in step 2. [1]

(iii) Methylpropene undergoes a reaction with hydrogen bromide.
Suggest a mechanism for this reaction and use it to predict the major product.
Explain your reasoning. [3]

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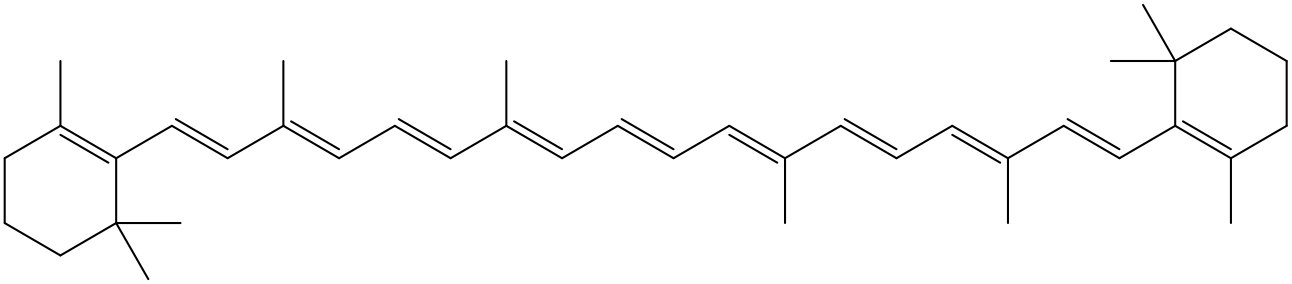
5 (b) (iv) Describe and explain the trend in the thermal stability of the hydrogen halides HC*l*, HBr and HI. Include an equation for the thermal decomposition reaction in your answer. [3]

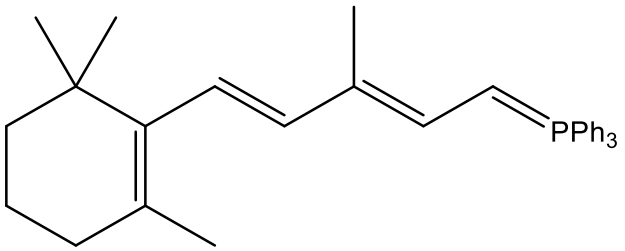
(v) Hence, by stating relevant information from the *Data Booklet*, suggest how the rate of the reaction will change in **(b)(iii)** when hydrogen chloride is used instead of hydrogen bromide. [2]

5 (c) Wittig reaction is also used in the industry to synthesise β-carotene. β-carotene is a food colouring that can be extracted from the pigmentation found in red-orange plants and fruits such as carrots. It can be synthesised using excess of an aldehyde and 2 molecules of phosphonium ylide.



β-carotene

The phosphonium ylide used to synthesise β-carotene is given below, where Ph, represents a phenyl group,



Suggest the structure of the aldehyde that can be used to produce β-carotene. [1]

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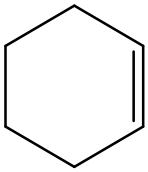
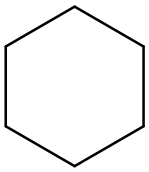
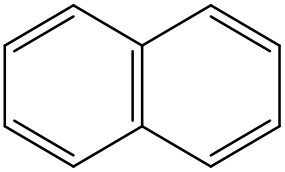
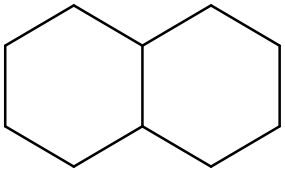
5 **(d)** The long conjugated hydrocarbon chain in β-carotene leads to its intense orange colour.

A conjugated system contains a series of alternating single and double bonds, in which there is a p orbital on each atom and electrons are delocalised in the molecule. This generally lowers the overall energy of the molecule and increases its stability.

The table below contains information about cyclohexene and naphthalene. Cyclohexene contains one carbon-carbon double bond and shows chemical properties common to other alkenes. Napthalene, $C_{10}H_8$, shows chemical properties common to aromatic compounds.

alkene	conditions for reaction with hydrogen	product	calculated enthalpy change of hydrogenation/ kJ mol^{-1}
 cyclohexene	room temperature, nickel catalyst	 cyclohexane	–118
 naphthalene	–	 decalin	?

(i) Calculate the enthalpy change of hydrogenation of naphthalene. [1]

(ii) The actual value for the enthalpy change of complete hydrogenation of naphthalene is –335 kJ mol^{-1}. Explain why this is so, in terms of hybridisation and interactions of the orbitals in the carbon atoms within a naphthalene molecule. [2]

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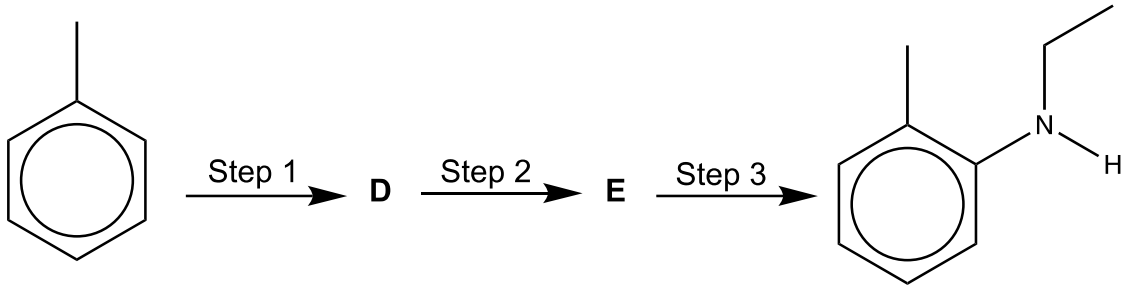
5 **(e)** Dyes possess colour as they have an extended conjugated system.
Compound **F** is used in the manufacture of dyes and paints. It can be synthesised from methylbenzene in three steps as shown.



F

(i) Suggest structures for the organic compounds **D** and **E**. [2]

(ii) Suggest reagents and conditions for each of the steps 1 and 2. [2]

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[Total: 20]

END OF PAPER

Additional answer space

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

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