Index No.	Name	Form Class	Tutorial Class 2CH_____	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY H2 9729/03

Paper 3 Free Response **1 September 2020**

Candidates answer on the Question Paper. 2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your index number and name, form class and tutorial 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.

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

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

Section	Question No.	For Examiner's Use
		Marks
A	1	
	2	
	3	
B		
Presentation of answers		
	TOTAL: 80 m	

Section A

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

1 Sodium borohydride, $NaBH_4$, reduces carbonyl compounds to secondary alcohols as shown below.

$$CH_3COCH_3 + NaBH_4 + H_2O \rightarrow CH_3CH(OH)CH_3 + BH_3 + NaOH$$

(a) (i) The kinetics of this reaction was studied using propanone in the presence of aqueous $NaBH_4$. Table 1.1 shows the experimental data obtained.

Table 1.1

experiment	initial concentration / mol dm^{-3}		initial rate of formation of $CH_3CH(OH)CH_3$ / mol dm^{-3} s^{-1}
	$[NaBH_4]$	$[CH_3COCH_3]$	
1	0.0100	0.200	6.60×10^{-5}
2	0.0080	0.200	5.28×10^{-5}
3	0.0100	0.100	3.30×10^{-5}

By showing appropriate working, deduce the order of reaction with respect to each compound. Hence write a rate equation for the reaction. [3]

(ii) Calculate the value of the rate constant, stating its units. [2]

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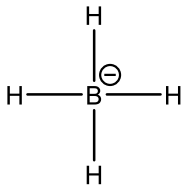
(b) The structural formula of the BH_4^- is shown below.



The reaction between propanone and sodium borohydride occurs in the following manner.

- In the first step, the BH_4^- ion transfers a hydride to the carbonyl carbon of propanone, forming the $CH_3CH(O^-)CH_3$ ion.
- In the next step, the $CH_3CH(O^-)CH_3$ ion accepts a proton from water to form $CH_3CH(OH)CH_3$.

(i) By referring to your rate equation in **(a)(i)** and the steps described above, name and describe the mechanism for the reaction between propanone and sodium borohydride.

In your answer, you should show all charges and lone pairs and show the movement of electrons by curly arrows. [3]

(ii) Experiment 1 was repeated under identical conditions using propanal. Explain how the initial rate of reaction will change. [2]

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(c) **(i)** Propanone reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate.

Draw the structure of the orange precipitate. [1]

(ii) Describe a simple chemical test that could distinguish between propanone and propanal. [2]

(iii) Suggest a suitable three step reaction pathway to convert propan-2-ol to 2-methylpropanoic acid. [5]

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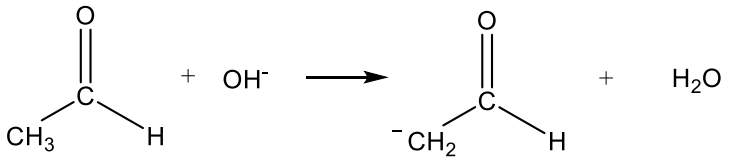
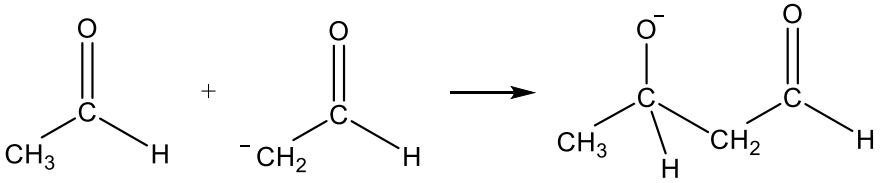
(d) In the presence of a strong base, carbonyl compounds undergo the aldol condensation to form a 3-hydroxy carbonyl compound.

Fig. 1.2 shows the aldol condensation of ethanal.

step 1



step 2



step 3

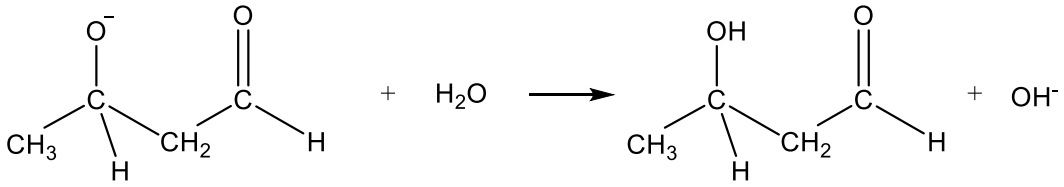
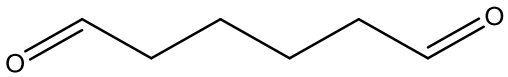


Fig. 1.2

(i) State the type of reaction in step 3. [1]

(ii) When hexanedial is reacted with a strong base, aldol condensation occurs and a product with the molecular formula $C_6H_{10}O_2$ is formed.



hexanedial

Suggest the structure of this product. [1]

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2 A neutral compound **A,** $C_6H_8O_4$, is used in production of paints and adhesives.

When compound **A** was heated with dilute hydrochloric acid, a mixture of compounds **C**, $C_4H_4O_4$, and **B** was obtained. When the mixture was distilled, compound **B** was obtained as a distillate.

When compound **B** was heated under reflux with acidified $KMnO_4$, only carbon dioxide gas and water were obtained.

Compound **C** exists as a pair of cis-trans isomers. Compound **C** decolourises Br_2 in CCl_4 and reacts with aqueous NaOH in a ratio of 1:2.

(a) Deduce the structures of compounds **A**, **B** and **C** and explain the reactions involved. [6]

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(b) The pK_{a1} values for the two isomers of compound **C** are given below in Table 2.1.

Table 2.1

	pK_{a1}
cis isomer of compound **C**	1.9
trans isomer of compound **C**	3.9

(i) Use the pK_{a1} values to suggest which isomer of compound **C** produces a more stable mono-anion when 1 mol of **C** is treated with 1 mol of NaOH. [1]

(ii) Draw the displayed formulae of the cis and trans isomers of the mono-anion of compound **C**.
Use your formulae to suggest an explanation for the relative stabilities of the cis and trans mono-anions of compound **C**. [4]

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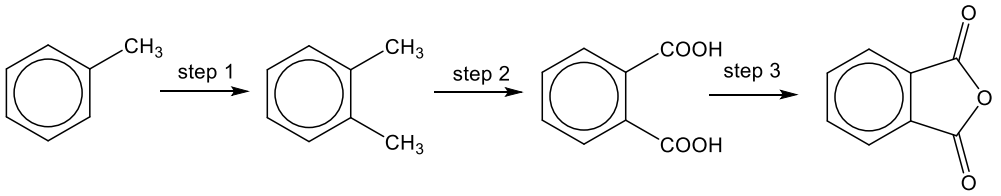
(c) **(i)** The following reaction scheme shows the synthesis of phthalic anhydride from methylbenzene.

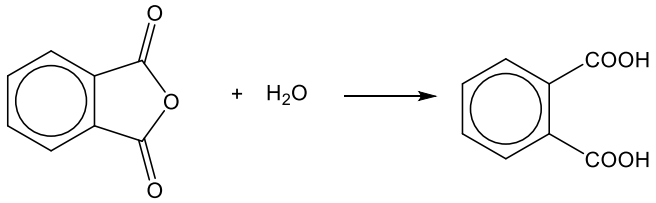


phthalic anhydride

State the reagents and conditions for steps 1 and 2. [2]

(ii) State the type of reaction occurring in step 3. [1]

(iii) Phthalic anhydride reacts with water in a 1:1 ratio as shown below.



phthalic anhydride

With reference to the above reaction, draw the structure of the product when phthalic anhydride reacts with compound **B** from **(a)** in a 1:1 ratio. [1]

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(d) An experiment was conducted to determine the enthalpy change of combustion of compound **B** and the following data was obtained.

amount of compound **B** used = 0.0250 mol
mass of water heated = 200 g
temperature rise = 19 ^{o}C
specific heat capacity of water = 4.2 J K^{-1} g^{-1}

(i) Draw a labelled experimental set-up that can be used to obtain the data above. [2]

(ii) Use the given data to calculate the enthalpy change of combustion of compound **B**. [2]

(iii) The actual enthalpy change of combustion of compound **B** is –715 kJ mol^{-1}.
Explain why your answer in **(d)(ii)** differs from the actual enthalpy change of combustion. [1]

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3 Butylamine, $CH_3CH_2CH_2CH_2NH_2$, is often used in the manufactures of pesticides. It has a pK_b value of 3.22.

25.0 cm^3 of 0.100 mol dm^{-3} aqueous butylamine was titrated with 0.100 mol dm^{-3} of dilute hydrochloric acid from a burette.

(a) **(i)** Calculate the initial pH of the solution of butylamine. [2]

(ii) Calculate the pH when 12.50 cm^3 of HC*l* is added. [1]

(iii) Sketch the titration curve you would expect to obtain when 30 cm^3 of 0.100 mol dm^{-3} of dilute hydrochloric acid is added to 25 cm^3 of 0.100 mol dm^{-3} butylamine.

Label the various key points on the curve. [3]

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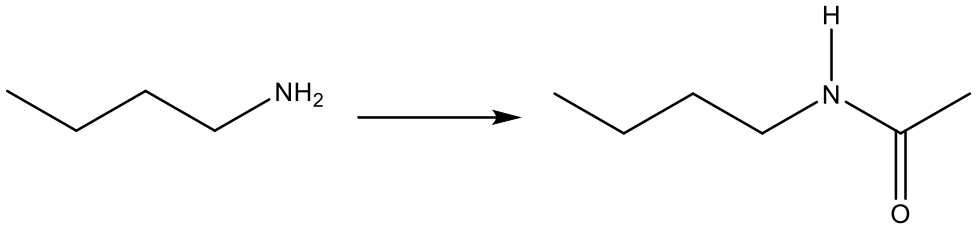
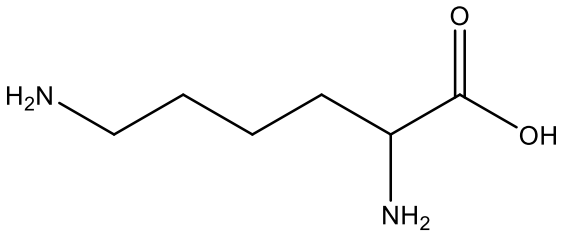
(b) **(i)** Butylamine can be converted to N-butylethanamide as shown below.



butylamine N-butylethanamide

State the reagents and conditions required for this conversion. [1]

(ii) Lysine is an amino acid with the following structure.



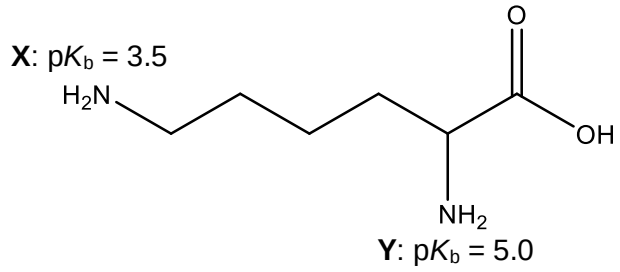
The melting points of lysine and N-butylethanamide are shown below in Table 3.1.

Table 3.1

compound	molecular formula	melting point / ^{o}C
lysine	$C_6H_{14}N_2O_2$	225
N-butylethanamide	$C_6H_{13}NO$	112

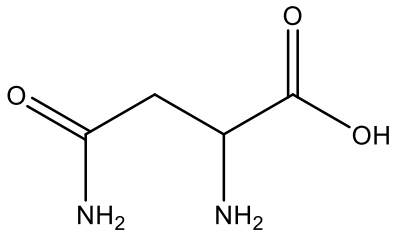
Explain why lysine has a higher melting point than N-butylethanamide. [2]

(iii) The pK_b values of the two amino groups of lysine, labelled as **X** and **Y,** are shown below.



Explain the difference in the pK_b values of the two amino groups labelled **X** and **Y**. [2]

(iv) Another amino acid, asparagine, has the following structure.



Describe a simple chemical test to distinguish asparagine from lysine. [2]

(v) The amino acid asparagine is able to act as a *buffer* in aqueous solution. Explain what is meant by the term *buffer*. [1]

(vi) With the aid of **two** equations, show how a solution of asparagine can act as a buffer. [2]

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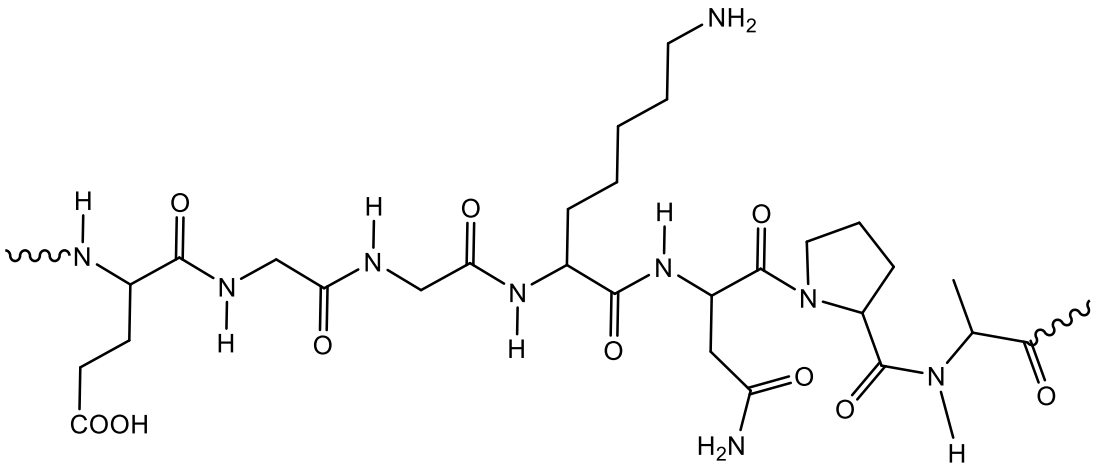
(c) Lysine and asparagine can be isolated from the protein tyrosinase, which catalyses the enzymatic browning of mushrooms.

A portion of the protein chain with seven amino acids is shown below.



(i) Suggest the reagents and conditions to hydrolyse proteins to their constituent amino acids. [1]

(ii) State the number of **different** amino acid residues that are present in this portion of the mushroom tyrosinase protein. [1]

(iii) Draw the structures of the amino acids **P** and **Q** from this portion of the mushroom tyrosinase protein which have the following properties:

P has no chiral carbon.
Q has a secondary amine group. [2]

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Section B

Answer **one** question from this section.

4 Calcium propanoate, $(CH_3CH_2COO)_2Ca$, forms calcium carbonate and pentan-3-one when heated.

$$(CH_3CH_2COO)_2Ca \longrightarrow CaCO_3 + CH_3CH_2COCH_2CH_3$$

Calcium carbonate occurs as chalk, marble and limestone. Finely ground chalk is incorporated in some toothpaste and cosmetics.

Pentan-3-one is one of the many volatile compounds in strawberry flavour and is used as a precursor to Vitamin E.

(a) (i) Define the term *standard enthalpy change of formation*, $\Delta H^{\ominus}_f$, of calcium carbonate. [1]

(ii) Write an equation for the thermal decomposition of calcium carbonate. [1]

(iii) Construct a fully labelled energy level diagram using the data given in Table 4.1 to calculate ΔH_f, the enthalpy change of formation of calcium carbonate.

Table 4.1

enthalpy change of combustion of carbon	-394 kJ mol^{-1}
enthalpy change of combustion of calcium	-635 kJ mol^{-1}
enthalpy change of thermal decomposition of calcium carbonate	$+178$ kJ mol^{-1}

[3]

(iv) Determine the minimum temperature for the spontaneous decomposition of calcium carbonate, given ΔS for the same reaction is $+163$ J mol^{-1} K^{-1}. [2]

(v) When heated, copper(II) carbonate decomposes in a similar manner as calcium carbonate.

Use data from the *Data Booklet* to suggest whether calcium carbonate or copper(II) carbonate has a higher decomposition temperature. Explain your reasoning. [3]

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(b) A solution contains 0.100 mol dm^{-3} magnesium nitrate and 0.100 mol dm^{-3} calcium nitrate. Solid sodium carbonate is added slowly to 100 cm^3 of this solution.

[$K_{sp}(MgCO_3) = 3.5 \times 10^{-8}$ mol^2 dm^{-6}; $K_{sp}(CaCO_3) = 2.8 \times 10^{-9}$ mol^2 dm^{-6}]

(i) State which metal ion is first precipitated. Calculate the concentration of carbonate ions in the solution needed for the first trace of precipitate to be seen. [1]

(ii) A student attempts to separate the two cations Mg^{2+} and Ca^{2+} by adding carbonate ions in a controlled manner.

Determine the concentration of the metal ion stated in **(b)(i)** when the **other** metal ion just begins to precipitate. [2]

(iii) The separation is considered effective when less than 1% of the metal ion remains in the solution. Hence, deduce if the above separation is effective. [1]

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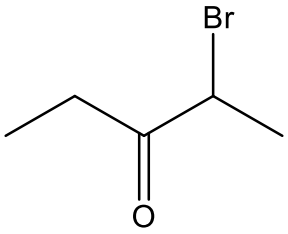
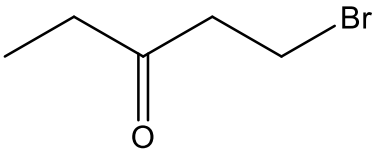
(c) There are two monobrominated isomers of pentan-3-one, compounds **E** and **F**.

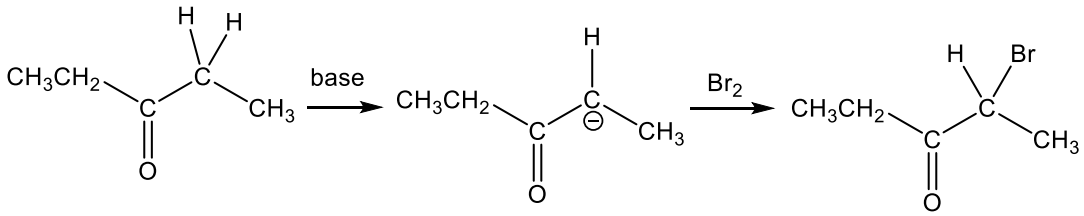


E



F

In the presence of a base, compound **E** can be formed from pentan-3-one, as shown in the scheme below.



anionic intermediate **E**

Suggest why the anionic intermediate is stable. [1]

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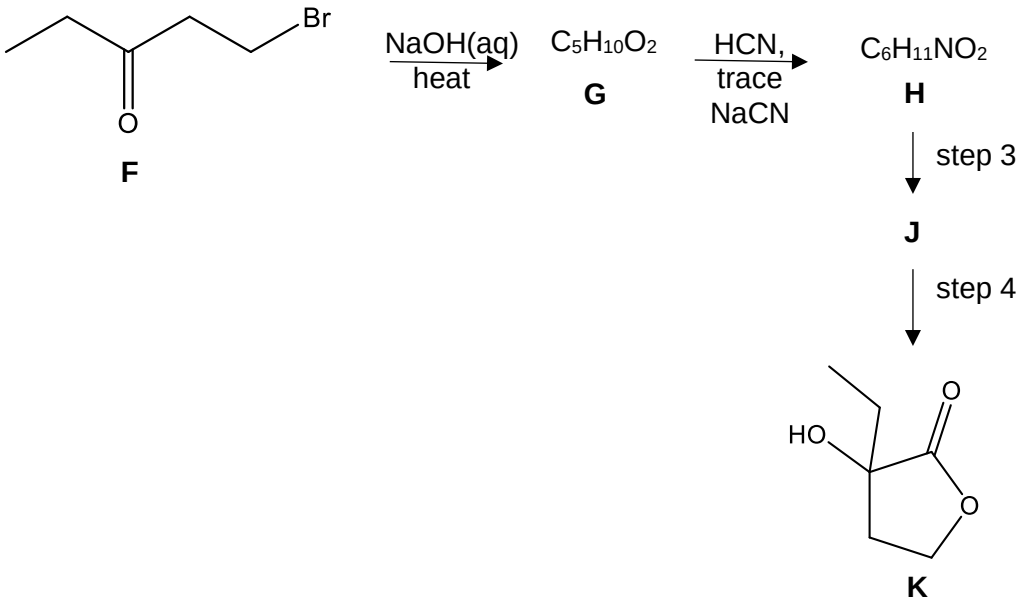
(d) Compound **K** can be made from compound **F** by a four-step synthesis, via key intermediates **H** and **J**.



One mole of compound **H** reacts with sodium metal to produce one mole of hydrogen gas. Compound **J** reacts with aqueous sodium carbonate.

(i) Suggest what the above observations indicate about the functional group(s) in **H**. [1]

(ii) Suggest the structures for compounds **G**, **H** and **J**. [3]

(iii) Suggest the reagents and conditions for step 4. [1]

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5 Calcium fluoride, CaF_2, is a Group 2 halide which occurs naturally in the mineral *fluorspar*. It is the major source of hydrogen fluoride, a chemical used to produce refrigerants and herbicides.

The data in Table 5.1 will be useful in this question.

Table 5.1

standard enthalpy change of formation of $CaF_2(s)$	-1220 kJ mol^{-1}
standard enthalpy change of formation of $Ca^{2+}(aq)$	-543 kJ mol^{-1}
standard enthalpy change of formation of $F^-(aq)$	-333 kJ mol^{-1}
standard enthalpy change of hydration of $Ca^{2+}(g)$	-1579 kJ mol^{-1}
standard enthalpy change of hydration of $F^-(g)$	-524 kJ mol^{-1}

(a) (i) Define the term *standard enthalpy change of solution* of CaF_2, $\Delta H^{\ominus}_{solution}$. [1]

(ii) The standard Gibbs free energy change of solution of CaF_2, $\Delta G^{\ominus}_{solution}$, is +64.4 kJ mol^{-1}.

Use relevant data given in Table 5.1 to calculate the $\Delta H^{\ominus}_{solution}$ and the standard entropy change of solution, $\Delta S^{\ominus}_{solution}$, of CaF_2. [3]

(iii) Construct a fully labelled energy cycle relating the lattice energy of CaF_2 and the $\Delta H^{\ominus}_{solution}$ of CaF_2. Use your cycle to calculate the lattice energy of CaF_2. [2]

(iv) Suggest, with reasons, how the magnitude of the lattice energy of CaF_2 might compare to that of

- $CaCl_2$
- CaO [2]

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(b) **(i)** When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$, in J mol^{-1}, is given by the following expression.

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

With reference to **(a)(ii)**, state the value of $\Delta G^{\ominus}_{ppt}$ of CaF_2. [1]

(ii) Hence, calculate a value for the K_{sp} of CaF_2. [2]

(iii) Calculate the concentration of Ca^{2+} in a saturated solution of CaF_2. [1]

(c) Group 2 halides have important applications in organic synthesis. One such example is the Grignard reagent, CH_3CH_2MgBr. The bond between magnesium and carbon is covalent.

(i) Explain why carbon bonds covalently to magnesium but not to calcium. [1]

The Grignard reagent, CH_3CH_2MgBr, reacts with carbon dioxide to form propanoic acid.

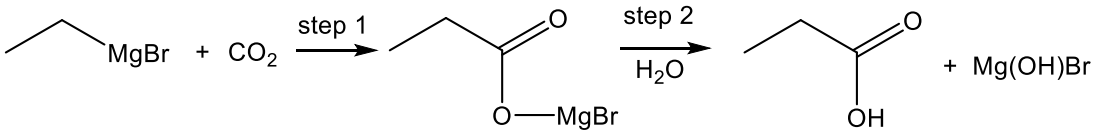

Fig. 5.1

(ii) State the type of reaction occuring in step 2. [1]

(iii) Likewise, the Grignard reagent can react with aldehydes to produce alcohols. By referring to the steps in Fig. 5.1, draw the structure of the aldehyde that can be used to synthesise butan-2-ol with the Grignard reagent, CH_3CH_2MgBr. [1]

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(d) Draw the structure of the ester formed between propanoic acid and butan-2-ol and state the reagents and conditions required for this conversion. [2]

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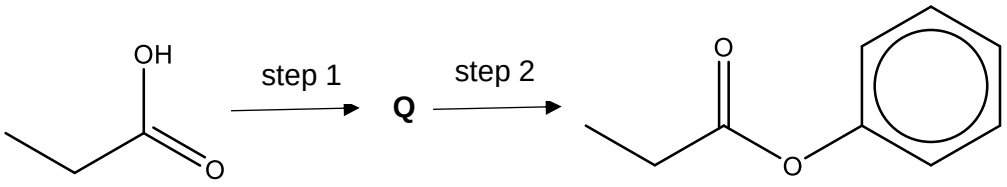
(e) Suggest the reagents and conditions you would use in a two-step synthesis of the ester phenyl propanoate and identify the intermediate **Q**.



phenyl propanoate

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Additional answer space

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