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

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY H2 **9729/03**

Paper 3 Free Response

1 September 2020

2 hours

Cover page

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** 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]

Comparing experiments 1 and 2,
When [$NaBH_4$] is increased 1.25 times, rate is increased 1.25 times.
Rate is directly proportional to [$NaBH_4$]
Order of reaction with respect to $NaBH_4$ = 1

Comparing experiments 1 and 3,
When [propanone] is doubled, rate is doubled.
Rate is directly proportional to [propanone]
Order of reaction with respect to propanone = 1

Rate = k [$NaBH_4$] [propanone]

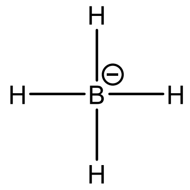
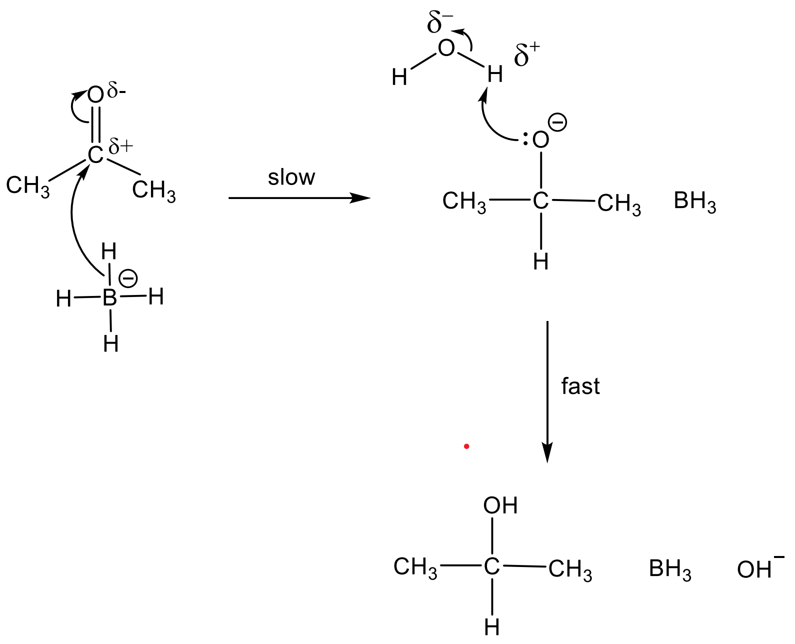
(ii) Calculate the value of the rate constant, stating its units.

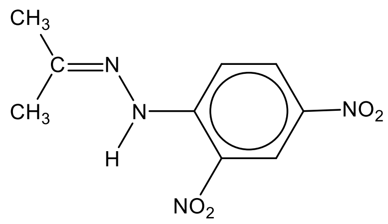
[2]

Using experiment 1:
$k = 6.60 \times 10^{-5} \div (0.01 \times 0.200)$
$= 0.0330$ mol^{-1} dm^{3} s^{-1}

Using experiment 2:
$k = 5.28 \times 10^{-5} \div (0.008 \times 0.200)$
$= 0.0330$ mol^{-1} dm^{3} s^{-1}

Using experiment 3:

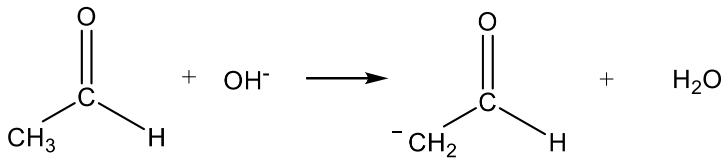
			$k = 3.33 \times 10^{-5} \div (0.01 \times 0.100)$ $= 0.0330\ mol^{-1}\ dm^3\ s^{-1}$
	(b)	The structural formula of the BH_4^- is shown below.  The reaction between propanone and sodium borohydride occurs in the following manner. • In the first step, BH_4^- ion transfers a hydride to the carbonyl carbon 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]
			Nucleophilic addition/Reduction 
		(ii)	Experiment 1 was repeated under identical conditions using propanal. Explain how the initial rate of reaction will change. [2]
			The rate of reaction will increase with propanal. Propanal has one less electron donating alkyl group, so its carbonyl carbon is more electron deficient and more reactive towards nucleophilic attack. OR

			The rate of reaction will increase when propanal is used. Propanal has one less alkyl group, so there is less steric hindrance around the carbonyl carbon for the nucleophilic attack.
	(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]
			Test: aqueous I_2, NaOH, warm / heat Observations: Propanone – yellow precipitate Propanal – No ppt/ soln remain yellow Test: $KMnO_4$, dilute H_2SO_4, heat Observations: Propanone – the solution remains purple Propanal – the solution decolourises Test: $K_2Cr_2O_7$, dilute H_2SO_4, heat Observations: Propanone – the solution remains orange Propanal – the solution turns green Test: Tollens' reagent, heat Observations: Propanone – no silver mirror Propanal – silver mirror is formed Test: Fehling's solution, heat Observations: Propanone – no red-brown ppt Propanal – red-brown ppt is formed
		(iii)	Suggest a suitable three step reaction pathway to convert propan-2-ol to 2-methylpropanoic acid. [5]
			$CH_3CH(OH)CH_3 \rightarrow CH_3CHClCH_3$ OR $CH_3CHBrCH_3$ OR CH_3CHICH_3 $\rightarrow CH_3CH(CH_3)CN \rightarrow CH_3CH(CH_3)COOH$ 1) I: $SOCl_2$ / PCl_5 / PCl_3 and heat / NaCl, conc H_2SO_4, reflux / dry HCl(g)/ concentrated HCl, anhydrous $ZnCl_2$ OR: PBr_3, heat/NaBr, conc H_2SO_4, reflux OR: NaI, conc H_2SO_4, reflux II: NaCN (ethanol), heat under reflux III: H_2SO_4(aq) heat under reflux

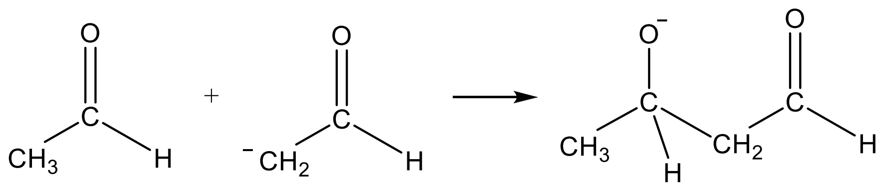
(d) In the presence of a strong base, carbonyl compounds undergo the aldol condensation to form a 3-hydroxy carbonyl compound.

Fig. 1.2 shows the aldol condensation of ethanal.

step 1



step 2



step 3

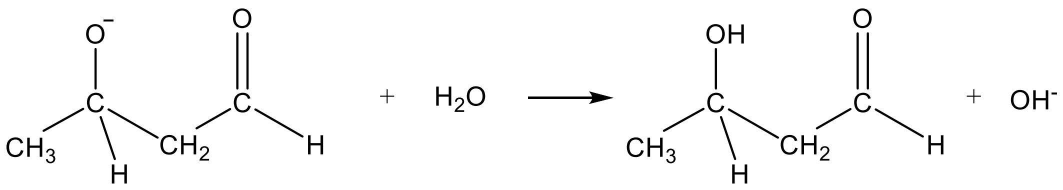
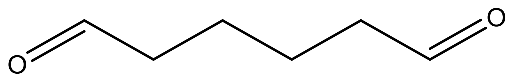


Fig. 1.2

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

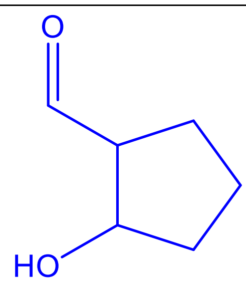
Step 3: Acid-base

(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]



[Total: 20]

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

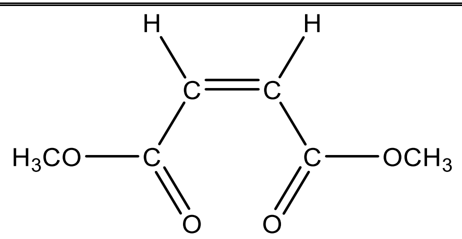
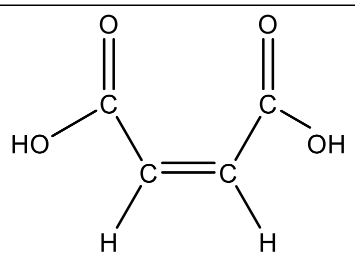
When compound **A** was heated with dilute hydrochloric acid, a mixture of compounds **C**, $C_4H_4O_4$, and **B** was obtained. When the mixture was distilled, compound **B** was obtained as a distillate.

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]

Reaction	Deduction
A neutral compound **A**, $C_6H_8O_4$was heated with dilute hydrochloric acid	<u>Acid hydrolysis</u> of <u>ester **A**</u> Degree of unsaturation in **A** = $\frac{[2(6)+2]-8}{2}$ = 3 Hydrolysis **A** is ester
Compound **C** reacts with Br_2 in CCl_4 in a 1:1 ratio	<u>Electrophilic addition of C=C in **C**</u> **C** exist as cis-trans isomers: 2 different groups attached to the same C of C=C Electrophilic addition Alkene or C=C present in **C**
Compound **C** reacts with NaOH in a 1:2 ratio.	<u>Acid base reaction between carboxylic acid</u> and NaOH. **C** is a carboxylic acid Acid base/neutralisation reaction Two COOH in **C** (or dibasic acid)
Compound **B**, was obtained as a distillate.	Compound **B** is <u>an alcohol</u>, since **C** is a carboxylic acid.
When compound **B** was heated under reflux with acidified $KMnO_4$, CO_2 was obtained.	**B** undergoes <u>oxidation</u> Since **C** has 4C and there are two COOH in **C**, <u>alcohol **B** has 1C</u> (or **B** is methanol)

Compound A	 Trans isomer accepted. They need not draw as trigonal planar
Compound B	CH_3OH
Compound C	 Trans isomer accepted. They need not draw as trigonal planar

(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 **C** produces a more stable mono-anion when 1 mol of **C** is treated with 1 mol of NaOH.

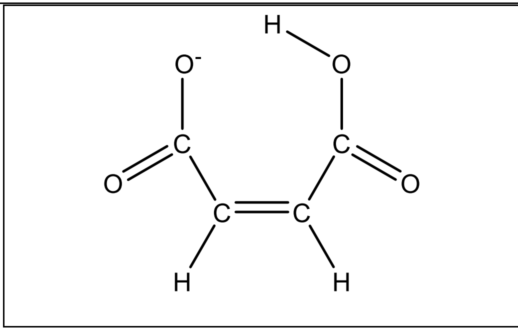
[1]

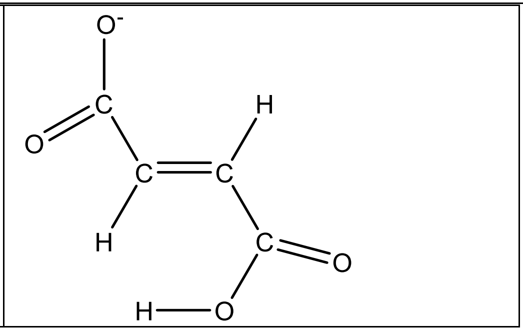
The <u>cis isomer produce a more stable</u> mono-anion as the pK_{a1} is lower, hence the cis isomer is more acidic.

(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]

Cis	Trans



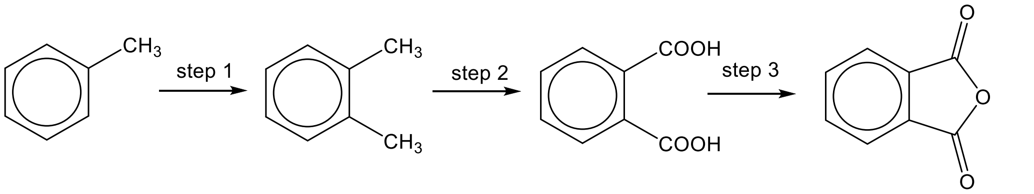


This cis mono-anion is more stable.

There is <u>intramolecular hydrogen bonding between the oxygen with the negative charge and the protonic H of the other COOH group</u>
Thus the <u>cis conjugate base/ monoanion is more stable</u>.

For the trans isomer, the oxygen with the negative charge is <u>too far away</u> from the COOH group <u>to form the intramolecular hydrogen bond</u>.

(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]

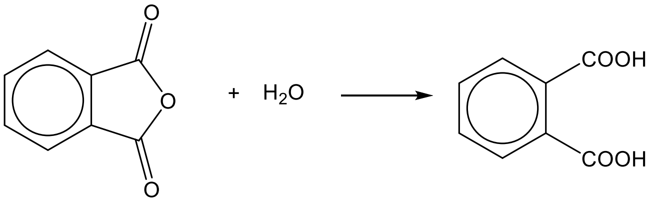
Step 1: CH_3Cl, $AlCl_3$
Step 2: $KMnO_4$, dilute H_2SO_4 or $H_2SO_4(aq)$, heat under reflux.

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

....[1]

Condensation

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

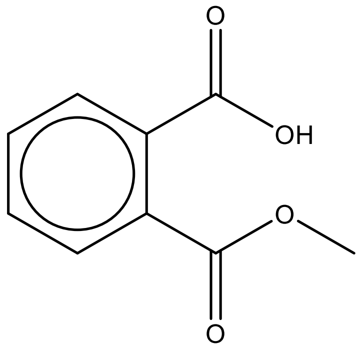


phthalic anhydride

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]

Answer:



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

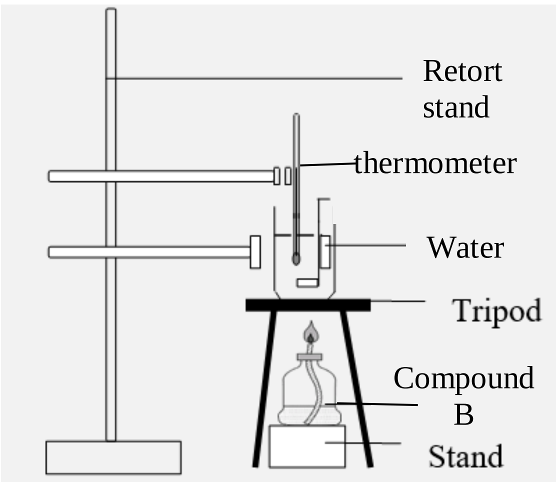
amount of compound **B** used = 0.0250 mol

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]



Compound B in spirit lamp
Water in beaker
Thermometer

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

Heat evolved = 200 x 4.2 x 19
= 15960J
= 15.96 kJ

Enthalpy change of combustion of **B** = –15.96 ÷ 0.0250
= –638 $kJmol^{-1}$

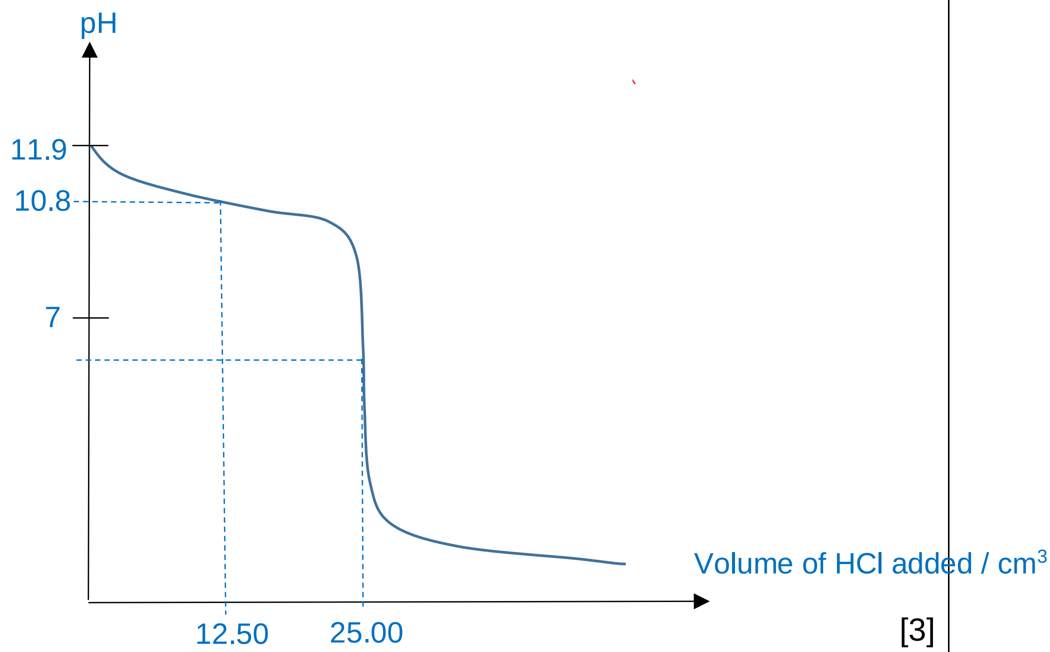
(iii) The actual enthalpy change of combustion of compound **B** is –715 kJ mol^{-1}.

			Explain why your answer in **(d)(ii)** differs from the actual enthalpy change of combustion. ....[1] There is <u>heat lost to surroundings/incomplete combustion</u>, thus the experimental enthalpy change of combustion is less exothermic. OR Heat capacity of beaker is not accounted for.
			[Total: 20]

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] $K_b = 10^{-3.22}$ $= 6.03 \times 10^{-4}$ moldm^{-3} $[OH^-] = \sqrt{0.100 \times 6.03 \times 10^{-4}}$ $= 7.76 \times 10^{-3}$ moldm^{-3} pH = 14 – lg(7.76×10^{-3}) = 11.9
		(ii)	Calculate the pH when 12.50 cm^3 of HC*l* is added. [1] At 12.50 cm^3, pOH = pK_b since this is max buffer capacity. pOH = 3.22 Hence, pH = 14 – 3.22 = 10.8

(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.

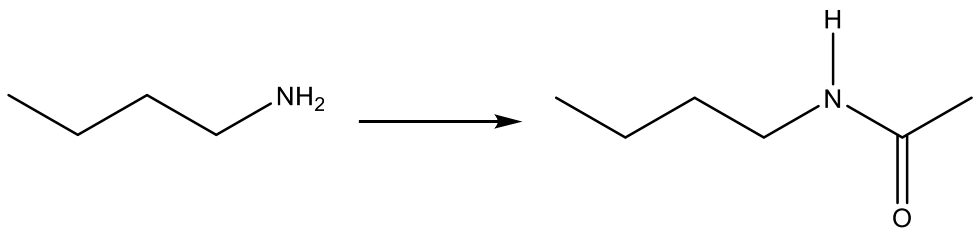
Label the various key points on the curve.



[3]

- Correct shape and axis (if missing units, just add in for them)
- Correct initial pH, ecf from (a)(i)
- Volume of HCl and pH at max buffer capacity from part aii
- Equivalence volume and pH < 7

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



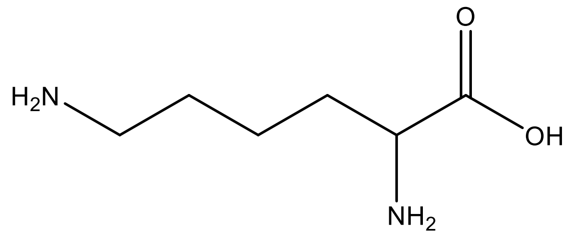
Butylamine N-butylethanamide

State the reagents and conditions required for this conversion.

....[1]

CH_3COCl

(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

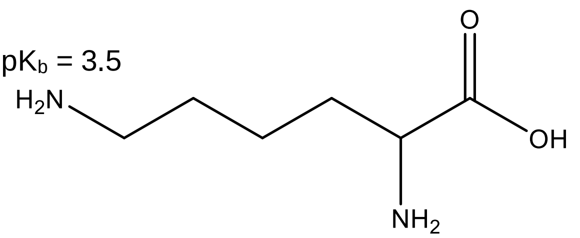
compound	molecular formula	melting point/°C
lysine	$C_6H_{14}N_2O_2$	225
N-butylethanamide	$C_6H_{13}NO$	112

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

Lysine exists as zwitterions, in a giant ionic lattice, thus there are electrostatic forces of attractions/ionic bonds are stronger than the hydrogen bondsbetween the simple molecules of N-butylethanamide is, hence require more energy to break.

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

X: $pK_b = 3.5$



Y: $pK_b = 5.0$

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

[2]

....

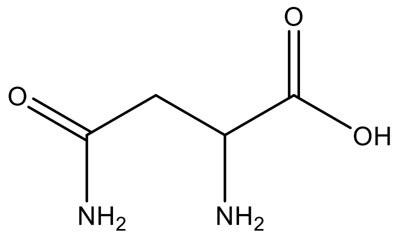
....

....

....

Amine group Y is closer to the electron-withdrawing COOH group than amine group X, thus the lone pair of electrons on amine group Y is less available for donation to H^+, hence is a weaker basewith larger pK_b.

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



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

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

Heat both asparagine and lysine with NaOH(aq)
Lysine: No pungent alkaline gas/no visible change/no change/no change/does not
Asparagine: Pungent NH_3 gas evolved turns damp red litmus paper blue.

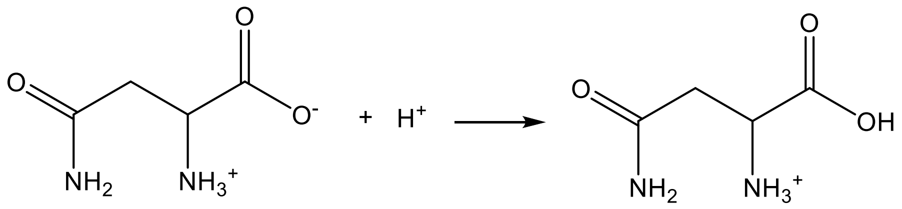
(v) The amino acid asparagine is able to act as a *buffer* in aqueous solution. Explain what is meant by the term *buffer*.

……………………………………………………………………………………[1]

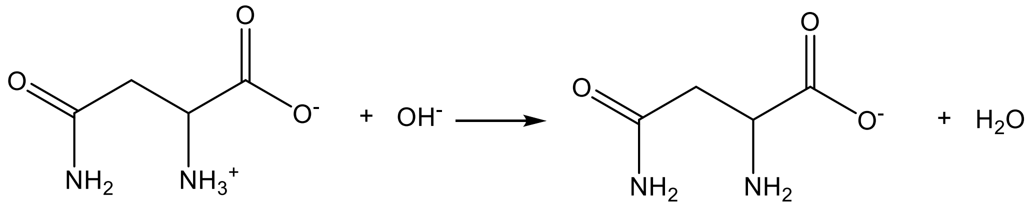
A buffer is able to resist pH changes when small amounts of strong acid or base is added.

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

Add acid:

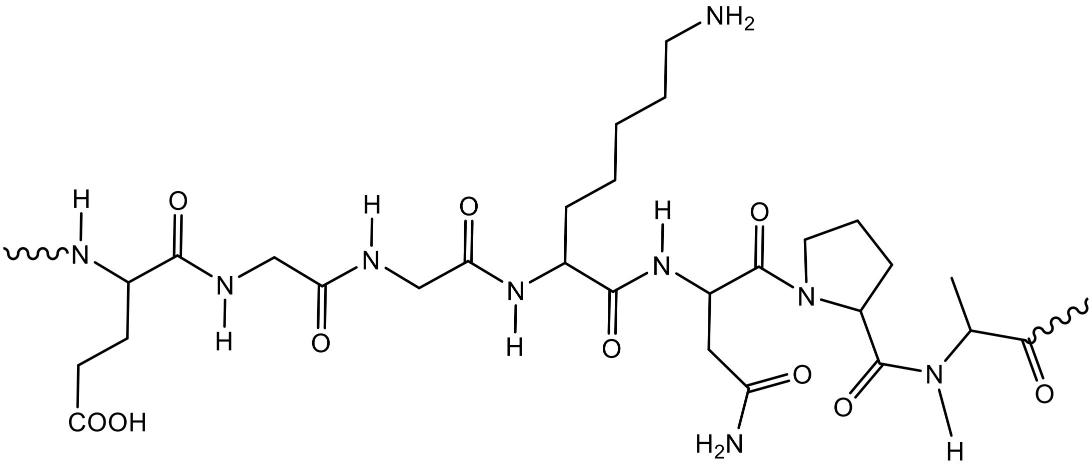


Add base:



(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]

Dilute HCl/H_2SO_4, heat under reflux for several hours
OR NaOH(aq), heat under reflux for several hours

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

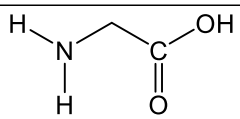
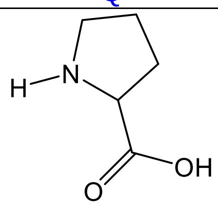
6

(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]

Answer:

P	Q
	

[20]

[Total: 20]

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]

Standard enthalpy change of formation of $CaCO_3$ is the heat change when one mole of $CaCO_3$(s) is formed from its constituent elements, Ca(s), C(s)& O_2(g) under standard conditions of 298 K and 1 bar. **[1]**

(ii) Write an equation for the thermal of calcium carbonate.

....[1]

$CaCO_3 \longrightarrow CaO + CO_2$

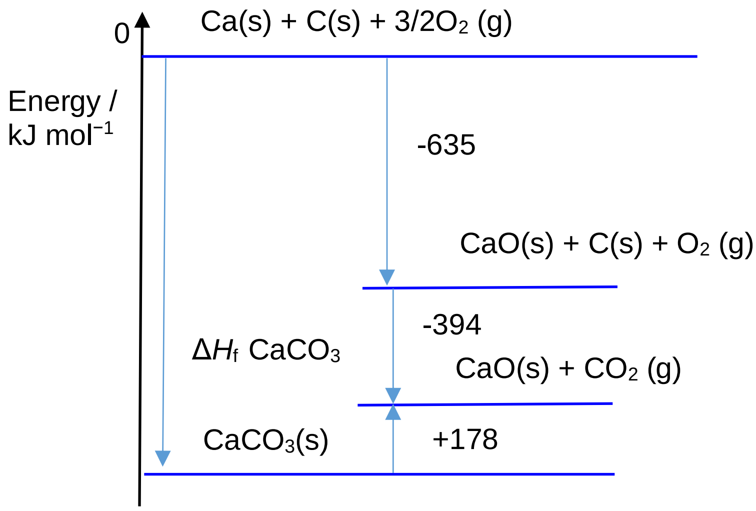
(iii) Construct a fully labelled energy level diagram using the data given in Table 4.1 and use your diagram to calculate ΔH_f, the enthalpy change of formation of calcium carbonate.

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]

Using Hess's law,
ΔH_f $CaCO_3$ = -635 + (-394) – (+178)
= **-1210 kJ mol^{-1}**



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

$\Delta G = \Delta H - T\Delta S$
$\Delta H - T\Delta S < 0$ (**$\Delta G < 0$** spontaneous reaction)
$T > \Delta H / \Delta S$
T > 178 x 1000 / 163
T> 1092 K
T > 1090 K (3 sig fig)

(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]

$CaCO_3$ will have a **higher** decomposition temperature.
Ionic radius of Ca^{2+} = 0.099 nm; Cu^{2+} = 0.073 nm

Size of Ca^{2+} is larger so its charge density is lower. Polarising power of Ca^{2+} is thus lower **and less able to distort/polarise the electron cloud of CO_3^{2-} ion, weakening the C-O covalent bond less** . Hence, $CaCO_3$ is **more stable to heat/ bonds in carbonate anion of $CaCO_3$ require more energy to break** and has a **higher decomposition temperature.**

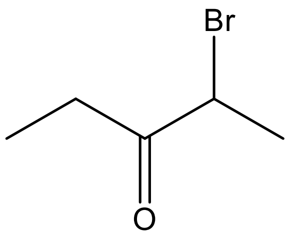
(b) A solution contains 0.100 mol dm^{-3} magnesium nitrate and 0.100 mol dm^{-3} calcium nitrate. Solid sodium carbonate is added slowly to 100 cm^3 of this solution.

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

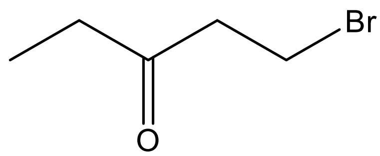
(i) State which metal ion is first precipitated. Calculate the concentration of carbonate ions in the solution needed for the first trace of precipitate to be seen. [1]

			Since K_{sp} of $CaCO_3$ is smaller (lower solubility), Ca^{2+} is precipitated first or $CaCO_3$ is precipitated. **$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 2.80 \times 10^{-9}$** **$0.100 \times [CO_3^{2-}] = 2.80 \times 10^{-9}$** **$[CO_3^{2-}] = 2.80 \times 10^{-8}$ mol dm^{-3}**
		(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] **$[CO_3^{2-}]$ when Mg^{2+} starts to precipitate** **$= 3.5 \times 10^{-8} \div 0.100$** **$= 3.5 \times 10^{-7}$ mol dm^{-3}** **Using K_{sp} of $CaCO_3$,** **$[Ca^{2+}] \times 3.5 \times 10^{-7} = 2.8 \times 10^{-9}$** **$[Ca^{2+}] = 0.00800$ mol dm^{-3}**
		(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]
			Percentage of **Ca^{2+} remaining** **= 0.008/0.1 x 100 = 8.00% >> 1% (ecf)** **The above separation is not effective.**

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

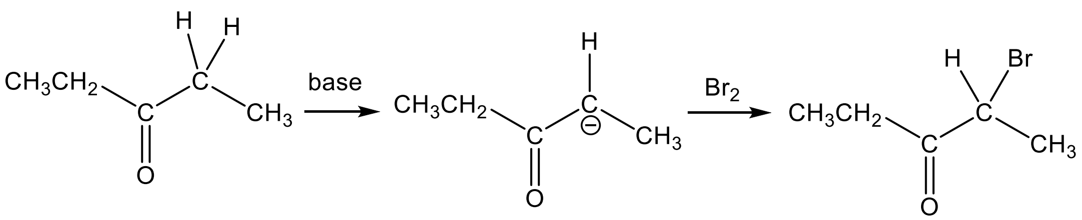


E



F

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

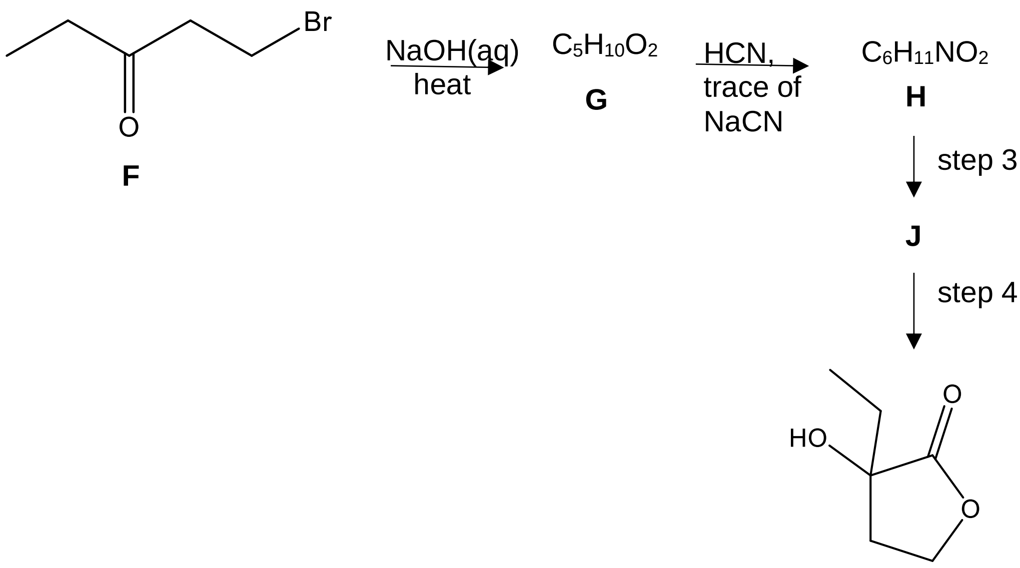


anionic intermediate **E**

Suggest why the anionic intermediate is stable. [1]

The negative charge can be delocalised into the electronegative oxygen, thus is effectively dispersed.

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



K

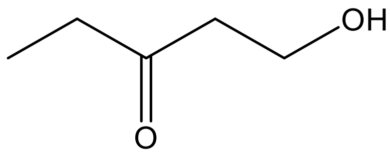
One mole of compound **H** reacts with sodium metal to produce one mole of hydrogen gas. Compound **J** reacts with aqueous sodium carbonate.

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

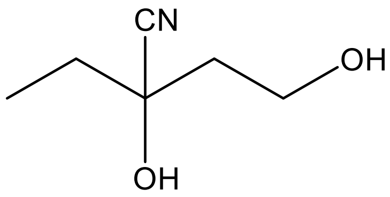
Compound H contains <u>two alcohols groups</u> as it undergoes redox reaction with Na.

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

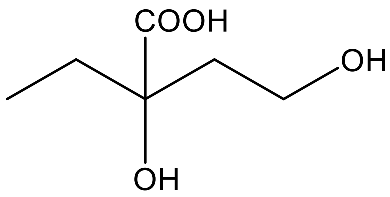
Compound G:



Compound H:



Compound J:



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

Step 4: catalytic/small amount of <u>concentrated H_2SO_4</u>, <u>heat</u> under reflux

[20]

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]

Standard enthalpy change of solution of CaF_2 is the heat change when one mole of CaF_2 (s) completely dissolved in infinite dilution in an aqueous solution under standard conditions of 298 K and 1 bar.

(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]

$$CaF_2(s) \longrightarrow Ca^{2+}_{(aq)} + 2\,F^-_{(aq)}$$

$$\Delta H^\ominus_{sol}(CaF_2) = \Delta H^\ominus_f(Ca^{2+}_{(aq)}) + 2\Delta H^\ominus_f(F^-_{(aq)}) - \Delta H^\ominus_f(CaF_{2(s)})$$
$$= -543 + 2(-333) - (-1220)$$
$$= +11.0 \text{ kJ mol}^{-1}$$

$$\Delta G^\ominus_{sol} = +64.4 \text{ kJ mol}^{-1}$$
$$= \Delta H^\ominus_{sol} - T\Delta S^\ominus_{sol}$$
$$64.4 = +11 - 298(\Delta S^\ominus_{sol})$$
$$\Delta S^\ominus_{sol} = -0.179 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

(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]

$$\begin{tikzcd}
CaF_2(s) \arrow[rr, "\Delta H^\ominus_{sol} = +11"] & & Ca^{2+}_{(aq)} & + & 2\,F^-_{(aq)} \\
& Ca^{2+}_{(g)} \arrow[ul, "L.E."] \arrow[ur, "-1579"'] & + & 2\,F^-_{(g)} \arrow[ur, "2(-524)"'] &
\end{tikzcd}$$

LE = -1579 + 2(-524) – (+11) = -2638 kJ mol^{-1} = -2640 kJ mol^{-1}

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

- $CaCl_2$
- CaO

[2]

Cl^- has larger ionic radius than F^-. Thus, the lattice energy of $CaCl_2$ is less exothermic than CaF_2 OR has a smaller magnitude.

O^{2-} is larger/ bigger ionic radius and has higher charge than F^-. Thus, the lattice energy of CaO is more exothermic than CaF_2 OR has a larger magnitude.

(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]

-64.4×10^3 J mol^{-1} or -64.4 kJ mol^{-1}

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

[2]

$$\Delta G^{\ominus}_{ppt} = 2.303\ RT \log K_{sp}$$
$$-64.4 \times 10^3 = 2.303 \times 8.31 \times 298 \log K_{sp}$$
$$K_{sp} = 5.10 \times 10^{-12}\ \text{mol}^3\ \text{dm}^{-9}$$

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

[1]

Let solubility of CaF_2 = x

$K_{sp} = [\mathbf{Ca^{2+}_{(aq)}}]\ [\mathbf{F^{-}_{(aq)}}]^2$

$5.10 \times 10^{-12} = 4x^3$

$x = 1.08 \times 10^{-4}$ mol dm^{-3}

(c) **(i)** 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.

Explain why carbon bonds covalently to magnesium but not to calcium.

[1]

The electronegativity difference between C and Ca is larger than between C and Mg, thus the bond between Ca and C is not covalent.

OR

The Mg^{2+} has a higher charge density than Ca^{2+} thus can polarise the electron cloud of alkyl group of the carbon to a greater extent, hence, the bond between C and Mg is covalent.

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

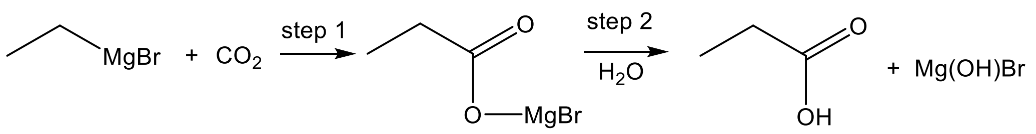


Fig. 5.1

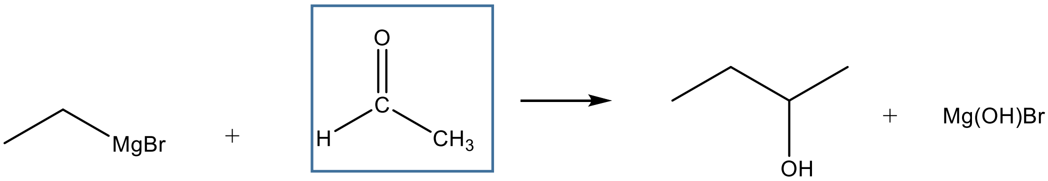
(ii) State the type of reaction occuring in step 2.

[1]

Hydrolysis

(iii) Likewise, the Grignard reagent can react with aldehydes to produce alcohols. By referring to the 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.

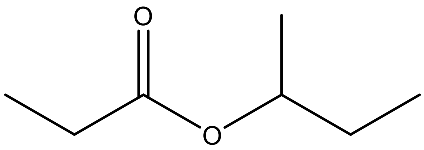
[1]



NOTE: The C=O group is converted to the CH_3CH_2 of the Grignard reagent and OH.

(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.

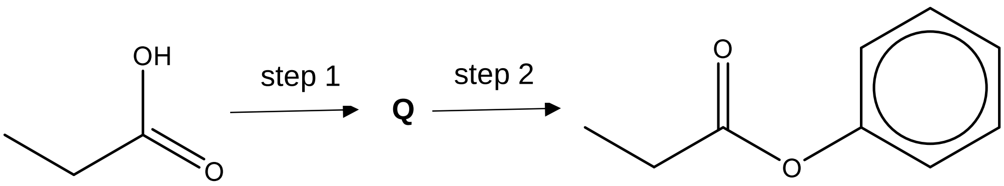
[2]



[1]

Catalytic amount of <u>concentrated H_2SO_4</u>, <u>heat</u> under reflux [1]

(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

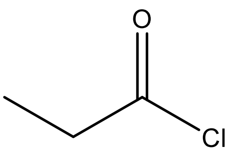
[3]

[20]

Step 1: PCl_5 or $SOCl_2$ or heat with PCl_3
or PBr_3 and heat but Q has to be drawn as acid bromide

Step 2: aq NaOH and <u>phenol</u> or sodium phenoxide

Intermediate Q



[Total: 20]