ANDERSON SERANGOON JUNIOR COLLEGE

2020 PRELIMINARY EXAMINATION

NAME:_____ ( ) **CLASS:** 20 /____

CHEMISTRY **9729/03**

Paper 3 Free Response **21 September 2020**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and register number 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 the booklet. The question number must be clearly shown.

Section A
Answer **all** the questions

Section B
Answer **one** question.

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

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.

For Examiner's Use	
1	**/16**
2	**/21**
3	**/23**
4*	**/20**
5*	**/20**
Total	**/80**

*Please circle the question you have attempted.

Paper 1	Paper 2	Paper 3	Paper 4	Percentage	Grade
/30	/75	/80	/55	/100	

This document consists of **32** printed pages.

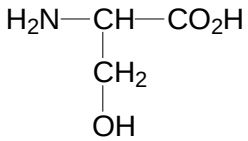
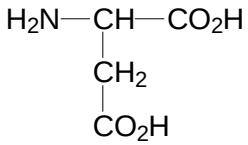
Section A

Answer **all** questions in this section.

1 Many naturally occurring organic compounds contain either acidic groups or basic groups or both. The strength of the acid or the base depends on the structure of the molecule.

(a) The pK_a values of ethanoic acid and two amino acids are given in Table 1.1 below.

Table 1.1

name	structure	pK_{a1}	pK_{a2}	pK_{a3}
ethanoic acid	CH_3COOH	4.7	–	–
serine (ser)		2.2	9.2	–
aspartic acid (asp)		1.9	3.7	9.6

(i) Suggest **two** reasons why the pK_{a1} value of serine is so much less than the pK_{a1} of ethanoic acid. [2]

(ii) Draw a **skeletal** structure for the dipeptide, asp–ser. [2]

Electrophoresis is a technique used to separate charged particles placed in an electric field. The system consists of two oppositely–charged electrodes connected by a conducting medium, typically a gel. The separation of the charged particles is based on their electrical charge and M_r.

A sample consisting of serine and aspartic acid was analysed by electrophoresis using a gel buffered at pH 5.7. The small quantity of the mixture was placed at the centre of the gel, at equal distance from the two electrodes.

(iii) Using the information given in Table 1.1, suggest the structures of the major species present in the buffer solution. Label the structures clearly. [2]

(iv) Hence, describe the relative positions of the two species in the gel after the separation by the electrophoresis process. Explain your answer.
You may find it helpful to draw a diagram to illustrate your descriptions. [2]

……

……

……

……

……

……

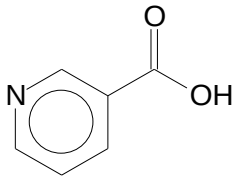
(b) A student prepared a buffer solution of pH 5.7 by adding solid sodium hydroxide to 200 cm^3 of 0.200 mol dm^{-3} ethanoic acid.

(i) With reference to the information in Table 1.1, calculate the mass of sodium hydroxide the student would have used. [2]

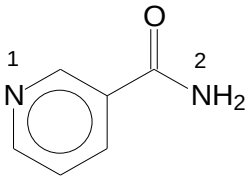
A buffer solution generally lost its effectiveness when one component of the buffer pair is less than about 10% of the other.

(ii) Calculate the percentage of ethanoic acid component present in the buffer solution in **(b)(i)** and hence comment on the effectiveness of the buffer. [2]

(c) Nicotinic acid and its amide, nicotinamide, are present in Vitamin B3 and are used to increase good cholesterol levels.



nicotinic acid



nicotinamide

The structure of nicotinamide consists of a single delocalised system of electrons which includes:

- an electron in the unhybridised p–orbital of the nitrogen atom in the six–membered ring
- electrons from the carbon atoms of the six–membered ring
- two electrons in the π bond of the >C=O group
- two electrons in lone pair on the nitrogen atom of the amide group

(i) State the number of delocalised electrons in one molecule of nicotinamide. [1]

(ii) Using the information provided, suggest the H–N–H bond angle in the NH_2 group in nicotinamide. [1]

(iii) Predict and explain the relative basicity of the two N atoms, labeled N1 and N2, in the nicotinamide molecule. [2]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

[Total: 16]

Question 2 starts on the next page.

2 **(a)** A lithium–iodine electrochemical cell can be used to generate electricity for a heart pacemaker. The cell is non–rechargeable and it consists of a lithium electrode and an inert electrode immersed in bodily fluids. When current flows, lithium is oxidised and iodine is reduced.

(i) Write two half–equations for the reactions taking place at the two electrodes. Hence, write the overall equation. [2]

(ii) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for this cell. [1]

(iii) A current of 2.5×10^{-5} A is drawn from this cell.

Calculate how long a pacemaker will last when 0.1 g of lithium electrode is remaining in the cell.
Assume the current remains constant throughout this period. Give your answer to the nearest day. [3]

(iv) Hence, suggest a reason why lithium–iodine battery can be used to power a heart pacemaker. [1]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

(b) Unlike the lithium–iodine cell, lithium–ion (Li–ion) batteries are designed to be recharged hundreds of times.

One type of lithium–ion battery consists of a cobalt oxide, CoO_2, electrode and a graphite electrode with lithium atoms inserted between the layers. An electrolyte of $LiPF_6$ dissolved in ethylene carbonate is used between the two electrodes.

During discharge, the Li atoms in the graphite electrode form Li^+ ions. Electrons are released and move through external circuit to the cobalt oxide electrode. The Li^+ ions migrate through the electrolyte and are incorporated into the cobalt oxide electrode. This is illustrated in Fig 2.1 in which C–C–C–C–C is a simplified representation of a layer of carbon atoms in graphite.

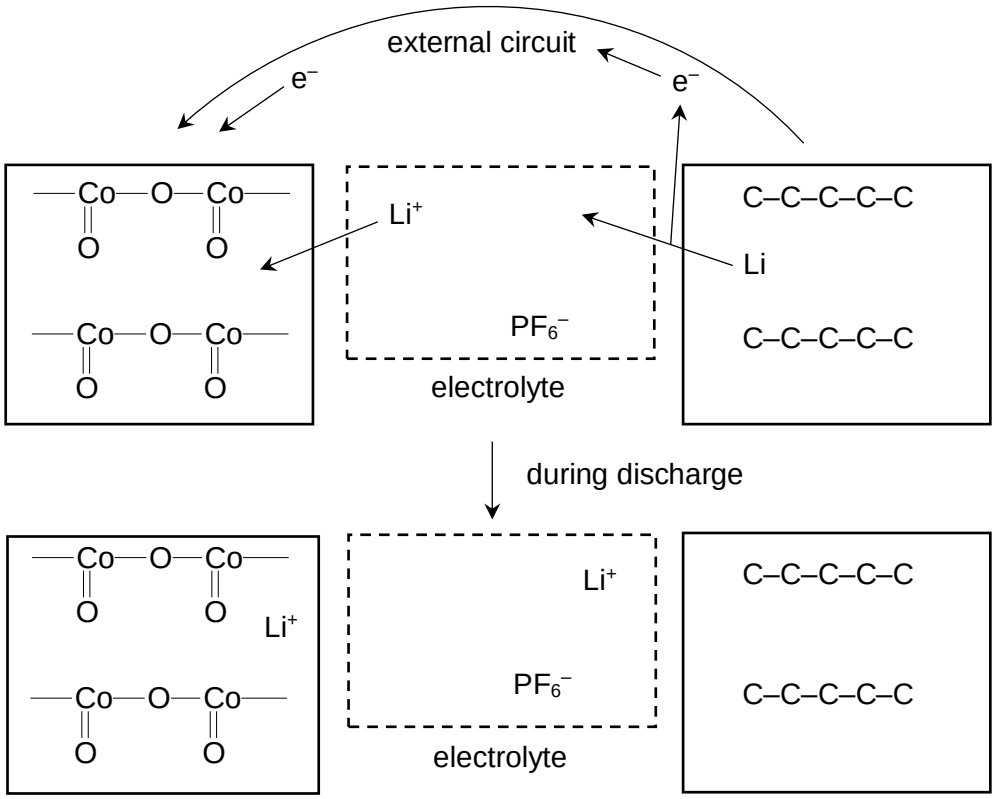


Fig 2.1

The overall redox equation during discharging can be represented as:

$$LiC_6 + CoO_2 \rightleftharpoons C_6 + LiCoO_2$$

where C_6 represents the graphite layers.

(i) Suggest the type of bonding between the lithium atoms and the layers of graphite. Explain your answer [1]

(ii) State the change in oxidation number of cobalt in the cobalt oxide electrode during discharging process.
Hence, or otherwise, identify if this electrode is the anode or cathode during discharge. [2]

(iii) The cell potential, E_{cell} is said to be related to the standard cell potential, $E^{\ominus}_{cell}$ by the Nernst equation:

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{F} \ln \frac{[LiCoO_2][C_6]}{[LiC_6][CoO_2]}$$

where concentration of the species are measured in the solid phase electrodes.

With reference to the Nernst equation, discuss how the cell potential changes as discharging takes place. [2]

(iv) During charging, the reverse of the discharging process takes place and eventually, all the lithium atoms will be stored between the graphite layers.

Suggest a property of graphite, other than its electrical conductivity, that allows the storage of lithium atoms upon charging. [1]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

(c) Zinc and silver are often present as impurities in crude copper obtained from minerals.

Explain, in terms of electrode reactions, how zinc and silver are removed in the industrial process of the purification of copper, using relevant data from the *Data Booklet*. Illustrate your answer with a labelled diagram. [4]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

(d) A set–up similar to what you have described in **(c)** can be used in copper electroplating.

Explain the effect, if any, each of the following changes have on the mass of copper plated if the duration of the electroplating process is kept constant.

- Doubling the concentration of copper ions in the electrolyte.
- Doubling the current of the electroplating process. [2]

……

……

……

……

……

……

……

……

……

(e) A fixed current was passed through two electrolytic cells connected in series for a known duration. The first cell contains aqueous copper(II) sulfate while the second cell contains aqueous silver nitrate. Inert electrodes were used in both cells.

Calculate the ratio $\frac{\text{mass of silver deposited}}{\text{mass of copper deposited}}$ under these conditions. [2]

……

……

……

……

……

……

……

……

……

……

……

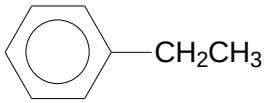
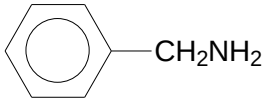
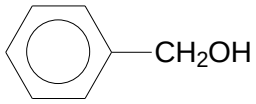
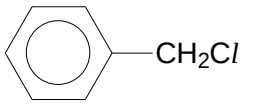
……

[Total: 21]

3 Organic compounds are molecules that contain carbon atoms covalently bonded to hydrogen atoms.

(a) The boiling points of some organic compounds are shown in Table 3.1.

Table 3.1

compound	formula	M_r	boiling point / °C
ethylbenzene		106.0	136
benzylamine		107.0	185
phenylmethanol		108.0	205
benzylchloride		126.5	179

Suggest explanations for these differences. [3]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

(b) **(i)** 2–methyl–1,3–butadiene, also called isoprene, is a colourless, volatile liquid hydrocarbon obtained in processing petroleum.

Draw the structures of the products **A** and **B** formed and suggest reagents and conditions for reaction **I** shown in Fig. 3.1.

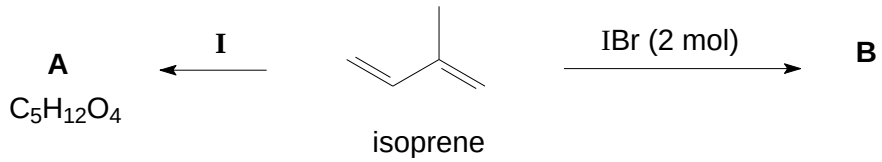
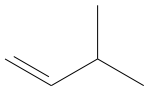


Fig. 3.1 [3]

Isoprene can be synthesised from the product obtained via a substitution reaction between compound **C** and a suitable halogen.



C

(ii) Suggest a suitable halogen and the condition for the substitution reaction. [1]

(iii) Draw the structure of the two possible products formed via the substitution reaction of **C** with the halogen and hence, determine the expected ratio in which they will be formed, assuming equal rate of substitution of H atom. [2]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

(c) Hydration of alkenes can be carried out by reacting alkenes with borane, BH_3 followed by treatment with alkaline hydrogen peroxide, H_2O_2.

An example of such a reaction is shown in Fig. 3.2.

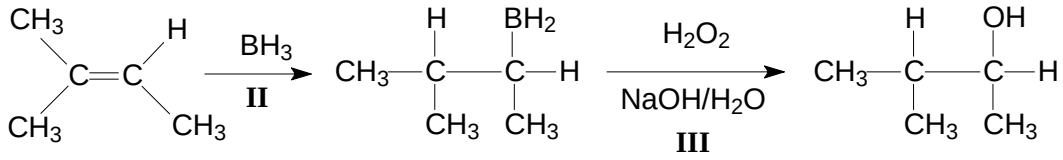


Fig. 3.2

Reaction **II** occurs via a mechanism similar to electrophilic addition and it involves the BH_3 acting as an *electrophile*.

(i) Explain what do you understand by the term *electrophile*. [1]

(ii) It is suggested that the mechanism for reaction **II** goes through the formation of a transition state as shown in Fig. 3.3.

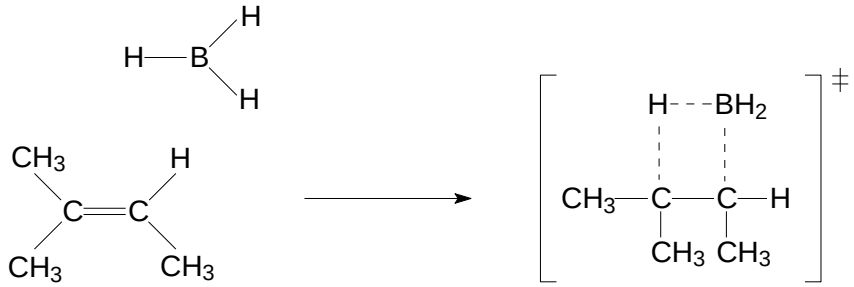


Fig. 3.3

Using information given in Table 3.2, complete Fig. 3.3. In your answer, indicate clearly the polarity of the B–H bond in borane by drawing $\delta+$ and $\delta-$ on the appropriate atoms and draw curly arrows for the movement of electrons.

Table 3.2

element	electronegativity
boron	2.0
hydrogen	2.2

. [2]

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

(iv) Two possible molecular arrangements of H_2O_2 exhibiting cis–trans isomerism, despite the absence of double bond to restrict rotation, is shown in Fig 3.4.

molecular arrangement 1 molecular arrangement 2

Fig 3.4

Using the principles of the Valence Shell Electron Pair Repulsion theory, explain the shape of the H_2O_2 molecule and suggest which molecular arrangement, 1 or 2, would result in a more stable molecule. [2]

(d) **(i)** Benzene rings are commonly found in many naturally occurring organic compounds.

Explain why benzene tends to undergo substitution reactions instead of addition reactions like alkenes. [2]

(ii) The position of substitution in the electrophilic substitution of arenes can be explained based on the stability of the intermediate carbocation formed.

Fig. 3.5 shows the possible carbocation intermediates that can be formed from the bromination of methylbenzene.

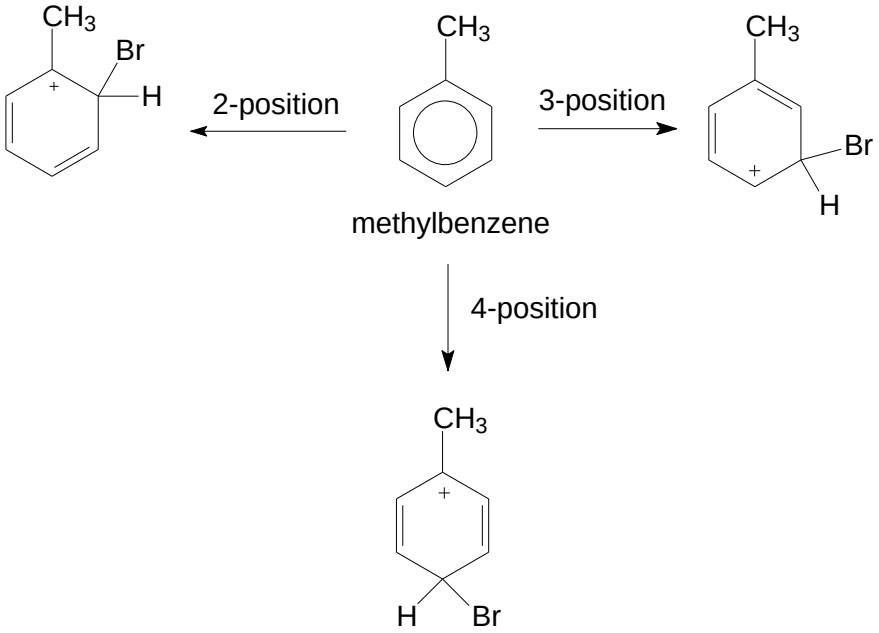


Fig. 3.5

Use the information and your knowledge about the stability of carbocation intermediates to suggest why the CH_3 group directs incoming electrophiles to the 2– and 4–positions in preference to the 3–position. [2]

(iii) Hence, suggest a synthesis of 3–bromobenzoic acid starting from methylbenzene according to the scheme in Fig. 3.6.

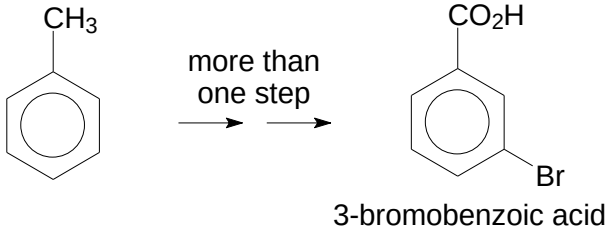


Fig. 3.6

[3]

……

……

……

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[Total: 23]

Section B starts on the next page.

Section B

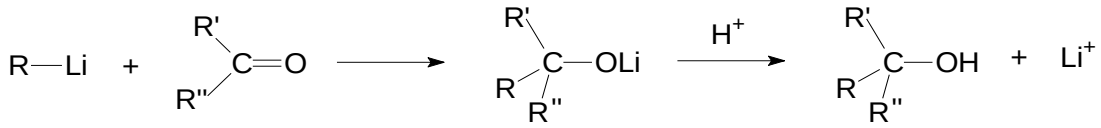
Answer **one** question from this section.

4 **(a)** Describe the reactions, if any, when separate samples of the oxides Na_2O, Al_2O_3 and P_4O_{10} are added to water. Write equations where appropriate and suggest the pH of any aqueous solution formed. [4]

(b) Lithium metal reacts with bromoalkanes to give organolithium compounds.

$$R–Br + 2Li \rightarrow R–Li + LiBr$$

The carbon–lithium covalent bond in organolithium compounds is polarised $\overset{\delta-}{C}–\overset{\delta+}{Li}$. These compounds are useful carbon–nucleophiles. They react with carbonyl compounds to give lithium alkoxides, which form alcohols on treatment with dilute acid as shown in Fig 4.1.



(R is alkyl; R' and R" are either alkyl or H)

Fig 4.1

(i) Butan–2–ol, $CH_3CH_2CH(OH)CH_3$ is formed when CH_3CH_2CHO reacts with CH_3Li in a similar two–step process.

Draw the mechanism for this reaction, assuming that CH_3Li produces the methyl anion, $:CH_3^-$, as the reacting species. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [2]

(ii) With reference to the mechanism you have described in **(b)(i)**, explain why the butan–2–ol formed does not rotate plane–polarised light. [1]

(iii) Deduce the structures of a suitable bromoalkane, RBr and a suitable carbonyl compound, R'R''CO, to synthesise each of the following isomeric alcohols.

- $CH_3CH_2CH_2CH(OH)CH_3$
- $(CH_3CH_2)_2CH(OH)$ [2]

……

……

……

……

……

……

……

……

……

……

……

……

(c) *p*–coumaric acid, $C_9H_8O_3$ (M_r = 164.0), occurs in tomatoes, carrots and strawberries and is thought to help prevent the development of stomach cancer. It is an aromatic compound with two substituents occupying positions 1 and 4 of the benzene ring.

8.2 g of *p*–coumaric acid reacts with excess sodium metal to give 1.2 dm^3 of hydrogen gas at room temperature and pressure conditions.

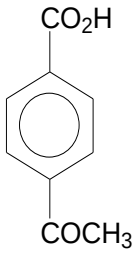
When solid $NaHCO_3$ is added to *p*–coumaric acid, compound **G** is formed, together with liberation of CO_2.

p–coumaric acid reacts with aqueous bromine to give compound **H**, $C_9H_7O_4Br_3$.

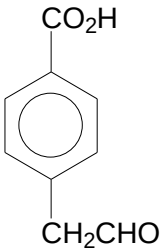
(i) Deduce the structures of compounds **G**, **H** and *p*–coumaric acid, explaining the reactions described. [6]

(ii) *p*–coumaric acid consists of two stereoisomers. State the type of isomerism shown here, and draw structures to illustrate your answer. [2]

Compounds **J** and **K** are two isomers of *p*–coumaric acid and their structures are given below.



J



K

(iii) When these two compounds are heated separately under reflux with alkaline $KMnO_4$ followed by acidification, the same compound is formed in each case.

Suggest the structure of this compound. [1]

(iv) Describe how compounds **J** and **K** could be distinguished using a simple chemical test. [2]

……

……

……

……

……

……

……

……

……

……

[Total: 20]

Question 5 starts on the next page.

5 **(a)** The halogens react with hydrogen to form hydrogen halides which are colourless gases at room temperature.

(i) With reference to the HC*l* molecule, explain the meaning of the term *bond energy*. [1]

Some bond energy values are given in the Table 5.1.

Table 5.1

bond	bond energy / kJ mol^{-1}
H–H	436
P–P	200
C*l*–C*l*	244
P–H	320
H–C*l*	431

(ii) The P–H bond energy is approximately the average of the H–H and P–P values. However, the H–C*l* bond energy is higher than the average of the H–H and C*l*–C*l* values.

Explain why this is so. [1]

(iii) Explain how the thermal stabilities of the hydrogen halides vary down the group. [2]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

(b) Chlorine finds various uses as organochlorine compounds.

Chloroethanoyl chloride, C*l*CH$_2$COC*l*, is used in the synthesis of the local anaesthetic, lidocaine, from 2,6–dimethylphenylamine as shown in Fig. 5.1.

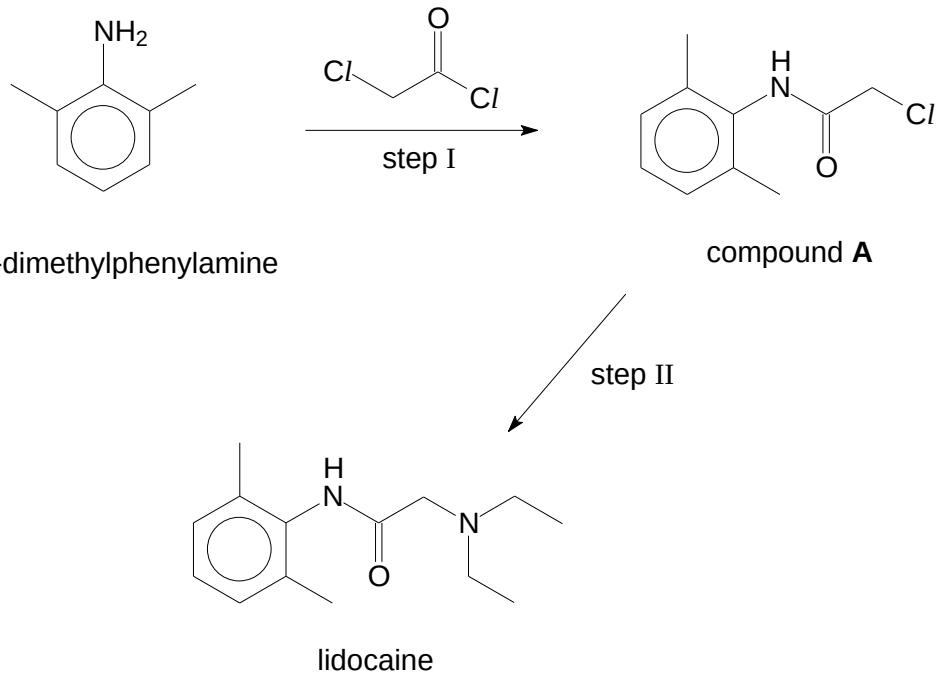
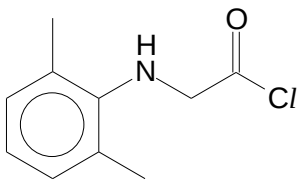


Fig. 5.1

(i) State the type of reaction that occur during step I. [1]

(ii) A student suggested that compound **B**, an isomer of compound **A**, was produced in Step I instead.



compound **B**

Explain clearly whether you agree with this suggestion. [2]

Step II proceeds by an S_N2 mechanism.

(iii) Draw the structure of the transition state formed in the mechanism. [1]

(iv) Suggest a reason which explains why step II did not proceed via S_N1 mechanism. [1]

(v) Suggest the **skeletal** formula of the product formed when lidocaine is reacted with lithium aluminium hydride. [1]

(c) Fig. 5.2 shows the reaction scheme involving chloroethanoyl chloride as a starting material.

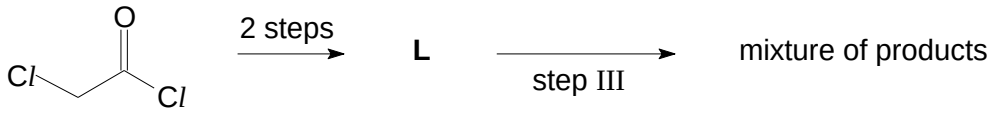


Fig. 5.2

Compound **L**, $C_5H_7O_2N$ is neutral and has a pleasant fruity smell.

Compound **M**, $C_3H_4O_4$ and **N**, C_2H_6O are two of the products formed in step III.

Effervescence is observed when solid sodium carbonate is added to compound **M**. One mole of compound **M** is neutralised by two moles of potassium hydroxide.

Upon adding alkaline aqueous iodine to compound **N**, a yellow precipitate is obtained.

(i) Deduce the structures of compounds **L**, **M** and **N** and suggest the reagents and conditions for step III. [4]

(ii) Hence, suggest the reagents and conditions for the 2–step synthetic route to form **L** from chloroethanoyl chloride. [2]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

(d) Chloroethanoyl chloride, C*l*CH_2COC*l,* has four non–cyclic isomers. None of the isomers contains O–C*l* bond.

One of these isomers, compound **P**, exhibits different chemical properties from the other three.

(i) Draw the structures of **all** four non–cyclic isomers of chloroethanoyl chloride and identify which isomer is compound **P**. [2]

(ii) Describe a chemical test you would conduct to distinguish compound **P** from the other three isomers. Include the observations expected in your answers. [2]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

[Total: 20]

Additional answer space

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