RAFFLES INSTITUTION
2021 YEAR 6 PRELIMINARY EXAMINATION

Higher 3

CANDIDATE NAME		CLASS	2 1 S 0
CENTRE NUMBER	S 3 0 1 6	INDEX NUMBER	

CHEMISTRY

9813/01

Paper 1

28 September 2021

2 hours 30 minutes

Candidates answer on the Question Paper.
Additional Materials: Data Booklet
Insert

READ THESE INSTRUCTIONS FIRST

Write your name, class and index 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 this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **two** questions.

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

The number of marks is given in brackets [ ] at the end of each question or part question.

Question	**Marks**
Section A (answer all)	
1	**/ 20**
2	**/ 20**
3	**/ 20**
Section B (answer two)	
4	**/ 20**
5	**/ 20**
6	**/ 20**
Total	**/ 100**

This document consists of **44** printed pages and **1** insert.

Section A

Answer **all** questions in this section.

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

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

1 **(a)** An example of a feldspar (aluminium based silicates) weathering reaction may be represented by the overall equation:

$$2KAlSi_3O_8 + 2CO_2 + 11H_2O \rightleftharpoons Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2K^+ + 2HCO_3^- \text{ ------ (1)}$$

As part of reaction (1), the silicate anions are involved. For example:

$$SiO_4^{4-} + H^+ \rightleftharpoons HSiO_4^{3-} \text{ and so on till}$$
$$H_3SiO_4^- + H^+ \rightleftharpoons H_4SiO_4$$

CO_2 reacts with water according to the following equations

$$CO_2(g) + aq \rightleftharpoons CO_2(aq) \text{ ------ (2)}$$
$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \text{ ------ (3)}$$
$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \text{ ------ (4)}$$
$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \text{ ------ (5)}$$

(i) The pK_{a1} values of H_2CO_3 and H_4SiO_4 are 6.35 and 9.84 respectively. By considering the structures of their conjugate bases, suggest two reasons for the relative pK_{a1} values of H_2CO_3 and H_4SiO_4. [2]

(ii) With reference to equations (2) to (5), comment on the implication of the pK_{a1} values in **(a)(i)** on the equilibrium between silicate and CO_2, and hence the thermodynamic feasibility of silicate weathering in CO_2 removal. [2]

(iii) SiO_2 has the following characteristics:

melting point / °C	solubility in water at 25 °C / mmol dm^{-3}	hardness	chemical reactivity
1713	2	very hard substance	reacts very slowly with bases

Explain the physical properties of SiO_2. [2]

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(iv) Silicic acid, H_4SiO_4, is usually used synonymously with silica, SiO_2. They exist in equilibrium in oceans.

Write an equation showing the formation of silica from silicic acid. Identify the type of reaction and describe the mechanism for the reaction using curly arrows for electron transfer. [3]

(v) By considering the information in **(a)(iii)** and **(a)(iv)**, suggest one positive and one negative impact on the effectiveness of reaction (1) in the removal of CO_2. [2]

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(b) Fig. 1 contains three graphs plotted to show pH, calcite saturation (Ω), and relative calcification levels as a function of atmospheric pCO_2 and increasing alkalinity of ocean waters. The colour gradient chart beside each graph indicates the colours that correspond to a range of values for each parameter.

Each graph has three arrows representing the following effects of ocean acidification from atmospheric CO_2:

- with no OAE,
- mitigation using air equilibrated OAE,
- mitigation using non equilibrated OAE.

For example, in graph **A** in Fig. 1, the vertical arrow showing no OAE tells us that for a given alkalinity of ocean water, as pCO_2 in the atmosphere increases, the acidity increases unmitigated, as the arrow goes upwards from the yellow region (pH ~ 8.6) to the blue region (pH ~ 8).

(i) With reference to graph **A** in Fig. 1, explain the arrows showing the changes of pH with non-equilibrated OAE and air-equilibrated OAE. [2]

(ii) By using the graphs in Fig. 1, explain how changing pH levels affect the relative calcification of marine organisms. [1]

(iii) When implementing Ocean Alkalinity Enhancement (OAE) as a method to remove carbon dioxide, we need to consider the impact of OAE on the marine ecosystem, including the various organisms (calcifying and non-calcifying) and food producers.

Comment on two ways how OAE would affect the marine ecosystem. [2]

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(c) **Refer to Abstract 2.**

The Arrhenius equation is given as

$$k = \mathrm{A}e^{-\frac{E_a}{\mathrm{RT}}}$$

where k is the rate constant, A is the Arrhenius constant, E_a is the activation energy, and T is the temperature.

In the hydrolysis of feldspar silicate, similar to reaction (1), the E_a in natural weathering conditions was found to be higher than those found previously under laboratory conditions.

(i) In the laboratories, researchers would typically grind up the minerals for kinetic experiments. Explain why the E_a found in natural weathering conditions was higher than those calculated from laboratory experiments. [2]

(ii) When global atmospheric CO_2 levels increase, the greenhouse effect also causes the temperature to rise. This increased temperature, in turn, increases the rate of the silicate weathering reaction (1) to remove CO_2. Thus, there is a negative feedback loop.

Explain why the higher than expected E_a would bring about more effective negative feedback against atmospheric pCO_2 increase by silicate weathering. [2]

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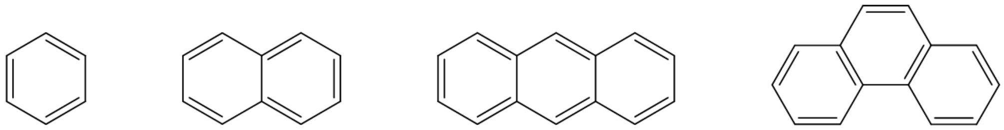
2 Aromatic compounds obey a set of rules known as Huckel's rules – they are fully conjugated cyclic systems containing (4n + 2) π electrons, where n = 0, 1, 2, etc.

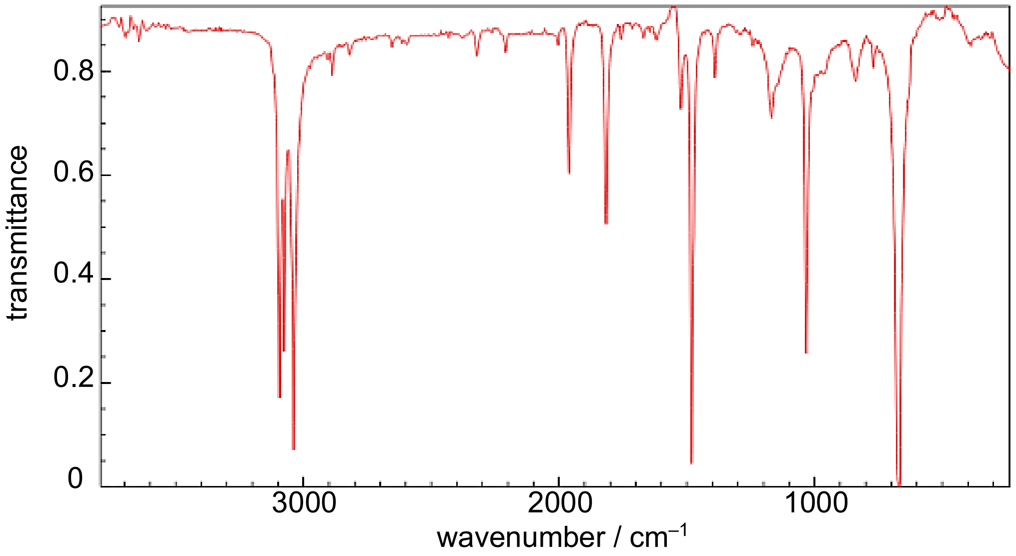
Some aromatic hydrocarbons are shown in Fig 2.1.



benzene naphthalene anthracene phenanthrene

Fig. 2.1

(a) The infra-red spectrum of benzene is given below.

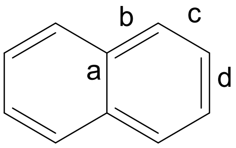


(i) Explain why absorption bands are observed in the infra-red spectrum of benzene. [1]

(ii) Sketch one possible vibrational mode in benzene which contributes to the absorption bands found at the 3000 to 3100 cm^{-1} region. [1]

(b) **(i)** Naphthalene has three possible uncharged resonance structures, one of which is shown in Fig. 2.1. Draw the other two uncharged resonance structures of naphthalene. [1]

(ii) Given that a typical C–C bond length is 1.54 Å and that of C=C is 1.34 Å, by considering the resonance structures in **(b)(i)**, comment on the carbon-carbon bond lengths (given in Å) observed in naphthalene.



bond	bond length / Å
a	1.42
b	1.42
c	1.37
d	1.41

[2]

(iii) Naphthalene undergoes electrophilic substitution more rapidly than benzene. Give two reasons to explain the greater reactivity in naphthalene. [2]

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(c) In an experiment, naphthalene was heated with CF_3COOD, a reagent which progressively incorporated deuterium into the naphthalene molecule via electrophilic substitution. The reaction was being monitored using ^1H NMR and Fig. 2.2 shows the relevant spectral peaks at selected reaction times.

The relative integration of the peaks, H_α/H_β, corresponds to the ratio of the ^1H content at the α and β positions of naphthalene. Fig. 2.3 shows how the H_α/H_β ratio changed with time until the system reached equilibrium, where about 80% deuteration of the naphthalene molecules was attained.

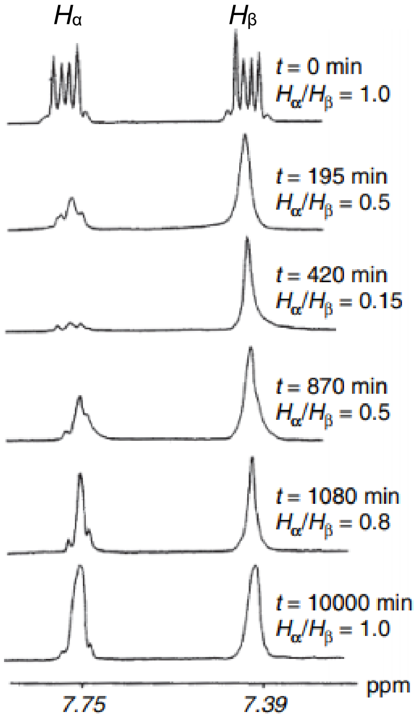


Fig. 2.2

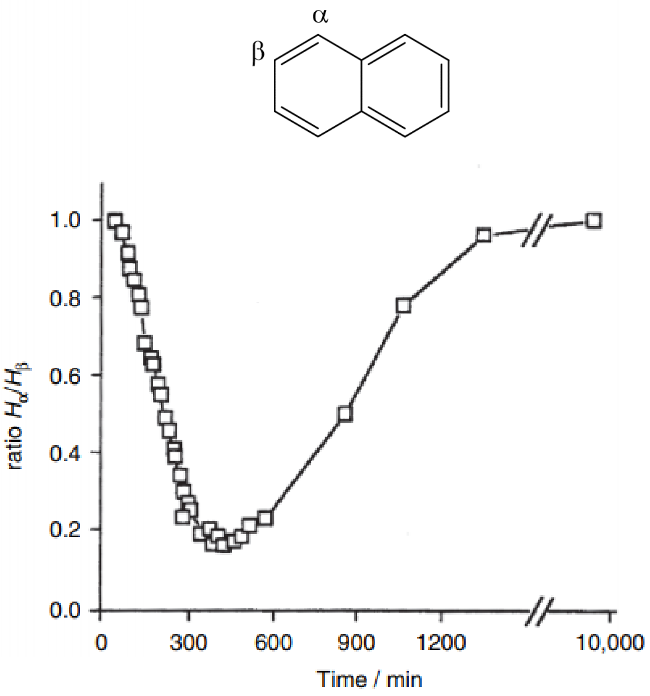


Fig. 2.3

(i) The ^1H NMR peaks corresponding to naphthalene are found at chemical shifts of 7.75 ppm and 7.39 ppm.

Explain why protons attached to aromatic rings are typically found significantly more downfield in a ^1H NMR spectrum than protons in alkyl groups. [1]

(ii) Using the data provided, deduce the kinetic product for the monodeuteration of naphthalene.

By comparing the deuteration at α and β positions, deduce which pathway goes through a lower energy transition state. Hence, determine the more stable carbocation by applying Hammond postulate. [4]

(iii) Deduce the thermodynamic product, supporting your answer from the data provided. [1]

(iv) Suggest a reason why there was a progressive loss of splitting pattern in the ^1H NMR peaks with time in Fig. 2.2. [1]

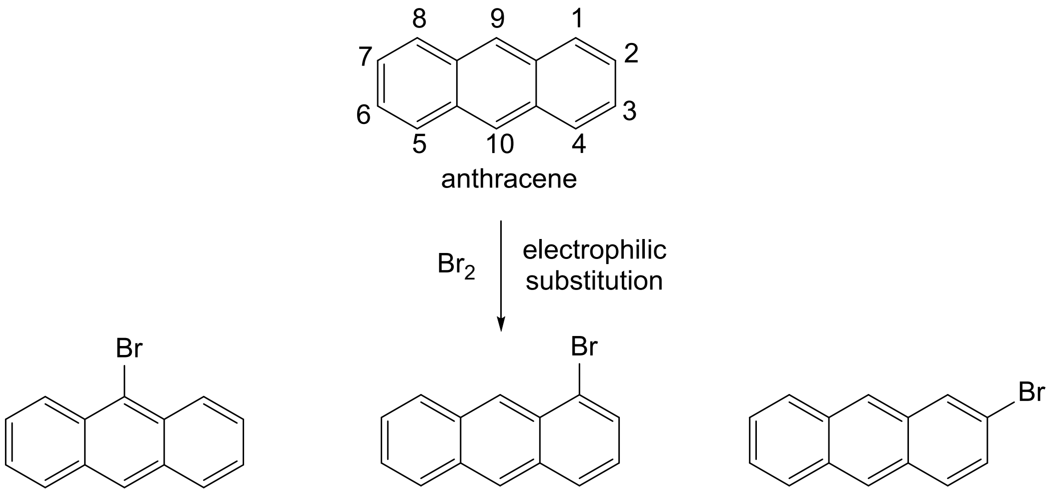
(d) The resonance energy of a compound is a measure of the extra stability of a conjugated system compared to a hypothetical structure with localised double bonds.

The resonance energies of some aromatic hydrocarbons are shown below.

compound	resonance energy / kJ mol^{-1}
benzene	151
naphthalene	255
anthracene	351
phenanthrene	385

The tricyclic aromatic compounds, anthracene and phenanthrene, undergo typical electrophilic substitution reactions. However, unlike benzene, they also take part in competing electrophilic addition reactions easily.

The diagram below shows how anthracene can undergo electrophilic substitution with bromine to give the addition product. Three monobrominated products are formed, with compound **A** being the major product.



A (major product)

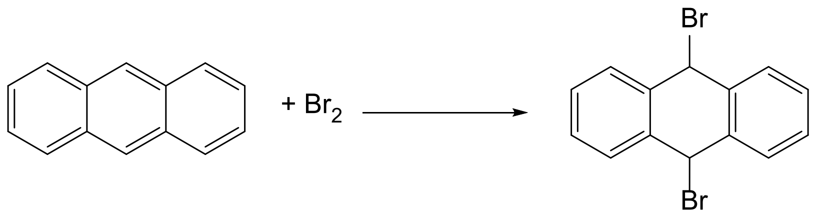
B

C

(i) Draw the carbocation intermediates in the formation of **A** and **B** respectively. [1]

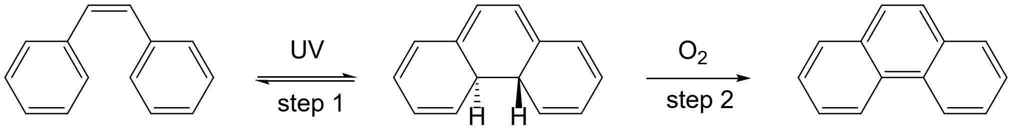
(ii) Hence, by calculating the loss in resonance energies in the formation of each intermediate in **(d)(i)**, explain why substitution is preferred at position 9 of anthracene instead of position 1. [2]

(iii) Anthracene can also undergo an electrophilic addition reaction with bromine.



Draw the mechanism for the above reaction between anthracene and bromine. [1]

(e) Phenanthrene can be synthesised from cis-stilbene in the presence of UV light and oxygen.



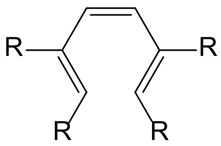
cis-stilbene

phenanthrene

Step 1 involves an electrocyclic ring closure reaction, which is a concerted reaction involving the formation of a new σ bond across the ends of a conjugated polyene. In this step, irradiation with UV light promotes an electron to the π LUMO of the conjugated system involved, resulting in the reaction.

A simplified structure of the π system involved in the step 1 is shown below.

Draw the π LUMO involved in step 1. Hence, explain how the formation of the new σ bond results in the configuration of the chiral centres observed in the intermediate.



[2]

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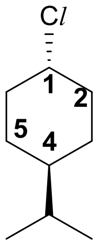
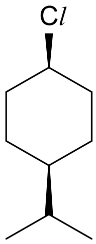
3 Elimination and substitution reactions are fundamental reactions in organic chemistry.

(a) Chlorocycloalkanes can undergo substitution reactions.



D



E

(i) State the stereochemical relationship between compounds **D** and **E.** [1]

(ii) Draw the Newman projection for the most stable conformer of compound **D** through the **C1**–**C2** and **C5**–**C4** bonds. [1]

(iii) Using appropriate diagrams, explain why the S_N2 reaction proceeds faster for compound **E** than **D**. [3]

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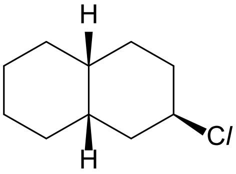
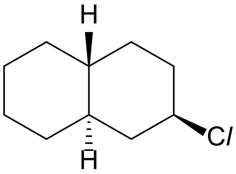
(b) Chlorocycloalkanes can also undergo elimination reaction.

Compounds **F** and **G** were heated with CH_3ONa in ethanol. Only one of the two compounds underwent the E2 elimination reaction.



F



G

Use suitable diagrams to illustrate the stereochemistry of the E2 elimination reaction and determine which of the isomers **F** or **G** can undergo the elimination reaction. Show why the other isomer **cannot** undergo an E2 elimination reaction. [3]

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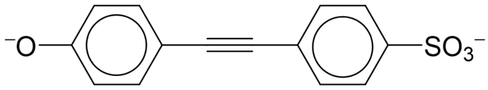
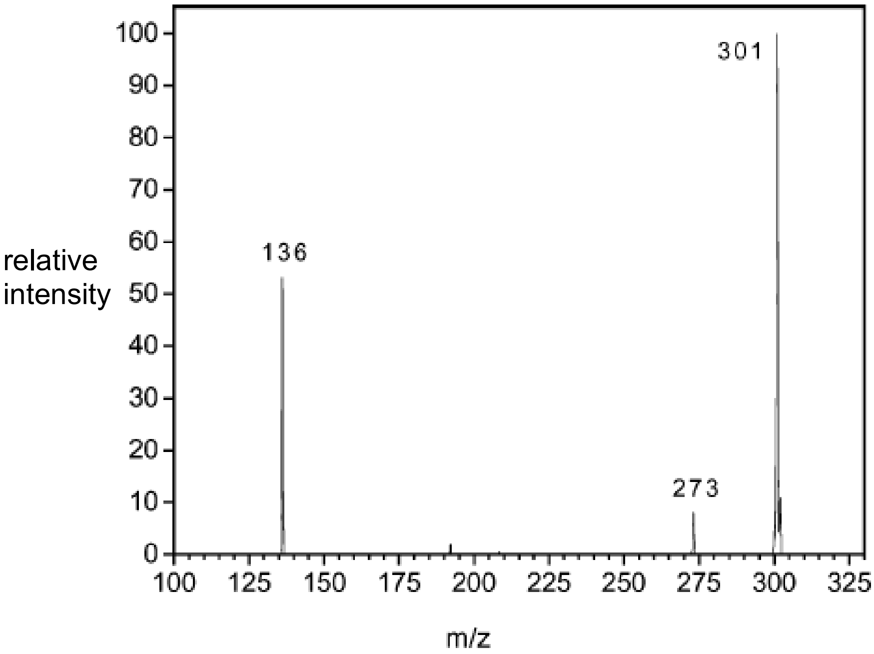
(c) Many elimination reactions are often accompanied by competing substitution reactions. In an experiment, the competition between elimination and substitution reactions was studied in a reaction between bromoethane and dianion **H**. The structure of dianion **H** is given below.



dianion **H**

In this study, the reaction was done in gas phase and monitored using a mass spectrometer which was operated under controlled conditions. There was no fragmentation of any species under these controlled conditions.

A mass spectrum for the reaction mixture between bromoethane and excess dianion **H** is given below.



(i) Predict if the experimental method above is used to study the competition between S_N1 and E1 or between S_N2 and E2 pathways. Suggest a reason why. [1]

(ii) Given that the $-SO_3^{-}$ moiety remains unreacted throughout the reaction, write the chemical equations when bromoethane and dianion **H** undergo

- an elimination reaction,
- a substitution reaction. [2]

(iii) Assign the three peaks in the mass spectrum to appropriate species in the reaction mixture. [2]

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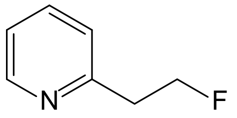
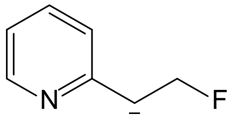
(d) In a separate study of an elimination reaction, compound **I** was reacted with sodium methoxide, CH_3ONa.



I

During the experiment, a short-lived intermediate **J** was isolated.



J

(i) Suggest a reason why intermediate **J** can be isolated. [1]

(ii) Draw the mechanism of the reaction between **I** and CH_3ONa to form the elimination product. [2]

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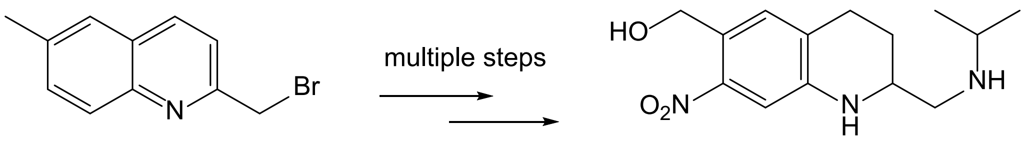
Compound **K**, an analog of compound **I**, is often used as a precursor for the synthesis of drugs to treat diseases caused by parasites. One such drug is oxamniquine.



K

oxamniquine

(iii) Explain why the λ_{max} value of **K** is higher than that of **I**. [2]

(iv) UV-Vis spectroscopy can be used to determine the content of active ingredients such as oxamniquine in a drug tablet.

A standard solution contains 0.030 mol dm^{-3} of oxamniquine, $C_{14}H_{21}N_3O_3$ (M_r = 279), in methanol. This solution has an absorbance of 0.831, in a cell with path length 1.0 cm.

The mass of 1 tablet containing oxamniquine is 1.50 g. The tabled was crushed and 0.90 g of the powder obtained was added to 50.0 cm^3 of methanol to extract the oxamniquine. The resultant solution gave an absorbance of 1.35, in a cell with path length 1.0 cm.

Calculate the percentage by mass of oxamniquine per tablet. [2]

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Section B

Answer **two** questions from this section.

4 **(a)** **(i)** Fool's gold refers to the mineral pyrite, FeS_2, where Fe has an oxidation state of +2.

Using only the valence shell atomic orbitals, draw the molecular orbital diagram for the molecular anion in pyrite. Label the molecular orbitals with σ or π symmetry clearly. [2]

(ii) Pyrite can be reduced by hydrogen to form FeS and hydrogen sulfide, H_2S.

Hydrogen sulfide reacts with methanol in the presence of a catalyst to form methanethiol, CH_3SH, the sulfur analogue of methanol.

$$CH_3OH + H_2S \rightarrow CH_3SH + H_2O$$

Explain why CH_3SH has lower pK_a than CH_3OH. [1]

(iii) Oxidation of CH_3SH changes the oxidation state of sulfur rather than carbon. CH_3SH undergoes mild oxidation to form a disulfide, CH_3SSCH_3. However, the corresponding mild oxidation of CH_3OH to a peroxide, CH_3OOCH_3, is not normally observed.

$$CH_3SH \xrightarrow{[O]} CH_3SSCH_3$$
$$CH_3OH \overset{[O]}{\not\longrightarrow} CH_3OOCH_3$$

Use relevant data from the *Data Booklet* to explain why the disulfide formation is favoured over that of peroxide. [2]

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(b) **(i)** Methyl thiocyanate, CH_3SCN, may be prepared from either CH_3SH or CH_3SBr using different reactions.

$$CH_3SH \xrightarrow{BrCN} CH_3SCN \quad \text{reaction 1}$$

$$CH_3SBr \xrightarrow{KCN} CH_3SCN \quad \text{reaction 2}$$

Table 4.1

element	electronegativity value
hydrogen	2.20
carbon	2.55
sulfur	2.58
bromine	2.96

Use the data given in Table 4.1 to deduce the different natures of the sulfur atoms in these substitution reactions. [2]

(ii) The infra-red absorption frequencies of the C≡N bonds in CH_3CN, CH_3SCN and CH_3OCN are shown in Table 4.2.

Table 4.2

compound	infra-red absorption frequency / cm^{-1}
CH_3SCN	2154
CH_3OCN	2260
CH_3CN	2267

Suggest why the infra-red absorption frequency of the C≡N bond in CH_3SCN is lower than that in

- CH_3CN,
- CH_3OCN. [3]

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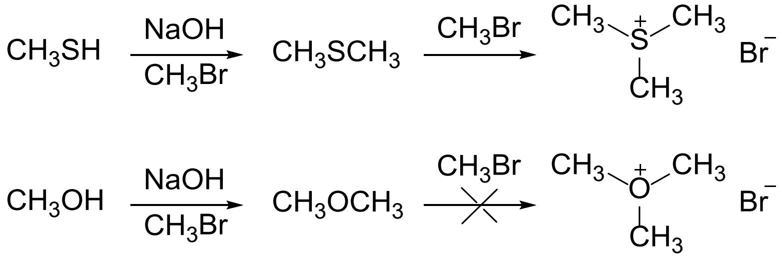
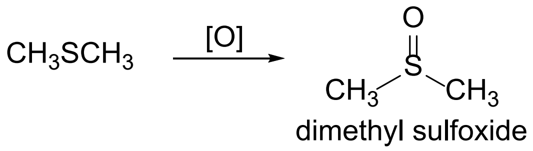
(c) **(i)** When treated with NaOH and CH_3Br, CH_3SH and CH_3OH yield dimethyl sulfide, CH_3SCH_3, and dimethyl ether, CH_3OCH_3, respectively.

Explain why only CH_3SCH_3 undergoes further reaction with CH_3Br to give a sulfonium salt.



[1]

(ii) Dimethyl sulfide, CH_3SCH_3, undergoes oxidation to form dimethyl sulfoxide.

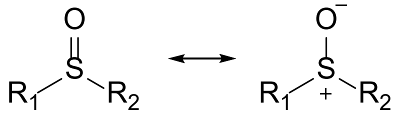


The bond energy of the π bond in S=O is about 140 kJ mol^{-1} while that in C=O is about 380 kJ mol^{-1}.

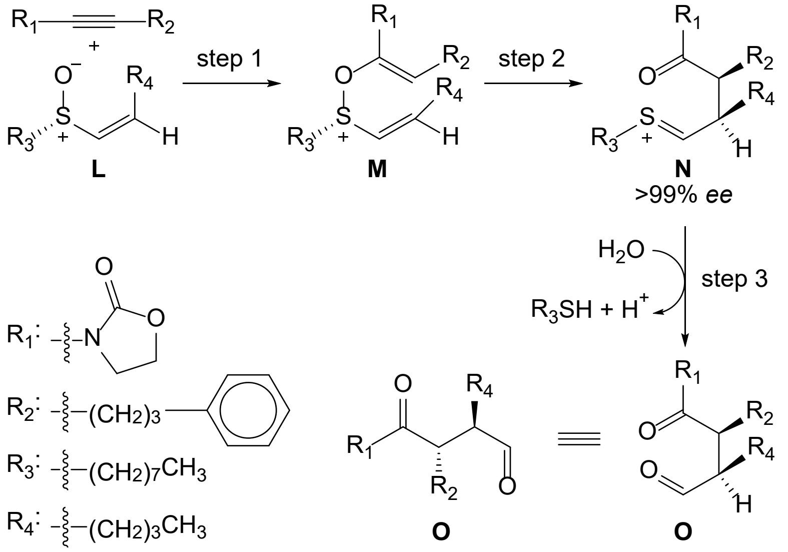
Draw a labelled diagram to show how orbitals overlap to form the π bond in dimethyl sulfoxide. Hence, suggest an explanation for the difference in bond energies. [2]

(iii) Besides the reason in **(c)(ii)**, explain why the infra-red absorption frequency of the S=O bond is significantly lower than that of the C=O bond in propanone. [1]

(d) Sulfoxides can be represented as a resonance hybrid of two hypothetical extremes.



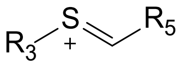
When R_1 is different from R_2, the sulfoxide is chiral and can be used to induce chirality in reactions. The following scheme shows enantiomerically pure sulfoxide **L** reacting to form **M**, which rearranges selectively to form one stereoisomer of **N** with excellent enantioselectivity. Subsequently, **N** undergoes hydrolysis to yield **O**.



(i) Using the *R*/*S* and *E*/*Z* convention, assign the stereochemistry at the sulfur atom and the double bond in **L.** [1]

(ii) Given that step 2 is a single step rearrangement, suggest the mechanism for step 2 and propose a structure for the chair-like transition state. [2]

(iii) Suggest the mechanism for step 3.

You may represent **N** as  . [2]

(iv) Suggest the structure of a sulfoxide that can give a diastereomer of **O**. [1]

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[Total: 20]

5 This question explores the chemistry of salmefamol, terbutaline and albuterol, which are structurally similar compounds used to treat asthma.

(a) $\mathrm{LiA}l\mathrm{H_4}$ and $\mathrm{NaBH_4}$ are common reagents used to reduce a variety of organic compounds. The reduction of carbonyl compounds using $\mathrm{LiA}l\mathrm{H_4}$ in dry ether, followed by the addition of aqueous acid, is shown in Fig. 5.1.

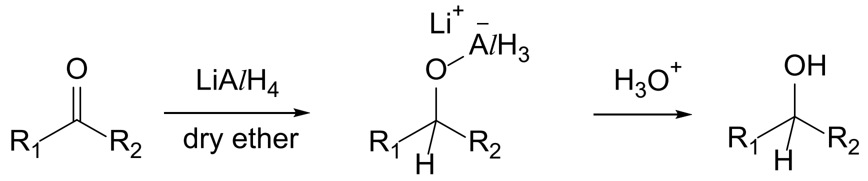

Fig. 5.1

$\mathrm{NaBH_4}$ reacts with carbonyl compounds by a similar mechanism. Unlike $\mathrm{LiA}l\mathrm{H_4}$, it is usually used in an alcoholic medium, although an excess of $\mathrm{NaBH_4}$ needs to be added.

A related reducing agent is lithium borohydride, $\mathrm{LiBH_4}$. It is known to be stronger than $\mathrm{NaBH_4}$, but weaker than $\mathrm{LiA}l\mathrm{H_4}$ with respect to its reducing power.

(i) Give two reasons for the greater reactivity of $\mathrm{LiA}l\mathrm{H_4}$ over $\mathrm{NaBH_4}$ in reduction reactions. [2]

(ii) Explain why an excess of $\mathrm{NaBH_4}$ must be added in an alcoholic medium. [1]

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LiA*l*H$_4$ can reduce both esters and amides.

Despite the similar chemical nature of esters and amides, they do not give the same type of products upon reduction by LiA*l*H$_4$. Fig. 5.2 shows the key intermediates and final products in the two reduction processes.

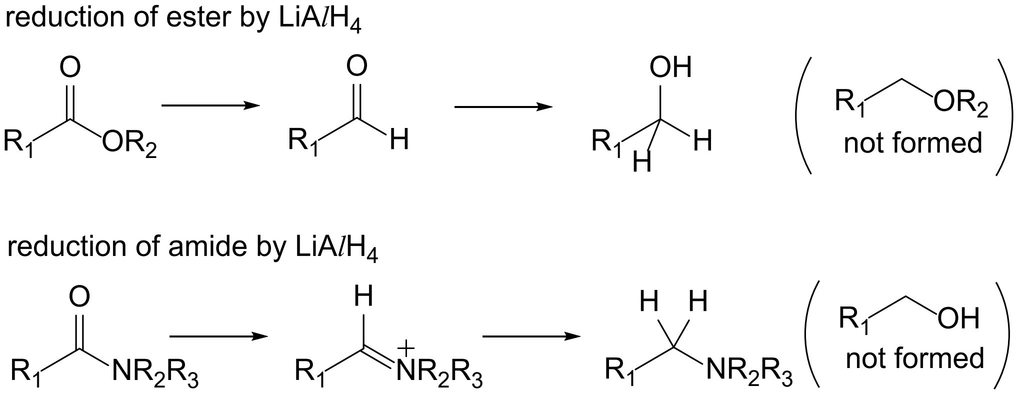

Fig. 5.2

(iii) By considering the information provided in Fig. 5.1 and Fig. 5.2, explain why esters and amides form different types of products upon reduction by LiA*l*H$_4$. [2]

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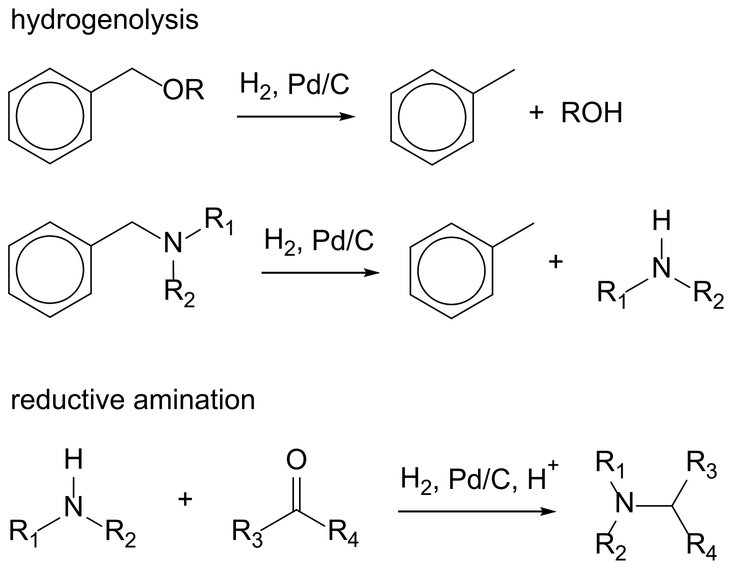
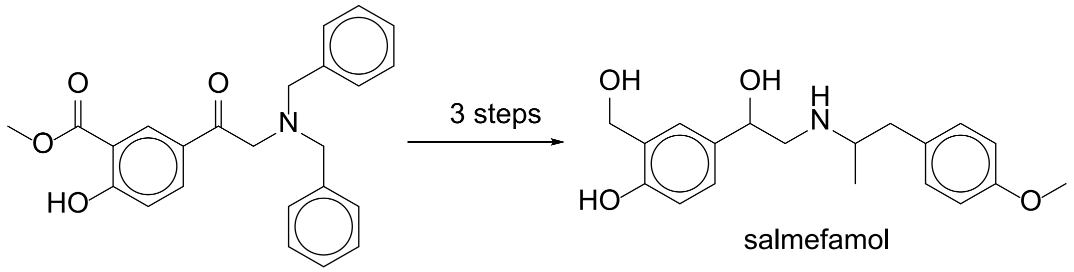
Hydrogen gas, in the presence of palladium catalyst on charcoal support, is used in several important reductive reactions. The reagent can remove a benzyl ($C_6H_5CH_2–$) group which is bonded to oxygen or nitrogen (known as hydrogenolysis), while it can also reliably monoalkylate amines with the use of a carbonyl compound in an acidic medium (known as reductive amination). These reactions are summarised in Fig. 5.3.



where R, R_1, R_2, R_3, R_4 = H, alkyl, aryl

Fig. 5.3

(iv) With the aid of the information provided in **(a)**, suggest a three step synthesis for salmefamol from the given starting material. In each step, a reducing agent must be used, and the intermediates and any other reagents should also be shown clearly.



[3]

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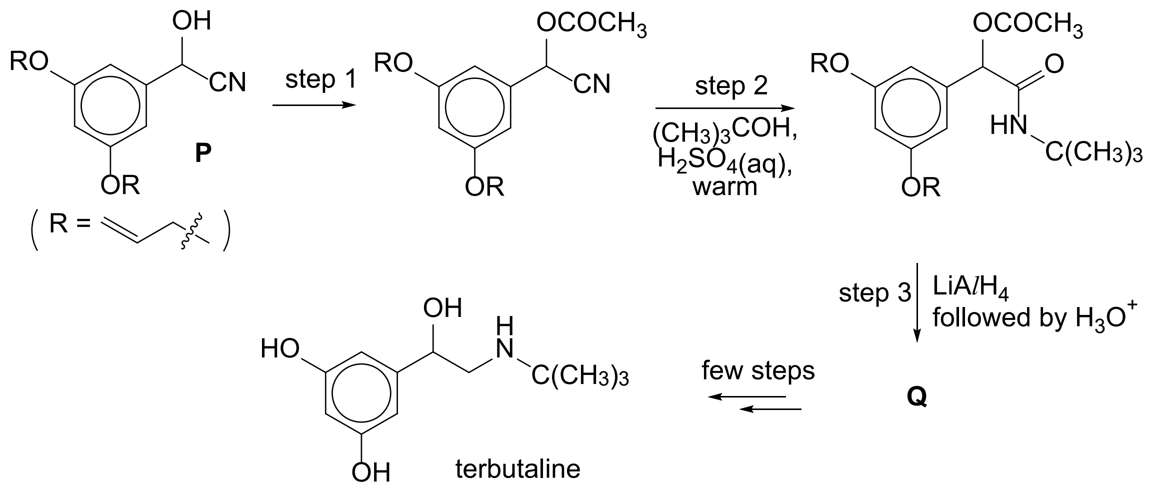
(b) The synthesis of terbutaline is as shown.



(i) Suggest a suitable reagent to be used in step 1. [1]

(ii) Draw the mechanism for step 2, given that the reaction involves an S_N1 reaction in the initial stage. You may represent the starting molecule of step 2 as R–CN. [3]

(iii) The researchers originally found that significant racemisation of an enantiomerically pure sample of **P** occurred in an acidic medium, which prompted them to introduce step 1 to maintain good retention of stereochemistry in the product.

Explain why racemisation of an enantiomer of **P** occurs in an acidic medium. [1]

(iv) Give the structure of intermediate **Q**. [1]

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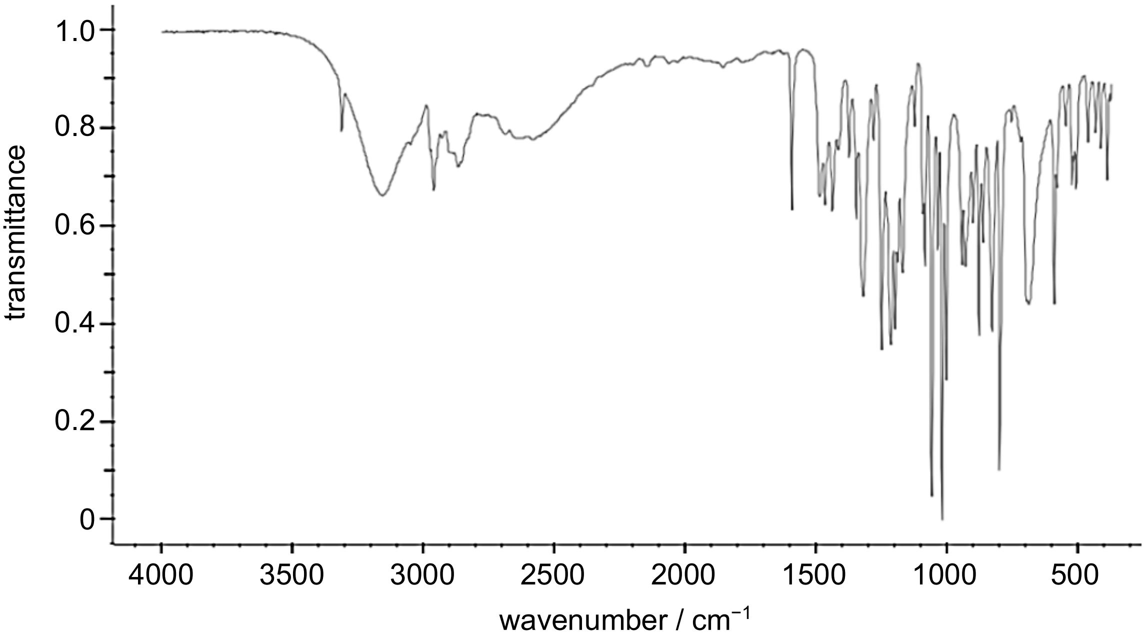
(c) Albuterol is structurally similar to terbutaline and contains the same type of elements.

The spectral data for albuterol is given below. Propose a structure of albuterol, giving your reasons. You do not need to assign the ^{1}H NMR peaks.

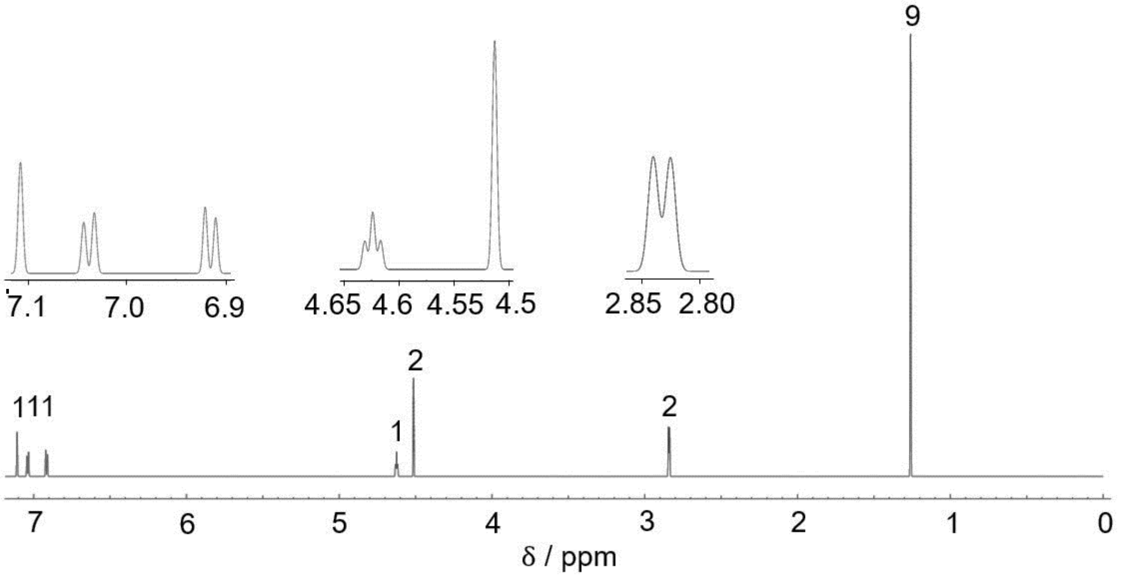
mass spectrum:

m/z	relative intensity
240	1
239 (M^+)	7
86	750
57	150

infra-red spectrum:



^{1}H NMR spectrum in D_2O:



In the absence of D_2O, there is an extra peak at chemical shift of 4.60 ppm (4H, broad). [6]

[Total: 20]

6 Merrilactone A ($C_{15}H_{18}O_6$), isolated from the pericarps of the *Illicium Merrillianum* plant, is found to mediate the growth and survival of neurons, hence playing an important therapeutic role in impeding the progress of neurodegenerative disorders.

(a) Part of the synthesis of Merrilactone A is shown in Fig. 6.1.

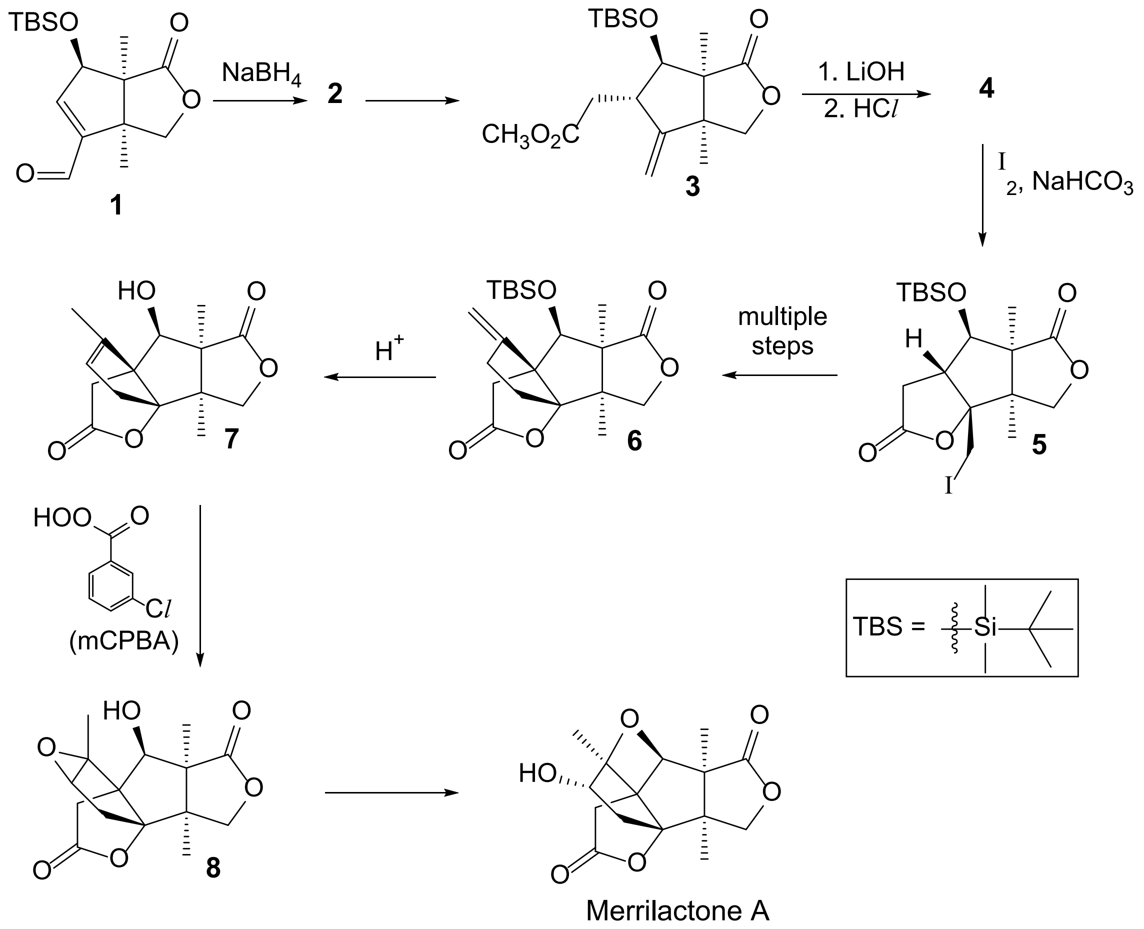


Fig. 6.1

(i) Draw the structure of intermediate **2**. [1]

(ii) Suggest a mechanism for the conversion of **3** to **4**. [2]

(iii) Suggest a mechanism for the conversion of **4** to **5**, showing clearly the stereochemistry involved. [2]

(iv) The –OTBS group is only converted to –OH group in **7**.

With reference to the structure of TBS, suggest how it reduces the reactivity of the –OH group. [1]

(v) Isomerisation of the alkene in **6** takes place in the presence of acid.

Suggest a reason why **7** is formed from the isomerisation reaction. [1]

(vi) Draw the structure of **8**, showing clearly the stereochemistry of the epoxide ring. Suggest why it is formed. [2]

(b) Intermediate **3** can also be formed by the following reaction pathway as shown in Fig. 6.2.

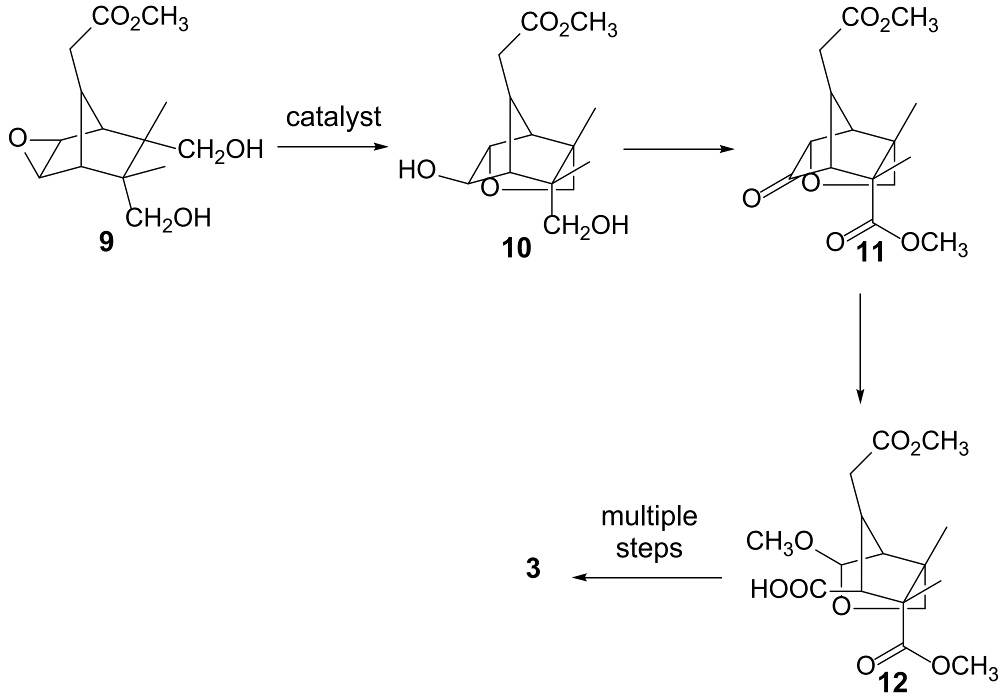
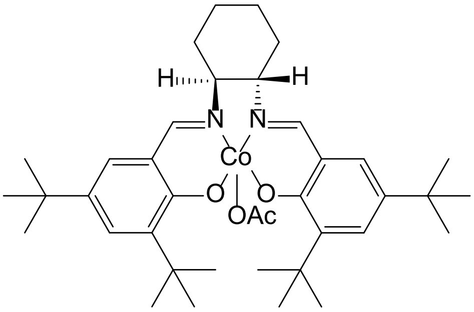


Fig. 6.2

(i) Deduce if compound **9** exhibits optical activity. [1]

The following chiral catalyst **R** is used in the conversion of compound **9** to intermediate **10**. It helps to control the stereospecificity of the reaction.



catalyst **R**

(ii) Identify the stereochemical configuration (*R* or *S*) at each of the chiral carbons in catalyst **R**. [1]

(iii) Suggest the structure of **10** if the enantiomer of catalyst **R** is used instead. [1]

(iv) Identify the type of reaction in the conversion of **11** to **12**. Explain your answer. [2]

(c) Merrilactone B ($C_{15}H_{20}O_6$) can also be isolated from the pericarps of the *Illicium Merrillianum* plant. It is structurally similar to Merrilactone A.

The ^1H NMR spectrum of Merrilactone B in the presence of D_2O is shown in Table 7.1.

Table 7.1

chemical shift δ / ppm	integration value	splitting pattern
1.14	3	singlet
1.22	3	singlet
1.42	3	singlet
1.89	2	triplet
1.96	2	triplet
2.33	2	singlet
3.96	2	singlet
4.03	1	singlet

A doublet signal in the ^1H NMR of Merrilactone A is replaced by a triplet signal at chemical shift of 1.96 ppm in the ^1H NMR of Merrilactone B.

(i) Suggest the structure of Merrilactone B.

Assign the peaks in the ^1H NMR spectrum to appropriate protons in Merrilactone B by labelling them in your structure. [4]

(ii) Hence, explain

- the splitting patterns of peaks at chemical shifts of 1.89 ppm and 1.96 ppm,
- the difference in chemical shift of peaks at 2.33 ppm and 3.96 ppm. [2]

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Additional page

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