H3

MINISTRY OF EDUCATION, SINGAPORE
in collaboration with
CAMBRIDGE INTERNATIONAL EDUCATION
General Certificate of Education Advanced Level

CANDIDATE NAME

CENTRE NUMBER | S | | | | |

INDEX NUMBER | | | | |

*0123456789*

**CHEMISTRY** **9813/01**

Paper 1 **For examination from 2026**

SPECIMEN PAPER **2 hour 30 minutes**

You must answer on the question paper.

You will need: Insert
Data booklet

**INSTRUCTIONS**

- Section A: answer **all** questions.
- Section B: answer **two** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and index number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen. Do **not** use correction fluid or tape.
- Do **not** write on any bar codes.
- You may use an approved calculator.

**INFORMATION**

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].
- The insert contains information for Question 1.



**Singapore Examinations and Assessment Board**

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**[Turn over**

## Section A

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

**1** 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.

**(a)** Suggest **two** positive outcomes of using carbon dioxide as a 'chemical feedstock'.

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..... [2]

**(b)** Use the data in Abstract 1 to calculate the volume of air, at room temperature and pressure, needed to produce 100 g of methanol. Show your working.

[3]

**(c)** Suggest whether propane or the electrolysis of water is preferred as a source of hydrogen. Give **two** reasons.

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..... [2]

**(d)** The overall reaction shown in step 4 of Figure 1.1 is not the usual method of reducing compounds such as **C** in the laboratory.

**(i)** Name the functional group in compound **C** created by the reaction in step 3.

..... [1]

**(ii)** Suggest a suitable reagent, other than $H_2$, that can be used in the laboratory to reduce **C**.

..... [1]

**(iii)** **C** is reduced using the reagent suggested in **1(d)(ii)**.
Draw the structural formula of the product of this reduction.

[1]

**(e)** Use information from Abstract 2 to calculate the time needed for 100 g of protein (composed of the 17 enzymes required for the cycle) to convert 10.0 g of $CO_2$ into organic molecules.

[3]

**(f)** By considering all the species added to the cycle described in Figure 1.2, and those produced by the cycle, construct an equation that represents the overall chemical transformation that occurs during one complete 11-step cycle.

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..... [2]

 

**(g)** The steps in the cycle in Figure 1.2 are numbered from 1 to 11.

Give the numbers of the steps that involve:

**(i)** net C–C single bond formation

..... [1]

**(ii)** reduction of an organic molecule (not including steps that involve $CO_2$)

..... [1]

**(iii)** oxidation of an organic molecule.

..... [1]

**(h)** The two abstracts each describe methods of converting a feedstock of carbon dioxide into useful products.

Comment on **one** advantage of each of the two methods.

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..... [2]

[Total: 20]

 

**2** Azo compounds contain the R—N=N—R functional group, where R = alkyl or aryl substituents.
The structural formulae of two azo compounds are shown.

| $CH_3N{=}NCH_3$ | $C_6H_5N{=}NC_6H_5$ |
|---|---|
| azomethane | azobenzene |

**(a)** Azo compounds exhibit *cis-trans* isomerism, similar to that in substituted alkenes.

**(i)** Explain the origin of *cis-trans* isomerism in substituted alkenes.
Suggest how a molecule of $CH_3N{=}NCH_3$ can also exhibit similar properties.

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..... [2]

**(ii)** *trans*-azobenzene is a planar molecule but *cis*-azobenzene is non-planar.
*trans*-azobenzene is more stable than *cis*-azobenzene.

Suggest an explanation for these two statements.
Draw structures of both *trans*-azobenzene and *cis*-azobenzene as part of your answer.

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..... [3]

 

**(b)** Azo compounds absorb strongly in the ultraviolet/visible region of the electromagnetic spectrum.

**(i)** State all types of electronic transition that could occur in a molecule of azomethane.

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..... [2]

**(ii)** A solution of *trans*-azobenzene absorbs ultraviolet light of wavelength 313 nm with molar extinction coefficient, $\varepsilon = 22\,020\ \text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1}$. At this wavelength, the absorbance of the solution in a cell of path length 10 cm is 1.28.

Calculate the concentration, in mol $\text{dm}^{-3}$, of *trans*-azobenzene in the solution.

[1]

**(c)** Azo compounds decompose when heated in the gas phase, according to the following steps.

step 1 $\text{R—N=N—R(g)} \rightarrow \text{R•(g)} + \text{N}_2\text{(g)} + \text{R•(g)}$ $\Delta H_1$

step 2 $\text{R•(g)} + \text{R•(g)} \rightarrow \text{R—R(g)}$ $\Delta H_2$

**(i)** Suggest the signs of the entropy changes for:

- step 1
- step 2
- the overall reaction (step 1 + step 2).

Explain each of your answers.

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..... [3]

**(ii)** Use bond energy values from the data booklet to calculate $\Delta H_1$.

[1]

In practice, the magnitude of $\Delta H_1$ varies according to the stability of R• relative to R—N=N—R.

**Table 2.1**

| R (in R—N=N—R) | $\Delta H_1$ / kJ mol$^{-1}$ |
|---|---|
| $CH_3$ | +33 |
| $(CH_3)_3C$ | +24 |
| $C_6H_5$ | +131 |

The stability of R• is affected by factors such as:

- the hybridisation of the orbital occupied by the single electron
- steric hindrance
- the electronic effect of substituents.

**(iii)** Use the data in Table 2.1 to suggest how each of these factors affects the relative stability of:

- $CH_3$• compared to $C_6H_5$•
- $CH_3$• compared to $(CH_3)_3C$•.

Explain your answer.

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..... [4]

**(d)** The O=O bond energy in the oxygen molecule, 496 kJ mol$^{-1}$, is similar to that of the N=N bond in azo compounds, 410 kJ mol$^{-1}$. The bonding in $O_2$ is therefore often represented by structure **I**.

O=O
structure **I**

However, the $O_2$ molecule is paramagnetic, meaning that it contains unpaired electrons. This can be represented by the alternative structure **II**. This suggests that it contains an O–O single bond, similar in strength to the O–O bond in $H_2O_2$, 150 kJ mol$^{-1}$.

•O–O•
structure **II**

Draw a molecular orbital diagram for the $O_2$ molecule and use it to explain why the $O_2$ molecule contains unpaired electrons but has a bond order of 2.

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..... [4]

[Total: 20]

 

**Turn over**

**3** A chemist can choose one of many synthetic routes to convert one compound into another. Figure 3.1 shows two routes for the synthesis of 4-bromophenylamine, **D**, from benzene.

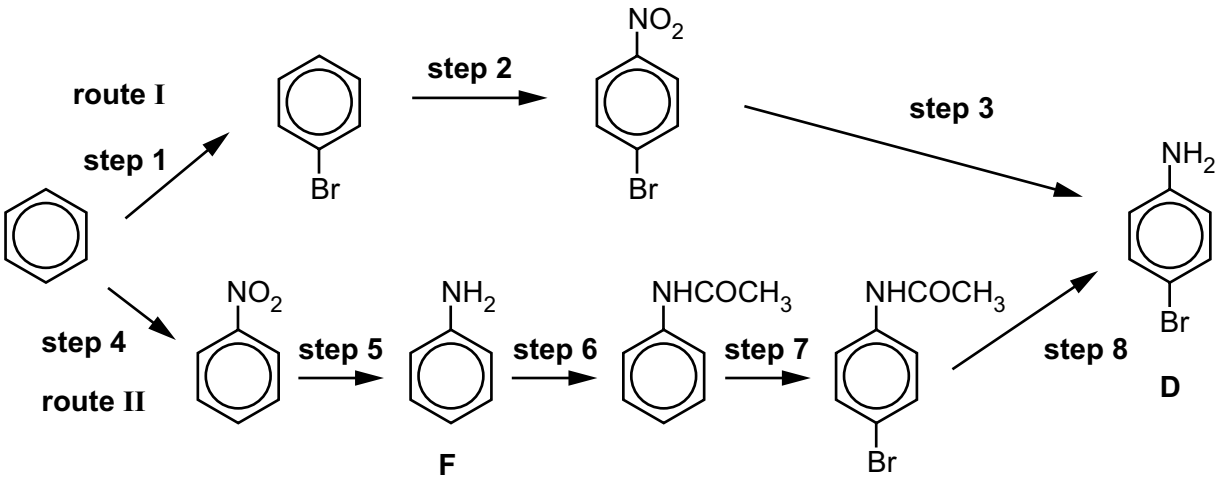


**Figure 3.1**

Table 3.1 lists the yields of each step and the reagents for some of the steps.

**Table 3.1**

| route | step | yield / % | reagent |
|---|---|---|---|
| **I** | 1 | 60 | $Br_2$ + A*l*$Br_3$ |
| **I** | 2 | 50 | conc $HNO_3$ + conc $H_2SO_4$ |
| **I** | 3 | 85 | Sn + conc HC*l*, then NaOH |
| **II** | 4 | 90 | conc $HNO_3$ + conc $H_2SO_4$ |
| **II** | 5 | 85 | Sn + conc HC*l*, then NaOH |
| **II** | 6 | 70 | *see* **(a)** |
| **II** | 7 | 70 | $Br_2$ in $CH_3CO_2H$ |
| **II** | 8 | 90 | *see* **(a)** |

**(a)** Suggest reagents for step 6 and for step 8.

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..... [2]

**(b)** The overall yield of route **II** is 33.7%.
Use the information in Table 3.1 to calculate the overall yield of route **I**. Hence determine the mass of benzene required to produce 10.0 g of **D** by this route.
[$M_r$: benzene, 78.0; **D**, 171.9]

[2]

**(c)** Apart from overall yield, suggest **one** other factor that needs to be considered when choosing a particular synthetic route.

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..... [1]

**(d)** The yield in step 2 is considerably lower than that in the similar transformation in step 4, due to the formation of another product, **E**.
Suggest the structure of **E**.

[1]

**(e)** Phenylamine, **F**, reacts more readily with $Br_2$ to form 2,4,6-tribromophenylamine and **cannot** be directly converted to **D** unlike benzene. **F** is a better nucleophile than benzene.

**(i)** Suggest why **F** is a better nucleophile than benzene.

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..... [1]

**(ii)** **F** is converted in step 6 to phenylethanamide, $C_6H_5NHCOCH_3$.
$C_6H_5NHCOCH_3$ is also a better nucleophile than benzene, but less reactive than **F**.
Suggest why.

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..... [1]

 

**(f)** By considering all the information stated earlier in this question, and your answer to **3(b)**, decide which of the two routes you would choose to make **D** from benzene in the laboratory. Explain your answer.

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..... [2]

[Total: 10]

 

Turn over

**4** Compound **G** was first used as an analgesic in 1887. **G** contains C, H, N and O, and is **not** a base. Its mass spectrum and $^{1}$H nuclear magnetic resonance (NMR) spectrum are shown in Figure 4.1 and Figure 4.2. The molecular ion peak in its mass spectrum is found at *m/z* 179, and the ratio of the peak heights of the M and M+1 peaks is 54:6.
The integration of each peak in the NMR spectrum is shown in brackets beneath each peak.

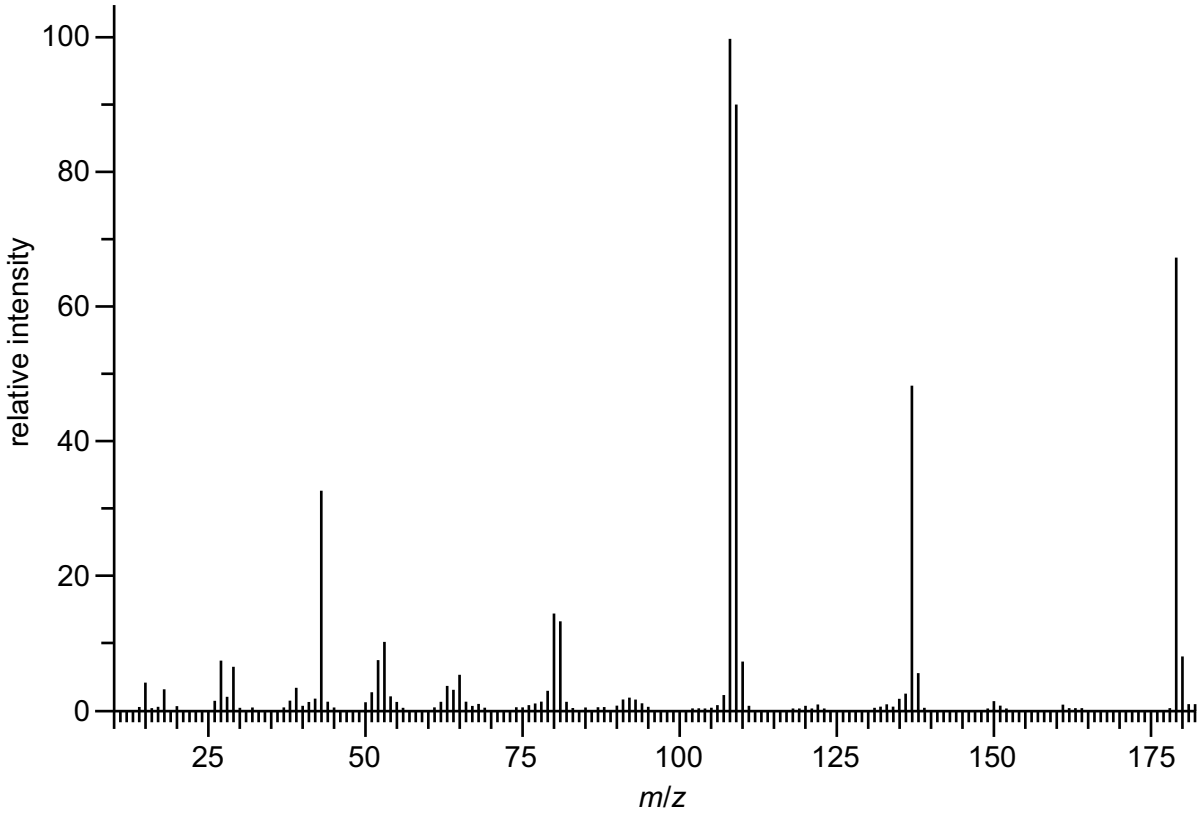


**Figure 4.1**

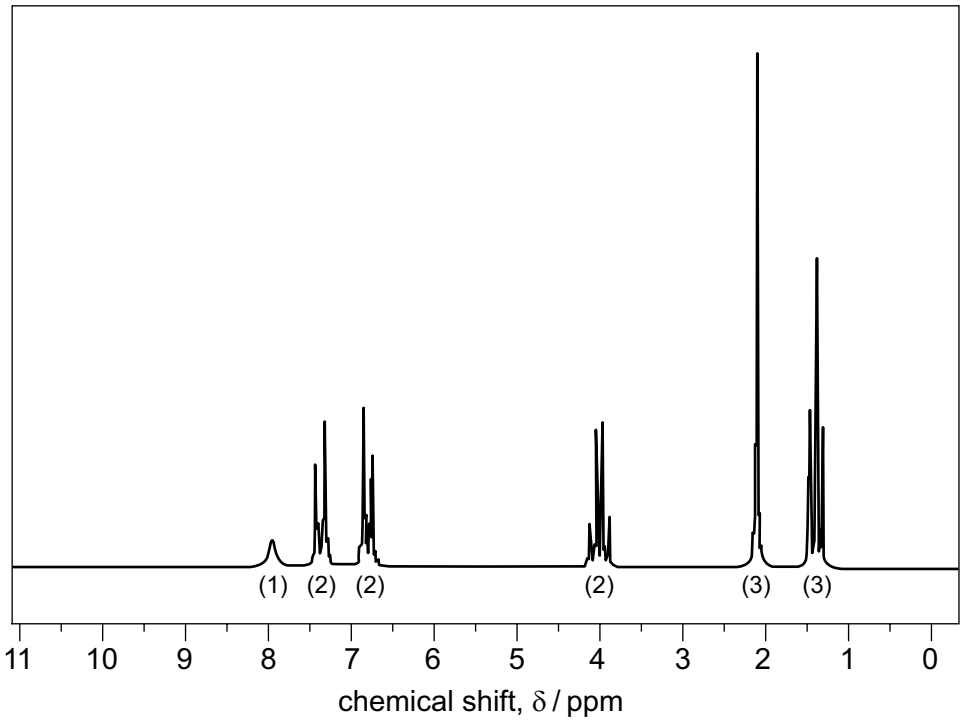


**Figure 4.2**

 

**(a)** Deduce the molecular formula of **G**. Explain your answer.

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..... [3]

**(b)** **(i)** Explain what can be deduced about the structure of **G** from its NMR spectrum. Your answer should refer to the chemical shifts of the peaks and their observed splitting patterns.

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..... [3]

**(ii)** Suggest the structure of the fragment at *m/z* 43 in the mass spectrum.

..... [1]

**(iii)** Predict the structure of **G**.

..... [1]

**(iv)** During fragmentation in the mass spectrometer, ions can sometimes pick up extra hydrogen atoms.
Suggest structures for three other abundant fragment ions in the mass spectrum of **G**.

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..... [2]

[Total: 10]

 

## Section B

Answer **two** questions from this section in the spaces provided.

**5** In physical organic chemistry, infra-red (IR) and ultraviolet (UV) spectroscopy can be used to monitor the progress of a reaction.

**(a) (i)** Explain the origin of IR absorptions of simple molecules.

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..... [2]

**(ii)** For each of the molecules, HC*l*, $CO_2$ and $NO_2$:

- predict, with reasons, the number of absorption bands in its IR spectrum
- identify the molecular vibrations which give rise to these absorptions.

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..... [5]

**(iii)** Explain the role of $CO_2$ in the greenhouse effect in terms of IR absorption.

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..... [1]

**(iv)** Suggest a factor which needs to be considered if IR were to be used as a way of monitoring the progress of a reaction.

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..... [1]

 

**(b)** When treated with sodium ethoxide, $C_2H_5ONa$, both menthyl chloride, **H**, and neomenthyl chloride, **J**, undergo elimination of $HCl$ by an E2 mechanism, but the rates and the products of the two reactions differ.

The conformation of the cyclohexane ring in which a bulky group such as $–CH(CH_3)_2$ is in the equatorial position is more stable than the conformation in which the bulky group is in an axial position.

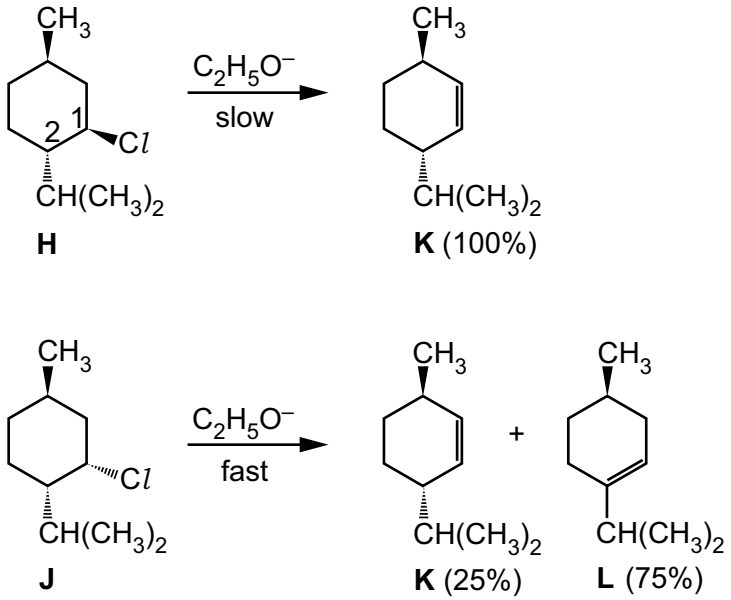


**Figure 5.1**

**(i)** Deduce the stereochemistry, *R* or *S*, at each of the carbon atoms 1 and 2 in **H**. Explain your answer.

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..... [2]

**(ii)** Draw the relevant ring conformations, using stereochemical projections and curly arrows, for the E2 reactions undergone by **H** and **J**, to explain:

- the stereochemistry of the reactions
- the slower rate of reaction of **H** compared to **J**
- the reaction of **H** to produce only alkene **K**, whereas **J** produces the isomeric alkene **L** as well as **K**
- the formation of more of alkene **L** compared to alkene **K**, in the reaction undergone by **J**.

[5]

**(c)** The potassium salt of 2-methylpropan-2-ol, $(CH_3)_3COK$, is a sterically-hindered strong base that can be used to convert chloroalkanes into alkenes. The stereochemistry of its reaction with some chlorocycloalkanes can be investigated by isotopic labelling with deuterium.

Figure 5.2 shows the products and yields from the base-catalysed elimination of $HCl$ / $DCl$ from two different chlorocycloalkanes, **M** and **N**.

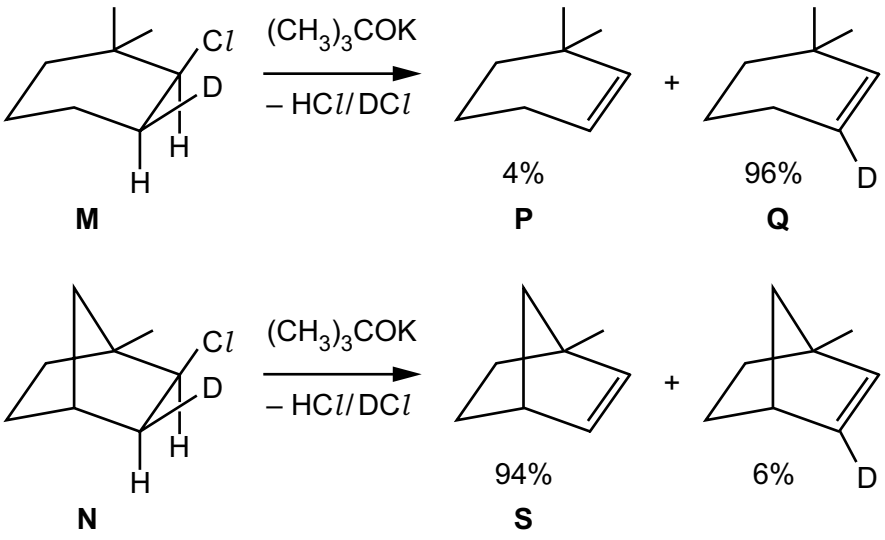


**Figure 5.2**

**(i)** State a method that will distinguish between compounds **P** and **Q**, and describe the measurements needed to identify which is **P** and which is **Q**.

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..... [1]

**(ii)** Explain, with the use of suitable diagrams, why **Q** and **S** are the major products of these elimination reactions. In your answer, you should consider the mechanism and type of elimination reaction that is occurring in each of the reactions shown in Figure 5.2.

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..... [3]

[Total: 20]

 

**6** **(a)** 2-chloro-3-methylbutane undergoes the reactions described in Figure 6.1.

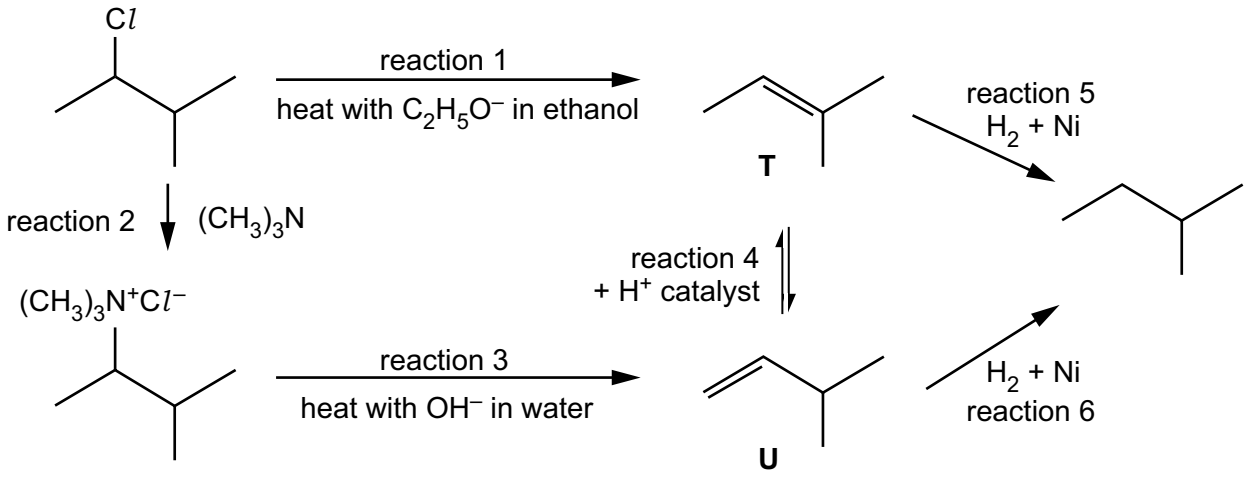


**Figure 6.1**

**(i)** Describe how the $^1$H NMR spectra of the alkenes **T** and **U** differ. In your answer, include approximate $\delta$ values, relative peak areas and the splitting patterns of two peaks in each spectrum.

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**(ii)** Discuss why reaction 1 produces alkene **T** whereas reaction 3 produces alkene **U**.

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..... [3]

**(iii)** Reaction 4 is a reversible reaction. The enthalpy changes for the two hydrogenations, reactions 5 and 6 in Figure 6.1, are given.

reaction 5 **T** + $H_2 \rightarrow CH_3CH_2CH(CH_3)_2$ $\Delta H_5^{\ominus} = -111\ kJ\ mol^{-1}$

reaction 6 **U** + $H_2 \rightarrow CH_3CH_2CH(CH_3)_2$ $\Delta H_6^{\ominus} = -126\ kJ\ mol^{-1}$

Use these data together with the equations shown to calculate the ratio [**T**]/[**U**] at equilibrium. State and explain any assumptions you have made in your calculation.

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

$$K_c = e^{-\Delta G^{\ominus} / RT}$$

$K_c$ is the equilibrium constant and R is the molar gas constant.

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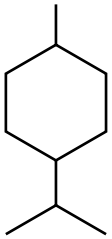
..... [3]

**(b)** The terpinenes are a group of isomers with the molecular formula $C_{10}H_{16}$. Each terpinene contains two carbon-carbon double bonds, and their carbon frameworks are identical to that of the saturated hydrocarbon, 2-(4-methylcyclohexyl)propane, **V**. They differ from each other in the positions of the double bonds.



2-(4-methylcyclohexyl)propane, **V**

There are 14 terpinenes, which can be grouped into different sets according to the positions of the two carbon-carbon double bonds.

There are five terpinenes in Set **I**. The terpinenes in Set **I** have structures in which both carbon-carbon double bonds are contained within the cyclohexane ring.

The structures of the terpinenes can be deduced by identifying their products of oxidation.

- Terpinene **W** is a terpinene in Set **I**.
  - When terpinene **W** is heated with a concentrated acidified solution of manganate(VII) ions, two compounds **X**, $C_4H_6O_3$, and **Y**, $C_6H_{10}O_3$ are produced.
  - **X** and **Y** contain both the ketone and carboxylic acid functional groups.
  - One of **X** and **Y** gives a yellow precipitate with alkaline aqueous iodine; the other compound (**X** or **Y**) gives no precipitate.

- Terpinene **Z** is also in Set **I**.
  - When terpinene **Z** is heated with a concentrated acidified solution of manganate(VII) ions, two moles of $CO_2$ are produced per mole of **Z**.
  - The other product from the oxidation of **Z** is compound **A**, $C_8H_{14}O_2$.
  - Compound **A** gives a yellow precipitate with alkaline aqueous iodine.

**(i)** Explain why the carbon-carbon double bonds in the terpinenes in Set **I** **cannot** show *cis-trans* isomerism.

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..... [1]

 

**(ii)** Draw the structures of the compounds, **W**, **X** and **Y**.
Identify which of **X** and **Y** gives a yellow precipitate with alkaline aqueous iodine.

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..... [3]

**(iii)** Write an equation for the oxidation of **Z** by a concentrated acidified solution of manganate(VII) ions.
In your answer use [O] to represent an atom of oxygen from the oxidising agent.
Draw the structures of **Z** and **A**.

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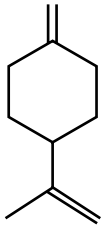
[3]

**(iv)** Terpinene **B** is in Set **II**. The terpinenes in Set **II** contain structures in which both carbon-carbon double bonds are outside the cyclohexane ring.

The structure of terpinene **B** is shown.



Deduce how many terpinenes, including terpinene **B**, are in Set **II**. Draw structures of any terpinenes in Set **II** (not including terpinene **B**)

[1]

**(v)** Draw the most stable conformation of **B**.
Explain your answer.

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..... [2]

[Total: 20]

 

**7** **(a)** The compound paroxetine is an antidepressant. It can be synthesised according to the scheme shown in Figure 7.1.

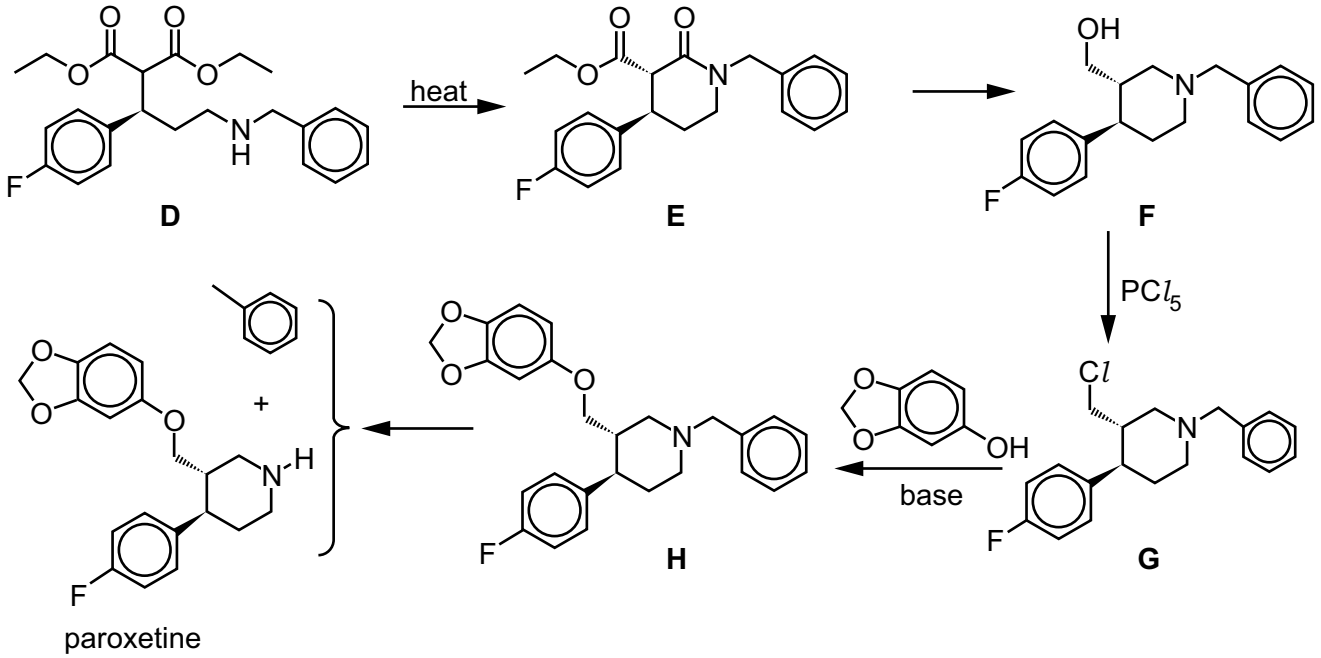


**Figure 7.1**

**(i)** Draw a diastereoisomer of paroxetine.

[1]

**(ii)** The specific rotation of a sample of paroxetine prepared by this route is 56.1°.
The specific rotation of optically pure paroxetine is 89.1°.

Calculate the percentage optical purity of this sample of paroxetine and the percentage of paroxetine in the sample, assuming the only impurity is its enantiomer.

[2]

During drug preparation there is often a rigorous separation of the two enantiomers of a chiral molecule.

**(iii)** Suggest a reason why rigorous separation of the two enantiomers of a chiral molecule is often necessary in drug preparation.

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..... [1]

**(iv)** Suggest why many of the psychiatric drugs provided by drug companies are nevertheless left as mixtures of enantiomers.

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..... [1]

**(v)** The conversion of **D** to **E** follows an addition-elimination mechanism, which overall sees substitution at the carbonyl group.

Suggest a mechanism for this reaction.
Aryl and substituted aryl rings can be represented by Ar.

[2]

**(vi)** Suggest the type of reaction that occurs during the conversion of **E** to **F**.

..... [1]

 

The mechanism for the conversion of **G** to **H** is shown in Figure 7.2. Only part of the structure of **G** has been shown. In Figure 7.2, base is represented by B.

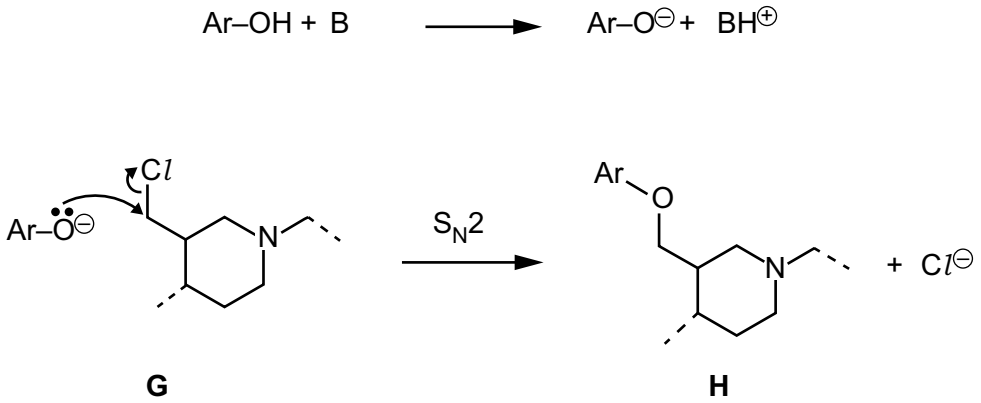


**Figure 7.2**

**(vii)** Write a rate equation for the C–O bond forming step.
Outline briefly how you could experimentally verify that this step follows an $S_N2$ mechanism.

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..... [3]

**(viii)** Predict how the rate of reaction would change if a base is **not** used.
Explain your answer.

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..... [1]

**(ix)** Describe the type of reaction occurring during the final step of this synthesis to form paroxetine.

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..... [1]

**(b)** Paroxetine and other molecules involved in its synthesis contain the ether functional group. Ethers are compounds in which an oxygen atom is bonded to two organic groups. Phenyl ethers can be prepared from phenol by the reaction scheme shown in Figure 7.3.

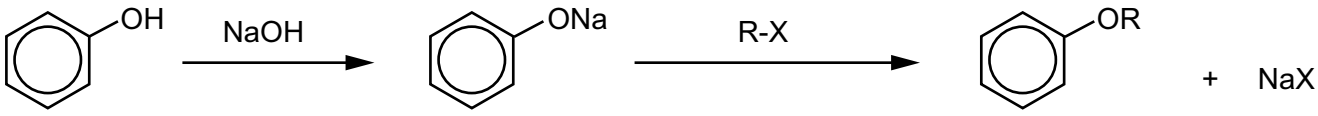
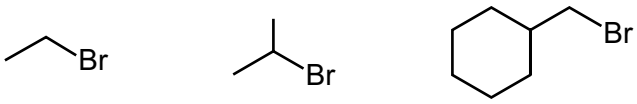



**Figure 7.3**

The reactions of **M**, **N** and **P** with phenol have the same mechanism.




**M** **N** **P**

**(i)** Predict the order of reactivity of phenol with compounds **M**, **N** and **P** under basic conditions.
Explain your answer.

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..... [3]

**(ii)** The reaction of **N**, 2-bromopropane, with phenol takes place quickly and gives a high yield.
For the reaction of 2-chloropropane with phenol, an equilibrium is established, and the yield is low. A small quantity of silver oxide, $Ag_2O$, is added to the reaction mixture to increase yield.

Explain why adding $Ag_2O$ to the mixture increases the yield.

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..... [2]

 

**(iii)** The reaction of **N** with potassium 2-methylprop-2-oxide, $(CH_3)_3COK$, does **not** produce the expected ether, $(CH_3)_3COCH(CH_3)_2$, but produces compound **Q**.
[$M_r$: **Q**, 42]

Suggest a structure for **Q**, and explain why this is formed instead of the ether.

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..... [2]

[Total: 20]

 

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