H

RAFFLES INSTITUTION
2022 YEAR 6 PRELIMINARY EXAMINATION
Higher 3

CANDIDATE NAME

CLASS 2 2 S 0

INDEX NUMBER

CHEMISTRY

9813/01

Paper 1

27 September 2022

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	/ 22
2	/ 17
3	/ 21
Section B (answer two)	
4	/ 20
5	/ 20
6	/ 20
Total	/ 100

This document consists of **40** printed pages and **1** insert.

Section A
Answer **all** questions in this section.

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) (i) Calculate the maximum total mass of H_2 produced when one tonne (1×10^6 g) of methane is used in steam methane reforming. [2]

(ii) Overall, it has been found that 0.465 tonnes of H_2 was produced per tonne of methane used.
Suggest **one** reason for the difference between this value and your answer in **(a)(i)**. [1]

(b) Permselectivity is a measure of the ability of a membrane to selectively allow a chemical species to pass through itself.

Explain how a membrane with high H_2 permselectivity can be used to increase the yield of the water-gas shift reaction. [2]

(c) Explain why pyrolysis is only feasible at higher temperatures. [1]

(d) (i) A typical alkaline electrolyser uses KOH(aq) as its electrolyte, with inert electrodes.

Write equations occurring at both the anode and the cathode. [2]

(ii) Calculate the minimum voltage required for the reaction to occur, assuming standard conditions. [1]

(iii) It is found that voltage required for electrolysis is higher when electrolysis takes place at high rate, for example, when operating at high current. However, this increase in voltage required is mitigated when the electrode is physically spinning in the electrolyte.

By considering the concentrations of chemical species at the surface of the electrode, explain the observations. [2]

(iv) The actual voltage required for the reaction to occur is larger than your answer in **(d)(ii)**. This difference between theoretical and actual voltage required is called the overpotential. The presence of overpotential indicates that electrochemical reactions are kinetically controlled.

Give a reason, other than that in **(d)(iii)**, to explain why the actual voltage required for the reaction to occur is larger than expected. [1]

(v) Since the electrolysis of water is energy intensive, the possibility of electrolysing aqueous methanol to produce hydrogen gas is considered.

$$CO_2 + 5H_2O + 6e^- \rightleftharpoons CH_3OH + 6OH^- \qquad E^\ominus = -0.81\ V$$

Suggest a reason why electrolysing methanol to produce hydrogen might be more energy efficient. [1]

(e) The choice of storing hydrogen depends on whether it is stored on-site as a source of energy or transported by vehicles.

With reference to information with Extract 2 and by considering the differences between both storage methods, explain your choice as to which is the optimal technology for

① on-site storage, and

② transport of hydrogen by vehicles.

[3]

(f) When assessing the "greenness" of a reaction, both the Atom Economy (AE) and E factor are usually used together.

(i) Explain how AE is a measurement of the greenness of a synthetic route to a product. [1]

(ii) Suggest one advantage and one limitation of using the AE as a green metric. [2]

(iii) With reference to the information provided in the question, determine the "greenest" process of hydrogen production. Show calculations where appropriate. [3]

[Total: 22]

2 In 2020, chemists have finally managed to synthesise *canataxpropellane*, one of the most complex natural products ever isolated. One of the steps which proved challenging in the synthesis involved a Diels-Alder reaction between **F** and **G** to give **H**.

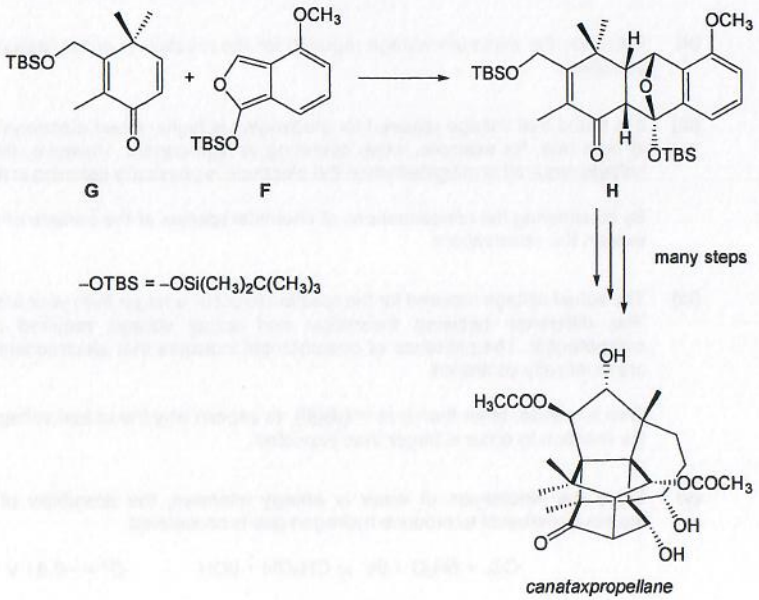


Fig. 2.1

The Diels-Alder reaction is a cycloaddition reaction between a conjugated diene and an alkene (also known as the dienophile) to form a six-membered ring.

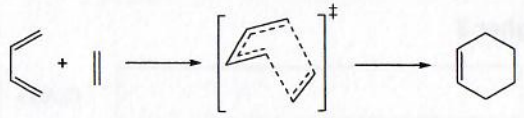


Fig. 2.2

(a) Both ethene and buta-1,3-diene absorb ultraviolet (UV) radiation.

(i) State the type of electronic transition that is responsible for the UV absorptions by the compounds. [1]

(ii) Suggest two ways the UV spectrum of buta-1,3-diene is expected to differ from that of ethene. Give reasons for your answer. [2]

(iii) Draw a molecular orbital diagram for the π system of buta-1,3-diene showing the linear combination of atomic orbitals. Label the HOMO and LUMO clearly. [1]

(b) The Diels-Alder reaction occurs when the HOMO of one reactant interacts with the LUMO of another reactant.

Fig. 2.3 shows the relative energy levels of the HOMOs and LUMOs of the reactants involved in both reactions in Fig. 2.1 and Fig. 2.2, except for the LUMO of **F**.

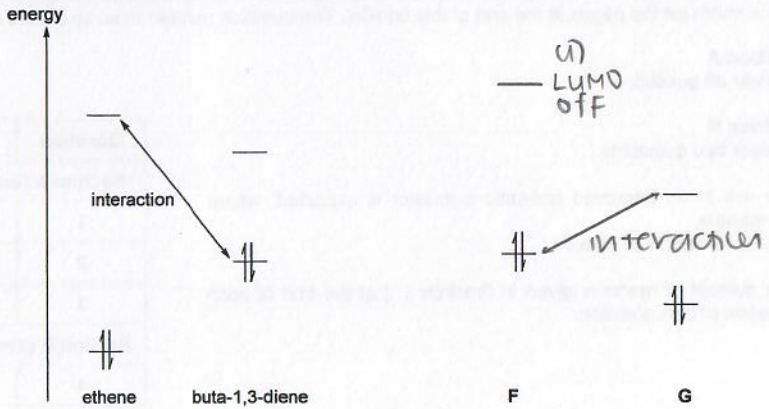
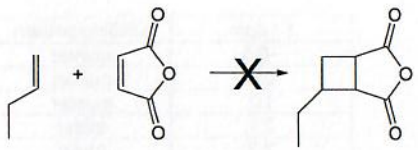


Fig. 2.3

(i) On Fig. 2.3, draw the energy level for the LUMO of **F**. [1]

(ii) With reference to Fig. 2.3, explain why the reaction between **F** and **G** is faster than that between ethene and buta-1,3-diene. [1]

(iii) In Fig. 2.4, when but-1-ene and maleic anhydride are mixed under Diels-Alder conditions, **I** cannot be obtained. Explain the observation by sketching the relevant HOMO and LUMO of the reactants.

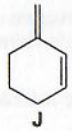


maleic anhydride **I**

Fig. 2.4

[2]

(iv) Explain whether **J** is expected to react with ethene via the Diels-Alder reaction.



J

[1]

(c) In the Diels-Alder reaction, the stereochemistry of the dienophile is preserved i.e. a *cis* arrangement of groups in a double bond will result in a *cis* arrangement in the new six-membered ring as shown in Fig. 2.5.

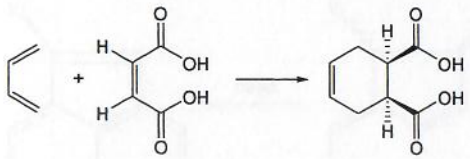


Fig. 2.5

For the diene, the two "outside" groups (labelled A) on the diene each end up on the same face of the new six-membered ring. Likewise, the two "inside" groups (labelled B) also end up on the same face of the new ring as shown in Fig. 2.6.

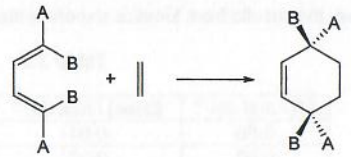
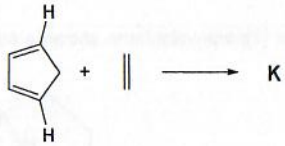


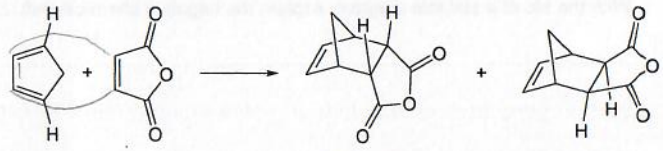
Fig. 2.6

(i) Draw the structure of the product **K** of the following reaction, showing clearly its stereochemistry.



[1]

When a substituted dienes reacts with a substituted dienophile, a pair of diastereomers (known as the *exo* and the *endo* products) are formed.



endo product *exo* product

Fig. 2.7

The *endo* product is kinetically favoured due to bonding interactions between the electron-deficient carbonyl group of the dienophile and the developing π bond at the back of the diene.

(ii) Explain how the bonding interactions favours the kinetic product. [1]

(iii) Upon prolonged heating of the reaction mixture, the *exo* product is favoured. Explain this observation. [2]

(iv) Using values from the *Data Booklet*, calculate the **average** enthalpy change of the reaction in Fig. 2.7. [1]

(v) Hence, on the same axes, draw the reaction profile diagrams for the formation of both *endo* and *exo* products. [1]

(vi) Table 2.1 shows the relative rate and ratio of the products for the reaction in Fig. 2.7 in different solvents.

Table 2.1

solvent	relative rate	*endo* : *exo* ratio
2,2,4-trimethylpentane	1	80:20
water	700	***x***

1. Explain the faster rate of reaction in water.

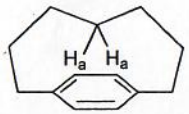
2. Suggest, with explanations, a value for ***x***.

[2]

[Total: 17]

3 Cyclophanes (*cyclo*-*ph*enyl-alk*anes*) are a class of hydrocarbons consisting of at least one aromatic unit and an aliphatic chain which forms a bridge between carbon atoms on the aromatic ring(s).

(a) The ^{1}H NMR of [7]paracyclophane shows a peak at δ = –0.6 ppm which corresponds to the protons, H_a.



[7]paracyclophane

With the aid of a suitable diagram, explain the negative chemical shift, δ, of H_a. [2]

.....

.....

.....

.....

.....

.....

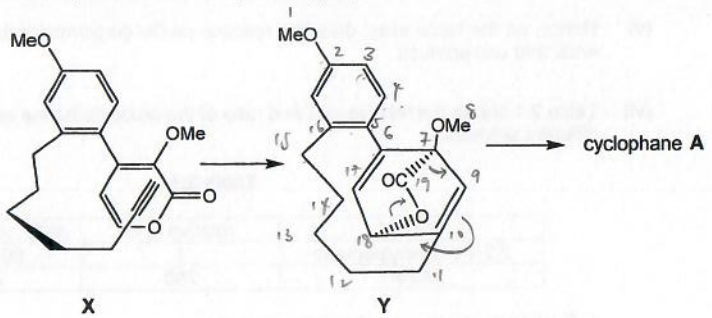
.....

.....

.....

.....

(b) The synthesis of cyclophane **A**, a derivative of Haouamine with anti-cancer properties, is shown. "Me" represents the methyl CH_3– group.



X **Y**

An intramolecular Diels-Alder reaction in **X** gives **Y** in the first step. The second step converts **Y** to **A** and CO_2 as a byproduct.

Cyclophane **A** is chiral.

Mass spectrometry of **A** gave abundant peaks at m/e values 15, 31, 95, 282 and 283. The relative abundances for the peaks at m/e 282 and 283 are 52 and 10.9 respectively.
The ^{1}H NMR spectrum of **A** is summarised in Table 3.1.

Table 3.1

δ / ppm	splitting pattern	integration
−0.5	quintet	2
0.9	quintet	2
1.2	quintet	2
2.1	triplet	2
2.3	triplet	2
3.7	singlet	3
3.8	singlet	3
6.9 – 7.5	multiplet	6

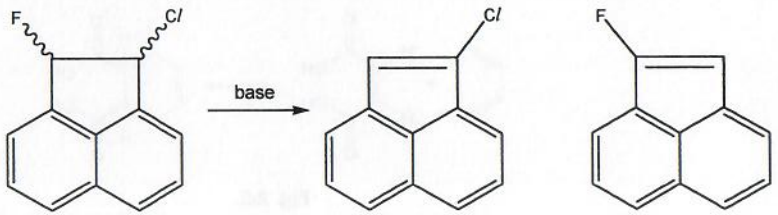
(i) Determine the molecular formula of **A**. [2]

(ii) Hence deduce the structure of **A**. Explain your reasoning, assigning the NMR signals to the H atoms in your structure . Using your structure, explain why **A** is chiral. [4]

(iii) Propose a single step mechanism for the reaction of **Y** to give **A**. [1]

(iv) **A** reacts with Br_2(aq) in a 1:5 ratio to give **B**, $C_{19}H_{21}O_5Br_5$. Suggest the structure of **B**. [1]

(c) When **J** was reacted with a base, **K** was observed to form, but not **L**,



J **K** **L**

not formed

Table 3.2 shows the results from kinetics experiments.

Table 3.2

[J] / mol dm^{-3}	[base] / mol dm^{-3}	rate / mol dm^{-3} s^{-1}
0.80	0.01	5.0×10^{-6}
0.80	0.02	1.0×10^{-5}
0.40	0.01	2.5×10^{-6}

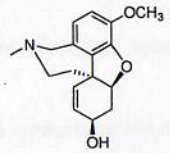
Similar observations were made with **any** stereoisomer of **J**.

(i) Using relevant values from the *Data Booklet*, explain why **L** is expected to be formed more readily than **K**. [1]

(ii) Determine the rate equation for this reaction. [1]

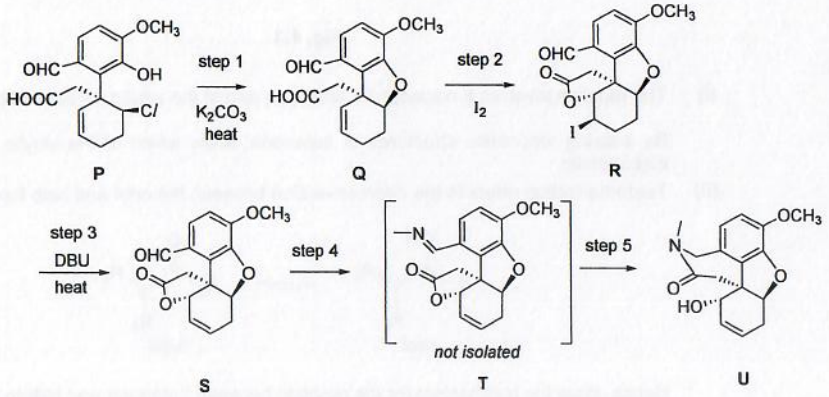
(iii) Considering all data and observations, suggest a mechanism for the elimination of **J** to **K**. [3]

(d) (–)-galanthamine, an inhibitor of acetylcholinesterase which enhances the cognitive functions of Alzheimer's patients, is another example of a cyclophane.



(–)-galanthamine

The following scheme shows the partial synthesis of (–)-galanthamine.



(i) The reaction in step 1 is catalysed by the weak base K_2CO_3. It was also found that **Q** was formed with >90% diastereomeric ratio. Propose the mechanism for step 1, accounting for the stereochemistry. [3]

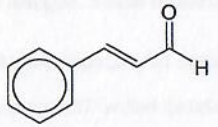
(ii) Identify the types of reactions that occur during each of the steps 4 and 5. Suggest the reagent for step 5. [3]

[Total: 21]

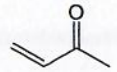
Section B

Answer **two** questions from this section.

4 α,β–unsaturated carbonyls, such as cinnamaldehyde and butanone, are compounds with a carbonyl group conjugated to an alkene.



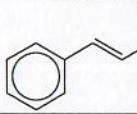
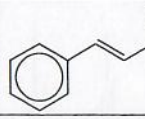
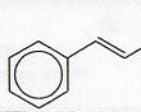
cinnamaldehyde



butenone

(a) The infra-red absorption frequency for the C=O bonds of cinnamaldehyde and some of its derivatives are given in Table 4.1.

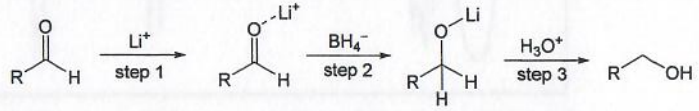
Table 4.1

compound	structure	wavenumber/ cm^{-1}
cinnamaldehyde		1677
cinnamamide		1664
cinnamoyl chloride		1688

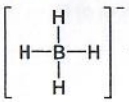
(i) Outline the principles of IR spectroscopy. [1]

(ii) Explain why the C=O absorption frequency for cinnamaldehyde is higher than cinnamamide but lower than cinnamoyl chloride. [2]

(b) $LiBH_4$ reduces aldehydes to its alcohol through the following steps.



(i) Draw a mechanism to show the single step mechanism in step 2.

Use  to represent BH_4^-. [1]

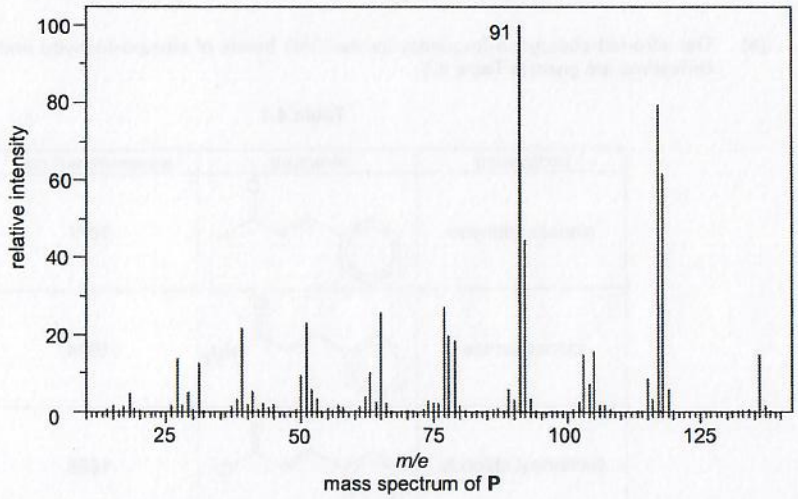
(ii) $LiBH_4$ reduces both esters and aldehydes. However, esters are reduced less readily than aldehydes.

By drawing resonance structures of both aldehydes and esters, explain why. [2]

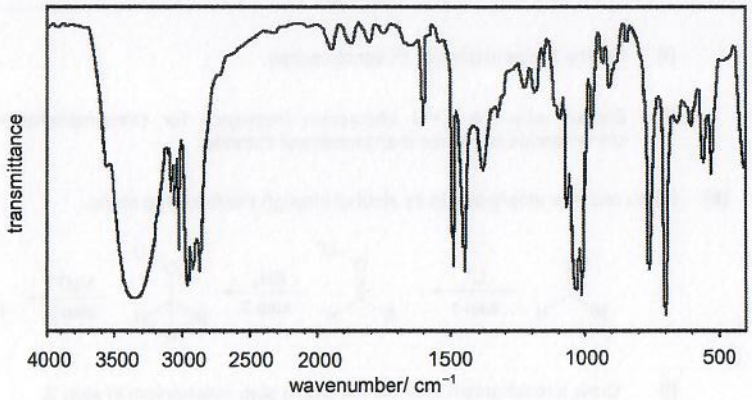
(iii) Unlike $LiBH_4$, $NaBH_4$ is unable to reduce esters. Suggest why. [1]

(c) When cinnamaldehyde is added into excess LiA/H_4, compound **P** is formed.

The mass spectrum for compound **P** is shown below. The molecular ion (M^+) peak has a *m/e* value of 136.



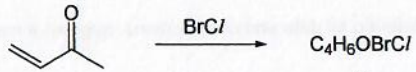
mass spectrum of **P**



infra-red (IR) spectrum of **P**

Using the spectral data, deduce the structure of compound **P**. Explain your reasoning fully. [3]

(d) Butenone reacts with BrC*l* to form a mixture of isomers (including stereoisomers).



Q

(i) Draw a mechanism to show the formation of **Q**. [2]

(ii) Deduce the molecular ion peaks in the mass spectrum of **Q** and their relative abundances. [2]

(e) Butenone also reacts with HBr as shown in Fig. 4.3.

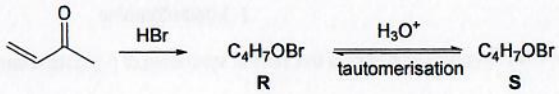


Fig. 4.3

(i) The reaction involves a nucleophilic attack on one of the vinylic carbons of butenone.

By drawing resonance structures of butenone, show which of the vinylic carbons is electrophilic. [1]

(ii) Tautomerisation refers to the interconversion between the enol and keto form.

Hence, draw the mechanism for the reaction between butenone and HBr to form **S**. [2]

(f) Butenone is used in the synthesis of the Wieland-Miescher ketone which is a versatile building block for the further synthesis of many different steroids.

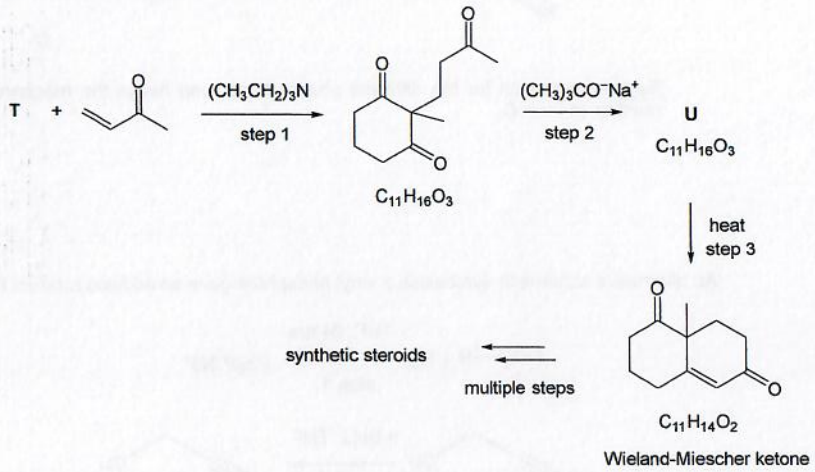


Fig. 4.4

(i) Explain why $(CH_3CH_2)_3N$ is a is a poor nucleophile. [1]

(ii) Reaction between butenone and **T** involves a nucleophilic attack on the vinylic carbon.

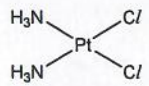
Draw the structure of the nucleophile. [1]

(iii) Suggest the structure of **U**. [1]

[Total: 20]

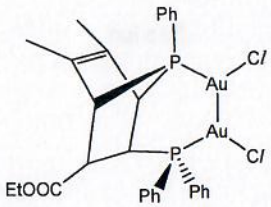
5 Organometallic complexes have many important applications such as catalysis and pharmaceuticals.

For example, cisplatin is an important early generation anti-cancer drug. However, its drawback is that it is also toxic to normal cells, causing severe side-effects.



cisplatin

A more recent development is a family of gold-based anti-cancer drug candidates. One such example is complex **A** which has the advantage of much higher selective cytotoxicity towards cancer cells.



A

Where Ph = phenyl C_6H_5–, Et = ethyl CH_3CH_2–

(a) Table 5.1 summarises some properties of various Fe(III) complexes, where $E^\ominus$ refers to electrode potentials for reduction to an Fe(II) product, and lg K_{stab} refers to the logarithm of the stability constant.

Table 5.1

complex	lg K_{stab}	$E^\ominus$ (M(III)/M(II)) / V
$[Fe(H_2O)_6]^{3+}$	0	+0.77
$[Fe(CN)_6]^{3-}$	43.6	+0.36
$Fe(OH)_3(H_2O)_3$	36	−0.56

The spectrochemical series lists ligands in order of the ΔE, which is the energy gap with respect to the splitting of d-orbitals within the complexes they form. A partial spectrochemical series is shown here.

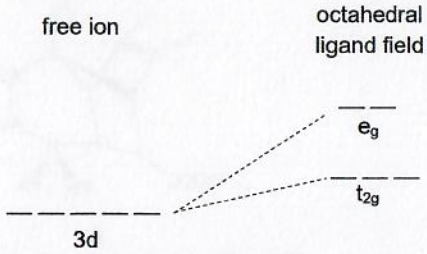
$$H_2O < PPh_3 < CN^-$$

Changes in ligands bound to a metal ion affects the properties of a complex. Most ligands can donate an electron pair to the metal ion, and are also termed as "σ donors", while some ligands are also known as "π acceptors" due to additional π interactions they can make with the metal ion.

(i) Explain why $Fe(OH)_3$ has a more negative $E^\ominus$ compared to $[Fe(H_2O)_6]^{3+}$. [1]

(ii) By considering the shape and geometry of the 3d orbitals, suggest a 3d orbital that may have π interactions with CN^- ligands in an octahedral complex. Draw a labelled diagram to illustrate the π interaction involving the LUMO of the CN^- with the 3d orbital of the Fe(III). [2]

(iii) The degenerate 3d orbitals in Fe^{3+} are split into 2 groups of different energy levels. They are termed e_g and t_{2g}.



Draw a partial MO diagram for the π interactions between CN^- ligands and the Fe(III) ion. Using your diagram, explain the high ΔE for CN^- complexes.

Hence or otherwise, and considering your answer to part **(a)(ii)**, explain the relative values of lg K_{stab} and $E^{\ominus}$ of $[Fe(CN)_6]^{3-}$ against $Fe(OH)_3(H_2O)_3$ and $[Fe(H_2O)_6]^{3+}$. [4]

(b) Both ammonia, NH_3, and triphenylphosphine, PPh_3, are possible ligands for gold(I) complexes. However, compared to ammonia, phosphine ligands tend to coordinate more strongly to gold(I) ions. By considering the frontier MOs, suggest a reason why. [1]

.....

.....

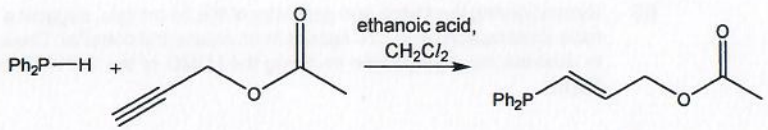
.....

.....

.....

(c) The syntheses of novel phosphine ligands are essential to the discovery of new metal-phosphorus complexes.

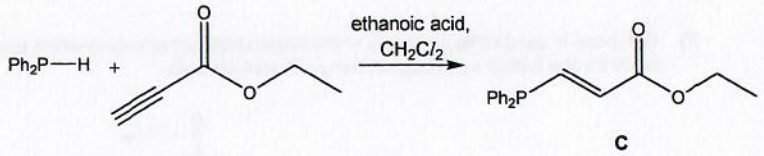
(i) The following methodology for the synthesis of a functionalised vinyl phosphine **B** was proposed.



B

However, the reaction could not take place.

With a different starting material, the following reaction to synthesise vinyl phosphine **C** was successfully carried out.

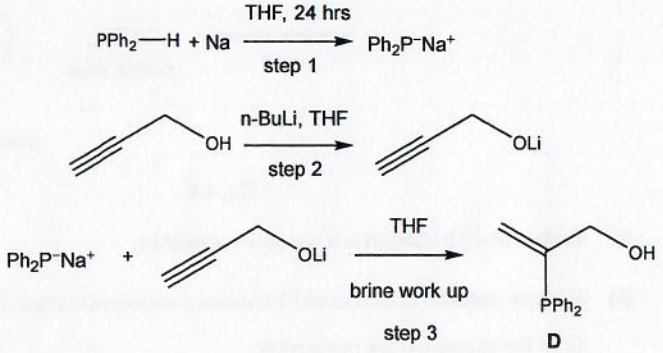


C

Suggest a reason for the different observations, and hence the mechanism for the reaction to form **C**.

[3]

An alternative scheme to synthesise a vinyl phosphine gave an addition product **D**:



D

where n-BuLi acts as a strong base.

(ii) The regiochemistry in product **D** is unexpected. Explain why. [1]

(iii) Suggest the mechanism in the step 3 to account for the regiochemistry in the formation of **D**. [2]

(d) Vinyl phosphine **D** is useful in the synthesis of a chiral bicyclic diphosphine ligand. Fig. 5.1. shows the scheme for the synthesis, where a Pd(II) dimeric complex ***R*-C9** is used as a promoter and chiral auxiliary to carry out asymmetric Diels-Alder reaction in step 3 to give ***R*-C12**.

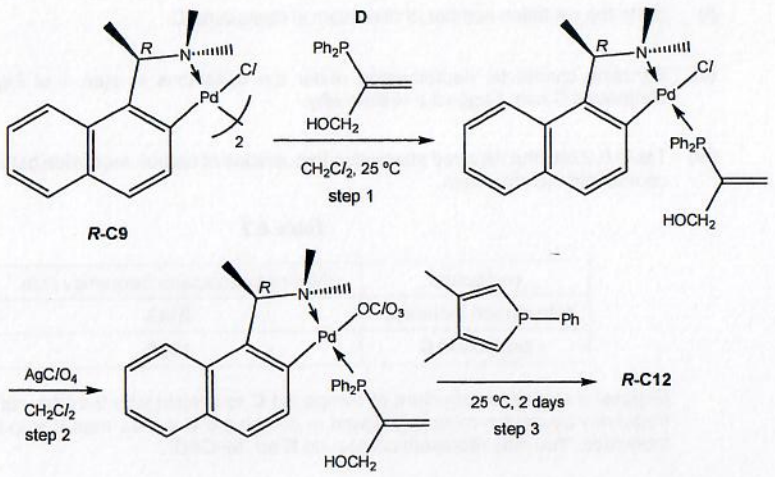
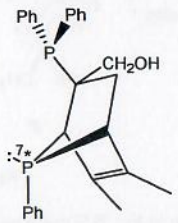


Fig. 5.1

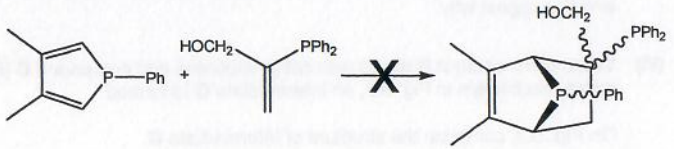
An intra-complex Diels-Alder reaction takes place in step 3. Treating ***R*-C12** with KCN(aq) liberates the diphosphine anti-cancer drug candidate, stereoisomer **F** nearly exclusively. Thus use of the *R* chiral auxiliary ***R*-C9** earlier enables the selective asymmetric synthesis of **F**.



F

(i) Using the *R* and *S* convention, assign the absolute configuration of the bridgehead 7-phosphorus atom in **F**. Your answer should include priority assignments as defined by the Cahn-Ingold-Prelog rules. [2]

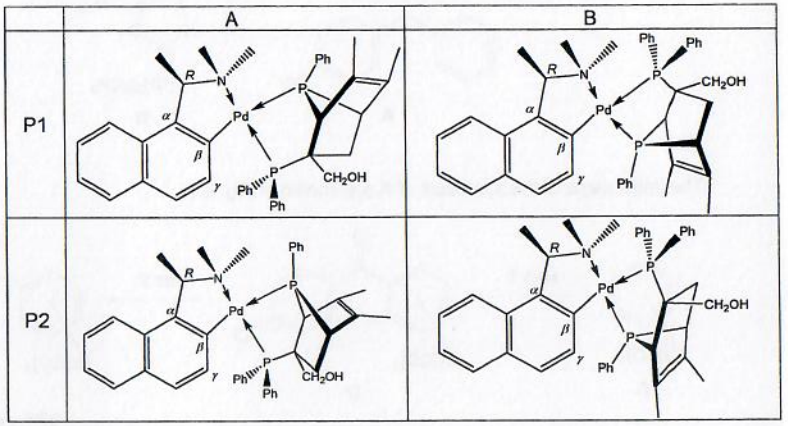
(ii) The intra-complex Diels-Alder reaction in step 3 does not take place if the Pd(II) complex is not present.



Suggest two reasons why coordination to the Pd(II) center promotes the reaction. [2]

(iii) Table 5.2 shows the 4 possible stereoisomers of ***R*-C12**, divided into two sets, P1 and P2.

Table 5.2



Set P1 gives **F** while set P2 does not.

The stereochemistry of the atoms around the Pd center may be visualised using Fig 5.2.

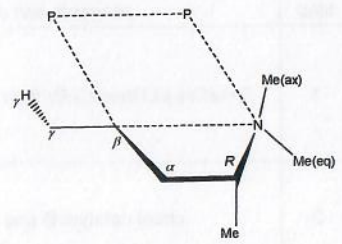


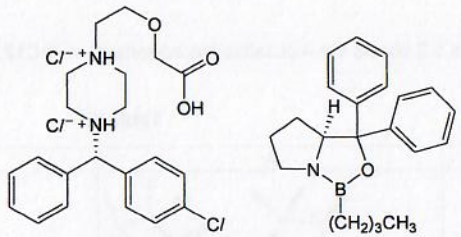
Fig. 5.2

The P atoms, β–C atom, and N atom are in the same plane.
On Fig. 5.2, fill out the diphosphine ligand for the one of the stereoisomers of ***R*-C12** in set P2, and hence explain why **F** is formed nearly exclusively via set P2 when the *R* chiral auxiliary is used.

[2]

[Total: 20]

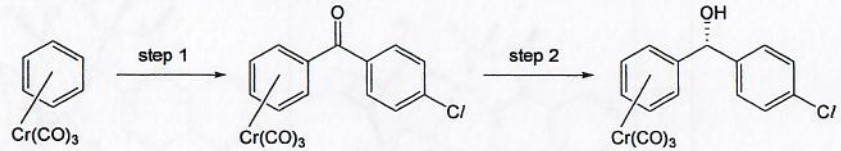
6 Zyrtec is a medicine used to relief common allergy symptoms, such as runny nose and sneezing, and it contains cetirizine dihydrochloride **A**, as the active ingredient. The first enantioselective synthesis of **A** was achieved using chiral catalyst **B**.



A

B

The initial steps of the synthesis of **A** are shown in Fig. 6.1.



C

D

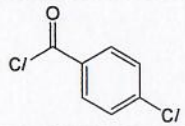
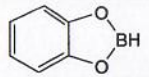
E

99% yield, 98% ee

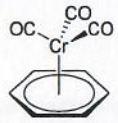
Fig. 6.1

Table 6.1 lists the reagents for the steps in Fig. 6.1.

Table 6.1

step	reagents and conditions
1	$CH_3(CH_2)_3Li$ then CuBr then 
2	chiral catalyst **B** and  (catecholborane)

(a) Compound **C** is a highly stable chromium complex consisting of three carbon monoxide ligands and a benzene ligand where all six π electrons are involved in coordination to the central transition metal. Compound **C** has a structure resembling an inverted piano stool where the $Cr(CO)_3$ group occupies one face of the benzene molecule.



C

(i) State the oxidation number of chromium in compound **C**. [1]

(ii) Benzene cannot be deprotonated under the conditions in step 1 of Fig. 6.1 while compound **C** can. Suggest a reason why. [1]

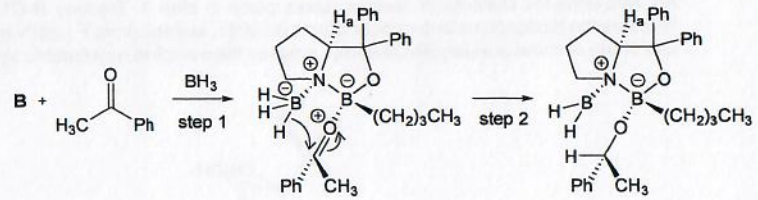
(iii) Table 6.2 lists the infra-red absorption frequencies of carbon monoxide before and after coordination to chromium.

Table 6.2

compound	infra-red absorption frequency / cm^{-1}
free carbon monoxide	2143
compound **C**	1990

Suggest a resonance structure of compound **C** to explain why the infra-red absorption frequency by carbon monoxide ligand in compound **C** is less than that in free carbon monoxide. You may represent compound **C** as $^{-}M{-}C{\equiv}O^{+}$. [2]

(b) Chiral catalyst **B** reduces carbonyl compounds using boranes enantioselectively via a mechanism shown in Fig. 6.2.



where Ph = phenyl

F

Fig. 6.2

Step 1 of the mechanism in Fig. 6.2 involves the coordination of the carbonyl compound and BH_3 with chiral catalyst **B** to give intermediate **F** with a rigid structure to prevent the carbonyl compound from rotating.

(i) Give reasons why chiral catalyst **B** reacts faster with BH_3 than catecholborane in step 1 of the mechanism in Fig. 6.2. [2]

(ii) In intermediate **F**, the BH_3 and carbonyl compound are *cis* relative to the tertiary hydrogen atom, H_a. By considering the shape of the bicyclic fused ring structure of **B** and **F**, suggest why. [1]

(iii) When chiral catalyst **B** reacts with catecholborane and compound **D** (Fig. 6.1) under the same mechanism in Fig. 6.2, an intermediate **G** is formed.

On Fig. 6.3, complete the structure of intermediate **G**. [1]

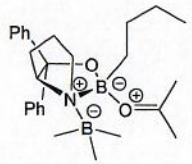
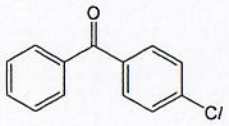


Fig. 6.3

(iv) In Fig 6.1, the enantioselective reduction of **D** gave **E** with an enantiomeric excess of 98%.

Predict and explain how the enantiomeric excess will change if compound **H** was reduced instead of **D**. [1]



H

(c) Moscher ester analysis is a method that can be used to determine the absolute configuration of compound **E** (Fig. 6.1).

Enantiomerically pure Moscher acyl chloride reacts with a chiral alcohol to form a Moscher ester with a conformation that allows the phenyl substituent to shield one of the substituents more than the other in the ^{1}H NMR as shown in Fig. 6.4.

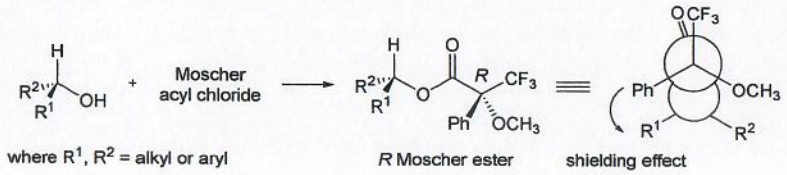


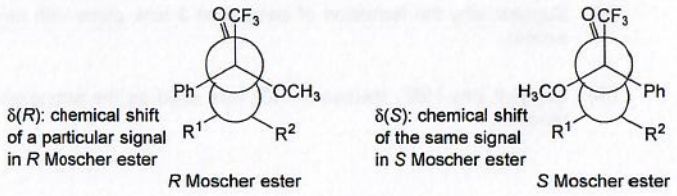
Fig. 6.4

(i) State the factor responsible for the shielding of the R^1 substituent in the *R* moscher ester in Fig. 6.4. [1]

(ii) Draw the structure and assign the absolute configuration of the Moscher acyl chloride required to synthesize *S* Moscher ester. Your answer should include priority assignments as defined by the Cahn-Ingold-Prelog rules. [2]

(iii) State the stereochemical relationship between the *R* and *S* Moscher esters of compound **E**. Explain your answer. [1]

(iv) By comparing the change in chemical shifts of a particular signal, $\Delta\delta$, in the ^{1}H NMR spectra of both *R* and *S* Moscher esters of compound **E**, it would be possible to determine the absolute configuration of the chiral alcohol as shown in Fig. 6.5.



$\Delta\delta = \delta(S) - \delta(R)$

Fig. 6.5

With the aid of a Newman projection of the *S* Moscher ester formed with **E**, deduce the sign of $\Delta\delta$ of the signal due to the protons on the phenyl ring that is coordinated to the $Cr(CO)_3$ group in the Moscher esters of compound **E**. [2]

(d) To complete the synthesis of cetirizine dihydrochloride, **A**, compound **E** underwent a substitution reaction to form compound **J** with no loss in enantiomeric excess as shown in Fig. 6.6.

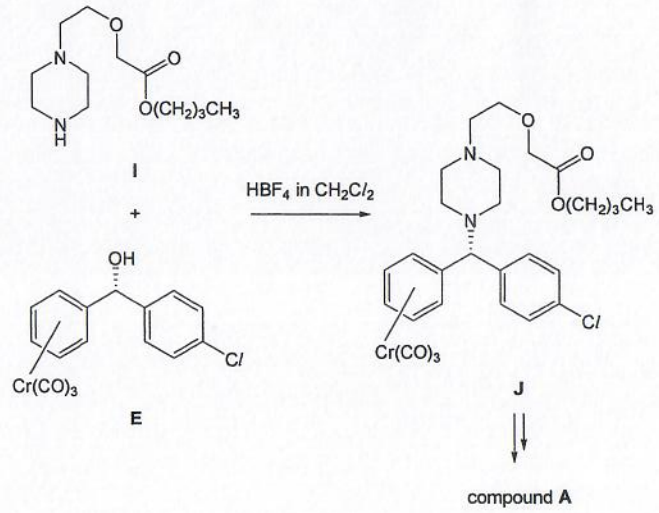


Fig. 6.6

(i) Given that the formation of compound **J** follows overall first order reaction kinetics, draw a mechanism that shows the formation of compound **J**. [3]

You may represent compound **E** as  and compound **I** as R_2N–H.

(ii) Suggest why the formation of compound **J** took place with no loss in enantiomeric excess. [1]

(iii) Suggest why HBF_4 instead of HC*l* was used as the strong acid in the substitution reaction. [1]

[Total: 20]

Information for Question 1

As part of the Paris agreement, countries have pledged to take action to keep global warming below 2 °C. To meet this reduction target, global annual greenhouse gas emissions will need to be reduced by 85% by 2050. The hydrogen economy is one of the ways to decarbonise economies, such as replacing vehicles powered by fossil fuels with those powered by hydrogen fuel cells.

Extract 1

Three common methods of producing hydrogen are steam methane reforming, pyrolysis, and the electrolysis of water.

Steam methane reforming involves a catalytic conversion of methane and steam to hydrogen and carbon oxides at temperatures of 850–900 °C. The process consists of two key steps – reforming and water-gas shift.

Reforming

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

Water-gas shift

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H^{\ominus} = -41.4\ kJmol^{-1}$$

To increase the yield of the reaction, a membrane with high H_2 permselectivity can be used after the water-gas shift reaction.

Pyrolysis is a process where thermal decomposition of the hydrocarbon occurs in the absence of oxygen at temperatures of 1100–1200 °C. The following equation shows the pyrolysis of methane.

$$CH_4 \longrightarrow C + 2H_2 \qquad \Delta H^{\ominus} = +74.9\ kJmol^{-1}$$

The electrolysis of water is done with an electrolyser, where an electrical current is applied to water to split it into hydrogen at the cathode and oxygen at the anode. To date, one commonly used electrolysis technology is the alkaline electrolyser.

Extract 2

At ambient temperature and atmospheric pressure, 1 kg of H_2 gas occupies a volume of 11 m^3. With such a low density of 0.09 kg m^{-3}, H_2 storage has become one of the key barriers restricting its wide-spread use. The main storage methods enable hydrogen to be stored physically as a gas or liquid, and on the surfaces or within the solids by adsorption and absorption, respectively.

High pressure gaseous hydrogen storage is currently the most common and mature method, achieving high pressures of up to 77 MPa using standard piston-type mechanical compressors.

Liquid hydrogen can be stored in cryogenic tanks through a double-step procedure of compression and cooling in a heat exchanger.

Solid-state storage provides another means of storing hydrogen. In a process of adsorption, a gas molecule interacts with several atoms at the surface of a solid where it is bonded and reversibly released when needed. Carbon nanotubes can store H_2 at quite low temperatures and pressures.

Alternatively, H_2 can react at elevated temperatures with many transition metals and their alloys to form hydrides.

Table 1.1 shows relevant information for the different approaches of storing hydrogen. Gravimetric density (ρ_m) is defined as the weight percentage of hydrogen stored of the total weight, while volumetric density (ρ_v) is the stored hydrogen mass per unit volume of the system.

Table 1.1

storage method	ρ_m (weight %)	ρ_v (kg m^{-3})	T (°C)	P (MPa)
high pressure gaseous H_2	13	40	ambient	77
cryogenic liquid	variable	70.8	−252.87	atmospheric
adsorbed on carbon nanotubes	10.8	41	−196.15	6
absorbed to form hydrides	3	150	ambient	atmospheric

Extract 3

In order to perform meaningful comparisons of different routes to synthesise a particular product, we need metrics to measure the greenness of each route. The two oldest green metrics, the atom economy (AE) and the E factor, are the simplest and most popular green metrics. AE is a theoretical number which assumes the use of exact stoichiometric quantities of starting materials and a theoretical chemical yield.

$$\text{AE (\%)} = \frac{\text{molecular weight of product}}{\text{sum of molecular weight of reactants}} \times 100\ \%$$

The E factor, in contrast, is the actual amount of waste produced in the process and takes into account waste from all auxiliary components, for example, solvent losses and chemicals used in workup.

$$\text{E factor} = \frac{\text{total mass of waste}}{\text{mass of final product}}$$

Copyright Acknowledgements:

Extract 1 and 2 (adapted from Nikolaidis, P., & Poullikkas, A. (2017). *Renewable and sustainable energy reviews, 67*, 597-611.)

Extract 3 (adapted from *Sheldon, R. A. (2018). ACS Sustainable Chemistry and Engineering, 6(1), 32-48.)*