TAMPINES MERIDIAN JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

CANDIDATE NAME

CIVICS GROUP

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **12 September 2024**

2 hours

Candidates answer on the Question Paper.

Additional materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your name and civics group in the spaces at the top of this page.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams and graphs.

Do not use paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

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.

For Examiner's Use		Percentage
Paper 1	**/ 30**	**/ 15**
Paper 2		
1	**/ 13**	
2	**/ 13**	
3	**/ 17**	
4	**/ 16**	
5	**/ 16**	
Paper 2 Total	**/ 75**	**/ 30**
Paper 3	**/ 80**	**/ 35**
Paper 4	**/ 55**	**/ 20**
Grand Total		**/ 100**

This document consists of **22** printed pages.

1 Some main group elements are similar to transition elements as they are capable of showing different oxidation states.

(a) Fig. 1.1 shows a sketch of the nine successive ionisation energies of element **A**, a main group element.

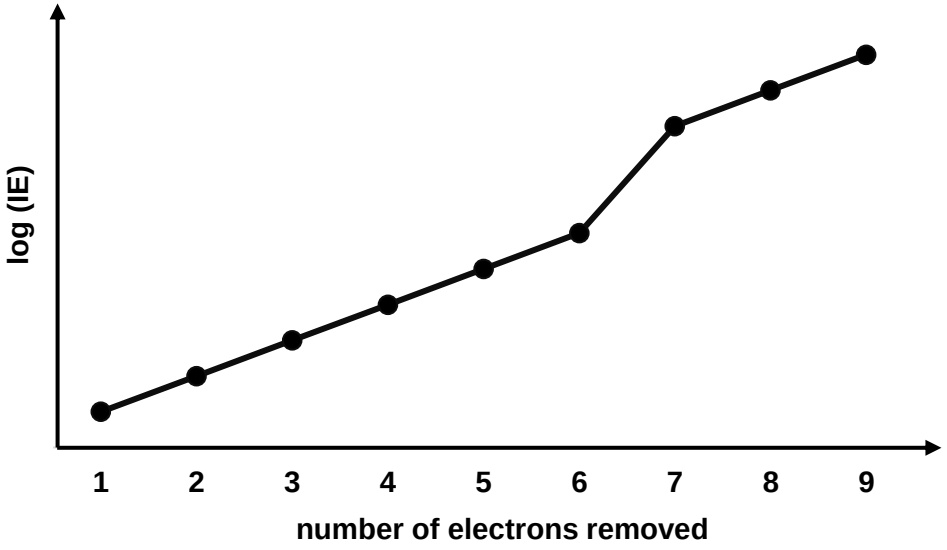

Fig. 1.1

(i) Write the equation for the third ionisation energy of element **A**.

..... [1]

(ii) Explain the general trend in successive ionisation energy shown in the graph of Fig. 1.1.

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..... [2]

(iii) Suggest, with reasoning, the group number of element **A** and state its identity, given that it belongs to Period 4.

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..... [2]

Transition elements form complexes that are responsible for the colour of many gemstones such sapphires and rubies.

(b) Define the term *transition element*.

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..... [1]

(c) In an isolated gas phase transition metal ion, the *d*-orbitals have the same energy. However, in the octahedral complex ion, $[Cr(H_2O)_6]^{3+}$, the d subshell is spilt into two energy levels.

(i) Complete the electronic configuration of Cr and Cr^{3+}.

Cr : $1s^2$ .....

Cr^{3+} : $1s^2$ ..... [1]

(ii) Explain why the splitting of *d*-orbitals occurs in the presence of ligands.

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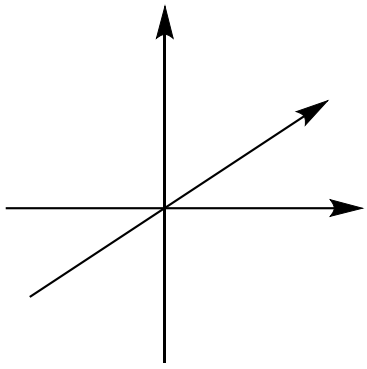
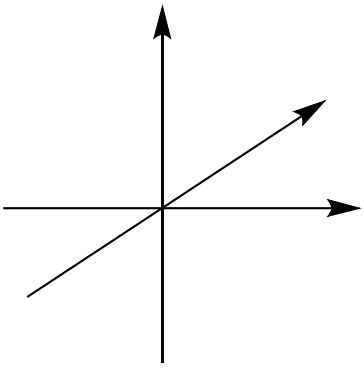
..... [1]

(iii) Draw and name the shape of one of the *d* orbitals in the lower energy level and one of the *d* orbitals in the upper energy level for the octahedral complex ion. Indicate the axes labels clearly.

	
Name of lower energy *d* orbital: _____	Name of upper energy *d* orbital: _____

[2]

(iv) Cr^{3+} ions forms a complex that gives rise to the red colour of rubies. Explain how the colour arises.

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..... [2]

(d) Chromium(III) picolinate, $Cr(C_5H_4N(COO))_3$, another bright red complex, is used to treat Type 2 diabetes. Picolinate is bidentate and forms an octahedral complex ion with chromium(III). The nitrogen atom in the benzene ring of picolinate has a lone pair of electrons available for coordination.

picolinate ligand

Using the information provided, draw the octahedral structure of chromium(III) picolinate in the space below showing the coordinate bonds clearly.

[1]

[Total: 13]

2(a) Magnesium oxide reacts reversibly with chlorine according to the following equation.

equation 2.1 $2MgO(s) + 2Cl_2(g) \rightleftharpoons 2MgCl_2(s) + O_2(g)$

Under certain conditions, a dynamic equilibrium is established.

(i) Explain what is meant by the term *dynamic equilibrium*.

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.....

..... [1]

(ii) At 1.00×10^5 Pa and 500 K, 70% of the initial amount of $Cl_2(g)$ has reacted with MgO.

Calculate the equilibrium constant, K_p for the reaction.

[2]

(iii) Predict and explain the effect of decreasing the volume of the system in equation 2.1 on the

- composition of reactants and products

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..... [2]

- equilibrium constant, K_p.

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..... [1]

(b) Hard water is water that contains high concentrations of calcium and magnesium ions.

Temporary hard water consists of dissolved hydrogencarbonate (HCO_3^-) ions. Heating HCO_3^- causes it to decompose according to equation 2.2. The carbonate then forms an insoluble metal carbonate with one of the metal ions according to equation 2.3, which gives the characteristic white 'scales' found in kettles used to boil such water.

equation 2.2 $2HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + CO_2(g) + H_2O(l)$

equation 2.3 $M^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons MCO_3(s)$ where M = Ca or Mg

(i) With reference to the equations given above, explain why the hardness of temporary hard water can be reduced by boiling.

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..... [1]

The numerical value of the solubility products of some of the compounds involved in the processes in part **(b)** are shown in Table 2.1.

Table 2.1

Compound	Solubility product, K_{sp}, at 25 °C
$CaCO_3$	2.8×10^{-9}
$MgCO_3$	3.5×10^{-8}
$Ca(OH)_2$	5.5×10^{-6}
$Mg(OH)_2$	1.8×10^{-11}

(ii) Deduce whether calcium or magnesium ion is likely to be precipitated out first in equation 2.3.

.....

..... [1]

Hard water can be softened by raising the pH of the water to precipitate out some metal ions.

A sample of hard water contained equal concentrations of calcium and magnesium ions at 8.00×10^{-3} mol dm^{-3} each. Its pH was raised to 10.0 at 25 °C.

(iii) By considering the relevant ionic product, deduce which metal ion will be precipitated out.

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..... [2]

(c) Phosphates from fertilizers used in agriculture could enter the water supply and combine with calcium ions present to form the sparingly soluble salt calcium phosphate, $Ca_3(PO_4)_2$. The value of K_{sp} for calcium phosphate is 1.0×10^{-26}.

(i) Write the K_{sp} expression and calculate the solubility, in mol dm^{-3}, of calcium phosphate. [2]

(ii) Suggest why calcium phosphate is expected to be less soluble in phosphoric acid than it is in water.

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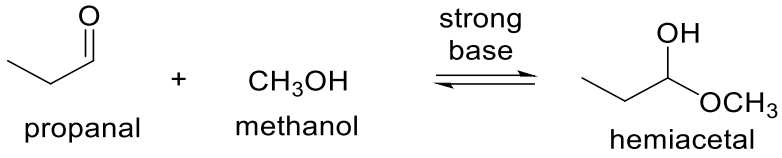
..... [1]

[Total: 13]

3(a) In the presence of a base catalyst, aldehyde can react with alcohol via nucleophilic addition to give hemiacetal. An example involving propanal and methanol is shown below.



This reaction occurs via a three-step mechanism.

Step 1 The base removes a proton to form a methoxide anion, CH_3O^-.

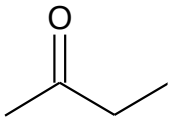
Step 2 The methoxide anion undergoes nucleophilic addition with the carbonyl group generating an anionic intermediate, in a rate determining step.

Step 3 The anionic intermediate abstracts a proton from a CH_3OH molecule.

Draw the mechanism for steps 2 and 3 of the reaction between propanal and methanol. In your answer, you should show all relevant charges, dipoles, and lone pairs; and show the movement of electrons using curly arrows.

[3]

(b) Butanone undergoes the same nucleophilic addition reaction with methanol.



butanone

Observations were made about the reactions as shown in Table 3.1.

Table 3.1

	Reaction between propanal and methanol	Reaction between butanone and methanol
Relative rate of reaction	faster	slower
Optical activity of product	does not rotate plane polarised light	does not rotate plane polarised light

(i) Draw the structure of the product formed from the reaction between butanone and methanol.

[1]

(ii) Explain the observations made about the two reactions in Table 3.1. Use the concepts of electronic and steric effects, and stereochemistry in your answer.

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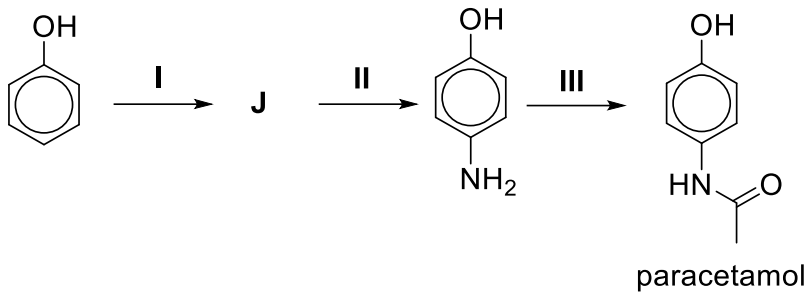
..... [3]

(c) Paracetamol is an over-the-counter medication used to treat pain and fever. It can be prepared from phenol via a three-step synthesis as shown below.



paracetamol

(i) Suggest the structure of compound **J**. [1]

(ii) Suggest the reagents and conditions for steps **II** and **III**.

step **II**: .....

step **III**: ..... [2]

(iii) Identify one possible organic side product with the molecular formula, $C_6H_4N_2O_5$, formed in step **I**. Suggest the reaction conditions to minimise its formation.

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..... [2]

(d) Amino acids are soluble in both dilute acids and dilute alkalis due to the ability to exist as zwitterions.

(i) Explain what is meant by the term zwitterion.

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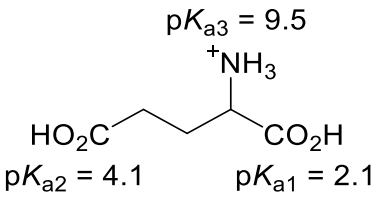
..... [1]

(ii) There are three pK_a values associated with glutamic acid: 2.1, 4.1 and 9.5.



Use the given pK_a values to suggest

1. the structure of the major species present in a solution of glutamic acid at pH 6.0 [1]

2. a pH at which the predominant species of glutamic acid is a zwitterion.

pH = ... [1]

(e) Compound **K** and **L** are isomers.

$CH_3COCH_2N(CH_3)_2$	$CH_3CH_2CON(CH_3)_2$
Compound **K**	Compound **L**

Which of the isomers is a stronger base? Explain.

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..... [2]

[Total: 17]

4 Two fatal explosions occurred at a hazardous chemical storage facility in Tianjin, China, almost a decade ago in August 2015. The chain of events which happened on that day is described below.

Stage 1: Fire

An overheated container of dry nitrocellulose was reported to cause the initial fire. Firefighters arrived at the scene to douse the flames with water.

Stage 2: Reaction between water and calcium carbide

Without prior knowledge of calcium carbide, $CaC_2(s)$, also being stored in the facility, the firefighters continued spraying water on the chemical which quickly fizzled and released an explosive gas, ethyne, $C_2H_2(g)$.

equation 4.1 $\quad CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$

Stage 3: First explosion

After the ethyne had mixed sufficiently with the surrounding air, one part of this explosive gas mixture was ignited by the pre-existing flames, causing the first explosion.

equation 4.2 $\quad C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(g)$

Stage 4: Second explosion

The heat from the first explosion initiated a runaway decomposition of about 800 tonnes (1 tonne = 1000 kg) of ammonium nitrate, $NH_4NO_3(s)$, which was stored nearby. This decomposition reaction produced a large quantity of gases under high temperatures and pressures. The rapid expansion of the gases outwards destroyed almost everything in their path.

equation 4.3 $\quad 4NH_4NO_3(s) \rightarrow 3N_2(g) + 2NO_2(g) + 8H_2O(g)$

The aftermath

This was one of the worst industrial disasters in China that caused many deaths and injuries due to improper storage of explosive chemicals.

(a) The carbon atoms in CaC_2 and C_2H_2 have similar hybridisation and hence they have similar bonding between the two carbon atoms.

(i) State the hybridisation of the carbon atoms in CaC_2 and C_2H_2.

.....[1]

(ii) Using structure and bonding, explain why CaC_2 is a solid at room temperature and pressure while C_2H_2 is a gas.

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..... [2]

(iii) The anion in calcium carbide has an approximate M_r of 24 and the cation has an approximate A_r of 40. Draw a dot-and-cross diagram to show the type of bonding present within a formula unit of calcium carbide. [1]

(b) The reaction of calcium carbide with water is exothermic and spontaneous.

(i) Using the data in Table 4.1, calculate the enthalpy change of reaction for equation 4.1. [2]

Table 4.1

	enthalpy change / kJ mol^{-1}
$\Delta H_f^{\ominus}$ (CaC_2(s))	–59.0
$\Delta H_f^{\ominus}$ (H_2O(l))	–285.8
$\Delta H_f^{\ominus}$ ($Ca(OH)_2$(s))	–985.2
$\Delta H_f^{\ominus}$ (C_2H_2(g))	+226.6

(ii) Explain why the reaction in equation 4.1 is spontaneous at all temperatures.

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..... [1]

(c) The first explosion was due to the combustion of ethyne, which is given in equation 4.2.

equation 4.2 $$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(g)$$

(i) Using bond energy values from the *Data Booklet*, show that the enthalpy change of combustion of ethyne is -1240 kJ mol^{-1}. [2]

(ii) Calculate the mass of ethyne needed to be completely burnt to raise the temperature of 1 kg of water from 30 °C to its boiling point, assuming 80% efficiency. [2]

(d) The second explosion caused by the decomposition of ammonium nitrate created an orange-brown fireball larger than the first one.

(i) Suggest a reason why this second explosion was more detrimental than the first.

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..... [1]

(ii) Calculate the total volume of gases produced, in m^3, when all the ammonium nitrate decomposed at 1000 °C and 1 atm. Hence, show that the diameter of the fireball is 186 m, assuming that the gases occupy a sphere. [3]

[Volume of sphere = $\frac{4}{3}\pi r^3$; where r = radius; diameter = 2r]

(iii) The diameter of the fireball was measured to be about 180 m, which was smaller than the calculated value in **(d)(ii)**. Suggest a reason why this was so.

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..... [1]

[Total: 16]

5(a) The use of *Data Booklet* is relevant to this question.

The materials used for filling dental cavities have evolved significantly over the centuries. French dentists were among the first to innovate by mixing mercury with other metals to create a material that could be used to fill cavities effectively.

About a hundred years ago, a common filling material was copper amalgam, comprising roughly 30% copper and 70% mercury. However, this copper amalgam proved to be unstable and corroded over time. The copper in the amalgam oxidised while oxygen was reduced, leading to the generation of Cu^{2+} ions, which caused teeth to develop a stain.

(i) Construct the overall equation for the oxidation of copper by oxygen in the air in an acidic medium.

.....

..... [1]

(ii) Calculate the standard cell potential, $E^{\ominus}_{cell}$, for this reaction. [1]

(iii) Given that $E^{\ominus}_{cell} = \frac{RT}{n\,F} \ln K_c$, determine the K_c value for the corrosion of the copper amalgam. [1]

In contrast, modern dental amalgams are composed of a mixture of silver, tin, and mercury. This amalgam contains three distinct solid layers: Ag_2Hg_3, Ag_3Sn, and Sn_8Hg.

Ag_3Sn, and Sn_8Hg layers each have their specific reduction potentials.

	$E^{\ominus}$
Sn^{2+} / Ag_3Sn	– 0.05 V
Sn^{2+}/ Sn_8Hg	– 0.13 V

(iv) Suggest and explain which of these layers is more likely to be corroded by oxygen.

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..... [1]

The electrochemical properties of dental amalgams can cause discomfort in some unexpected situations. For instance, if a person accidentally bites down on a piece of aluminum foil used in candy wrappers and it comes into contact with a dental filling, an electrochemical cell is created in the mouth. This "cell" generates a small electric current that can result in a sharp, sudden pain. In this electrochemical reaction, the Sn^{2+} ions formed from the amalgam reacts with the aluminum and this leads to the formation of tin metal.

(v) Write the overall equation for the electrochemical reaction between the Sn^{2+} ions in the amalgam and aluminium.

..... [1]

Small pieces of gold leaf can be used to decorate luxurious desserts. Unlike aluminium, gold does not induce pain when bitten.

(vi) Suggest why biting on a piece of gold metal does not cause the pain that aluminium foil does.

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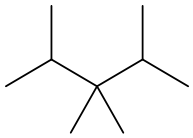
..... [1]

(b) Scientists are studying 2,3,3,4-tetramethylpentane, which has a molecular formula of C_9H_{20}. During the investigation, they study the free radical substitution chlorination of this alkane to understand the distribution of chlorinated products.



2,3,3,4-tetramethylpentane

(i) Draw the structures for all possible monochlorinated isomers of 2,3,3,4-tetramethylpentane. [2]

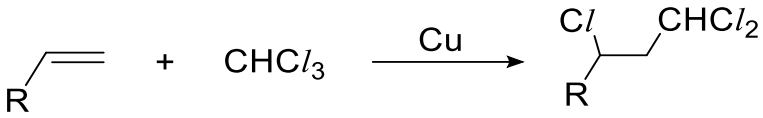
(ii) It is found by experiment that during this type of reaction, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates as shown in Table 5.1.

Table 5.1

Reaction	relative rate
$RCH_3 \rightarrow RCH_2Cl$	1
$R_2CH_2 \rightarrow R_2CHCl$	4
$R_3CH \rightarrow R_3CCl$	5

Calculate the expected relative ratio of the monochlorinated isomers produced from the chlorination of 2,3,3,4-tetramethylpentane, using the information in Table 5.1 and the number of hydrogen atoms of each (primary, secondary or tertiary) within the molecule. [1]

(c) The Kharasch addition is a copper-catalysed free radical addition reaction where compounds such as excess $CHCl_3$ are added to terminal alkenes.



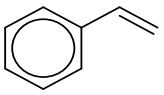
The reaction proceeds via the following steps.

- The initiation step involves the formation of a dichloromethyl free radical ($•CHCl_2$) from $CHCl_3$ by the abstraction of the chlorine atom.
- The first propagation step involves $•CHCl_2$ adding to a terminal alkene molecule to form a free radical intermediate. The relative stabilities of free radical intermediates are similar to the relative stabilities of carbocations.
- In the second propagation step, the free radical intermediate formed in the step 2 reacts with **excess** $CHCl_3$ to form the final product and regenerate $•CHCl_2$.

(i) Write equations for the first and second propagation steps in this reaction between $•CHCl_2$ and styrene. (curly arrows are not required) In your answer, show clearly the structure of the free radical intermediate that is formed in the first propagation step.

[2]

You can represent styrene as $Ph–CH=CH_2$ in your drawing.



= $PhCH=CH_2$

stryene

In the above reaction, more than one possible free radical intermediate can be generated. Explain why one free radical intermediate is likely to be formed in greater proportion.

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.....

..... [1]

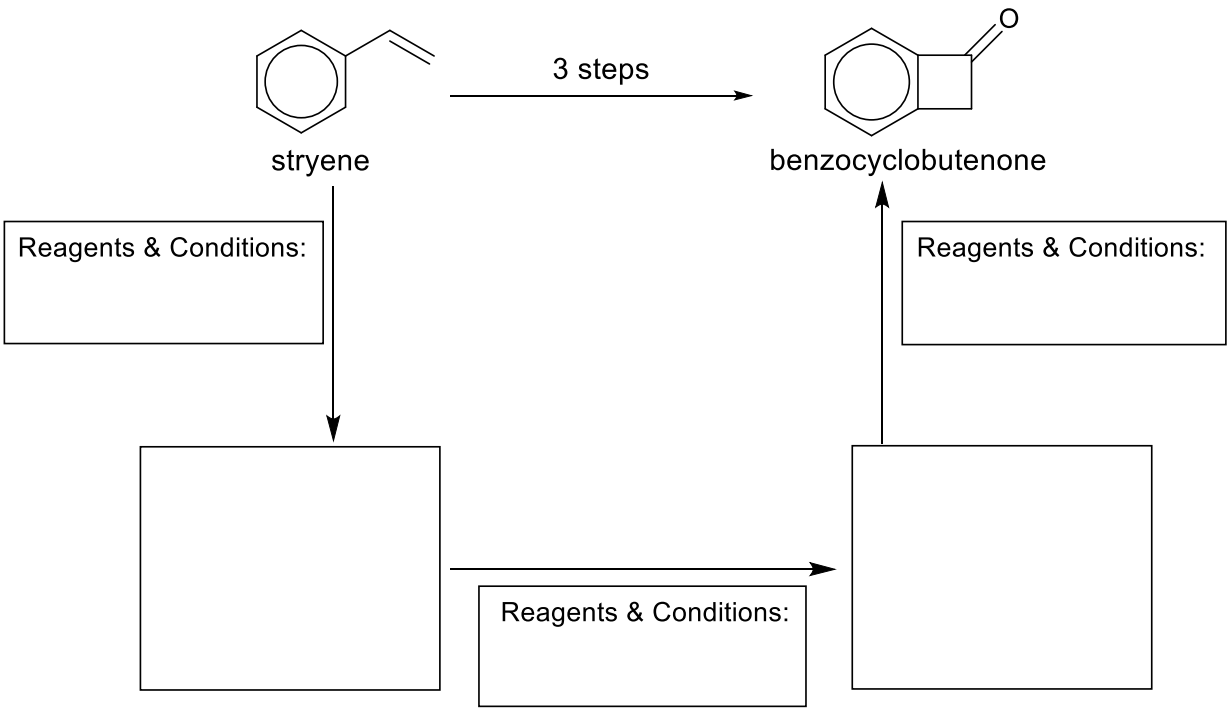
If excess styrene is used, the free radical intermediate formed in the first propagation step will react with styrene to generate another radical of larger molecular mass.

(ii) Compound **B** with a molecular formula of $C_{17}H_{17}CI_3$ is formed in a reaction that involves excess styrene reacting with $CHCI_3$ in 2:1 mole ratio.

Suggest the structure of compound **B**. [1]

(d) Benzocyclobutenone can be synthesised from styrene in three steps.

Suggest reagents and conditions for each step. Draw the structures of the intermediate compounds. [3]



[Total: 16]