Cambridge Pre-U

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

CHEMISTRY **9791/03**

Paper 3 Part B Written **October/November 2020**

2 hours 15 minutes

You must answer on the question paper.

You will need: Data booklet

INSTRUCTIONS

- Answer **all** 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 candidate 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 or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working, use appropriate units and use an appropriate number of significant figures.

INFORMATION

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

For Examiner's Use	
1	
2	
3	
4	
5	
6	
Total	

This document has **20** pages. Blank pages are indicated.

1 This question is about weak acids.

(a) Ethanoic acid is a weak acid with a pK_a value of 4.76.

(i) State what is meant by the term *weak acid*.

....

.... [1]

(ii) Write the expression for the acid dissociation constant, K_a, for ethanoic acid in terms of concentrations.

K_a =

[1]

(iii) Calculate the pH of a 0.150 mol dm^{-3} solution of ethanoic acid.

Give your answer to **two** decimal places.
Show your working.

pH = ... [3]

(b) Chloroethanoic acid, $CH_2C\mathit{l}COOH$, and its sodium salt, $CH_2C\mathit{l}COONa$, can be used to make a buffer solution. The pK_a of chloroethanoic acid is 2.89.

(i) State what is meant by a *buffer solution*.

....

.... [1]

(ii) Explain how a solution of chloroethanoic acid and its sodium salt form a buffer solution. Use equations in your answer.

....

....

....

....

....

....

.... [3]

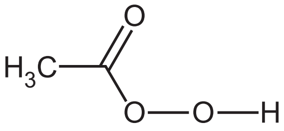
(iii) Calculate the mass of sodium chloroethanoate, $CH_2C\mathit{l}COONa$, that must be added to 250 cm^3 of 0.200 $mol\,dm^{-3}$ chloroethanoic acid, $CH_2C\mathit{l}COOH$, to form a buffer solution with a pH of 3.00.
Show your working.

mass of $CH_2C\mathit{l}COONa$ to be added = ... g [3]

(c) Acidic strength can be compared using pK_a values.

acid	formula	pK_a
chloroethanoic acid	$CH_2ClCOOH$	2.89
ethanoic acid	CH_3COOH	4.76
peroxyethanoic acid	CH_3COOOH	8.20

Peroxyethanoic acid is an example of a peroxyacid. Peroxyacids contain the COOOH functional group.



peroxyethanoic acid

Suggest why chloroethanoic acid has a lower pK_a than ethanoic acid and why peroxyethanoic acid has a higher pK_a than ethanoic acid.

....

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....

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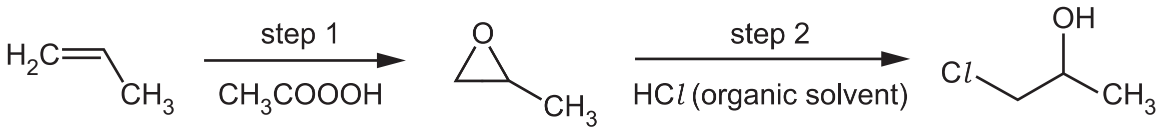
....

....

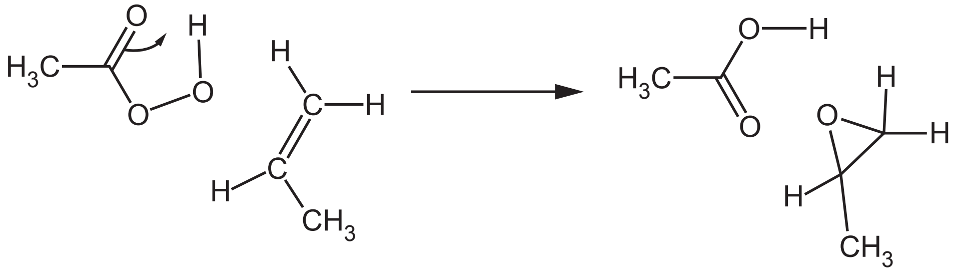
.... [4]

(d) Peroxyethanoic acid is used in the synthesis of 1-chloropropan-2-ol. An epoxide intermediate is formed.



(i) The reaction mechanism for step 1 is known as the 'butterfly mechanism' and it involves the movement of four pairs of electrons. The movement of one of the pairs of electrons is shown in the diagram.

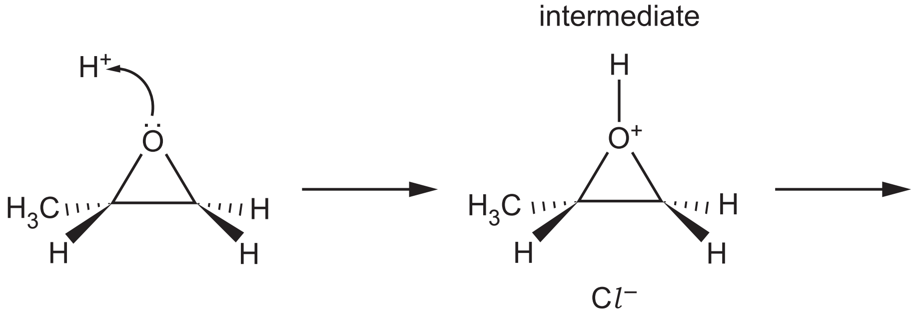
By drawing appropriate curly arrows on the diagram, suggest the other **three** electron pair movements.



[3]

(ii) Step 2 forms a mixture of products. Protonation of the epoxide oxygen occurs first, followed by the attack of the chloride ion on either $\delta+$ carbon of the intermediate species.

- Suggest the name of the reaction mechanism.
- Complete the reaction mechanism. Include all relevant lone pairs of electrons, dipoles and curly arrows.
- Comment on the formation of **structural** isomers in the products.



name of reaction mechanism ....

comment ....

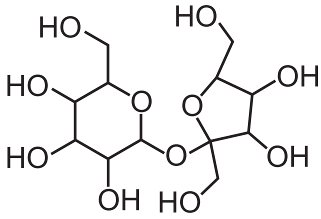
....

....

[4]

[Total: 23]

2 The structure of sucrose is shown.



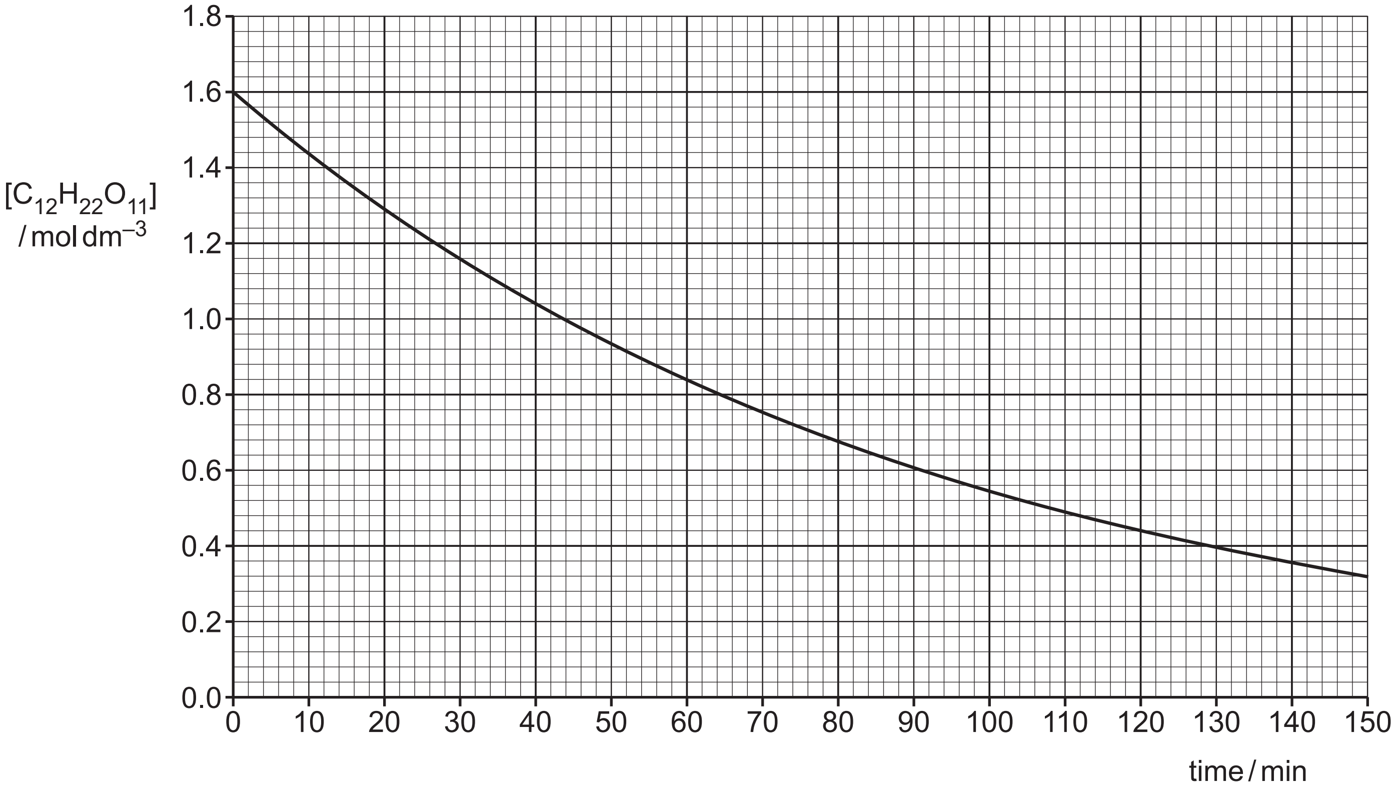
sucrose, $C_{12}H_{22}O_{11}$

Sucrose can be hydrolysed using an acid catalyst.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} 2C_6H_{12}O_6$$

A series of experiments is carried out to investigate the kinetics of this reaction.

(a) In one experiment, the change in the concentration of sucrose, $[C_{12}H_{22}O_{11}]$, is recorded over time.



(i) By determining two half-lives, show that the rate of reaction is first order with respect to $[C_{12}H_{22}O_{11}]$. Draw construction lines on the graph.

....

....

.... [2]

(ii) Suggest why, in this experiment, $[H^+]$ is constant as $[C_{12}H_{22}O_{11}]$ decreases.

.... [1]

(b) The rate of reaction was also found to be first order with respect to $[H^+]$, but zero order with respect to $[H_2O]$.

(i) State the rate equation for this reaction.

rate = ... [1]

(ii) Give units for the rate constant, *k*.

units = ... [1]

(c) Further experiments were conducted and the following information about the reaction found.

rate constant, *k*, at 25 °C = 1.73×10^{-4} (units not shown)
pre-exponential factor, *A* = 1.51×10^{15} (units not shown)

Calculate the activation energy, in kJ mol^{-1}, at 25 °C for the reaction.

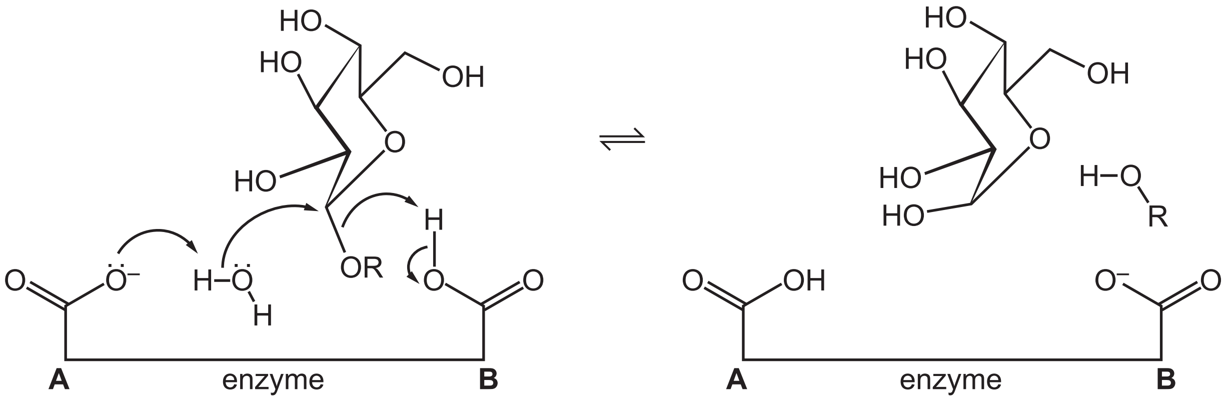
Use the appropriate equation from the Data Booklet.
Show your working.

activation energy = ... kJ mol^{-1} [3]

(d) Sugars like sucrose are an essential part of a healthy diet. In the body, they are broken down into simpler sugars by enzymes.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{enzyme}} 2C_6H_{12}O_6$$

A typical mechanism for this reaction is shown. Two functional groups on the enzyme are labelled **A** and **B** and the structure of the enzyme is simplified.



In this reaction, one of the functional groups on the enzyme acts as an acid and the other as a base.

(i) State which of the functional groups, **A** or **B**, acts as a Brønsted-Lowry acid in the forward reaction. Explain your answer.

....

.... [1]

(ii) Explain, with reference to functional groups **A** and **B**, why the enzyme is effective only within a narrow pH range.

....

....

.... [1]

(iii) Sketch a graph on the axes below to show the effect of pH on the rate of reaction.

[1]

[Total: 11]

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3 An organic compound, **X**, is analysed.

(a) **(i)** **X** is found to contain 52.5% carbon and 7.5% hydrogen by mass, with the rest being oxygen.

The mass spectrum of **X** has a molecular ion signal at *m/z* = 160.

Show that the molecular formula of **X** is $C_7H_{12}O_4$.

[3]

(ii) The mass spectrum of **X** also shows a small signal at *m*/*z* = 161.

Explain the origin of this signal and determine its height as a percentage of the molecular ion signal.

explanation ....

....

height = ... % [2]

(iii) The mass spectrum of **X** also shows a signal at *m*/*z* = 131. The species responsible for this signal contains four oxygen atoms.

Construct an equation for the formation of the species responsible for this signal.

Use molecular formulae.

.... [3]

(b) The proton NMR spectrum of **X** shows only three peaks with the following properties.

δ / ppm	splitting pattern	integral
1.3	triplet	0.50
3.4	singlet	0.17
4.2	quartet	0.33

(i) Explain why the peak at δ = 4.2 ppm is further downfield than the other peaks and suggest what causes this shift.

....

....

.... [2]

(ii) The peak at δ = 1.3 ppm is split into a triplet.

What information does this splitting pattern give about the structure of **X**?

.... [1]

(iii) What do the following chemical test results show about the structure of **X**?

- **X** does not react with acidified sodium dichromate(VI).

....

- **X** reacts with aqueous acid, forming ethanol as one of the products.

....

....

[2]

(iv) The carbon-13 NMR spectrum of **X** shows four peaks. Draw the skeletal structure of **X**.

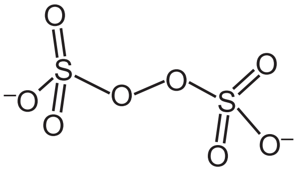
[1]

(c) Another compound, **Y**, is a structural isomer of **X**.
1 mol of **Y** reacts exactly with 1 mol of sodium carbonate.
Y has four peaks in its carbon-13 NMR spectrum and three peaks in its proton NMR spectrum.
Suggest a structure for **Y**.

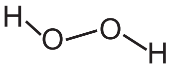
[2]

[Total: 16]

4 The peroxodisulfate ion, $S_2O_8^{2-}$, consists of two units bridged by an O–O single bond, similar to that in hydrogen peroxide. The O atoms in this O–O single bond have an oxidation number of −1 as do the O atoms in the O–O single bond of hydrogen peroxide.



peroxodisulfate ion



hydrogen peroxide

(a) Peroxodisulfate ions react with iodide ions to form iodine and sulfate ions, SO_4^{2-}, in a redox reaction.

The ionic equation for this reaction is given.

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

(i) Use oxidation numbers to complete the following for this reaction.

element oxidised .... from .... to ....

element reduced .... from .... to .... [2]

(ii) The half-equations for the reaction are shown.

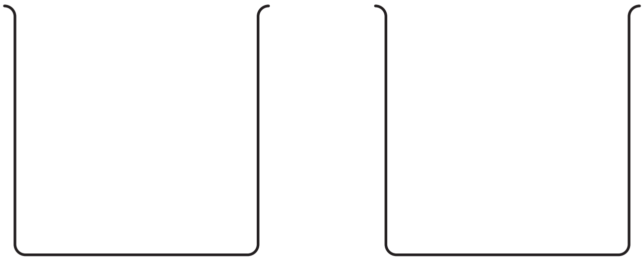
$$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq) \qquad E^\ominus = +0.54\,V$$

$$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq) \qquad E^\ominus = +2.01\,V$$

Calculate $E^\ominus_{cell}$ for the reaction.

$E^\ominus_{cell}$ = ... [1]

(iii) Complete and label the diagram of the electrochemical cell, consisting of two half-cells, that could be used to measure a value for E_{cell} for this reaction.



[4]

(iv) Describe this cell using standard cell notation.

.... [1]

(v) Some silver nitrate, $AgNO_3$, is added to the iodide/iodine half-cell.

State and explain the effect, if any, on the potential of this half-cell.

Hence state the effect, if any, on the overall cell potential.

....

....

....

....

.... [4]

(b) When peroxodisulfate ions and iodide ions are mixed in solution, the reaction is very slow because it has a relatively high activation energy.

(i) Suggest why the activation energy is high for this reaction.

....

.... [1]

(ii) Describe how you might follow the progress of this reaction.

....

....

....

.... [2]

(c) The reaction between peroxodisulfate ions and iodide ions can be catalysed by the addition of Fe^{3+}(aq) ions.

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^\ominus = +0.77\,V$$

(i) What type of catalyst is Fe^{3+}(aq) in this reaction? Explain your answer.

....

....

.... [2]

(ii) The catalysed reaction proceeds in two steps. The first step involves the reaction of Fe^{3+} with I^-.

Write equations for each step.

step 1 ....

step 2 ....
[2]

(iii) Suggest whether $Fe^{2+}(aq)$ would also act as a catalyst in this reaction. Explain your answer.

....

.... [1]

(iv) Comment on the suitability of $V^{3+}(aq)$ and the suitability of $Mn^{3+}(aq)$ as catalysts for the reaction.

Use the relevant half-equations.

$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$ $E^\ominus = +0.54\,V$

$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$ $E^\ominus = +2.01\,V$

$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$ $E^\ominus = -0.26\,V$

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $E^\ominus = +0.77\,V$

$Mn^{3+}(aq) + e^- \rightleftharpoons Mn^{2+}(aq)$ $E^\ominus = +1.49\,V$

....

....

....

....

....

.... [3]

[Total: 23]

5 This question is about iron.

(a) Complete the electronic configurations.

Fe atom $1s^2$ ....

Fe^{3+} ion $1s^2$ ....

[2]

(b) Aqueous iron(II) and iron(III) compounds contain $[Fe(H_2O)_6]^{2+}(aq)$ and $[Fe(H_2O)_6]^{3+}(aq)$ complex ions respectively.

(i) Explain what is meant by the term *complex ion*.

....

.... [2]

(ii) Draw a three-dimensional diagram of the $[Fe(H_2O)_6]^{2+}(aq)$ ion.

Name the shape of the ion and state the O-Fe-O bond angle.

name of shape ....

bond angle ....

[3]

(iii) Explain why a solution of Fe^{2+} ions is coloured.

....

....

....

....

....

....

.... [4]

(c) When sodium hydroxide is added to a solution of $Fe^{2+}(aq)$, a precipitate of iron(II) hydroxide, $Fe(OH)_2$, forms.

$Fe(OH)_2$ has a K_{sp} value of 8.0×10^{-16} at 298 K.

(i) Write the expression for $K_{sp}(Fe(OH)_2)$.

$K_{sp} =$

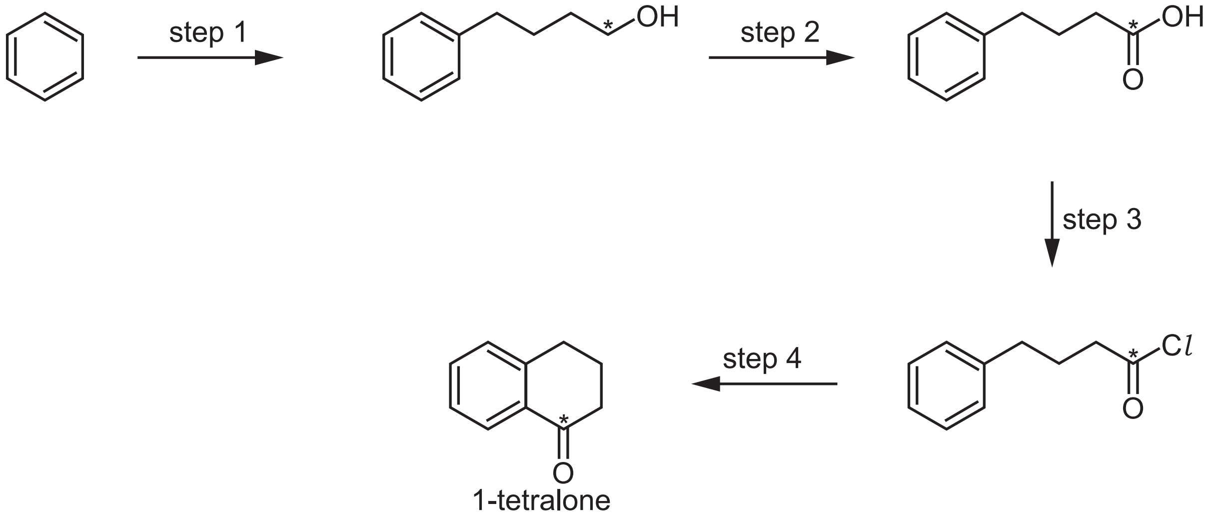
[1]

(ii) Calculate the solubility at 298 K, in $mol\,dm^{-3}$, of $Fe(OH)_2$.
Show your working.

solubility of $Fe(OH)_2$ = ... $mol\,dm^{-3}$ [3]

[Total: 15]

6 Benzene can be used to make 1-tetralone, $C_{10}H_{10}O$, in the following synthesis.



(a) Suggest reagents and conditions for each of the four steps.

step 1 ....

step 2 ....

step 3 ....

step 4 ....

[5]

(b) One of the carbon atoms is marked with an asterisk, *.

State how this carbon changes its functional group level, FGL, in this synthesis and categorise the reactions of the following steps.

(i) Step 2: FGL goes from .... to ....

The reaction in step 2 is .... [2]

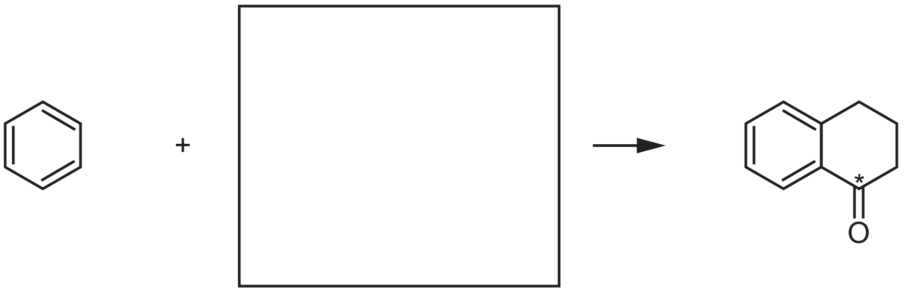
(ii) Step 3: FGL goes from .... to ....

The reaction in step 3 is .... [2]

(iii) Step 4: FGL goes from .... to ....

The reaction in step 4 is .... [2]

(c) Suggest the structure of an organic reagent that could form 1-tetralone from benzene in a single step.



[1]

[Total: 12]

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