EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2021
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME							
CIVICS GROUP	**2**	**0**	**–**			REGISTRATION NUMBER	

CHEMISTRY

9729/02

Paper 2 Structured Questions

16 September 2021
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not use paper clips, highlighters, glue or correction fluid.
Write your name, civics group, registration 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.
Answer all questions on the **Question Paper**
The number of marks is given in brackets [ ] at the end of each question or part question.

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

For Examiner's Use	
Paper 2	
1	/ 15
2	/ 12
3	/ 13
4	/ 15
5	/ 20
Total	**/ 75**

This document consists of **19** printed pages and **1** blank page.

For Examiner's Use

1 Nitrosyl chloride, NO*Cl* decomposes at temperatures above 100 °C to form nitrogen monoxide and chlorine as shown in the equation below.

$$2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$$

(a) A sample of NO*Cl* was allowed to decompose at 127 ºC and 147 atm. Assuming that NO*Cl* behaves ideally, show that its initial concentration is 4.48 mol dm^{-3}.

[2]

(b) A student pointed out that the assumption in **(a)** that NO*Cl* behaves ideally is not valid. Suggest and explain **two** possible reasons why this may be so.

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.....[2]

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(c) The change in the concentration of NOCl was monitored as the decomposition reaction occurred over time. The data obtained is shown in Fig. 1.1.

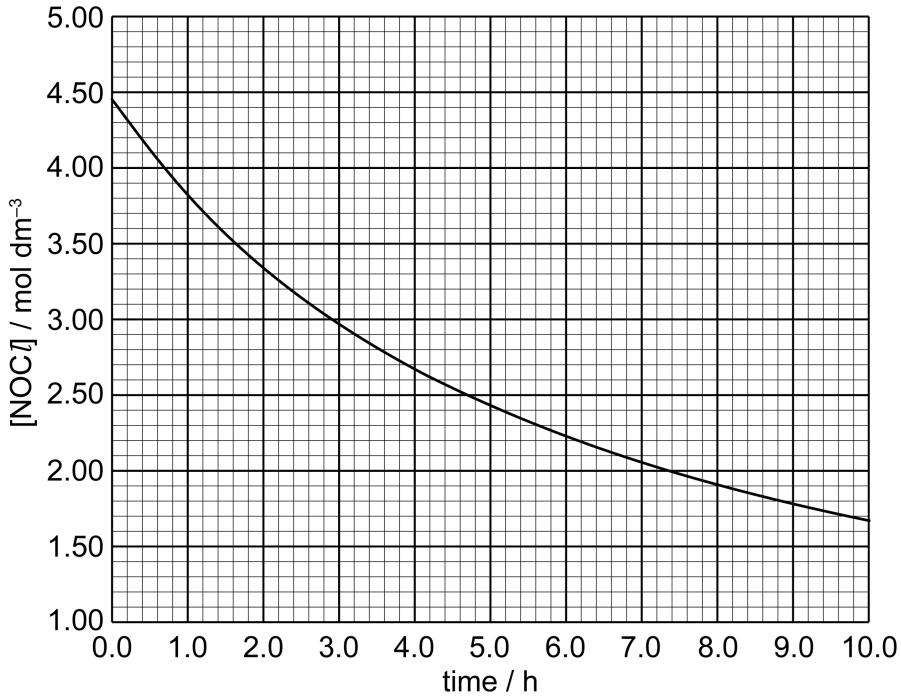

Fig. 1.1

(i) Using Fig. 1.1, show that the reaction is second order with respect to NOCl.

[3]

(ii) Given that the rate equation is $\text{rate} = k[\text{NOC}l]^2$, calculate the rate constant of the reaction, stating its units clearly.

[2]

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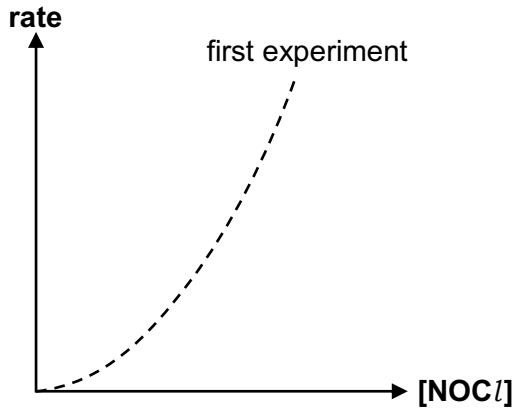
(iii) A second experiment was conducted under the same conditions, but using half the initial concentration of NOC*l*.

On the axes provided below, sketch the graph that will be obtained using data from the second experiment, relative to that provided for the first experiment.



[1]

(d) (i) Define *half-life*.

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.....

..... [1]

(ii) The rate equation for the second-order decomposition of NOC*l* can also be represented in the following manner:

$$\frac{1}{[\text{NOC}l]_t} - \frac{1}{[\text{NOC}l]_0} = kt$$

where $[\text{NOC}l]_t$ = concentration of NOC*l* at time, *t*,

$[\text{NOC}l]_0$ = original concentration of NOC*l*, and

k = rate constant

Using this equation, derive an expression for the half-life of the reaction.

[1]

For Examiner's Use

(iii) Hence, state and explain whether the half-life of a second-order reaction will increase or decrease as the reaction proceeds.

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.....[1]

(e) The reverse of the decomposition reaction can also occur such that NOCl is formed from NO and Cl_2.

Given that a possible mechanism for the reaction is as shown below, suggest the rate equation for the reaction.

Step 1: $NO + NO \rightleftharpoons N_2O_2$ (fast)

Step 2: $Cl_2 + N_2O_2 \xrightarrow{\text{slow}} 2NOCl$

[2]

[Total: 15]

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2 During the 2000s, researchers looked into creating high-capacity rechargeable batteries for use in energy storage in renewable energy generation. The zinc-cerium battery shown in Fig. 2.1 is one example of such a rechargeable battery involving redox flow.

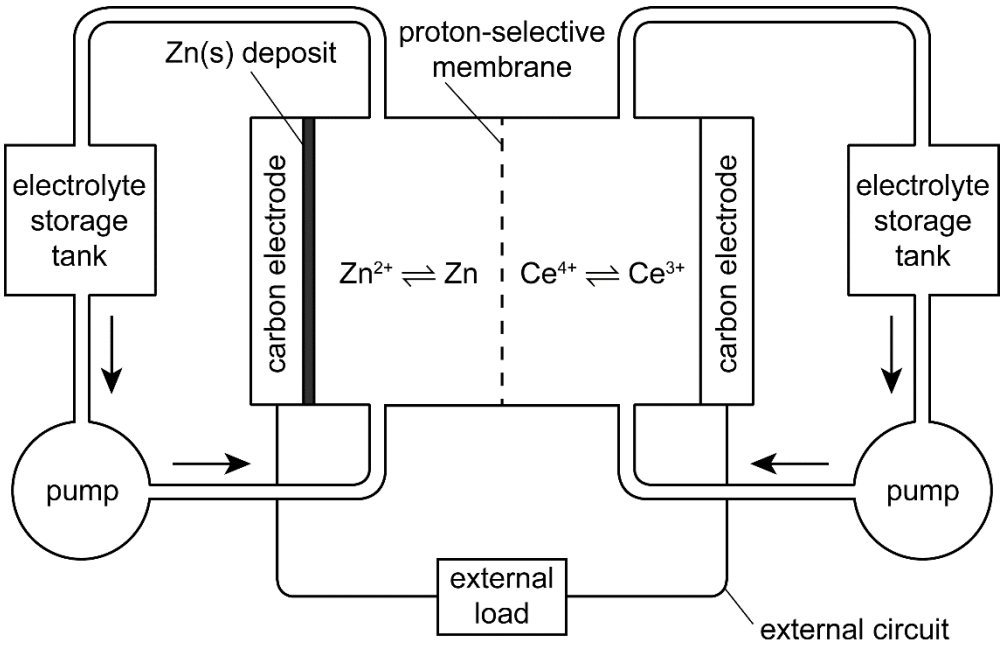

Fig. 2.1

The half-cells are made up of the following:

half-cell	electrolyte	electrode
Zn^{2+}/Zn	$Zn(CH_3SO_3)_2(aq)$, $CH_3SO_3H(aq)$	carbon-based polymer (similar to graphite) with fine Zn metal particles on surface
Ce^{4+}/Ce^{3+}	$Ce(CH_3SO_3)_3(aq)$, $Ce(CH_3SO_3)_4(aq)$, $CH_3SO_3H(aq)$	carbon-based polymer (similar to graphite)

The two electrolytes, consisting of methanesulfonic acid, CH_3SO_3H, and the respective salts, are separated by a proton-selective membrane.

(a) During the discharge process, the Zn^{2+}/Zn half-cell undergoes oxidation.

(i) Identify the polarity of the electrodes for the half-cells during the discharge process.

Zn^{2+}/Zn: ..... Ce^{4+}/Ce^{3+}: ..... [1]

(ii) Draw on Fig. 2.1 the direction of electron flow in the external circuit during the discharge process. [1]

For Examiner's Use

(iii) Write the overall equation for the reaction during the discharge process.

.....[1]

(iv) Given that $E^{\ominus}\left(Ce^{4+}\middle|Ce^{3+}\right) = +1.44\ V$, with the aid of the *Data Booklet*, calculate the $E^{\ominus}_{cell}$ for the reaction during the discharge process.

[1]

(v) Hence, calculate the standard Gibbs free energy in kJ mol^{-1}.

[1]

(b) Methanesulfonic acid dissociates fully in water. During the discharging process, the Zn^{2+}/Zn half-cell becomes more positive than the Ce^{4+}/Ce^{3+} half-cell over time.

(i) Explain how the proton exchange membrane maintains electrical neutrality.

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.....[1]

When a high concentration of methanesulfonic acid was used, it was found that cerium(III) methanesulfonate, $Ce(CH_3SO_3)_3$, precipitates out in the electrolyte.

(ii) Suggest the effect on E_{cell} when a higher concentration of methanesulfonic acid was used as the electrolyte. Explain your answer.

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.....[2]

For Examiner's Use

(c) Although the zinc-cerium battery has potential in renewable energy storage, some side-reactions hinder its application.

During the **charging process**, the electromotive force used is large enough to drive these side-reactions to be thermodynamically feasible.

Using relevant values from the *Data Booklet,* identify one side-reaction during the charging process and explain why it will occur.

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.....[2]

(d) Suggest

(i) why the carbon-based polymer can be used as a suitable material for the electrode for the Ce^{3+}/Ce^{4+} half-cell.

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.....[1]

(ii) why the zinc-cerium battery has a short lifespan, by considering the possible reactions occurring at the Zn^{2+}/Zn half-cell.

.....

.....[1]

[Total: 12]

For Examiner's Use

3 Double indicator acid-base titrations are used in scenarios where there is more than one end-point to a titration. Hence, it can also be used to determine the composition of mixtures of acids, as well as the pH of buffer solutions formed from polyprotic acids.

A typical example of a polyprotic acid is carbonic acid, where:

$$H_2CO_3(aq) + H_2O(l) \text{ É } H_3O^+(aq) + HCO_3^-(aq) \qquad pK_{a1} = 6.36$$

$$HCO_3^-(aq) + H_2O(l) \text{ É } H_3O^+(aq) + CO_3^{2-}(aq) \qquad pK_{a2} = 10.3$$

(a) Explain why the value of pK_{a2} is higher than that of pK_{a1}.

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.....[1]

A buffer solution was prepared by mixing Na_2CO_3 and $NaHCO_3$. To determine the pH of the buffer solution, a double-indicator titration was performed where 25.0 cm^3 of the buffer was titrated against 0.200 mol dm^{-3} HC*l*. Phenolphthalein (pK_{In} = 9.3) was used as an indicator for the first end-point.

After the first end-point was attained, methyl orange (pK_{In} = 3.7) was added as the second indicator to the same mixture to determine the second end-point.

The first end-point occurred at 16.90 cm^3. An additional titre volume of 19.20 cm^3 was required to reach the second end point.

The reaction between CO_3^{2-} ions and HC*l* occurred in two stages, with HCO_3^- as the intermediate product.

$$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq)$$

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$$

(b) (i) Calculate the concentration of CO_3^{2-} present in the buffer solution initially.

[1]

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(ii) Hence or otherwise, calculate the volume of hydrochloric acid used to fully react with the HCO_3^- present in the buffer solution initially.

[1]

(iii) Using your answer to **(b)(ii)**, calculate the concentration of HCO_3^- present in the initial buffer solution.

[1]

(iv) Hence, calculate the initial pH of the buffer solution.

[1]

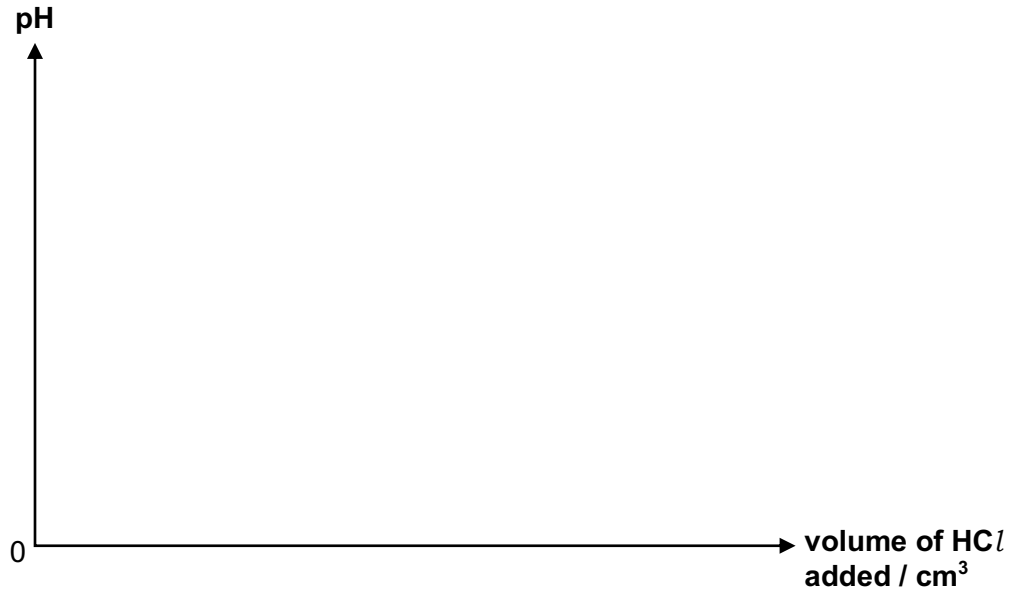
(v) Calculate the pH of the mixture attained at the second equivalence point.

[3]

(vi) By considering the initial concentrations of Na_2CO_3 and $NaHCO_3$, calculate the volume of HCl that must be added to 25.0 cm^3 of the buffer to produce a resultant mixture with a pH of 10.3.

[2]

(c) Using the information provided in the question, as well as your answers from **(b)(iv)** – **(b)(vi)**, sketch a graph to show the pH changes that occur when 50.00 cm^3 of 0.200 mol dm^{-3} HCl is added to 25.0 cm^3 of the initial buffer solution.



[2]

(d) Explain why ethanoic acid cannot be used in place of hydrochloric acid for this titration.

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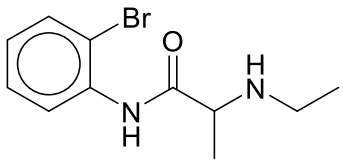
.....[1]

[Total: 13]

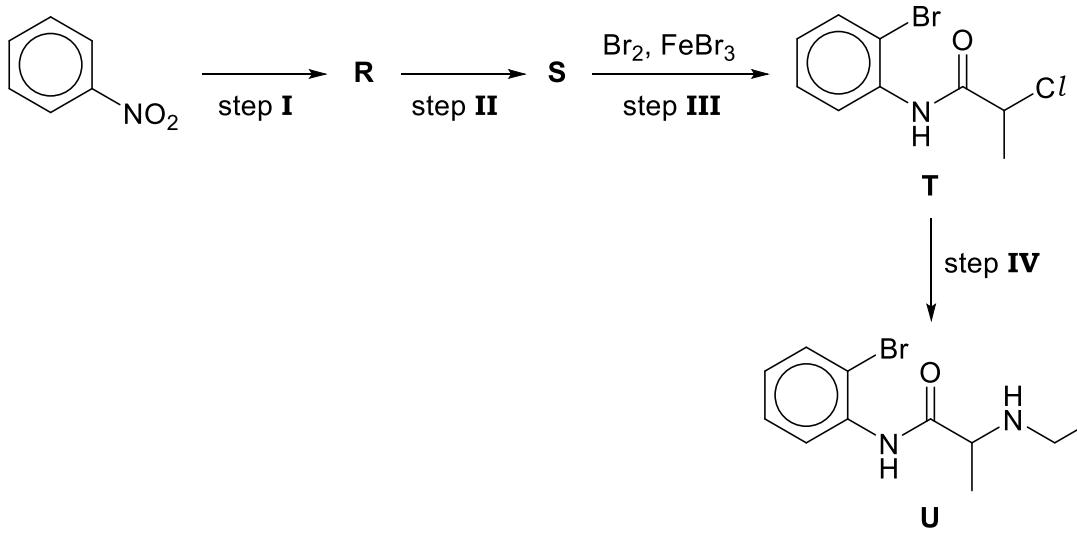
For Examiner's Use

4 Compound **U** was developed in the drug discovery process for an anaesthetic.



U

(a) The following synthetic scheme shows the synthesis of compound **U**.



(i) Draw the structures of the organic compounds **R** and **S**.

R	**S**

[2]

(ii) State the reagents and conditions for steps **I**, **II** and **IV**.

step **I**:.....

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

step **IV**: .....

[3]

For Examiner's Use

(iii) Suggest why bromination cannot be carried out in step **I**.

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.....[1]

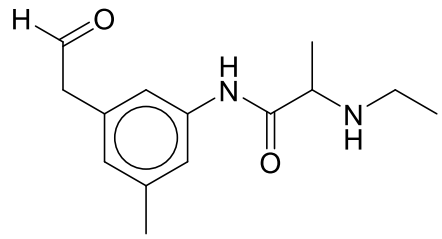
(iv) Describe the mechanism for the reaction in step **III**.

[3]

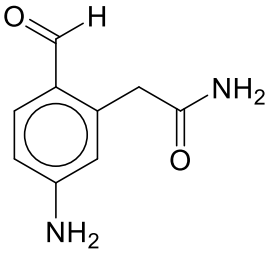
For Examiner's Use

(b) During the process of drug discovery, the following four compounds, **W** to **Z**, were also developed.

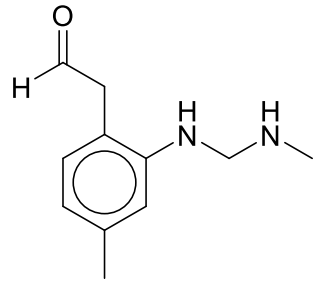
W:



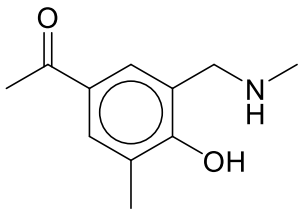
X:



Y:



Z:



Describe three simple chemical tests that could be carried out in sequence to distinguish between compounds **W**, **X**, **Y** and **Z**. State the expected observations for each test.

Test 1: .....

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Observations: .....

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Test 2: .....

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Observations: .....

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Test 3: .....

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Observations: .....

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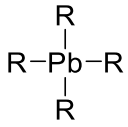
[6]

[Total: 15]

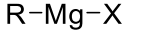
For Examiner's Use

5 Organometallic chemistry is the study of compounds containing, and reactions involving, metal–carbon bonds. In addition, other bonds such as metal–nitrogen and metal–halogen bonds, are also of interest.

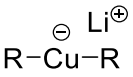
Common examples of organometallic compounds are



organolead



organomagnesium (Grignard reagents)



organocuprate (Gilman reagents)

where R = alkyl groups; X = C*l*, Br or I

(a) Tetraethyllead, $(C_2H_5)_4Pb$, is an example of an organolead compound, that for much of the 20th century was the chief antiknock agent for automotive gasoline, or petrol.

(i) State and explain the shape of the tetraethyllead molecule.

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.....[2]

In the car engine, tetraethyllead burns to deposit solid lead and lead(II) oxide, PbO, which destroy the engine. Hence, lead scavengers such as 1,2-dibromoethane and 1,2-dichloroethane are used in conjunction with tetraethyllead, forming gaseous lead(II) bromide and lead(II) chloride in the engine instead.

(ii) Explain why $PbCl_2$ and $PbBr_2$ are more volatile than PbO.

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.....[2]

Organometallic compounds tend to act as carbon-based nucleophiles.

(b) With reference to the bonding in organometallic compounds, suggest why they tend to act as carbon-based nucleophiles.

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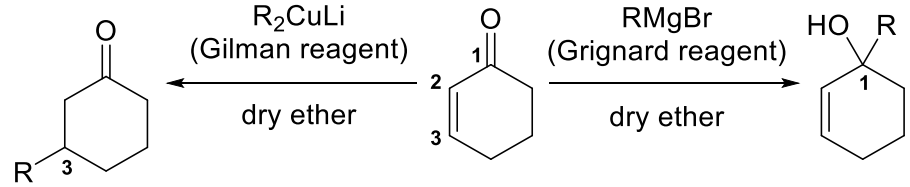
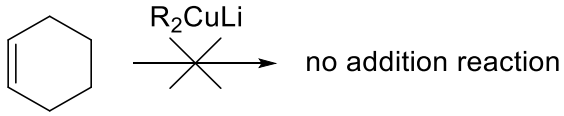
.....[1]

Both Gilman reagents and Grignard reagents act as carbon-based nucleophiles, adding across double bonds. However, the addition product with cyclohex-2-en-1-one differs for the two reagents.



3-alkylcyclohexan-1-one cyclohex-2-en-1-one 1-alkylcyclohex-2-en-1-ol

Nonetheless, Gilman reagent does not react with cyclohexene.



(c) (i) Explain why Gilman reagent does not react with cyclohexene.

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.....[1]

(ii) With the aid of a suitable diagram, explain why Gilman reagent reacts with carbon-3 of cyclohex-2-en-1-one but not carbon-2, using the concept of electronegativity and delocalisation in your answer.

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.....[2]

(iii) With reference to the structure of the cyclohex-2-en-1-one and the relative polarity of the metal–carbon bonds, suggest why Gilman reagent reacts preferentially with carbon-3 of cyclohex-2-en-1-one but Grignard reagent reacts with carbon-1, the carbonyl carbon.

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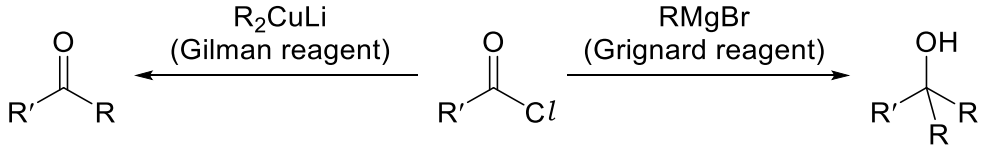
.....[2]

Another reaction where Gilman reagents and Grignard reagents give different product is in their reaction with acyl chlorides.



Gilman reagents react with acyl chloride to give ketones, while Grignard reagents react to give tertiary alcohols.

(d) (i) State the type of reaction undergone by the acyl chloride with Gilman reagent.

.....[1]

(ii) The reaction with Grignard reagents involves another type of reaction. State this second type of reaction.

.....[1]

(iii) Draw the skeletal formula of the product obtained when 3-methylpentanoyl chloride reacts with the Grignard reagent, CH_3CH_2MgBr.

[1]

Gilman reagents are also effective nucleophiles for substitution reactions with organyl halides, in what is known as the Corey-House synthesis, as shown below. Grignard reagents, on the other hand, perform very poorly in this reaction.

$$\underset{\text{organyl halide}}{R'-X} \xrightarrow[\text{dry ether}]{R_2CuLi} R'-R$$

where R = methyl, 1º, 2º, 3º alkyl, aryl, alkenyl
R′ = methyl, 1º, cyclic 2º alkyl, aryl, alkenyl
X = Br or I

(e) (i) What evidence suggest an S_N2-type mechanism in the Corey-House synthesis?

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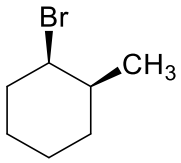
.....[1]

(ii) The S_N2-type mechanism in the Corey-House synthesis can be established by using the following cyclic secondary bromide as an organyl halide substrate.



State the observation which will confirm a S_N2-type mechanism.

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.....[1]

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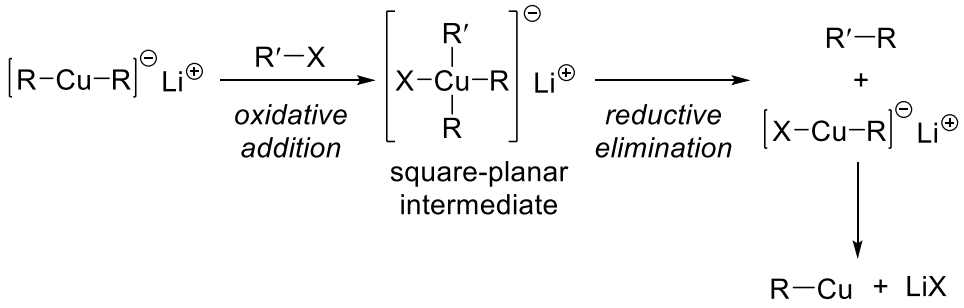
The Corey-House synthesis is believed to proceed via first *oxidative addition* of the organyl halide to give a square planar copper-containing intermediate, which then undergoes *reductive elimination* to provide the product, R′–R.



(f) **(i)** State the oxidation state of copper in

- the square-planar intermediate: .....
- $[X–Cu–R]^-$: .....

[2]

(ii) With reference to **(f)(i)**, suggest why the second step is known as *reductive elimination*.

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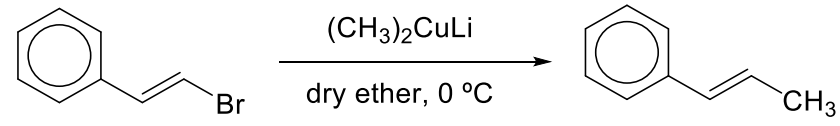
.....[2]

Unlike the reaction of organyl halides with aqueous sodium hydroxide, where aryl and alkenyl halides are unreactive, alkenyl and aryl bromide and iodide reacts readily with Gilman reagents. For example,



an alkenyl bromide

(g) Explain why alkenyl halides are unreactive towards aqueous sodium hydroxide.

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.....[1]

[Total: 20]

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