Name: ( )	Class: 21S0____

RAFFLES INSTITUTION
2021 YEAR 6 TERM 2 TIMED PRACTICE

Higher 2

CHEMISTRY

9729

23 March 2021

2 hours

READ THESE INSTRUCTIONS FIRST

Write your name, index number and civics tutorial group in the spaces provided on this cover sheet.

This paper consists of two sections **B** and **C**.

Section B (35 marks) consists of 2 structured questions.
Answer all questions in the spaces provided on the Question Paper.

Section C (40 marks) consists of 2 free-response questions.
Answer all questions in the spaces provided on the Question Paper.

If additional space is required, you should use the blank spaces, blank pages and the pages at the end of this booklet. The question number must be clearly shown.

You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.

Write in dark blue or black pen. You may be subject to penalty for writing answers in pencil.

Question	Marks
B1	/ 13
B2	/ 22
C1	/ 21
C2	/ 19
Total	/ 75
Percentage	/ 100
Penalty	
Overall	/ 100
Grade	

Section B (35 marks)

This section consists of **2** questions.

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

1 Ammonia, NH_3, is an important reagent in organic and inorganic chemical reactions.

The solubility of ammonia in water is different from that in organic solvents.

When aqueous ammonia is shaken with an organic solvent, an equilibrium is established.

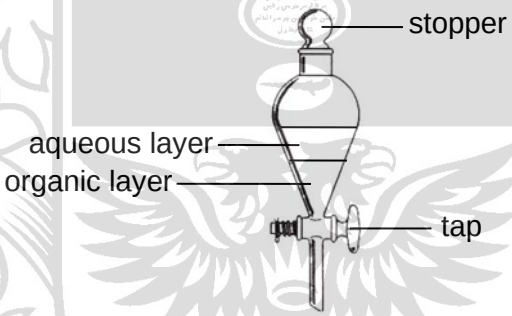
$$NH_3(org) \rightleftharpoons NH_3(aq), \quad K_D = \frac{[NH_3(aq)]}{[NH_3(org)]}$$

The equilibrium constant, K_D, is known as the distribution coefficient. It is the ratio of the concentration of ammonia in water to the concentration of ammonia in the organic solvent.

When trichloromethane is used as the organic solvent, the value of K_D at 25 °C for the above equilibrium is known to be *approximately* 25.

The accurate value of K_D can be determined by the distribution of ammonia into the two layers followed by an acid-base titration.

A student poured 50 cm^3 of 1.04 mol dm^{-3} aqueous ammonia into a separating funnel, followed by 50 cm^3 of trichloromethane. The stopper was replaced and the separating funnel was shaken. The ammonia originally in the aqueous layer was redistributed into the aqueous and organic layers.



separating funnel

Since the volumes of the aqueous and organic layers are equal, $[NH_3(aq)] + [NH_3(org)] = 1.04$ mol dm^{-3}.

The student obtained 25.0 cm^3 of the **aqueous** layer and titrated it against 0.100 mol dm^{-3} hydrochloric acid. She decided that the concentration of ammonia in the aqueous layer was too high and needed to be diluted before titration.

(a) Use the approximate value of K_D to calculate the volume of 0.100 mol dm^{-3} hydrochloric acid required to titrate 25.0 cm^3 of the aqueous layer, and explain why the concentration of ammonia in the aqueous layer would have been unsuitable for use in the student's titration.

[3]

(b) Plan a procedure for the determination of the concentration of ammonia in the aqueous layer.

You may assume that you are provided with:

- the separating funnel and its contents, prepared by the student, which has reached equilibrium,
- 0.100 mol dm^{-3} hydrochloric acid,
- the apparatus and chemicals normally found in a school Chemistry laboratory.

Your plan should include:

- calculation of an appropriate volume of the aqueous layer to be used for dilution,
- the procedure you would follow to
  - obtain the volume of the aqueous layer from the separating funnel without the organic layer,
  - dilute the aqueous layer to an appropriate volume,
  - carry out the titration.

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[6]

(c) A mixture of aqueous ammonia and ammonium chloride can be used to prepare a buffer solution (pK_b of NH_3 = 4.75).

(i) Write two equations to show how the buffer solution can control pH.

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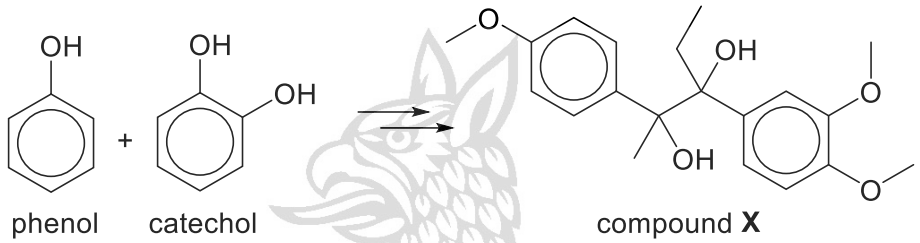
……[2]

(ii) Calculate the mass of solid ammonium chloride to be added to 1 dm^3 of 0.80 mol dm^{-3} aqueous ammonia to form a buffer solution of pH 9.0.

[2]

[Total:13]

2 Compound **X** can be synthesised from phenol and 1,2-dihydroxybenzene (catechol) in several steps.



(a) The following table compares the pK_a values of phenol with catechol.

compound	pK_{a1}	pK_{a2}
phenol	10.0	–
catechol	9.45	12.8

(i) Calculate the pH of a 0.750 mol dm^{-3} solution of aqueous phenol.

[2]

(ii) Draw the structure of the monoanion of catechol and explain why catechol has a lower pK_{a1} than phenol.

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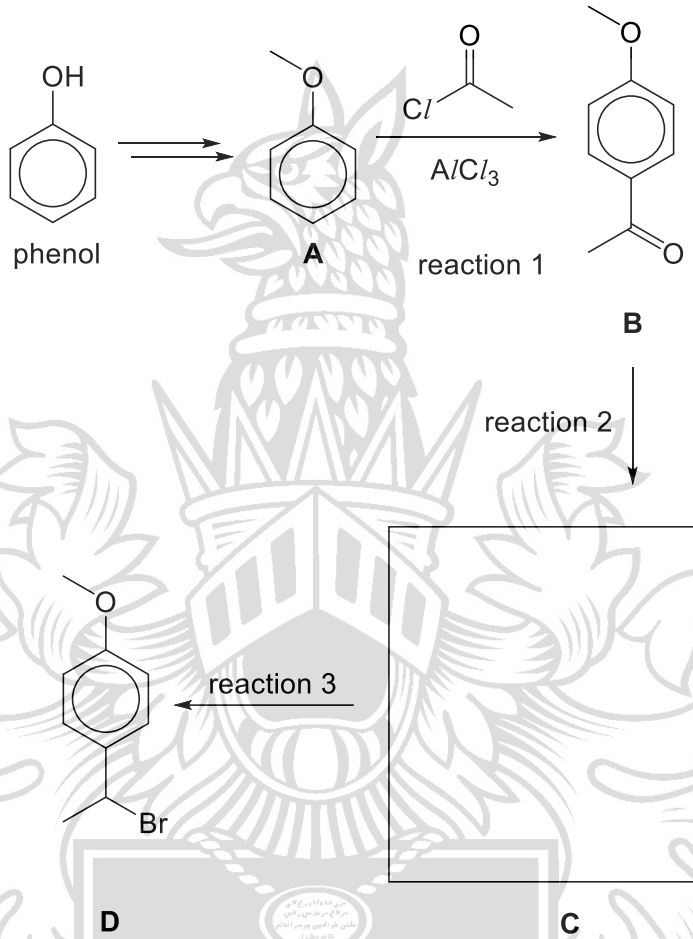
……[2]

(b) Phenol can be converted to intermediate **D** via a series of steps.



In the above reactions, the $-OCH_3$ group remains unaltered.

(i) Draw the structure of compound **C** in the above reaction scheme and state the reagents and conditions required for reactions 2 and 3.

reaction 2 .....

reaction 3 .....

[3]

Reaction 1 occurs in several steps.

The first step involves the reaction between CH_3COCl and $AlCl_3$ to form an *electrophile*.

(ii) Explain what is meant by an *electrophile*.

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……..…….....[1]

(iii) Write an equation for the reaction between CH_3COCl and $AlCl_3$ and state the role of $AlCl_3$ in the reaction.

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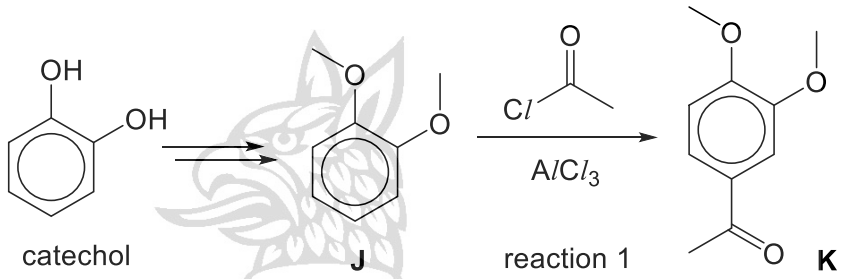
……....[2]

(iv) The benzene ring of **A** is then attacked by the electrophile in an electrophilic substitution reaction to form **B**.

Draw the mechanism of the electrophilic substitution reaction. Use curly arrows to indicate the movement of electron pairs and show the structures of any intermediates.

[2]

(v) Compound **J**, obtained from catechol, undergoes a similar reaction as compound **A** when treated with CH_3COCl and $AlCl_3$ in reaction 1.



Predict whether compound **J** undergoes reaction 1 more readily than compound **A**. Explain your answer.

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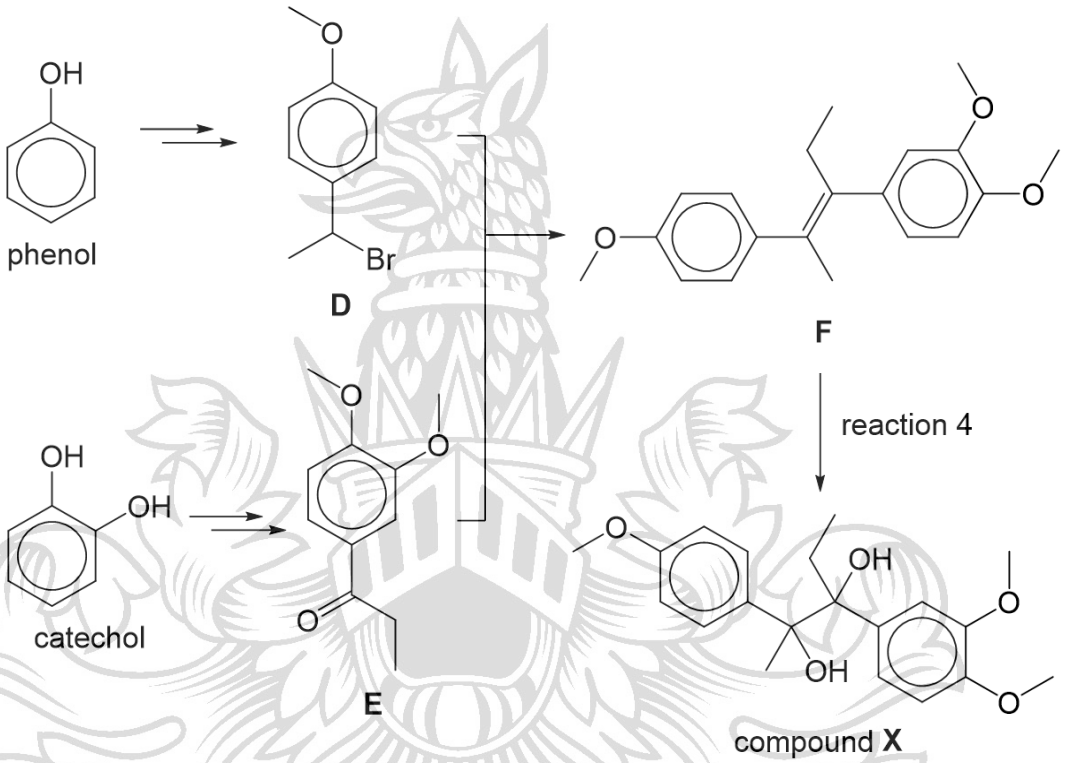
……[2]

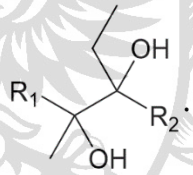
(c) The reactions between intermediates **D** and **E** result in compound **F**. Reaction 4 converts compound **F** to compound **X**.



(i) State the reagents and conditions required for reaction 4.

reaction 4 .....[1]

(ii) State the type of stereoisomerism which occurs in compound **X** and draw two structures to illustrate this isomerism.

You may represent compound **X** as 

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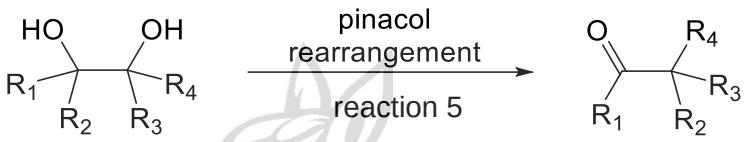
Type of stereoisomerism : .....

[2]

(d) 1,2-Diols such as compound **X** can undergo pinacol rearrangement to form the corresponding carbonyl compound. One such example is given below.

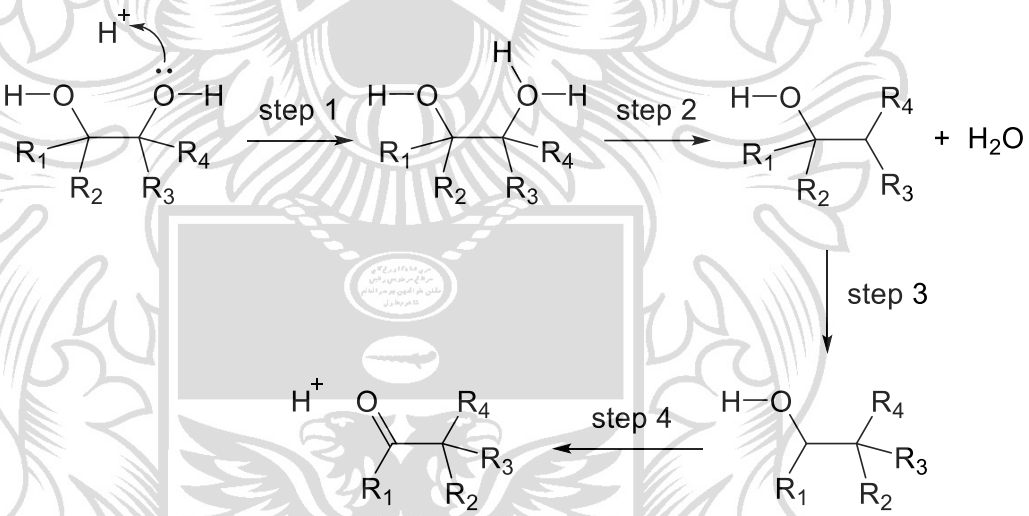


(i) The mechanism of the pinacol rearrangement occurs over several steps.

- Step 1 involves the protonation of an –OH group.
- Step 2 involves the loss of a water molecule to form a carbocation.
- Step 3 involves the migration of an alkyl group.
- Step 4 involves the breaking of the O–H bond to form a C–O π bond.

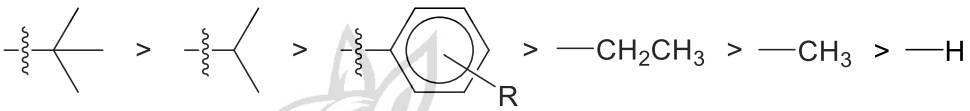
For **each of the steps 1, 2, 3 and 4,**

- label **one** positive charge on the intermediate;
- draw **one** curly arrow to show the movement of electrons during the reaction.



[3]

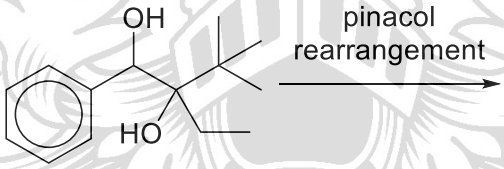
(ii) In reaction 5, it is observed that the group which migrates follows the priority of migration listed below.

1. 

2. For substituted aryls, the more electron-rich aryl group will have a higher migration priority.

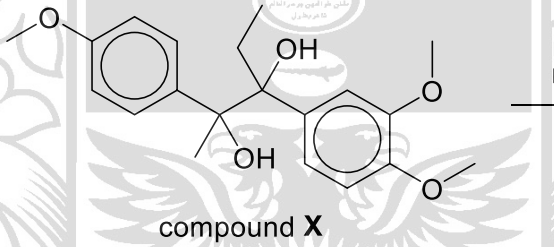
With the aid of the information provided, draw the structures of compounds **G** and **H** in the boxes provided below.

①



G

②



compound **X**

pinacol
rearrangement

H

[2]

[Total: 22]

Section C (40 marks)

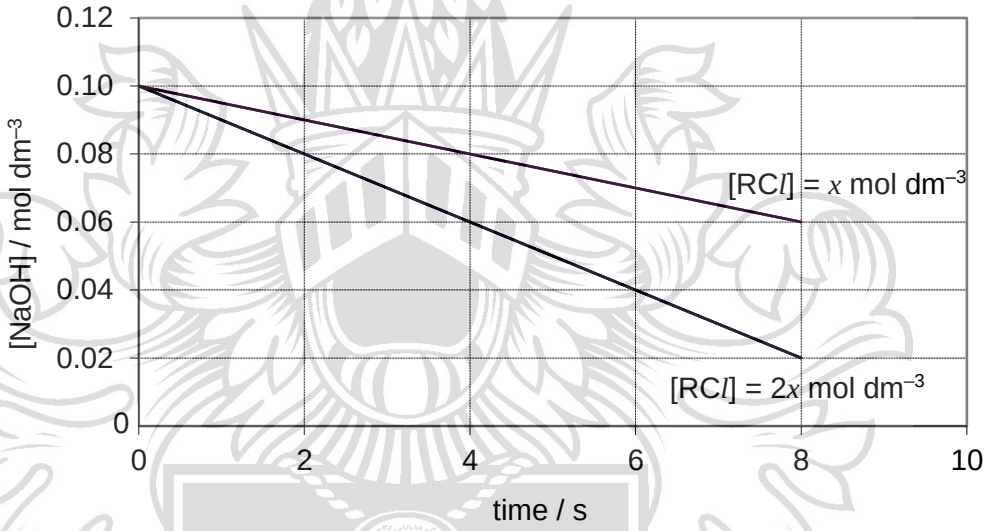
This section consists of **2** questions.

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

1 Two experiments were carried out to investigate the kinetics of the reaction between aqueous sodium hydroxide and a chloroalkane, RC*l*, at temperature T °C.

In each experiment, the concentration of the chloroalkane was in large excess over the concentration of aqueous sodium hydroxide.

The results of the experiments are shown below.



(a) **(i)** Use the graph to determine the orders of reaction with respect to sodium hydroxide and RC*l*. [2]

(ii) Write the rate equation and state the name of the mechanism. [2]

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(b) Suggest the structure of a non-cyclic four-carbon chloroalkane that will undergo the mechanism in **(a)(ii)**. Explain your answer using the concepts of electronic and steric effects. [3]

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(c) The reaction between SH^- and RC*l* proceeds via the **same mechanism** as that of OH^- and RC*l*.

A student made the following suggestion.

"Since SH^- is a stronger nucleophile than OH^-, the reaction between SH^- and RC*l* will be faster than if OH^- were used."

(i) The SH^- anion is usually obtained from sodium hydrogensulfide, NaSH.

Draw the "dot-and-cross" diagram of NaSH. [1]

(ii) Comment on the validity of the underlined words in the students' suggestion. [2]

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Phosphorus, sulfur and chlorine are Period 3 elements.

(d) Arrange these three elements in order of increasing melting point and account for the order in terms of their structure and bonding. [3]

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(e) Compound **J**, $C_{10}H_{14}O$, is an aromatic and optically active compound which does not react with hot acidified sodium dichromate(VI). **J** reacts with phosphorus pentachloride to give compound **K**, $C_{10}H_{13}Cl$. **K** is also optically active.

Compound **K** reacts with hot ethanolic potassium hydroxide to yield compound **L**, $C_{10}H_{12}$. **L** is not chiral but exhibits cis-trans isomerism. **L** reacts with hot acidified potassium manganate(VII) to give **M**, C_8H_8O and **N**, $C_2H_4O_2$. **M** gives a positive iodoform test but not **N**.

Deduce the structures of compounds **J** to **N**, explaining the reactions described. [8]

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[Total : 21]

2 Aluminium oxide, Al_2O_3, is a useful reagent in organic and inorganic reactions, and has unique acid-base properties.

(a) The acid-base behaviour of Al_2O_3 shows similarities and differences to that of phosphorus(V) oxide, P_4O_{10}.

State one similarity and one difference in the acid-base behaviour of Al_2O_3 and P_4O_{10}. Write equations for all the reactions described. [5]

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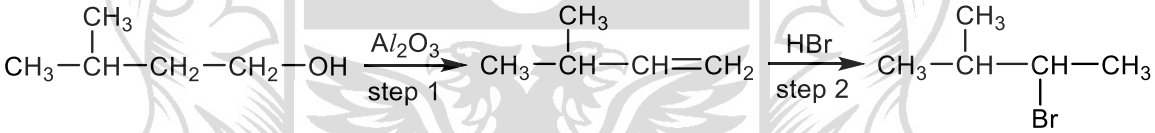
(b) Aluminium oxide is involved in the conversion of 3-methylbutan-1-ol to 2-bromo-3-methylbutane, as shown in the following scheme.



(i) Name the type of reaction which occurs in step 1 and suggest alternative reagents and conditions for the reaction. [2]

(ii) Describe the mechanism of the reaction in step 2, showing curly arrows, charges, dipoles and any relevant lone pairs. [3]

(iii) Explain why 1-bromo-3-methylbutane is formed as a minor product in step 2. [1]

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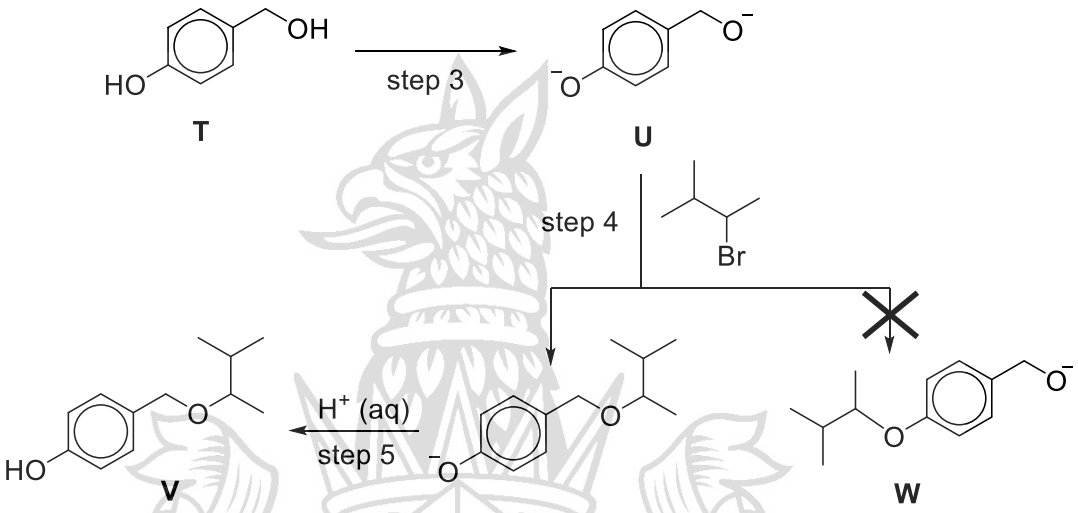
(c) 2-Bromo-3-methylbutane is required in the synthesis of compound **V**. The reactions involved are shown in the following reaction scheme.



(i) Suggest a suitable reagent for step 3. [1]

(ii) Intermediate **U** reacts with an equimolar amount of 2-bromo-3-methylbutane. Since phenoxide is a weak nucleophile, compound **W** is not formed.

Explain why phenoxide is a weak nucleophile. [2]

(iii) In step 4, the same reaction is carried out using 2-iodo-3-methylbutane instead of 2-bromo-3-methylbutane.

Suggest and explain the effect of this change on the rate of reaction in step 4. [1]

(iv) Draw the structure of the product formed between compound **V** and Br_2(aq). [1]

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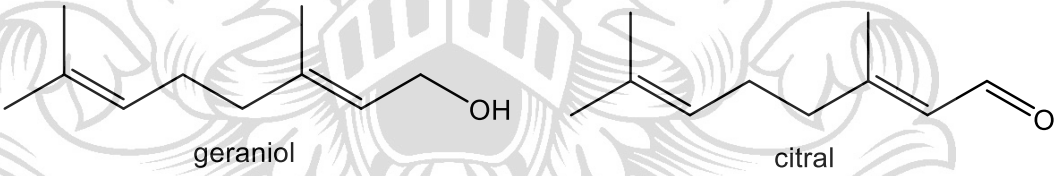
(d) Geraniol and citral are flavour compounds which can be derived from citrus fruits.



geraniol citral

(i) Suggest a simple chemical test that can be used to distinguish between geraniol and citral. You should state the observations for each compound. [1]

Suggest reagents and conditions which can be used to convert

(ii) geraniol to citral. [1]

(iii) citral to geraniol. [1]

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[Total : 19]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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