Second Semester Examination
Academic Session 2020/2021

July 2021

KOT423 – ORGANIC CHEMISTRY III

Duration: 2 hours

Please check that this examination paper consists of **TEN (10)** pages of printed material before you begin the examination.

Section A: Answer **ALL THREE (3)** questions.

Section B: Answer any **ONE (1)** question.

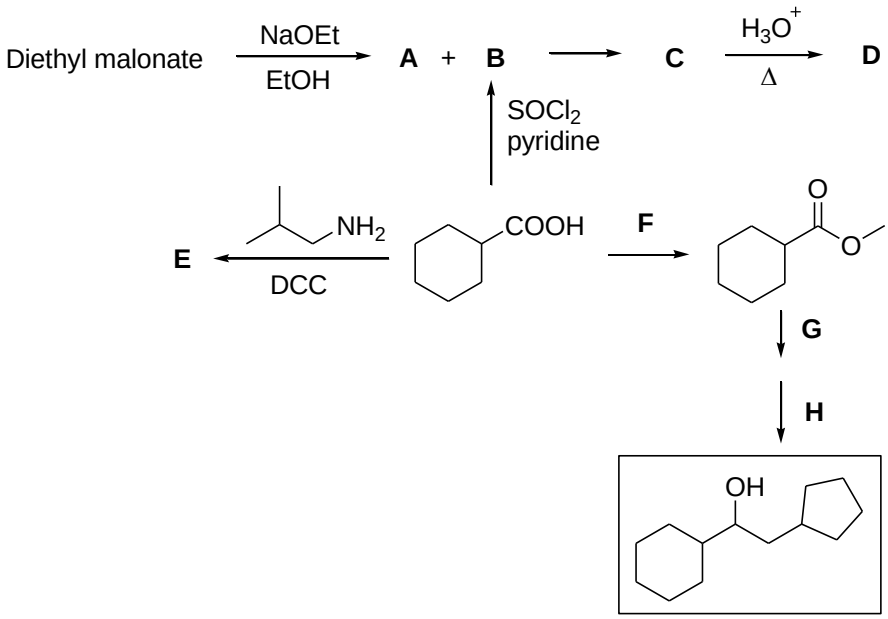
Answer each question on a new page.

You may answer the question either in Bahasa Malaysia or in English.

If a candidate answers more than five questions, only the answers to the first five questions in the answer sheet will be graded.

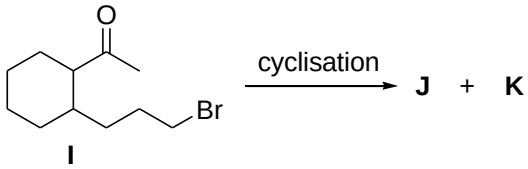
SECTION A: Answer **ALL THREE (3)** questions.

1. (a) In the reactions shown below, propose the products (**A** – **E**) and reagents and reaction conditions (**F** – **H**).



(10 marks)

(b) In the reaction given below, compound **I** forms two different products, **J** and **K**.



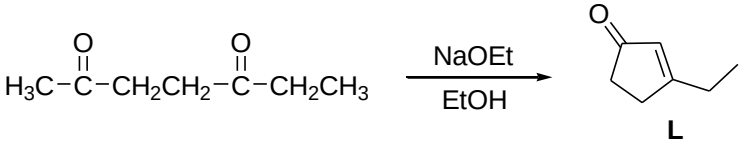
I

(i) Propose the suitable reagents and reaction conditions needed for the formation of **J** and **K**.

(ii) Draw the products **J** and **K**.

(5 marks)

(c) Intramolecular cyclisation of 2,5-heptanedione shown below forms compound **L**. Illustrate the mechanism of this transformation.

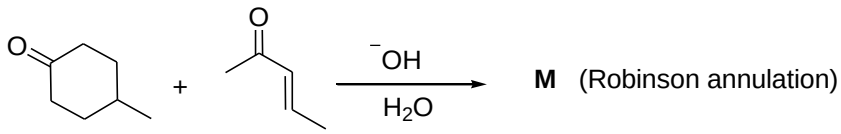


L

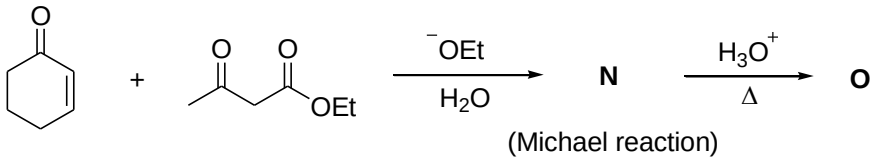
(5 marks)

(d) Give the products **M** – **O** in the following reactions.

(i)



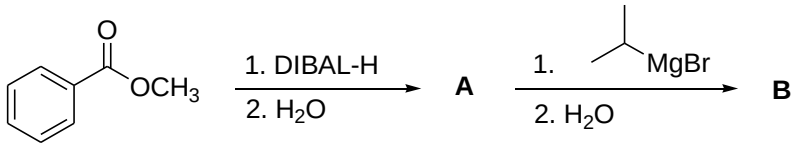
(ii)



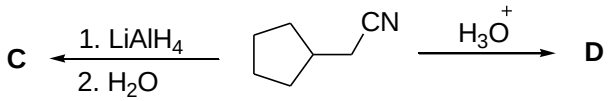
(5 marks)

2. (a) Give the products **A-F** in the following reactions.

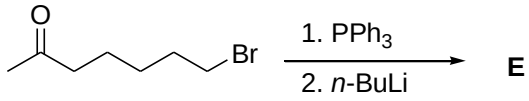
(i)



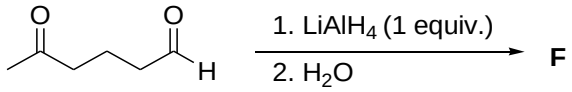
(ii)



(iii)



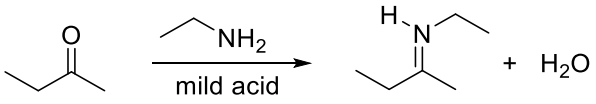
(iv)



(6 marks)

(b) Give a brief explanation for the following statements.

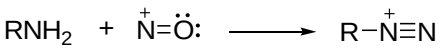
(i) The reaction below will not occur if strong acid is used.



(ii) Phenylacetic acid, $PhCH_2COOH$, is difficult to be prepared via a malonic ester synthesis pathway.

(4 marks)

(c) Aliphatic primary amines react with nitrosonium ion to form the diazonium salt.



(i) Give a stepwise mechanism for this reaction.

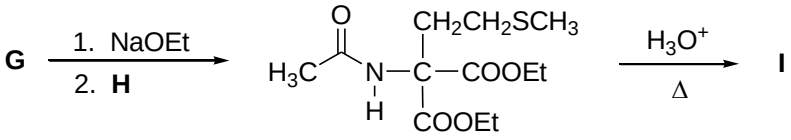
(ii) Describe the stability of the diazonium salt formed.

(iii) Illustrate the reaction of aliphatic secondary amines with the nitrosonium ion.

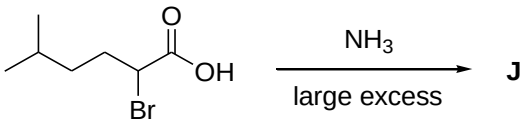
(10 marks)

(d) Give the structures of **G** - **J** in the reactions below:

(i)



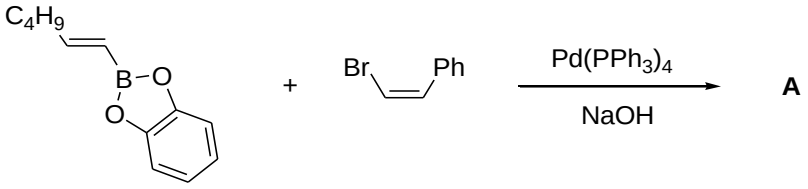
(ii)



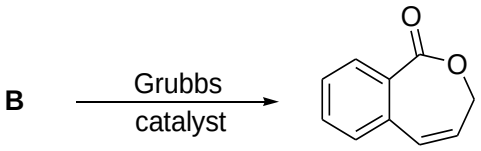
(5 marks)

3. (a) Give the structures of compounds **A** to **D** in the following reactions.

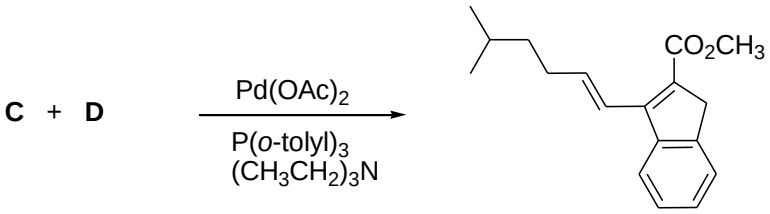
(i)



(ii)

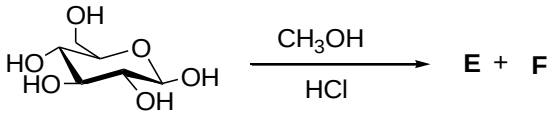


(iii)



(4 marks)

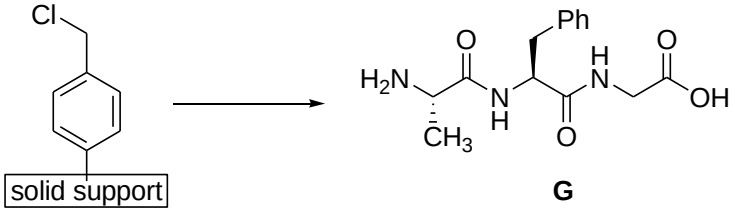
(b) Reaction of β-D-glucose with methanol in acidic media forms two anomeric glycosides, **E** and **F**. Draw a mechanism for these glycosides formation.



β-D-glucose

(5 marks)

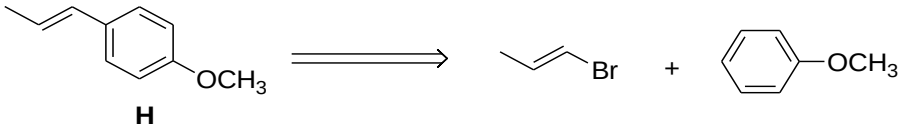
(c) Based on the scheme below, show a stepwise synthesis of peptide **G**.



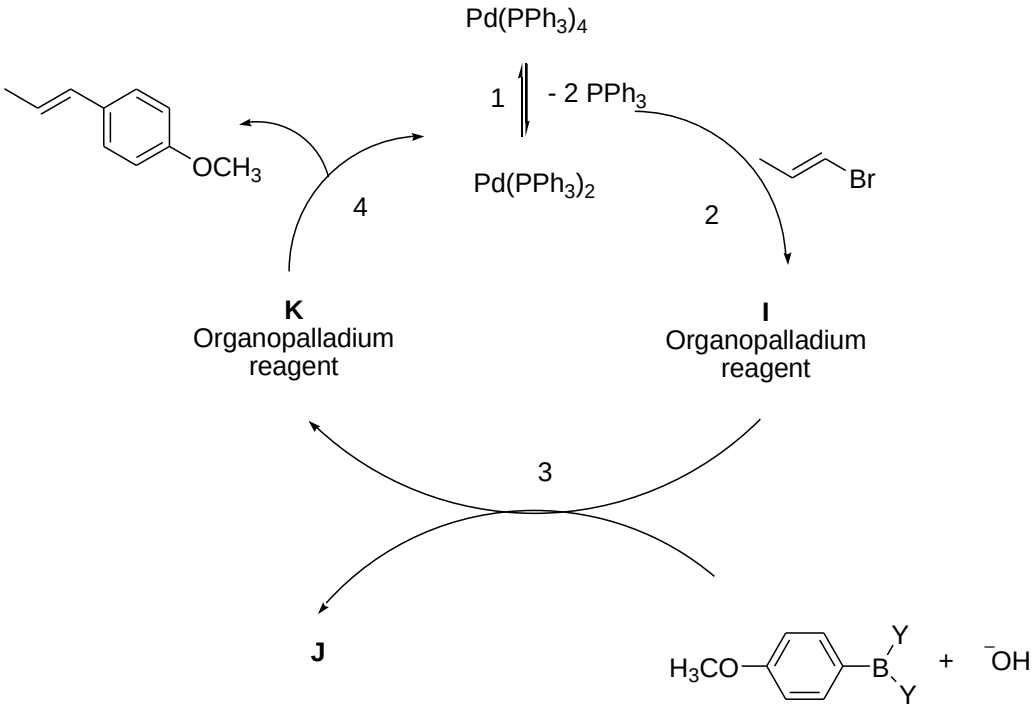
G

(6 marks)

(d) The catalytic cycle for the Suzuki reaction below shows the synthesis of compound **H** from 1-bromopropene.



H



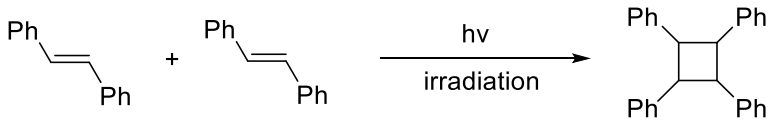
(i) Propose the structures of **I**, **J** and **K**.

(ii) Give the reaction names for steps 2 and 4 in the catalytic cycle.

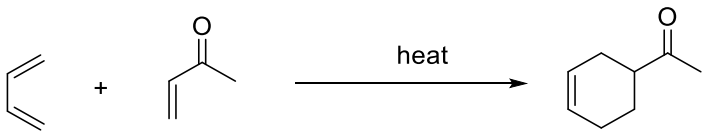
(5 marks)

(e) Illustrate the frontier orbitals in each molecules, which are involved in the cycloaddition reactions below.

(i) A [2+2] cycloaddition



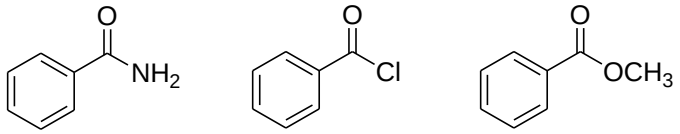
(ii) A [4+2] cycloaddition



(5 marks)

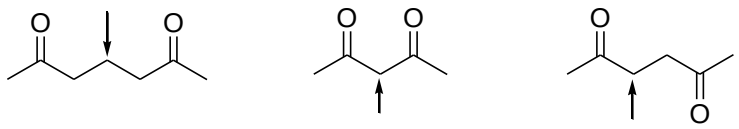
SECTION B: Answer only **ONE (1)** question.

4. (a) (i) Rank the carboxylic acid derivatives in order of increasing reactivity for nucleophilic acyl substitution with brief explanation.



I **II** **III**

(ii) For the dicarbonyl compounds listed below, rank the protons (shown by the arrows) in the order of increasing acidity with brief explanation.

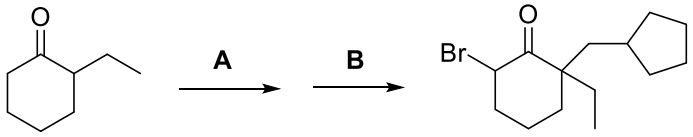


I **II** **III**

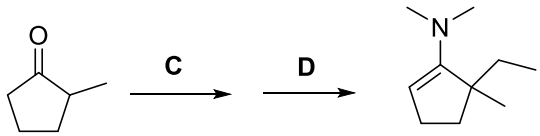
(7 marks)

(b) Propose suitable reagents and reaction conditions (**A** – **D**) needed in the following reactions.

(i)

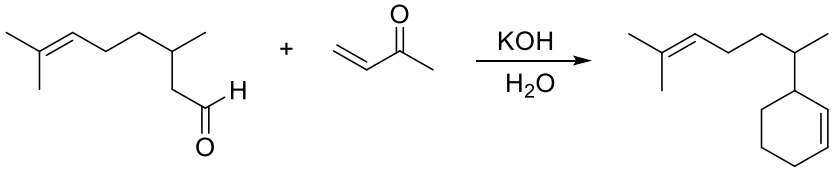


(ii)



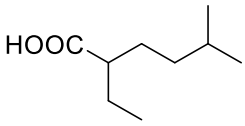
(6 marks)

(c) Robinson annulation is a Michael reaction followed by an intramolecular Aldol reaction. Show the mechanism (with curved arrows) for the transformation shown below.



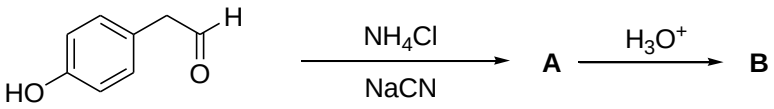
(7 marks)

(d) Propose the synthesis steps via a Malonic ester synthesis to form the compound shown below.



(5 marks)

5. (a) 4-Hydroxyphenylacetaldehyde is a yeast metabolic pathway intermediate. It undergoes the Strecker synthesis to form an intermediate **A** before producing the final product **B**, as illustrated below.



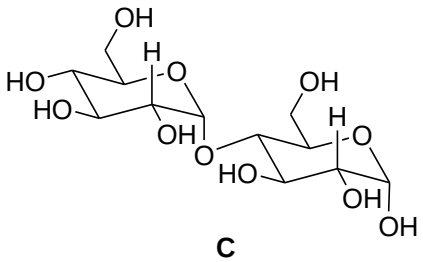
4-Hydroxyphenylacetaldehyde

(i) Draw the structures for **A** and **B**.

(ii) Draw the mechanism for the transformation of 4-hydroxyphenylacetaldehyde to **A**.

(8 marks)

(b) The structure of a carbohydrate **C** is given as below.



C

(i) Give the name of the monosaccharide that form **C**.

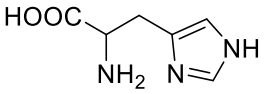
(ii) Give the name of the glycosidic linkage in **C**.

(iii) Show the conversion of the monosaccharide in **C** from chair conformation to Fischer projection.

(iv) Show the conversion of the monosaccharides in **C** into a pentose.

(10 marks)

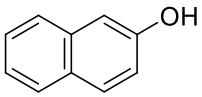
(c) The structure of histidine, an amino acid is given below. Draw the structures of histidine in solution at pH 1, and at pH 12.



Histidine

(2 marks)

(d) The Brady's test in KUT 206 lab course can be used to distinguish aromatic and aliphatic amines. Explain by showing the possible reactions how ethylamine and aniline can be distinguished using the Brady's test by reacting each of them with HNO_2, followed by a reaction with the alkaline solution (NaOH) of 2-naphthol.



2-Naphthol

(5 marks)