

FINAL EXAMINATION MAY 2024 SEMESTER

COURSE :

YBB2013 - ORGANIC CHEMISTRY II

DATE

1 AUGUST 2024 (THURSDAY)

TIME

9:00 AM - 12:00 NOON (3 HOURS)

INSTRUCTIONS TO CANDIDATES

- 1. Answer **ALL** questions in the Answer Booklet.
- Begin EACH answer on a new page in the Answer Booklet.
- 3. Indicate clearly answers that are cancelled, if any.
- Where applicable, show clearly steps taken in arriving at the solutions and indicate ALL assumptions, if any.
- 5. DO NOT open this Question Booklet until instructed.

Note

- i. There are **EIGHT (8)** pages in this Question Booklet including the cover page and appendices.
- ii. DOUBLE-SIDED Question Booklet.

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 a. Illustrate the mechanism using the curved arrows and draw the major product of each pericyclic reaction, clearly indicating the relative stereochemistry.

[3 marks]

ii. Me heat

[3 marks]

iii.

[4 marks]

 Illustrate the complete and detailed mechanism with curved arrows for the intramolecular esterification of 4-hydroxybutanoic acid to produce cyclic ester.

[10 marks]

2. a. i. Under basic hydrolysis conditions, a nitrile goes through a primary amide intermediate before becoming a carboxylate. Draw the mechanism with the curved arrows for the reaction below.

$$R-C \equiv N \xrightarrow{HO^-} R \xrightarrow{NH_2} HO^- \xrightarrow{HO^-} R \xrightarrow{O} + NH_3$$

[8 marks]

ii. Explain why it is not a facile method for converting nitriles into carboxylates.

[2 marks]

b. The following reaction shows the acetoacetic ester synthesis.

i. Complete the two steps acetoacetic ester synthesis by naming the reagent A and drawing the structure of compounds I and II.

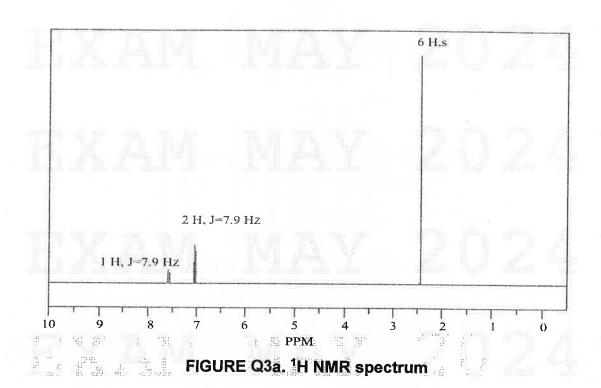
[3 marks]

ii. Compound II can be hydrolyzed in the presence of basic condition and subsequent acidification to produce mono-butylacetoacetic acid. If heat is applied after acidification, decarboxylation takes place to produce 2-heptanone. Draw the detailed mechanism with curved arrows for this transformation.

[7 marks]

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a. Determine the molecular formula and draw the structure of the unknown compound that has the ¹H and ¹³C NMR spectra and following data:
 MW (g/mol) = 107; Elemental analysis; C, 78.50; H, 8.41; N, 13.08



200 180 160 140 120 100 80 60 40 20 0 PPM

FIGURE Q3a, ¹³C NMR spectrum

[5 marks]

b. A peptide with nine amino acids has the following composition: Asn Cys Gln Gly Cys lle Leu Pro Tyr (not in sequence). It also has Cys as the N-terminal residue and Gly as C-terminal. Partial acid hydrolysis gave these peptide sequence as below. Determine the sequence of the original peptide.

Asn-Cys

Cys-Tyr

Tyr-Ile-Gln

Cys-Pro-Leu

lle-Gln

Leu-Gly

Gln-Asn-Cys

[5 marks]

c. Cyclic structure of *D*-glucose is presented below.

i. Draw the opened Fisher structure of α -D-glucose based on monosaccharide nomenclature.

[2 marks]

ii. Determine whether the structure is classified as an acetal, ketal, hemiacetal, or hemiketal. Justify your answer.

[2 marks]

iii. Acid-catalyzed addition of methanol to D-(+)-glucose results in the formation of anomeric methyl acetals called glucosides. Illustrate the complete mechanism with curved arrows for the formation of α- and β-glucosides and label them correctly.

[6 marks]

- a. The Strecker reaction, followed by a hydrolysis reaction, is an excellent method for synthesizing amino acids. This reaction involves the conversion of an aldehyde or ketone into an amino acid through a multi-step process.
 - i. Draw the detailed mechanism with curved arrows for the conversion of aldehyde to α -aminonitrile as shown below.

[5 marks]

ii. Draw the detailed mechanism with curved arrows for the hydrolysis of a-aminonitrile α-amino acid.

$$\begin{array}{c|c} CN & H_3O^+ & COO^- \\ + & H_2O & R & NH_3 \end{array}$$

[6 marks]

 Predict the structure of products formed when the fatty acid below reacts with the following reagents.

$$R \longrightarrow O$$
OH

i. SOCl2

[3 marks]

ii. Br2

[3 marks]

iii. Methanol in the presence of H+

[3 marks]

5. a. The noncyclic acid anhydride as the target molecule (TM) is given below.

i. Name the compound and indicate the synthons and corresponding synthetic equivalents

[5 marks]

ii. Using retrosynthetic analysis, provide a possible general scheme of the synthesis of the compound.

[5 marks]

b. Design the retrosynthesis analysis and illustrate the complete mechanism with curved arrows to produce the structure below.

[10 marks]

-END OF PAPER-

JIP BRAM MAY ZUZGI

APPENDIX ECULAR ORBITALS **MOLECULAR ORBITALS**

Orbital	Orbital Diagram	Homo / Lumo
ψ ₂ * / π ₂ *		LUMO
Ψ1/π1	001	НОМО

				Orbital	Orbital Diagram	Homo / Lumo
			Tal T	ψ ₄ / π ₄ *		
	Orbital	Orbital Diagram	Homo / Lumo			
	ψ ₂ * / π ₂ *		LUMO	ψ ₃ / π ₃ *		FUMO
Ψ2 7 112	Ψ2 / 112		LOWIG	ψ ₂ / π ₂		номо
	ψ ₁ / π ₁	0 1	НОМО	Ψ1/π1	00001	
		影影		Ψιλιιι	8 8 8	

Orbital	Orbital Diagram	Homo / Lumo	
ψ ₆ / π ₆ *	0 0 0 0 0	-20	
ψ ₅ / π ₅ *		-	
ψ4 / π4*	9 9 9 9 9	LUMO	
ψ3/π3	9 9 9 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	НОМО	
ψ2 / π2		44	
ψ1/π1	000001	51	