

FOURTH YEAR EXAMINATION FOR THE AWARD OF THE DEGREE OF BACHELOR OF SCIENCE IN INDUSTRIAL CHEMISTRY

SECOND SEMESTER 2021/2022 (FEBRUARY-JUNE, 2022)

CHEM 462: ADVANCED HETROCYCLIC CHEMISTRY

STREAM: : Y4S2 TIME: 2 HOURS

DAY: MONDAY, 8.00 AM - 11.00 AM DATE: 00/05/2022

INSTRUCTIONS:

1. Do not write anything on this question paper.

2. Answer ALL Questions in Section A and any other two in Section B.

SECTION A (40MKS)

1. a. Draw the following compounds.

(8 marks)

- i. cis-2,3-Diphenyloxacyclopropane
- ii. 3-azacyclobutanone
- iii. 1,3-oxathiacyclopentane;
- iv. 2-butanoyl-1,3-dithiacyclohexane;

b. Name the following compounds.

(8 marks)

c. Give the expected product of each of the following reaction sequences. (6 marks)

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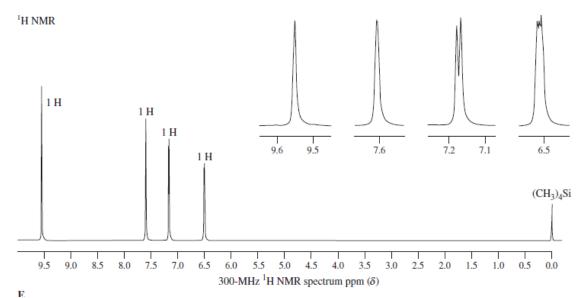
- d. Rank the following compounds in increasing order of basicity: water, hydroxide, pyridine, pyrrole and ammonia. (5 marks)
- e. Give the reasons as to why isPyrrole is a much weaker base than azacyclopentane (pyrrolidine). (4 marks)
- f. in the following reaction scheme compound E is a valuable synthetic starting material. The following sequence convertsit into furethonium, which is useful in the treatment of glaucoma. What is the structure of furethonium? (7 marks)

Aldopentoses
$$\xrightarrow{\mathbf{H}^+, \Delta} C_5H_4O_2$$
 \mathbf{E}

1. NH₃, NaBH₃CN
$$E \xrightarrow{\mathbf{2. Excess CH_3I, (CH_3CH_2)_2O}} \text{furethonium}$$

SECTION B (30MKS)

2. The commercial synthesis of a useful heterocyclic derivative requires treatment of a mixture of aldopentoses (derived from corncobs, straw, etc.) with hot acid under dehydrating conditions. The product, E, has 1H NMR spectrum E, shows a strong IR band at 1670 cm21, and is formed in nearly quantitative yield. Identify compound E and formulate a mechanism for its formation. (15mks)



3. Quinolines are heterocycles that are widely used in medicinal chemistry because of the diversity of biological activity — including anticancer utility — that their derivatives display. A short synthesis of 3-cyldihydroquinolines (which may be converted into 3-acylquinolines by mild oxidation) is shown below. Propose a mechanism for this process. (15 marks)

4. Starting with benzenamine (aniline) and pyridine, propose a synthesis for the antimicrobial sulfa drug sulfapyridine.

$$\begin{array}{c|c} N & O \\ \parallel & \\ NHS & \\ O \\ \hline Sulfapyridine \\ \end{array}$$