

**UNIVERSITY OF SWAZILAND
SUPPLEMENTARY EXAMINATION 2011**

TITLE OF PAPER : Advanced Organic Chemistry

COURSE NUMBER : C403

TIME : Three Hours

INSTRUCTIONS : Answer any **FOUR** Questions.
Each Question carries 25 Marks

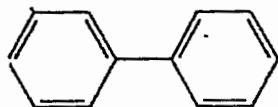
You must not open this paper until the Chief Invigilator has granted permission to do so.

SECTION A

POLYCYCLIC AROMATIC HYDROCARBONS

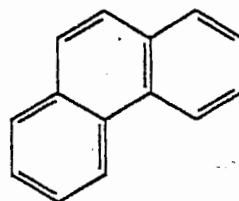
Question 1

- (a) Write the sequence of reactions that correctly describe a rational synthesis of each of the following polycyclic aromatic hydrocarbons. In each case show all reagents, reaction conditions and intermediate products. (16)



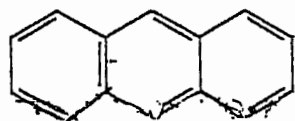
(i)

(4 marks)



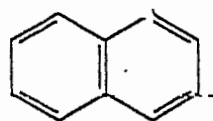
(ii)

(5 marks)



(iii)

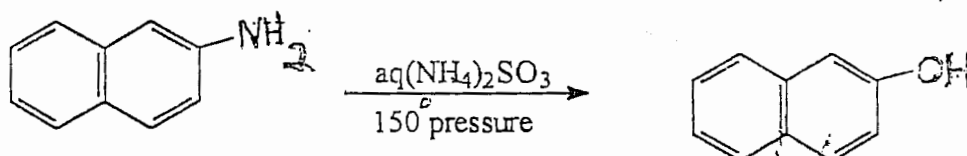
(3 marks)



(iv)

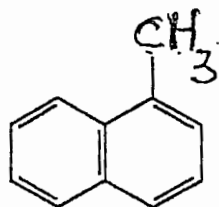
(4 marks)

- (b) Write out the mechanism for conversion of 2-amino naphthalene to 2-naphthol, showing every intermediate involved in the Bucherer reaction. (4)

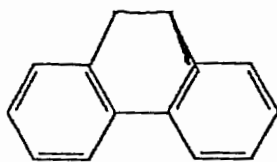


- (c) Write the structure of the expected dominant product in the mono-nitration of each of the following compounds.

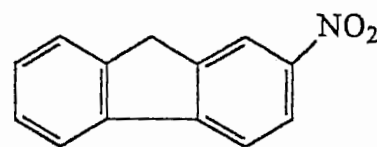
(5)



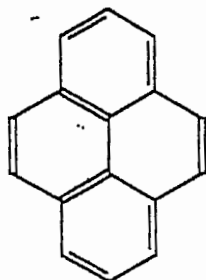
(i)



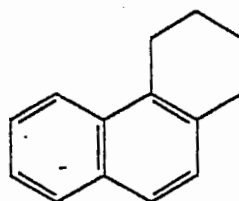
(ii)



(iii)



(iv)

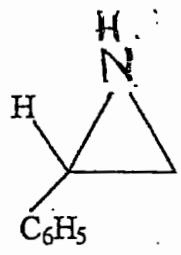


(v)

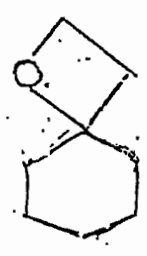
SECTION B
HETEROCYCLIC COMPOUNDS

Question 2

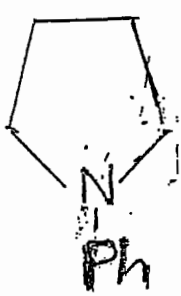
(a) Outline a synthesis for each of the following non-aromatic heterocyclic compounds. (15)



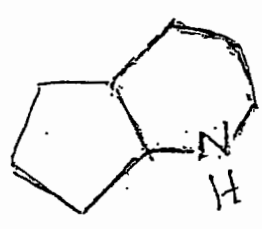
(i)
(6 marks)



(ii)
(3 marks)

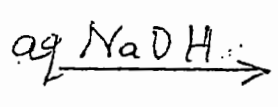
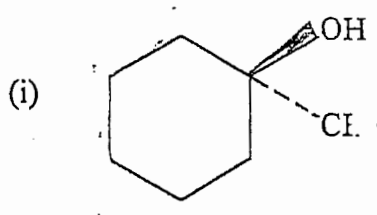


(iii)
(3 marks)



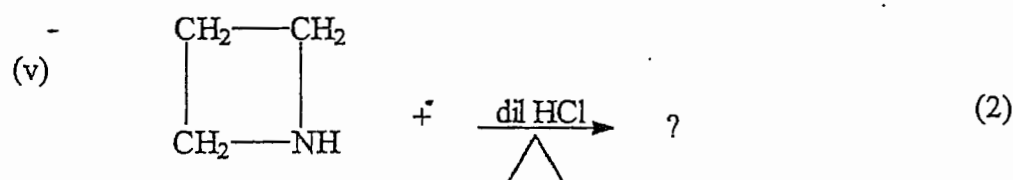
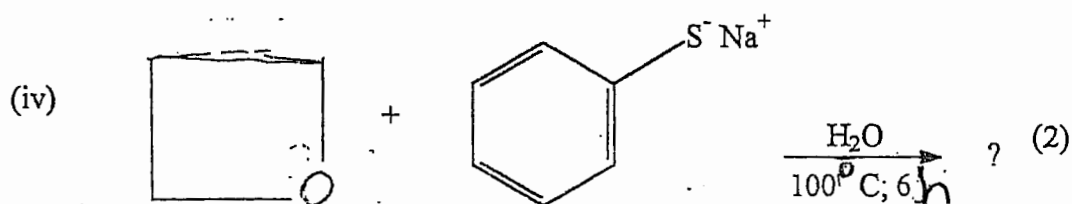
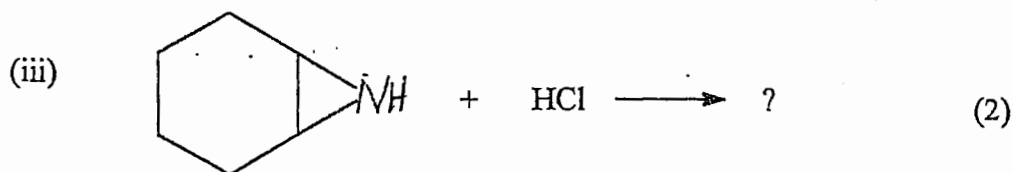
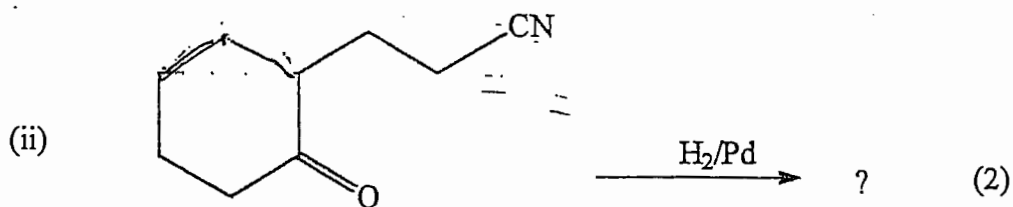
(iv)
(3 marks)

(b) What is the structure of the main product expected from the following reactions. (10)



?

(2)



Question 3

(a) Account for the following facts.

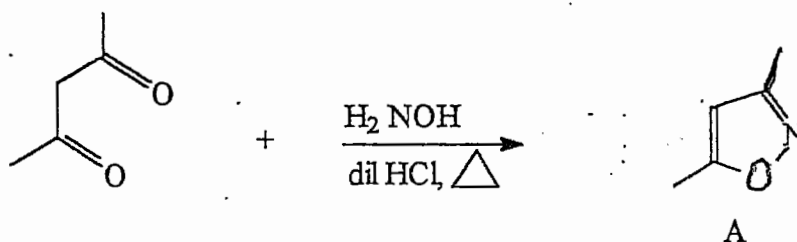
(i) Compared to other azoles, imidazole and pyrazole have relatively high boiling points and are the only solids at room temperature. (2)

(ii) Pyridine is more basic than pyrrole even though both compounds have lone pairs of electrons on nitrogen that can be protonated in an acid base reaction (2)

(iii) Electrophilic substitution occurs predominantly at the α -position [C-2] in furan, pyrrole and thiophene. (2 marks)

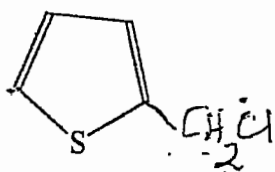
- (iv) The most preferred orientation in electrophilic substitution reactions in indole is C-3. (2)

- (b) (i) The isoxazole ring system A may be synthesized by the reaction of hydroxylamine with a 1,3-dicarbonyl compound or its equivalent as shown vide infra.



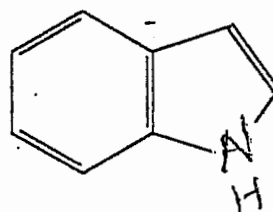
Write the mechanism for this reaction. (3)

- (ii) Outline a synthesis for each of the following compounds starting from non-heterocyclic reagents.



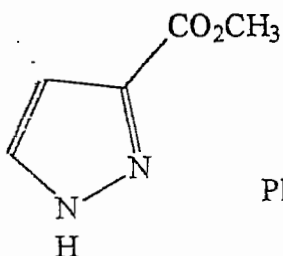
(ii)

(2 marks)



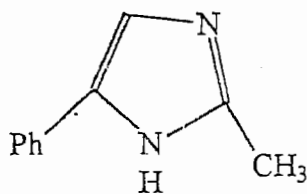
(iii)

(3 marks)



(iv)

(2 marks)

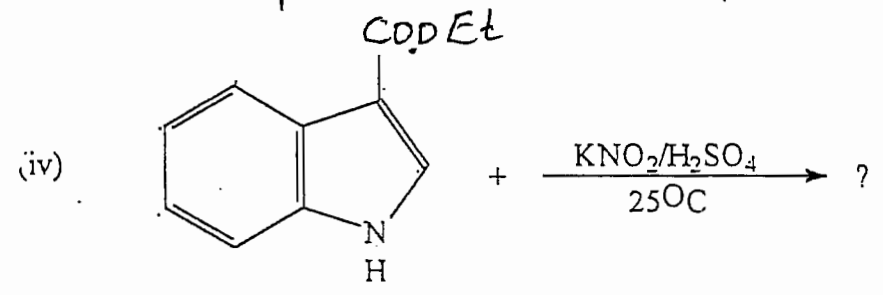
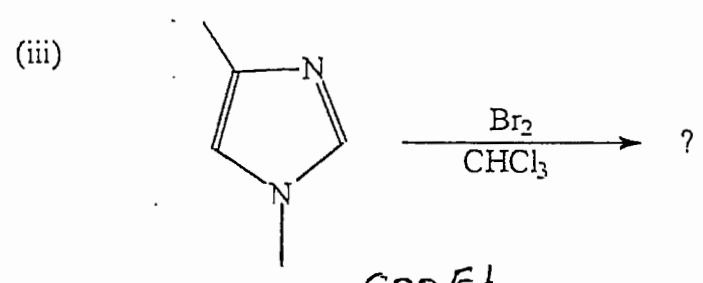
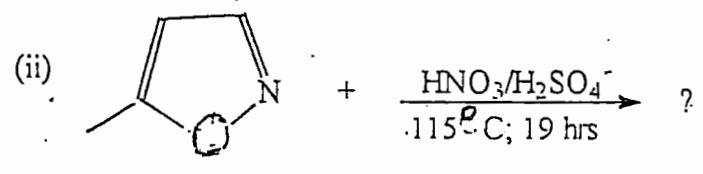
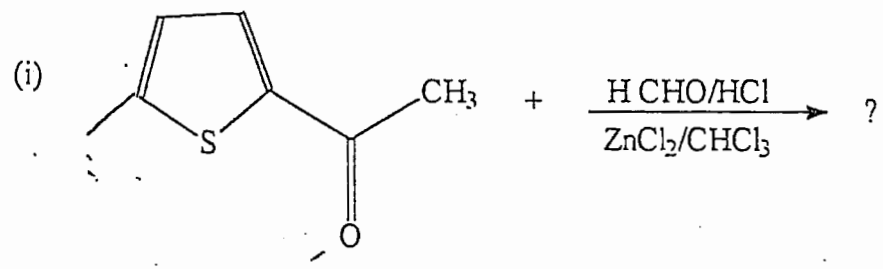


(v)

(3 marks)

C

(c) Write the structure of the main product expected from the following reactions (4)

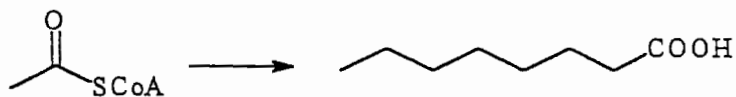


SECTION C
NATURAL PRODUCTS

8

Question 4 (Fatty Acids and Carbohydrates)

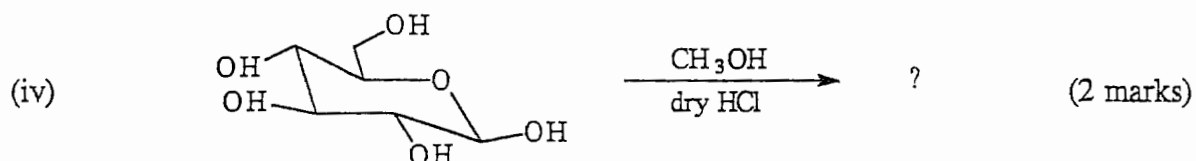
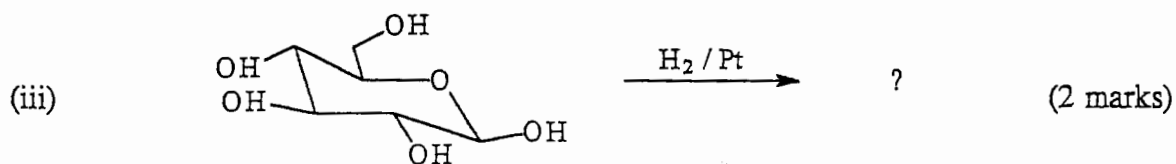
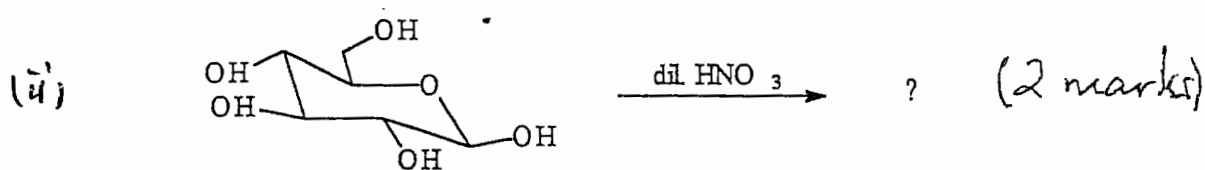
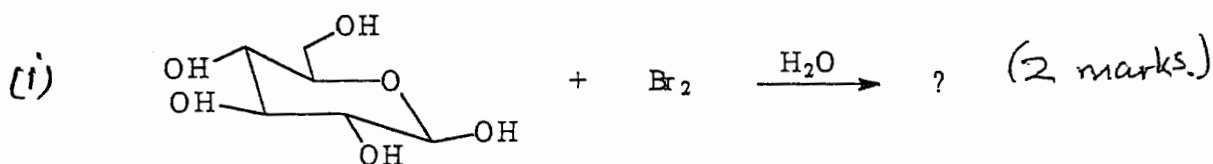
- (a) (i) Outline the process of fatty acid biosynthesis from acetylcoenzyme A to Octanoic acid. (4 marks)



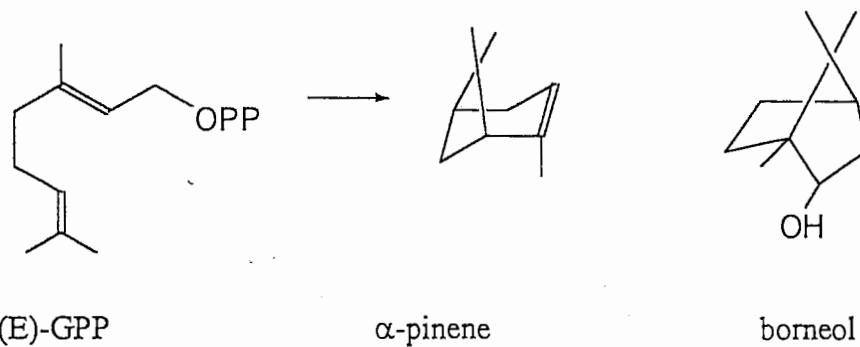
- (ii) Explain how energy is stored in the fatty acid during the synthesis process.

(2 marks)

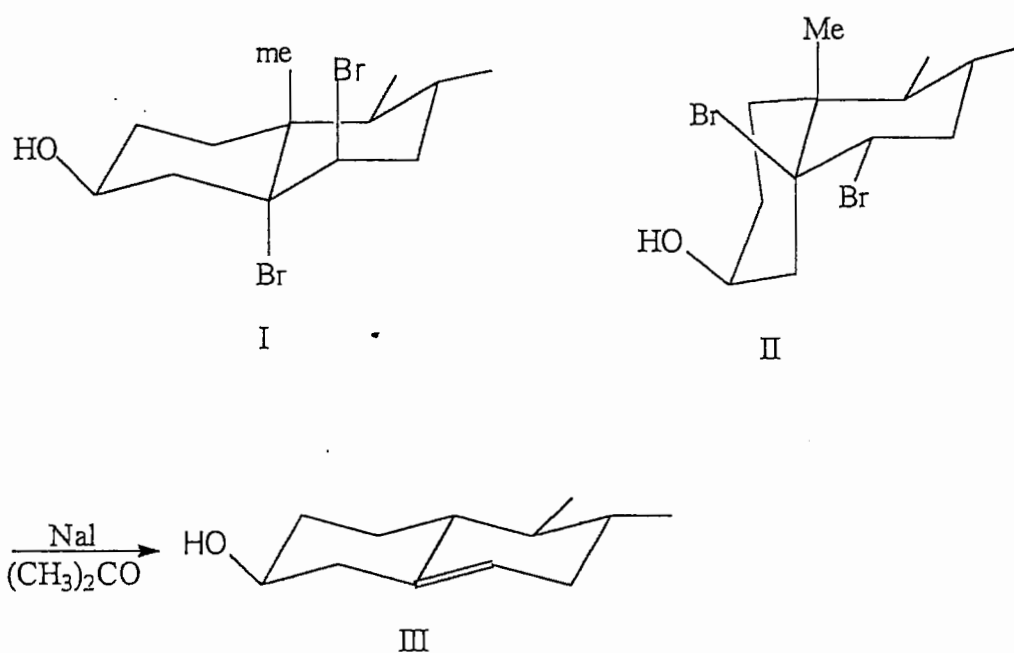
- (b) Draw the structure of the principal product of the reaction of β -D-Glucose with each of the following reagents.



- (c) Outline the biosynthesis of α -pinene and borneol from (E)-geranyl pyrophosphate. (6)

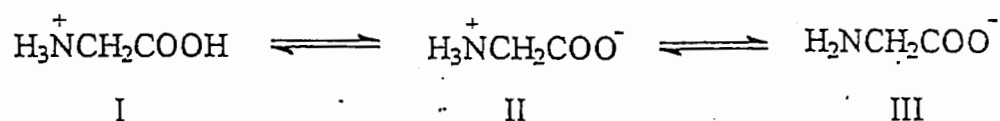


- (d) Both compounds I and II are debrominated by sodium iodide in acetone to compound III, but compound I reacts much faster than compound II. Why? Explain your reasoning clearly. (5)



Question 5 (Amino Acids)

- (a) Amino acids exist as Zwitterions (inner salts) and participate in acid-base equilibria as outlined in scheme 1, in which the three species, the cation (I), the neutral Zwitterion (II) and the carboxylate anion (III) are each predominantly present in solution at some characteristic pH.

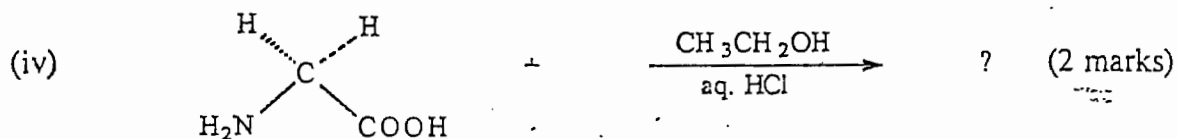
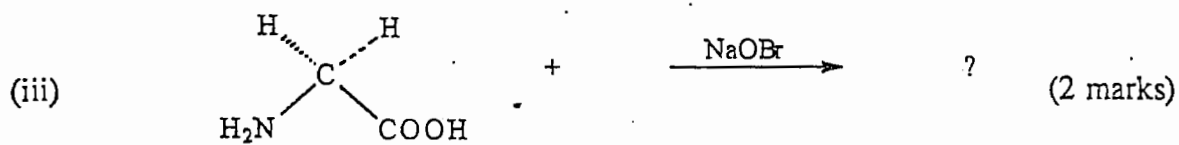
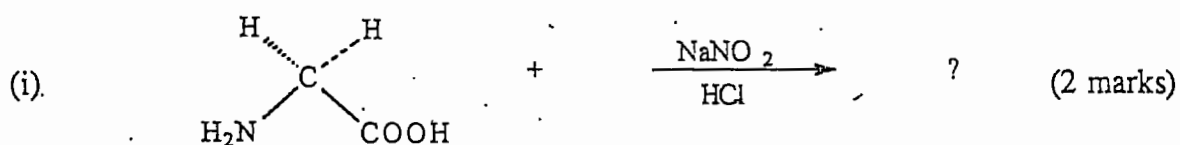


Scheme 1: Zwitterionic character of Amino Acids

Study scheme 1 and answer the following questions:

- i. Which species is present when the solution is strongly acidic (pH < 2)? (2 marks)
- ii. Identify and draw the structure of the predominant form of the Zwitterion present in the solution when the pH is near neutral. (2 marks)
- iii. When the pH of the solution is 13, indicate the predominant form of amino acid present in the solution. (2 marks)
- iv. Which of the two functional groups (NH₃⁺, COOH) in the amino acid molecule is more basic than the other? (1 mark)

(b) Draw the structure of the principal product of the reaction of glycine with the following reagents: (8 marks)



(c) Give, in outline form, the three common general methods by which amino acids can be synthesized in the laboratory. (10 marks)

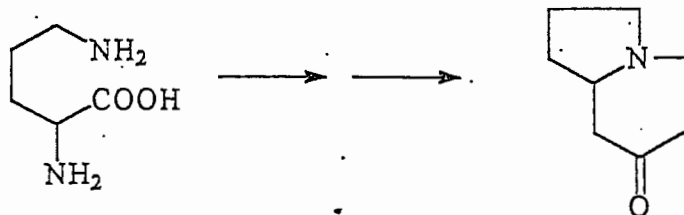
Question 6 (Alkaloids)

(a) Write a short essay on natural alkaloids with specific focus on the following general aspects:

- i. Definition
- ii. Occurrence and distribution
- iii. Properties
- iv. Isolation
- v. Importance in human health care

(9 marks)

(b) Give a brief outline of the biosynthesis of the alkaloid hygrine from ornithine.

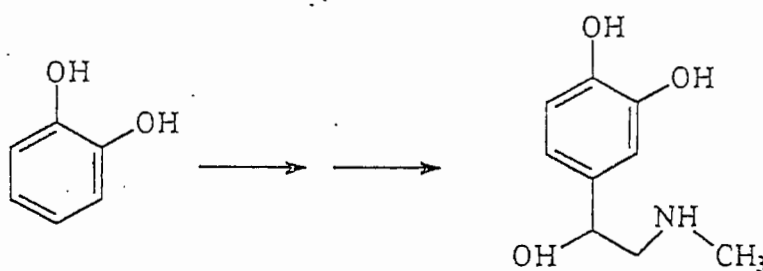


Ornithine

Hygrine

(8 marks)

(c) Outline the sequence of steps and show the appropriate reagents in the synthesis of adrenaline from catechol.



Catechol

Adrenaline

(8 marks)