

**UNIVERSITY OF SWAZILAND  
MAIN EXAMINATION 2008/09**

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**TITLE OF PAPER** : **ADVANCED ORGANIC CHEMISTRY**

**COURSE NUMBER** : **C403**

**TIME** : **THREE HOURS**

**INSTRUCTIONS** : **ANSWER ANY FOUR  
QUESTIONS. EACH QUESTION  
CARRIES 25 MARKS.**

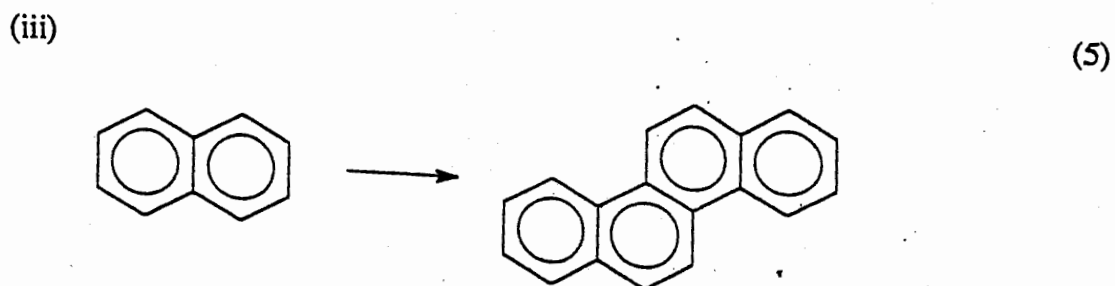
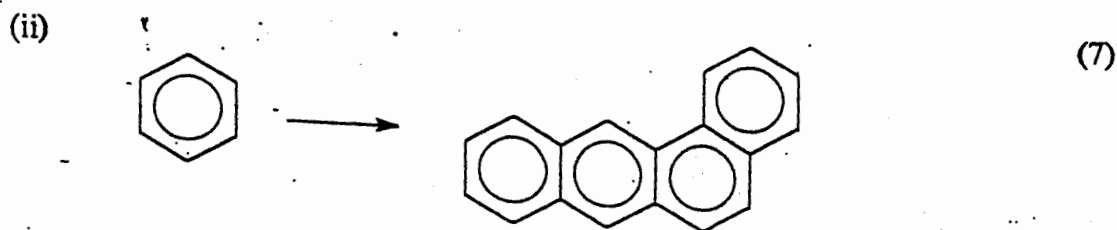
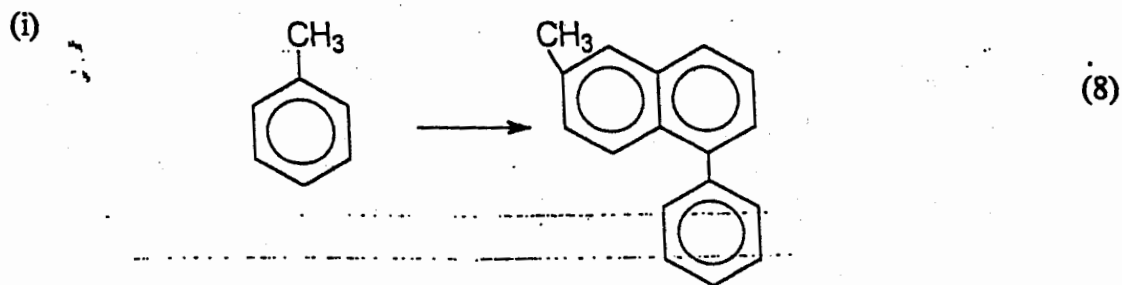
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**QUESTION 1**

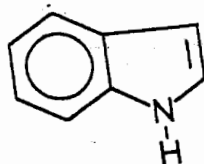
(a) 4-Nitrophenyl is nitrated in position 4 of the other ring. Account for this orientation of electrophilic attack. (5)

(b) Give all steps in the following transformations:



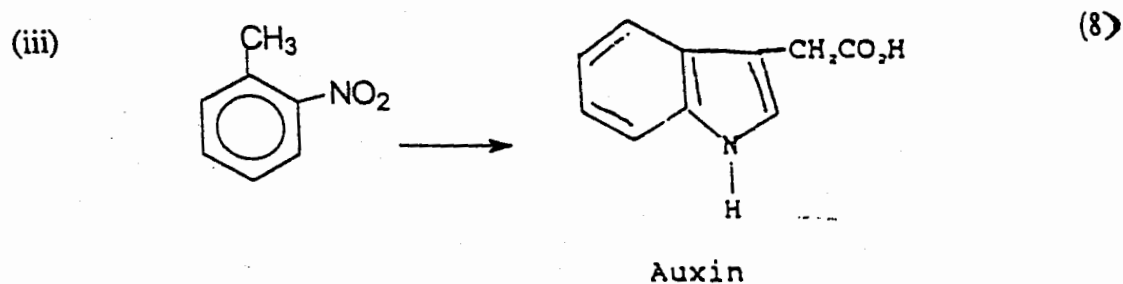
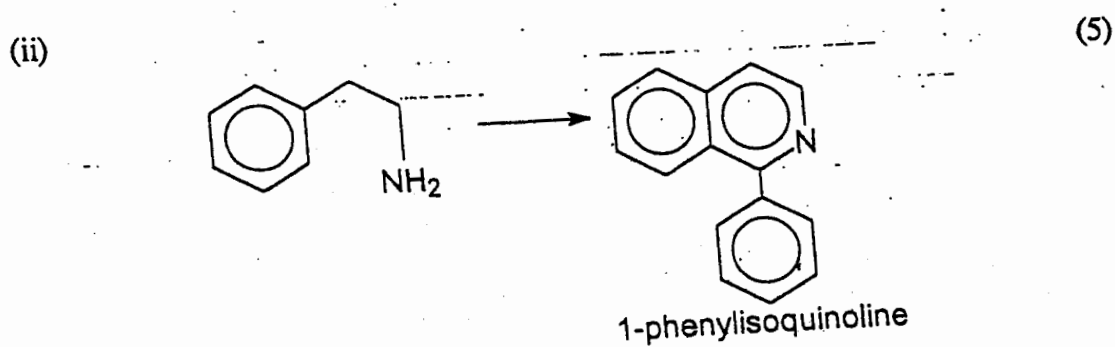
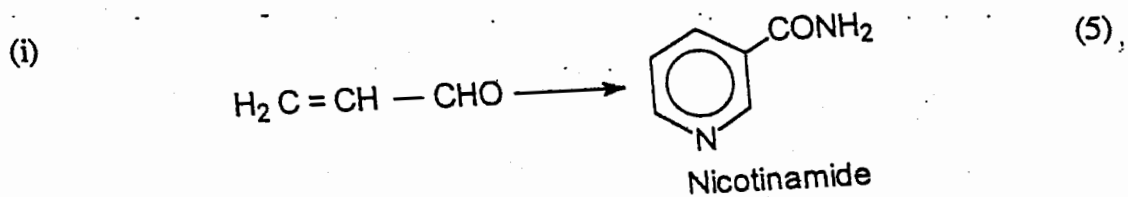
## QUESTION 2

- (a) Use the resonance structures of indole to decide on the orientation of electrophilic attack on indole. (7)



Indole

- (b) Show all steps in the following syntheses:



### **QUESTION 3**

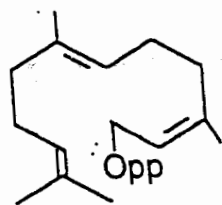
- (a) Starting with D-glyceraldehyde, outline the synthesis of aldotetroses, using the Kiliani-Fisher method. (6)
- (b) Give the configurations of all the aldopentoses expected from the above aldotetroses by the Kiliani-Fisher method. (4)
- (c) (i) What do you understand by the term "reducing sugar" ? (2)  
(ii) Explain with suitable structures why lactose and maltose are reducing sugars but sucrose is not. (7)
- (d) What are the products of the reaction of glucose with each of the following reagents? The names and formulas of the products are essential. (6)
- (i) Bromine water
  - (ii) Aqueous nitric acid
  - (iii) Hydrogen in presence of nickel catalyst.

### **QUESTION 4**

- (a) A tetrapeptide is subjected to total amino acid analysis and found to contain serine, valine, alanine and glycine. Edman degradation gives a tripeptide and the N-phenylthiohydantoin of valine. A second Edman degradation of the tripeptide gives a dipeptide and the N-phenylthiohydantoin of serine. The dipeptide is analysed by the Sanger method and the N-(2,4-dinitrophenyl)-alanine is isolated. What is the structure of the original tetrapeptide? Write equations illustrating the entire degradation sequence. (15)
- (b) Write the steps in the synthesis of glycine using ethylchloroacetate through Gabriel's phthalimide synthesis. (4)
- (c) What are the products of the reaction of glycine with each of the following? (6)
- (i)  $\text{CH}_3\text{COCl}$
  - (ii)  $\text{HNO}_2$
  - (iii)  $\text{NOCl}$

### QUESTION 5

- (a) Outline the synthesis of farnesyl pyrophosphate from isopentenyl pyrophosphate. (5)

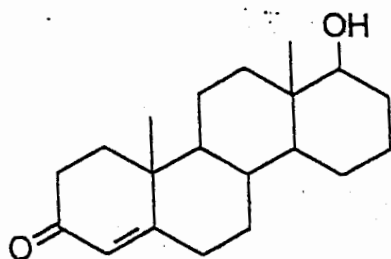


Farnesyl pyrophosphate

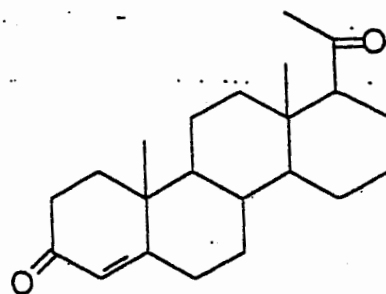
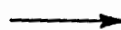
- (b) Show all the steps in the following transformations:

(i)

(5)



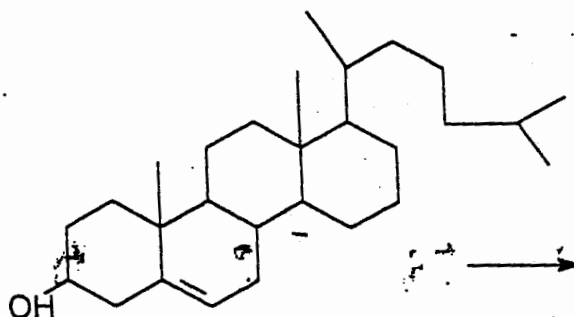
Testosterone



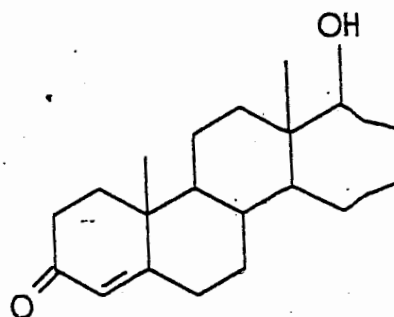
Progesterone

(ii)

(8)



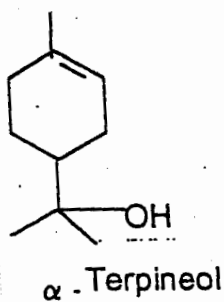
Cholesterol



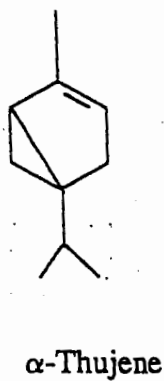
Testosterone

(c) Write the mechanisms for the synthesis of the following compounds from geranyl pyrophosphate:

(i) (3)



(ii) (4)



### QUESTION 6

- (a) Write the structure of nicotine and give the experimental evidences in support of the structure. (10)
- (b) Write briefly on alkaloids indicating what they are, their major sources, how they are usually isolated from their sources and their importance to human beings. (7)

- (c) Outline the steps in the following synthesis of adrenaline from catechol. Explain how such a synthesis gives rise to a racemic mixture while the biosynthesized adrenaline is stereochemically pure. (8)

