UNIVERSITY OF SWAZILAND
FINAL EXAMINATION 2007

TITLE OF PAPER	:	Advanced Organic Chemistry
COURSE NUMBER	:	C403
TIME	:	Three Hours
INSTRUCTIONS	:	Answer any **FOUR Questions.** Each Question carries 25 Marks.

This Paper contains eleven (9) printed pages.

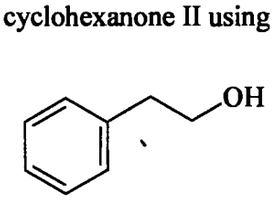
You must not open this paper until the Chief Invigilator so has granted permission to do.

SECTION A

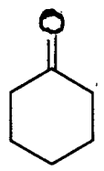
POLYCYCLIC AROMATIC HYDROCARBONS AND HETEROCYCLIC COMPOUNDS

Question 1 **Polycyclic Aromatic Hydrocaborns**

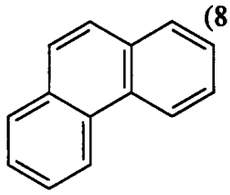
(a) Show a practical synthesis of phenanthrene III starting with 2 – phenylethanol I and cyclohexanone II using other suitable reagents. (8 marks)



I



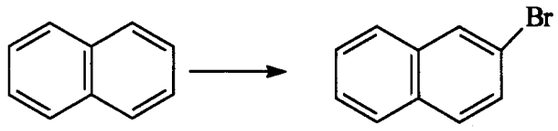
II



III

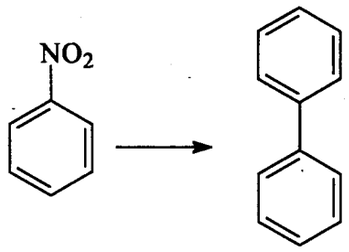
(b) Write a sequence of reactions showing all the suitable reagents and reaction conditions for laboratory synthesis of the following compounds.

(i) 2 – Bromonapthalene(II) from naphthalene (I) (3 marks)



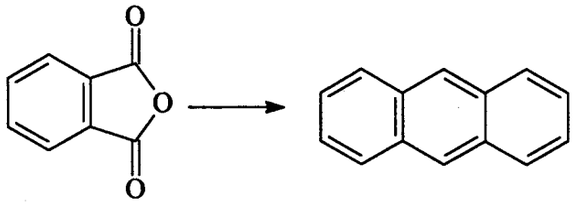
(I) (II)

(ii) Biphenyl (IV) from nitro-benzene (III) (3 marks)



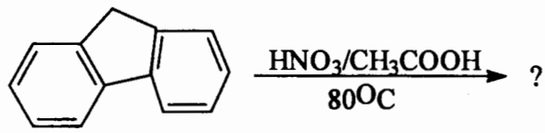
(III) (IV)

(iii) Anthracene VI from phthalic anhydride (V) (3 marks)

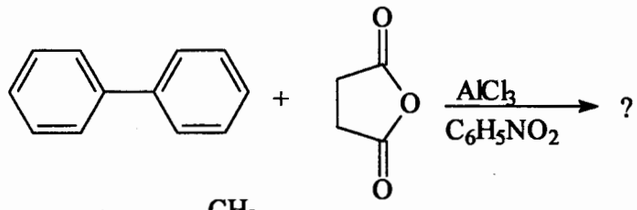


(V) (VI)

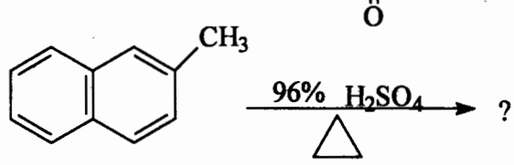
(c) Each of the following reactions has been reported in the chemical literature and proceeds clearly in good yield. Write down the structure of the principal product in each case.

(i) 

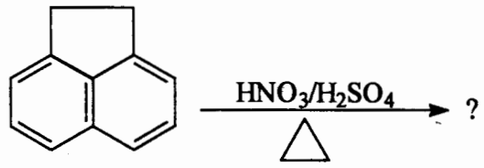
(2 marks)

(ii) 

(2 marks)

(iii) 

(2 marks)

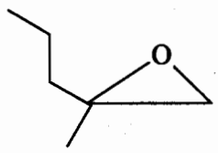
(iv) 

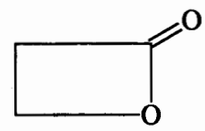
(2 marks)

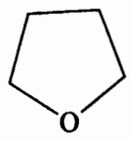
HETEROCYCLIC COMPOUNDS

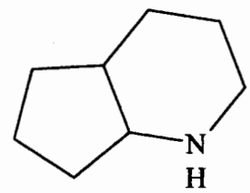
Question 2

(a) Outline a synthesis for each of the following non-aromatic heterocyclic compounds. (2 marks each)

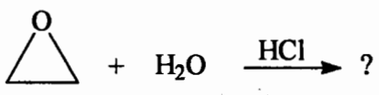
(i) 

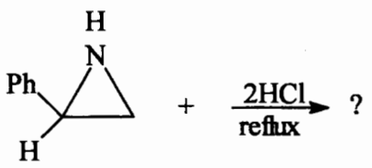
(ii) 

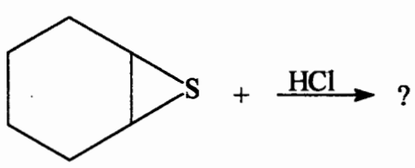
(iii) 

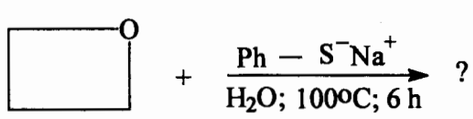
(iv) 

(b) Draw the structure of the main product expected from each of the following reaction of non aromatic heterocyclic compounds. (1 mark each)

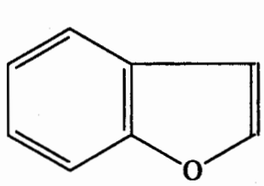
(i) 

(ii) 

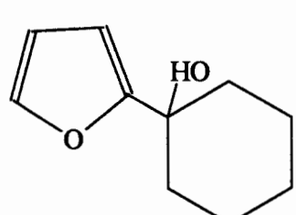
(iii) 

(iv) 

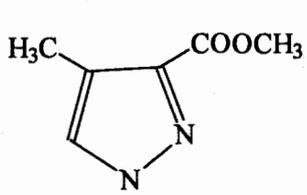
(c) Outline a synthesis for each of the following compounds from the corresponding non-heterocyclic reagents or unsubstituted heterocyclic systems.

(i) 

(3 marks)

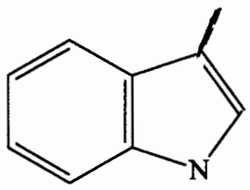
(ii) 

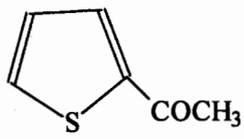
(3 marks)

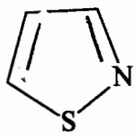
(iii) 

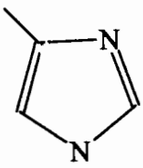
(3 marks)

(d) Predict and draw the major product expected from the following reactions of heterocyclic aromatic compounds. (1½ marks each)

(i)  + Br_2 $\xrightarrow[25^oC]{CH_3COOH}$?

(ii)  $\xrightarrow[ZnCl_2/CHCl_3]{CH_2O/HCl}$?

(iii)  + $\xrightarrow[115^oC;\ 19\ hrs]{HNO_3/H_2SO_4}$?

(iv)  + Br_2 $\xrightarrow{CHCl_3}$?

SECTION B

NATURAL PRODUCTS

Question 3

(a) (i) Explain why the melting point of a fat molecule depends on the amount of unsaturation in the fatty acid component of the fat. (3 marks)

(ii) By considering the formation of butanoic acid from two molecules of acetyl coenzyme A, describe briefly, the major elements of fatty acid biosynthesis. (4 marks)

(iii) Trimyristin is a white crystalline fat compound m.p 54 – 55°C, obtainable from nutmeg, and is the principal constituent of nutmeg butter. Hydrolysis of trimyristin with hot aqueous sodium hydroxide gives an

excellent yield of myristic acid, m.p. 52 – 53°C, as the only fatty acid. What is the structure of trimyristin. (3 marks)

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

(i) Br_2/H_2O

(ii) Dil.HNO_3

(iii) H_2/Pt (8 marks)

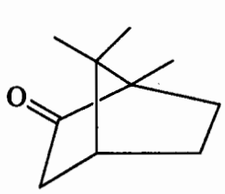
(iv) CH_3OH/dry HCl

(c) Starting from D-Glyceraldehyde describe the steps involved in the synthesis of D-threose. (7 marks)

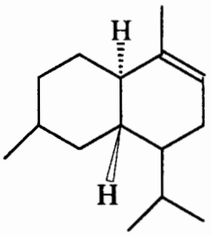
Question 4 **Terpenes and Steroids**

Structure

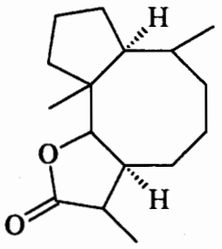
(a) (i) The following terpenes are made up of more than one isoprene unit. Draw the compounds and with dotted lines or cycles, identify the five carbon fragments corresponding to the isoprene units in each compound



Camphor



β-cadinene



Ambrosin

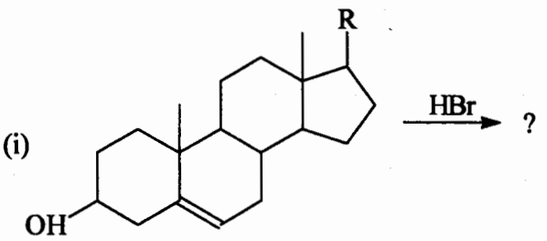
(ii) Which two structural factors determine the course and rate of reaction of steroids. (2 marks)

(iii) With diagrams and suitable examples, describe briefly how these factors work. (2marks)

Reactions

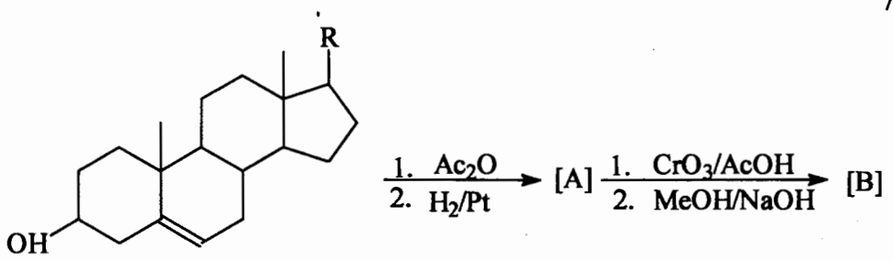
(b) Predict and draw the structure of the principal organic product expected from each of the following reactions of steroid compounds.

(i)



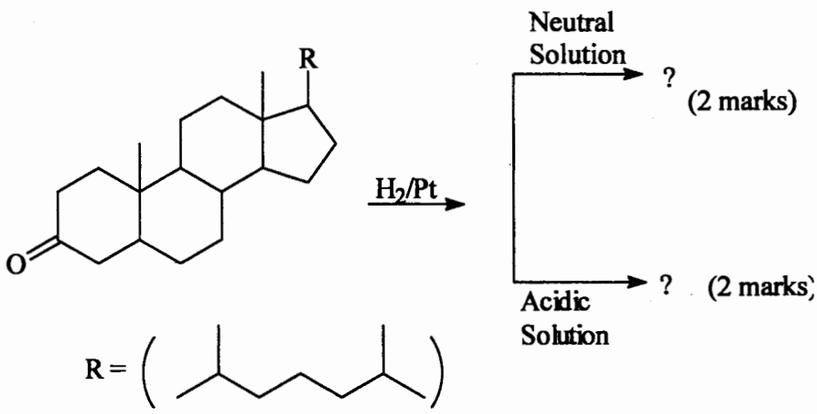
(2 marks)

(ii)



(4 marks)

(iii)

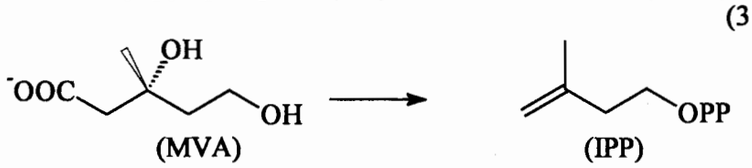


Biosynthesis

(c) Outline the main steps and show the key reactions in the biosynthesis of the following compounds.

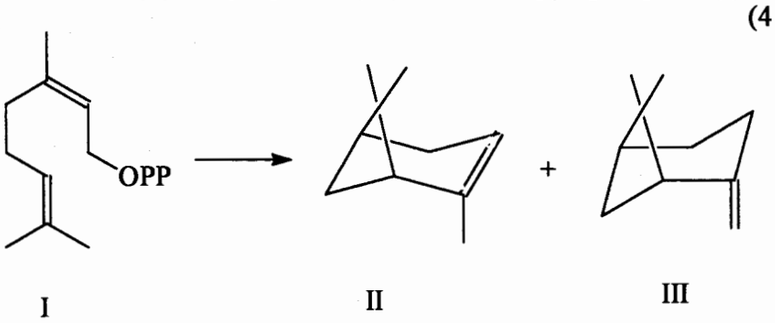
(i) iso – Pentenyl pyrophosphate (IPP) from mevalonic acid (MVA)

(3 marks)



(ii) α – Pinene (II) and β – pinene (III) from nerol pyrophosphate (I)

(4 marks)

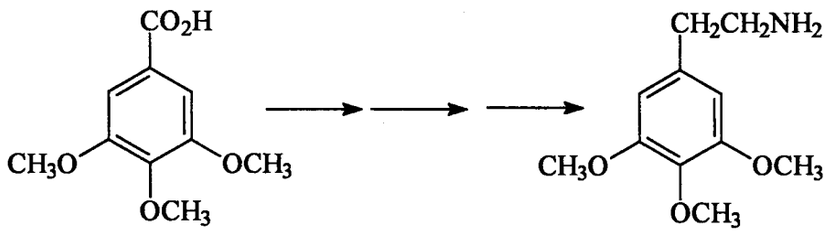


Question 5

(a) Write a short essay on natural alkaloids, with specific focus on the following general aspects. (6 marks)

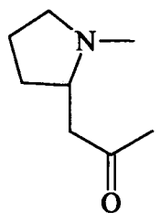
(i) Definition
(ii) Occurrence and distribution
(iii) Properties
(iv) Isolation and purification
(v) Importance in human health care

(b) Outline the synthesis of the hallucinogenic compound mescaline from 3,4,5-trimethoxy benzoic acid. Indicate other necessary reagents. (6 marks)

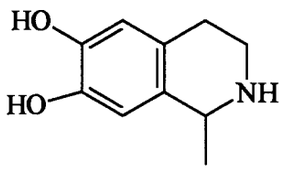


3,4,5-trimethoxybenzoic acid Mescaline

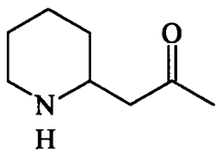
(c) Outline a biosynthetic pathway for each of the following alkaloid compounds. (13 marks)



(i)
(5 marks)



(ii)
(4 marks)



(iii)
(4 marks)

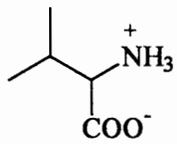
Question 6 Amino Acids, Peptides and Proteins.

(a) Outline a synthesis of Alanine from propionic acid. (5 marks)

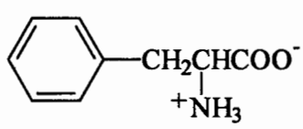
CH_3CH_2COOH CH_3CHCOO^- with NH_3

Propionic Acid Alanine

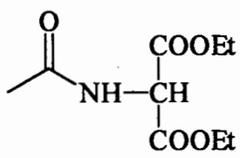
(b) Outline the steps in the preparation of Valine by the Strecker Synthesis. (5 marks)



(c) Using diethylacetamidomalonae and any other appropriate reagents, outline a synthesis of phenylalanine. (7 marks)



Phenylalanine



Diethylacetamidomalonate

(d) Predict and draw the structure of the major product of the reaction of glycine with the following reagents. (12 marks)

(i) $NaNO_2$ and dilute HCl
(ii) Acetic anhydride $[(CH_3CO)_2O]$
(iii) NaOBr
(iv) CH_3CH_2OH and dry HCl