

**UNIVERSITY OF SWAZILAND
FINAL EXAMINATION 2013**

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 11 (eleven) printed pages.

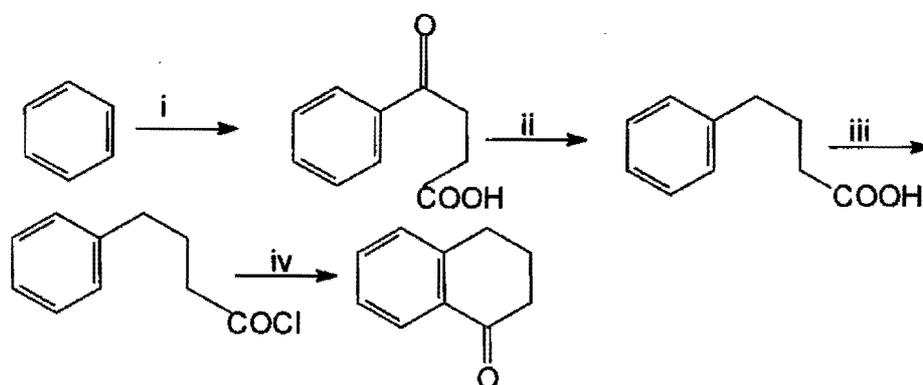
You must not open this paper until the Chief Invigilator so has granted permission to do.

SECTION A

POLYCYCLIC AROMATIC HYDROCARBONS AND HETEROCYCLIC COMPOUNDS

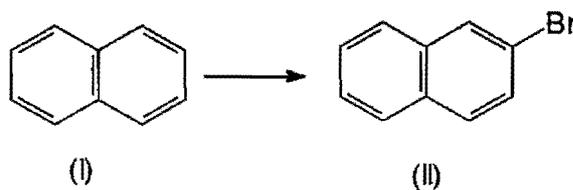
Question 1 Polycyclic Aromatic Hydrocarbons

- (a) A standard synthetic sequence for building a six membered cyclic ketone onto an existing aromatic ring is shown in outline as follows:

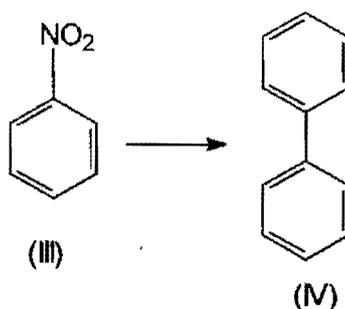


- (i) Specify the reagents and general reaction conditions necessary for each of the steps in (i) to (iv). (8 marks)
- (b) Write a sequence of reactions showing all the suitable reagents and reaction conditions for laboratory synthesis of the following compounds.

- (i) 2-Bromonaphthalene(II) from naphthalene (I). (3 marks)

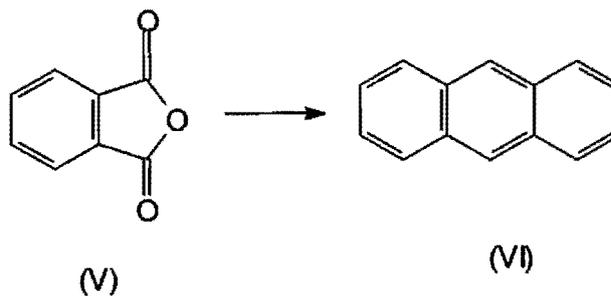


- (ii) Biphenyl (iv) from benzene(III). (3 marks)

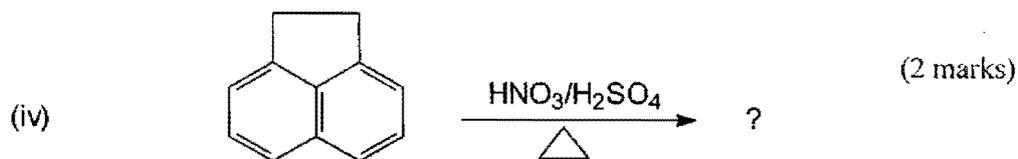
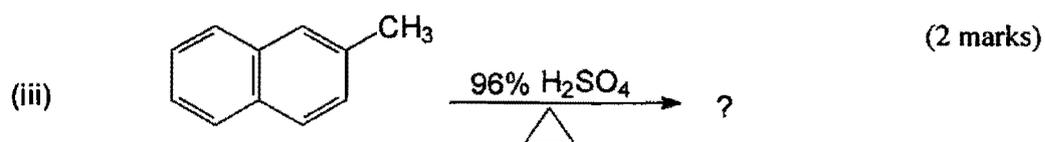
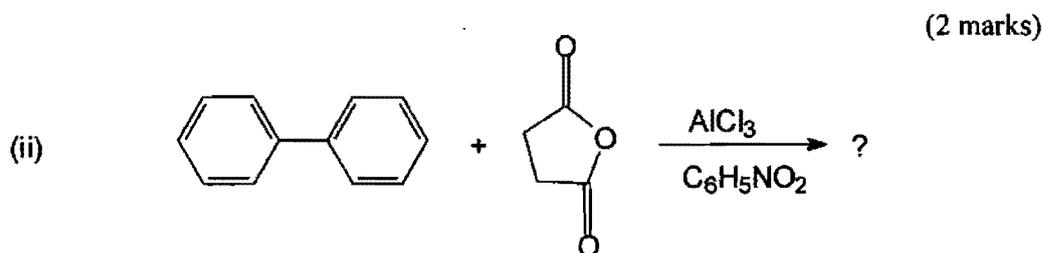
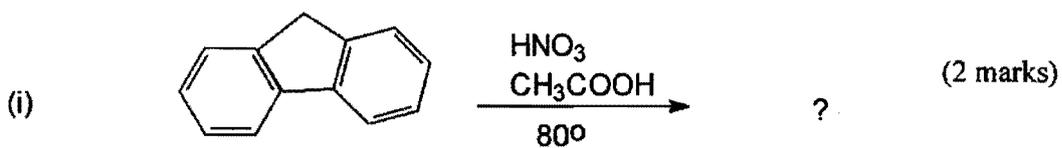


(iii) Anthracene VI from phthalic anhydride (V).

(3 marks)



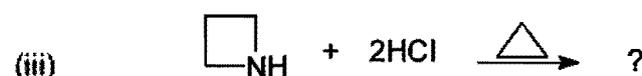
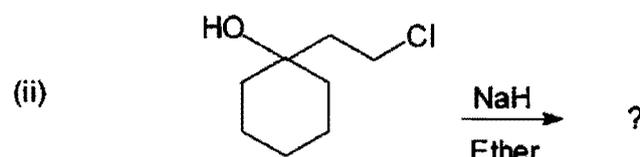
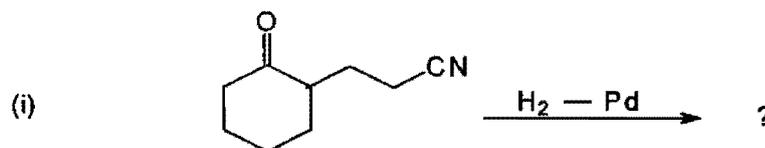
(c) Each of the following reactions has been reported in the chemical literature and proceeds cleanly in good yield. Write down the structure of the principal product in each case.



Question 2 **Heterocyclic Compounds**

Non Aromatic Heterocycles

- (a) Write down the structure of the principal product from each of the following reactions. (6 marks)



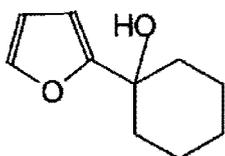
Aromatic heterocycles

- (b) (i) Briefly describe the structure and bonding characteristics in pyrrole and thiophene in terms of orbital hybridization. (2 marks)

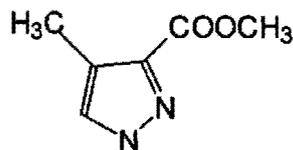
Explain the following factual observations:

- (ii) Pyridine is more basic than pyrrole even though both of them have lone pair of electrons on nitrogen which can be protonated in an acid-base reaction. (2 marks)
- (iii) Thiophene is more aromatic than furan. (2 marks)

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

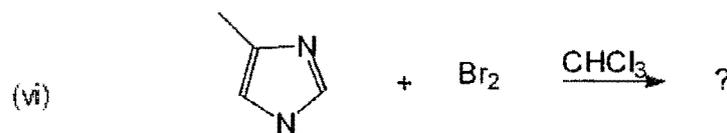
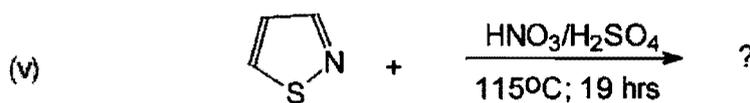
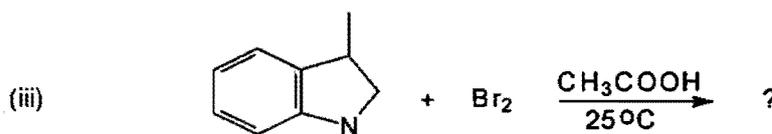


(i) (5 marks)



(ii) (2 marks)

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



SECTION B**NATURAL PRODUCTS****Carbohydrates, Fatty Acids and Derivatives****Question 3**

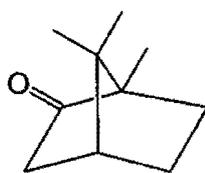
- (a) (i) Explain why the melting point of a fat molecule depends on the amount of unsaturation in the fatty acid component of the fat. (3 marks)
- (ii) By considering the formation of butanoic acid from two molecules of acetyl coenzyme A, describe briefly, the major elements of fatty acid biosynthesis. (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, $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$, 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) $\text{Br}_2/\text{H}_2\text{O}$
- (ii) dil.HNO_3
- (iii) H_2/Pt (8 marks)
- (iv) $\text{CH}_3\text{OH}/\text{dry HCl}$
- (c) Starting from D-Glyceraldehyde describe the steps involved in the synthesis of D-threose. (7 marks)

Question 4 Terpenes and Steroids

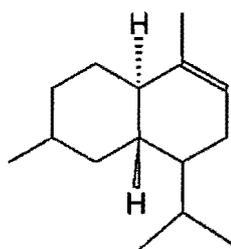
Structure

- (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.

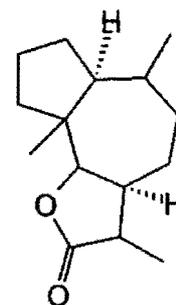
(4 marks)



Camphor



β -cadinene

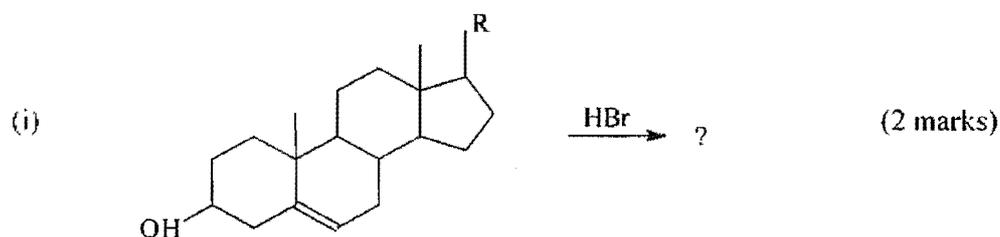


Ambrosin

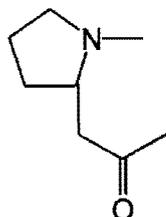
- (ii) Which two structural factors determine the course and rate of reaction of steroids? (2 marks)
- (iii) With diagrams and suitable examples, describe briefly how these factors work. (2 marks)

Reactions

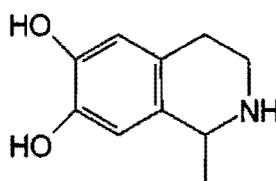
- (b) Predict and draw the structure of the principal organic product expected from each of the following reactions of steroid compounds.



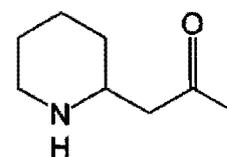
- (c) Outline a biosynthetic pathway for each of the following alkaloid compounds. (13 marks)



(i)
(5 marks)



(ii)
(4 marks)

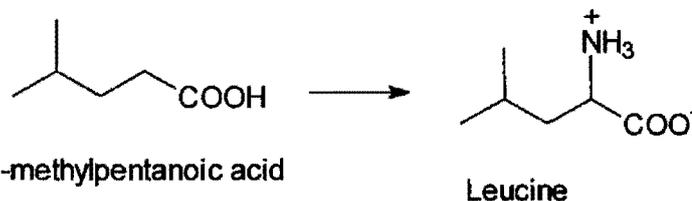


(iii)
(4 marks)

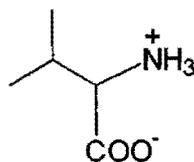
Question 6

Amino Acids, Peptides and Proteins.

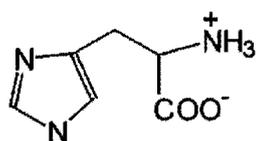
- (a) Suggest a synthesis of Leucine from 4-methylpentanoic acid. (5 marks)



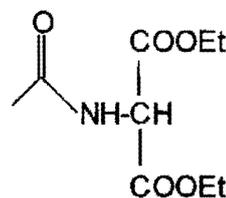
- (b) Outline the steps in the preparation of Valine by the Strecker Synthesis. (5 marks)



- (c) Using diethylacetamidomalonate and any other appropriate reagents, outline a synthesis for histidine. (7 marks)



histidine



Diethylacetamidomalonate

- (d) Glycine undergoes acid catalysed esterification more slowly than does propionic acid. Explain. (4 marks)
- (e) Write the structural formula of the Glycylalanine (Gly-ala) dipeptide showing:
- (i) the constitution and
 - (ii) the stereochemistry at the α -carbon atom. (4 marks)