# UNIVERSITY OF SWAZILAND
# FINAL EXAMINATION 2011

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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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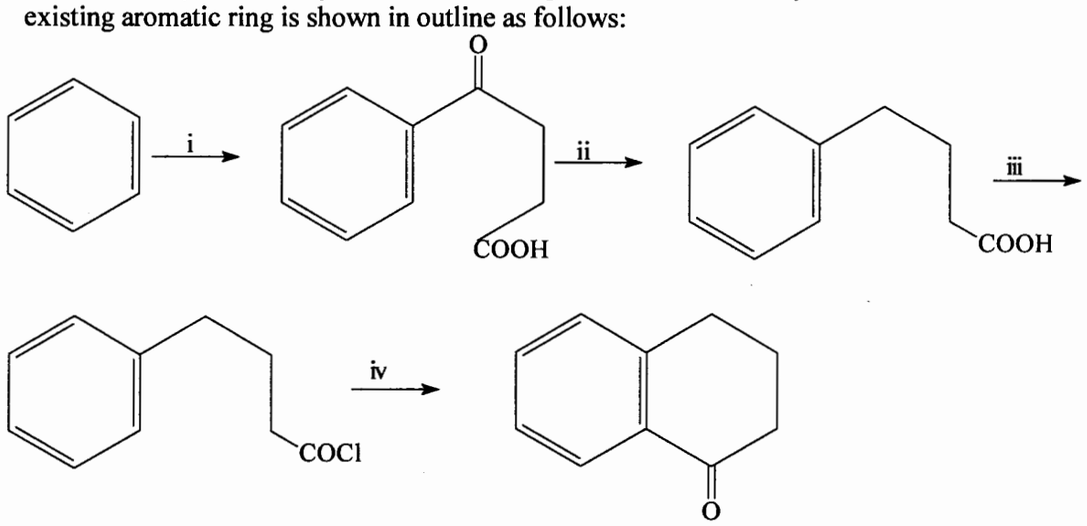
This Paper contains ten (10) printed pages.

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

**Question 1** ***Polycyclic Aromatic Hydrocarbons***

**Synthesis**

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

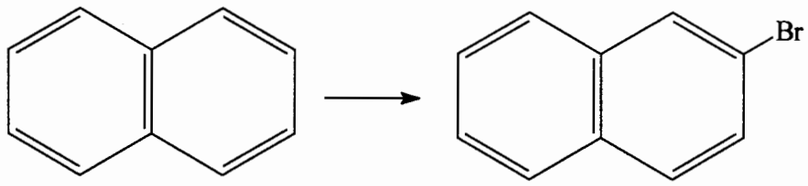



Specify the reagents and general reaction conditions necessary for each of the steps in (i) to (iv). (8 marks)

**Reactions**

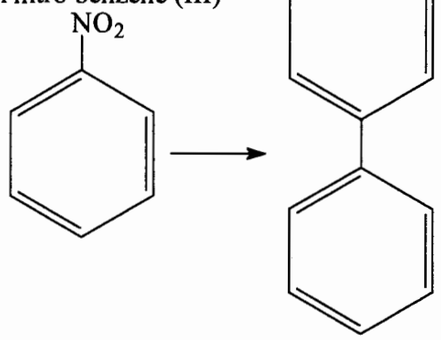
(b) Write a sequence of reactions showing al the suitable reagents and reaction conditions for laboratory synthesis of the following compounds.

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



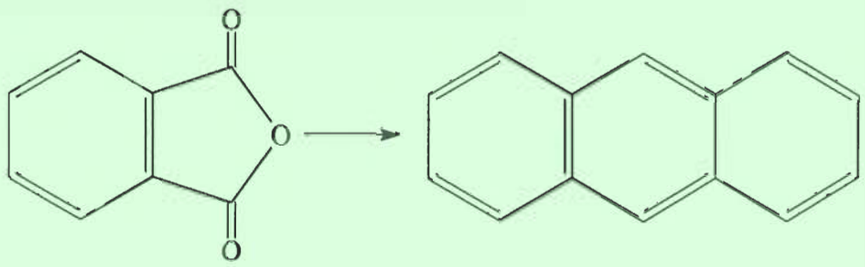

(I) (II)

(ii) Biphenyl (iv) from nitro benzene (III) (3 marks)



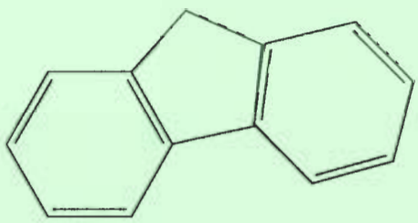

(III) (IV)

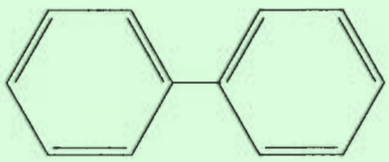
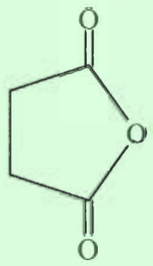
(iii) Anthracene VI from phthalic anhydride (V)

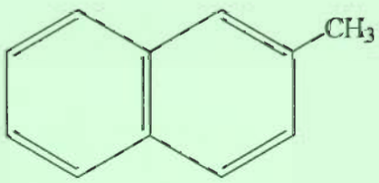


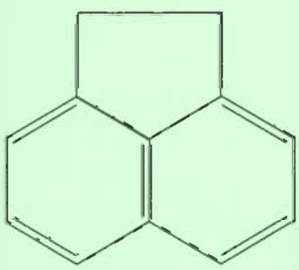
(V) (VI)

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

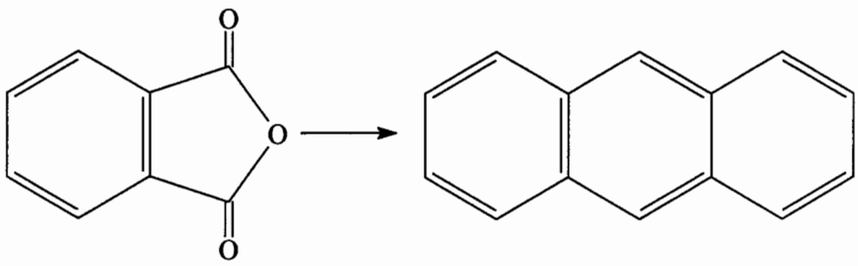
(i)  $\xrightarrow[80^{O}C]{HNO_3/CH_3COOH}$ ? (2 marks)

(ii)  +  $\xrightarrow[C_6H_5NO_2]{AlCl_3}$ ? (2 marks)

(iii)  $\xrightarrow[\triangle]{96\%\ H_2SO_4}$ ? (2 marks)

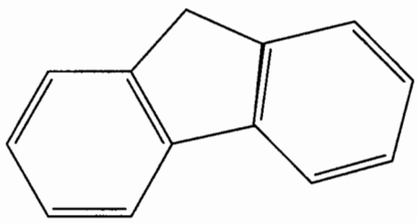
(iv)  $\xrightarrow[\triangle]{HNO_3/H_2SO_4}$ ? (2 marks)

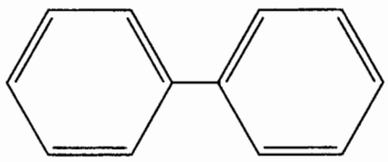
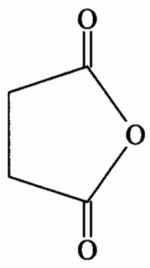
(iii) Anthracene VI from phthalic anhydride (V)

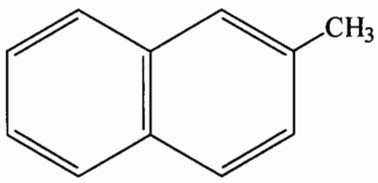


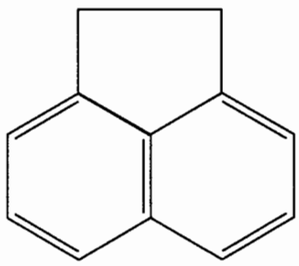
(V) (VI)

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

(i)  $\xrightarrow[80^{o}C]{HNO_3/CH_3COOH}$ ? (2 marks)

(ii)  +  $\xrightarrow[C_6H_5NO_2]{AlCl_3}$ ? (2 marks)

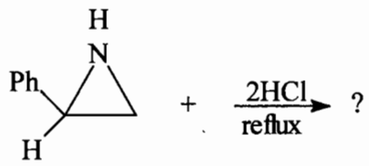
(iii)  $\xrightarrow[\Delta]{96\%\ H_2SO_4}$ ? (2 marks)

(iv)  $\xrightarrow[\Delta]{HNO_3/H_2SO_4}$ ? (2 marks)

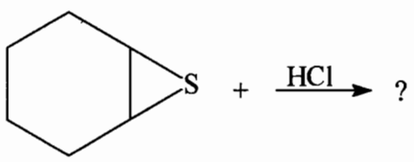
## Question 2

### I Non Aromatic Heterocycles

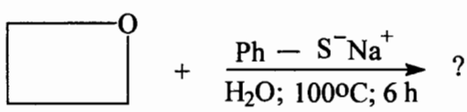
(a) Write down the structure of the principal product from each of the following reactions.

(i) 

(2 marks)

(ii) 

(2 marks)

(iii) 

(2 marks)

### Aromatic Heterocycles

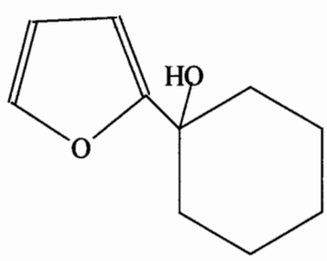
(b) (i) Briefly describe the structure and bonding characteristics in pyrrole and thiophene in terms of orbital hybridization. (2 marks)

Explain the following factual observations:

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

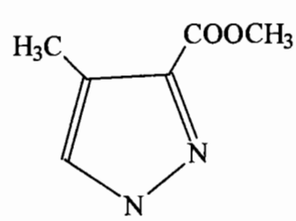
(iii) Thiophene is more aromatic than furan. (2 marks)

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




(VII)

(5marks)

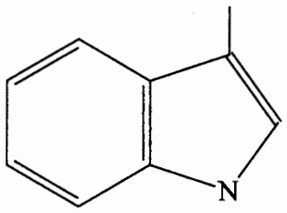



(VIII)

(2 marks)

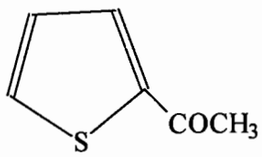
(d) Predict the major product expected from each of the following reactions of heterocyclic aromatic compounds. (1½ marks each)

(i)



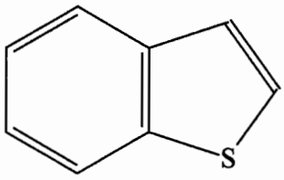

$+ \ Br_2 \xrightarrow[25^{O}C]{CH_3COOH} ?$

(ii)



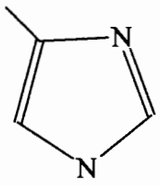

$\xrightarrow[ZnCl_2/CHCl_3]{CH_2O/HCl} ?$

(iii)




$+ \ CH_2O \xrightarrow{HCl} ?$

(iv)




$+ \ Br_2 \xrightarrow{CHCl_3} ?$

**Question 3**

**Carbohydrates, Fatty Acids and Derivatives**

(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$^{O}$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$^{O}$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. $HNO_3$ (8 marks)

(iii) $H_2/Pt$

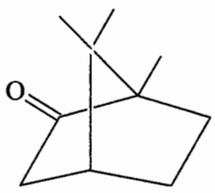
(iv) $CH_3OH$/dry HCl

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

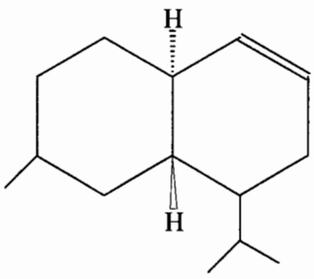
**Question 4** **Terpenes and Steroids**

**Structure**

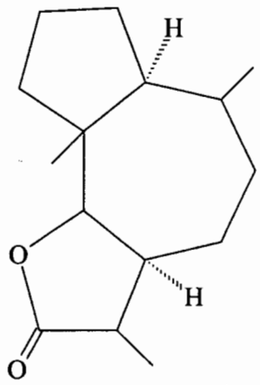
(a) (i) The following terpenes are made up of more than one isoprene unit. Draw the compounds and with dotted line or cycles, identify the five carbon fragments corresponding to the isoprene units in each compound. (4 marks)




Camphor




β-cadinene




Ambrosin

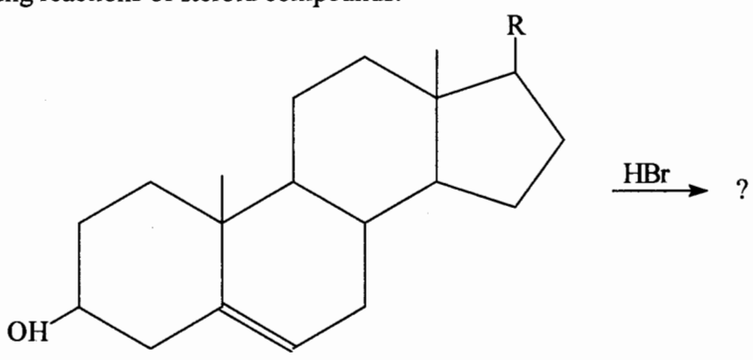
(ii) Which two structural factors determine the course and rate of reaction of steroids? (2 marks)

(iii) With a diagram and a suitable example, describe briefly how one of these factors work. (2 marks)

**Reactions**

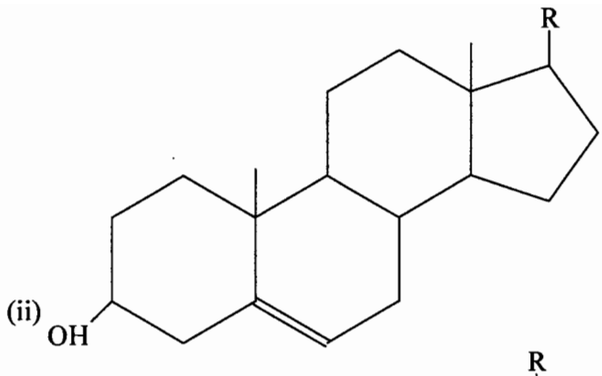
(b) Predict and draw the structure of the principal organic product expected from each of the following reactions of steroid compounds.

(i)




(2 marks)

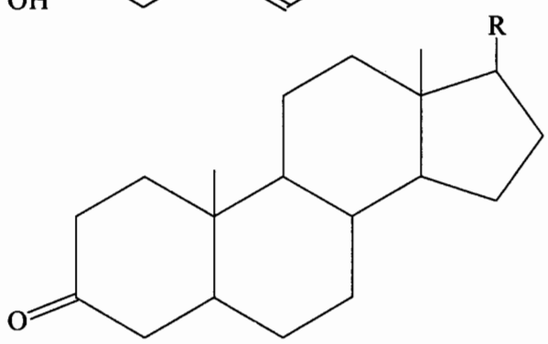
(ii)




1. $Ac_2O$ / 2. $H_2/Pt$ → [A] 1. $CrO_3/AcOH$ / 2. MeOH/NaOH → [B]

(4 marks)

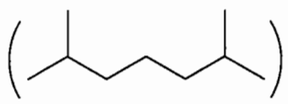
(iii)




$H_2/Pt$ →

Neutral Solution → ? (2 marks)

Acidic Solution → ? (2 marks)

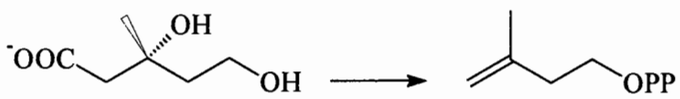
R = 

**Biosynthesis**

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

(i) iso-Pentenyl pyrophosphate (IPP) from mevahemic acid (MVA)

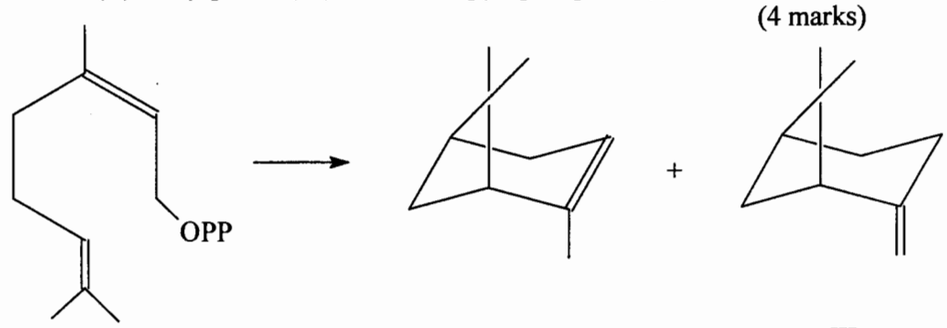
(3 marks)




(MVA) (IPP)

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

(4 marks)




I II III

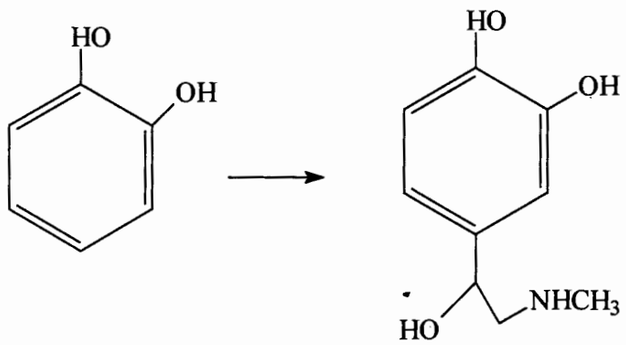
## Question 5

**Alkaloids**

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

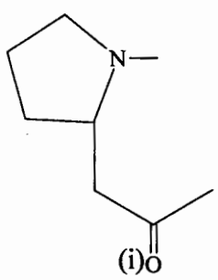
(i) Definition
(ii) Occurrence and distribution
(iii) Properties
(iv) Isolation and purification
(v) Importance in human health care.

(b) From the commercially available compound 2-hydroxyphenol and any other suitable reagents, outline a laboratory synthesis of the important neurotransmitter adrenalin. (6 marks)



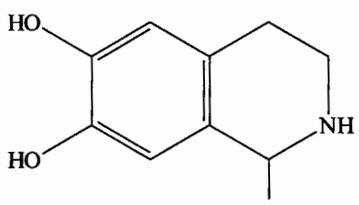

2-hydroxyphenol ± adrenalia

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



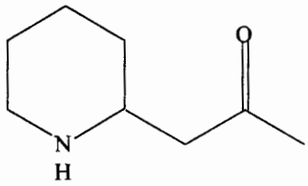

(i)

(5 marks)




(ii)

(4 marks)

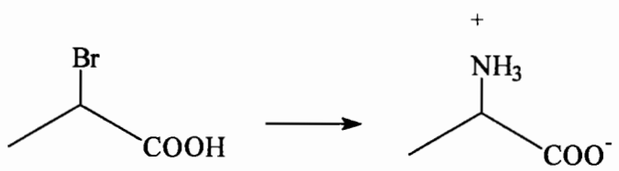



(iii)

(4 marks)

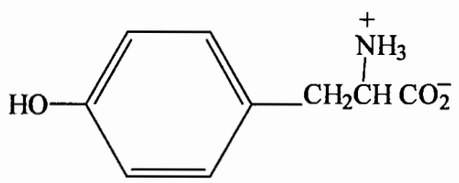
**Question 6** **Amino Acids, Peptides and Proteins**

(a) Outline a synthesis of DL-alanine from α-bromopropanoic acid. (5 marks)



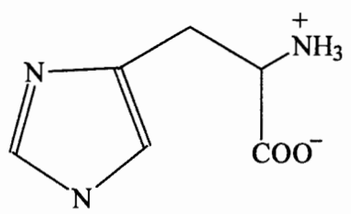

α-bromopropanoic acid DL-alanine

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

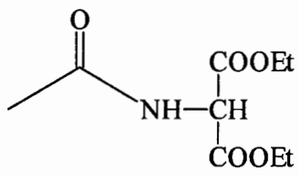



DL-tyrosine

(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)