

UNIVERSITY OF SWAZILAND
SUPPLEMENTARY EXAMINATION 2014

TITLE OF PAPER : Advanced Organic Chemistry

COURSE NUMBER : C403

TIME : Three Hours

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

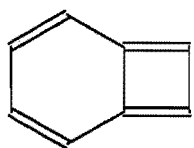
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This Paper contains ten (10) printed pages.

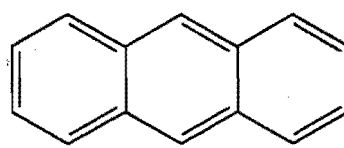
You must not open this paper until the Chief Invigilator so has granted permission to do.

Question 1 *Structure and Properties of Biphenyl Naphthalene Anthracene and Phenanthrene*

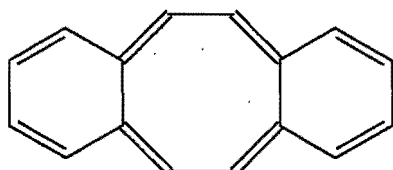
- (a) Write the correct structure for the most stable resonance form of structure for each of the following compounds. (5 marks)



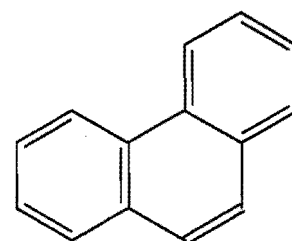
(i)



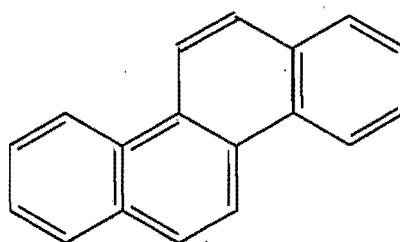
(ii)



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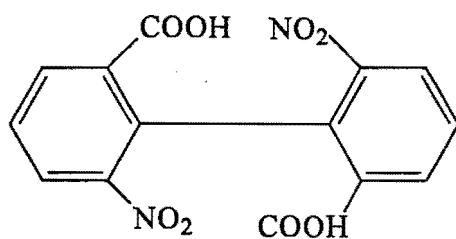


(iv)

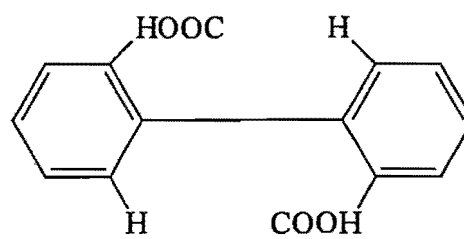


(v)

- (b) (i) Briefly describe the structure of biphenyl. Indicate the elements of biphenyl structure that explain its physical properties. (3 marks)
- (ii) Explain why the optical resolution of compound (2) is possible when the same optical resolution of compound (3) is normally unsuccessful. (3 marks)



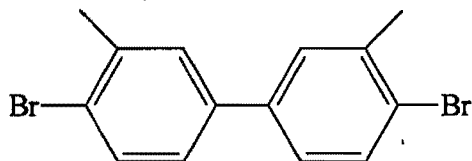
(2)



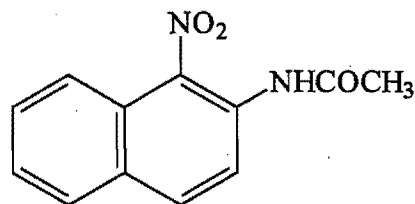
(3)

(c) *Synthesis*

Write the sequence of reactions that correctly describe a rational synthesis of each of the following compounds. Start with the simplest and most available hydrocarbon and, in each case, show all reagents reaction conditions and intermediate products:



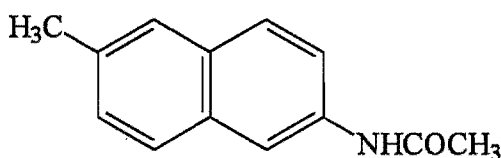
(i) (4 marks)



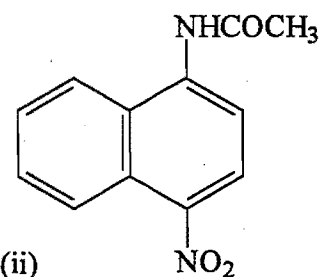
(ii) (4 marks)

(d) *Reaction*

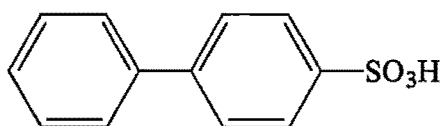
- (i) Explain why electrophilic substitution occurs in naphthalene preferentially at C - 1 rather than at C - 2. (4 marks)
- (ii) Write the structure of the expected dominant product on the mononitration of each of the following compounds. (2 marks)



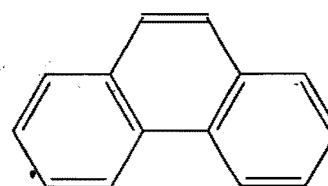
(i)



(ii)



(iii)



(iv)

(Each correct structure = 1/2 marks)

Question 2

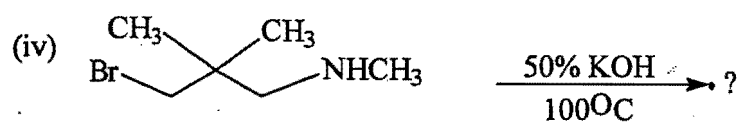
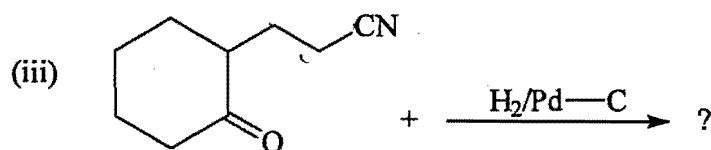
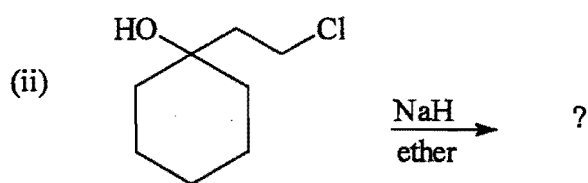
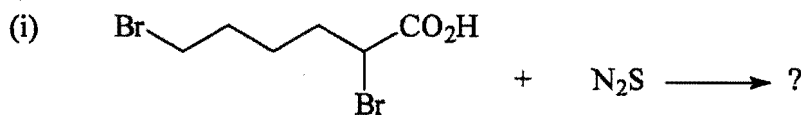
(a) Write the correct structure for each of the following compounds:

(4 marks)

- (i) 2 - Phenylaziridine
 (ii) 3 - azetidone
 (iii) 2,5 - Dihydrofuran
 (iv) 3 - Methyltetrahydropyran

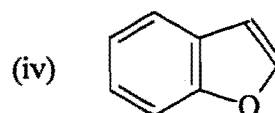
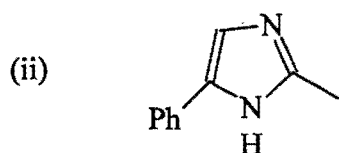
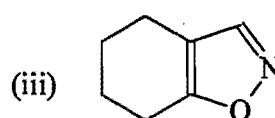
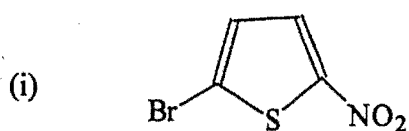
(b) Predict and give the major product from each of the following reactions:

(4 marks)

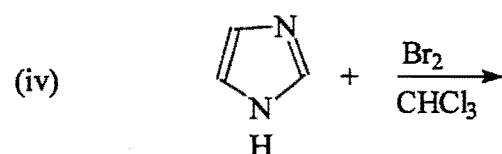
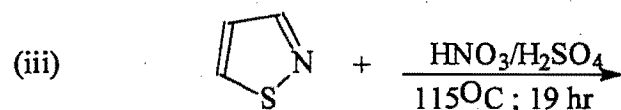
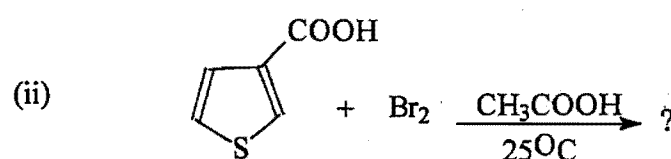
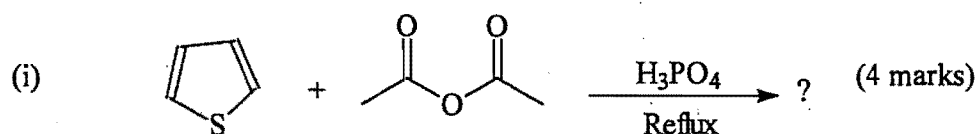


- (c) (i) Briefly describe the orbital structure and bonding characteristics of pyrrole and imidazole. (3 marks)
- (ii) Explain the following observations:
- (a) Compared with other azoles, pyrazole and imidazole are solids at room temperature and have higher boiling points. (2 marks)
- (b) Furan, pyrrole and thiophene undergo electrophilic substitution predominantly at C-2. (1 marks)
- (c) Pyridine is more basic than pyrrole. (1 marks)

- (d) Give a brief outline of a synthesis for each of the following heterocyclic compounds. (1½ marks each)

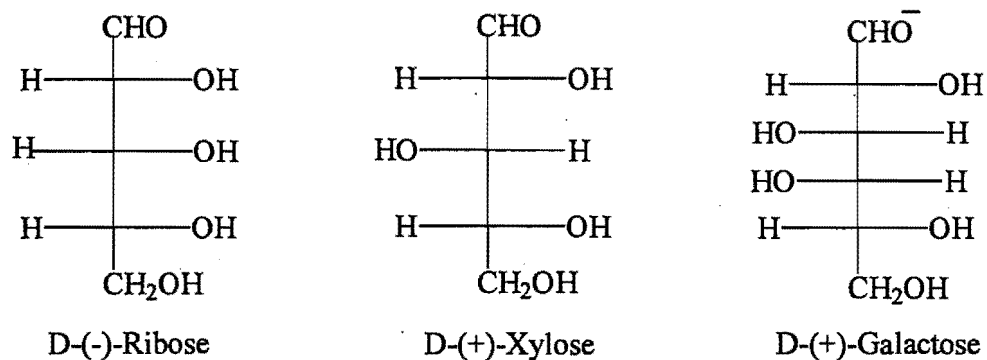


- (e) Write the structure of the main product expected from each of the following reactions of heterocyclic aromatic compounds.

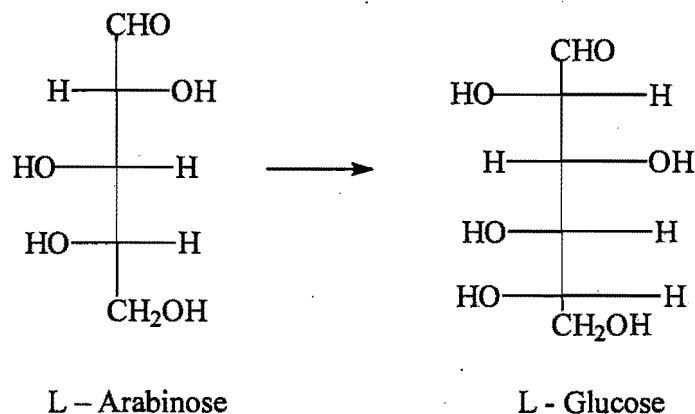


Question 3 Carbohydrates

- (a) Write the Harworth formulas corresponding to the α – and β – pyranose forms of D – Xylose, D – Ribose and D – Galactose. (9 marks)



- (b) Show the steps and reagents in the synthesis of L-Glucose from L-Arabinose (8 marks)

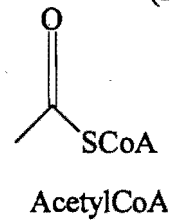
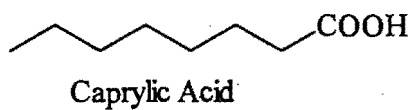


- (c) Give the structure of the product of the reaction of D-glucose with the following reagents: (8 marks)

- (i) bromine in water ($\text{Br}_2/\text{H}_2\text{O}$)
- (ii) Nitric acid
- (iii) Acetic anhydride in pyridine
- (iv) Hydroxylamine ($\text{HO} - \text{NH}_2$)
- (v) Sodium borohydride in water ($\text{NaBH}_4/\text{H}_2\text{O}$)

Question 4 Lipids**(a) Fatty Acids**

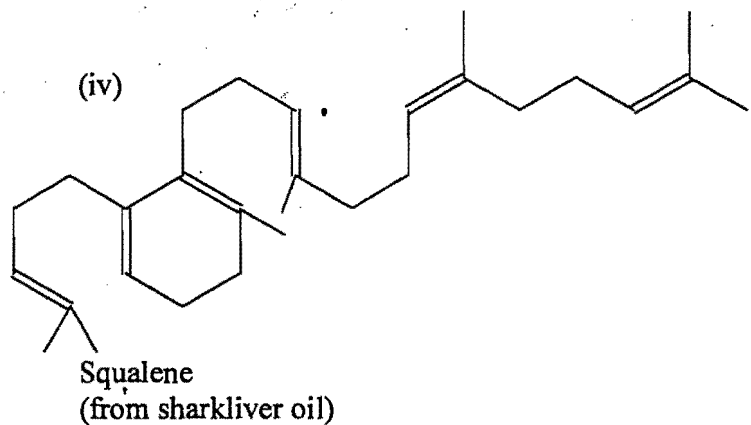
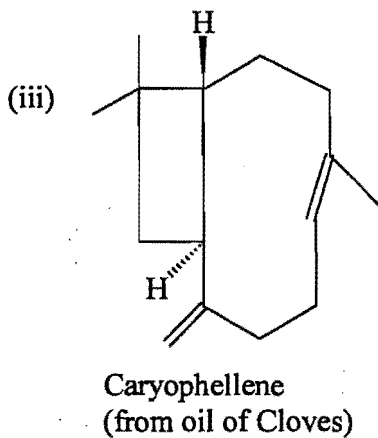
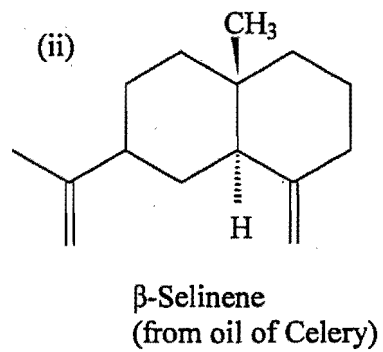
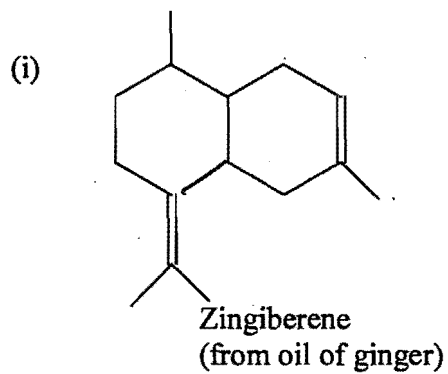
- (i) The physical properties (m.p. appearance etc) of fats, waxes and oils normally depend on the degree of unsaturation in the fatty acid component. Explain. (2 marks)
- (ii) Outline the sequence of biological reactions involved in the biosynthesis of caprylic acid (C_8) from acetylCoA. (3 marks)



- (iii) Give a brief summary of the typical reactions of fatty acids. (3 marks)

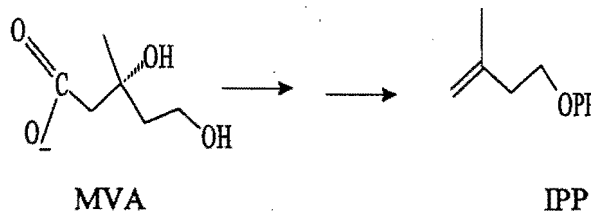
Terpenes

- (b) Show the isoprene units in each of the following terpenes, and classify each terpene as a monoterpene etc. (1 mark each)

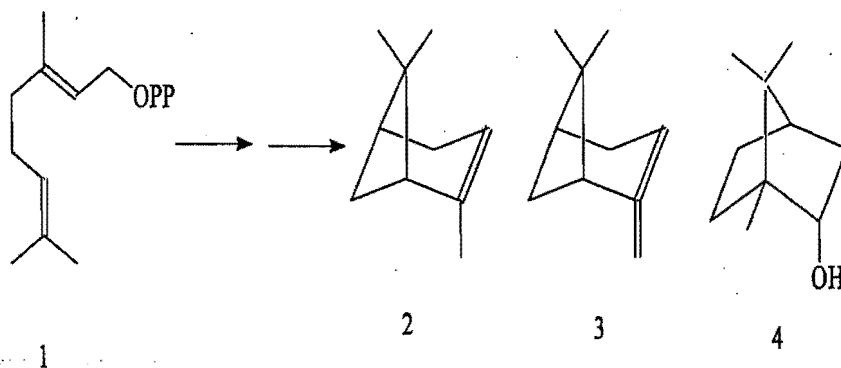


(c) Show the main steps and outline the key reactions in each step that are involved in the biosynthesis of the compounds named vide infra (below).

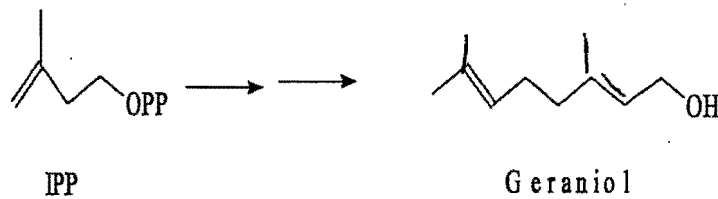
(i) iso-Pentenylpyrophosphate (IPP) from mevalonic acid (MVA). (2 marks)



(ii) α -Pinene(2), β -Pinene (3) and borneol. 1 (4) from E-Geranyl pyrophosphate (1) (3 marks)

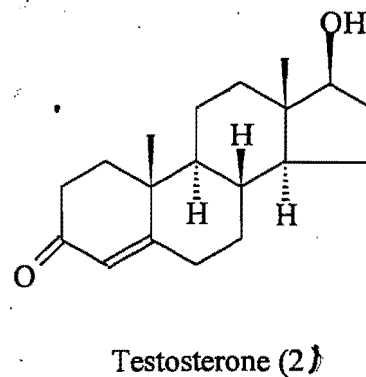
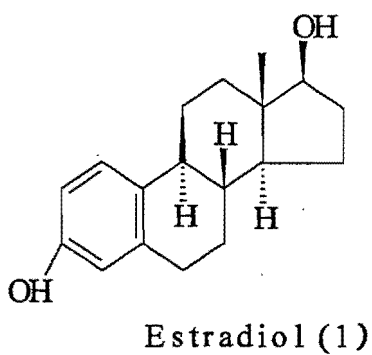


(iii) Geraniol from IPP (2 marks)



Steroids

(d) The structures of the estrogen estradiol (1) and the androgen testosterone 2 are shown vide infra

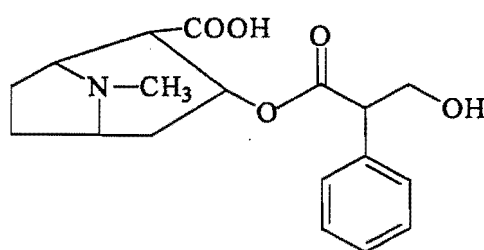


Examine these structures closely and answer the following questions:

- (i) Indicate the structural differences between the two compounds. (2 marks)
- (ii) Estrogens, for example, Estradiol, are easily separated from androgens (testosterone), on the basis of one of their chemical properties. What is the property and how could such separation be accomplished? (2 marks)
- (iii) Name any two features of the steroid structure that determine the course, rate and stereo chemical outcome of their reactions. (2 marks)

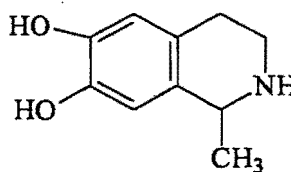
Question 5 Alkaloids

- (a) Outline a biosynthesis for the following compounds.



Hyosyamine

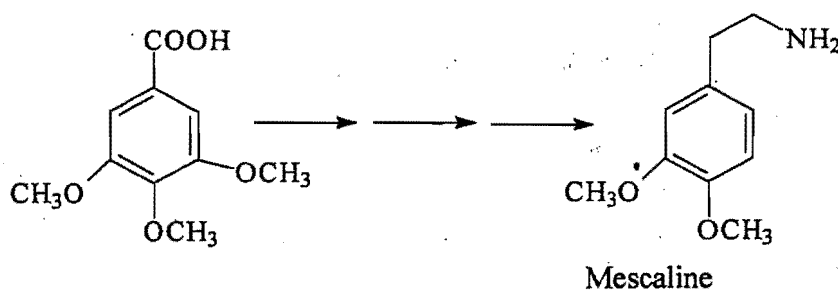
(13 marks)



Pellotine

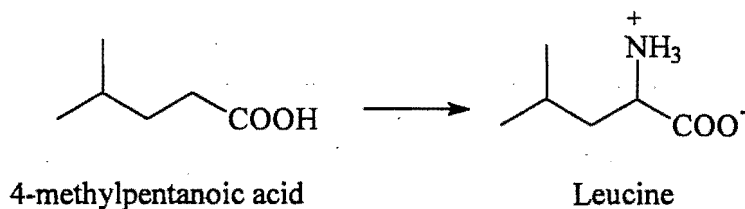
(6 marks)

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

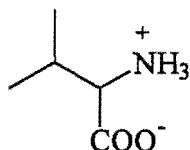


Question 6 Amino Acids

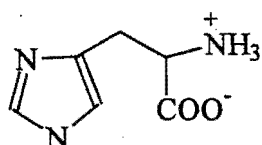
- (a) Suggest a synthesis of Leucine from 4-methylpentanoic acid. (4 marks)



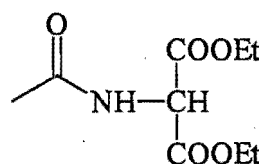
- (b) Outline the steps in the preparation of Valine by the Strecker Synthesis. (4 marks)



- (c) Using diethylacetamidomalonate and any other appropriate reagents, outline a synthesis for histidine. (5 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:
- the constitution and
 - the stereochemistry at the α -carbon atom. (4 marks)
- (f) Predict and draw the structure of the major product of the reaction of glycine with the following reagents. (4 marks)
- NaNO_2 and dilute HCl
 - Acetic anhydride $[(\text{CH}_3\text{CO})_2\text{O}]$
 - NaOBr
 - $\text{CH}_3\text{CH}_2\text{OH}$ and dry HCl