UNIVERSITY OF SWAZILAND

FIRST SEMESTER MAIN EXAMINATION 2008/2009

TITLE OF PAPER	:	**ORGANIC CHEMISTRY**
COURSE NUMBER	:	**C303**
DURATION (TIME)	:	**THREE (3) HOURS**
INSTRUCTIONS	:	**ANSWER ANY FOUR (4) QUESTIONS. EACH QUESTION CARRIES 25 MARKS.**

CAUTION	:	**DO NOT OPEN THIS PAPER UNTIL PERMISSION TO DO SO HAS BEEN GRANTED.**

SECTION A: Instrumental Methods of Structure Determination
NMR Spectroscopy

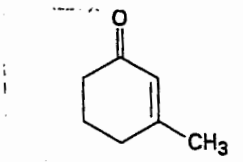
QUESTION ONE

(a) Nuclear magnetic resonance (NMR) spectroscopy is the most valuable spectroscopic technique available to organic chemists. It is the method of structure determination that organic chemists turn to first. Give a brief summary of the fundamental principles on which NMR spectroscopy is based. [6 marks]

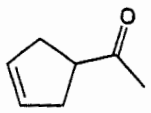
(b) Explain why all protons in a molecule do not absorb radio-frequency (rf) energy at the same time. [6 marks]

(c) Propose a structure for a compound $C_5H_{12}O$, that fits the following ^1H NMR data: 0.92 δ (3H, J = 7 Hz), 1.2 δ (6H, singlet), 1.50 δ (2H, quartet, J = 7 Hz), 1.64 δ (1H, broad singlet). [6 marks]

(d) How could you use ^1H NMR, ^{13}C NMR, and IR spectroscopy to help you distinguish between the following structures: [7 marks]



3-Methylcyclohex-2-enone



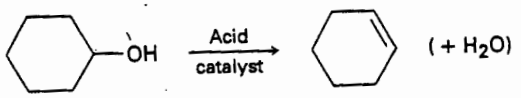
Cyclopent-3-enyl methyl ketone

SECTION B: Organic Reactions

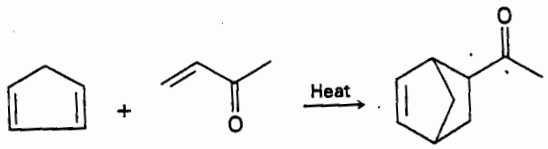
QUESTION TWO

(a) Identify the following reactions as additions, eliminations, substitutions, or rearrangements:

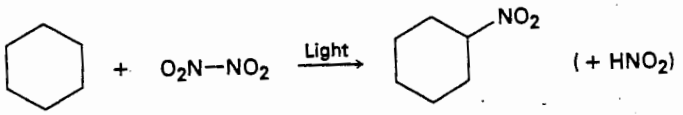
(i) $CH_3CH_2Br + NaCN \longrightarrow CH_3CH_2CN\ (+ NaBr)$ **(4 marks)**

(ii) 

(4 marks)

(iii) 

(4 marks)

(iv) 

(4 marks)

(b) The naturally occurring molecule α–terpeneol is biosynthesized by a route that includes the following step:

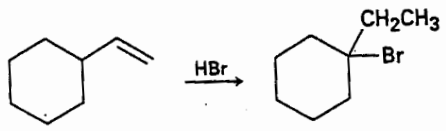
Carbocation α-Terpineol

(i) Propose a likely structure for the isomeric carbocation intermediate. [4 marks]

(ii) Show the mechanism of each step in the biosynthetic pathway, using curved arrows to indicate electron flow. [5 marks]

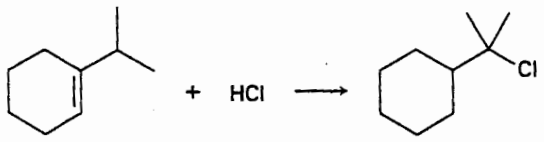
QUESTION THREE

(a) On treatment with HBr, vinyl cyclohexane undergoes addition and rearrangement to yield 1-bromo-1-ethylcyclohexane. Propose a mechanism to account for this result. [6 marks]

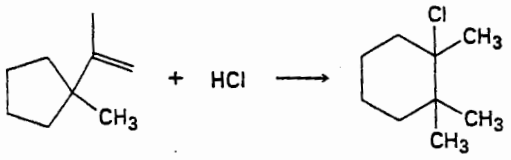


Vinylcyclohexane 1-Bromo-1-ethylcyclohexane

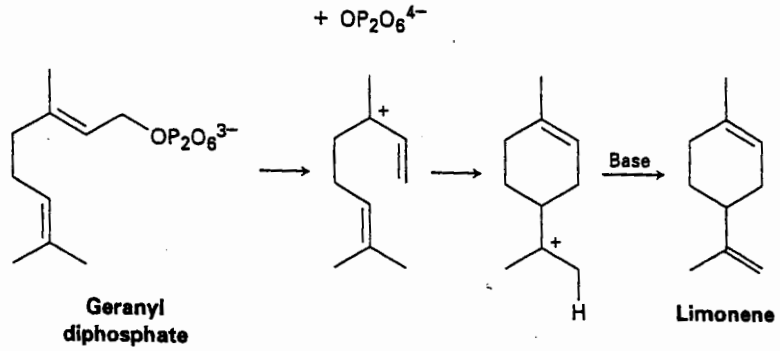
(b) Addition of HCl to 1-isopropylcyclohexene yields a rearranged product. Propose a mechanism, showing the structure of the intermediate and using curved arrows to indicate electron flow in each step. [6 marks]



(c) Addition of HCl to 1-isopropenyl-1-methylcyclopentane yields 1-chloro-1,2,2-trimethylcyclohexane. Suggest a mechanism, showing the structures of the intermediate and using curved arrows to indicate electron flow. [7 marks]



(d) Limonene, a fragrant hydrocarbon found in lemon and oranges, is biosynthesized from geranyldiphosphate by the following pathway. Add curved arrows to show mechanism of each step. Which step involves an alkene electrophilic addition? (The ion $OP_2O_6^{4-}$ is the diphosphate ion, and "base" is an unspecified base in the enzyme that catalyzes the reaction). [6 marks]

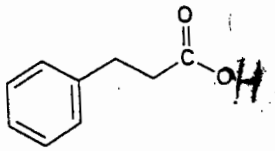


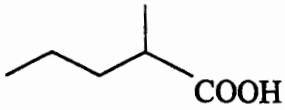
SECTION C: Synthesis

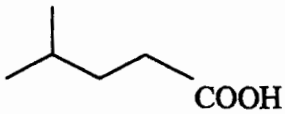
QUESTION FOUR

How could you use a malonic ester synthesis to prepare the following compounds? Show all the steps in each case.

(a)  [6 marks]

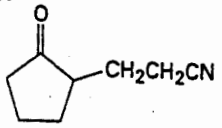
(b)  [6 marks]

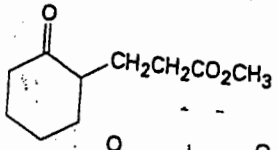
(c)  [7 marks]

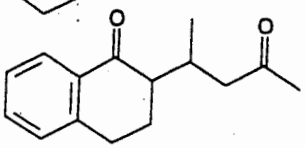
(d)  [6 marks]

QUESTION FIVE

Show how you might use the Stock Enamine reaction to prepare the following compounds:

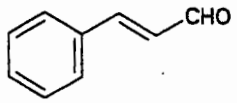
(a)  [9 marks]

(b)  [8 marks]

(c)  [8 marks]

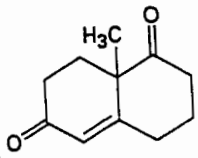
QUESTION SIX

(a) Cinnamaldehyde, the aromatic constituent of cinnamol oil, can be synthesized by a mixed aldol condensation. Show the starting materials you would use, and write the reaction. [8 marks]



Cinnamaldehyde

(b) The so-called Wieland-Miescher ketone is a valuable starting material used in the synthesis of steroid hormones. Show how you might prepare it from cyclohexane-1,3-dione. [8 marks]



Wieland–Miescher ketone

(c) The Darsens reaction shown below involves a two-step, base-catalysed condensation of ethylchloroacetate with a ketone to yield an epoxy ester. The first step is a carbonyl condensation reaction, and the second step is an SN^2 reaction. Write both steps, and show their mechanism. [9 marks]