UNIVERSITY OF SWAZILAND
FIRST SEMESTER FINAL EXAMINATION 2010

TITLE OF PAPER	:	Introductory Organic Chemistry
COURSE NUMBER	:	C203
TIME	:	Three Hours
INSTRUCTIONS	:	Answer any **FOUR Questions**. Each Question carries 25 Marks.

This Examination Paper Contains 9 (Nine) Printed Pages Including This Page

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

Question 1

(a) (i) Name the four (4) kinds of organic reactions, and give one suitable example of each kind. **(3 marks)**

(ii) Describe the reorganization of atoms and bonds that occur to reactant molecules during the progress of each kind of reaction named above. **(4 marks)**

Explain the following terms:

(iii) Nucleophile **(3 marks)**

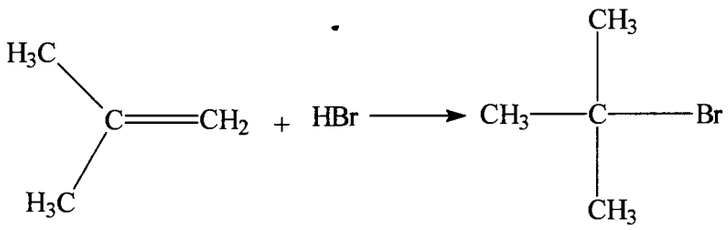
(iv) Electrophile **(3 marks)**

In each case give an appropriate example to illustrate your answer.

(b) (i) What is a reaction mechanism? **(2 marks)**

(ii) Describe two general kinds of mechanism by which reactions take place. **(4 marks)**

(c) Reaction of HBr with 2-methyl propene yields 2 – bromo – 2 – methylpropane.



(i) What is the structure of the carbocation formed? **(3 marks)**

(ii) Show the mechanism of the reaction. **(3 marks)**

Question 2

(a) Sketch an energy diagram for the following:

(i) A fast exergonic reaction. **(3 marks)**

(ii) A slow exergonic reaction **(3 marks)**

(iii) A fast endergonic reaction **(3 marks)**

(iv) A slow endergonic reaction. **(3 marks)**

(b) The reaction of hydroxide ion (HO^-) with chloromethane (CH_3Cl) to yield methanol is an example of a general reaction type called a nucleophilic substitution reaction.

$$HO^- + CH_3Cl \rightleftharpoons CH_3OH + Cl^-$$

(i) Write a mechanism for this reaction. **(4 marks)**

Given the value of ΔH^O for the reaction is -75 kJ/mol, and the value of ΔS^O is +0.054 J/K.mol.

(ii) What is the value of ΔG^O (in kJ/mol, at 298 K? **(3 marks)**

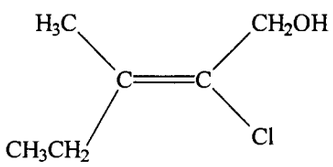
(iii) Is the reaction exothermic or endothermic? **(3 marks)**

(iv) Is it exergonic or endergonic? **(3 marks)**

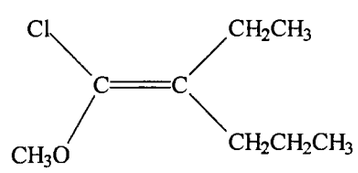
Question 3

(a) Assign *E* or *Z* configuration to the following alkenes: **(4 marks)**

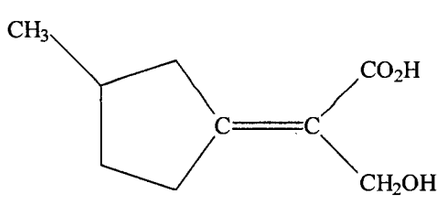
(i) (a)



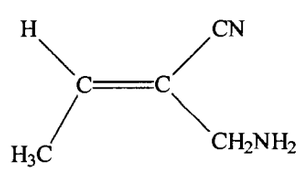
(b)



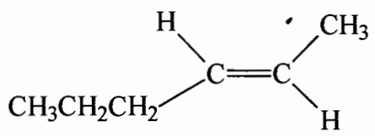
(c)



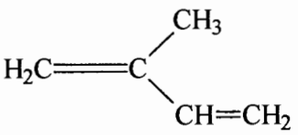
(d)



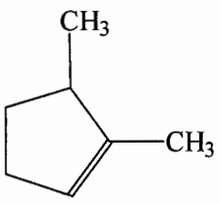
(ii) Name the following alkenes. **(4 marks)**



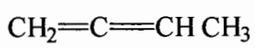
(a)



(b)



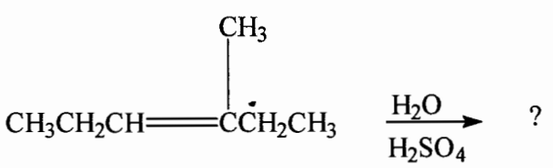
(d)



(d)

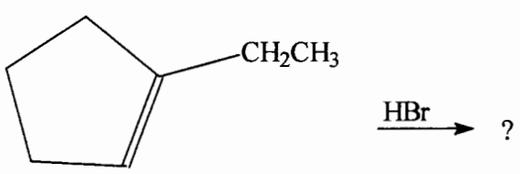
(iii) Predict the major product in each of the following reactions: **(4 marks)**

(a)

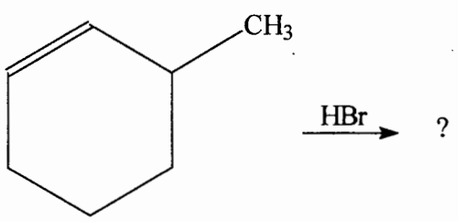


(Addition of H_2O occurs)

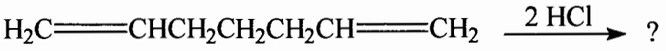
(b)



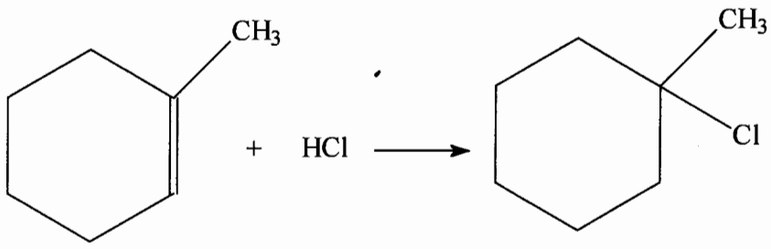
(c)



(d)



(b) Consider the following reaction:

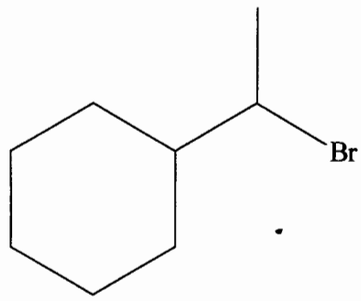


(i) Write the complete stepwise mechanism for this reaction. **(4.5 marks)**

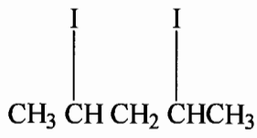
(ii) Draw a qualitative reaction energy diagram for this reaction. Label the position of all reactants, intermediates and products. **(4.5 marks)**

Predict the structure of the alkene you would use to prepare each alkylhalide below: **(4 marks)**

(iii)

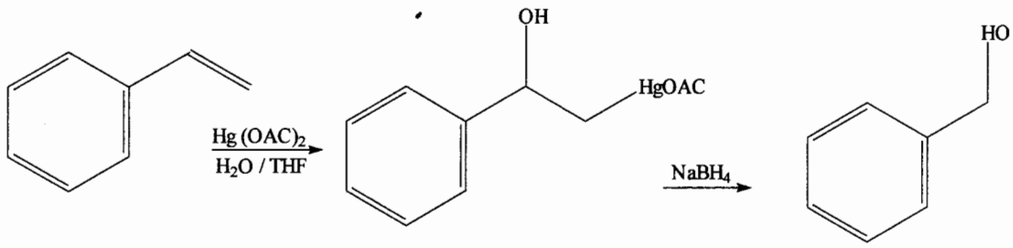


(iv)



Question 4

(a) Consider the reaction sequence below to answer the following questions:



(i) Write a complete reaction mechanism for the first step of this reaction in sequence. Show all electronflow with fishhook arrows and show all intermediate structures. **(8 marks)**

(ii) The intermediate in the first step of this reaction sequence is called: **(2 marks)**

(a) carbocation (b) cycloniumion

(c) mercuriniom ion (d) mercapto species.

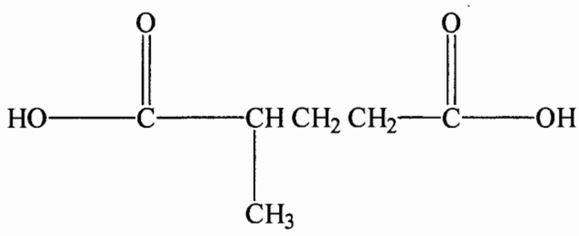
(iii) In the second step of this reaction sequence, the organomercury compound is treated with sodium borohydride, $NaBH_4$, to yield the alcohol product. This replacement of a carbon-mercury bond with a carbon-hydrogen bond is termed: **(2 marks)**

(a) an oxidation (b) a reduction

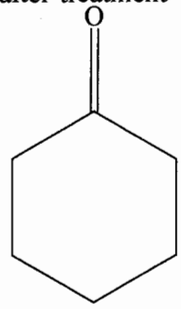
(c) a hydroxylation (d) a cycloaddition.

(b) To answer the questions below consider the following information:

In an abandoned laboratory has been found a flammable liquid A, in a bottle bearing only the "Compound A: C_7H_{12}". After verifying the molecular formular by elemental analysis, you find that Compound A reacts with 1 mol equivalent of hydrogen; and, after treatment with acidic $KMnO_4$, compound A gives the dicarboxylic acid C (see below). Another bottle from the same laboratory is labeled "Compound B (isomer of A)". Compound B also reacts with 1 mol equivalent of hydrogen, but yields cyclohexanone after treatment with acidic $KMnO_4$.



Compound C



Cyclohexanon

(i) How many degrees of unsaturation does Compound A posses? **(3 marks)**

(ii) Suggest structures for A and B. **(8 marks)**

(iii) What was the other product formed in the $KMnO_4$ oxidation of B. **(2 marks)**

Question 5

(a) Briefly explain the following terms and give appropriate examples as necessary.

(i) Chiral molecule **(2 marks)**
(ii) Constitutional isomers **(2 marks)**
(iii) Diastereomers **(2 marks)**

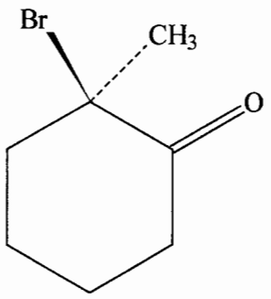
The specific rotation of a compound may be calculated from the observed rotation according to the expression.

$$[\alpha] = \frac{100\alpha}{cl}$$

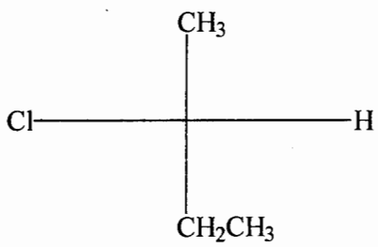
Where α = Observed rotation
c = Concentration of the sample in grams per 100 mL of solution.
l = length of the polarimeter in decimeters (one decimeter = 10 cm)

(iv) Cholesterol when isolated from natural sources is obtained as a single enantiomer. The observed rotation α of a 0.3 g sample of cholesterol in 15 mL of chloroform solution contained in a 10 cm polarimeter tube is -0.78^{O}. Calculate the specific rotation of cholesterol. **(2 marks)**

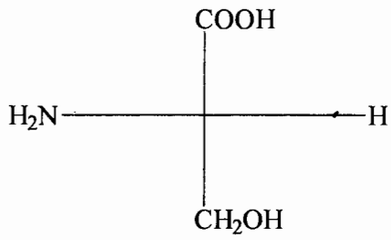
(b) Specify the configuration as R and S in each stereogenic centre of the following molecules. **(1½ marks each, total 9 marks)**



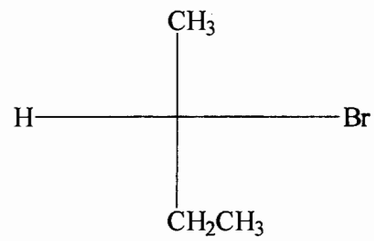
(i)



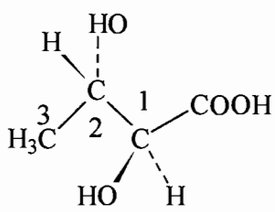
(ii)



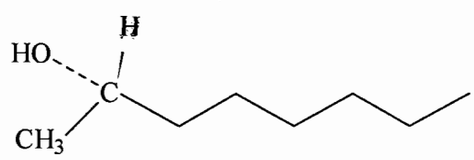
(iii)



(iv)



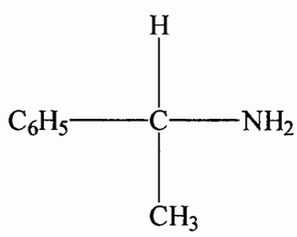
(v)



(vi)

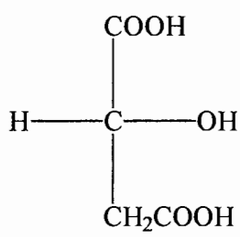
(c) The chemical reactions involved in the formation of diastereomers and their conversion to separate enantiomers are simple acid-base reactions. Through such reactions, naturally occurring (S)-(-)-malic acid (I) is often used to resolved racemic forms of amines. One such amine that has been resolved this way is 1-phenylethylamine (2)

(i) Briefly describe how the resolution of 1-phenylethylaine (2) into a pair of enantiomers may be achieved using (S)-(-)-malic and (2). **(6 marks)**



(2)

1-Phenylethylamine
(racemic mixture)



(1)

(S)-(-)-Malic Acic

(ii) In the resolution of 1-phenylethyl amine using (S)-(-)-malic acid, the compound obtained by recrystallization of the mixture of diastereomeric salts in (R)-1-phenylethylamm onium (S)-malate. The other component of the mixture is more soluble and remains in solution in the recrystallizatin solvent. What is the name and configuration of the more soluble salt? **(2 marks)**

Question 6

Tactaric acid [HO_2C-CH(OH)CH(OH)CO_2H)] was an important compound in the early history of stereochemistry. Two naturally occurring forms of tartaric acid are optically in active. One form has a melting point of 206 ^{O}C, the other a melting point of 140 ^{O}C. The inactive tartaric acid with a melting point of 206 ^{O}C can be separated into two optically active forms of tartaric acid with the same melting point (170 ^{O}C). One optically active tartaric acid has $[\alpha]_D^{25} = +12^O$; the other $[\alpha]_D^{25} = -12^O$. All attempts to separate the other inactive tartaric acid (m.p. 140 ^{O}C) into optically active compounds fail.

(a) How many stereoisomers of tartaric acid are possible. **(6 marks)**

(b) Write the three dimensional structure and the corresponding Fischer projection formula of the tartaric acid with the melting point 140 ^{O}C? **(7 marks)**

(c) What are the possible Fischer projection structures for the optically active tartaric acids with the melting points of 170 ^{O}C? **(6 marks)**

(d) What is the nature of the forms of tartaric acid with

(i) A melting point 206 ^{O}C? **(3 marks)**

(ii) A melting point of 140 ^{O}C? **(3 marks)**