# UNIVERSITY OF SWAZILAND
# FINAL DECEMBER EXAMINATION 2007

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

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This Examination Paper Contains 6 (Six) Printed Pages Including This Page

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

## SECTION A: CHEMICAL BONDING

### Question 1

(a) Name any five elements in the periodic table which are most commonly associated with the majority of organic compounds. (5 marks)

(b) Using the principles and rules that govern the distribution of electrons in atomic orbitals, write the ground state electron configuration for each atom named in (a) above. (5 marks)

(c) Why is knowledge of electron configuration of an element important in the study of molecular structure and properties of carbon compounds. (5 marks)

(d) With the aid of suitable diagrams and formulas, explain the following terms:

(i) An orbital (4 marks)
(ii) Lewis Structure (3 marks)
(iii) Chemical Bond (3 marks)

### Question 2

(a) Briefly describe the structure and bonding characteristics of ammonia molecule ($NH_3$) in terms of the following three modes of bonding:

(i) The Lewis model (3 marks)
(ii) Valence Shell Electron Pair Repulsion (VSEPR) theory. (3 marks)
(iii) Orbital hybridization (3 marks)

(b) (i) Write two resonance structures for the formate ion $H\overline{C}O_2$. (3 marks)

(ii) Explain what these structures predict for:

(1) The carbon-oxygen bond lengths of the formate ion. (2 marks)

(2) The electrical charge on the oxygen atoms. (2 marks)

(c) Write the dot structure, the dash structure and the bond – line formular for each of the following molecules:

(i) $(CH_3)_2\ CHOH$ (3 marks)
(ii) $(CH_3)_2\ CH\ CH_2CH_2CH_2OH$ (3 marks)
(iii) $CH_3\ \ddot{O}\ CH_3$ (3 marks)

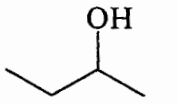
## SECTION B: STEREOCHEMISTRY

**Question 3**

(a) Briefly explain the following terms and give examples:

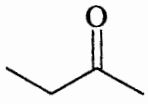
(i) Optical isomers (3 marks)
(ii) Diastereoisomers (3 marks)
(iii) Walden inversion. (3 marks)

(b) (i) Write the sequence of reaction that describes the synthesis of 2 – butanol (I) by the nickel catalysed hydrogenation of butanone (II) (2 marks)




2-Butanol

I




But - 2 - one

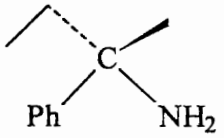
II

(ii) Use an appropriate diagram to illustrate the stereochemical aspects of the reaction of butanone with hydrogen in the presence of a nickel catalyst. (2 marks)

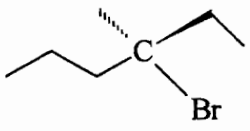
(iii) Explain why the 2 – butanol products are obtained in equal amounts as a racemate. (2 marks)

(iv) Suggest a method for synthesis of 2 – butanol which does not produce a racemic mixture. (2 marks)

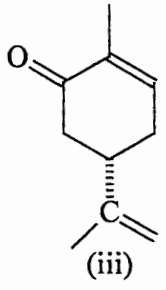
(c) Specify the configuration as R and S in each stereogenic centre of the following molecules:



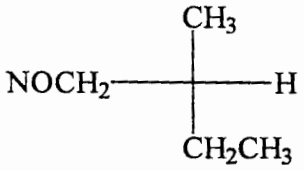

(i)




(ii)




(iii)




(vi)

(8 marks)

**Question 4**

(a) Examine the Fischer projection structure for 2,3-dihydroxybutanoic acid molecule in Figure I and answer the following questions:.

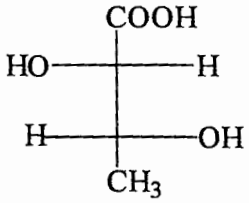



Figure I: Fischer projection structure for 2,3-dihydroxybutanoic acid

(i) How many stereoisomers of 2,3-dihydroxybutanoic acid are possible? (2 marks)

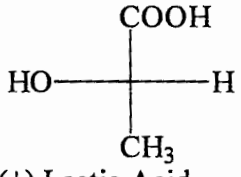
(ii) Draw Fischer projection structure for all the possible stereoisomers of 2,3-dihydroxybutanoic acid. (3 marks)

(iii) Write a three dimensional structure for each of the following compounds:

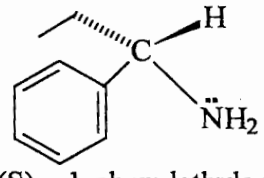
(a) (2S, 3R) – 2,3 – Dihydroxybotanoic acid. (2 marks)

(b) (2S, 3S) – 2,3 – Dihydroxybutanoic acid (2 marks)

(b) (i) Briefly outline a sequence of reactions that describes the resolution of the racemic form of latic acid (1) using optically pure (S) – 1 – phyenyl ethylamine (2). (6 marks)




(±) Lactic Acid
(1)




(S) – 1-phenylethylamine
(2)

(iii) In the resolution of lactic acid using (S)-1-phenylethylamine, the compound obtained by recrystallization of the mixture of diastereomeric salts is (S) - phenylethylammonium – (R) – lactate. The other component of the mixture is more soluble and remains in solution in the re-crystalization solvent. What is the name and configuration of the more soluble salt? (3 marks)

(c) Describe briefly how an enzyme could be used in the resolution of a racemic modification. (7 marks)

## SECTION C: REACTIONS AND SYNTHESIS OF ORGANIC COMPOUNDS

**Question 5**

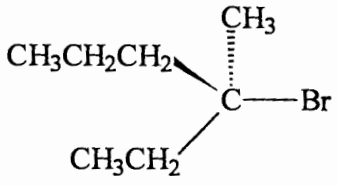
(a) Write a brief and full explanation of the following terms:

(i) Chemical reaction (2 marks)
(ii) The reaction profile (3 marks)
(iii) Reaction mechanism (3 marks)

(b) (i) List the most important factors which affect the rates of substitution by:

- $S_N^2$ mechanism
- $S_N^1$ mechanism (3 marks)

Heating optically active (S) – 3 – bromo – 3 – methylhexane with aqueous acetone affords two products A and B (see reaction below).

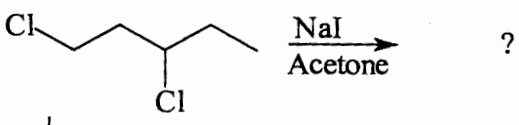



(ii) Draw the correct structure for compounds A and B. (2 marks)

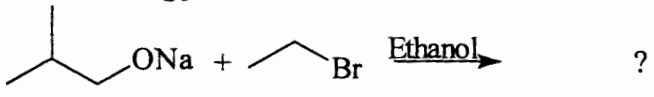
(iii) Write a valid mechanism for the formation of the products A and B. (2 marks)

(iv) What is the name of the reaction involved in the transformation of (S) – 3 – bromo-3-methylhexane to compounds A and B. (2 marks)

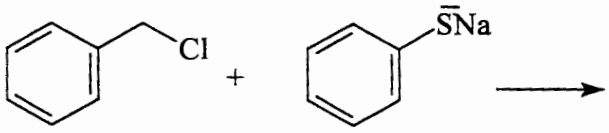
(c) Write the structure of the main product expected from the following reactions:

(i) 

(2 marks)

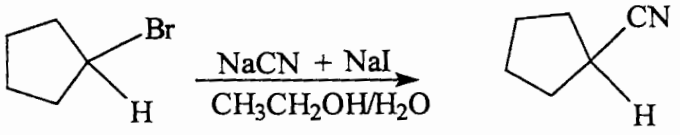
(ii) 

(2 marks)

(iii) 

(2 marks)

(v) The reaction of cyclopentenyl bromide (1) and sodium cyanide to give cyclopentanyl cyanide (2), (shown below) proceeds faster if a small amount of sodium iodide (NaI) is added to the reaction mixture. Suggest a reasonable mechanism to explain the catalytic function of sodium iodide. (2 marks)




(1) (2)

**Question 6**

Diethylmalonate is prepared commercially by hydrolysis and esterification of ethylcyanoacetate. The preparation of ethylcyanoacetate proceeds via ethylchloroacetate and begins with acetic acid.

$NCCH_2COOCH_2CH_3$ Ethylcyanoacetate

(a) Write a sequence of reactions that describe the synthesis of Diethylmalonate. (10 marks)

(b) Write three general formulas corresponding to the three classes of aliphatic amines. Name the classes and give an example of the common compounds in each class. (6 marks)

(c) Give a sequence of reactions showing how each amine cited in (b) above would react with nitrous acid.

(d) Write the sequence of reactions which describe the preparation of a diazonium salt from aniline. Give the structure of the product expected from the reaction of the resulting diazonium salt with water. (3 marks)