UNIVERSITY OF SWAZILAND
FIRST SEMESTER FINAL EXAMINATION 2006

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 10 (Ten) 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) (i) Write the ground state electron configuration of hydrogen, carbon nitrogen, oxygen and sulphur elements in tabular form, showing:

1. the z number and
2. the distribution of electrons among the various orbitals of each element. (4 marks)

(ii) The number of electrons and the disposition of those electrons among various orbitals in an atom determines the kind of bonds the atom forms. Give further explanation of this statement. (3 marks)

(b) (i) List the three common models of chemical bonding and write a brief summary complete with examples, explaining each model. (4 marks)

(ii) Write a complete Lewis structure for each of the following chemical species :

- Methylcation ($^{+}CH_3$)
- The chlorate ion (ClO^{-}_3)
- Isocyanic acid (O = CNH) (3 marks)

(iii) Boron trifluoride (BF_3) reacts with ammonia to form a compound ($BF_3{}^{+}NH_3$) (3 marks)

- What factors account for the reaction taking place so readily?
- What formal charge is present on boron and nitrogen in the product?
- What hybridization state would you expect for both boron and nitrogen in the product?

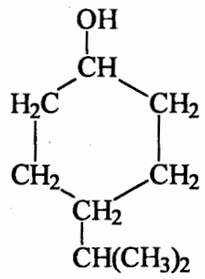
(c) (i) Describe the bonding characteristics and shape of BF_3 and ethylene ($CH_2 = CH_2$) in terms of orbital hybridization model of bonding. (3 marks)

(ii) Write a bond line formula for each of the following condensed structures. (3 marks)

(1) $(CH_3)_2\,C = CHCH_2CH_3$ (2) $CH_3\,CH_2\,N(CH_3)_2$

(3) $CH_3\,CHCl\,CH_2CH_3$ (4) $(CH_3)_2CH\,CH_2\,CH_2\,CH_2OH$

(5) $(CH_3)_2CH\ CH_2\ CH_2\ COCH_3$ (6)



(iii) Write the correct three dimenstional structure for each of the following molecules. (2 marks)

1. HC(BrClI)
2. BF_3
3. CH_4
4. CH_2BrCH_2Cl

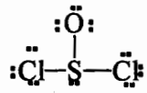
Question 2

(a) Explain the following terms as completely as possible. Use appropriate examples and illustrations to illuminate your answer. (6 marks)

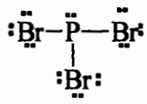
(i) Formal charge
(ii) Resonance

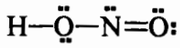
(b) Calculate the formal charge on each of the atoms in the following Lewis structures: (7 marks)

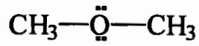
(i) Thionyl chloride:



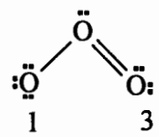
(ii) Phosphorus tribromide:



(iii) Nitrous acid: 

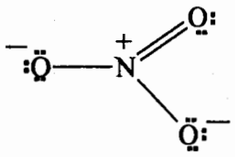
(iv) Dimethylether : 

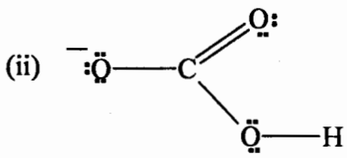
(v) Ozone :

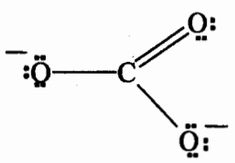


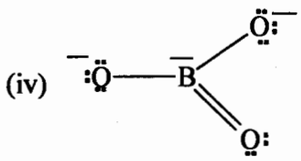
1 3

(c) Using curved arrows, show how an equivalent resonance structure can be generated for each of the following anions: (6 marks)

(i) 

(ii) 

(iii) 

(iv) 

(d) (i) Distinguish between the resonance concept and polar covalent bonds. (3 marks)

(ii) Specify the geometric shape of the following compounds: (3 marks)

- Ammonia $\ddot{N}H_3$
- Carbon dioxide CO_2
- Methane CH_4

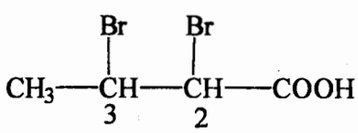
SECTION B: STEREOCHEMISTRY

Question 3

(a) Briefly explain the following terms and give suitable examples to illustrate your answer: (8 marks)

(i) Constitutional isomers
(ii) Absolute configuration
(iii) Fisher projection
(iv) Resolution

(b) The compound 2,3-dibromo butanoic acid (1) incorporates two stereogenic centres at C – 2 and C – 3 as shown.

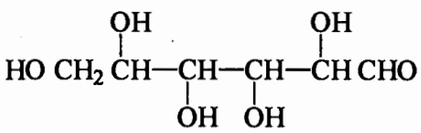


(1)

(i) Specify absolute configuration at C – 2 and at C – 3 as (R) or (S) (2marks)

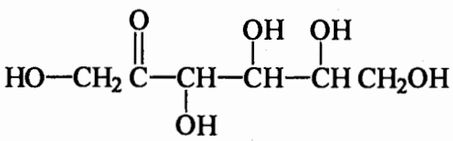
(ii) How many stereo isomers of compound 1 are possible? (2 marks)

One class of carbohydrates called hexoses has the constitution



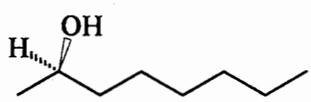
(iii) How many stereoisomeric hexoses are possible for this structure? (2 marks)

(iv) A second category of six – carbon carbohydrates called 2 – hexuloses has the constitution:

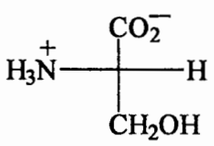


Write down the number of possible stereoisomeric 2 – hexuloses. (3 marks)

(c) Specify the configuration as R or S in each of the following molecules:



(i)



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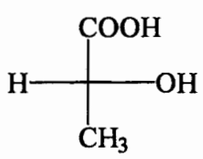

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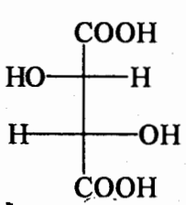

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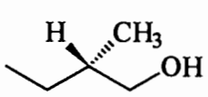
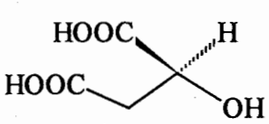


(v)



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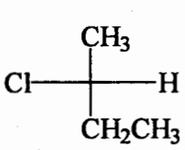

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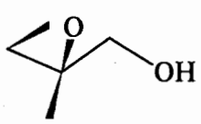


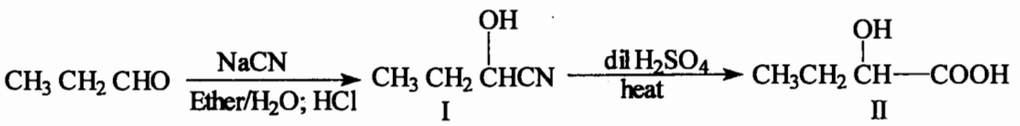
(viii)

(8 marks)

Question 4

(a) The sequence of reactions below describes a synthesis of 2-hydroxybutanoic acid II through the cyanohydrin compound I.

The sequence:



Examine the sequence and answer the following questions as completely as you can:

(i) In what stereochemical (or optical) form is the 2 – hydroxybutanoic acid II produced? (2 marks)

(ii) Explain why compound II is obtained in the stereochemical form identified in (i) above? (2 marks)

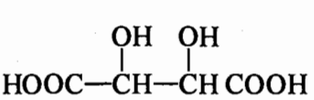
(b) Draw the Fischer projection structure for: (6 marks)

(i) (R) – 2 – Hydroxy propanoic acid.

(ii) (S) – 2 – Amino butanedioic acid.

(iii) (2R, 3R) – 2,3 – Dichloropropanoic acid

(c) (i) Outline a procedure for separating the enantiomers of tartaric acid from each other. (5 marks)



Constitutional formular of Tartaric acid.

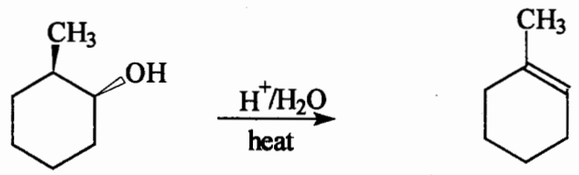
(ii) In the resolution of 1-phenylethylamine using (S)-(-)-malic acid as the resolving agent the compound obtained by re-crystallization of the mixture of diastereomeric salts is (R) – 1 – phenylethylammonium (S) Malate. The other component of the mixture is more soluble and remains in solution in the recrystallization solvent. What is the configuration of the more soluble salt?
(2 marks)

(d) Outline any two viable procedures for the synthesis of chiral molecules in a laboratory. (8 marks)

SECTION C: REACTIONS AND SYNTHESIS OF ORGANIC COMPOUNDS

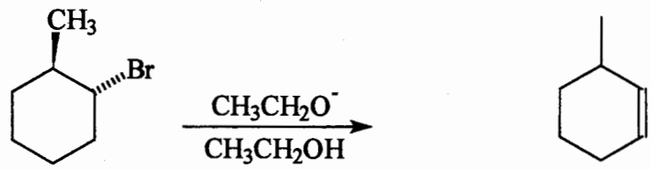
Question 5

(a) The sequence of reaction shown below describes an acid catalysed dehydration of trans-2-methylcyclohexanol (1) to 1-methyl cyclohexene (2) as the major product.



(1) (2)

However, when trans - bromo - 2 - methylcyclohexane is subjected to dehydrohalogenation as indicated below, the major product is 3 - methyl cyclohexene (3)

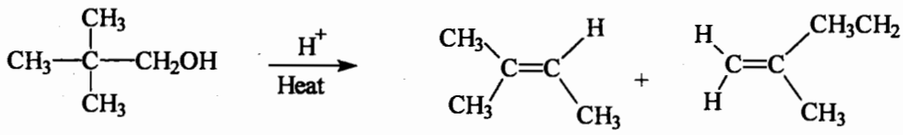


(3)

Write a reasonable mechanism that accounts for the formation of the product in each reaction. (8 marks)

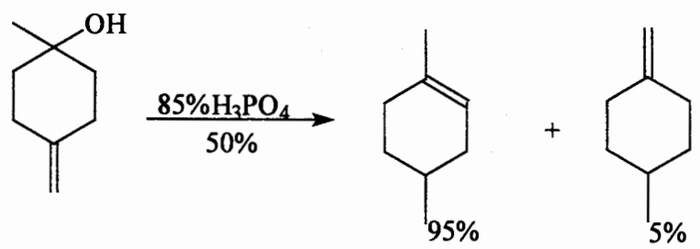
(b) The following reactions are examples of acid – catalysed dehydration of alcohols. Such reactions normally produce a mixture of isomeric alkenes, as shown in the schemes below.

(1)

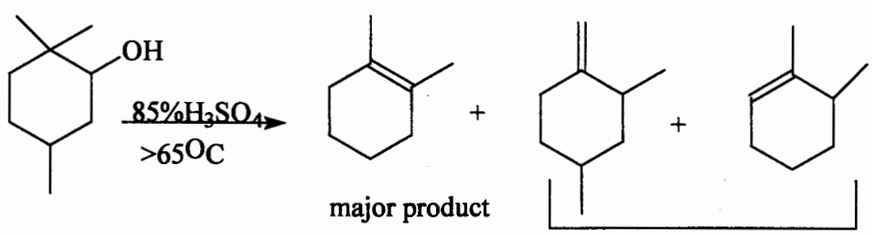


major product minor product

(2)



(3)

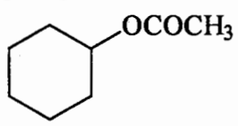


(i) Write a plausible mechanism in each case, showing all the steps in the formation of the products. (6 marks)

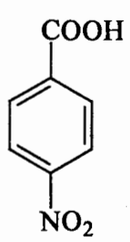
(ii) Explain the essential role performed in these reactions by the acid catalyst. (3 marks)

(c) Write the sequence of reactions showing reagents and conditions, for the synthesis of:

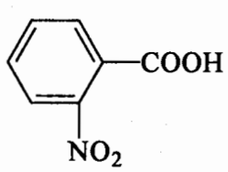
(i) Cyclohexyl acetate



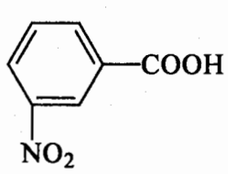
(ii) p-Nitrobenzoic acid



(iii) O-Nitrobenzoic acid



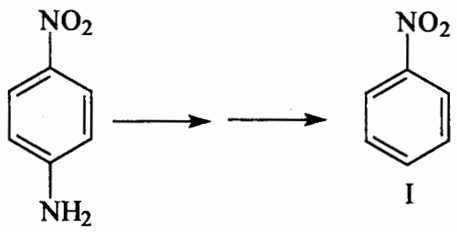
(iv) M-Nitrobenzoic acid



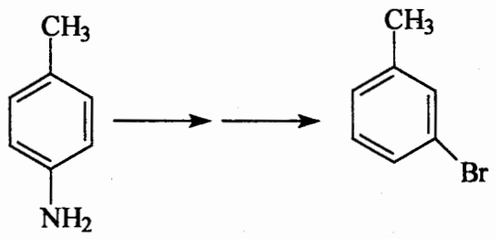
(4 marks)

(d) Show all the reagents, reaction conditions and intermediates involved in the following functional group transformations: (4 marks)

(i)

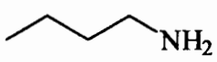


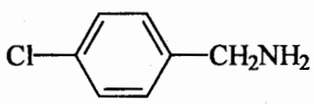
(ii)



Question 6

(a) Outline a general laboratory method for the synthesis of the following amine compounds.

(i) Butylamine 

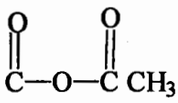
(ii) p - chlorobenzylamine 

(b) (i) Describe the bonding characteristics of the amine (NH_2) group. (3 marks)

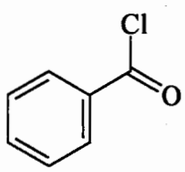
(ii) Show how the structure of this group influences its reactivity and physical properties. (2 marks)

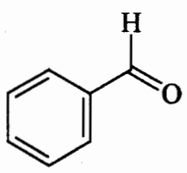
(iii) Write the structure of the major product of the reaction of ethyl amine $CH_3CH_2NH_2$ with the following reagents: (5 marks)

(1) $NaNO_2/HCl$ at 0^oC.

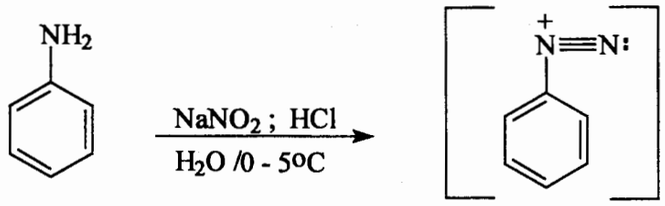
(2) Acetic anhydride 

(3) HBr

(4) Benzoyl chloride 

(5) Benzaldehyde 

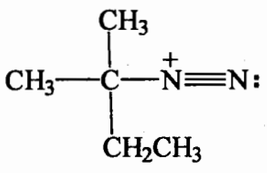
(c) (i) Outline the sequence of steps in the diazotization reaction of aniline with nitrous acid. (Scheme 1) (3 marks)



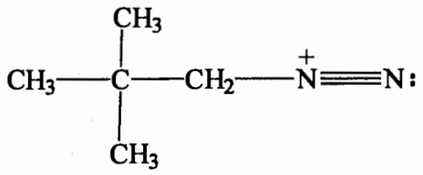
aniline benzenediazonium chloride

SCHEME 1

(ii) After formation from the respective amines by diazatization process, the diazonium ions (1) and (2) were allowed to decompose freely in the reaction mixture. In each case, show all the major products of decomposition. (3 marks)



(1)



(2)

(iii) Diazonium salts are used in the synthesis of many benzonoid compounds. Give two specific examples that illustrate organic synthesis using diazonium salts. (3 marks)