UNIVERSITY OF SWAZILAND
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 Paper contains 9 printed pages excluding this page.

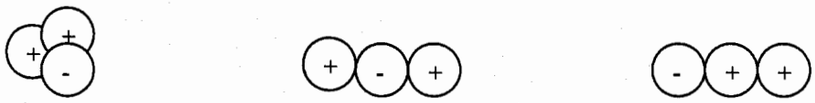
You must not open this paper until the Chief Invigilator so has granted permission to do.

SECTION A: STRUCTURE AND CHEMICAL BONDING

Question 1

(a) (i) Using carbon as an example, explain how the ground state electron configuration determines the ability of carbon to form many types of bonds to other elements. (3 marks)

(ii) Of the orbital overlaps represented below, one is bonding, one is antibonding, and the other is non bonding (neither bonding nor antibonding). Which pattern of orbital overlap corresponds to which interaction? Why? (3 marks)



A B C

(b) (i) Write the Lewis structure for NH_3 . (2 marks)
(ii) Predict its shape on the basis of VSEPR theory (2 marks)
(iii) Describe bonding characteristics in ammonia in terms of orbital hybridization. (3 marks)

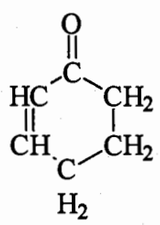
(c) Rewrite the following using the bond line formulas: (6 marks)

(i) $(CH_3)_2N\,CH_2CH_3$

(ii) $CH_3CH(CH_3)CH_2CH_2CH_2OH$

(iii) $CH_2{=}CHCH_2CH_2CH{=}CHCH_3$

(iv)



(d) Write three-dimensional formulas for each of the following molecules: (6 marks)

(i) CH_3Cl (ii) CH_4 (iii) CH_2Cl_2

(iv) CH2BrCl (v) BCl_3 (vi) CH_3CH_2Cl

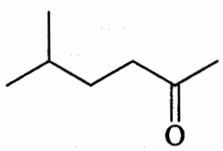
Question 2

(a) Explain the following terms as completely as possible using suitable examples and illustrations. (5 marks)

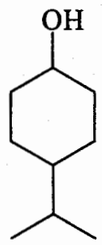
(i) Covalent bond
(ii) An orbital
(iii) Formal charge
(iv) Constitutional isomerism
(v) Resonance

(b) (i) Write a dash formula for each of the following bond-line formulas: (3 marks)

(1)



(2)



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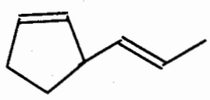
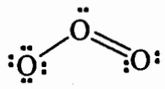


(ii) Assign any necessary formal charges to the atoms in ozone structure given below: (1 mark)

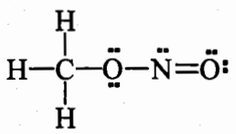


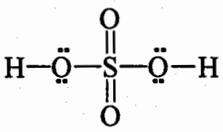
(iii) Write another equivalent resonance structure for ozone. (1 mark)

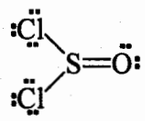
(iv) What do these resonance structures predict about the relative lengths of the two oxygen - oxygen bonds of ozone? (1 mark)

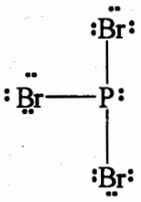
(v) The structure above and the one you have written assume an angular shape for the ozone molecule. Is this shape consistent with VSEPR theory? Explain your answer. (2 marks)

(c) Determine the formal charge on each atom in the following Lewis structures, and specify the net charge on each molecule as a whole. (6 marks)

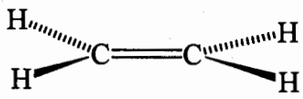
(i) 

(ii) 

(iii) 

(iv) 

(d) Describe the geometric shape and bonding characteristics in ethylene in terms of orbital hybridization. (6 marks)



ethylene

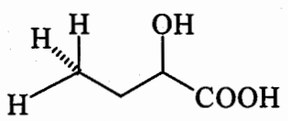
SECTION B: STEREOCHEMISTRY

Question 3

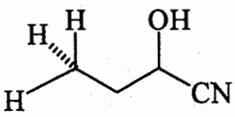
(a) Briefly explain the following terms and give examples to illustrate: (6 marks)

(i) Chirality
(ii) Stereochemistry
(iii) Optical activity
(iv) Diastereomers
(v) Meso compound

(b) (i) Write the sequence of reactions that describe the synthesis of 2-hydroxy butanoic acid through a cyano hydrin intermediate. (3 marks)



2-hydroxybutanoic



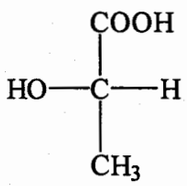
Cyanohydrin

(ii) In what stereochemical form is 2-hydroxybutanoic acid obtained? Why? (3 marks)

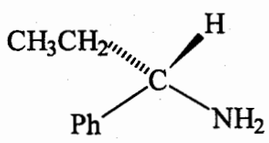
(c) Write the Fischer projection formulae of the following compounds. (9 marks)

(i) (R) - 2 - Hydroxy propanoic acid
(ii) (S) - 2 - Aminobutanedioic acid
(iii) (2R, 3R) - 2,3 - Dichloropropane

(d) Describe briefly how (S) – (1) - phenylethylamine may be used to resolve a racemic mixture of lactic acids. (4 marks)



Lactic acid

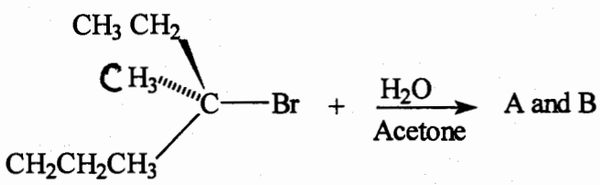


(S)-(1)-Phenylethylamine

SECTION C: ORGANIC REACTIONS, SYNTHESIS AND MECHANISM

Question 4

(a) Heating (S) - 3 - bromo - 3 - methylhexane with aqueous acetone results in the formation of two alcohol products. A and B as described by the following equation:



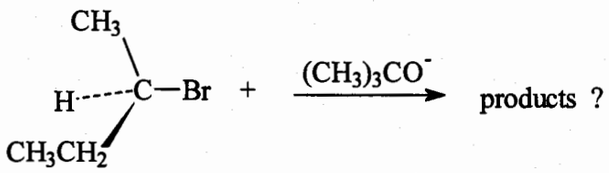
(i) What are the structures of A and B? (4 marks)

(ii) Write a valid mechanism for the reaction and predict the optical nature of the products A and B. (4 marks)

(b) Using (R) - 2 - bromobutane: (7 marks)

(i) Show how the E2 elimination leads to the formation of two products.
(ii) Indicate the major product and
(iii) Explain why the formation of the major product is predominant.

The E2 reaction:

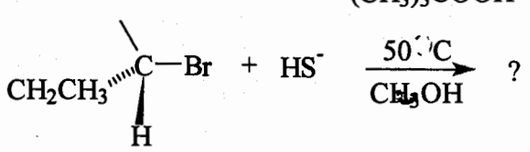


(R) - 2 - Bromobutane

(c) Write the structure of the product or (products) that you would expect to be formed in each of the following reactions. In each case give the mechanism (S_N1, S_N2, E1 or E2) by which the product is formed and predict the relative amount of each (ie. Would the product be the only product, the major product, or a minor product). (10 marks)

(i) $CH_3CH_2CH_2Br + CH_3O^- \xrightarrow[CH_3OH]{50^oC}$?

(ii) $CH_3CH_2CH_2Br + (CH_3)_3CO^- \xrightarrow[(CH_3)_3COOH]{50^oC}$?

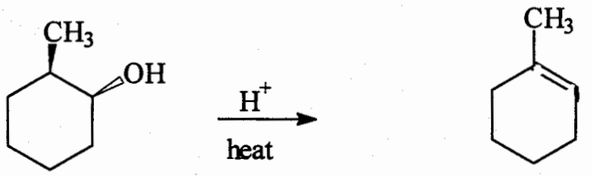
(iii 

(iv) $(CH_3CH_2)_3\,CBr + \bar{O}H \xrightarrow[CH_3OH]{50^oC}$?

(v) $[CH_3CH_2]_3\,C\,Br \xrightarrow[CH_3OH]{25^oC}$?

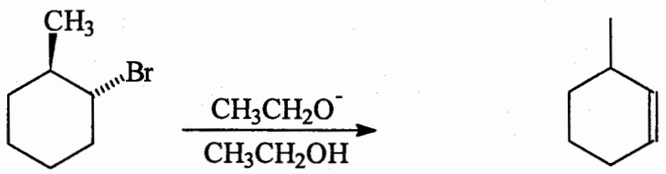
Question 5

(a) When trans-2-methylcyclohexanol (1) is subjected to acid catalysed dehydration, the major product is 1-methylcyclohexene



(1) (2) 1 - methylcyclohexene

However, when trans - bromo - 2 - methylcyclohexane is subjected to dehydrohalogenation the major product is 3 - methyl cyclohexene

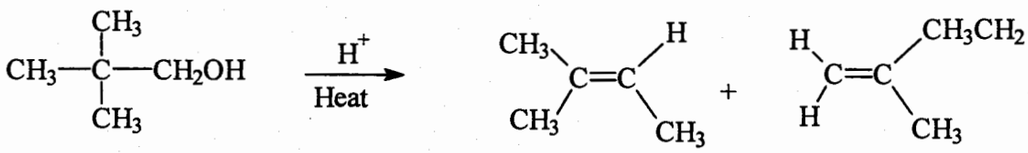


heat 3 - methylcyclohexene

Account for the different products of these two reactions. (8 marks)

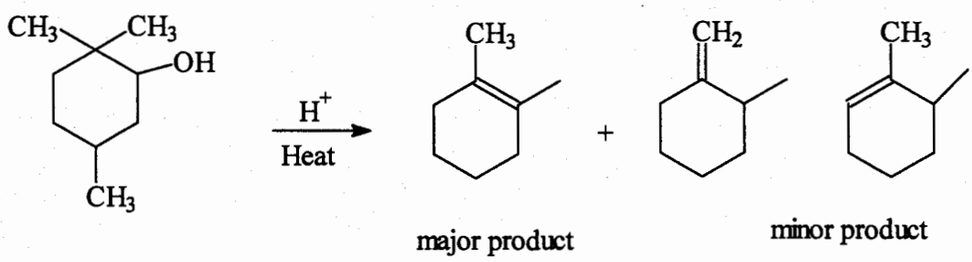
(b) Write step by step mechanism, that account for each of the following reactions and explain the relative amounts of proportions of the isomers obtained in each instance. (9 marks)

(i)



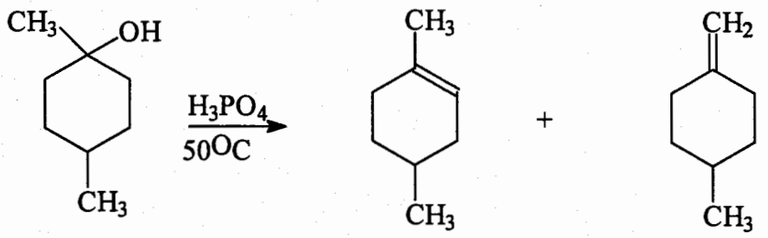
major product minor product

(ii)



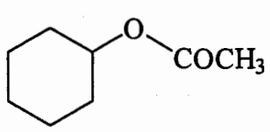
major product minor product

(iii)



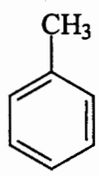
(95%) (5%)

(c) (i) Show the reagents and reaction conditions for the laboratory synthesis of cyclohexyl acetate.



cyclohexylacetate

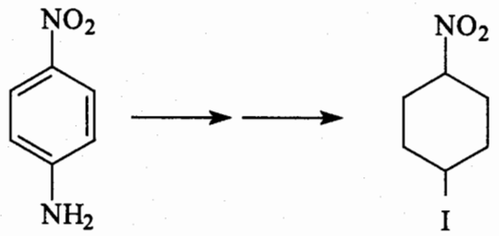
(ii) Starting with toluene, outline a synthesis of:
- (a) p-nitrobenzoic acid
- (b) o-nitrobenzeoic acid
- (c) m-nitrobenzoic acid



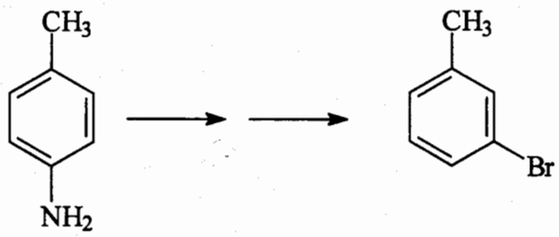
toluene

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

(i)

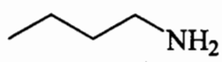


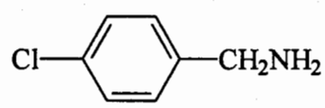
(ii)



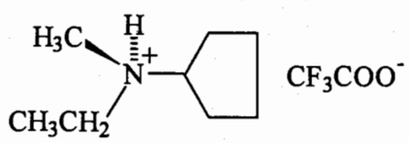
Question 6

(a) Give one specific example of the general laboratory methods for the synthesis of the following amine compounds.

(i) Butylamine  (4 marks)

(ii) p - chlorobenzylamine  (4 marks)

(iii) The compound N-ethyl N-methyl cyclopentyl ammonium trifluroroacetate [A] is clearly chiral. However, all attempts to resolve the compound to its enantiomers fail. Explain why? (2 marks)



A

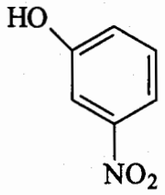
(b) Write the sequence of reactions that best describe what happens when:

(i) A solution of sodium nitrite ($NaNO_2$) in water is acidified. (3 marks)

(ii) A primary and a secondary amine each reacts with an acidified solution of sodium nitrite at 0^oC. (4 marks)

(c) Outline the most major reactions describing method of synthesis of the following benzene compounds in the laboratory form amines. (8 marks)

(i)



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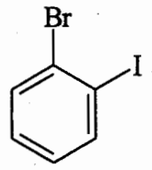

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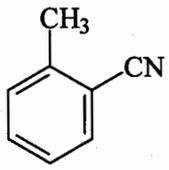

(iv)