TECHNICAL UNIVERSITY OF MOMBASA

FACULTY OF APPLIED AND HEALTH SCIENCES

DEPARTMENT OF PURE AND APPLIED SCIENCES

UNIVERSITY EXAMINATION FOR

BACHELOR OF TECHNOLOGY IN APPLIED CHEMISTRY

ACH 4204 : STEREOCHEMISTRY AND CONFORMATIONAL ANALYSIS

END OF SEMESTER EXAMINATION

SERIES: MAY 2016

TIME: 2 HOURS

DATE: 17TH MAY 2016

Instructions to Candidates

You should have the following for this examination

-Answer Booklet, examination pass and student ID

This paper consists of FIVE questions. Attempt Question ONE and any other TWO.

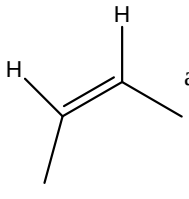
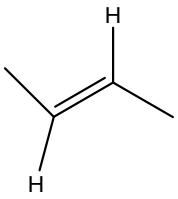
Do not write on the question paper.

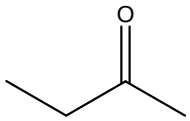
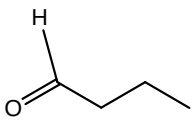
Question ONE

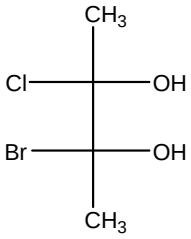
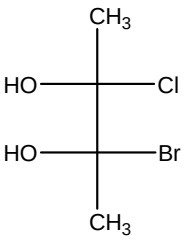
a) Explain the following terms
   i) Trans isomer
   ii) Chiral centre
   iii) Fischer projection
   iv) Dextrorotatory isomer

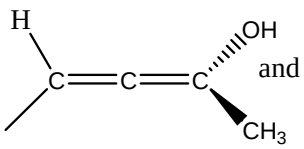
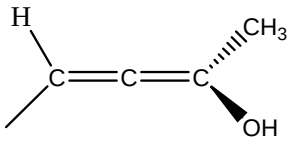
(8marks)

b) Indicate with reason whether the following pairs of compounds are identical, diastereomers, enantiomers or constitutional isomers.

i)  and 

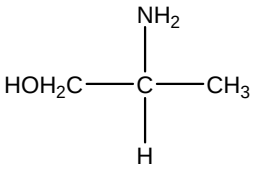
ii)  and 

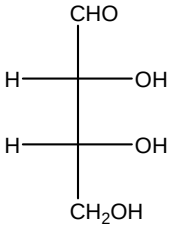
iii)  and 

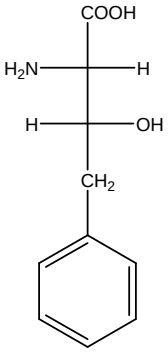
iv)  and 

(8marks)

c) Redraw and assign R or S configuration to all the stereocentres in each of the following compounds.

i) 

ii) 

iii) 

(5marks)

d) Draw the most stable chair conformations of the following compounds and state whether they are optically active or optically inactive.

i) Trans -1-ethyl-2-propylcyclohexane
ii) Trans- 1,4- dibromocyclohexane
iii) Cis-2-methylcyclohexanol

(6marks)

e) The conformational free energy of a fluoro group is -1.0 KJmol^{-1} at 25^{0}C. Calculate the conformational equilibrium constant of fluorocyclohexane.

(3marks)

Question TWO

a) Differentiate between the following terms
   i) Pro-R and Pro-S
   ii) Re-face and Si-face
   (4marks)

b) 28mg of a sample of Mandelic acid was dissolved in 1 cm^3 of ethanol and the solution placed in a 10cm polarimeter cell. An optical rotation of $+4.34^0$ was measured at 20^0C with light of wavelength 589nm.

   i) Calculate the specific rotation of the sample. (4marks)
   ii) If the specific rotation of pure (R) – Mandelic acid is +158 work out the % optical purity . (3marks)
   iii) Calculate the % of (R)- and (S)- Mandelic acid in the sample.
   (3marks)

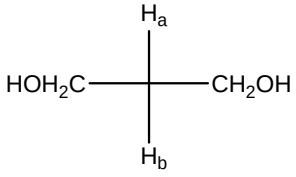
c) Using Newmann projections draw the preferred conformation(s) of the following compounds and give reason(s) for your choice.
   i) $ClCH_2CH_2Cl$ (2marks)
   ii) $HOCH_2CH_2OH$ (2marks)
   iii) $CH_3CH_2CH_2CH_3$ (2marks)

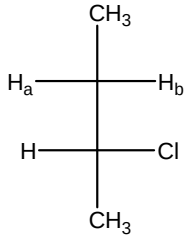
Question THREE

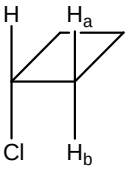
a) i) Explain the term allenes. (2marks)
   ii) State and explain the conditions for allenes to be chiral or achiral.
   (4marks)

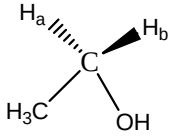
b) Draw the cis and trans forms of 4-t-butylcyclohexanol dash structures.
   (4marks)

c) Indicate with reason whether the hydrogen atoms Ha and Hb in each of the following compounds are homotopic, enantiotopic or diastereotopic.

i) 

ii) 

iii) 

iv) 

   (8marks)

d) Explain the term threo enantiomer
   (2marks)

Question FOUR

a) Explain the following terms

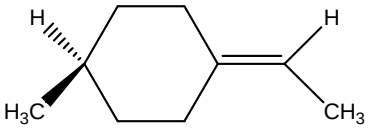
i) Biphenyls

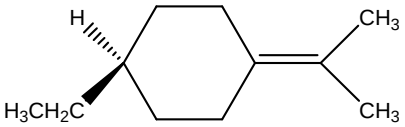
ii) Spiranes

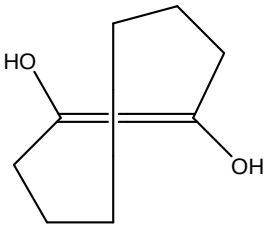
iii) Helical molecules

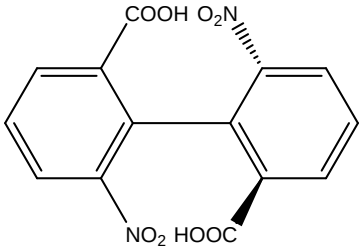
(6marks)

b) Indicate whether the following molecules are chiral or achiral and explain your answer.

i) 

ii) 

iii) 

iv) 

(7marks)

c) At 32^0C the dipole moment of gaseous 1,2- dichloroethane was found to be 1.12D. Given that $\mu_{gauche} = 3.2D$ and $\mu_{anti} = 0$ calculate

i) The % of each of the anti and gauche conformers at 32^0C.

(3marks)

ii) The equilibrium constant K.

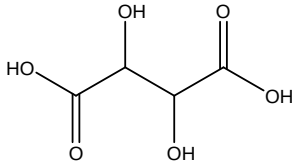
(2marks)

iii) The Gibbs free energy difference (ΔG^{θ}) between the two conformations given that $\Delta G^{\theta} = -RT\ln K$ and $R = 8.314 Jmol^{-1}K^{-1}$

(2marks)

Question FIVE

a) Using the compound below to answer questions that follow



i) Determine the maximum number of stereoisomers possible for this compound. (2marks)

ii) Draw the Fischer projections of the stereoisomers.

(6marks)

iii) Which of the isomers in (ii) above are optically inactive. Explain your answer. (2marks)

b) i) Explain the term sigmatropic reaction.

(2marks)

ii) Differentiate between [2,3] and [3,3] – sigmatropic rearrangements giving an example of reactions in each case.

(6marks)

c) Explain how enzymes act as resolving agents in resolution of enantiomeric mixture of 5- norbornen-2-ol.

(2mks)