SCIENCE

## COURSE CODE: CHEM 412

COURSE TITLE: ADVANCED STEREOCHEMISTRY \& REACTION MECHANISM
STREAM: SESSION VIII

DAY: WEDNESDAY
TIME:
2.00-4.00 P.M.

DATE:
08/04/2009

## INSTRUCTIONS:

Attempt all questions.
Each question $=171 / 2$ Marks

## PLEASE TURN OVER

## QUESTION ONE

(a) Define each of the following terms
(i) Enantiomer
(ii) Chiral centre
(iii) Racemic mixture
(iv) Optical activity
(b) Identify the chiral centres of the following molecules (Use asterisk *) [4 mks]
(b) (i)

(ii) 3-Methylcyclopent-1-enol
(iii) 2-chloro-2-methylbutane (iv)

(c) Assign R and S configurations to the following molecules
(i)

(ii)


(iv)

(d) Briefly explain the effect of plane-polarized light when it is passed through a 50:50 racemic mixture
[ $1 \frac{1}{2} \mathrm{mks}$ ]

QUESTION TWO
(a) Define the following terms:
(i) Conformations
(ii) Conformational analysis
(b) (i) Draw the axial and equatorial conformations of ethylcyclohexane
[1 mk]
(ii) With a reason state the most stable configuration of ethylcyclohexane [ $11 / 2 \mathrm{mks}$ ]
(c) The Gibbs free energy difference between the axial and equatorial conformers of methylcyclohexane is $7.6 \mathrm{~kJ} / \mathrm{mol}$. Show mathematically that at equilibrium the equatorial conformer is $95 \%$ and the axial conformer is $5 \%$ of the mixture $\left[\mathrm{T}=25^{\circ} \mathrm{C}\right.$, $\mathrm{R}=0.082058 \mathrm{~L} . \mathrm{atm} \mathrm{K} \mathrm{Kol}^{-1}$ ]
(d) Briefly explain the following terms
[6 mks]
(i) 1,3-steric strain
(ii) Torsional strain
(iii) Diastereomers

## QUESTION THREE

(a) Define the following terms

## [17 ½ Marks]

(i) HOMO
(ii) LUMO
(iii) Nucleophile
(iv) Leaving group
(v) Mechanism
(b) (i) Using molecular orbitals explain how acetone $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{O}$ can act as both an electrophile and a nucleophile
(c) Consider the following reaction

(i) State the importance of the reagents $\mathrm{H}_{2} \mathrm{O}$ and THF in the reaction [2 mks]
(ii) Using curly arrows propose a mechanism for the above reaction
[ $4 \frac{1}{2} \mathrm{mks}$ ]
(iii) With the help of frontier molecular orbitals show the HOMO - LUMO interactions in the above reaction

## QUESTION FOUR [17 ½ Marks]

(a) Define the following terms:
[4 mks]
(i) Electrocyclic reactions
(ii) Concerted reaction
(iii) Stereospecific reaction
(iv) Conrotatory process
(b) With the aid of orbital diagrams show the products $\mathrm{A}, \mathrm{B}, \mathrm{C}$ and D of the following reactions:


Trans,trans - 2,4-hexadiene


Trans, cis, trans - 2,4,6 - octatriene
hv

D
(c) State the products of the following reactions:

(ii)

(d) Using NaCN as HOMO and acetone as LUMO explain the term Burgi - Dunitz trajectory
[ $31 / 2 \mathrm{mks}$ ]

