KABARAK



UNIVERSITY

EXAMINATIONS

2008/2009 ACADEMIC YEAR

FOR THE DEGREE OF BACHELOR OF EDUCATION 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 = 17 ½ Marks

PLEASE TURN OVER

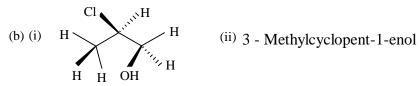
QUESTION ONE

[17 ½ Marks]

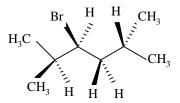
(a) Define each of the following terms

[4 mks]

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

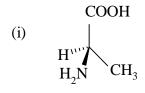


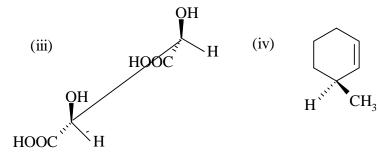
(iii) 2-chloro-2-methylbutane (iv)



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

[8 mks]





(d) Briefly explain the effect of plane-polarized light when it is passed through a 50:50 racemic mixture [1 ½ mks]

(a) Define the following terms:

[3 mks]

- (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

[1 ½ mks]

(c) The Gibbs free energy difference between the axial and equatorial conformers of methylcyclohexane is 7.6 kJ/mol. Show mathematically that at equilibrium the equatorial conformer is 95% and the axial conformer is 5% of the mixture $[T = 25^{\circ}C,$

$$R = 0.082058 \text{ L.atm } \text{K}^{-1} \text{ mol}^{-1}$$

[6 mks]

(d) Briefly explain the following terms

[6 mks]

- (i) 1,3 steric strain
- (ii) Torsional strain
- (iii) Diastereomers

QUESTION THREE

[17 ½ Marks]

(a) Define the following terms

[5 mks]

- (i) HOMO
- (ii) LUMO
- (iii) Nucleophile
- (iv) Leaving group
- (v) Mechanism
- (b) (i) Using molecular orbitals explain how acetone $(CH_3)_2C=O$ can act as both an electrophile and a nucleophile [4 mks]
- (c) Consider the following reaction

- (i) State the importance of the reagents H_2O and THF in the reaction [2 mks]
- (ii) Using curly arrows propose a mechanism for the above reaction

[4 ½ mks]

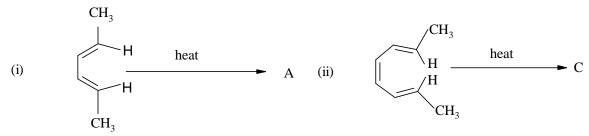
(iii) With the help of frontier molecular orbitals show the HOMO - LUMO interactions in the above reaction [2 mks]

QUESTION FOUR [17 ½ Marks]

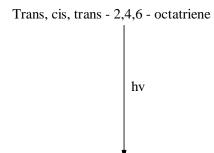
(a) Define the following terms:

[4 mks]

- (i) Electrocyclic reactions
- (ii) Concerted reaction
- (iii) Stereospecific reaction
- (iv) Conrotatory process
- (b) With the aid of orbital diagrams show the products A, B, C and D of the following reactions: [8 mks]



Trans, trans - 2,4 - hexadiene



D

hv B (c) State the products of the following reactions:

[2 mks]

(i)
$$CH_3CH_2$$
 — CH_3 — CH_3 — CH_3 — CH_2O

(d) Using NaCN as HOMO and acetone as LUMO explain the term Burgi – Dunitz trajectory [3 ½ mks]