



MAASAI MARA UNIVERSITY

**REGULAR UNIVERSITY EXAMINATIONS
2022/2023 ACADEMIC YEAR
FIRST YEAR SECOND SEMESTER**

**SCHOOL OF PURE, APPLIED AND HEALTH
SCIENCES
MASTERS OF SCIENCE (MSc)**

COURSE CODE: CHE 8219

**COURSE TITLE: ADVANCED STEREOCHEMISTRY AND
CONFORMATIONAL STUDIES**

DATE: 20TH APRIL 2023

TIME: 1100 – 1300HRS

INSTRUCTIONS TO CANDIDATES

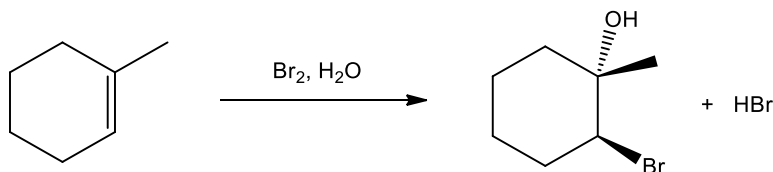
This examination paper consist of two sections **A** and **B**. Section **A** is compulsory. Answer any other TWO questions in section **B**.

This paper consists of 7 printed pages. Please turn over:

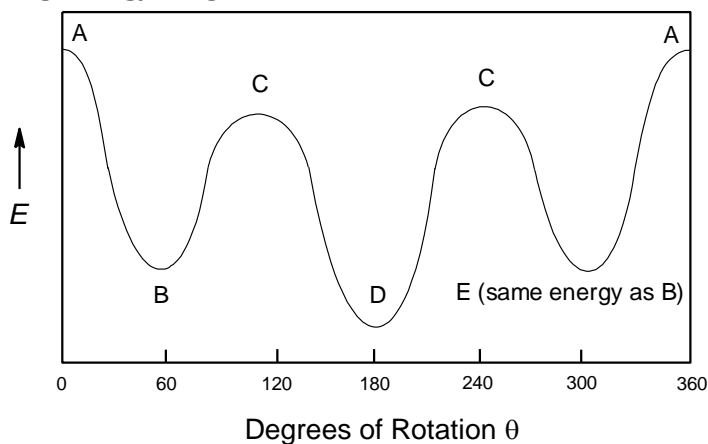
SECTION A

Question ONE (30 marks)

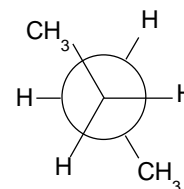
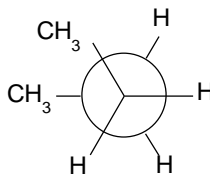
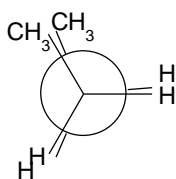
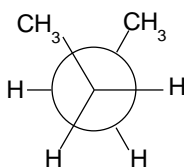
- a) Distinguish between the following terminologies using relevant examples where applicable. (8 marks)
- Enantiotopic and homotopic hydrogens
 - Erythro and threo stereochemical descriptors
 - Configurational isomers and constitutional isomers
 - Chiral and achiral molecule
- b) Which isomer would you expect to undergo E₂ elimination faster, *trans*-1-bromo-4-*tert*-butylcyclohexane or the *cis*-1-bromo-4-*tert*-butylcyclohexane? Justify your choice (3 marks)
- c) Draw a detailed, stepwise mechanism showing how the products of the reaction below are formed. (4 marks)



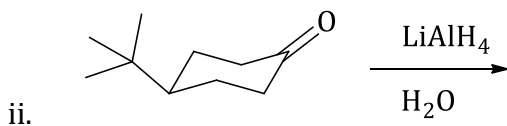
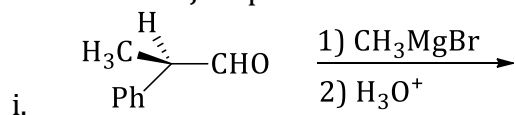
- d) Using the following energy diagram:



Label the following Newman Projections with the appropriate letter (A, B, C, D or E) to correspond to the appropriate energy level. (4 marks)

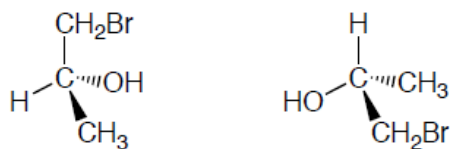


e) Provide the MAJOR products for the following reactions (4 marks)

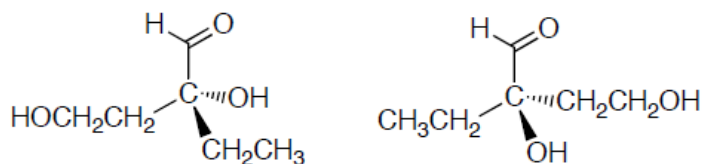


f) Are the following pairs of compounds identical, or are they a pair of enantiomers? Briefly explain (4 marks)

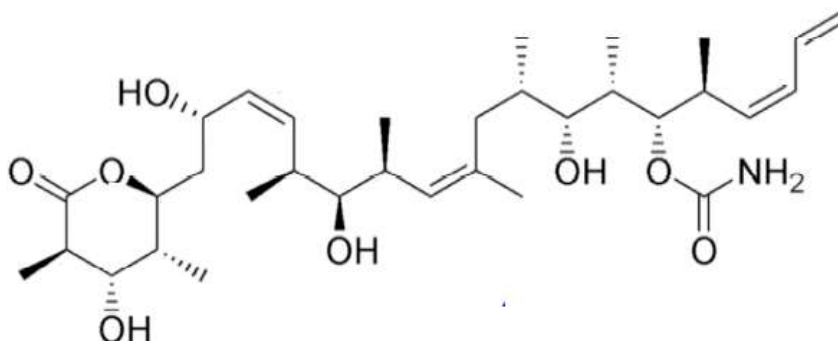
i.



ii.



g) Discodermolide, a natural product isolated in 1990 from a marine sponge, is a potent inhibitor of tumor cell growth. How many asymmetric centers are there in Discodermolide? Mark each one with a star (*) (3 marks)



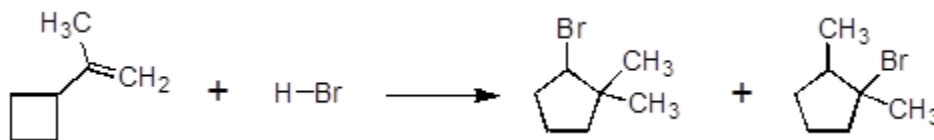
SECTION B

Question TWO (20 marks)

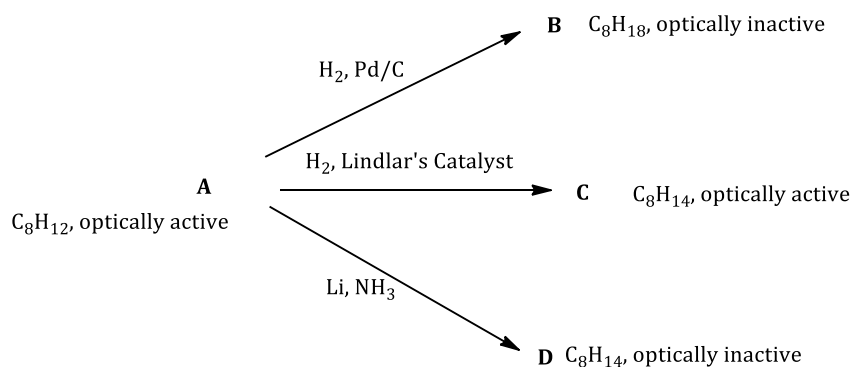
a) Give brief definitions of the following stereochemistry terms and where applicable provide relevant examples. (8 marks)

- i. Racemic mixture
- ii. Chirotopicity
- iii. Meso compound
- iv. Epoxidation

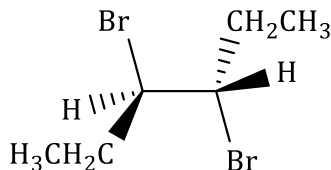
b) Propose a mechanism for the following reaction: (4 marks)



c) Based on the information below, determine the possible structures of compounds **A**, **B**, **C**, and **D**. (4 marks)

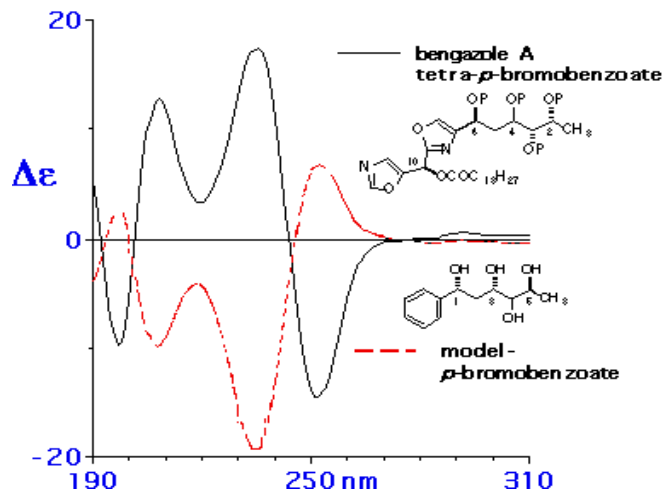


d) Design a synthesis of (3R, 4S)-3,4-dibromohexane shown below starting with acetylene ($HC\equiv CH$) **ONLY** as your starting material. (4 marks)

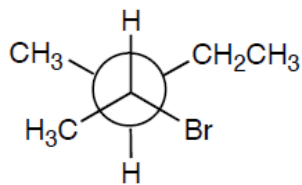
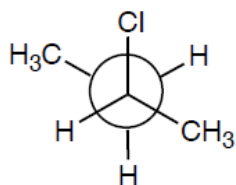


Question THREE (20 marks)

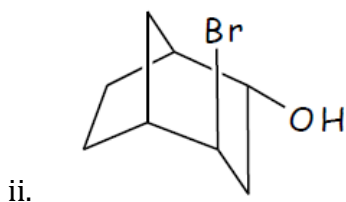
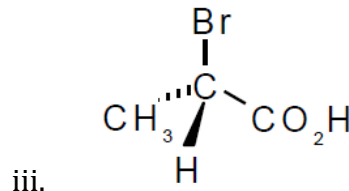
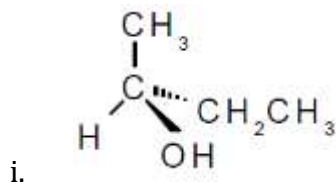
- a) The pictorial diagram below was obtained from circular dichroism of 4-bromobenzoate. How does CD spectroscopy help in analysis of chirality? (2 marks)



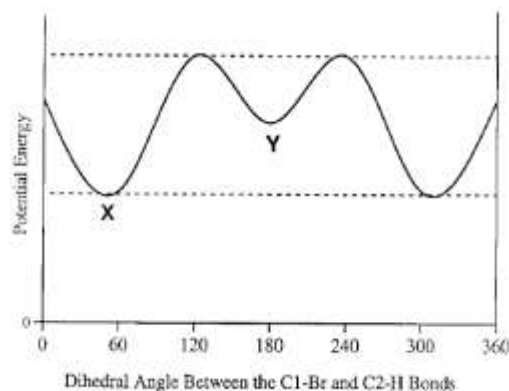
- b) Name the following compounds, include R or S designations: (4 marks)



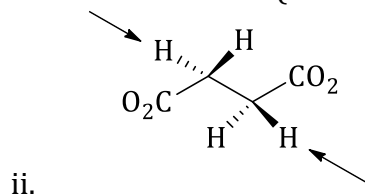
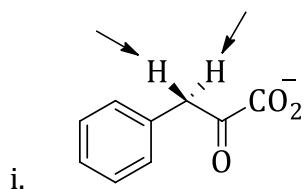
- c) Identify the asymmetric carbon(s) in each of the following compounds and determine whether it has the (R) or (S) configuration: (6 marks)



- d) Below is a conformational energy diagram showing the energy changes that occur as a molecule of 1-bromo-2-methylpropane rotates around the C1-C2 bond. (C1 is the carbon bonded to the bromine). Using Newman projections, show the conformations of 1-bromo-2-methylpropane at the points labeled X and Y in the diagram. (4 marks)

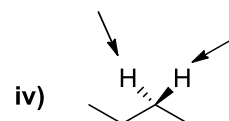
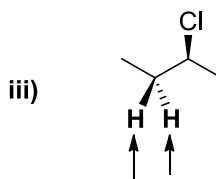
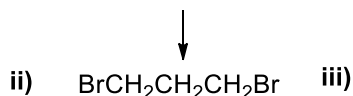
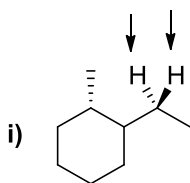


- e) Identify the highlighted hydrogens in the molecules shown below as either pro-R or pro-S (4 marks)



Question FOUR (20 marks)

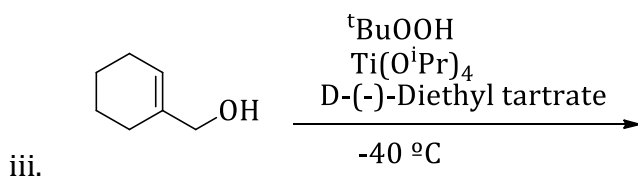
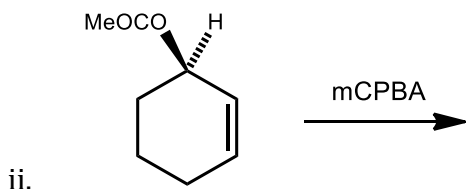
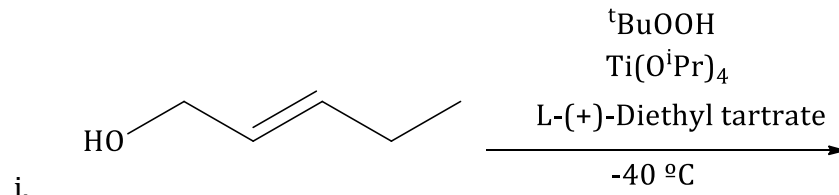
- a) Consider the following organic molecules.



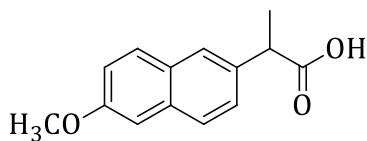
Indicate whether the hydrogens (pointed with arrows) are homotopic, enantiotopic or diastereotopic. Do these hydrogens have same or different chemical shifts? Briefly explain. (4 marks)

b) Using clear examples, distinguish between stereospecific reaction and stereoselective reaction. (4 marks)

c) Provide the products for the following reactions. Pay attention to stereochemistry where applicable. (6 marks)



d) Many chiral drugs must be prescribed as a single enantiomer. Naproxen (shown below) is an anti-inflammatory drug, which is mandated to be sold at greater than 97% enantiomeric excess (e.e.). The specific rotation of the R-enantiomer (in CHCl_3) is $+65.5^\circ$. A quality control chemist samples a 50 kg batch of Naproxen produced at a pharmaceutical industry. She dissolved 2.6 g of product in 10 mL of chloroform and measured an optical rotation of $+15.2^\circ$ in a 10 cm (1 dm) polarimeter.



- Draw the R-enantiomer of Naproxen (2 marks)
- Calculate the optical purity of the sample and determine whether it meets the standards for it to be marketed? (4 marks)

//END