



KISII UNIVERSITY
UNIVERSITY EXAMINATIONS
SPECIAL EXAMINATION
FOURTH YEAR EXAMINATION FOR THE AWARD OF
THE DEGREE OF BACHELOR OF EDUCATION SCIENCE
FIRST SEMESTER 2021/2022
(JULY, 2022)

CHEM 436: ADVANCED STEREOCHEMISTRY AND REACTION
MECHANISM

STREAM: Y4 S1

TIME: 2 HOURS

DAY: MONDAY, 3.00 PM – 5.00 PM

DATE: 025/07/2022

INSTRUCTIONS:

- 1. Do not write anything on this question paper.***
- 2. Answer Question ONE (Compulsory) and any TWO Questions.***

1. Explain the following terms: (6marks)

- (i) Stereoisomer (ii) Epimerisation (iii) Resolution (iv) Stereoisomer specific reaction
(v) Conformational isomerism (iv) Enantiomer

2. Explain these observations:

(i) Trans-ethyl-4-tertbutylcyclohexane carboxylate reacts with 70% ethanolic NaOH at 25⁰C twenty times faster than Cis-form. (4 marks)

(ii) The boat conformation of cyclohexane is 29 KJ/mol above the chair conformation in potential energy. (3 marks)

(iii) A substitution is more stable in equatorial position than in axial position. (3marks)

3. Draw the possible chair conformations of trans- and cis-1,3-dimethylcyclohexane.

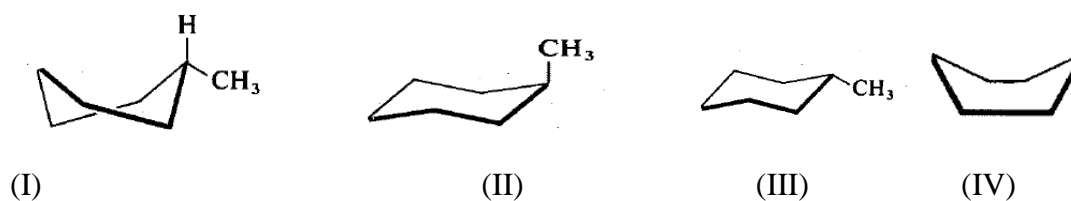
Is the cis or the trans isomer likely to be the more stable? Explain. (3marks)

4. Write the structures of the eight branched-chain isomers of heptane $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$. Name each by the IUPAC system. (6marks)

5. (I) Explain the interconversion of figure I, II and III. (3marks)



6. Sketch the appropriate energy curve for cyclohexane and 1-methylcyclohexane conformations and therefore draw the corresponding conformation structure at each maximum or minimum. (6marks)



7. Using cross formulas, which of the following compounds are chiral and achiral? (6marks)

- (a) 2-chloropentane
- (b) 1-chloro-2-bromobutane
- (c) 3-chloropentane
- (d) 1-chloro-2-methylpentane
- (e) 2-chloro-2-methylpentane
- (f) 3-chloro-2-methylpentane

SECTION B (30 marks)

8.(a) Draw and specify as R or S the enantiomers (if any) of: (6marks)

(i) 3-chloro-1-pentene

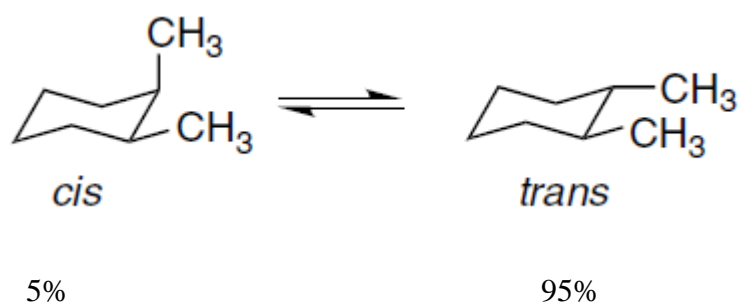
(ii) 3-chloro-4-methyl-1-pentene

(iii) $\text{HOOCCH}_2\text{CHOHCOOH}$, malic acid

(iv) $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{NH}_2$

(v) $\text{C}_6\text{H}_5\text{CHOHCOOH}$, mandelic acid

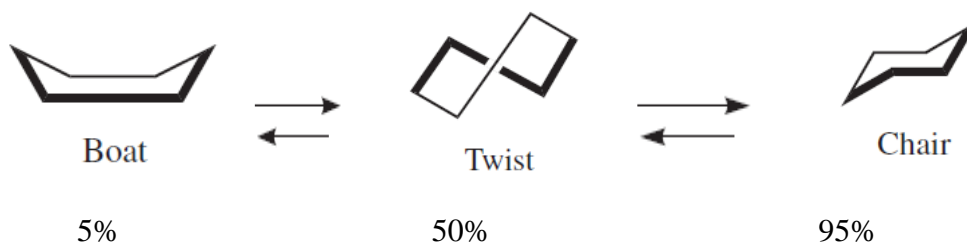
(b). Explain why two compounds below, trans form exist 95% and cis exist 5%. (4marks).



(c) (i) When 28 mg was dissolved in 1 cm^3 of ethanol and the solution placed in a 10 cm long polarimeter cell, an optical rotation α of -4.35° was measured (that is, 4.35° to the left) at 20°C with light of wavelength 589 nm. What is the specific rotation of the acid? (3marks)

(ii) If the enantiomeric excess is 95%, how much of each enantiomer is present. (2marks)

10. The diagrams below show the ring inversion of isomers:



(a) Explain the following observation: (5marks)

(i) The twist form is (6.3 kJ mol^{-1}) more stable than the boat form.

(ii) The chair form is more stable than the twist form by (21 kJ mol^{-1}).

(iii) The chair form is more stable than the boat form by (28 kJ mol^{-1}).

(iv) Boat form is easily ring inverted into twist form.

(v) It is not easy to convert chair form into twist form.

(b). The substitution of an axial substituent proceeds faster than the substitution of an equatorial substituent. Explain the observation. (2marks)

(c). Explain the causes of the following bond strains: (4marks)

(i) Torsional strain (ii) steric strain (iii) angle strain (iv) conformational inversion

(d) Give the absolute configuration and R/S specification of compounds below: (4marks)

