KENYATTA UNIVERSITY

UNIVERSITY EXAMINATIONS 2011/2012

SECOND SEMESTER EXAMINATION FOR THE DEGREE OF MASTER OF SCIENCE

SCH 534: ADVANCED STEREOCHEMISTRY AND CONFORMATIONAL ANALYSIS

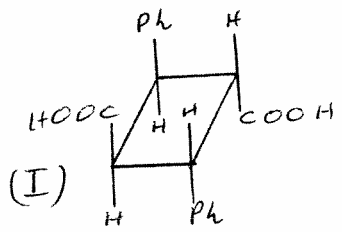
DATE: Friday 30th March 2012 **TIME: 2.00p.m – 5.00p.m**

INSTRUCTION: Answer ALL questions

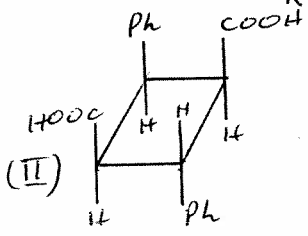
Q1. (a) The *meso* stereoisomer of butane-2,3-diol is populated equally (50:50) by the two gauche conformations; no *anti* conformation is present. On the other hand, although optically active stereoisomers are also populated by two gauche conformations, these are present in unequal proportions.
(i) Explain this difference with the help of appropriate 3-dimensional representations (e.g. Newman or sawhorse projections) of conformational structures resulting from rotation about the central C-C of the *meso* and any one of the two optically active isomers. **[10 marks]**
(ii) Which of the two gauche conformations of the optically active stereoisomers is likely to predominate? Why? **[3 marks]**

(b) Draw pairs of chair conformational structures of the following cyclohexane derivatives. On the basis of different factors (steric, electronic, H-bonding etc) between the substituents, predict the likely equilibrium position of each conformational pair. Briefly indicate the bases of your predictions.
(i) *Cis*- and *trans*-1,2-dibromocyclohexane
(ii) *Cis*- and *trans*-1-bromo-2-methylcyclohexane
(iii) Cis- and *trans*-1-bromo-2-hydroxycyclohexane **[12 marks]**

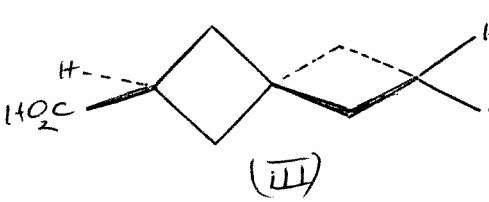
Q2. Taking into account the 3-dimensional structures of the following compounds, identify their symmetry elements (C*n*, σ, *i* and and S*n*) and classify each into symmetric, dissymmetric or asymmetric, and chiral or achiral:
(i) *Cis*- and *trans*-1,2-dibromocyclopropane **[5 marks]**
(ii) α-Truxilic acid (I) and its isomer (II) **[6 marks]**
(iii) Spiro[3,3]heptane-2,6-dicarboxylic acid (III) and its tri-carboxyl analogue (IV) **[6 marks]**
(iv) Tetramethyl-spiro-(1,1')-dipyrrolidium salts represented by (V) and (VI) **[8 marks]**



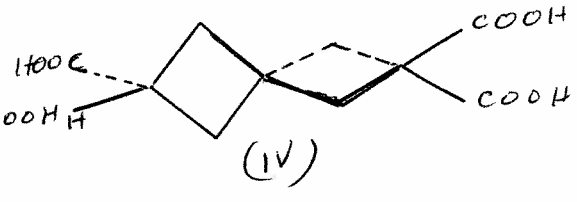
(I)



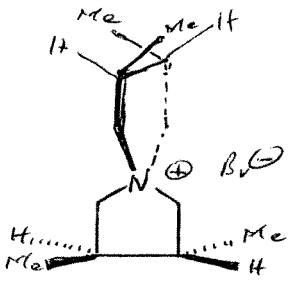
(II)



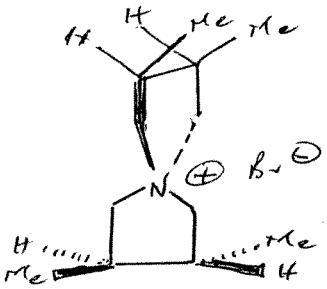
(III)



(IV)



(V)

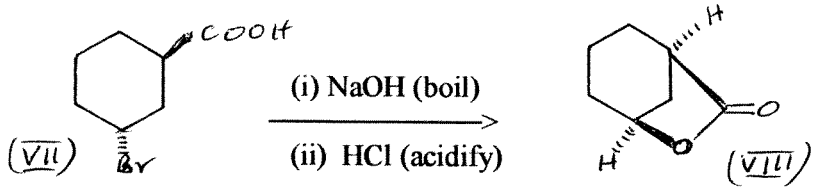


(VI)

Q3. Account **fully** for the following differences in the reactivity of stereoisomers with the help of conformational and stereo-structural analyses.

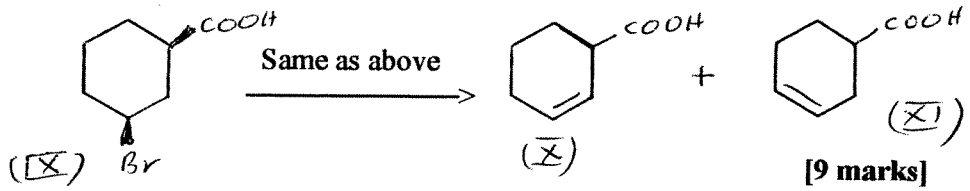
(i) Treatment with the base pyridine, racemic 1,2-dibromo-1,2-diphenylethane loses HBr to yield *trans*-1-bromo-1,2-diphenylethene; on the other hand, the meso dibromo compound loses Br_2 to yield *trans*-diphenylethene. Account fully for this difference between the isomers. **[8 marks]**

(ii) Boiling trans-1-bromo-3-carboxylcyclohexane (VII) with NaOH followed by neutralisation with HCl gives the lactone (VIII) formed by internal nucleophilic substitution:



(VII) (VIII)

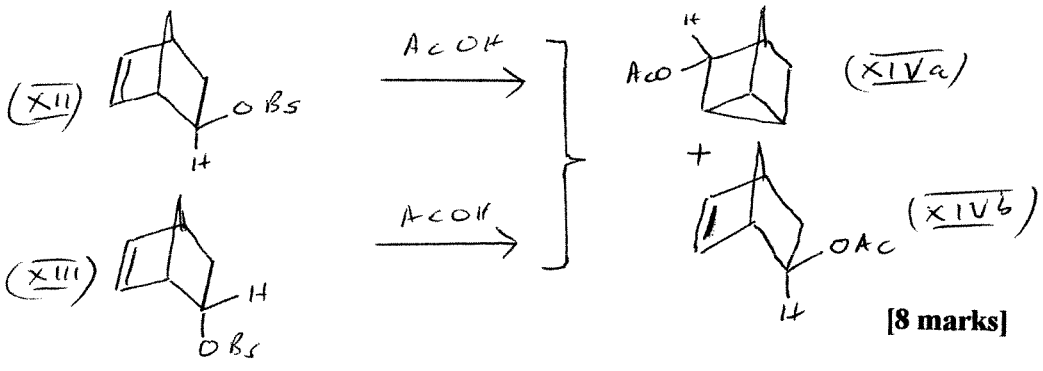
However, similar treatment of the *cis* analogue (IX) gives a mixture of two elimination products (X) and (XI):



(IX) (X) (XI)

[9 marks]

(iii) Acetolysis of *exo*-5-norbornenyl brosylate (XII) and its *endo*-isomer (XIII) proceed at very different rates, the exo-isomer reacting 8000 times faster than the endo-isomer. However, both give the same products (XIVa and XIVb).



(XII) (XIII) (XIVa) (XIVb)

[8 marks]

Q4. (a) Explain the terms conrotatory and disrotatory with respect to electrocyclic conversion of butadiene to cyclobutene. Which is facilitated by heat (Δ) and which by light (hυ)? Include consideration of symmetry of the orbitals involved in the conversions. **[5 marks]**

(b) Disrotatory ring opening of cis-5,6-dimethylcyclohexadiene follows only one of two possible pathways. What product is formed and why? What facilitates the reaction? **[6 marks]**

(c) (i) Light (hυ) induces reaction of two ethene (ethylene) molecules to give cyclobutane, but no reaction is facilitated by heat. Explain. **[6 marks]**

(ii) Explain the following differences in the course of the reaction between two butadiene molecules induced by light (hυ) and heat (Δ), respectively. **[8 marks]**