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PG (NEW) CBCS
M.Sc. Semester-IV Examination, 2020
CHEMISTRY
PAPER: CEM 403
ADVANCED ORGANIC CHEMISTRY-IV

Full Marks: 40   **Time: 2 Hours**

Answer any <u>one</u> question from the following (within 250 words): 40X1=40

1. (a) In the following thermal rearrangements a particular diastereomer (as shown) is formed. Identify at which face of the olefin (Re or Si) the migration takes place. Offer an explanation why the other diastereomer is not formed?
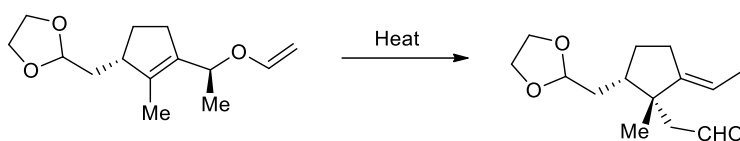
   (b) cis-1-Benzoyl-2-phenylcyclohexane furnishes a monobromination product when subjected to acid catalysed bromination. The corresponding trans isomer fails to react. Explain with reason(s). What happens when trans-1-acetyl-2-phenylcyclohexane is so treated?

2. The abbreviated configurational names for the diastereomers of perhydrophenanthrene are:

   (i) t-tr-t   (ii) t-tr-c   (iii) t-ci-t   (iv) t-ci-c   (v) c-tr-c   (vi) c-ci-c

   Now answer the following:

   (i) Which diastereomer(s) can be called meso?

   (ii) Which can exist as resolvable dl pair?

   (iii) Which exists as non-resolvable dl pair?

   (iv) Whose conformational structure does not have the central ring in chair form?

   (v) Whose torsion angle signs for the two ring juncture bonds within the central ring are different?

   (vi) Arrange all the diastereomers in order of their increasing enthalpy.

3. Write down the conformers of both the enantiomers of cis-1-decalone and trans-1-decalone. Designate stereocenters with R/S notation. Label the conformers of cis-decalone as steroidal or non-steroidal.

(1)

4. Comment on the chirality, relative stability and sign of torsion angles at ring junction in the central ring of (i) cis-c-cis- and (ii) trans-t-trans isomers of perhydroanthracene.

5. (-) trans-10-Methyl-2-decalone exhibits negative Cotton effect in the ORD curve. Deduce its absolute configuration by the application of octant rule and specify its stereocenters in terms of (R, S) nomenclature. Explain with the help of energy profile diagram the principle of enantioselective reactions.

6. Derive Curtin-Hammett principle for a case where more stable conformer gives major product. State the conditions under which Curtin-Hammett principle is valid. Give reasonable mechanism to account for the following transformation.
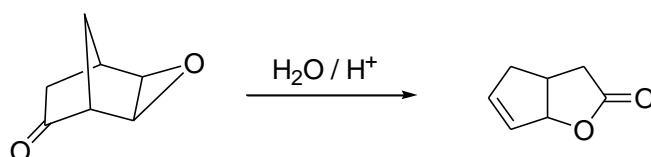
7. Compare and contrast cis-decalin and cis-1,2-dimethylcyclohexane in respect of (i) symmetry and chirality and (ii) relative stability of the conformers. What is Brewster rule?

8. How do you achieve the following stereoselective synthesis in one or more step(s)?
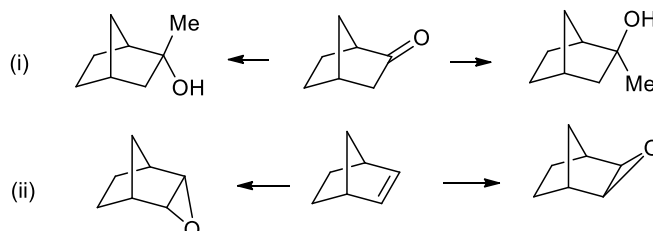
9. Explain with the help of Cieplak model, giving orbital interpretation, the diatereomeric composition of the products in the following reactions when substituent (Z) is varied as shown:

| Z	Percentage of	
	P_1 (E-isomer)	P_2 (Z-isomer)
-Cl	59	41
4-Cl-C_5H_4	60	40
4-HO-C_5H_4	44	56
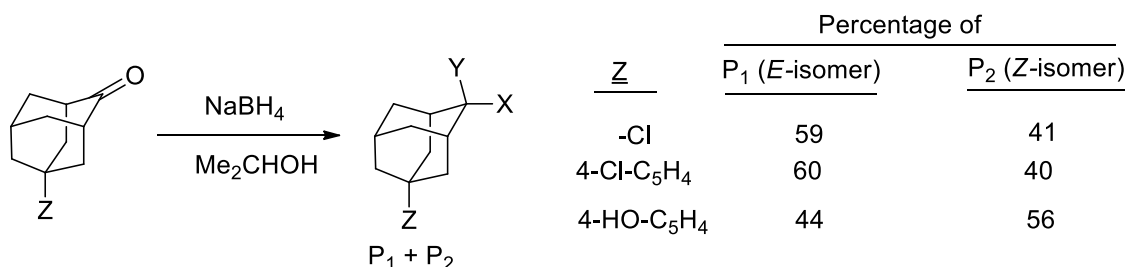
10. What is circular dichroism? Calculate ΔG at 25 °C for cis-4-methylcyclohexanol from the given rates of acetylation as follows:

    Cyclohexanol   : 3.76 units

    cis-4-tert-Butylcylcohexanol   : 2.89 units

    trans-4-tert-Butylcyclohexanol   : 10.65 units

11. Identify the compounds A – E in the following transformations and explain your answer:
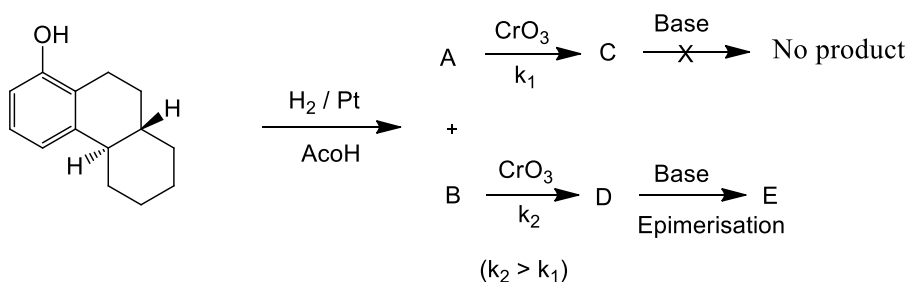
12. (-)-Menthone having 2R, 5R configuration, shows only a positive Cotton effect CD curve in water, but exhibits a strong negative Cotton effect in isooctane. Explain these observations. Define the molar ellipticity.

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