CHEM6394: Stereochemistry
Prof. Ognjen Š. Miljanić

Second Midterm Exam
April 2, 2024

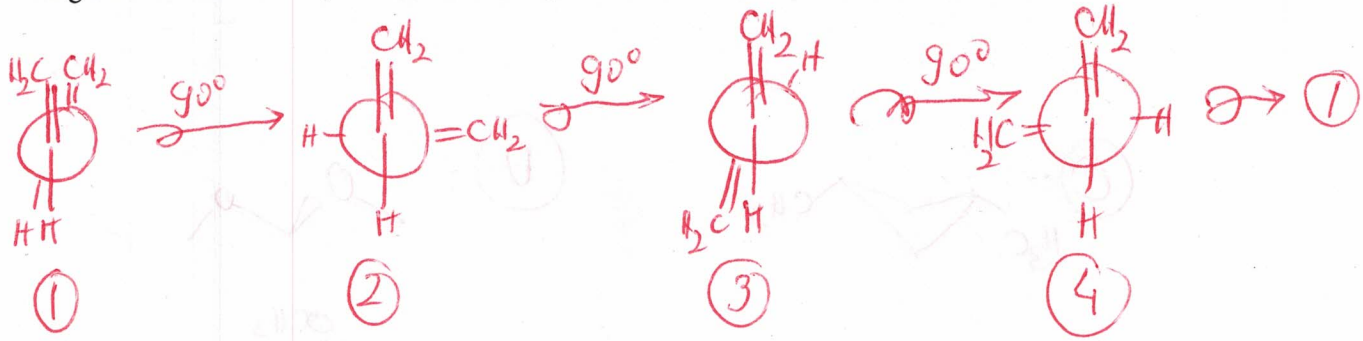
Name: Answer Key
(print legibly) Last First

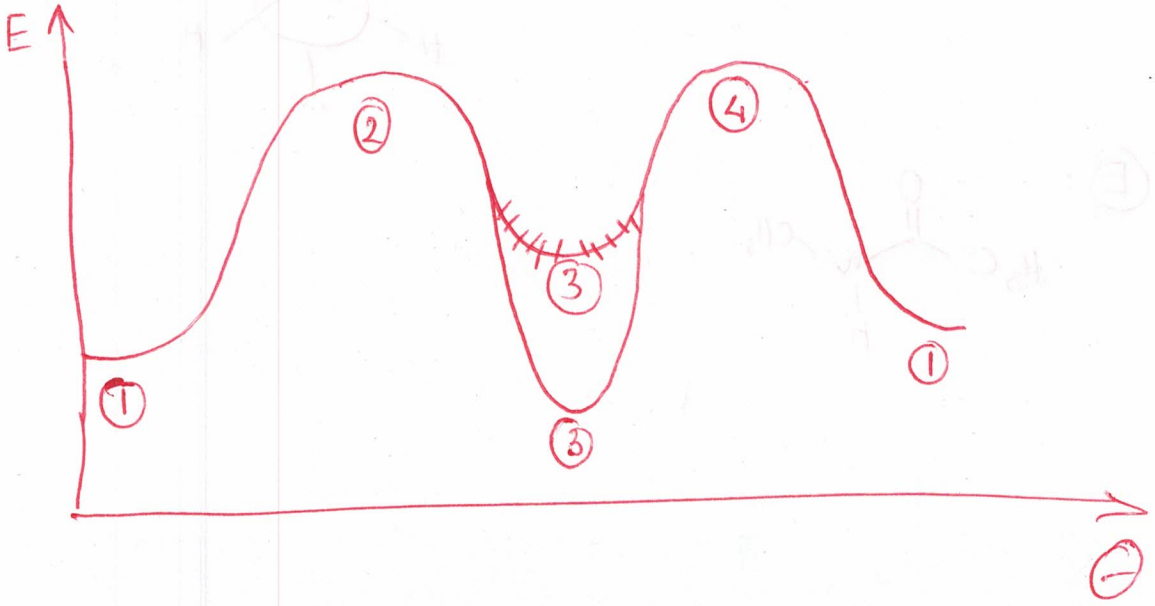
Last 4 Digits of Student ID Number: N/A

Read all directions very carefully. Write your answer legibly in the designated spaces. Total number of points is 200. This exam is supposed to have six (6) pages, with the last page intentionally left blank.

50

1. Draw the approximate conformational energy diagram for the rotation around the C2–C3 bond in 1,3-butadiene. Use Newman projection formulas to show the key conformations through which the molecule goes during this rotation. Clearly denote local and global minima and maxima on your diagram. *50 points*

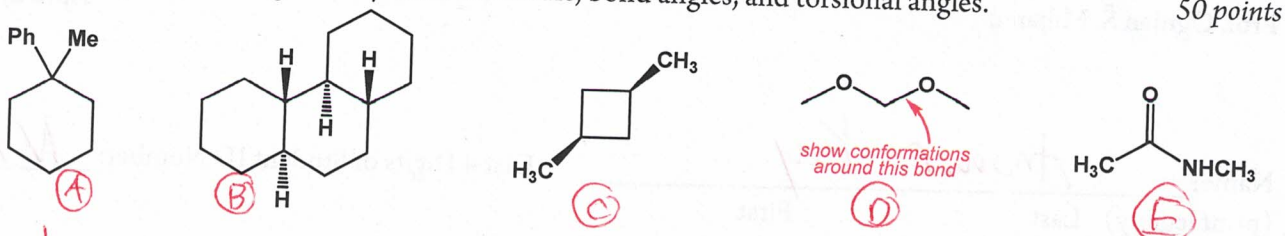


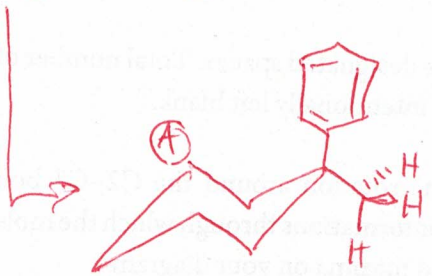


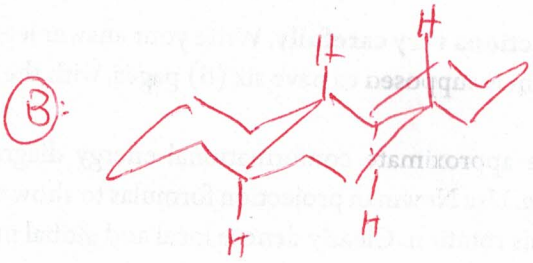
DO NOT WRITE IN THIS SPACE
200
FINAL SCORE

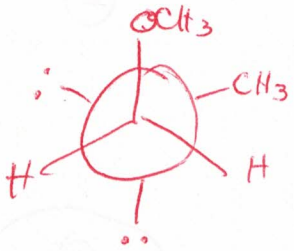
50

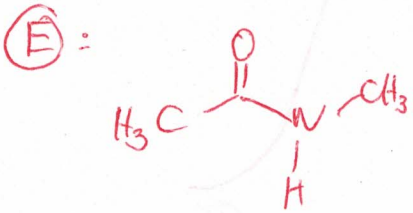
2. Draw the most stable conformations of the molecules and the radical shown below. Be very specific in highlighting the overall geometry of the molecule, bond angles, and torsional angles. *50 points*





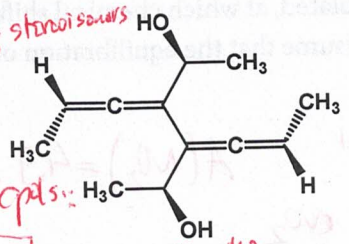






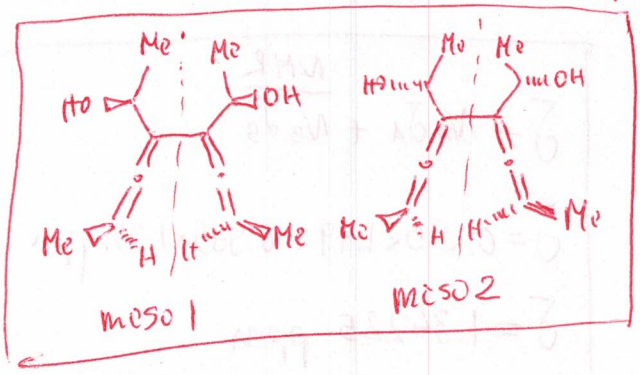
(20)

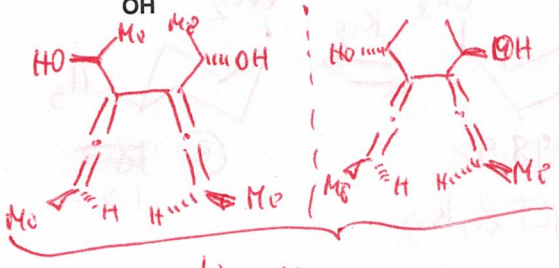
3. Draw all the stereoisomers of the allene shown below. Clearly identify enantiomeric and diastereomeric relationships. Assume completely free rotation around all single bonds, and no free rotation around the double bonds. *20 points*



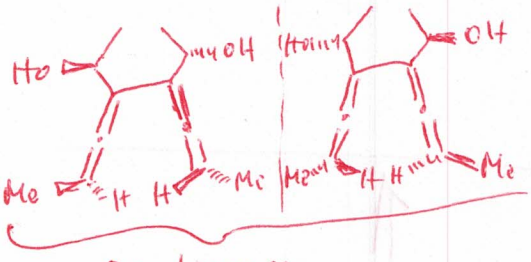
4 stereocenters = up to $2^4 = 16$ stereoisomers

Let's redraw in a way which makes it easier to find meso cpds:

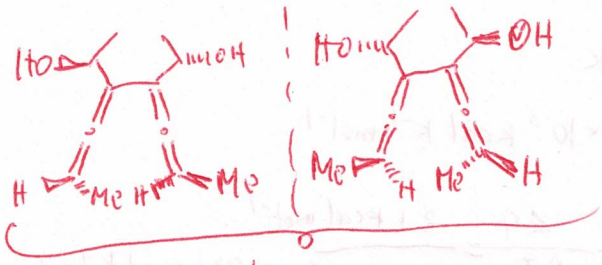




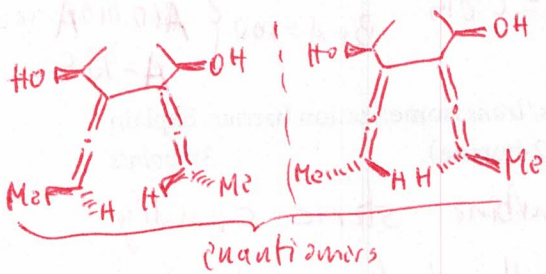
enantiomers



enantiomers



enantiomers



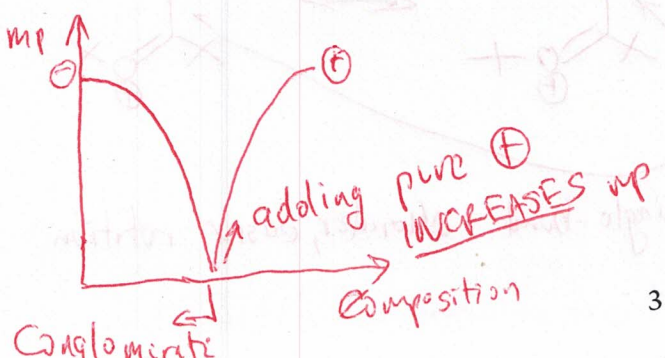
enantiomers

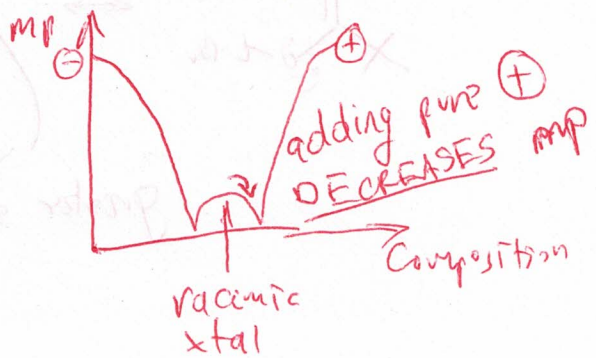
All other relationships are diastereomeric. Why is there only 10 isomers? Because a combination of a symmetry plane and a C_2 axis results in enantiomers which are identical to other cpds. See printout on the back!

(10)

4. Briefly describe how you could distinguish a racemic crystal from a conglomerate of enantiopure crystals without using X-ray diffraction. *10 points*

You could distinguish them by the different response of their melting points to the addition of pure enantiomer:



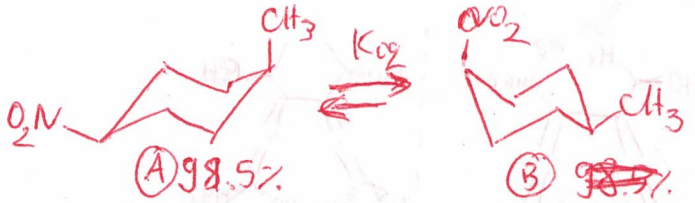


40

4. The *A* value for the methyl group is 1.8 kcal mol^{-1}, and that for the nitro group is 4.9 kcal mol^{-1}. What percentage of *cis*-4-nitromethylcyclohexane has the methyl group in the axial position at 100 °C? Show your work. In the ^{1}H NMR spectra, the axial methyl group appears at 1.34 ppm and the equatorial at 1.49 ppm. Using the percentages you just calculated, at which chemical shift would you expect the averaged peak for the methyl group in this compound? Assume that the equilibration of the two chair forms is faster than the NMR timescale.

40 points

$A(CH_3) = 1.8$ kcal mol^{-1} $\quad A(NO_2) = 4.9$ kcal mol^{-1}



(A) 98.5% (B) ~~98.5%~~ 1.5%

$\Delta G = -RT \ln K_{eq}$

$\Delta G = 4.9 - 1.8$ kcal mol^{-1} $= 3.1$ kcal mol^{-1}

$T = 373$ K

$R = 1.987 \times 10^{-3}$ kcal K^{-1} mol^{-1}

$$\ln K_{eq} = -\frac{\Delta G}{RT} = \frac{3.1 \text{ kcal mol}^{-1}}{373 \text{ K} \times 0.001987 \text{ kcal K}^{-1} \text{ mol}^{-1}}$$

$\ln K_{eq} = -4.182 \Rightarrow K_{eq} = e^{-4.182} = 0.015 \longrightarrow B/A = 0.015$

$B + A = 100$ } $A + 0.015A = 100$

$A = 98.5\%$

$$\overline{\delta} = N_A \delta_A + N_B \delta_B \quad \text{(NMR)}$$

$\overline{\delta} = 0.015 \times 1.49 + 0.985 \times 1.34$ ppm

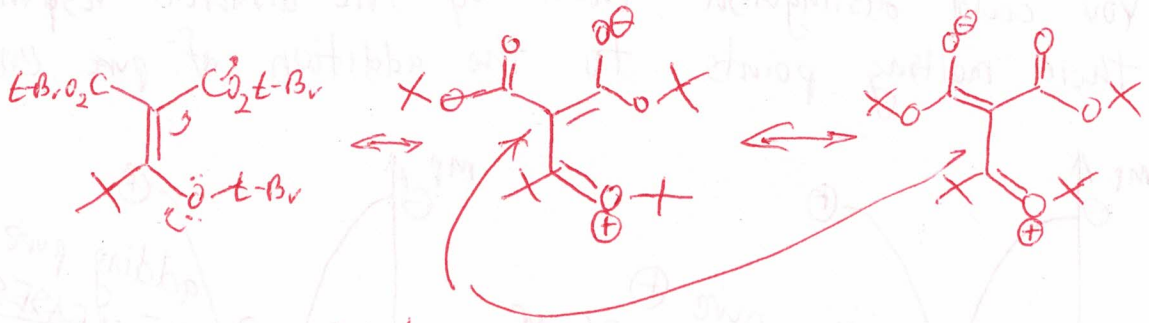
$\overline{\delta} = 1.34225$ ppm

30

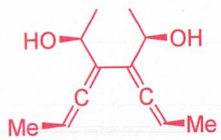
6. Draw a molecule of your choice which has a C=C bond with a very low *cis*/*trans* isomerization barrier. Explain why this barrier would be significantly lower than in simple alkenes (e.g., 2-butene).

30 points

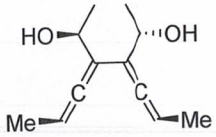
to lower the rotation barrier, we need to combine steric crowding around the double bond with a push-pull electronic character:



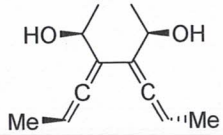
greater single-bond character, easier rotation



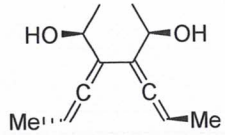
A
achiral, σ



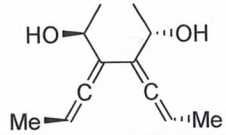
B



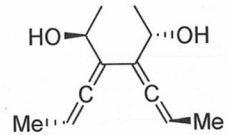
C



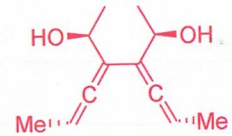
D
enantiomer of C



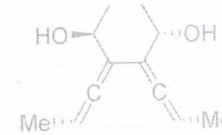
E



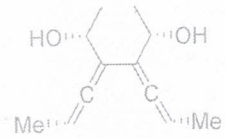
F



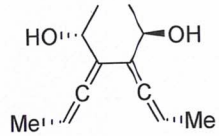
G
achiral, σ



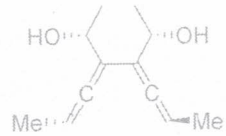
H
identical to B



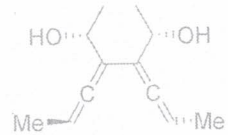
A'
identical to A



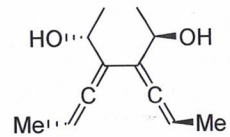
B'
enantiomer of B



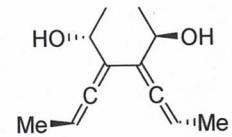
C'
identical to D



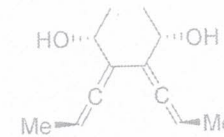
D'
identical to C



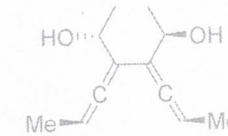
E'
enantiomer of E



F'
enantiomer of F



G'
identical to G



H'
identical to B'

Chart for the Determination of Point Groups