Name: _____   Last 4 Digits of Student ID Number: _____

(print legibly)   Last   First

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.

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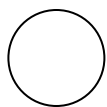
2. Draw the most stable conformations of the molecules and the radical shown below. Be very specific in highlighting the overall geometry of the molecule, bond angles, and torsional angles.   *50 points*

Ph   Me

H   H

H

H

CH$_3$

H$_3$C

O   O

show conformations around this bond

O

H$_3$C   NHCH$_3$
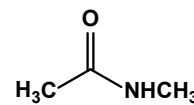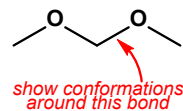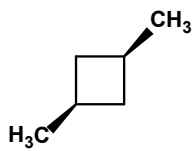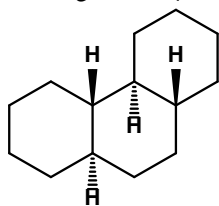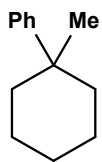
3. Draw all the stereoisomers of the allene shown below. Clearly identify enantiomeric and diastereomeric relationships. Assume completely free rotation around all single bonds, and no free rotation around the double bonds. *20 points*
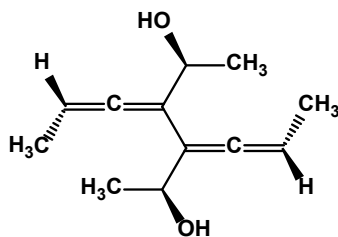
4. Briefly describe how you could distinguish a racemic crystal from a conglomerate of enantiopure crystals without using X-ray diffraction. *10 points*

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*

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*

Chart for the Determination of Point Groups

MOLECULE

LINEAR — YES → i? — YES → $D_{\infty h}$
i? — NO → $C_{\infty v}$
LINEAR — NO → TWO OR MORE C_n, $n > 2$

TWO OR MORE C_n, $n > 2$ — YES → i? — NO → T_d
i? — YES → C_5? — YES → T_h
C_5? — NO → O_h

TWO OR MORE C_n, $n > 2$ — NO → C_n?
C_n? — NO → σ_h? — YES → C_s
σ_h? — NO → i? — YES → C_i
i? — NO → C_1

C_n? — YES → SELECT C_n WITH HIGHEST n; $n C_2 \perp C_n$

SELECT C_n ... — YES → σ_h? — YES → D_{nh}
σ_h? — NO → $n\sigma_v$? — NO → D_n
$n\sigma_v$? — YES → D_{nd}

SELECT C_n ... — NO → σ_h? — YES → C_{nh}
σ_h? — NO → $n\sigma_v$ — YES → C_{nv}
$n\sigma_v$ — NO → S_{2n}? — YES → S_{2n}
S_{2n}? — NO → C_n

THERE IS IN PRINCIPLE AN INFINITE NUMBER OF POINT GROUPS, BUT IN REALITY ONLY ABOUT TWO DOZEN ARE USED

Point groups that lack reflection symmetry (ie that don't have σ, i, or S_n elements) cannot be superimposed with their mirror images: they are CHIRAL.