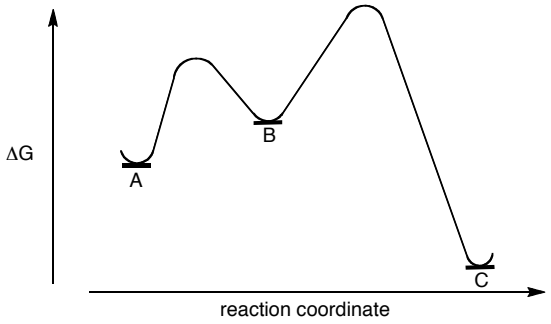
Name: _____

CHEM 633: Advanced Organic Chem: Physical
Problem Set 3
Due 11/20/16

Please do not look up references until after you turn in the problem set unless otherwise noted.
For the following problems, please use Excel (or another graphing program), when necessary. Please submit your graphs with your problem set.

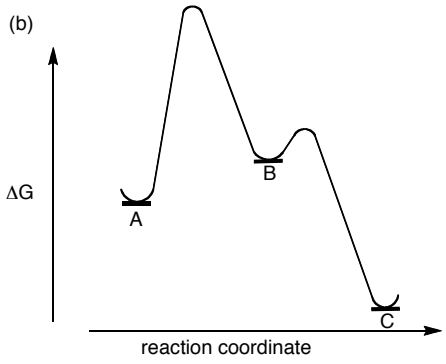
1. Consider the following theoretical reaction coordinate diagrams, describing the transformation of starting material **A** into product **C** via intermediate **B**. For each reaction coordinate diagram, please answer the following questions:
(a) Is there a possibility that intermediate **B** may be observable using standard spectroscopic methods, such as NMR spectroscopy?
(b) If there is the possibility that **B** may be observable, what is the maximum possible energy difference between **A** and **B** to allow observation of **B** by NMR spectroscopy? Please explain your reasoning.

(a)



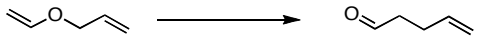
(a) Can **B** be observed?
(b) Maximum possible energy difference?

(b)



(a) Can **B** be observed?
(b) Maximum possible energy difference?

2. The temperature-dependent rates of rearrangement of allyl vinyl ether (eq 1) was studied in the gas phase.



(1)

Temp (K)	k (s^{-1})
469.1	2.875×10^{-3}
469.4	3.021×10^{-3}
473.7	3.838×10^{-3}
427.7	0.120×10^{-3}
456.7	1.166×10^{-3}
451.6	0.788×10^{-3}
440.2	0.341×10^{-3}

a. Provide a depiction of the transition structure for this transformation.

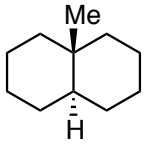
b. Draw a reaction coordinate diagram for this transformation, clearly labeling all intermediates and transition states.

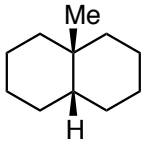
c. Determine $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ from the data (in kcal/mol and eu, respectively).

d. Explain whether your proposed transition structure is consistent with the experimentally measured value of $\Delta S^{\ddagger}$.

3. Which of the following is more stable? Why?

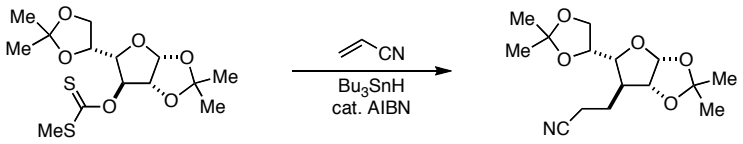
4. (a) Please draw the lowest energy conformation of these methyl-substituted decalins.

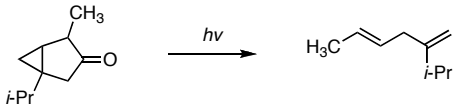


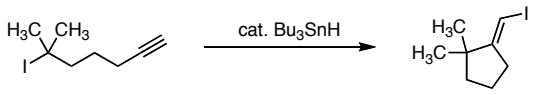


(b) Please estimate the energy difference between the lowest energy conformations of the diastereomers in part a.

5. ***From <u>The Art of Writing Reasonable Organic Reaction Mechanisms</u>, Ch. 5:*** Please draw reasonable arrow-pushing mechanisms for the following transformations:






H3C CH3
I
cat. Bu3SnH
H3C
H3C
I