

Name: Answer Key

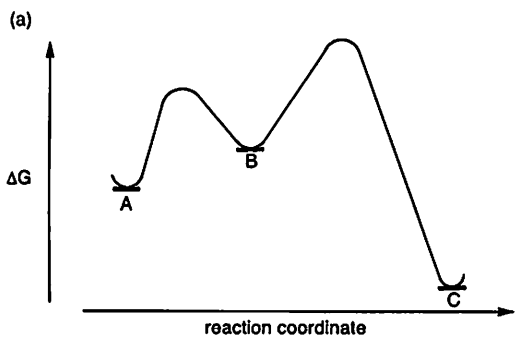
CHEM 633: Advanced Organic Chem: Physical
Problem Set 3
Due 11/20/16

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) Can **B** be observed?

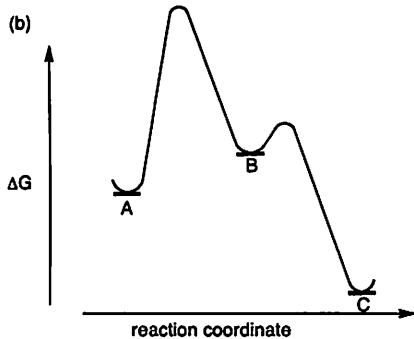
Yes

(b) Maximum possible energy difference?

$$\text{Max } K_{eq} \text{ for } A \rightleftharpoons B \approx 100$$

$$\Delta G_{298}^{\circ} = -RT \ln K_{eq}$$

$$\Delta G_{298}^{\circ} = +2.8 \text{ Kcal/mol}$$



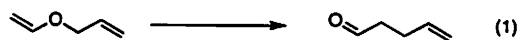
(a) Can **B** be observed?

No

(b) Maximum possible energy difference?

N/A

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



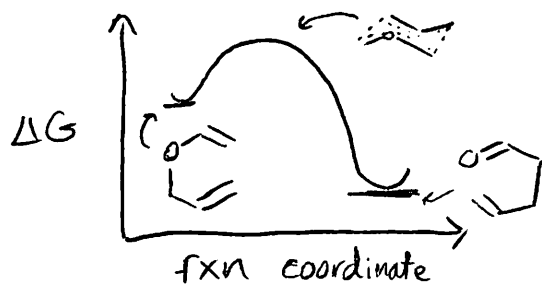
Temp (K)	k (s ⁻¹)
469.1	2.875×10^{-3}
469.4	3.021×10^{-3}
473.7	3.838×10^{-3}
427.7	0.120×10^{-3}
456.7	1.166×10^{-3}
451.6	0.788×10^{-3}
440.2	0.341×10^{-3}

Reference:
JACS, 1950, 72
p 3155

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 ΔH^\ddagger and ΔS^\ddagger from the data (in kcal/mol and eu, respectively).

$$\Delta H^\ddagger = +29.5 \text{ kcal/mol}$$

$$\Delta S^\ddagger = -8.0 \text{ eu}$$

(from graph)

$$y = \underbrace{-29.490}_{\text{slope} = -\Delta H^\ddagger \text{ (kcal/mol)}} x + \underbrace{-7.9536}_{\text{y-intercept} = \Delta S^\ddagger \text{ in e.u.}}$$

d. Explain whether your proposed transition structure is consistent with the experimentally measured value of ΔS^\ddagger .

A negative ΔS^\ddagger indicates an increased order in the TS. This is similar (in both sign + magnitude) to other pericyclic rxns where bond breaking + bond making occur.

Rxn
concerted cope

ΔS^\ddagger (e.u.)
-13.8 to -11.7

Ref.
Acc. Chem. Res 2009, 42, p169
JACS 1964, 86, p899

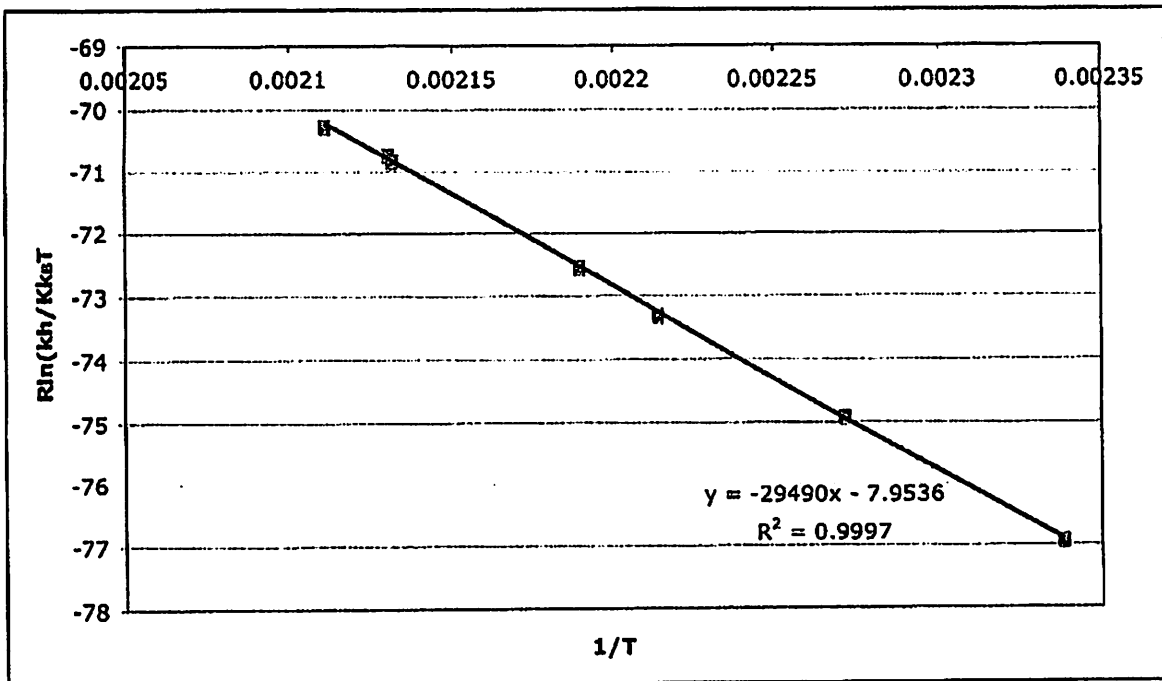
allyl methyl
ether fragmentation

-11.6

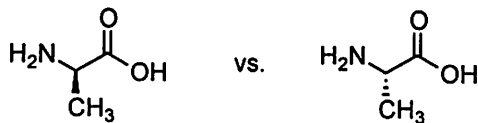
JACS, 1973, 95, p5234

For #2

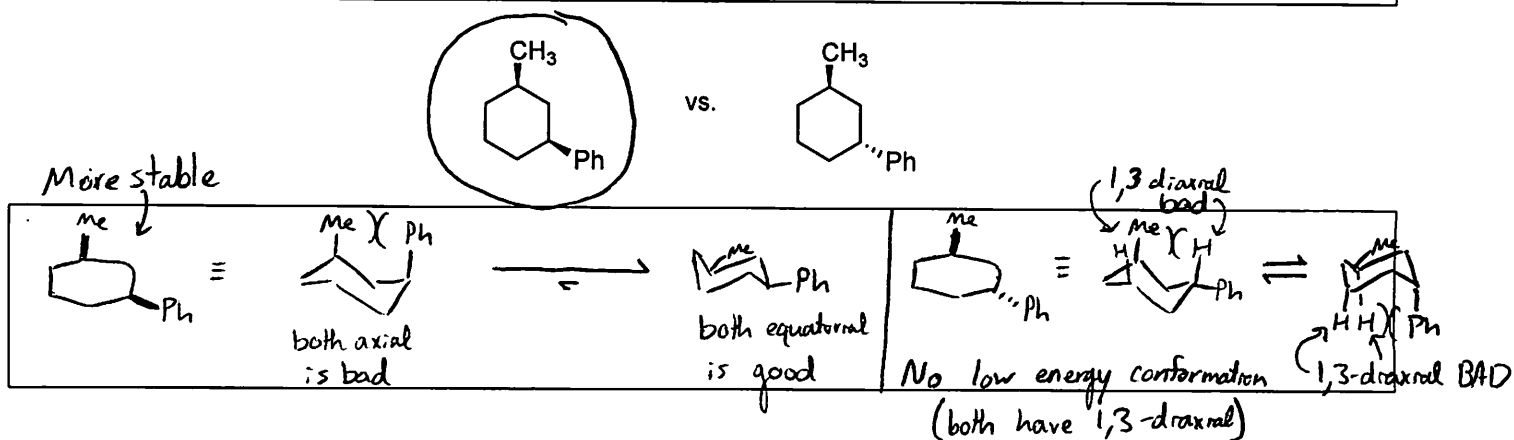
Temp (K)	$k(s^{-1})$	$k(s^{-1})$	$1/T$	kh/Kk_bT	$R\ln(kh/Kk_bT)$
469.10	2.875×10^{-3}	0.002875000	0.002131742	2.94228E-16	-70.80911298
469.40	3.021×10^{-3}	0.003021000	0.002130379	3.08972E-16	-70.71229908
473.70	3.838×10^{-3}	0.003838000	0.002111041	3.88967E-16	-70.25641483
427.70	0.120×10^{-3}	0.000120000	0.002338087	1.34695E-17	-76.91527905
456.70	1.166×10^{-3}	0.001166000	0.002189621	1.22568E-16	-72.54296797
451.60	0.788×10^{-3}	0.000788000	0.002214349	8.3769E-17	-73.29656862
440.20	0.341×10^{-3}	0.000341000	0.002271695	3.71891E-17	-74.90442356



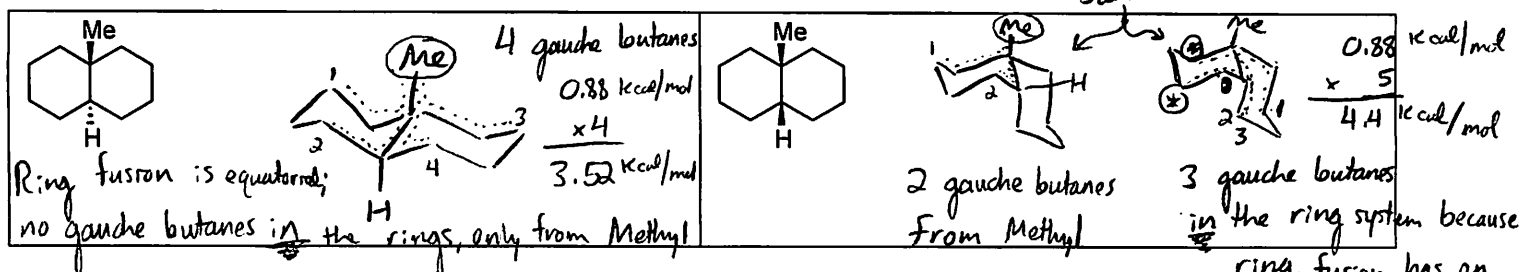
3. Which of the following is more stable? Why?



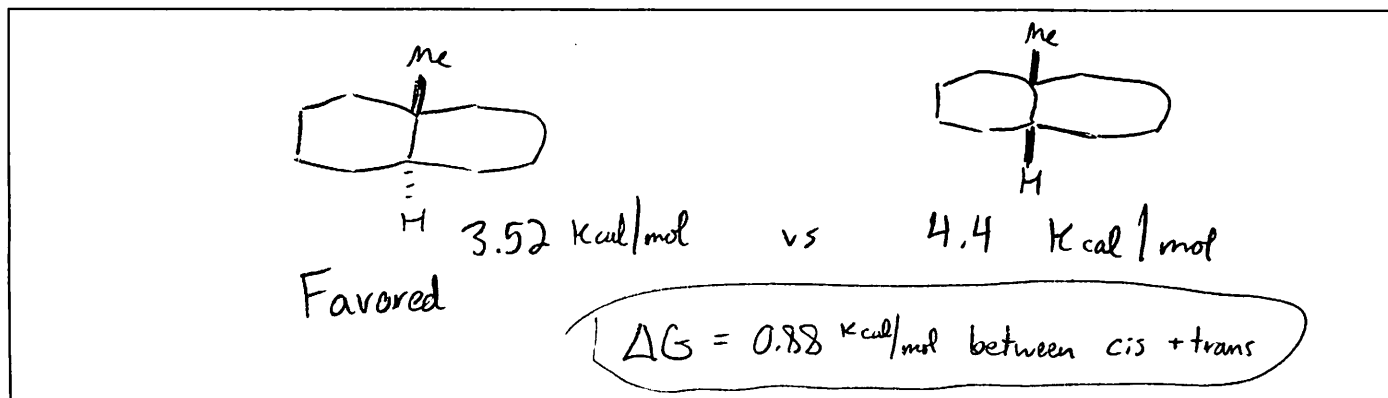
Equally stable; enantiomers have the same connectivity + conformations (except mirrored).



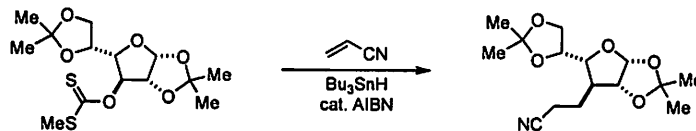
4. (a) Please draw the lowest energy conformation of these methyl-substituted decalins.



(b) Please estimate the energy difference between the lowest energy conformations of the diastereomers in part a. ring fusion has an axial carbon.



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



AIBN Formation

