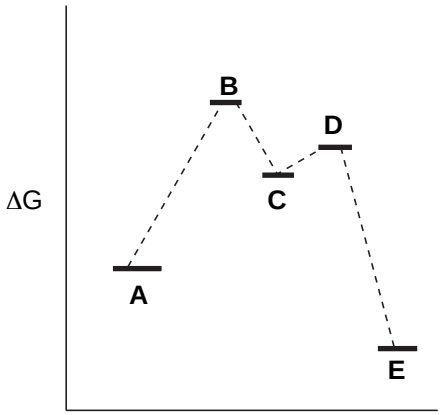
Chem 131(231) A; exam 1

1 [33 total]. Direct your attention to the potential energy diagram. Suppose that it refers to a reaction where **A** and **E** are neutral substances (i.e., they are not charged), while **C** is charged. The overall transformation converts **A** to **E**.



[a; 2 pts] Label the rate determining step.

[b; 2,4 pts] Suppose one switches from a nonpolar to a polar solvent. How would the rate of the reaction be effected? Explain.

[c; 2,4 pts] Which step is faster – the conversion of **A** to **C**, or **C** to **E**? Explain.

[d; 2,3; 2,3; 5 pts] Does the first transition state come late or early? How about the second? In each instance, what is the basis for your answer? What is the name of the postulate that deals with these topics?

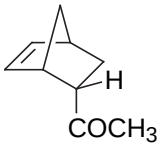
[e; 4 pts] Illustrate on the diagram, the quantity that determines how much of **A** and **E** will be present, assuming equilibrium has been reached.

[2a 10 pts; 2b) 2,2; 2,2 pts = 18 pts total]

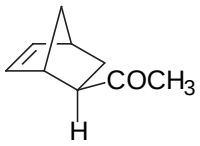
2. When cyclopentadiene is allowed to react with methyl vinyl ketone, the bicyclic ketone **A** is produced. When **A** is heated, it reverts to cyclopentadiene, methyl vinyl ketone, and a mixture of the bicyclic ketones **A** and **B**, with **B** dominant at equilibrium.

[a] Draw a potential energy surface that illustrates these observations.

[b] Which product is kinetically preferred? ... thermodynamically preferred?

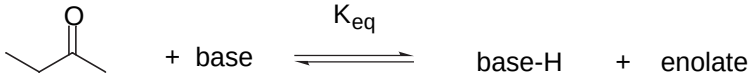


A



B

3 [26 total]. Focus your attention upon the following reaction.



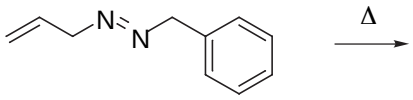
[a; 5,5 pts] Draw the structure of the two enolates that can be formed.
[b; 3,3 pts] Specify which enolate is expected to dominate under thermodynamic control. Do the same for kinetic control.
[c; 5,5 pts] Determine K_{eq} when LDA is used as the base. Do the same for sodium methoxide.

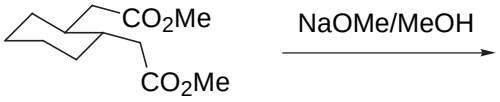
4 [10 pts total].

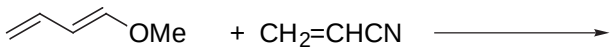
[a; 5 pts] Specify the general equation that relates K_{eq} to the thermodynamic free energy change.

[b; 5 pts] Suppose that a ketone is in equilibrium with its enolate and that the ratio of the two substances is 80/20 at 25 °C. Set up the equation that would allow you to determine the free energy difference between the two substances.

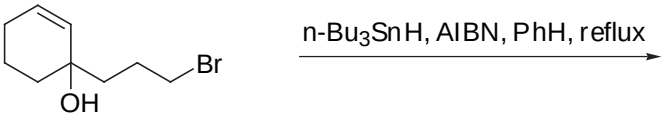
5 [5 pts each: 20 total]. Complete the following.

[a] 

[b] 

[c] 

specify stereochemistry

[d] 

6 [10 pts]. Formulate a mechanism for the acid catalyzed conversion of acetone dimethyl ketal to acetone.