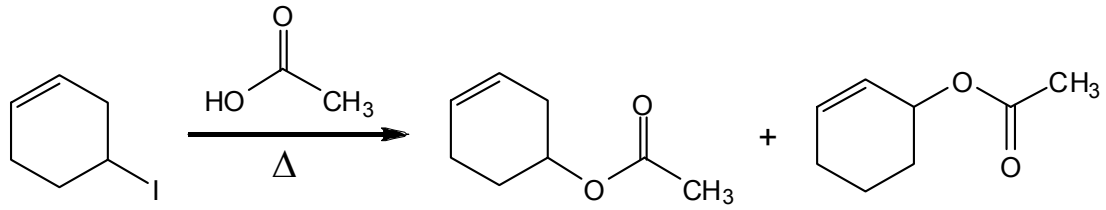
Chemistry 2331H Tuesday, October 22

Workshop 16
Drawing Potential Energy Diagrams

The reaction shown below proceeds by S_N1 to give two products: one (**P1**) by normal substitution, and the other (**P2**) involving 1,2-hydride shift of the intermediate cation. In this Workshop, we will try to interpret product preference by drawing potential energy diagrams.



SM **P1** **P2**

a. Using "electron pushing", write a mechanism for each of the two products.

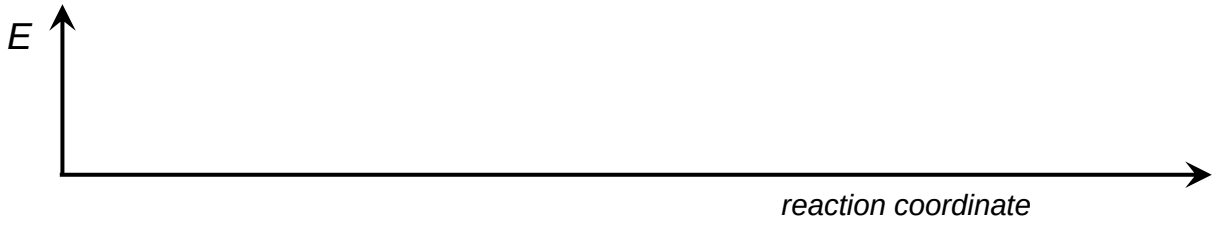
b. In class, we discussed how carbocations can undergo rearrangement if the rearranged cation is more stable. Would that be true in this case, and why?

c. In the space on the next page, draw a potential energy diagram for the reaction **SM** → **P1**. Each of the molecules that you drew in your mechanism for **P1**—starting materials, intermediates, and **P1** product—you should draw as a "well" in your potential energy diagram, and each of the steps in your mechanism should be drawn as a "hump" that the molecule has to go over.

d. Now, let's combine **SM** → **P1** and **SM** → **P2** into the same diagram. For this part of the problem, we'll assume that product **P2** predominates. On the next page, redraw your diagram for **SM** → **P1**, draw a potential energy diagram for the entire reaction that would explain this preference. Make sure your diagram illustrates:
   - Two potential energy curves, one for each product.
   - The relative potential energies of all starting materials, transition states, intermediates, and products. Show which energies correspond to which chemical structures in your arrow-pushing mechanism.
   - Which step/barrier is rate-determining, and which step/barrier is product determining.

e. How would you re-draw your diagram if the product **P1** was favored?

(c) **SM** → **P1**



(d) **SM** → **P1** and **SM** → **P2**, assuming **P2** is favored:

(e) **SM** → **P1** and **SM** → **P2**, assuming **P1** is favored: