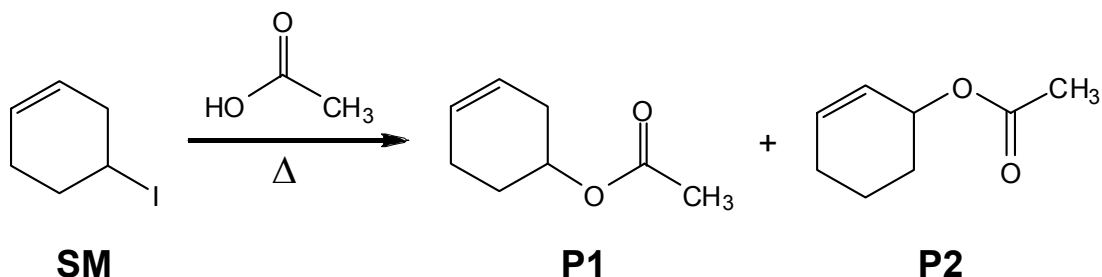


Workshop 15
Drawing Potential Energy Diagrams

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.



- Using “electron pushing”, write a mechanism that explains the formation of each of the two products.
- 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?
- In the space on the next page, draw a potential energy diagram for the reaction **SM** \rightarrow **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.
- Now, let’s combine **SM** \rightarrow **P1** and **SM** \rightarrow **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** \rightarrow **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.
- 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:

