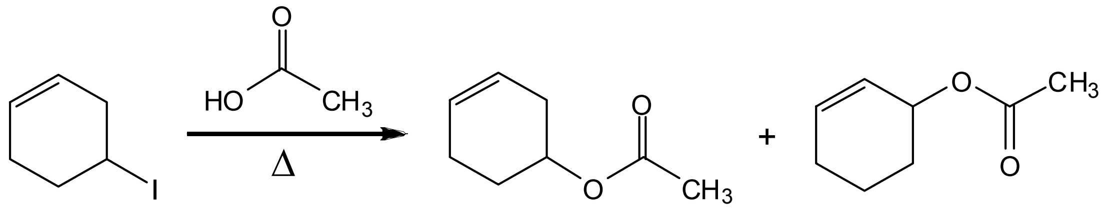
Chemistry 2301

Workshop 15 Solutions
Drawing Potential Energy Diagrams



SM **P1** **P2**

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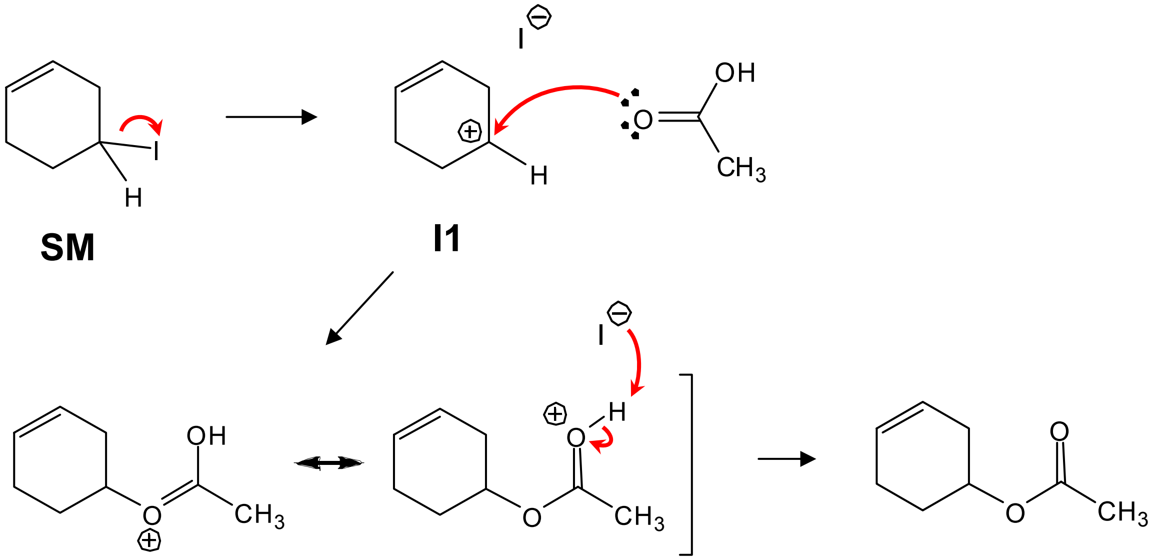
a.

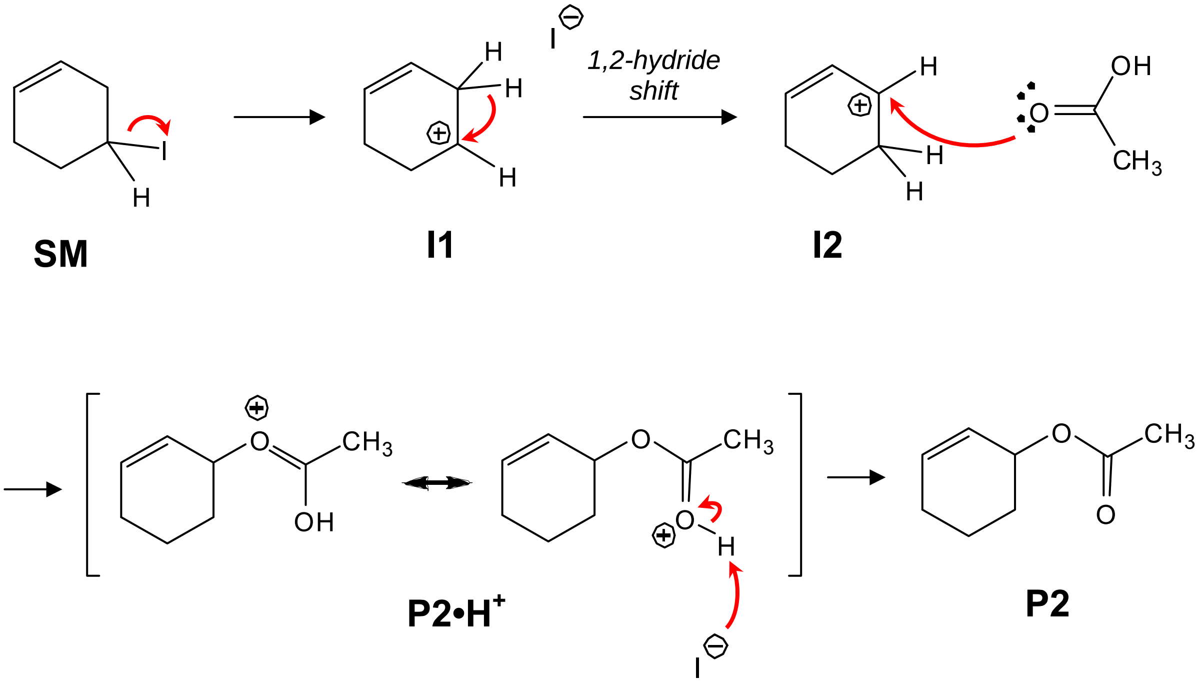


SM **I1**

P1•H$^+$ **P1**

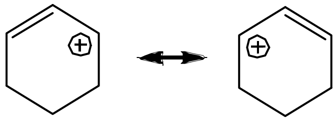
So, the potential energy curve for this first reaction needs to have <u>four</u> wells—one for starting material, one for product, and two intermediates—and three barriers to go over.

(Why did I use the double-bonded oxygen as the nucleophile? If I do, the intermediate **P1•H$^+$** is resonance-stabilized. If I don't, it isn't.)



The 1,2-hydride shift actually adds an intermediate here (**I2**), so this potential energy curve will have five wells, and four barriers.

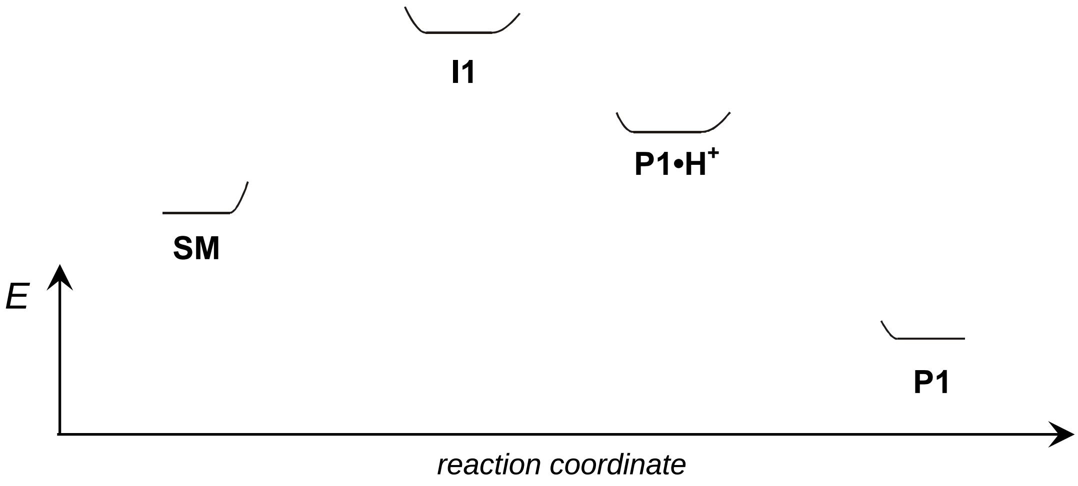
b. The intermediate **I2** has resonance structures, whereas **I1** does not.



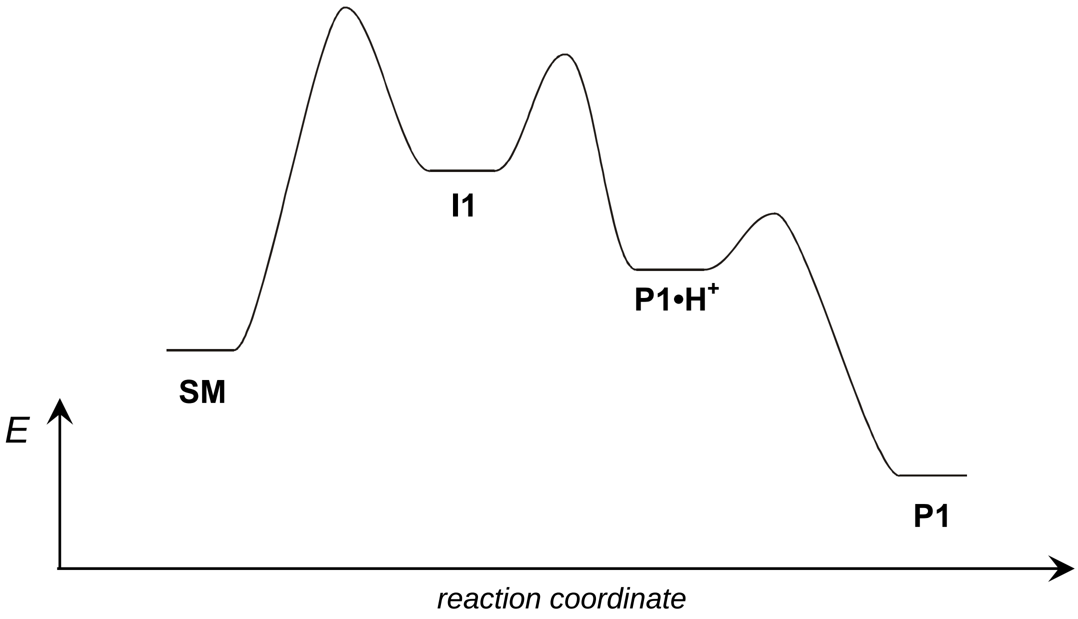
I2

So I would expect **I2** to be a more stable carbocation than **I1**.

c. Let's draw the diagram for the first reaction first. In this mechanism, the two intermediates (**I1** and **P1•H$^+$**) are both charged and relatively unstable, whereas the starting materials and products are neutral and relatively happy. We might start to draw our diagram by drawing just wells (next page):

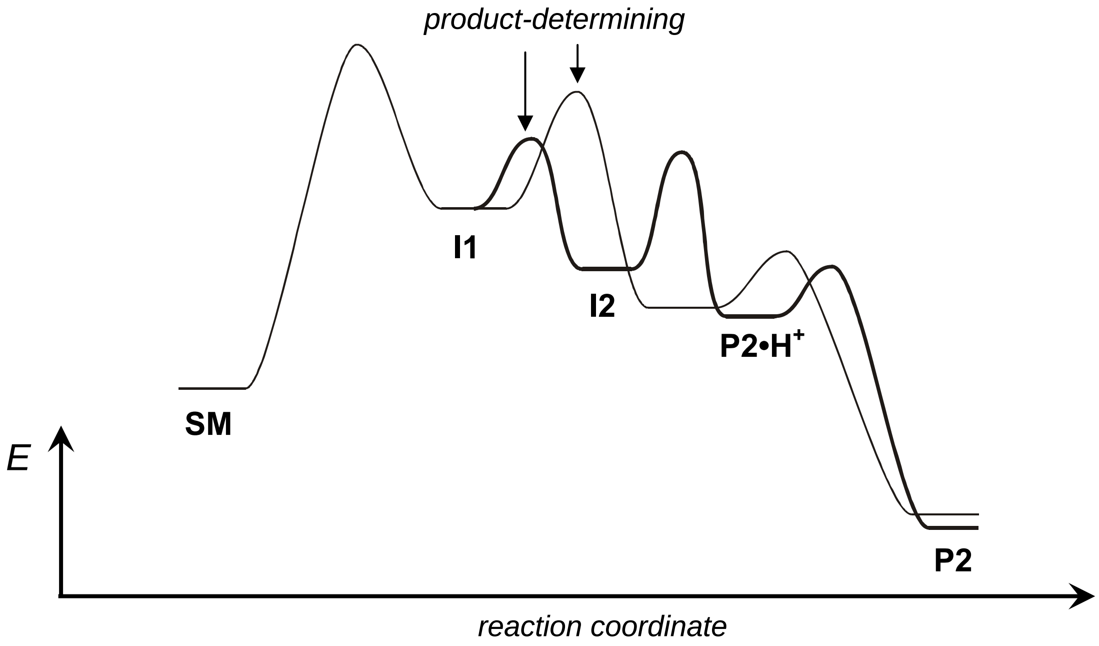


I’ve drawn **P1•H$^+$** below **I1** in energy—they’re both unstable cations, but I1 has an unfilled octet, whereas **P1•H$^+$** just has a cation on an electronegative atom. Let’s put some barriers on the plot:



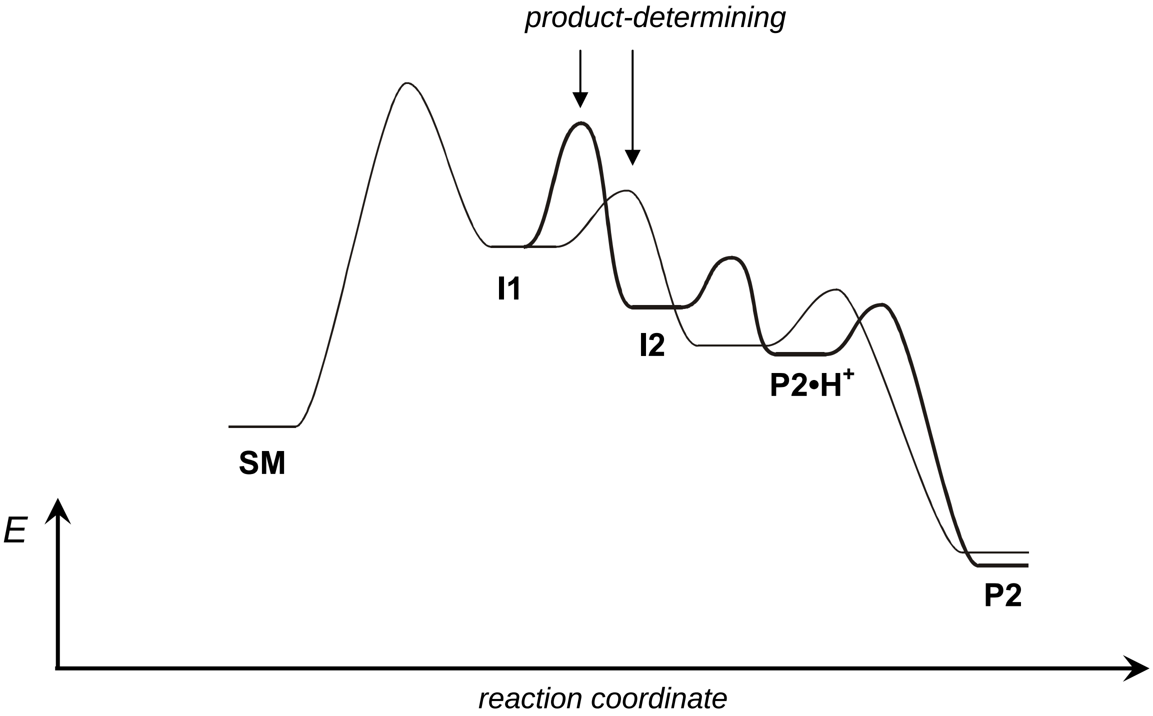
The last barrier we know will be low—proton transfer is extremely fast. I’ve drawn the first barrier as the highest one, assuming that the reaction goes forward (and not back to starting materials).

d. Okay, let's add the other reaction. We know that **I2** is lower in energy than **I1** from part (b). But how do the subsequent intermediates compare? There's no difference in stabilizing interactions between the two products, or in the protonated versions of these products—so **P1** and **P2** should be about the same energy, as should **P1•H$^+$** and **P2•H$^+$**.



Using the "bowling ball" analogy, the rate of the reaction is determined by the step with the highest barrier—the first—but the ratio of products is determined by the fork in the path that happens after the first step. The way I drew things above, the 1,2-hydride shift step has a lower barrier than the direct sunstitution (**I1 → P1•H$^+$**) step, and so the reaction would choose the **P2** fork.

e. However, what if the 1,2-hydride shift had the higher barrier? Well, then the **P1** product would be favored. (See next page.) All of the intermediate and product energies are the same in this graph, but the hydride shift barrier is higher, and that switches the fork towards making **P1**.


product-determining
I1
I2
P2•H+
SM
E
P2
reaction coordinate