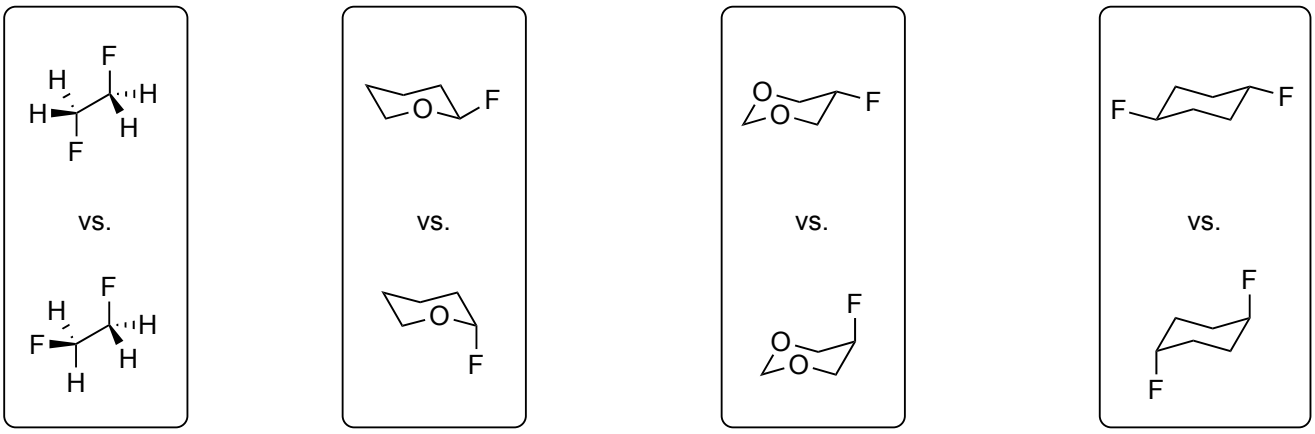
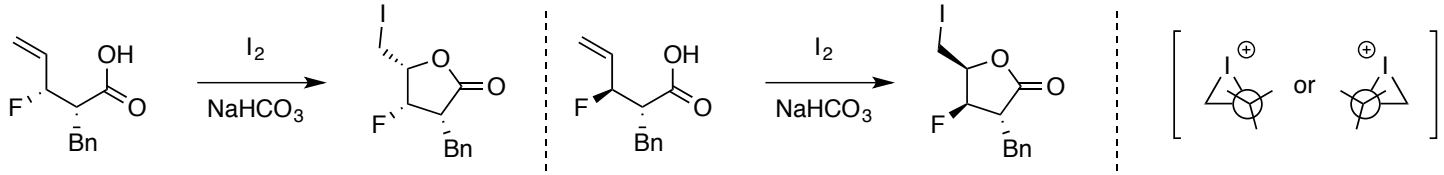
Problem Set #012 (Ross)

(1) Circle the most stable conformation for each pair of conformers.



Stereoelectronic effects: a bridge between structure and reactivity, Igor V. Alabugin,

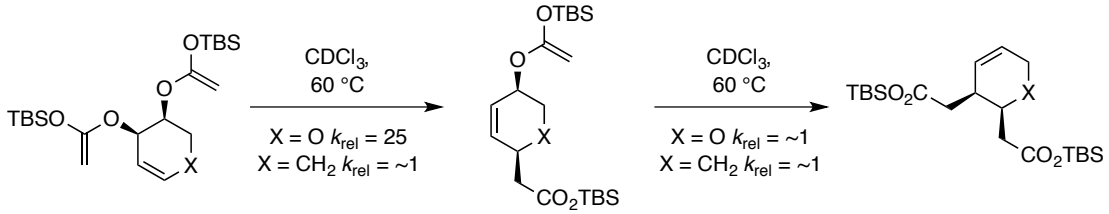
(2) The allylic fluoride **1** undergoes iodolactonization to give lactone **2** through an intermediate like **5**. The analogous allylic fluoride **3** gives rise to lactone **4** through an intermediate like **6**. Determine the conformation of this key intermediate, and rationalize why this is the preferred conformation.



1 ***2*** ***3*** ***4*** ***5*** ***6***

Tredwell, M,; Luft, J. A. R.; Schuler, M.; Tenza, K.; Houk, K. N.; Gouverneur, V. *Angew. Chem. Int. Ed.* **2008**, *47*, 357.

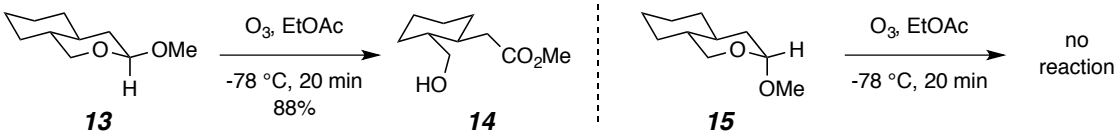
(3) In the course of developing a synthetic route to pseudomonic acid antibotics Dennis Curran and Young-Ger Suh observed that the Claisen rearrangement of **7** to **8** occurred 10–25 times than the Claisen rearrangement of **8** to **9**. However, when the carbocyclic analogue **10** was subjected to the same conditions the rearrangement of **10** to **11** occurred at approximately the same rate as **11** to **12**. Rationalize the difference in reactivity for the transformation of **7** to **8** compared to **10** to **11**.



X = O ***7*** X = CH_2 ***10*** | X = O ***8*** X = CH_2 ***11*** | X = O ***9*** X = CH_2 ***12***

Curran, D.P.; Suh, Y. *J. Am. Chem. Soc.* **1984**, *106*, 5002.

(4) Delongchamps and coworkers have shown that the ozonolysis of acetal **13** to give hydroxy ester **14** occurs rapidly at -78°C. However, the isomeric acetal **15** does not react under these conditions. Rationalize this experimental outcome. (Hint: the anomeric proton of **13** is more hydridic than **15**)



13 ***14*** ***15***

Li, S.; Deslongchamps, P. *Tet. Lett.* **1993**, *34*, 7759.