Dr. Andreana Group Meeting – Fun Problem Set 3

(Credit: Dr. Evans CCB Problem Sets)

Problem 1

Takeda and co-workers have recently reported the mechanistically interesting ring extension reaction illustrated below (Org. Lett. 2000, 2, 1903).

Provide a plausible mechanism for this transformation in the space below. Ignore the stereochemical aspect of this transformation.

Problem 2

The following transformation was recently reported by Barriault and Deon in conjunction with their synthesis of arteannium M (*Org. Lett.* **2001**, *3*, 1925-1927). Provide a mechanism for the illustrated thermal rearrangement(s) of **A** to **B**. Where stereochemical issues are at stake, provide clear three dimensional drawings to support your answer.

Problem 3

Please provide a rationale for the stereoselective synthesis of cyclic ethers in a single step shown by Sinha and coworkers (*Org. Lett.* **2004**, *6*, 123). Be sure to provide clear 3D drawing to account for the observed stereoselectivity. (Note: An excess of Bu₂BOTf (> 2 equiv) is necessary for the reaction to proceed.)

Problem 4

In Amos Smith's synthesis of the natural product, phorboxazole, (J. Am. Chem. Soc. **2001**, 123, 10942) the following acetate \mathbf{F} was treated with $ZnCl_2$ and an enoisilane to afford pyran \mathbf{G} . Provide a mechanism for this reaction and indicate what is the predominant diastereomer by providing a detailed depiction of the transition state. Assume an aqueous workup of the reaction.

Answer Key

Problem 1

Problem 2

Equatorial disposed side chain favored over Axial

Problem 3

Problem 4