Dr. Andreana Group Meeting - Fun Problem Set 3

(Credit: Dr. Evans CCB Problem Sets)

Problem 1a

Scheidt and co-workers have recently disclosed the following reaction catalyzed by an *N*-heterocyclic carbene (*J. Am. Chem. Soc.* **2007**, *129*, 10098-10099). Please provide a mechanism that accounts for the high levels of selectivity.

Problem 1b

Scheidt and co-workers have reported the following transformation utilizing an *N*-heterocyclic carbene as a catalyst (*Angew. Chem.* **2007**, *46*, 3107). Please provide a detailed mechanism and an explanation for the high levels of diastereo— and enantioselectivity.

Problem 2a

In Heathcock's recent synthetic approach to the *Stemma* alkaloids, an interesting series of transformations were used (Heathcock, JOC, 2001, 66, 7751).

Please provide a mechanism for each reaction and identify the structure of intermediate A.

Problem 2b

The fumagillin natural products possess several interesting biological properties including antibiotic activity against *Staphylococcus auereus*. In Sorensen's recent synthesis of fumagillol (*Angew. Chem, Int. Ed.* **1999**, *38*, 971), intermediate **1** was transformed into its a-oxygenated counterpart **3** through the indicated reaction sequence.

CHO Me

Me

RNH-OH

$$-H_2O$$

A

 ACO
 ACO

in the space below, identify the structure of intermediate A and provide a mechanism for the transformation of 1 into 2.

Answer Key

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CHO Me

Me

RNH-OH

$$-H_2O$$

A acetyl chloride

 Et_3N
 Et_3N

In the space below, identify the structure of intermediate A and provide a mechanism for the transformation of 1 into 2.