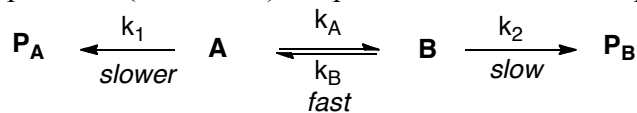


VanNieuwenhze Group Problem Set

November 17, 2009

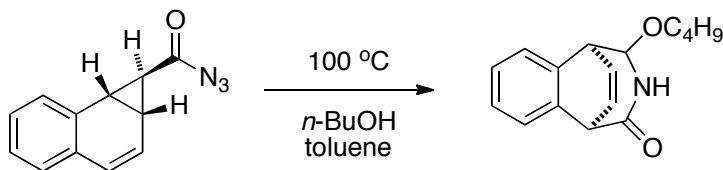
- 1) Consider the following scenario: You have a rapidly equilibrating mixture of two conformers (**A** and **B**) from which two products (**P_A** and **P_B**) are produced. In this example $k_2 > k_1$.



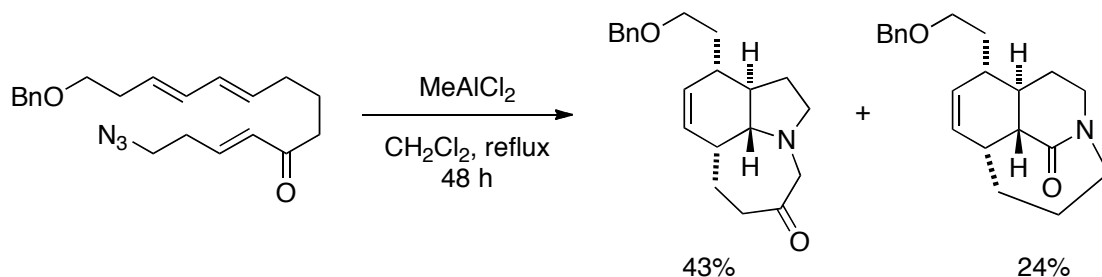
Part A. Draw a reaction coordinate diagram that reflects the situation where the equilibrium population of conformers is the same as the product ratio.

Part B. What do these conditions imply with respect to free energy relationships?

- 2) In a classic chemical transformation first disclosed by Doering and Goldstein, the acyl azide shown below was heated in the presence of *n*-butanol to afford a 1 : 1 mixture of diastereomers. Provide a mechanism for this transformation.



- 3) In a recent report of a formal synthesis of stenine, a tandem cyclization reaction afforded the following products. Propose a mechanism that accounts for each of the products, their relative stereochemistry, and their relative distribution.



- 4) Aube' has reported the transformations below and has documented that the observed product is dependent on the tether length between the azide and carbonyl functional groups. Provide a mechanism for each transformation and rationalize their differences in reactivity.

