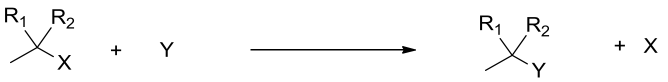
Problems - Set 2: Kinetics and Thermodynamics

Problem 1

Consider substitution reaction of an alkyl halide

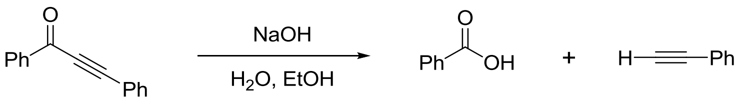


Give two possible reaction profiles corresponding to an S_N1 and S_N2 reaction, clearly labeling the important parts of the diagram.

Problem 2

For the above reaction in the S_N2 case, show the mechanism with the transition state including the breaking and forming bonds. Also draw the mechanism for S_N1 reaction showing the intermediates.

Problem 3



This reaction shows third order kinetics as the rate expression is rate=[ketone][OH^-]^2. Suggest a mechanism that explain these observations and draw the energy profile.

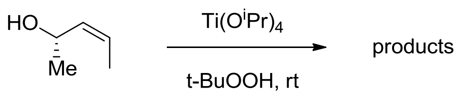
Problem 4

Consider the reaction between Br_2 and 1,3-butadiene

Draw energy profile diagram and explain the difference between the formations of these 2 products.

Problem 5

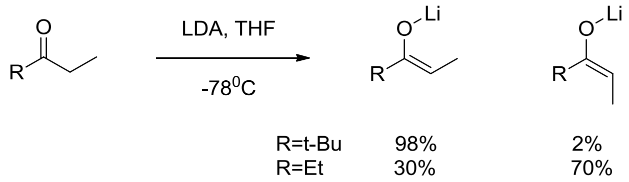
Draw the major/minor products expected from this epoxidation reaction:



The theoretical transition state energy $\Delta\Delta G^{++}$ = -1.43 kcal/mol, and experimentally the product ratio = 91:09. Determine whether this reaction obeys the Curtin-Hammett principle by calculating the expected ratio of products based on the theoretical $\Delta\Delta G^{++}$ value.

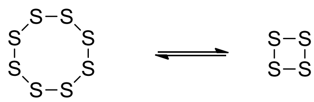
Problem 6

Use the proportion of enolates shown for the two cases (R=t-Bu and R=Et) to determine the difference in the free energies of activation at -78°C, assuming that enolate formation is kinetically controlled?



Problem 7

Elemental sulfur normally exists as an eight-membered ring (S_8), but it can also be found in a number of other states. How would entropy and enthalpy affect the equilibrium between sulfur in these two forms?



Problem 8

Enantiomerically pure α-amino acids are isomerized into their racemic mixtures. What is the Gibbs Energy of this reaction at 25°C?

Problem 9

The following reaction has a standard entropy of 35cal·mol^{-1}·K^{-1}. At which temperature will you obtain a full conversion (conversion ~ 99%) of the starting material?