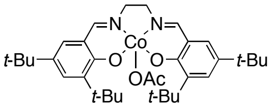
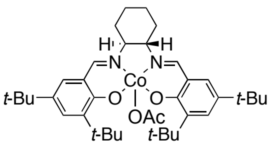
Due in class: Monday, Feb. 26th, 2007 at 12:05 pm.

1. The cobalt complexes shown below catalyze the addition of water to propylene oxide.

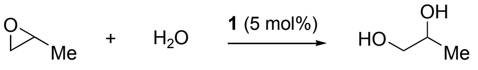


1



2
(single enantiomer)

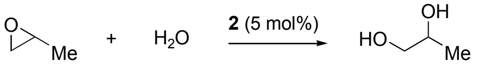
a.



racemic

100%

b.



racemic

50%

When catalyst **1** is used, complete conversion to the diol is observed. However, when catalyst **2** is used, the addition of water proceeds to 50% (a significant drop in the reaction rate is observed beyond this point).

Explain these results, provide clear energy diagrams for equations a and b consistent with your explanation, and describe the stereochemical relationship between the products of equations a anb b.

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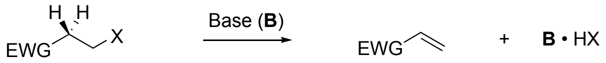
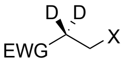
2. Consider the following reaction (EWG = electron withdrawing group, X = leaving group):



A

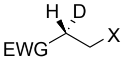
a) Propose two possible mechanisms for this transformation.

b) Compare the reaction of **A** with that of doubly deuterated derivative **A**-d_2. Predict the isotopic effect in each of your proposed mechanisms for part "a" of this question and explain your reasoning, including the use of a free energy diagram.



A-d_2

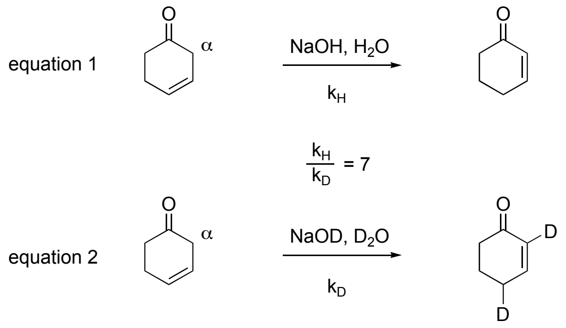
c) If the mono-deuterated derivative **A**-d_1 is used in the above experiment, provide the sturcture and ratio of the expected products in accord with each of your proposed mechanisms.



A-d_1

3. Base-catalyzed isomerization of 3-cyclohexenone to 2-cyclohexenone was achieved in H_2O and D_2O.

The rate of this isomerization in H_2O was found to be seven times faster than in D_2O. The incorporation of deuterium in the α-position of 3-cyclohexenone was found to be faster than the olefin isomerization.

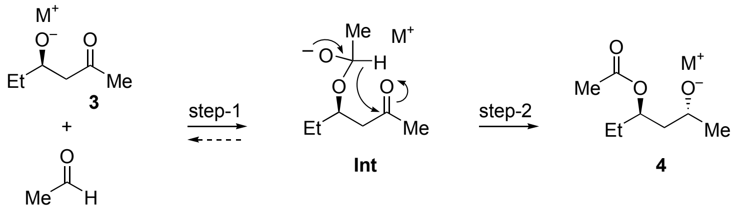


a) Provide a mechanism for the transformation depicted in equation 1 including arrow pushing.

b) Draw a reaction coordinate diagram for your answer to 3a. Clearly label all important features of the diagram.

c) Which is the rate-determining step? Explain your reasoning.

4. Treatment of alkoxide 3 with acetaldehyde gives ester 4:



a) Draw a reaction coordinate diagram consistent with step-1 being the rate-determining step. What would this imply about the reversibility of step-1?

b) Draw a reaction coordinate diagram consistent with step-2 being the rate-determining step. What would this imply about the reversibility of step-1?

c) Provide a drawing and a description of the transition state structure for formation of the intermediate (Int) based on the Hammond Postulate consitent with your answer to 4a.

d) Consider your answer to 4a. Would you expect the rate to be faster in a polar or in a non-polar solvent? Use a reaction coordinate diagram to explain your reasoning.

e) Provide a rate law for your answer to 4a.