Cumulative Examination

Organic Chemistry

January 18, 2018

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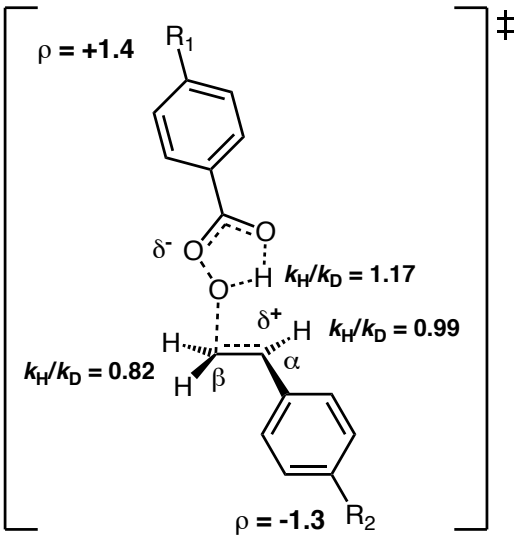
Attempt All Questions (100 Total Points)

Question 1 (50 points)

Bartlett first proposed the "butterfly" mechanism for alkene peroxidation in 1950. In this model, the transition state resembles a spiro system with the terminal oxygen of the peracid reagent centered over the middle of the two alkene carbon atoms. Studies of the reaction of substituted (R_1) peroxybenzoic acids with substituted (R_2) styrenes, by Hanzlik and Shearer, generated the kinetic isotope and Hammett study data shown below.



a. For each of the three kinetic isotope experiments, indicate whether a significant KIE is observed and, if so, if it is a) primary or secondary, or b) normal or inverse.

15 pts

b. What can be inferred about the degree to which the acidic hydrogen atom is transferred to the carbonyl oxygen atom in the transition state from the k_H/k_D value observed for the reaction with $C_6H_5CO_3D$.

5 pts

c. Compare the kinetic isotope data observed for the alkene hydrogens. Which of the two carbon atoms (α or β) is more pyramidal at the transition state? *Rationale your answer*.

10 pts

d. Given the observed rho (ρ) value for the alkene, would the rate of reaction be increased or decreased by electron-donating substituents (R_2)?

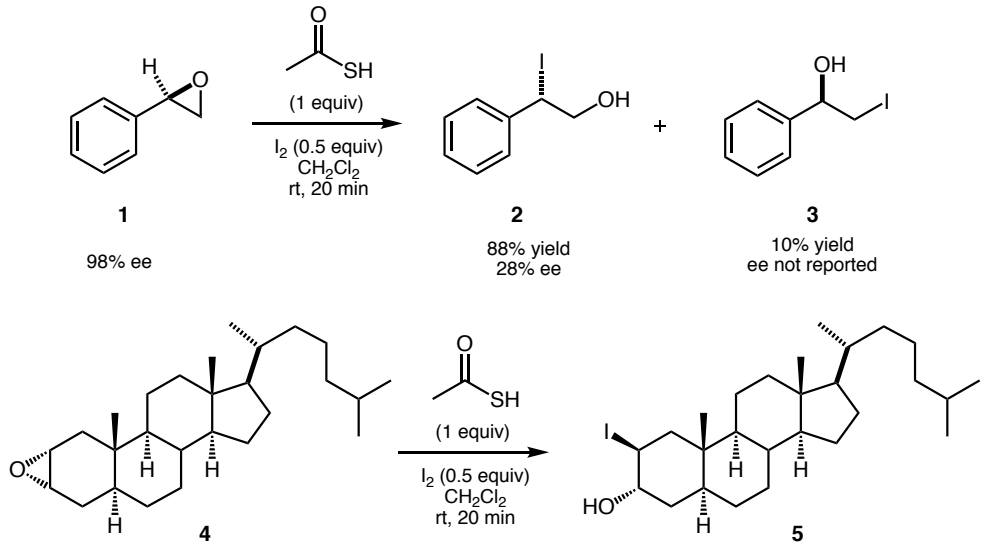
10 pts

e. Why is *meta*-chloroperbenzoic acid a stronger epoxidizing agent that perbenzoic acid? In your answer, refer to the observed rho (ρ) value of +1.4.

10 pts

Question 2 (50 points)

Treatment of thiolacetic acid with 0.5 molar equivalents of iodine generates hydrogen iodide (H-I, pK_a = -9.5) that converts epoxides to vicinal iodohydrins. Two examples are shown below.



a. Provide a rationalization for the erosion of stereochemical integrity during the opening (*R*)-2-phenyloxirane (**1**).

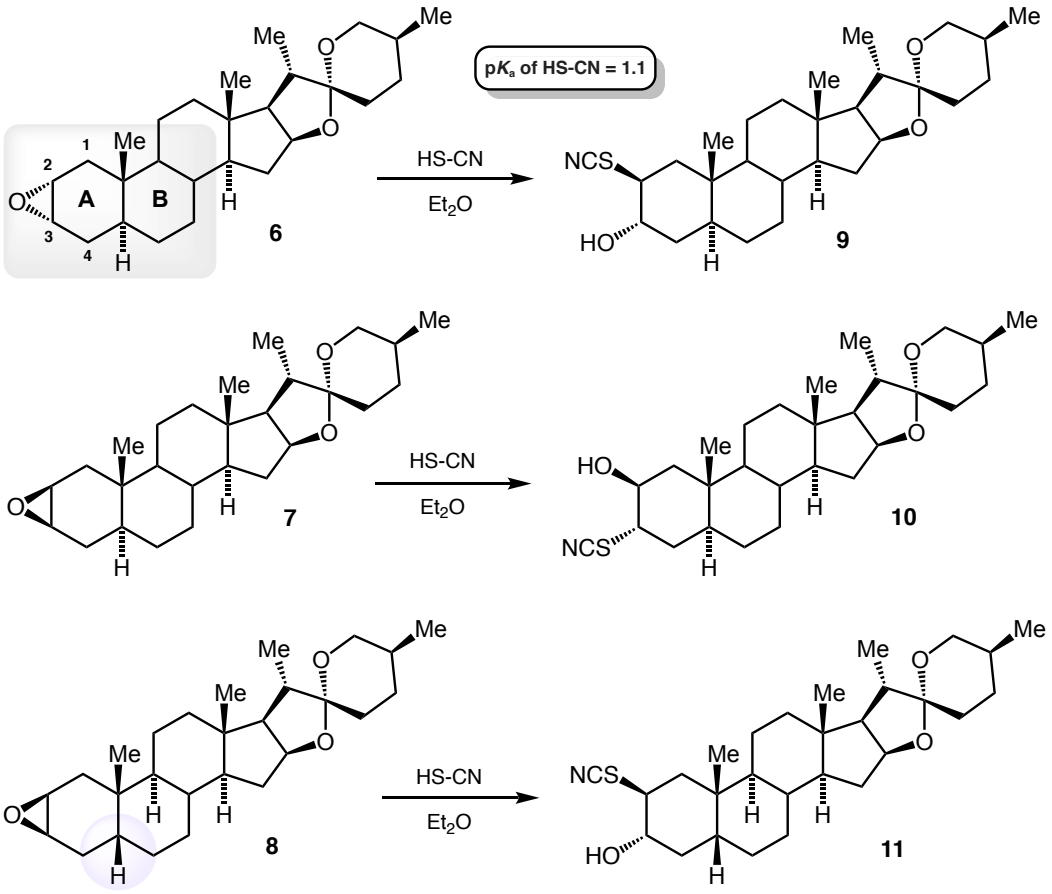
5 pts

b. Using a diagram, account for the complete regioselectivity observed during the reaction of steroidal epoxide **4**.

15 pts

Question 2, Cont'd

c. Rationalize the regioselectivity of the ring opening reaction of saponin epoxides **6**-**8** with thiocyanic acid. Use diagrams, but limit your drawing the structure in the grey box for each answer. Pay attention to the trans ring fusion (highlighted in purple) of substrate **8**



30 pts