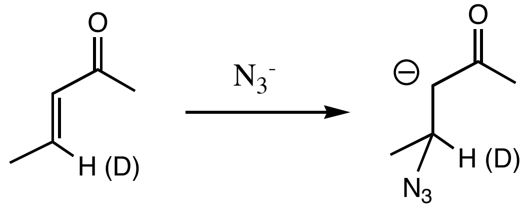
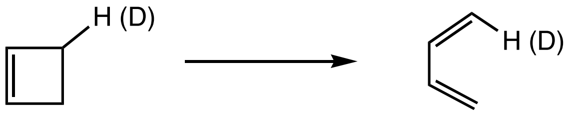
Additional Problems for Kinetics II

1. State whether the following reactions will show a normal or inverse, primary or secondary, kinetic isotope effect. Explain your reasoning.

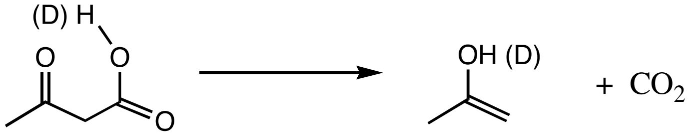
A.



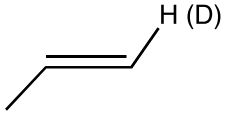
B.



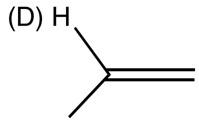
C.



2. The following isotope effects are found for the ozonolysis of various deuterium-substituted propenes. What do these isotope effects tell you about the mechanism?

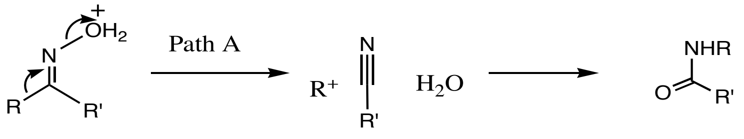


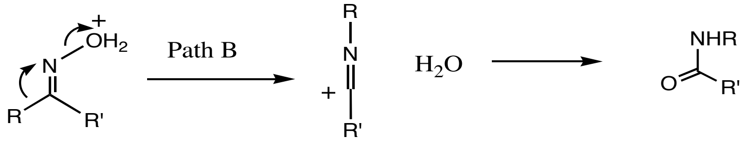
KIE = 0.88



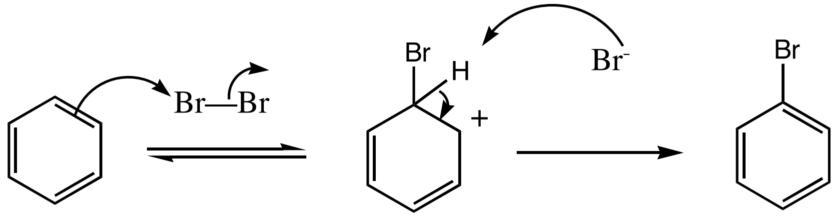
KIE = 0.88

3. The acid-catalyzed Beckmann rearrangement of oximes to amides has two possible rate-determining steps, the first one in each path shown below. Explain how you would use a Hammett plot analysis to distinguish these possibilities. Note that the R group trans to the departing water is the only one that migrates.

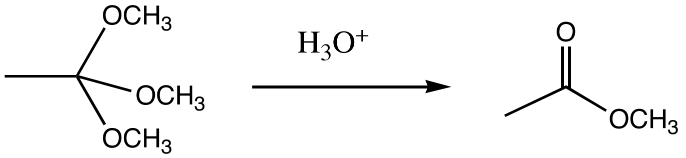




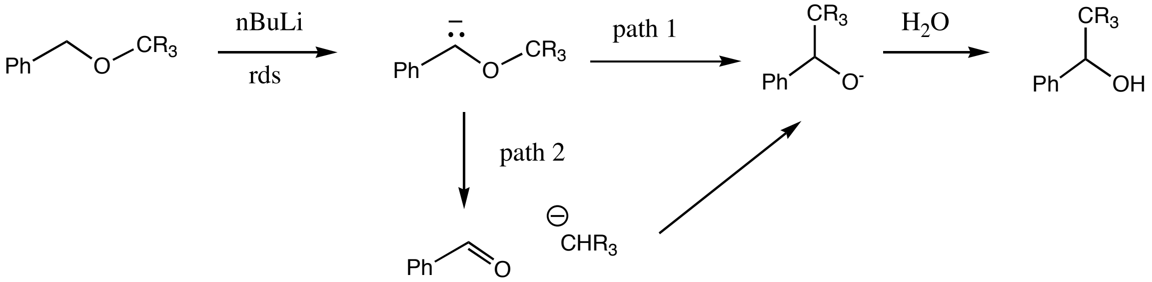
4. Explain how one would perform a Hammett plot study for the following reaction. Do you expect a positive or negative ρ value?



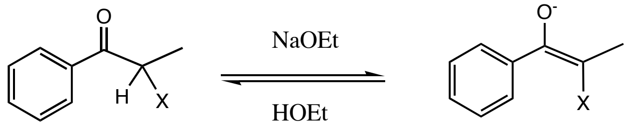
5. How can one distinguish if the orthoester shown below hydrolyzes in acidic water by an S_N1 or S_N2 mechanism? Note that the relevant SN2 mechanism would involve nucleophilic attack at a methyl group.

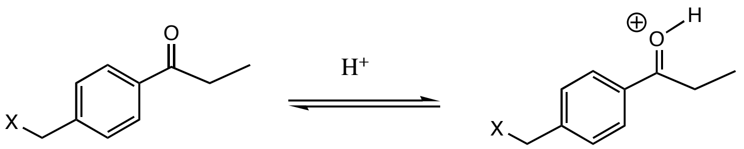


6. Two possible mechanisms for the Wittig rearrangement of benzyl ethers are shown below. Path 1 involves concerted intramolecular migration of CR_3, whereas path 2 involves a heterolysis. In either mechanism, the deprotonation step is rate –determining. How would you apply the following experiments to distinguish between the two mechanisms: cross-over, product stereochemistry.

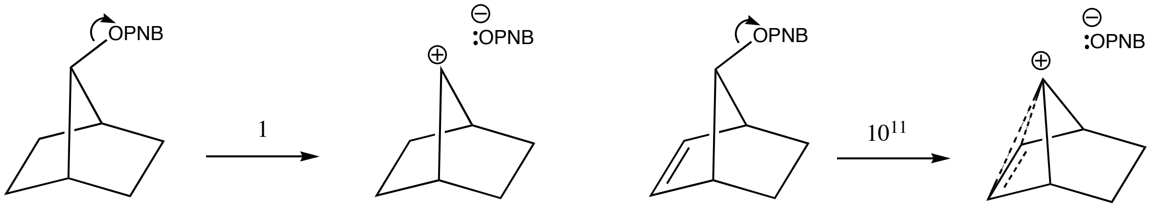


7. In the following reactions substituent X was varied between electron-donating and electron-withdrawing. If you use the usual σ values, do you expect a positive or negative ρ value for each equilibrium? Should each reaction be more or less sensitive to the X-substituent than benzoic acid? Explain your reasoning.

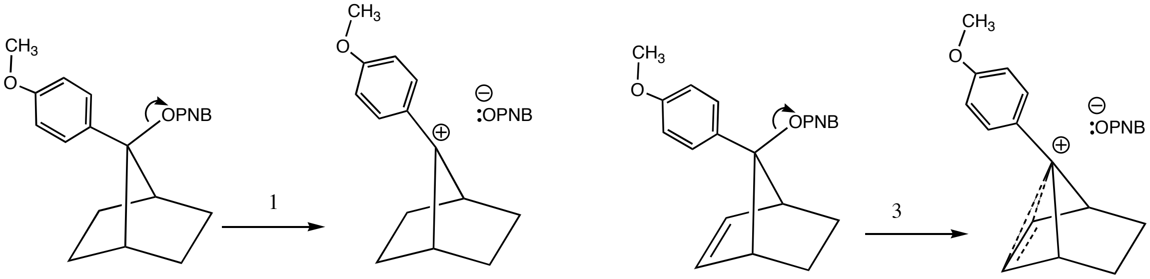




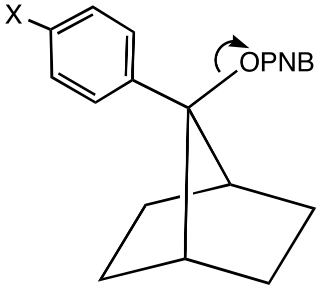
8. The relative rates of the SN1 reactions of the following two alkyl p-nitrobenzoates are show. The reason for the dramatic difference in the rate of departure of the nitrobenzoate leaving groups is the stabilization from the alkene to form a non-classical carbocation (three-center, two-electron bond)



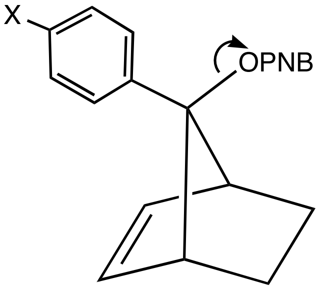
   a. When p-anisyl is placed in the reactant as shown below, the 10^{11} rate enhancement by the double bond is reduced to only a factor of 3. Explain why the introduction of this substituent changes the relative reactivity from the example given above.



   b. The ρ values for the SN1 reaction of the following compounds were measured using σ^+ values. Interpret these values in light of the information given above. Do these ρ values support or contradict the conclusions based on the difference in relative rates of the two comparisons given above?



$\rho = -5.17$



$\rho = -2.30$

c. When H and CF_3 are the X groups shown above, the relative rates of the SN1 reaction of the norbornene structure compared to the norbornane analog are 41 and 35,000, respectively. Why are these relative rates higher than when X=OMe?