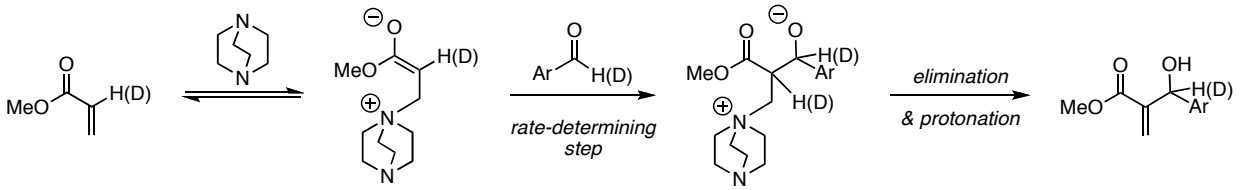
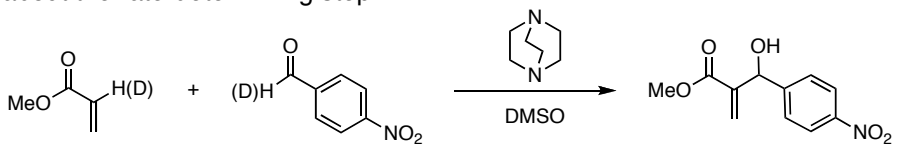
CHEM 633: Advanced Organic Chem: Physical
Problem Set 7
Due on 10/27/09

For the following problems, please use Excel (or another graphing program), when necessary. Please submit your graphs with your problem set.

1. (a) The generally accepted mechanism of the Baylis–Hillman reaction is shown below. If this mechanism is correct, please predict the isotope effects that should be observed at the indicated positions.

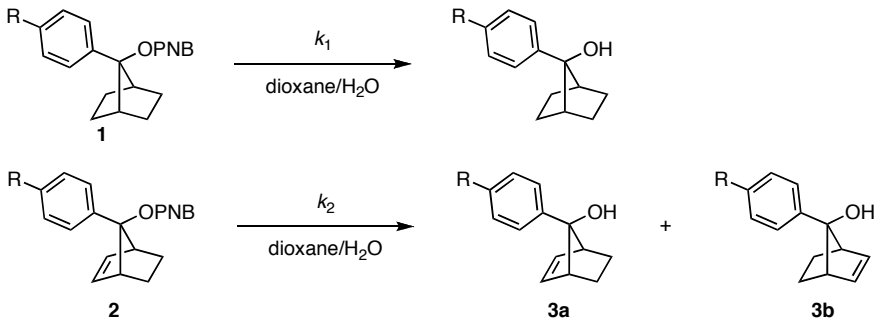


(b) In a recent study, the following isotope effects were measured. What do these isotope effects suggest about the rate-determining step?



$k_H/k_D = 5.2 \pm 0.6$ $k_H/k_D = 0.75 \pm 0.05$

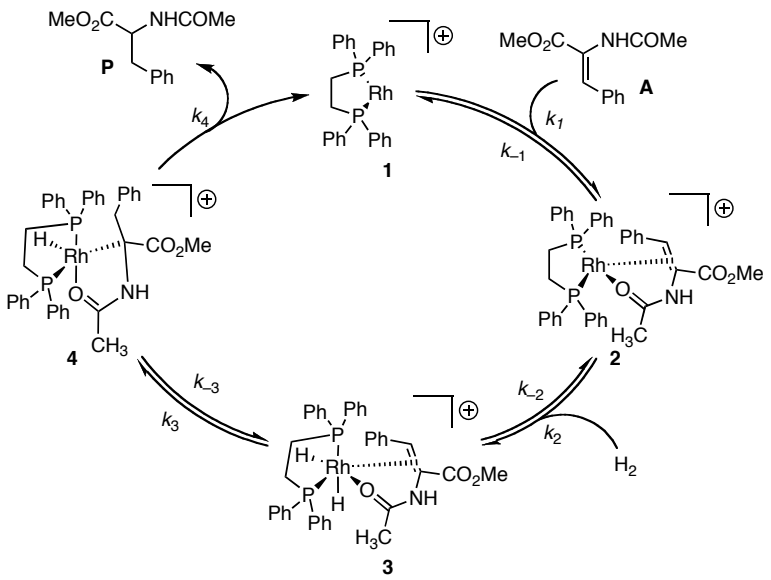
2. The solvolysis of bicyclic *para*-nitrobenzoate (PNB) derivatives **1** and **2** has been studied (Remember: solvolyses proceed via S_N1 mechanisms).



R	σ+	$k_{1,25\,°C}$ (s^{-1})	$k_{2,25\,°C}$ (s^{-1})	Product distribution
NMe_2	–1.70	2.42×10^{-2}	1.08×10^{-2}	10:1 **3a**/**3b**
OMe	–0.78	1.54×10^{-7}	5.18×10^{-7}	10:1 **3a**/**3b**
H	0	1.02×10^{-10}	4.23×10^{-9}	**3a** only
CF_3	0.61	8.52×10^{-15}	2.94×10^{-10}	**3a** only
3,5-bis-CF_3	1.04	1.20×10^{-16}	3.06×10^{-11}	**3a** only

(a) Generate a Hammett plot for each set of substrates using the σ+ values provided.
(b) One the basis of the stereochemical and rate data, depict the solvolysis reactions of **1** and **2** where R = CF_3 on a single reaction coordinate diagram. Provide clear depictions of transition structures and intermediates. You may assume the starting materials are isoenergetic.
(c) Provide an explanation for the differences in the Hammett plots of the hydrolyses of **1** and **2**.

3. The Rh(I)-catalyzed hydrogenation of methyl-(*Z*)-acetamidocinnamate (**A**) has been studied. The catalytic cycle shown below has been proposed.



(a) Write a "one plus" catalytic rate expression for this catalytic cycle. You may use generic observable constants for each of the terms in the rate law (C_1, C_2, etc.)

(b) Assuming that the second step (**2** –> **3**) is rate-limiting and all subsequent steps to regenerate **1** are rapid and irreversible, write down a simplified "one plus" catalytic rate expression. Use the rate constants depicted in the catalytic cycle above, and assume that any steps prior to the rate-limiting step are rapid and reversible compared with the rate-limiting step. (ie, use the pre-equilibrium approximation). Express your rate law in terms of **A**, H_2, and $[Rh]_{total}$.

(c) Assuming that the second step (**2** –> **3**) is rate-limiting and all subsequent steps to regenerate **1** are rapid and irreversible, apply the steady-state approximation to **2** and derive a rate law for the reaction in terms of **A**, H_2, and $[Rh]_{total}$.

(d) Show that the equations derived in (b) and (c) are equivalent when k_2 is small compared with k_{-1}.

4. What is "tunneling?" Please provide an example of tunneling from the literature.

5. Please show why 6.5 is the maximum kinetic isotope effect for a "normal" organic reaction.

6. Please choose a catalytic reaction from the recent literature.

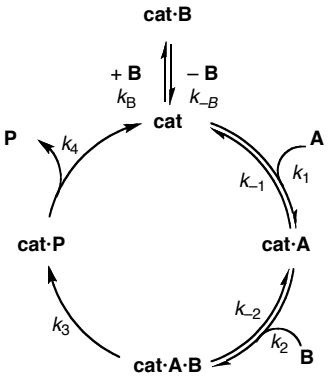
(a) Propose a mechanism for your chosen reaction.

(b) Identify two possible rate-limiting steps of your catalytic cycle.

(c) Derive rate laws for your catalytic cycle corresponding to the possible rate-limiting steps you identified in (b).

(d) Propose experiments to determine which step is rate-limiting.

7. Consider the following catalytic cycle, in which the catalyst is unproductively and reversibly bound by react **B**.



(a) Will this reversible binding by **B** be detectable using a same-excess experiment?

(b) Please depict the expected plot of relative rate vs. [**A**] from your same-excess experiment.

(c) Please write a "1+" expression for the catalytic cycle and explain your reasoning for your answer to (a).