CH 630
Midterm Exam 2
Monday, November 24

Please write answers in the blue books provided. You may use numerical calculators, molecular model kits or drawing templates, but nothing with chemical information on it.

1. (60 points) Reaction of 1-chloro-1,1-diphenylethane (**I**) in acetonitrile leads to formation of 1,1-diphenylethane (**IV**). Addition of methanol in amounts up to 10 mol-% increases the rate of disappearance of the alkyl chloride, and results in generation of 1-methoxy-1,1-diphenylethane (**III**) as well as the alkene.

A. Write a reasonable mechanism for formation of all products. Assign mechanistic rate constants to each transformation.

B. Show the rate expression for formation of each of the two products (d[**III**]/dt and d[**IV**]/dt) in terms of observable or controllable species concentrations.

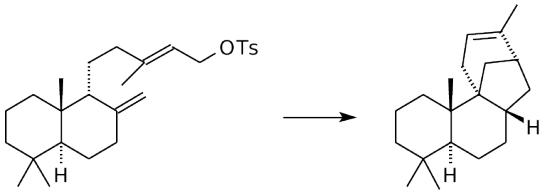
C. When d_3-**I** is used, the observed kinetic isotope effect on formation of **III** is 0.88 for 5.66 mol-% CH_3OH. Explain how to interpret this.

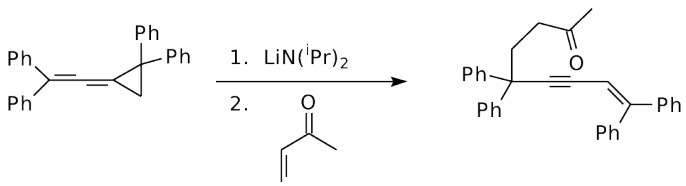
D. When d_3-**I** is used, the observed kinetic isotope effect on formation of **IV** is 1.63 for 5.66 mol-% CH_3OH. Explain how to interpret this.

E. The KIE in each case varies with the amount of methanol present (as does the overall rate of reaction). Suggest what this fact tells you about your mechanism, and predict how each KIE ought to vary with [CH_3OH].

F. If you were to examine a series of compounds that had substituents on one of the aryl rings, describe what you would predict for the linear free energy relationship (log k vs. σ).

2. (20 points) Provide a reasonable mechanism for each of the following reactions.





3. Preparation of chiral carbanions (as their lithium salts) has been attempted via reaction of chiral silanes with methyllithium:

Describe the configurational stability you expect for the carbanion. Be sure to address each of the following:
-Inherent configurational stability of a free carbanion (compared to isoelectronic analogs)
-Impact of electronic interaction with the sulfone
-Counterion and aggregation effects
-Whether the pKa of the conjugate acid should play a role in configurational stability.