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-diphenylethene (**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.
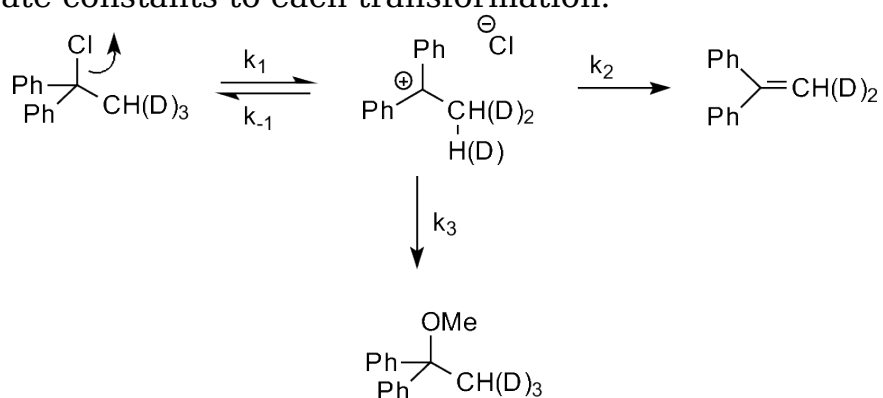
B. Show the rate expression for formation of each of the two products ($d[$**III**$]/dt$ and $d[$**IV**$]/dt$) in terms of observable or controllable species concentrations. If II is the carbocation, a steady-state intermediate,

$d[$**III**$]/dt = k_2[$**II**$]$; $d[$**IV**$]/dt = k_3[$**II**$][MeOH]$

$d[$**II**$]/dt \sim 0 = k_1[$**I**$] - k_{-1}[$**II**$][Cl^-] - k_2[$**II**$] - k_3[$**II**$][MeOH]$

Collecting terms and dividing,

$[$**II**$] = k_1[$**I**$]/(k_{-1}[Cl^-] + k_2 + k_3[MeOH])$

Substituting:

$d[$**III**$]/dt = k_1 k_2[$**I**$]/(k_{-1}[Cl^-] + k_2 + k_3[MeOH])$;
$d[$**IV**$]/dt = k_1 k_3[$**I**$][MeOH]/(k_{-1}[Cl^-] + k_2 + k_3[MeOH])$

Note that any further simplification requires assumptions about the relative magnitudes of k_{-1}, k_2 and k_3. These expressions as listed satisfy what the question asks.

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.

An inverse kinetic isotope effect that stems primarily from an inductive effect (roughly 0.96 per D).

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.

This is a normal KIE, but it's not immediately clear whether it is primary or secondary. One must first determine the per-D KIE: the cube root of 1.63 is 1.18. Few secondary KIEs are this high. However, it could as well be a primary KIE (for H-transfer) coupled to a secondary KIE based on rehybridization. The latter should be normal (1.10/D?), so the primary KIE is still small—only about 1.35. It must therefore be a very asymmetric proton transfer.

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 $[CH_3OH]$.

The KIE is expressed on a post-RDS step in each case. The solvent change alters the polarity of the mixture, which by itself is enough to alter the location of the transition state for the proton transfer. The substitution will also be affected so far as the stability of the cation will affect the ZPE.

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).

You are developing positive charge at the benzylic position in the RDS, so there should be a large, negative ρ value.

2. (20 points) Provide a reasonable mechanism for each of the following reactions.
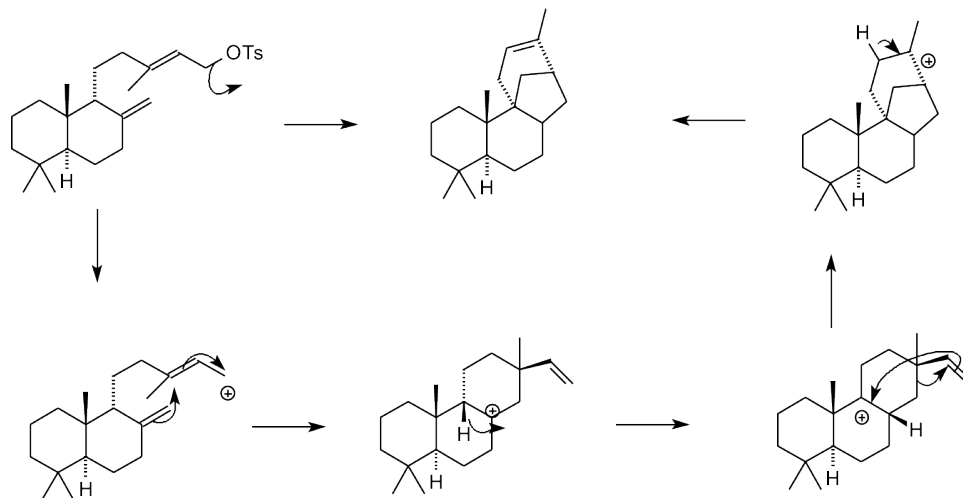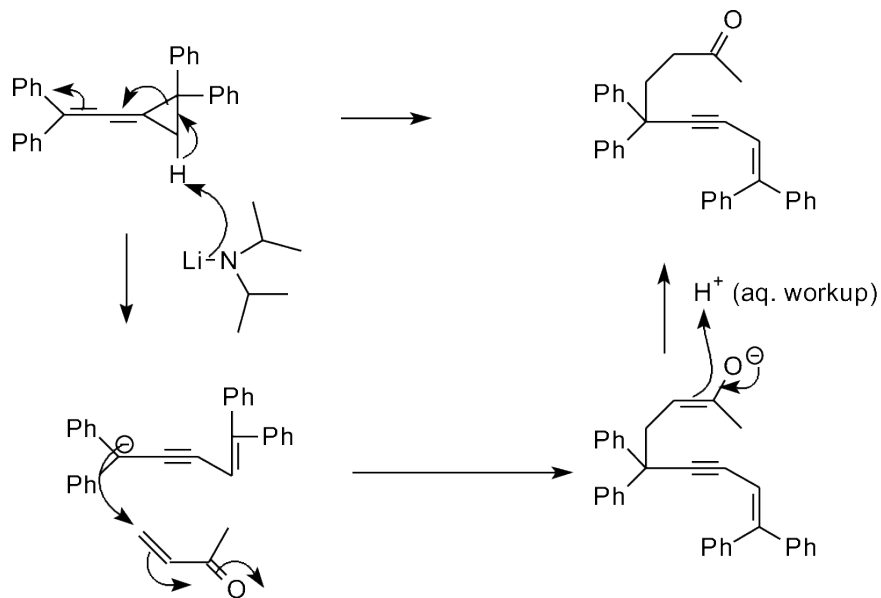
3. Preparation of chiral carbanions (as their lithium salts) has been attempted via reaction of chiral silanes with methyllithium:

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.

Generation of the alkyllithium should be stereospecific.

The fate of the product depends on several factors:
(1) If the free carbanion forms, it should be of similar configurational stability to an amine. (I.e., not very.) However, since carbon is less electronegative than nitrogen, the electrons will be less stable at the transition state, where they occupy an unhybridized p orbital. Therefore, configurational stability might be expected, but at very low temperature.

(2) The electron withdrawing effect of the sulfone will enhance acidity, but whether it will affect configurational stability depends on its ability to pi-bond to

the alpha carbon. The current thinking is that it will not: d-pi-p-pi bonding is thought to be weak.

(3) Association of the lithium counterion via covalent bonding should enforce configurational stability.

(4) Aggregation might favor dissociation, unless the presence of the sulfone oxygen ligates lithium and reduces steric congestion.