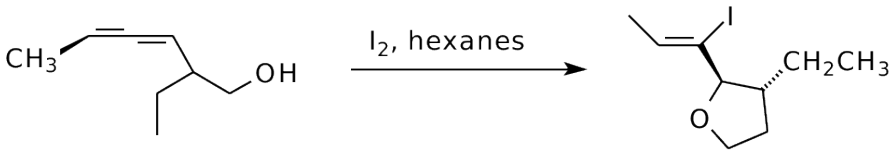
CH 630
Final Exam
Wednesday, December 10, 2008

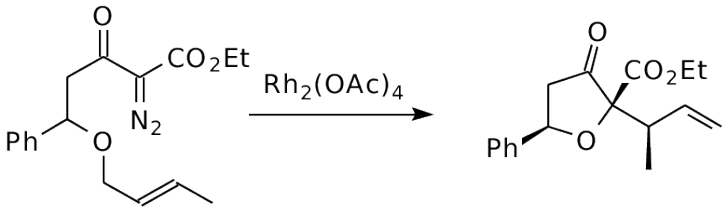
Please place answers in the blue books provided. You may use molecular models, numerical calculators or drawing templates, but no books, notes or other materials with chemical information.

1. (100 points) Write a plausible mechanism for each of the following transformations described in recent literature. Note that each should involve a reactive intermediate that we have discussed.

A.

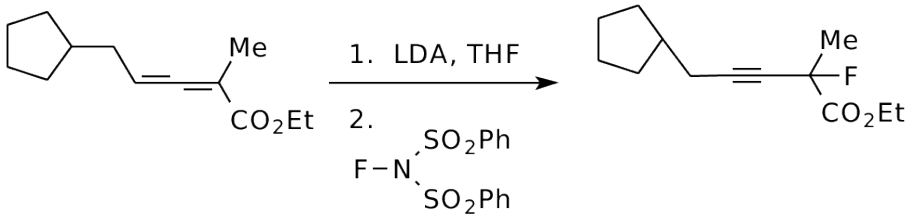


B.

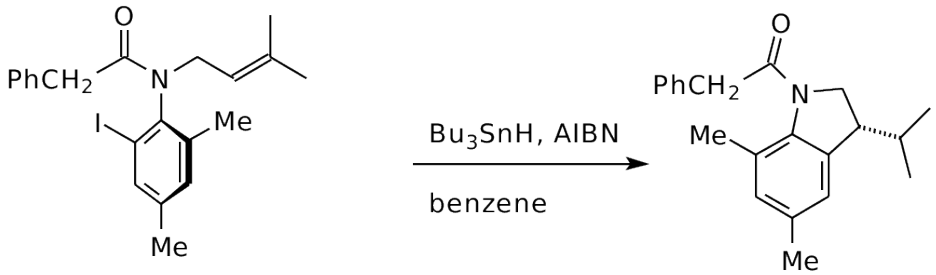


C.

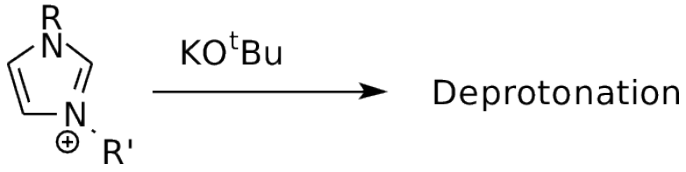
D.



E.



2. (25 points) Imidazolium salts can be prepared by a number of routes and deprotonated:



Provided R and R' are bulky enough (e.g., 2,6-dimethylphenyl), the deprotonation product can be stable in solution and even isolable.

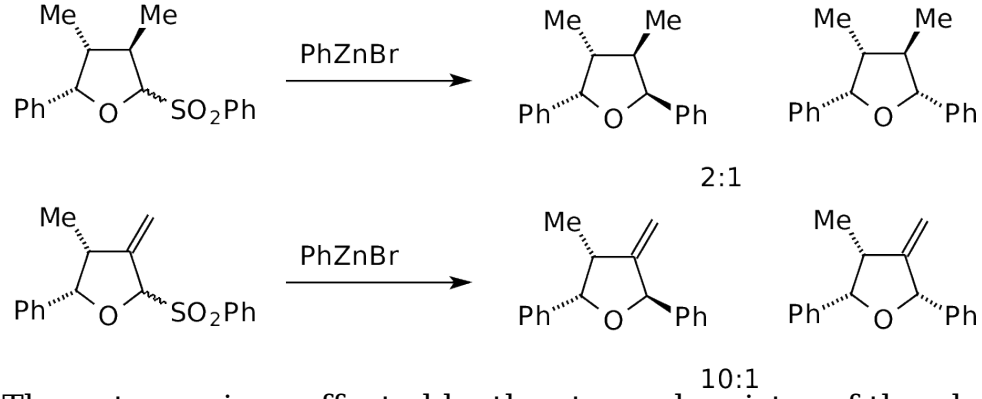
A. Identify the preferred site of deprotonation.

B. Draw resonance structures for the deprotonation product.

C. From your answer to (B), it should be evident why isolation of the deprotonation product requires steric bulk on the nitrogen. Explain why, and show the product you expect to form when there is little steric bulk (e.g., R, R' = Me).

3. (25 points) Alkyl and aryl zinc halides are significantly less basic than Grignard or alkyllithium reagents, yet still potent nucleophiles.

Consider the following two transformations:

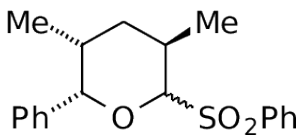


The outcome is unaffected by the stereochemistry of the phenylsulfonyl group.

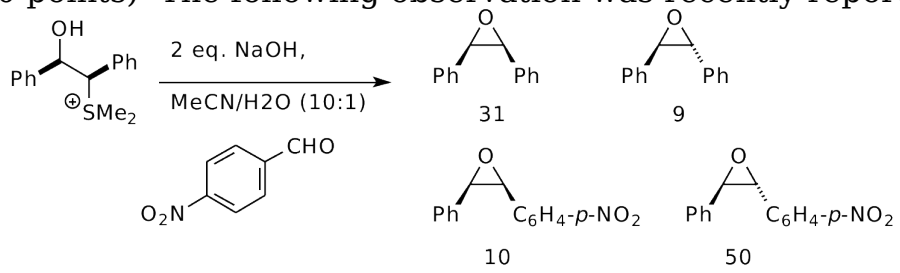
A. Show a reasonable mechanism for the transformation.

B. Each transformation goes through a similar intermediate. Draw a 3-dimensional projection that clearly depicts the steric interactions that control selectivity in forming the products.

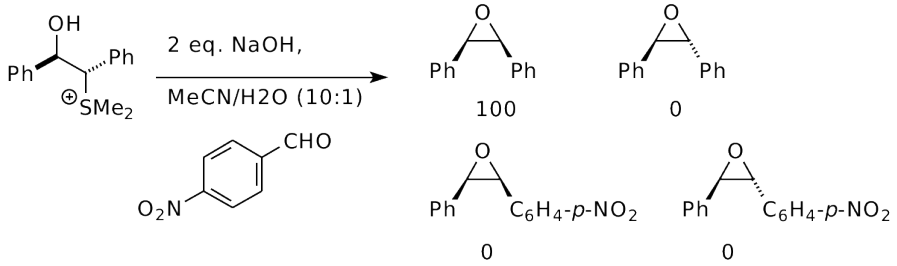
C. Predict (and explain your prediction) selectivity for a similar reaction of the following substrate:



4. (50 points) The following observation was recently reported:



But:



A. Identify the initial site of deprotonation.

B. Show Newman projections for the favored conformer for the anion that forms.

C. Show a mechanism that explains the incorporation of the *p*-nitrophenyl group into products from the *syn* isomer.

D. Explain the absence of incorporation of the *p*-nitrophenyl group into the product from the *anti* isomer.

E. When the reaction is performed with $NaOD/D_2O$ in place of $NaOH/H_2O$, different outcomes are seen:
-the *syn* isomer gives 5% deuteration of the ring in the cis epoxide, and 100% deuteration in the trans epoxide.
-The *anti* isomer gives no deuteration at all.

Explain.