Institut für Chemie
und Biochemie

Modern Synthetic Methods **Name:**
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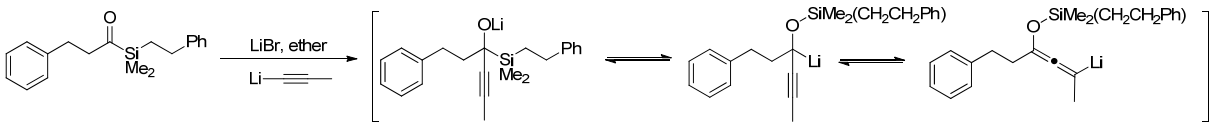
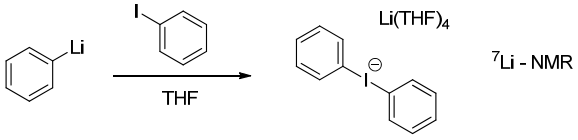
Problem Set No. 2_Key

1. Answer the following questions derived from Reich J. Org. Chem. **2012**, *77*, 5471:

a. How can the Brook Rearrangement be used to produce lithiated allenes?



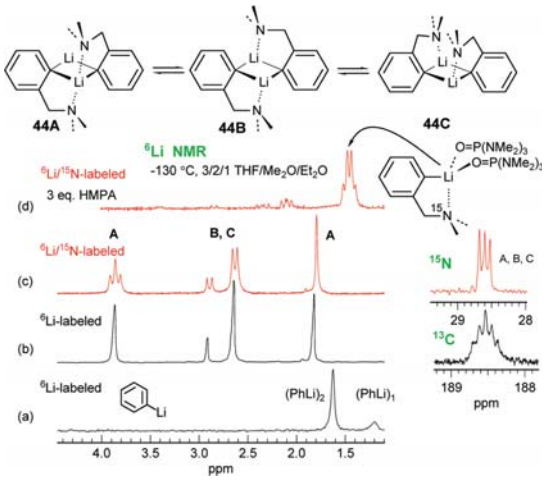
b. What is the product that forms when 1 eq. of phenyl lithium is added to 1 eq. of iodobenzene? How was the structure characterized?



c. How does the addition of HMPA alter the structure of organolithium species.

Tends to produce solvent separated ion pairs.

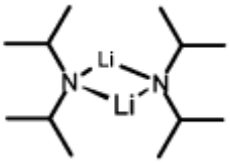
d. What is the structure of *o*-(dimethylaminomethyl)phenyllithium in THF and in THF with 3 eq. of HMPA?



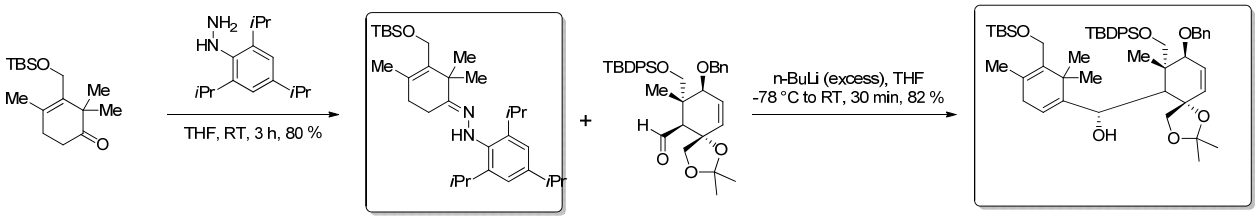
e. What impact on does addition of HMPA have on the chemoselectivity associated with addition to cyclohexenone?

For certain (soft) nucleophiles, the selectivity can switch from 1,2 to 1,4 selectivity (see Figure 18 in Reich's paper).

f. Draw the structure of LDA in 3THF:2Et_2O



2. The following sequence was used by Nicolaou et al. (*J. Am. Chem. Soc.* **1994**, *116*, 591.) to synthesize the anti-cancer agent Taxol. Fill-in the blanks and provide an arrow pushing mechanism for the last step.



3. Supplement the schemes with starting materials or products!