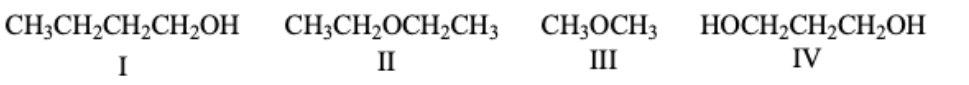
Organic Chemistry for Life Sciences: CHM 224

Problem Set Chapter 14 *and* Organometallics

Name_____

DUE: Friday February 23rd

1. Rank the following compounds in decreasing order of boiling points (highest to lowest).

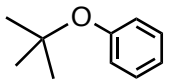


- I: 5 heavy atoms; polar; H-bonding
- II: 5 heavy atoms; polar
- III: 3 heavy atoms; polar
- IV: 5 heavy atoms; polar; DOUBLE H-bonding

A) II>IV>I>III
B) I>IV>II>III
C) IV>I>II>III
D) III>II>I>IV
E) IV>II>I>III

2. Ethers are subject to reaction with atmospheric O_2 to form potentially explosive peroxides. However, tert-butyl phenyl ether does not form a peroxide with O_2. This is likely because:

A. tert-butyl phenyl ether cannot be synthesized
B. the peroxide formed from tert-butyl phenyl ether is especially unstable
C. O_2 cannot react with tert-butyl phenyl ether to form a peroxide
D. tert-butyl phenyl ether is not a strong enough nucleophile

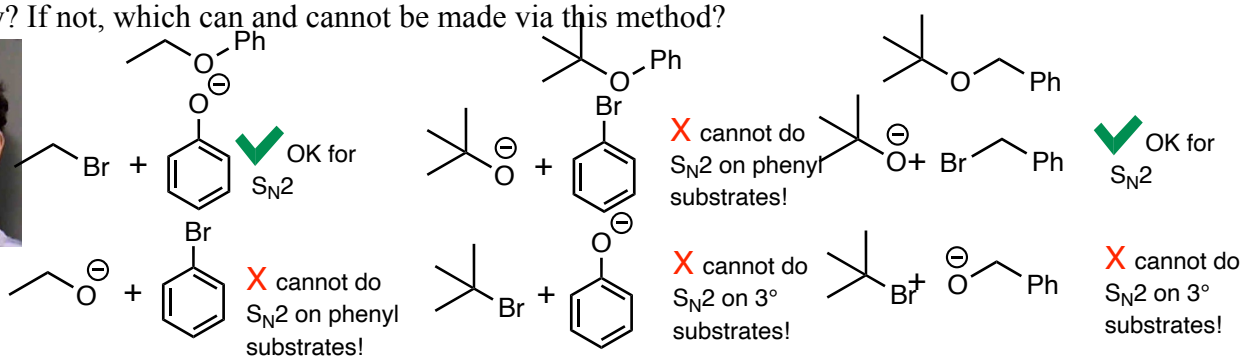


tert-butyl phenyl ether

- as discussed in class, peroxide formation begins with hydrogen abstraction of a hydrogen on the carbon adjacent to the ether oxygen
- diphenyl ether does not have a hydrogen on the adjacent carbon and is therefore incapable of reacting with oxygen in this way

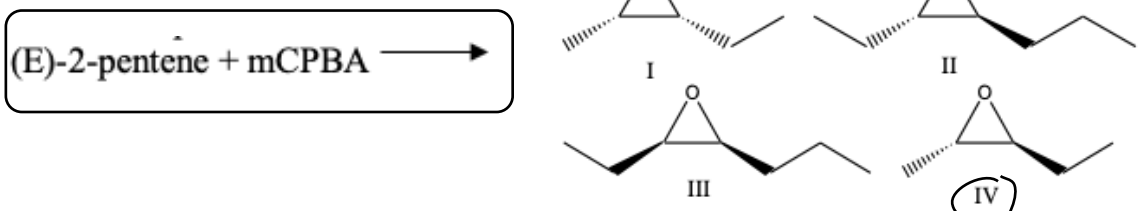
3. Jimmy says he can make all of the compounds below using the Williamson ether synthesis. Do you agree with Jimmy? If not, which can and cannot be made via this method?


Jimmy

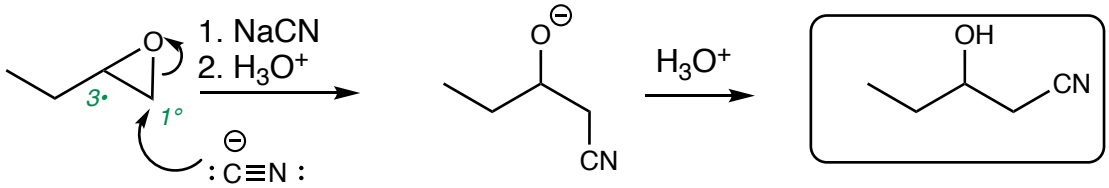


Jimmy is incorrect, only two of the compounds CAN be made by the Williamson ether synthesis, but the middle compound CANNOT! Sorry Jimmy!

4. Predict the product for the following reaction:

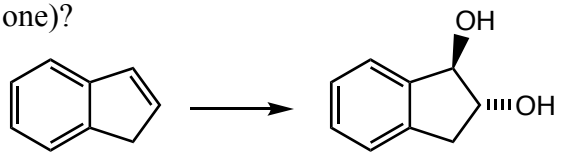


5. Predict the major product from the following reaction of an epoxide with NaCN:



NOTE that nucleophilic attack occurs preferentially at the more reactive (less sterically congested) 1° carbon atom!

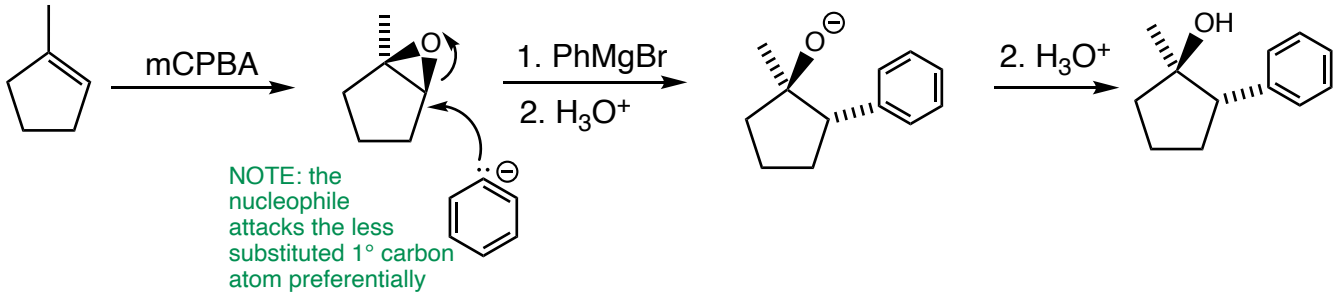
6. Which set of reaction conditions will successfully complete the transformation below (may be more than one)?



A. i) BH_3•THF ii) NaOH, H_2O_2
B. i) $Hg(OAc)_2$, H_2O ii) $NaBH_4$
C. i) $KMnO_4$, NaOH, H_2O
D. i) mCPBA ii) NaOH iii) H_3O^+

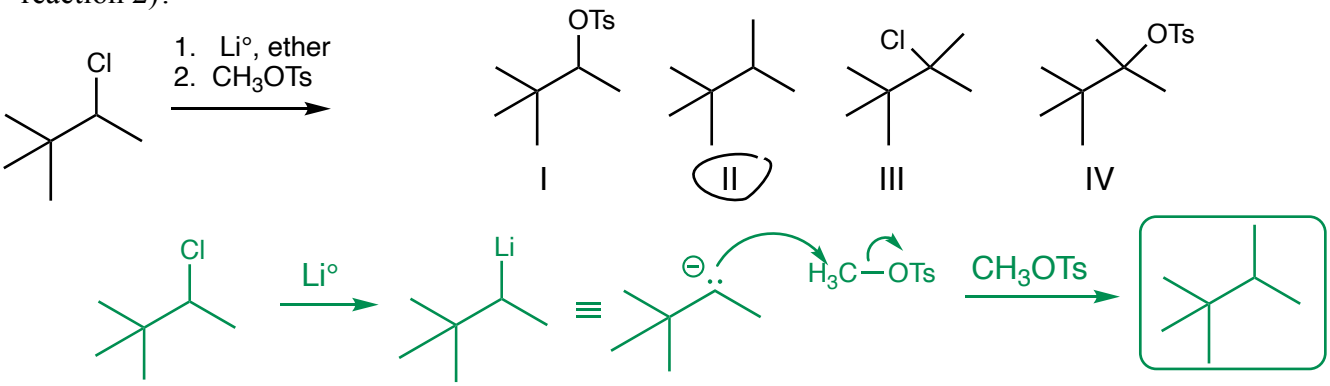
A results in hydration (addition of H and OH) only
B and C result in formation of the cis-diol

7. Predict the products for the following sequence of reactions (include proper stereochemistry):

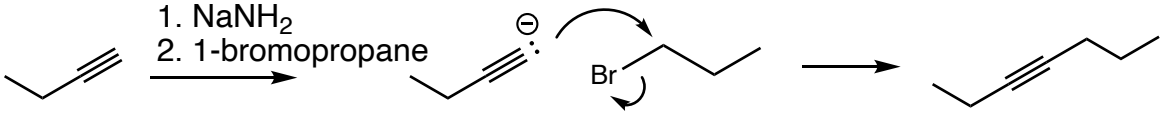


NOTE: the nucleophile attacks the less substituted 1° carbon atom preferentially

8. What is the final product expected from the following sequence of reactions (i.e., do reaction 1 and then reaction 2)?

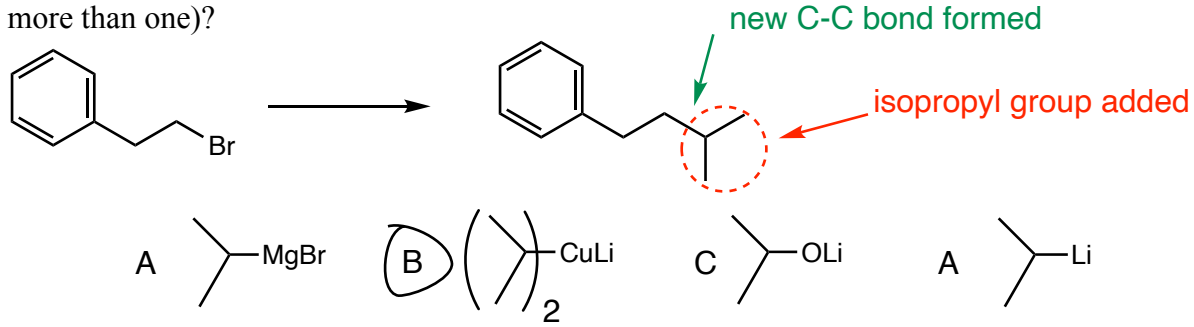


9. What is the final product expected from the following sequence of reactions



deprotonation of terminal alkyne by $NaNH_2$

10. Which of the following organometallics will sucessfully complete the following reaction as written (may be more than one)?



• only organocuprates are successful in S_N2 reactions with alkyl halides (other than methyl substrates)