Chem 332, Professor Fox Problem Set #4 Use additional paper

1. Provide the reagents



3) Rationalize the following observations:



Deprotonation with 1 equiv of base gives the most stable anion, which is then alkylated



BuLi is a strong enough base to remove a second proton. Alkylation of the less stablized anion is fastest.

4. Provide a mechanism for the formation of 1 and 2



5. Circle the product, and explain using your knowledge of molecular orbitalsof the following transformation



6. The conversion of Dewar benzene (**3**) to benzene is extremely exothermic (by 60 kcal/mol), yet it occurs only very slowly under thermal conditions. However, photolysis converts Dewar benzene into benzene very readily. Explain why, using your knowledge of electrocyclic rearrangements to determine the problem with a concerted thermal ring opening, and why a concerted photochemical ring opening should be facile.



For this problem, we need to think about ring opening. Construct the MO's and fill in the electrons as you did for problem 5. The opening has to be conrotatory to give the thermal HOMO .



this analysis shows that a thermal opening would give benzene with a trans double bond. This would be even more strained than **3**

Photochemically, we change the symmetry of the HOMO, and a concerted electrocyclic ring opening would be disrotatory. This could give a product with two cis double bonds, as is found in benzene.

