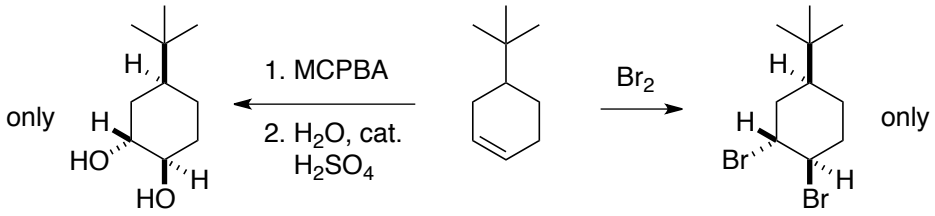
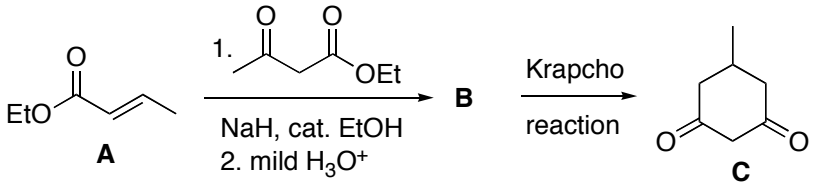
CHEM 330

Problem set 4

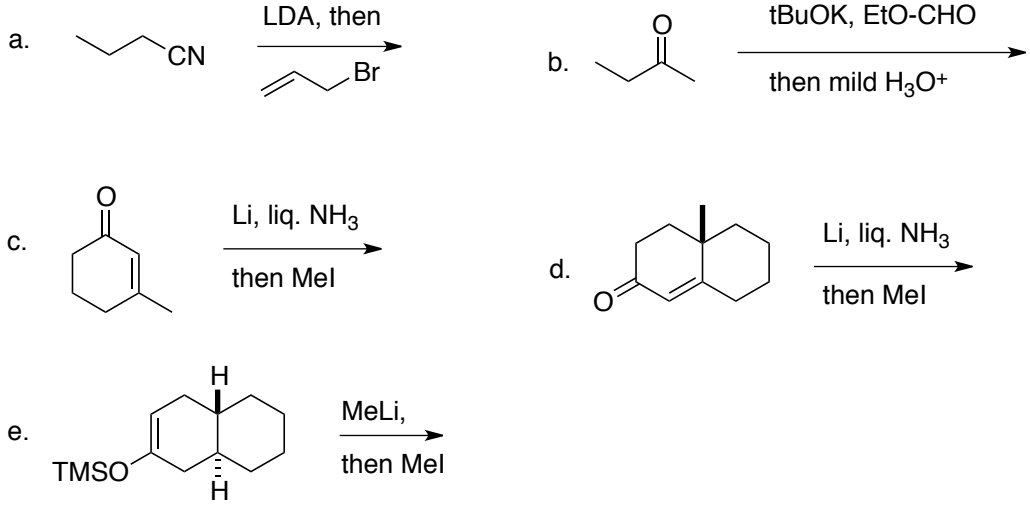
1. The stereochemical course of a number of reactions of cyclohexenes and related systems can be rationalized based on the notion that the ring tends to evolve toward a chair conformer during the reaction. Draw accurate mechanisms to illustrate how this principle accounts for the so-called *Fürst-Plattner rule*, which states that electrophilic cyclohexene derivatives (epoxides, halonium ions, ...) react with nucleophiles to form *trans*-diaxial products selectively; e.g.:



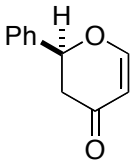
2. Reaction of ethyl crotonate, **A**, with ethyl acetoacetate under the conditions outlined below leads to a product, **B**, which upon Krapcho reaction furnishes diketone **C**. Identify **B** and write an accurate mechanism for its formation.



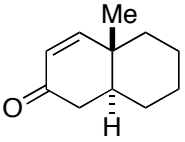
3. Predict the structure of the major product arising from each of the following reactions and, where appropriate, provide a brief rationale for the anticipated stereochemical outcome.



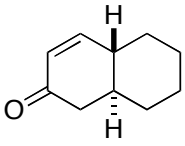
4. Predict the structure of the major product arising from the following Cu-mediated reactions and provide a brief rationale for the anticipated stereochemical outcome.

a. 

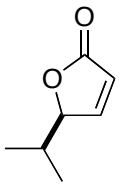
1. CH_2=$CHCu(PBu_3)_2$
2. MeI

b. 

Me_2CuLi, then
TMS-Cl, Et_3N

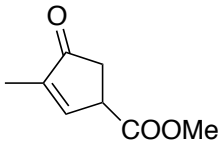
c. 

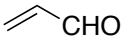
Me_2CuLi, then
CH_2=CH-CH_2Br
Et_3N

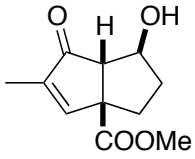
d. 

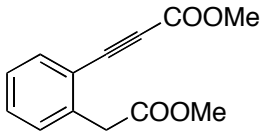
1. $(CH_2$=$CH)_2CuLi$
2. CH_2=CH-COOEt
Et_3N
3. Mild H_3O^+

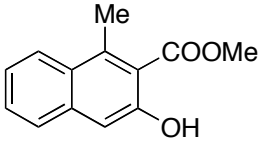
5. Write accurate mechanisms for the following known reactions:

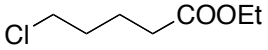
a. 

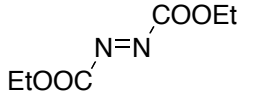


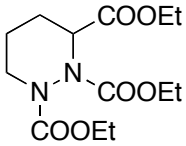
cat. CH_3ONa


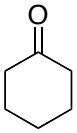
b. 

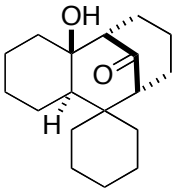
Me_2CuLi, then
mild H_3O^+


c. 

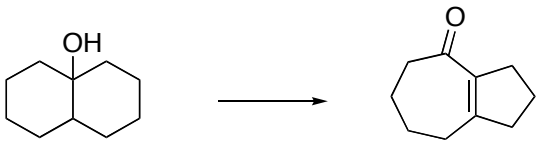
LDA, then add


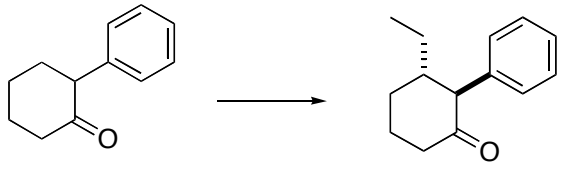


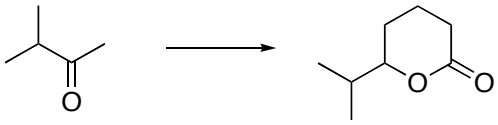
d. 

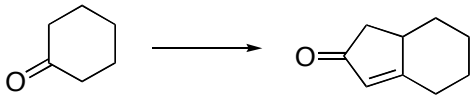
Excess EtONa
then mild H_3O^+


6. Propose a method to achieve the following transformations:

a 

b. 

c. 

d. 

e.