CHEM 330

Final Exam
December 11, 2007

Your name: _____

This a closed-notes, closed-book exam

The use of molecular models is allowed

This exam contains 12 pages

Time: 2h 30 min

1. _____ / 20
2. _____ / 20
3. _____ / 30
4. _____ / 40
5. _____ / 30
6. _____ / 40
7. _____ / 30
8. _____ / 40

TOTAL _____ / 250 = _____ / 100

This exam counts for 45% of your CHEM 330 final grade

1. (20 pts.) Write a chemical equation to show an example of the following reactions (**do not** write mechanisms – just the reactions).

   a. Baylis-Hillman reaction:

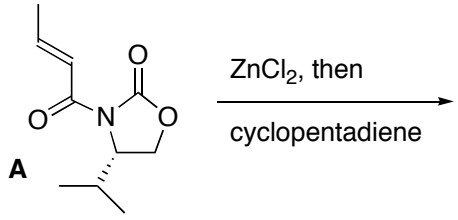
   b. Prasad Reduction:

   c. Cannizzaro reaction:

   d. Mukaiyama aldol reaction:

   e. Swern oxidation:

2. (20 pts.) A highly stereoselective reaction ensues when compound **A** below is treated with 1 equivalent of $ZnCl_2$, followed by cyclopentadiene. The result is product **B**.
   (i) Draw the structure of **B** in the box;
   (ii) Sketch an approximate transition state structure that accounts for the observed stereoselectivity.



A

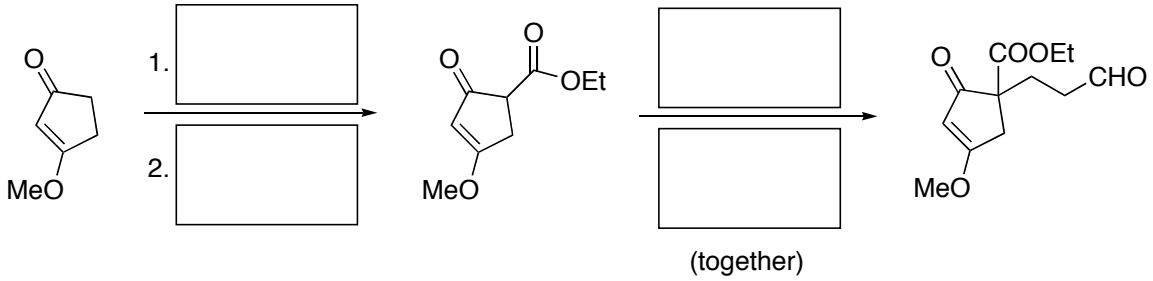
$ZnCl_2$, then

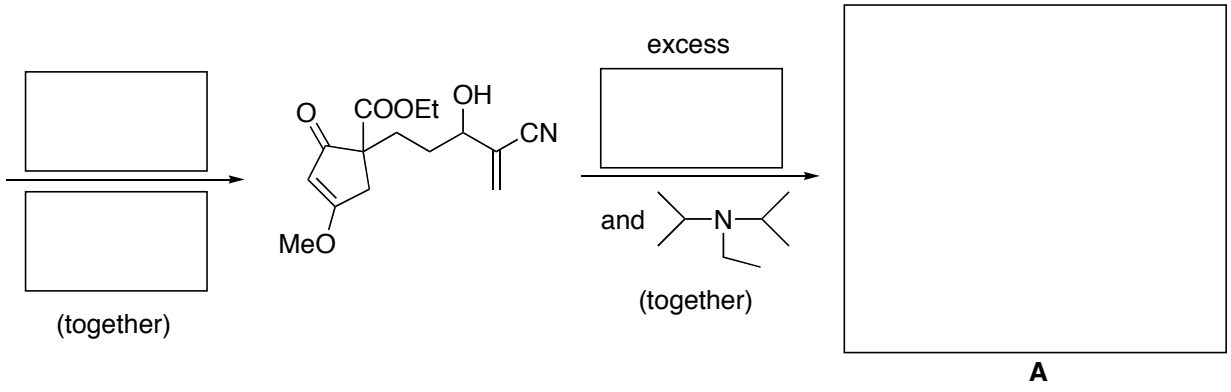
cyclopentadiene

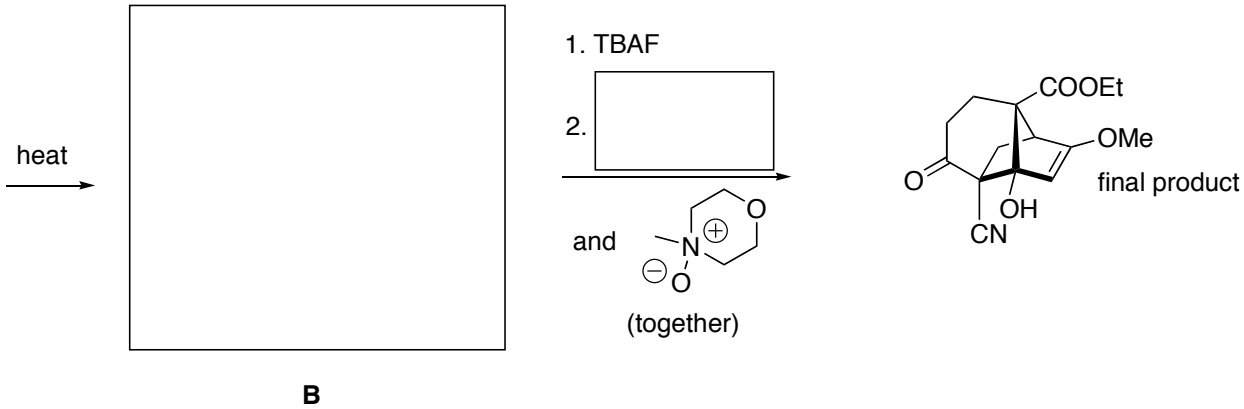
B

approximate transition state structure:

3. (30 pts.) Complete the reaction diagram shown below by indicating all missing reagents / products. Each box corresponds to **one** reagent / product. **Note**: aqueous workup steps are understood and are not to be included in your answers.



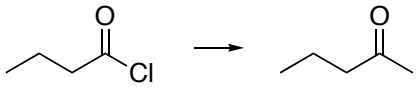




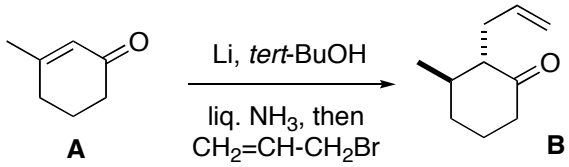
4. (40 pts) Check the appropriate box to indicate whether the following statements are true or false.

a. The copper atom undergoes reductive elimination in the following reaction: **true** ☐ **false** ☐

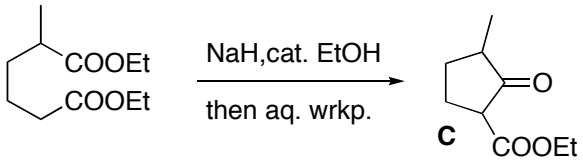
b. The following transformation may be induced by the use of MeMgBr: **true** ☐ **false** ☐



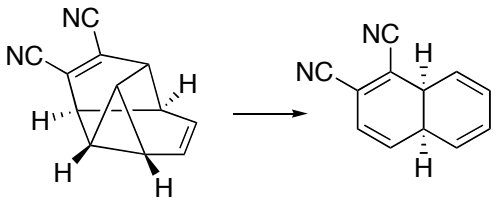
c. Treatment of **A** with Li and tert-BuOH in liquid NH_3, followed by allyl bromide, results in formation of **B**: **true** ☐ **false** ☐



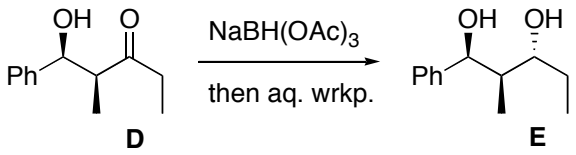
d. The reaction shown below will give compound **C** as the major product: **true** ☐ **false** ☐



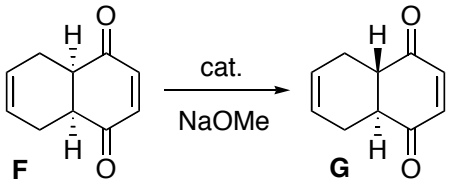
e. The reaction shown below is a retro-Diels-Alder: **true** ☐ **false** ☐



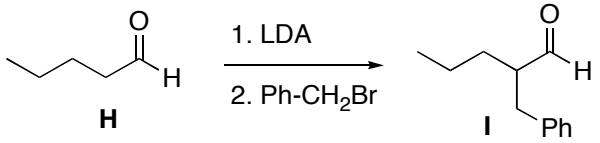
f. Treatment of **D** with $NaBH(OAc)_3$ followed by aqueous workup yields **E** as the major product: **true** ☐ **false** ☐



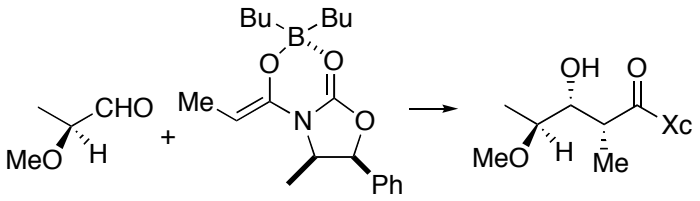
g. Reaction of **F** with NaOMe yields compound **G**: **true** ☐ **false** ☐



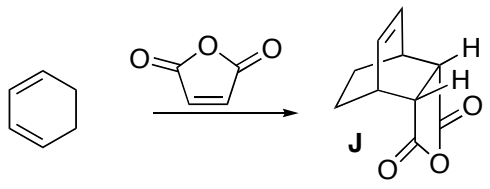
h. Compound **H** may be converted to **I** as follows: **true** ☐ **false** ☐



i. Substrate and reagent in the reaction shown below are stereochemically matched: **true** ☐ **false** ☐

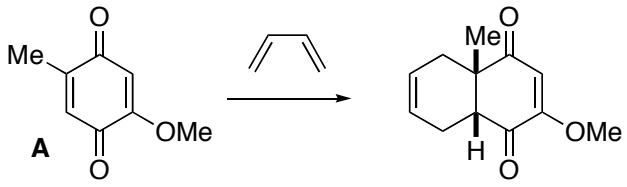


j. Compound **J** forms when 1,3-cyclohexadiene reacts with maleic anhydride: **true** ☐ **false** ☐



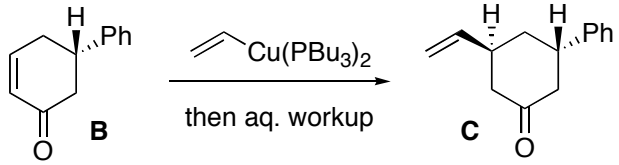
5. (30 pts.) Provide a succinct explanation for the following experimental observations:

(a) Benzoquinone **A** undergoes Diels-Alder reaction with butadiene selectively at the methyl-substituted double bond,



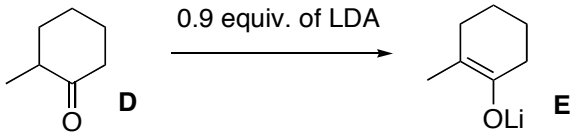
because:

(b) The Noyori copper reagent shown below adds stereoselectively to enone **B** to form **C**,



because:

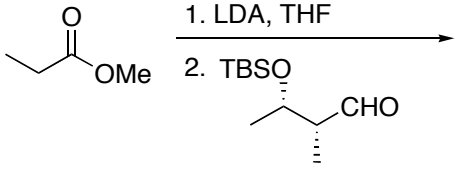
(b) Reaction of ketone **D** with a *defect* of LDA produces enolate **E**,



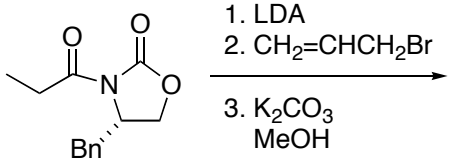
because:

6. (40 pts) Predict the structure of the major product expected from the following reactions. Notes: **(i) it is not necessary to draw mechanisms; (ii) aqueous workups at appropriate stages are understood.**

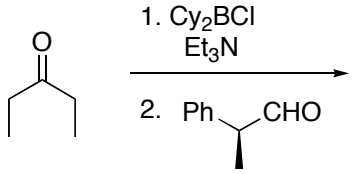
a.



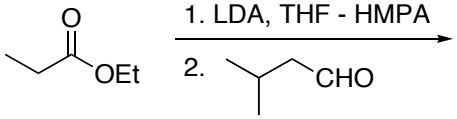
b.



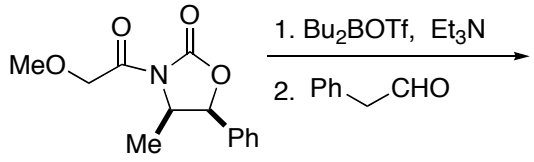
c

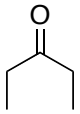


d.



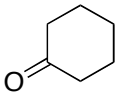
e.



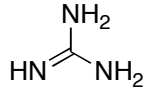
f. 

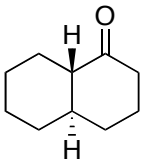
1. 9-BBN-OTf
   Et_3N

2. PhCHO
3. $NaBH(OAc)_3$

g. 

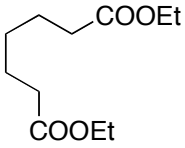
1. excess tBuOK,
   1 equiv. of
   EtOOC-COOEt

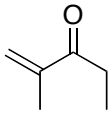
2. 

h. 

1. LDA, then PhSeBr
2. MCPBA, then heat

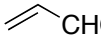
3. Me_2CuLi, then Et_3N
   and

i. 

1. NaH, cat. EtOH
2.  , cat. DBU

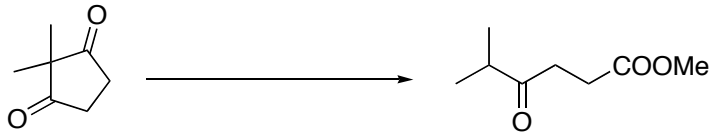
3. tBuOK

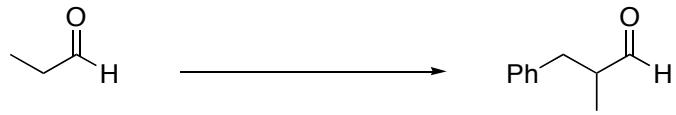
j. 

1. 

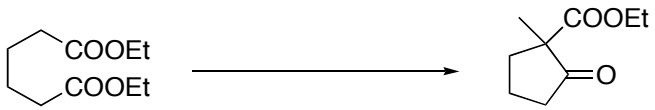
2. excess HCHO,
   aq. NaOH

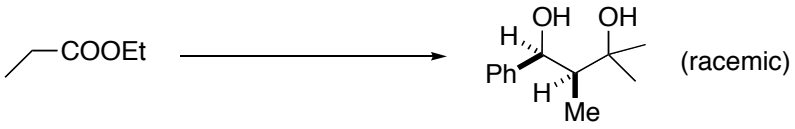
7. (30 pts.) Indicate all the reagents that are necessary to effect the following transformations. Provide your answers as a numbered list of reagents, in the correct order, written over/under the reaction arrows, according to the format of question 6 above.

a. 

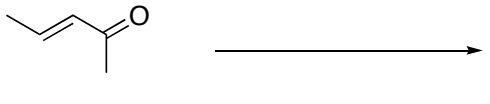
b. 

c. 

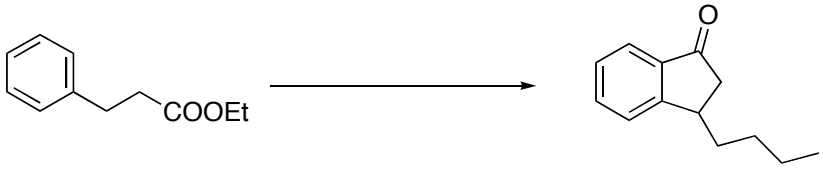
d. 

e. 

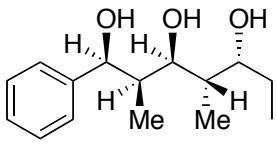
(racemic)

f. 

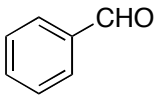
(racemic)

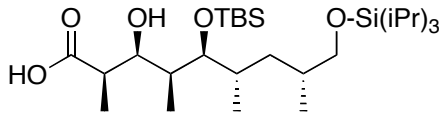
g. 

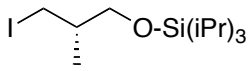
8. (40 pts) Propose a method to achieve the enantioselective synthesis of the molecules shown below starting with the indicated building blocks. Be careful about protecting groups and configurations of stereocenters. Assume the availability of all needed reagents, auxiliaries, etc. Present your answer as a flowchart. **It is not necessary to draw mechanisms**.

a. 

from:



b. 

from: 

(cf. J. Org. Chem. **2006**, *71*, 9853)

Happy Holidays !