**CHEM 330**

**Final Exam**
December 4, 2008

**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. _____ / 20
4. _____ / 30
5. _____ / 40
6. _____ / 40
7. _____ / 40
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. Barton-McCombie deoxygenation:

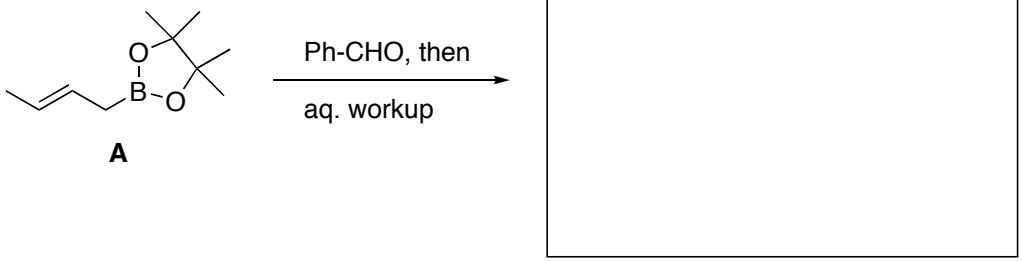
   b. Yonemitsu reaction:

   c. Cannizzaro reaction:

   d. A sigmatropic reaction:

   e. Parekh-Doering oxidation:

2. (20 pts.) The reaction of benzaldehyde with compound **A** below, followed by the usual aqueous workup, yields a product **B**, mw = 162, as a single diastereomer.
   (i) Draw the structure of **B** in the box;
   (ii) Propose a mechanism to account for the formation of **B** and sketch an approximate transition state structure that rationalizes the observed diastereoselectivity.



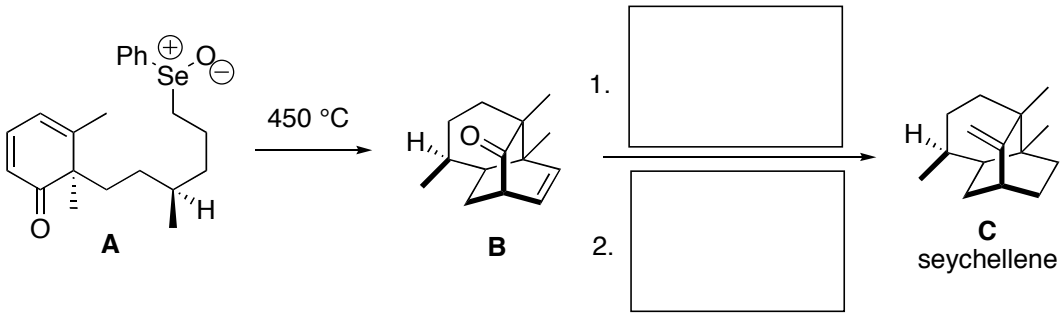

**A**

**B**: mw = 162

mechanism and approximate transition state structure:

3. (20 pts.) Seychellene, **C**, is a component of patchouli extract, an essential oil of interest in perfumery. A synthesis of seychellene involved heating compound **A** to 450°C for a few seconds, whereupon **B** was obtained. Intermediate **B** was then converted into **C** in two steps.

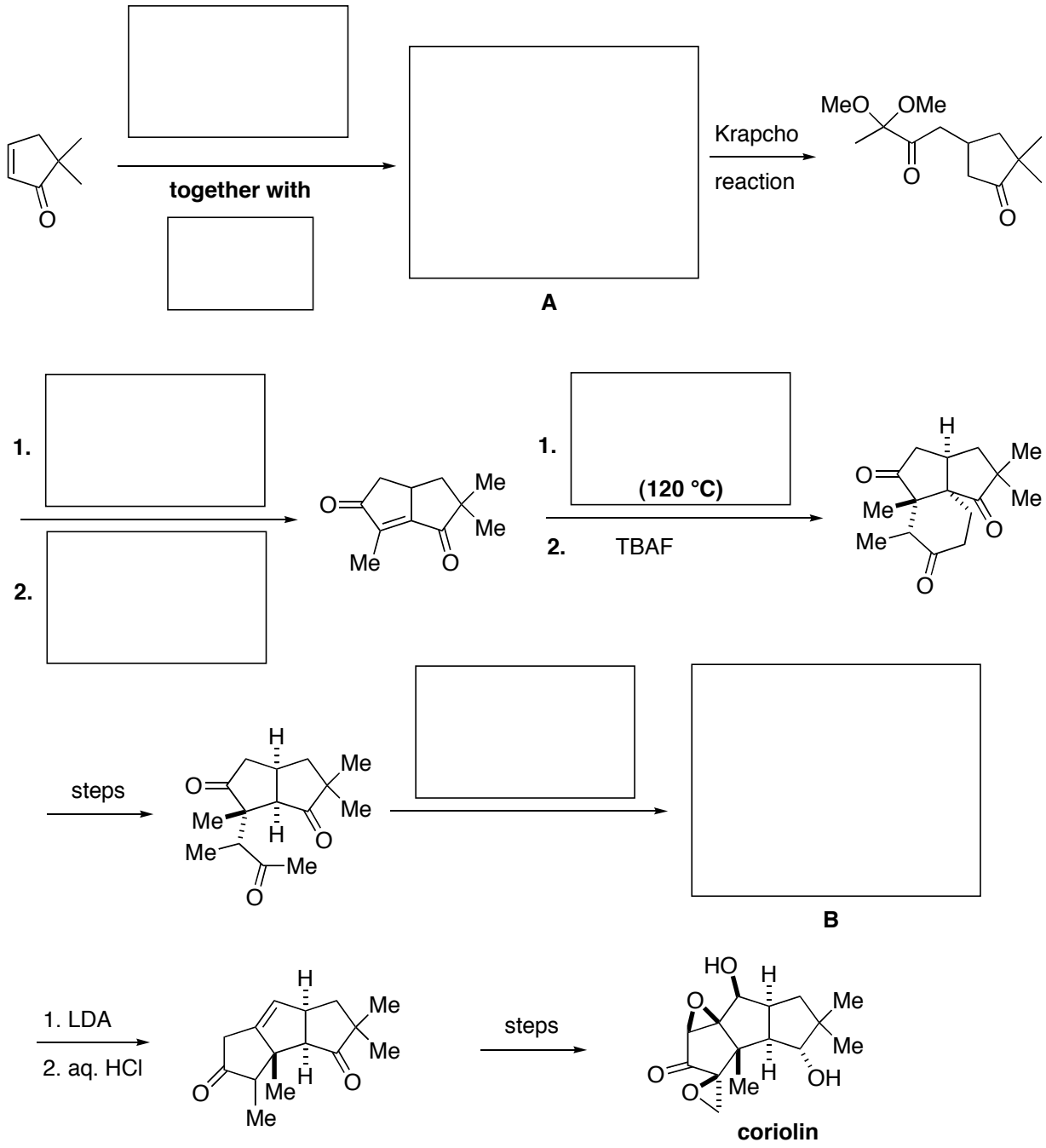
   a. Write the missing reagents required to advance **B** to **C** in the appropriate boxes
   b. Write a mechanism for the conversion of **A** into **B**
   c. Advance a succinct explanation as to why such a high temperature was necessary to effect this transformation (write in the box below).




| The reaction required such a high temperature probably because: |
| --- |
| |

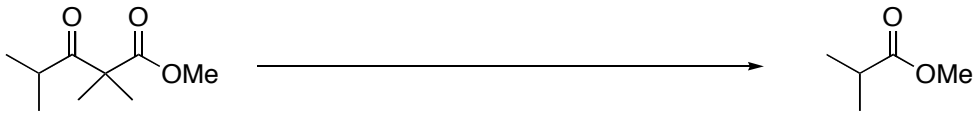
4. (30 pts.) A synthesis of the antitumor agent, coriolin, proceeded as outlined in the reaction scheme below. Complete this diagram by indicating all missing reagents / products. Each box corresponds to **one** reagent / product.

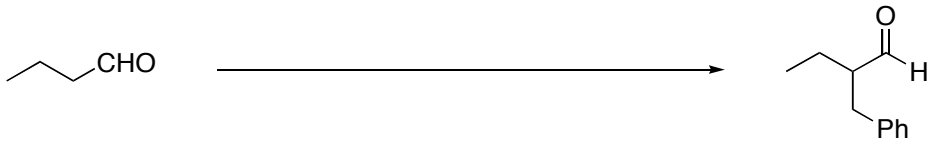
   **Note**: aqueous workup steps are understood and are not to be included in your answers.

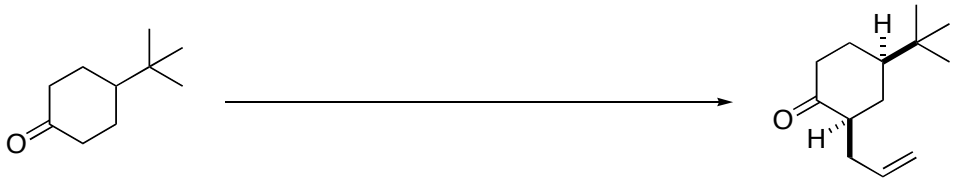


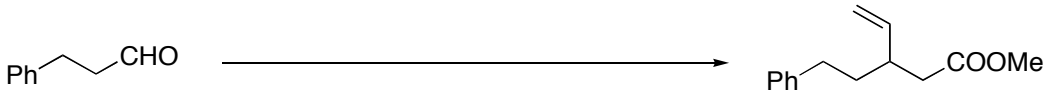
5. (40 pts.) Complete the following equations by indicating all the reagents that are necessary to effect the transformations shown. Provide your answers as a numbered list of reagents, in the correct order, written over/under the reaction arrows.

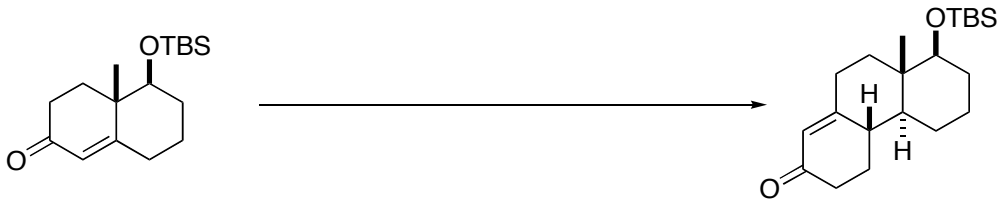
   **Note**: aqueous workups are understood and are not to be included in your answers.

a. 


b. 

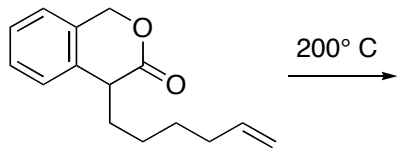

c. 

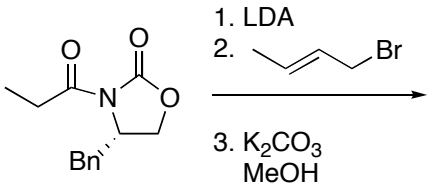

d. 

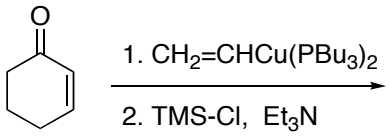

e. 

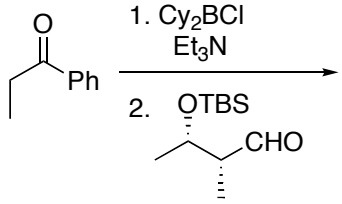
6. (40 pts.) Predict the structure of the major product expected from the following reactions. Note: **It is not necessary to draw mechanisms**.

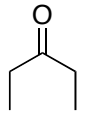
**Note**: aqueous workups at the end of each step are understood

a. 


b. 

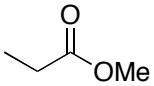

c. 


d. 

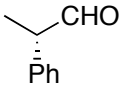
e. 

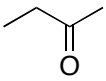
1. 9-BBN-OTf
   $Et_3N$
2. PhCHO

3. $Et_2BOMe$
   $NaBH_4$

f. 

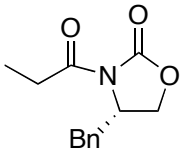
1. LDA, THF

2.  then aq. wrkp.

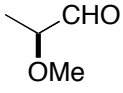
g. 

1. excess NaH,
   cat.EtOH, 1 eq.

$(EtO)_2CO$
2. Ph-$CH_2$Br
3. Aq. wrkp.

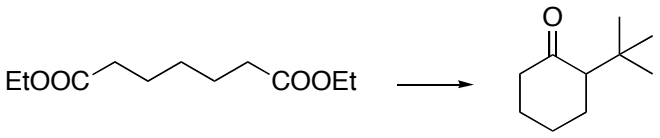
h. 

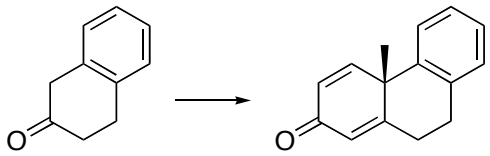
1. $Bu_2BOTf$,
   $Et_3N$

2.  then aq. wrkp.

7. (40 pts.) Propose a method to accomplish the transformations shown below. In each case, a multistep sequence (= not just one reaction, but several) may be necessary. Assume the availability of all required reagents (e.g, bases, alkyl halides, etc.). Present your answer as a flowchart that clearly shows all intermediate products.

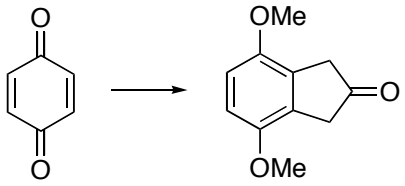
Note: **It is not necessary to draw mechanisms**.

a. 

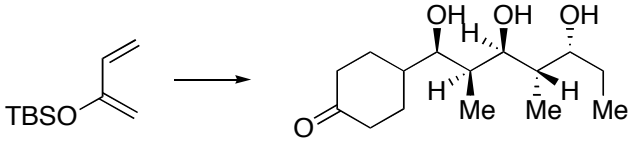

b. 

(racemic)

c.

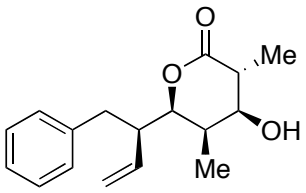


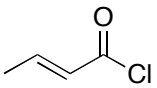

d.

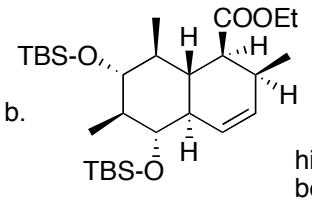


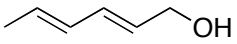

(this enantiomer)

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. 

starting with 

b. 


starting with 


hint: the last step of the synthesis must be an intamolecular Diels-Alder reaction

*Happy Holidays !*