

UNIVERSITY OF WINDSOR
SCHOOL OF PHYSICAL SCIENCES
CHEMISTRY AND BIOCHEMISTRY

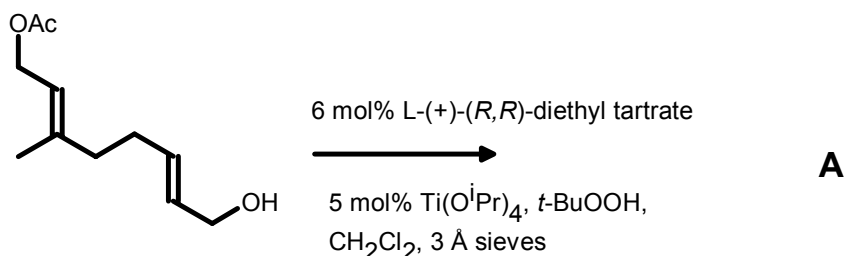
Chemistry 59-531/431
Final Examination

Dec. 14, 1998
Time: 3 hours

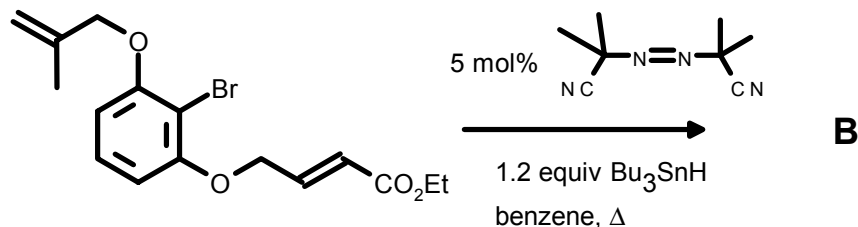
Answer all questions in the exam booklet.

1. Do any eight (8) 'letters'. (40 marks) Provide the major reaction product in each of the following transformations. Include stereochemical (relative and or absolute) information where it is relevant. Mechanisms are not necessary, but showing your work may be a help.

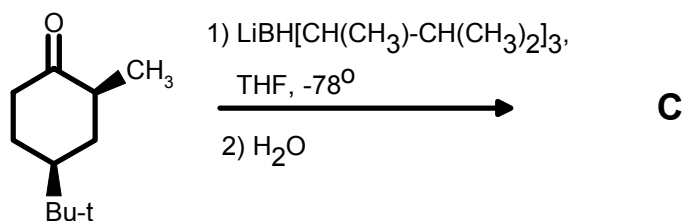
a)



b)

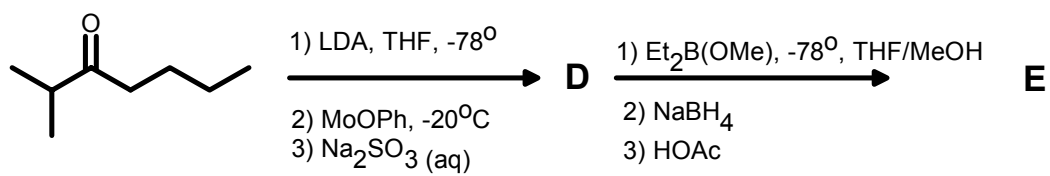


c)

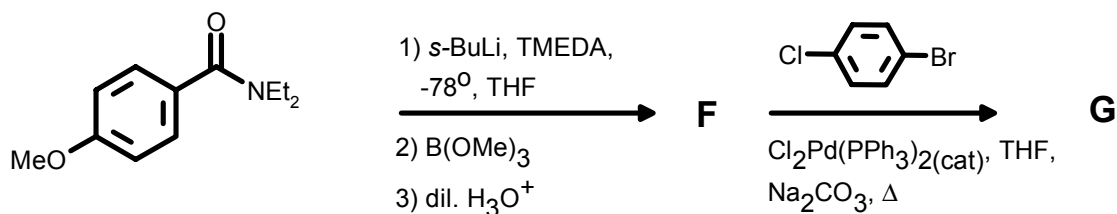


Note: In my notes, I appear to have written $\text{LiBH}[\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_2]_2$; this is incorrect. The reagent is called "LS-Selectride".

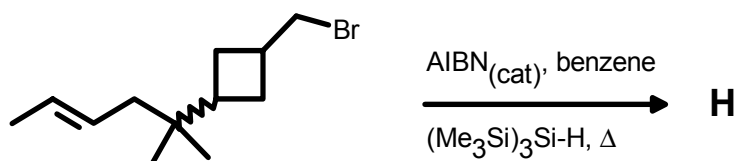
d)



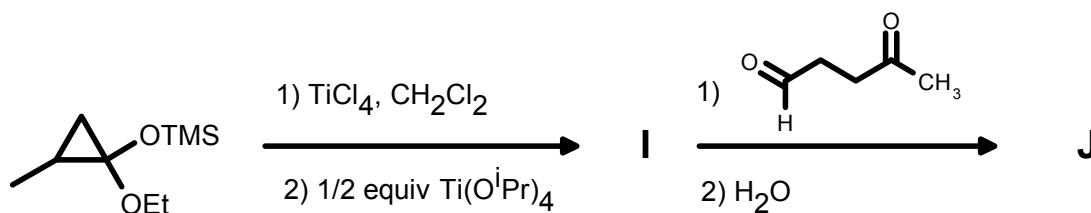
e)



f)

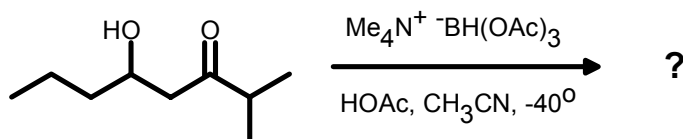


g)



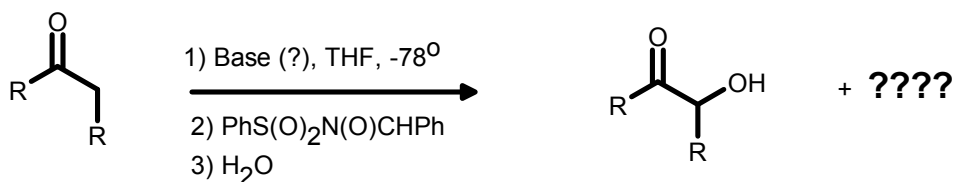
2. (Total 20 marks)

a) One of the reagents for reducing β -hydroxy ketones with excellent diastereoselectivity is $\text{Me}_4\text{N}^+ \text{BH(OAc)}_3$. Show by way of intermediates and transition state(s) why such selectivity is observed, and of course the final product, including relative stereochemistry (and the stereochemical descriptor used for it).



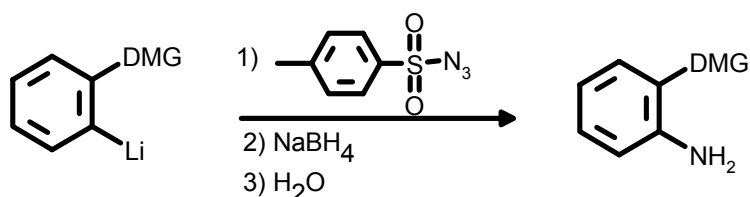
b) Do i) or ii), but not both.

i) One of the best methods of incorporation oxygen as an electrophile employs the oxaziridines developed by the Davis group. Show the mechanism of this oxygenation and how the most common side product occurs. What is responsible for this side product, and how is it minimized normally?

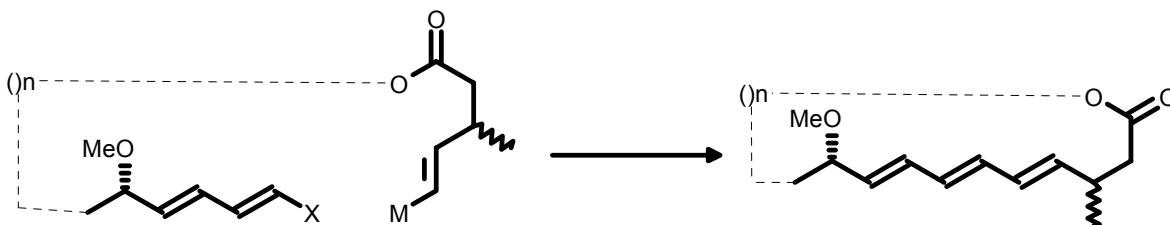


You'll notice I left the nature of the base out here. Clearly this is important to part of the answer.

ii) Aryllithiums are most often aminated ($\text{E}^+ = \text{" +NH}_2\text{"}$) by treating it with tosyl azide, followed by a reduction. Show the mechanistic steps of this reaction.



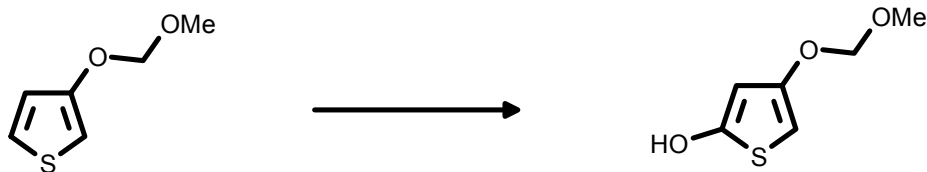
3. The critical, final bond forming step in Prof. Robert Maleczka's (Friday's seminar speaker) proposed synthesis of Amphidinolide A is the following (I've left much of the rest of the molecule out). Given your choice, and keeping in mind the other functional groups present in the molecule and the fact that you're closing a 20 membered ring, what would choose for the actual substrate (M especially, and include the X too) and the conditions of the reaction? What would be the worst of the 4 common choices for M? (10 marks)



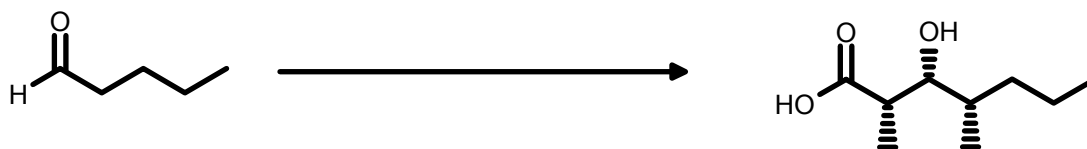
4. Do any seven (5) of the following, including b).

Show by equation how you would prepare the illustrated below from the given starting material. You may use any other reagents which you deem fit. Show all reagents, conditions, and isolable intermediates. Mechanisms are not necessary, but may be a help. (Total 50 marks)

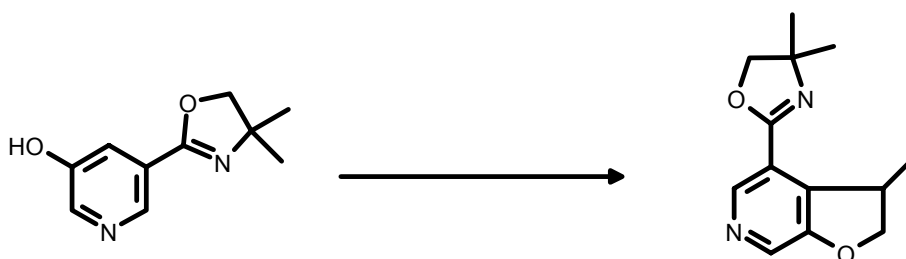
a)



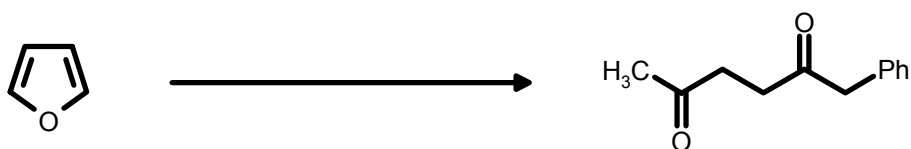
b)



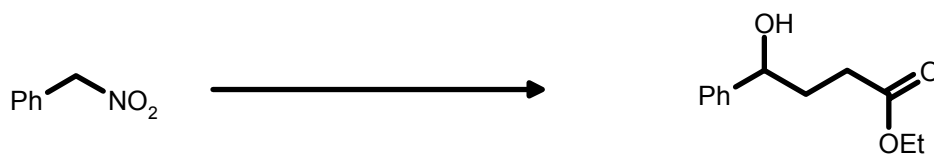
c)



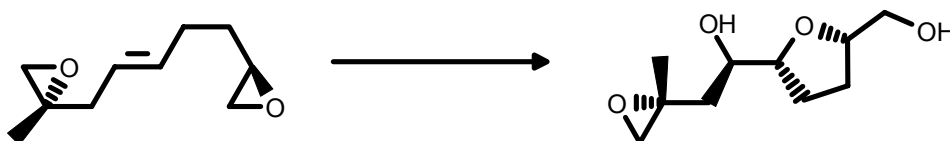
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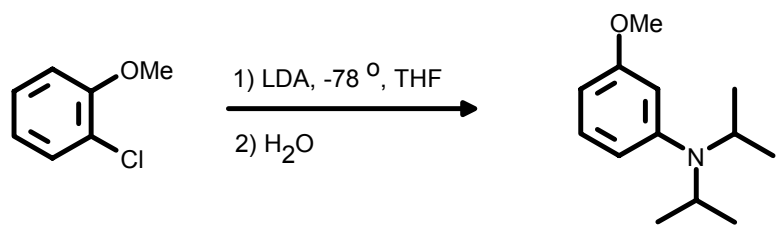
e)



f)



Bonus: Halides, by virtue of being $-I$ groups, can also be metallation directing (DMG's), albeit weak ones. The question is, why does the following odd type of substitution, called *cine* substitution, occur in the following reaction?



Assorted Cheat-sheet info

Baldwin's Rules for Ring Closure

For tetrahedral substrates:

- a) 3- to 7- exo-tet favoured
- b) 5- to 6- endo-tet disfavoured

For trigonal substrates

- a) 3- to 7- exo-trig favoured
- b) 3- to 5- endo-trig disfavoured
- c) 6- to 7- endo-trig favoured

For digonal substrates

- a) 3- to 4- exo-dig disfavoured
- b) 5- to 7- exo-dig favoured
- c) 3- to 7- endo-dig favoured

The structure of MoOPh is:

