

UNIVERSITY OF WINDSOR  
SCHOOL OF PHYSICAL SCIENCES  
CHEMISTRY AND BIOCHEMISTRY

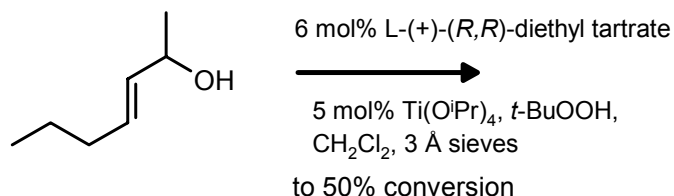
Chemistry 59-531/431  
Final Examination

Dec. 14, 2000  
Time: 3 hours

Answer all questions in the exam booklet.

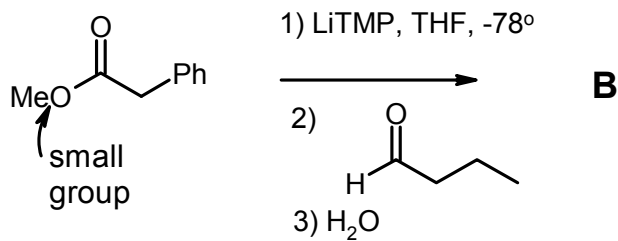
1. Do any eight (8) 'letters', including e. (40 marks) Provide the major reaction product in each of the following transformations. Include stereochemical (relative and or absolute) information where it is relevant. Mechanisms are not necessary, but showing your work may be a help. A warning, though...if you do the 1<sup>st</sup> letter of a series, you must do them all (i.e. you can't do D but not E and I but not J).

a)



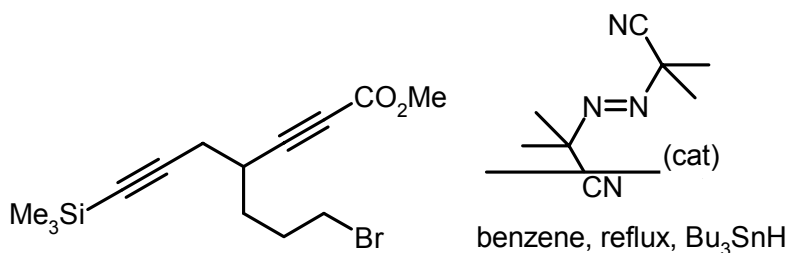
**A** two compounds

b)



**B**

c)

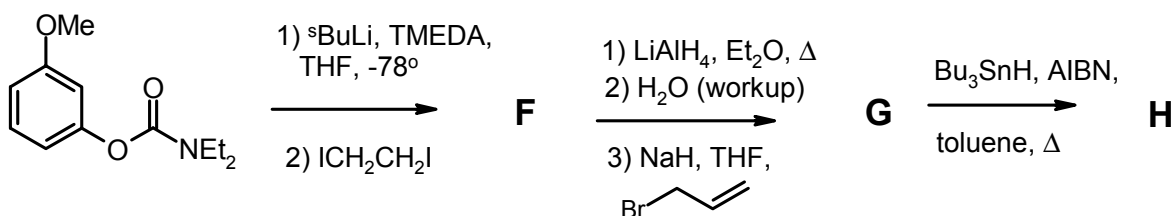


**C**

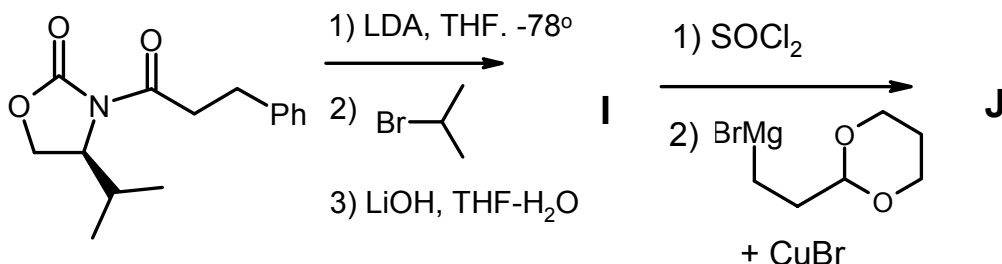
d)



e)

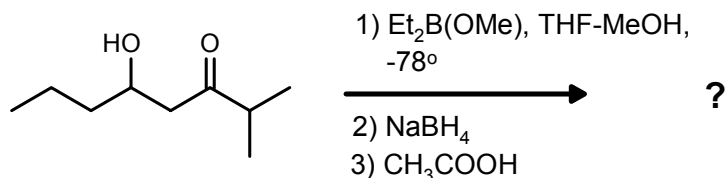


f)



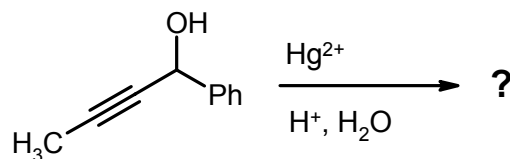
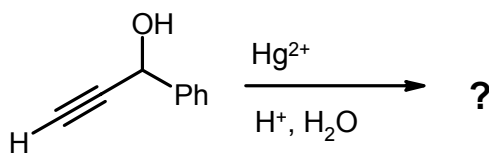
## 2. (Total 20 marks)

a) One of the series reagents for reducing  $\beta$ -hydroxy ketones with excellent diastereoselectivity employs  $\text{Et}_2\text{B}(\text{OMe})$ , followed by  $\text{NaBH}_4$  and a protic (usually acetic acid) workup. 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).

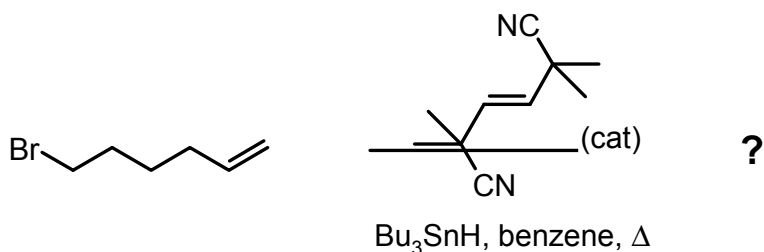


b) **Do i) or ii), but not both.**

i) Propargyl alcohols serve as effective 1,2-dioxygenated synthons only when the 'other' end of the alkyne is unsubstituted. Show by mechanism of hydrolysis why the left structure is effective in this regard, and why the right structure is not.



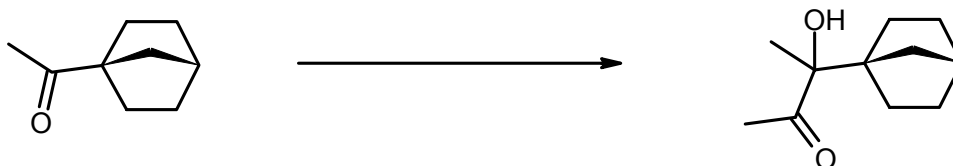
ii) Show the mechanistic steps of an AIBN,  $\text{Bu}_3\text{SnH}$  induced radical cyclization reaction of 5-hexenyl bromide. Show all reasonable initiation and propagation steps. Termination steps are *not* necessary here.



3. Do any seven (5) of the following.

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)**

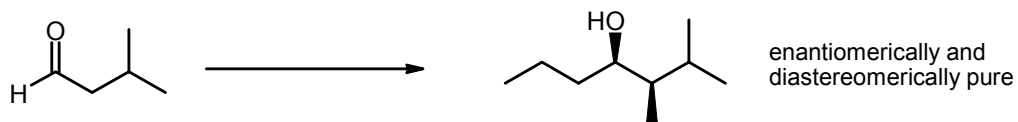
a)



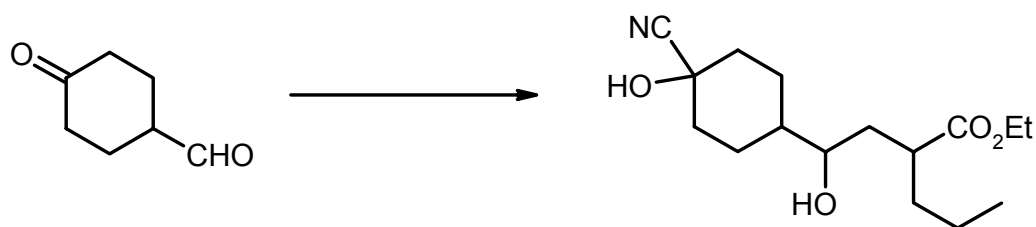
b)



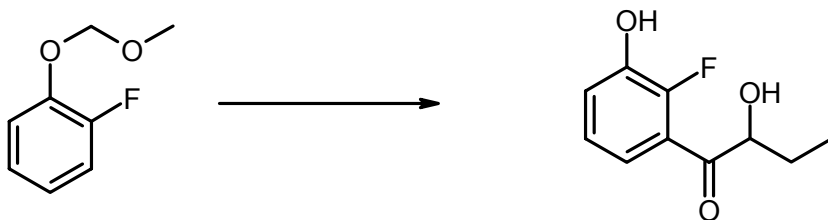
c) (next page)



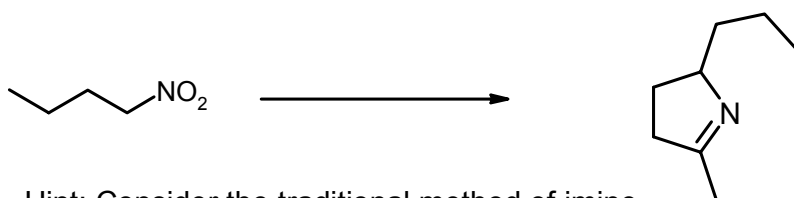
d)



e)

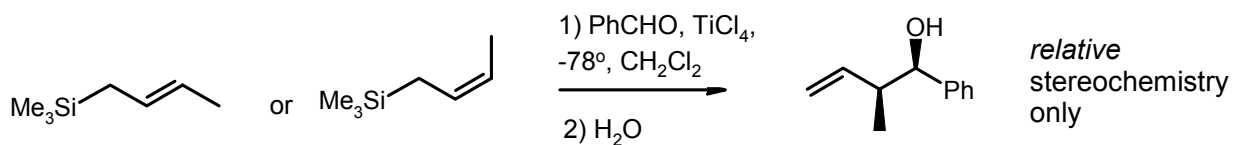


f)



Hint: Consider the traditional method of imine formation first.

**Bonus:** Unlike aldol type reactions, the Lewis acid mediated reactions of allylsilanes (or allyltins) with aldehydes gives pretty reliable *syn* stereochemistry regardless of the stereochemistry of the allylsilane (allyltin). Propose a reasonable transition state explanation for why this is the case.



## 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:

