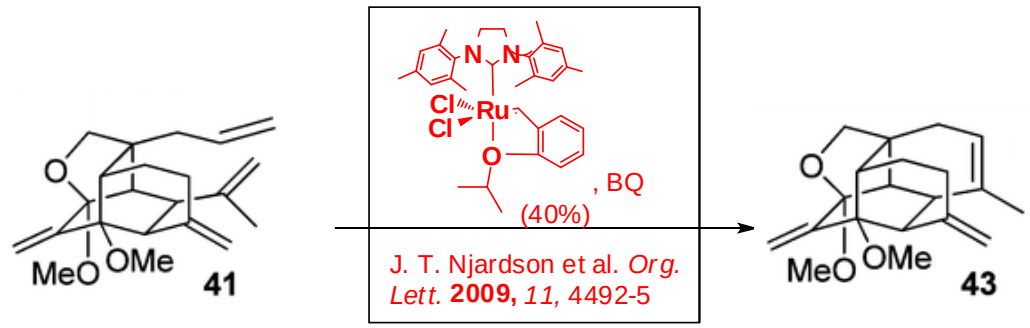
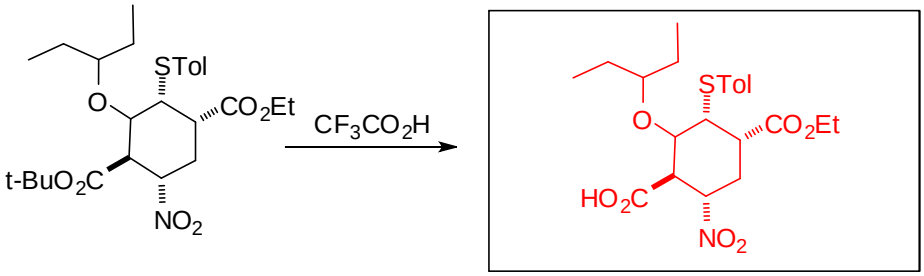
Advanced Organic Chemistry: Synthesis Name:___Johnny Damon_____
CHEM 311/511
Problem Set #4
Due: Tuesday October 27, 2009

1. Provide the necessary information, products or reagents, to complete the following reactions. Undergraduates must complete ten of the twelve boxes and graduate students must complete all twelve. (10 pts.)

a)

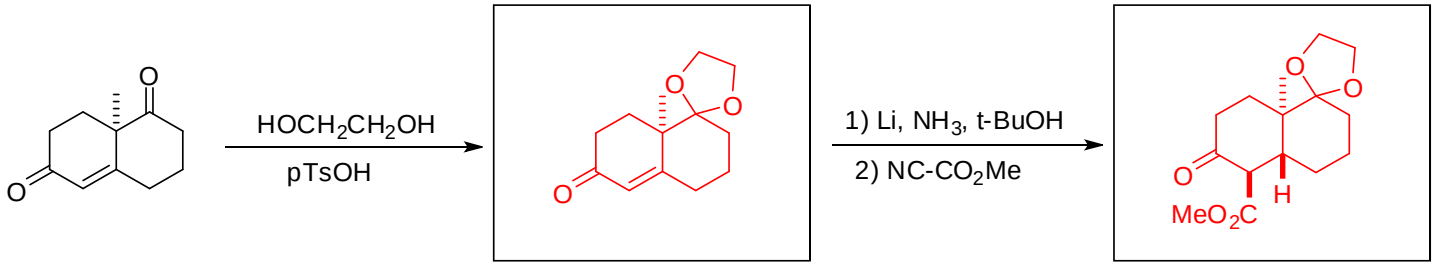


b)



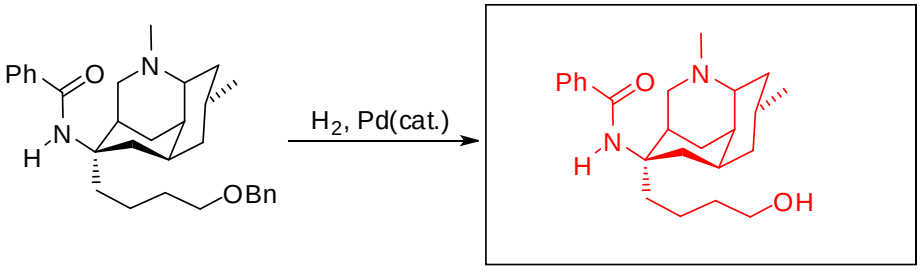
Y. Hayashi et al. *Angew. Chem. Int. Ed*. **2009,** *48,* 1307.

c)



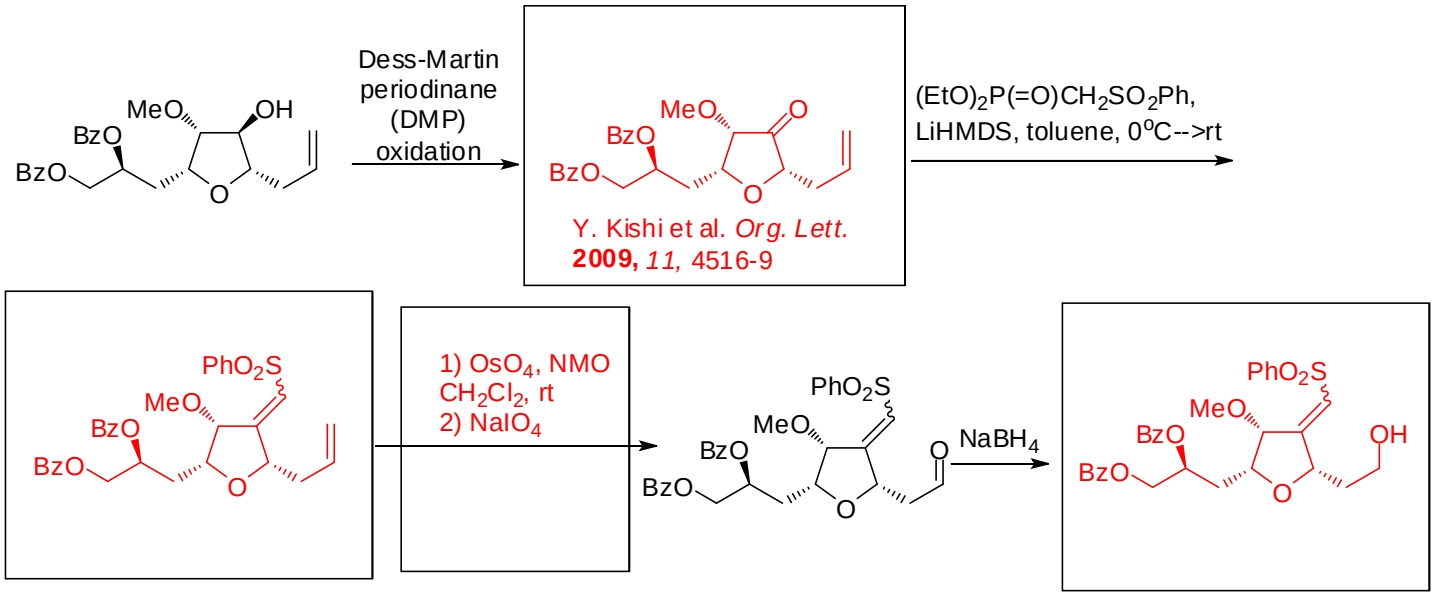
E. A. Theodorakis et al. *JOC* **2001,** *66,* 8843.

d)



L. E. Overman et al. *JACS* **2008,** *130,* 11297.

e)



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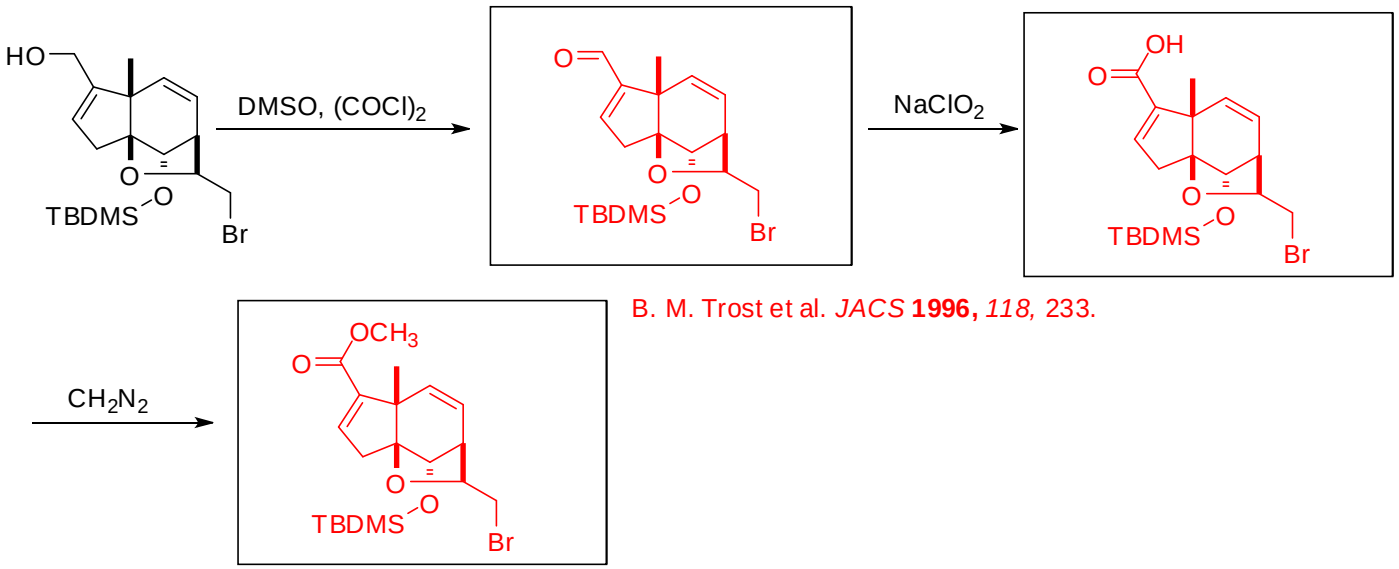


B. M. Trost et al. *JACS* **1996,** *118,* 233.

2. Mechanistic questions. Undergraduates must complete two of three questions and graduate students answer all three. (5 pts.)

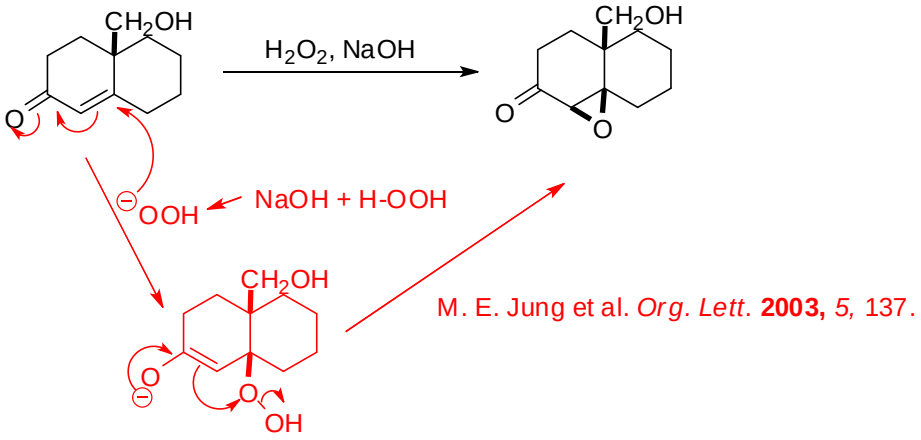
a) Explain the regioselectivity of the reaction in question 1a.

Ruthenium alkylidene initial reacts with least hindered, monosubstituted alkene, then reacts with the most accessible disubstituted alkene to form a thermodynamically stable cyclohexene ring. Of the other two disubstituted alkenes, one is not accessible and the second would form a rather strained cycloheptene ring.

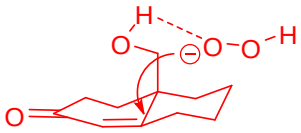
b) Explain the regioselectivity or chemoselectivity of the reaction in question 1c (first box).

The acetal forms from attack of the diol on the more electrophilic carbonyl; that is the non-conjugated carbonyl. The conjugated carbonyl is made less electrophilic due to resonance.

c) Provide a mechanism for the following reaction and suggest a reason for the reaction diastereoselectivity.

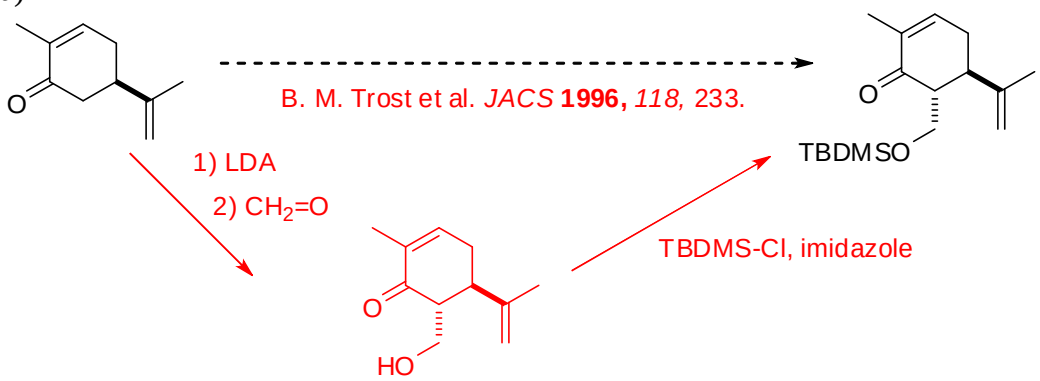


The reaction occurs syn to the hydroxymethyl group probably because the hydroxymethyl group hydrogen bonds with the hydroperoxide anion directing addition to the top face of the molecule.

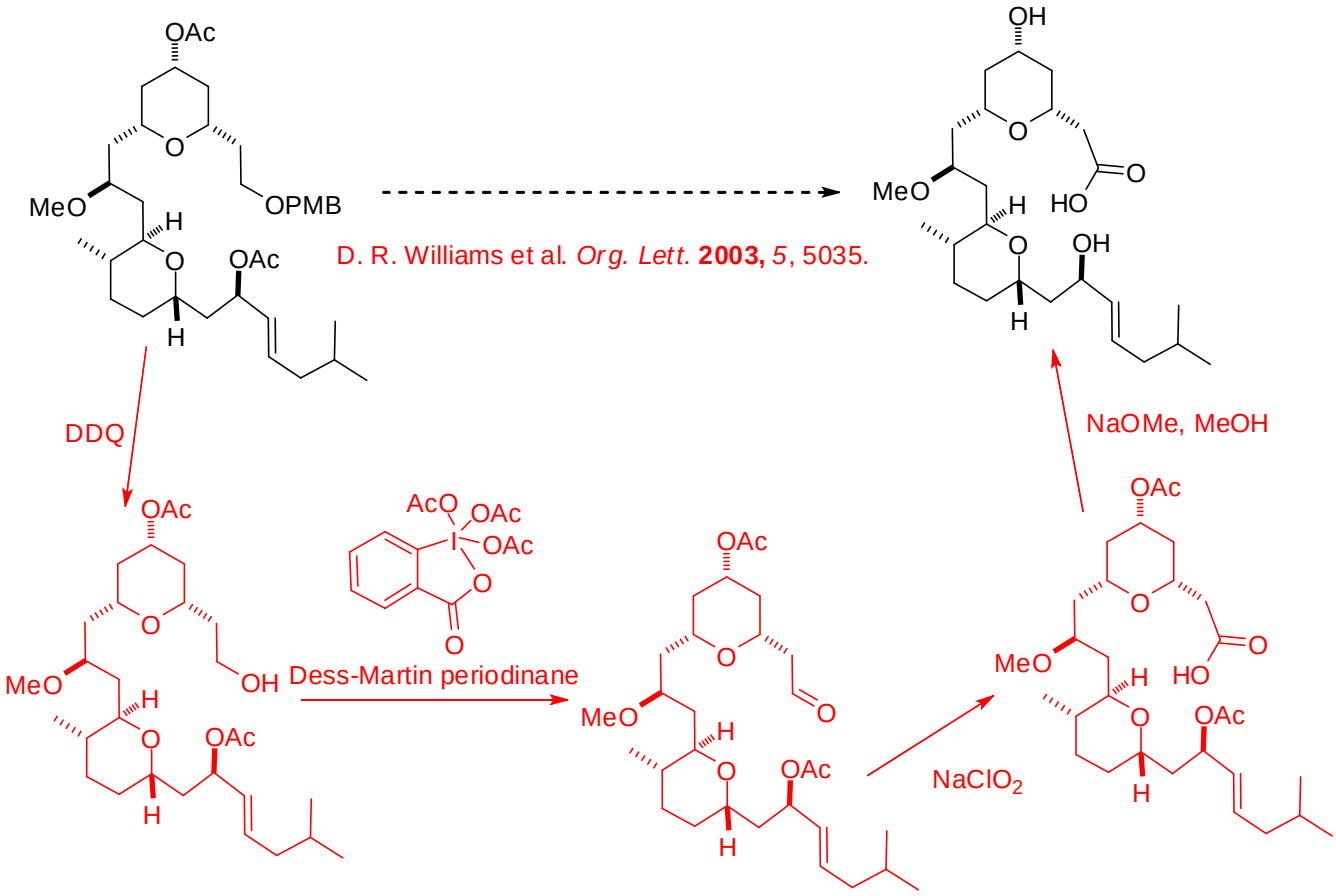


3. Synthesis questions. Undergraduates choose one question and graduate students do two. (5 pts.)

a)



b)


OAc
MeO
OPMB
H
O
OAc
H
D. R. Williams et al. Org. Lett. 2003, 5, 5035.
OH
MeO
O
HO
O
H
OH
H
DDQ
NaOMe, MeOH
OAc
MeO
OH
H
O
OAc
H
AcO
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I
OAc
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Dess-Martin periodinane
OAc
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H
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OAc
MeO
O
HO
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H
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OAc
H