Chem 220a

Problem Set 9

Chapters 10 and 11

Due: Monday, November 29, 2004

(but don't wait 'til the last minute)

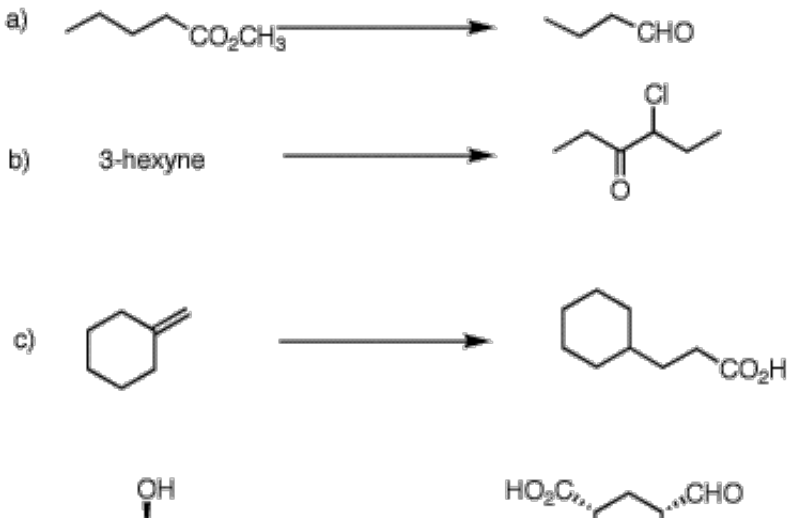
The topic of oxidation levels of organic compounds is addressed in passing on pg. 446. We will consider the issue in more detail as described in Oxidation Levels.The alcohol module in ORGO will give you a good review of some of the fundamental reactions discussed in class and in Chapters 10 and 11.

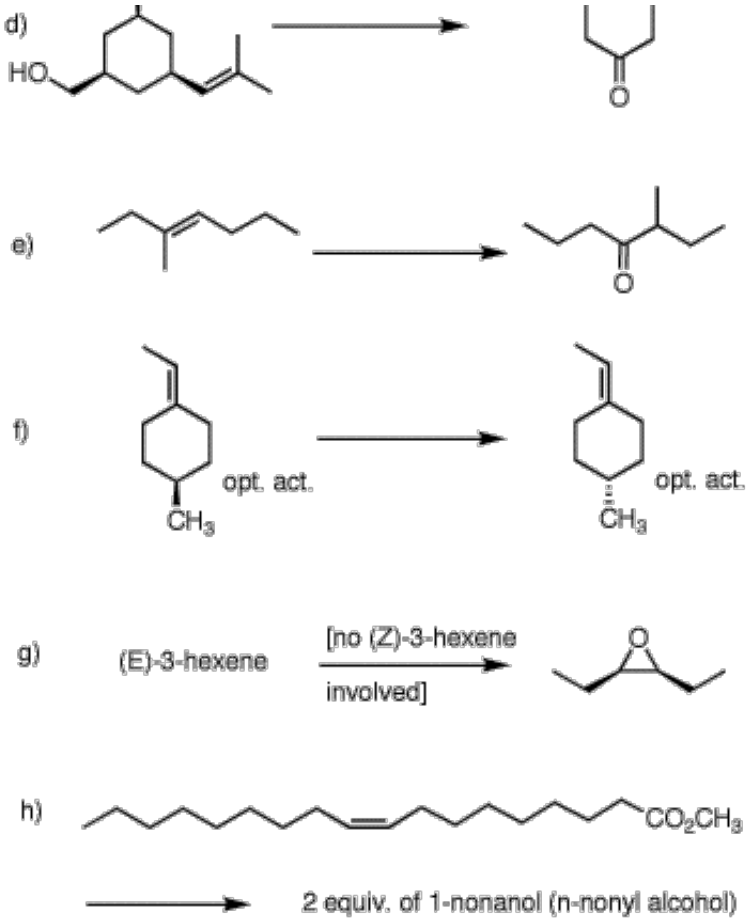
Victor Grignard (1871-1935)

Co-Nobel Prize in Chemistry (1912)

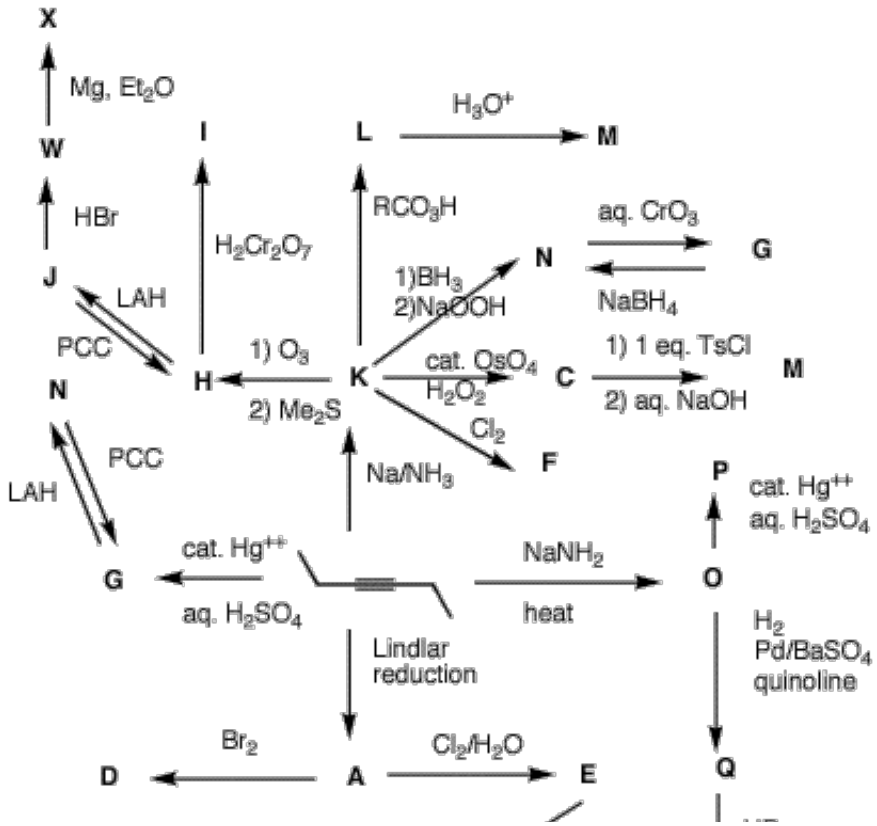
1. (20 pts) Compound **A** ($C_6H_{12}O_2$) reacts with 2 equiv. of an aliphatic Grignard reagent **B** to produce a single compound **C**. Treatment of **C** with H_2SO_4 readily affords only **D**, which upon ozonolysis gives **E** and formaldehyde. What are the structures of **A-E**? Explain and illustrate.

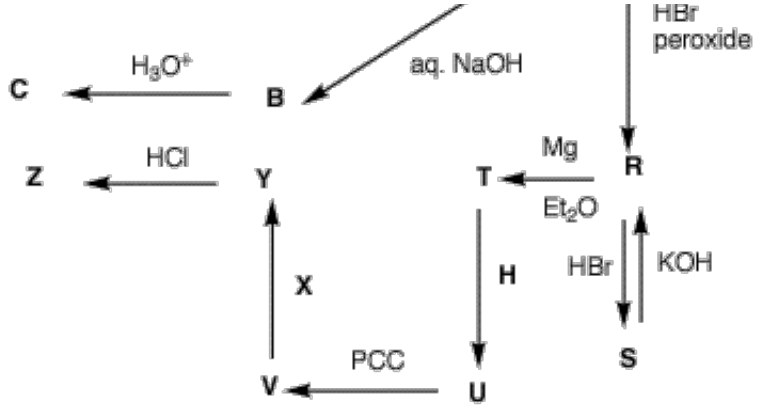
2. (40 pts) Provide reagents and intermediate compounds in the following transformations. Each reaction requires more than one set of conditions.





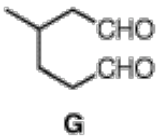
3. (100 pts) The Maze of Reactions: Provide the structures **A-Z**. Pay attention to stereochemistry and conditions. For additional exercises of this type, see the Web of Reactions. For a single page version of the Maze, click here.





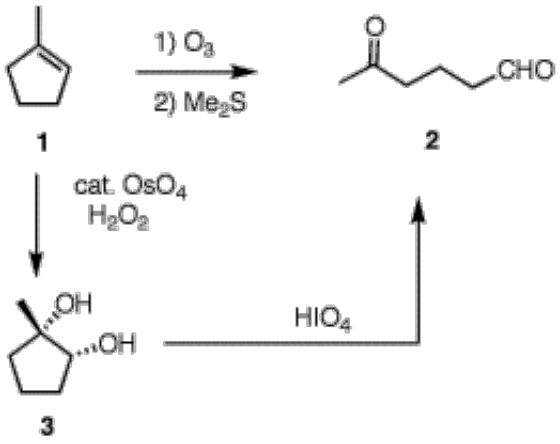
4. (30 pts) How many grams of potassium dichromate are required to oxidize 0.1 moles of ethanol to acetic acid? Show the balanced redox reaction and the rest of your calculations.

5. (30 pts) An optically-active component ((*R*)-**A**) of citronella oil has the formula $C_{10}H_{20}O$. Treatment of **A** with PBr_3 provides **B**, which forms Grignard reagent **C**. Addition of isobutyraldehyde [$(CH_3)_2CHCHO$] to **C** leads to compound **D**. Treatment of **D** with H_2SO_4 gives optically inactive **E** ($C_{14}H_{26}$). Oxidation of **A** with PCC provides **F**, which upon ozonolysis gives optically active dialdehyde **G**. What are the structures of **A-G**? Explain and illustrate. Pay attention to absolute (*R* vs. *S*) stereochemistry.

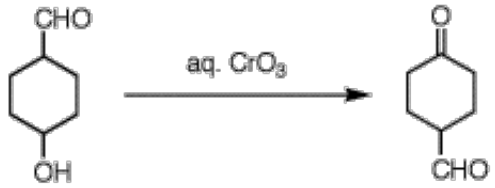


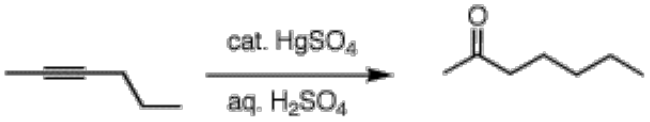
G

6. (20 pts) Your text (pg. 473) illustrates the sequence of reactions **1** --> **3** --> **2**. [The text doesn't specify catalytic OsO_4, but it is.] This procedure, which you will notice is the equivalent of ozonolysis (**1** --> **2**), is a two step procedure; the diol 3 is isolated. Explain what will happen if HIO_4 replaces H_2O_2 as the stoichiometric reagent. What about the use of $KMnO_4$ in place of H_2O_2? Assume that HIO_4 and $KMnO_4$ can oxidize Os(VI) to Os(VIII).

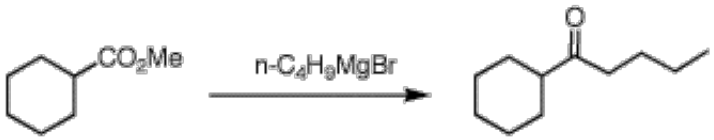


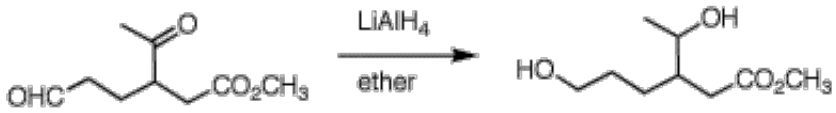
7. (60 pts) Each of the following reactions has a fatal flaw. What are they? How would you change the conditions of each reaction to accomplish the transformations?

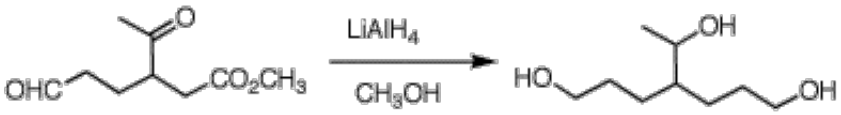
a) 

b) 

c) but-3-yn-1-ol
1) 1 eq. CH_3MgBr
2) acetaldehyde
hex-3-yn-1,5-diol

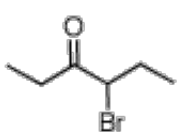
d) 

e) 

f) 

8. (60 pts) In each of the following reactions, determine whether the process is an oxidation, a reduction, or an electroneutral process. Give the total electron change in each case and provide the reaction conditions.

a) (*Z*)-3-hexene ⟶ $CH_3CH_2CO_2H$

b) (*E*)-3-hexene ⟶ 

c) 3-hexyne ⟶ 3-hexanone

d) 

e) 

f)