Chem 220 - Organic Chemistry

Problem Set 9

Chapters 10 and 11, Alcohols

New Due Date: Monday, November 29, 2010

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. As you master the chemistry of alcohols, you should try the Web of Reactions.

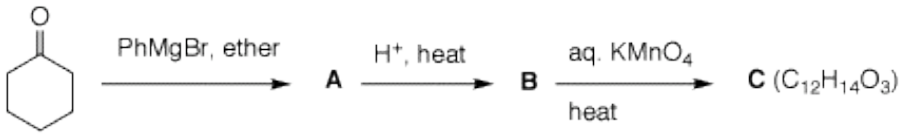
1. How many grams of $KMnO_4$ in aqueous KOH are required to oxidize 20 grams of 1,2-cyclohexanediol to adipic acid? [Note: MnO_2 is the reduction product of permanganate. This is a redox reaction from Gen. Chem. Go here for help. Derive the balanced equation and show your work.].

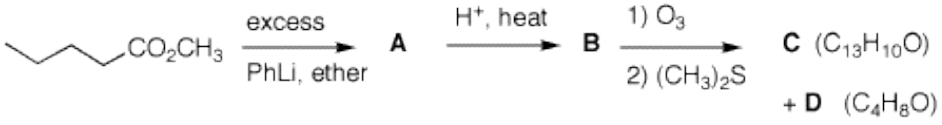
Victor Grignard (1871-1935)

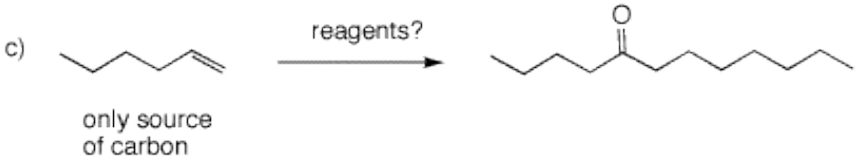
Co-Nobel Prize in Chemistry (1912)

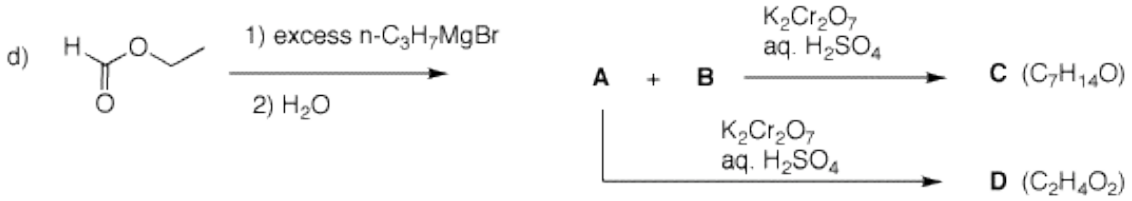
2. Optically-active compound **A** ($C_{10}H_{20}O_2$) reacts with $LiAlH_4$ in ether to form a single optically-inactive compound **B** ($C_5H_{12}O$). Bromide **C** is converted into its Grignard reagent **D**. Reagent **D** reacts with **A** to form optically-active **E** ($C_9H_{20}O$) and (*S*)-**B**. What are the structures **A-E**? Explain and illustrate.

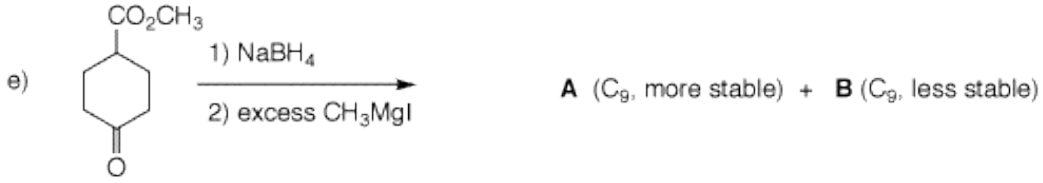
3. Predict the products and/or reagents in each of the following examples. Justify your answers.

a) 

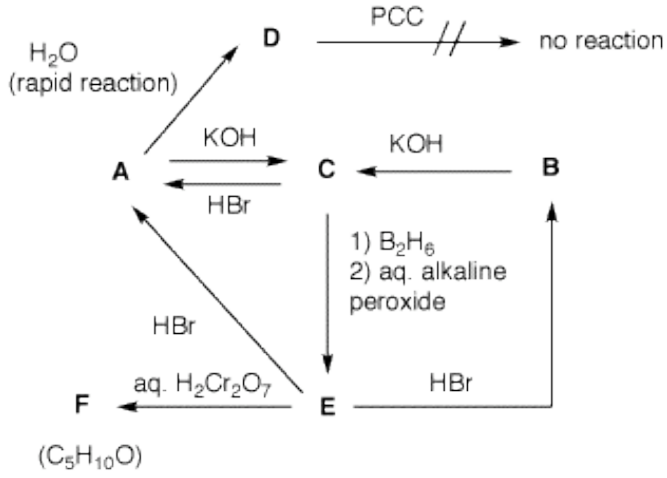
b) 

c) 

d) 

e) 

4. Two bottles on a shelf have had their labels fall off. Both of the labels read "$C_5H_{11}Br$". A student decides to run some reactions on the contents of bottle **A** and **B** to determine the structures of the two compounds. From the flow chart determine the structure of **A** and **B** and identify **C-F**. Show your reasoning. [**Hint:** Draw all of the structures of $C_5H_{11}Br$. Eliminate non-contenders? Only the major product in the formation of **C**



should be considered.]

5. Neosporol (**1**), which is shown in two views, was successfully synthesized from racemic ketone **2**, whose synthesis is well beyond the scope of this question. The immediate problem was to convert ketodiol **2** into triol **3**. [The fact-oid-s have been altered slighted to facilitate the question. (*J. Am. Chem. Soc.*, **1993**, *115*, 2581)] When an excess of methyllithium was used to convert the ketone function of **2** into the tertiary alcohol of **3**, only ketodiol **2** was recovered upon aqueous workup. A Jmol structure of neosporol is provided. Move the structure around to compare it with the two views of neosporol **1**.

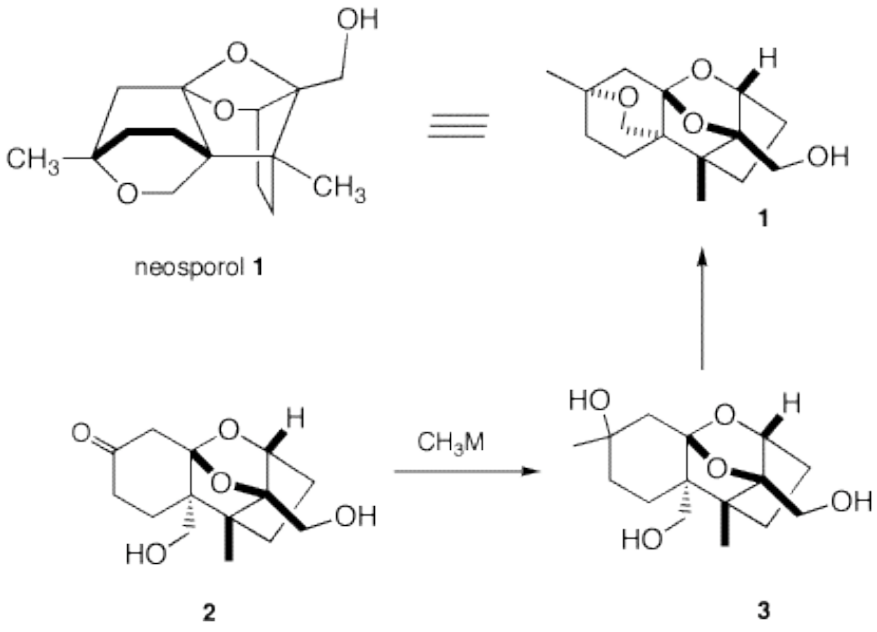
a) What is the minimum amount of methyllithium required in this reaction? Explain?

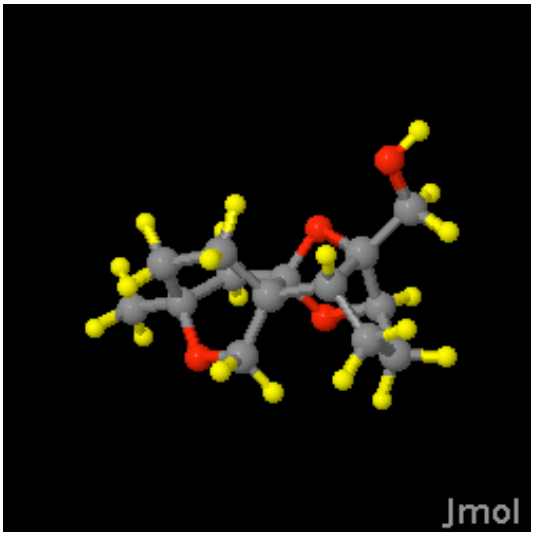
b) What events occurred prior to aqueous work up? [Hint: Generally, organolithium and Grignard reagents undergo addition but they are also the conjugate bases of weak acids.] What was the fate of the ketone group?

When methyl magnesium bromide was employed, both **2** and a mixture of the diastereomers of **3** were obtained. Complete conversion of **2** to **3** (5/1 mixture of diastereomeric tertiary alcohols) was effected cleanly with the cerium reagent, CH_3CeCl_2.

c) Draw the structures of the two diastereomers of **3**, i.e., provide stereochemistry in structure **3**.]

d) Provide conditions and a mechanism for the conversion of **3** to **1**. Is it necessary to separate the diastereomers of **3** prior to forming **1**?





Neosporol

(How to manipulate

Jmol structures)

(Larger Version)