Chem 225b - Comprehensive Organic Chemistry

Problem Set 9

Chapters 9 and 10, Alcohols

Due: Monday, April 14, 2008

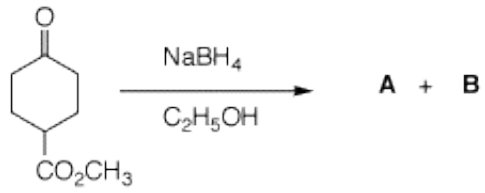
The alcohol module in ORGO will give you a good review of some of the fundamental reactions discussed in class and in Chapters 8 and 9. As you master the chemistry of alcohols, you should try the Web of Reactions.

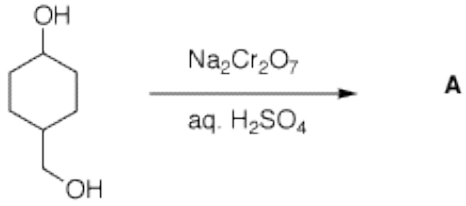
1. How many grams of $K_2Cr_2O_7$ in aqueous H_2SO_4 are required to oxidize 20 grams of cyclohexanol to cyclohexanone? [This is a redox reaction from Gen. Chem. Derive the balanced equation and show your work.]

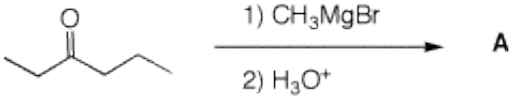
Victor Grignard (1871-1935)

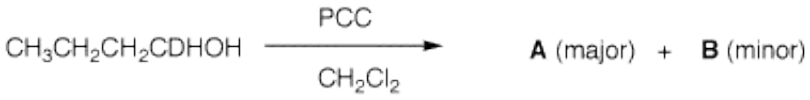
Co-Nobel Prize in Chemistry (1912)

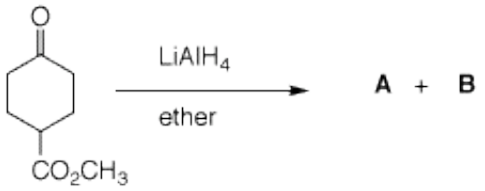
2. Predict the products in each of the following examples. Justify your answer.

a) 

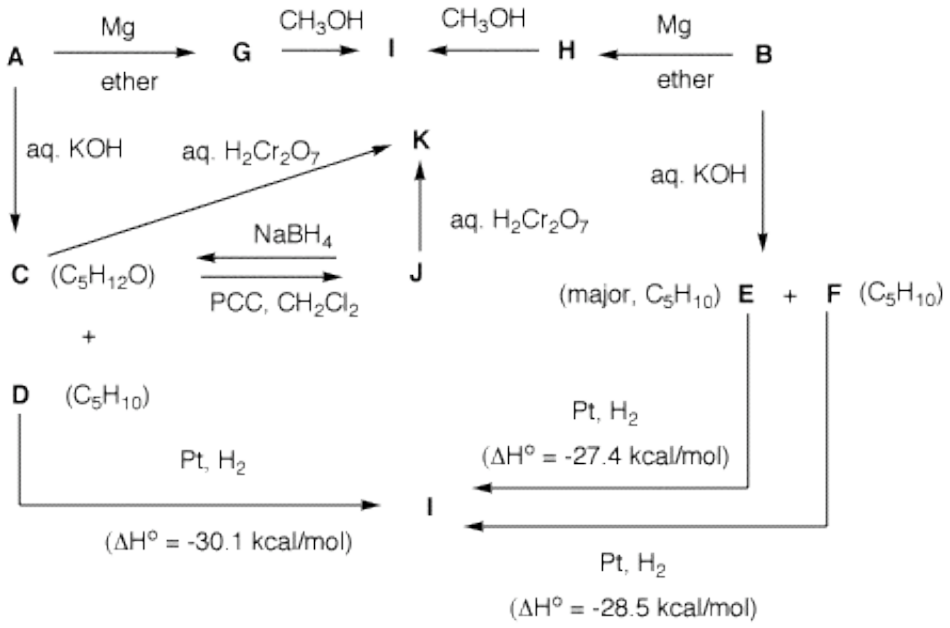
b) 

c) 

d) 

e) 

3. Two bottles on a shelf have had their labels fall on the desktop. 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. She also has access, as do you, to heats of formation. From the flow chart below, determine the structure of **A** and **B** and identify **C-I**. [Note: The mixture **C** and **D** is derived from **A**.] Show your reasoning.



4. When organometallic reagents add to aldehydes and ketones, there is only one addition. Aldehydes give secondary alcohols and ketones afford tertiary alcohols. Esters (RCO_2CH_3), which are derivatives of carboxylic acids and are at the same oxidation level as each other, undergo addition of an organometallic reagent (R'M) twice to yield a tertiary alcohol, RR'_2COH. The reaction cannot be stopped after the first addition. It is also true that carboxylic acids are at a higher oxidation level than aldehydes by two electrons. Provide an explanation for these results and provide a mechanism for the process.

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 isolated upon aqueous workup.

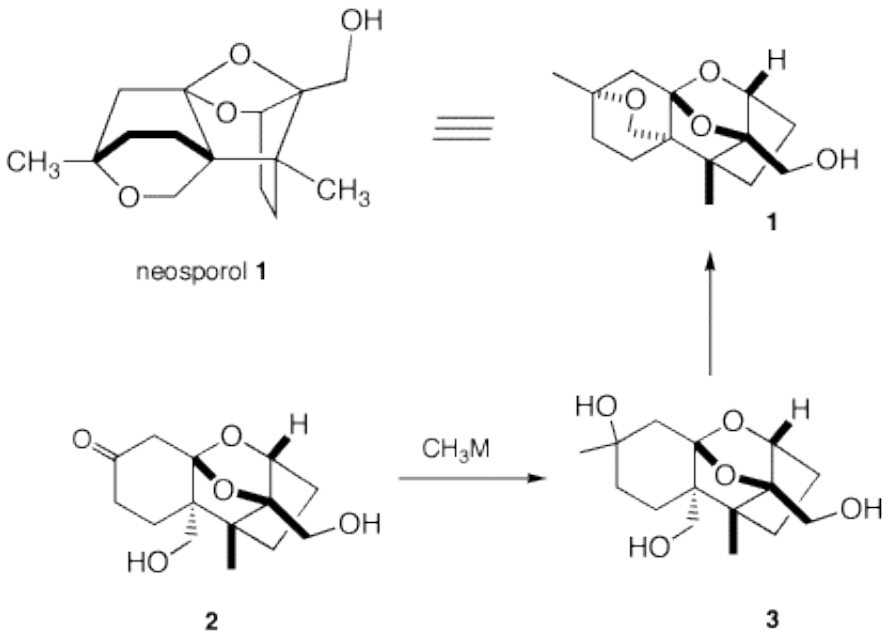
a) What is the minimum amount of methyllithium required in this reaction? Explain?

b) What events occurred prior to aqueous work up? 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**.

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**?



6. 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 (*R*)-**B**. What are the structures **A-E**? Explain and illustrate.