

Chem 220 - Organic Chemistry

Problem Set 9

Chapters 9 and 10, Alcohols

Due: Monday, November 16, 2009

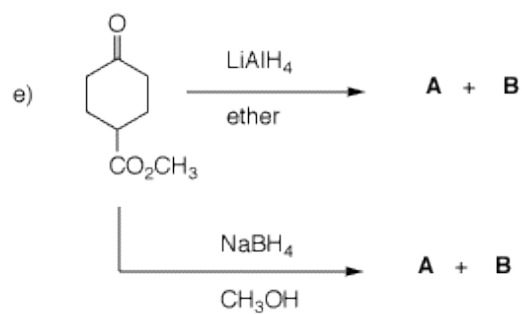
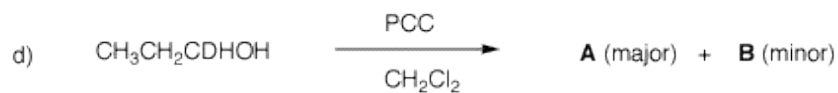
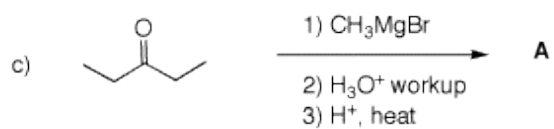
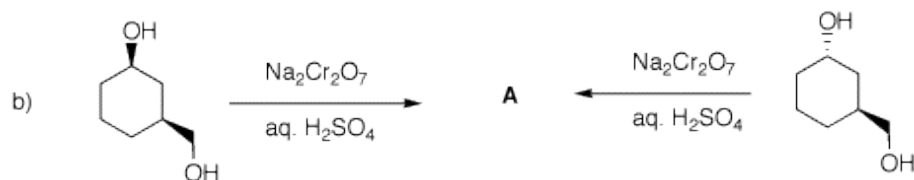
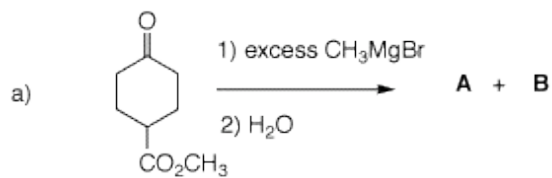
The alcohol module in [ORGO](#) will give you a good review of some of the fundamental reactions discussed in class and in Chapters 8 and 9. As you master the chemistry of alcohols, you should try the [Web of Reactions](#).

1. How many grams of $K_2Cr_2O_7$ in aqueous H_2SO_4 are required to oxidize 30 grams of cyclopentanol to cyclopentanone? [This is a redox reaction from Gen. Chem. Derive the balanced equation and show your work.]
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 in each of the following examples. Justify your answer.



Victor Grignard (1871-1935)

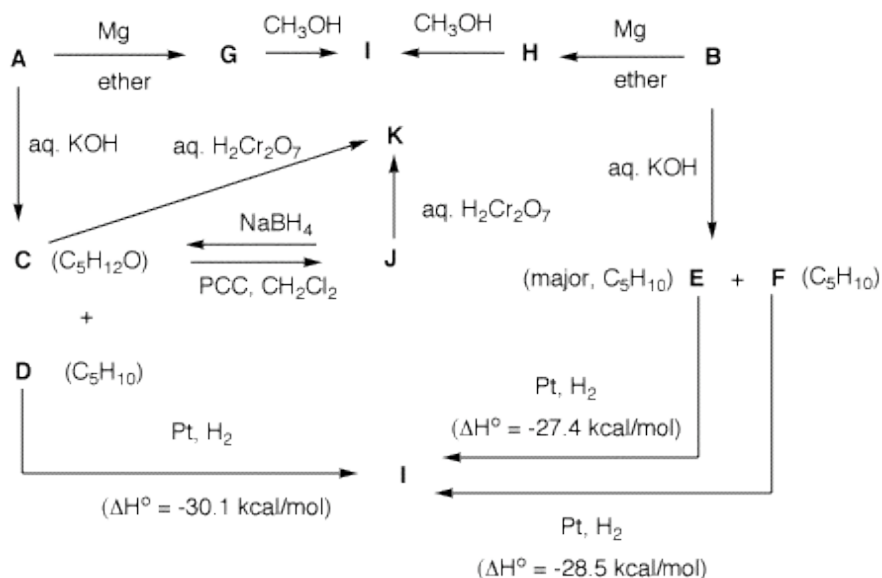
[Co-Nobel Prize in Chemistry \(1912\)](#)



4. Two bottles on a shelf have had their labels fall on the desktop. Both of the labels read "C₅H₁₁Br". 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. [**Hint:** Draw all of the structures of $C_5H_{11}Br$. What does **I** tell you about **A** and **B**?]



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 factoids have been altered slightly to facilitate the question. (*J. Am. Chem. Soc.*, **1993**, *115*, 2581)] When an excess of methyl lithium 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 methyl lithium required in this reaction? Explain?

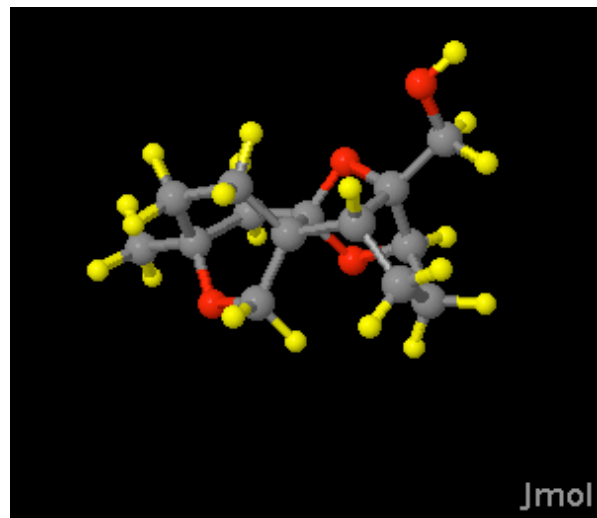
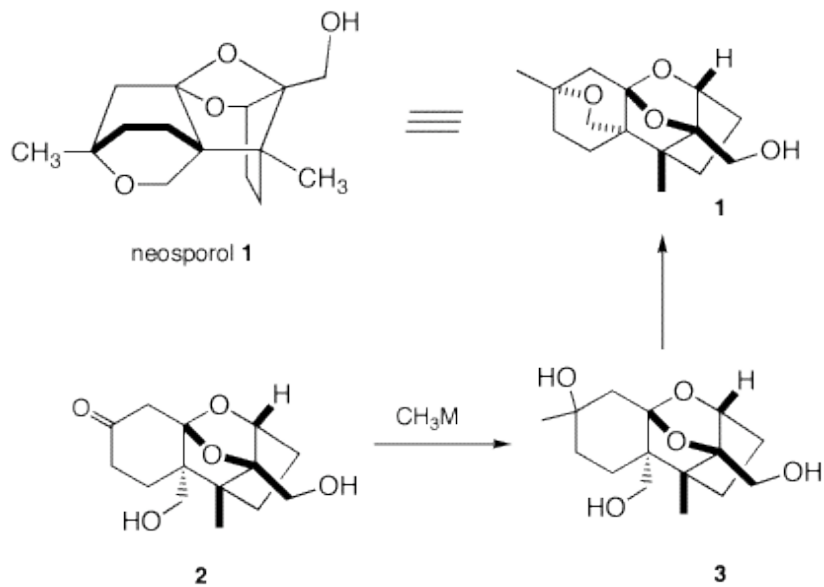
b) What events occurred prior to aqueous work up? [Hint: Generally, Grignard reagents undergo addition but they are also the conjugate bases of weak acids.] What was the fate of the ketone group?

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](#))