

Chem 225b

Comprehensive Organic Chemistry

Problem Set 7

Chapter 8

Due: Monday, March 27, 2006

We have discussed Degree of Unsaturation (D.U.) as it relates to hydrocarbons. How do you find the D.U. if other atoms are present? Fear not! There is an [html document](#) and an independent, different [Powerpoint](#) presentation on this topic. The subject of oxidation levels of organic compounds is a useful concept. Check it out here [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 8 and 9.

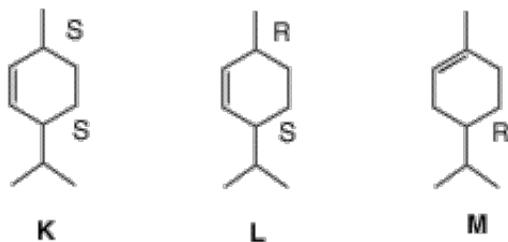


Victor Grignard (1871-1935)

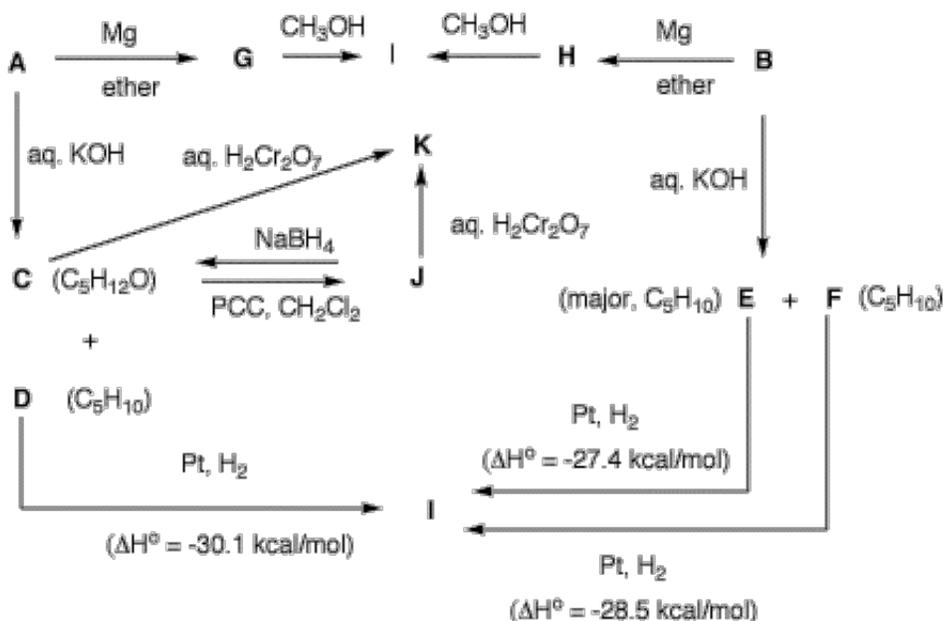
[Co-Nobel Prize in Chemistry \(1912\)](#)

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.]
2. (*R*)-(-)-Carvone is reduced in the presence of hydrogen to form two carvomenthones, **A** and **B** ($C_{10}H_{18}O$). **A** is less stable than **B**. (Use what you know about cyclohexane to make this evaluation.) Reduction of **A**

with NaBH_4 provides **C** and **D** while **B** gives **E** and **F**. Compounds **C-F** are converted to their respective tosylates **G-J** and their rates of elimination and products formed upon exposure to EtONa/EtOH were studied. Rates of elimination: $\text{G} > \text{H}$ and $\text{I} > \text{J}$. Tosylate **G** forms only **K**, **H** forms **M** and **I** forms **M** (major) and **L** (minor). What are the structures **A-J**? Explain all transformations involved.



3. Two bottles on a shelf have had their labels fall on the desktop. Both of the labels read " $\text{C}_5\text{H}_{11}\text{Br}$ ". A student decides to run some reactions on the contents 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**. Show your reasoning.



4. For EtOH ($\text{pK}_a = 15.9$) + NaOH in equilibrium with EtONa + H_2O ($\text{pK}_a = 15.7$),

a) What is the value of K_{eq} ? Show work.

b) How much of each base is present?

c) When n-butyl bromide reacts with excess 0.1 M KOH in ethanol, more of n-butylethyl ether is formed than n-butyl alcohol. Assume that hydroxide and ethoxide have the same rate constant for this reaction, how much of each compound is produced? Why?

5. 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, undergo addition of an organometallic reagent ($\text{R}'\text{M}$) twice to yield a tertiary alcohol, $\text{RR}'_2\text{COH}$. 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.