

## Chem 220 - Organic Chemistry

### Problem Set 8

#### Chapter 9, Alkynes

Due: November 9, 2009

#### Connections

Aluminum was once a precious metal although it was plentiful. The problem was how to remove it from its ore.

[Friedrich Wöhler](#), of urea synthesis fame, was able to accomplish this feat but by an impractical method. He was to meet a

young chemist, [Frank Jewett](#), recently arrived in Göttingen from Yale.

Aware of the difficulty Wöhler had had and probably encouraged by Wöhler, Jewett, as a professor at



Friedrich Wöhler (1800-1884)

(Wöhler possessed a wry sense of humor)

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Oberlin College, passed the problem onto [Charles Martin Hall](#), a young student at the college. Hall solved the problem in his family garage. Thus was born Alcoa. At the same time in Spray, North Carolina, [Thomas Willson](#), a Canadian, and American James Moorhead were unsuccessfully trying to refine aluminum using an electric arc. Unsuccessful in purifying aluminum, they sought calcium metal. Heating coal tar and lime in an electric furnace they obtained a brittle material that produced a combustible gas upon exposure to

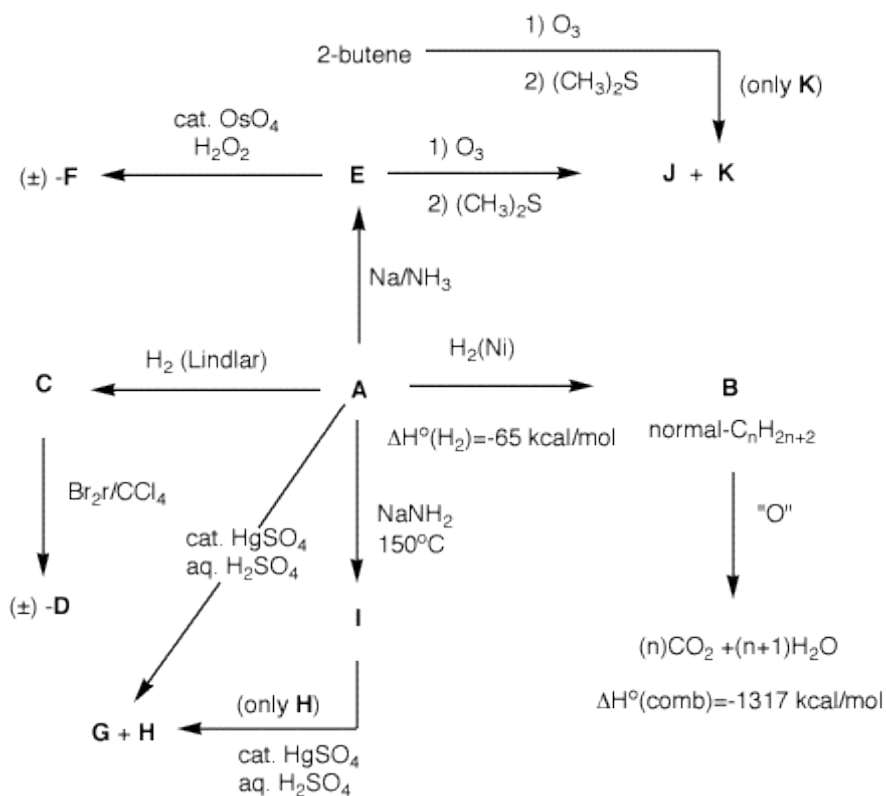


Charles Martin Hall (1863-1914)

water. The material was not calcium nor was the gas hydrogen. The pair was calcium carbide and acetylene, the basis for Union Carbide (RIP).

The alkyne module in [ORGO](#) gives a good review of acetylene chemistry.

1. Determine the structures **A-K**. Explain your reasoning.



2. Provide reagents for the following reactions. Explain your reasoning.

- a) 2-butyne  $\longrightarrow$  3-octyne (2-Butyne is the only source of carbon.)
- b) 4-octyne  $\longrightarrow$  meso-4,5-dibromooctane
- c) 4-octyne  $\longrightarrow$  d,l-4,5-dihydroxyoctane
- d) 4-octyne  $\longrightarrow$  meso-4,5-dihydroxyoctane
- e) 4-octyne  $\longrightarrow$  d,l-4,5-dibromooctane

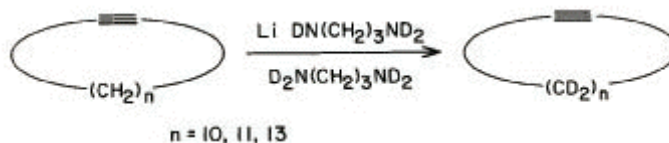
3. Design a synthesis of [muscalure](#) [(Z)-tricos-9-ene], the sex attractant of the common housefly, *Musca domestica*. As a source of carbon you have available 1-butyne, 1-pentyne and acetylene. You may use 1-pentyne and acetylene only once, i.e., only seven of the carbons may be provided by these two alkynes. All reagents are available.

4. Estimate the [heat of formation](#) of 1-,2-,3- and 4-octyne. Equilibration of any one of these isomers with KOH at 200°C produces about as much 2-octyne as 3-octyne both of which individually exceed the amount of 1-octyne. However, the amount of 4-octyne is less than the amount of 2- or 3-octyne. Explain. [Hint: 2- and 3-octyne have an entropic advantage over 4-octyne.]

5. Two bottles are found on a laboratory shelf labeled "alkyne **A**" and "alkyne **B**". Hydrogenation of **A** or **B** over a platinum catalyst gives the same alkane **C**. Compound **A** reacts with  $H_2$  in the presence of Lindlar's catalyst to form **D**. Compound **D** reacts with  $O_3$  to form a single compound **E**,  $C_3H_6O$ . On the other hand, compound **B** reacts with aq.  $H_2SO_4$  in the presence of  $HgSO_4$  to give two ketones **J** and **K**. Under the same conditions, **A** gives only **J**. Compound **B** also reacts with  $Na/NH_3$  to give **F**, which itself reacts with  $Br_2/H_2O$  to give a pair of constitutional isomers, **G** and **H**. Treatment of either **G** or **H** with aqueous NaOH gives the same compound **I**,  $C_6H_{12}O$ , that is also formed by the reaction of **F** with peracid. What are the structures of **A-K**? Explain and illustrate. [Note: **G** and **H** are not distinguished from one another. Pay attention to stereochemistry.]

6. The reaction on the right, which was conducted on three different cycloalkynes, was reported in 1985 by Suzanne Abrams and Angela Shaw of the National Research Council of Canada. Rather than use  $NaNH_2$  as your text suggests, they used the lithium salt of tetradeutero-1,3-diaminopropane in tetradeutero-1,3-diaminopropane as a solvent at room temperature.

a) Name the alkynes used in these experiments.  
 [Note: Not surprisingly, cyclooctyne was found to be unstable to the reaction conditions.]



b) The base in this experiment is formed by adding n-butyllithium to the solvent, tetradeutero-1,3-diaminopropane. Use the [pKa](#) table to explain why this is a sound way to prepare this base.

c) Provide an explanation (mechanism) as to how each methylene group becomes deuterated.  
 [Hint: Such reactions are often called "zipper" reactions. Why?]