

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



Friedrich Wöhler (1800-1884)

(Wöhler possessed a wry sense of humor) [1](#) [2](#)

professor at 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

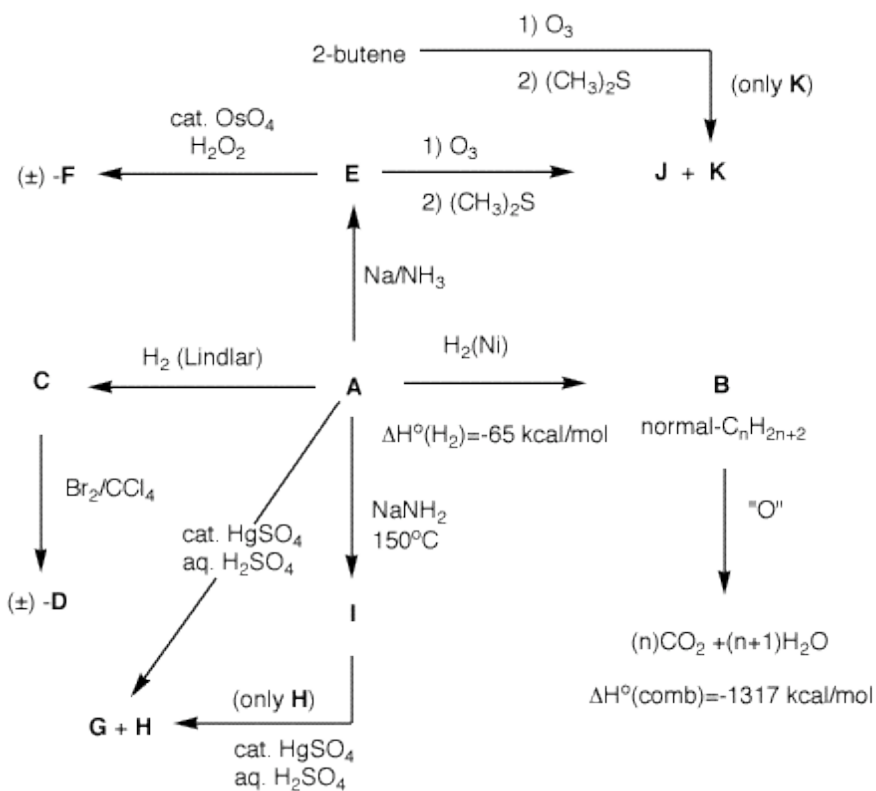


Charles Martin Hall (1863-1914)

exposure to 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

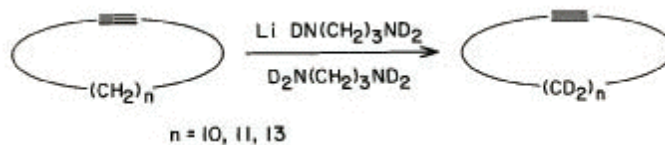
3. Design a synthesis of **muscalure** [(Z)-tricos-9-ene], the sex attractant of the common housefly, *Musca domestica*. As a source of carbon you have available 1-butyne, 1-pentyne and acetylene. You may use 1-pentyne and acetylene only once, i.e., only seven of the carbons may be provided by these 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 H₂ in the presence of Lindlar's catalyst to form **D**. Compound **D** reacts with O₃ to form a single compound **E**, C₃H₆O. On the other hand, compound **B** reacts with aq. H₂SO₄ in the presence of HgSO₄ to give two ketones **J** and **K**. Under the same conditions, **A** gives only **J**. Compound **B** also reacts with Na/NH₃ to give **F**, which itself reacts with Br₂/H₂O to give a pair of constitutional isomers, **G** and **H**. Treatment of either **G** or **H** with aqueous NaOH gives the same compound **I**, C₆H₁₂O, 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 NaNH₂ 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?]