Chem 220 - Organic Chemistry

Problem Set 8

Chapter 9, Alkynes

Due: November 8, 2010

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 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 Corporation (RIP).

The alkyne module in ORGO gives a good review of acetylene chemistry.

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

a) 2-butyne ⟶ 3-octyne (2- Butyne is the only source of carbon.)

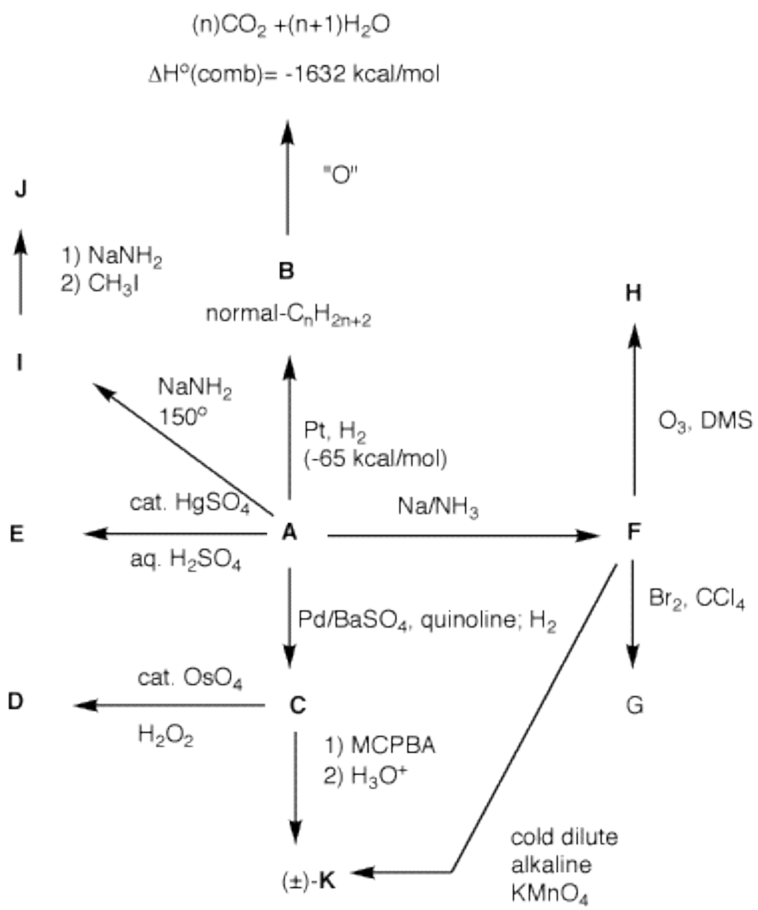
b) 4-octyne ⟶ meso-4,5-dibromooctane

c) 4-octyne ⟶ d,l-4,5-dihydroxyoctane

d) 4-octyne ⟶ meso-4,5-dihydroxyoctane

e) 4-octyne ⟶ d,l-4,5-dibromooctane

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



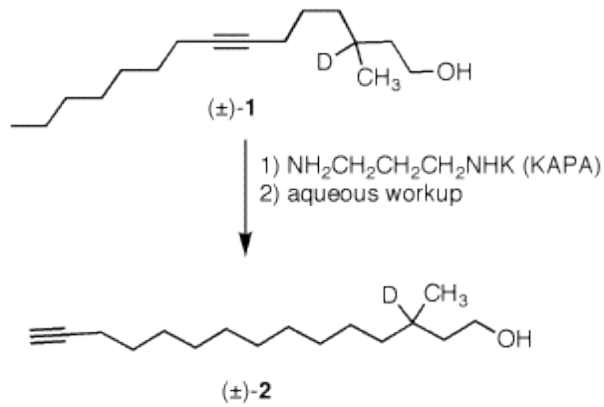
3. Design a synthesis of muscalure [(Z)-tricos-9-ene], the sex attractant of the common housefly, *Musca domestica*. As a source of carbon you have available 1-butyne, 1-pentyne and acetylene. You may use 1-pentyne and acetylene only once, i.e, only seven of the carbons may be provided by these two alkynes. 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^{o}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. When racemic acetylenic alcohol **1**, which bears a deuterium atom at the asymmetric carbon, was exposed to the potassium salt of 1,3-diaminopropane (KAPA, in place of $NaNH_2$) in 1,3-diaminopropane as a solvent, racemic **2** was obtained in a "zipper" reaction after aqueous workup with 97% of the deuterium retained.



a) How many equivalents of KAPA are required in this reaction? Explain.

b) What can be concluded from the the near perfect retention of deuterium in **2**?
c) If compound **1** were of the (*R*)-configuration with hydrogen in place of deuterium, what would the structure of **2** be? Why?
d) What is the role of the aqueous workup? How would you prepare (±)-**2** bearing an additional deuterium attached to the terminal sp-hybridized carbon.? Explain and illustrate.