

Due: Monday, November 1, 2004

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 Gottingen from Yale. Aware of the difficulty Wöhler had had and probably encouraged by Wöhler, Jewett, as a 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, [Thomas Willson](#), a Canadian, and American James Moorhead were unsuccessfully trying to refine aluminum in Spray, NC 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 water. The material was not calcium nor was the gas hydrogen. The pair was calcium carbide and acetylene. Thus was born Union Carbide.

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

1. Two bottles are labeled "**A** - C₈H₁₄" and "**B** - C₈H₁₄". Compound **A** liberates 65 kcal/mol of heat upon hydrogenation to form n-octane. Compound **B** also provides n-octane upon hydrogenation. When treated with Na/NH₃, **A** forms **C**. Compound **C** undergoes ozonolysis to form a single substance **D**. Compound **B** forms succinaldehyde **E** (Cf. pg. 903) and **F**. Treatment of **B** with Br₂/CCl₄ provides two racemic tetrabromides, **G** and **H**. What are the structures **A-H**? Explain and illustrate. [**G** and **H** are not distinguishable.]
2. Design a synthesis of muscalure. As your sources of carbon, you have acetylene, 1-bromopentane, and 2-octyne available to you. All reagents are also available.
3. When (Z,Z)-1,5-cyclooctadiene is treated with borane at ambient temperature, two boranes (C₈H₁₅B) **A** and **B** are formed. When the mixture is heated at elevated temperature, only **A** is observed and the mass balance is excellent (i.e., **B** is not destroyed.). Treatment of **A** with alkaline peroxide converts **A** into achiral **C** (C₈H₁₆O₂). The diastereomer of **C**, namely **D**, which is not formed, is also achiral. When **B** is exposed to alkaline peroxide, compound **E** is formed. **E** is achiral but its diastereomer **F** is a racemate.

a) What are the structures of **A-F**? Explain and illustrate all reactions.

b) When 1-hexyne is exposed to **A**, **G** is formed. **G** reacts with alkaline peroxide to form **H** and **C**. What are **G** and **H**? Provide mechanisms (curved arrow formalisms) for the formation of **C** and **H**.

4. In the first column is a list of 19 compounds. Their assigned numbers are in the second column that is labeled **From**. For example, you are being asked to convert 1 **To** 2, 13, 3, and 4. The first transformation is how do you go from 3-hexyne (1) to 1-hexyne (2). You are to make a list 1 ---> 2 "answer" for each of the 25 transformations. If a number appears twice in a row (e.g., two sixes in row 3), this means that there are two answers. These transformations require one or two steps. Imagine that you were asked to prepare 8 from 1. You can work this synthesis backwards (or forwards) from 8 --> 5 --> 4 --> 1 by following the red numbers.

Compound	From	To	To	To	To
3-hexyne	1	2	13	3	4
1-hexyne	2	16	11	12	18
(E)-3-hexene	3	6	6	9	10
(Z)-3-hexene	4	10	5	17	17
cis-2,3-diethyloxirane	5	8			
trans-2,3-diethyloxirane	6	10			
d,l-3,4-dibromohexane	7	2			
d,l-3,4-dihydroxyhexane	8				
meso-3,4-dibromohexane	9				
meso-3,4-dihydroxyhexane	10				
hexanal (Table 18-3)	11				
2-hexanone (Table 18-3)	12				
3-hexanone (Table 18-3)	13				
2-hexanol (Table 10-1)	14				
1-hexanol (Table 10-1)	15				
1-hexene	16	2	14	15	19
3-hexanol (Table 10-1)	17				
2-heptyne	18				
1-bromohexane	19	15	16	14	