Chem 220 - Organic Chemistry

Problem Set 8

Solution Set

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

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 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 water. The material was not calcium nor was the gas hydrogen. The pair was calcium carbide and acetylene, the

Friedrich Wöhler (1800-1884)

(Wöhler possessed a wry sense of humor) 1 2

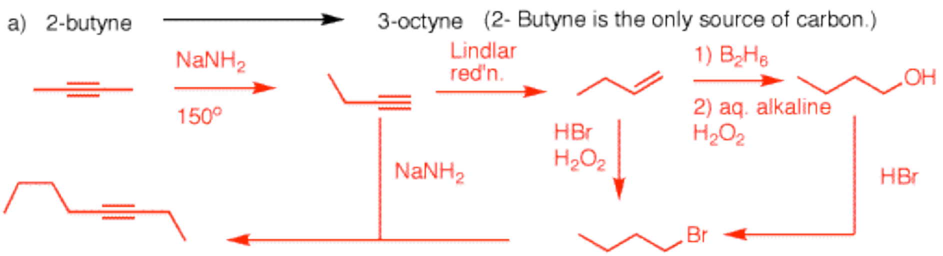
Charles Martin Hall (1863-1914)

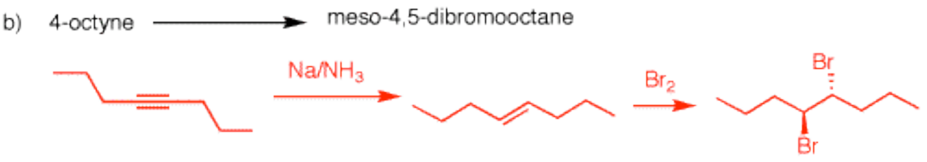
basis for Union Carbide Corporation (RIP).

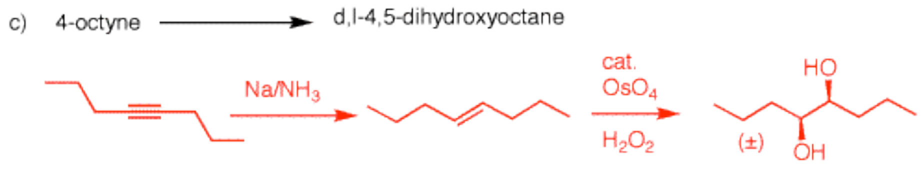
The alkyne module in ORGO gives a good review of acetylene chemistry.

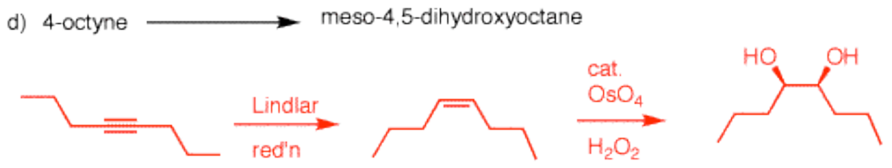
1. Provide reagents for the following reactions. Explain your reasoning. *a) 4 + 4 = 8! This is an alkyne alkylation. Isomerize 2-butyne to 1-butyne. Split the pot of 1-butyne. Use one portion of 1-butyne to form 1-bromobutane by either of the paths shown. Form the anion of 1-butyne and alkylate with 1-bromobutane. When 1-butyne is formed as its sodium salt in the first step, you can save 1/2 as the anion in preparation for the alkylation.*

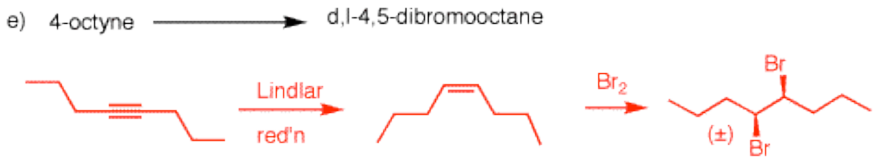
b) You want meso. Anti addition of bromine to an (E)-double bond.
c) You want a racemate. Syn addition of OsO_4 to an (E)-double bond.
d) You want meso. Syn addition of OsO_4 to a (Z)-double bond.
e) You want a racemate. Anti addition of bromine to a (Z)-double bond.





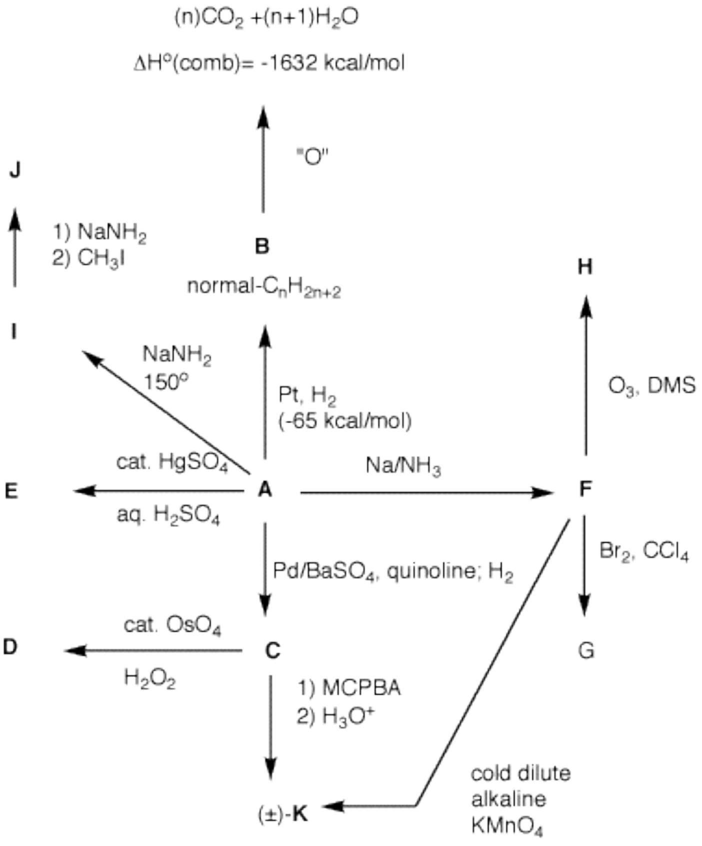






2. Determine the structures **A-K**. Explain your reasoning. *Given that this chapter is about alkynes and all the reactions conducted on compound **A** are applicable to alkynes, it is likely that **A** is an alkyne. [If it quacks like a duck ...]. Because **B** is a normal chain alkane, **A** must be a normal chain as well. The heat of hydrogenation (-65 kcal/mol) is ~ twice the value of an alkene hydrogenation, i.e., absorption of two equivalents of H_2. Is **A** an internal or terminal alkyne? Go to the Heats of Formation Tables! From the heats of formation of 1-butyne, 2 butyne and n-*

butane, we calculate that the heat of hydrogenation of 1-butyne is -69.5 kcal/mol while 2-butyne affords a value of -64.5 kcal/mol. A is an internal alkyne. Since you should know that increasing an alkane chain by a $-CH_2-$ *group adds ~ -157 kcal/mol to the heat of combustion, figure out the heat of combustion of n-butane.* $\Delta H^o_{comb}(n\text{-}C_4H_{10}) = \Delta H^o_{comb}(4C+5H_2) - \Delta H_f{}^o(n\text{-}C_4H_{10}) = -(4 \times 94.05) - (5 \times 68.3) + 30.0 = -341.5 - 376.2 + 30.0 = -687.7$ *kcal/mol. Therefore, the number of* ***additional*** $-CH_2-$ *groups in* ***B*** *can be determined: -1632 = -157n - 688. Then n = 6. Therefore,* ***B*** *is a* C_{10} *compound, n-decane,* $C_{10}H_{22}$*. Is* ***A*** *2-, 3-, 4- or 5-decyne? Follow the path* ***A*** *-->* ***F*** *-->* ***H****.* Na/NH_3 *reduces internal alkynes to (E)-alkenes. Ozonolysis of* ***F*** *gives only one product,* ***H****.* ***A*** *must be symmetrically substituted, i.e., 5-decyne! F is (E)-5-decene and* ***H*** *is the five carbon, straight chain aldehyde, pentanal. With* ***A*** *and* ***F*** *known, the rest fall into place:*



G *= meso-5,6-dibromodecane (anti addition to a symmetrically substituted double bond.)*

C *= (Z)-5-decene (syn addition to a triple bond; Lindlar)*

D *= meso-5,6,dihydroxydecane (syn addition to a symmetrically substituted double bond.)*

E *= 5-decanone (one product from hydration of a symmetrical alkyne).*

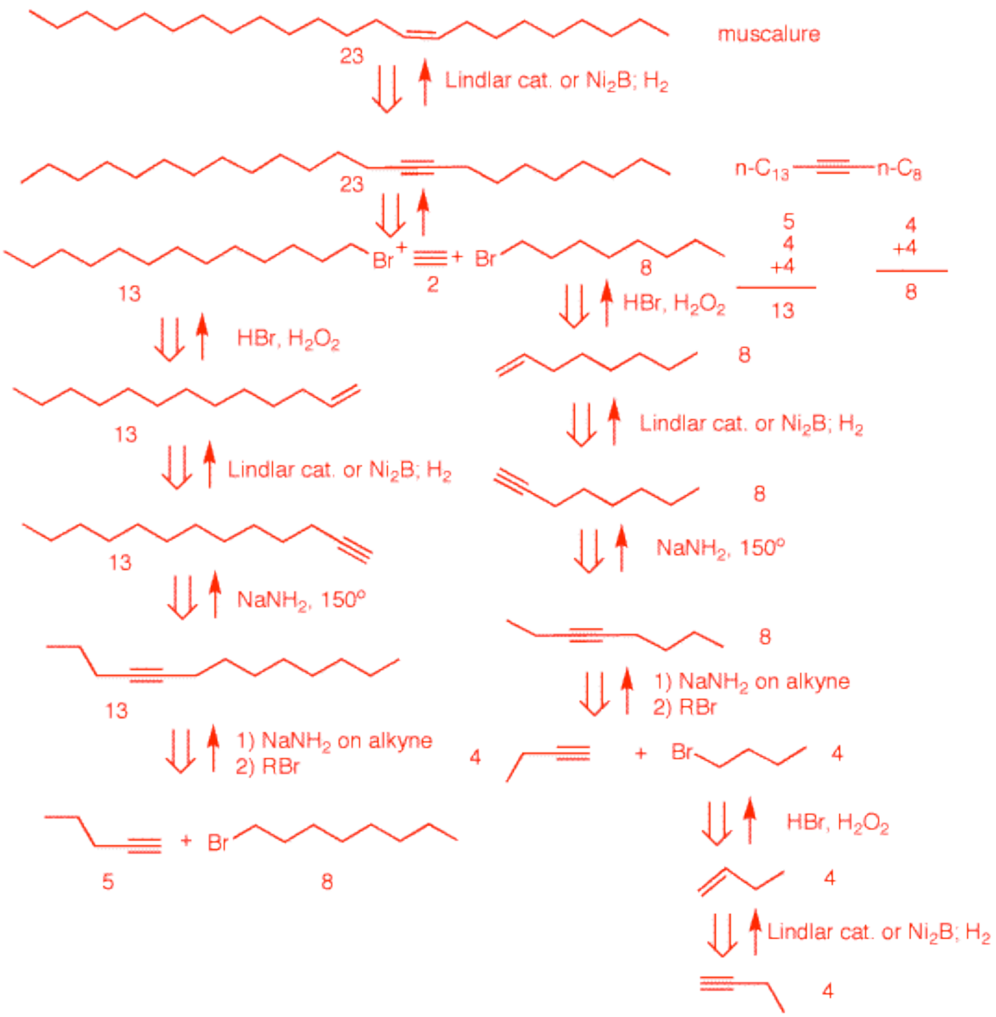
I *= 1-decyne ("zipper" reaction)*

J *= 2-undecyne (methylation of the anion of* ***I****)*

K *= rac.-5,6-dihydroxydecane (syn epoxidation of (Z)-double bond; anti opening with aqueous acid.)*

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. *Muscalure is a C_{23} straight chain alkene with a (Z)-double bond at C_9. Given the ground rules of the problem, use a double acetylene alkylation along with syn reduction to afford muscalure. One needs to prepare 1-bromotridecane (C_{13}) and 1-bromooctane: 13 = 5 + 4 +4; 8 = 4 + 4. {Note: acetylene and 1-pentyne are used once. Follow the retrosynthetic arrows to see how 1-bromooctane is prepared. As in* ***1a****, there is more than one way to convert a terminal alkene to a primary bromide. 1-Bromooctane is also used in the synthesis of 1-bromotridecane. How will you know if your synthesis was a success? Flies will swarm about you.*

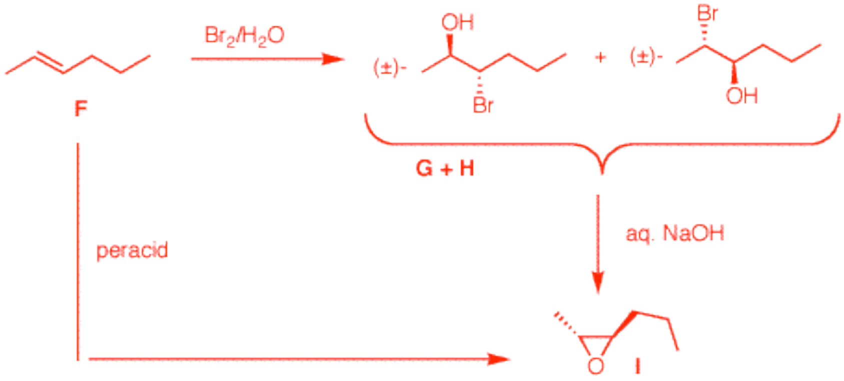


4. Estimate the heat of formation of 1-,2-,3- and 4-octyne. Equilibration of any one of these isomers with KOH at 200°C produces about as much 2-octyne as 3-octyne both of which individually exceed the amount of 1-octyne. However, the amount of 4-octyne is less than the amount of 2- or 3-octyne. Explain. [Hint: 2- and 3-octyne have an entropic advantage over 4-octyne.] *Using the heats of formation table, one obtains the values for the three hexynes. The estimate for 3-octyne and 4-octyne can come from 3-hexyne. The value for 3-decyne comes from NIST (National Institute of Standards and Technology) as do the reported values. The correction is -5 kcal/mol/CH_2 increase in chain length. Less terminal alkyne is expected than internal alkyne because the former have a higher heat of formation. There are two ways to form 2- and 3-octyne but only one way to form the symmetrical 4-octyne.*

Alkyne	ΔH_f^o Hexynes (kcal/mol)	Correction for Chain Length (kcal/mol)	Estimated ΔH_f^o for Octynes (kcal/mol)	Reported Values ΔH_f^o (kcal/mol)
1-hexyne	+29.2			
2-hexyne	+25.7			
3-hexyne	+25.2			
3-decyne	+5.2			
1-octyne (from 1-				

1-octyne (from 1-hexyne)		-10	+19.2	+19.3
2-octyne (from 2-hexyne)		-10	+15.7	+15.2
3-octyne (from 3-hexyne)		-10	+15.2	?
3-octyne (from 3-decyne)		+10	+15.2	?
4-octyne (from 3-hexyne)		-10	+15.2	+14.4

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**. ***A*** *and* ***B*** *have the same connectivity of carbon atoms.* Compound **A** reacts with H_2 in the presence of Lindlar's catalyst to form **D**. ***A*** *forms a (Z)-double bond.* Compound **D** reacts with O_3 to form a single compound **E**, C_3H_6O. ***D*** *is a symmetrically substituted double bond (single monofunctional product) as is* ***A*** *a symmetrically substituted triple bond.* ***E*** *cannot be acetone because ozonolysis would have produced it from 2,3-dimethyl-2-butene (tetramethylethylene), which cannot be derived from an alkyne.* ***E*** *must be propionaldehyde,* CH_3CH_2CHO*. Therefore,* ***D*** *is (Z)-3-hexene and* ***A*** *is 3-hexyne.* 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**. ***B*** *is either 1-hexyne or 2-hexyne. 1-Hexyne would give only 2-hexanone upon* Hg^{++}*-catalyzed hydration. 2-Hexyne would give 2- and 3-hexanone. These two ketones are* ***J*** *and* ***K***; ***B*** *is 2-hexyne.* Under the same conditions, **A** gives only **J**. *Since* ***A****, 3-hexyne, affords only* ***J*** *under these conditions,* ***J*** *must be 3-hexanone and* ***K*** *is 2-hexanone.* Compound **B** also reacts with Na/NH_3 to give **F**, *(**F** is (E)-2-hexene)* which itself reacts with Br_2/H_2O to give a pair of constitutional isomers, **G** and **H**. *Anti addition of the elements of HOBr gives* ***G*** *and* ***H****. See below*. 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. *Halohydrin formation followed by base treatment gives an even number of* S_N2 *inversions of stereochemistry: two. Peracid gives zero inversions. Therefore, the two reaction sequences give the same trans epoxide* ***I****.* What are the structures of **A**-**K**? Explain and illustrate. [Note: **G** and **H** are not distinguished from one another. Pay attention to stereochemistry.]

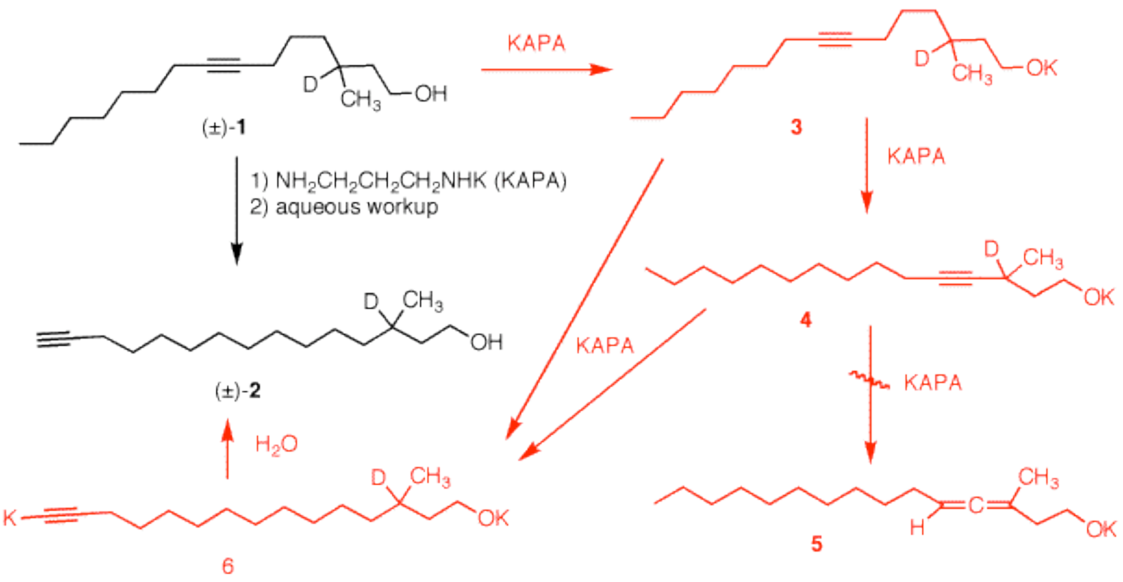


6. When racemic acetylenic alcohol **1**, which bears a deuterium atom at the asymmetric carbon, was exposed to the potassium salt of 1,3-diaminopropane

(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. *The diamine has a pKa (Table) similar to ammonia (pKa = 35). Its conjugate base (KAPA) will deprotonate the alcohol (pKa = 16) to form **3**. The zipper reaction requires only catalytic KAPA but the terminal alkyne 2 (pKa = 25) requires stoichiometric base for deprotonation. At least two equivalents of KAPA are required.*

b) What can be concluded from the the near perfect retention of deuterium in **2**? *The zipper reaction can migrate the triple bond three bonds to*



*the right (structure **4**) but it can't abstract the deuterium to form allene **5**. If **5** were formed, the zipper could still move the triple bond to the left to form **2**. This inability to remove the deuterium is not a deuterium isotope effect. It is a kinetic issue wherein the propargylic CH_2 (next to the triple bond) are more acidic than propargylic methine hydrogens (or deuterium atoms).*

c) If compound **1** were of the (*R*)-configuration with hydrogen in place of deuterium, what would the structure of **2** be? *Why? The inability to form **5**, which is racemic, means that the there is no configurational change at the asymmetric carbon. Compound **2** would be optically active and of the (R)-configuration.*

d) What is the role of the aqueous workup? *To protonate the* *dianion 6.* How would you prepare (±)-**2** bearing an additional deuterium attached to the terminal sp-hybridized carbon.? Explain and illustrate. *"Protonate" with D_2O which will add deuterium to the acetylene anion and the alkoxide. Wash this compound with water, which will exchange -OD for -OH and leave the alkyne deuterium bond as well as the original C-D bond unaffected.*