Chem 220 - Organic Chemistry

Problem Set 8, Solution Set

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 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

Friedrich Wöhler (1800-1884)

(Wöhler possessed a wry sense of humor) 1 2

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. *Structure A seems to be the center of action. From its reactions it appears to be an alkyne. How do we learn about its structure? Hydrogenation over a nickel catalyst affords a straight chain alkane **B** (normal chain). The heat of hydrogenation is too much for a double bond. Using 3-hexyne and 1-hexyne as models for internal and terminal alkynes in the <u>heats of formation table</u>, the respective heats of the respective heats of hydrogenation are -65.5 and -69.2 kcal/mol for the two alkynes. The heat of formation of n-hexane is -39.9 kcal/mol, the product of hydrogenation. Clearly, A looks like an internal alkyne. The heat of combustion of this n-alkane gives a clue to the chain length. Compute the heat of combustion of n-hexane (C_6H_{14}) from the elements: 6 C (-94.05 kcal/mol) + 7H_2 (-68.3 kcal/mol) = -1042 kcal/mol. The heat of combustion of n-hexane is -1042 - (-40 (ΔH_f^o)) = -1002*
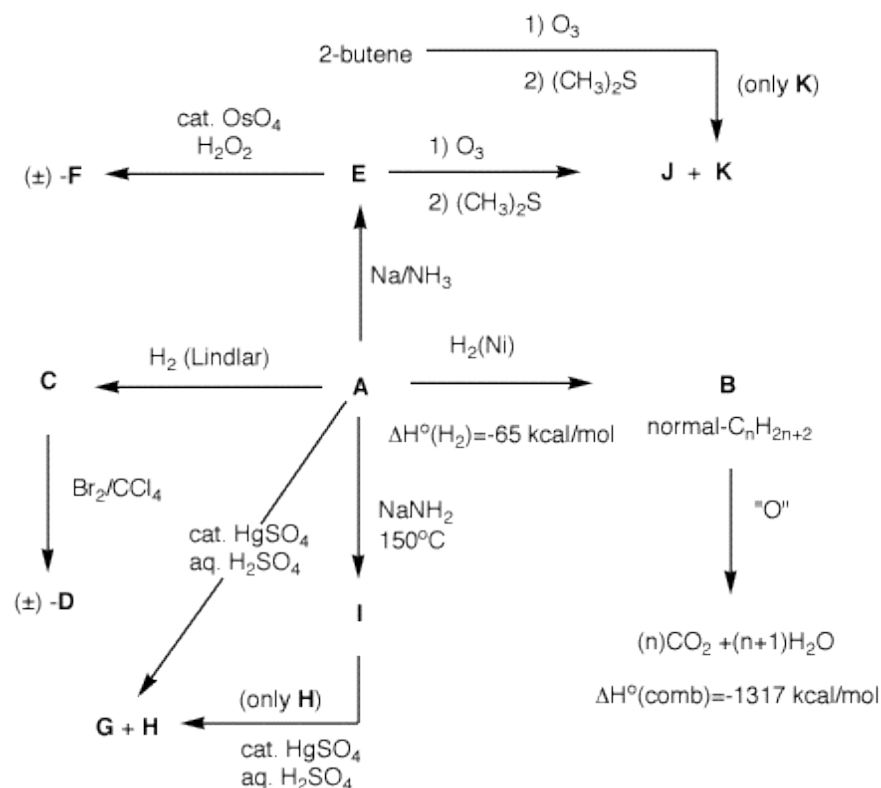
Note: There is another way to find the number of carbons and hydrogens in B:

$$\Delta H^o(comb) = \Delta H^o(comb\ C_n) + \Delta H^o(comb\ H_{n+1}) - \Delta H_f^o$$

$$\Delta H^o(comb) = nC + (n+1)H - 5n$$

(The term 5n is -5 kcal/mol/CH_2 where n = # carbons.) Now,

-1317 = -94.05n + [(n+1)(-68.3)] - (-5n)
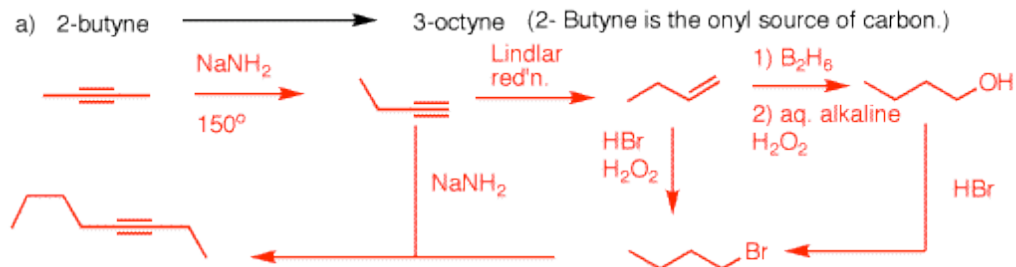
-1249 = -157n

n = 7.9 or C = 8

n = 7.9 or C = 8.

*kcal/mol. This value is less negative than -1317 kcal/mol by -315 kcal/mol. The heat of combustion for an unstrained -CH_2- group is -157 kcal/mol. The value -315 kcal/mol accounts for two more -CH_2- groups. Thus, **B** is n-octane. A is either 2-, 3- or 4-octyne. Na/NH_3 reduction of **A** gives **E**, which contains an (E)-double bond. Ozonolysis of **E** gives two products. This eliminate a symmetrical alkyne for **A** and symmetrical alkene for **E**. **K** is acetaldehyde since it is the only product of ozonolysis of 2-butene. Therefore, **J** is hexanal (C_6 straight chain aldehyde). **A** is 2-octyne; **E** is (E)-2-octene. Syn, 1,2-addition of two hydroxyl groups to **E** gives **F** [(2R*, 3R*)-2,3-octanediol] as a racemate]. Lindlar reduction of **A** affords **C** [(Z)-2-octene]. **C** upon anti addition of Br_2 gives **D**, (±)-(2R*, 3R*)-2,3-dibromooctane. $NaNH_2$ isomerization of **A** forms **I** (1-octyne). Hydration of the terminal alkyne **I** gives only **H**, 2-octanone, which also forms along with **G** (3-octanone) upon hydration of **A**.*
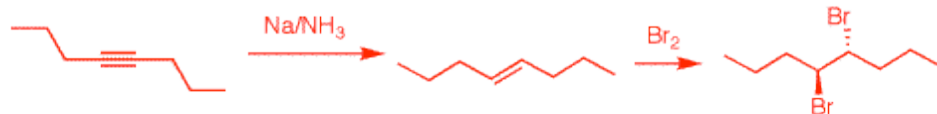
2. Provide reagents for the following reactions. Explain your reasoning.

*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 OsO₄ to an (E)-double bond.
d) You want meso. Syn addition of OsO₄ to a (Z)-double bond.

a) 2-butyne $\longrightarrow$ 3-octyne   (2- Butyne is the onyl source of carbon.)

b) 4-octyne $\longrightarrow$ meso-4,5-dibromooctane

c) 4-octyne $\longrightarrow$ d,l-4,5-dihydroxyoctane
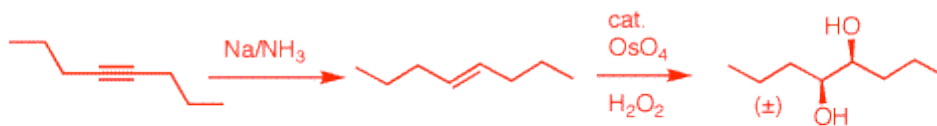
d) 4-octyne $\longrightarrow$ meso-4,5-dihydroxyoctane

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.

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: actylene and 1-pentyne are used once. Follow the retrosynthetic arrows to see how 1-bromooctane is prepared. As in 2a, there is more than one way to convert a terminal alkene to a primary bromide. 1-Bromooctane is also used in the synthesis
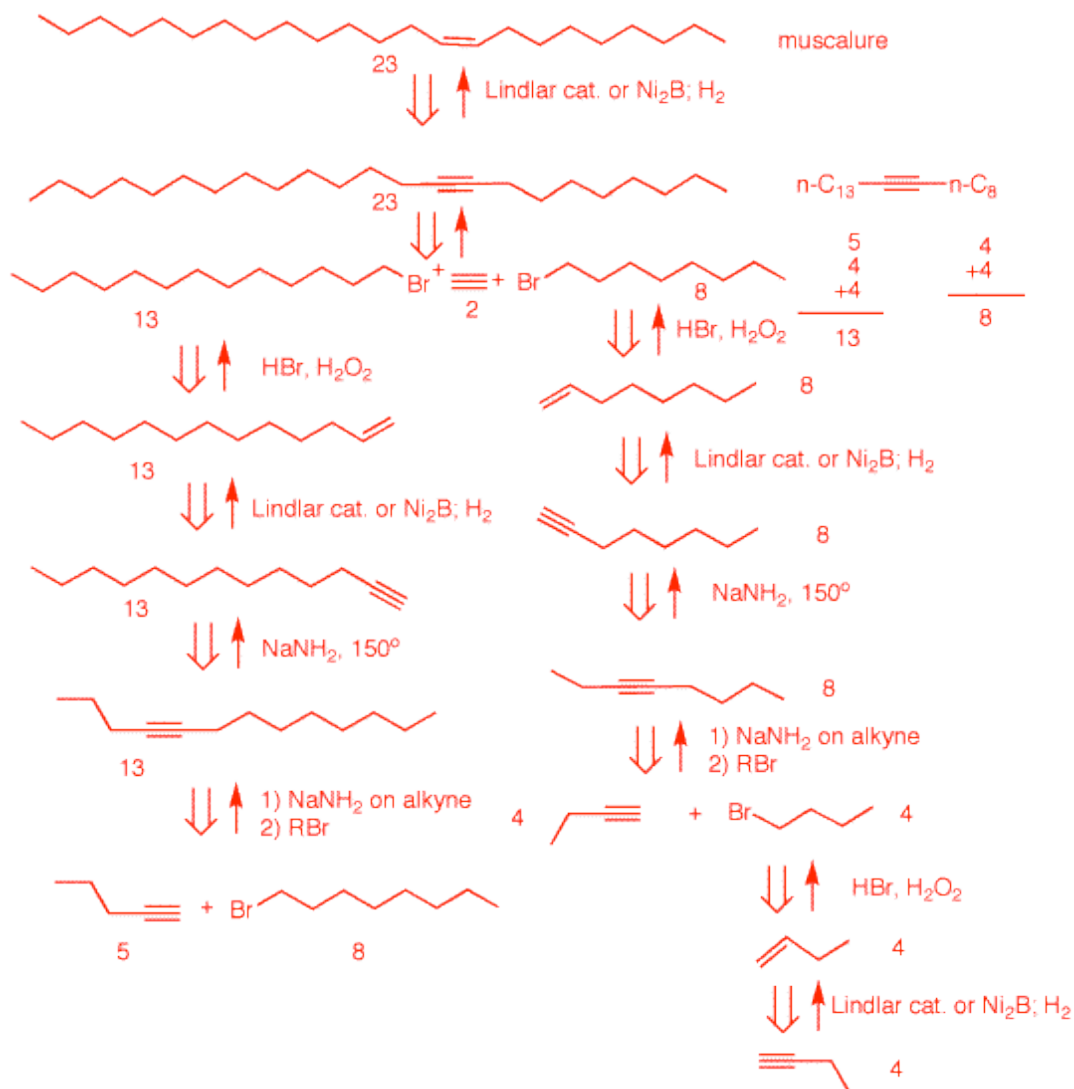
of 1-bromotridecane.
How will you know if
your synthesis was a
success? Flies will
swarm about you.

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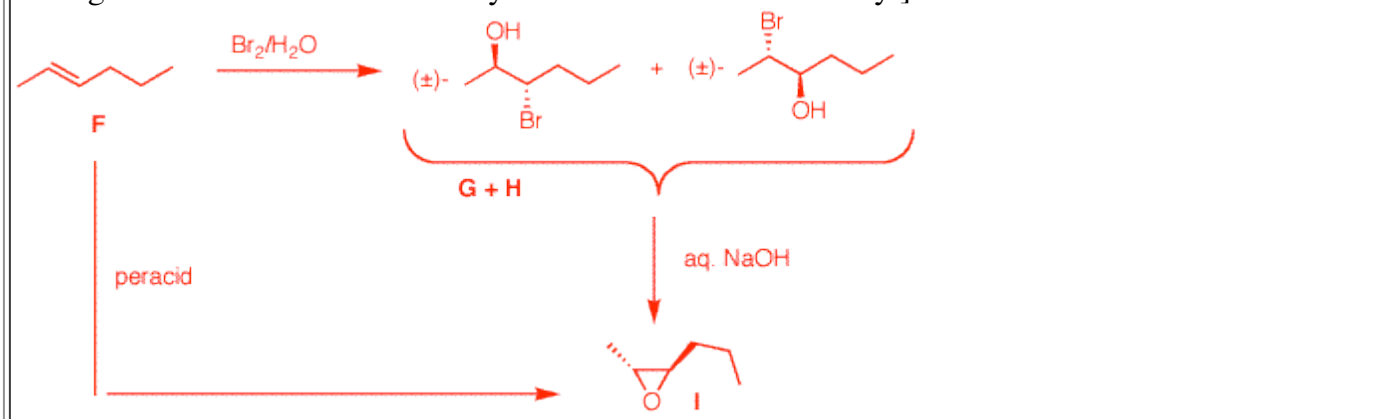
6. The reaction on the right, which was conducted on three different cycloalkynes, was reported in 1985 by Suzanne Abrams and Angela
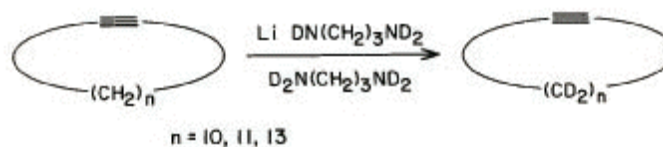
Shaw of the National Research Council of Canada. Rather than use $NaNH_2$ as your text suggests, they used the lithium salt of tetradeutero-1,3-diaminopropane in tetradeutero-1,3-diaminopropane as a solvent at room temperature.

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

n = 10; Cyclododecyne
n = 11; Cyclotridecyne
n = 13; Cyclopentadecyne

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.

n-Butyllithium is the conjugate base of the "acid" butane, pKa = ~50. 1,3-Diaminopropane can be modeled by ethylamine, pKa = 35. The amine is the weaker acid; it is deprotonated by n-butyllithium.

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

If internal normal alkynes can be isomerized to terminal alkynes, then the same thing happens with cycloalkynes, except that there is no irreversible last step. The final position of the triple bond can be between any two contiguous carbons. Propargylic hydrogens are to triple

cyclododecyne

(propargylic H's shown)
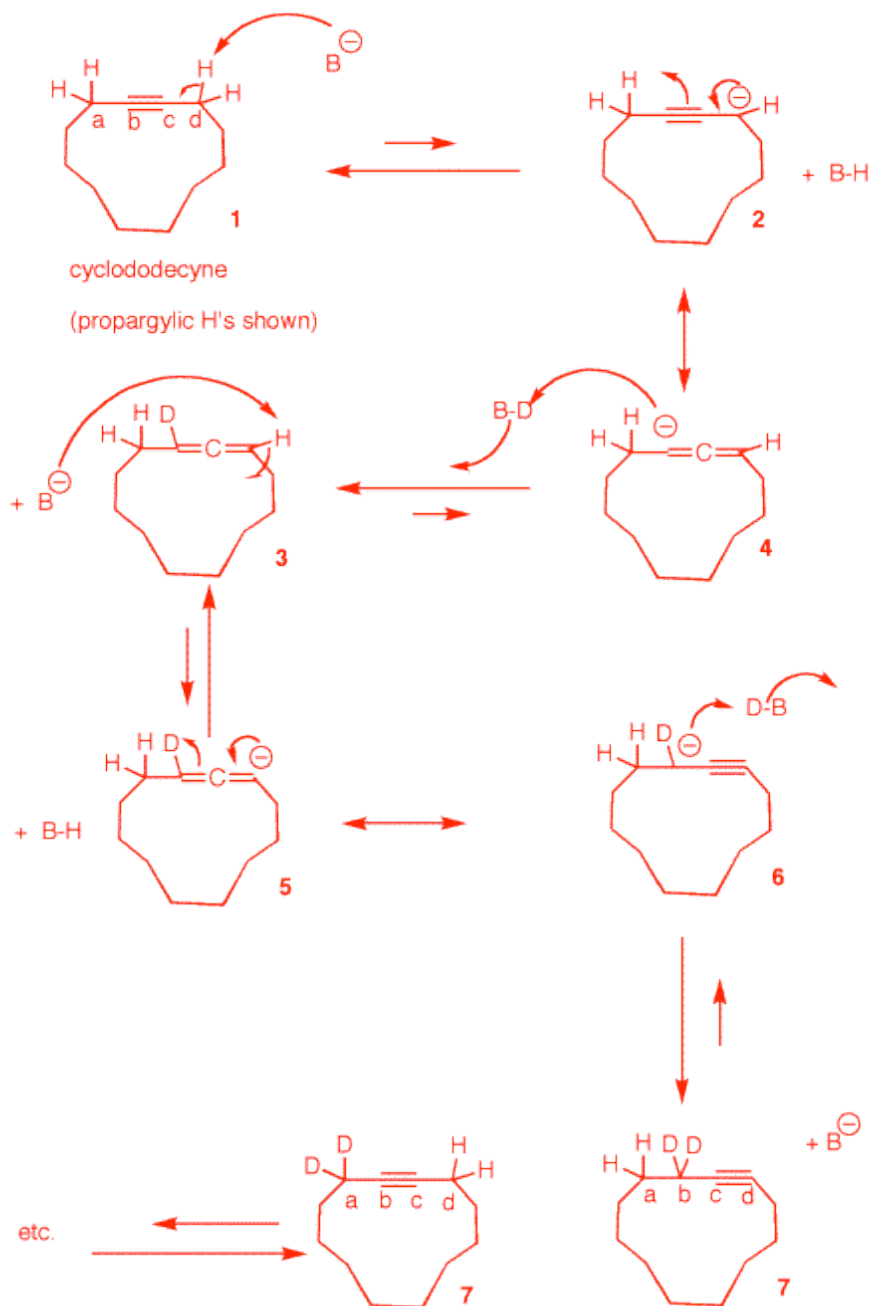
bonds what allylic hydrogens are to double bonds. They are about the same pKa as the amine and are reversibly deprotonated to form a propagylic anion **2** who resonance structure is allenyl anion **4**. [In this mechanism, the amide base is B$^-$; the deuterated amine is B-D.] Deuteration of anion 4 leads to deutereated allene **3**. Deprotonation of the vinyl hydrogen of allene **3** affords allenyl anion **5** whose resonance structure is deuterated propargyl anion **6**. Deuteration of this species provides dideuterated cyclododecyne. Note that the position of the triple bond in **1** was between carbons a and b. In **7** the triple bond is between carbons c and d. The triple bond "zippers" its way around te ring.