

Alkynes, Part I

Reading: Wade chapter 9, sections 9-1- 9-8

Study Problems: 9-29, 9-32, 9-36

Key Concepts and Skills:

- Explain why alkynes are more acidic than alkanes or alkenes; show how to generate nucleophilic acetylide anions and heavy-metal derivatives.
- Propose effective single-step and multi-step syntheses of alkynes.
- Show how the reduction of an alkyne leads to an alkene with the desired stereochemistry

Lecture Topics:

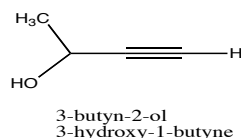
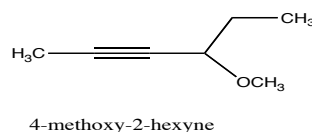
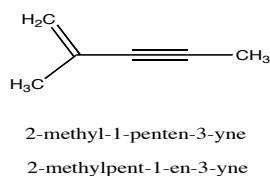
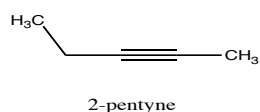
I. Structure of Alkynes

Alkynes contain the carbon-carbon triple bond; each triple bond introduces two degrees of unsaturation, and thus a compound containing only one triple bond has the molecular formula C_nH_{2n-2} .

Nomenclature

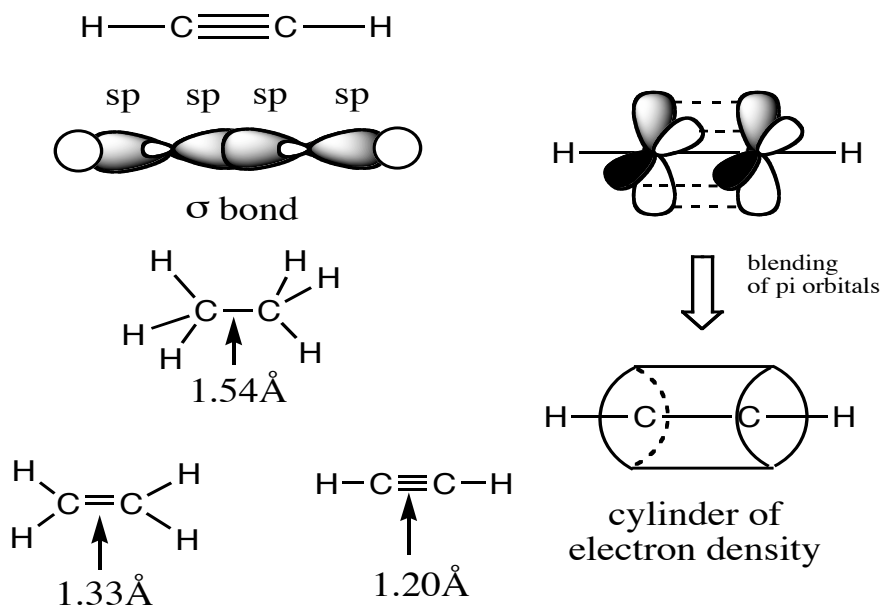
Again, we find the longest chain containing the alkyne and use that as a base name. Number the substituents as usual. Compounds also containing double bonds are named as enynes, and containing alcohols (which have a higher priority than triple bonds) are called ynols.

Examples:



Alkynes are linear with sp hybridization at carbon; each sp carbon has two unhybridized p -orbitals which overlap to form two π bonds perpendicular to each other. The electron density of the two π bonds blend to form a cylinder of electron density around the sigma bond axis. Note also that C-C triple bonds are shorter than C-C single or C-C double bonds because of the high degree of s character (50%) for the overlapping sp orbitals

which form the central C-C sigma bond. Remember that s orbitals are closer to the nucleus, and thus electrons in s orbitals are more tightly held.



II. Acidity of Terminal Alkynes

HA	A ⁻	s character	pKa
		25%	50
		33%	44
$\text{H}-\text{C}\equiv\text{C}-\text{H}$		50%	25

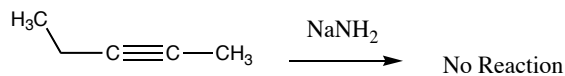
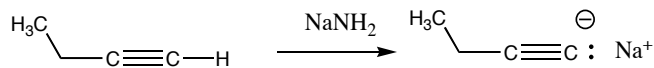
Terminal alkynes are more acidic than alkenes or alkanes; the negative charge on the conjugate base is in a carbon sp orbital. The negative charge in an sp hybrid orbital is more stable than in an sp² or sp³ orbital because it is closer to the nucleus. Electrons in orbitals with high s character have less charge separation.

Note: NH_3 (HA) \rightarrow NH_2^- (A⁻) (pKa=35)

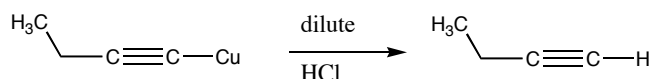
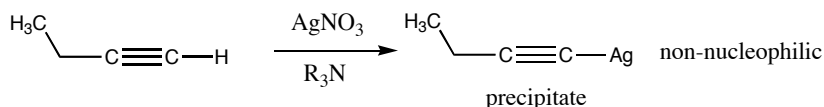
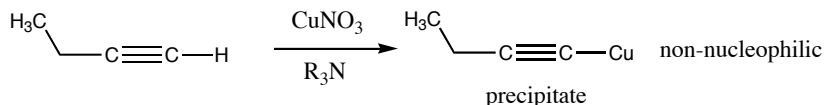
CH_3OH (HA) \rightarrow CH_3O^- (A⁻) (pKa=16)

Thus, terminal alkynes may be deprotonated by H_2N^- , but not by CH_3O^-

Only terminal alkynes can be deprotonated, internal alkynes are unaffected by base treatment:



Testing for terminal alkynes:

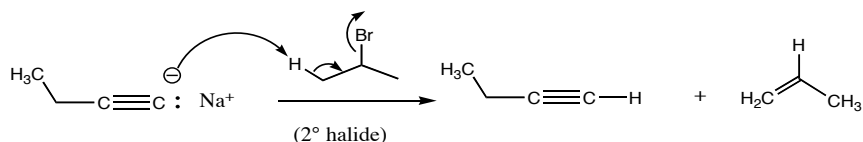
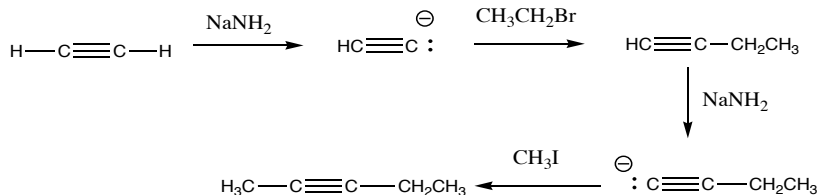
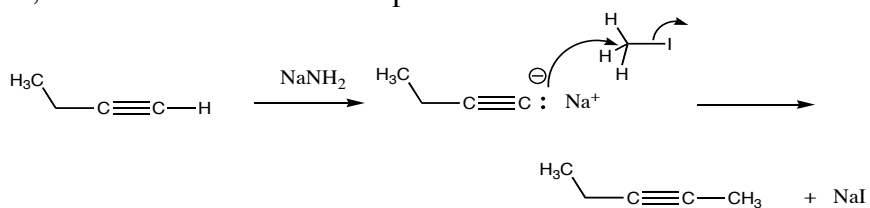


Terminal alkynes also react with Cu(I) and Ag(I) salts to form copper acetylides and silver acetylides, respectively. These insoluble compounds form characteristic precipitates that indicate the presence of terminal (and not internal) alkynes. A mild acidification with dilute HCl re-forms the terminal alkyne.

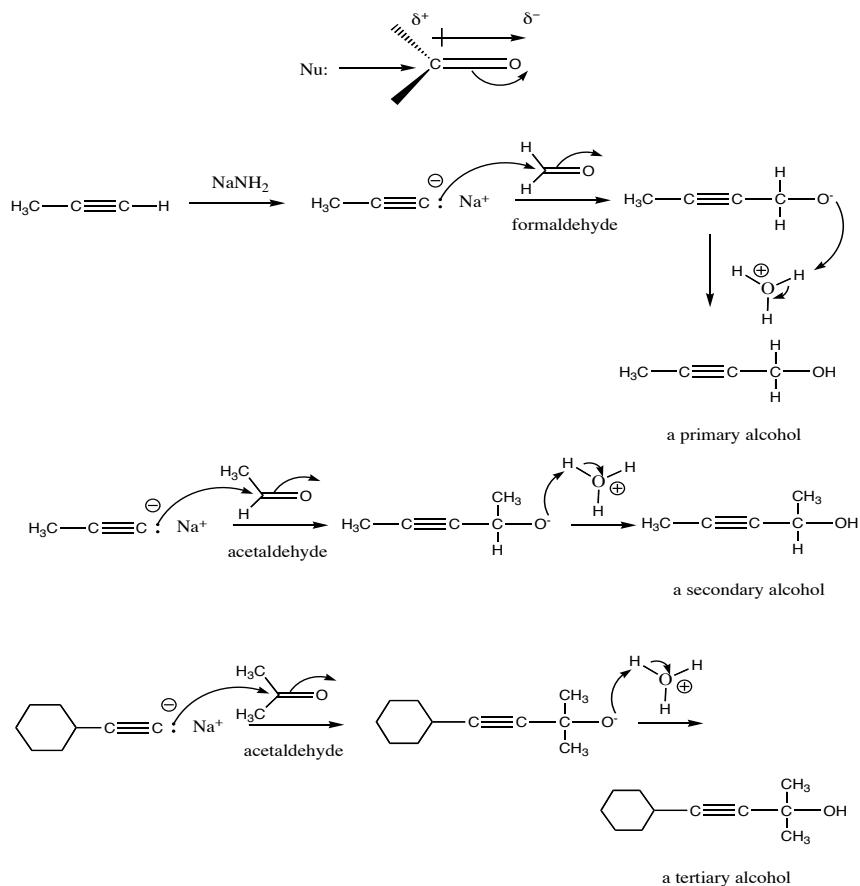
III. Alkyne Synthesis

a. Alkylation of acetylide anions

Alkali-metal acetylides (Li, Na) are good nucleophiles that can react with unhindered (methyl, primary) alkyl halides to form internal alkynes in good yields. With secondary alkyl halides, E2 elimination often takes place.

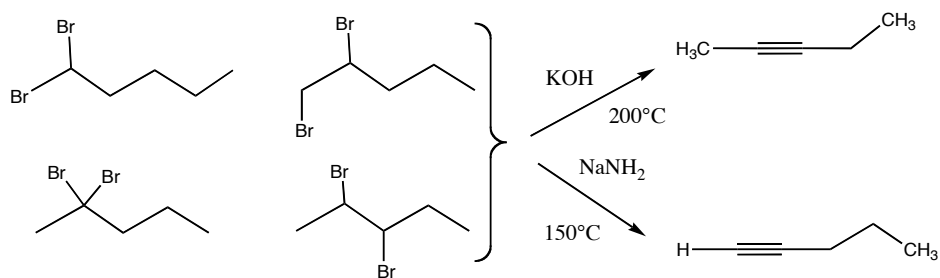
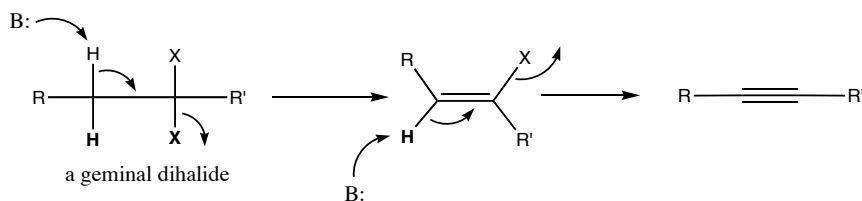
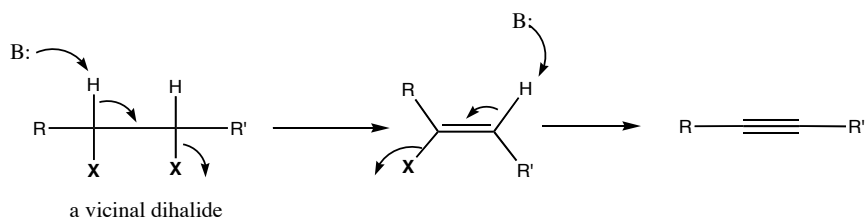


Alkynes can also attack the carbonyl groups of aldehydes and ketones to form primary, secondary, and tertiary alcohols. Note that the dipole of the carbonyl group places a partial positive charge on the carbonyl carbon, thus making that carbon a good electrophile for attack by the nucleophilic alkynyl anion:

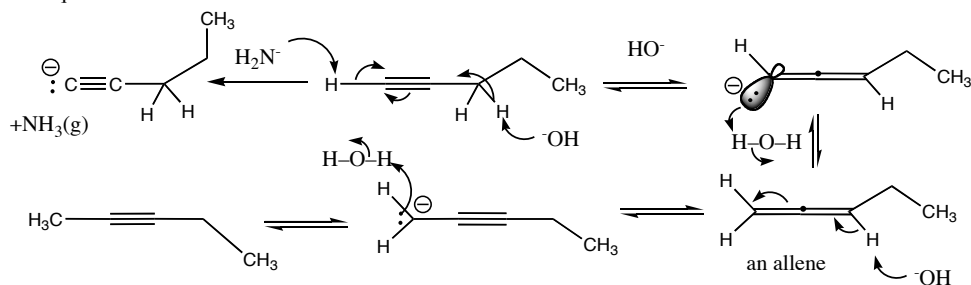


b. Synthesis of alkenes by elimination reactions (E2)

Elimination of two molecules of H-X from vicinal or geminal dihalides occurs under basic conditions. Low yields are sometimes encountered because of base-catalyzed rearrangements, leading to multiple products. With KOH at 200°C , the most stable (internal) alkyne is produced in excess. With NaNH_2 , which can deprotonate terminal alkynes irreversibly, the terminal alkyne is produced in excess:

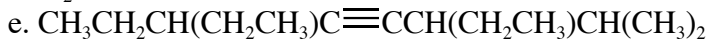
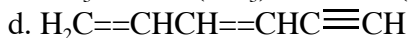
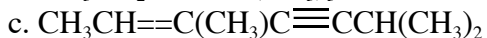
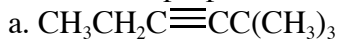


Base-promoted isomerization: only NH_2^- irreversibly deprotonates terminal alkyne, removing it from the equilibria:



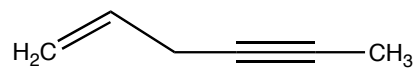
Additional Problems for practice:

1. Provide proper IUPAC names for the following:

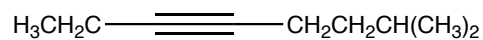


2. How might you prepare the following compounds from acetylene and any needed alkyl halide?

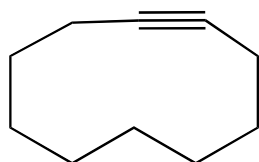
a.



b.

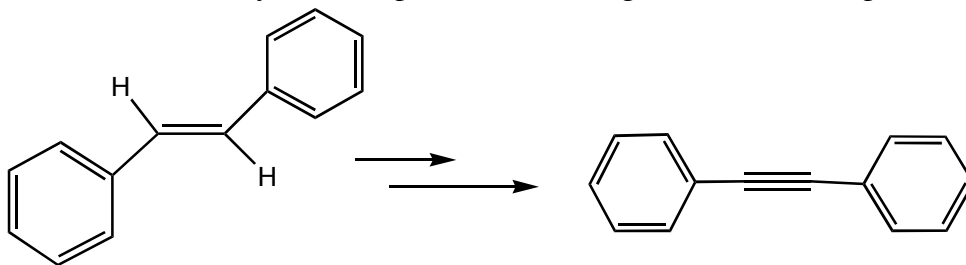


c.

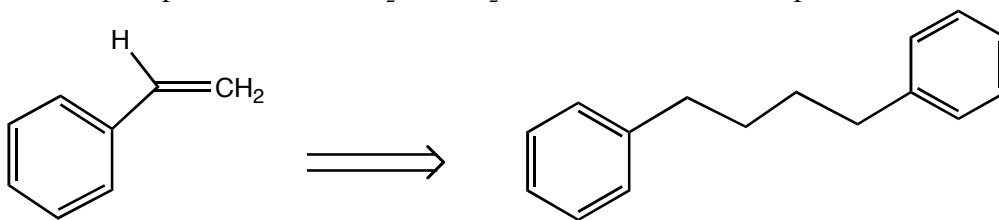


cyclodecyne

3. How would you accomplish the following conversion (2 steps):



4. Assuming that H_2/Pd can reduce alkynes to alkanes, how would you synthesize the following compound starting with styrene, and using only the reagents Br_2 , $\text{HBr}/\text{peroxides}$, NaNH_2 , and H_2/Pd ? More than one step is needed.



styrene