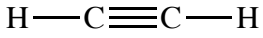
Lecture Notes
Chem 51B
S. King

Chapter 11 Alkynes

I. Introduction: Alkynes are hydrocarbons with carbon-carbon triple bonds.



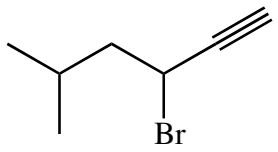
terminal alkyne:

internal alkyne:

II. Nomenclature:

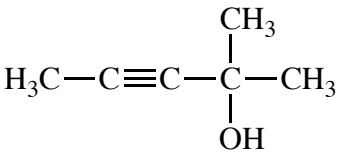
Simple alkynes are named much like alkenes, except the ending is changed from **-ane** to **-yne.**

- Number the chain from the end closest to the triple bond.
- Substituents are named as they are in alkenes.



- If an –OH group or double bond is also present in the molecule, number giving the alcohol and/or double bond priority over the triple bond.

Priority: –OH > Alkene > Alkyne

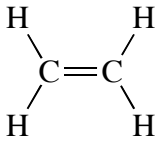


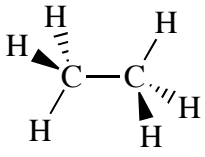
One group containing a carbon-carbon triple bond is used in common nomenclature:

the propargyl group:	*Example:*
$HC{\equiv}CCH_2$——	$HC{\equiv}CCH_2OH$

III. Acidity of 1-Alkynes

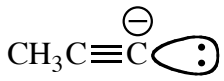
1-Alkynes *(terminal alkynes)* are significantly more acidic than the corresponding alkene or alkane:

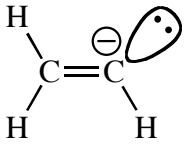


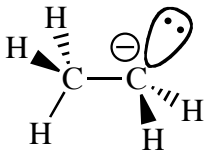


Why is acetylene so much more acidic than ethane?

look @ conjugate bases on the next page:

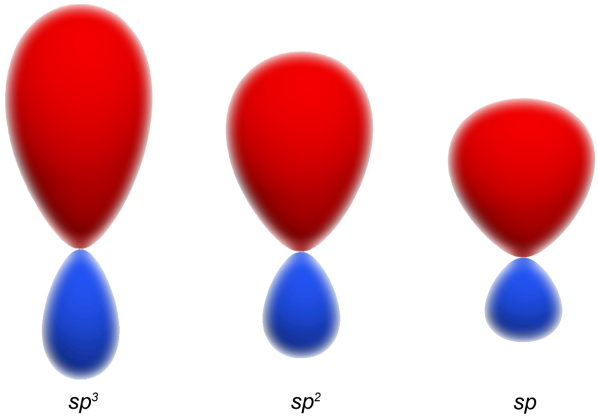




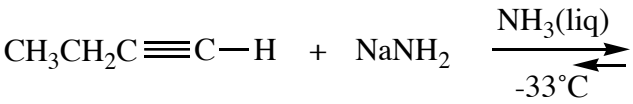


- When carbon has more "***s character,***" the electrons are closer to the nucleus - in effect, carbon w/ more ***s-character*** is more electronegative - electrons are pulled in toward the nucleus ∴ they are lower in energy and less available for reaction.

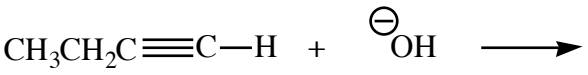
Compare an sp^3, sp^2 and sp orbital:



☞ A terminal alkyne can be deprotonated by a strong base. When deprotonating an acid, you must choose a base that is *stronger than the conjugate base formed* when you remove the proton. An amide ion ($^{-}NH_2$) or H^- work well for alkynes because they are stronger bases than acetylide ion:

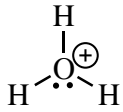
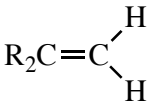
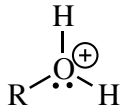
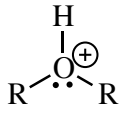
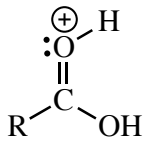


Don't try to use NaOH for this! It is not a strong enough base *(it is a weaker base than acetylide ion)*!!

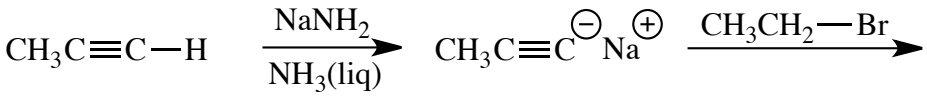


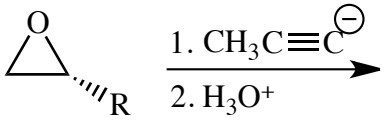
Relative Acidities:

Approximate pK_a values *(rounded to nearest 5)*

< 0	5	10	15	25	35	45	50
			ROH	$RC{\equiv}CH$			CH_4
			H_2O				RCH_3
							
							

The anion derived from deprotonation is a ***good nucleophile***. It reacts with **primary halides** and **methyl halides** to give internal alkynes, and epoxides to give alcohols:

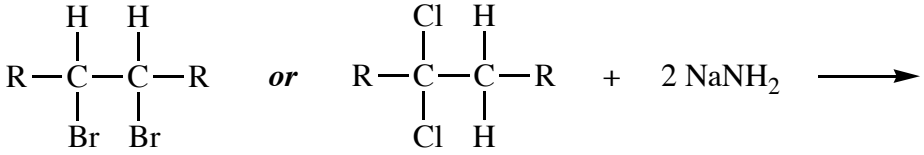




☞ ***Careful!*** *Acetylide ion is a great nucleophile but also a strong base! Use primary or methyl alkyl halides or tosylates only. Reaction with secondary alkyl halides will give E2 rather than SN2 reaction.*

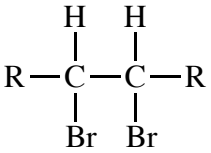
IV. Preparation of Alkynes

Alkynes are prepared by treating vicinal or geminal dihalides with two equivalents of strong base (Chapter 8.10). The base we will use is NH_2^-.



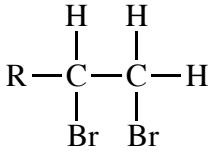
vicinal dihalide *geminal dihalide*

This is a double elimination:



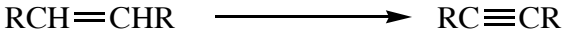
☞ ***Careful!*** *If you are making a terminal alkyne, you need 3 equivalents of NH_2^-. Why? As soon as the terminal alkyne is formed, it will be deprotonated by the strongly basic NH_2^- (acid/base reactions are faster than E2 reactions). If you don't use 3 equivalents, you will run out of base and will get incomplete conversion.*

Count NH_2^- molecules:



✶✶ If you are making a terminal alkyne, you must add a final protonation step!

Vicinal dihalides are made from alkenes and bromine! The conversion of an alkene to an alkyne, therefore, involves two steps:



or if terminal, three steps:

V. Electrophilic Addition Reactions of Alkynes

The π-bonds of alkynes are electron rich, and like alkenes, react with electrophilic reagents to give electrophilic addition products. The same electrophilic reagents that add to alkenes also add to alkynes. Because the product of an electrophilic addition reaction is an alkene, a second electrophilic addition can occur.

A. Addition of Hydrogen Halides to Alkynes

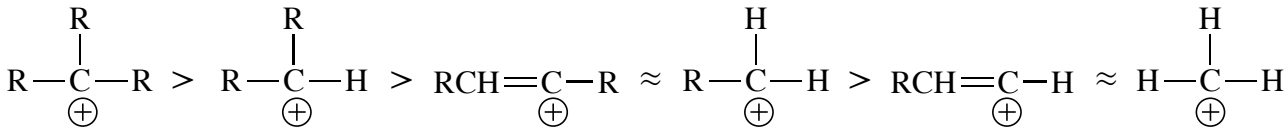
Alkynes undergo addition reactions with hydrogen halides.

Mechanism:

Important point about this mechanism: There is some doubt about whether a vinylic cation is actually formed in this reaction. *Why?*

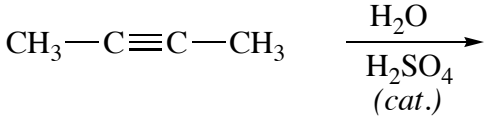
1) vinyl cations are very unstable 2) trans products predominate 3) more than one halogen appears in the rate law!

Look at the stability of a vinylic cation:



B. Addition of Water to Alkynes: Hydration

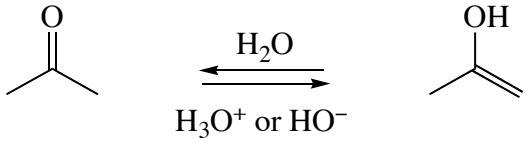
Addition of water in the presence of a strong acid catalyst forms ketones:



Mechanism:

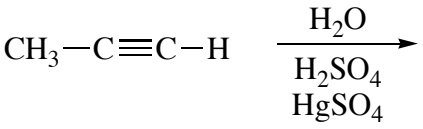
☛ **Important points about this reaction:**

- Carbonyl compounds with α-hydrogens are in equilibrium with vinylic alcohol isomers called enols. The two isomers that interconvert are called ***tautomers***.

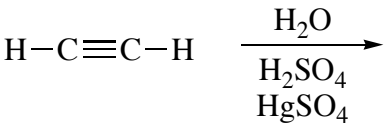


- **Tautomerization**: The conversion of an enol to a ketone by protonation at the carbon atom of the double bond, and deprotonation at the oxygen atom.
- ***Most*** carbonyl compounds are considerably more stable than their corresponding *enols*, so **when an *enol* is formed in a reaction, it will automatically convert to its *keto* form in the presence of a trace of acid or base.**
- The addition of water to alkynes follows Markovnikov's rule:

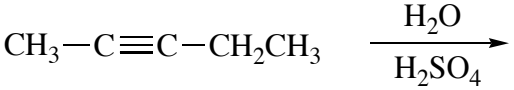
- Terminal alkynes are less reactive and require the use of an additional catalyst, $HgSO_4$:



- The product is always a ketone except when acetylene is hydrated:



- Unsymmetrical internal alkynes will give mixtures of products:



C. Addition of Bromine and Chlorine to Alkynes

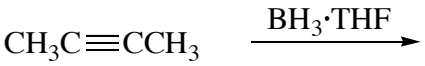
Alkynes undergo addition reactions with bromine and chlorine.

1 equivalent halogen:

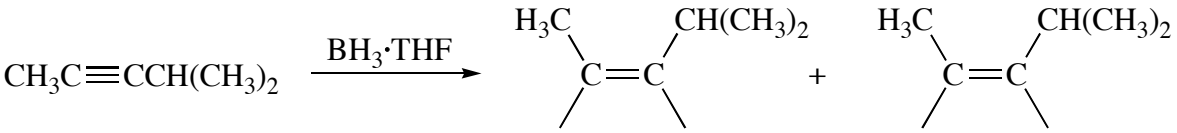
2 equivalents halogen:

D. Hydroboration/Oxidation of Alkynes

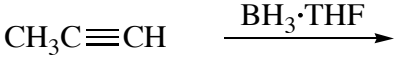
Like alkenes, alkynes undergo hydroboration when treated with borane reagents.



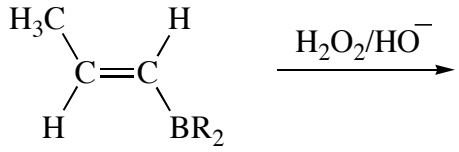
Unsymmetrical alkynes **give mixtures:**

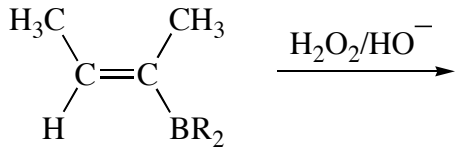


Terminal alkynes **also undergo hydroboration:**



Oxidation of the hydroboration product provides a route to aldehydes or ketones (terminal alkynes give *aldehydes*, and internal alkynes give *ketones*.)

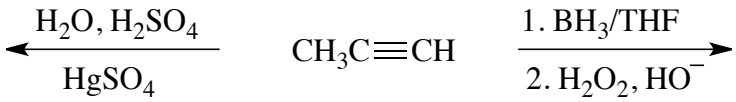




Mechanism for base-catalyzed tautomerization:

Don't do this:

Compare the result obtained when a terminal alkyne undergoes acid catalyzed hydration *vs.* hydroboration/oxidation.



VII. Designing Syntheses: Part 1

In planning a synthesis, we have to consider four things:

1. Construction of the carbon skeleton
2. Functional group interconversion
3. Control of regiochemistry
4. Control of stereochemistry

Example: Prepare the following compound from acetylene: