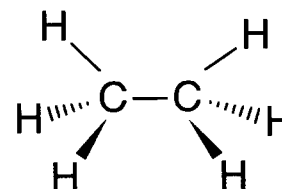
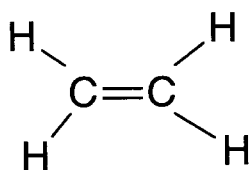


Sean  
Chem 333  
204  
**Chapter 9: Alkynes** (omit 9 - 6B)

**Structure:** compare to alkene and alkane



BDE of triple bond =

BDE of double bond =

BDE of C-C bond =

BDE of first  $\pi$  bond:

BDE of second  $\pi$  bond:

**Percent s character/ Importance:**

sp hybrid orbital -

sp<sup>2</sup> hybrid orbital -

sp<sup>3</sup> hybrid orbital -

Physical Properties:

Since nonpolar compounds - similar to the alkanes/alkenes of corresponding molecular mass

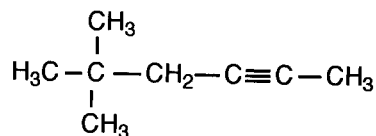
Common Names: Acetylenes     HC $\equiv$ CH

terminal alkyne: CH<sub>3</sub>CH<sub>2</sub>-C $\equiv$ C-H

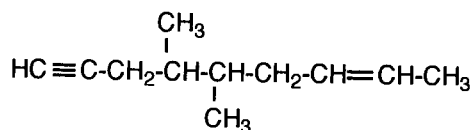
internal alkyne: CH<sub>3</sub>-C $\equiv$ C-CH<sub>3</sub>

Alkyne Nomenclature:

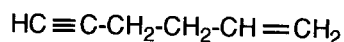
1. Choose longest chain that contains the triple bond. Suffix is "yne" (or diyne, triyne, etc.) Triple bonds gets priority when it is the only functional group present.



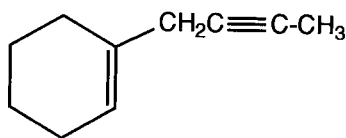
2. Compounds with double and triple bonds in the longest chain are called "enynes." Numbering an enyne begins with the end that gives the multiple bonds the lowest possible numbers (double or triple may have the lower number).



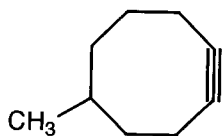
If the numbering is the same from either direction, the double bond has priority and receives the lower number.



3. If the triple bond is not part of the parent name, name as an alkynyl side chain.



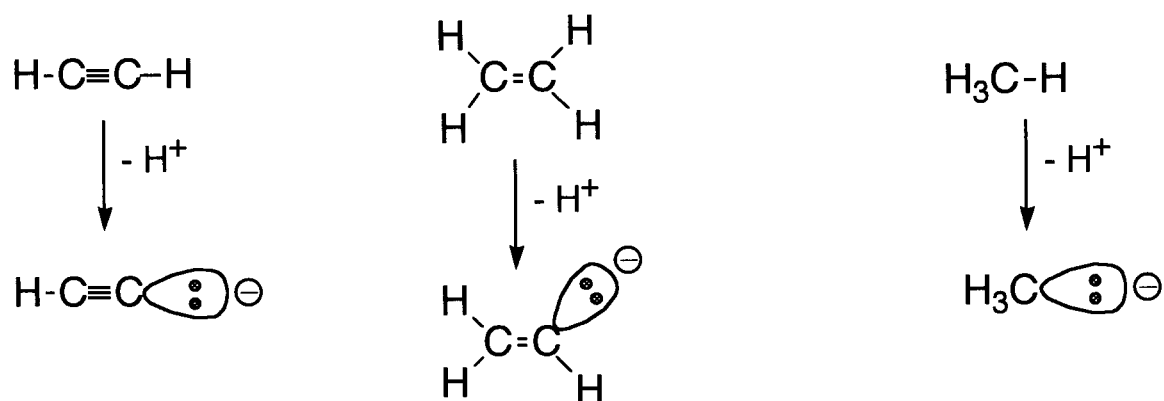
4. Cyclic alkynes (ring size of at least 8 carbons necessary): Triple bond is understood to be between carbons 1 and 2.



Note: True bond angle of sp carbon is not reflected in the structure above!

## ALKYNE ACIDITY

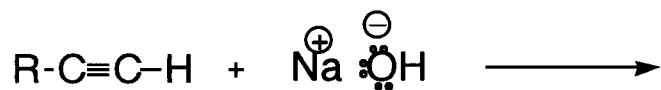
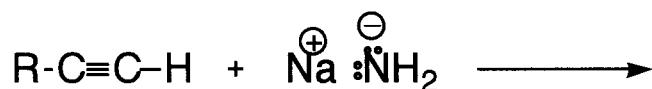
Compare the  $pK_a$  values of hydrocarbons:



other  $pK_a$  values:  $\text{H}_2\text{SO}_4$      $\text{CH}_3\text{CO}_2\text{H}$      $\text{H}_2\text{O}$      $\text{CH}_3\text{CH}_2\text{OH}$

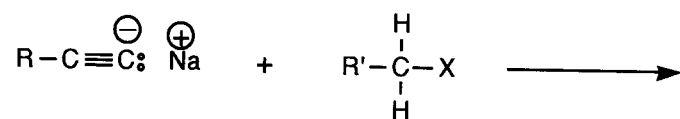
## FORMATION OF ACETYLIDE ANIONS:

Strong bases such as  $\text{NaNH}_2$ , organolithium reagents, and Grignard reagents can deprotonate a terminal alkyne to form an acetylide anion. (Hydroxide is NOT strong enough.)

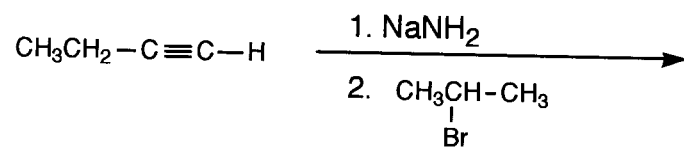
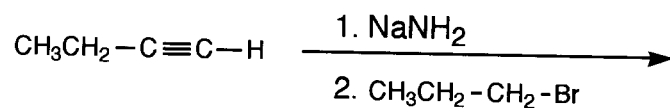


## Reactions of Acetylide Anions:

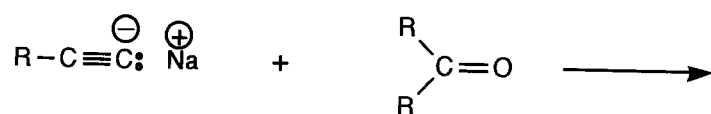
### A. Alkylation of the acetylide anion - a substitution reaction ( $S_N2$ )



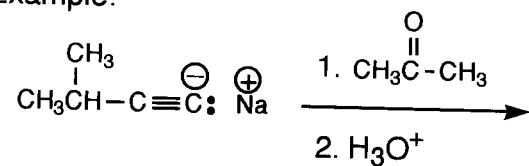
### Examples:



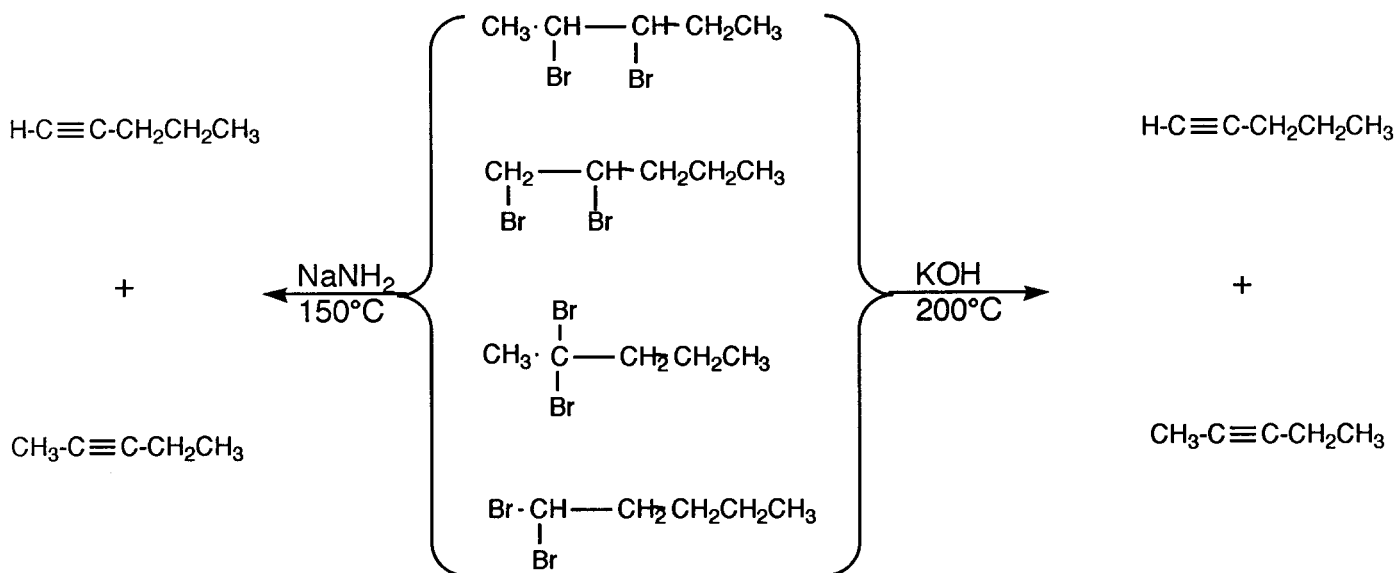
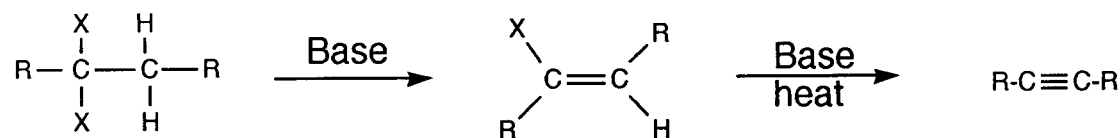
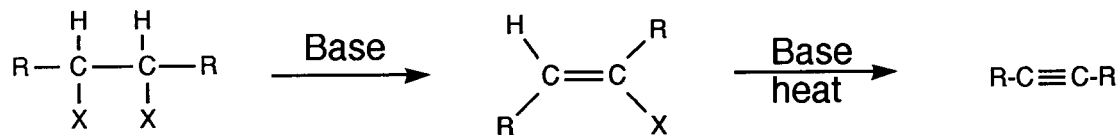
### B. Addition to carbonyl groups (aldehydes and ketones):



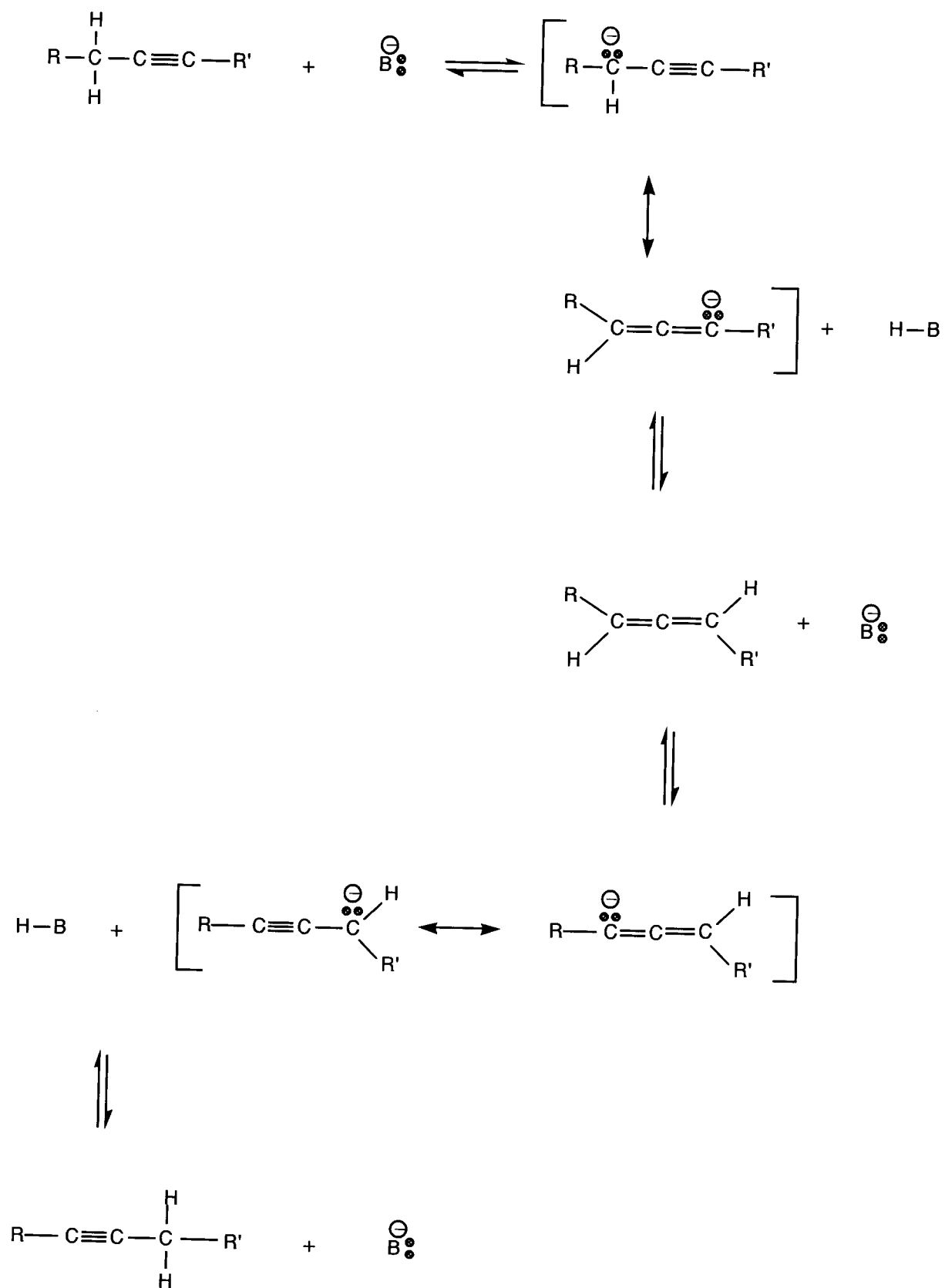
### Example:



# Synthesis of Alkynes: Dehydrohalogenation of vicinal and geminal dihalides



## Base Catalyzed Rearrangement of Alkynes

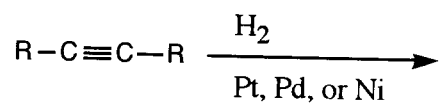


## REACTIONS OF ALKYNES

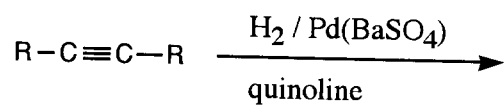
### I. Addition of H<sub>2</sub>

#### A. Catalytic Reduction (Hydrogenation)

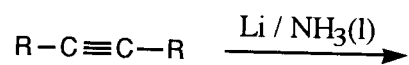
##### 1. Reactive catalysts:



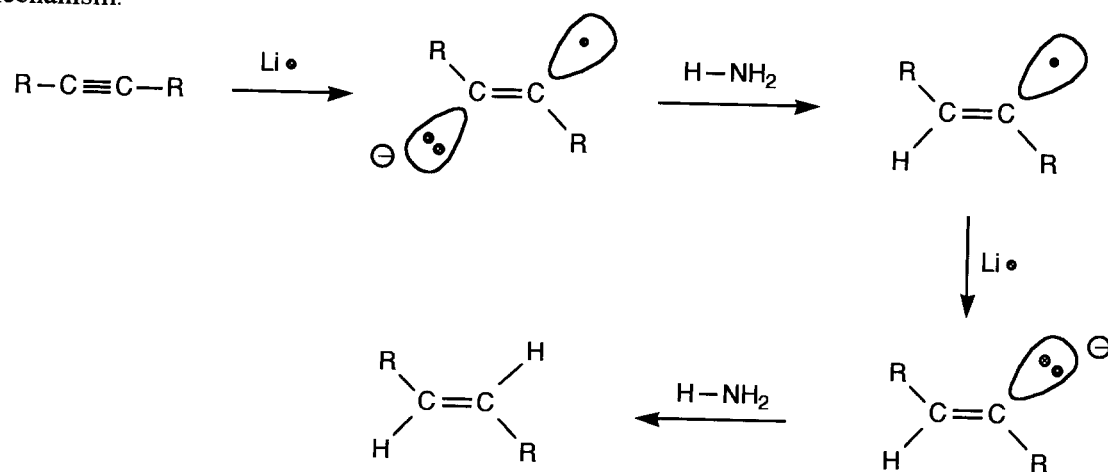
##### 2. Lindlar's catalyst:



#### B. Dissolving Metal Reduction

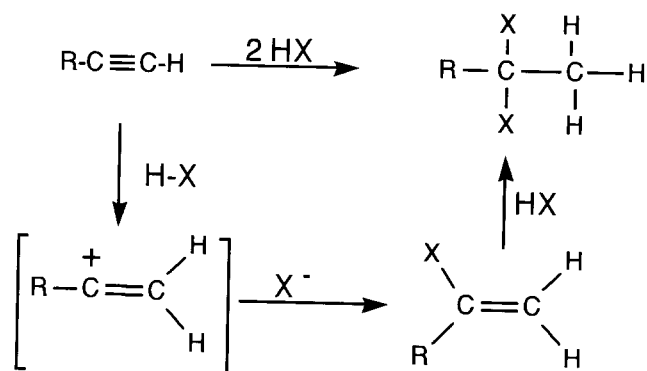


##### Mechanism:

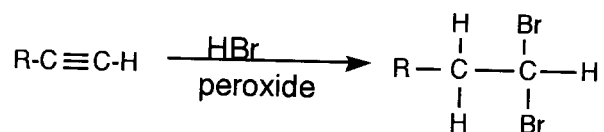


## Reactions of Alkynes (continued):

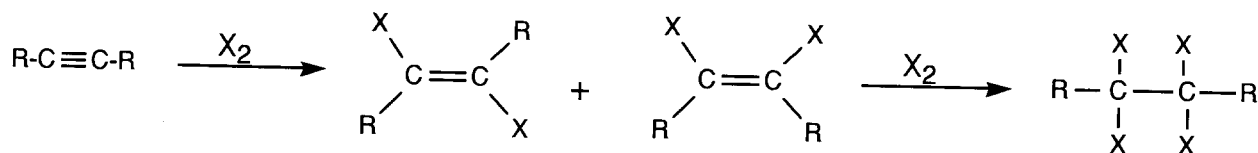
### II. Addition of H - X (HCl, HBr, HI):



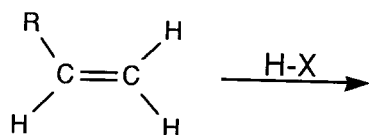
### addition of HBr/peroxide:



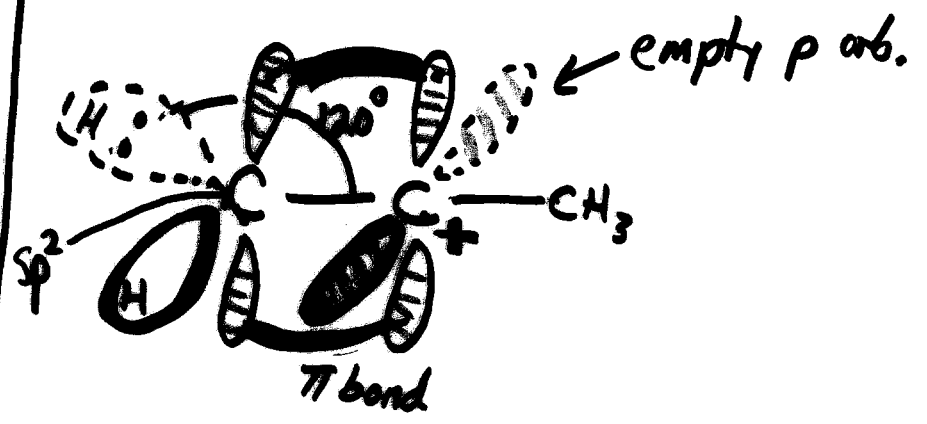
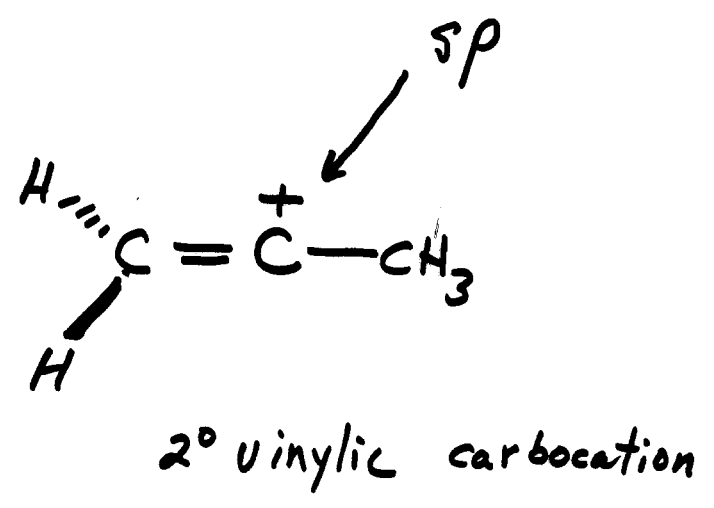
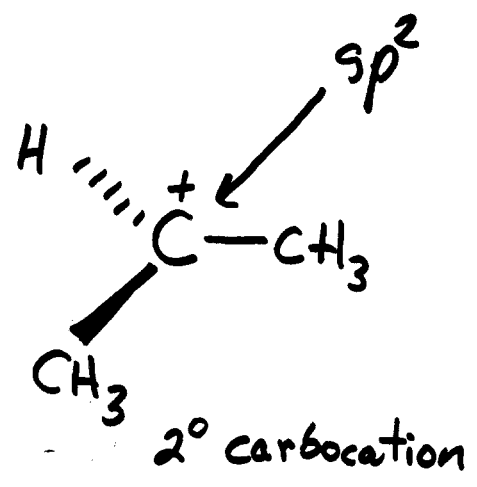
### III. Addition of X<sub>2</sub> (Br<sub>2</sub> or Cl<sub>2</sub>):



### Reactivity of Alkyne vs Alkene and Stability of the Vinyl Carbocation:







stabilization by  
2 methyl groups

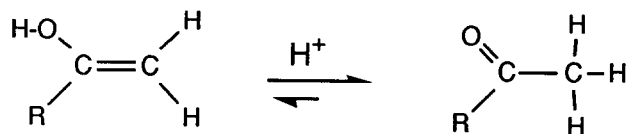
stabilization by only  
one methyl group

## IV. Addition of H-OH (Hydration)

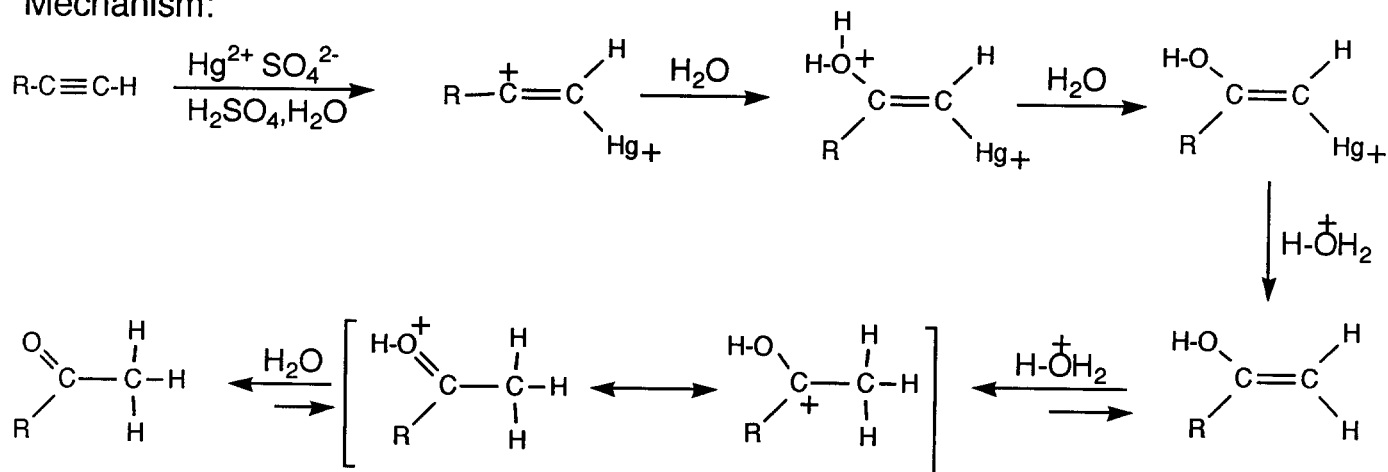
## A. Mercuric Ion - catalyzed hydration:



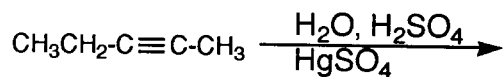
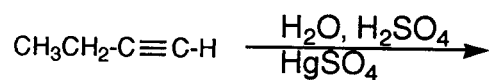
tautomers: special constitutional isomers that are interconvertible by a rapid EQ



## Mechanism:

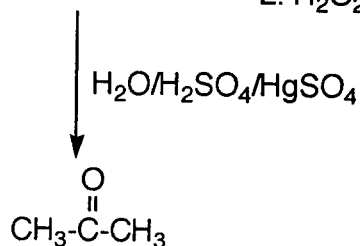
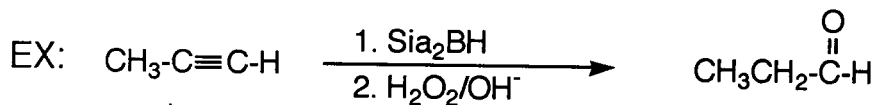
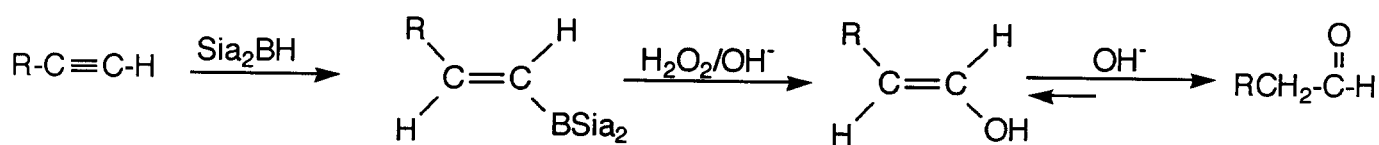
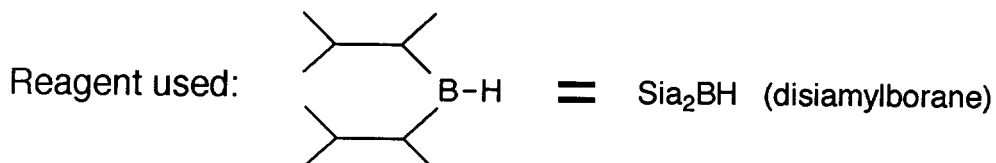
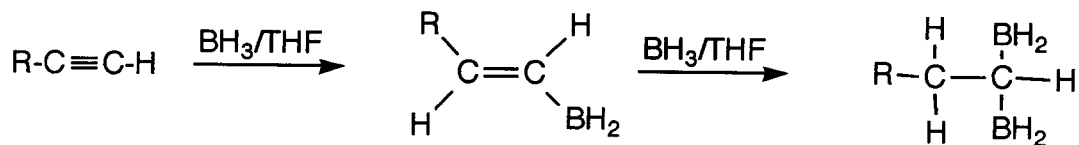


## Examples:



## Addition of H-OH to alkynes (continued)

B. Hydroboration/oxidation (non-Mark) - first step similar to addition of borane to alkene, but must use a hindered borane to prevent double addition:



## V. Oxidation of alkynes:

