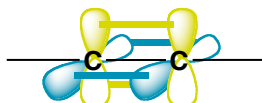


## Chapter 8 - Alkynes: An Introduction to Organic Synthesis

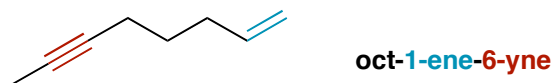
## Alkyne Structure

Alkynes are  $sp$  hybridized and have linear geometry. In general, the  $\pi$ -bonds of alkynes are more reactive than alkenes. Much of the chemistry of alkynes mirrors alkenes with a few twists. The difference stems from the presence of the second  $\pi$ -bond which can react further in a particular transformation. For, example, addition reactions often occur twice on alkynes.



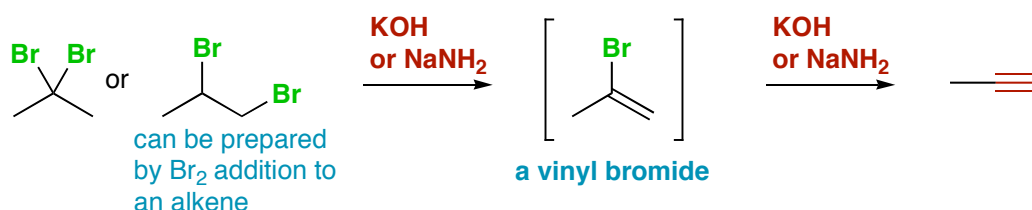
## Naming Alkynes

Alkynes are named similar to alkenes. Alkenes will have priority for the lowest number if it is equidistant from the end of the chain, otherwise, whichever is closest to an end gets the lowest number.



## Preparation of Alkynes

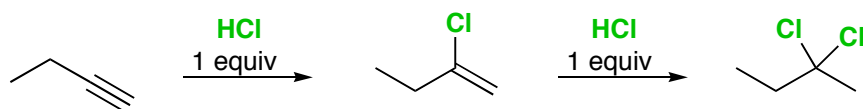
Alkynes are prepared by elimination reactions of vinyl halides. These can be prepared by elimination of dihalides. Thus, you could do sequential eliminations to form a triple bond.



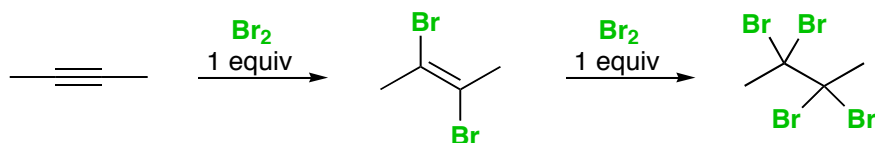
## Electrophilic Addition to Alkynes

The addition of electrophiles to alkynes is very similar to alkenes, but the reaction can occur twice. Terminal alkynes (on the end of a double bond) will generally proceed with Markovnikov addition whereas internal alkynes often give mixtures of regioisomers.

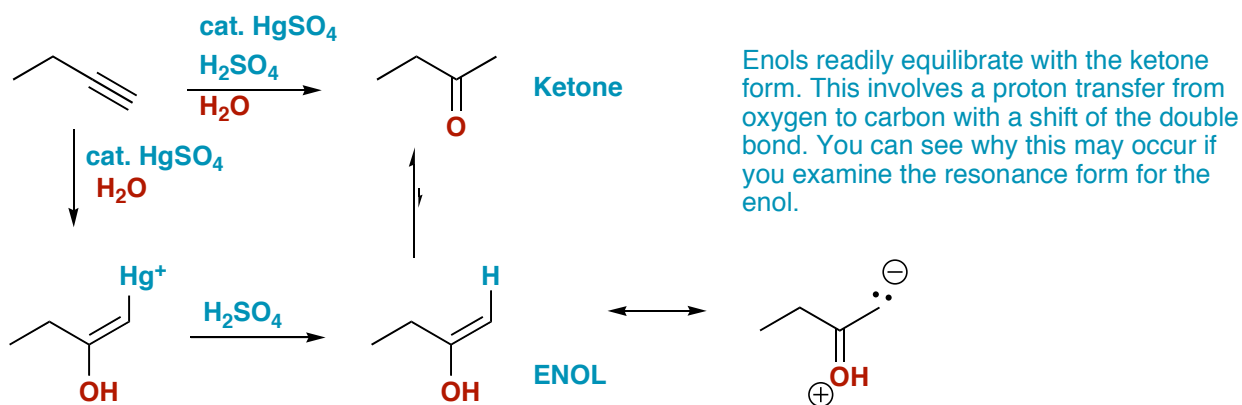
The addition of  $\text{HX}$  can be controlled by limiting the electrophile to one equivalent. A second equivalent, if present will add again to form a dihalide.



The addition of bromine or chlorine will proceed just like with an alkyne. The initial addition of one equivalent will selectively form the trans dihalide due to the bridging intermediate.



The hydration of alkynes occurs in a slightly different fashion than with alkenes. First, only a catalytic amount of mercury salt is required as the intermediate vinyl mercury species readily protonates in the presence of acid. Secondly, the product of the hydration, an enol, readily isomerizes (tautomerizes) to the more stable ketone form.



## Hydrogenation of Alkynes

Alkynes can be hydrogenated just like alkenes all the way to the alkane with Pd/C catalysis. In order to stop the reaction after the first addition of hydrogen, you need a 'poisoned', or less reactive catalyst. Lindlar's catalysts foots the bill here. This is a Pd catalyst whose reactivity has been tempered by the addition of quinoline.

