Chapter 9
Alkynes

Alkynes are hydrocarbons that contain a carbon-carbon triple bond. They have the formula C_nH_{2n-2}.

Nomenclature:

The parent is the longest chain that contains the triple bond. Change the parent alkane into alkyne (-ane of alkane to –yne of alkyne). Number the chain so as to give the first carbon of the triple bond the lowest number.

$CH_3-C\equiv C-H$

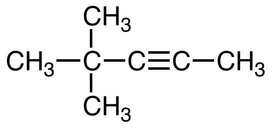
propyne

$CH_3CH_2-C\equiv C-H$

1-butyne

$CH_3-C\equiv C-CH_3$

2-butyne



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-C\equiv C-CH_3$$

4,4-dimethyl-2-pentyne

The simplest alkyne is ethyne, C_2H_2, more commonly called acetylene. Terminal alkynes are at the end of the chain and disubstituted alkynes have substituents at either end of the triple bond.

$H-C\equiv C-H$

acetylene (or ethyne)

$R-C\equiv C-H$

terminal alkyne

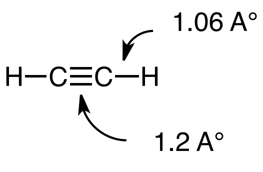
$R-C\equiv C-R'$

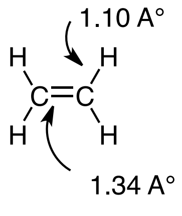
disubstituted alkynes

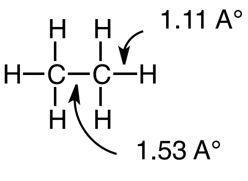
Alkynes have physical properties that are similar to alkanes and alkenes. They have relatively low density and low solubility in water.

Bonding

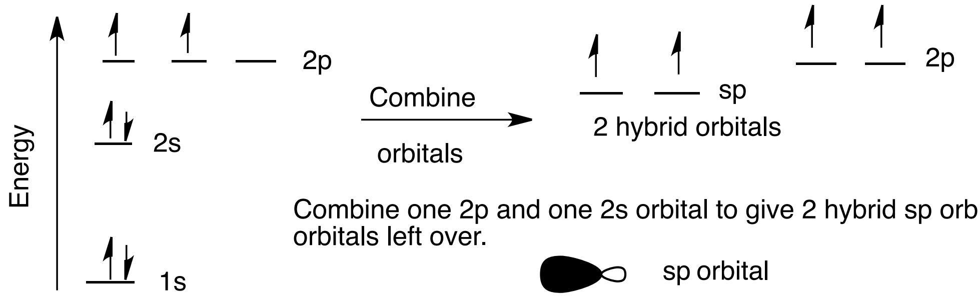
Alkynes are linear with sp-hybridized carbons. The triple bond is shorter and strong than a double bond and both are shorter and stronger than a single bond. The sp carbon-hydrogen bond is also shorter and stronger than an sp^2 carbon-hydrogen bond.



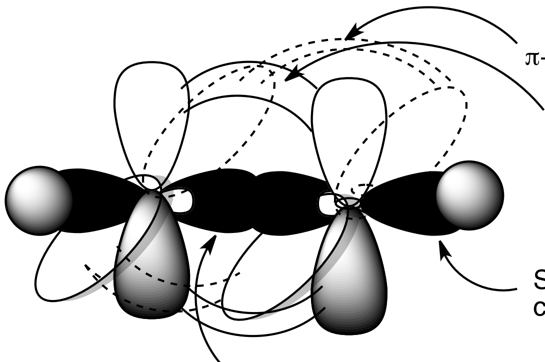




Recall from Chapter 2 that we form sp hybrid orbitals by combining one s orbital and one p orbital and there are two p orbitals left over to form the two mutually perpendicular π−bonds.



Combine one 2p and one 2s orbital to give 2 hybrid sp orbitals with two 2p orbitals left over.



π−bond formed from overlap of two 2p orbitals

Second π−bond formed from overlaps of the other pair of 2p orbitals.

The two π−bonds are mutually perpendicular.

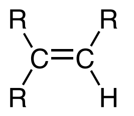
Sigma C-H bond formed from overlaps of carbon sp orbital and 1s orbital of hydrogen.

Sigma C-C bond from end-to-end overlap of two carbon sp orbitals.

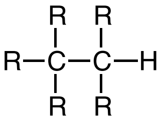
The two sp-hybridized carbon atoms have 50% s character. This greatly increases the electronegativity of the carbon and makes the sp carbon-hydrogen bond much more acidic than an sp^2 carbon-hydrogen bond or an sp^3 carbon-hydrogen bond.

$R-C\equiv C-H$

pKa 26



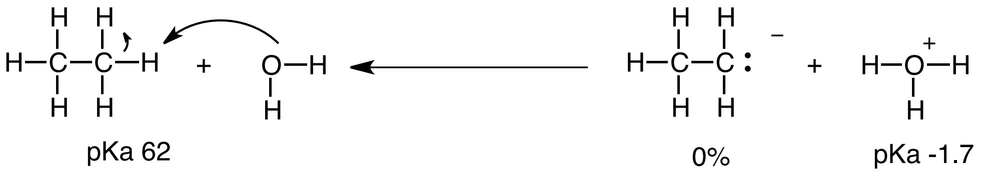
pKa 45



pKa 62

The more s character in the hybrid, the more electronegative the carbon since on average an electron in an s-orbital is closer to the nucleus and more strongly held than an electron in a p-orbital.

Ethane (pKa 62) is a very weak acid and is not ionized by any known base. A weak base such as water forms no carbanion.

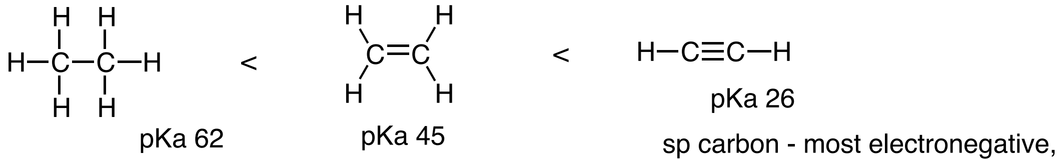


Recall that the acidity parallels the electronegativity of the atom involved:

CH_4 < NH_3 < H_2O < HF

CH_4	NH_3	H_2O	HF
pKa 60	pKa 36	pKa 15.7	pKa 3.1
weakest acid, carbon is least eletronegative atom			strongest acid, fluorine is most electronegative atome

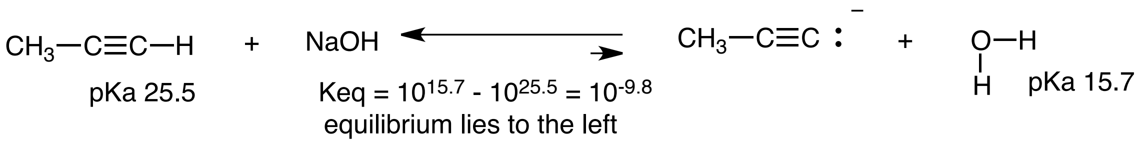
This is similar to the trend in carbon acidities:



sp^3 carbon - least electronegative, least acidic

sp carbon - most electronegative, most acidic

As a general rule, in order for the base to deprotonate the acid, the pKa of the conjugate acid of the base must be larger than the pKa of the acid.

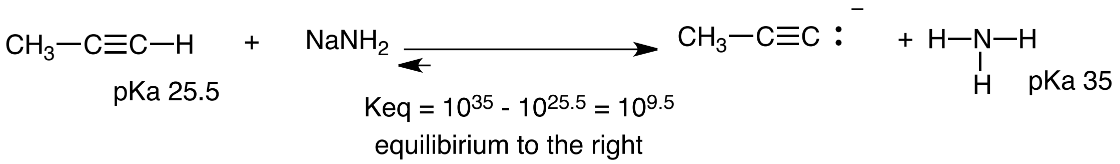


Keq = $10^{15.7} - 10^{25.5} = 10^{-9.8}$
equilibrium lies to the left

Here the pKa of H_2O is 15.7; this is smaller than the pKa of propyne. Therefore, hydroxide is not strong enough to deprotonate the acid and the equilibrium constant is unfavorable.

(Note: to find the equilibrium constant for any acid-base reaction, simply subtract the pKa's. Remember, these are exponents for the equilibrium constant, Keq. The sign of the exponent will be negative if the equilibrium lies to the left – unfavorable - and the sign will be positive if the equilibrium lies to the right - favorable.)

But treatment of propyne with sodium amide (pKa NH_3 =35) provides the acetylide anion in yield. The equilibrium lies well to the right.

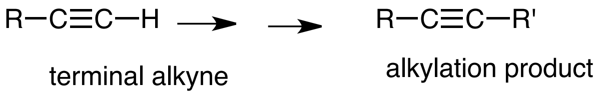


$$CH_3{-}C{\equiv}C{-}H + NaNH_2 \rightleftharpoons CH_3{-}C{\equiv}C:^{-} + H{-}\underset{H}{\underset{|}{N}}{-}H$$

Again, remember the correlation between pKa and base strength. The conjugate base of a strong acid will be a weak base. It does not hold onto the proton very strongly. And, the conjugate base of a weak acid is a strong base. The higher the pKa of an acid, the stronger is the conjugate base. The carbanion of ethane is one of the strongest bases in chemistry.

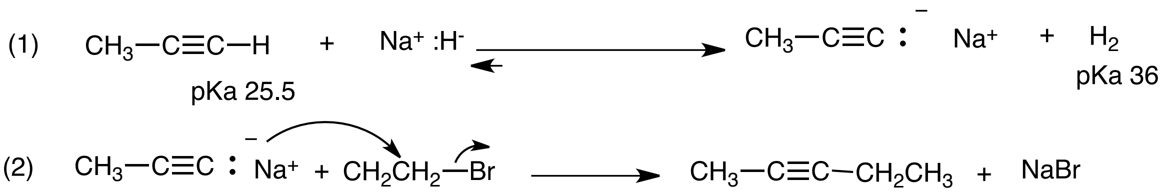
Alkylation of Terminal Acetylenes

The acetylide anions are excellent nucleophiles and will undergo S_N2 reactions with primary alkyl halides to form new carbon-carbon bonds.



$$R{-}C{\equiv}C{-}H \longrightarrow \longrightarrow R{-}C{\equiv}C{-}R'$$

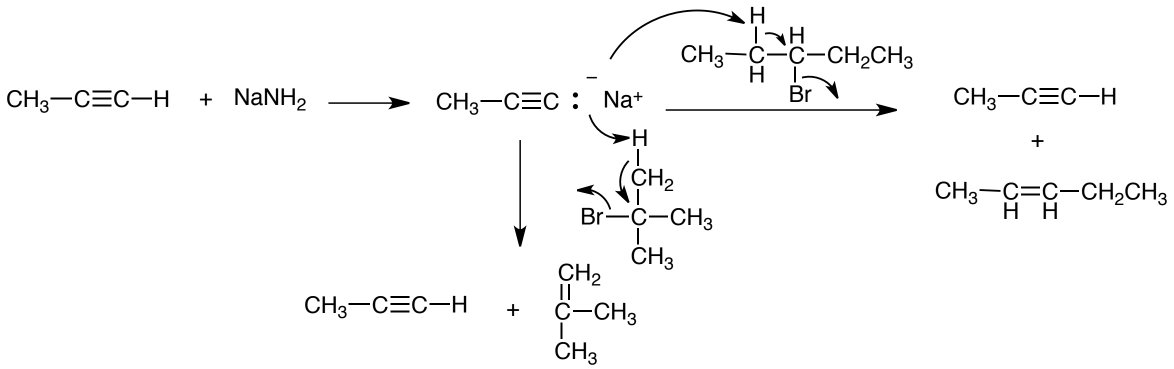
There are two steps in the synthesis:
(1) Deprotonation of the alkyne with very strong bases such as sodium amide or sodium hydride.
(2) Addition of an alkylating agent (R'X), a primary alkyl halide.



$$(1)\quad CH_3{-}C{\equiv}C{-}H + Na^+ :H^- \rightleftharpoons CH_3{-}C{\equiv}C:^{-}\ Na^+ + H_2$$

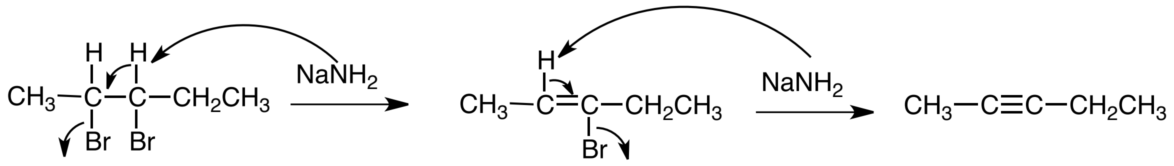
$$(2)\quad CH_3{-}C{\equiv}C:^{-}\ Na^+ + CH_2CH_2{-}Br \longrightarrow CH_3{-}C{\equiv}C{-}CH_2CH_3 + NaBr$$

The acetylide anion is a very strong base (it is a weak acid) and therefore it will cause competing elimination reactions with secondary or tertiary alkyl halides. The alkyl halide must be a primary or methyl halide.

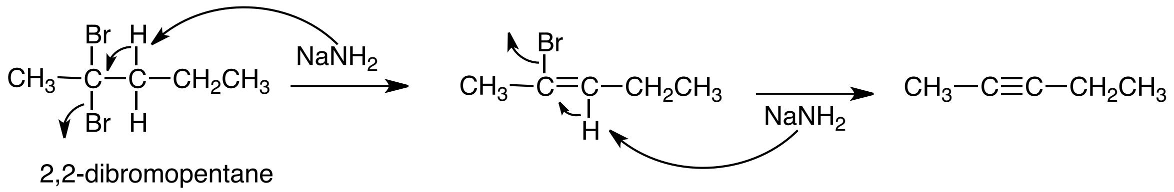


Preparation of Alkynes by Elimination Reactions

Vicinal dihaloalkanes (1,2-dihaloalkanes) or geminal dihaloalkanes (1,1-dihaloalkanes) can undergo two elimination reactions using two equivalents of a strong base such as sodium amide to give alkynes. A strong base is needed in the second step because the vinyl sp^2 C-H and C-Br bonds are much harder to cleave than the sp^3 C-H and C-Br bonds.

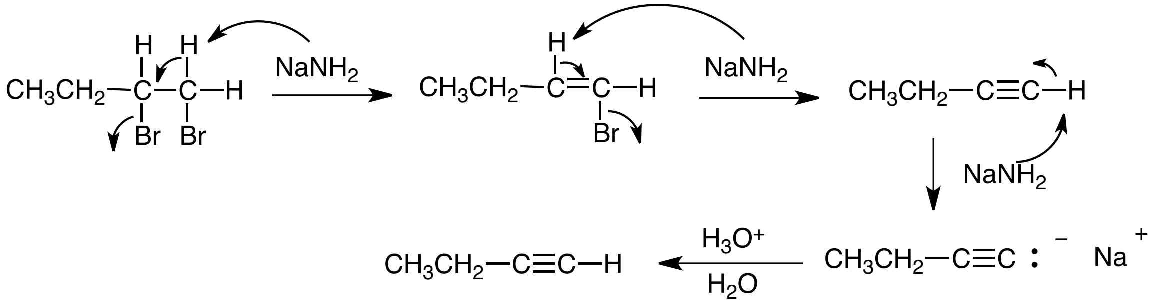


2,3-dibromopentane (vicinal dihaloalkane)

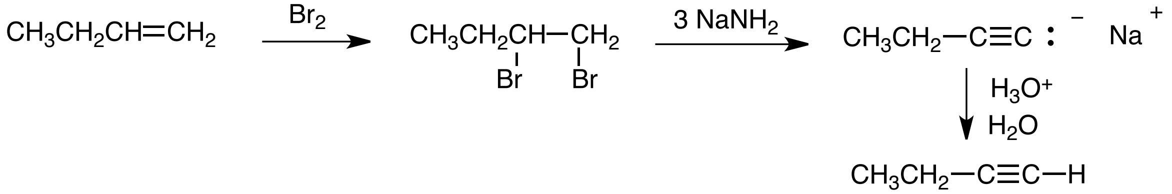


2,2-dibromopentane
(geminal dihaloalkane)

If we are making a terminal alkyne, we need to use a full three equivalents of the strong since one of the equivalents will react with the product that is formed. We do not want the final deprotonation step to occur but there is no way to prevents its happening. Then, in order to isolate the neutral terminal alkyne, we must add the proton back by adding aqueous acid.



We can convert an alkene to an alkyne in two steps. In step one we add molecular bromine to the double bond to give a vicinal di-halide. Then in step two we treat it with base to form the alkyne. Again, if we are forming a terminal alkyne, we must use three equivalents of the base and then do an acidic workup.



$$CH_3CH_2CH{=}CH_2 \xrightarrow{Br_2} CH_3CH_2\underset{Br}{CH}{-}\underset{Br}{CH_2} \xrightarrow{3\ NaNH_2} CH_3CH_2{-}C{\equiv}C{:}^{-}\ Na^{+} \xrightarrow[H_2O]{H_3O^+} CH_3CH_2{-}C{\equiv}C{-}H$$

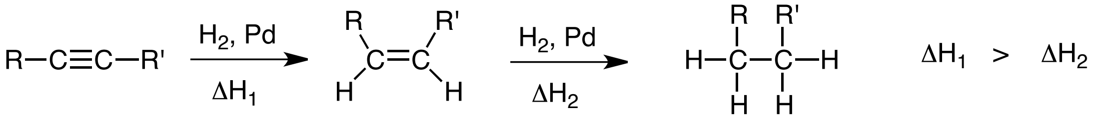
Reactions of Alkynes

Hydrogenation of Alkynes

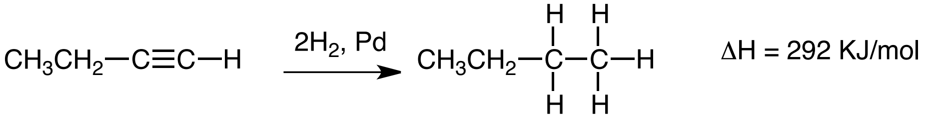
Alkynes will react with molecular hydrogen in the presence of a noble metal catalyst such as palladium, platinum, nickel, rhodium to give the fully hydrogenated alkane.

$$R{-}C{\equiv}C{-}R' \quad + \quad 2H_2 \xrightarrow[\text{(or Pt, Ni, Rh)}]{Pd} R{-}CH_2{-}CH_2{-}R'$$

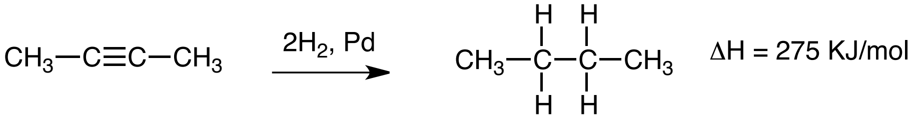
The heat of hydrogenation of an alkyne is greater than twice the heat of hydrogenation of an alkene. The addition of the first mole of hydrogen is more exothermic than addition of the second mole.



The heat of hydrogenation of 1-butyne is greater than the heat of hydrogenation of 2-butyne. The internal triple bond is more stable than the terminal triple bond. It is a disubstituted alkyne and had two alkyl groups that release electron density to the electron deficient triple bond.



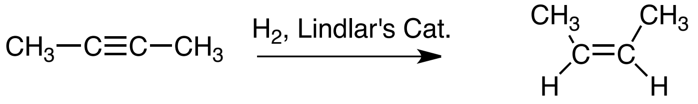
$$CH_3CH_2-C\equiv C-H \xrightarrow{2H_2,\ Pd} CH_3CH_2-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H \qquad \Delta H = 292\ KJ/mol$$



$$CH_3-C\equiv C-CH_3 \xrightarrow{2H_2,\ Pd} CH_3-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-CH_3 \qquad \Delta H = 275\ KJ/mol$$

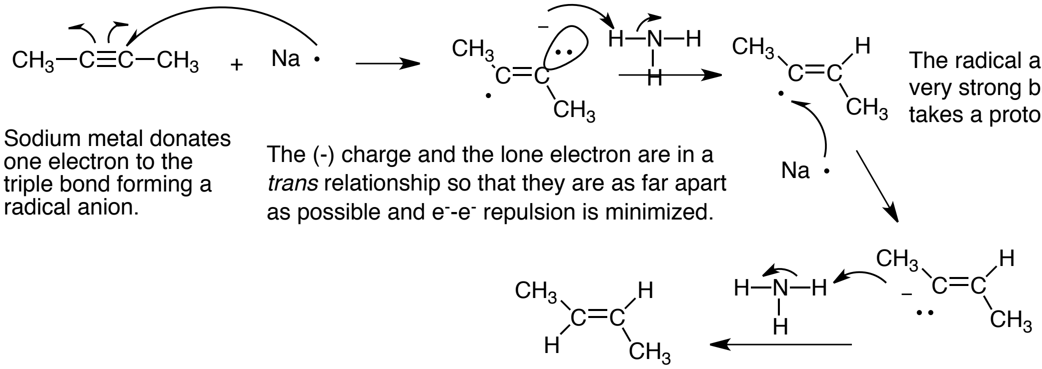
It is difficult to stop the hydrogenation at the alkene stages since the alkene is more reactive than the alkyne. It is more easily reduced.

One way to isolate the alkene intermediate is to use a special, less reactive catalyst such as Lindlar's Catalyst. This is a special form of palladium that has been poisoned with lead and calcium carbonate and quinolone. It will reduce alkynes but will not reduce alkenes.



Syn addition of the hydrogen to give the *cis*-alkene.

To make *trans*-alkenes, we use a dissolving metal reduction with either sodium or lithium in liquid ammonia. Ammonia is a gas at room temperature but has a boiling point of -38°C. It is a convenient solvent at low temperatures since it also provides a source of protons in the strongly basic reaction conditions. The actual reducing agent is an electron donated by the lithium or sodium metal to the liquid ammonia solution.



Sodium metal donates one electron to the triple bond forming a radical anion.

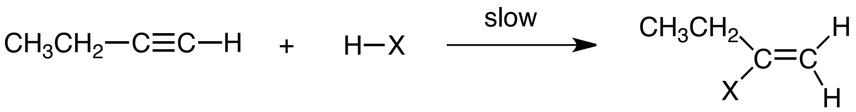
The (-) charge and the lone electron are in a *trans* relationship so that they are as far apart as possible and e$^-$-e$^-$ repulsion is minimized.

The radical anion is a very strong base and takes a proton from NH_3.

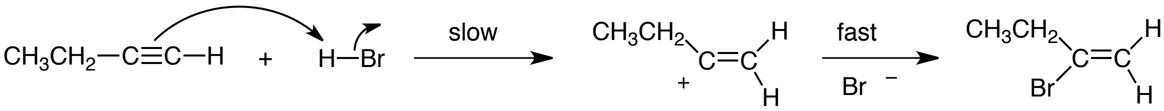
Another molecule of sodium donates a second electron to make an anion which then abstracts a proton from the solvent NH_3.

Addition of Hydrogen Halides

Hydrogen halides react with triple bonds in a manner analogous to hydrogen halide addition to alkenes but there are some important differences in the mechanism. The regioselectivity follow's Markovnikov's rule. This indicates that there is some carbocation character but the reaction follows third order kinetics.



One possible mechanism would be nucleophilic attack of the triple bond π–electrons on the proton of the H-Br molecule to give a free vinyl carbocation intermediate.



vinyl carbocation

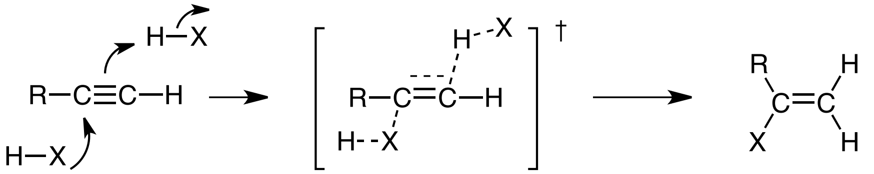
There are some problems with this mechanism, however.

(1) Vinyl carbocations are very high in energy and very hard to form. The rate of reaction of alkynes would then be expected to be much, much slower than for alkenes. Though the rate of reaction is slower for alkynes, it is not that much slower.

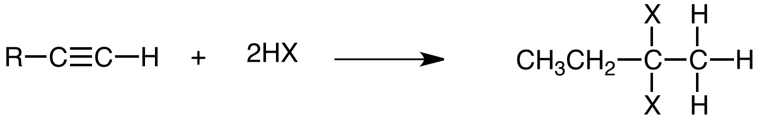
(2) The other major problem with this proposed mechanism is that it does not account for the observed third order kinetics. We see that the rate expression for this reaction is first order in alkyne and second order in H-X, third order overall.

Rate = k[alkyne] $[HX]^2$

A mechanism that fits these facts is shown below. Attack by the π–electrons of the triple bond is concerted with attack by the halogen of a second molecule of H-X. This is called an Addition-Electrophilic-Termolecular mechanism (Ade3). There is some carbocation character, however, since we do see Markovnikov regioselectivity with the hydrogen adding to the terminal end of the alkyne and the nucleophilic halogen adding to the more substituted carbon.

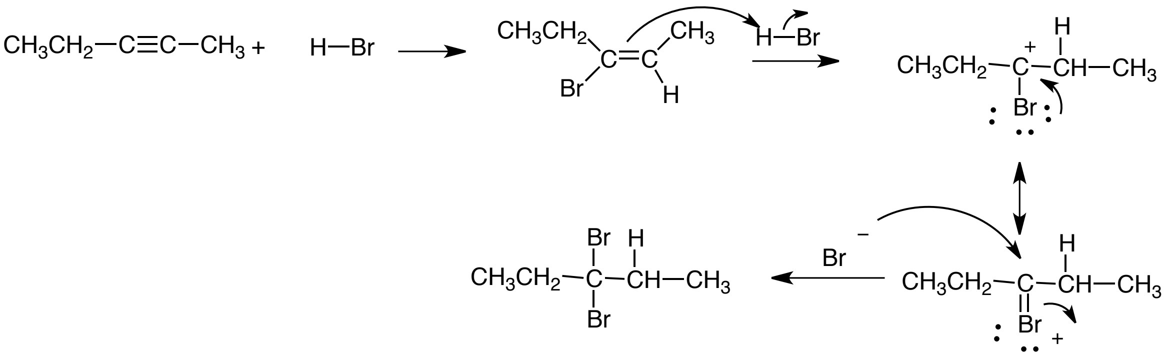


If we add an excess of HX, we get double addition to form the geminal dihalides. Both halogens add to the same carbon.

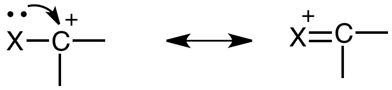


geminal dihalide

In the example below, the first step is the Ade3 addition of the first molecule of H-Br to the alkyne to form the vinyl alkyne intermediate. The second hydrogen adds so as to form the carbocation with the (+) charge on the carbon that already has a bromine atom. Bromine is very electron rich, with three sets of lone pair. These lone pair help to stabilize the adjacent carbocation by donation of electron density.



This is a general rule: any atom with a lone pair (nitrogen, oxygen, halogen) will stabilize an adjacent carbocation by resonance donation of the lone pair.

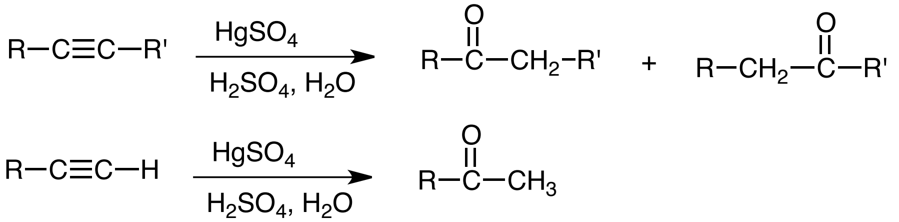


X = N, O, S, halogen, etc.

resoance stabilized carbocation

Hydration of Alkynes

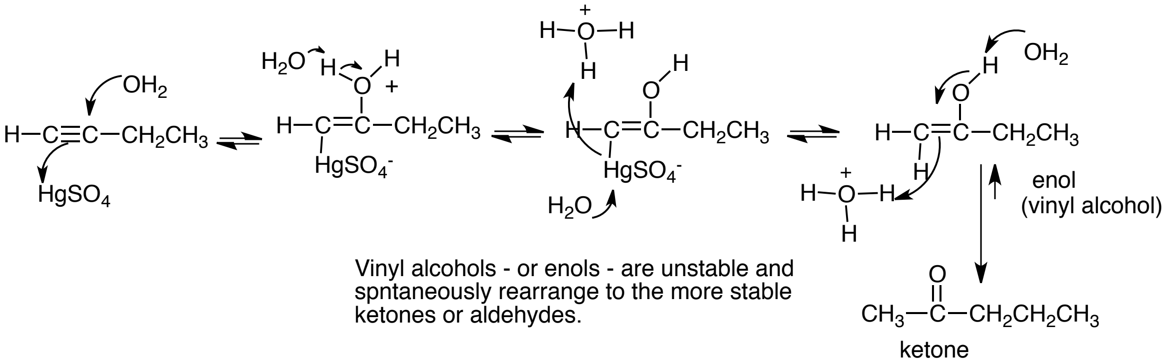
Water can be added to alkynes to form ketones. With disubstituted alkyne, a mixture of regioisomers can be formed but with terminal alkynes, methyl ketones are produced in accordance with Markovnikov's rule. A strong Lewis acid such as mercury sulfate ($HgSO_4$) is used to facilitate the initial electrophilic addition.



$$R-C\equiv C-R' \xrightarrow[H_2SO_4,\ H_2O]{HgSO_4} R-\overset{O}{\overset{\|}{C}}-CH_2-R' + R-CH_2-\overset{O}{\overset{\|}{C}}-R'$$

$$R-C\equiv C-H \xrightarrow[H_2SO_4,\ H_2O]{HgSO_4} R-\overset{O}{\overset{\|}{C}}-CH_3$$

This reaction is essentially acid-catalyzed Markovnikov addition to an alkyne with addition of the H^+ to the less substituted or terminal end of the alkyne and the formation of the more substituted carbocation intermediate, which is then attacked by the water. The role of the Hg is to help stabilize the sp2 carbocation by acting as a Lewis acid and by donating electrons through the d-orbitals to the π-system. The vinyl alcohol intermediate (also called an enol as we shall see in the second semester) is unstable and rapidly rearranges to the more stable ketone. The C=O bond is more stable than the C=C bond.



enol
(vinyl alcohol)

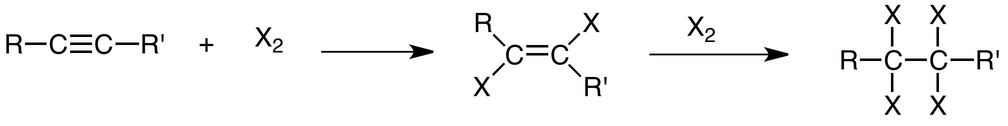
Vinyl alcohols - or enols - are unstable and spntaneously rearrange to the more stable ketones or aldehydes.

ketone

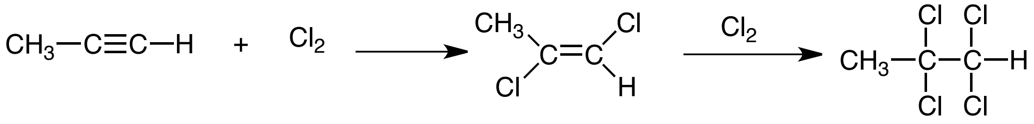
The C=O double bond is stronger than the C=C double bond.

Addition of Halogens

Addition of one equivalent of a halogen gives the *trans*-vicinal dihalides. Addition of two equivalents gives the tetra-halogenated species.

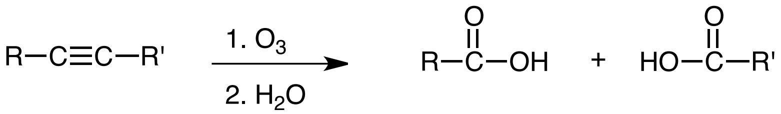


For example:



Ozonolysis

Ozonolysis of alkynes gives two carboxylic acids.



$$R-C\equiv C-R' \xrightarrow[\text{2. } H_2O]{\text{1. } O_3} R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \;+\; HO-\overset{\overset{\displaystyle O}{\|}}{C}-R'$$