Alkynes

Alkynes or acetylenes are compounds that contain a carbon–carbon *triple* bond.
E.g.

$H{-}C{\equiv}C{-}H \qquad CH_3CH_2{-}C{\equiv}C{-}H \qquad H_3C{-}C{\equiv}C{-}CH_3$

acetylene

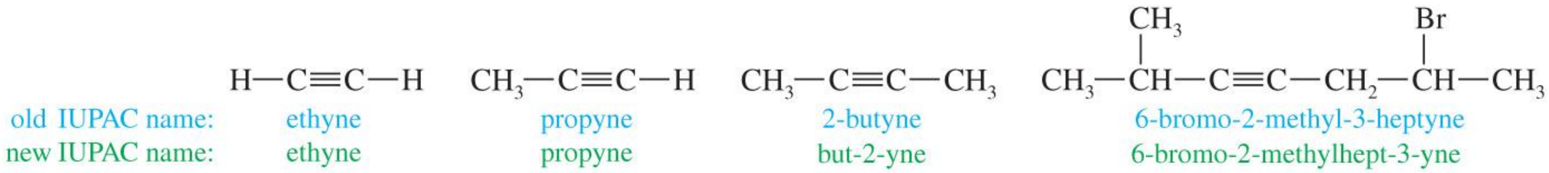
The triple bond results in a molecular formula of $\mathbf{C_nH_{2n-2}}$

Ethane	C_2H_6	0 elements of unsaturation
Ethene	C_2H_4	1 element of unsaturation
Ethyne	C_2H_2	2 elements of unsaturation

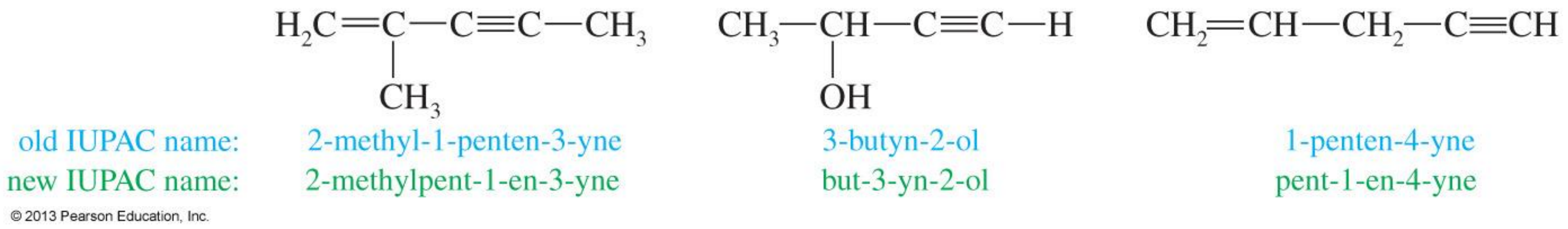
The triple bond contributes two *elements of unsaturation*.

Nomenclature of Alkynes

IUPAC nomenclature is similar to that for alkenes, except the *–ane* ending is replaced with *–yne*.
The chain is numbered from the end closest to the triple bond.



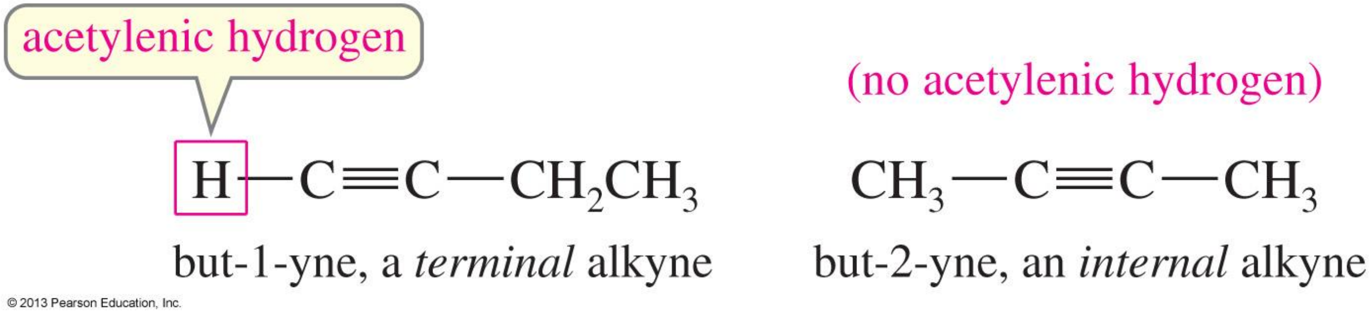
When additional functional groups are present, the suffixes are *combined*.



Terminal and Internal Alkynes

The *position* of the triple bond can alter the reactivity of the alkyne.

Compounds with triple bonds at the *end* of a molecule are called terminal alkynes. (Terminal C-H groups are called *acetylenic hydrogens*).



If the triple bond is flanked by alkyl groups on *both* sides it is an internal alkyne.

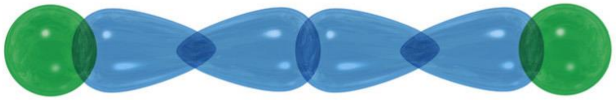
Electronic Structure of Alkynes

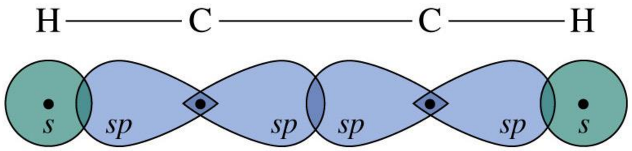
The triple bond consists of one σ bond and two π bonds.
Each carbon is bonded to two other atoms, and there are no nonbonding electrons.

Carbon requires two hybrid orbitals to bond to the atoms, thus sp hybrids are used.

The sp orbitals are linear and oriented at 180°.

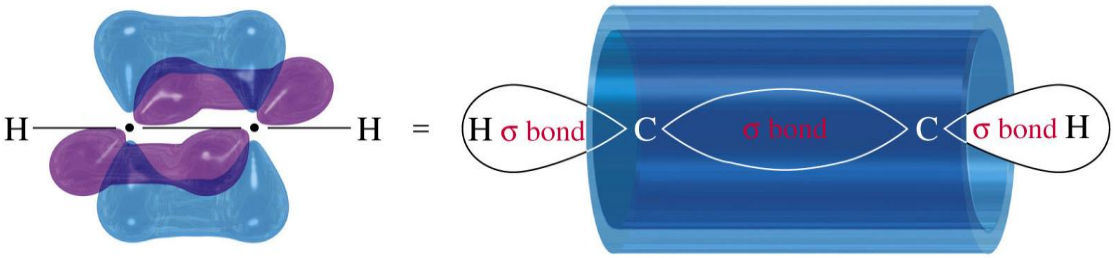
The C-C bond is formed from sp-sp overlap.
The C-H bond is formed from sp-s overlap.





The creation of sp hybrids leaves 2 free p orbitals – these create the two π bonds.

The p orbitals overlap just as for an alkene, except there are two π bonds at right angles to one another.



overlap of *p* orbitals

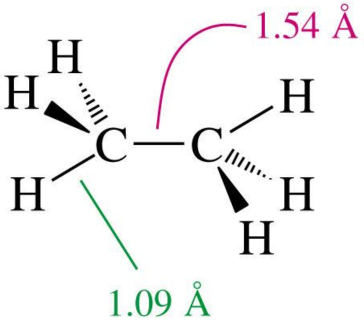
cylinder of electron density

This generates a cylinder of electron density around the sigma bond.

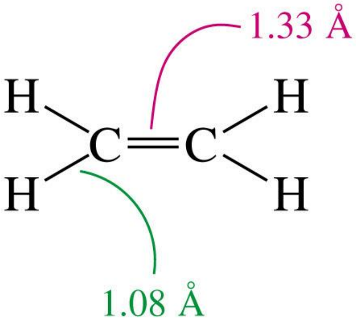
The C-C bond length for ethyne is 1.20Å which is *shorter* than ethane (1.54Å) and ethene (1.33Å).

The C-H bond length in ethyne is 1.06Å which is also *shorter* than in ethane (1.09Å) or ethene (1.08Å).

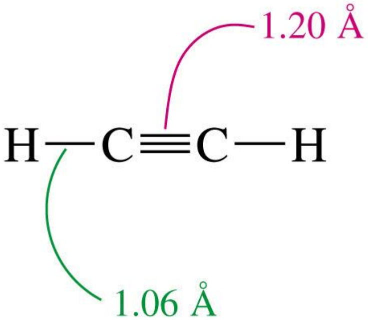
This is because the C-H bond contains more s character ($sp^3 \rightarrow sp^2 \rightarrow sp$) which gives *stronger* bonds.



ethane



ethene

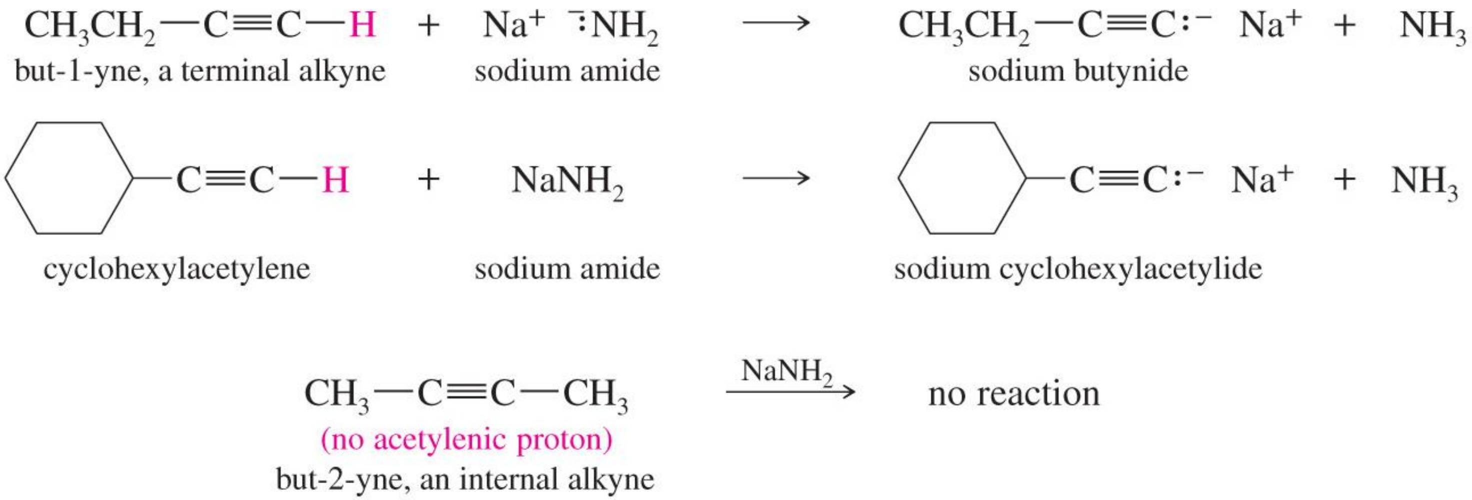


ethyne

Acidity of Alkynes

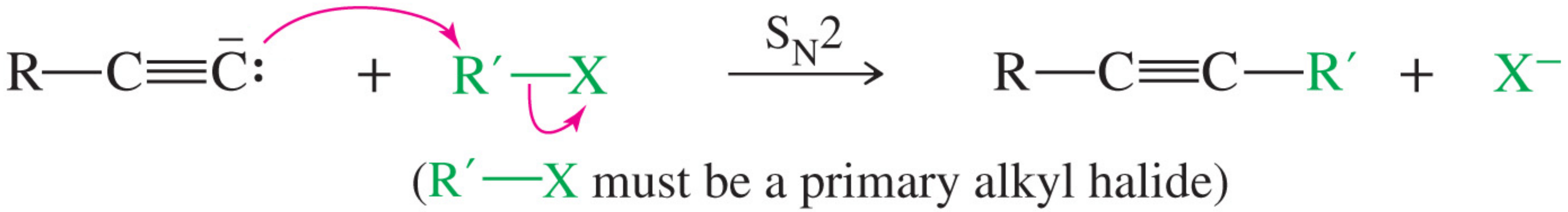
Terminal alkynes are **acidic**, the end hydrogen can be removed as a proton by a strong base.

E.g.



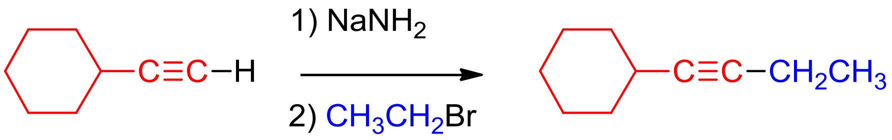
Synthesis of Alkynes

The carbanions produced are called *acetylides*, and are strong nucleophiles.

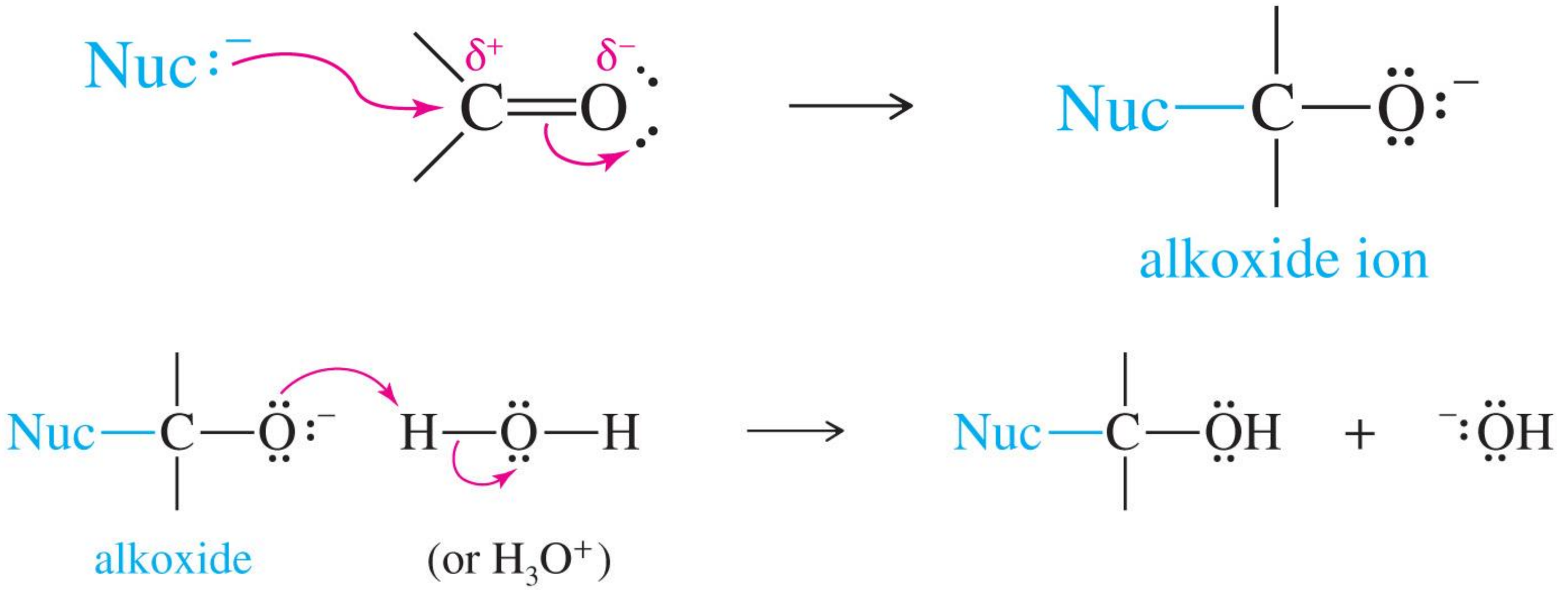


They can react in S_N2 displacements of halides or tosylates from primary unhindered substrates to produce *internal* alkynes.

E.g.

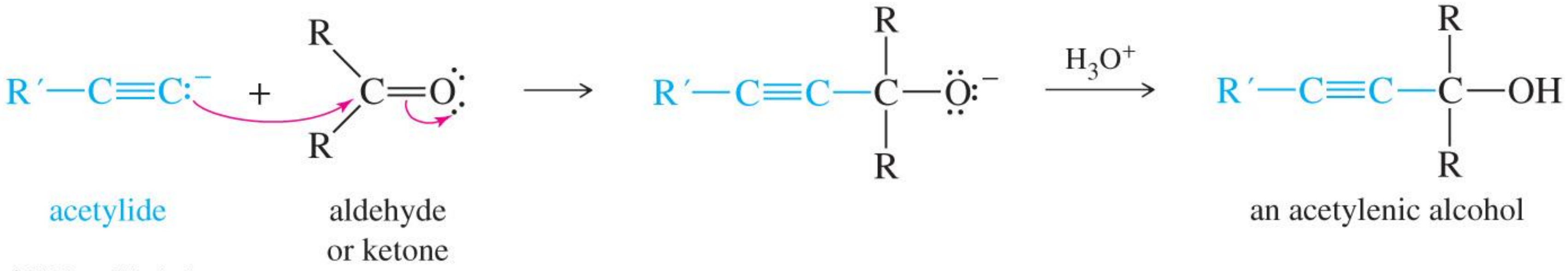


Carbonyl Reactions

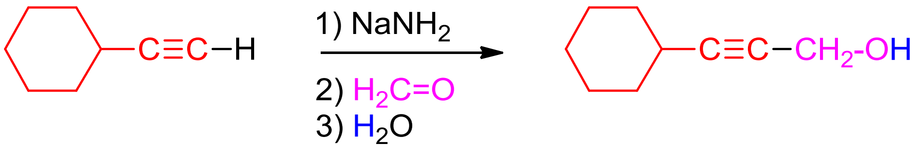


Acetylides will also attack other standard electrophiles like carbonyls to generate alcohols. (These reactions are very similar to Grignard type reactions).

Therefore with the acetylide as the nucleophile:

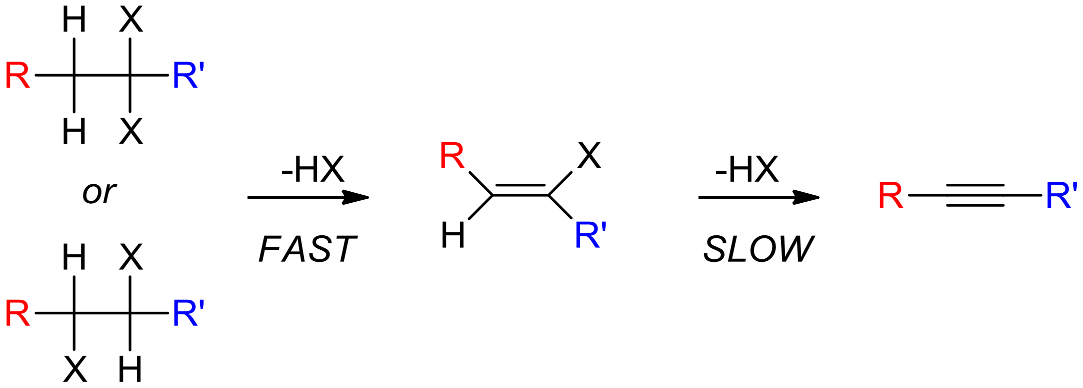


E.g.



Synthesis of Alkynes via Elimination

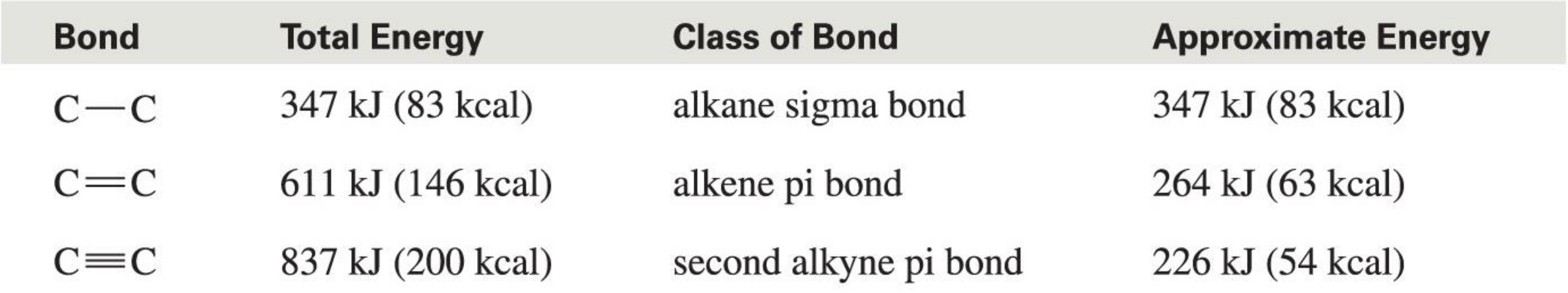
In the same way that alkenes are produced by elimination of H-X, alkynes can be produced by elimination of 2 moles of H-X from a *geminal* or *vicinal* dihalide.



Strongly basic conditions (KOH or $NaNH_2$, high temps) are required for this transformation, and often the molecule may not be stable to these conditions and may be destroyed or will rearrange.

Bond Strengths

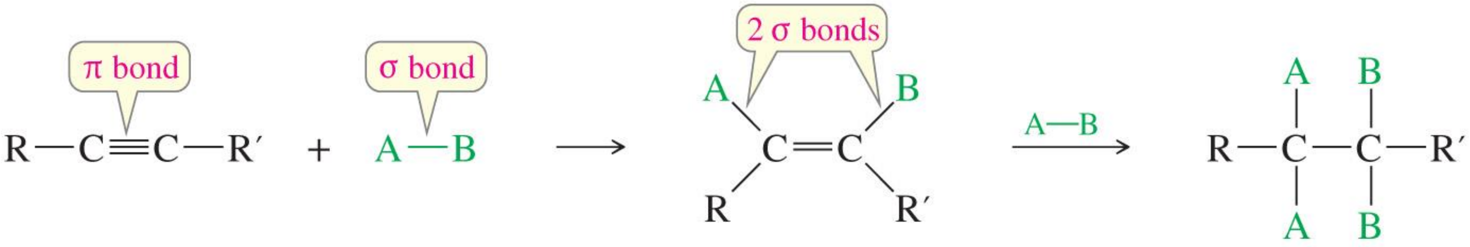
Recall that the π bond of an alkene is *weaker* than its σ bond.



Bond	Total Energy	Class of Bond	Approximate Energy
C—C	347 kJ (83 kcal)	alkane sigma bond	347 kJ (83 kcal)
C=C	611 kJ (146 kcal)	alkene pi bond	264 kJ (63 kcal)
C≡C	837 kJ (200 kcal)	second alkyne pi bond	226 kJ (54 kcal)

The sum of the two π bonds in an *alkyne* is **weaker** than the sum of two *alkene* π bonds.

The triple bond is **electron rich** and acts as a nucleophile (just like a double bond).

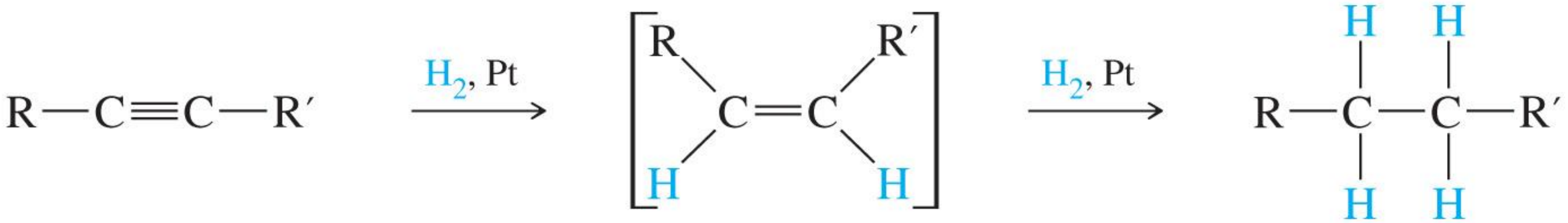


Since addition reactions convert π bonds into σ bonds, these reactions are typically **exothermic**.

Alkynes can add up to *two molecules* across the triple bond.

Addition of Hydrogen

Hydrogen in the presence of a catalyst will add twice to alkynes to generate alkanes.



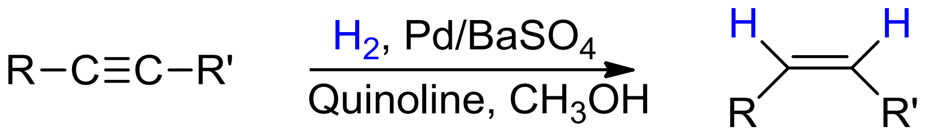
This reaction proceeds through a *cis* alkene intermediate, but **cannot** be stopped at this stage except with the use of a special catalyst.

$$\underset{\text{but-1-yne}}{H—C{\equiv}C—CH_2CH_3} \;+\; 2\,H_2 \xrightarrow{Pt} \underset{\substack{\text{butane}\\(100\%)}}{H—CH_2—CH_2—CH_2CH_3}$$

$$\underset{\text{but-2-yne}}{CH_3—C{\equiv}C—CH_3} \;+\; 2\,H_2 \xrightarrow{Pt} \underset{\substack{\text{butane}\\(100\%)}}{CH_3—CH_2—CH_2—CH_3}$$

The special catalyst is: Lindlar's catalyst

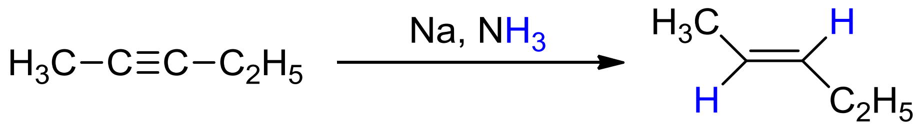
This is a partially deactivated (poisoned) catalyst consisting of barium sulfate, palladium and quinoline (the poison).



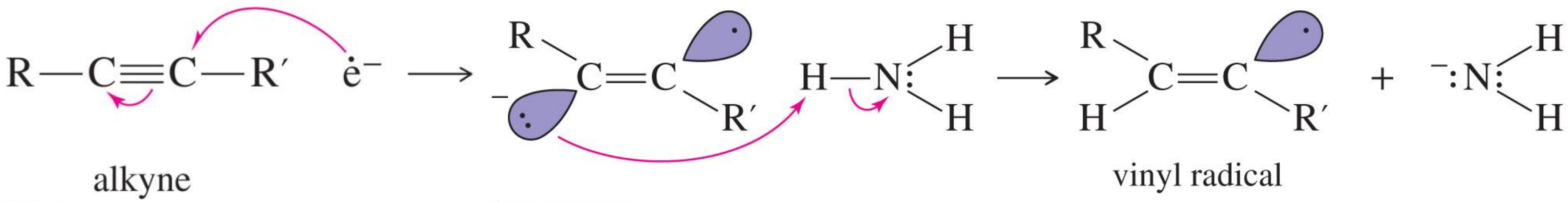
The hydrogens are delivered simultaneously to the same side of the alkyne, creating *syn* addition (*cis* alkenes).

Trans Alkenes

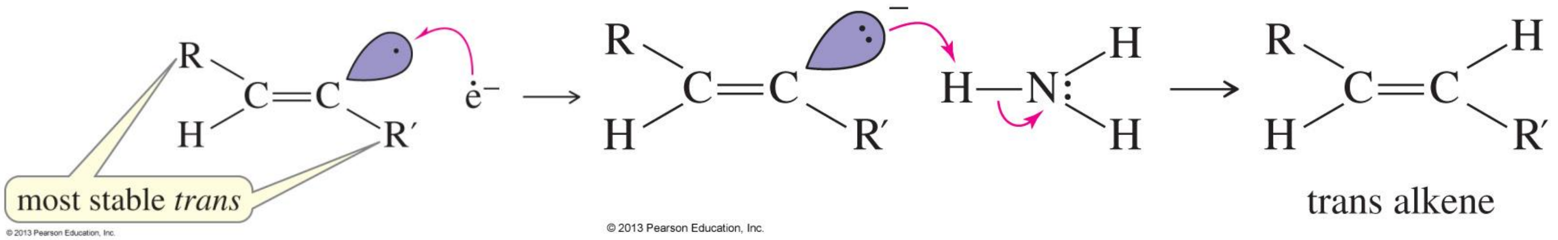
These can be produced by the action of sodium metal in liquid ammonia.



An electron is added to the triple bond, generating a radical anion, which is protonated to generate a vinyl radical.



The radical accepts another electron which produces an anion, which in turn gets protonated, giving the alkene with **anti** stereochemistry.

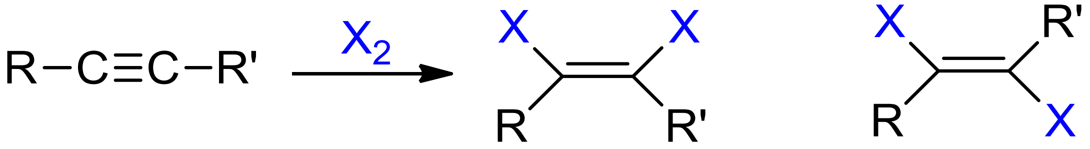


The anti stereochemistry arises from the two alkyl groups being as far away from each other as possible at the vinyl radical stage.

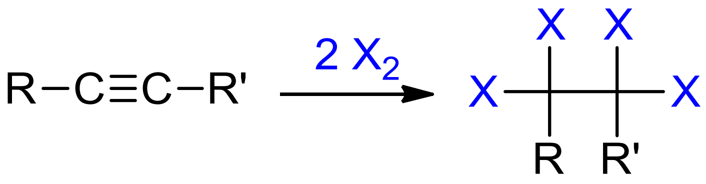
Addition of Halogens

Chlorine and bromine add in an analogous fashion as for alkenes.

If only one mole of halogen is added then a dihaloalkene is produced, and a mixture of *syn* and *anti* addition is observed.

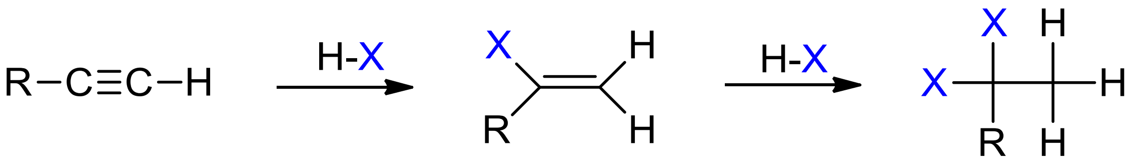


It is usually hard to control the addition of just one equivalent of halogen and it is more common to add two equivalents to generate tetrahalides.



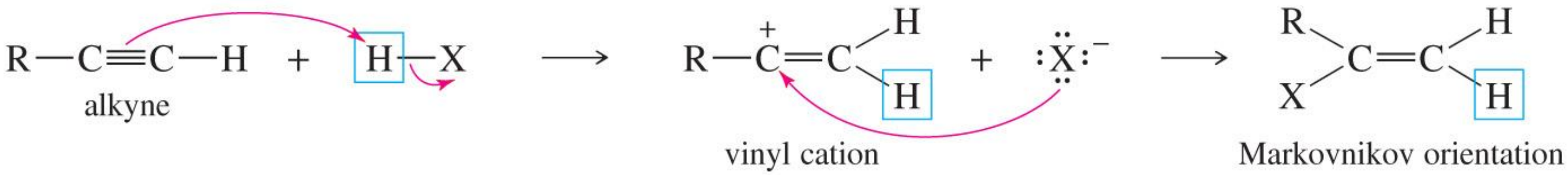
Addition of Hydrogen Halides

H-X can be added to alkynes just like to alkenes.

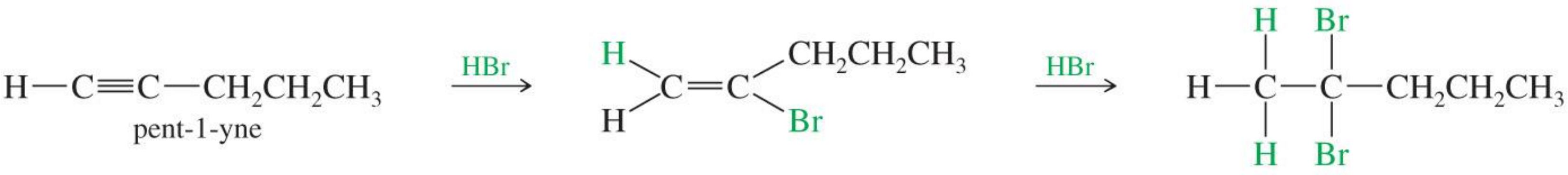


For **terminal** alkynes, the products have orientation as dictated by Markovnikov’s rule.

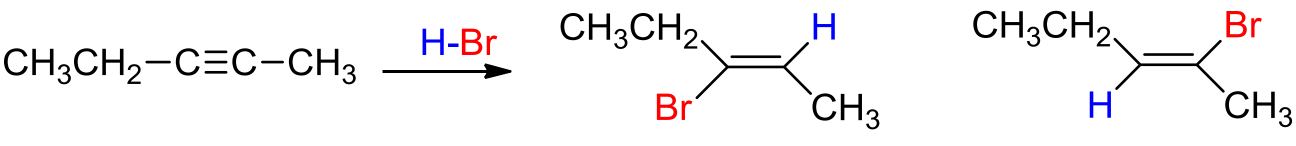
The vinyl cation is more stable with positive charge on the **more** substituted carbon.



The second mole of H-X will usually add with the same orientation as the first.



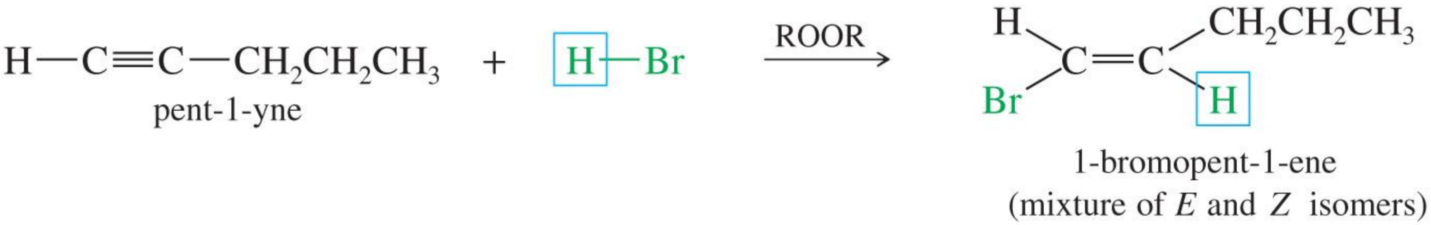
Internal alkynes show little selectivity since both intermediate cations are equally substituted.



E *and* Z

E *and* Z

The *peroxide effect* is also observed with the addition of H-Br and peroxides to generate anti-Markovnikov products.



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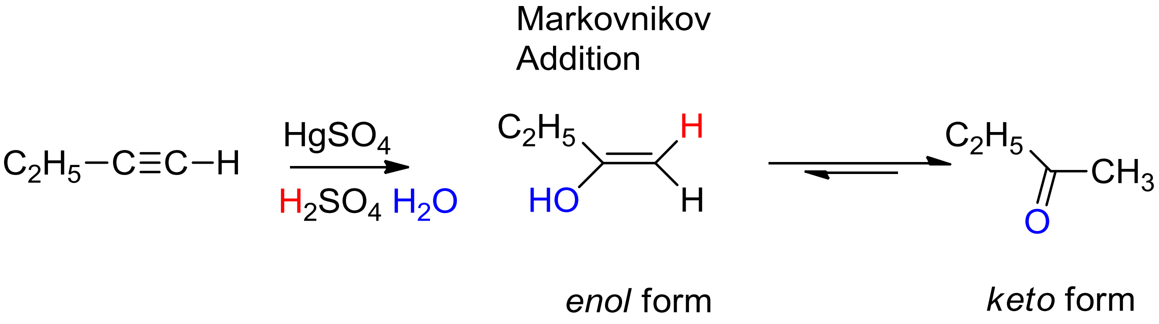
Hydration of Alkynes to Ketones and Aldehydes

There are two different methods:

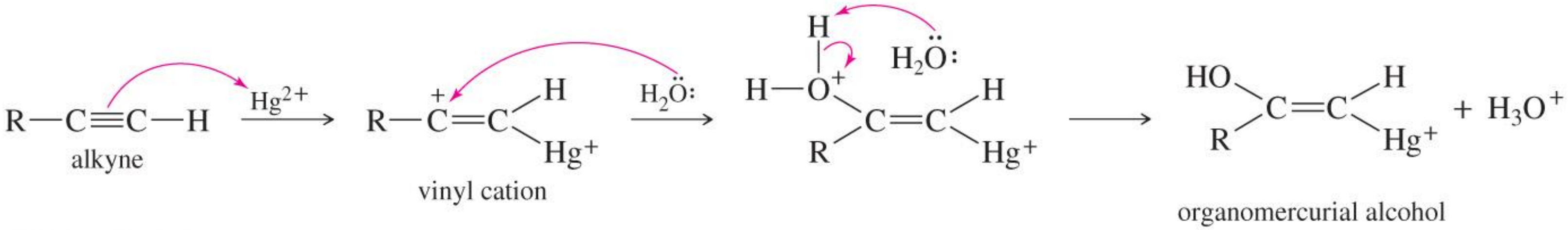
Mercuric-ion catalyzed hydrations

A mixture of mercuric sulfate and aqueous sulfuric acid is used to perform addition of water across the triple bond.

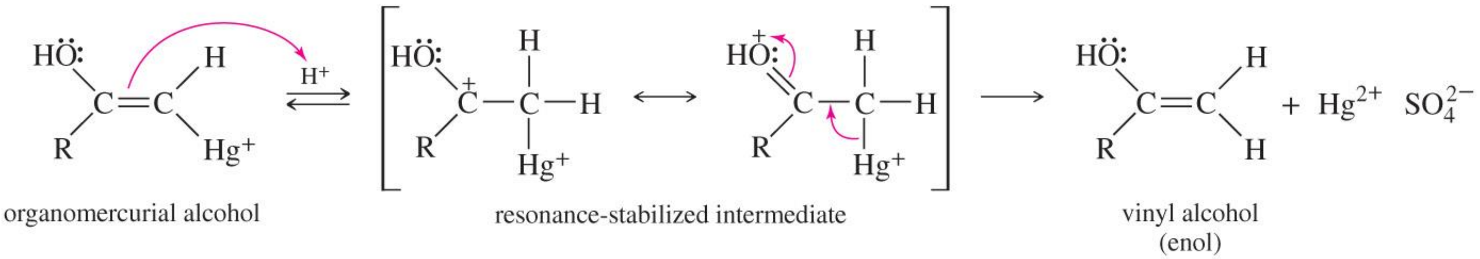
The orientation is Markovnikov, and the initial products are enols.



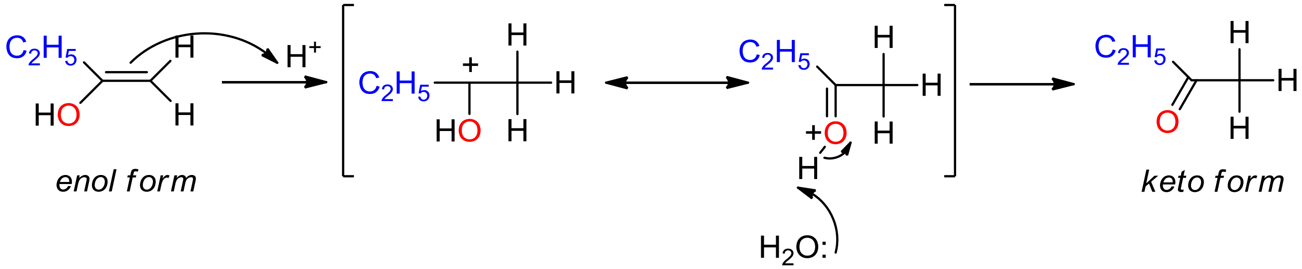
Electrophilic addition of the Hg^{2+} ion generates a vinyl cation, which is attacked by a nucleophilic water molecule.



Deprotonation gives an organomercurial alcohol which, under acidic conditions, has the mercury replaced by a hydrogen, to generate a vinyl alcohol (*enol*).



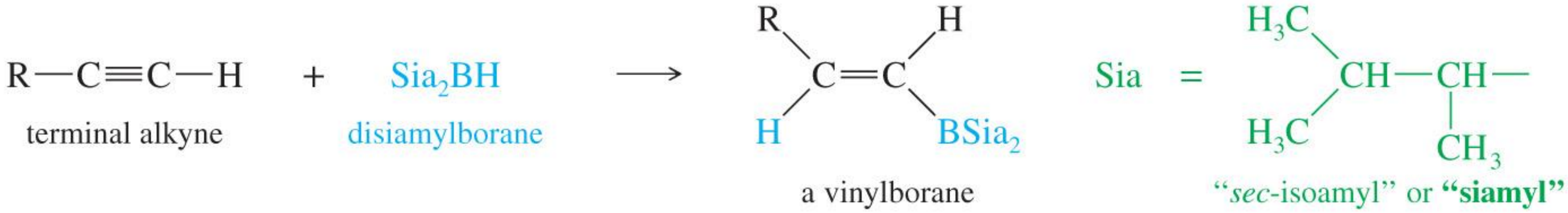
Enols tend to be unstable, and isomerise to their more stable ketone form.
Enols are always in equilibrium with their ketone form – this is an example of *keto-enol tautomerism*.



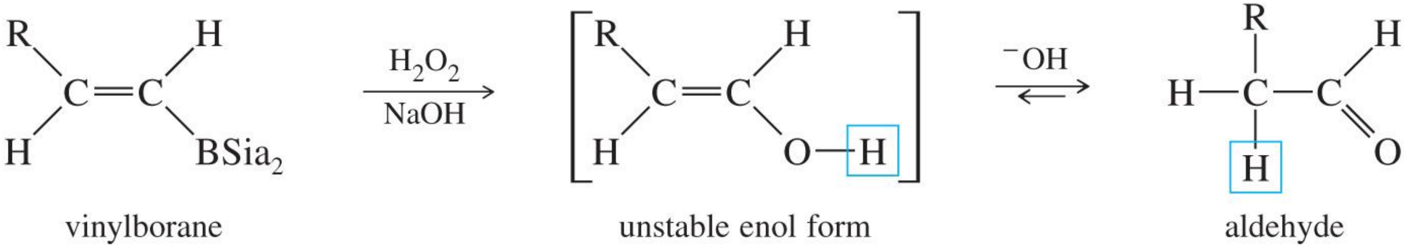
Hydroboration-Oxidation

Previously we saw hydroboration-oxidation of alkenes gave *anti-Markovnikov* addition of water across the double bond.

The same occurs for alkynes, except a sterically hindered dialkylborane must be used to prevent the addition of two borane molecules. (Usually di(*sec*-isoamyl)borane is used).



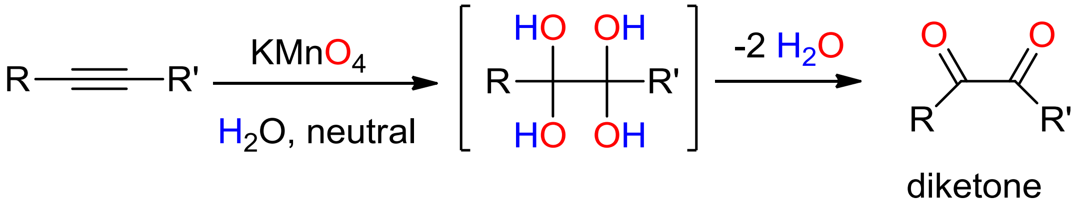
A vinyl borane is produced with anti-Markovnikov orientation, which then is oxidized using basic hydrogen peroxide to an *enol*, which tautomerises into the more stable *keto* form.



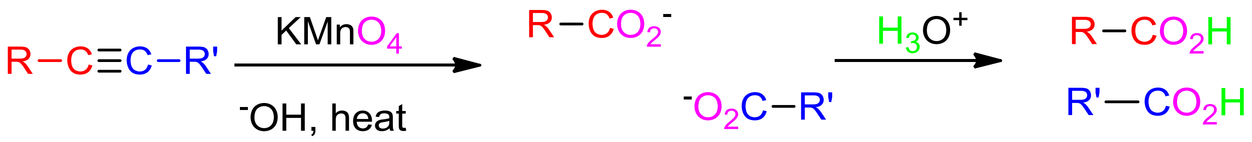
Terminal alkynes are converted into aldehydes.

Oxidation of Alkynes

Under mild (cold, neutral) conditions the reaction of potassium permanganate with an alkyne can generate a diketone.

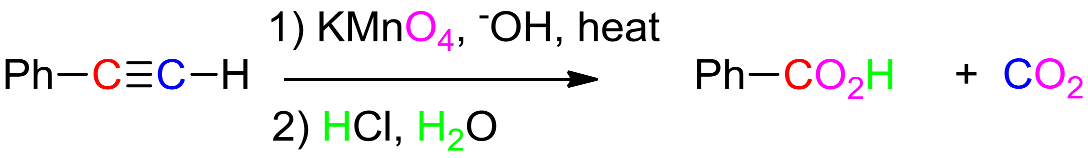


If the mixture becomes too warm or basic, the oxidation proceeds further to generate two carboxylate anions, which on acidification generates two carboxylic acids.



$$R-C\equiv C-R' \xrightarrow[^{-}OH,\ heat]{KMnO_4} R-CO_2^- \quad ^{-}O_2C-R' \xrightarrow{H_3O^+} R-CO_2H \quad R'-CO_2H$$

Terminal alkynes are similarly cleaved to give a carboxylic acid and carbon dioxide.



$$Ph-C\equiv C-H \xrightarrow[2)\ HCl,\ H_2O]{1)\ KMnO_4,\ ^{-}OH,\ heat} Ph-CO_2H + CO_2$$

Ozonolysis

Ozonolysis of an alkyne followed by hydrolysis gives similar products to those obtained from permanganate oxidative cleavage, except *terminal* alkynes yield formic (methanoic) acid.