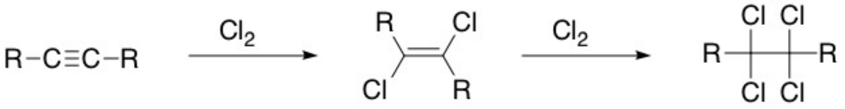
CHEM 261 Nov 20, 2018

Addition reactions of Alkynes

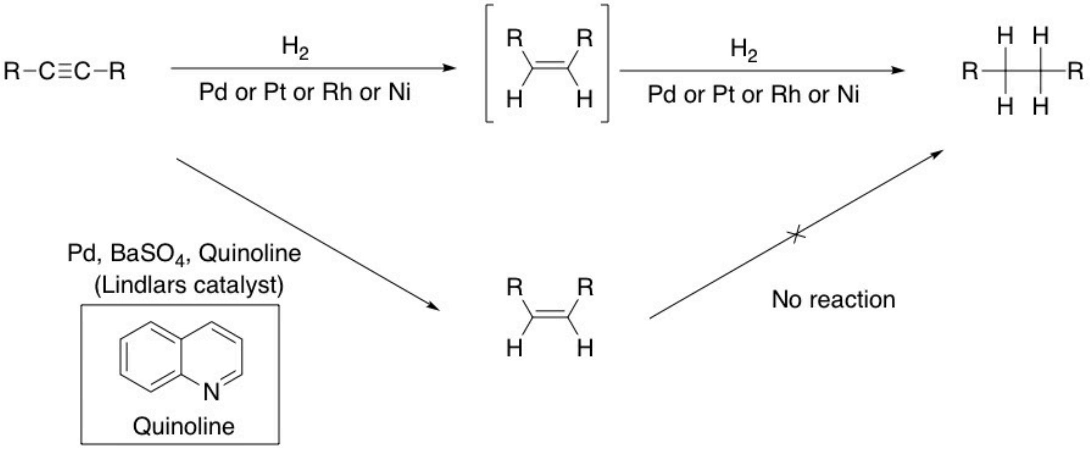
Alkynes are more polar as they have more negative charge between the two carbons. They are always more reactive than alkenes and so can be utilized in all addition reactions that alkenes can, except react faster.

The carbon-carbon triple bond is composed of two pi bonds and a sigma bond

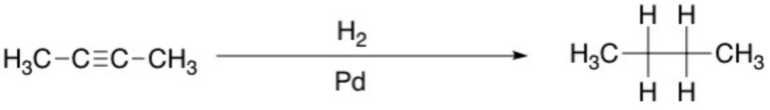


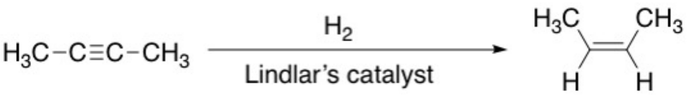
The first addition to the alkyne is anti, which forms the trans alkene.

Hydrogenation of Alkynes

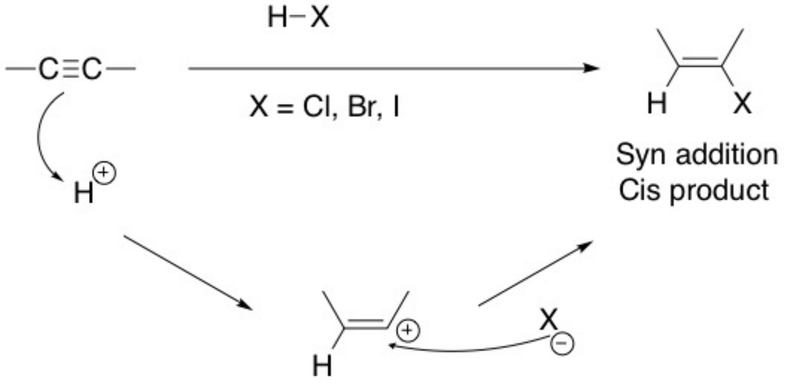


Example: 2-butyne



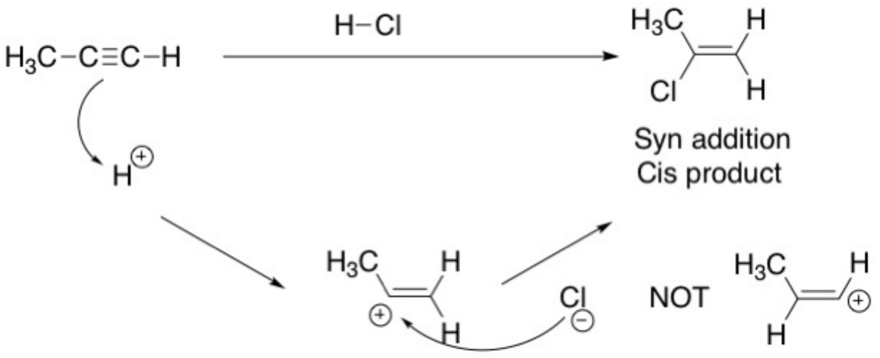


HX Addition

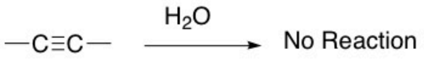


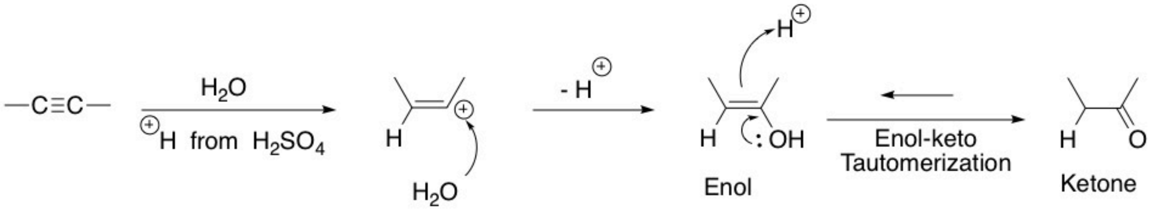
RECALL: Addition of HX across the double bond occurs in Markovnikov fashion

Example: 1-propyne



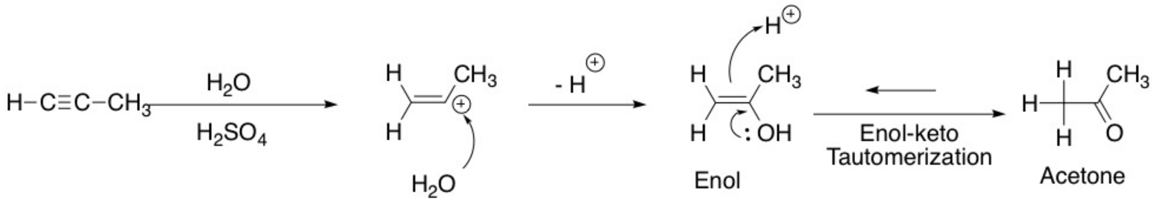
Addition of H_2O



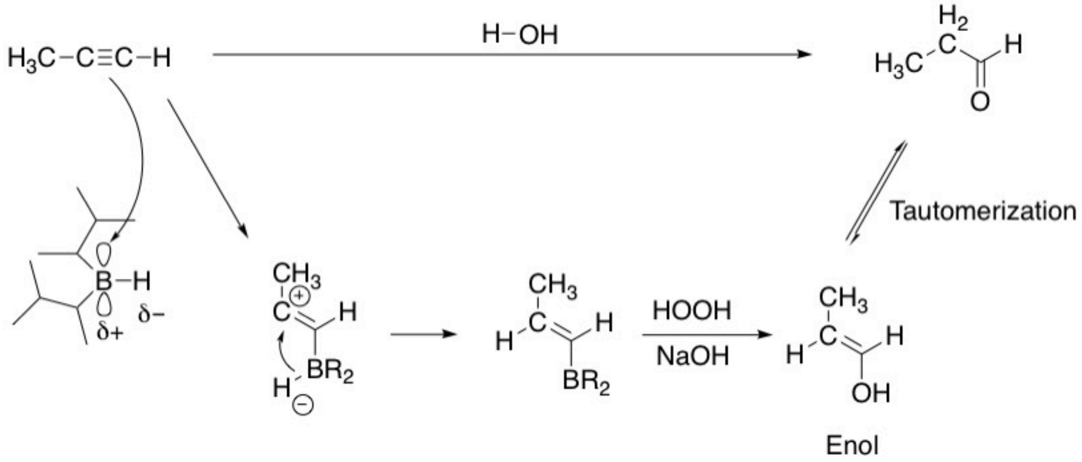


Tautomers are rapidly interconverting structural isomers. In the above example, the ketone and enol are tautomers.

Example: 1-propyne

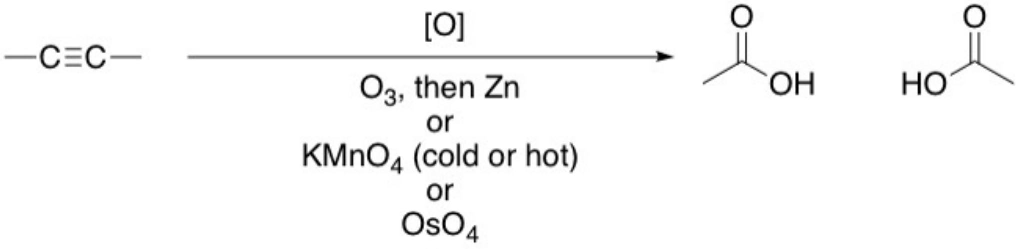


What if we want addition in anti-Markovnikov fashion?
Then we use a borane reagent!



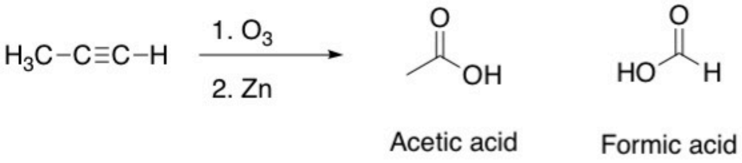
Notice how in the above examples with 1-propyne, depending on which reagents are used one can carry out a Markovnikov addition leading to a ketone or an anti-Markovnikov addition leading to an aldehyde.

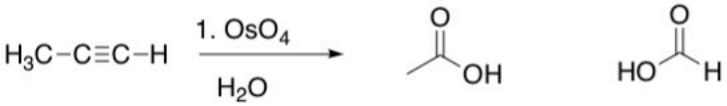
Oxidation of Alkynes

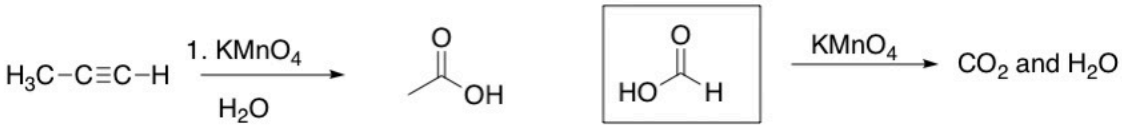


Any of the reagents shown can be used on an alkyne to produce the acids shown on the right.

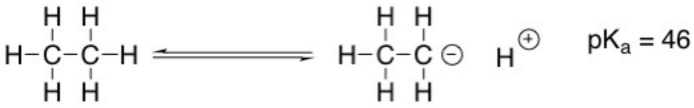
Examples: 1-propyne

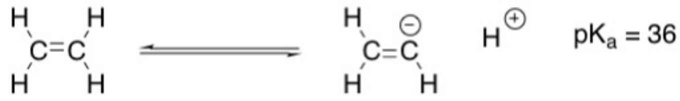


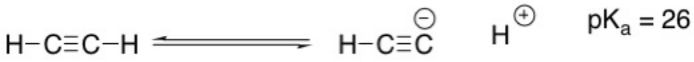




Synthesis of Alkenes and Alkynes

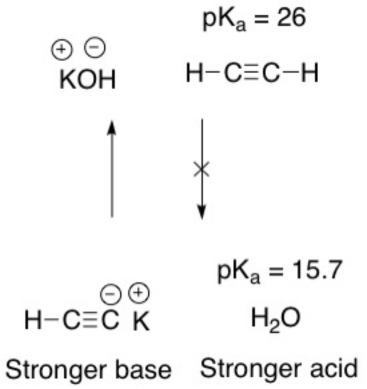


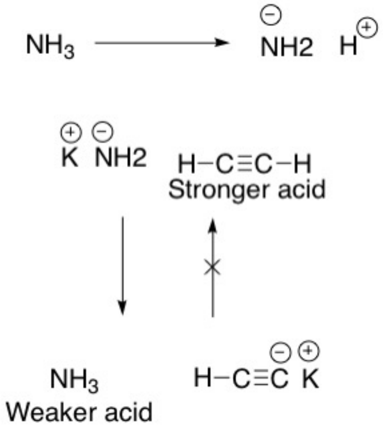




Equilibrium lies to the left in each of these reactions as alkanes, alkenes, and alkynes are very weakly acidic.

Deprotonating acetylenes

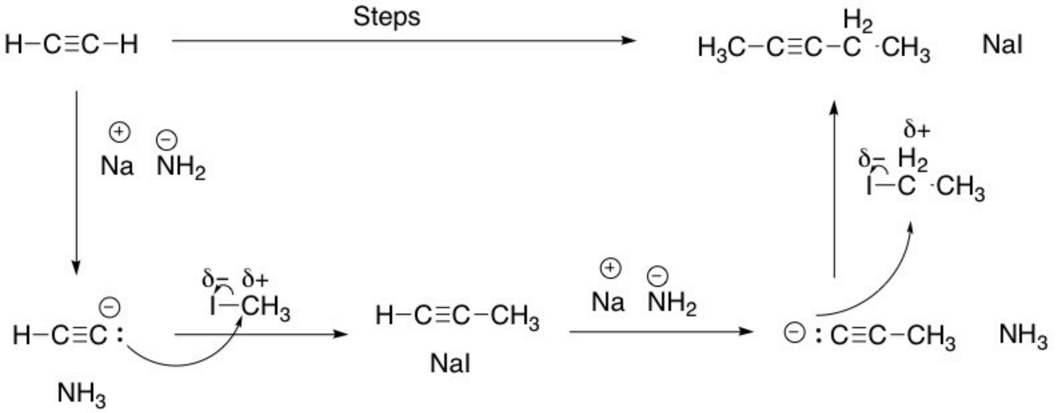




KOH will not deprotonate acetylene because it is a weaker base than acetylenes conjugate base (acetylide).

On the other hand KNH_2 will deprotonate acetylene, as the resulting acetylide is a weaker base. Ammina pKa is 36

Organic synthesis example:



Both substitution reactions involving methyl iodide and ethyl iodide are S_N2, as the primary and secondary carbons will not hold the positive charge that is characteristic of an S_N1 intermediate (tertiary carbocation).