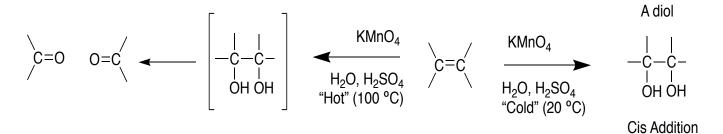
Oxidation Reactions of Alkenes (Addition Reactions)

Potassium Permanganate: KMnO4

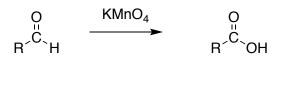
κ[⊕] 0[⊖] 0 0″ 0

Purple crystals in H₂O and H₂SO₄

General Scheme:

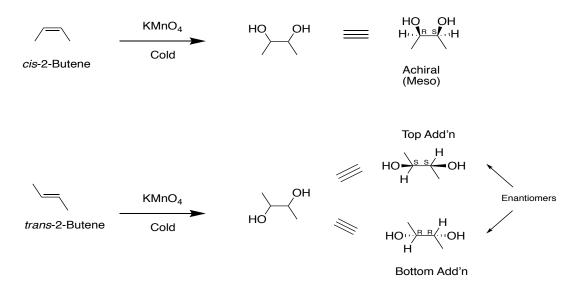


Reaction with aldehydes:

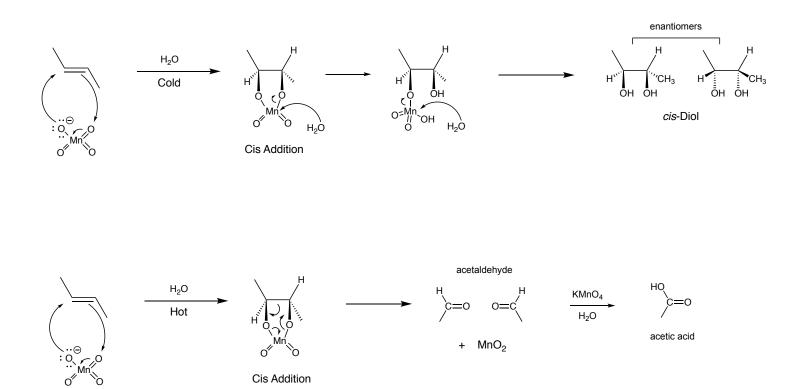


$$\begin{array}{c} O \\ H \\ C \\ H \end{array} \xrightarrow{\mathsf{KMnO}_4} \\ \mathsf{CO}_2 + \\ \mathsf{H}_2 \\ \mathsf{CO}_2 + \\ \mathsf{H}_2 \\ \mathsf{CO}_2 + \\ \mathsf{H}_2 \\ \mathsf{CO}_2 + \\ \mathsf{CO}_2 \\ \mathsf{H}_2 \\ \mathsf{CO}_2 + \\ \mathsf{CO}_2 \\ \mathsf{CO}_2 + \\ \mathsf{CO}_2 \\$$

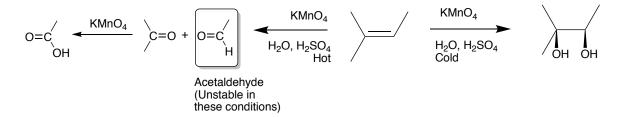
Example 1:



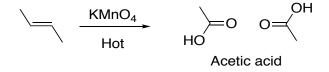
Mechanism:

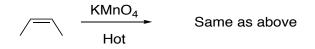


Example 2:

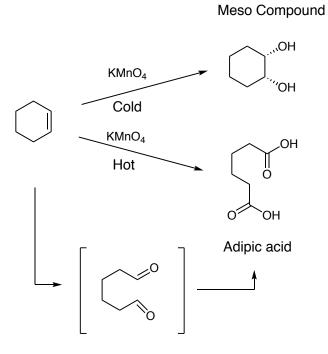


Example 3:





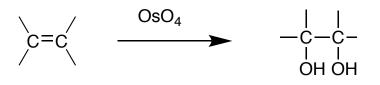
Example 4:



Osmium Tetraoxide: OsO4

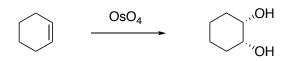
Toxic, Volatile

General Scheme:

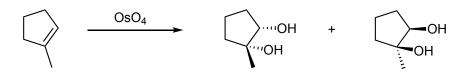


Syn/Cis Addition

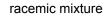
Example 1:



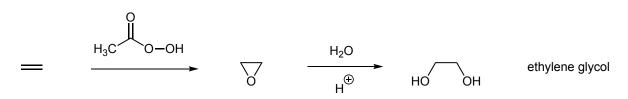
Example 2:



Z-1-methylcyclopent-1-ene



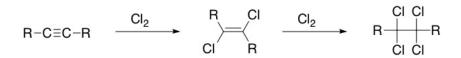
Recall:



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

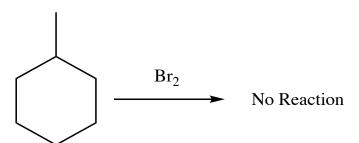


The first addition to the alkyne is anti, which forms the trans alkene.

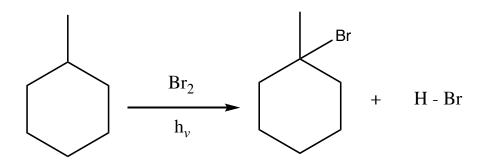
Recall:

Halogenation of alkanes: (radical source)

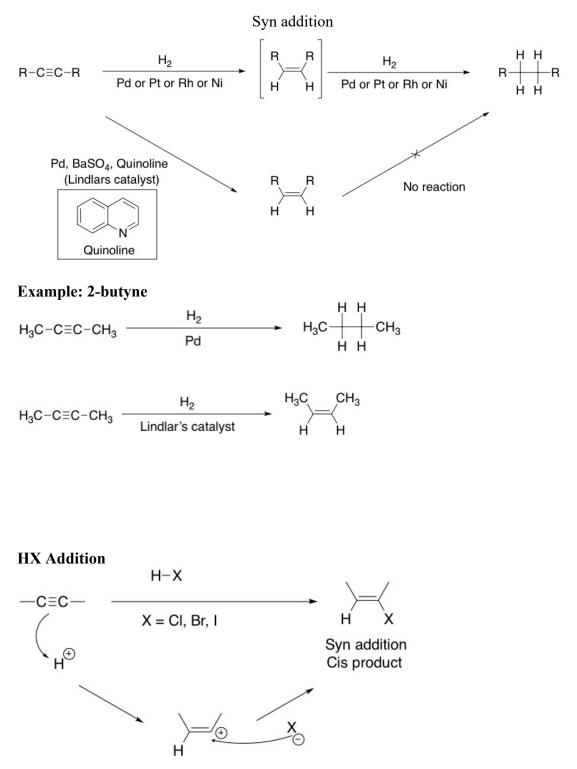
Example:



- requires light or heat to cause a reaction between the starting material and halogen.

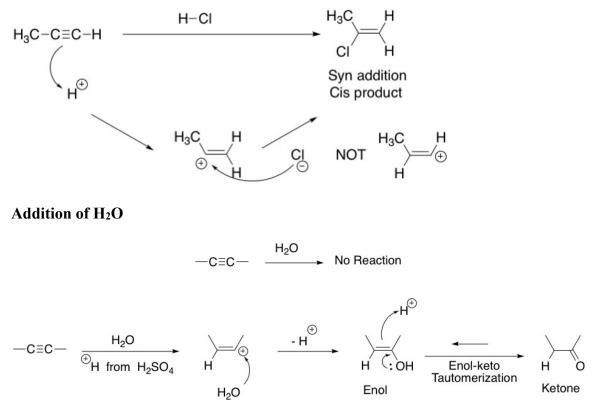


Hydrogenation of Alkynes



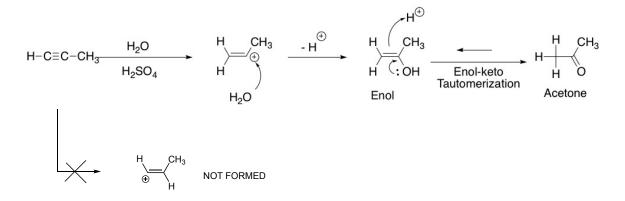
RECALL: Addition of HX across the double bond occurs in Markovnikov fashion

Example: 1-propyne

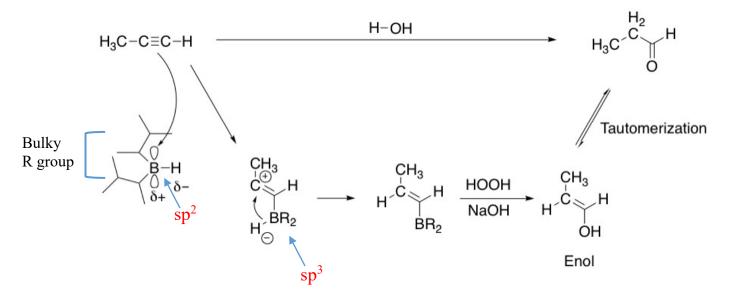


Tautomers are rapidly interconverting structural isomers. In the above example, the ketone and enol are tautomers.

Example: 1-propyne

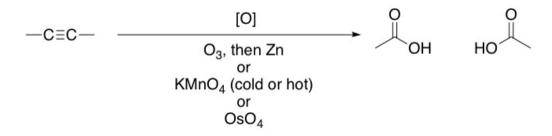


What if we want addition in anti-Markovnikov fashion? Then we use a borane reagent!



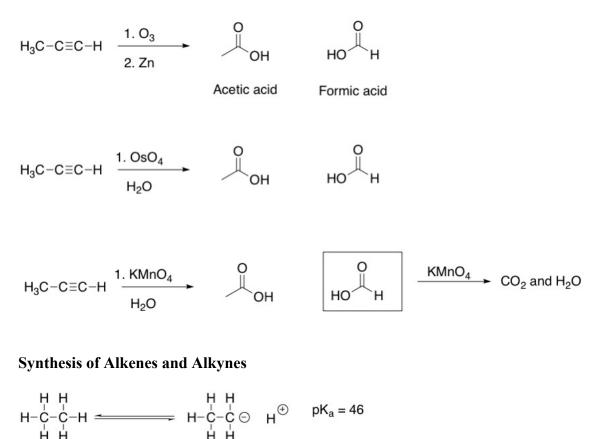
Notice how in the above examples with 1-propyne, depending on which reagents are used one can carry out a Markovnikov addition leading to a ketone or an anti-Markovnikov addition leading to an aldehyde.

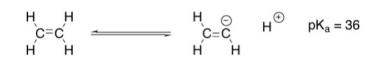
Oxidation of Alkynes



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

Examples: 1-propyne

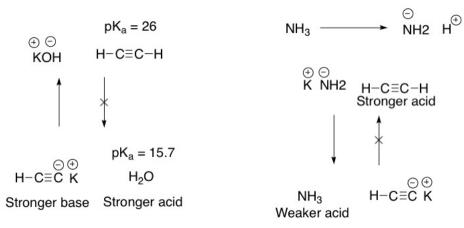




 $H-C\equiv C-H \xrightarrow{\frown} H-C\equiv C H^{\oplus} pK_a = 26$

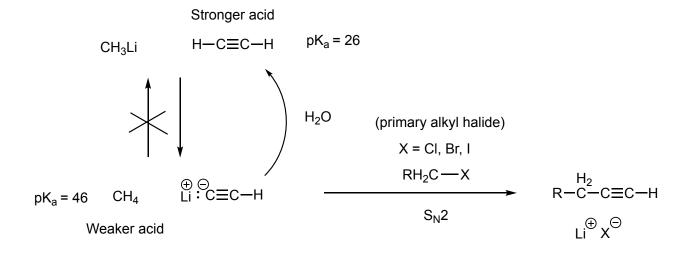
Equilibrium lies to the left in each of these reactions as alkanes, alkenes, and alkynes are very weakly acidic.

Deprotonating acetylenes

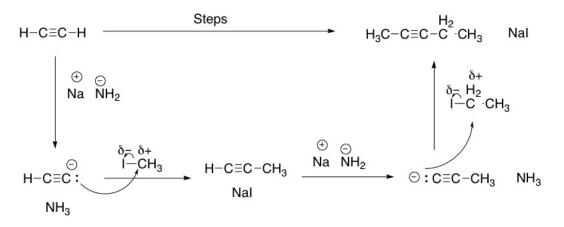


KOH will not deprotonate acetylene because it is a weaker base than acetylenes conjugate base (acetylide).

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



Organic synthesis example:



Both substitution reactions involving methyl iodide and ethyl iodide are $S_N 2$, as the primary and secondary carbons will not hold the positive charge that is characteristic of an $S_N 1$ intermediate (tertiary carbocation).