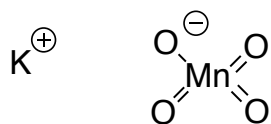


Oxidation of Alkenes:

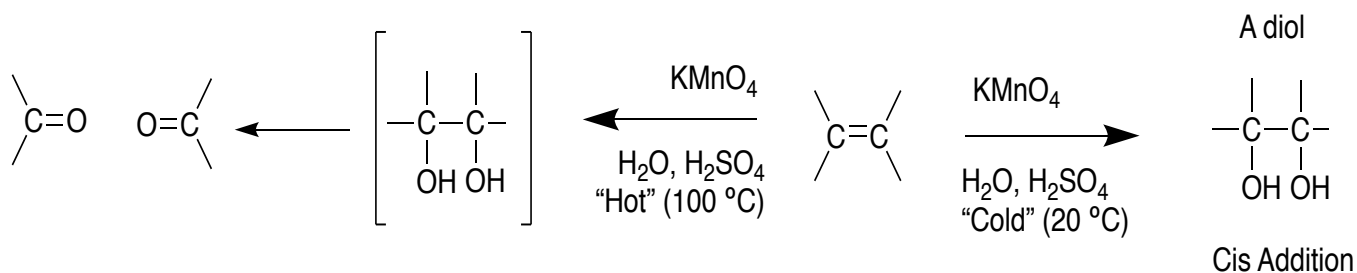
Potassium Permanganate: KMnO_4



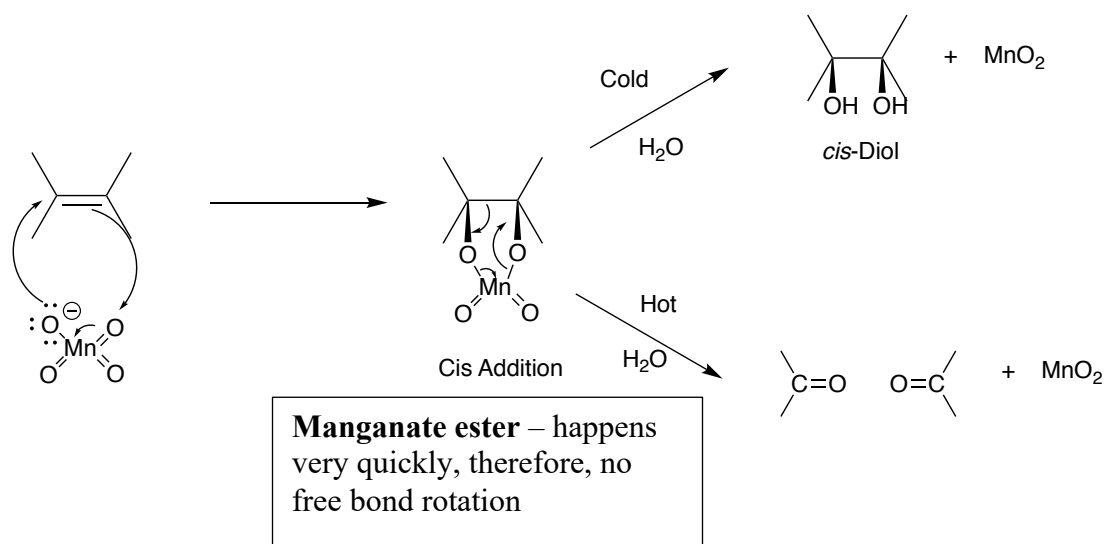
Purple crystals in H_2O and H_2SO_4

- Frequently used in acid solutions
- Used to kill fungi – dissolves the membrane of fungi
- Good oxidizing agent (wants to grab electrons)

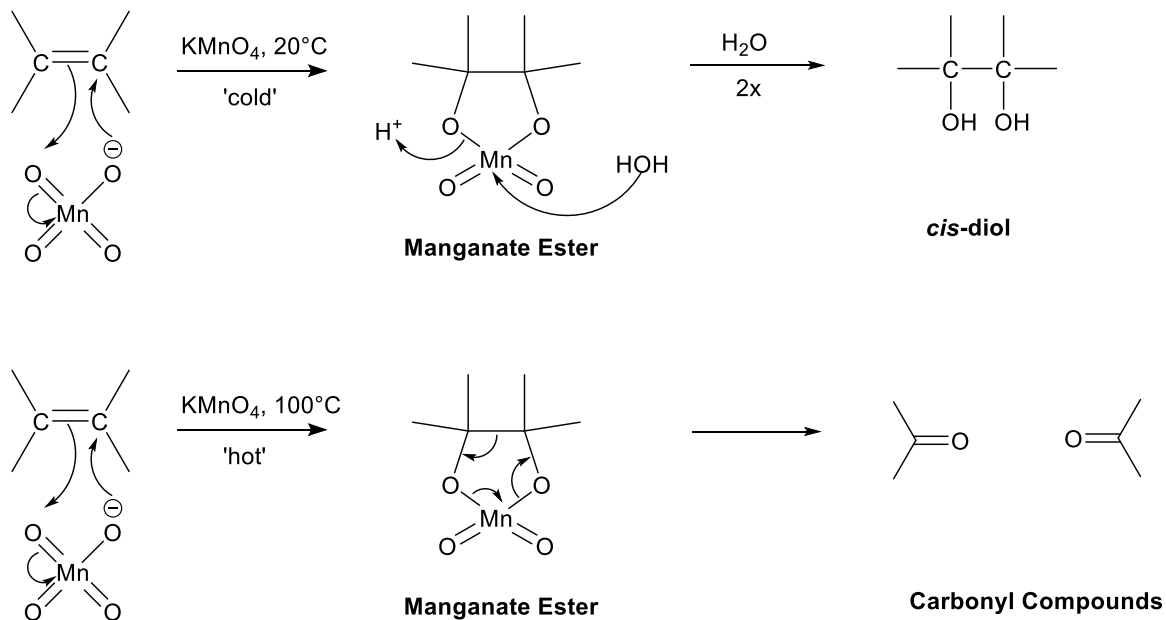
General Scheme:



Mechanism:



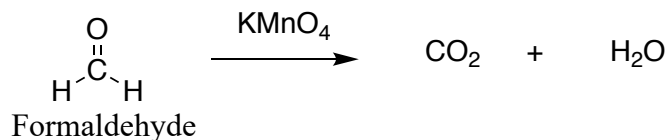
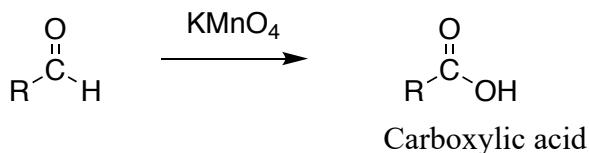
A closer look:



- Reaction of alkenes with 'cold' KMnO_4 is stereospecific (cis/syn addition)
- Under 'cold' reaction conditions, H_2O attacks the manganate ester twice to form the *cis*-diol. The reaction is **stereospecific**.
- Under 'hot' reaction conditions, there is enough energy to break the C-C bond on the manganate ester, resulting to the formation of carbonyl compounds (i.e., ketone, aldehydes, carboxylic acids, etc.)

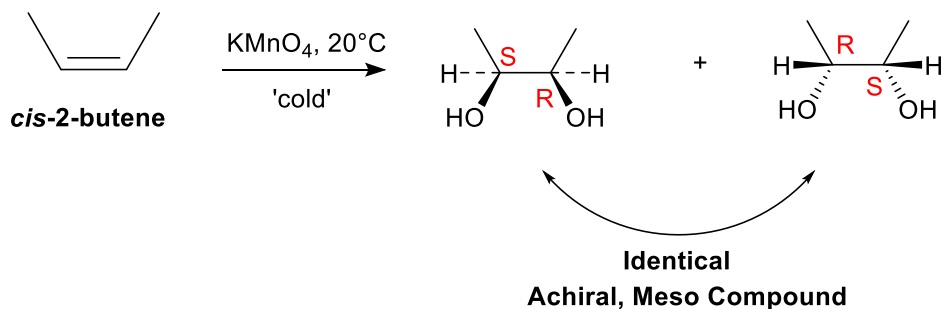
Reaction with aldehydes:

- In 'hot' KMnO_4 oxidations, aldehydes are oxidized further. Ketones, on the other hand, won't get oxidized further.

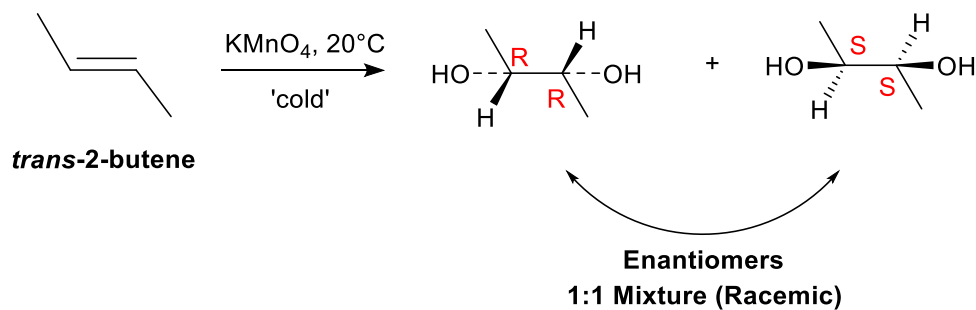


- Formaldehyde
 - o disinfectant – used to preserve cadavers
 - o is further oxidized to form CO_2 and H_2O in the presence of excess KMnO_4

cis-2-butene vs *trans*-2-butene

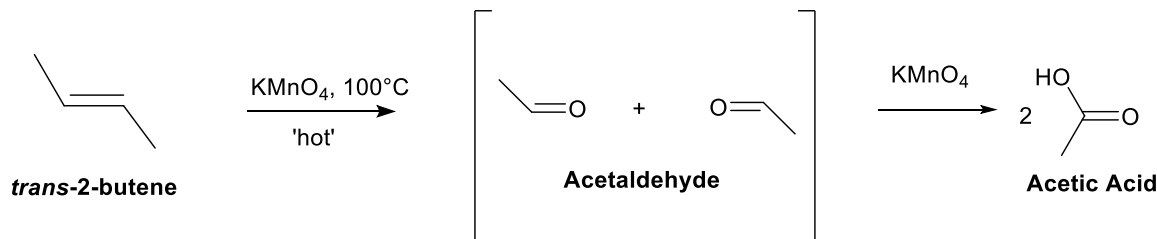


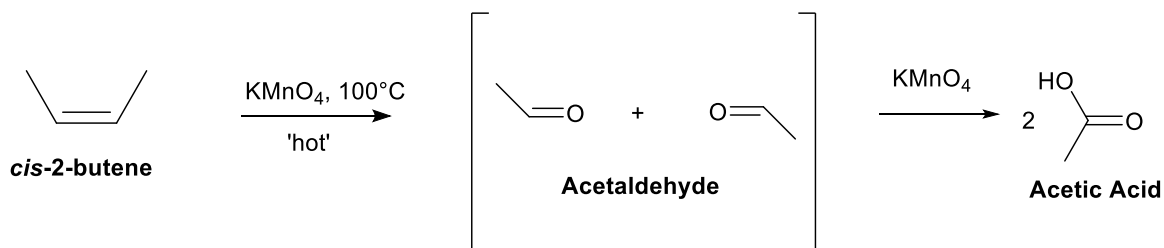
- 'Cold' KMnO_4 – 50/50 chance that KMnO_4 attaches from the top or from the bottom due to the planar structure of the *cis*-2-butene



- Chance of the reaction going from the top or the bottom is 50/50
- 1:1 mix of enantiomers (racemic mixture)
- Reaction is stereospecific
- Initial addition of the permanganate on the double bond is concerted – all bonds break and form at the same time

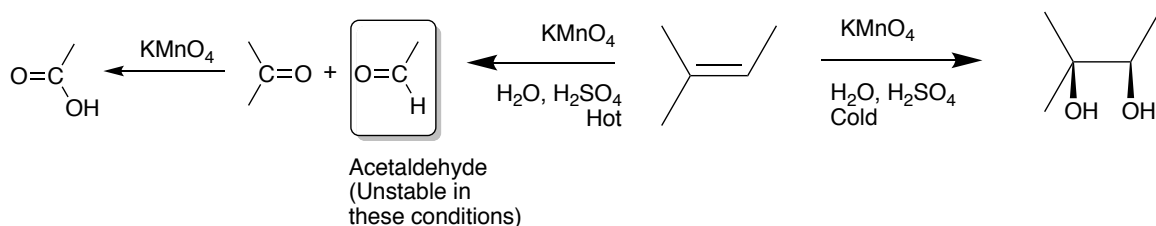
'Hot' Permanganate Oxidation



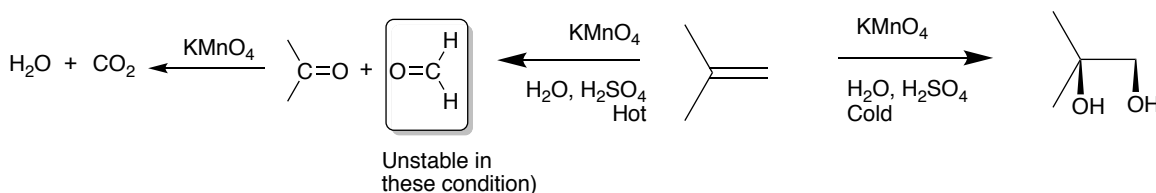


- Hot (100°C) KMnO_4 oxidation of 2-butene cleaves the double bond to form 2 molecules of acetic acid
- High temperature provides enough energy to break the C–C double bond in the manganate ester to initially form acetaldehyde which is then further oxidized to acetic acid
- Same oxidation products for *cis*-2-butene and *trans*-2-butene – breaking the C–C bond in the permanganate ester results in the loss of stereochemistry

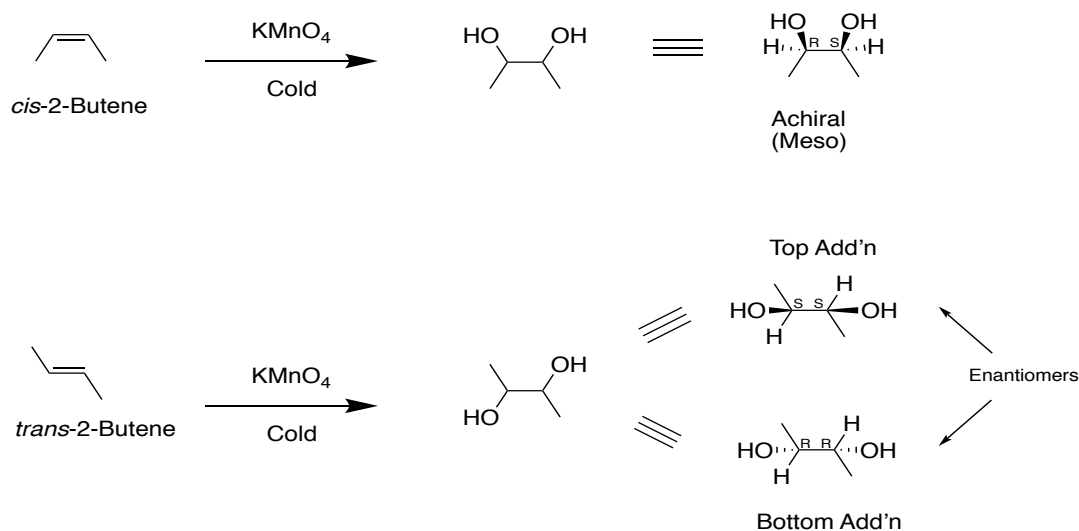
Example 1:



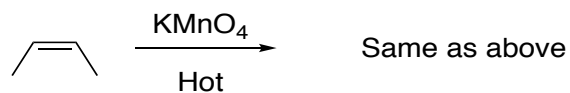
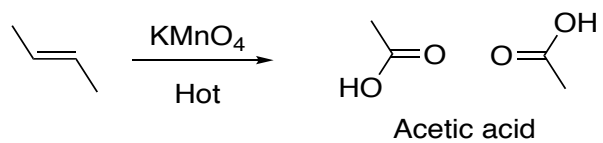
Example 2:



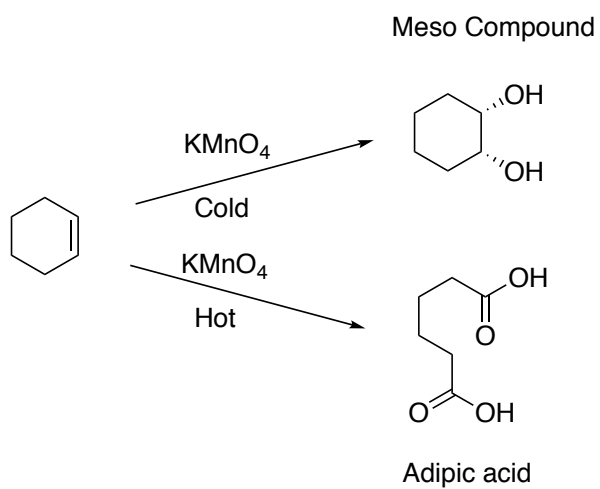
Example 3: see discussion above



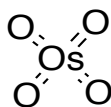
Example 4:



Example 5:



Osmium Tetraoxide: OsO_4



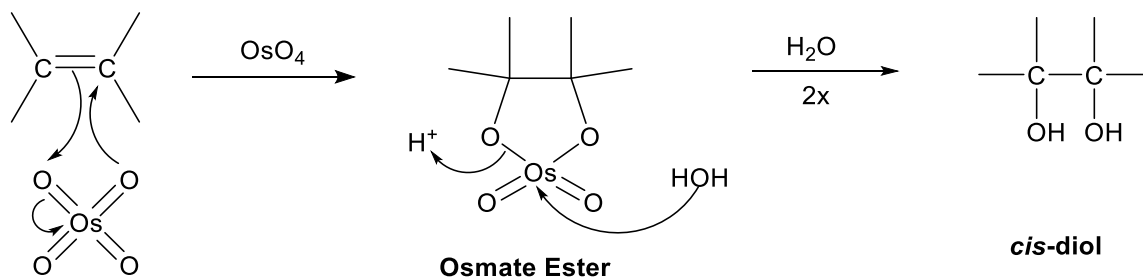
Toxic, Volatile

General Scheme:



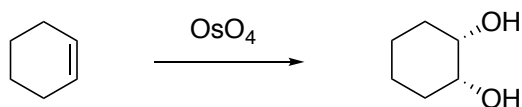
Syn/Cis Addition

Mechanism:



- OsO₄ adds across the double bond to form osmate ester
- Osmate ester (very stable) is then attacked by H₂O to form *cis* diols
- Reaction is stereospecific (syn/cis addition)

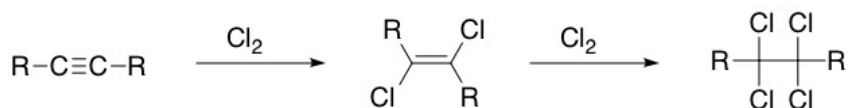
Example 1:



Addition reactions of Alkynes

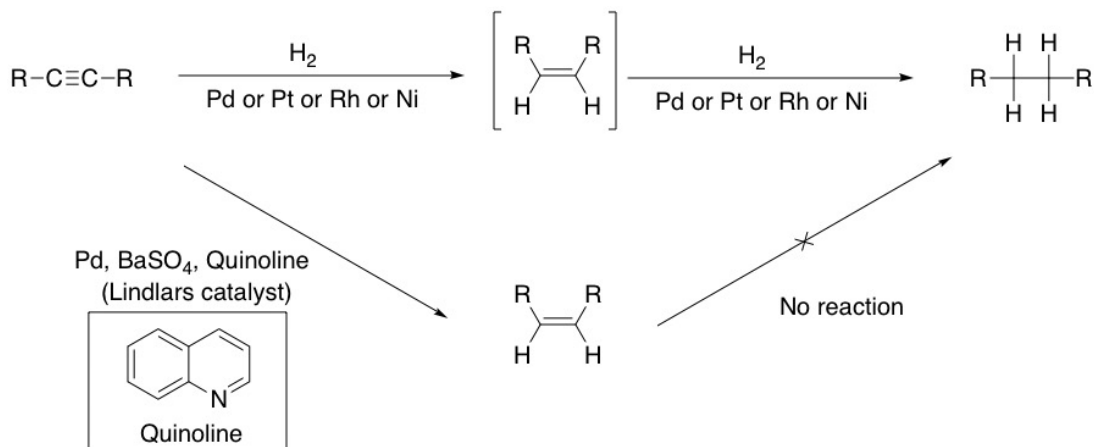
Alkynes are more polar as they have more negative charge between the two carbons. They are always more reactive than alkenes and so can be utilized in all addition reactions that alkenes can, except react faster.

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



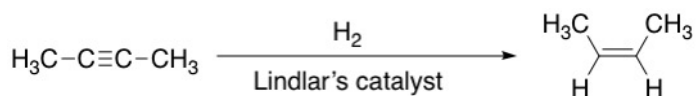
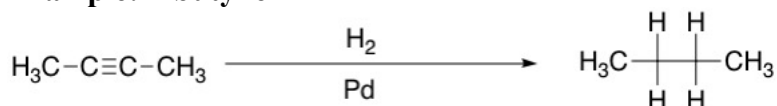
The first addition to the alkyne is anti, which forms the trans alkene.

Hydrogenation of Alkynes



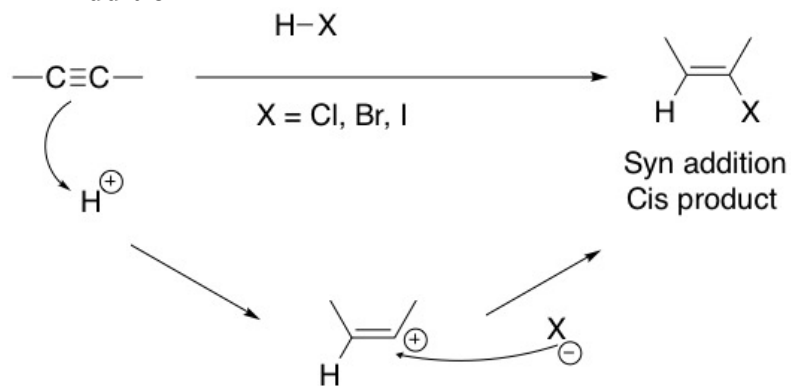
- **Lindlar's catalyst** – quinoline complexes with the metal and deactivates it. Hence, the hydrogenation reaction stops at the alkene.

Example: 2-butyne



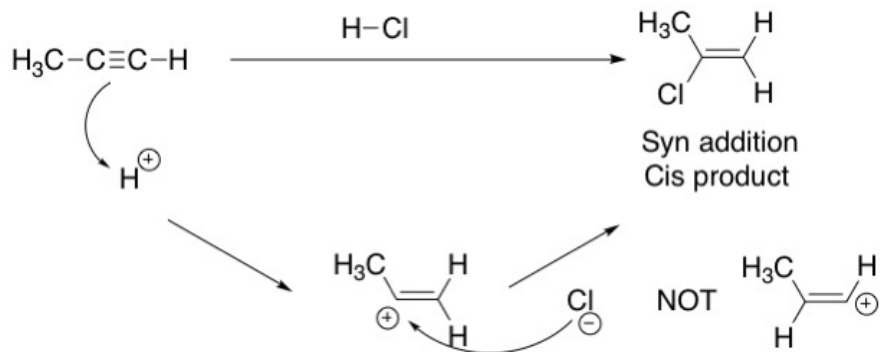
- Reaction is stereospecific – H atoms are added on the same side of the double bond

HX Addition



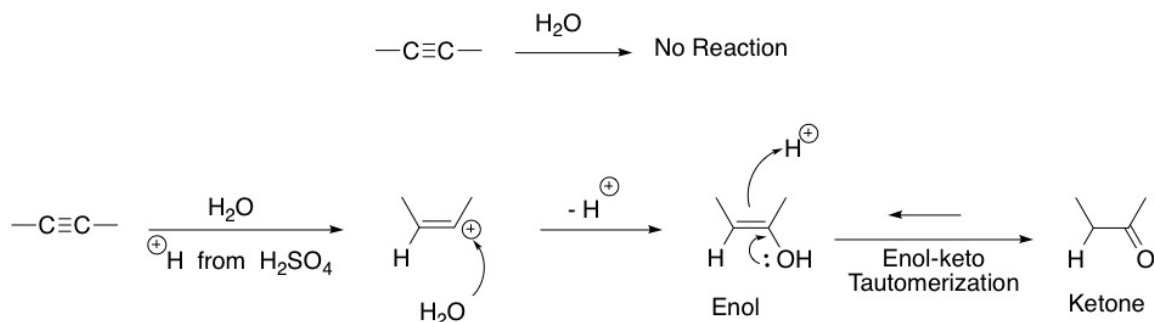
RECALL: Addition of HX across the double bond occurs in Markovnikov fashion – the positive end of the added adds to the least substituted end of a multiple bond.

Example: 1-propyne



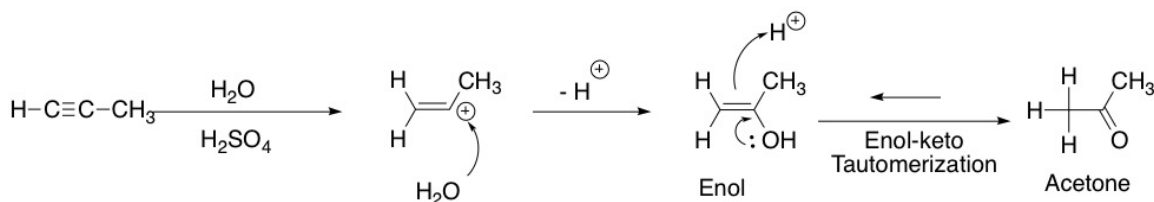
Addition of H_2O

- Needs the presence of acid (H^+) such as H_2SO_4 for the reaction to proceed
- H_2O is not electrophilic enough to pull the electrons from the multiple bond



- **Enols** are generally unstable and tends to isomerize to the **keto form** (generally favoured over the enol – less thermodynamically energetic) – this process is called **tautomerization**
- **Tautomers** are rapidly interconverting structural isomers. In the above example, the ketone and enol are tautomers. **Note:** these are not resonance forms since the position of the H atom is changed.

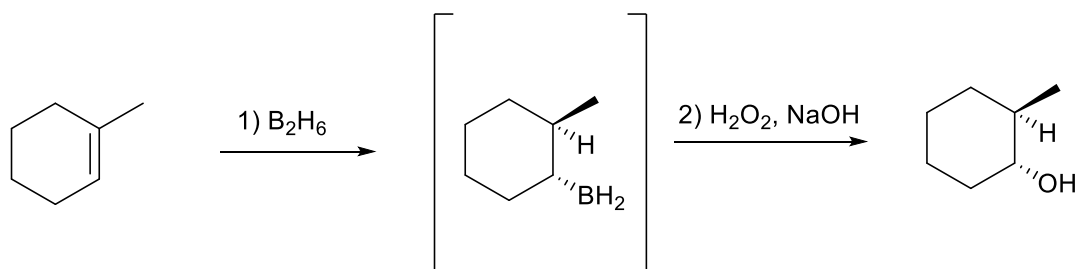
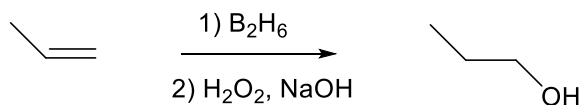
Example: 1-propyne



Hydroboration - Oxidation

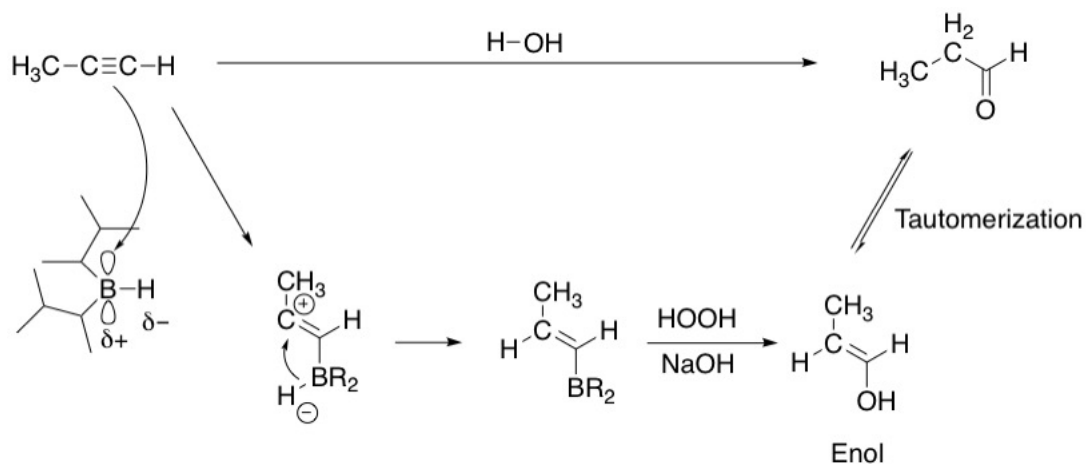
What if we want addition in anti-Markovnikov fashion?
Then we use a borane reagent!

RECALL: Hydroboration of alkenes



- Cis/syn addition
- Oxidation with $\text{H}_2\text{O}_2/\text{NaOH}$ replaces the C-B bond with retention of configuration

Hydroboration of Alkynes



- Can use diborane but generally use sterically hindered organoborane to prevent multiple additions across the multiple bond

Note: Notice how in the above examples with 1-butyne, 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.