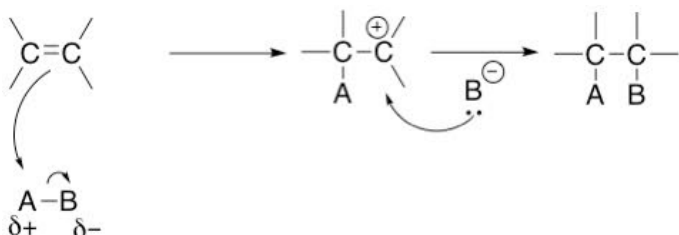
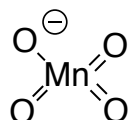


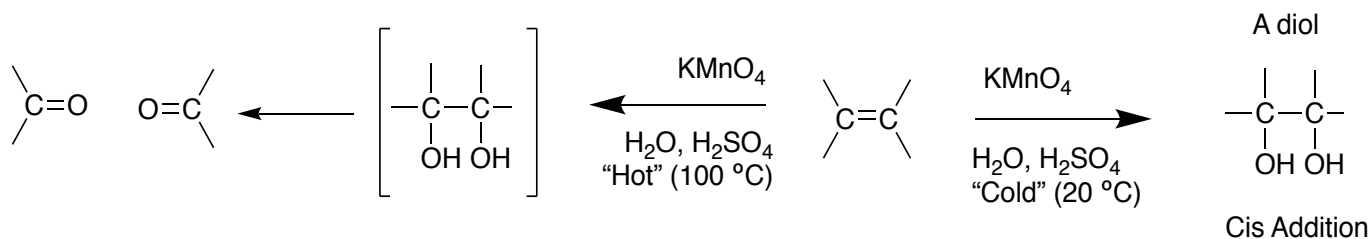
**RECALL:****Addition Reactions**

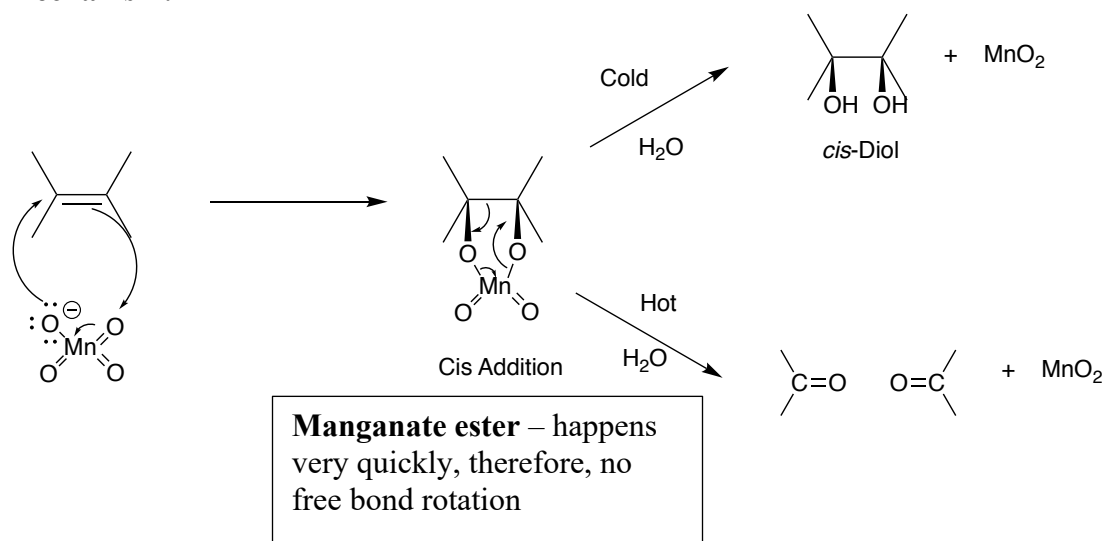
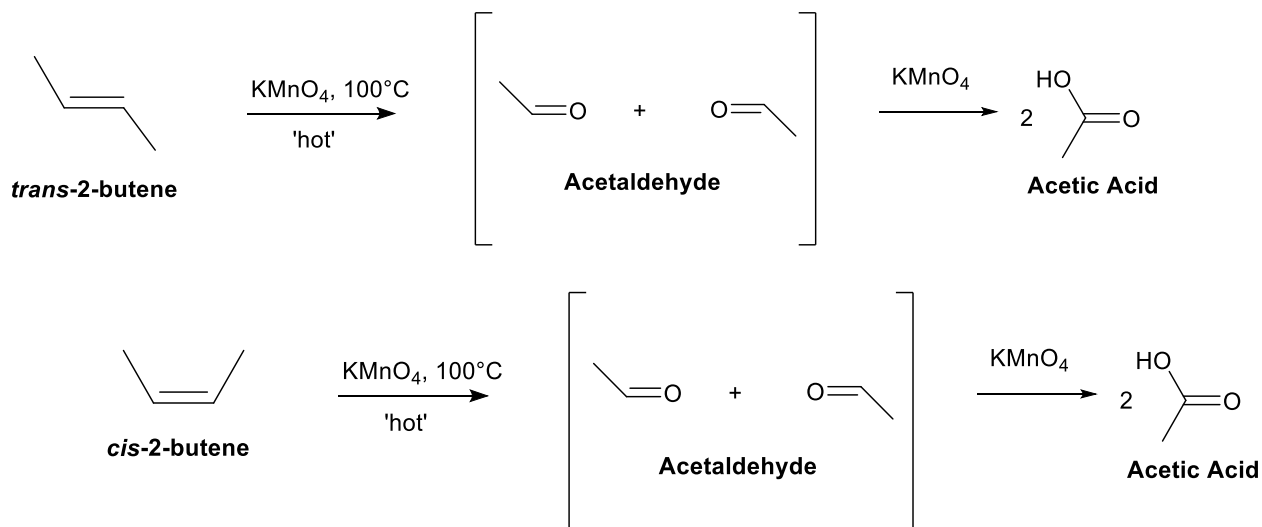
- Occurs on double bonds and triple bonds

**Oxidation of Alkenes:****Potassium Permanganate: KMnO<sub>4</sub>**

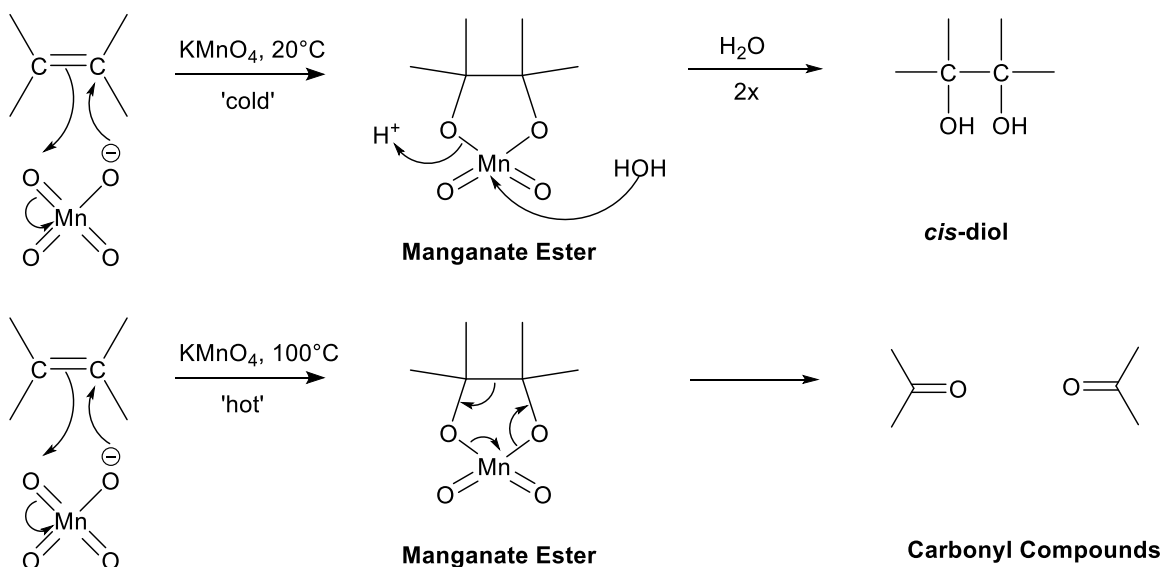
Purple crystals in H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub>

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

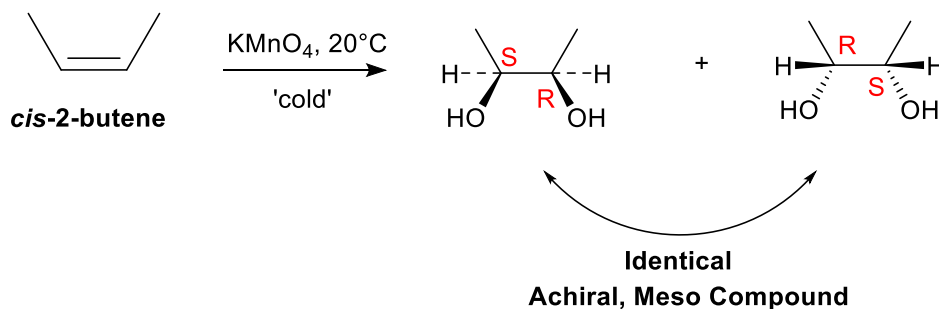
**General Scheme:**

**Mechanism:****'Hot' Permanganate Oxidation**

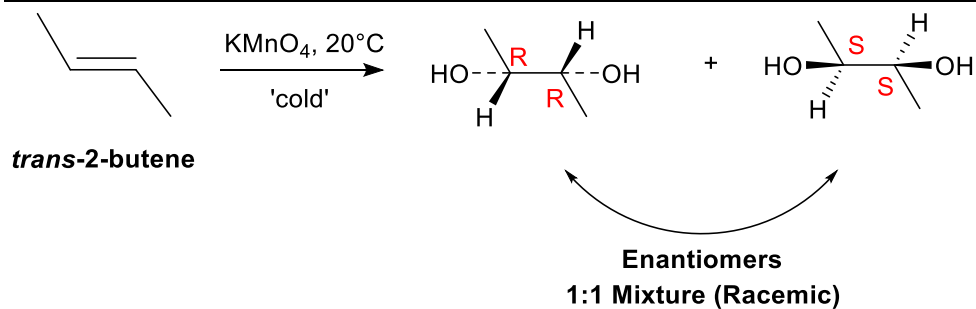
- Hot (100°C) KMnO<sub>4</sub> oxidation of 2-butene cleaves the double bond to form 2 molecules of acetic acid
- High temperature provides enough energy to break the C–C double bond in the manganate ester to initially form acetaldehyde which is then further oxidized to acetic acid
- Same oxidation products for *cis*-2-butene and *trans*-2-butene – breaking the C–C bond in the permanganate ester results in the loss of stereochemistry

**A closer look:**

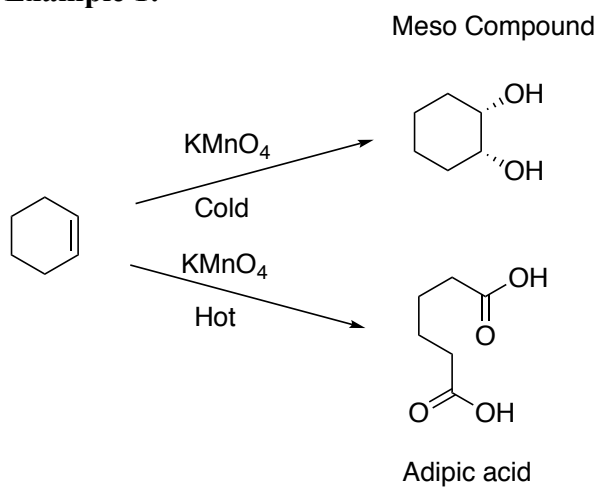
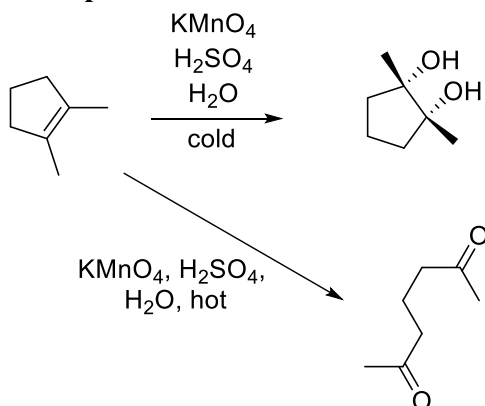
- Reaction of alkenes with 'cold' KMnO<sub>4</sub> is stereospecific (*cis*/syn addition)
- Under 'cold' reaction conditions, H<sub>2</sub>O attacks the manganate ester twice to form the *cis*-diol. The reaction is **stereospecific**.
- Under 'hot' reaction conditions, there is enough energy to break the C–C bond on the manganate ester, resulting to the formation of carbonyl compounds (i.e., ketone, aldehydes, carboxylic acids, etc.)

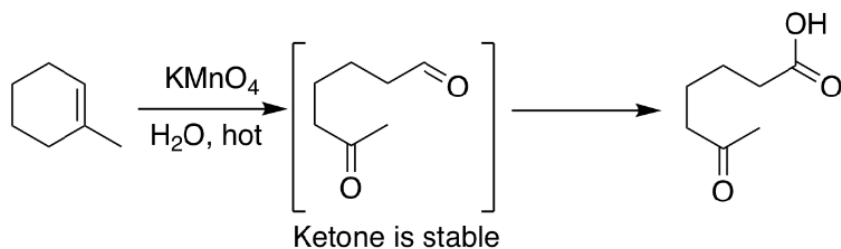
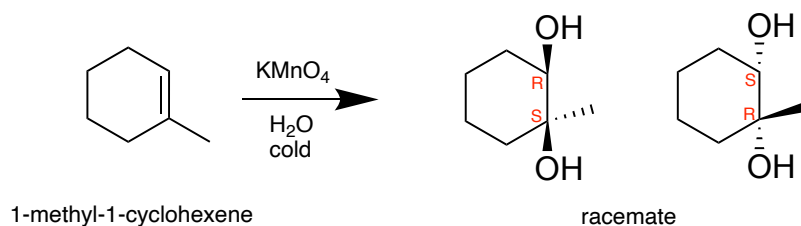
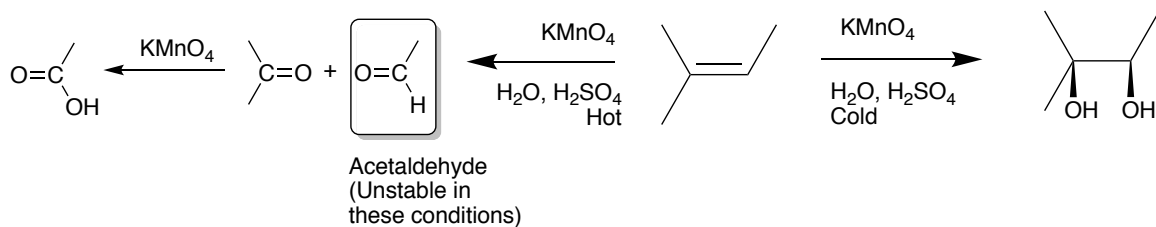
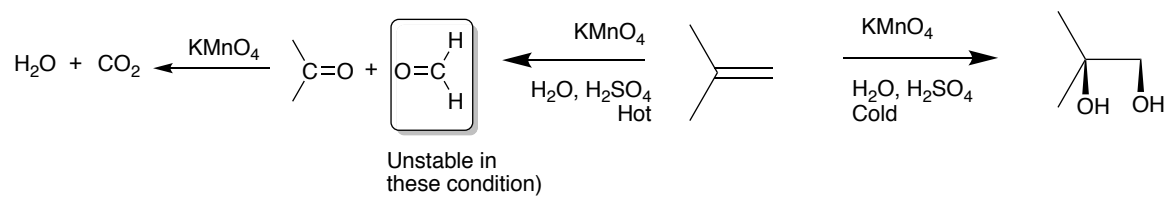
**'Cold' Permanganate Oxidation*****cis*-2-butene vs *trans*-2-butene**

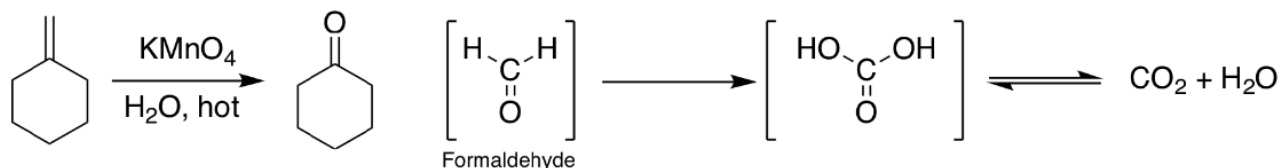
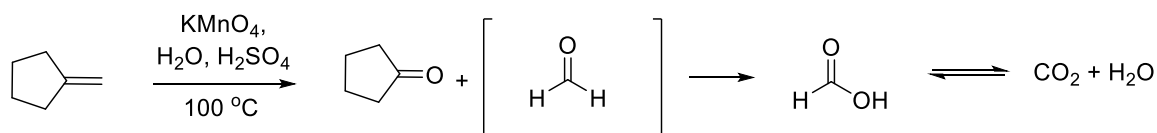
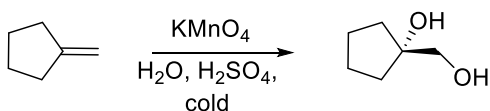
- 'Cold' KMnO<sub>4</sub> – 50/50 chance that KMnO<sub>4</sub> attaches from the top or from the bottom due to the planar structure of the *cis*-2-butene



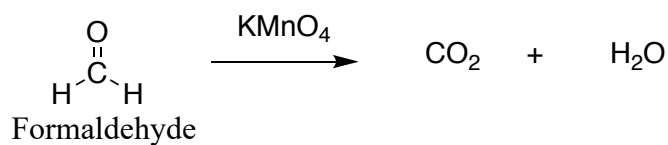
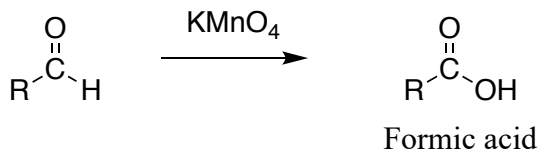
- Chance of the reaction going from the top or the bottom is 50/50
- 1:1 mix of enantiomers (racemic mixture)
- Reaction is stereospecific
- Initial addition of the permanganate on the double bond is concerted – all bonds break and form at the same time

**Example 1:****Example 2:**

**Example 3:****Example 4:****Example 5:****Example 6:****Example 7:**

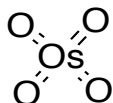
**Example 8:****Reaction with aldehydes:**

- In 'hot'  $\text{KMnO}_4$  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  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the presence of excess  $\text{KMnO}_4$

**Osmium Tetraoxide:  $\text{OsO}_4$**

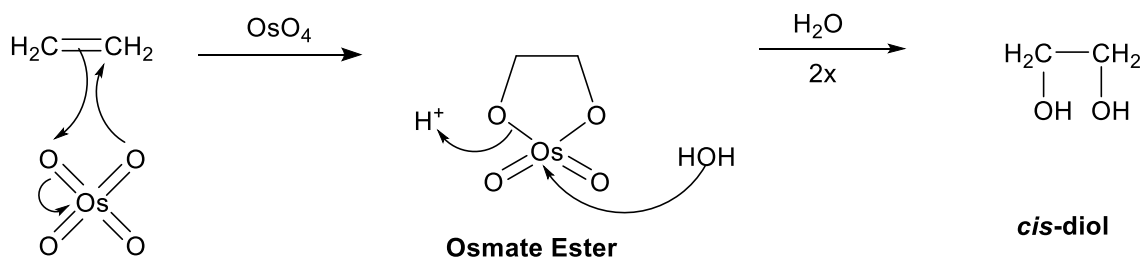


Toxic, Volatile

**General Scheme: (No over oxidation)**

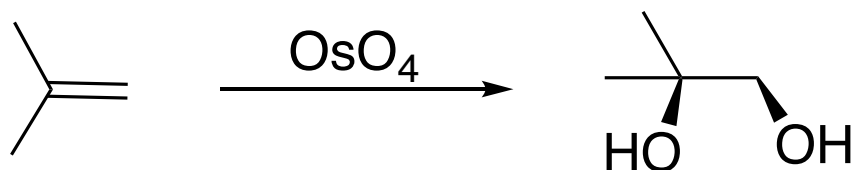


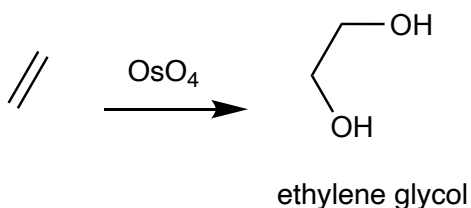
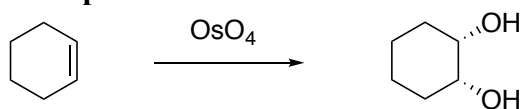
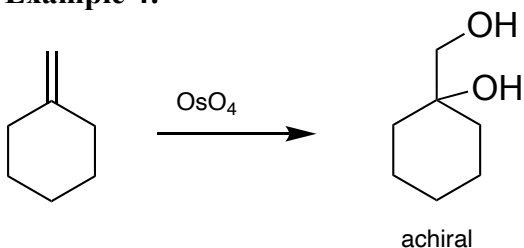
**Mechanism:**



- OsO<sub>4</sub> adds across the double bond to form osmate ester
- Osmate ester (very stable) is then attacked by H<sub>2</sub>O to form *cis* diols
- Reaction is stereospecific (*syn/cis* addition)

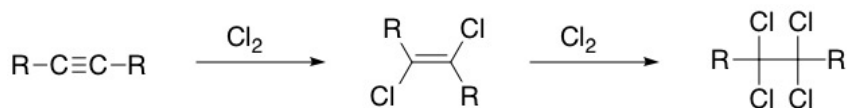
**Example 1: 2-methylpropene**



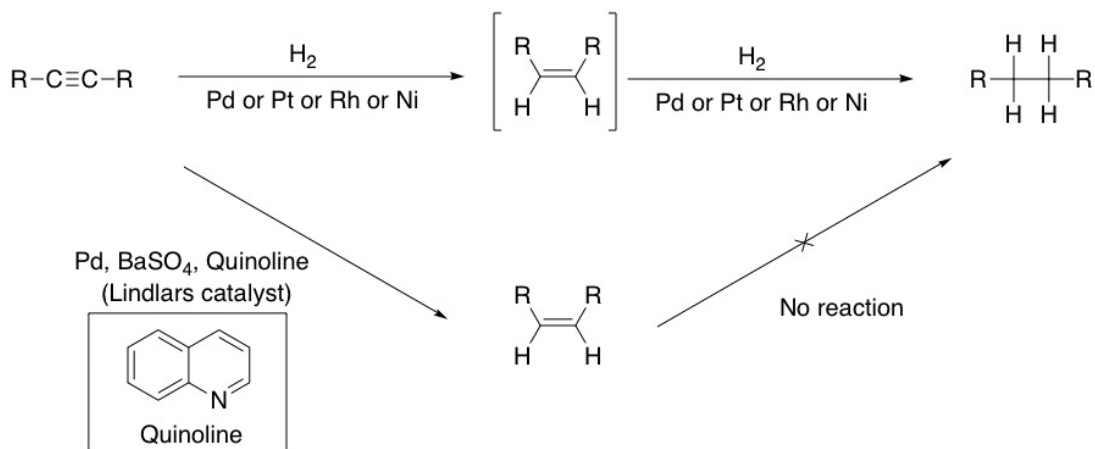
**Example 2:****Example 3:****Example 4:****Addition reactions of Alkynes**

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.

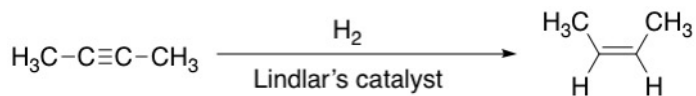
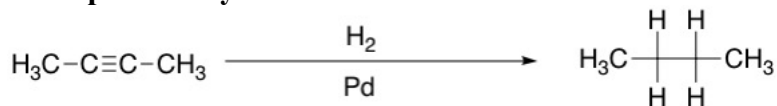
The carbon-carbon triple bond is composed of two pi bonds and a sigma bond



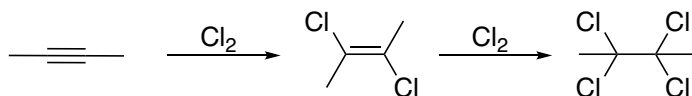
The first addition to the alkyne is anti, which forms the trans alkene.

**Hydrogenation of Alkynes**

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

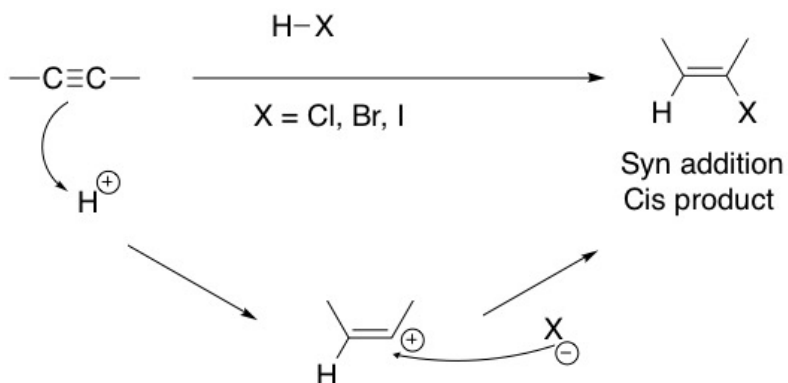
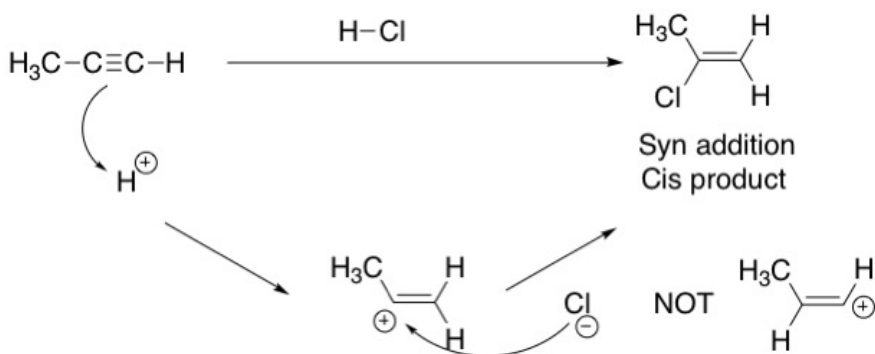
**Example: 2-butyne**

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

**Halogenation of Alkynes****Example: 2-butyne**

**HX Addition**

Follows Markovnikov rules (the most substituted end of the alkene will harbour the cation)

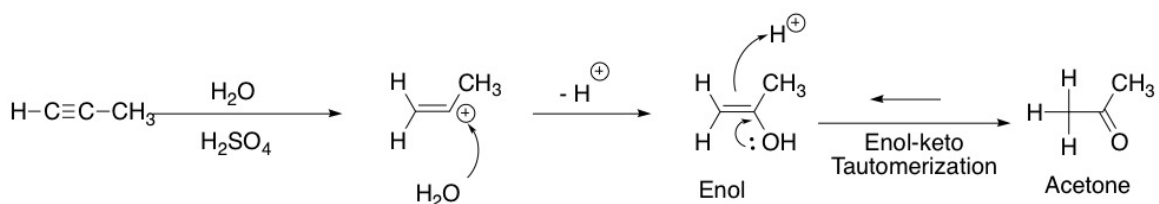
**Example 1: 2-butyne****Example 2: 1-propyne**

RECALL: Addition of HX across the double bond occurs in Markovnikov fashion— the  $\text{H}^+$  adds to the least substituted end of a multiple bond, and  $\text{Cl}^-$  to the most substituted end to form 2-chloro-1-propene

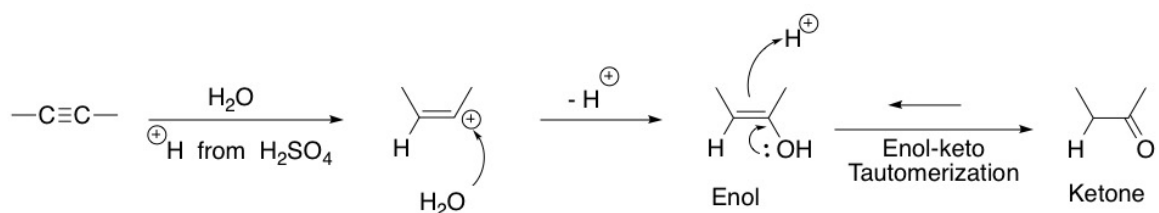
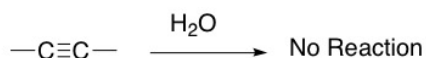
**Addition of  $\text{H}_2\text{O}$** **Example 1: 1-propyne**

- $\text{H}_2\text{O}$  or ROH by itself cannot add to the double bond. Need an acid ( $\text{H}^+$ ) to pull the electrons from the double bond.

- $\text{H}_2\text{SO}_4$  ( $\text{H}^+$ ) is a catalyst, meaning that it is not transformed or used up in the reaction but is present to lower the activation energy.

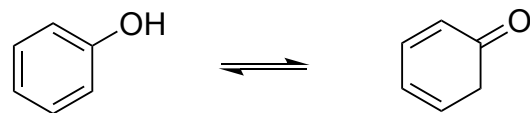


### Example 2: 2-butyne



- **Enols** are generally unstable and tend to isomerize to the **keto form (generally favored 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.

### Unique Example where the enol is favored is phenol



phenol

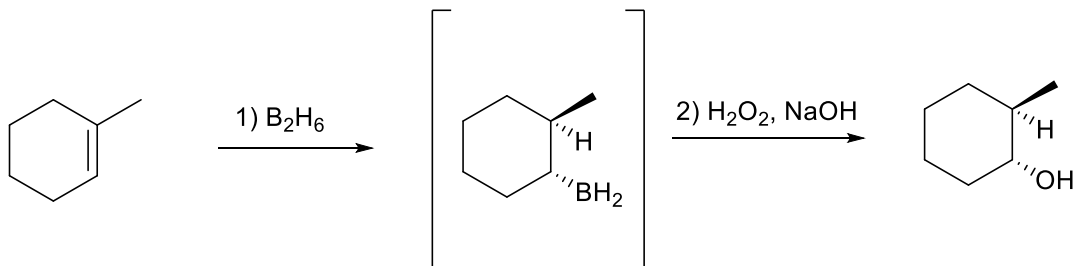
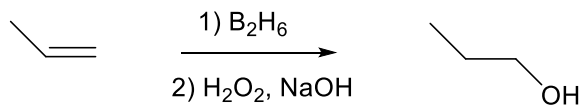
enol is favored

ketone is disfavored

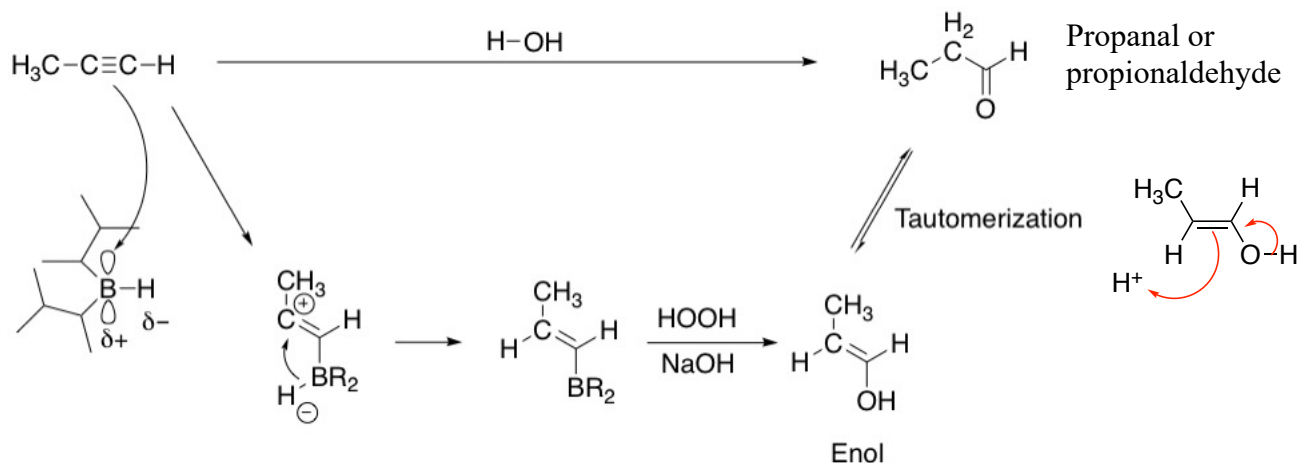
tautomers are structural isomers, not resonance structures

### Hydroboration - Oxidation

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

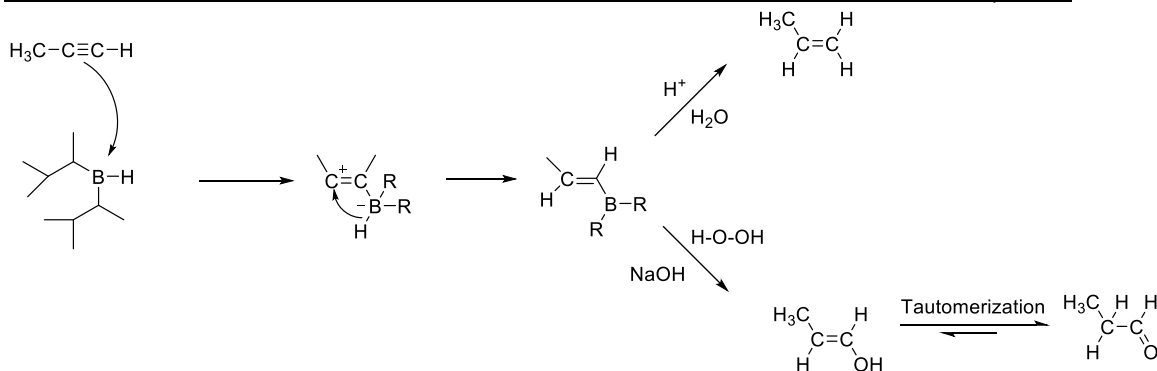
**RECALL:** Hydroboration of alkenes

- Cis/syn addition
- Oxidation with  $H_2O_2/NaOH$  replaces the C-B bond with retention of configuration

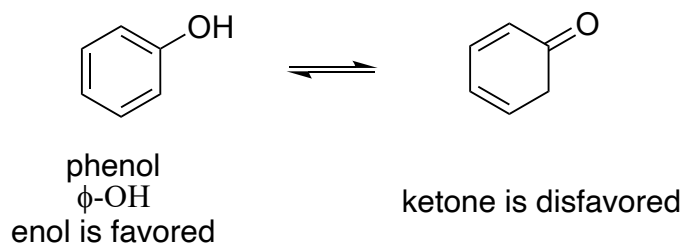
**Hydroboration of Alkynes**

- 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-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.



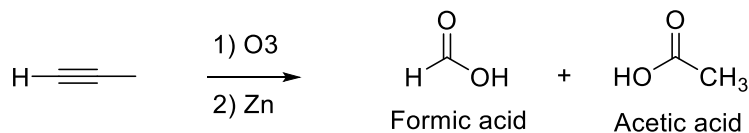
Unique Example where the enol is favored is phenol



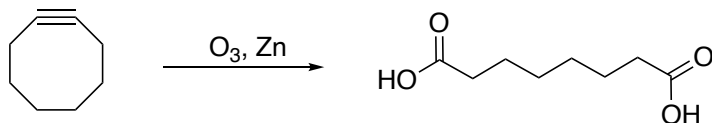
tautomers are structural isomers, not resonance structures

### Oxidations of Alkynes (Examples/Summary)

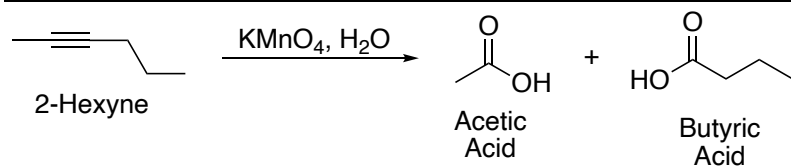
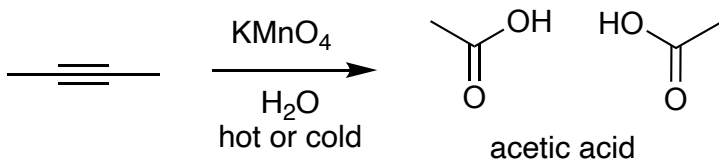
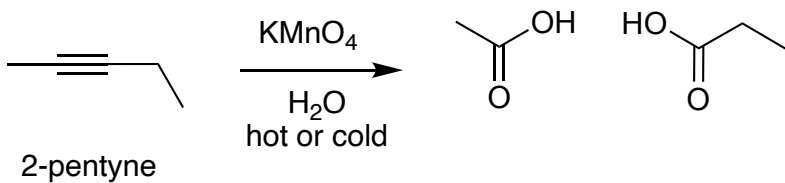
#### Example 1: Ozonolysis of 1-propyne



#### Example 2: Ozonolysis of Cyclooctyne



#### Example 3:

**Example 4: 2-butyne****Example 5: 2-pentyne****Example 6: propyne**