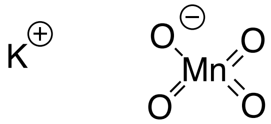
CHEM 261 Notes Winter 2025 March 25, 2025

Recall:

Addition Reactions

Oxidation of Alkenes:

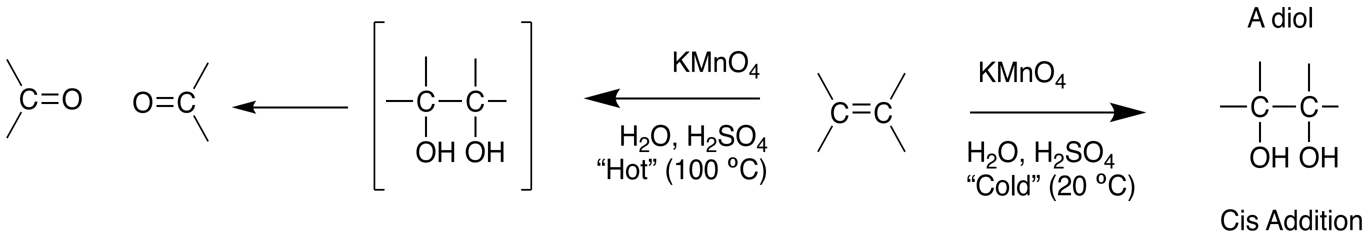
Potassium Permanganate: $KMnO_4$



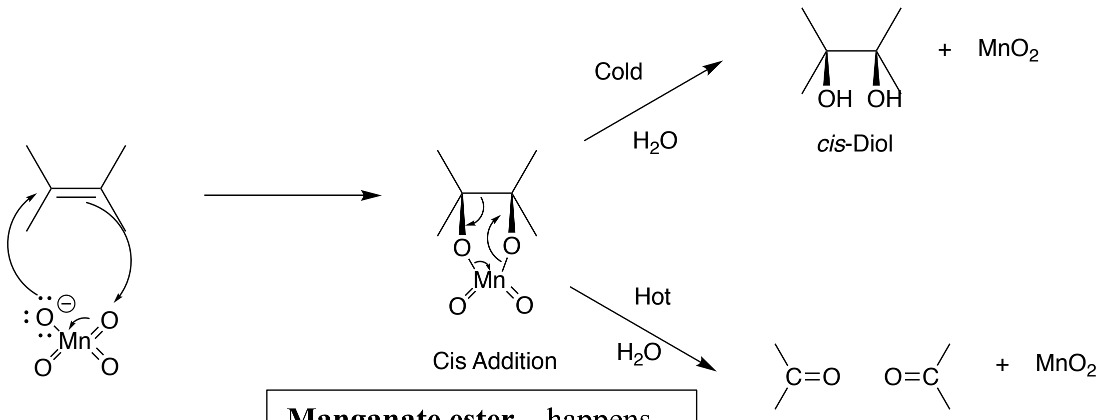
Purple crystals in H_2O and H_2SO_4

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

General Scheme:

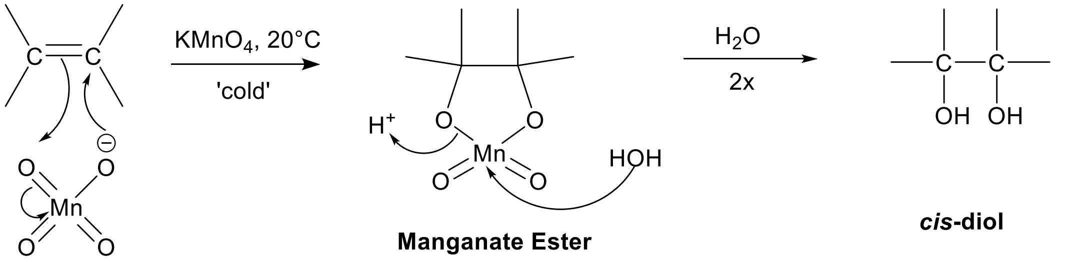


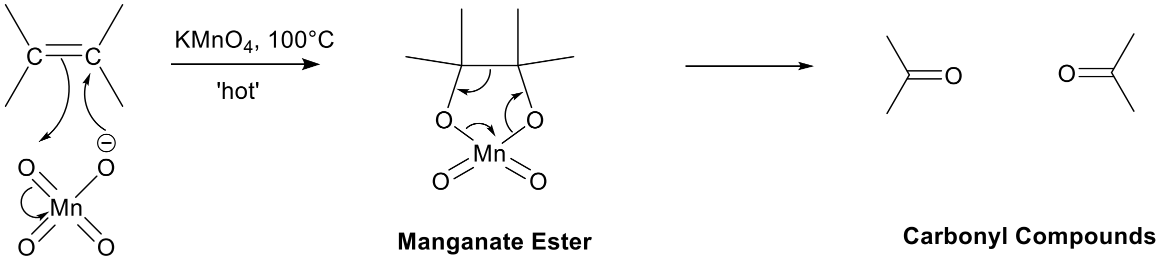
Mechanism:



Manganate ester – happens very quickly, therefore, no free bond rotation

A closer look:

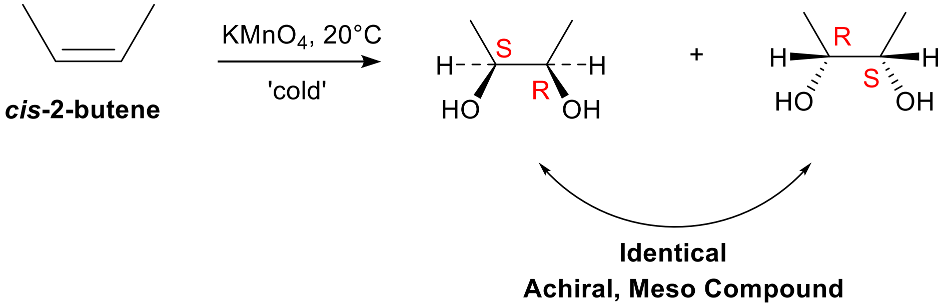




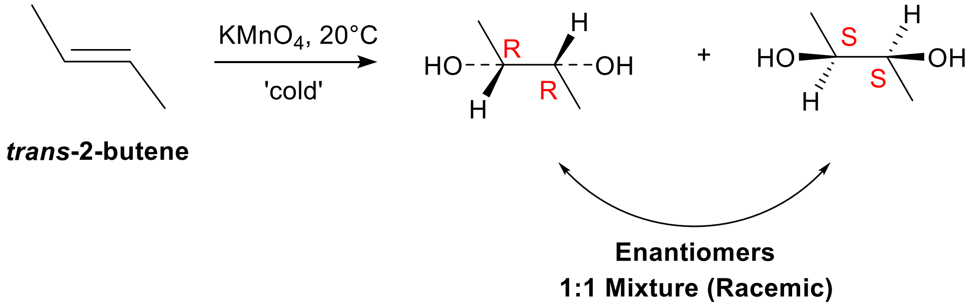
- Reaction of alkenes with 'cold' $KMnO_4$ is stereospecific (cis/syn addition)
- Under 'cold' reaction conditions, H_2O attacks the manganate ester twice to form the *cis*-diol. The reaction is **stereospecific**.
- Under 'hot' reaction conditions, there is enough energy to break the C–C bond on the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

'Cold' Permanganate Oxidation

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

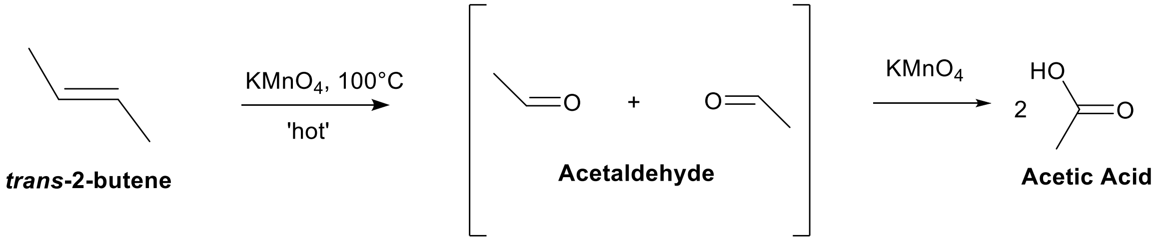


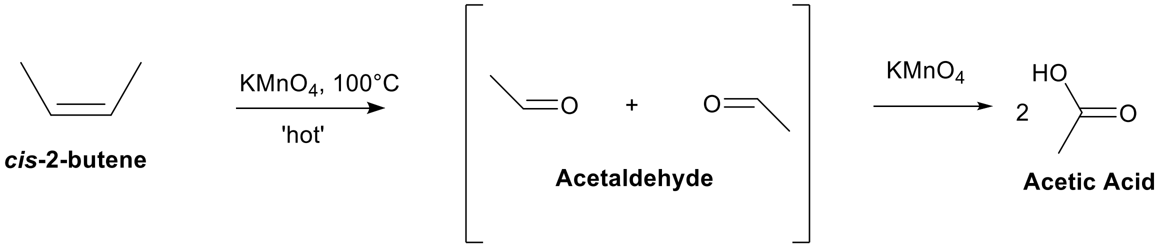
- 'Cold' $KMnO_4$ – 50/50 chance that $KMnO_4$ attaches from the top or from the bottom due to the planar structure of the *cis*-2-butene



- 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

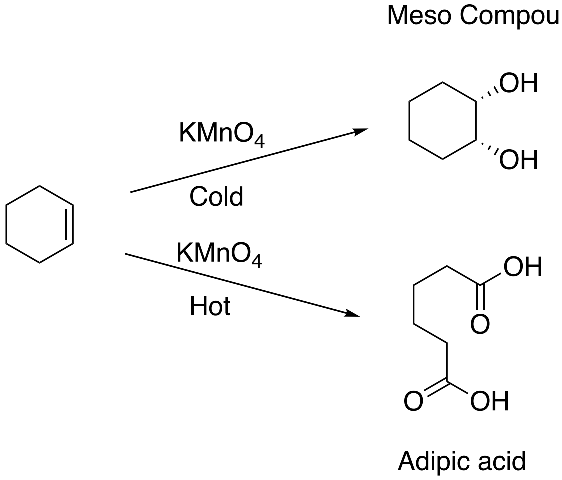
‘Hot’ Permanganate Oxidation



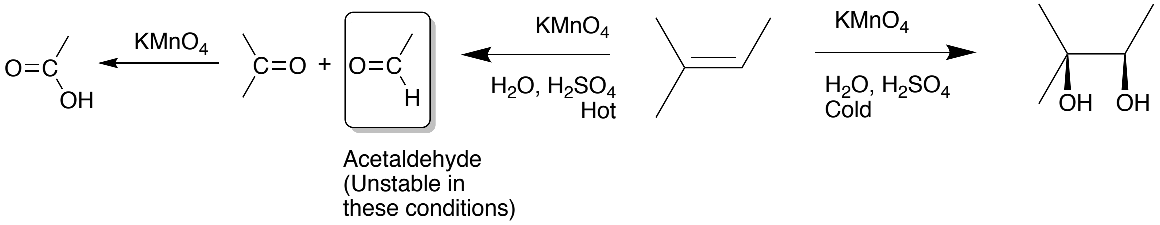


- Hot (100ºC) $KMnO_4$ oxidation of 2-butene cleaves the double bond to form 2 molecules of acetic acid
- High temperature provides enough energy to break the C–C double bond in the manganate ester to initially form acetaldehyde which is then further oxidized to acetic acid
- Same oxidation products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

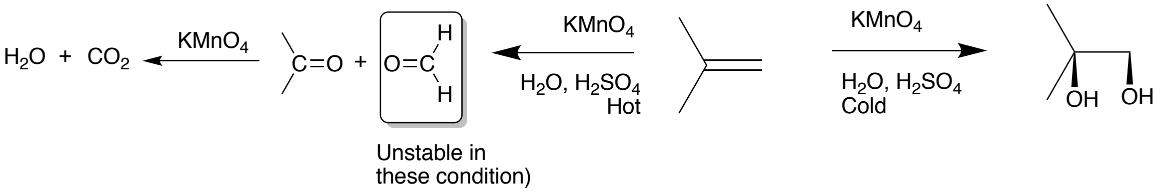
Example 1:



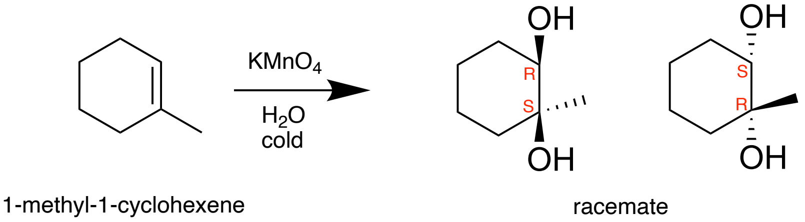
Example 2:



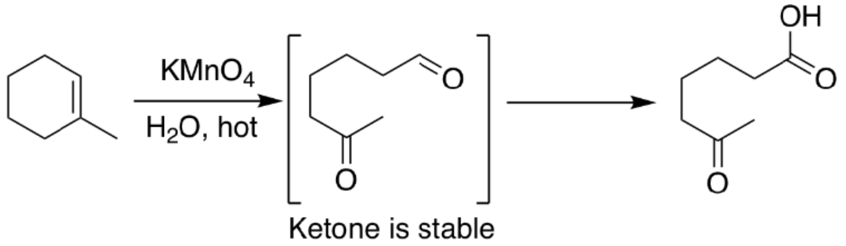
Example 3 :



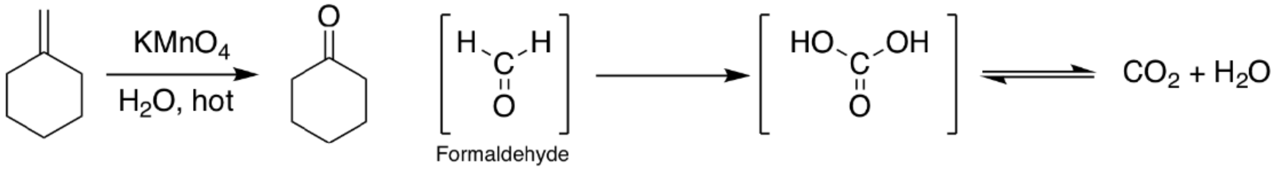
Example 4:



Example 5:

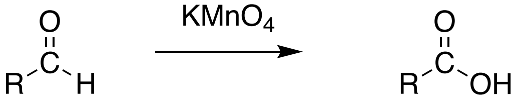


Example 6:

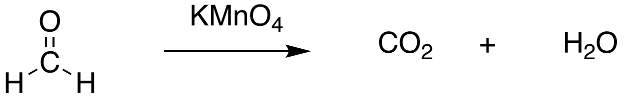


Reaction with aldehydes:

- In 'hot' KMnO$_4$ oxidations, aldehydes are oxidized further. Ketones, on the other hand, won't get oxidized further.



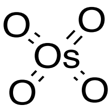
Formic acid



Formaldehyde

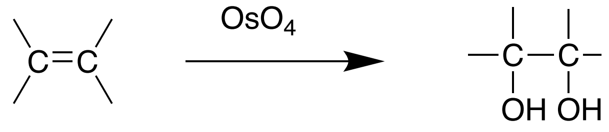
- Formaldehyde
  - disinfectant – used to preserve cadavers
  - is further oxidized to form CO_2 and H_2O in the presence of excess $KMnO_4$

Osmium Tetraoxide: OsO_4



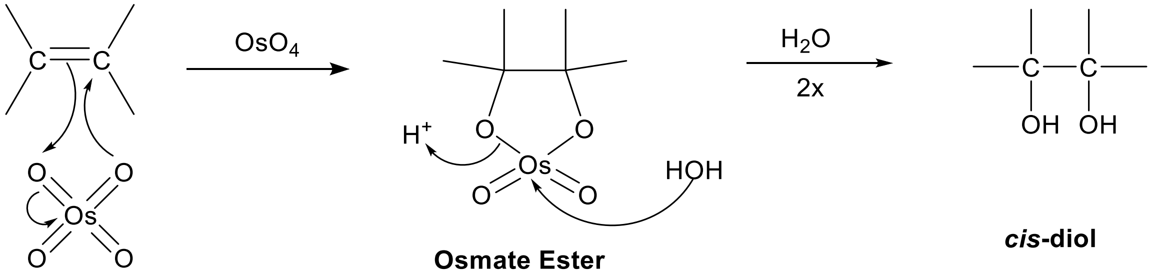
Toxic, Volatile

General Scheme:



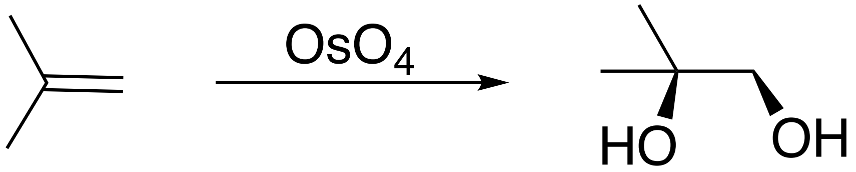
Syn/Cis Addition

Mechanism:

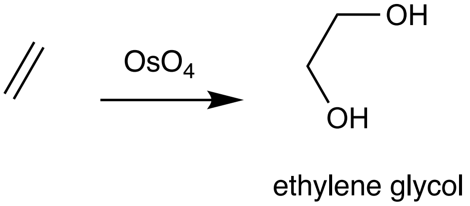


- OsO_4 adds across the double bond to form osmate ester
- Osmate ester (very stable) is then attacked by H_2O to form *cis* diols
- Reaction is stereospecific (syn/cis addition)

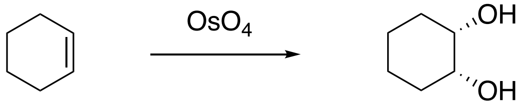
Example 1: 2-methylpropene



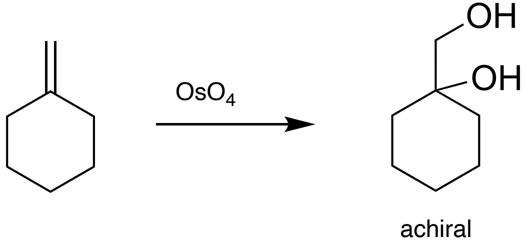
Example 2:



Example 3:



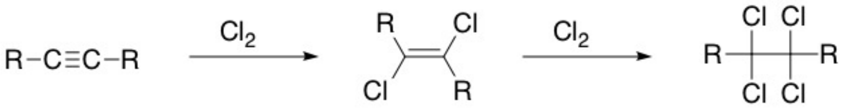
Example 4:



Addition reactions of Alkynes

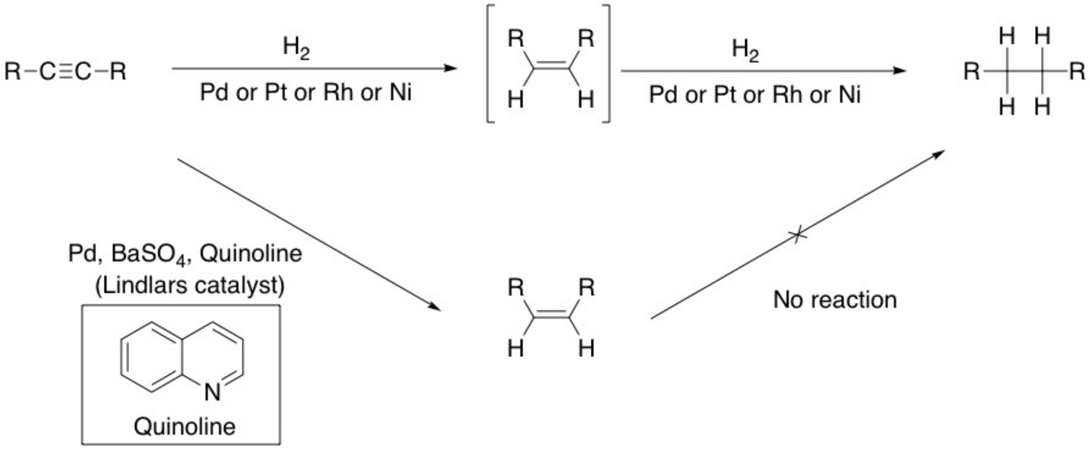
Alkynes are more polar as they have more negative charge between the two carbons. They are always more reactive than alkenes and so can be utilized in all addition reactions that alkenes can, except react faster.

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



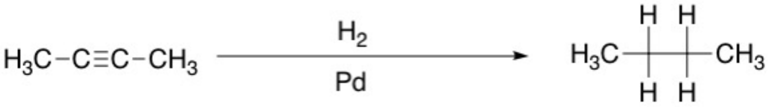
The first addition to the alkyne is anti, which forms the trans alkene.

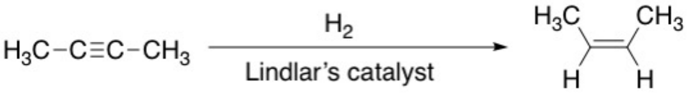
Hydrogenation of Alkynes



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

Example: 2-butyne

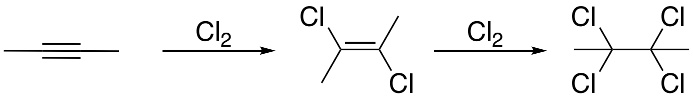




- Reaction is stereospecific – H atoms are added on the same side of the double bond

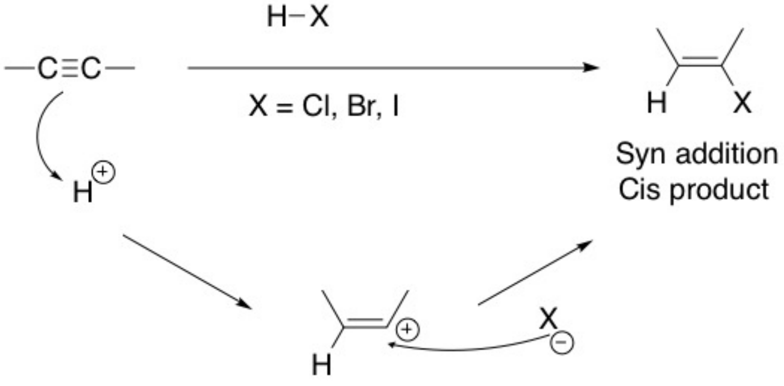
Halogenation of Alkynes

Example: 2-butyne

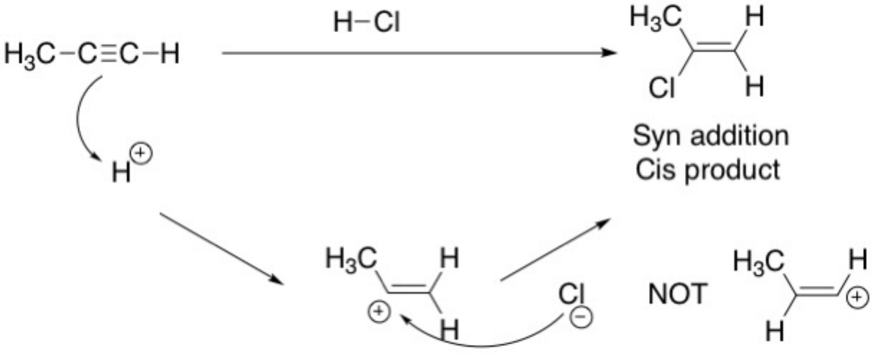


HX Addition

Example 1: 2-butyne



Example 2: 1-propyne

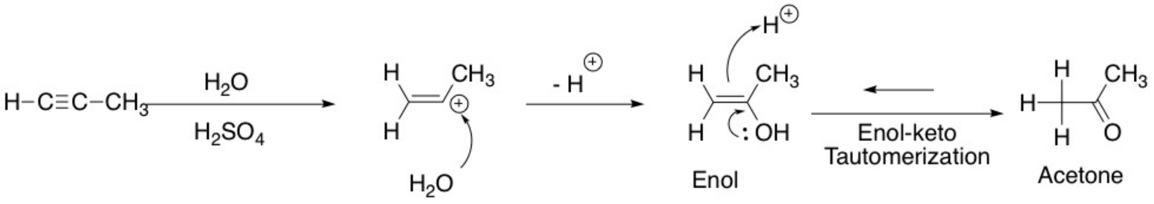


RECALL: Addition of HX across the double bond occurs in Markovnikov fashion– the H^+ adds to the least substituted end of a multiple bond, and Cl- to the most substituted end to form 2-chloro-1-propene

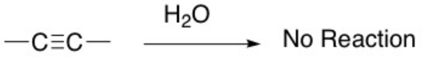
Addition of H_2O

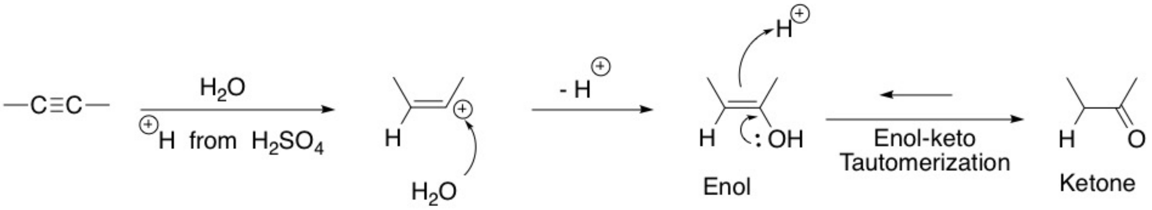
Example 1: 1-propyne

- H_2O or ROH by itself cannot add to the double bond. Need an acid (H^+) to pull the electrons from the double bond.
- H_2SO_4 (H^+) is a catalyst, meaning that it is not transformed or used up in the reaction but is present to lower the activation energy.



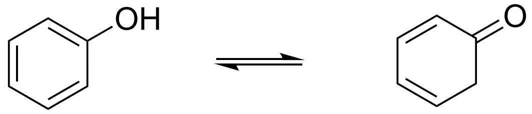
Example 2: 2-butyne





- **Enols** are generally unstable and tend to isomerize to the **<u>keto form (generally favored over the enol</u>** – 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



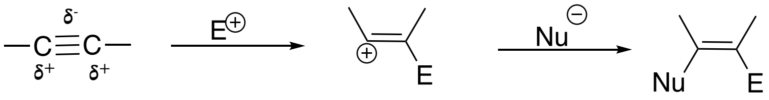
phenol

enol is favored

ketone is disfavored

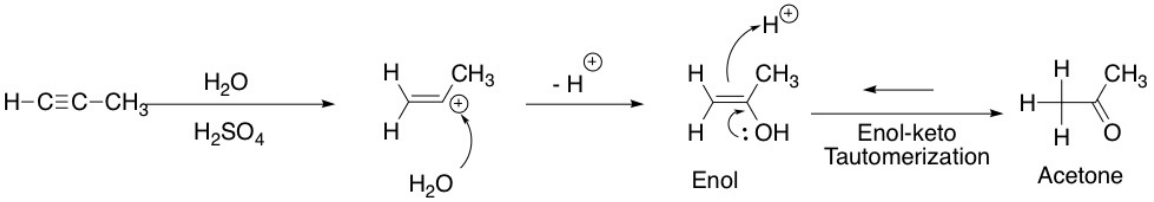
tautomers are structural isomers, not resonance structures

RECALL:



Note: Electrophile like H+ adds in less substituted C (Markovnikov rule) and nucleophile (e.g. Cl^-, H_2O, etc) adds to the more substituted C.

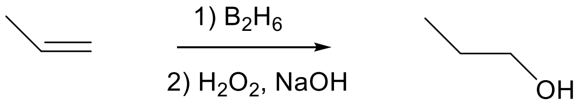
Addition of H_2O to Alkyne

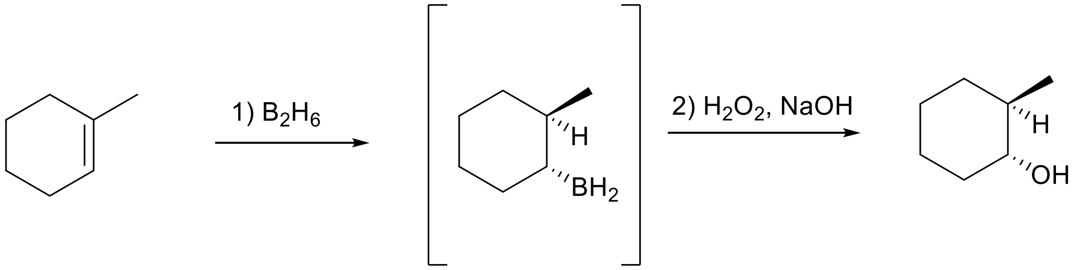


Hydroboration - Oxidation

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

RECALL: Hydroboration of alkenes

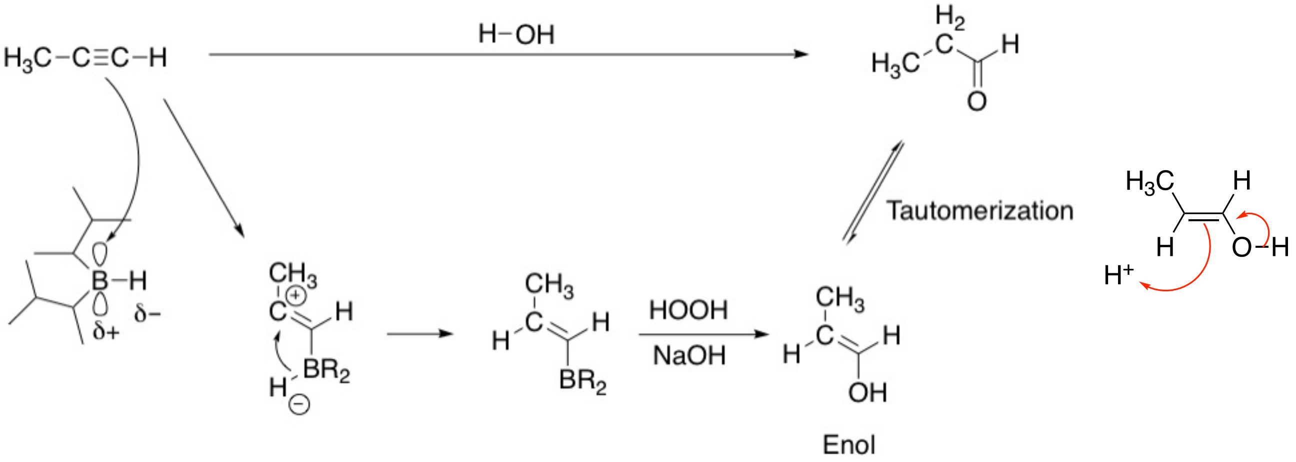




- Cis/syn addition
- Oxidation with H_2O_2/NaOH replaces the C–B bond with retention of configuration

Hydroboration of Alkynes

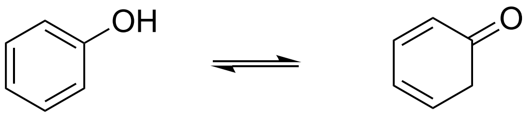
Propanal or
propionaldehyde



- 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



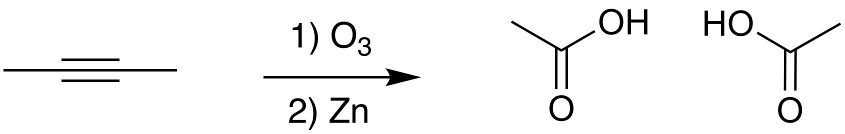
phenol
ϕ-OH
enol is favored

ketone is disfavored

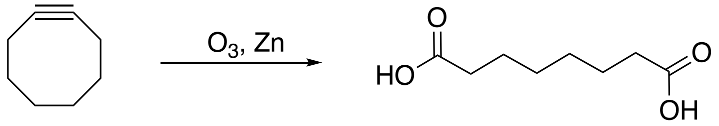
tautomers are structural isomers, not resonance structures

Oxidations of Alkynes

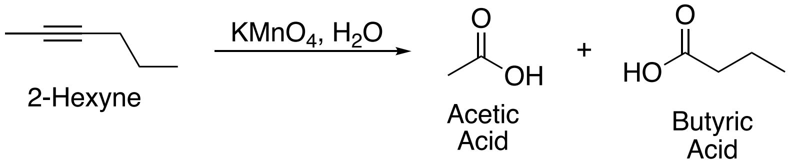
Example 1: Ozonolysis of 2-butyne



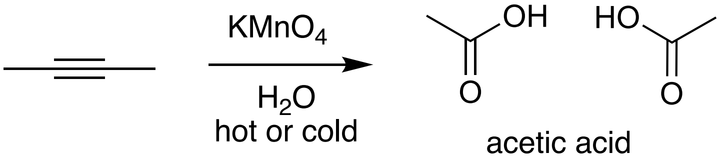
Example 2: Ozonolysis of Cyclooctyne



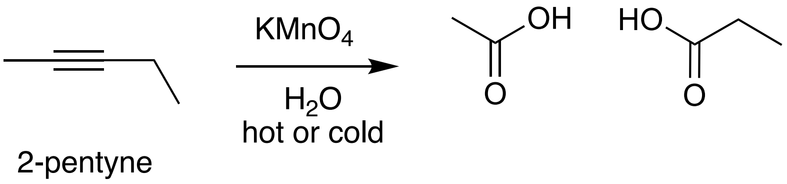
Example 3:



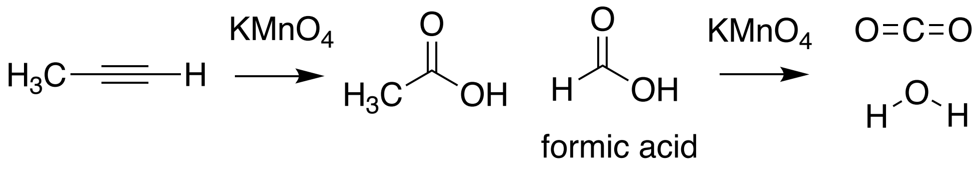
Example 4: 2-butyne



Example 5: 2-pentyne

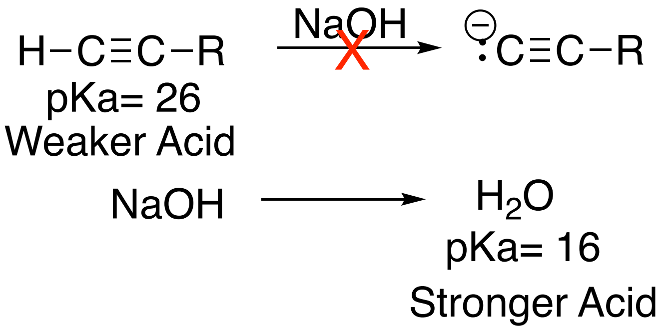


Example 6: propyne



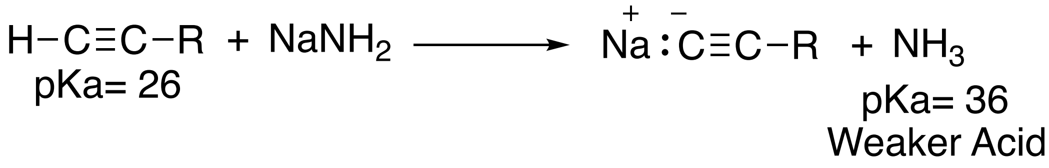
Special Reaction for Terminal Alkynes

Recall:

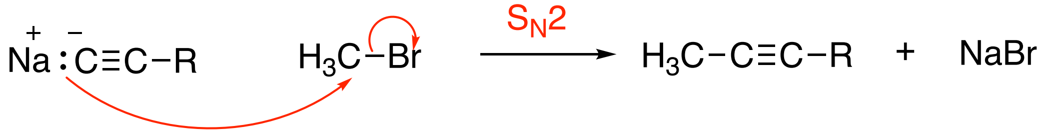


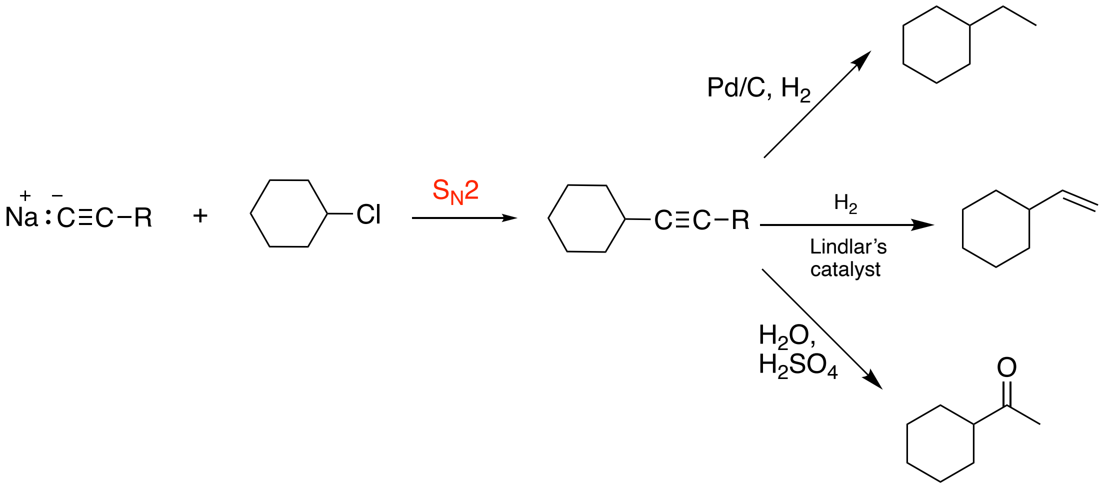
Note: this reaction will not occur because the reaction will form a stronger acid (H_2O) as compared to acetylene

However,

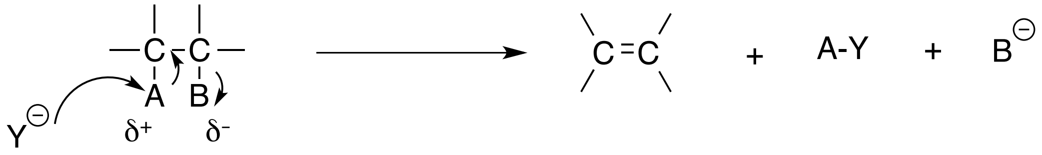


Reaction of Acetylide anion

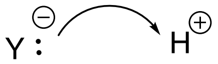




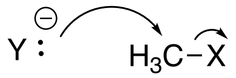
Elimination Reactions:



Base vs. Nucleophile:



vs.



Base

Nucleophile

Elimination (E_1 and E_2)

Substitution (S_N1 and S_N2)

2 Types of Mechanisms: E_1 and E_2

<u>E_2 Reaction</u> (E=Elimination)**:**

- Rate depends on two concentrations
- Stereospecific
- Concerted (bonds being formed and broken at the same time)
    - No intermediate
- follows Zaitsev Rule: most substituted alkene will be the major product

- Anti-periplanar geometry
- 1º, 2º, 3º, but especially primary and secondary

E_1 Reaction

- Rate depends on the concentration of one species
- Carbocation intermediate
- Teritiary carbon preferred
- Favored by heat, acid