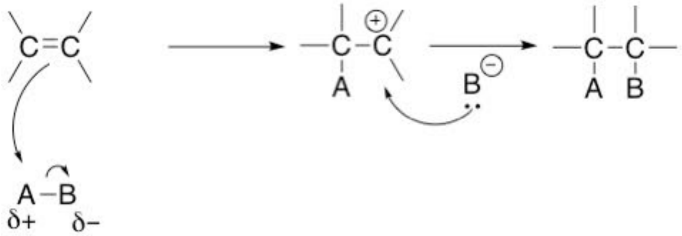
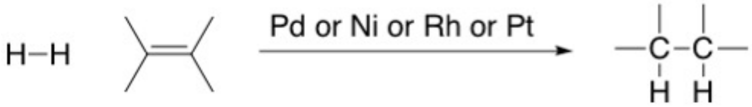
RECALL:

Addition Reactions

- Occurs on double bonds and triple bonds

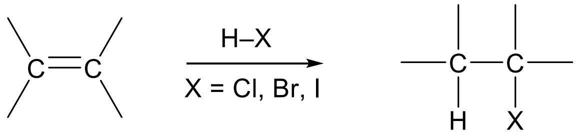


Hydrogenation Addition of H_2



- cis or syn addn
- stereospecific

Hydrogen Halide (HX) Addition

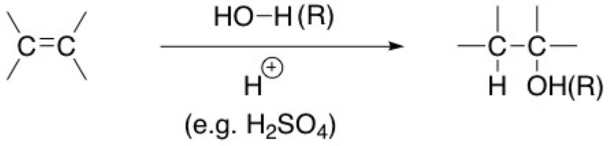


Reaction generally leads to syn/cis addition

Addition of H_2O and ROH (Hydration and Ether Formation)

HO−H or RO−H

Addition R = Alkyl



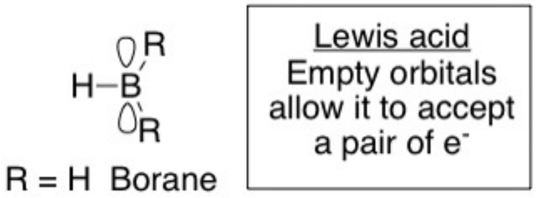
Not Stereospecific

Hydration formation

- H_2O or ROH by itself cannot add to the double bond. Need an acid (H^+) to pull the electrons from the double bond.

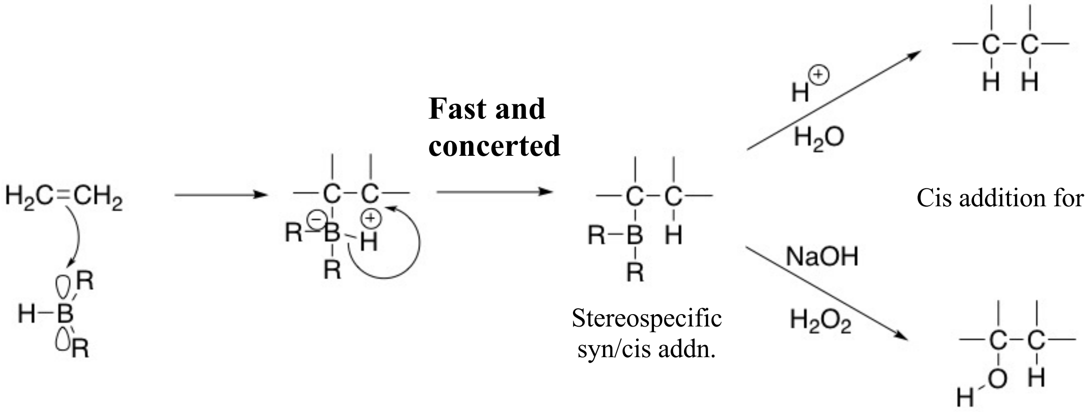
- H_2SO_4 (H^+) is a catalyst, meaning that it is not transformed or used up in the reaction but is present to lower the activation energy.

Hydroboration



Lewis acid
Empty orbitals allow it to accept a pair of e⁻

- B when stable and uncharged has 3 bonds and no lone pairs
- Borane forms partial bonds with another borane molecule to form B_2H_6 (diborane)
- Borane is a hydride (H^-) donor



Fast and concerted

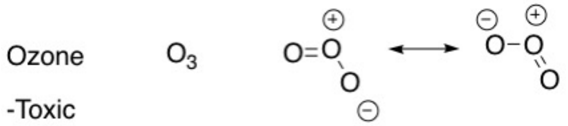
Like H_2/ Cat. (Pd, Pt, Ni, Rh)

Cis addition for both reactions

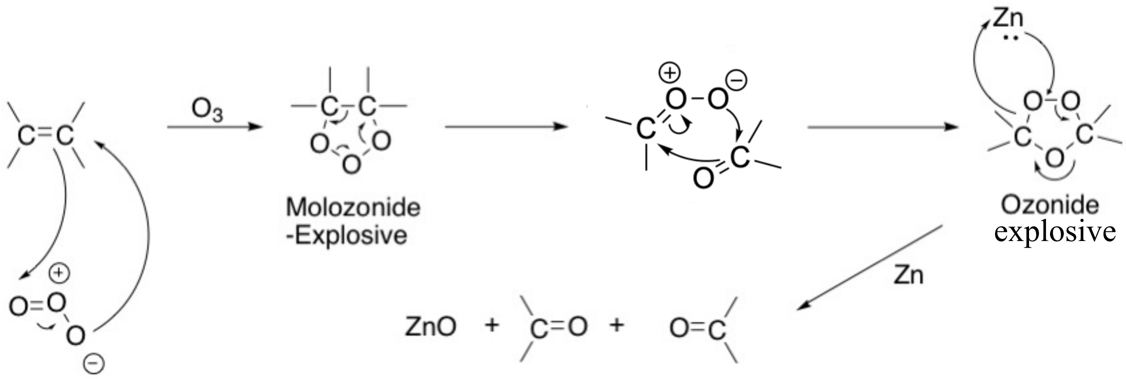
Stereospecific syn/cis addn.

Concerted reaction: bond breaking and bond formation happens in a single step
Anti-Markovnikov: the hydrogen ends up on the more substituted C in a double bond. It is SYN.

Ozonolysis (lysis = cleavage) – cleavage by ozone (O_3)

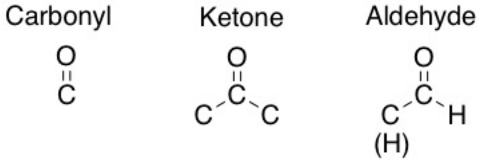


- Use double-headed arrow to indicate resonance (↔)
- Highly reactive (always looking for negative charge such as the negative charge in a double bond)
- Concerted and stereospecific

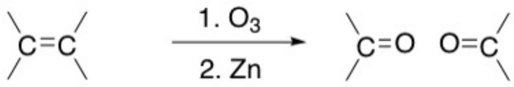


- Reaction is irreversible

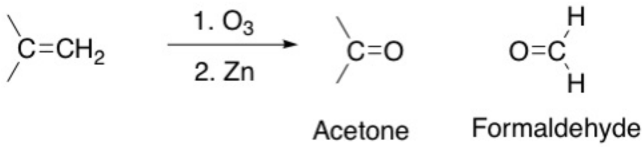
Examples of carbonyl groups

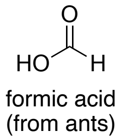


Reaction scheme of ozone

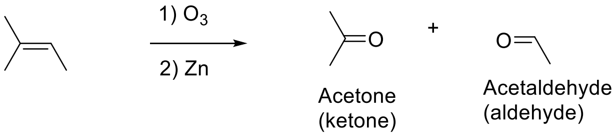


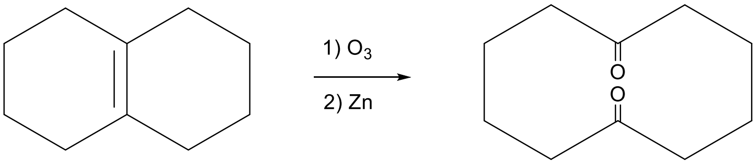
Example

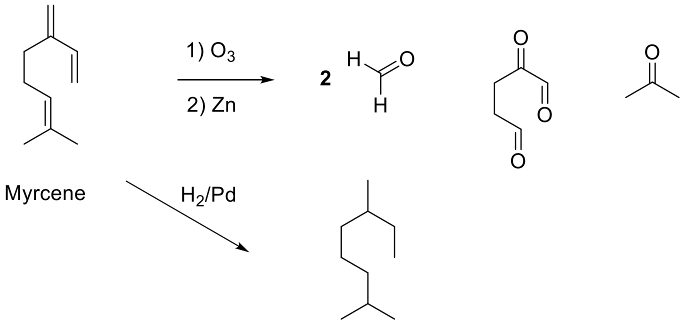




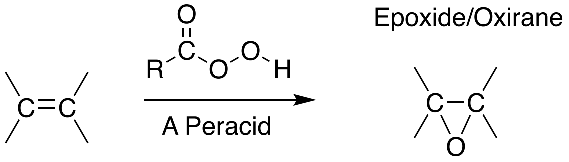
More examples





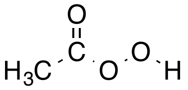


Epoxidation:



Syn/Cis Addition
Stereospecific

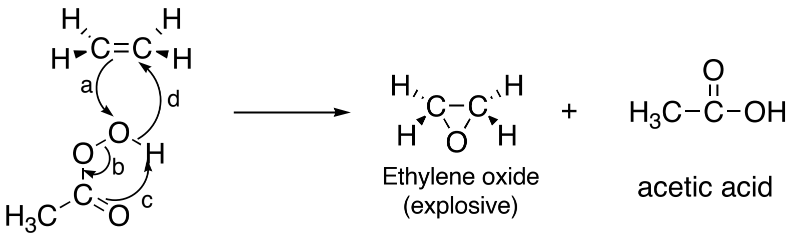
Example of
a peracid



$$H_3C-\overset{\overset{\large O}{\|}}{C}-O-O-H$$

Concerted (bonds break and form at the same time)

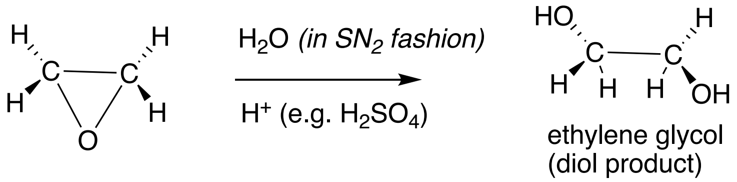
Mechanism:



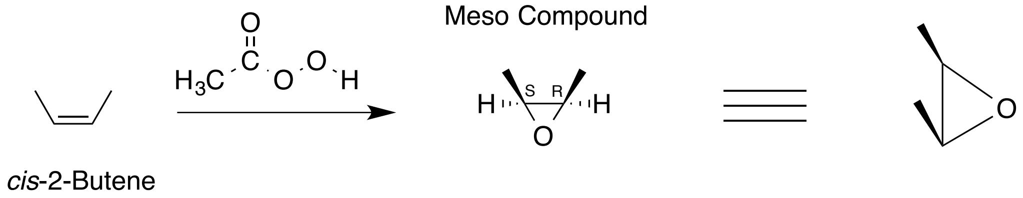
Ethylene oxide
(explosive)

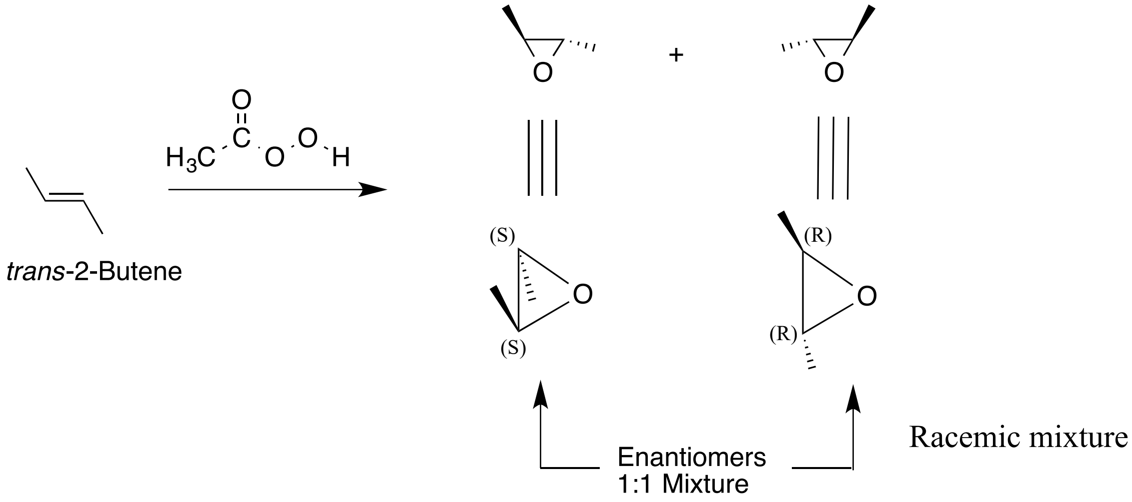
acetic acid

to quench ethylene oxide:



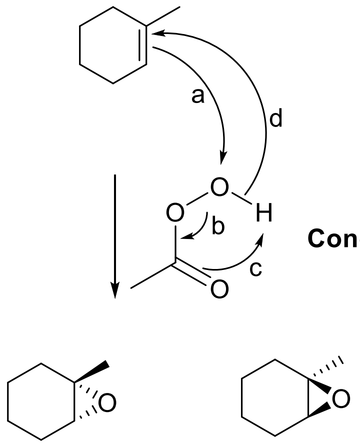
Example 1: *trans-* vs *cis-*Butene





The possibility of epoxidation from the top is 50% and from the bottom is 50% so a 1:1 mixture of enantiomers is form (racemic mixture).

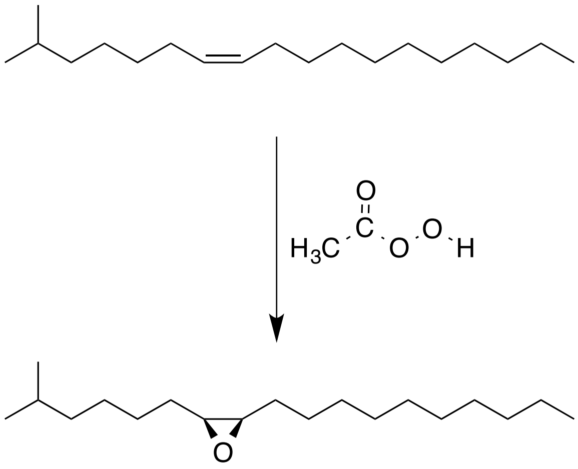
Example: 1-methyl-1-cyclohexene



Concerted Stereospecific

Racemic mixture (1:1)
cis/syn addition

Example 2: 2-Methyl-7-octadecene

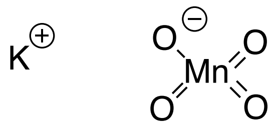


Sex pheromone for Gypsy Moth

biologically, only one enantiomer is active (one shown) – racemate produced by peracetic acid

Oxidation of Alkenes:

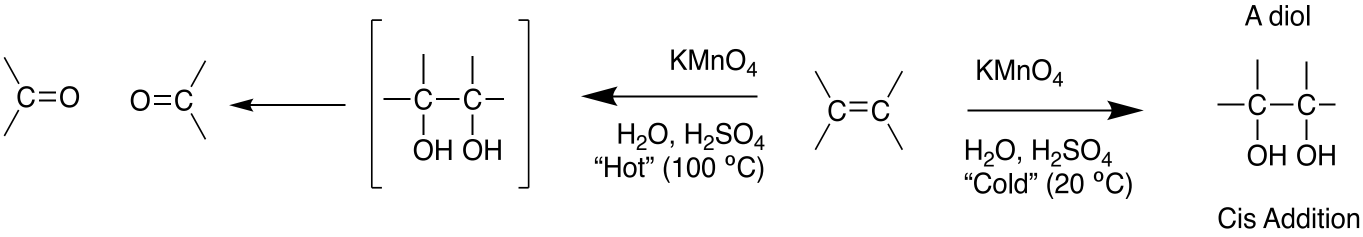
Potassium Permanganate: $KMnO_4$



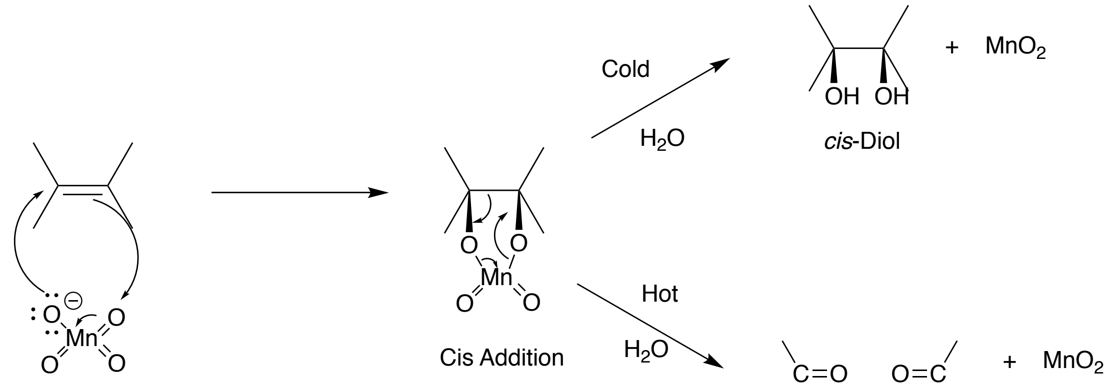
Purple crystals in H_2O and H_2SO_4

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

General Scheme:

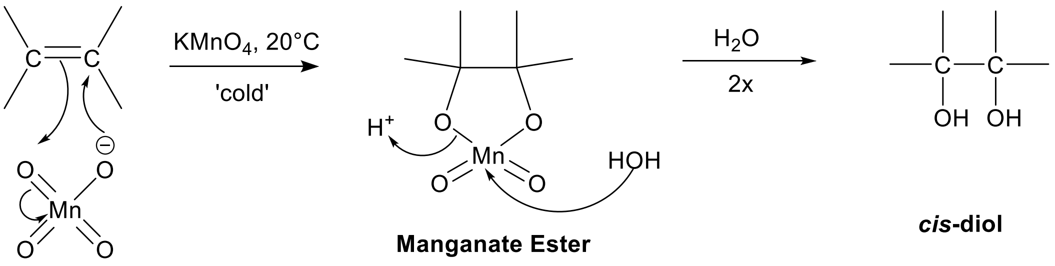


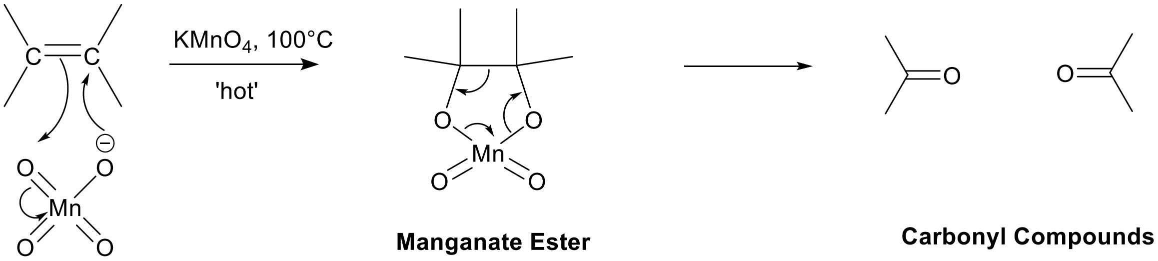
Mechanism:



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

A closer look:

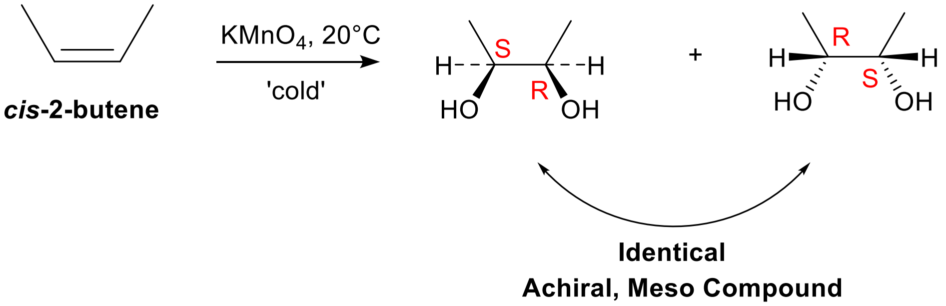




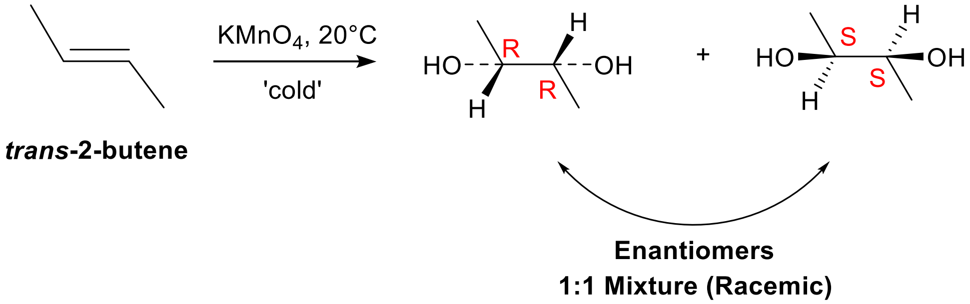
- Reaction of alkenes with ‘cold’ $KMnO_4$ is stereospecific (cis/syn addition)
- Under ‘cold’ reaction conditions, H_2O attacks the manganate ester twice to form the *cis*-diol. The reaction is **stereospecific**.
- Under ‘hot’ reaction conditions, there is enough energy to break the C–C bond on the 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



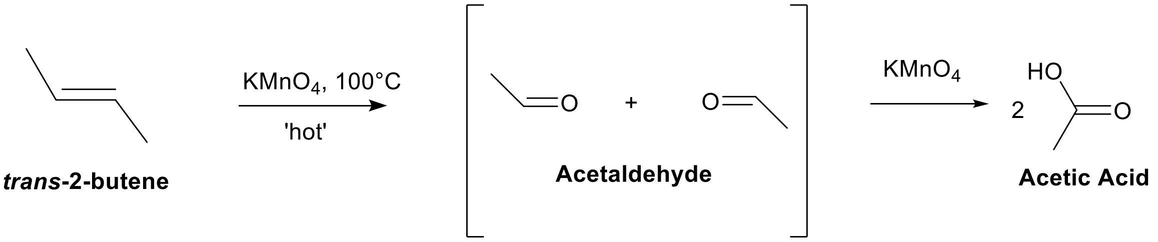
- ‘Cold’ $KMnO_4$ – 50/50 chance that $KMnO_4$ attaches from the top or from the bottom due to the planar structure of the *cis*-2-butene

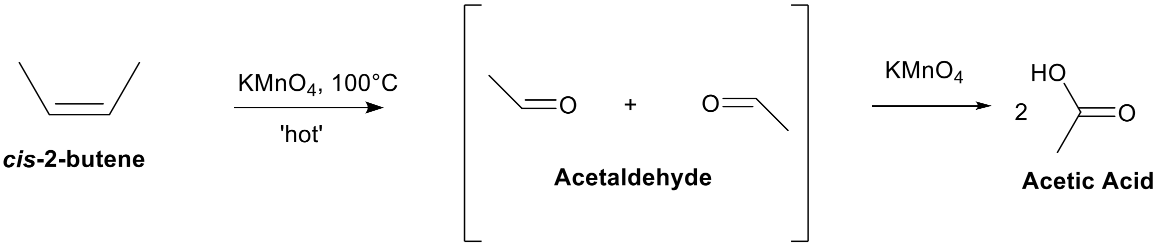


- Chance of the reaction going from the top or the bottom is 50/50
- 1:1 mix of enantiomers (racemic mixture)
- Reaction is stereospecific

- Initial addition of the permanganate on the double bond is concerted – all bonds break and form at the same time

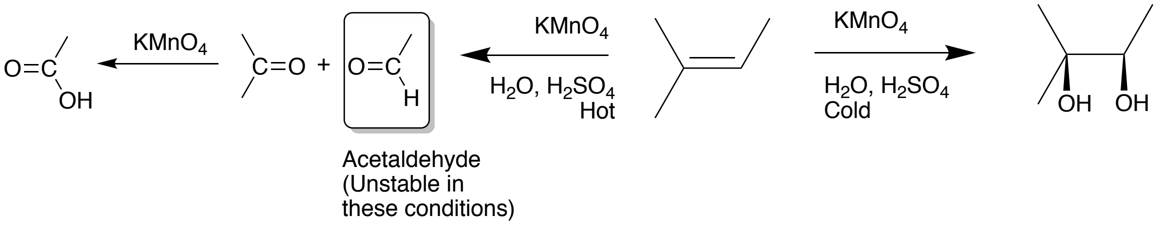
‘Hot’ Permanganate Oxidation



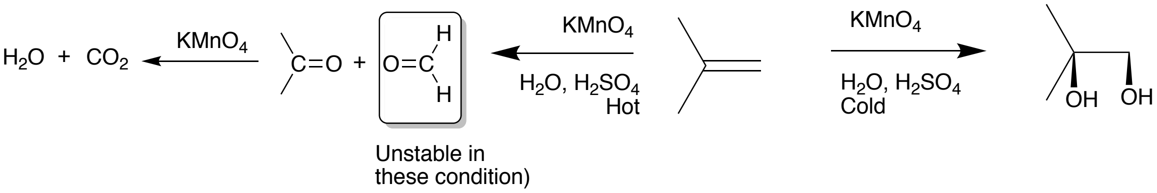


- Hot (100ºC) $KMnO_4$ oxidation of 2-butene cleaves the double bond to form 2 molecules of acetic acid
- High temperature provides enough energy to break the C–C double bond in the manganate ester to initially form acetaldehyde which is then further oxidized to acetic acid
- Same oxidation products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

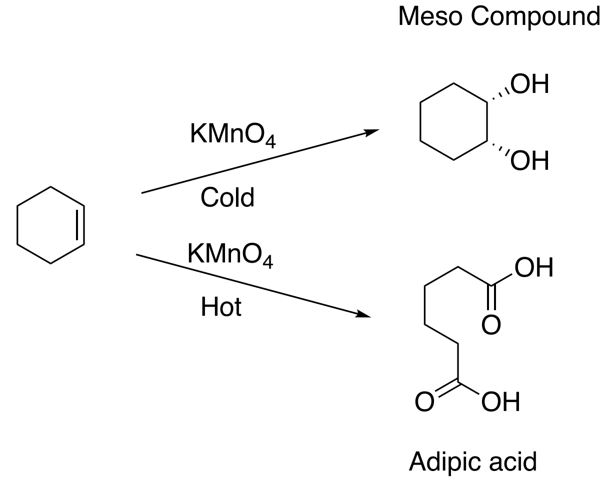
Example 1:



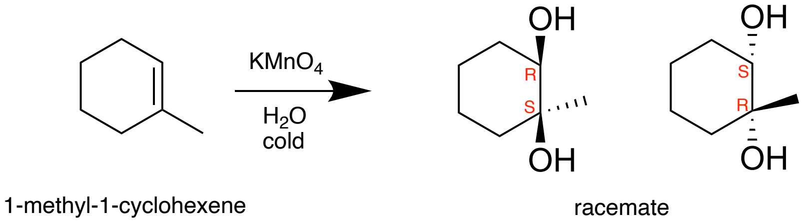
Example 2:



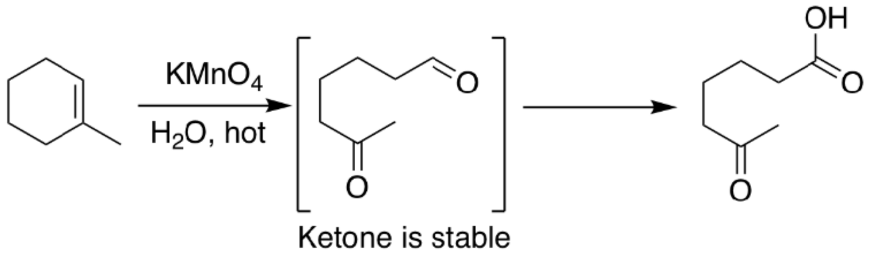
Example 3:



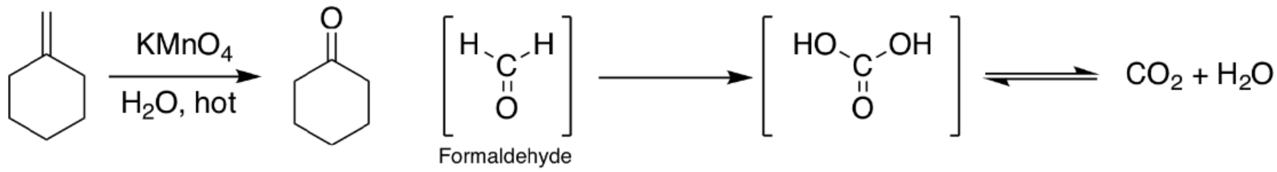
Example 4:



Example 5:

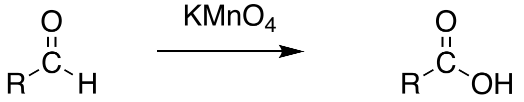


Example 6:

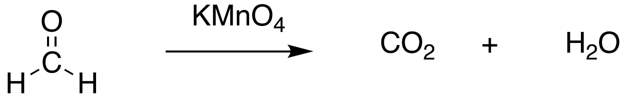


Reaction with aldehydes:

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



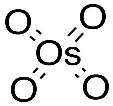
Formic acid



Formaldehyde

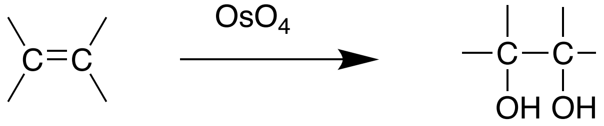
- Formaldehyde
  - disinfectant – used to preserve cadavers
  - is further oxidized to form CO_2 and H_2O in the presence of excess $KMnO_4$

<u>Osmium Tetraoxide: OsO_4</u>



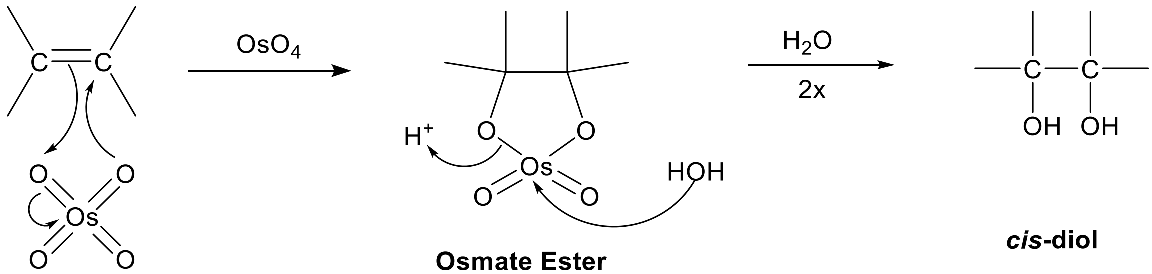
Toxic, Volatile

General Scheme:



Syn/Cis Addition

Mechanism:



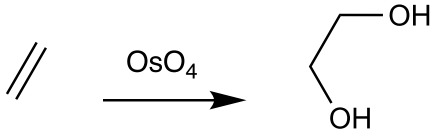
Osmate Ester

***cis*-diol**

- 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

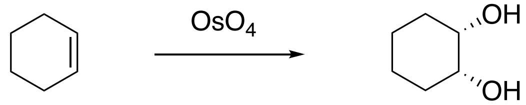
- Reaction is stereospecific (syn/cis addition)

Example 1:

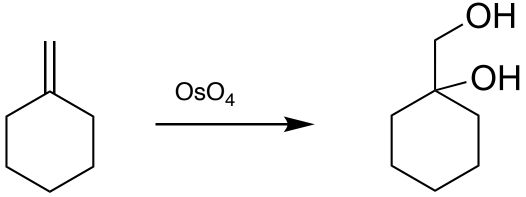


ethylene glycol

Example 2:



Example 3:

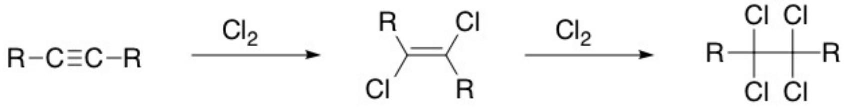


achiral

Addition reactions of Alkynes

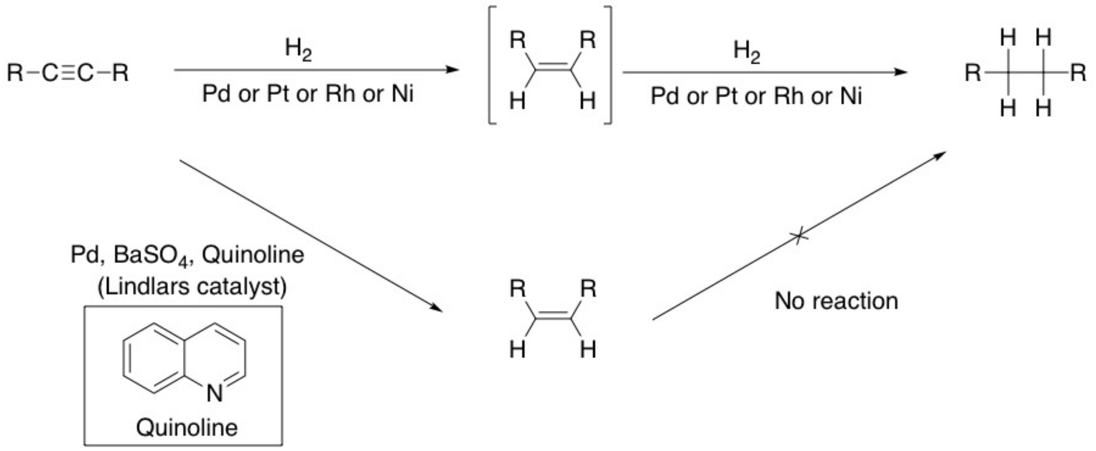
Alkynes are more polar as they have more negative charge between the two carbons.
They are always more reactive than alkenes and so can be utilized in all addition reactions that alkenes can, except react faster.

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



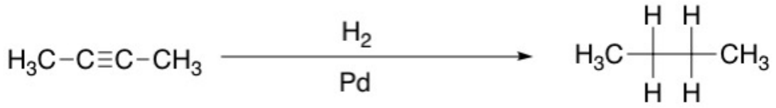
The first addition to the alkyne is anti, which forms the trans alkene.

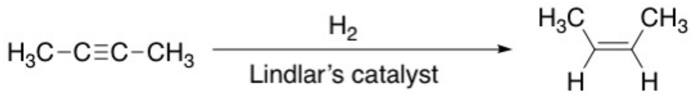
Hydrogenation of Alkynes



- **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