# **Recall:**

## **Addition Reactions**

- Occurs on double bonds and triple bonds



### **Ozonolysis**

Ozone

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

O<sub>3</sub>



**Example:** 



# **Epoxidation:**





Epoxide/Oxirane

Syn/Cis Addition Stereospecific

Concerted (bonds break and form at the same time)

### Mechanism:



to quench ethylene oxide:





ethylene glycol (diol product)

## 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 2: 1-methyl-1-cyclohexene



### 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: KMnO4



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:



- 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'  $KMnO_4 - 50/50$  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**



### CHEM 261 Notes

November 19, 2024

- 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

## Example 1:

#### Meso Compound



Adipic acid

## Example 2:



racemate

November 19, 2024

# Example 4:



1-methyl-1-cyclohexene

### **Example 5:**



Ketone is stable

Example 6:



# **Reaction with aldehydes:**

- In 'hot' KMnO<sub>4</sub> 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<sub>2</sub> and H<sub>2</sub>O in the presence of excess KMnO<sub>4</sub>

# Osmium Tetraoxide: OsO4

Toxic, Volatile

# **General Scheme:**



- OsO4 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:



ethylene glycol

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.

FALL 2024 November 19, 2024

### **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 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<sub>2</sub>O

### **Example 1: 1-propyne**

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



- Enols are generally unstable and tend to isomerize to the <u>keto form (generally</u> <u>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

ketone is disfavored

enol is favored

tautomers are structural isomers, not resonance structures