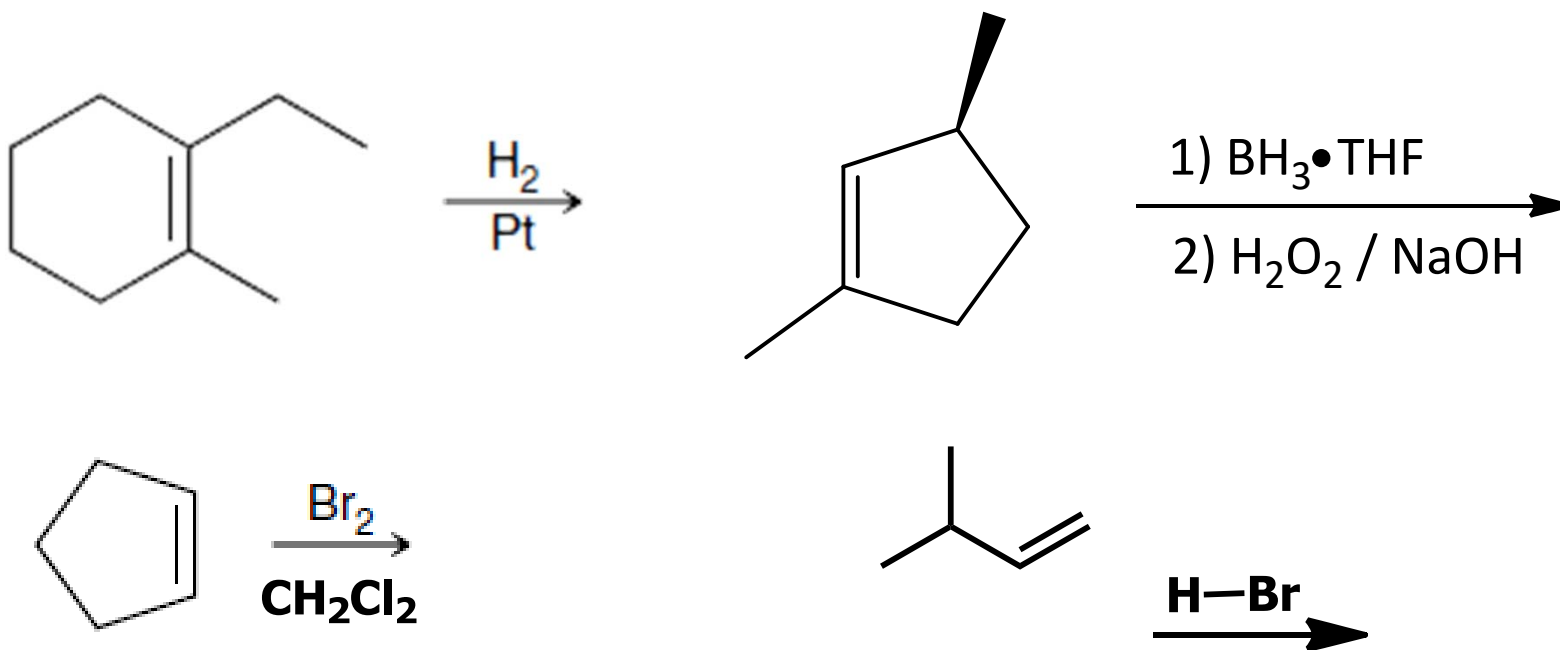


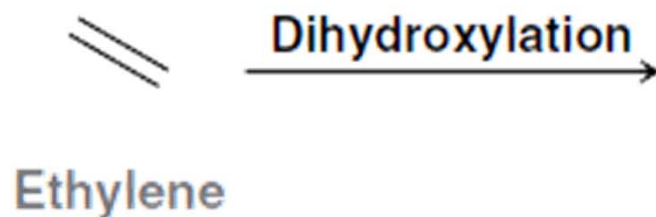
# Chapter 8 part 5:

## Oxidative Cleavage

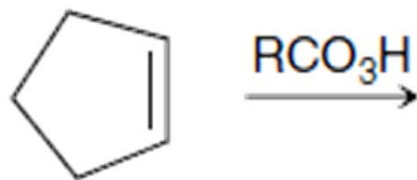


# Anti Dihydroxylation

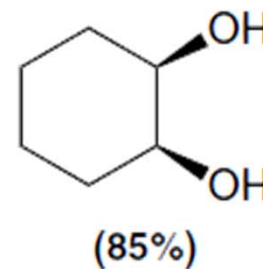
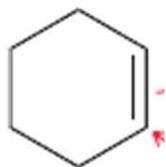
- Dihydroxylation occurs when two –OH groups are added across a C=C double bond.



- ANTI dihydroxylation is achieved through a multi-step process.

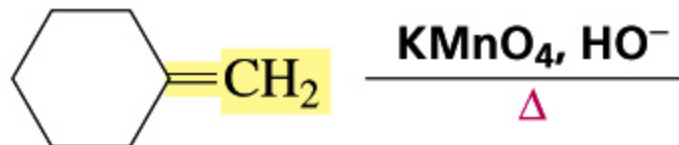
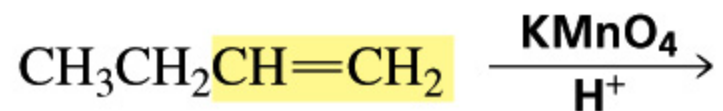
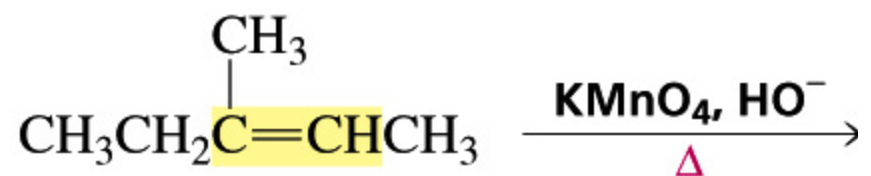


# Syn Dihydroxylation



- Diols are often further oxidized by  $\text{MnO}_4^{1-}$ , and  $\text{MnO}_4^{1-}$  is reactive toward many other functional groups as well.
- The synthetic utility of  $\text{MnO}_4^{1-}$  is limited.

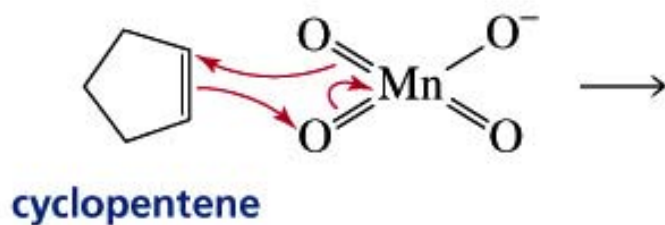
# Syn Dihydroxylation



# Hydroxylation of Alkenes

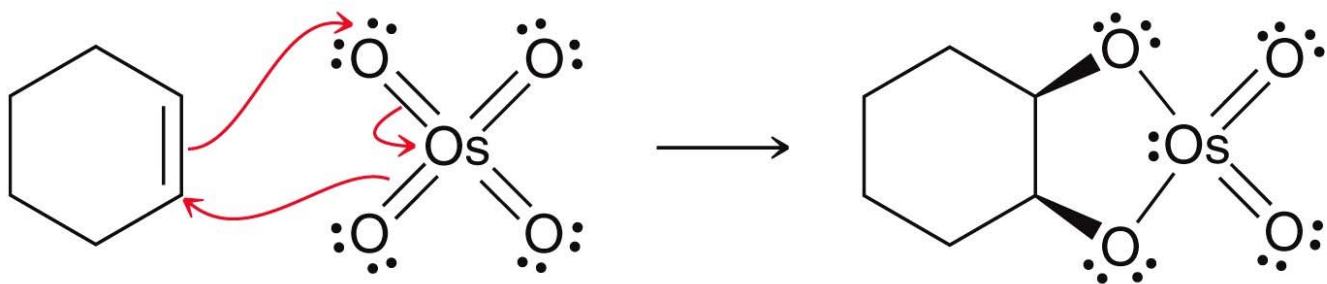


## Mechanism for *cis*-Glycol Formation

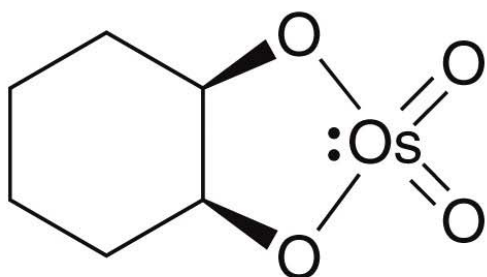


# Syn Dihydroxylation

- Like other ***syn*** additions, *syn* dihydroxylation adds across the C=C double bond in ONE step

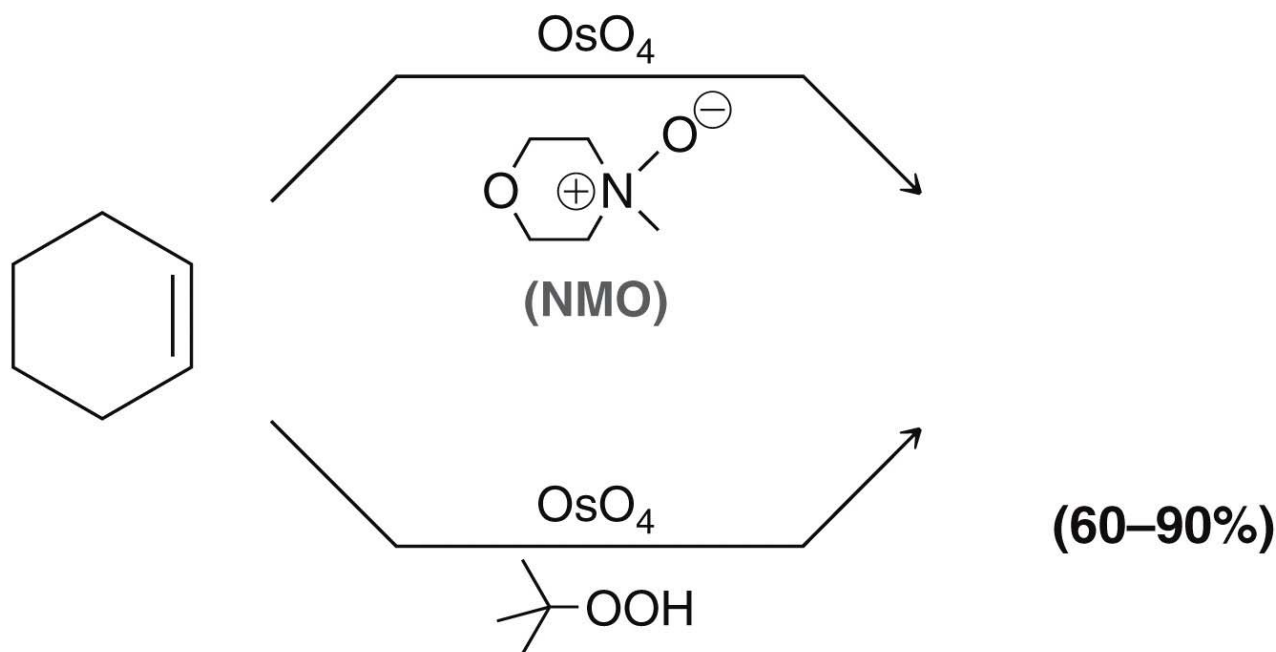


A cyclic osmate ester



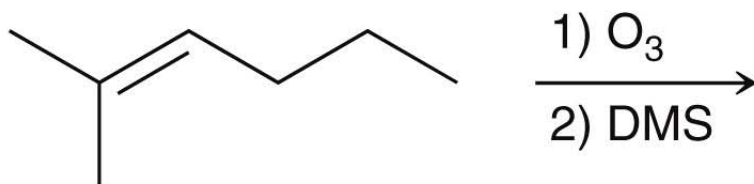
# Syn Dihydroxylation

- Because  $\text{OsO}_4$  is expensive and toxic, conditions have been developed where the  $\text{OsO}_4$  is regenerated after reacting, so only catalytic amounts are needed



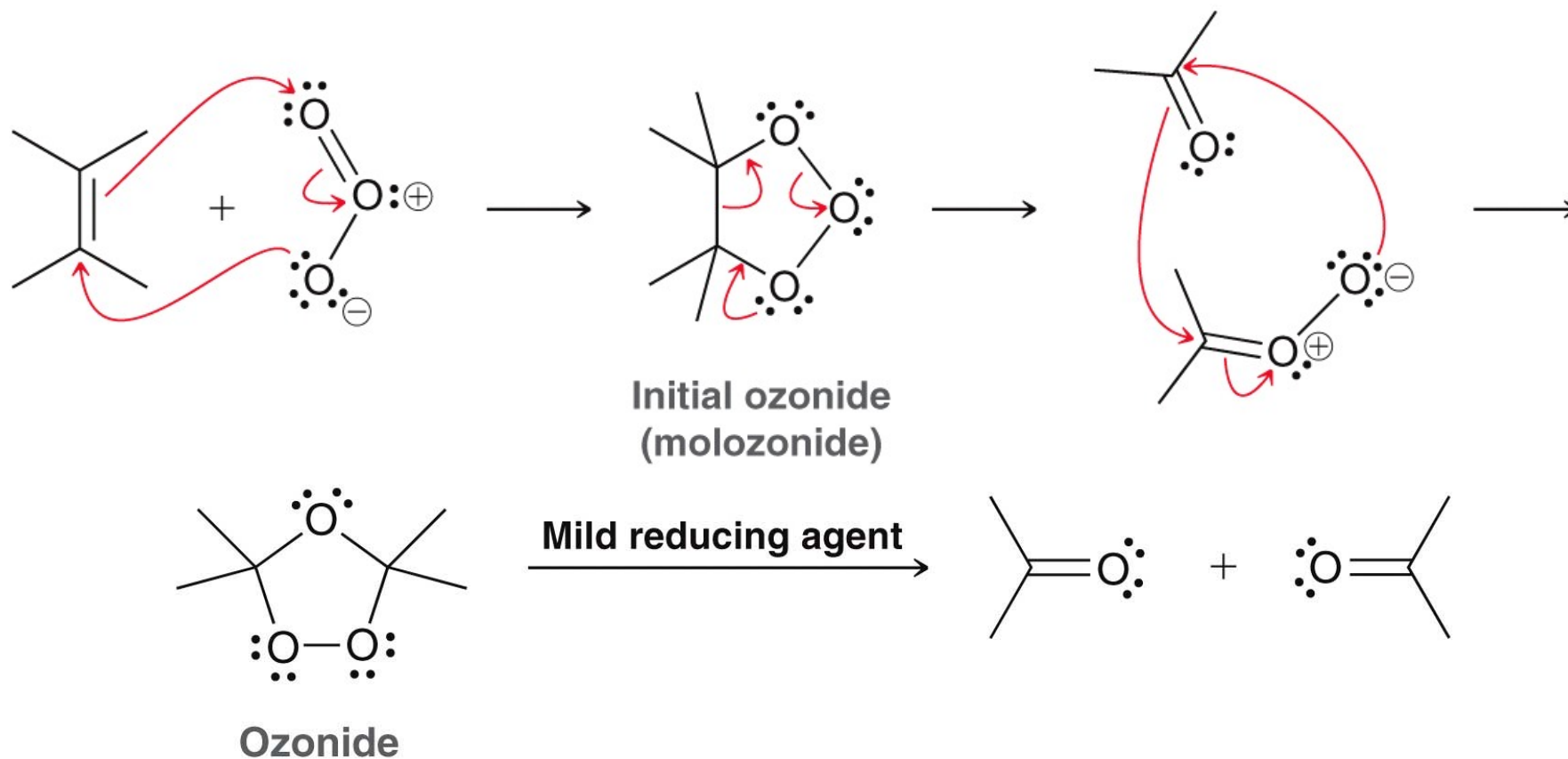
# Oxidative Cleavage with O<sub>3</sub>

- C=C double bonds are also reactive toward oxidative cleavage
- Ozonolysis is one such process



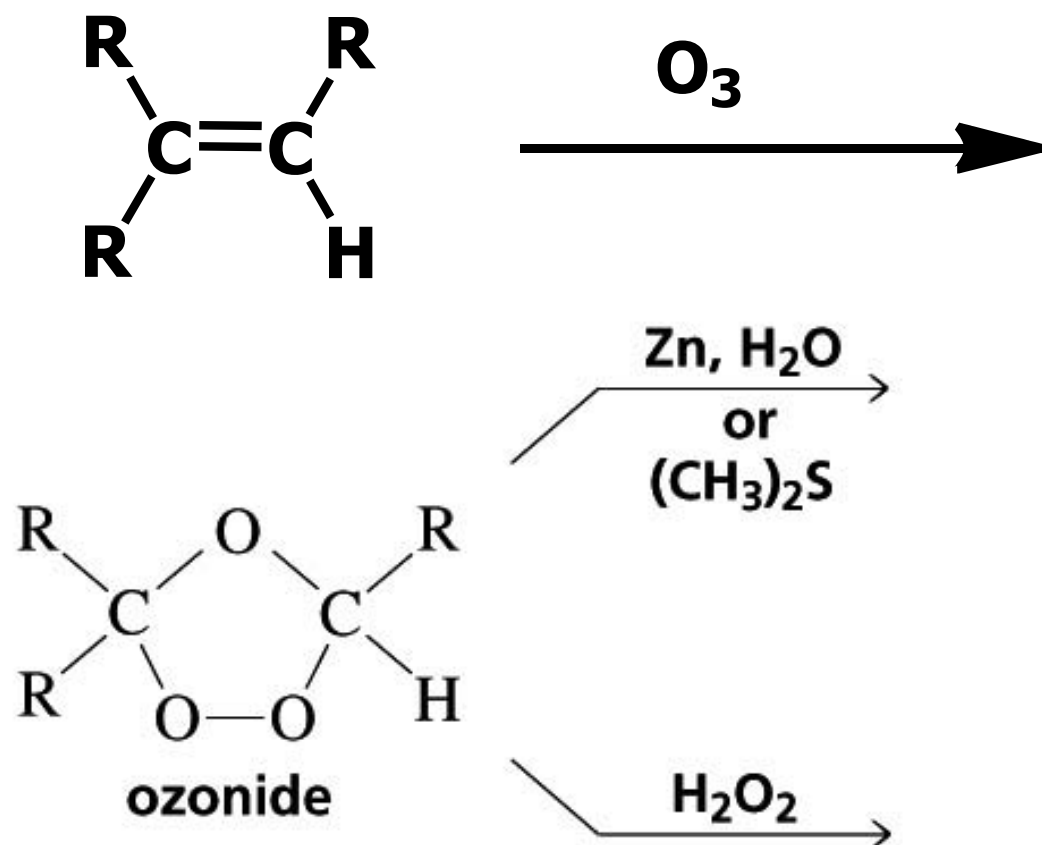


# Oxidative Cleavage with $O_3$



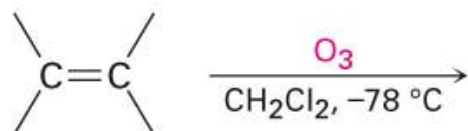
- Common reducing agents include dimethyl sulfide (DMS) and  $Zn/H_2O$ .

# Oxidative Cleavage of Alkenes by Ozonolysis



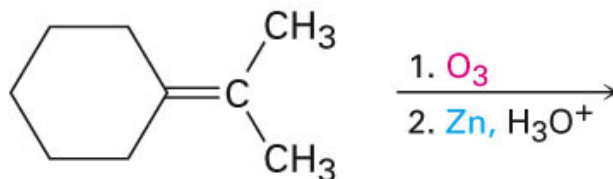
Ozonides can be cleaved to carbonyl compounds with a reducing agent

# Examples of Ozonolysis of Alkenes



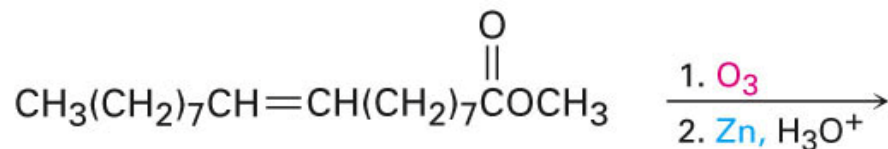
## An alkene

The molozonide is unstable because it has two O–O bonds. The ozonide is more stable.



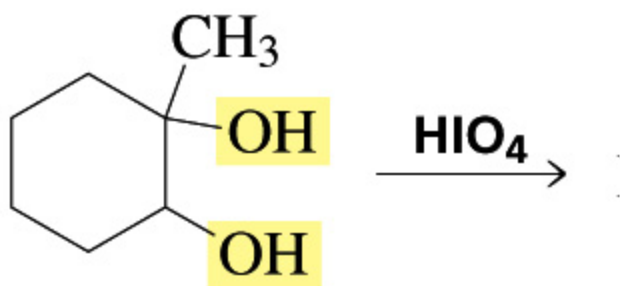
### Isopropylidenecyclohexane (tetrasubstituted)

Used in determination of structure of an unknown alkene



### Methyl 9-octadecenoate (disubstituted)

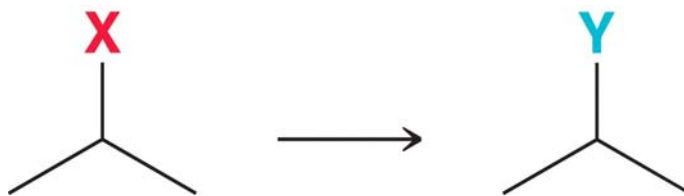
# Cleavage of 1,2-Diols



- Reaction of a 1,2-diol with **periodic** (*per-iodic*) acid,  $\text{HIO}_4$ , cleaves the diol into two carbonyl compounds
- Sequence of diol formation with  $\text{OsO}_4$  followed by diol cleavage is a good alternative to ozonolysis

# One Step Syntheses

- To set up a synthesis, assess the reactants and products to see what changes need to be made
- Label each of the processes below



# For Next Time....

Next week Chapter 9

Suggested Homework Problems Chapter 8

# 1, 2, 5, 9, 12,13, 18, 24, 27, 31, 42-46, 52, 57,62,63

Suggested Homework Problems Chapter 9

# 1,7,9,13,18,20,32-37, 41,44,52,57