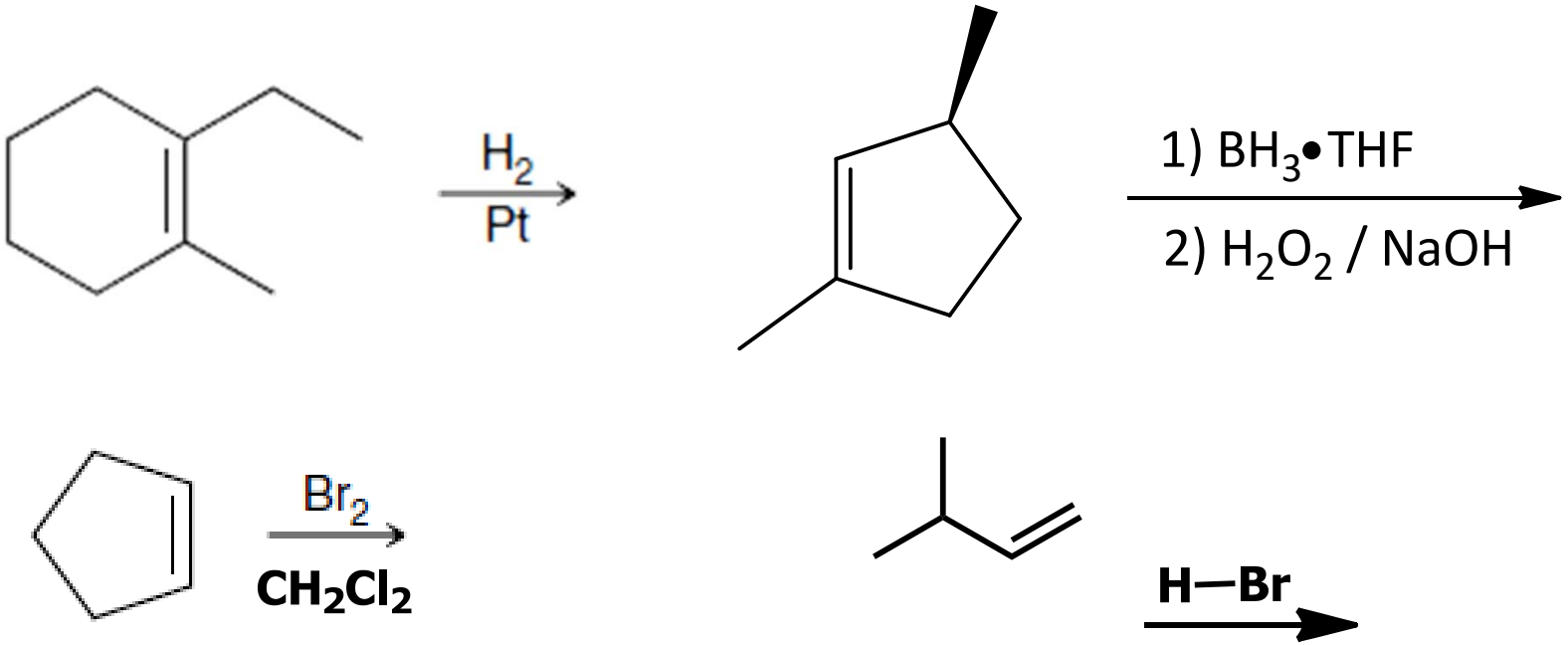
Chapter 9 part 5:

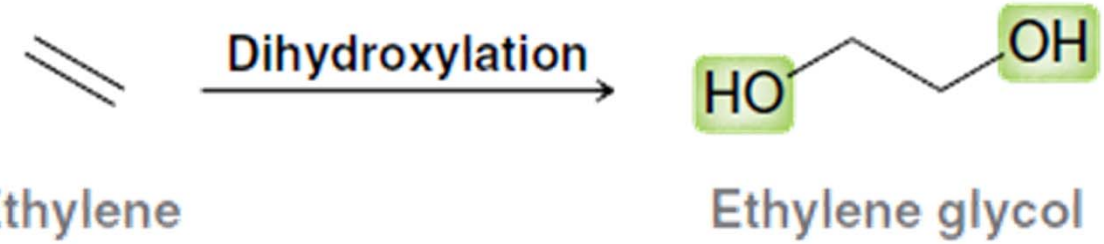
Oxidative Cleavage

- Today (9.8-9.13) Halogenation and Oxidative Cleavage

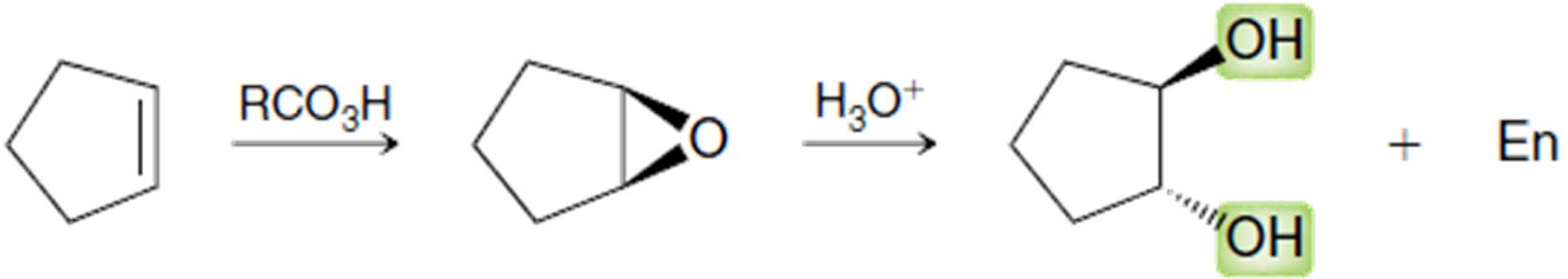


Anti Dihydroxylation

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

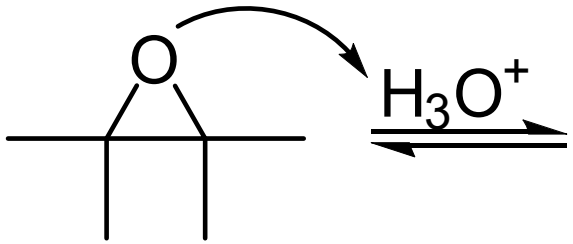


- ANTI dihydroxylation is achieved through a multi-step process.



Anti Dihydroxylation

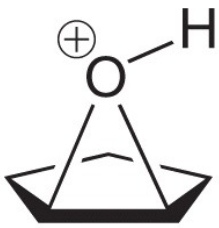
- Nucleophile attacks **more** substituted carbon of a protonated epoxide
- Inversion of configuration at site of nucleophilic attack
- Water is a poor nucleophile, so the epoxide is activated with an acid



Mild acid reacts with epoxides in water to generate anti 1,2-diols

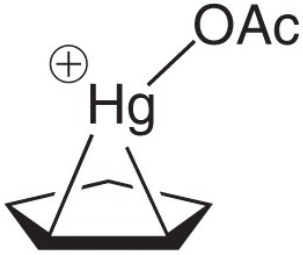
Anti Dihydroxylation

- Note the similarities between three key intermediates



A protonated epoxide

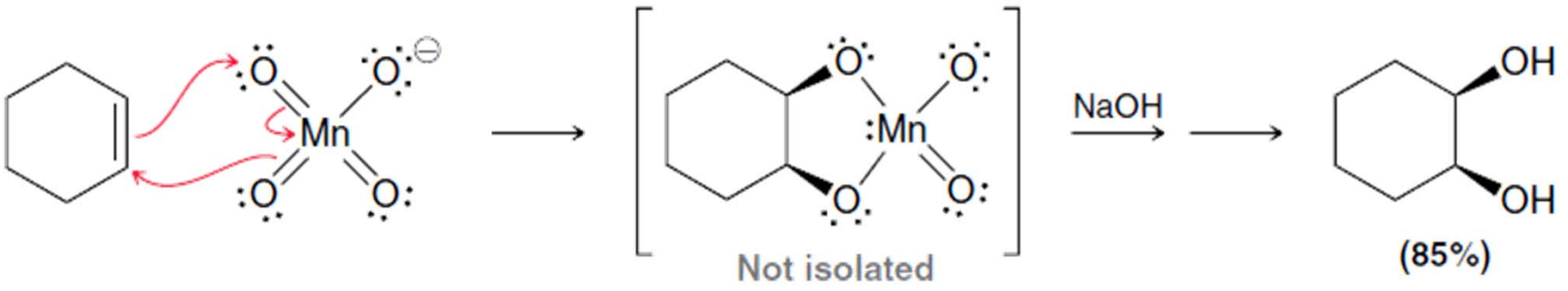
A bromonium ion



A mercurinium ion

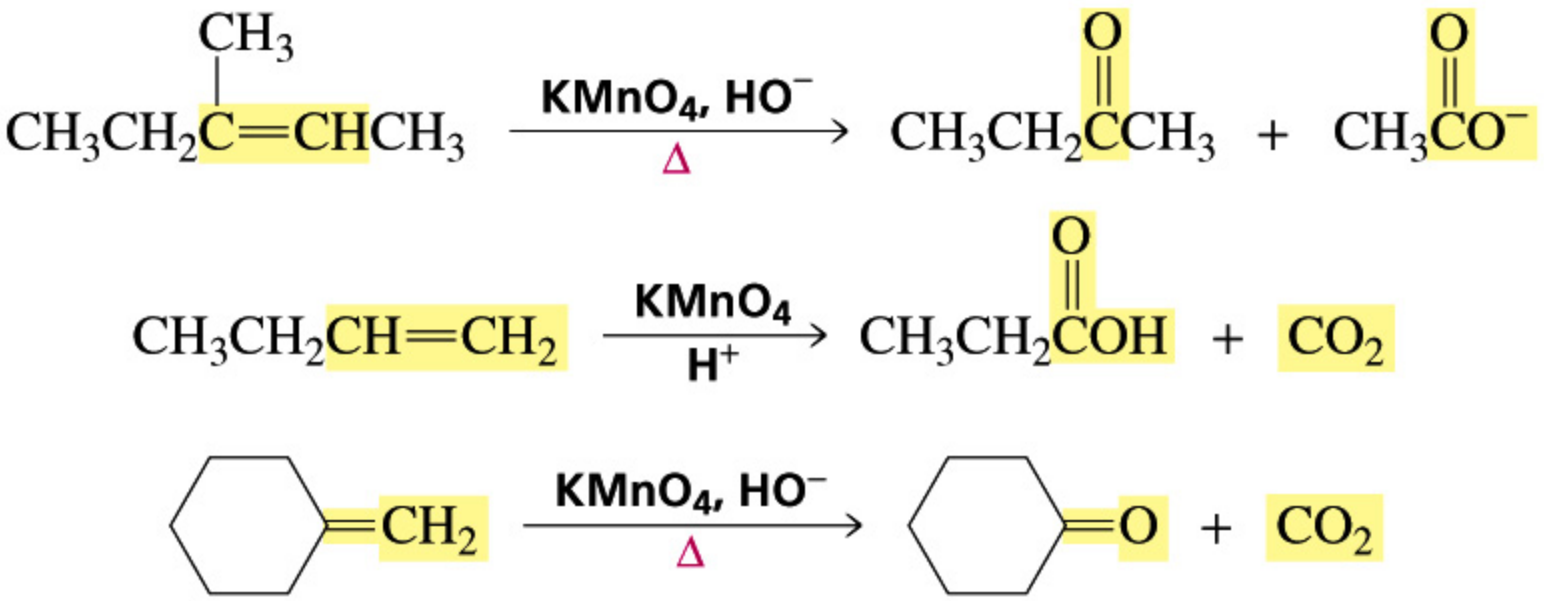
- Ring strain and a +1 formal charge makes these structures GREAT electrophiles
- They also each yield ***anti*** products, because the nucleophile must attack from the side opposite the leaving group

Syn Dihydroxylation



- Diols are often further oxidized by MnO_4^{1-}, and MnO_4^{1-} is reactive toward many other functional groups as well.
- The synthetic utility of MnO_4^{1-} is limited.

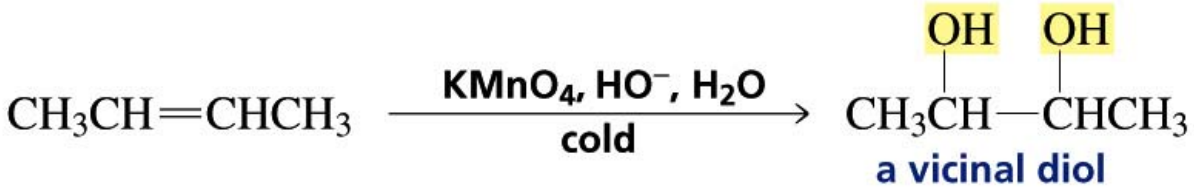
Syn Dihydroxylation



A peroxyacid, OsO_4, and (cold basic) $KMnO_4$ break only the π bond of the alkene

Ozone and acidic $KMnO_4$ break both the π bond and the σ bond

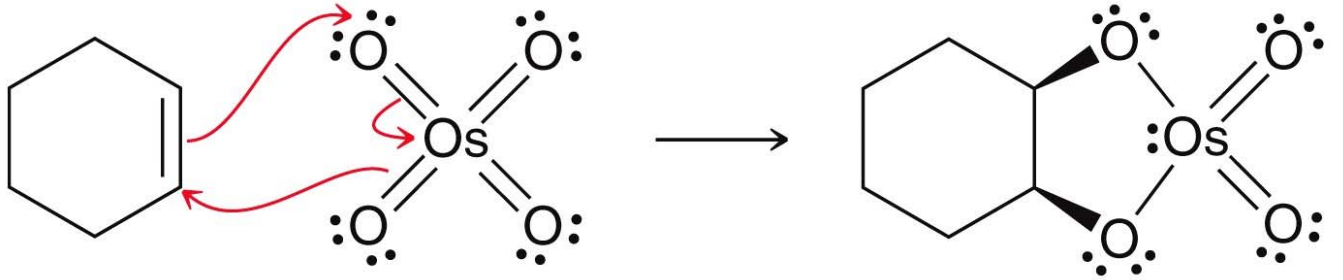
Hydroxylation of Alkenes



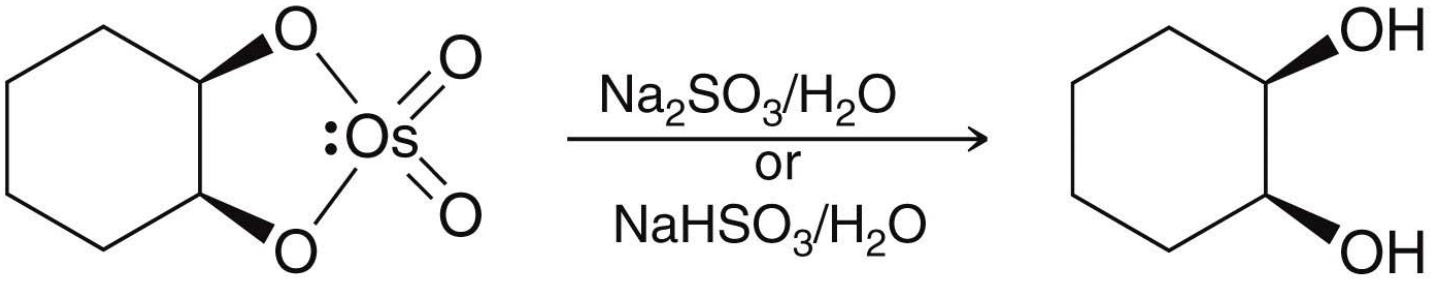
Mechanism for *cis*-Glycol Formation

Syn Dihydroxylation

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

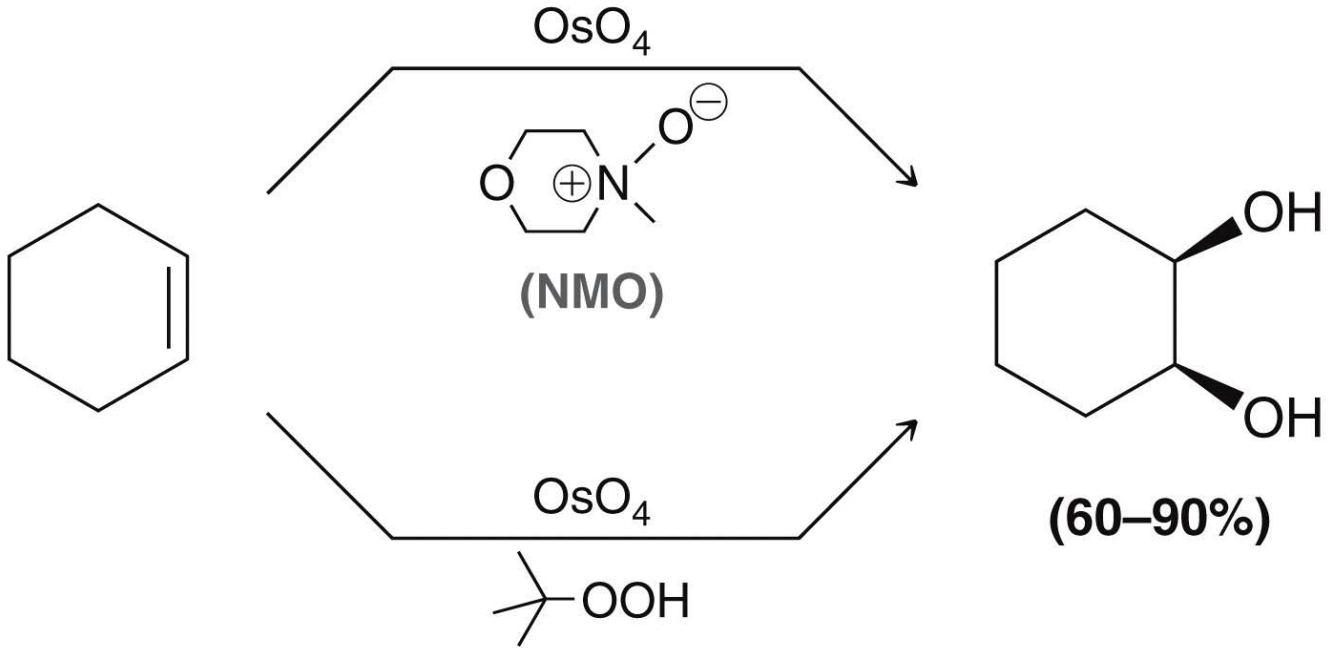


A cyclic osmate ester



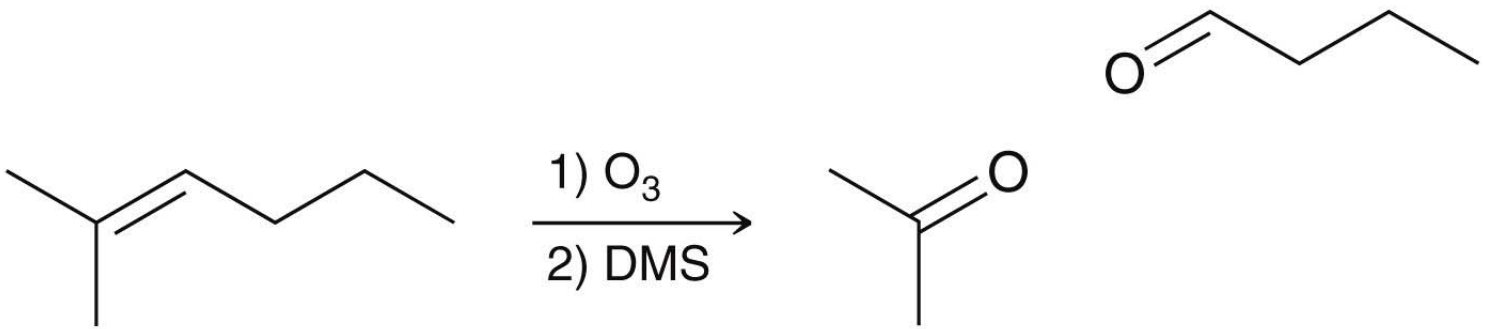
Syn Dihydroxylation

- Because OsO_4 is expensive and toxic, conditions have been developed where the OsO_4 is regenerated after reacting, so only catalytic amounts are needed

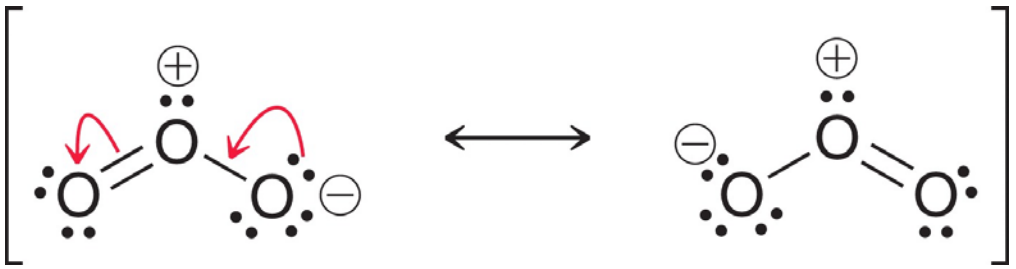


Oxidative Cleavage with O_3

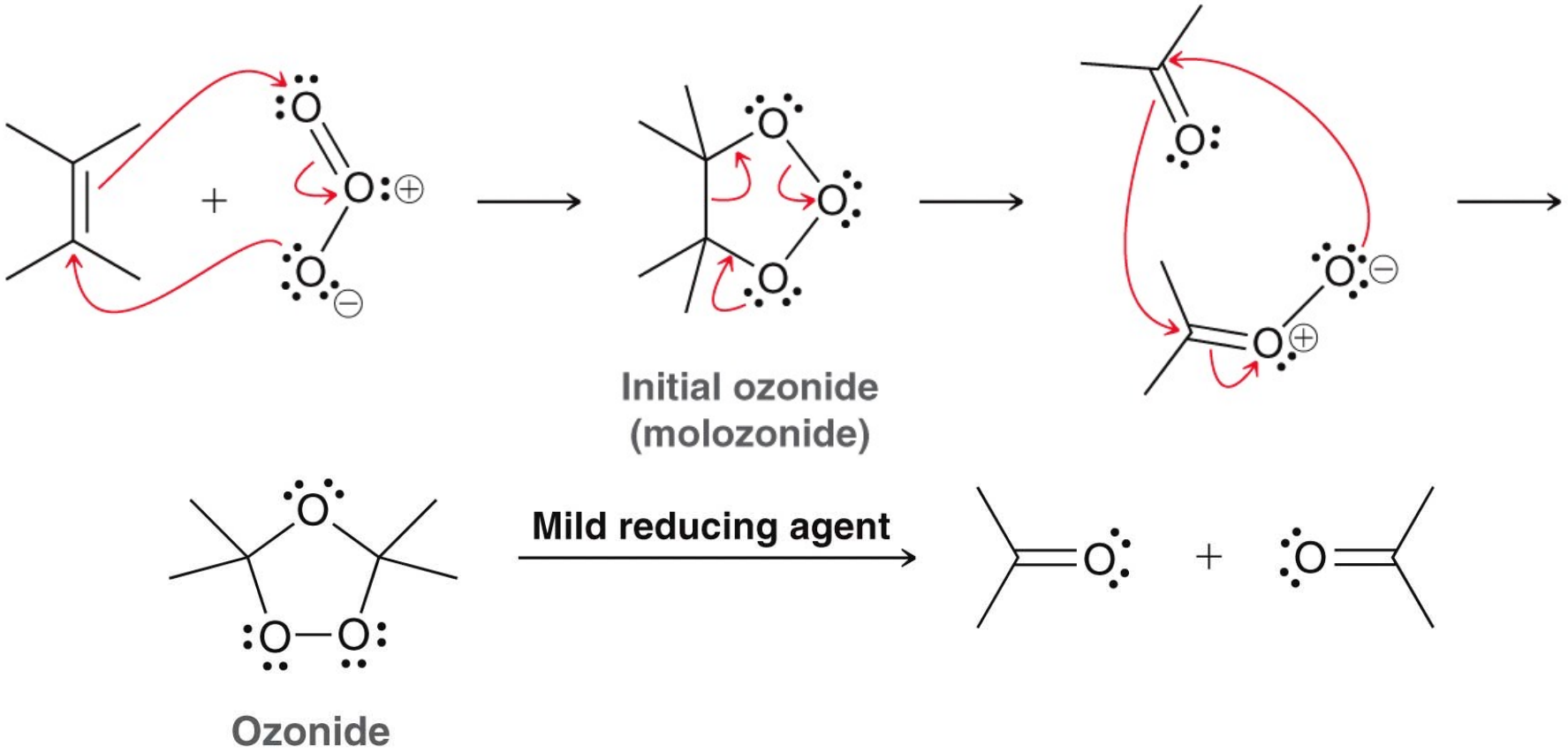
- C=C double bonds are also reactive toward oxidative cleavage
- Ozonolysis is one such process



- Ozone exists as a resonance hybrid of two contributors

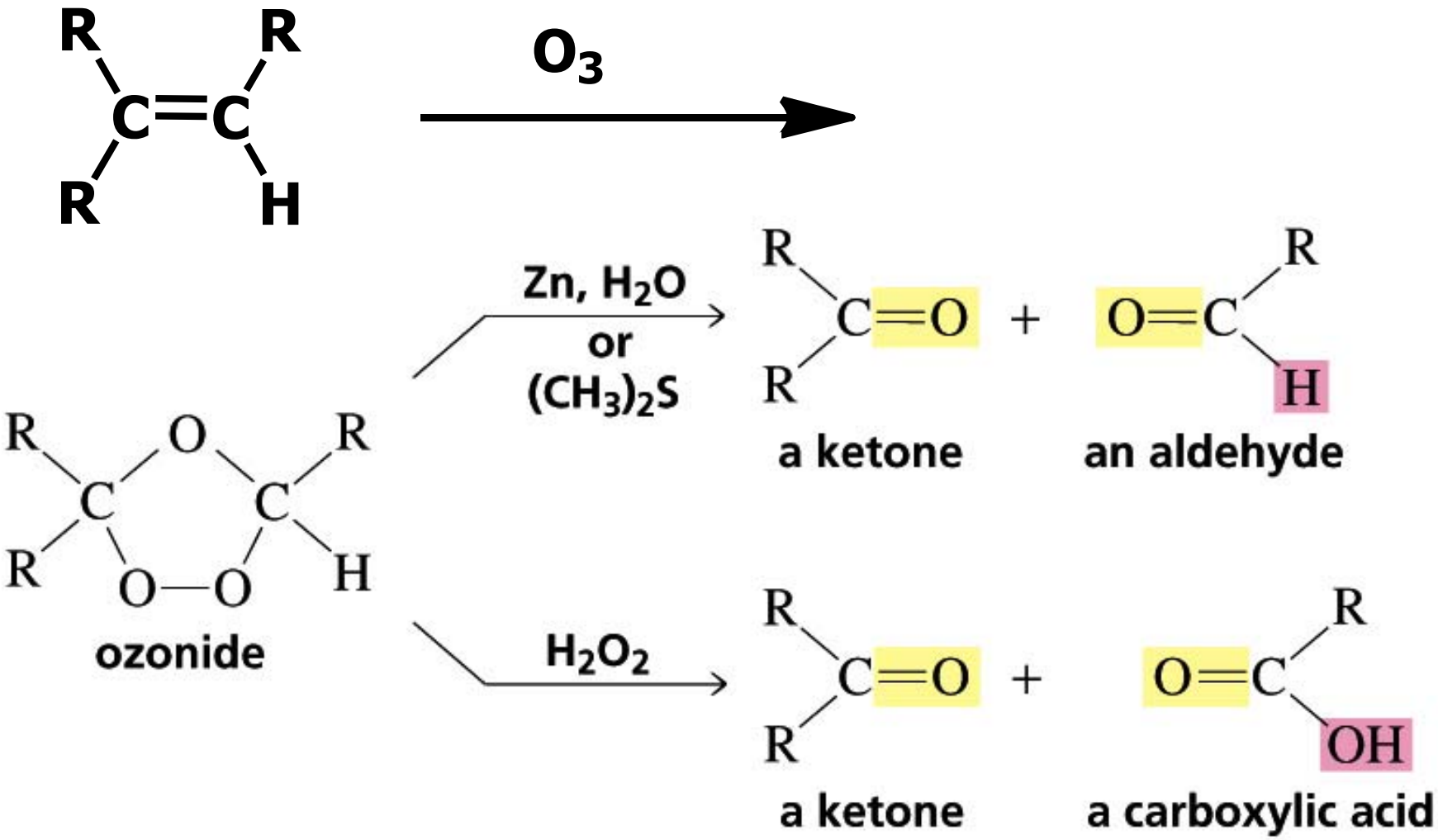


Oxidative Cleavage with O_3



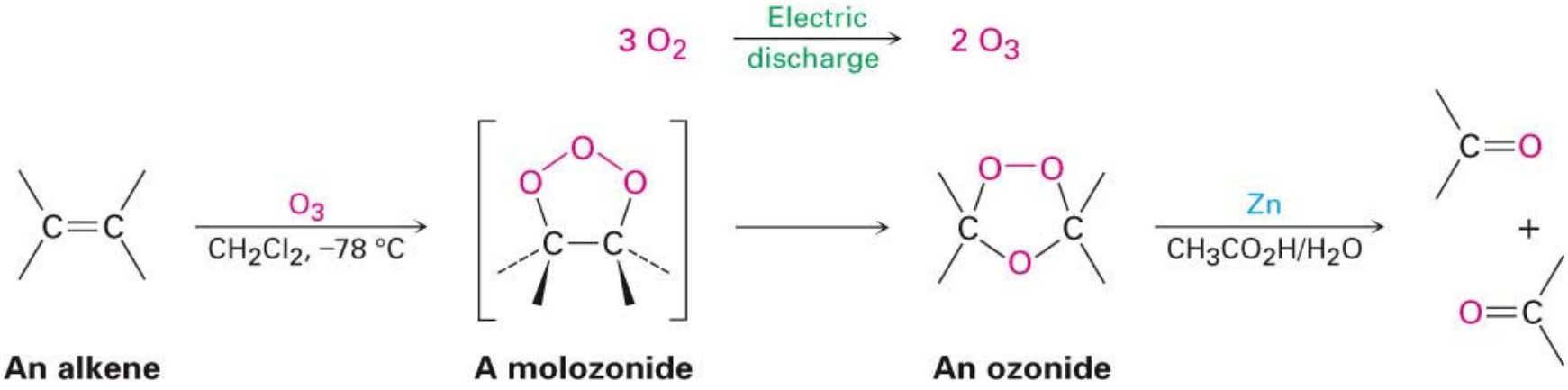
- Common reducing agents include dimethyl sulfide and Zn/H_2O.

Oxidative Cleavage of Alkenes by Ozonolysis

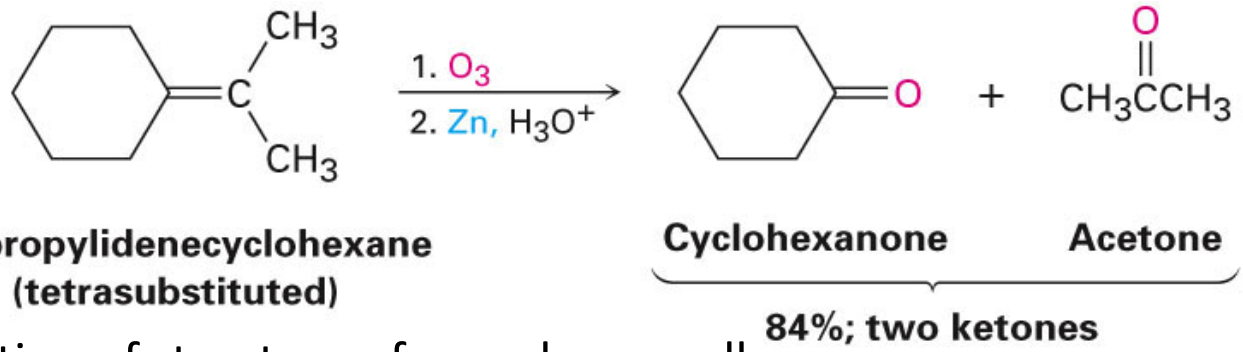


Ozonides can be cleaved to carbonyl compounds with a reducing agent

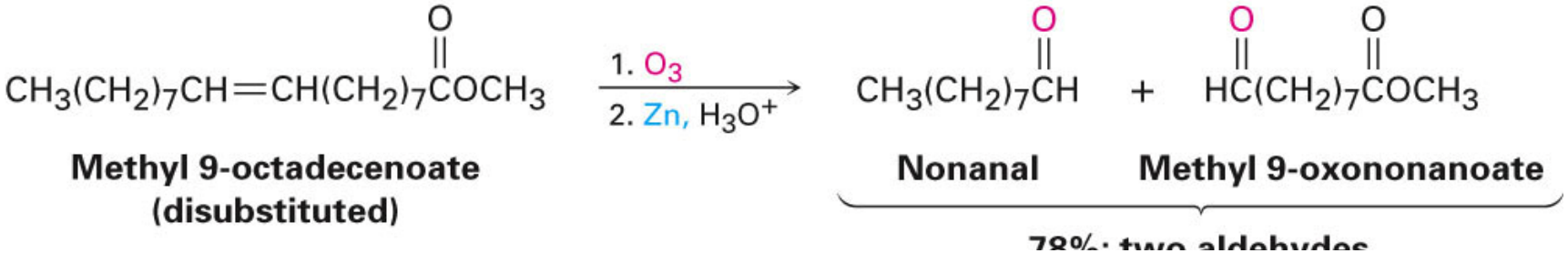
Examples of Ozonolysis of Alkenes



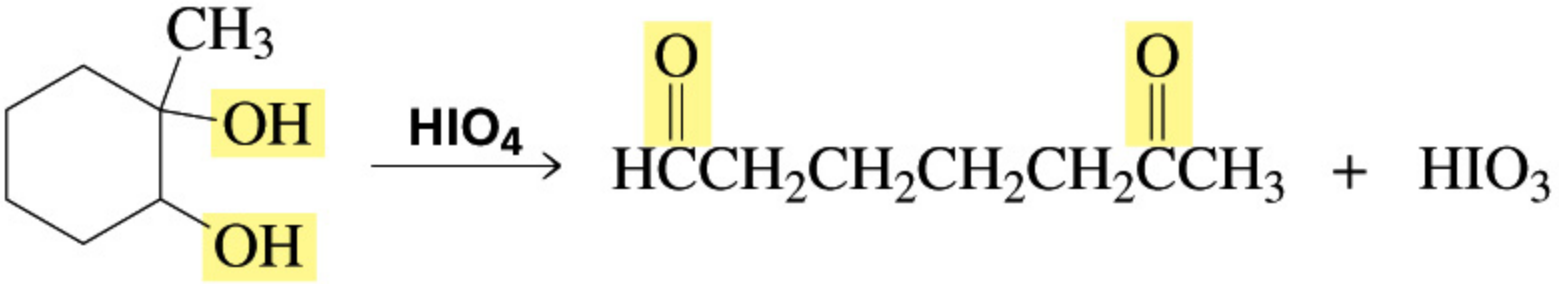
The molozonide is unstable because it has two O–O bonds. The ozonide is more stable.



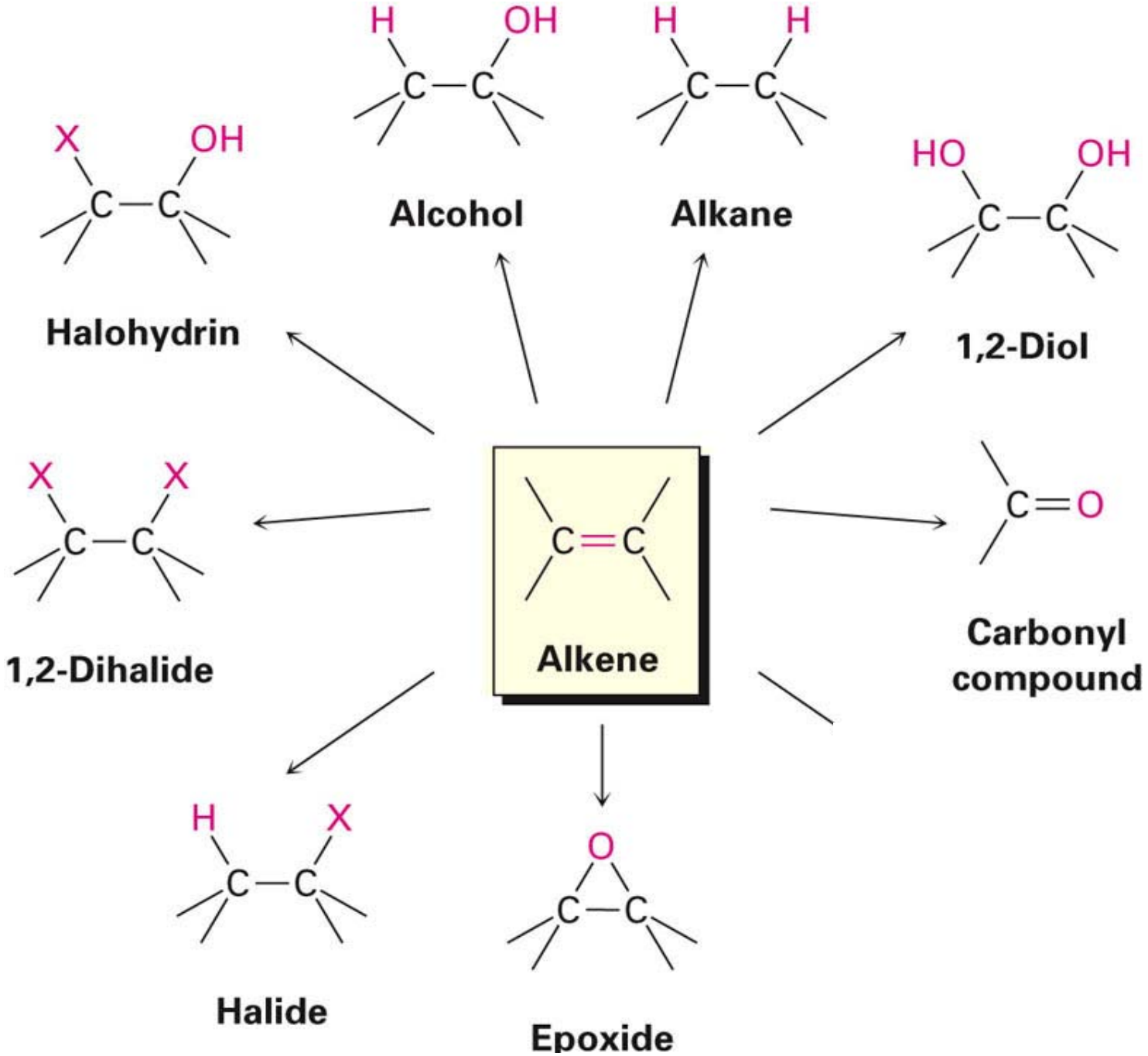
Used in determination of structure of an unknown alkene



Cleavage of 1,2-Diols



- Reaction of a 1,2-diol with **periodic** (*per-iodic*) acid, HIO_4 , cleaves the diol into two carbonyl compounds
- Sequence of diol formation with OsO_4 followed by diol cleavage is a good alternative to ozonolysis

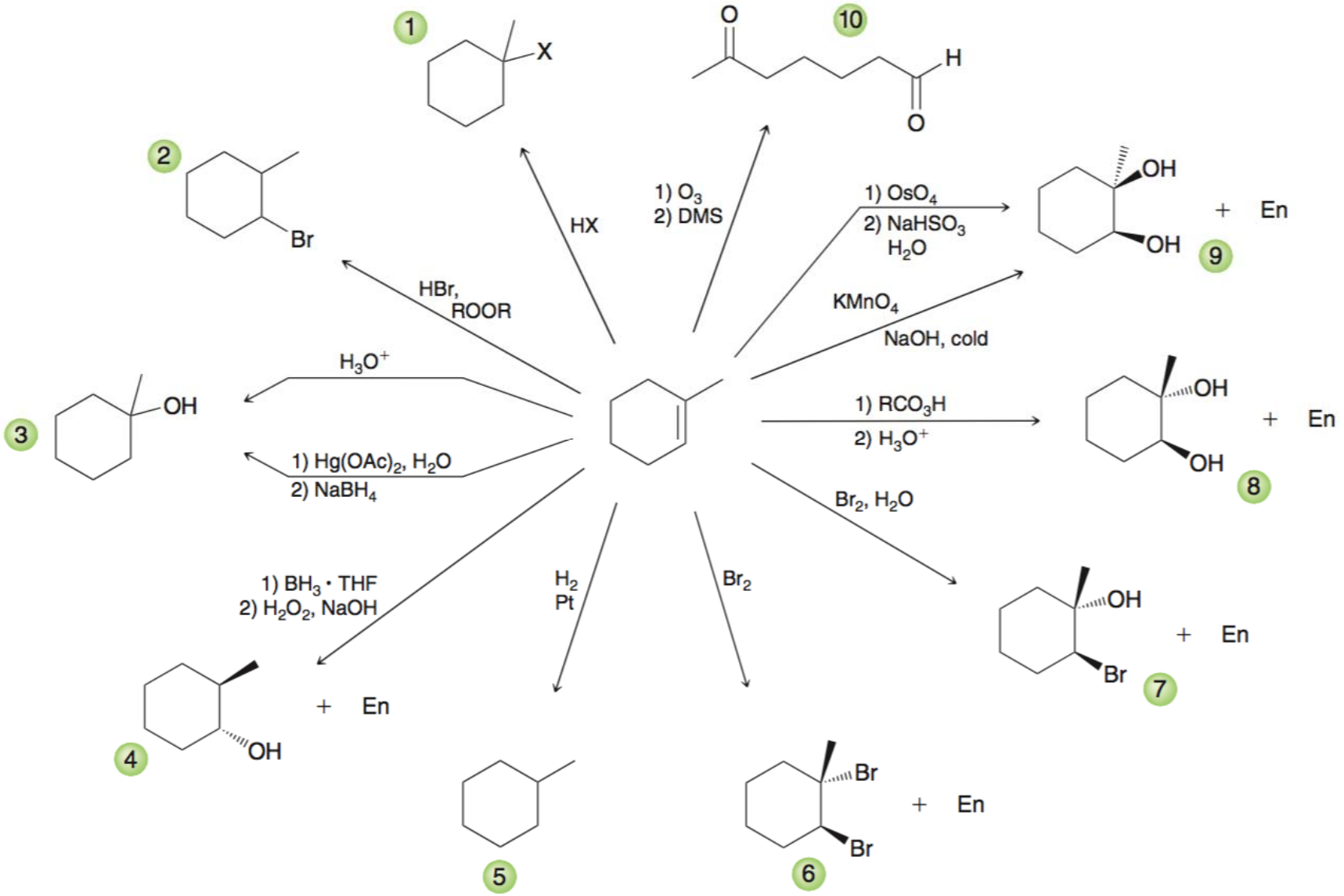

H
OH
H
H
X
OH
HO
OH
Alcohol
Alkane
Halohydrin
1,2-Diol
X
X
C=O
1,2-Dihalide
Alkene
Carbonyl compound
H
X
O
Halide
Epoxide

Review of Addition Reactions

- **Ten reactions of alkenes covered in this chapter:**

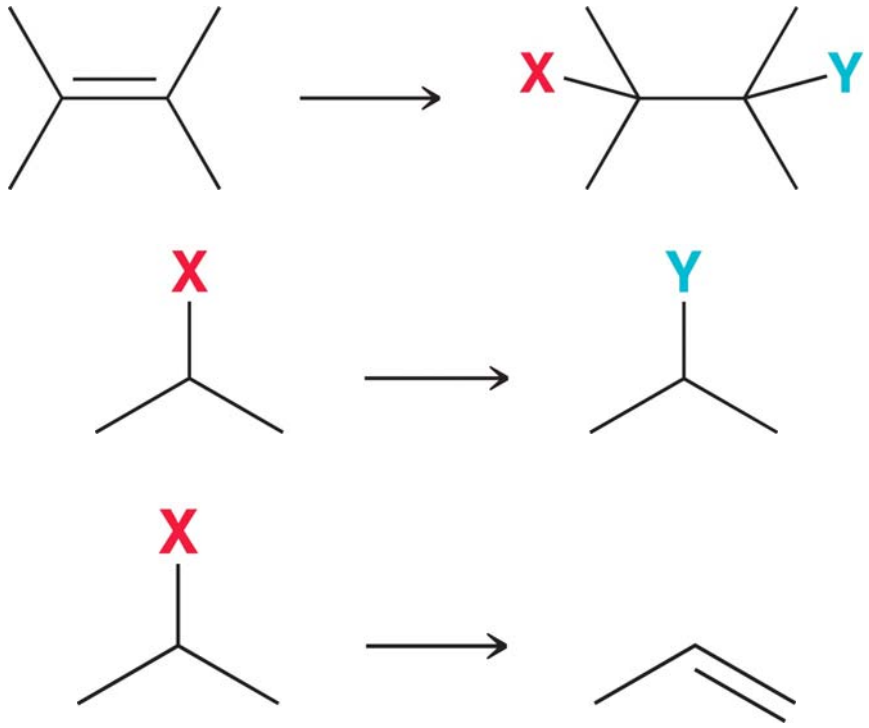
1. Hydrohalogenation (Markovnikov)
2. Hydrohalogenation (*anti*-Markovnikov)
3. Acid-catalyzed hydration and oxymercuration-demercuration
4. Hydroboration-oxidation
5. Hydrogenation
6. Bromination
7. Halohydrin formation
8. *Anti* dihydroxylation
9. *Syn* dihydroxylation
10. Ozonolysis

Review of Addition Reactions



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….

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

MONDAY Chapter 9 Alkynes (9.1-9.4)
Wednesday (9.4-9.7) Reactions with Alkynes
Friday (9.7- 9.11)

Oxidative Cleavage with O_3

- Predict the major product(s) for the reactions below.