

Alkenes 7: Oxidation of Alkenes

Chemistry 318/310M

Sessler

Lecture 22

“Sessler’s Picks”

Recommended Problems for Those Cramming for Exam II
(Note: As always, those not on this list are still fair game!)

3.9, 3.10, 3.11, 3.15, 3.16, 3.19-3.22, 3.28-3.30, 3.31, 3.35, 3.36

5.11-5.14, 5.17, 5.18, 5.20

6.15-6.17, 6.19-6.22, 6.24-6.27, 6.29-6.33, 6.36, 6.37, 6.39-6.42, 6.47,
6.49

7.2, 7.5, 7.6, 7.12-7.17, 7.19-7.24

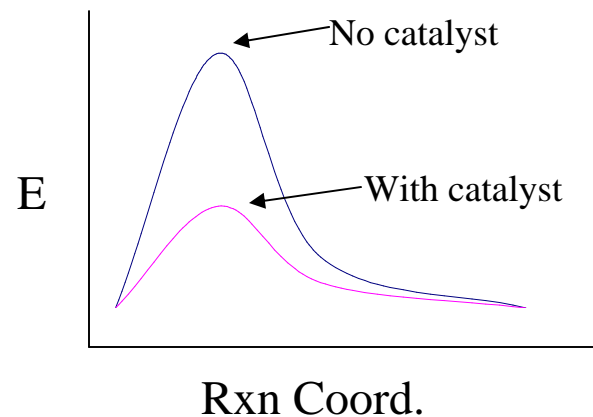
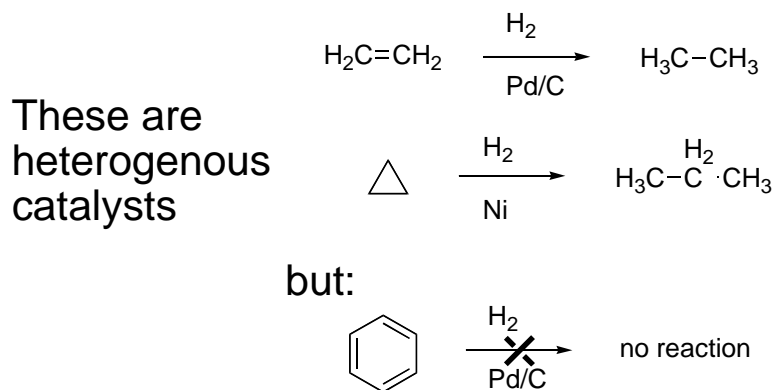
Oxidation and Reductions of Alkenes

- Earlier we saw how π bonds reacted as Lewis bases (electron donors) with electrophiles.
- Now we consider oxidation & reduction reactions of alkenes.

Reduction

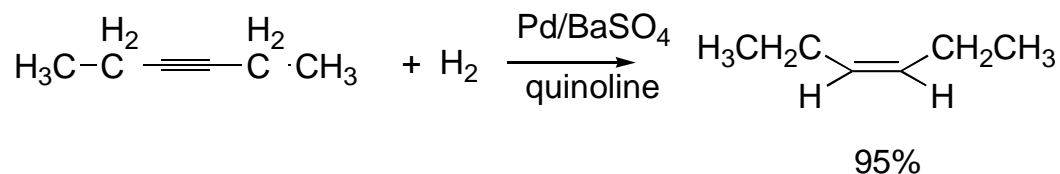
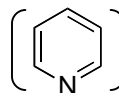
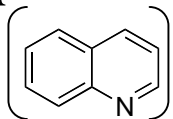
Review: catalytic hydrogenation: certain transition metals, especially: Pd, Pt, and Ni catalyze the addition of H₂ to alkenes and strained hydrocarbons.

1)



These catalysts are not very selective. It is not generally possible to stop at the alkene stage in reducing alkynes unless the catalyst is poisoned to make it less active. This is not our problem yet, but will be when we get to a discussion of alkynes. Still, it is nice to see the chemistry involved since it shows how catalysts can be modified.

2) A popular poisoned catalyst is Lindlar's catalyst in which palladium is deposited on BaSO_4 and then treated with quinoline a chemical cousin of pyridine.

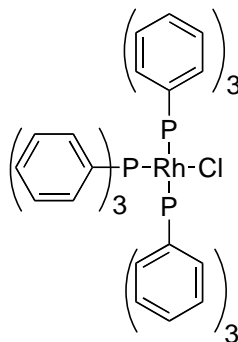


notice how cis alkene is formed

(Z)-3-hexene

You can now see a second reason for showing this: It provides a way of making cis alkenes!

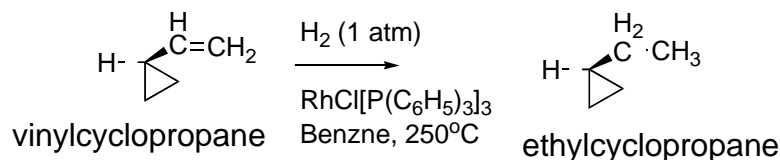
3) A second popular, less active, catalyst is Wilkinson's hydrogenation catalyst. This is an homogenous catalyst in that it dissolves into the reaction mixture.



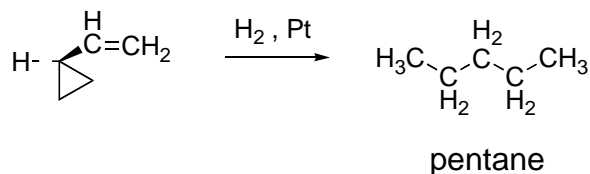
Wilkinson's hydrogenation catalyst
 $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$

The mechanism of action involves organometallic intermediates (species with carbon bound to metals) and is actually quite complex. You are not required to know it.

You should know that Wilkinson's catalyst is very selective:



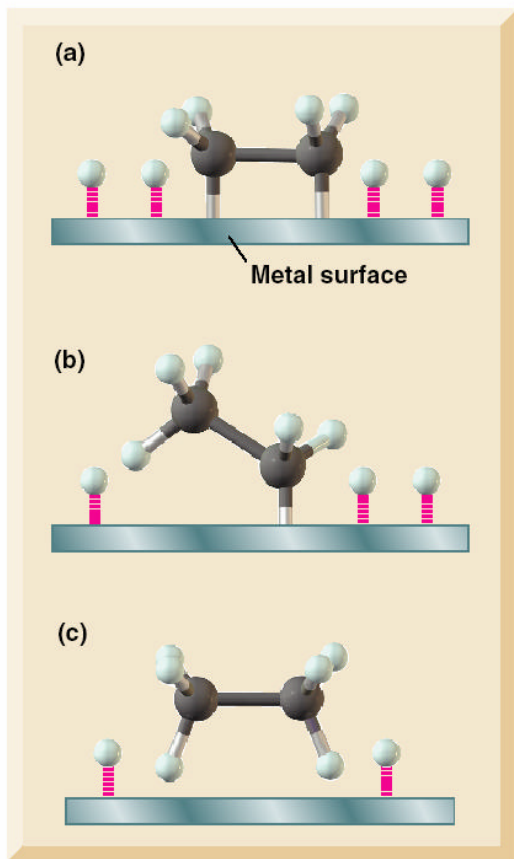
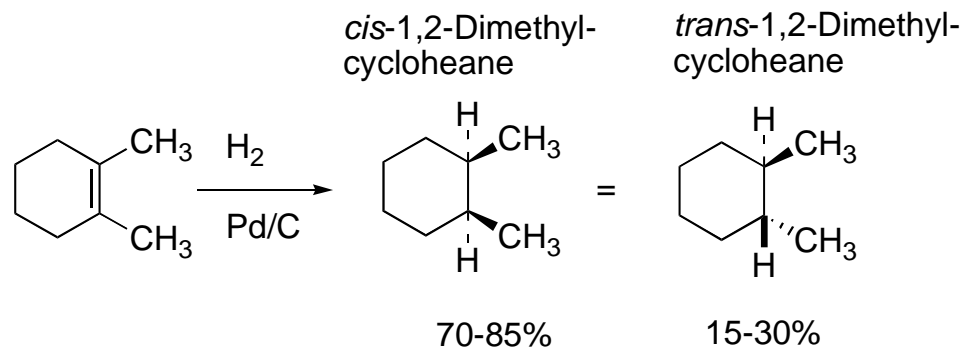
but:



Stereochemistry of Hydrogenation

Catalytic hydrogenation is stereoselective favoring syn-addition

ex:

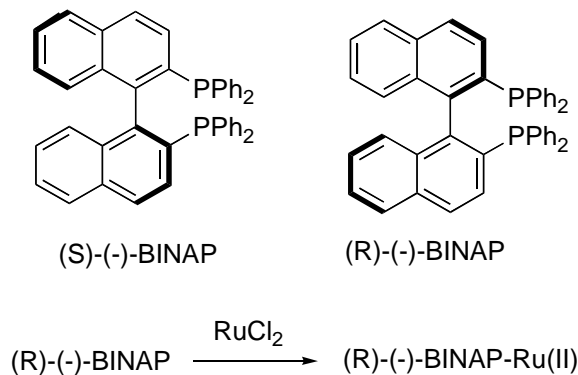


Mechanistic rationalization for syn-addition

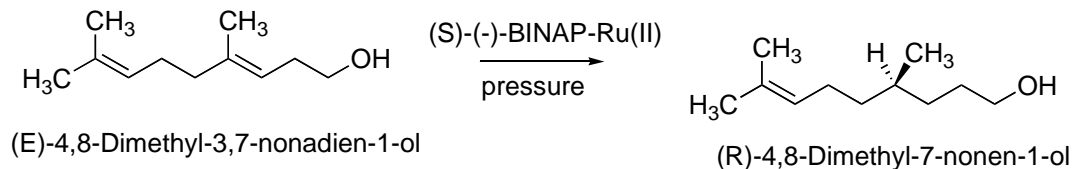
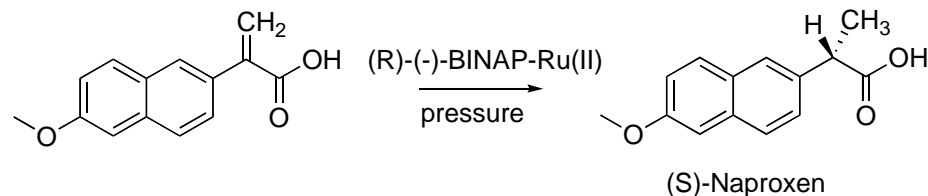
Enantioselective Hydrogenation:

Here, key idea is to make a soluble hydrogenation catalyst that has a defined stereochemical configuration. The transition state is thus expected to be diastereotopic and thus favoring the formation of one enantiomer.

How to make the catalyst:



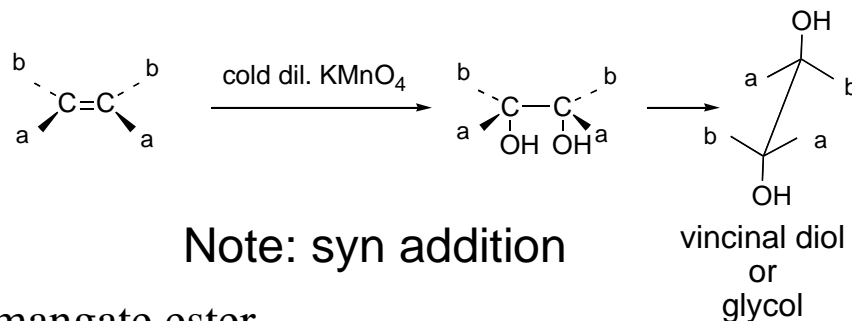
Two Sample Reactions:



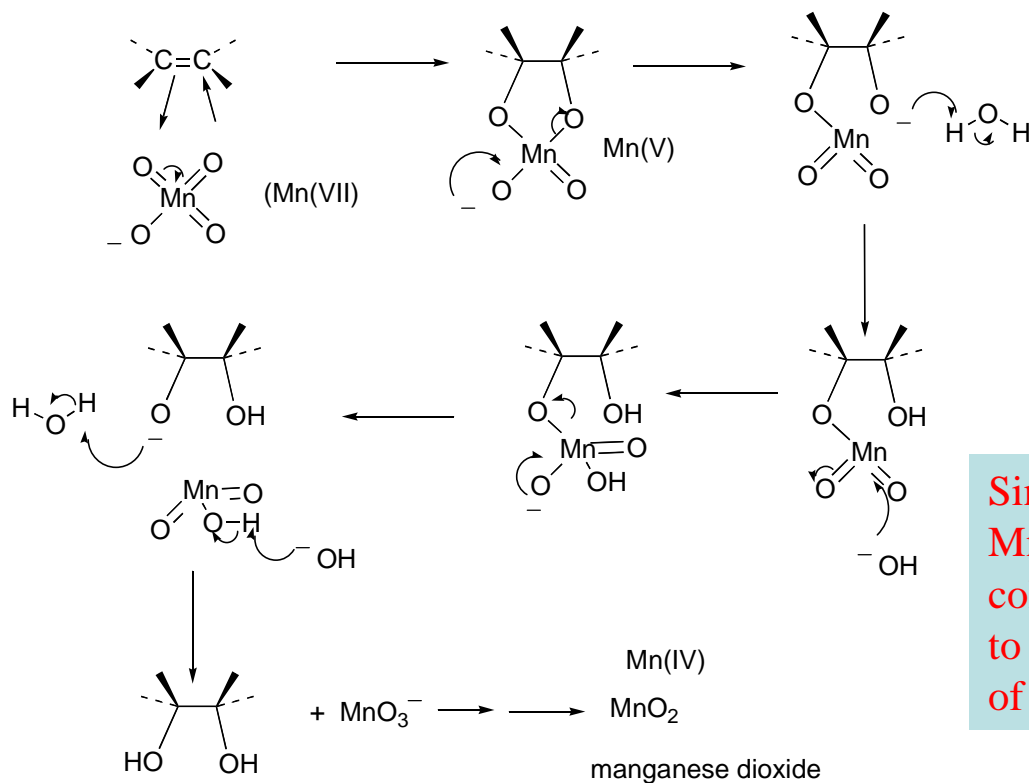
Oxidation of Alkenes

1) Oxidation of alkenes with aqueous potassium permanganate

In the presence of cold, dilute KMnO_4 aq. alkenes are oxidized to glycols.



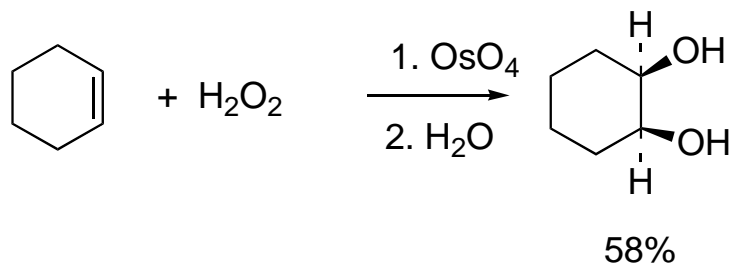
Mech: Key step is formation of cyclic manganate ester.



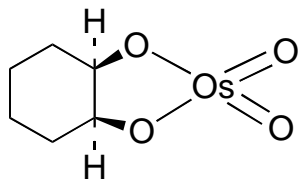
Mechanism is fair game for final but is not on Exam II

Since MnO_4^- is purple and MnO_2 is light brown; this color change can be used to assay for the presence of an alkene: Baeyer test.

2) A similar reaction occurs with osmium tetroxide: Since osmium tetroxide is very toxic and very expensive, one uses it as a catalyst only, and some other oxidizing agent. Peroxides work well.

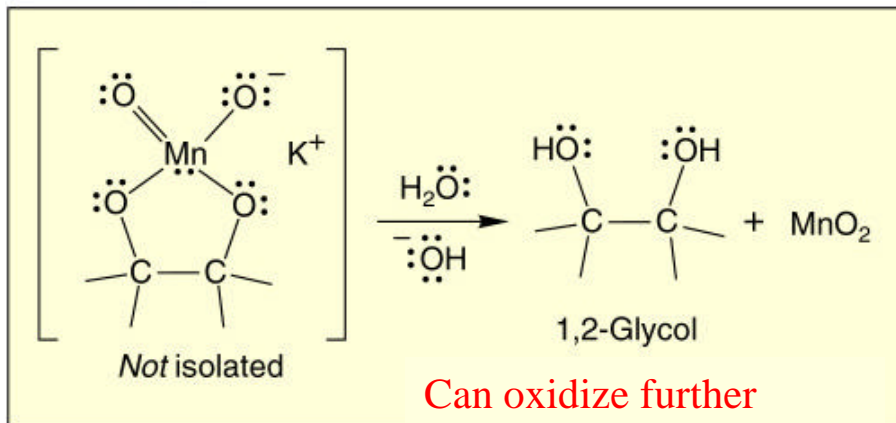


The key intermediate is the osmate ester:

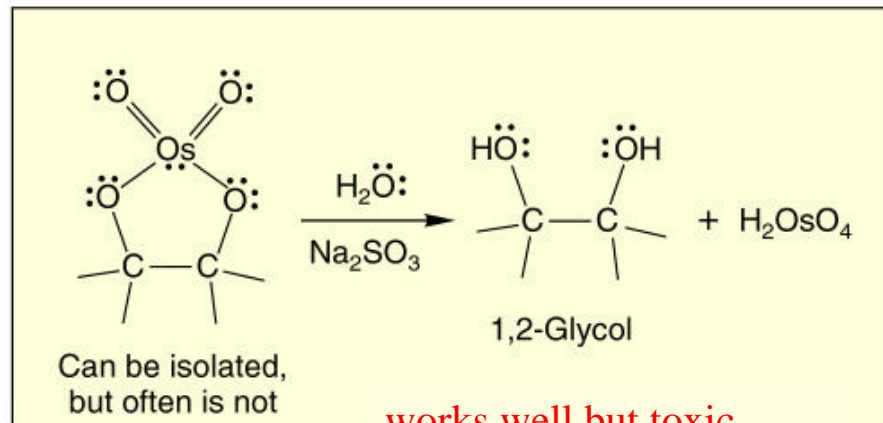


QuickTime™ and a
Sorenson Video decompressor
are needed to see this picture.

General cases

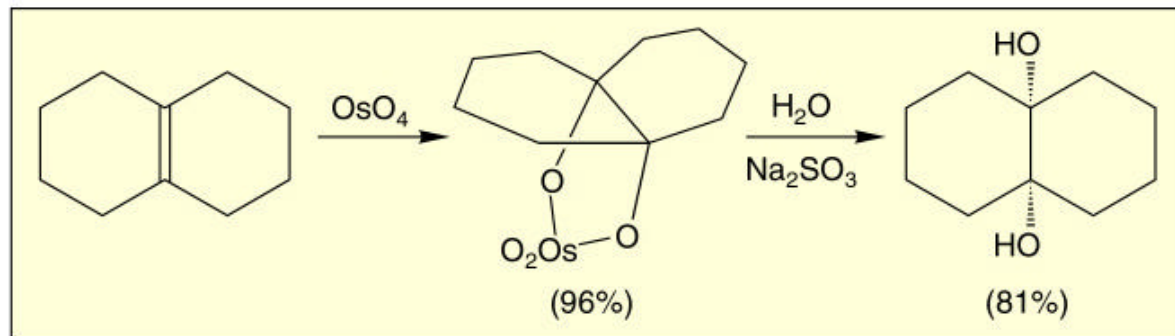
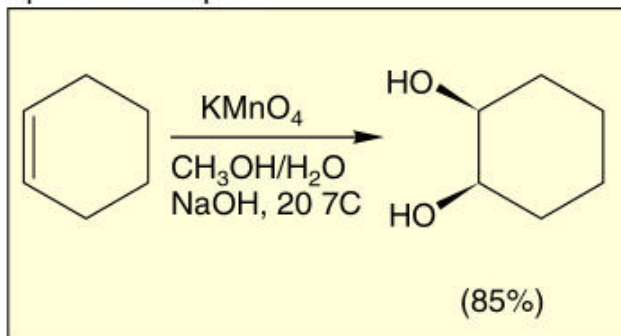


Can oxidize further
(hence low yields)



works well but toxic

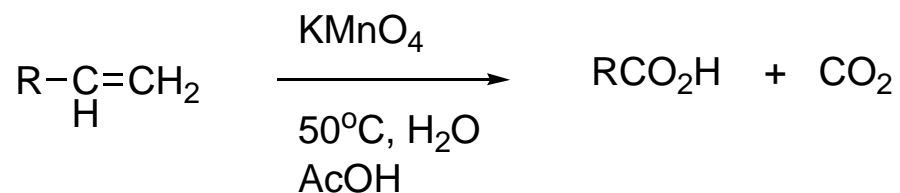
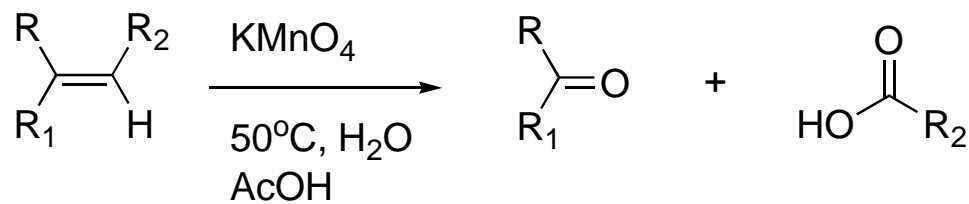
Specific examples



- These metal-containing five-membered rings can react further to generate 1,2-diols, which are also called 1,2-glycols (a.k.a. cis diol).
- OsO₄ used catalytically with hydrogen peroxide or (CH₃)₃OOH (t-butyl hydroperoxide) as main oxidant.

3) Cleavage of carbon-carbon bonds by permanganate. This is not in book but expected knowledge.

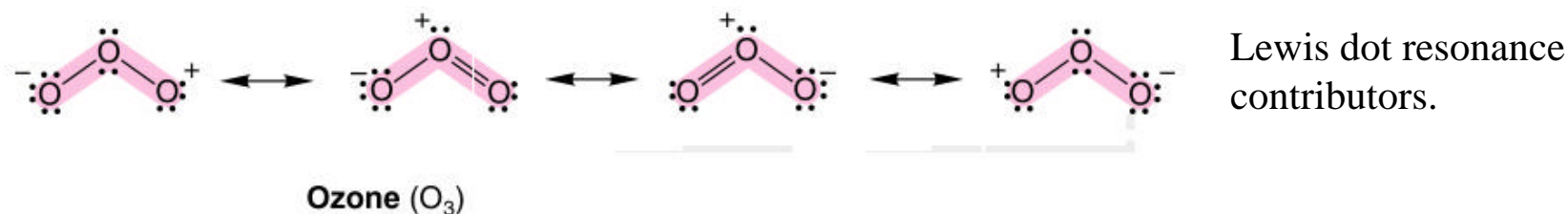
a) Alkenes are cleaved by warm, acidic solutions of KMnO_4 (aq.) to give carboxylic acids, ketones or CO_2 depending on the structure.



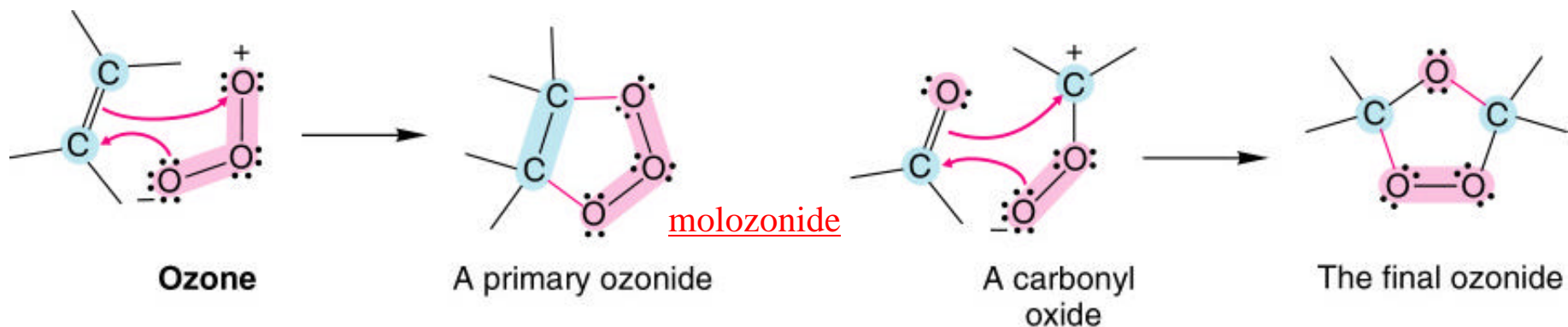
Yields generally low, so not useful preparatively. However, this chemistry is very useful to establish structure.

4) Ozonolysis of alkenes

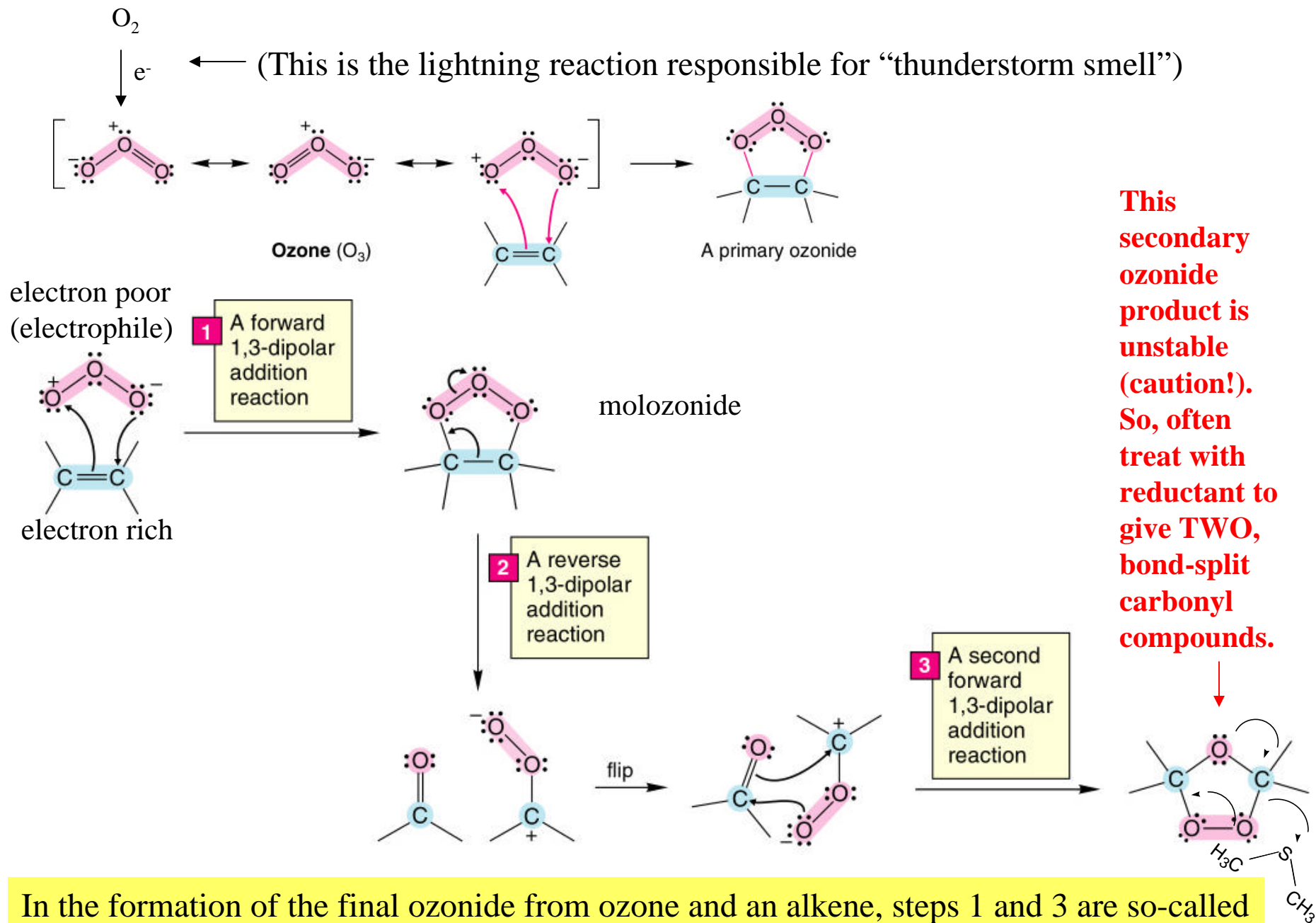
Ozone, O_3 , from electric discharge on O_2



Reaction of alkenes with ozone gives rise to a molozonide (primary ozonide) which rearranges to an ozonide.

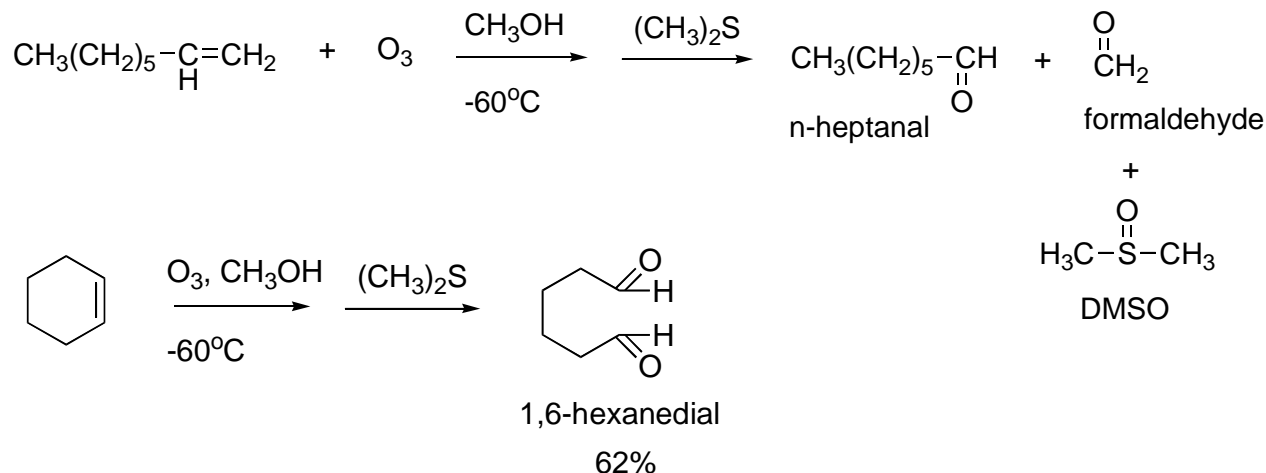


Ozonides can be isolated, but often explode, so decomposed in situ either reductively or oxidatively.

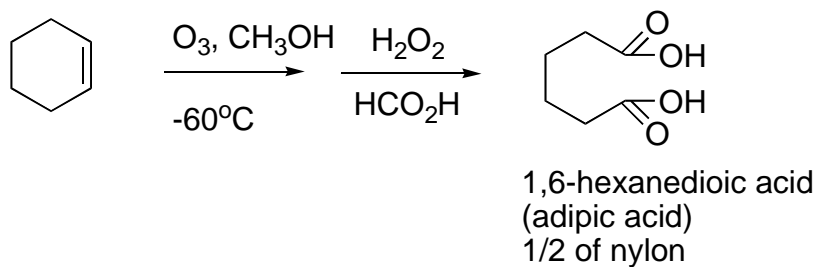


In the formation of the final ozonide from ozone and an alkene, steps 1 and 3 are so-called 1,3-dipolar addition reactions, where one part of the incoming molecule is the electrophile and the other the nucleophile. Step 2 is a reverse 1,3-dipolar addition.

a) Reductive work-up: $(\text{CH}_3)_2\text{S}$ (most popular), but also Zn^0 , H_2/Pd , etc.



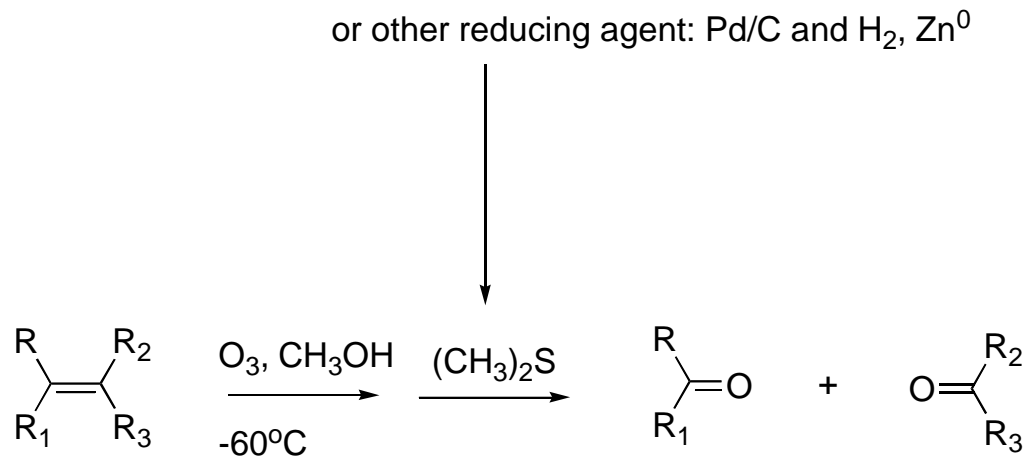
b) oxidative work-up:



Because of explosion risk, oxidative work-ups are generally not as common.

Structure Determination by Ozonolysis

Upon reductive work-up, get two carbonyl-containing compounds



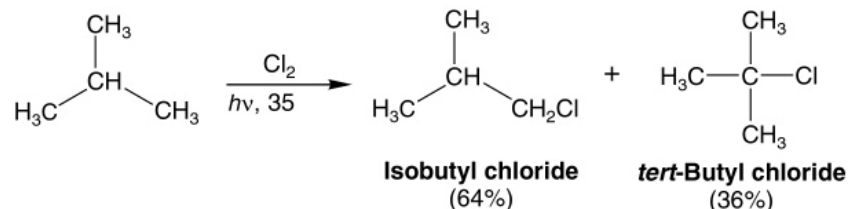
- You can see that for terminal alkenes (R_2 and $\text{R}_3 = \text{H}$) you get formaldehyde and either an aldehyde or ketone depending on whether R or R_1 is a proton or both are alkyls.
- For internal alkenes 2 aldehydes, an aldehyde and ketone, or two ketones are possible. **Try problem 6.13 for practice.**

MAKE SURE you understand KMnO_4 ,
 OsO_4 and O_3 .

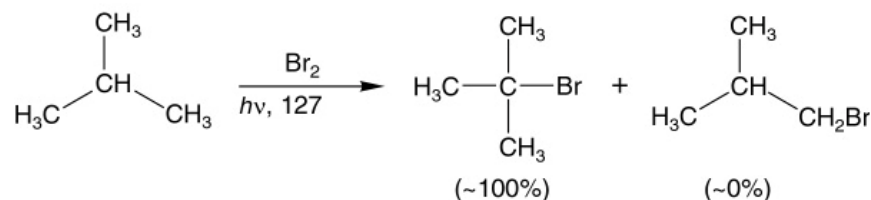
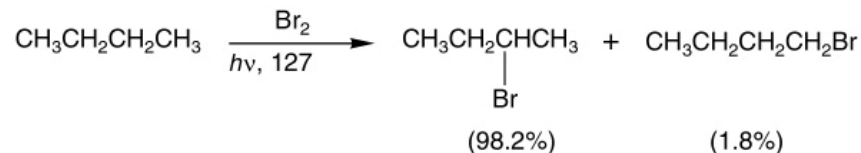
At this point you do not need to know the mechanisms. However, you do need to know the reactions “backwards and forwards” so you can use this chemistry to solve structure determinations.

Now, on to Chapter 7...

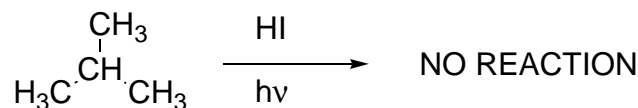
New Chemistry. We Must Explain: What's Going on Here?!



The photochlorination of isobutane gives *tert*-butyl chloride and isobutyl chloride. For a chlorine atom, abstraction of a tertiary hydrogen is favored over abstraction of a primary hydrogen by a factor of about 5 on a per hydrogen basis.



Photobromination is far more selective than photochlorination



Iodination = No reaction...**explain these findings!!**