

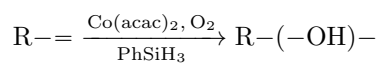
Week 7

Reactions of Alkynes

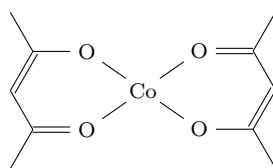
7.1 Methods of Hydration

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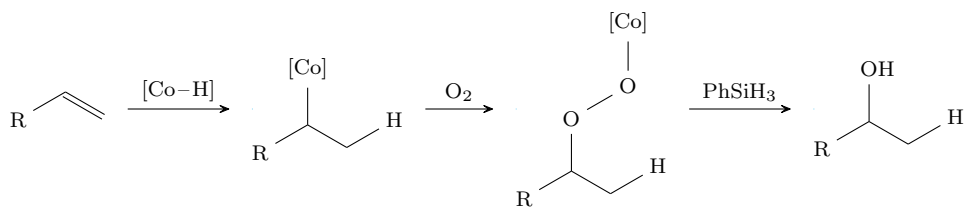
- Mukaiyama Hydration.
 - A “greener” method.
- General form.



- Mechanism:



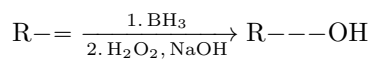
(a) Cobalt catalyst.



(b) Mechanism.

Figure 7.1: Mukaiyama hydration mechanism.

- Note that $\text{Co}(\text{acac})_2$ is a catalyst.
- Hydroboration/oxidation of alkene.
 - Nobel Prize (1979).
 - Discovered by a UChicago undergrad, H. C. Brown.
- General form.



- Regioselective (anti-Markovnikov).

- Stereospecific (H and OH add cis).
- Covers BH_3 with its empty p orbital that makes it a good Lewis acid and dimerizes to B_2H_6 with its “3C-2e” bond in the gas phase.

• Mechanism:

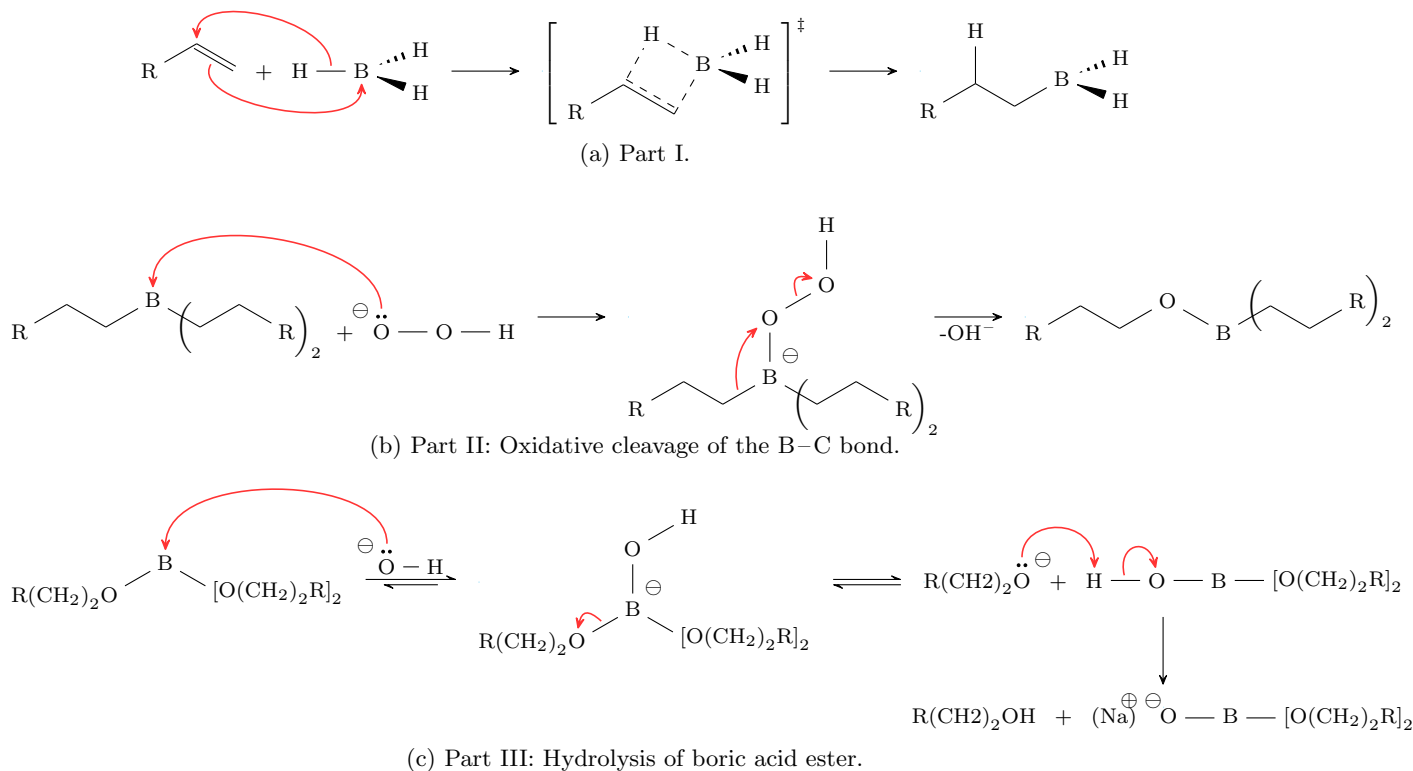


Figure 7.2: Hydroboration mechanism.

- The step in Part I is a concerted step (this is key for cis addition).
 - BH_3 adds the way it does in part I (with the H put on the more substituted carbon) due to sterics (bulky group attaches to the less bulky side) and electronics (the π -bonding electrons of the alkene connecting to the boron first will create a partial positive charge, and it is more stable to have that partial positive on the more substituted position).
 - The alkene does not attack an H on BH_3 because said H's are not acidic (it is the boron that is electron deficient).
 - Each part repeats an additional two times with the product of the n^{th} run the reactant of the $(n + 1)^{\text{th}}$ run to create the reactant of the next part.
 - In part II, mixing H_2O_2 with OH^- yields a deprotonated peroxide (O_2H^-).
 - The final product of part II is the boric acid ester.
 - Part III has a borate salt as a final byproduct.
 - The mechanism implies that the hydrogen added comes from BH_3 , and the oxygen added (as part of the hydroxide) comes from H_2O_2 .
- If we add to an alkene borane, and then a strong acid and heat, we end up hydrogenating it.
 - Summary of alcohol synthesis:
 - If you want Markovnikov addition, use...

- Acid-catalyzed hydration.
 - Oxymercuration/reduction.
 - Mukaiyama hydration.
- If you want anti-Markovnikov addition, use...
 - Hydroboration.
- Ozonolysis of alkenes.
 - An **oxidation** reaction (adding oxygen or removing hydrogen).
 - Treat an alkene with ozone and dimethyl sulfide to cleave the C=C bond and add oxygen onto each carbon, forming carbonyls (and associated groups).
 - Note that if we consider the resonance structures of ozone, we will find that charge separation is unavoidable, i.e., that the molecule must have a plus and a minus charge somewhere. This makes it very reactive.
- Mechanism.

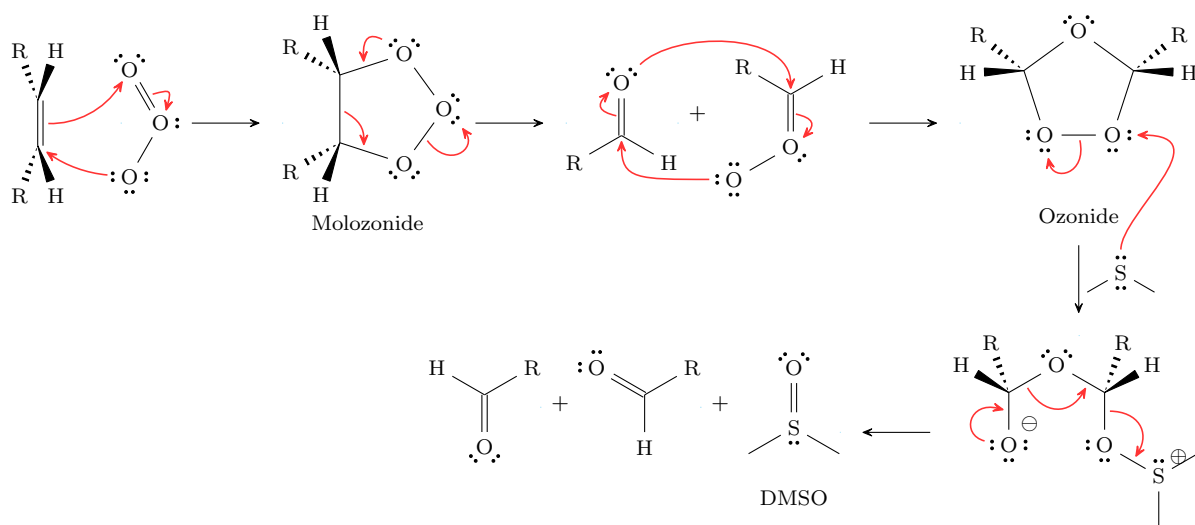


Figure 7.3: Ozonolysis of alkenes.

- The first step of the reaction is a concerted 3 + 2 addition.
 - The ozonide intermediate is more stable than the molozonide owing to its symmetry.
 - Motivation for the last intermediate to split is eliminating charge separation.
- Dihydroxylation of alkene (creation of a 1,2-diol).
- General form.

$$R- \xrightarrow[2. \text{NaHSO}_3]{1. \text{OsO}_4} R-(\text{-OH})-\text{-OH}$$
 - Stereospecific (cis).
 - Compare to bromination, which gives the trans-product (the difference is for mechanistic reasons).
 - The product is a 1,2-diol, or a vicinal diol.

- Mechanism.

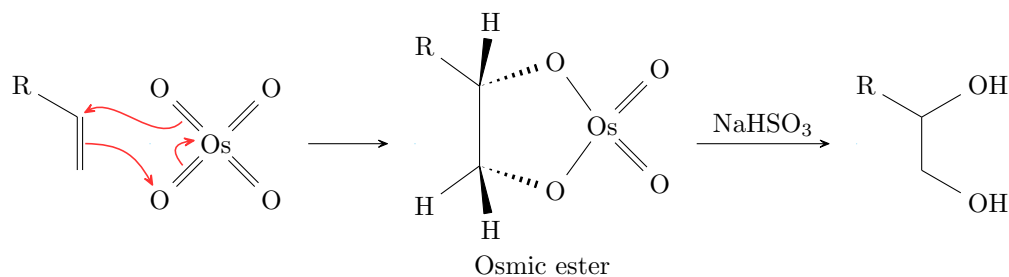


Figure 7.4: Dihydroxylation.

- The first step is concerted, once again.
- Osmium gets reduced in the first step (oxidation number goes from +8 to +6).
- In the second step, sodium bisulfite cleaves the two osmium oxygen bonds in a very complex process.
- Problems: OsO_4 is very expensive and very toxic.
- Solutions:
- UpJohn process (1976).
 - The same as dihydroxylation but with only 1% OsO_4 and NMO (N-methylmorpholine oxide) and H_2O added second instead of NaHSO_3 .
- Sharpless asymmetric dihydroxylation.
 - Nobel prize (2001).
 - Gives high ee for each product.
 - Conditions are catalytic potassium osmium salt ($\text{K}_2\text{OsO}_2(\text{OH})_4$), potassium carbonate (K_2CO_3), and potassium iron cyanate ($\text{K}_3\text{Fe}(\text{CN})_6$).
- Alkene dihydrogenation.