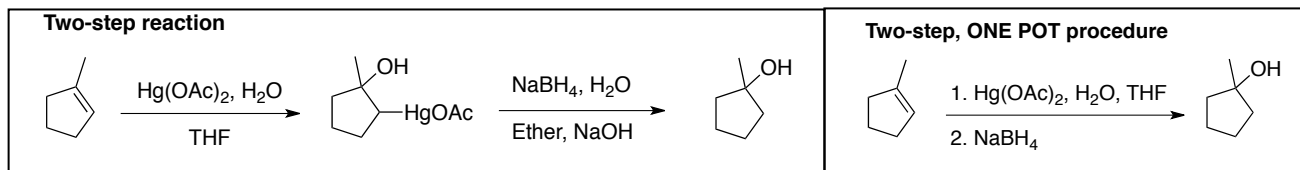


CHAPTER 8. ALKENES: REACTIONS AND SYNTHESIS

Hydration of Alkenes by Oxymercuration-Reduction

- concerted formation of three-membered ring intermediate
- addition of water occurs through anti stereoselectivity
- nucleophilic attack occurs at most highly substituted carbon
- NaBH_4 replaces HgOAc with hydrogen



This is a two-step process, but is most commonly done as a “one-pot procedure” (upper right).

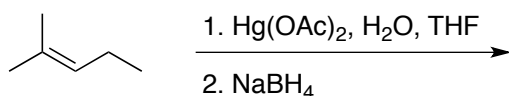
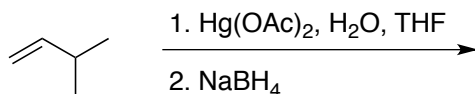
First step is an in-solution dissociation of mercuric acetate to form an electrophilic mercury ion:



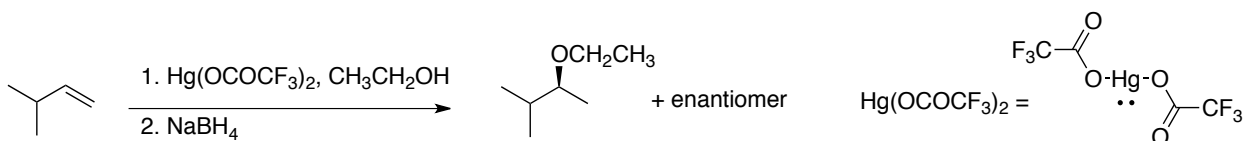
A great electrophile

Now draw a mechanism showing reaction of methylcyclopentene with the electrophile to form of a three-membered bridged mercurinium ion (just like with Br_2). Then use water and acetate to get you to the alcohol (with the HgOAc still attached). Finally, NaBH_4 replaces the HgOAc with a hydrogen (mechanism unimportant).

Can you predict the products of the following reactions? Make sure to include stereochemistry when relevant.

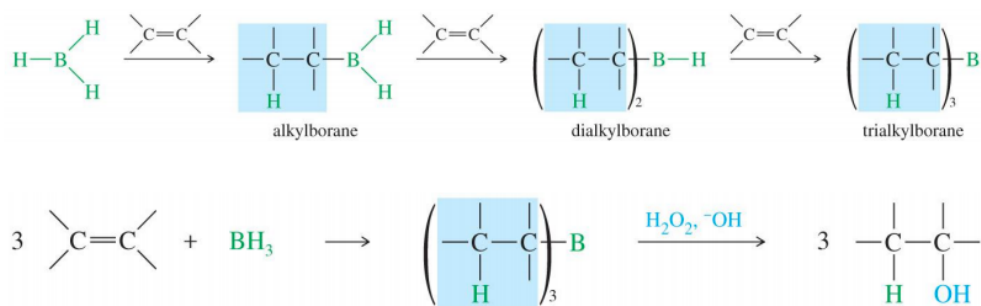


In addition to alcohols, you can also make ethers using this method. Draw a mechanism for the following conversion:

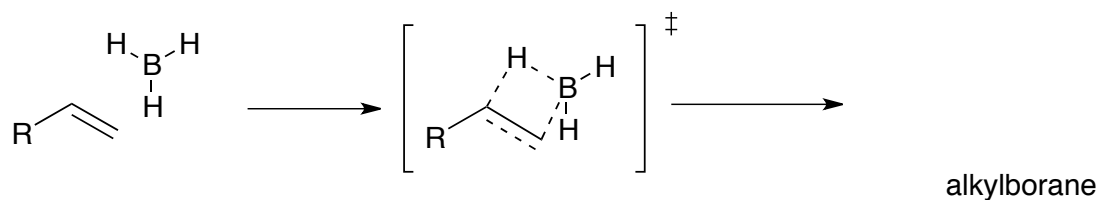


Hydroboration-Oxidation

- concerted *syn*-addition of B-H
- three equivalents of alkene can react with each mole of BH₃
- addition of hydride to the most highly substituted carbon leads to the **anti**-Markovnikov alcohol



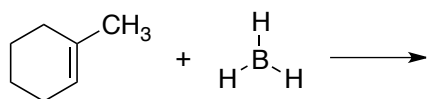
Add two curved arrows to the left-most structures that lead to the formation of a four-membered transition state, as shown for the addition of BH₃ to the generic alkene shown below:



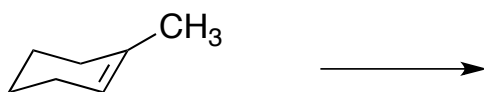
Draw a mechanism that shows how the trialkylborane is converted to the trialkylborate:



Draw a mechanism for and the structure of the transition state after the addition of BH_3 to methylcyclohexene:

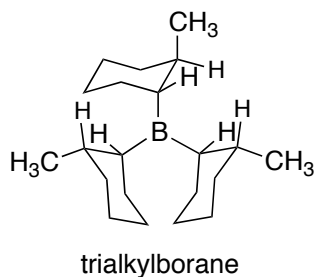


Now let's do this in three dimensions - draw the transition state:



You should have drawn a structure that shows a *cis* relationship between the BH_2 and H you just added, and a *trans* relationship between the BH_2 and the CH_3 .

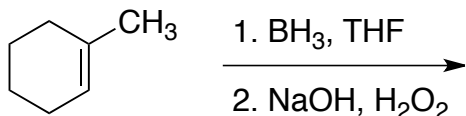
Each molecule of BH_3 can react with three alkenes to form a trialkylborane that looks like this,



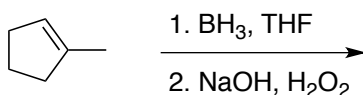
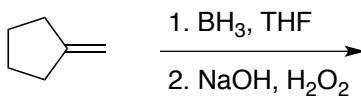
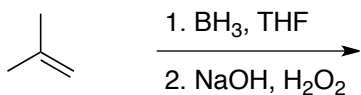
but this structure is FAR too complex to work with, so let's simply use R to represent the methylcyclohexane:



Given what you know about how BH_3 adds to an alkene, and without drawing each step of the mechanism, predict the organic product(s) of this reaction?



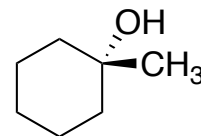
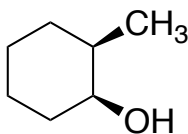
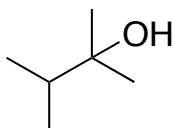
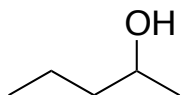
Draw structures of the alcohols formed by hydroboration/oxidation of each alkene - make sure to include stereochemistry when relevant (not all structures will be chiral):



Both (*E*)- and (*Z*)-3-hexene are subjected to a hydroboration-oxidation sequence. How are the products from these two reactions related to each other?

- A) The (*E*)- and (*Z*)-isomers generate the same products but in differing amounts.
- B) The (*E*)- and (*Z*)-isomers generate the same products in exactly the same amounts.
- C) The products of the two isomers are related as constitutional isomers.
- D) The products of the two isomers are related as diastereomers.
- E) The products of the two isomers are not structurally related.

Which of the following alcohols could *not* be made selectively by hydroboration-oxidation of an alkene?



Referring to the three ways you've learned to make alcohols, which of the following is the best reaction sequence to accomplish a Markovnikov addition of water to an alkene with minimal skeletal rearrangement?

- A) water + dilute acid
- B) water + concentrated acid
- C) oxymercuration-demercuration
- D) hydroboration-oxidation
- E) none of the above