

CH203 Lecture 13

October 21, 2010

John. A. Porco, Jr.

BOSTON
UNIVERSITY

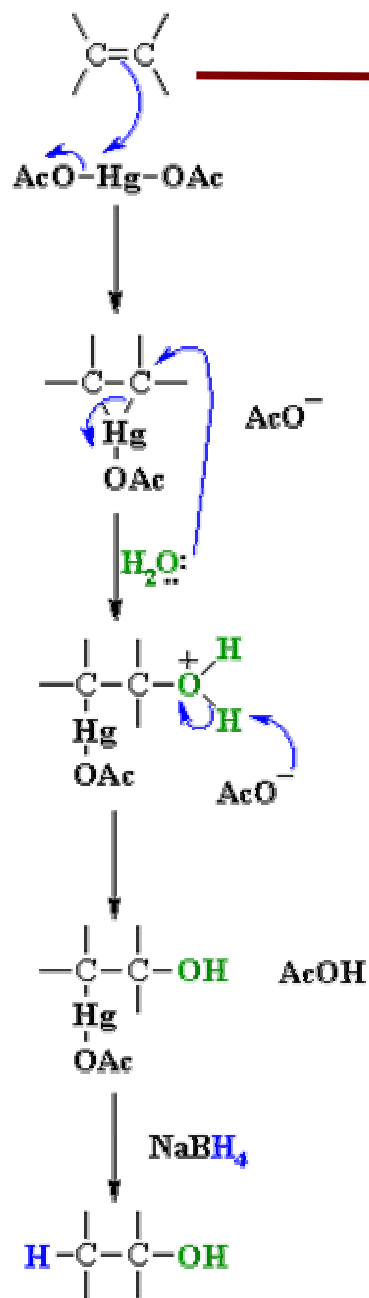
Department of Chemistry

porco@bu.edu

Announcements

- **Exam II: Thursday November 4,
2010 8 AM – 9:20 AM**
- **Practice Exam 2: By Friday
October 29**
- **Review Session: Monday
November 1nd 7-8 pm STO B50**

Oxymercuration-Demercuration



Step 1:

The π electrons act as the nucleophile with the electrophilic Hg and loss of an acetate ion as a leaving group, forming the mercurinium ion.

Step 2:

Water functions as a nucleophile and attacks one of the mercury substituted carbons resulting in cleavage of the $\text{C}-\text{Hg}$ bond.

Step 3:

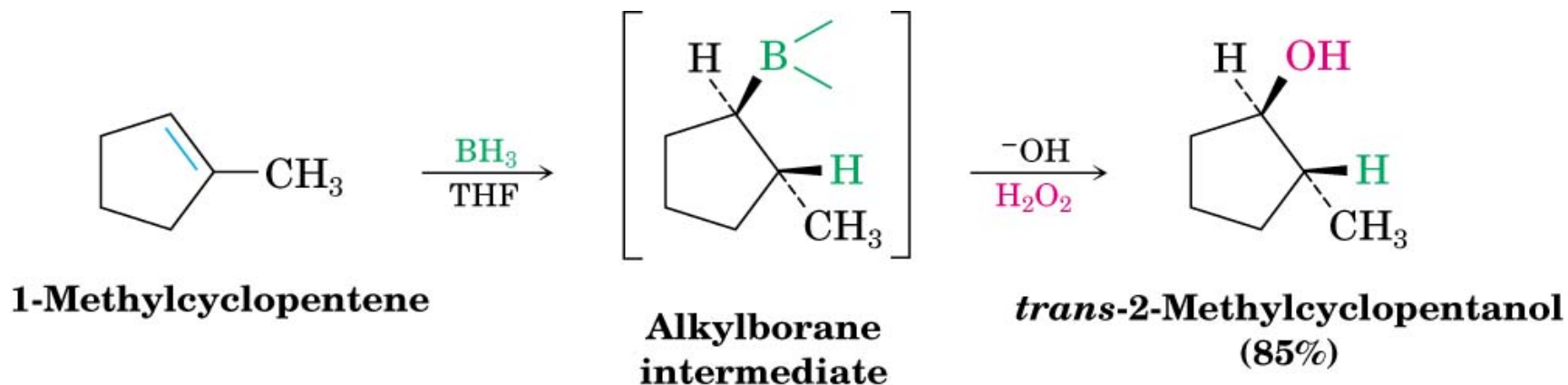
The acetate ion functions as a base deprotonating the oxonium ion to give the alcohol. This completes the oxymercuration part of the reaction.

Step 4:(mechanism not shown)

The hydride reduces the Hg off, creating a $\text{C}-\text{H}$ bond while breaking the $\text{C}-\text{Hg}$ bond. This is the demercuration part of the process

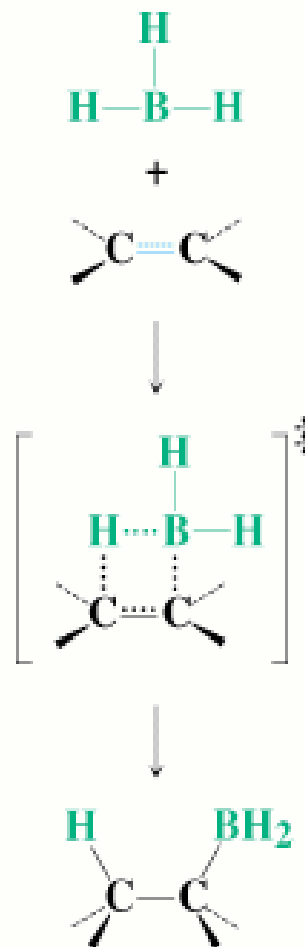
Orientation in Hydration via Hydroboration

- Regiochemistry is opposite to Markovnikov orientation
 - OH is added to carbon with most H's
- H and OH add with **syn stereochemistry**, to the same face of the alkene (opposite of anti addition)



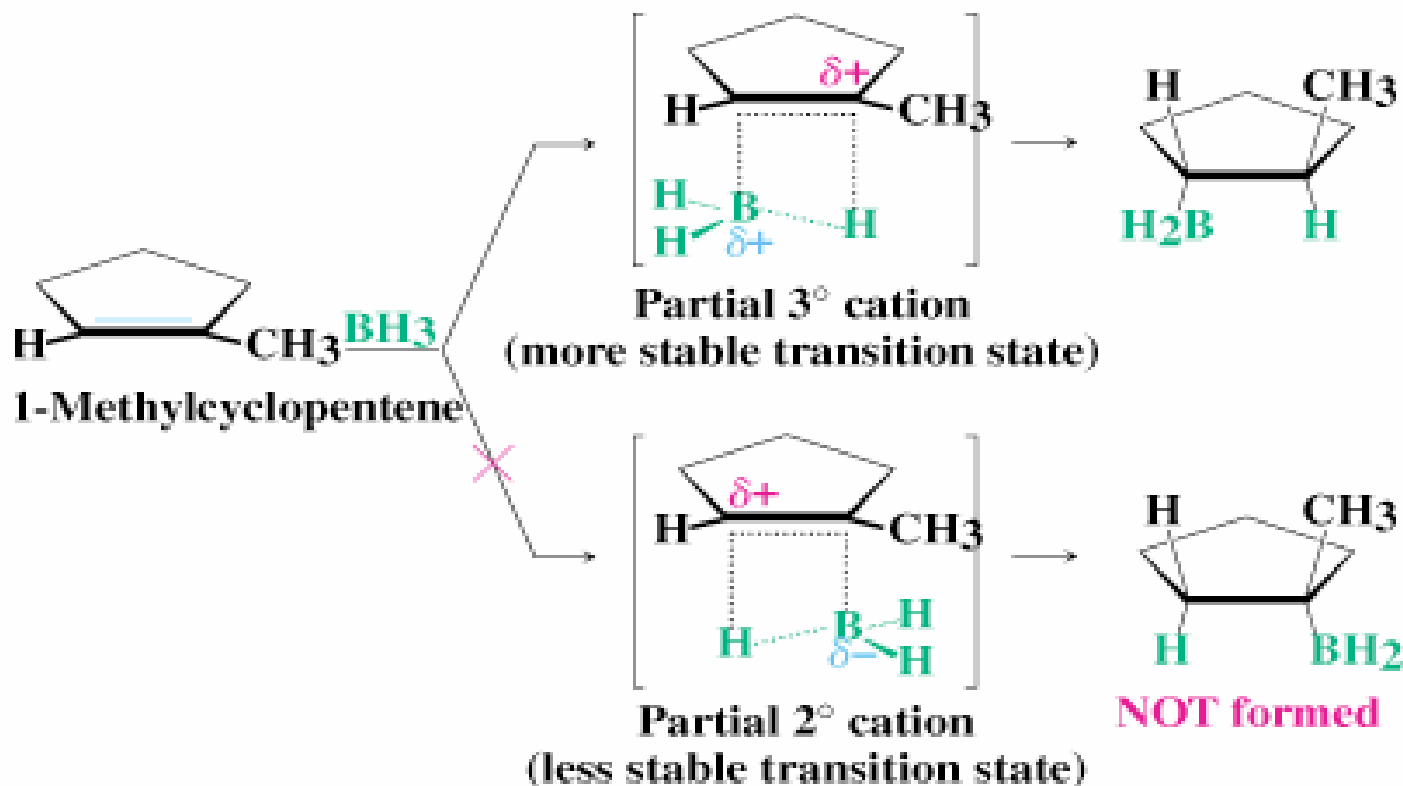
Mechanism of Hydroboration

- Borane is a Lewis acid
- Alkene is Lewis base
- Transition state involves anionic development on B
- The components of BH_3 add across $\text{C}=\text{C}$
- **Syn** addition



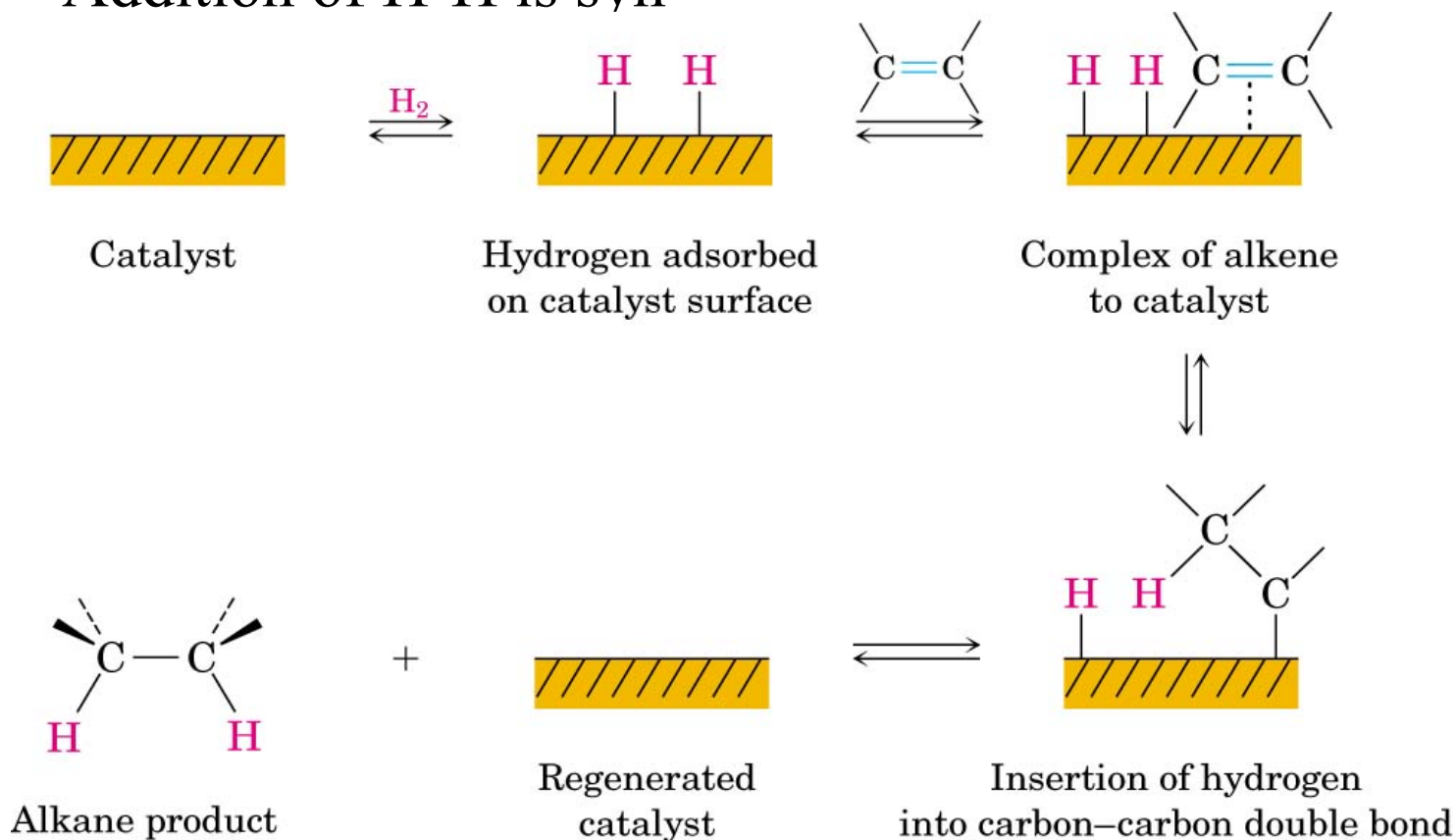
Hydroboration, Electronic Effects Give Anti-Markovnikov

- More stable carbocation is also consistent with steric preferences



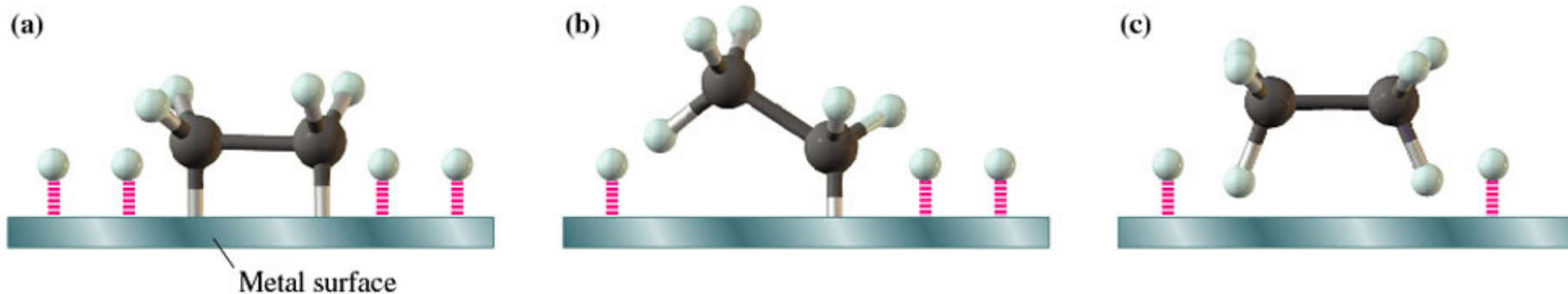
Mechanism of Catalytic Hydrogenation

- Heterogeneous – reaction between phases
- Addition of H-H is syn



Reduction of Alkenes

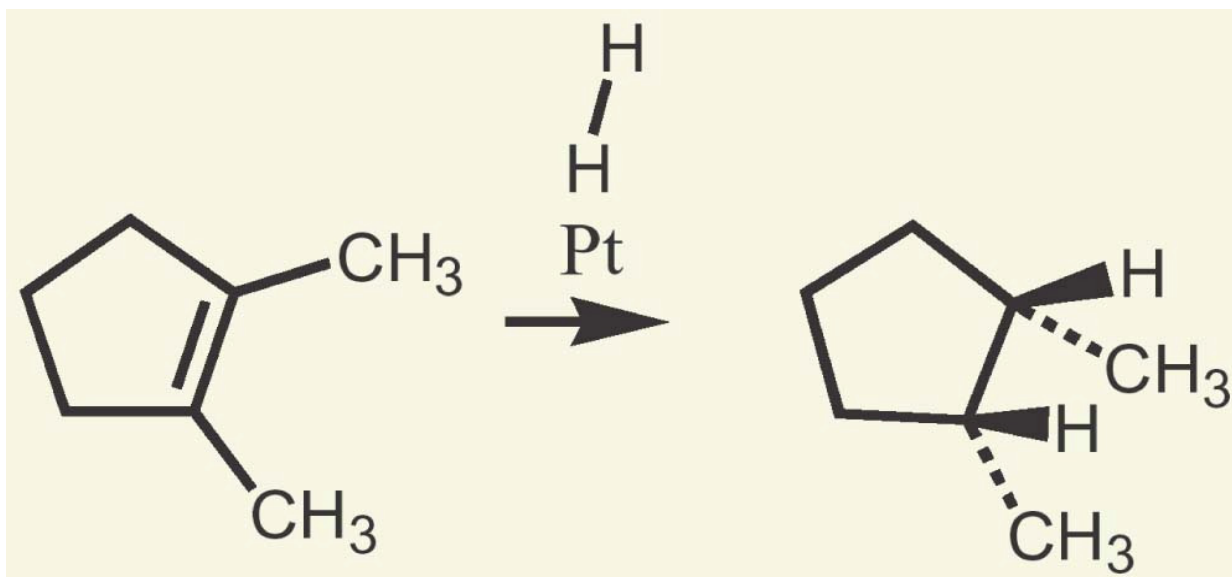
- Mechanism of catalytic hydrogenation



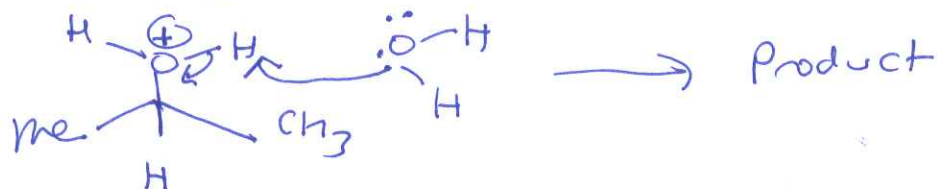
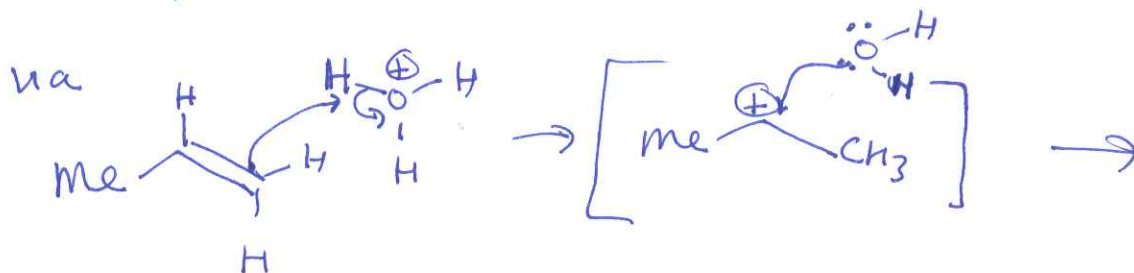
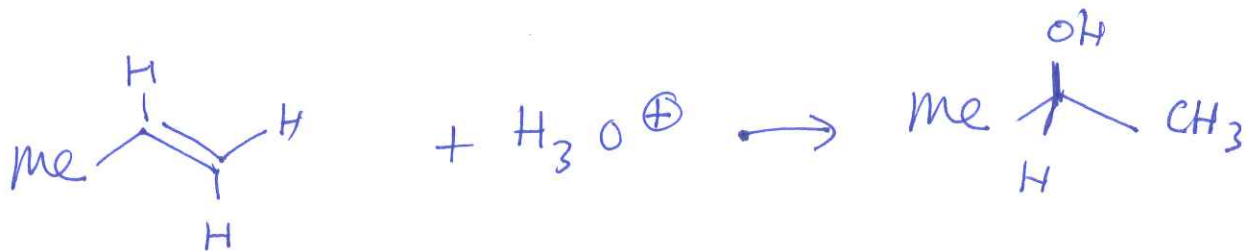
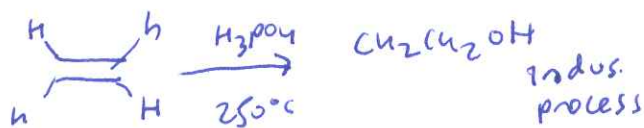
Reduction of Alkenes:

Hydrogenation

- Addition of H-H across C=C
- Reduction in general is addition of H₂ or its equivalent
- Requires Pt or Pd as powders on carbon and H₂
- Hydrogen is first adsorbed on catalyst
- Reaction is heterogeneous (process is not in solution)



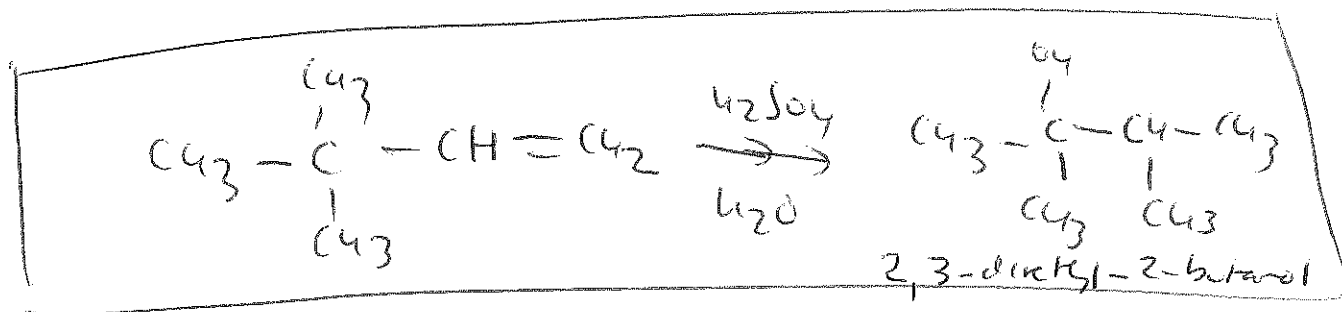
Acid - Catalyzed Hydration of Alkenes



- produce more highly substituted alcohol by Markovnikov's rule.

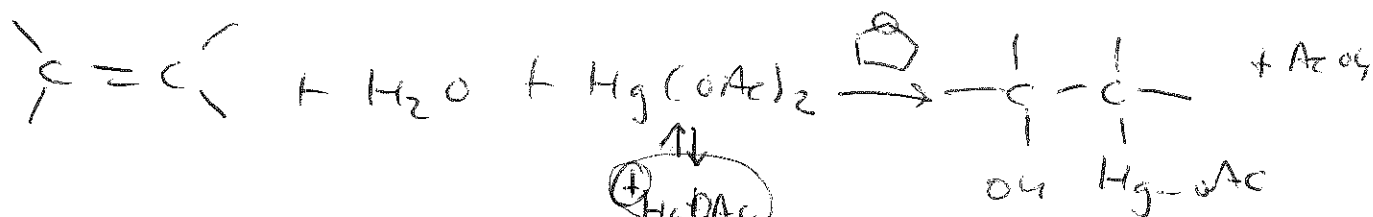
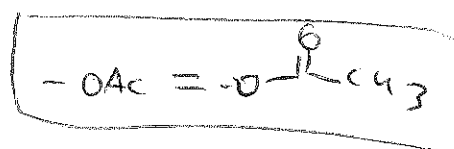
The rate det. step in the hydration mechanism is step 1 (formation of carbocation).

Also can be complicated by rearrangements:

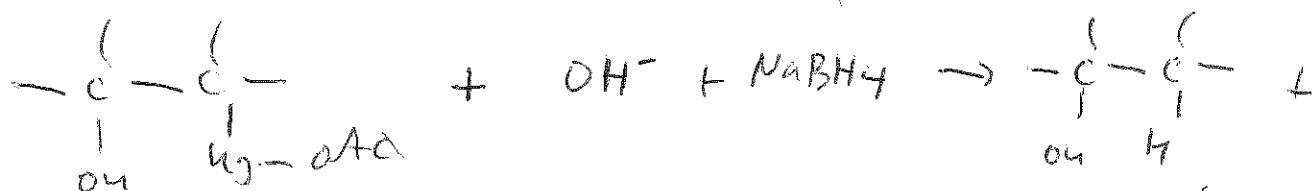


Another useful procedure for preparing alcohols from alkenes involves oxymercuration-demercuration

Step 1: oxymercuration



Step 2: demercuration



Slide shows that net orientation of addition of H + OH is in accord with Markovnikov's rule.

MECHANISM FOR REACTION OF ALKENES WITH $\text{Hg}(\text{OAc})_2 / \text{H}_2\text{O}$

Step 1:

The $\text{C}=\text{C}$ π electrons act as the nucleophile with the electrophilic Hg and loss of an acetate ion as a leaving group, forming the mercurinium ion.

Step 2:

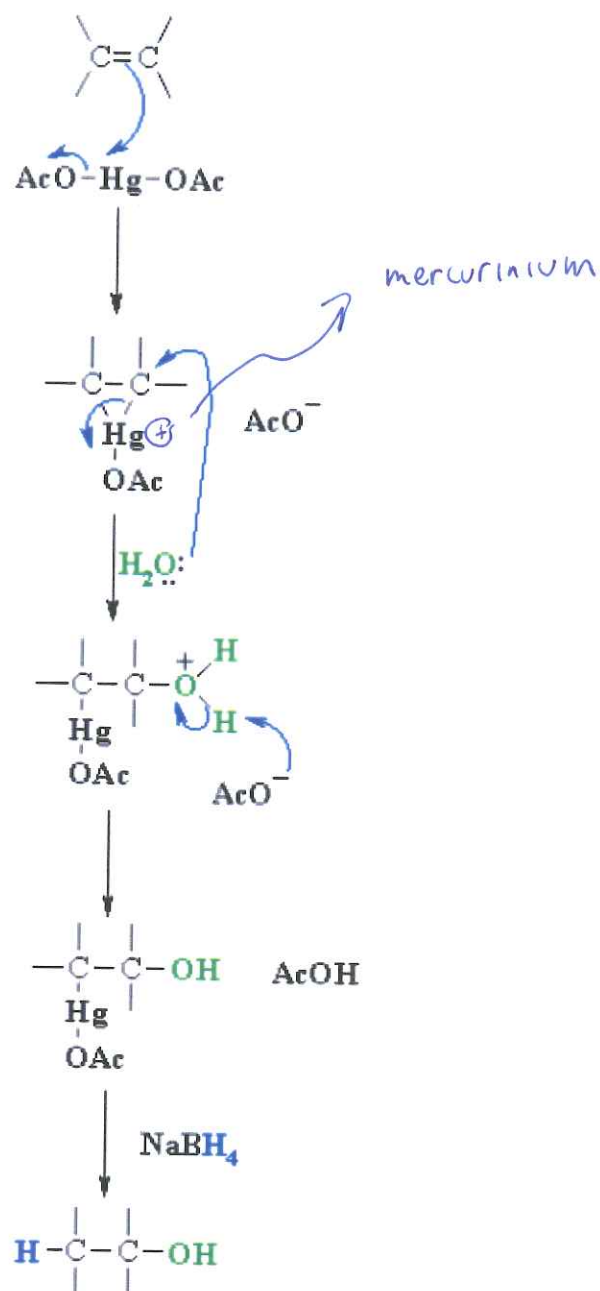
Water functions as a nucleophile and attacks one of the mercury substituted carbons resulting in cleavage of the $\text{C}-\text{Hg}$ bond.

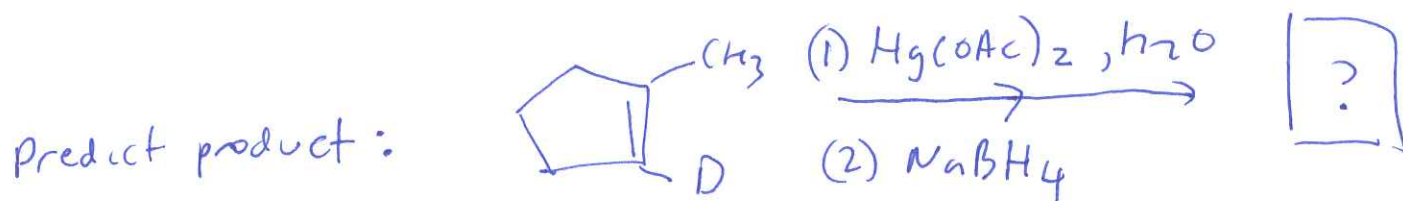
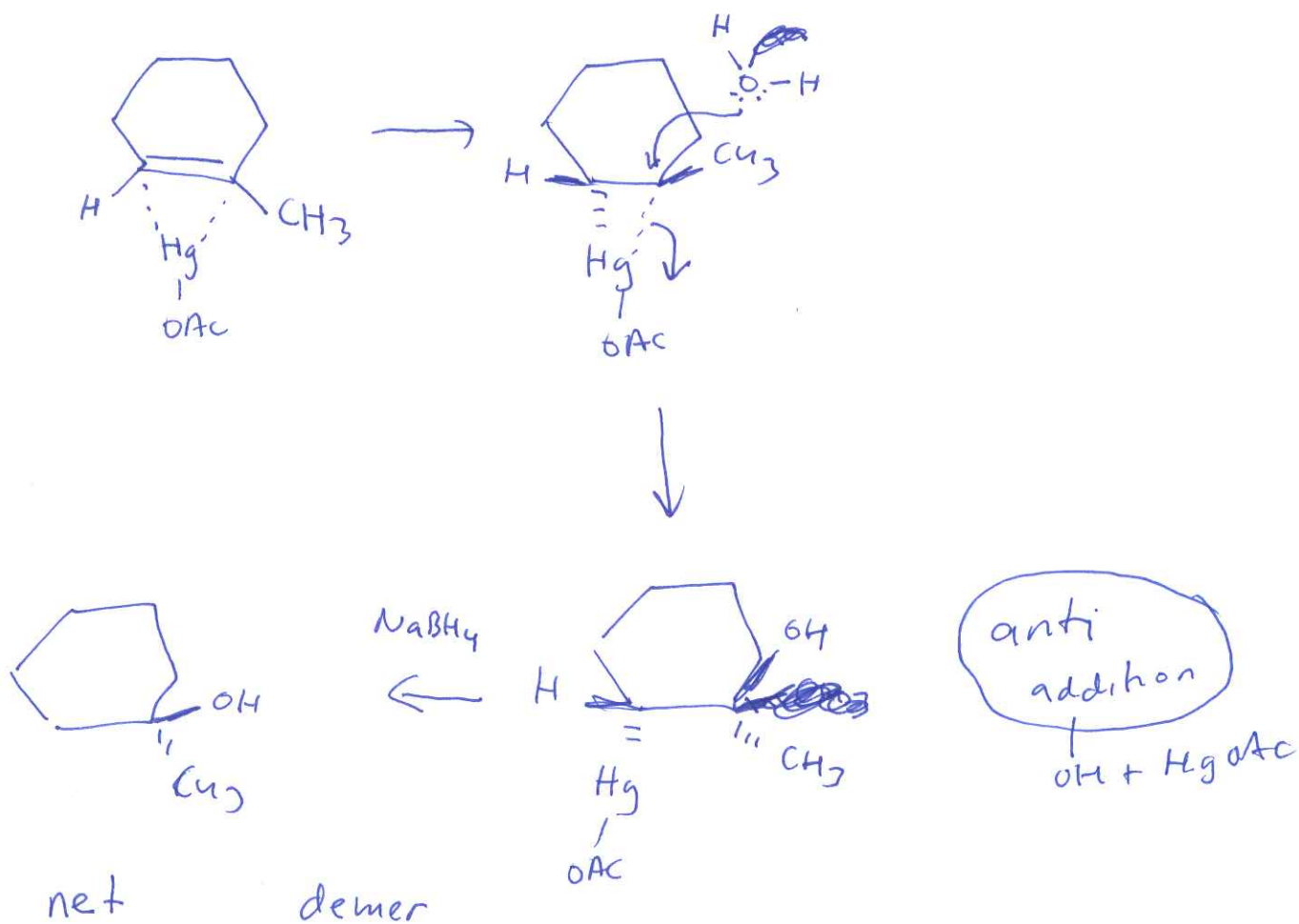
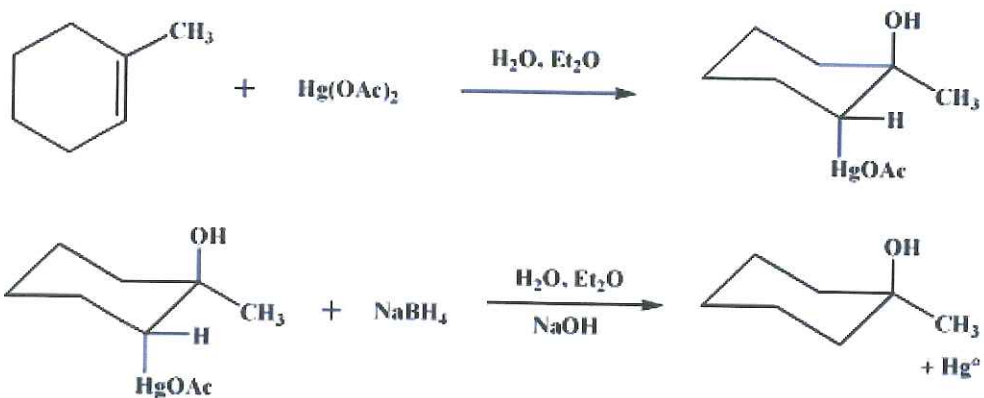
Step 3:

The acetate ion functions as a base deprotonating the oxonium ion to give the alcohol. This completes the oxymercuration part of the reaction.

Step 4: (mechanism not shown)

The hydride reduces the Hg off, creating a $\text{C}-\text{H}$ bond while breaking the $\text{C}-\text{Hg}$ bond. This is the demercuration part of the process.



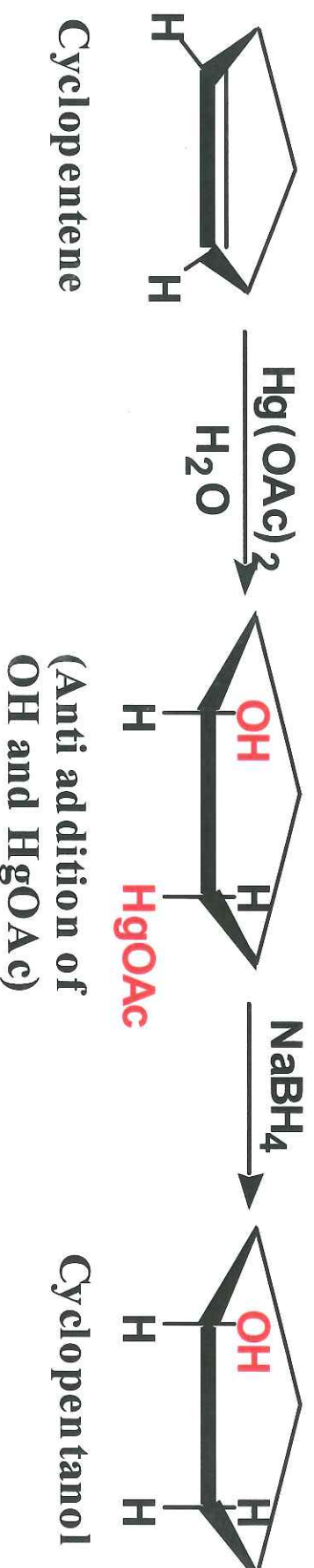


Oxymercuration/Reduction

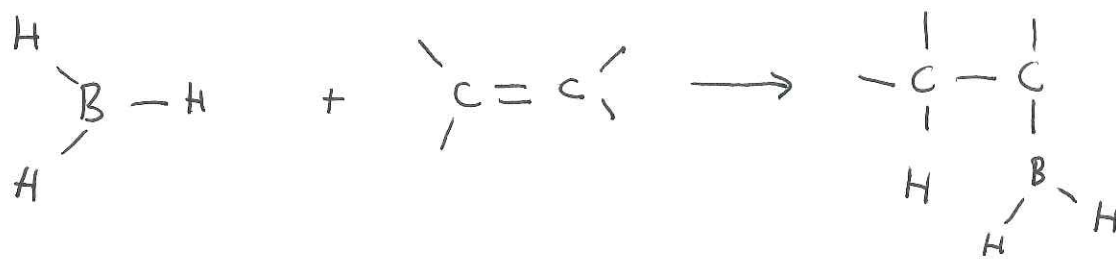
- an important feature of oxymercuration/reduction is that it occurs without rearrangement



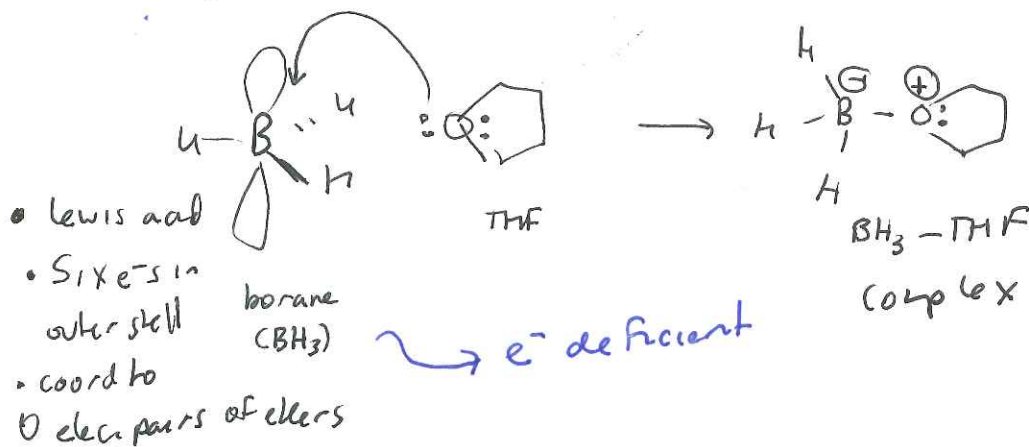
- oxymercuration occurs with anti stereoselectivity



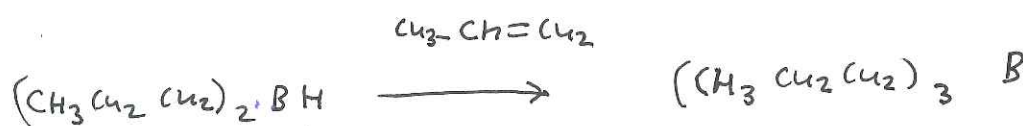
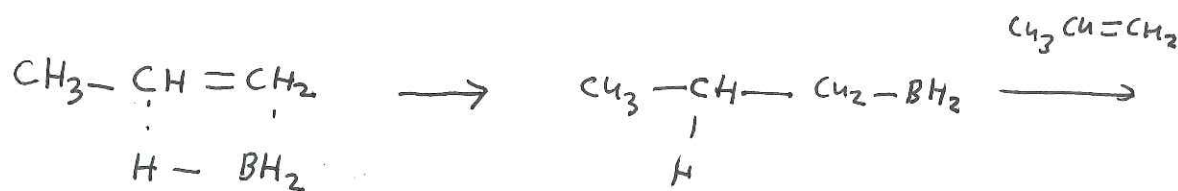
Hydroboration of Alkenes



boron
hydride



Mechanism



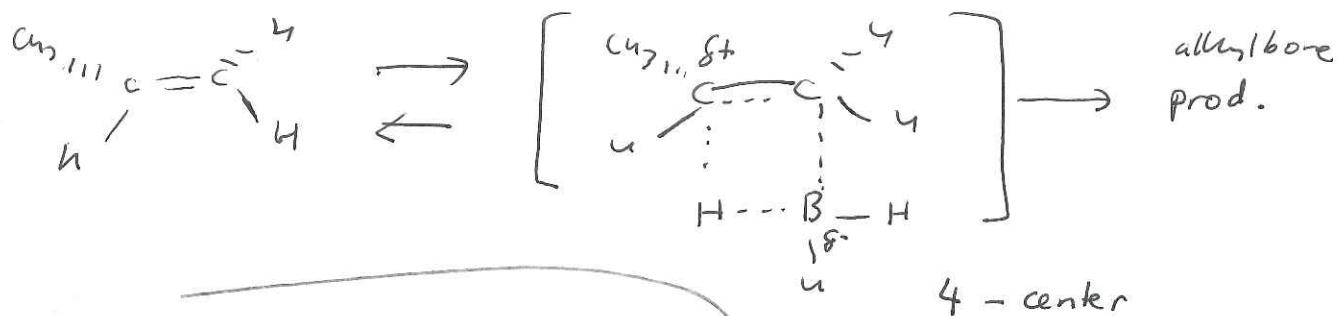
1) B-H adds consecutively to three molecules of alkene $\rightarrow$ trialkylborane

2) In each addition step the B atom becomes attached to the less subst. C atom of the alkene $\rightarrow$

"anti-Markovnikov"
H atom attached to C atom with few H atoms

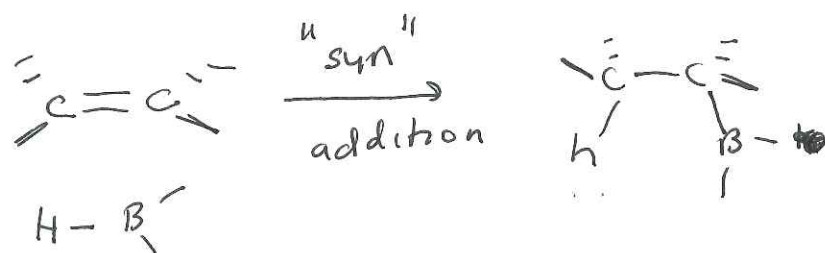
"regioselective"





- π electrons of double bond donated to vacant p orbital
- 4-center t.s. in which B atom is partially bonded to less subst C atom
- e^- s shift away from more subst C. atom + towards B atom $\therefore$ more subst C atom develops part pos. charge

Stereochemistry

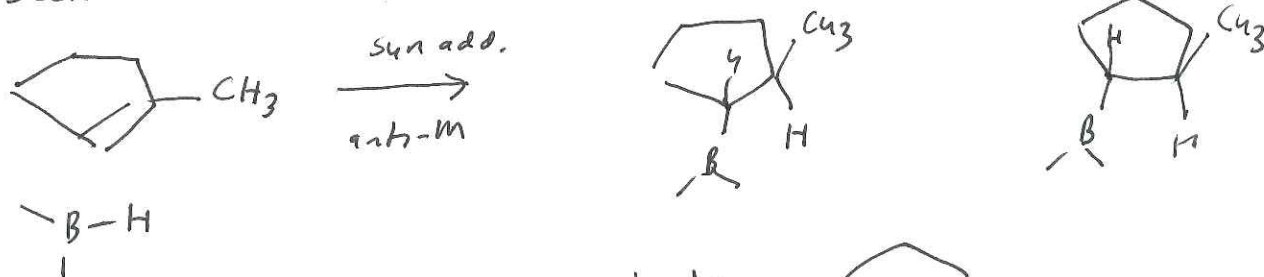


hydroboration

- regioselective
- syn stereoselect.

t.s. for hydroboration requires that the B + H atom add to the same face of the alkene

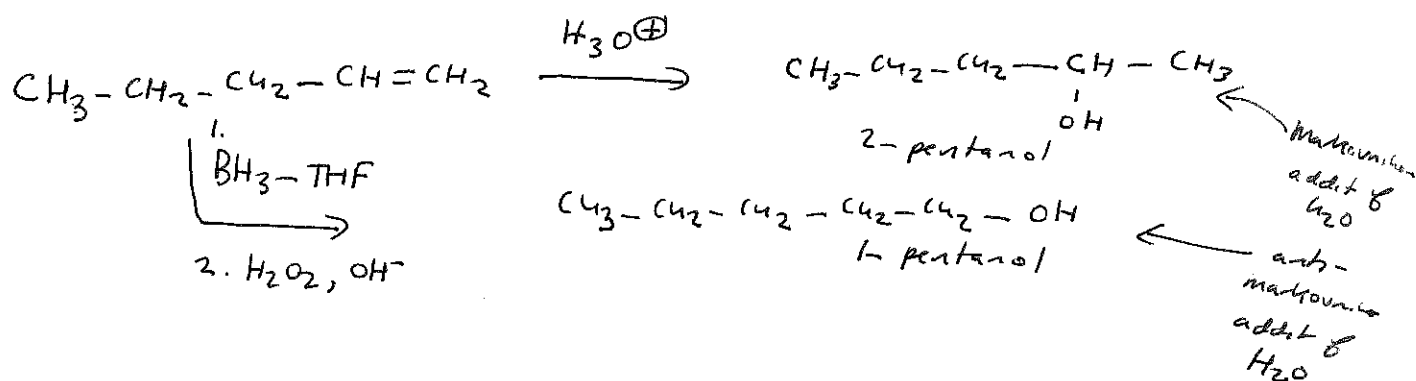
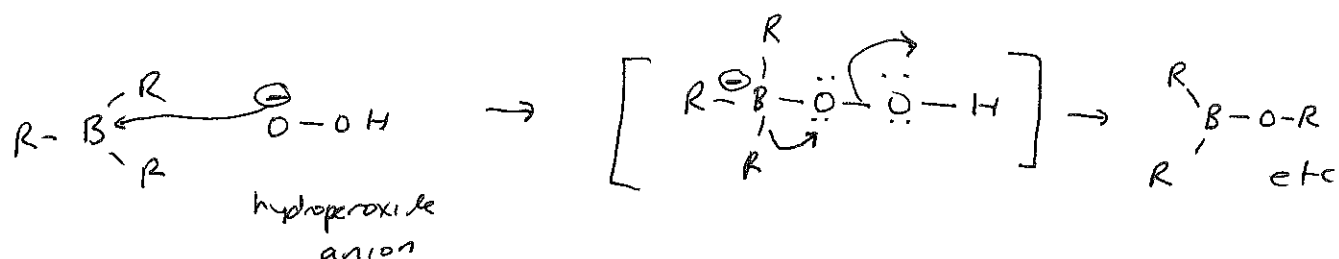
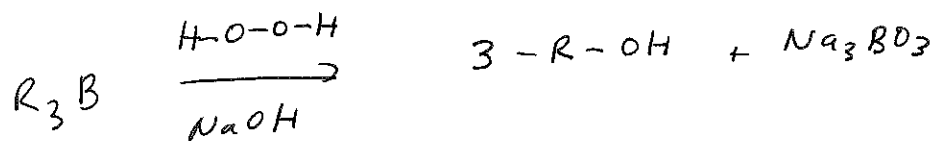
Seen most readily in the following example:



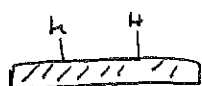
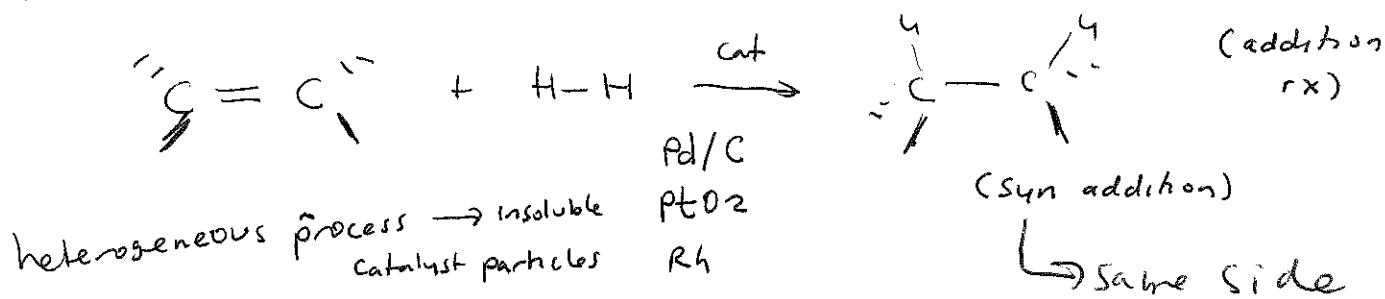
Sterics also likely involved:



The Alkyl boranes produced in the hydroboration step are generally not isolated but oxidized + hydrolyzed to alcohols



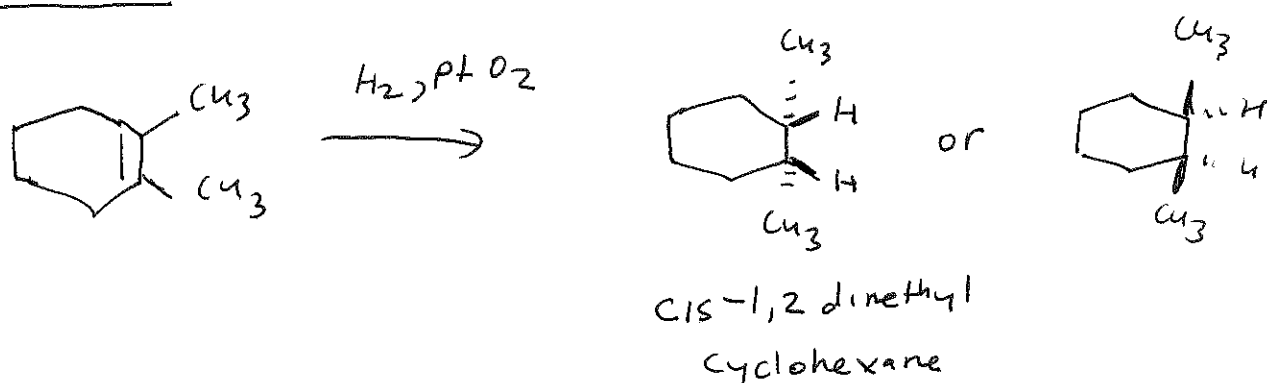
Reduction of alkenes : hydrogenation



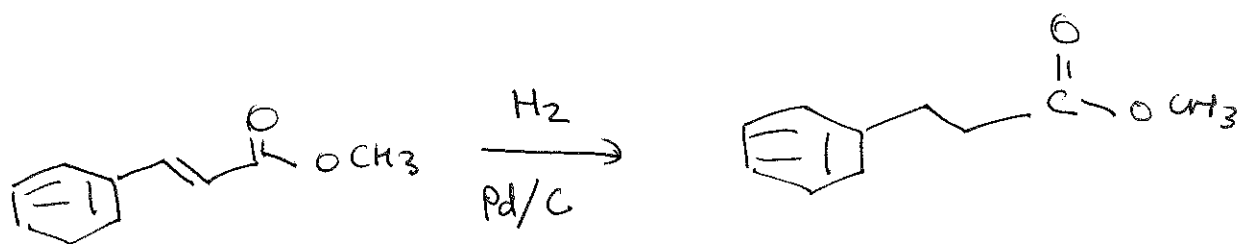
• Function of catalyst is to absorb H atoms which are delivered to the alkene

• As a consequence both H atoms generally from the same side of the molecule

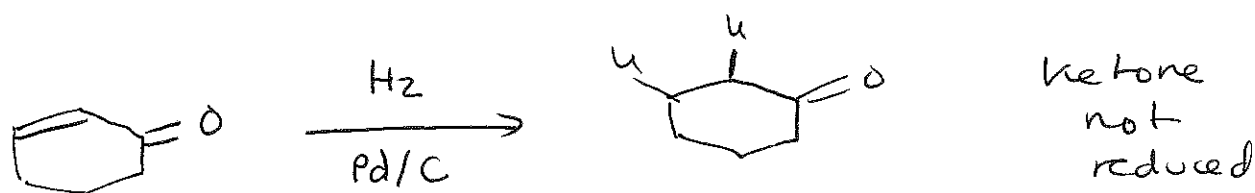
Example



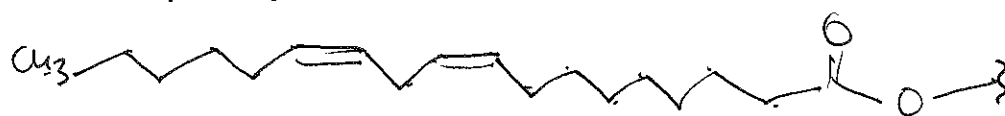
Hydrogenations are quite selective for alkenes relative to other functionality (aldehydes, ketones, esters, nitrile) "chemoselective"



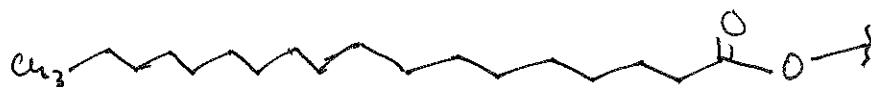
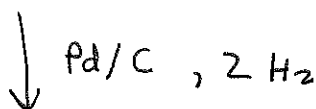
* aromatic ring is not reduced even though it contains apparent double bonds



unsat. vegetable oils



linoleic acid ester



stearic acid ester

(C18)

Reaction Stereochemistry

- treating (*R*)-BINAP with ruthenium(II) chloride forms a complex in which ruthenium is bound in the chiral environment of the larger BINAP molecule
- this complex is soluble in CH_2Cl_2 and can be used as a homogeneous hydrogenation catalyst



- using (*R*)-BINAP-Ru as a hydrogenation catalyst, (*S*)-naproxen is formed in greater than 98% ee

