Course Chem 343 Lecturer Gellman (11 am)

Day Monday Date 10/10/11

Notes Taken By Travis Total # of Pages 4

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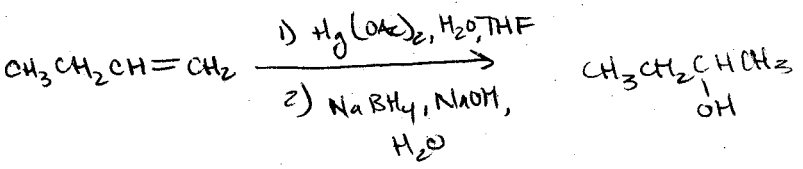
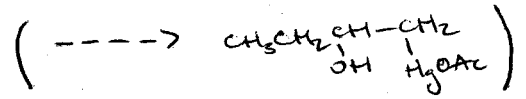
RECALL: Oxymercuration - Reduction of Alkenes (to Alcohols, Markovnikov)

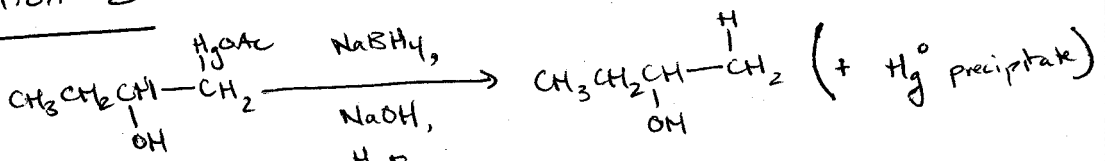


From LAST CLASS:

Reaction 1: oxymercuration



Now Reaction 2:



[C-Hg bonds are quite toxic, typically not isolated]

Comments:

1) Mechanism is unclear
2) "Reduction" - $Hg^{2+} \rightarrow Hg^{0}$ (in replacing C-Hg bond with C-H bond)
3) The above equation isn't balanced...
   ex: (what happens to Boron?)
   * focus is on transformation of organic molecule, other reactants are less important to us. *

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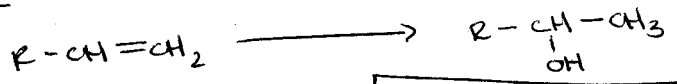
Overall:

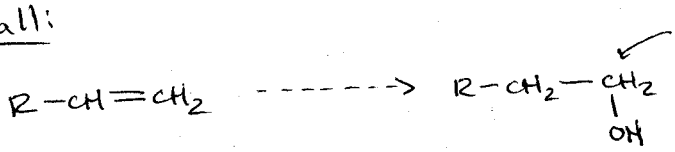


"Markovnikov Selectivity"

Hydroboration-Oxidation of Alkenes

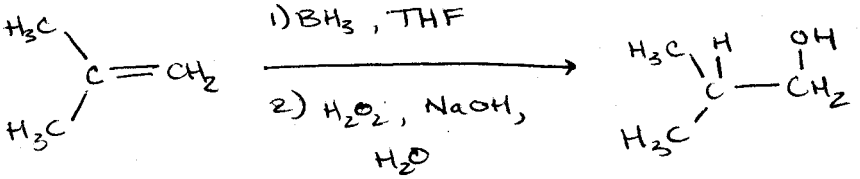
↳ Allows formation of Anti-Markovnikov alcohols

Overall:



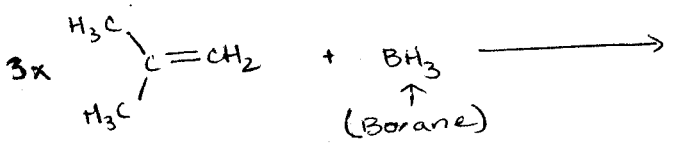
*Note: Reagent choice determines regiochemistry of product alcohol

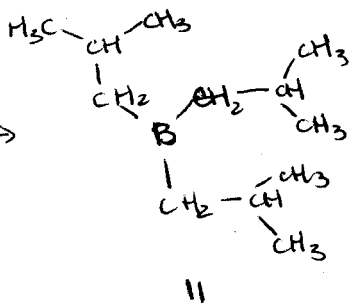
Ex:

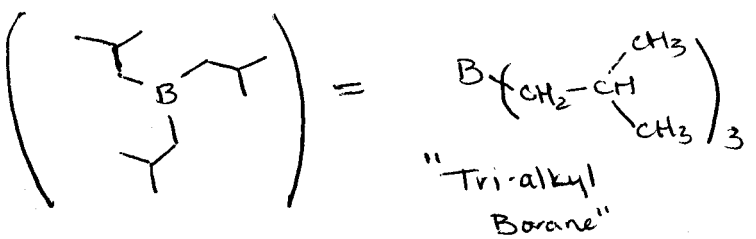


(2 steps)

Reaction #1: Hydroboration







"Tri-alkyl Borane"

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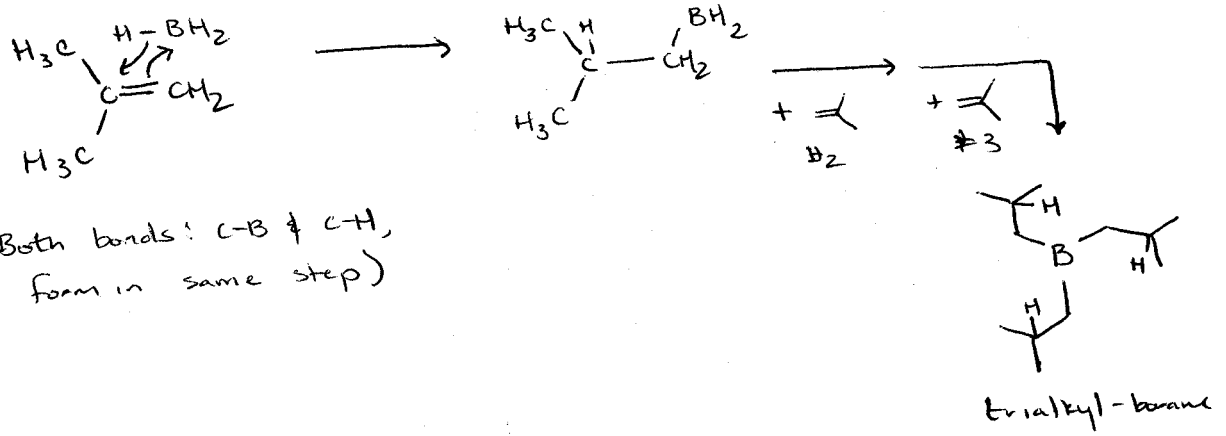
Mechanism of Addition of B–H to an Alkene π-bond:

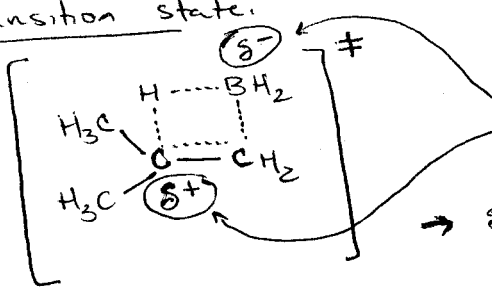


(Both bonds: C–B & C–H, form in same step)

What is the origin of selectivity? (why does Boron go to the less-substituted C)?

Two Rationales:

① Partial charges develop transiently in the transition state.



Partial charges develop

→ δ+ preferentially occurs on more substituted carbon

② Sterics:

BH_2 is bigger than H, so BH_2 will prefer to associate with the less substituted carbon.

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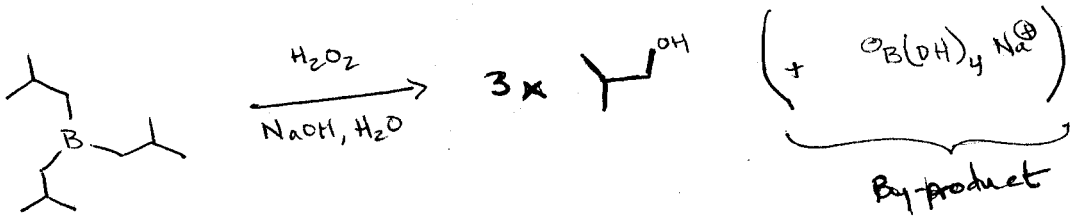
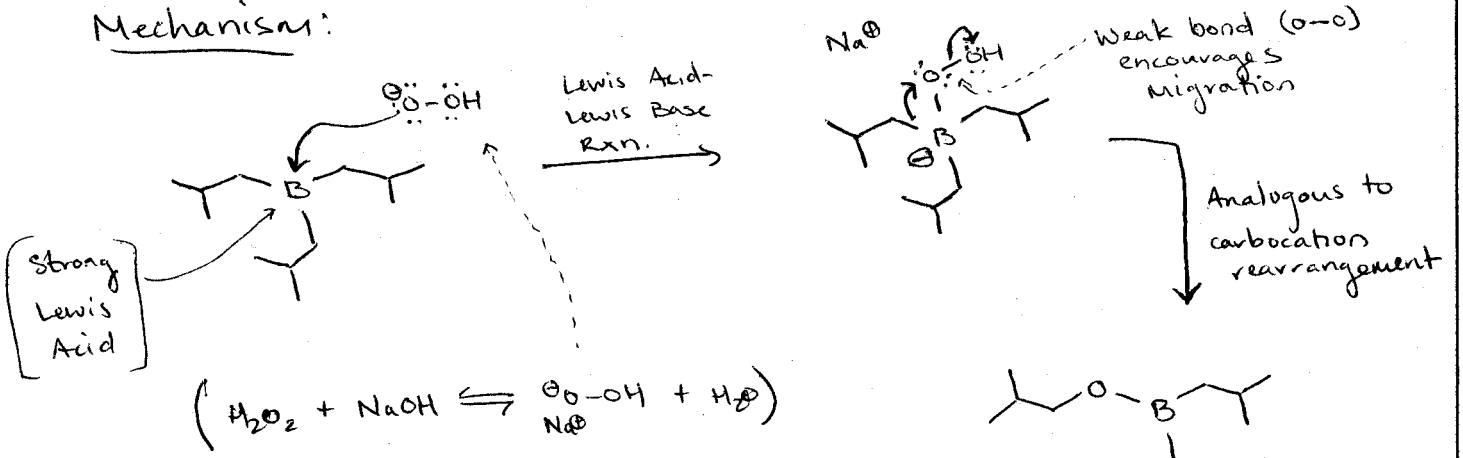
Step #2: Oxidation



Mechanism:



Note: Breaking the high-energy O-O bond provides the thermodynamic driving force for this reaction ("drives this rxn")