Course 342 Lecturer Prof. Gellman

Day Wednesday Date 10/10/17

Notes Taken By Marlies Hoger Total # of Pages 3

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Recall: Rxns of alkenes...

Oxymercuration - Reduction

overall:

$R-CH=CH_2 \longrightarrow R-\underset{OH}{\underset{|}{C}}H-CH_3$ ("Markovnikov")

Hydroboration - Oxidation

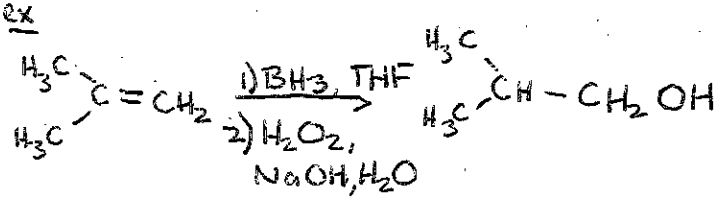
Overall:

$R-CH=CH_2 \longrightarrow R-CH_2-\underset{OH}{\underset{|}{C}}H_2$ "Anti-Markovnikov"

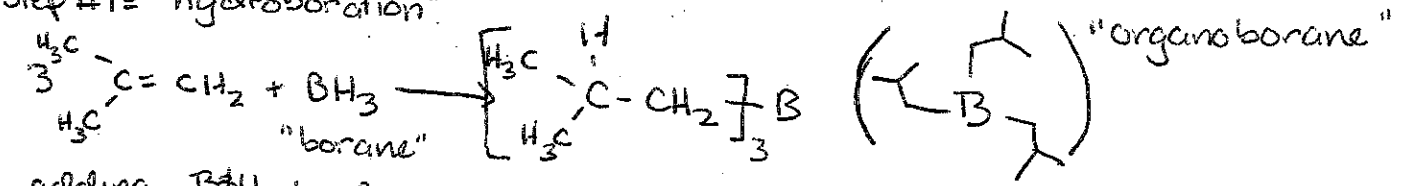
-OH on less substituted C

This type of complementary regioselectivity is extremely useful from a synthetic perspective

ex

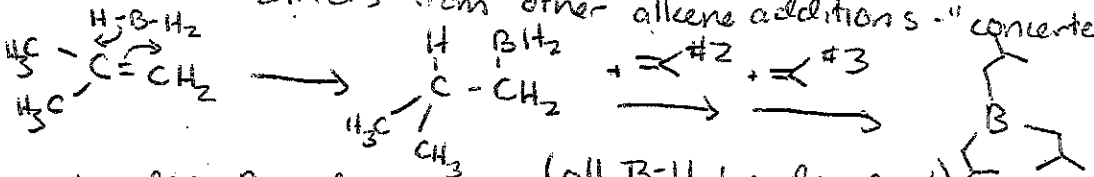


Step #1 = "hydroboration"



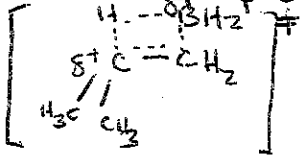
- adding B-H bonds across double bond

mechanism - differs from other alkene additions - "concerted"



- why does B end up on less substituted C? (all B-H bonds react)

2 factors proposed: # 1 = partial charges at TS



transient δ^+ on C,

δ^- on B $\Rightarrow \delta^+$ will prefer to be at more substituted C

Course 343-2 Lecturer Prof. Gellman

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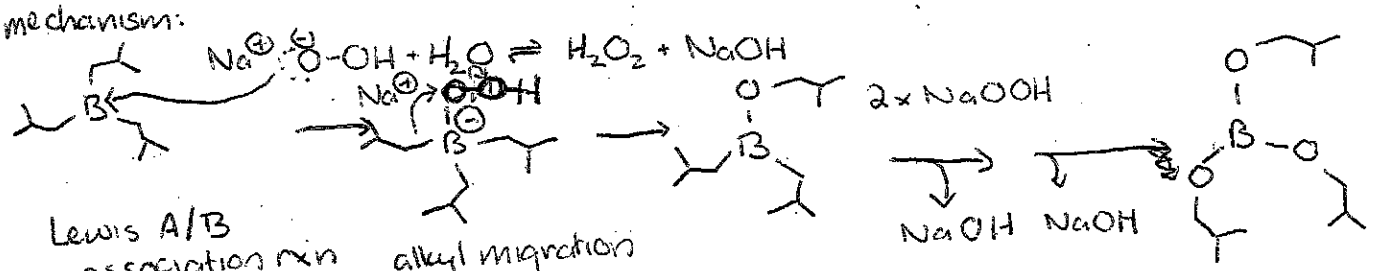
#2. Sterics

- BH_2 larger than H, prefers less substituted C

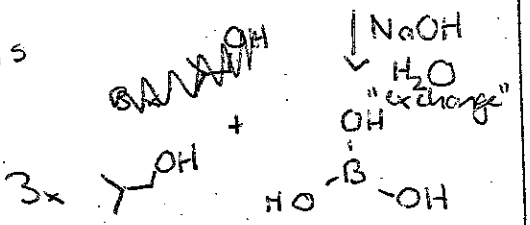
Step #2: "Oxidation"

mechanism:

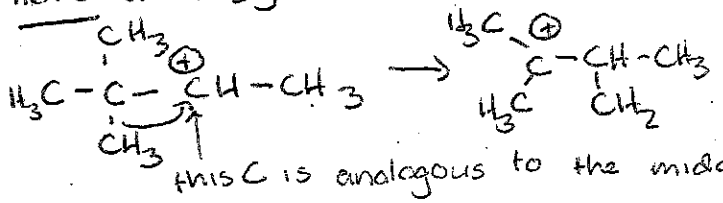


Lewis A/B association rxn — alkyl migration to O

- any bond between 2 electronegative atoms is reactive (both want the e⁻)
  ↳ so the O-O bond is weak ⇒ reactive



note analogy:



Ozonolysis of Alkenes

ozone: O_3 — very reactive!

overall rxn process(es):

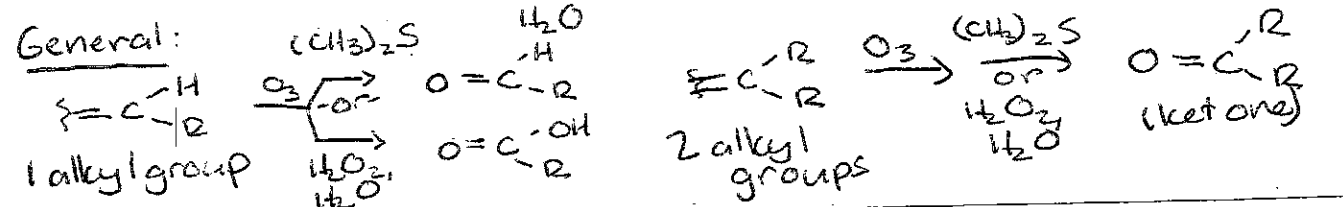
$CH_3-CH=CHCH_2CH_3 \xrightarrow{1)\ O_3\ \ 2)\ (CH_3)_2S}$ aldehydes

replace C=C w/ 2 C=O

alternative (2nd step): $(H_3C-S-CH_3)$

$CH_3-CH=CHCH_2CH_3 \xrightarrow{1)\ O_3\ \ 2)\ H_2O_2,\ H_2O}$ carboxylic acids

General:



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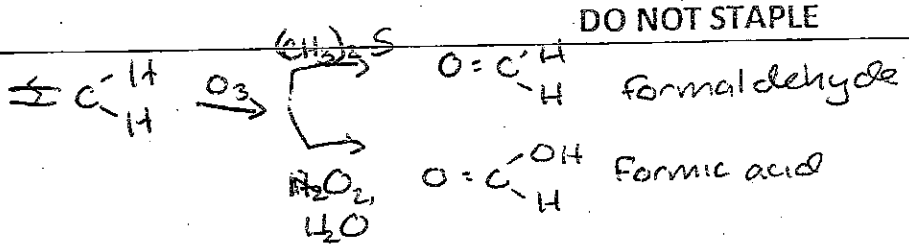

Exam

≥ 92 = doing well

85-91 = solid

75-84 = concern

< 75 = trouble