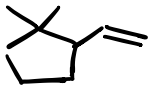
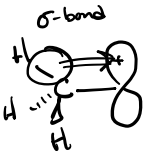
Alkene Rxns (Electrophilic Addition)

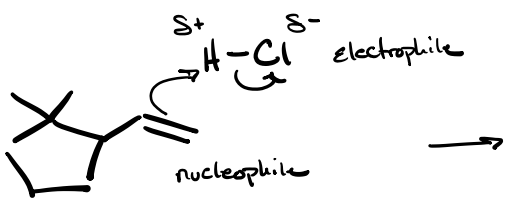


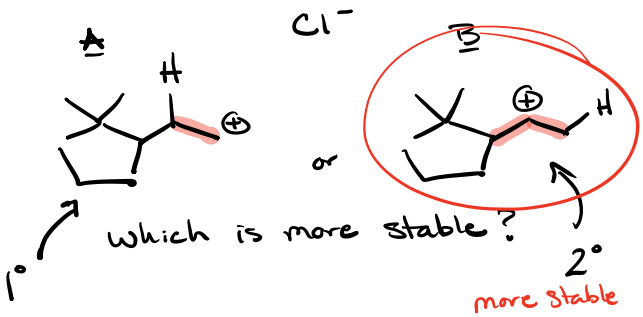
HCl



Hyperconjugation
⇒ Induction
Donation

Mechanism



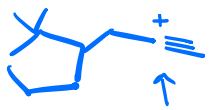


more stable
lower E_A
major

C^+ stability

more stable $3° > 2° > 1°$

Conformation

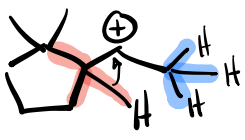


no Resonance

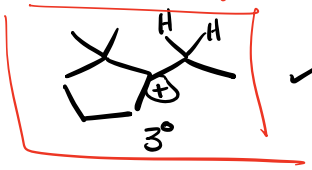
Sp Carbocation

2° sp^2 w/ Conjugation
Extremely Stable

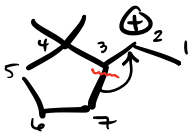
Is there a more stable C^+ that can form?
(by a single Hydride or Alkyl Shift?)



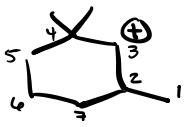
1,2-hydride shift



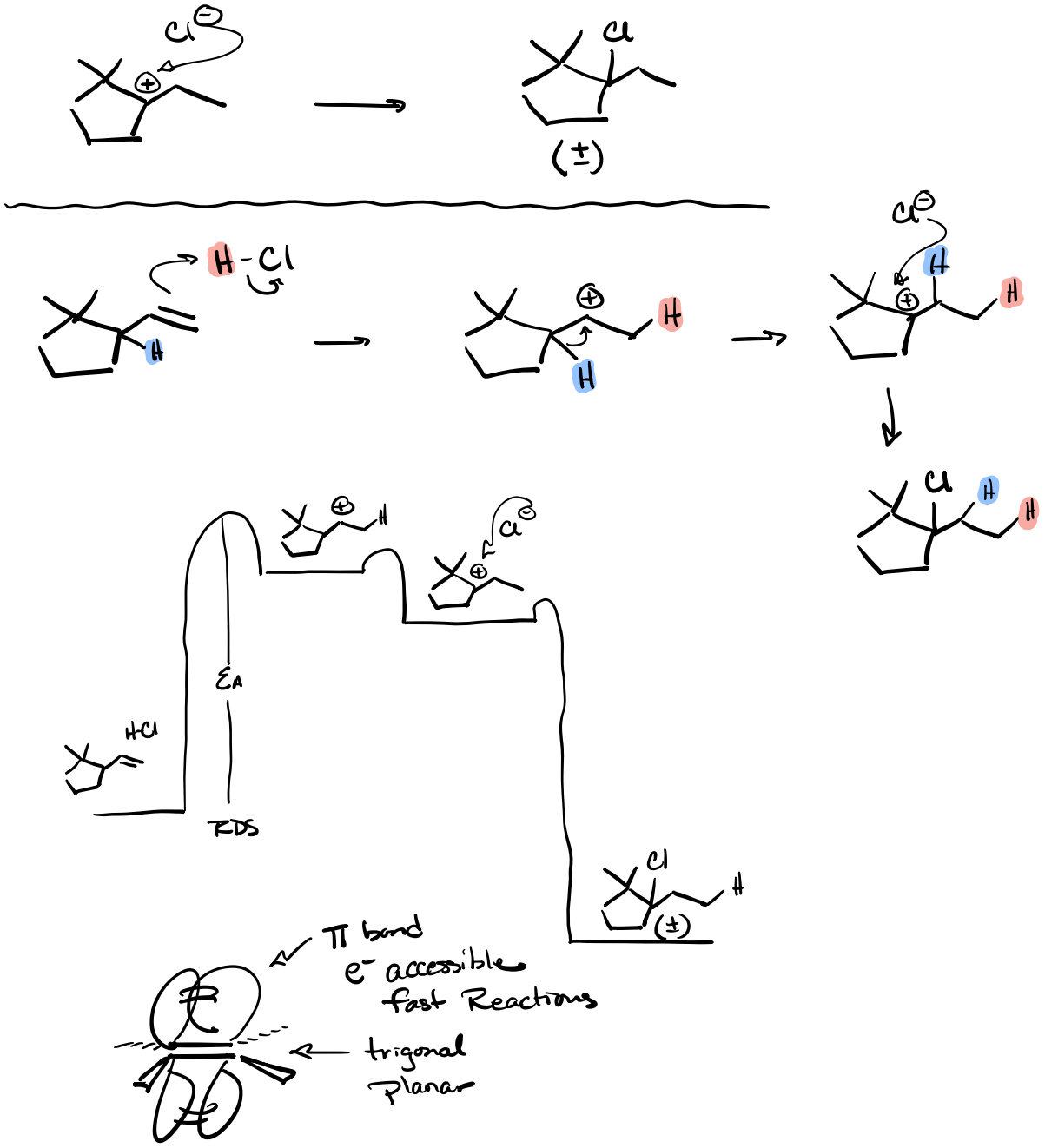
✓ more stable



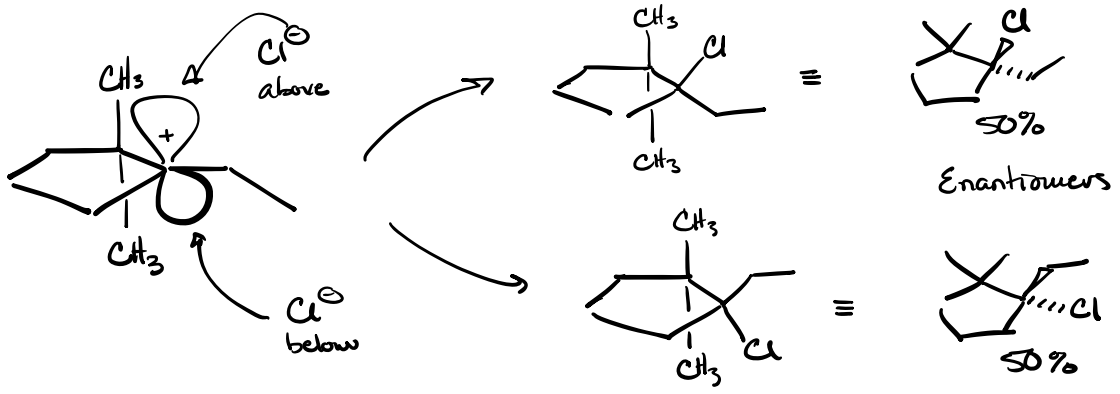
1,2-Alkyl Shift



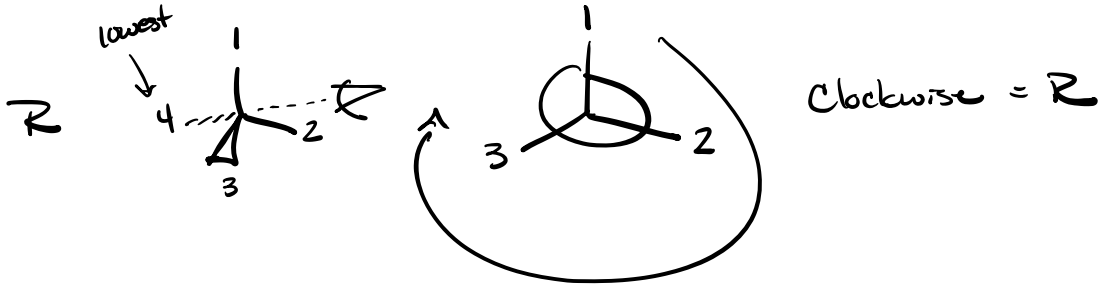
✗ not as stable

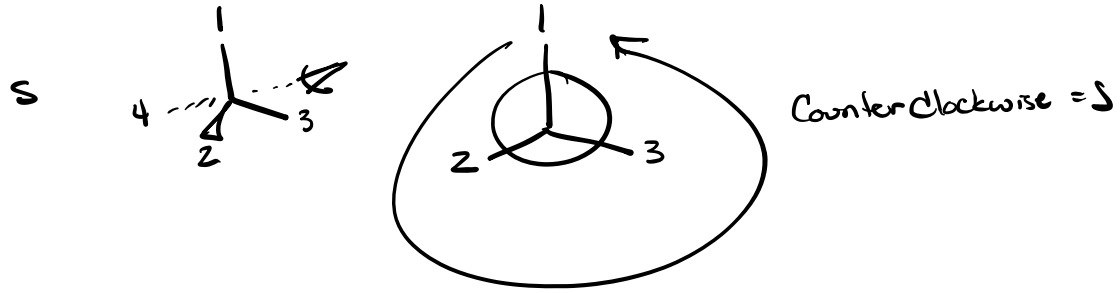


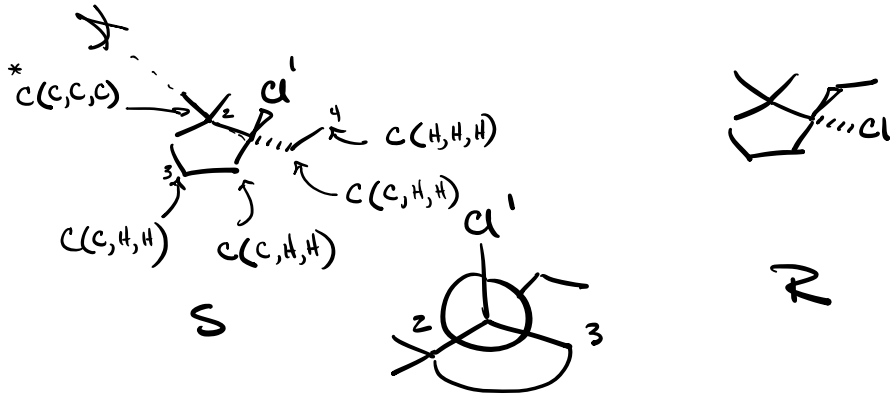
1. Protonate
2. Decide which direction (more stable C^+)
3. Hydride & Alkyl Shift
4. Nucleophilic attack on C^+



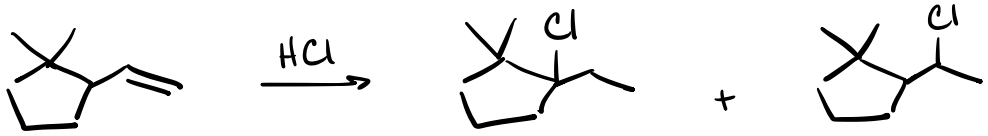
50%R & 50%S = Racemic = (±)







R



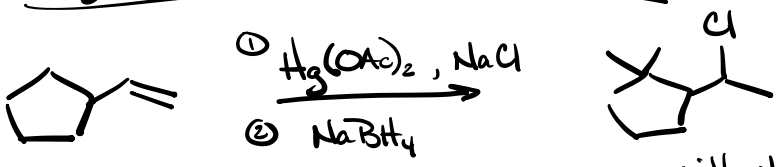
major

by 1,2-hydride shift

minor

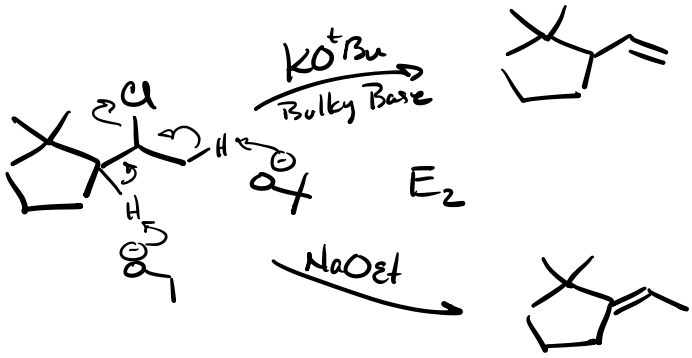
How can we make this major?

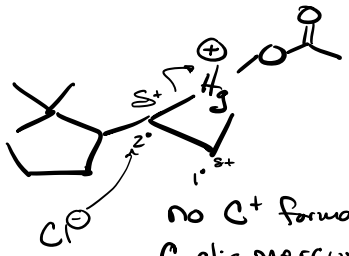
Oxymercuration – demercuration



without hydride shift

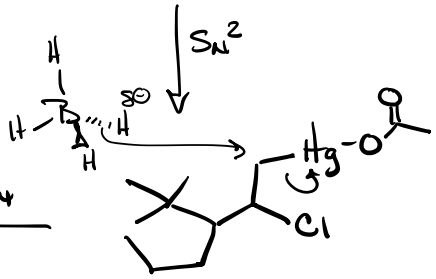
⇒ no C+ formation



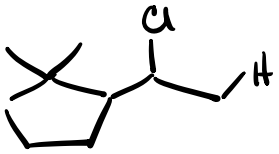


no C^+ formation

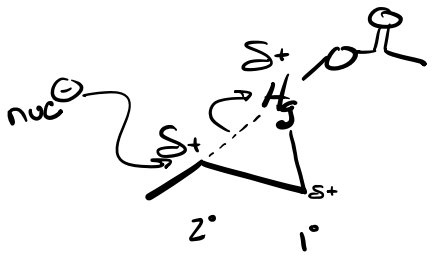
Cyclic mercurium ion

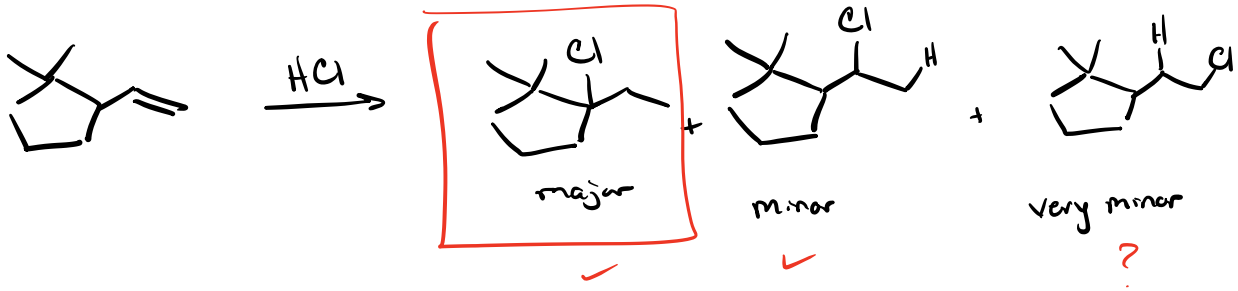


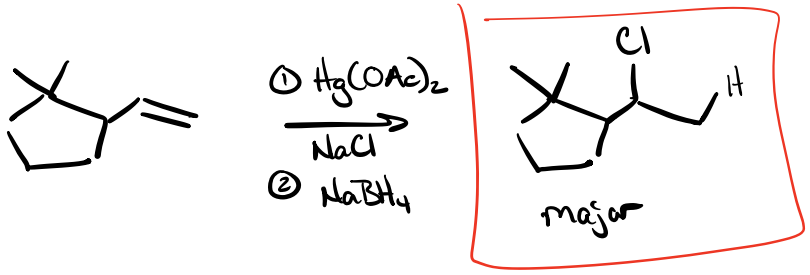
III

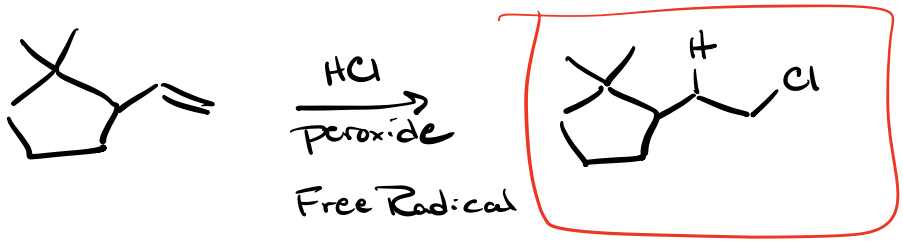


direct 1,2 substitution without shifts



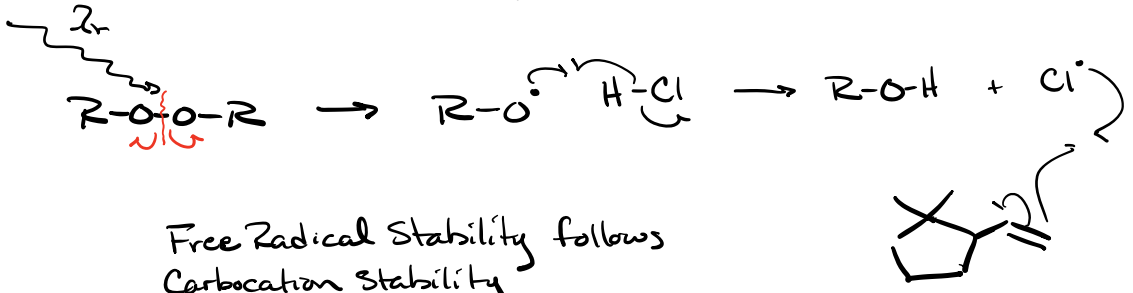

HCl
Cl
major
Cl
H
minor
H
Cl
very minor
?


① Hg(OAc)2
NaCl
② NaBH4
Cl
H
major

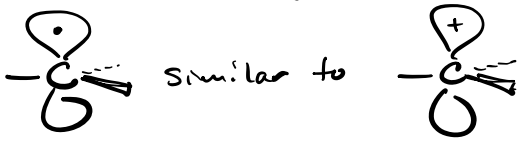

HCl
Peroxide
Free Radical
H
Cl

Free Radical with Peroxide

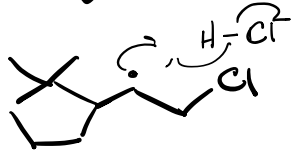
R-O-O-R peroxide
often with light or heat
(hν) (Δ)



Free Radical Stability follows Carbocation Stability



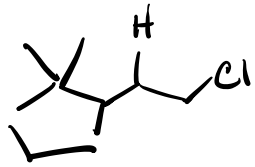
* Key Step



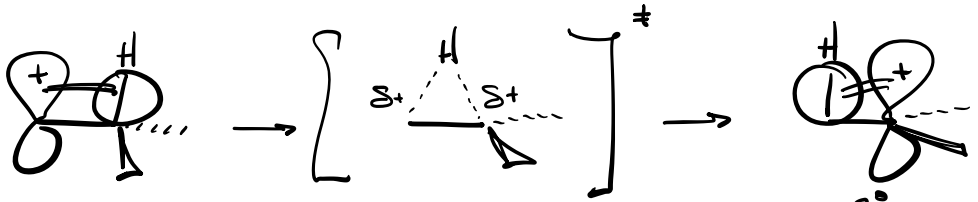
2°

Halogen adds first

* No Alkyl or hydride shifts w/ free Radicals



C⁺ shift



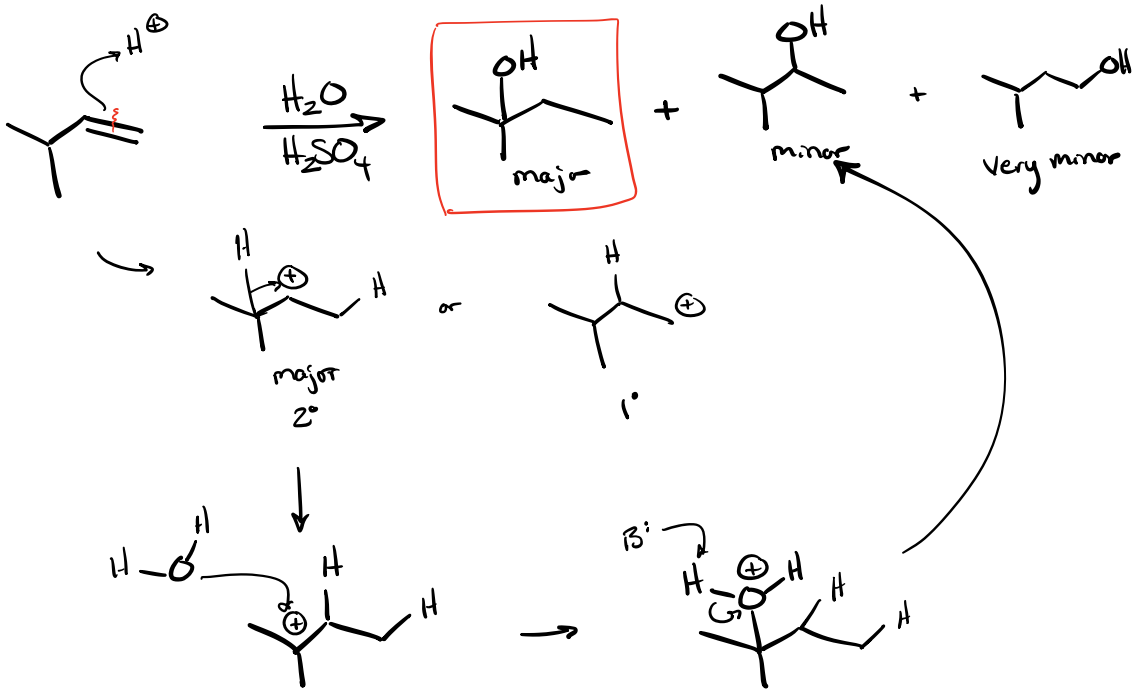
1°

1,2-hydride Shift

3°

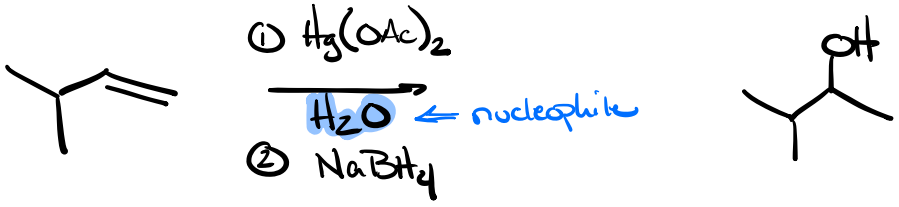
Free Radical

Less e⁻ difficient

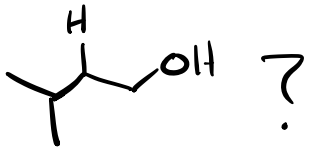


Question How do I prevent Shift?

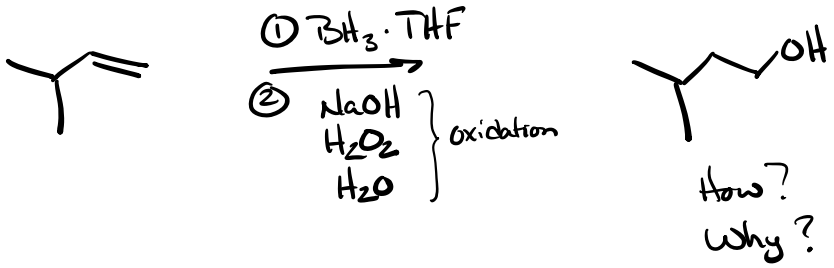
Oxymercuration - Demercuration

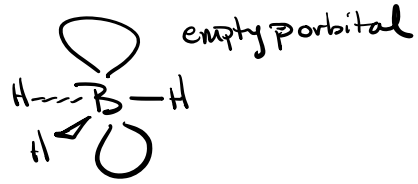


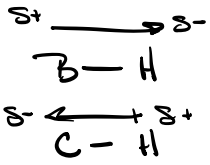
Question ⇒ What if I want the anti-Markovnikof product?



?

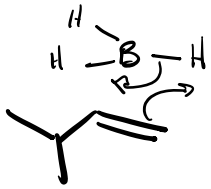




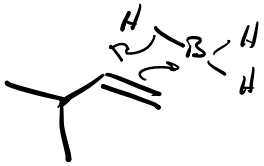


$H:^{\ominus}$ hydride

$H^{\oplus}$ proton

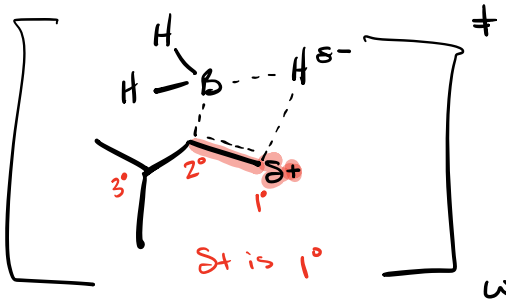


or

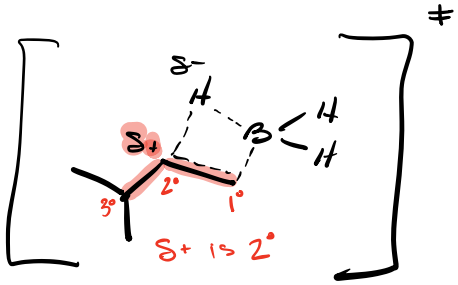


Concerted

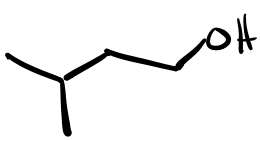
Concerted



Which is Lower in Energy?

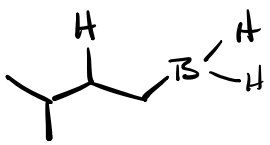


More stable
Lower E_A
Faster Reaction



Major

oxidation



Review for Exam

Star Chart alkene