Course Chem 343 Lecturer Gellman (11 am)

Day Friday Date October 7, 2011

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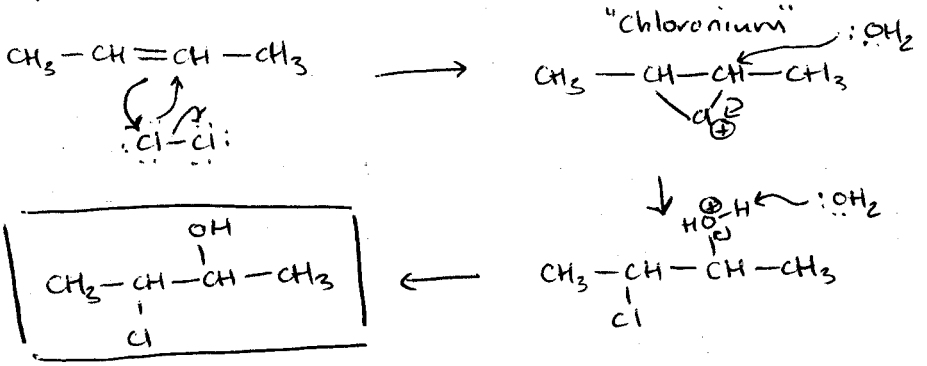
Recall: Halohydrin Formation

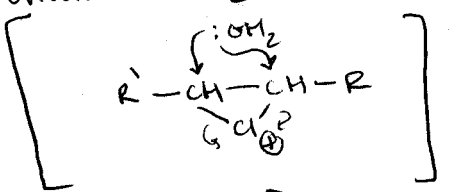
Ex: $CH_3-CH=CH-CH_3 \xrightarrow{H_2O} CH_3-CH(Cl)-CH(OH)-CH_3$ (+ Cl_2)

Mechanism:



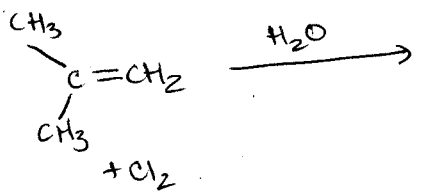
What about unsymmetrical alkenes? (Regioselectivity?)

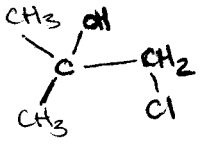
→ where does water attack if both sides of chloronium are not the same

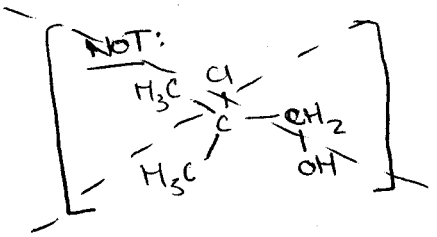


$(R' \neq R)$

???







WHY?

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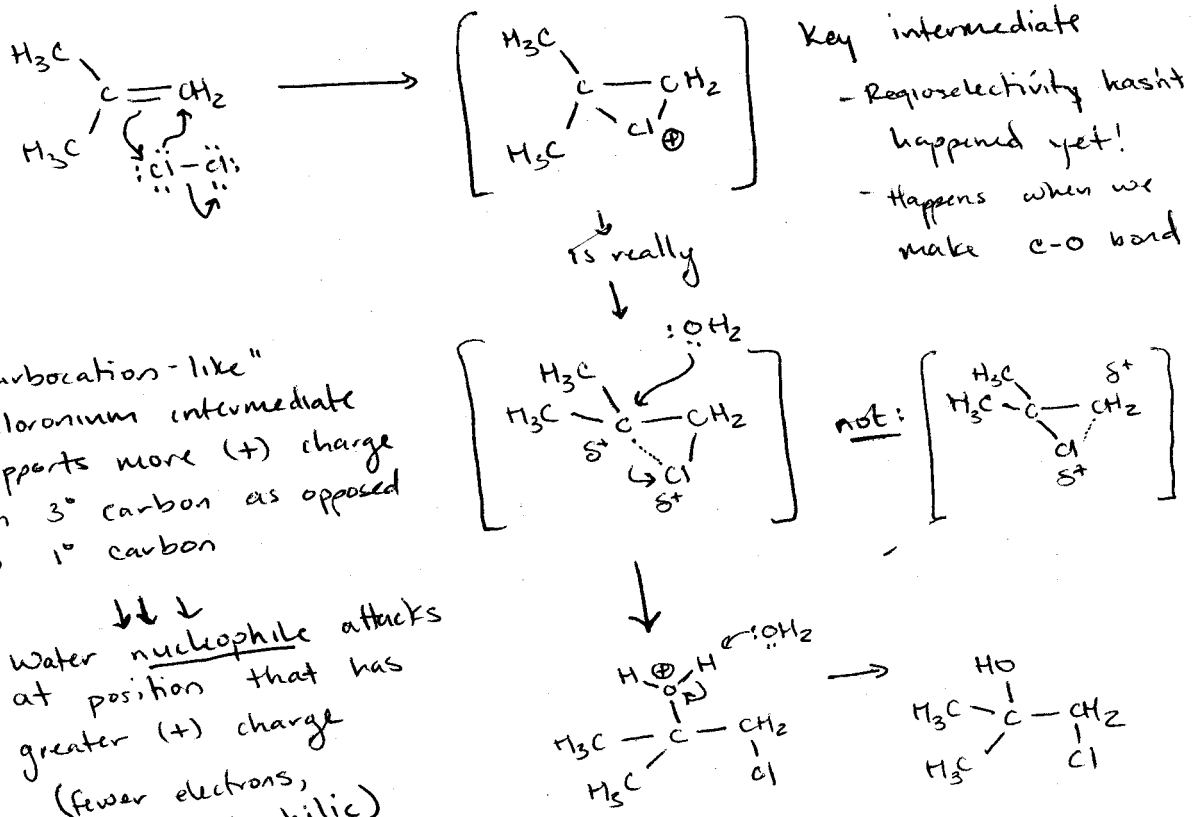
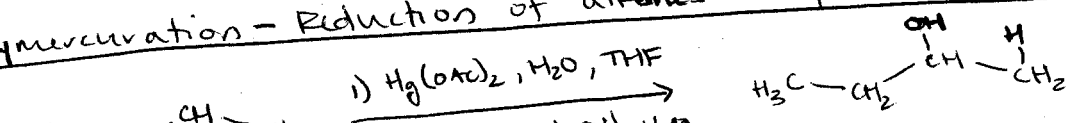


Oxymercuration – Reduction of alkenes to produce alcohols



* Markovnikov Product

[See text: p. 186]

Note: Separate steps must clearly be indicated!!

(ex: 1), 2), , 3),)

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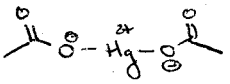
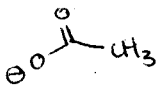
→ Focus on two steps separately:

First Step:

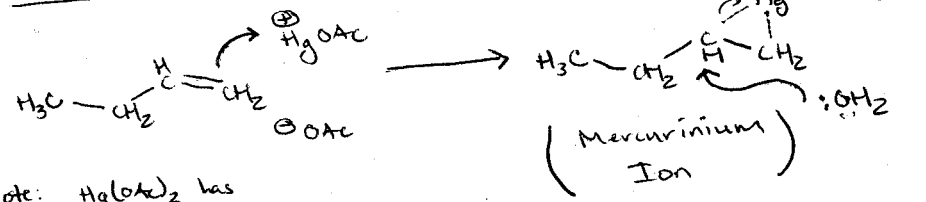
$Hg(OAc)_2$ = $Hg^{2+}(^{\ominus}OAc)_2$ or 

$^{\ominus}OAc$ = 

"Acetate"

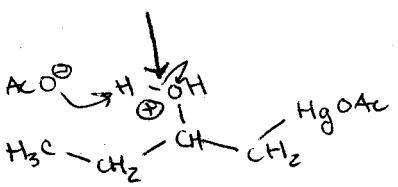
(solvent) THF =  (type of ether, often miscible with H_2O)

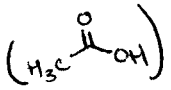
Mechanism of First step

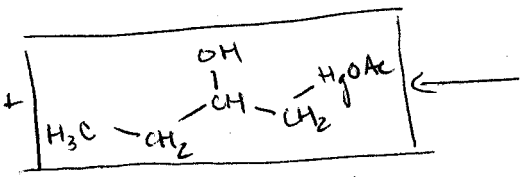


(note: $Hg(OAc)_2$ has dissociated)

(Mercurinium Ion)



AcOH 



Stable product of first step ("Oxymercuration")

Note: ① "Organometallic" species - has carbon bound to a metal

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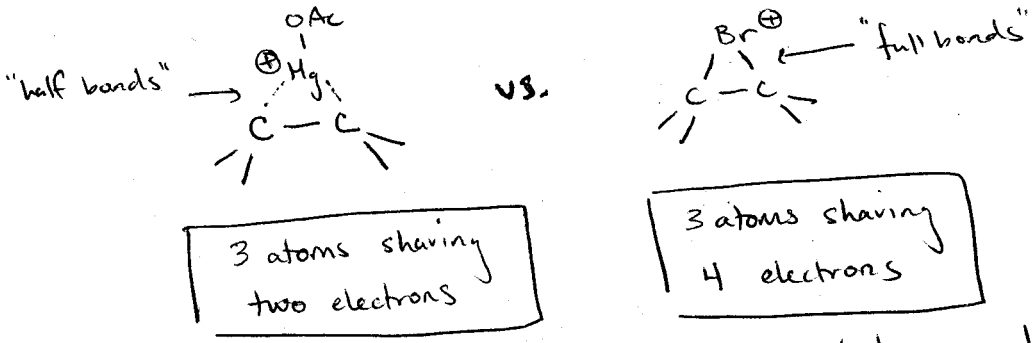
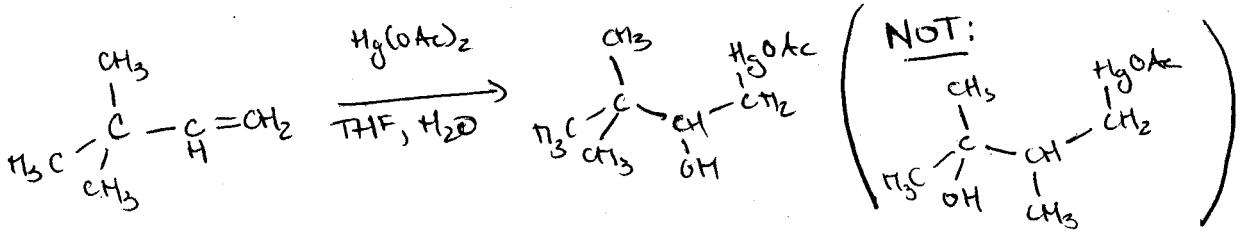
Contrast: Mercurinium Ion vs. Bromonium Ion



(Contrasts with representation in textbook)

Mercurinium & Bromonium Ions
↳ Similar reactivity but different electronic structure

Note: In neither oxymercuration nor halohydrin formation do we envision a carbocation (C⊕) alternative
→ Why? - Carbocations will rearrange



** No rearrangement, no carbocation