Course Chem 343 11 AM Lecturer Gellman

Day Monday Date 11/28/11

Notes Taken By Herndon Total # of Pages 4

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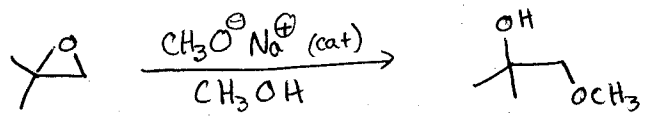
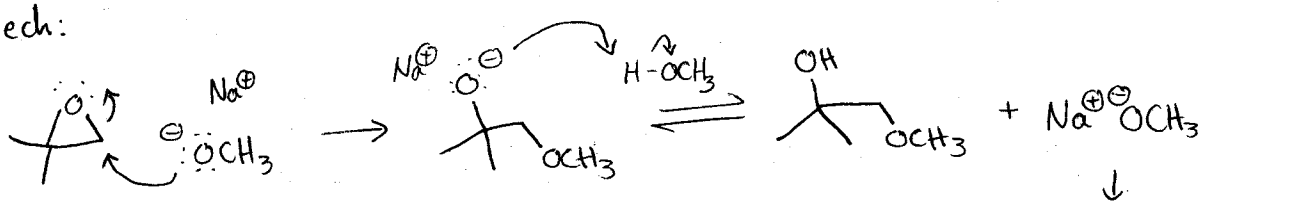
Recall: Rxns of epoxides with nucleophiles ("ring strain")

(1) $S_N2$ rxns w/ alkoxides (+ others)

Ex:




Mech:



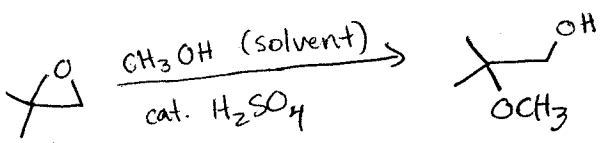

Comments:

1) Recall: alkoxides are <u>not</u> good $S_N2$ LGs - special case b/c of ring strain

2) $S_N2$ selectivity influenced by steric repulsion - explains why attack occurs @ less substituted C.

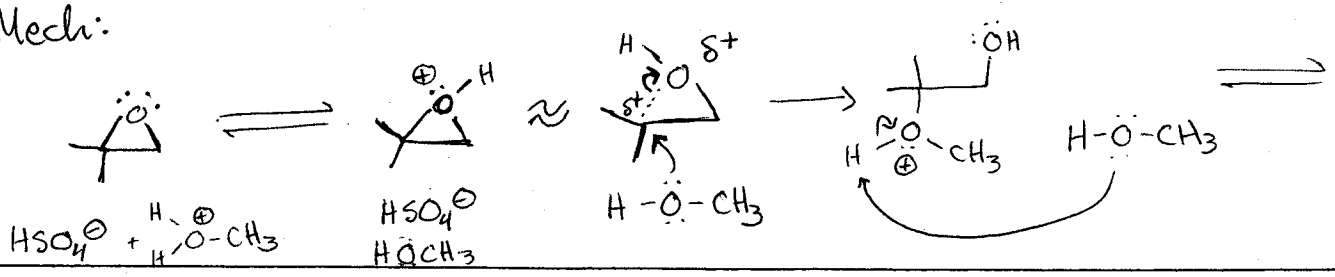
(2) Epoxide ring-opening under acidic conditions

Ex:




Isomer of previous product!

Mech:



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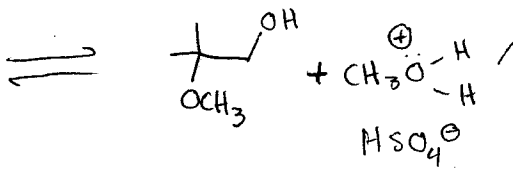
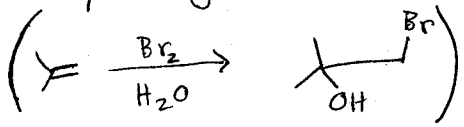
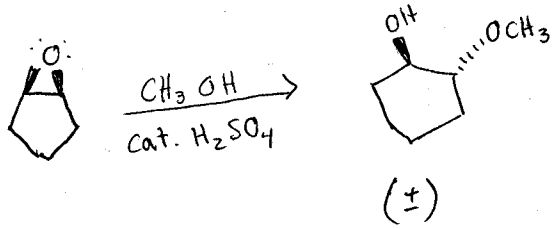



regenerated ⇒ catalyst acid

Recall: Regioselectivity argument here parallels argument for halohydrin formation



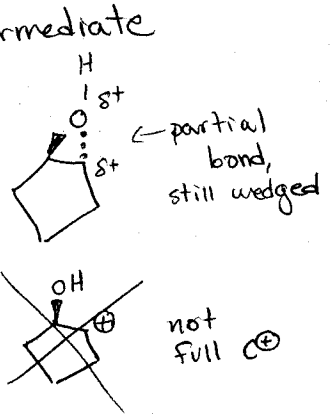

Another example: highlights stereochemical issue



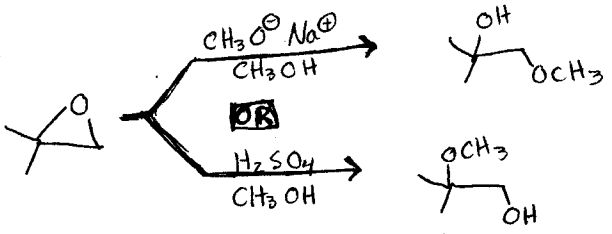

(anti addition)

(±)

Intermediate

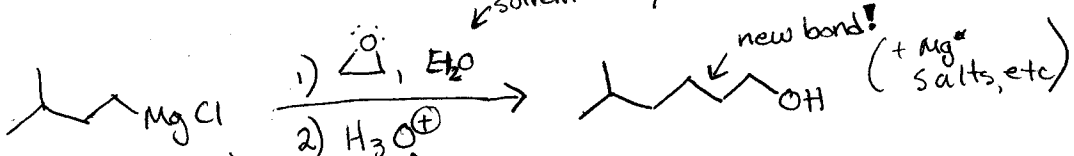



Note: Thus, alkoxide vs. acid catalysis provides predictable access to alternative regioisomers from unsymmetrical epoxides




(3) Epoxide opening w/ organometallic reagents (carbanion-like reactivity)

Ex:




(grignard reagent)

"water with some acid in it"

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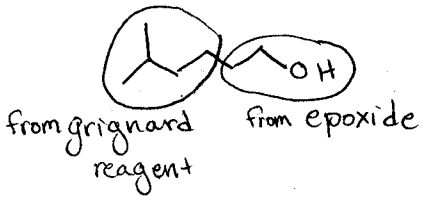
Find SM in product

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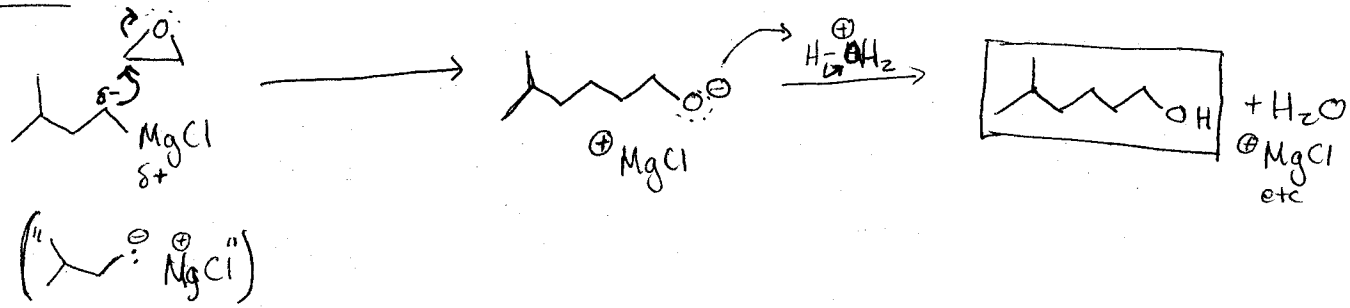
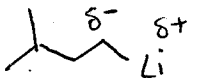



("MgCl")

Comments:

(i) See text - Mg from another grignard reagent coordinates to epoxide oxygen: "Lewis Acid activation"

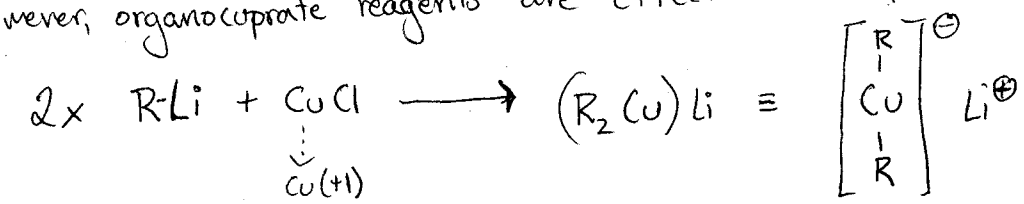
(ii) Organolithium reagents are <u>not</u> effective for epoxide opening




looks similar, doesn't react same as grignard in this case

→ produces complex mixture upon rxn with epoxides

(iii) However, organocuprate reagents are effective for epoxide opening



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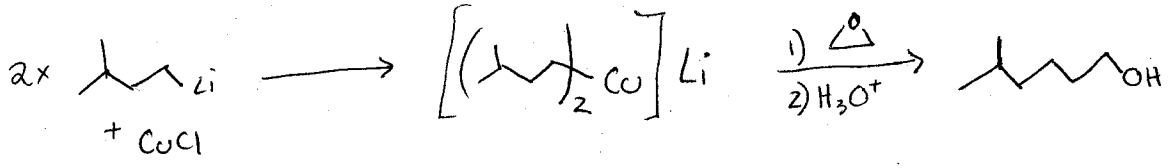
Thus,




Final note: Form new C-C bond! Very exciting.

(iii) ↗