Course Chem 343 Lecturer Gellman
Day Monday Date 11-23-15
Notes Taken By Lu Liu Total # of Pages 4

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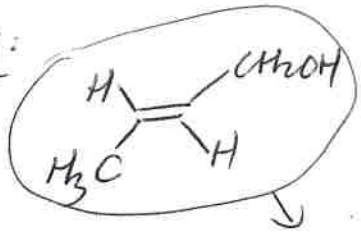
Exam 3. Week 2 Dec. Through Chap. 11

Review Session Tues 1 Dec, B371, 5pm

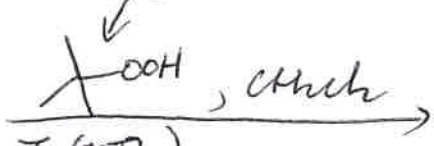
Recall Synthesis of epoxides....

3) Asymmetric epoxide synthesis ⟶ "Sharpless epoxidation"

Ex:



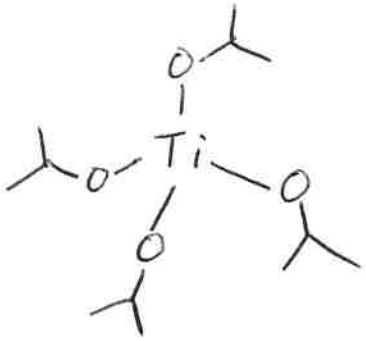
oxidant



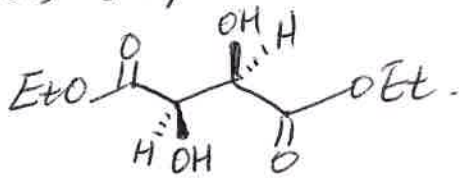
Ti(OiPr)3
(+)-DET

(>95% this enantiomer)

Ti(OiPr)3 =



(+)-DET =



"Diethyltartrate"

source of enantiomer preference in the product!
("Asymmetric induction")

Practical importance ⟶ (+)-DET is readily available, therefore, use of (+)-DET under "Sharpless condition" must provide

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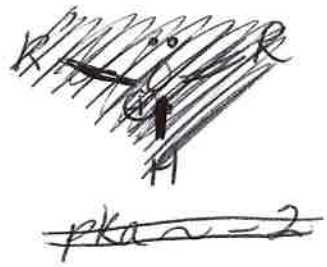
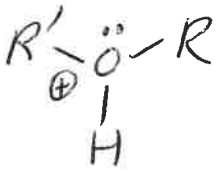
Reactions of ethers

In general, most ethers are not very reactive. However, under acidic conditions, rxns can occur, esp. for ethers involving 3° carbon.

Recall: Ether O is a Brønsted base.



~~pKa ~ -2~~



pKa ~ -2

--> SN1. E1 reactivity (or SN2., if 1° R or R').

Consider: one "R" = 3°

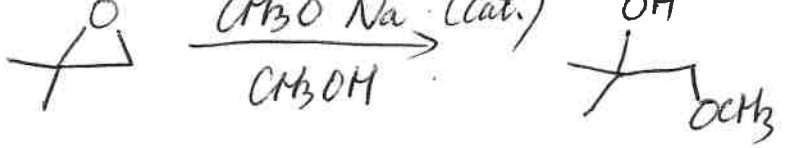
You fill in mech.

"acid-catalyzed ether cleavage".

Rxns of epoxides w/ nucleophiles

→ Rxns driven by ring strain.

① SN2 rxns w/ alkoxides (& comparable nucleophiles).

Ex. 

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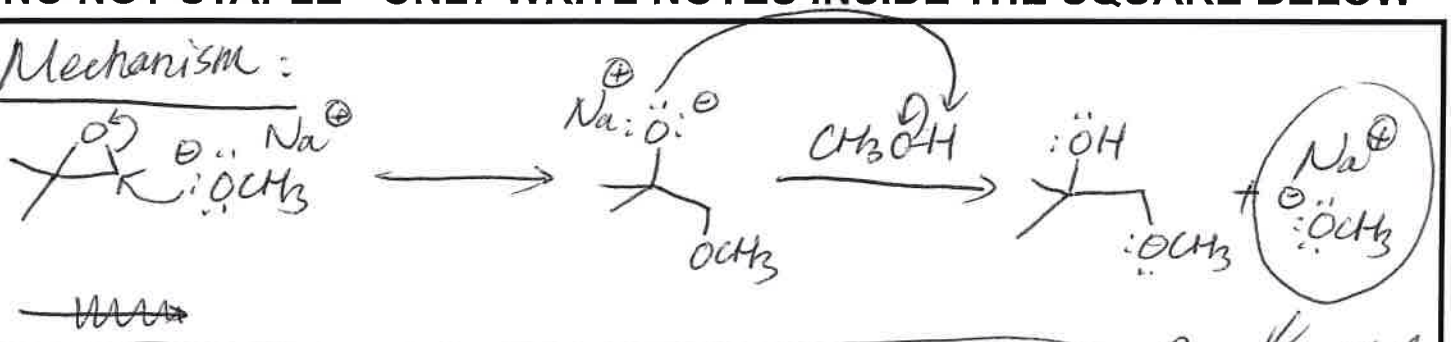
Mechanism:

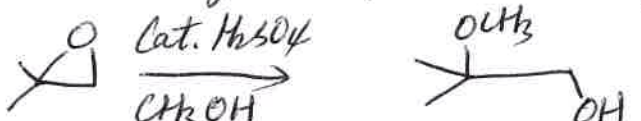


Regenerated ∴ Catalyst

Note: Alkoxides generally are terrible LGs, but OK here because of relief of ring strain.

Because SN2 mech very sensitive to steric environment @ electrophile C, preference for 1° C (vs. 3° C).

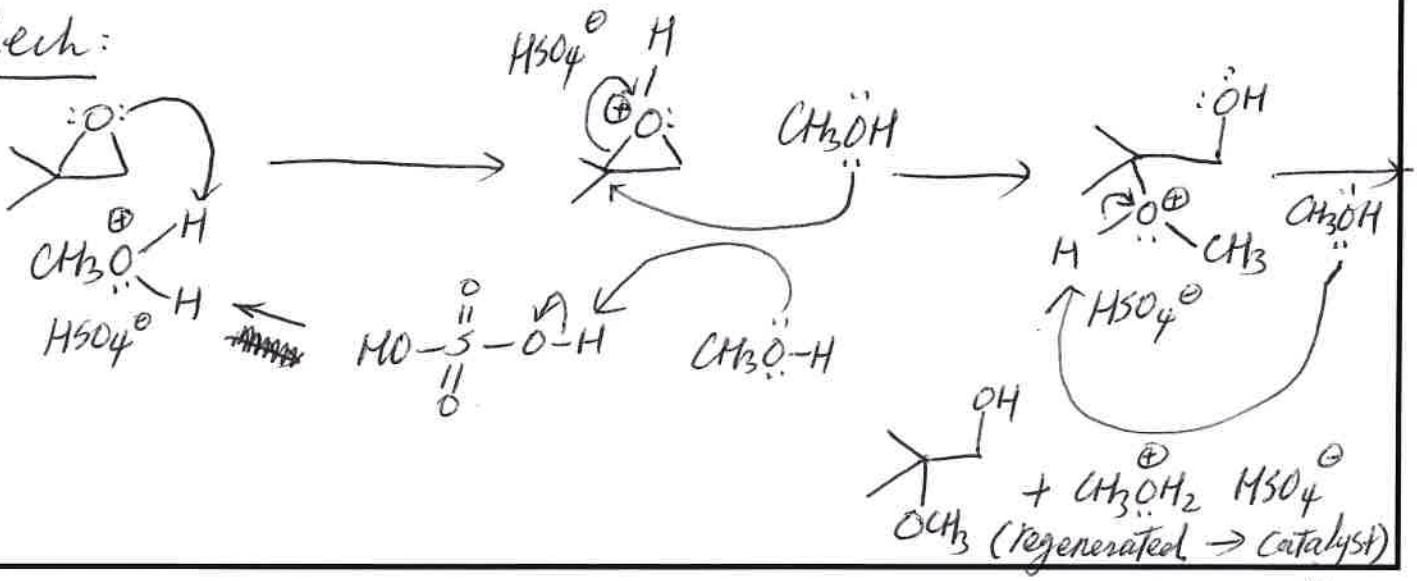
2) Acid-catalyzed epoxide opening

Ex 

(solvent & reactant)

(Note: isomeric w/ previous product)

Mech:



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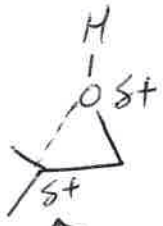
Origin of "regioselectivity"? i.e. Why does CH_3OH attack more-substituted C?

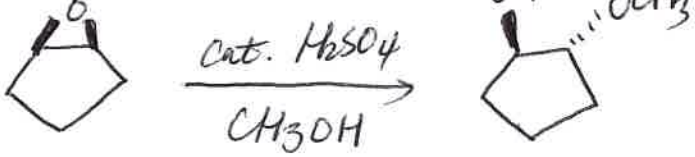
Answer:  is really 



CH_3OH attracted here

Recall halohydrin formation!

Another example:



(±)

Trans only (no Cis)

2nd example shows strictly backside attack ("S_N2-like")

But, 1st example seems to argue against S_N2 b/c of preference for 3° C.

3) Epoxide opening w/ organometallic ~~Reg~~ reagents (form new C–C bond)

Ex: