Course Chem 343 Lecturer Gellman

Day Friday Date 11-20-15

Notes Taken By Lu Liu Total # of Pages 5

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Recall Rxns of Ethers...

Special case. Epoxides.

→ Ring strain leads to unusual (and useful reactivity).

Synthesis of Epoxides

1) Alkene + "peracid"

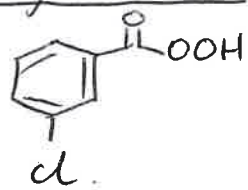
Recall:  

Note: Weak bond (2 electronegative atoms...)

"per-carboxylic acid" ("peracid")

(Recall: peroxide = HO-OH)

Specific case

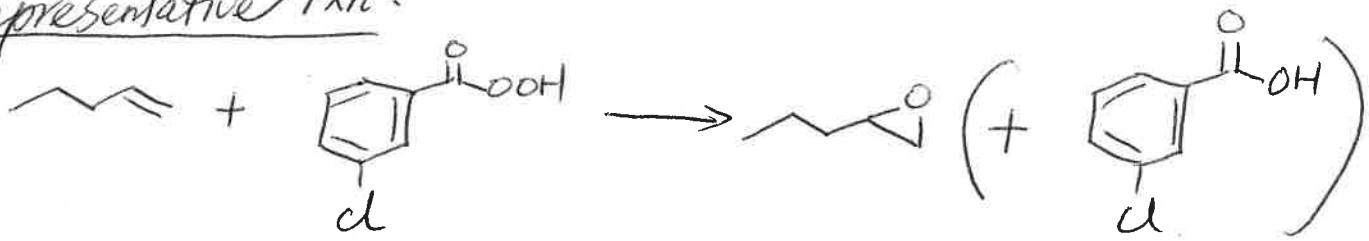


→ commercially available!

meta-chloroperbenzoic acid

(mCPBA)

Representative rxn:



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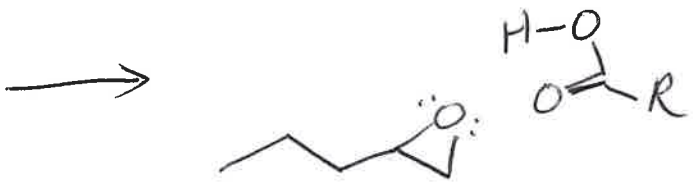
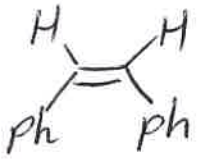
Recall: Alkene + Br_2/Cl_2

Mech:

(Note: Ar = "Aryl" - aromatic fragment)

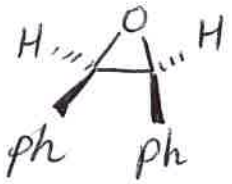


Stereochemical evidence supports hypothesis of concerted mech.



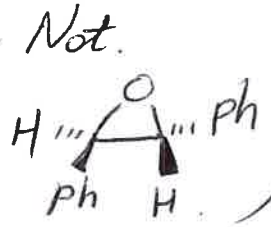
cis

mCPBA →



cis epoxide (only)

(Not.



(±))

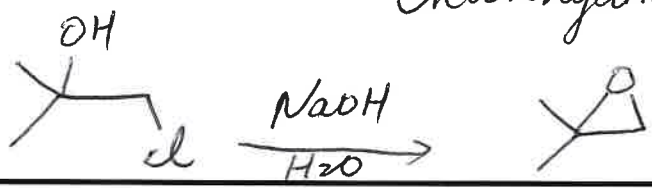
Fill in how to get this product.

2) Cyclization of halohydrins

Recall: 

;

"chlorohydrin"

New: 

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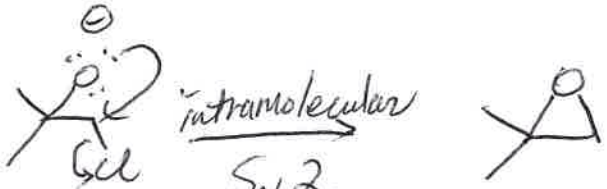
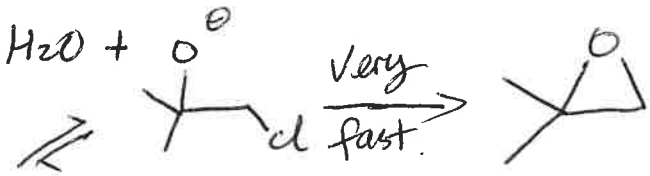
Comments:

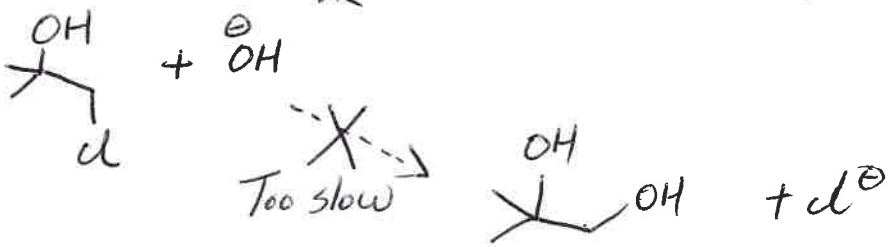
1) Mech:
Key step: 

2) Recall previous discussions of S_N2 rxn of alkoxides w/ alkyl halides; need for quant. deprotonation to generate alkoxide. (NaH)

Why do we not worry about quant. deprotonation in this case?

→ Intramolecular rxns have intrinsic advantages over intermolecular rxns, esp. when forming 3-6 membered rings.

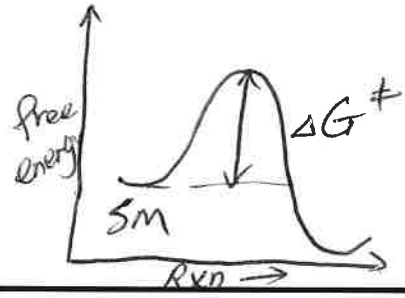
In graphics, 



(intermol.)

Reactivity ≈ energy of activation

$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$



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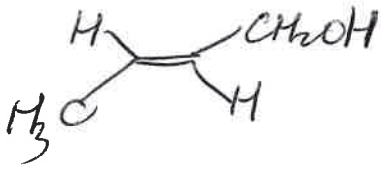
$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ → entropy of activation
↓
enthalpy of activation

Intramolecular rxns are much less entropically unfavorable than intermolecular.

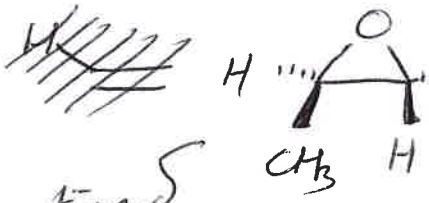
Stereochemistry in intramolecular rxn....

3) [§ 11.11] Asymmetric ~~epox~~ epoxide synthesis.
(i.e. synthesis of chiral expoxides that favors one enantiomer over the other).

Consider:

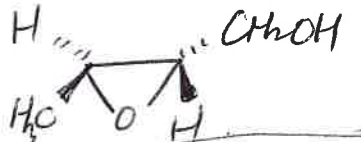


mCPBA →



enantiomers

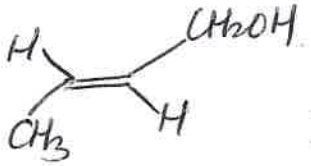
+



product is racemic

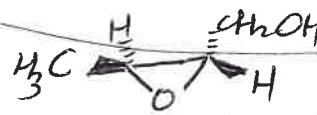
Sharpless epoxidation:

(~1980)



→OOH

$Ti(OiPr)_4$
CH_2Cl_2, (+)-DET



> 95% this enant.

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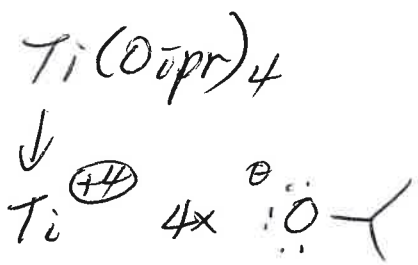
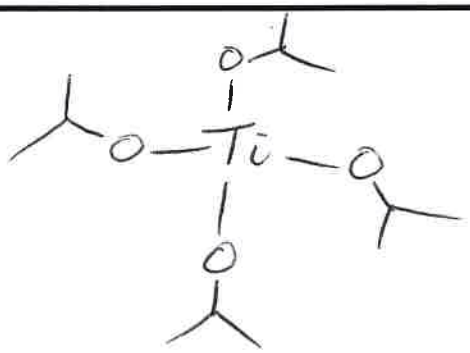
$Ti(OiPr)_4$





(+)-DET