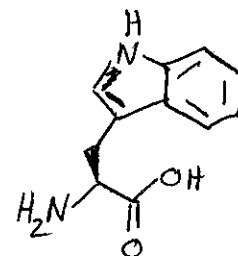
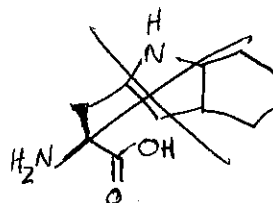
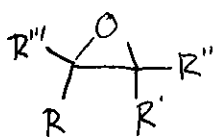


Course Chem 343 11 AM Lecturer Gellman
Day Wednesday Date 11/23/11
Notes Taken By Herndon Total # of Pages 5

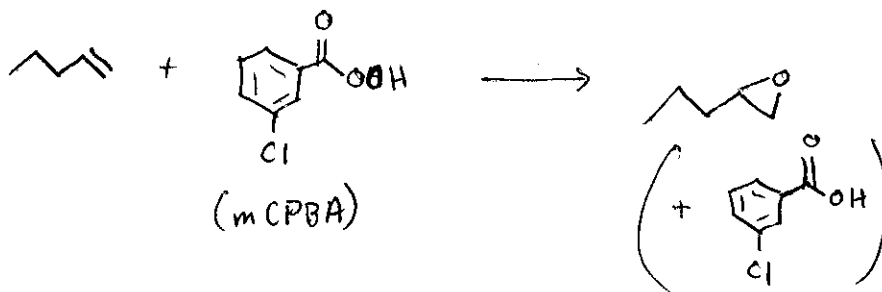
Submit a *Single-sided Copy* to the Office
DO NOT STAPLE

Recall: Epoxides...

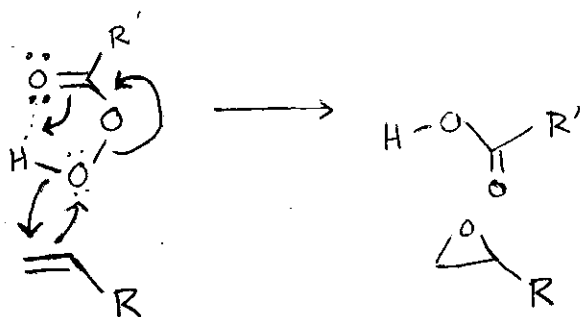


Synthesis...

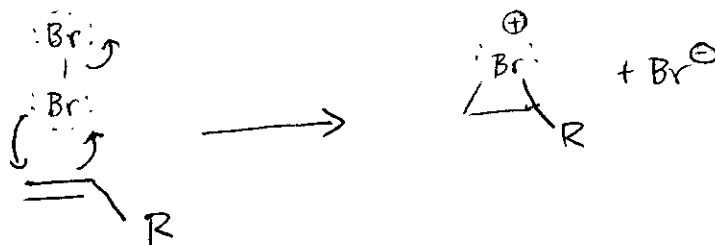
1) Peracid



Mechanism:

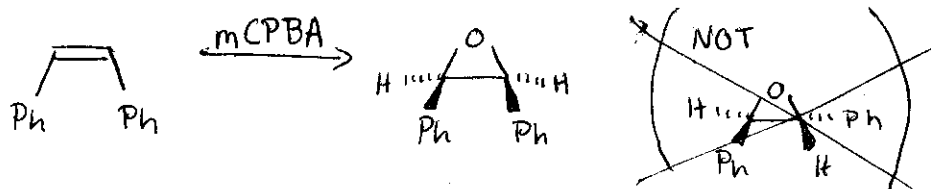


Recall:



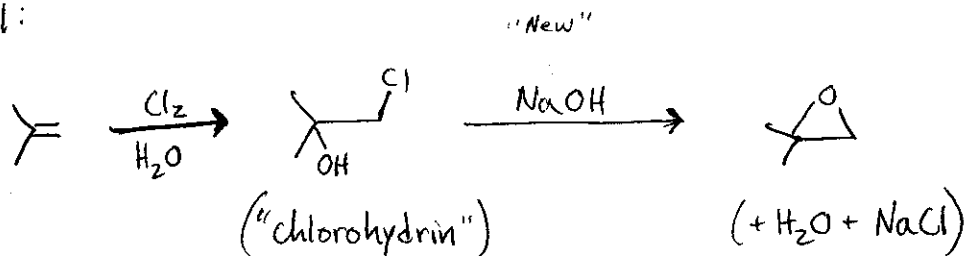
Submit a *Single-sided Copy* to the Office
 DO NOT STAPLE

Evidence for concerted mechanism from stereochemistry

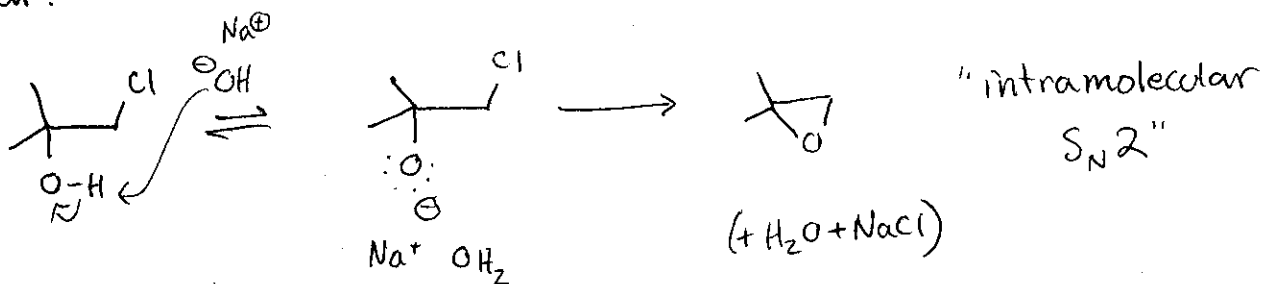


2) Cyclization of halohydrins

Recall:



Mech:

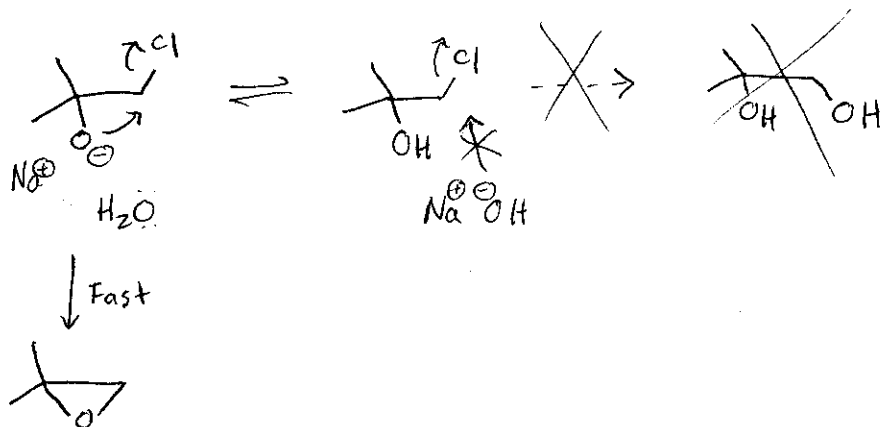


Recall: Williamson ether formation (ether via intermolecular S_N2)-
 need quantitative alkoxide formation

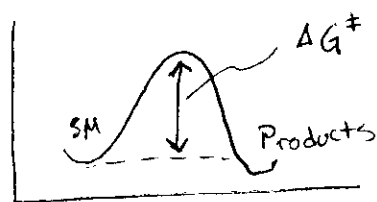
* NaOH OK for epoxide formation because of intrinsic advantage
 of this intramolecular reaction

Submit a *Single-sided Copy* to the Office
 DO NOT STAPLE

Consider:



"Reactivity" $\approx$ activation energies ($\Delta G^\ddagger$)

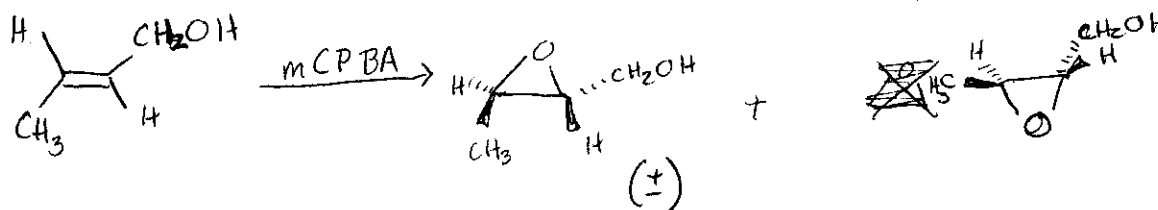


$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$$

$\downarrow$ enthalpy (of activation) $\downarrow$ entropy (of activation)

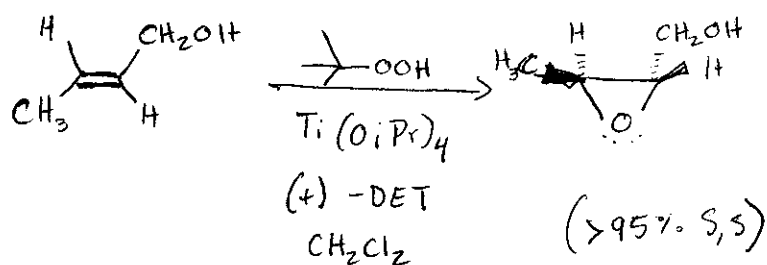
3) Asymmetric epoxide synthesis ("Sharpless epoxidation")

$\downarrow$
 form one enantiomer in preference to the other



Submit a *Single-sided Copy* to the Office
 DO NOT STAPLE

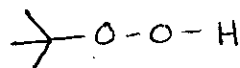
Sharpless:



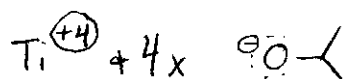
Comments

1) Oxidant

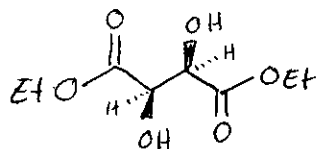
"t-butyl hydroperoxide"



2) Ti(OiPr)_4



3) (+)-DET single enantiomer of chiral molecule



Note: (-)-DET (you fill in) readily accessible

Mechanism? Source of enantioselectivity?

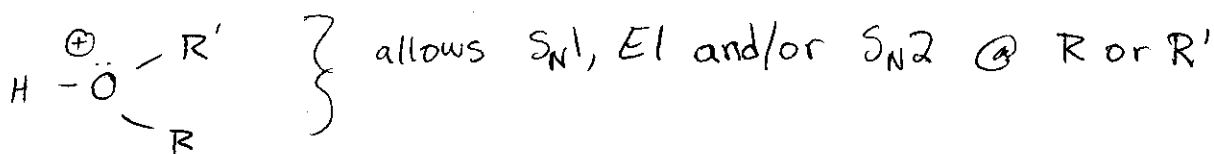
You fill in if you can....

Submit a *Single-sided Copy* to the Office
 DO NOT STAPLE

Reactions of Ethers ($R-O-R'$)

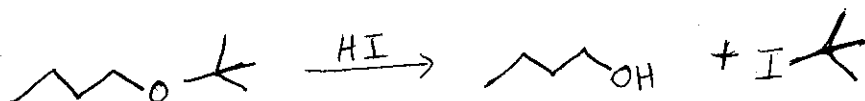
→ ethers are in general fairly unreactive

However, subject to elimination and/or substitution in presence of strong acids

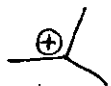


($pK_a \sim -2$)

See pp 492-495. One example:



Rxn occurs via



Rxns of epoxides (unusually reactive) - more reactive than most ethers because of ring strain

1) S_N2 rxn w/ alkoxides (+ other nucleophiles)

