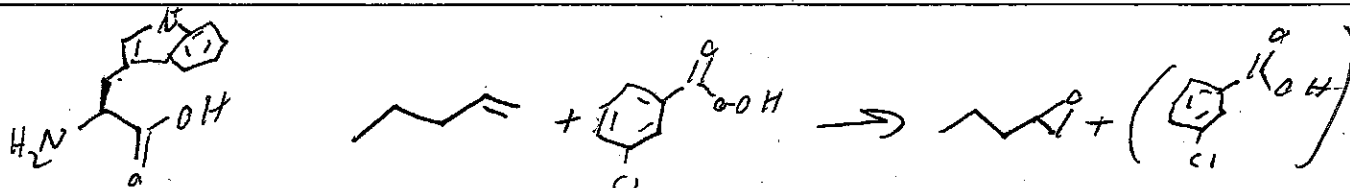
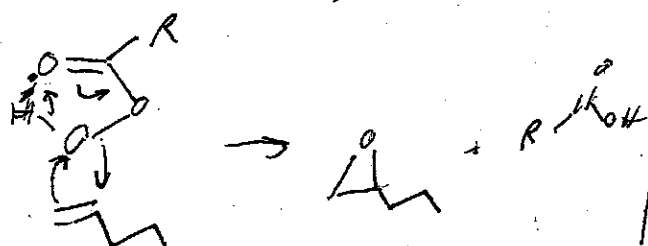


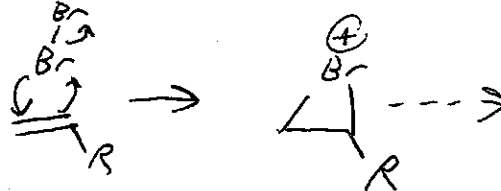
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Mechanism (concerted)

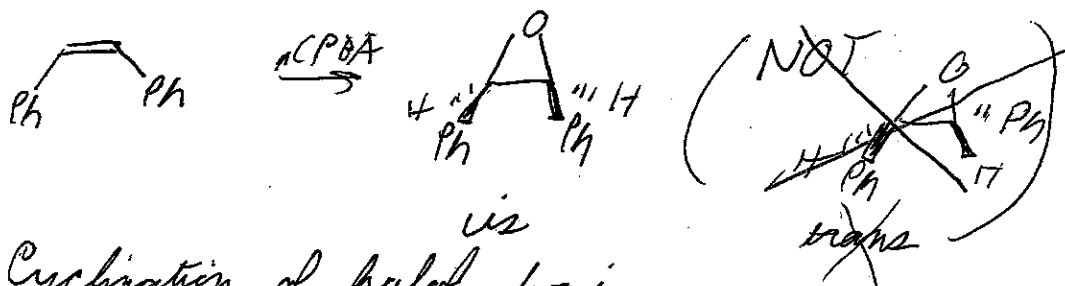


Recall:

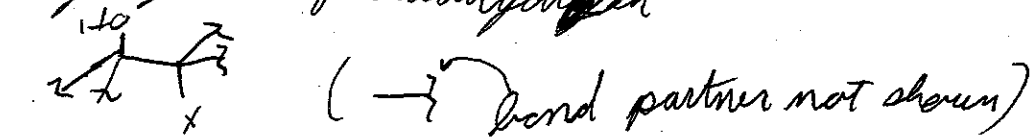


Evidence for concerted mechanism from stereochemistry

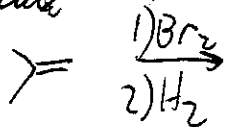
ex



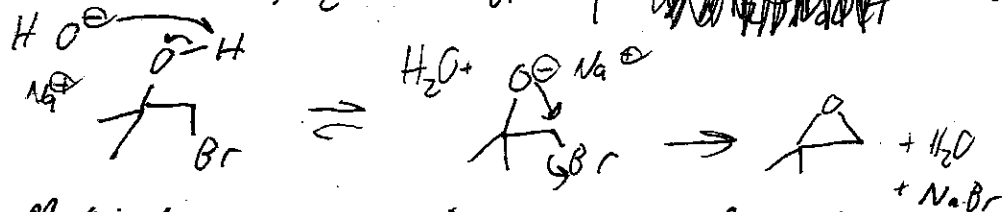
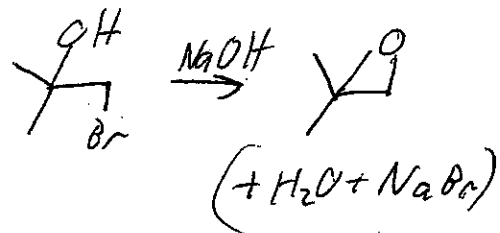
2) Cyclization of halohydrin



Recall:

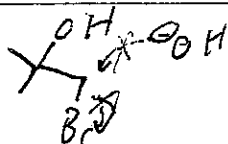


New:



Note: do not require a strong base (like NaH) for this intramolecular SN2. Taking advantage of intrinsic reactivity edge of internal nucleophile.

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Intramolecular: Common observation on
3-6 membered rings

Reactivity $\approx$ activation energy



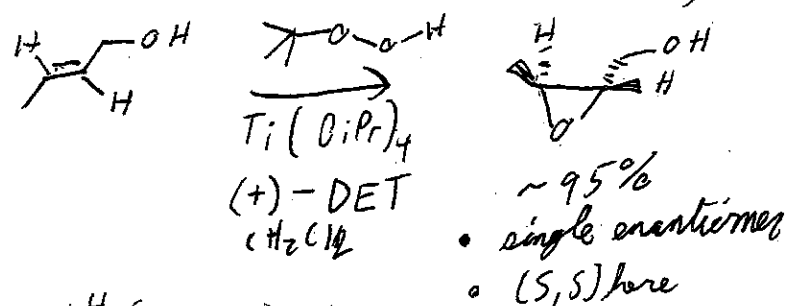
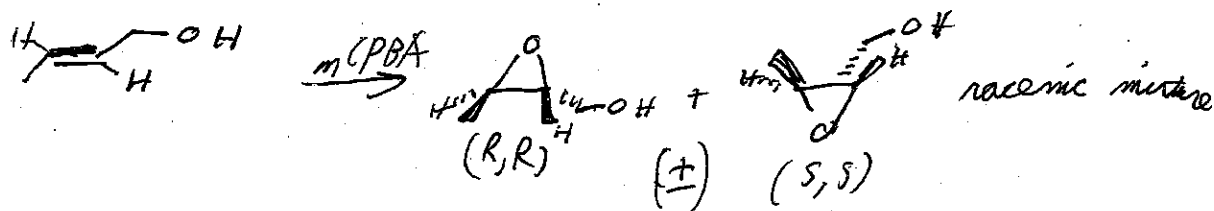
$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

enthalpy (of activation)

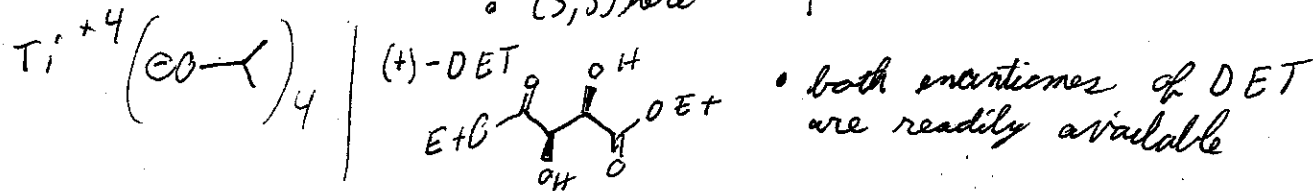
entropy (of activation)

3) Sharpless Epoxidation

Predict



Note
1) oxidant is TB_4OOH
~~tert-butyl hydroperoxide~~ (tert-butyl hydroperoxide)



source of chirality - turns achiral S_{on} into chiral product

Mechanism?

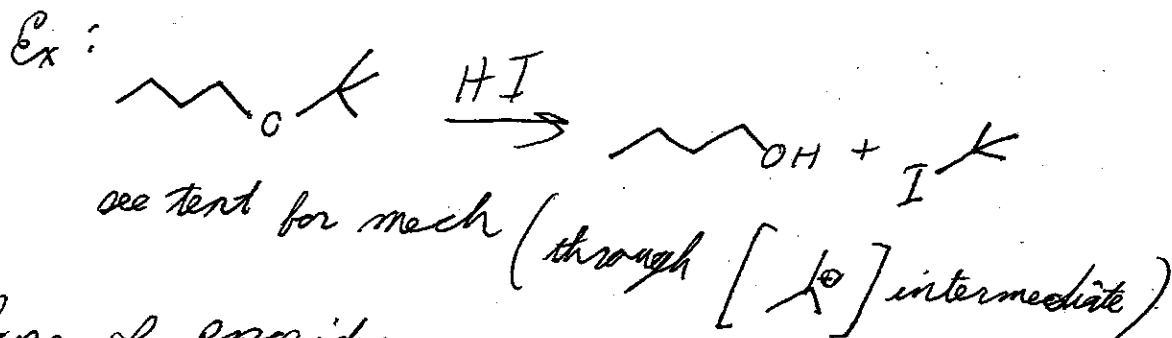
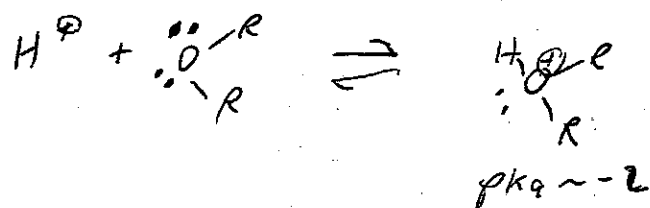
- not completely understood; coordination of Ti to ~~alcohol~~ ^{alcohol} ~~hydroperoxide~~
- see text for picture of proposed transition state

Course CHEM 343 Lecturer Gellman
Day Wed 1:20 PM Date 11/24/11
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Rxns of ethers

- Most ethers are not reactive under most conditions
- However, strongly acidic conditions promote substitution &/or elimination rxns ($E1$, S_N1 , or S_N2)
- see pp 452-455



Rxns of epoxides

More possibilities b/c of ring strain