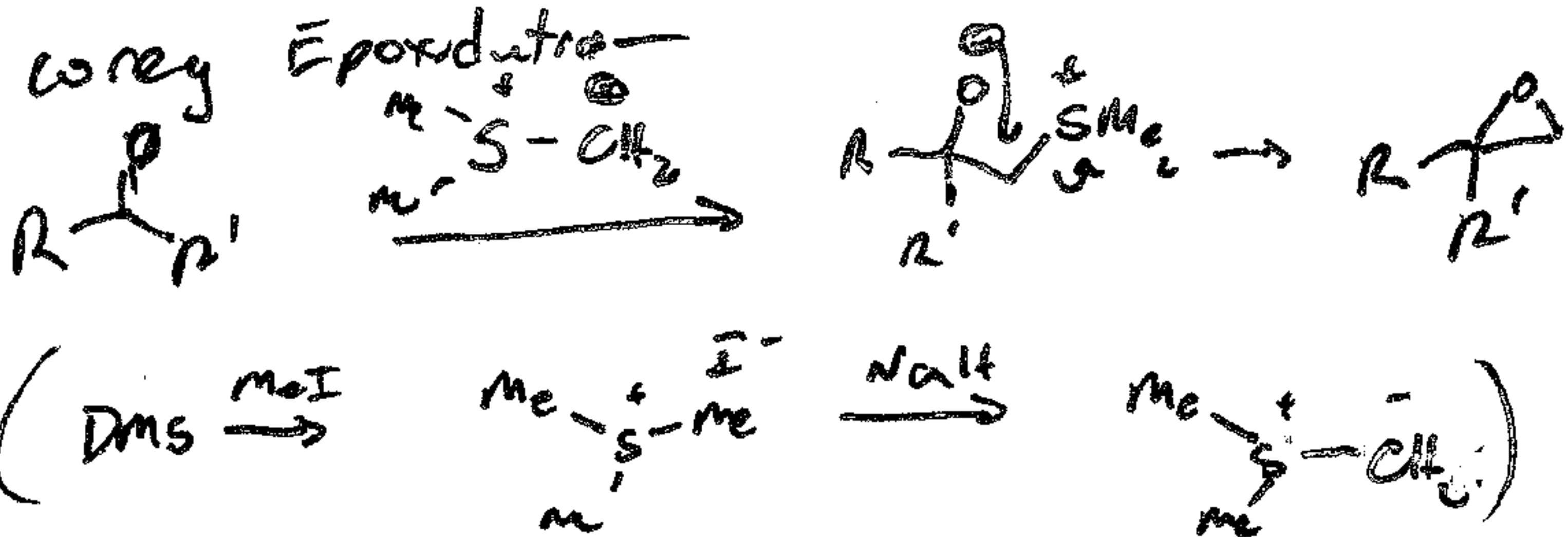
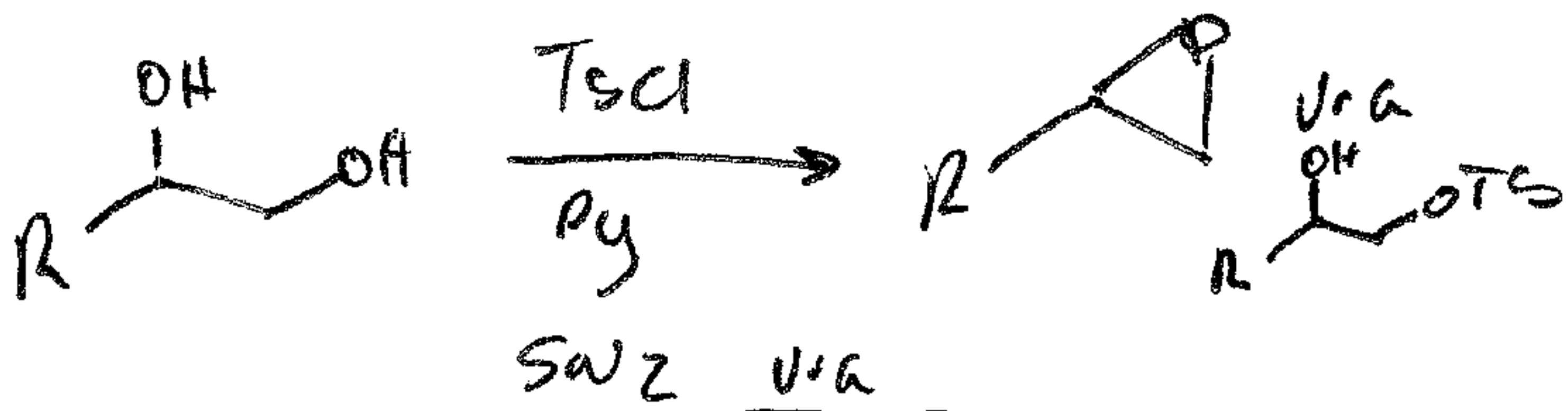


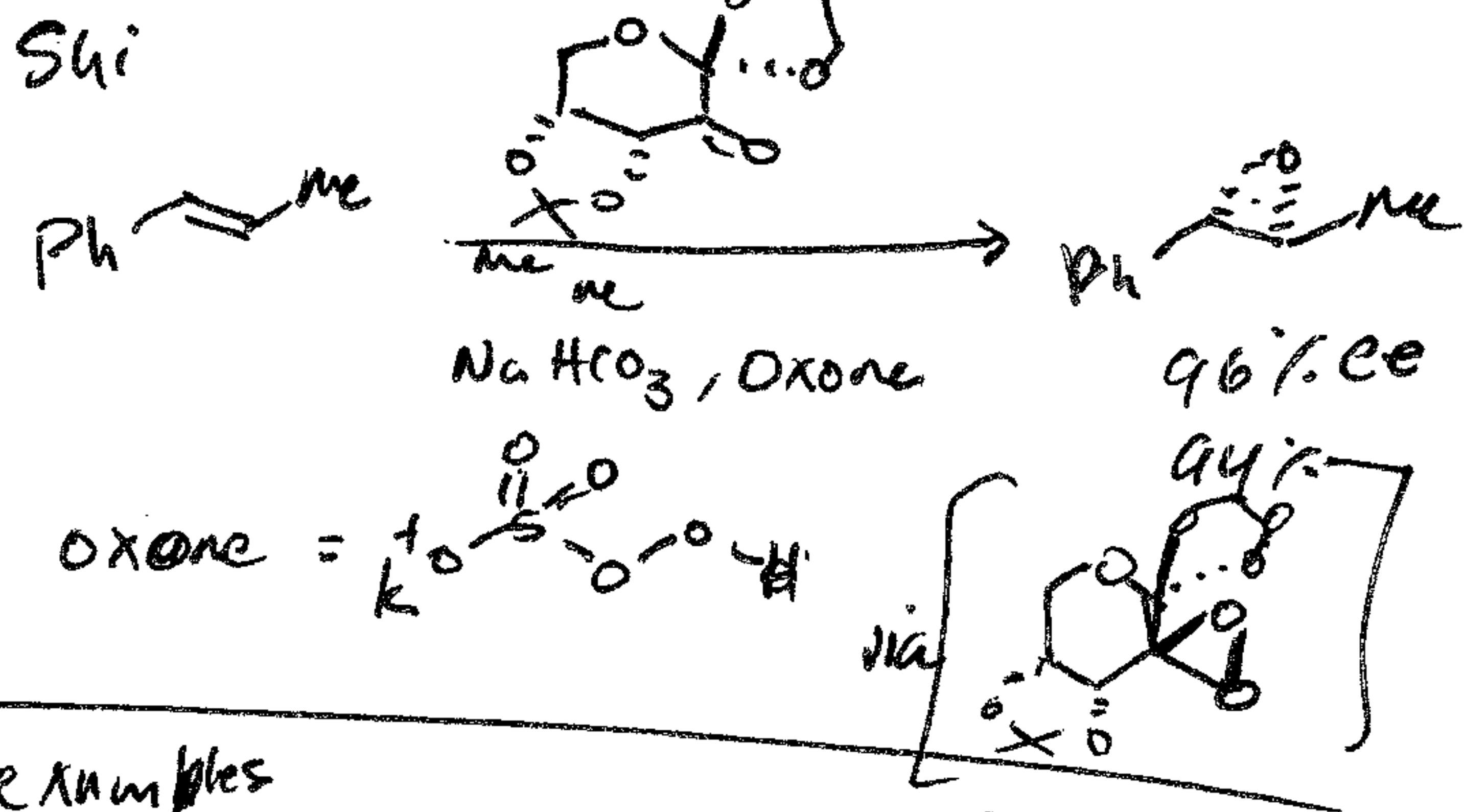
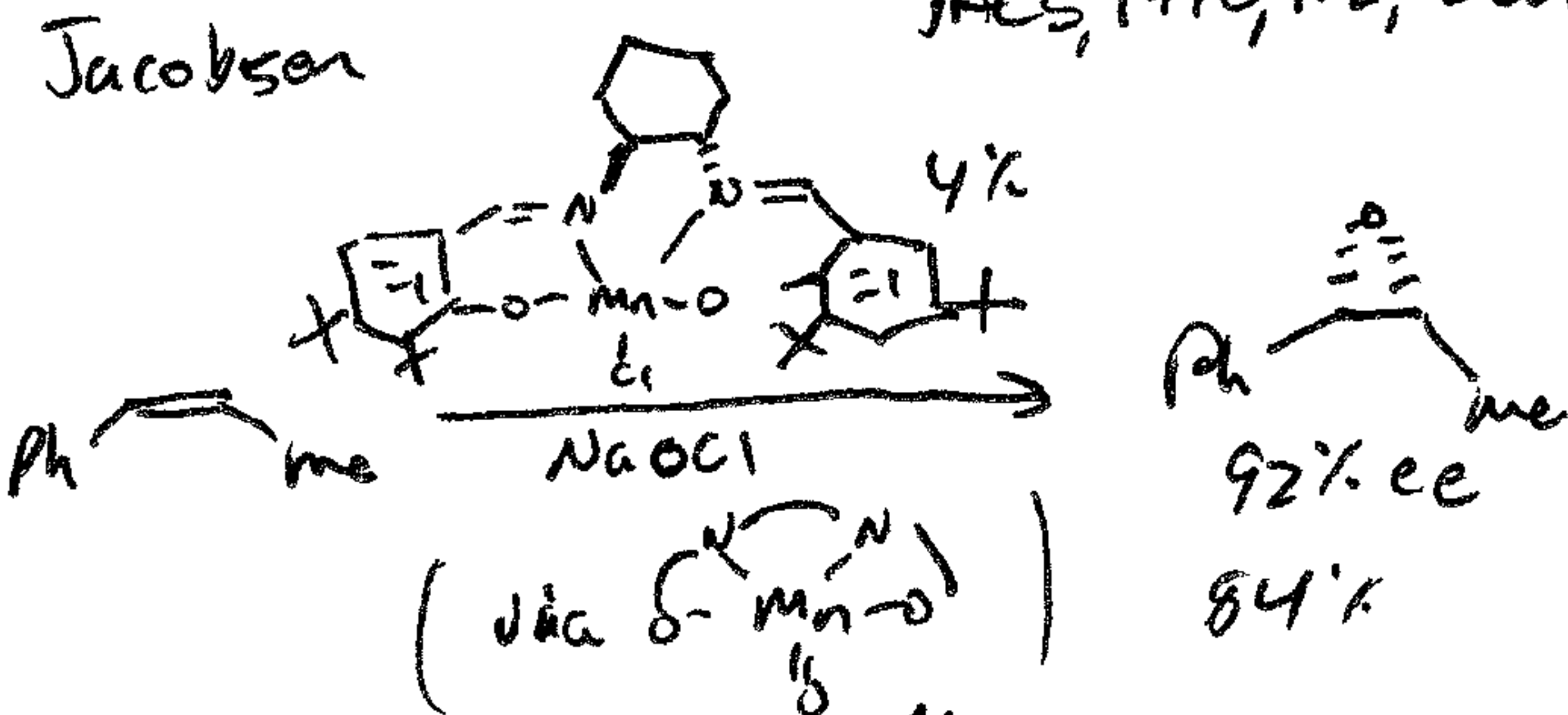
Strained Rings

Epoxides - Recall previously discussed alkene epoxidation




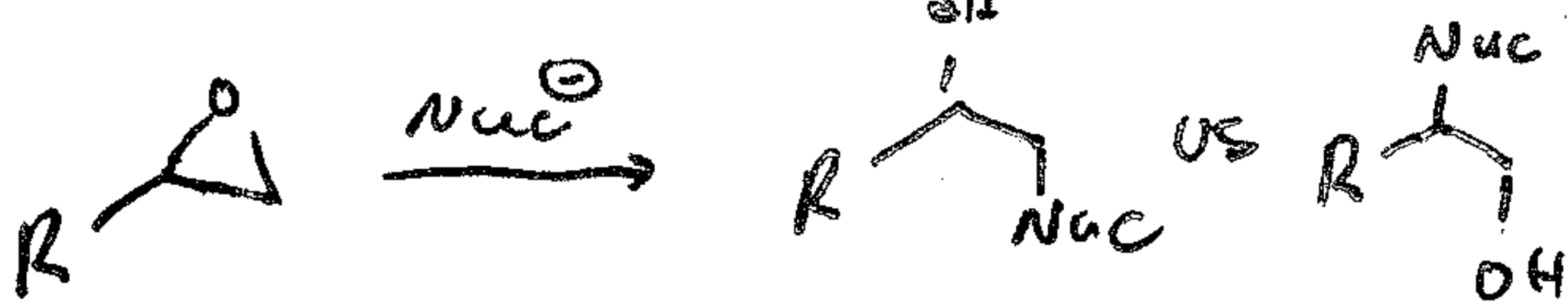
Other Enantioselective Epoxidations

JACS, 1990, 112, 2801

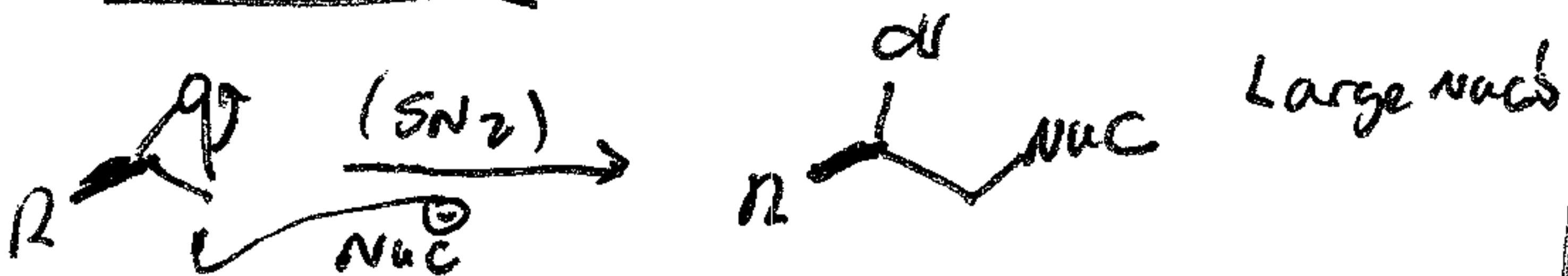


Epoxide Ring Opening

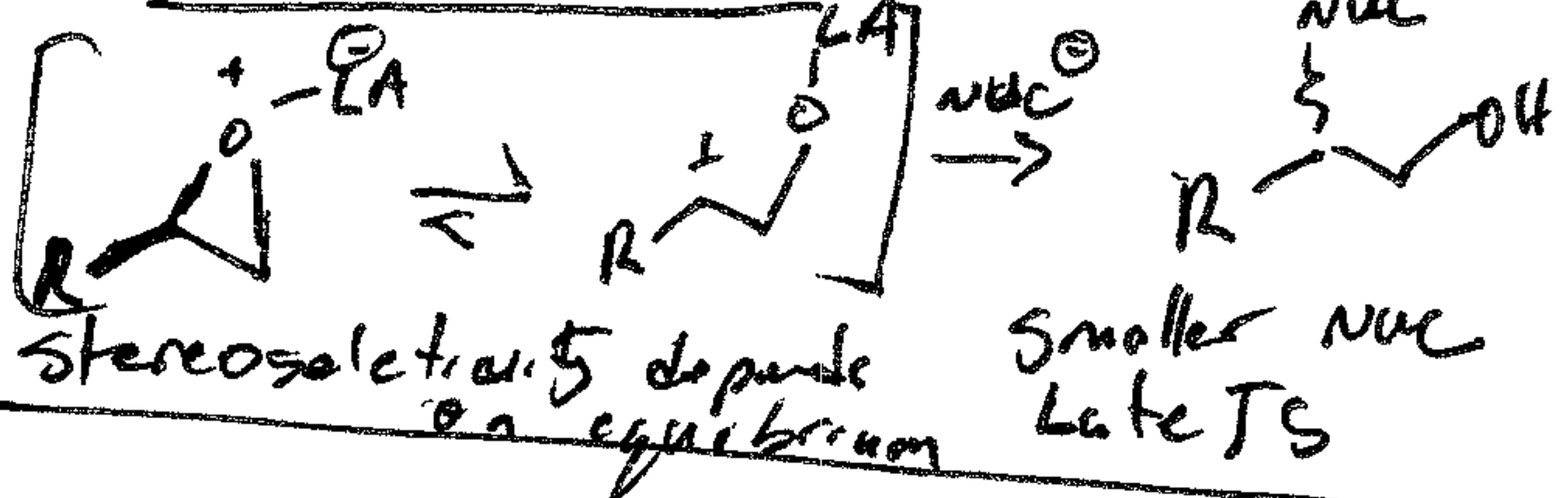
 Ring strain = great LG.



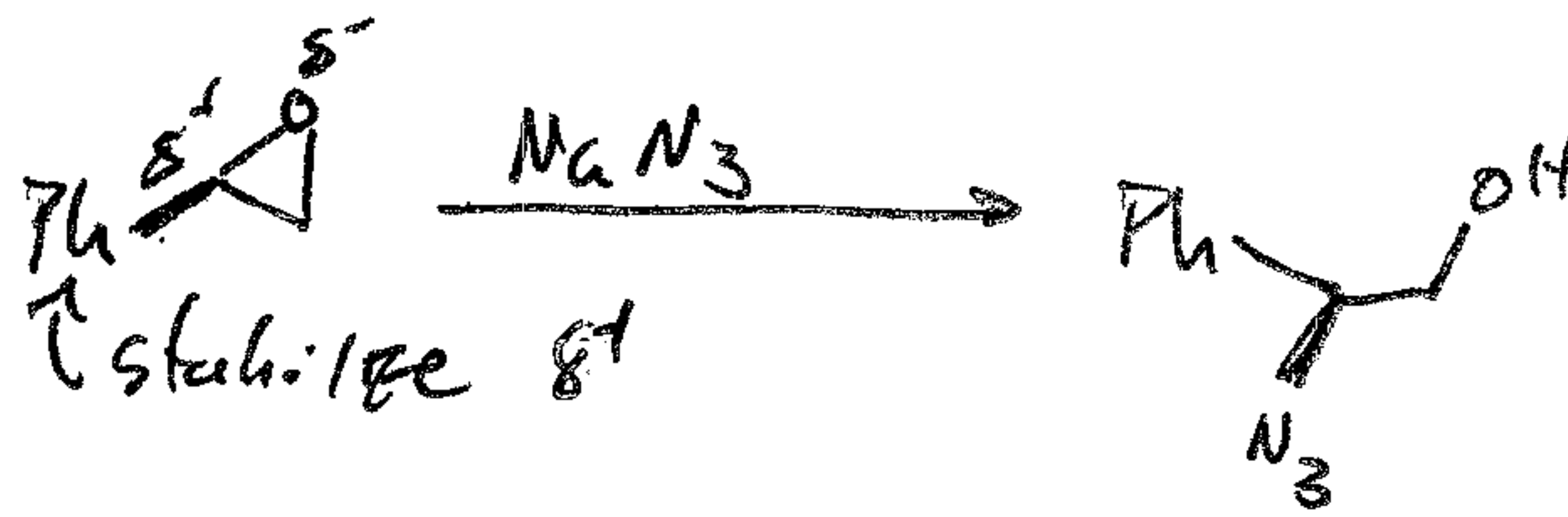
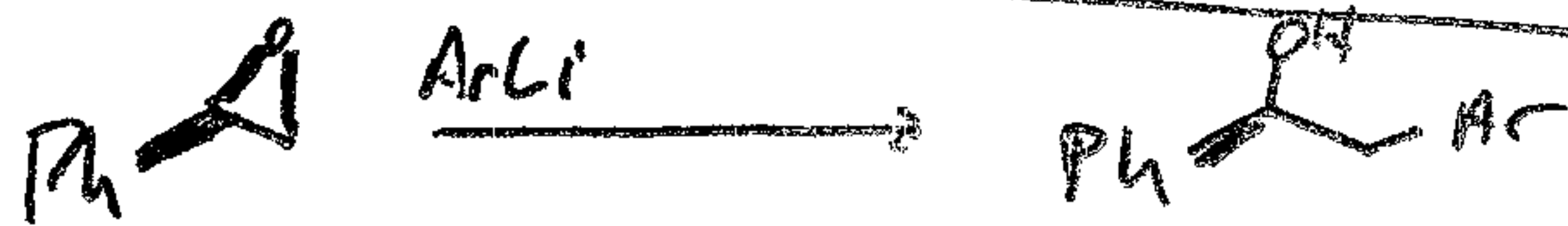
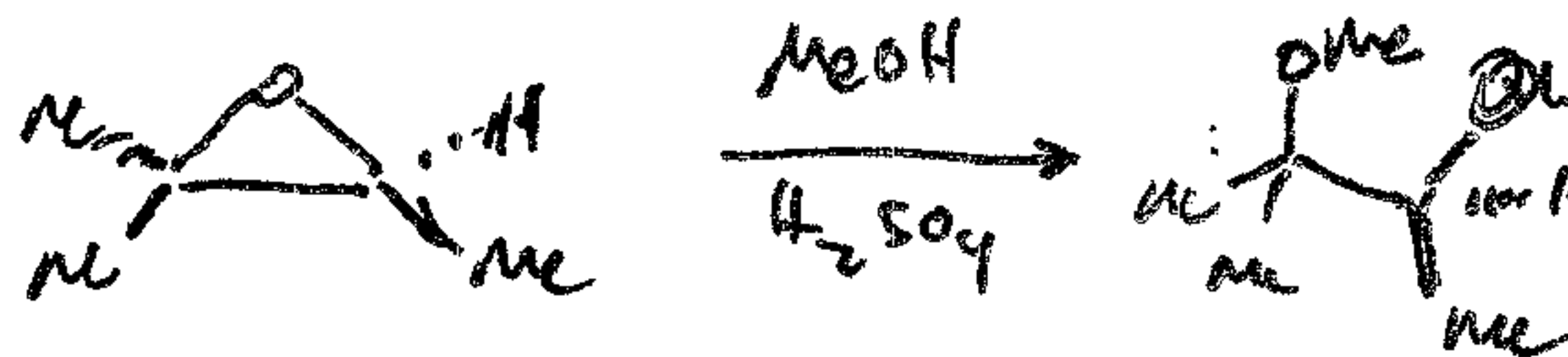
steric control



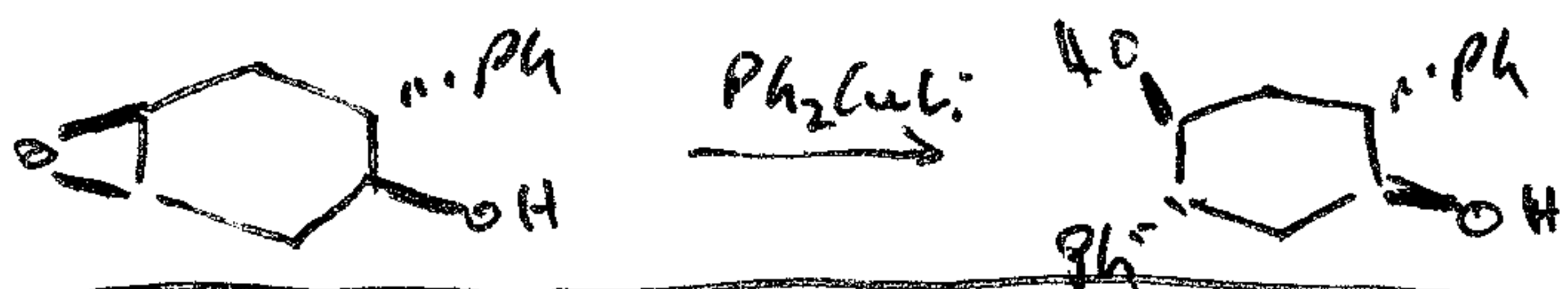
Electronic control



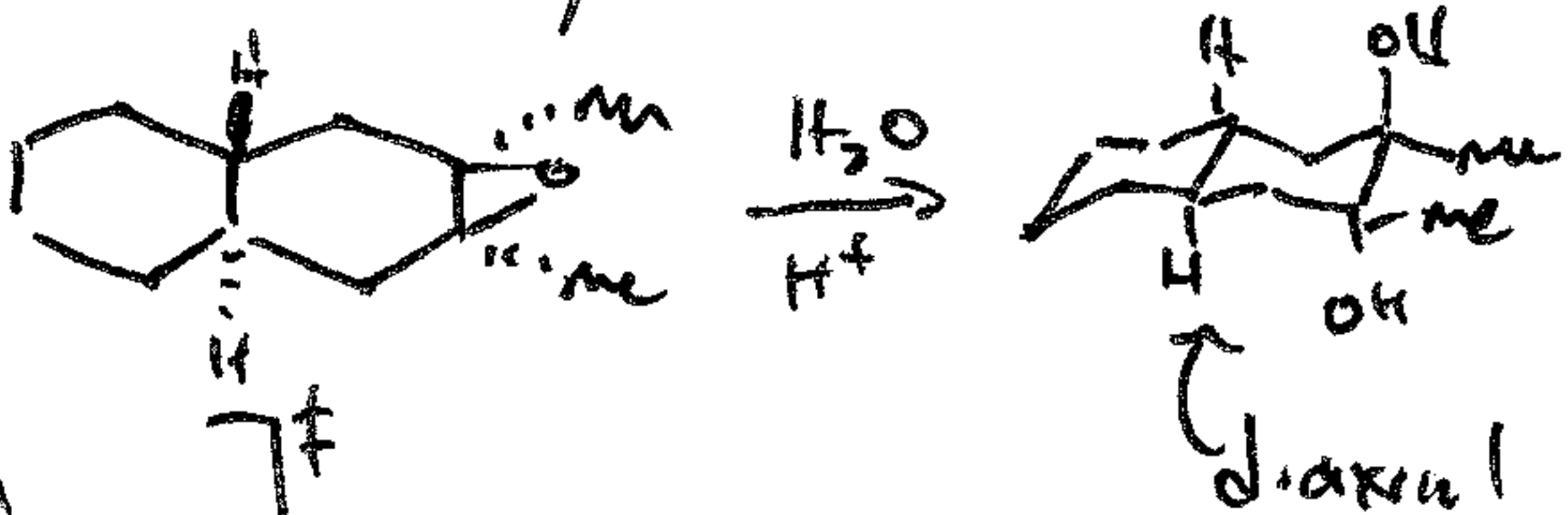
Examples



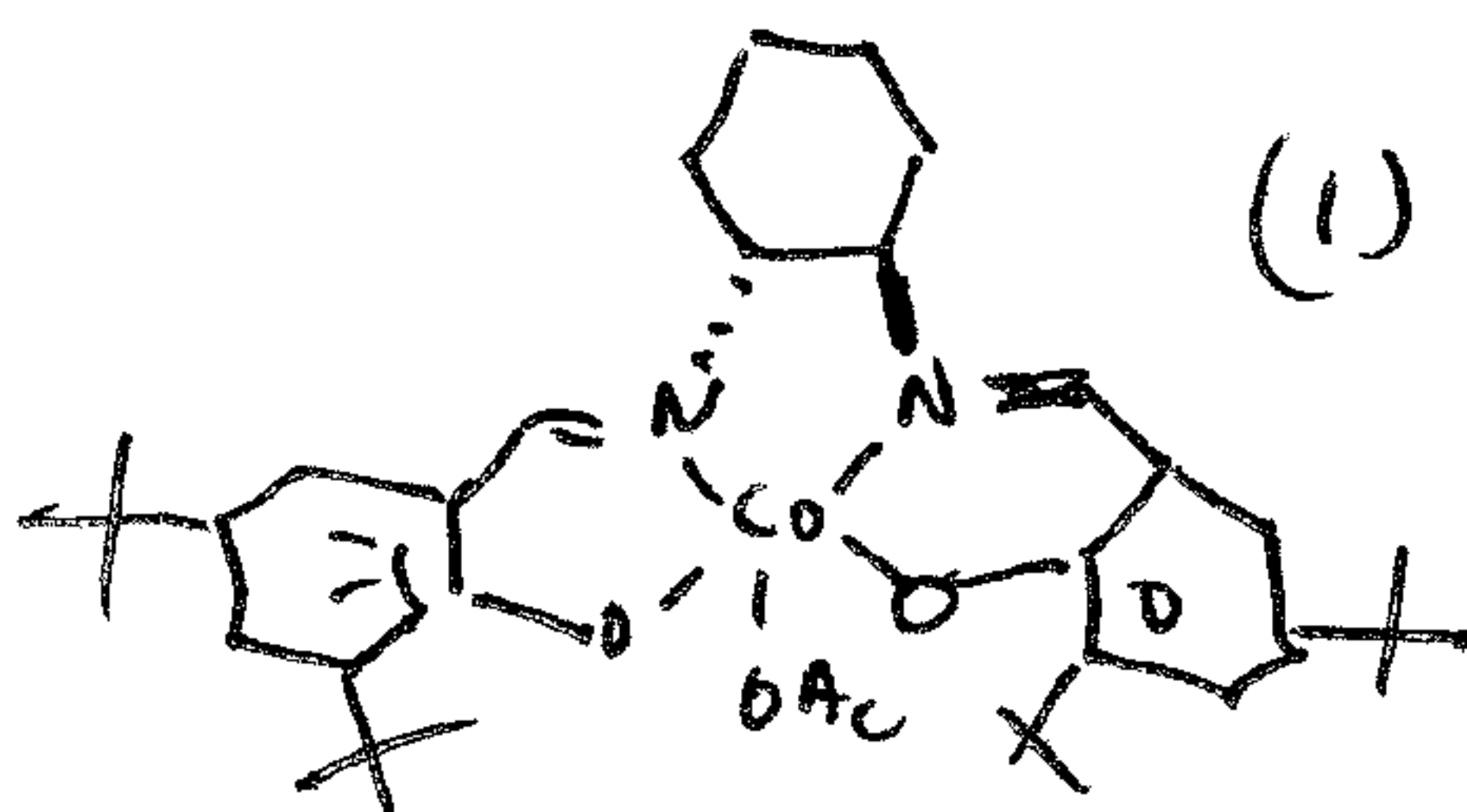
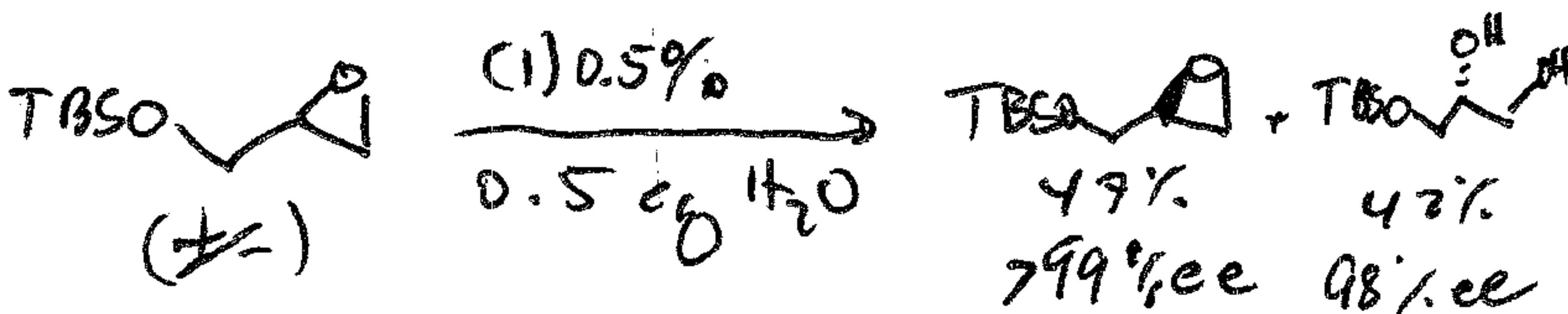
Organocuprates also good nuc



stereocontrol cyclohexene oxides

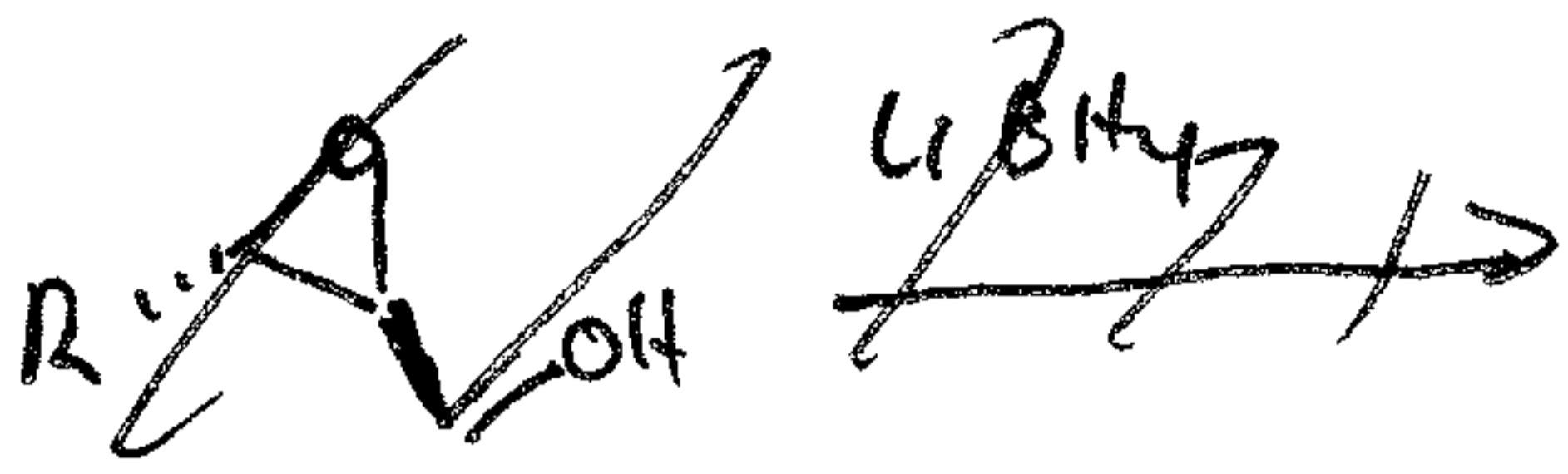


Jacobsen - HKR Science, 1997, 277, 936



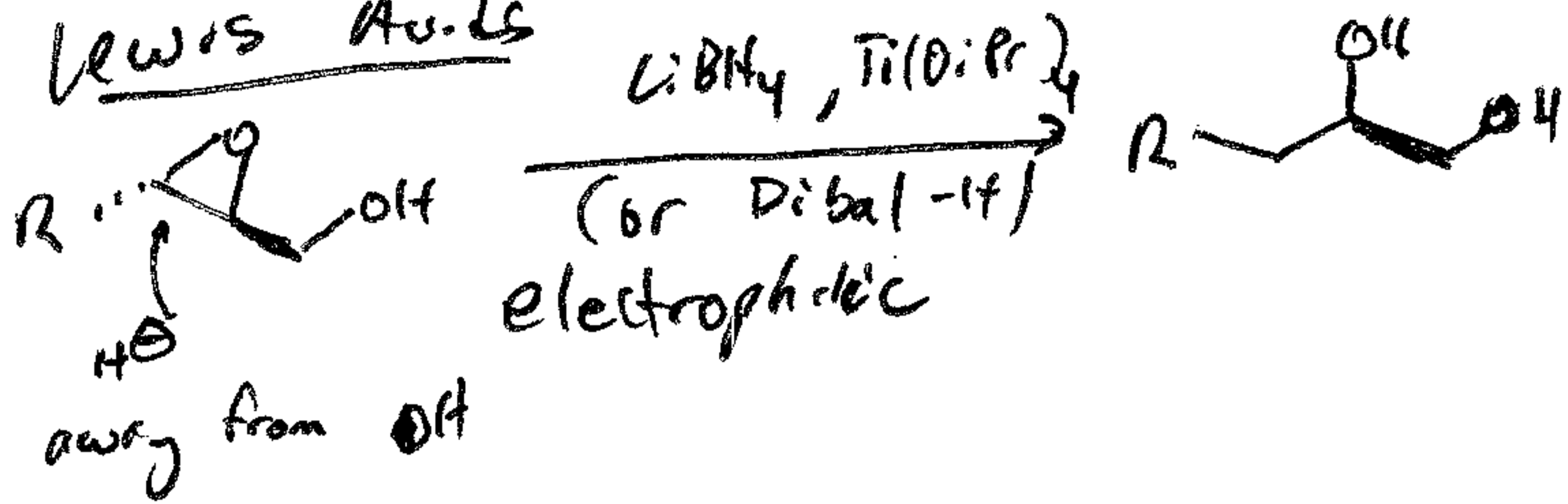
1ent reacts faster than the other

Epoxide Reduction

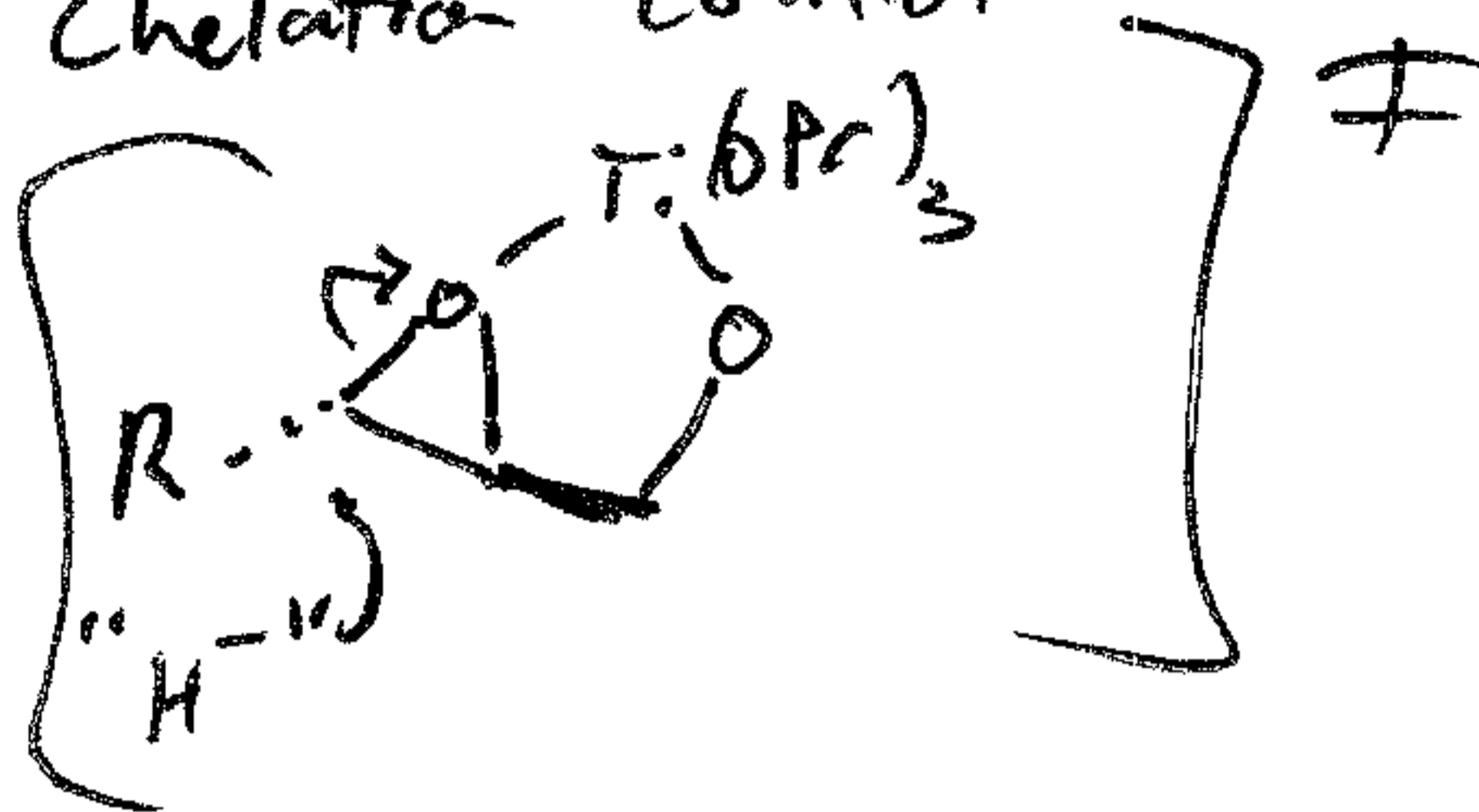


Allylic alcohols

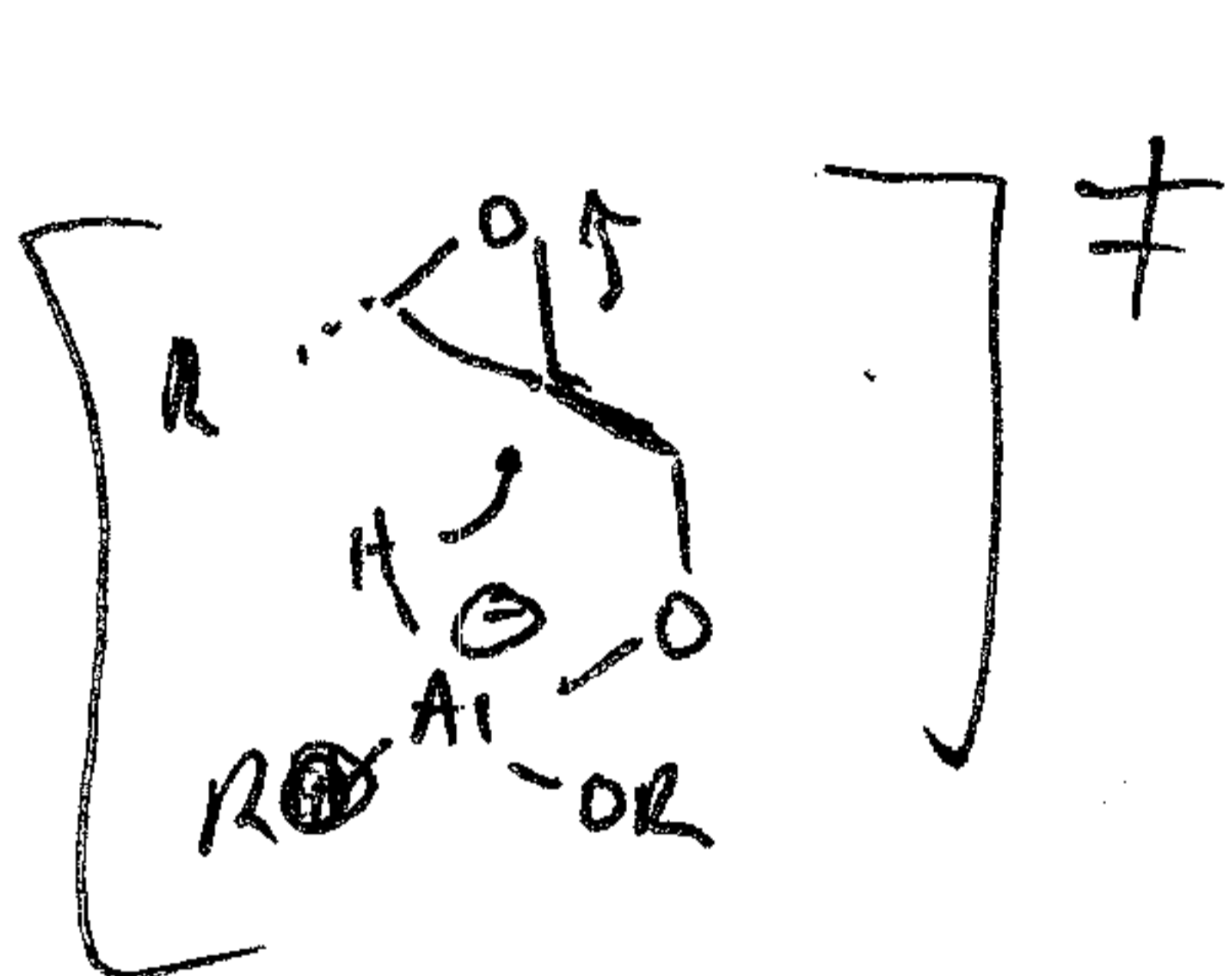
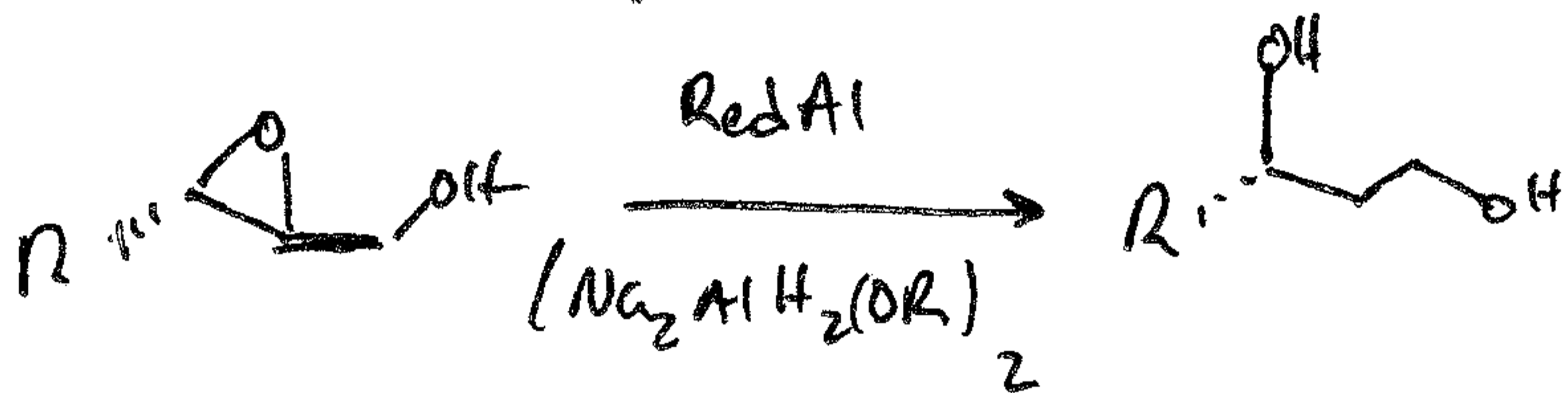
Lewis Acids



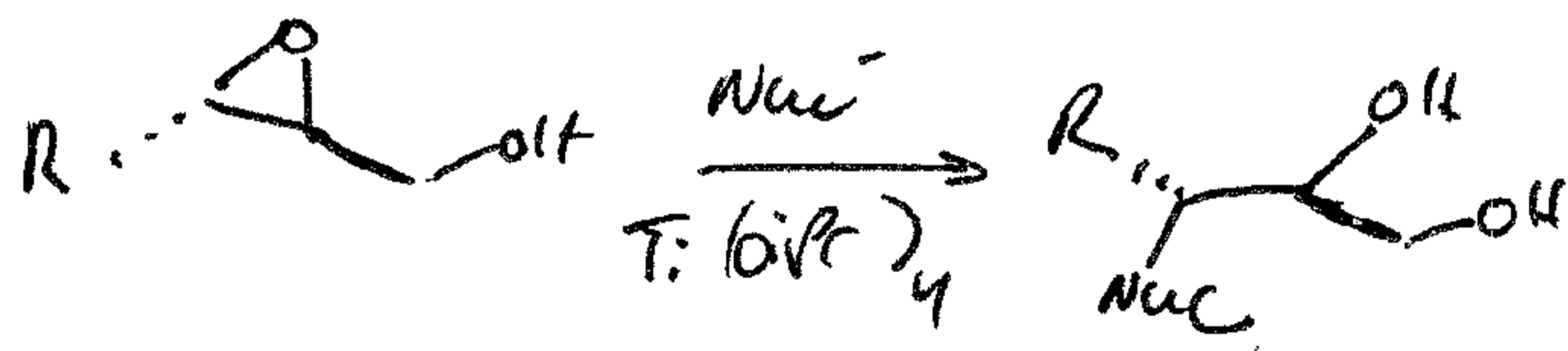
Chelation Control



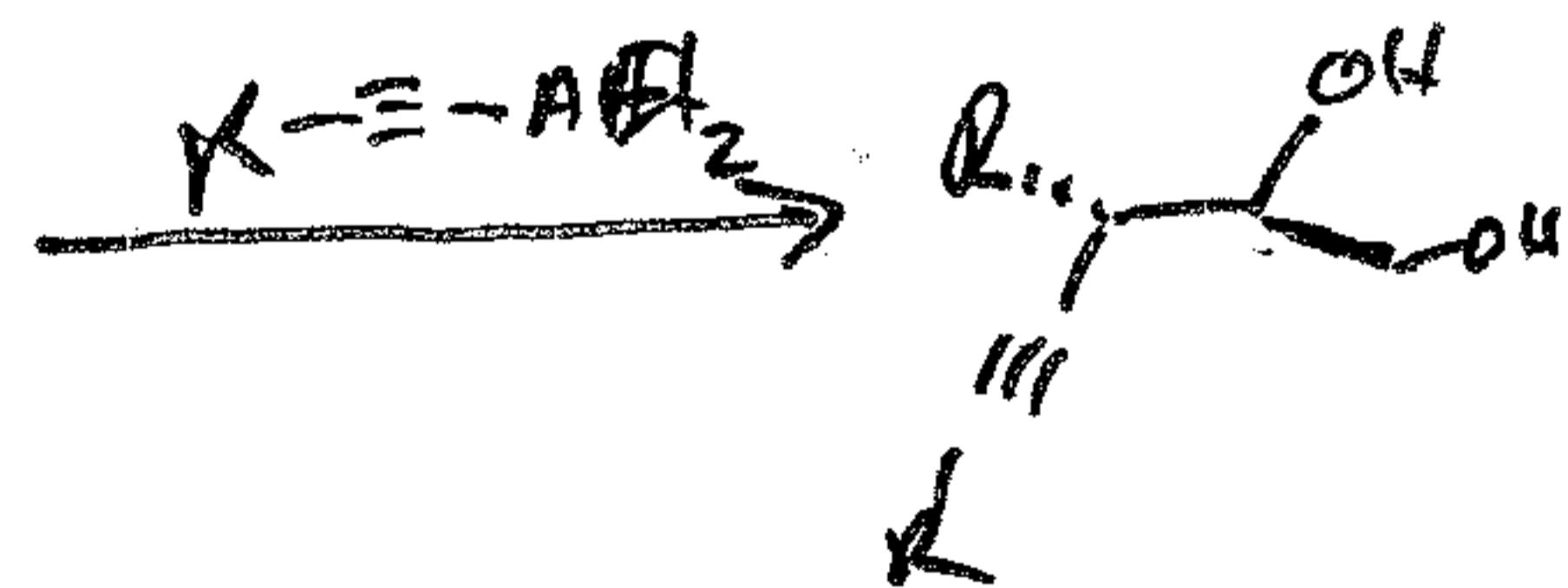
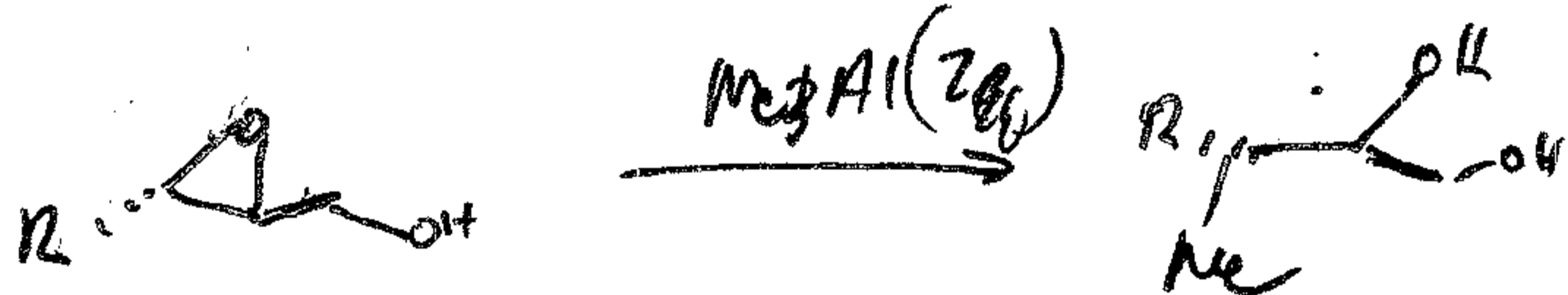
Internal Delivery



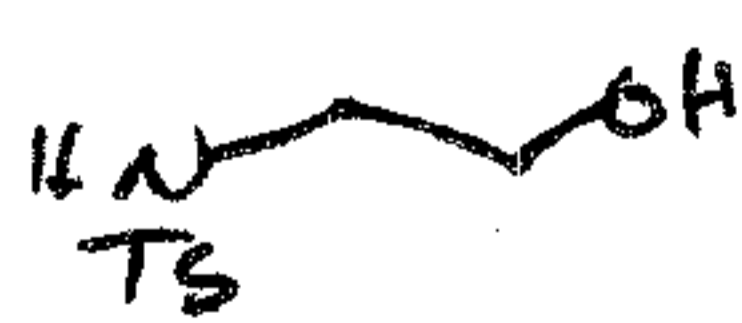
Similar w/ other nucleos



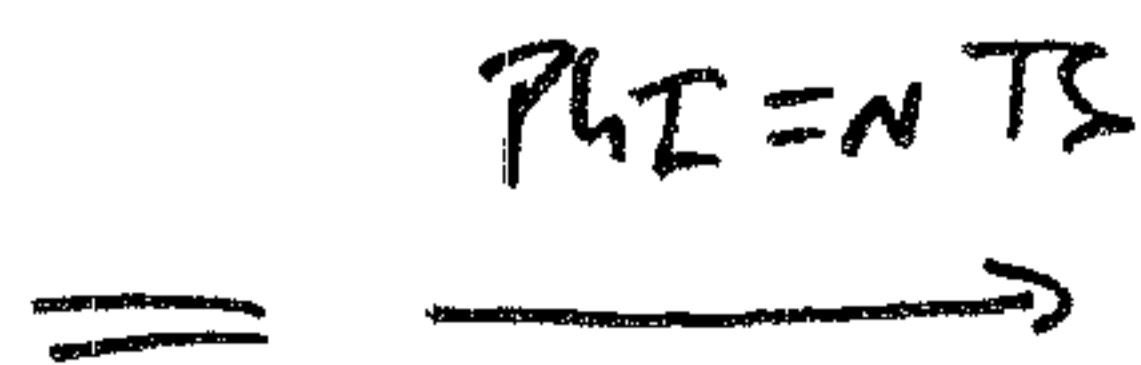
Carbon-Nucleos



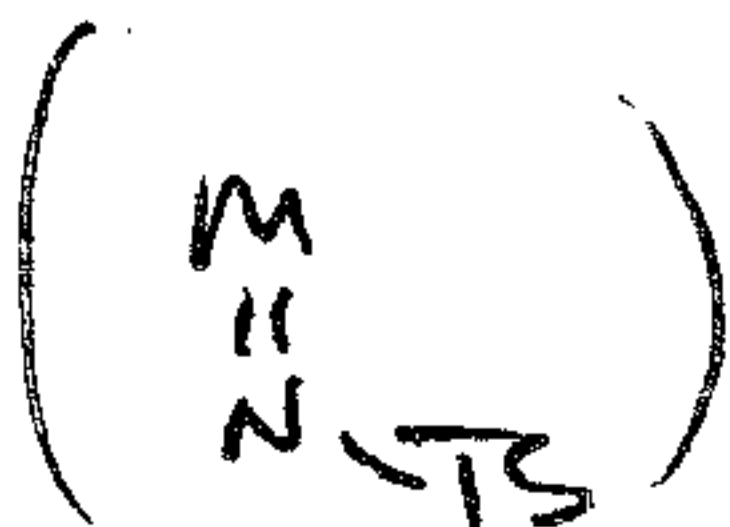
Azidines (generally less useful than epoxides)



EWG generally required for ring-opening



(can be chiral)

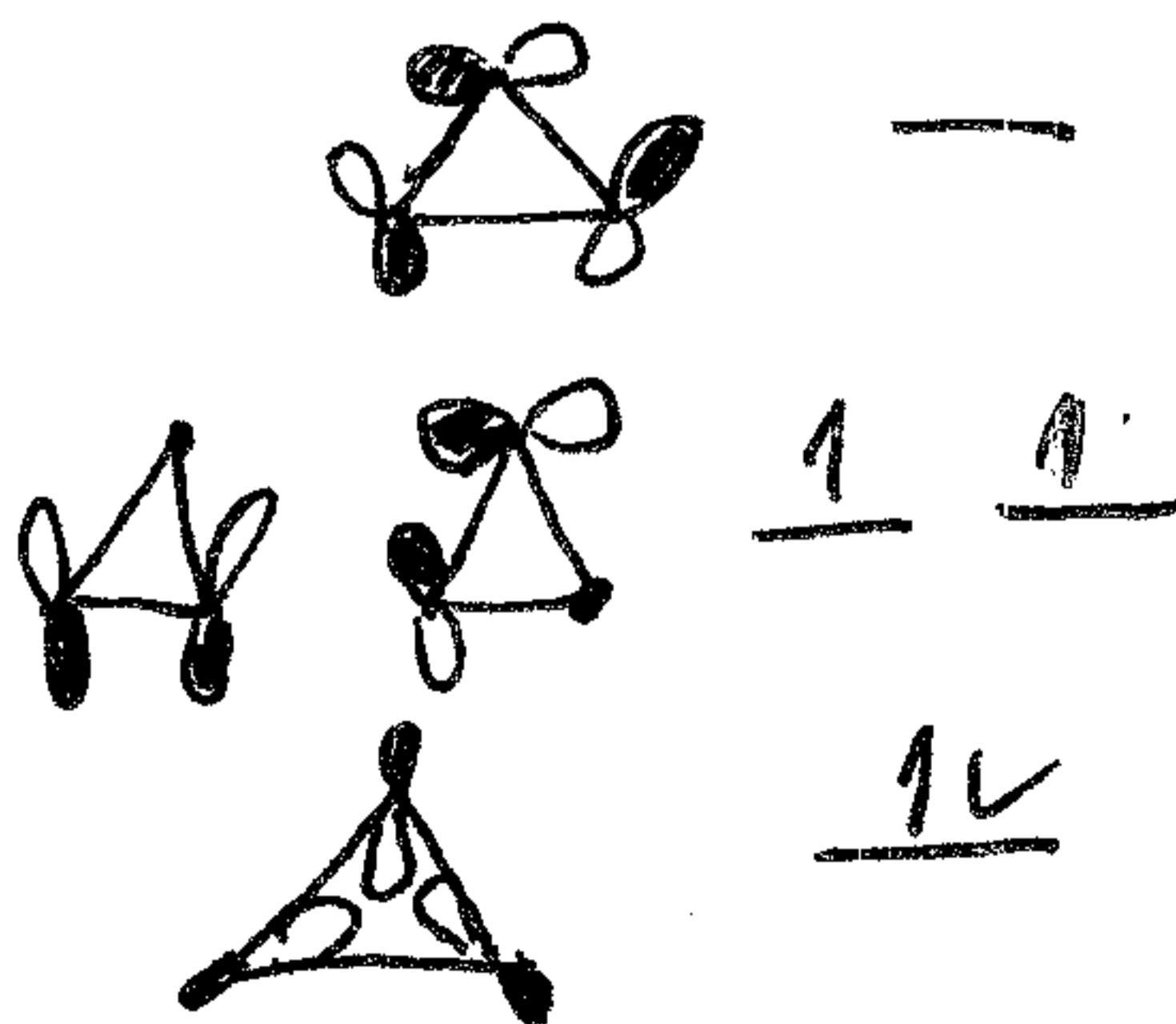


Evans, 1994, 116, 2742

Cyclopropanes

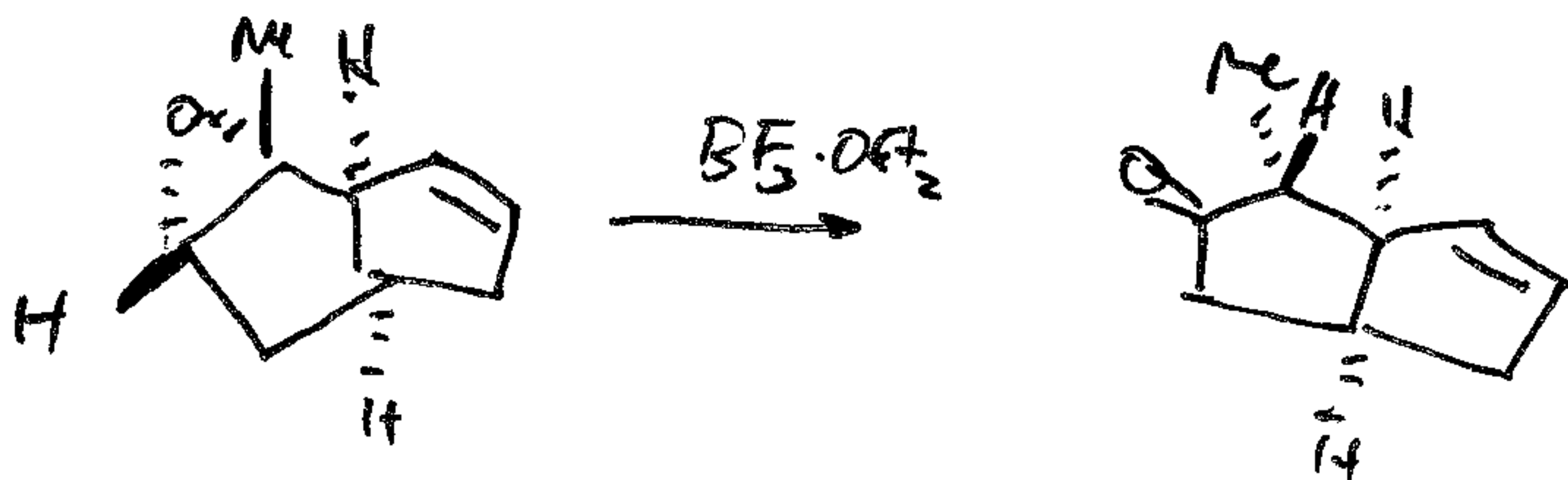
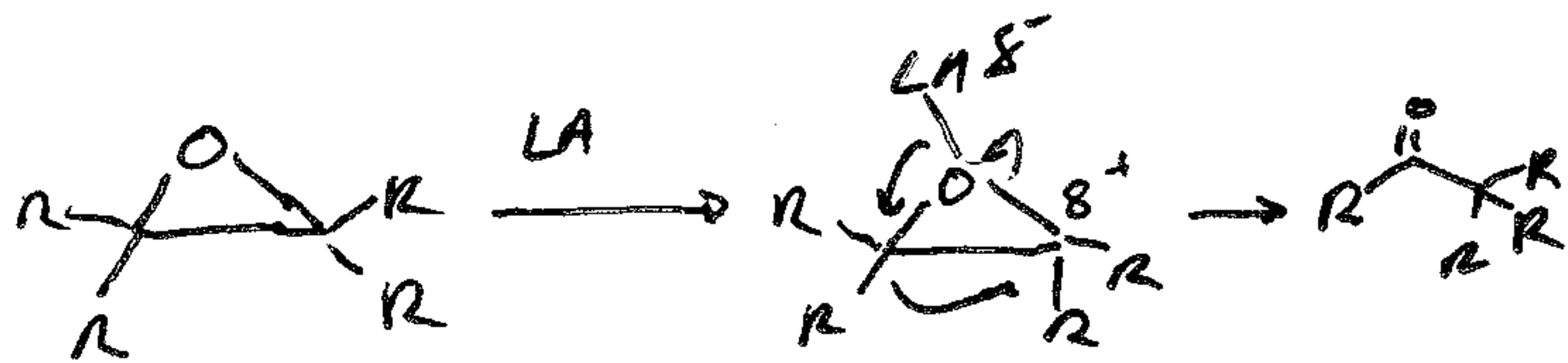
walsh orbitals

27 kcal/mol ring strain

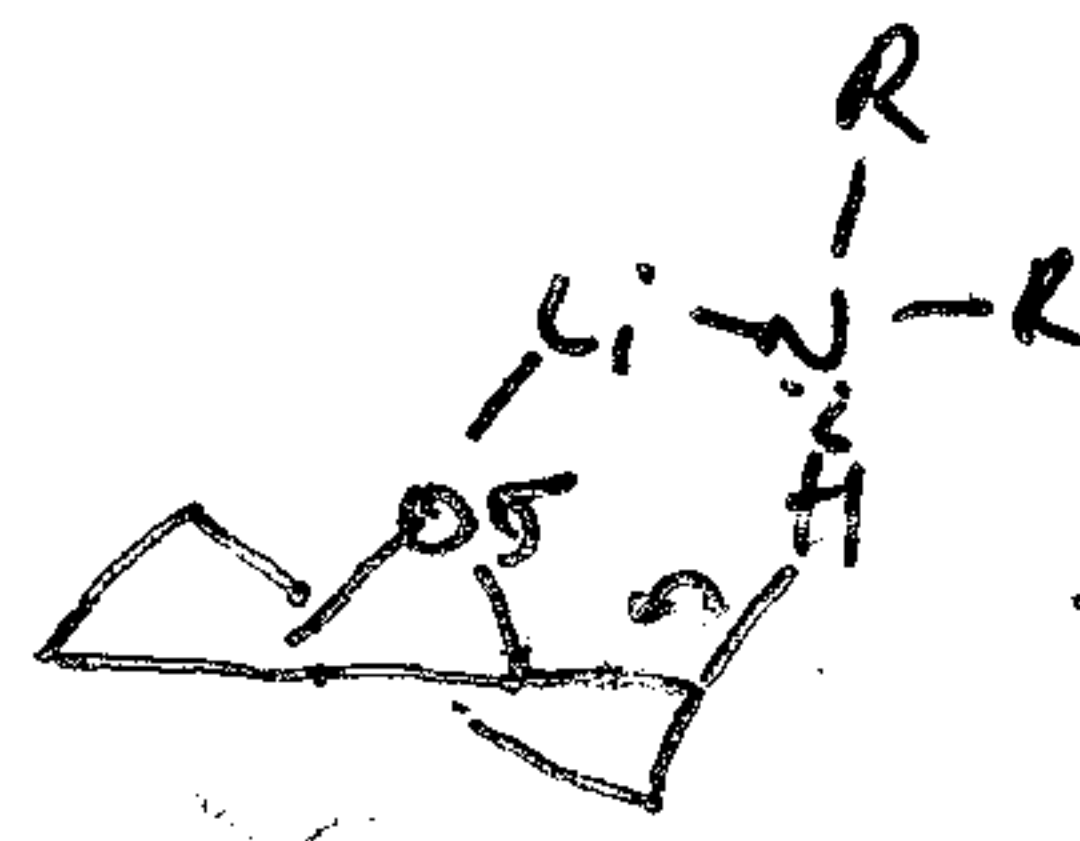
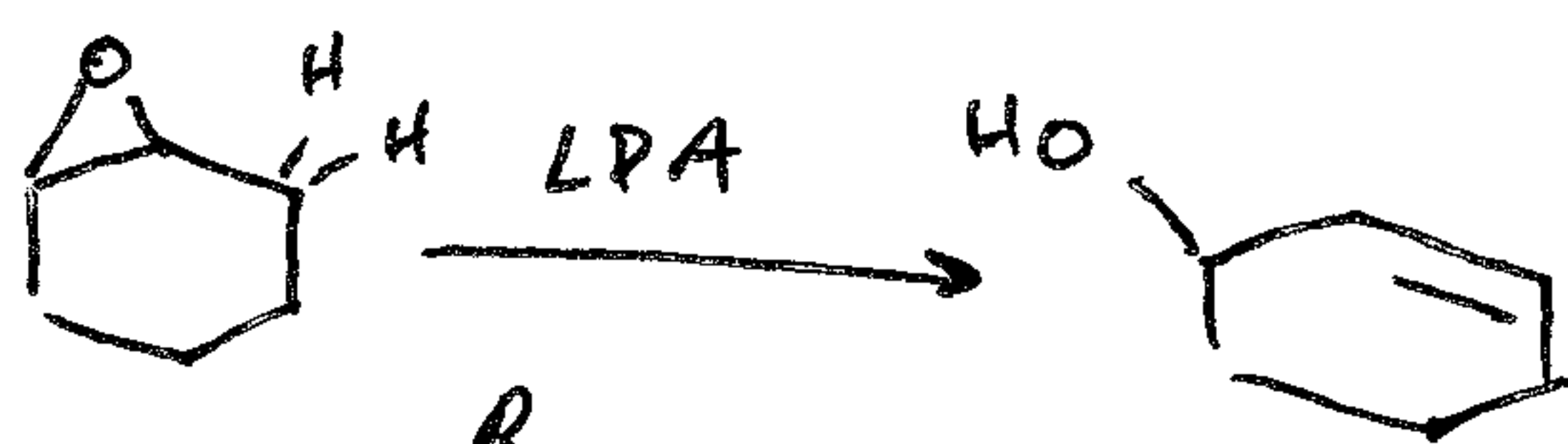


σ bond have π character

Epoxide Rearrangements

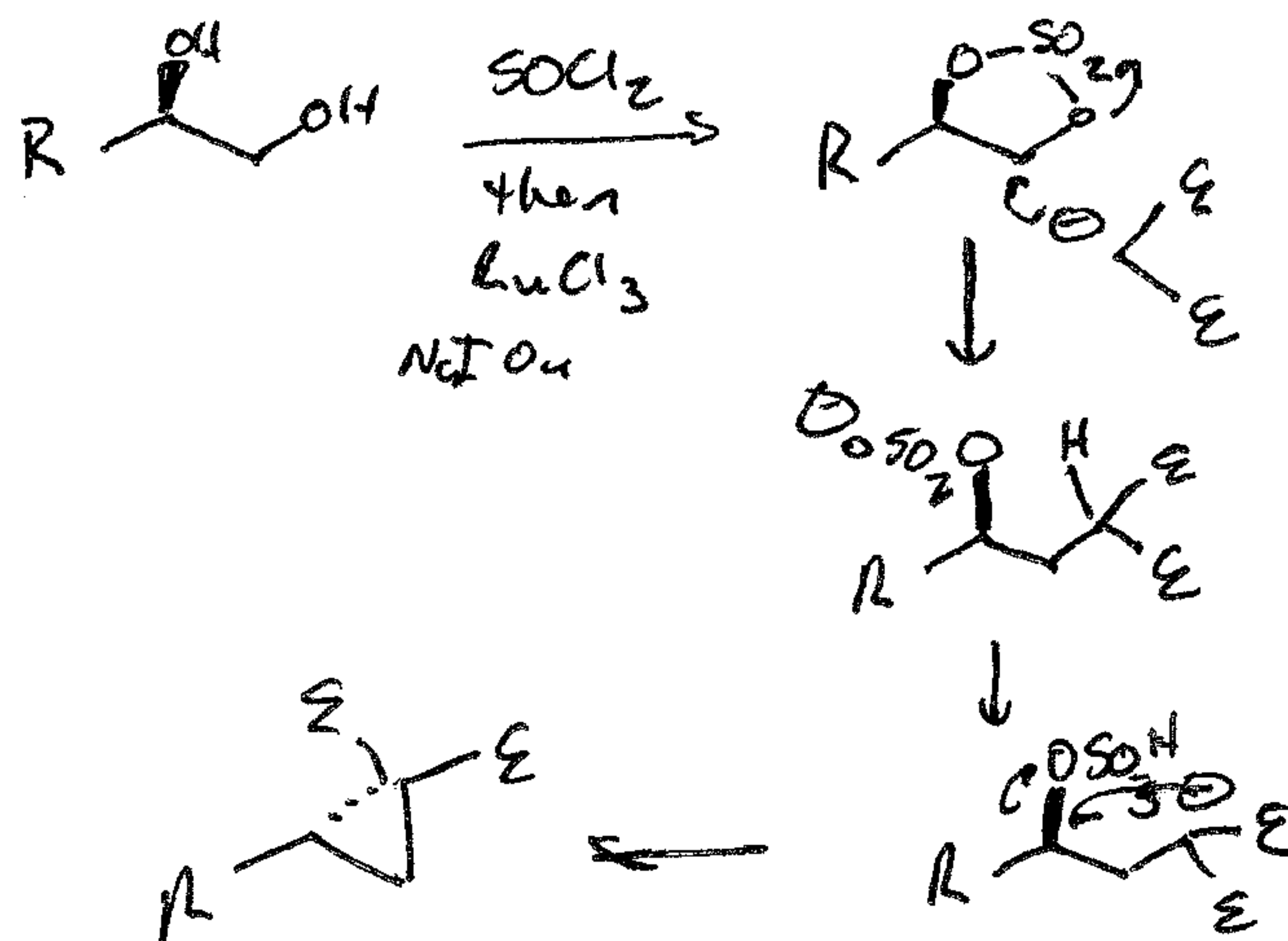
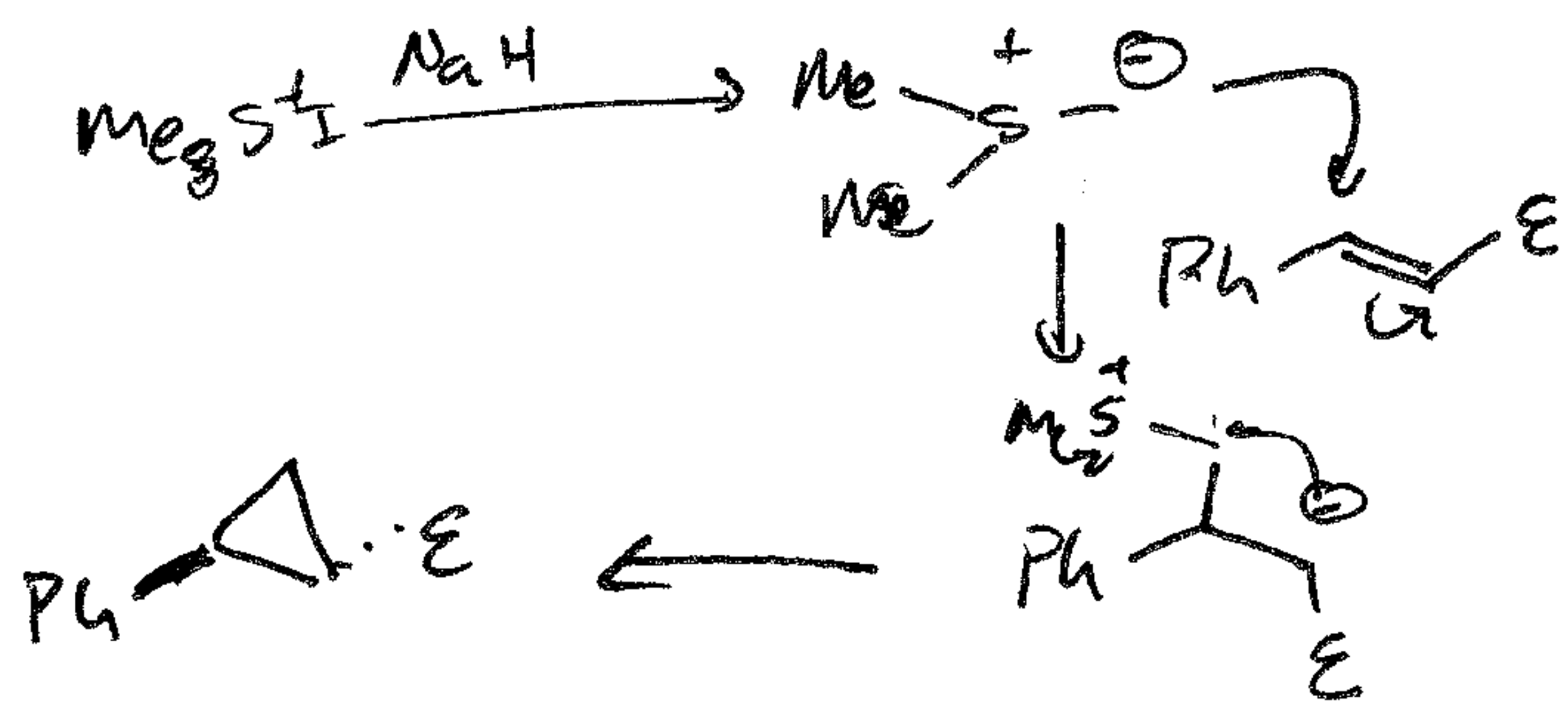
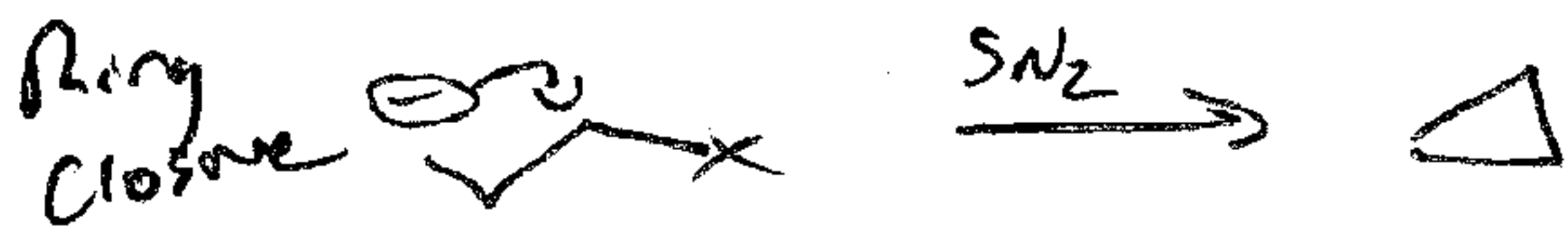


Epoxide Fragmentation

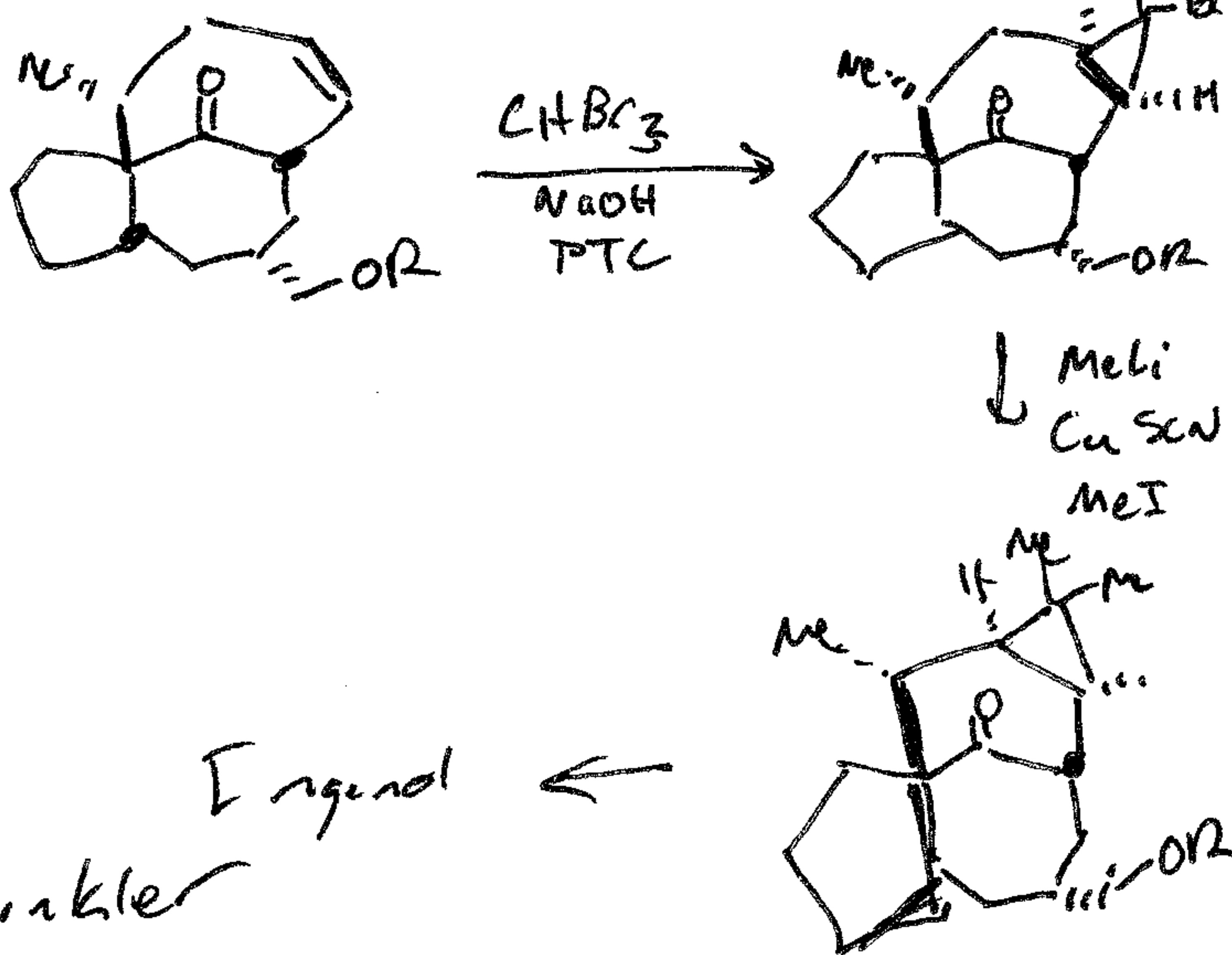
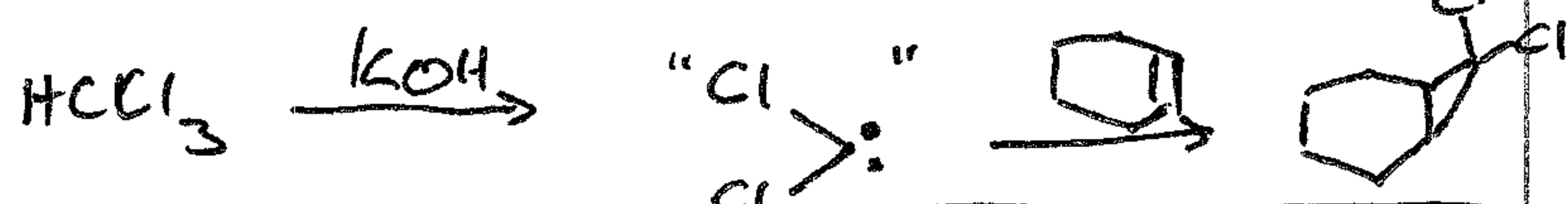


does not have to be cyclic.

Cyclopropane Synthesis

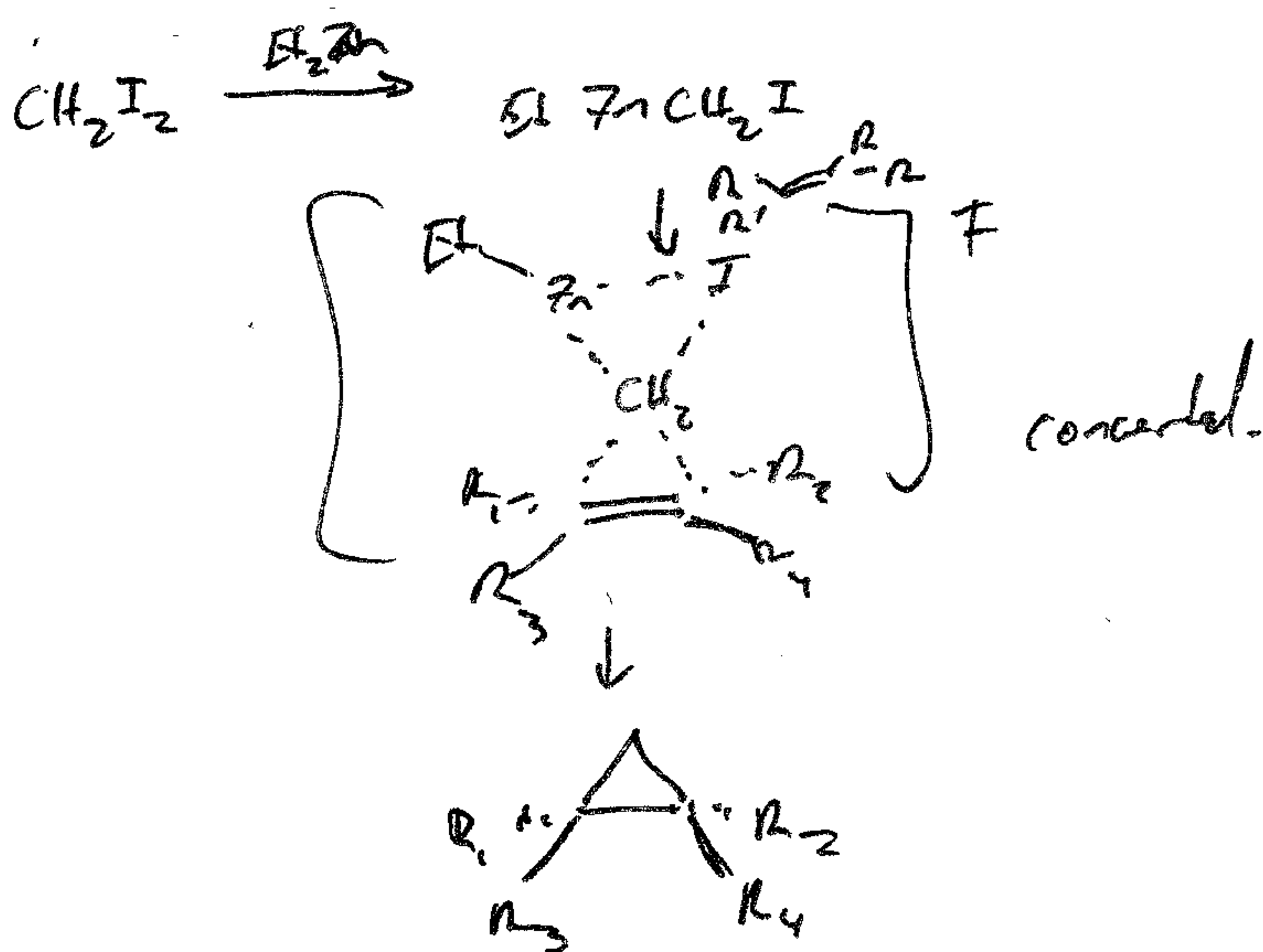
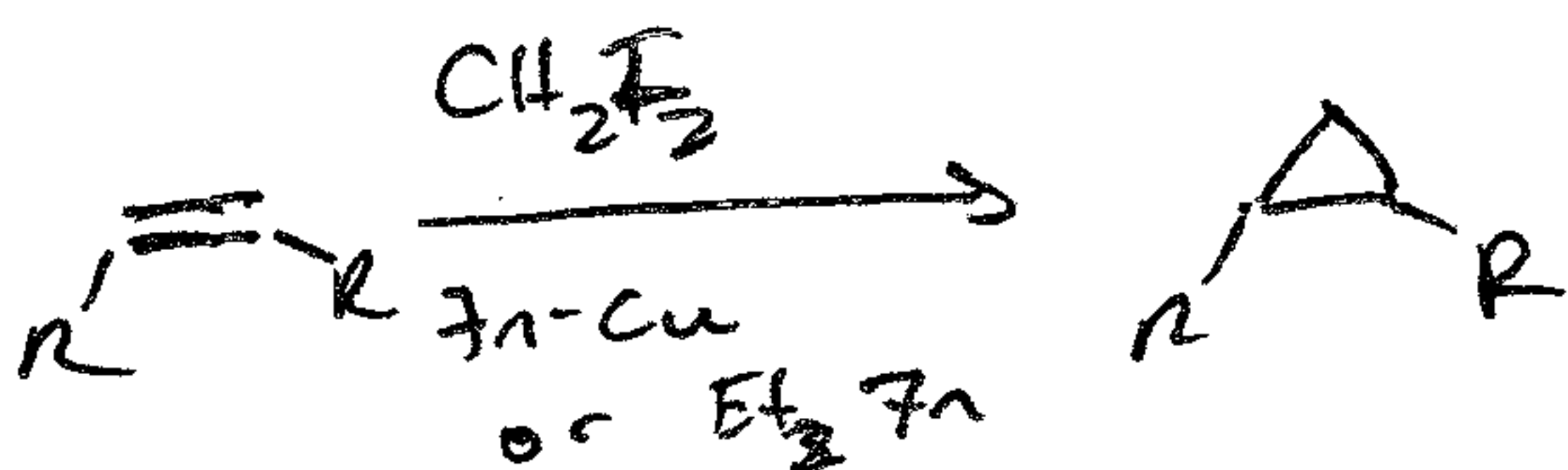


2+1 - Approaches

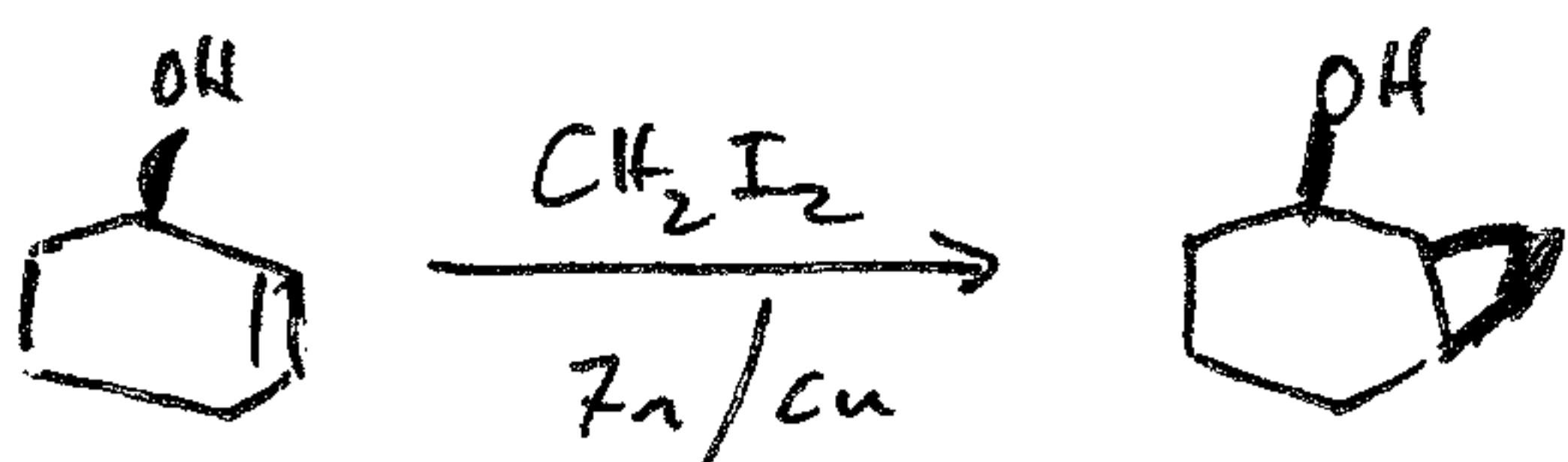


Ingenol
Winkler
JACS, 2002, 124, 9726

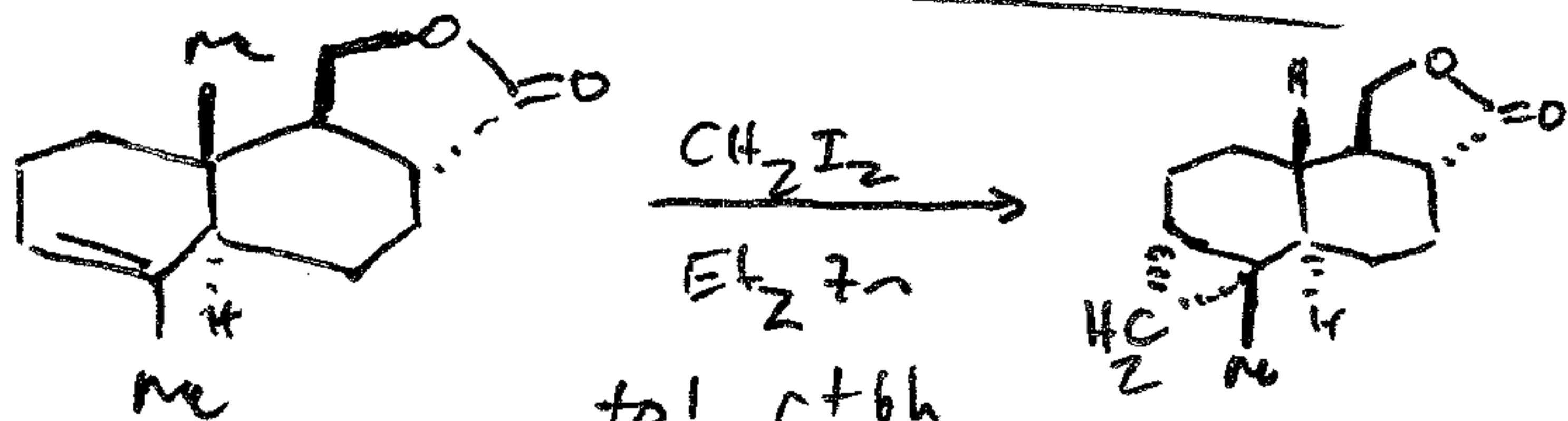
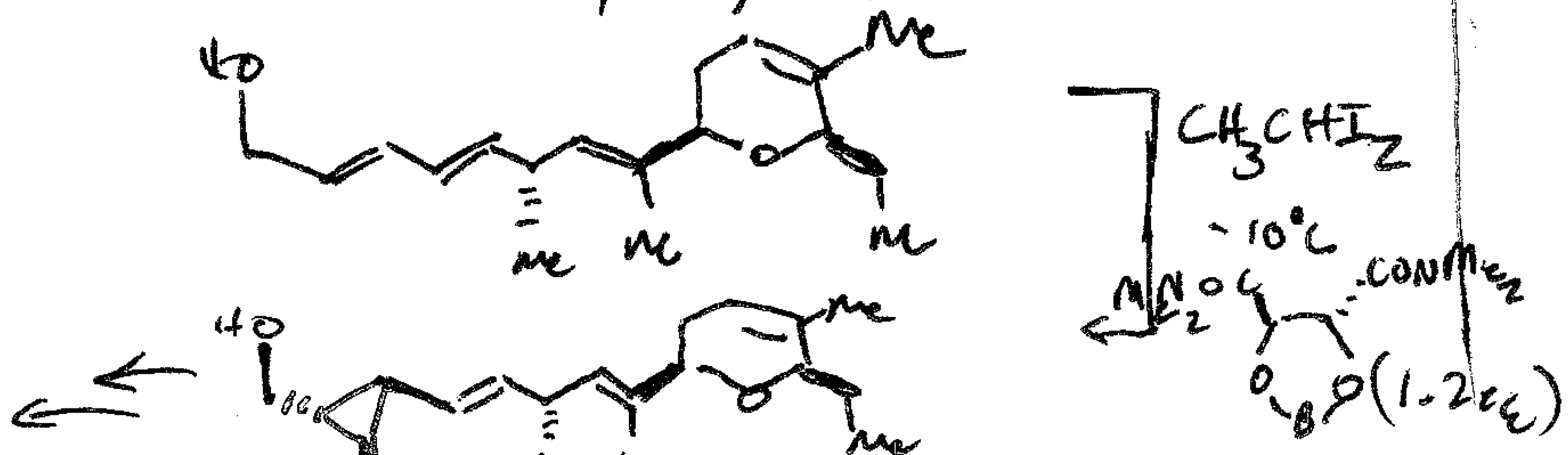
Simmons-Smith Reaction



Allylic Alcohols

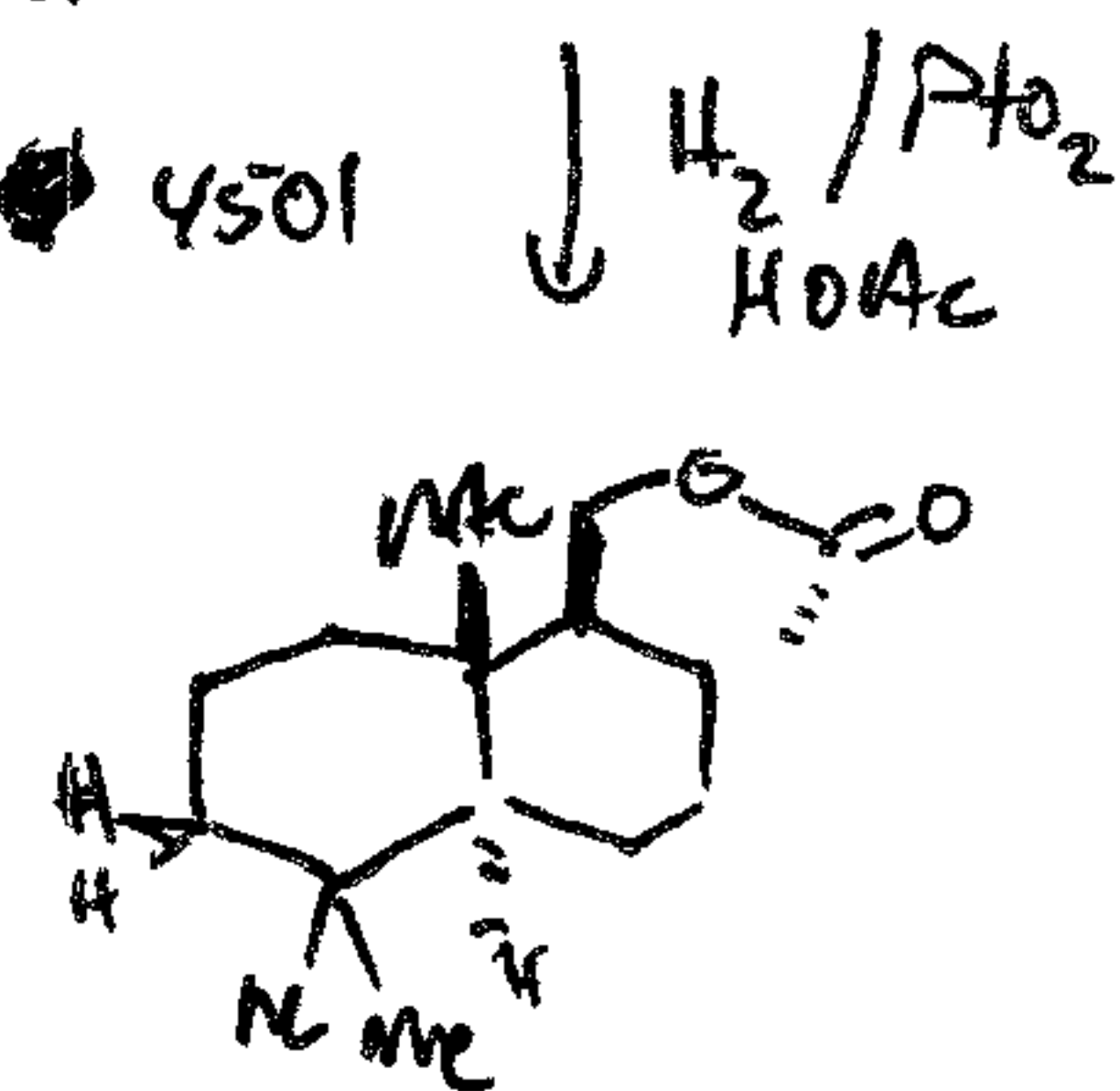


ENS - JACS, 2001, 123, 10772

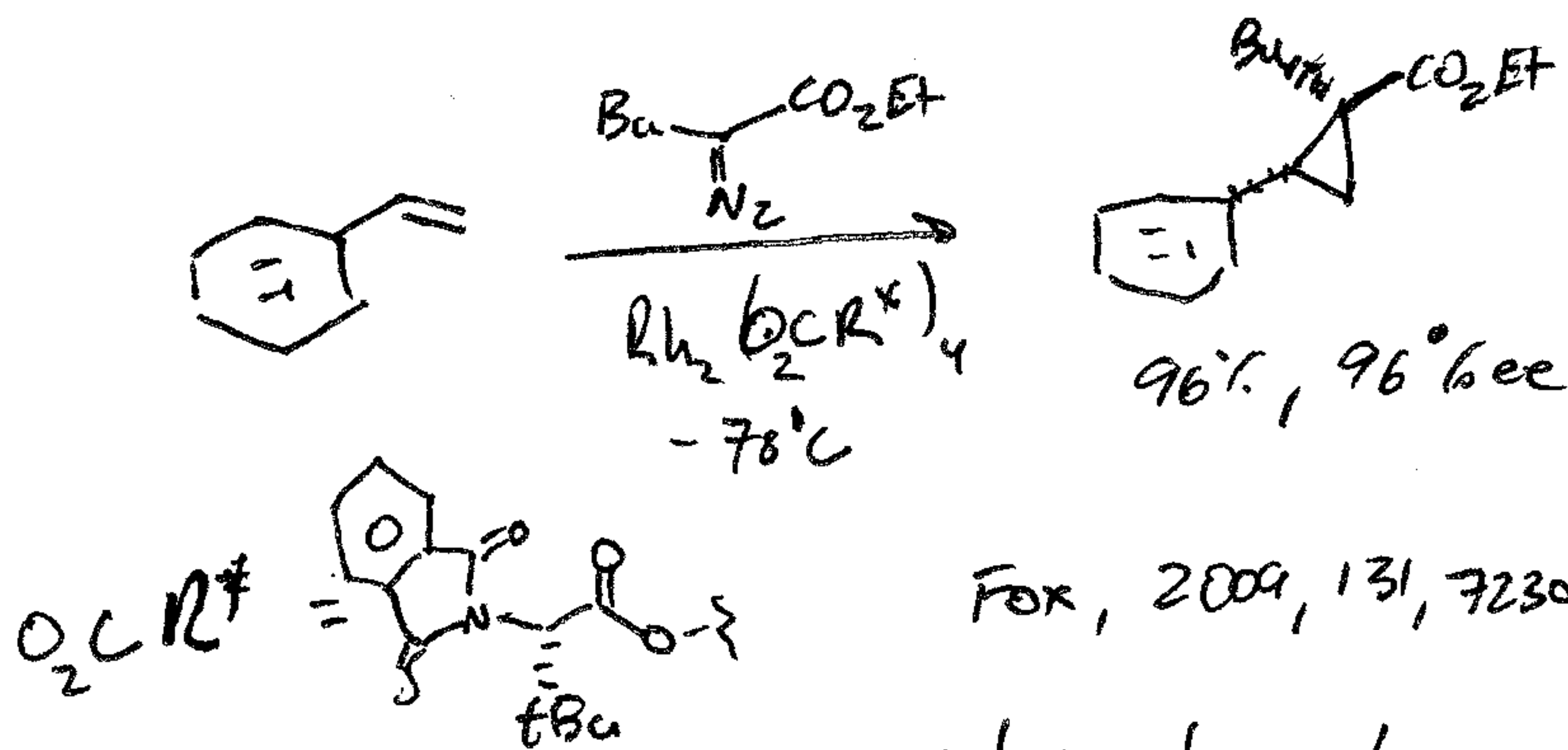
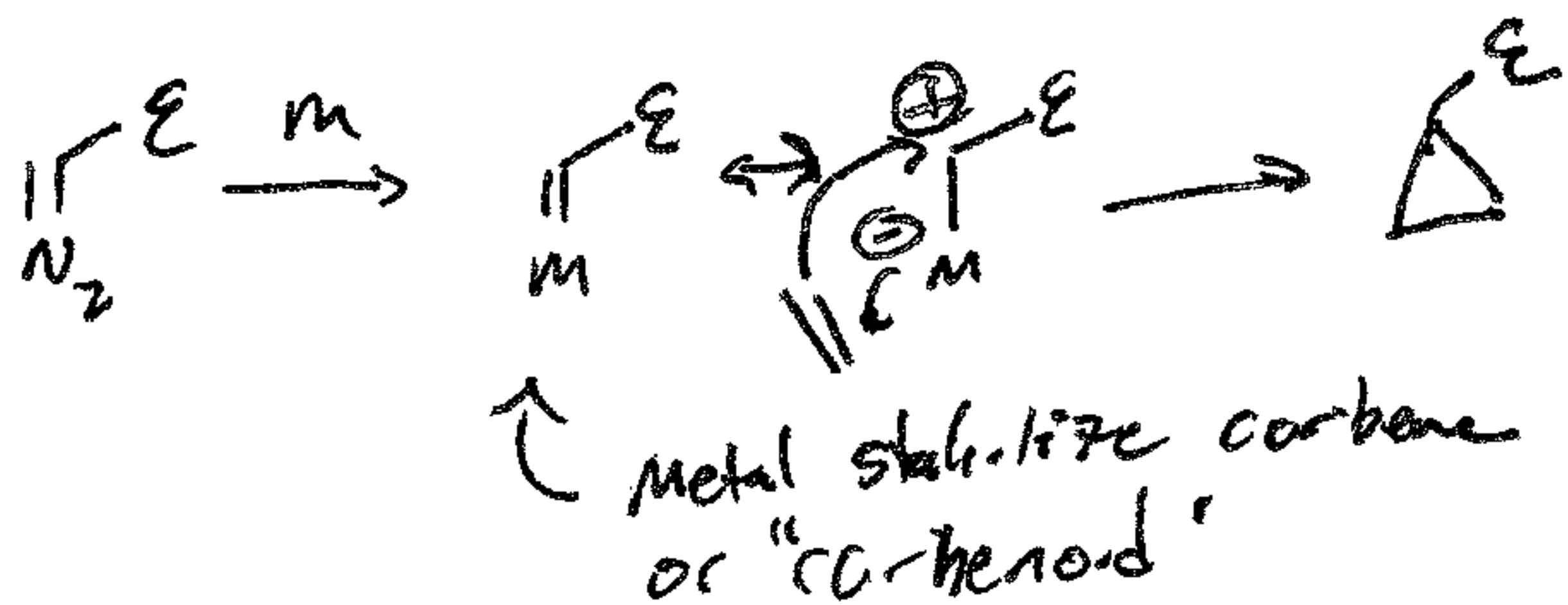
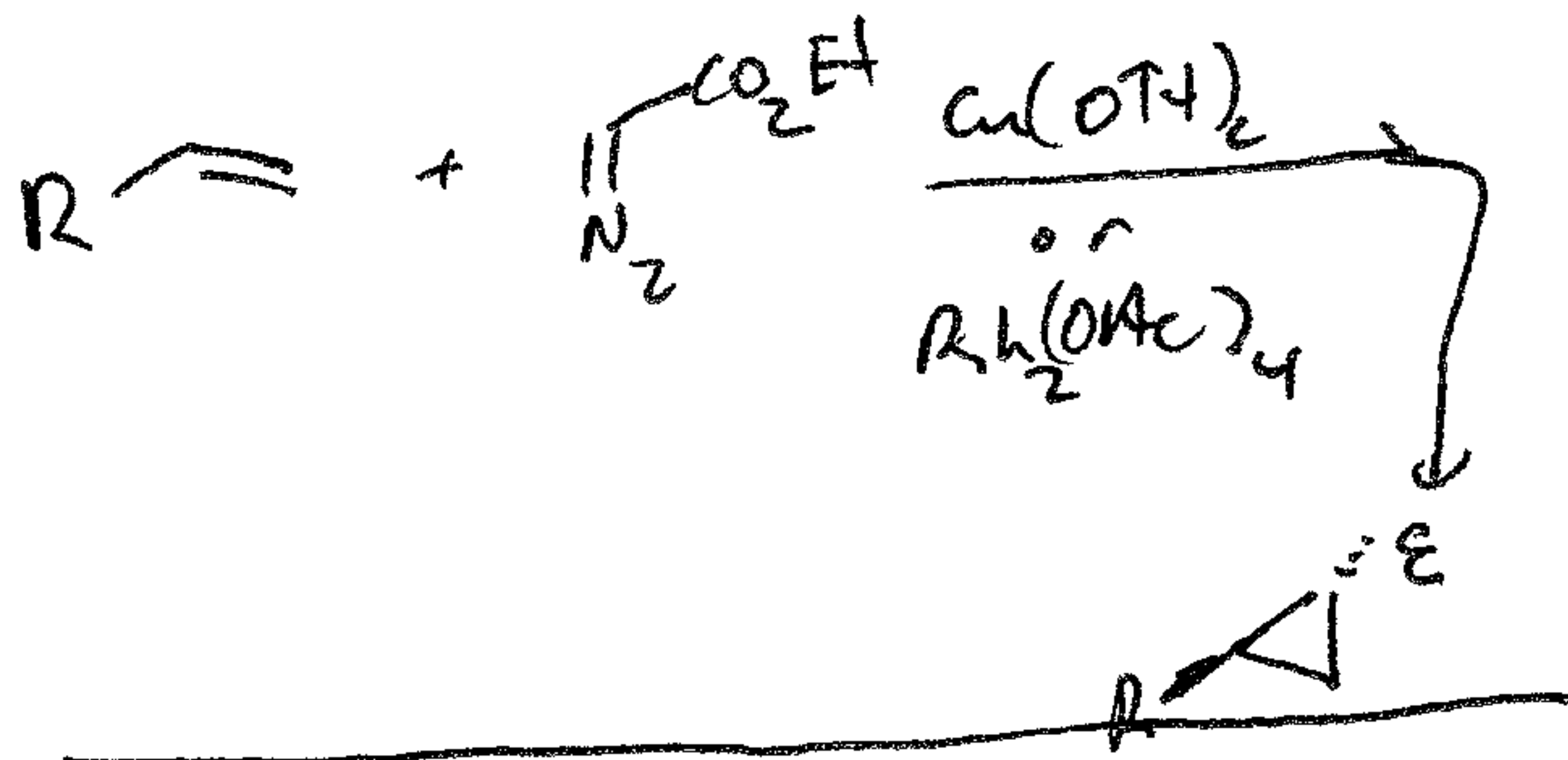


Taber JOC, 2002, 67, 4501

trans-dihydro
con fertifolin

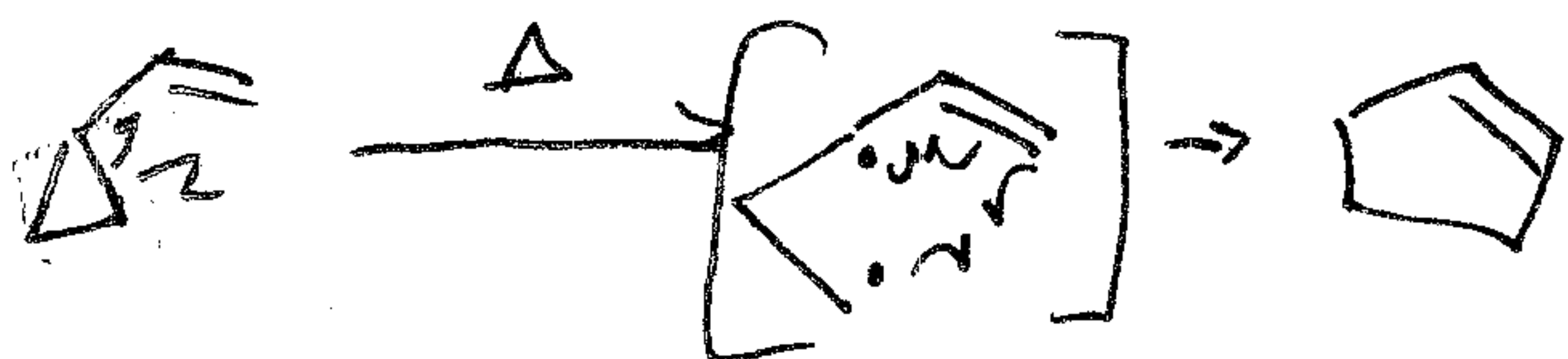


Diazo - Chemistry



Recall Recall Divinyl cyclopropane Rearr.

Vinyl cyclopropane Rearr.



Anton - accelerated \equiv concerted.

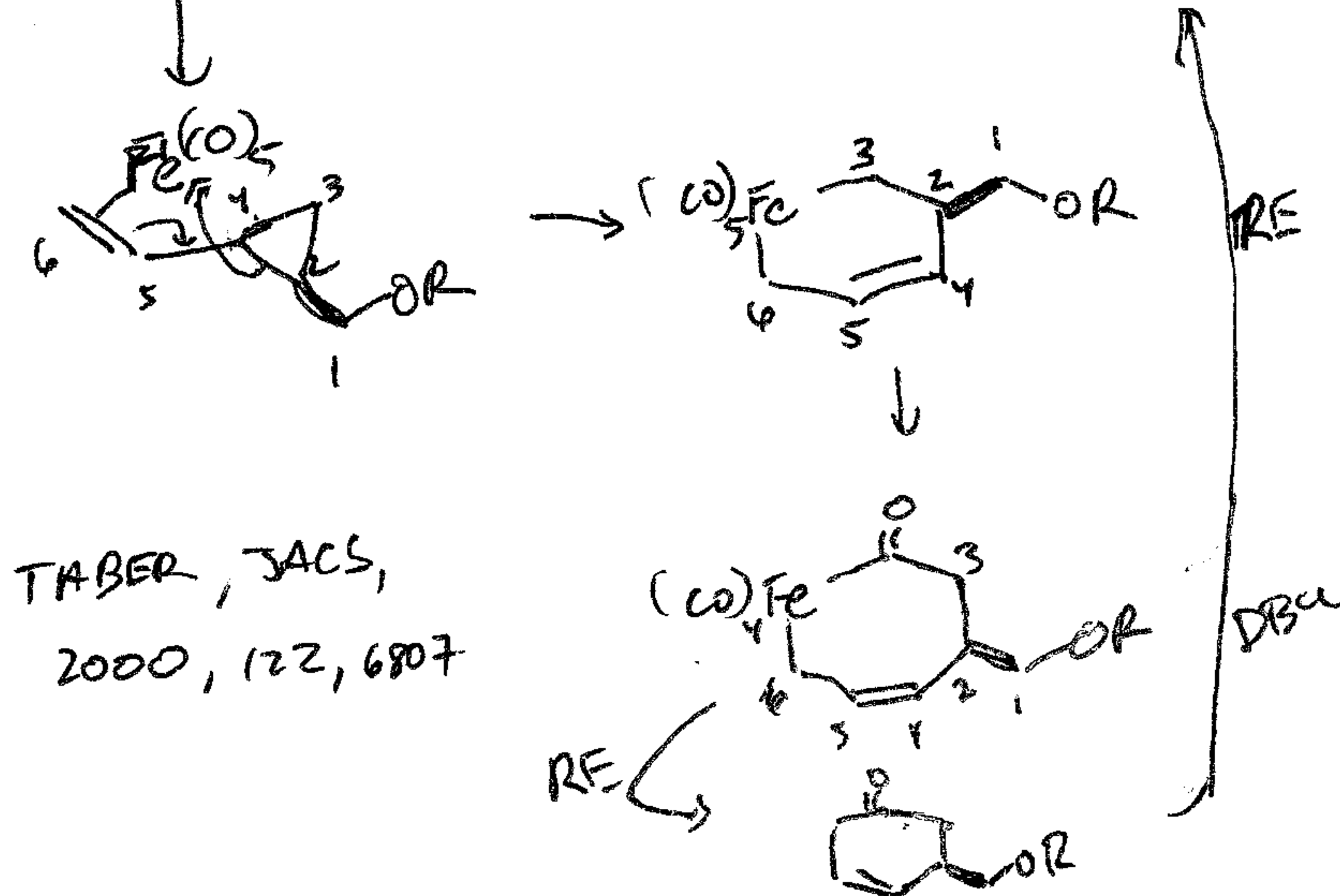
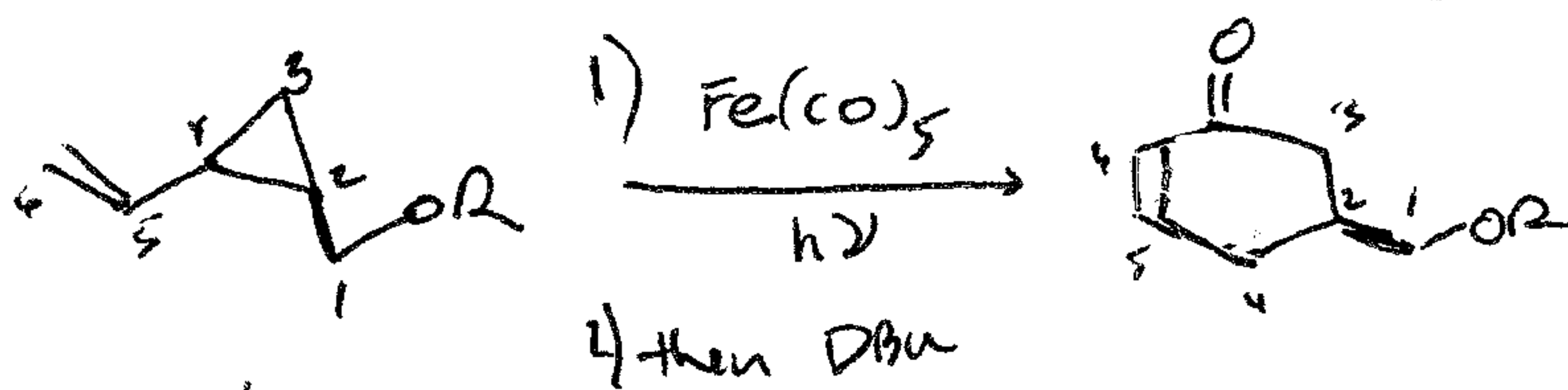
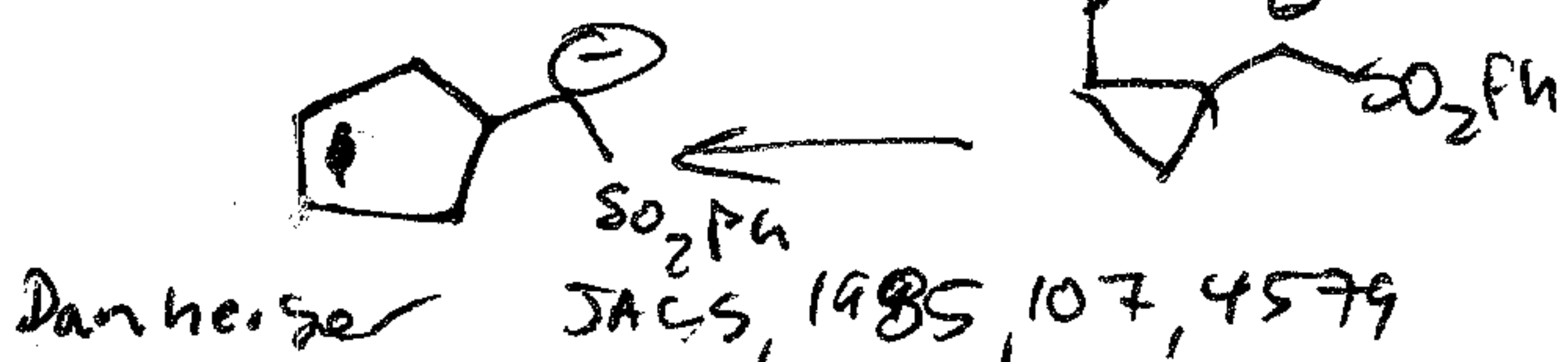
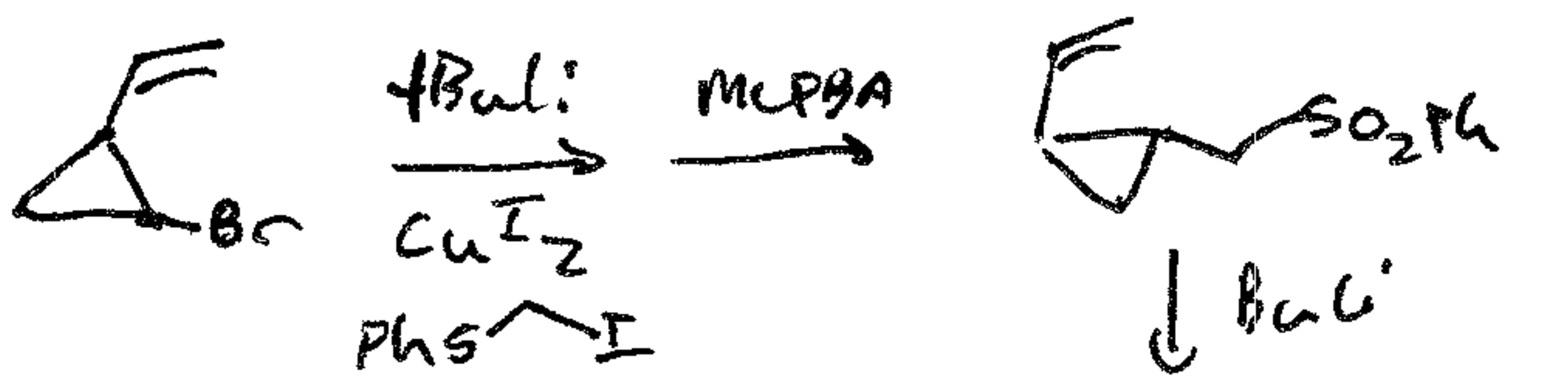
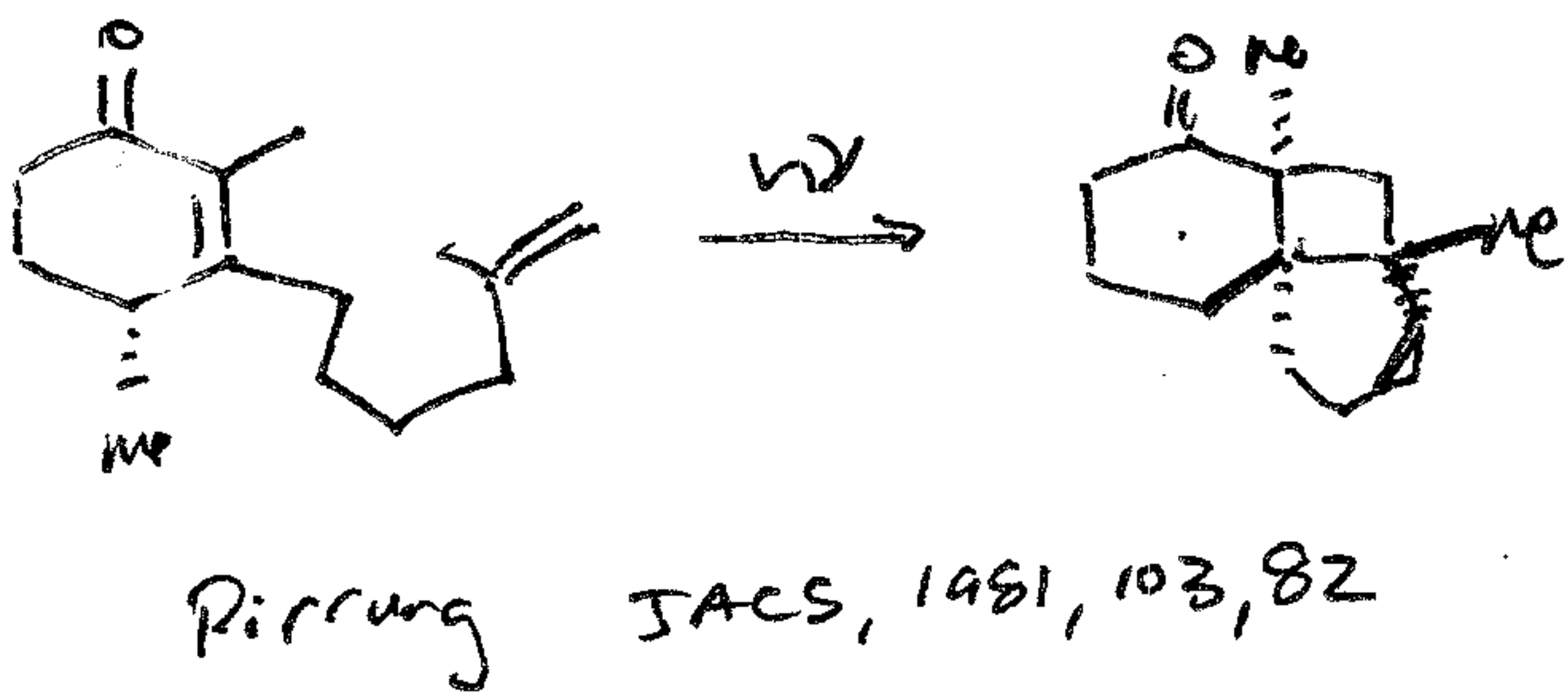
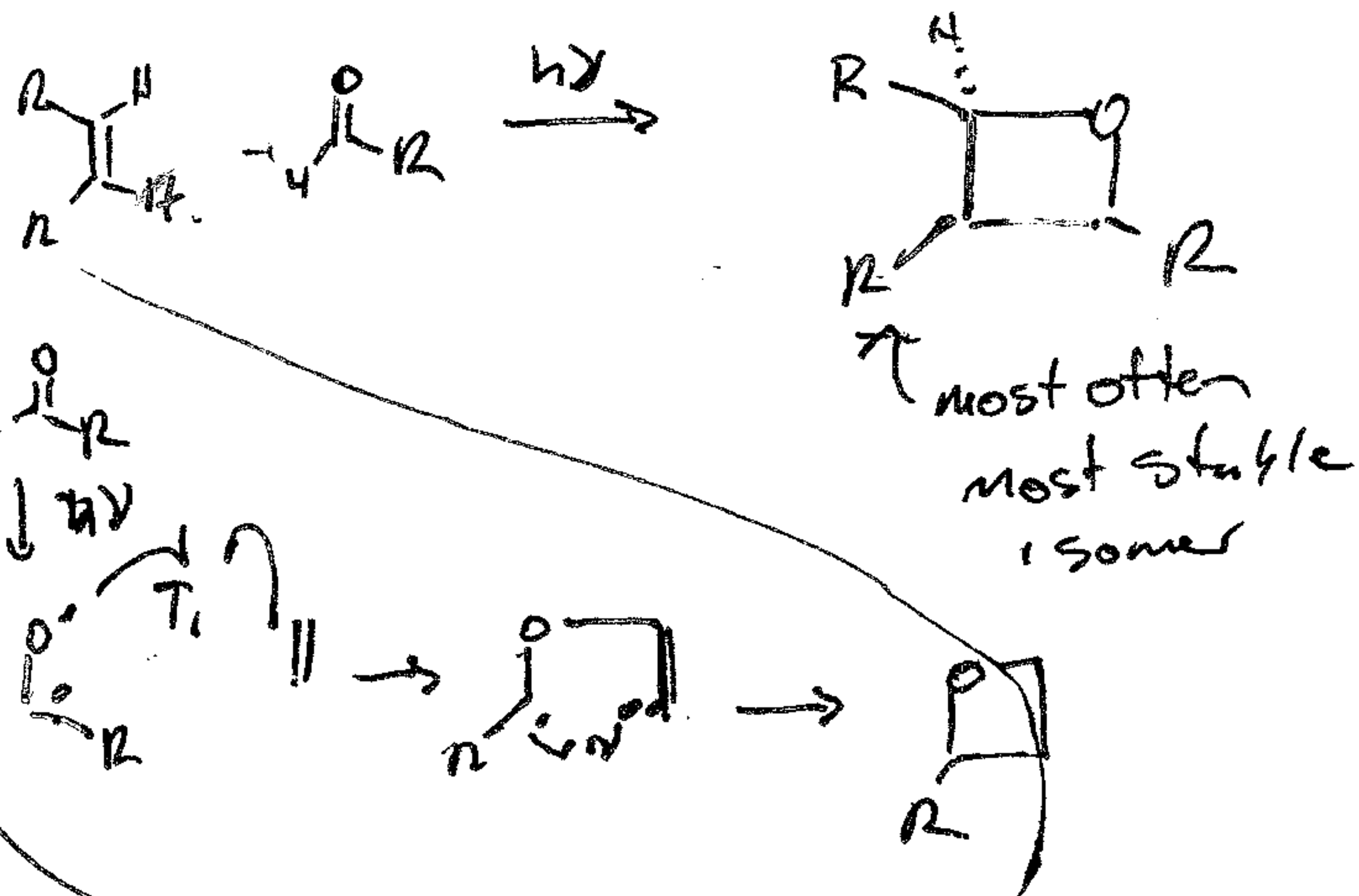


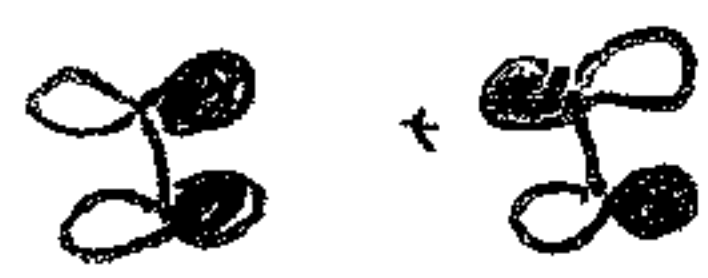
Photo 2+2



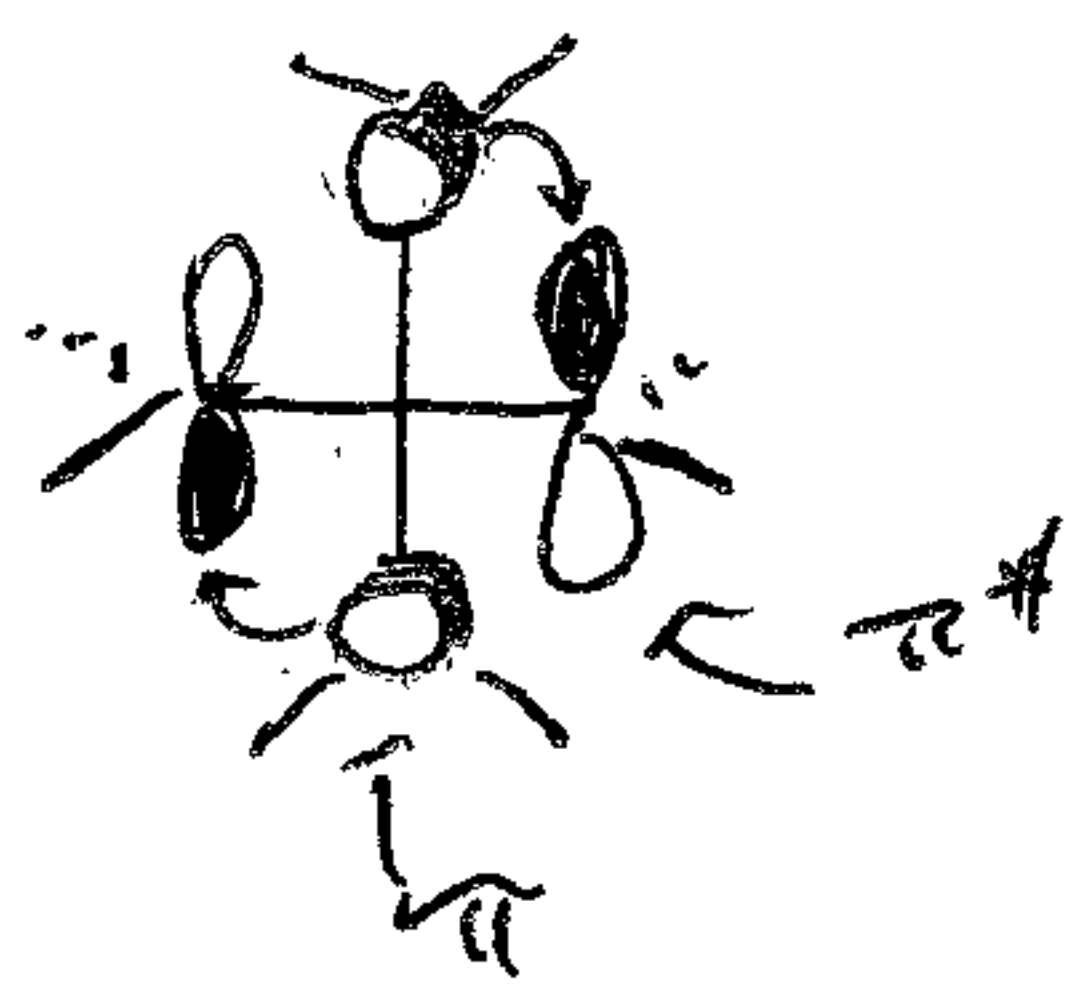
Paterno-Büchi Reaction



Thermal $2+2$

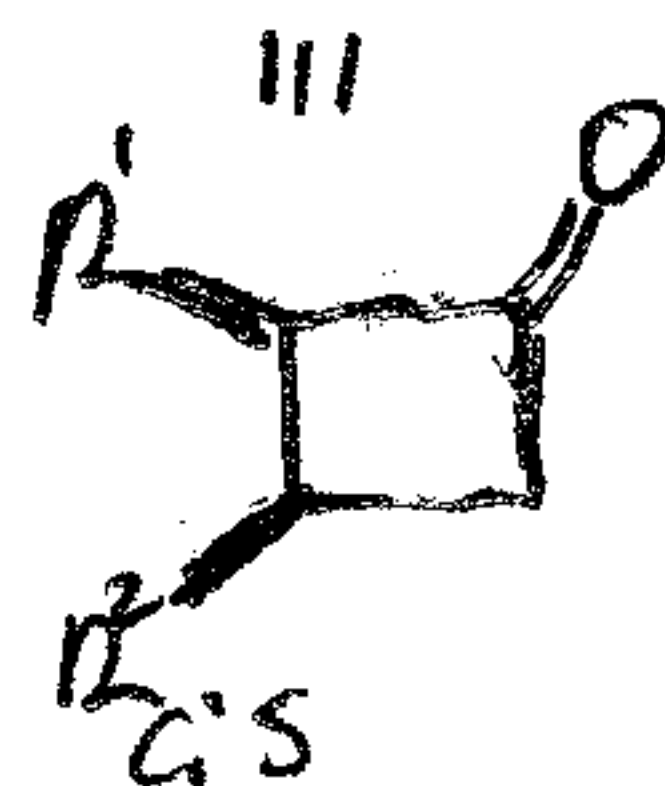
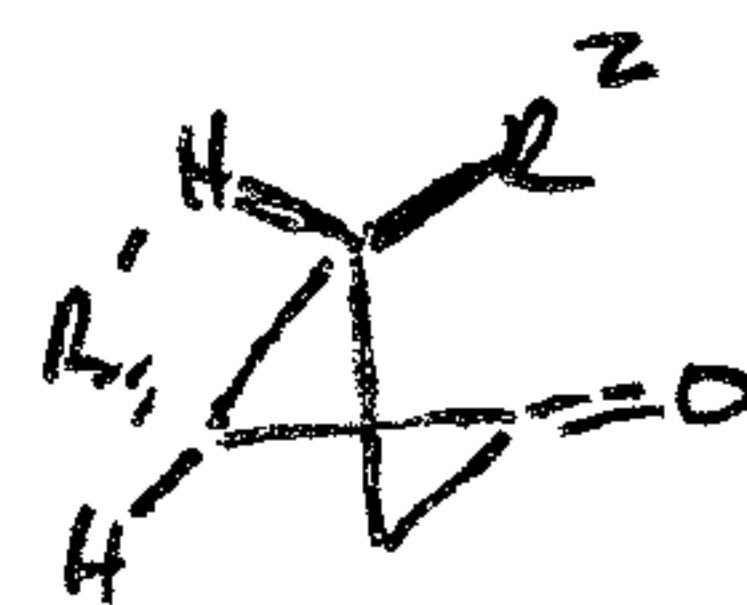
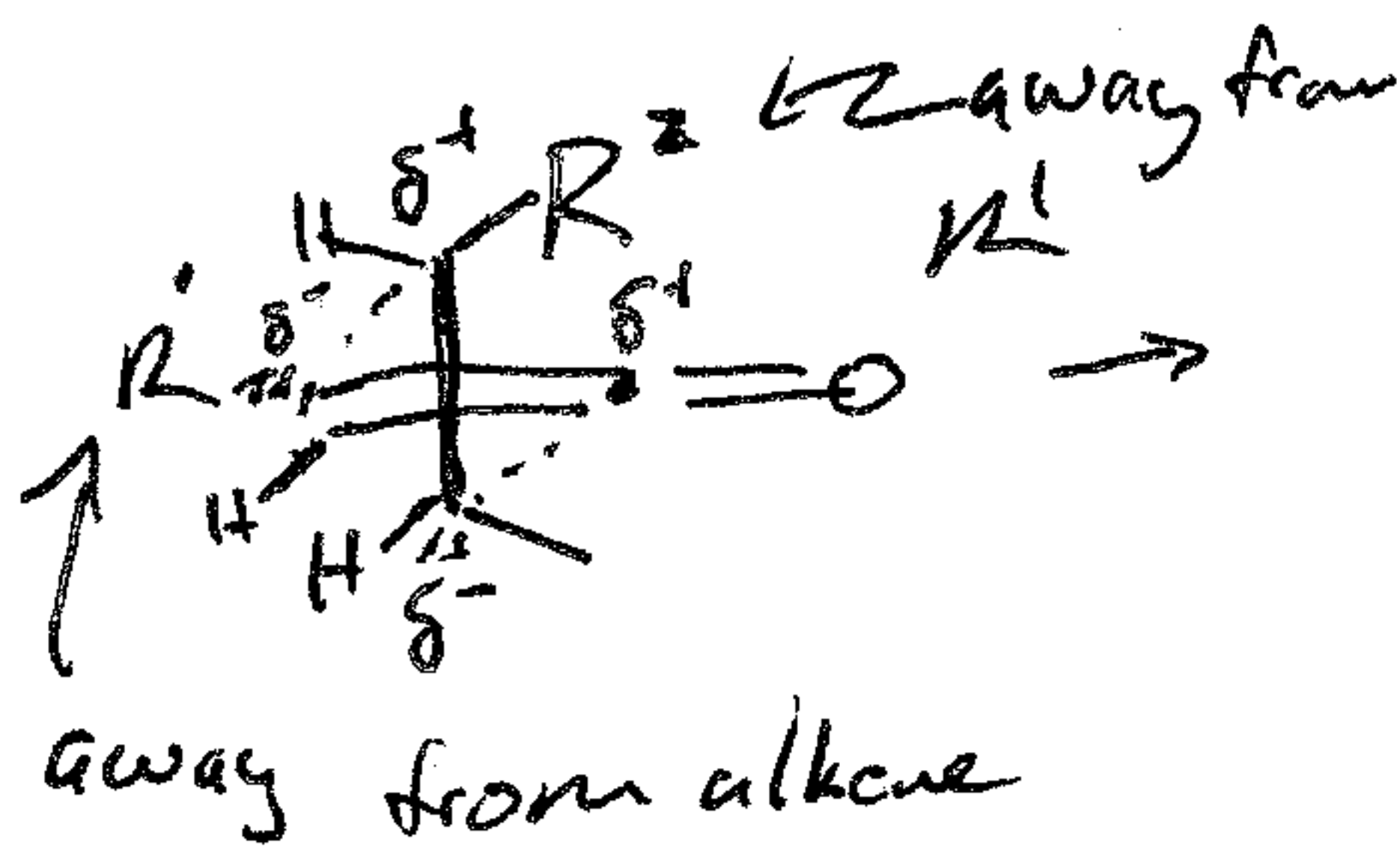


orbital forbidden



antarafacial is allowed

most often w/
ketenes, ~~alkenes~~, etc...



avored

Note on ketone formation

