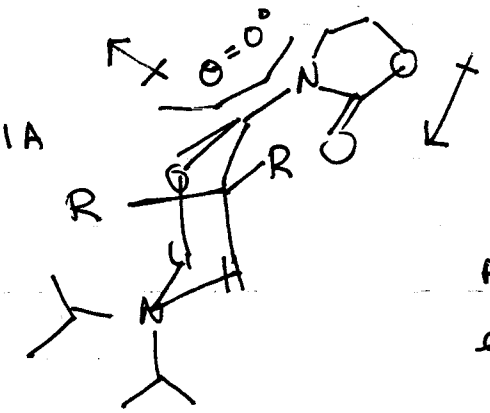
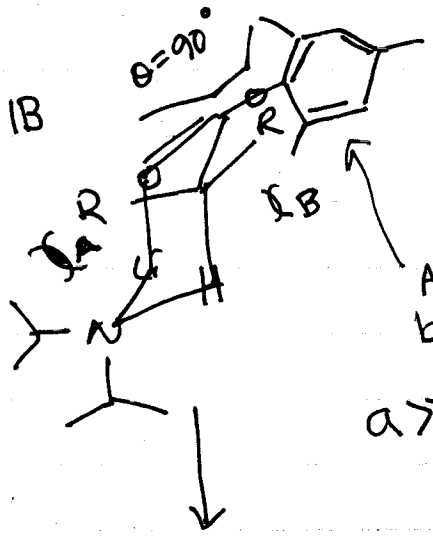
PS 1 Answer Key



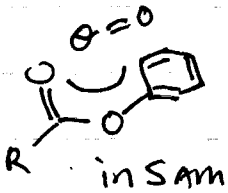
dipole minimization

axial R vastly favored to equatorial R which runs into (C=O)

Z enolate only!

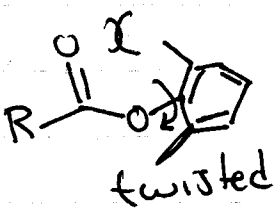


exaggerated but

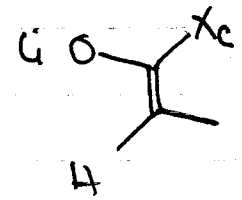


in same plane

Appears small because of twist



a >>>> B

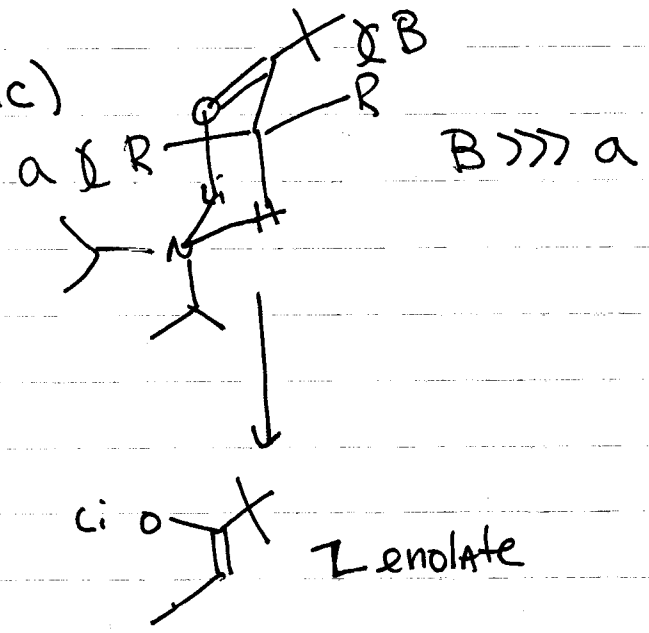


E enolate predominates

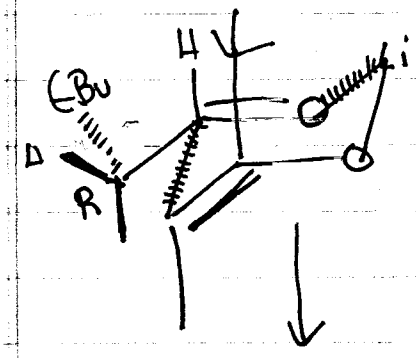
Yamamoto enolate

P.S. 1

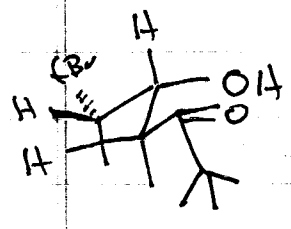
1c)

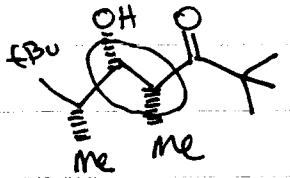


2) The Aldol reaction



can't really ring flip because enolate geometry fixed. But, axial tBu is very bad. The De will probably suffer



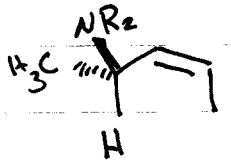


Syn stereochem expected with Z enolate

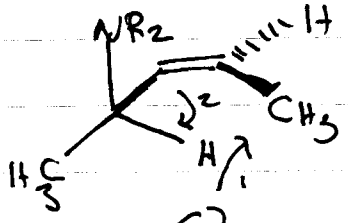
I started with opposite enantiomer of the aldehyde

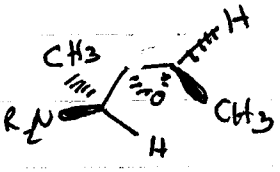
PS1

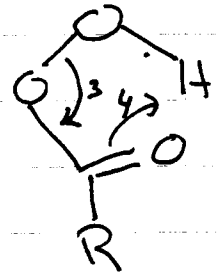
3) Two ways to think about this
felkin or Allylic strain

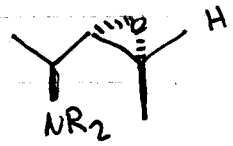


$NR_2 > CH_3$
react from
bottom face

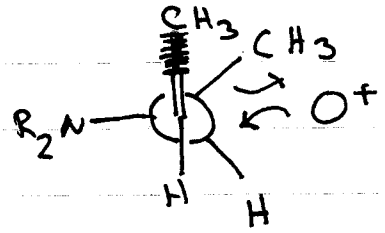






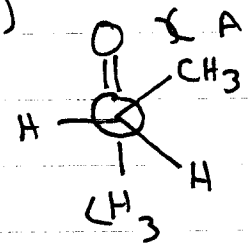


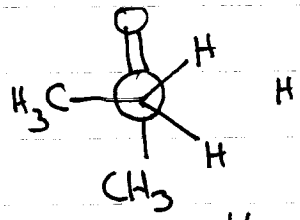
Felkin idea



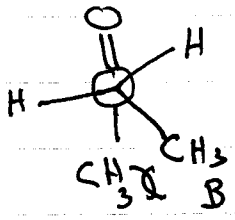
Both models give same product

4)





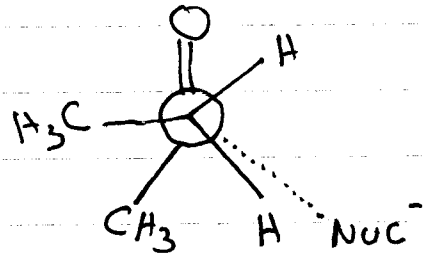
C No problem



B > A > C
less ⟶ more

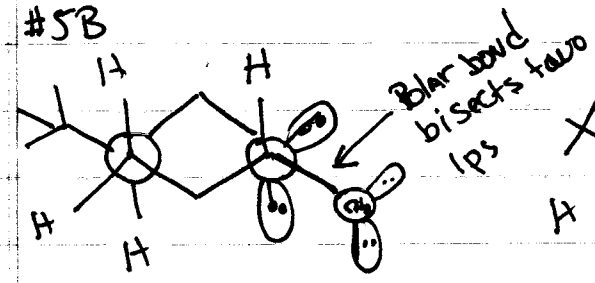
This the GS basis of the Felkin Model

TS

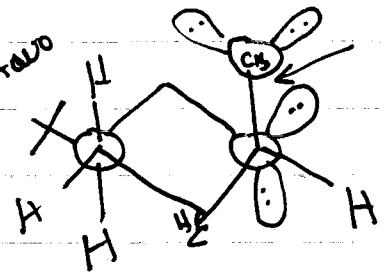


109° Attack vector
sp^2 carbon not really sp^2 any more

#5B

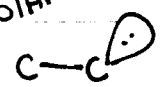


A



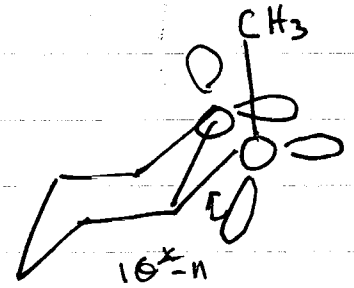
B

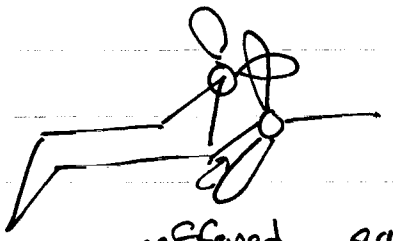
polar bond bisects one lp



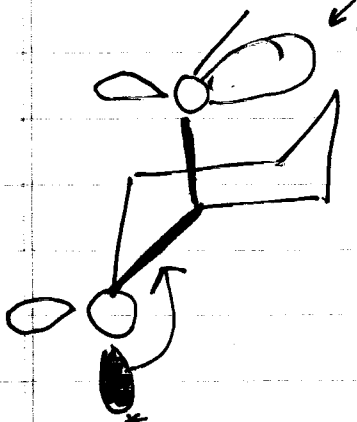
A has more electrostatic repulsions

#5C

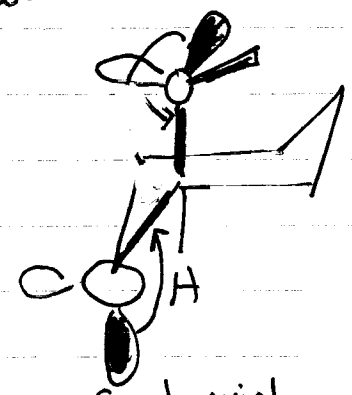




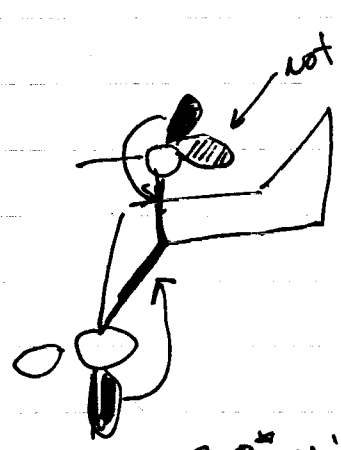
preffered eq conformer



10*-n interaction



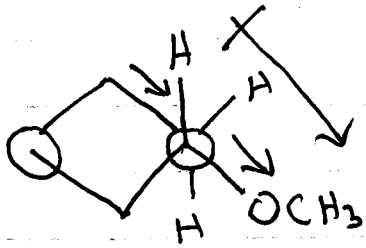
prefered AXIAL conformer



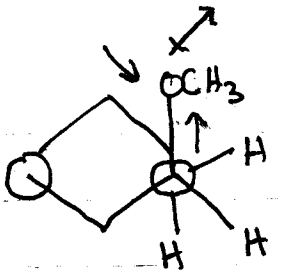
2 σ*_N interaction

2σ*_N interacti

5a) dipole consideration

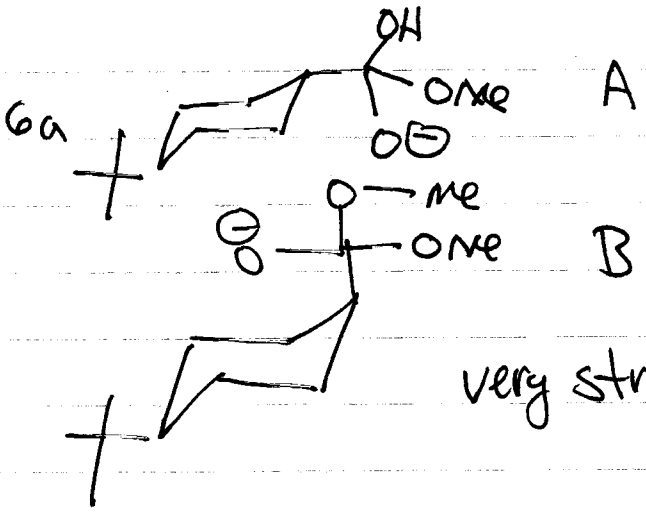


vectors additive
big dipole



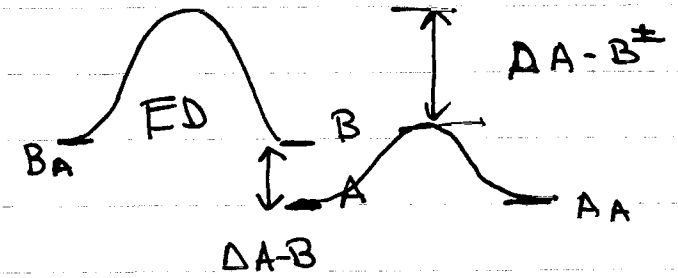
∪
small dipole

5d) calculate kcal go look up what gauche lp C-O bond is worth



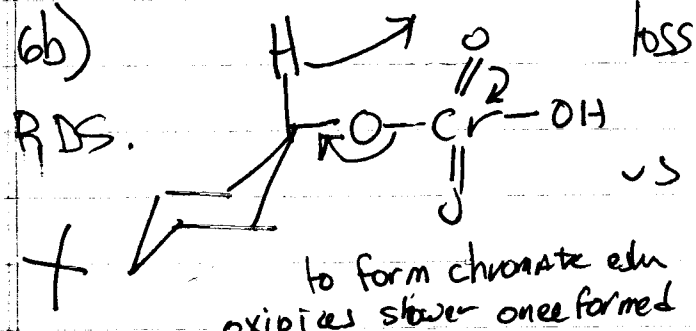
RDS probably Addition of LiOH

very strained



an axial ester only cost less than 1.1 kcals ()
but TS looks like axial tButyl group (
∴ would estimate that the $\Delta A^{\ddagger}-B^{\ddagger}$ > 4.5 kcals higher in energy.

6b)

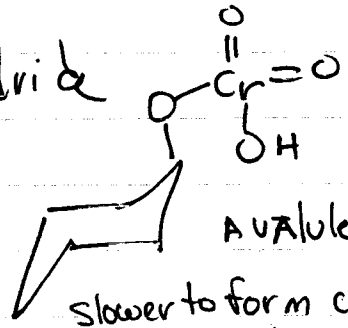


RDS.

to form chromate ester oxidizes slower once formed

vs

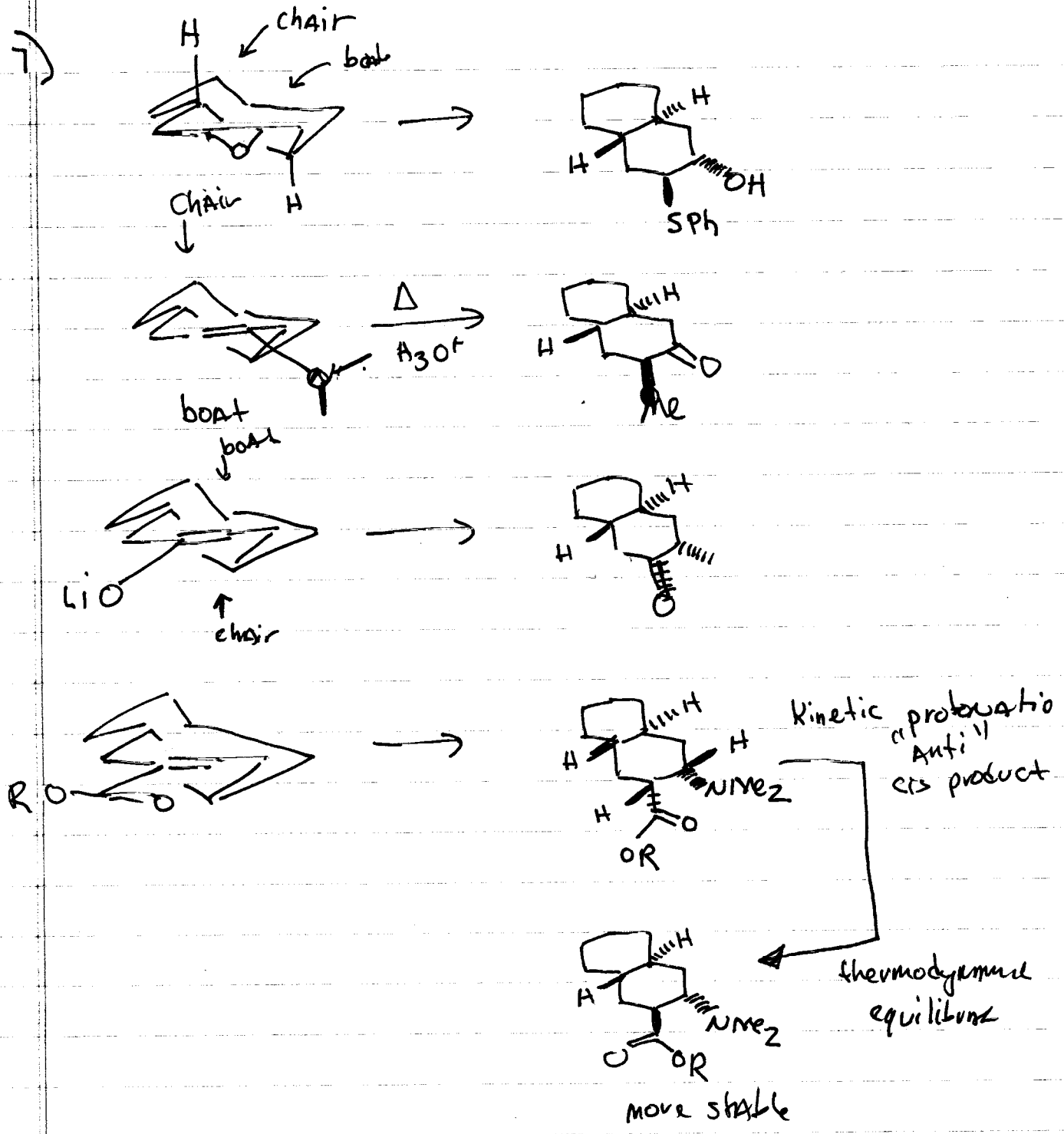
loss of hydride



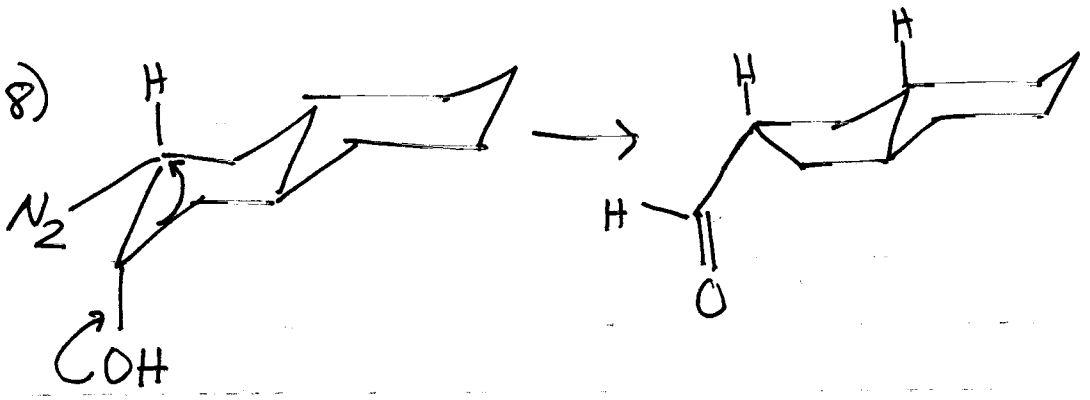
A value ≃ .71

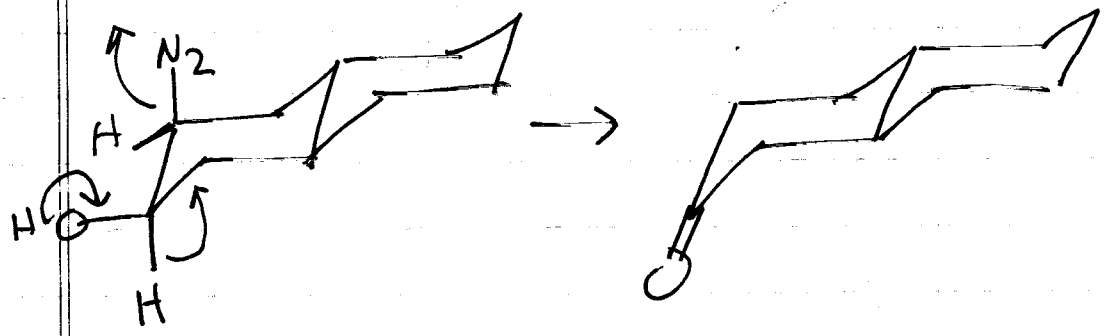
slower to form chromate ester once formed oxidizes faster

not as bad because ≠ to tButyl
However Axial Alcohol requires more energy to form Chromate ester ∴ slower to oxidize

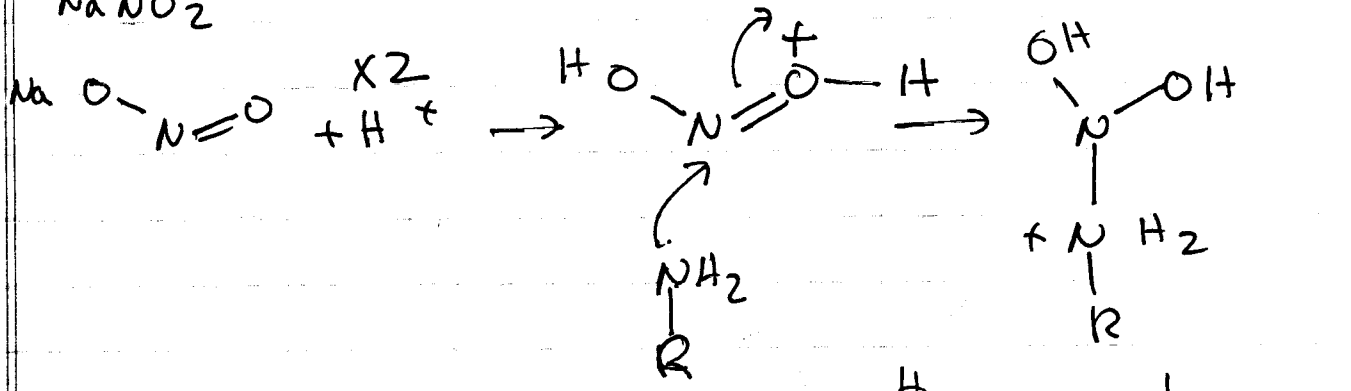

H
chair
boat
chair
H
H
H
OH
SPh
Δ
A3OT
boat
H
H
Me
boat
LiO
chair
H
H
R
O
O
H
H
NMe2
H
O
OR
Kinetic protonation
"Anti"
cis product
thermodynamic
equilibrium
H
H
NMe2
O
OR
more stable

8)

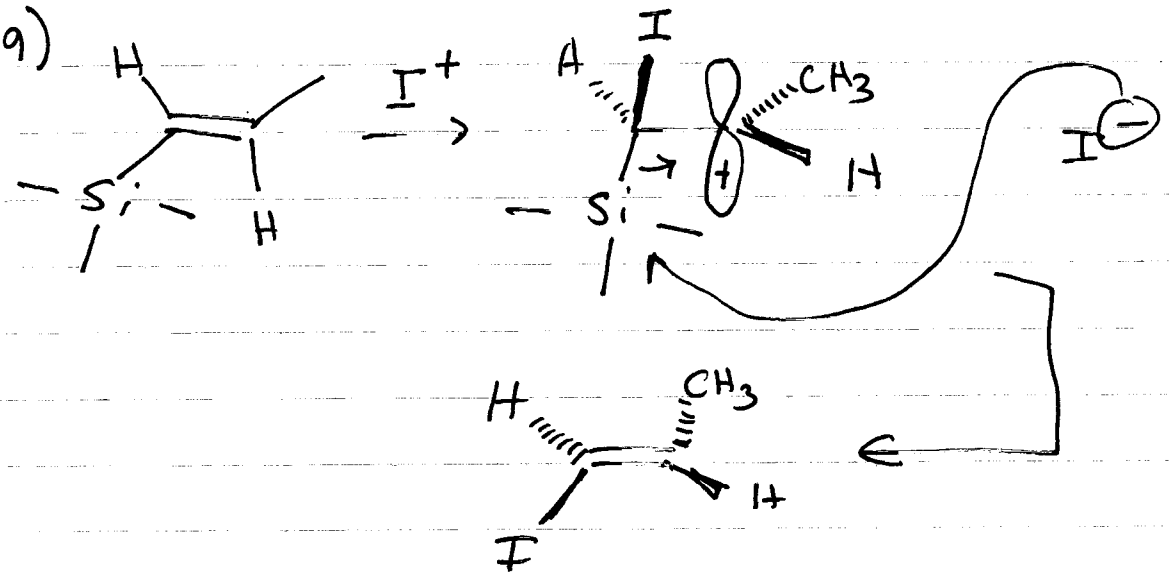


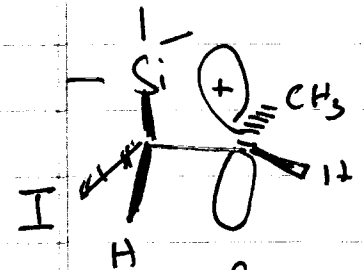


$NaNO_2$



9)

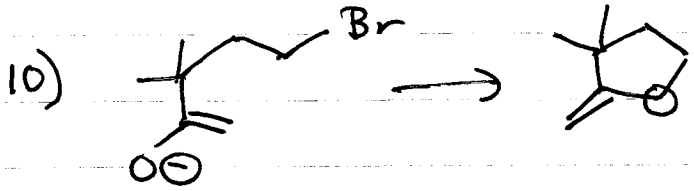


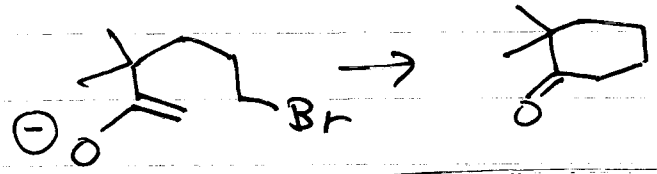


unfavored

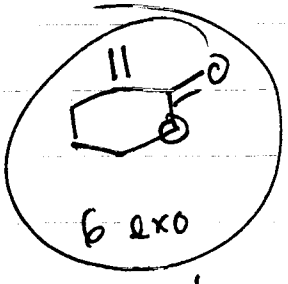
gauché between I vs CH_3

10)





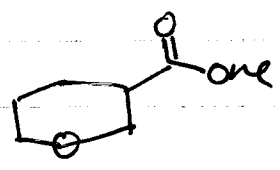
exo and endo dont really apply to
At least
it can align these
two cases



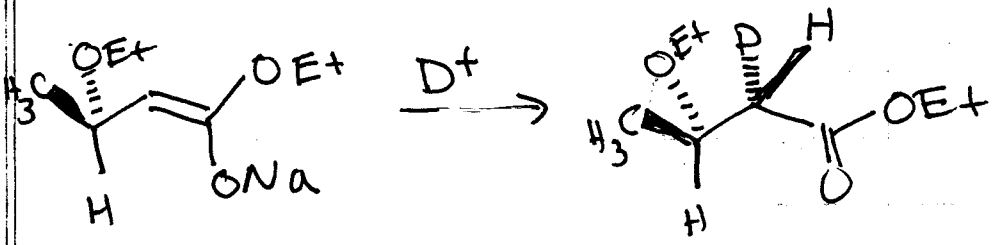
6 exo

favored

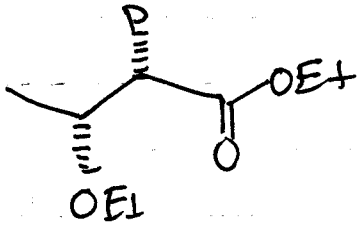
vs



6 endo



OEt smaller than CH_3
D^+ add to on OEt side



if could β-elim