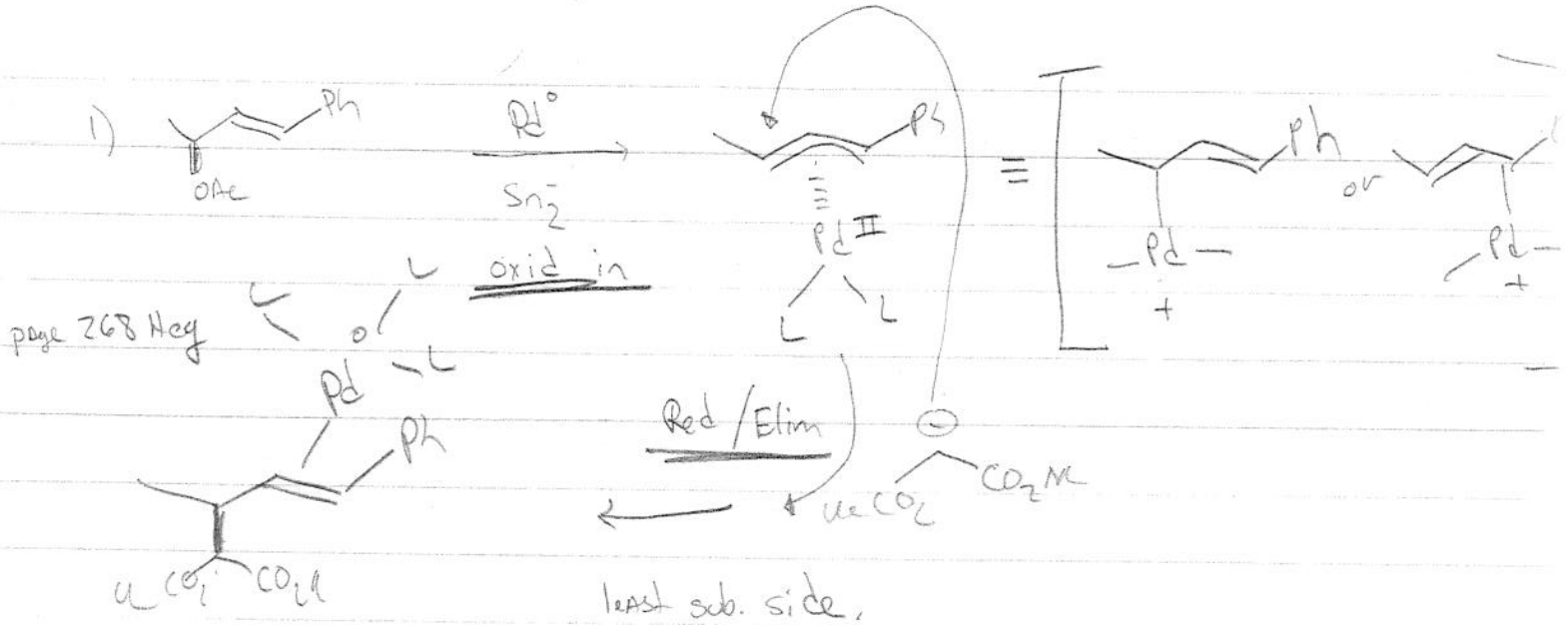
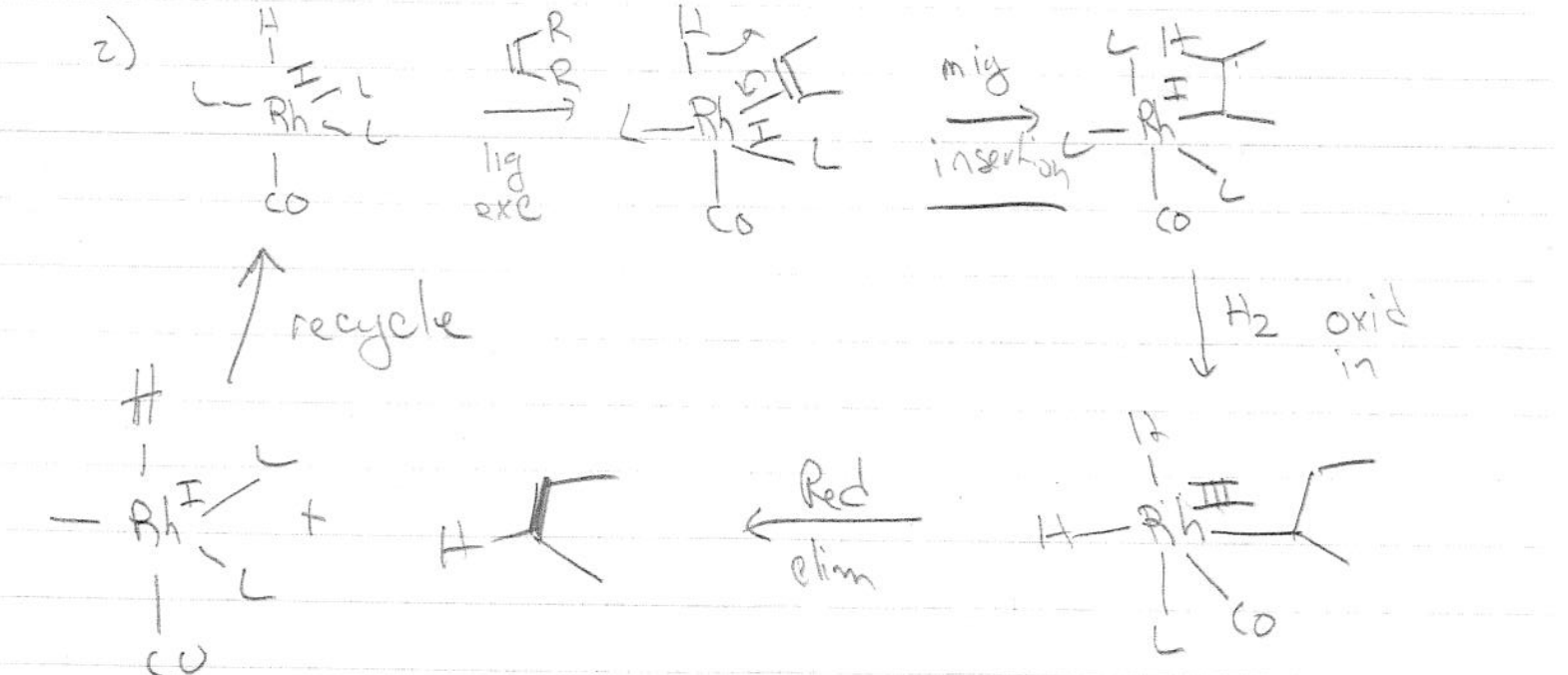
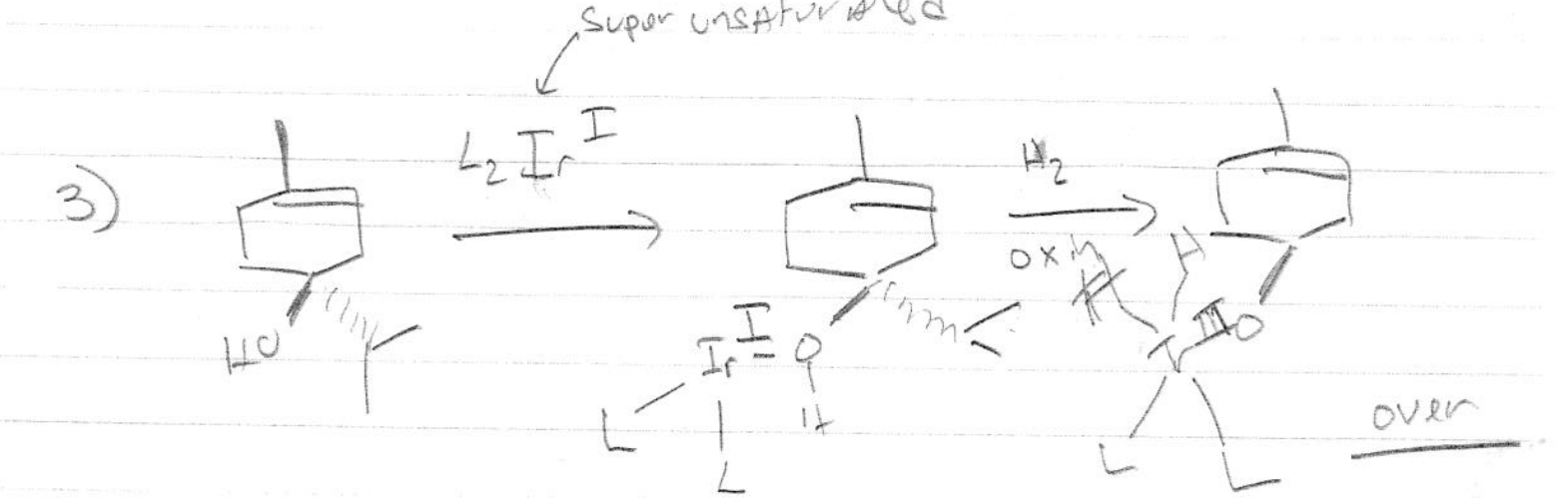
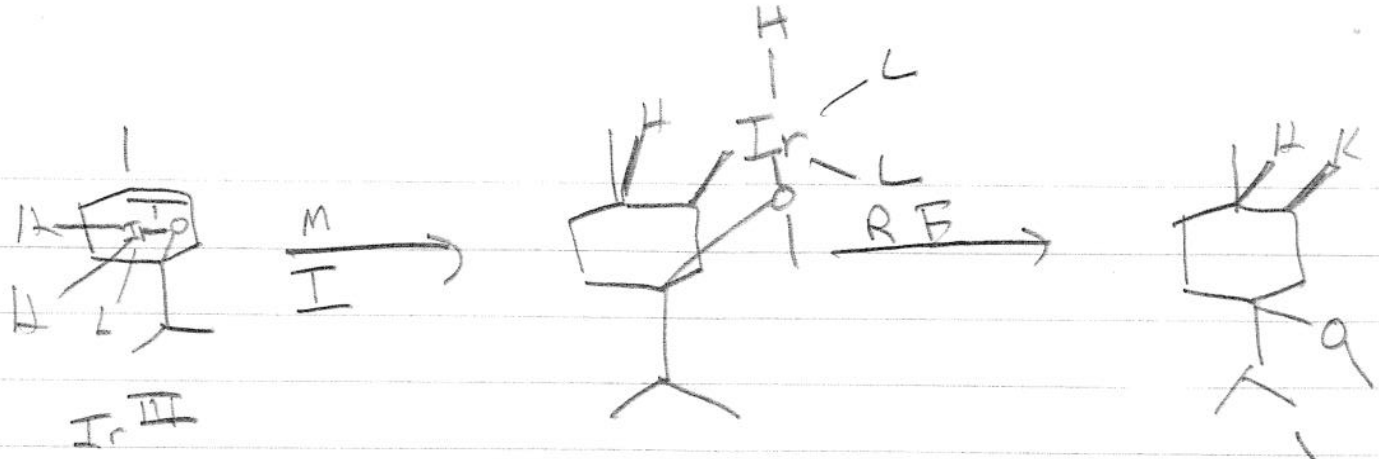
Problem Set IV

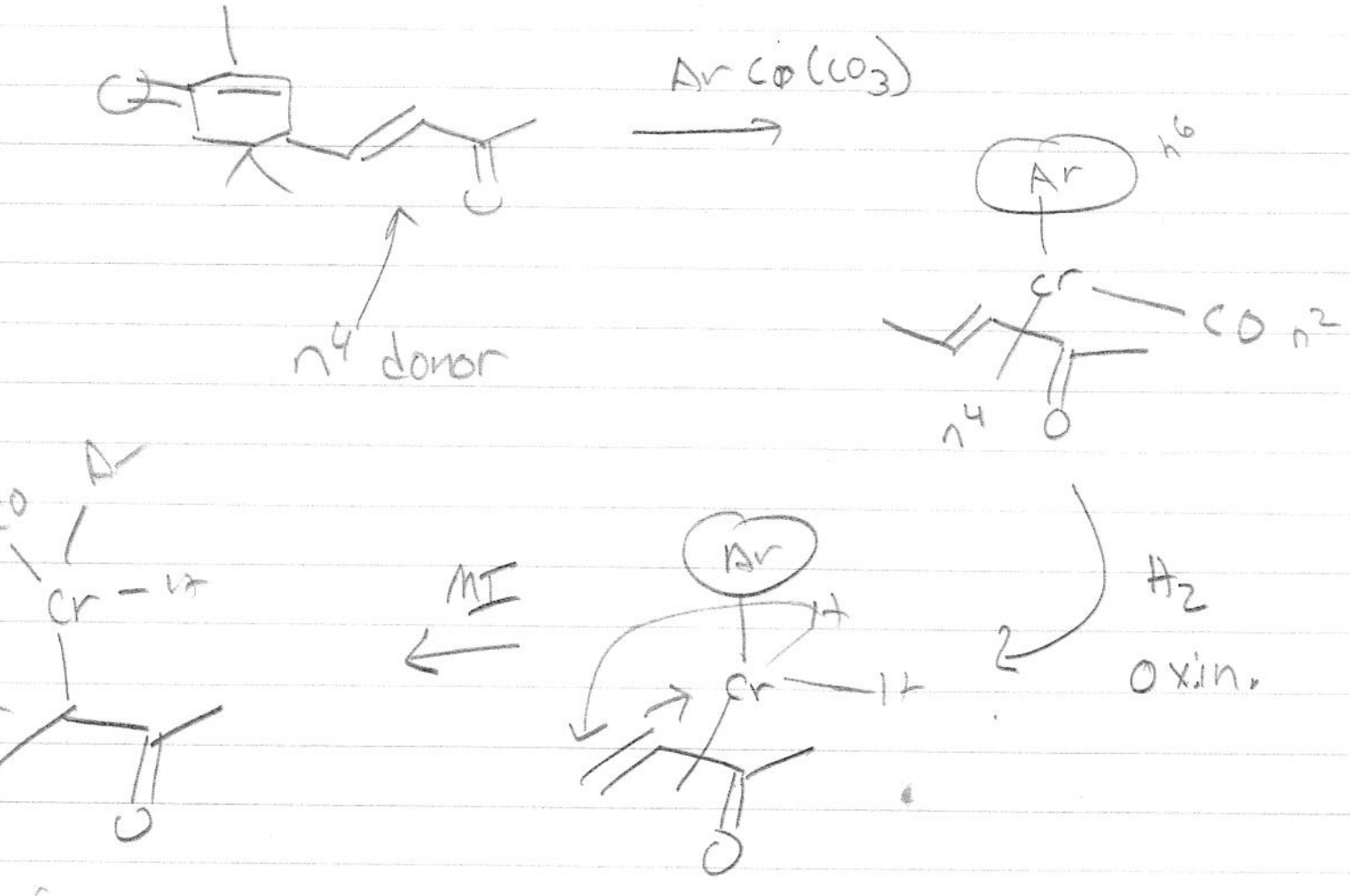


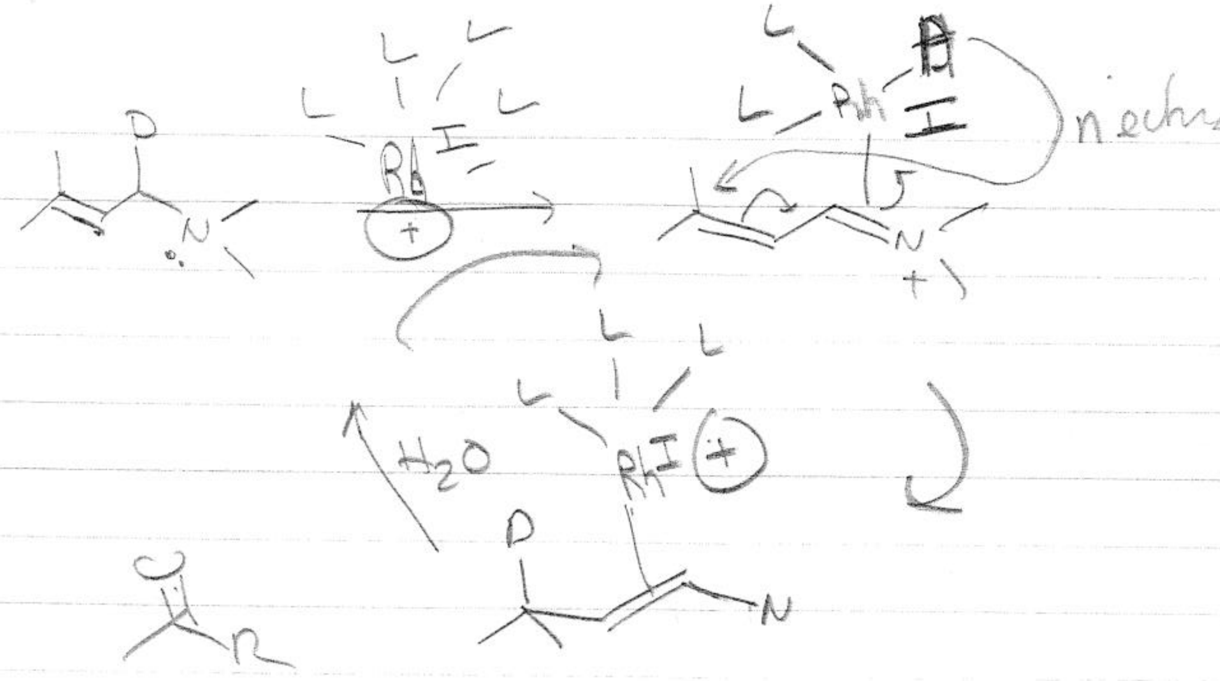


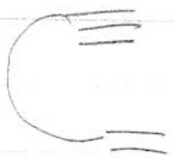


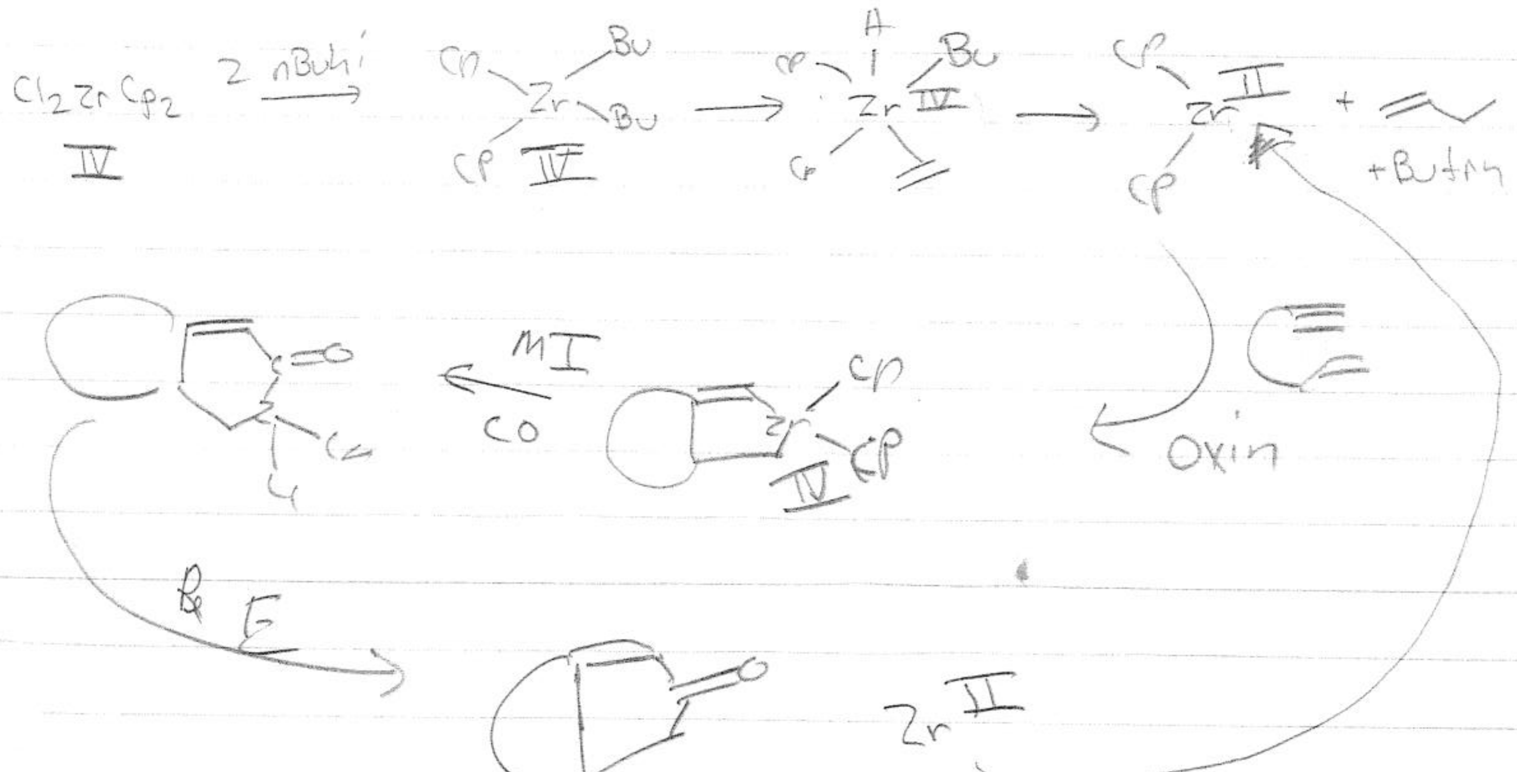

I
Ir III
M
I
H
L
Ir
RF
super
unsaturated
12 e⁻
Ir L2

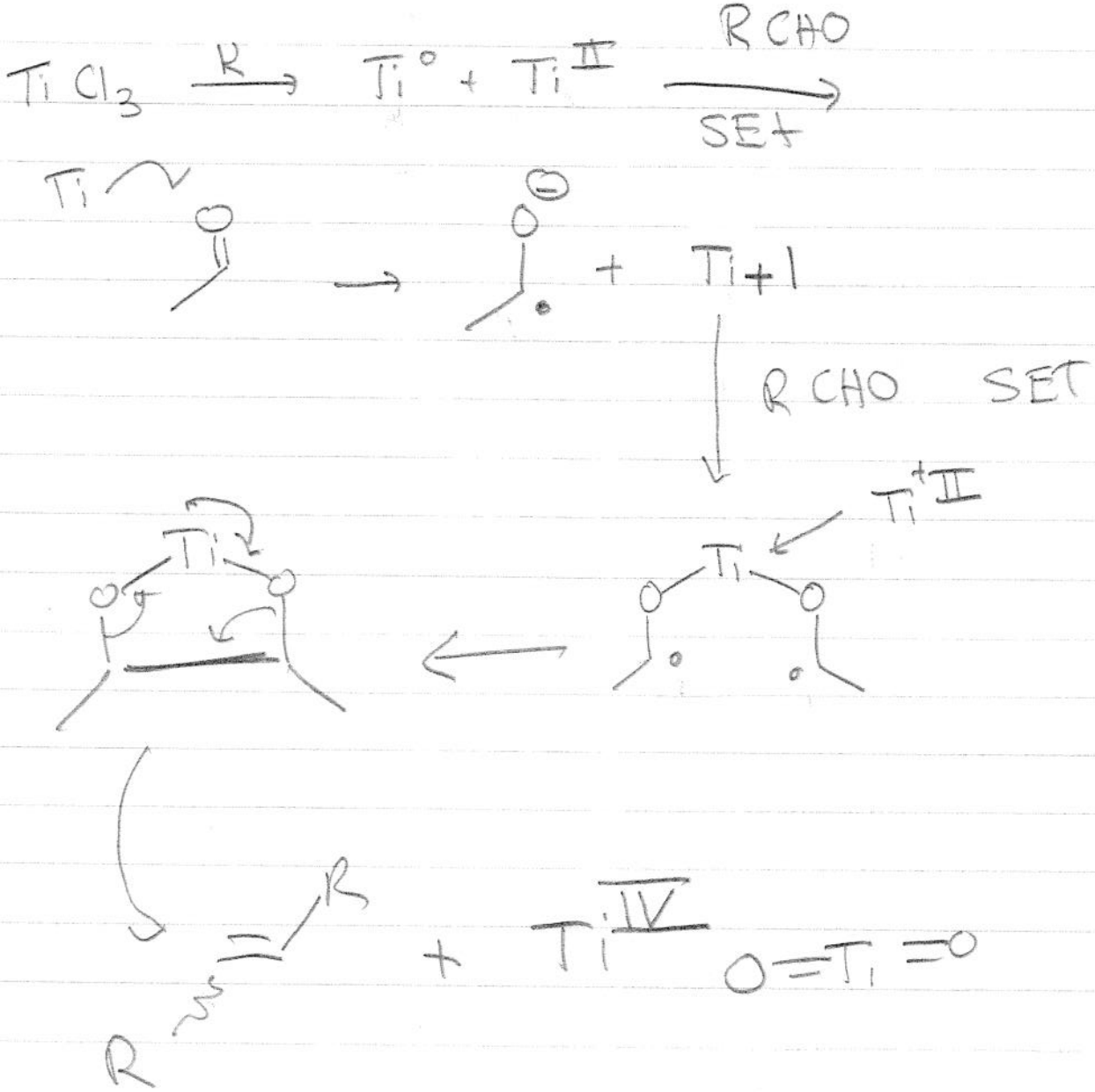
IV

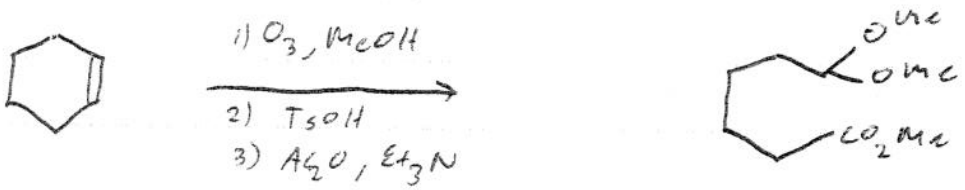

Ar Co(CO3)
η4 donor
Ar
η6
Cr
CO
η2
η4
O
MI
H2
Oxin.
red
elim


H2O
Rh

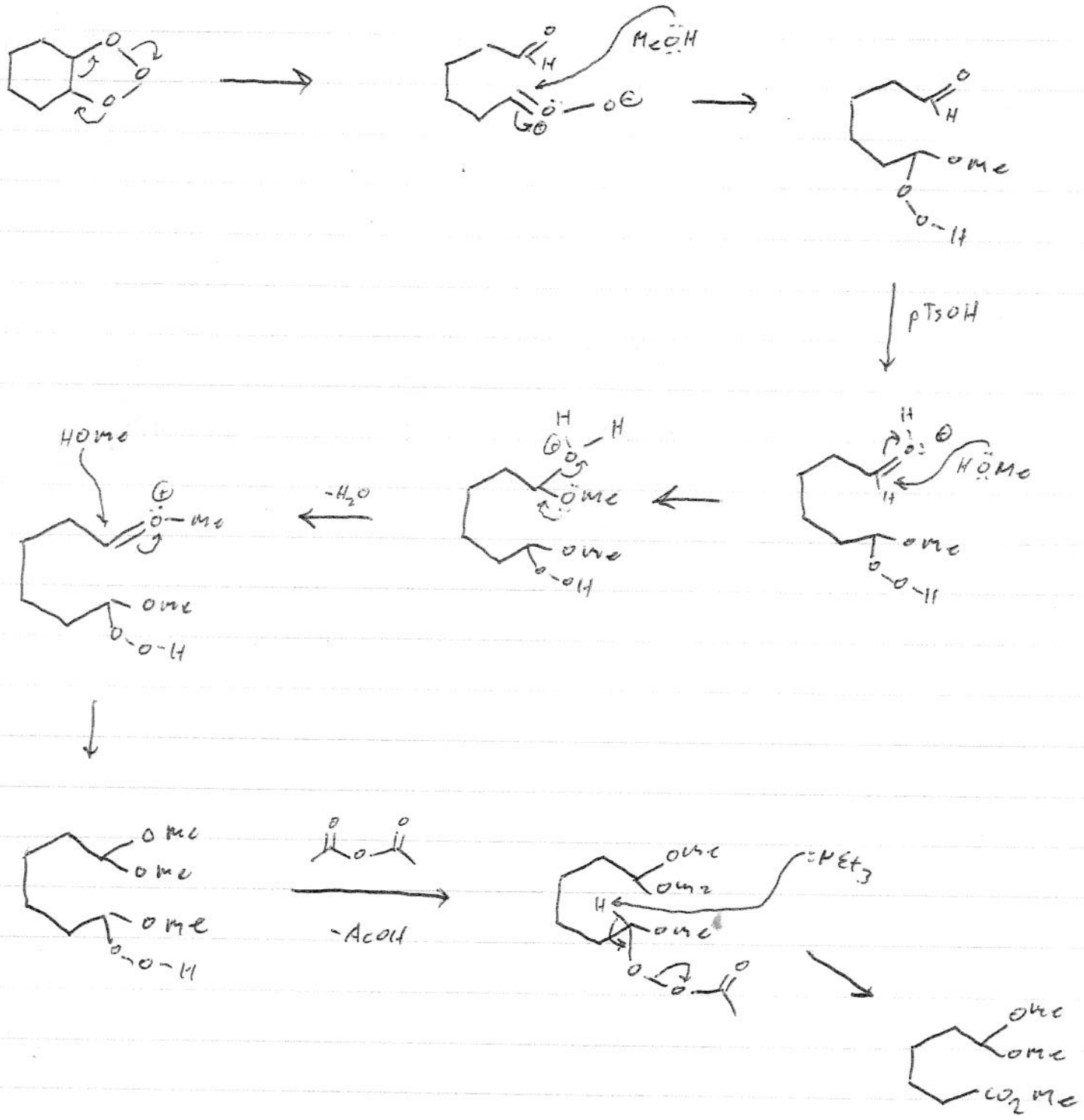



Cl2ZrCp2
2 nBuLi
Oxin
CO
Zr II

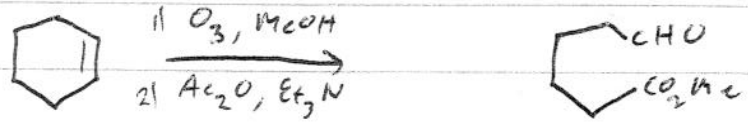

TiCl3
K
Ti° + Ti II
RCHO
SET
Ti
Ti+1
RCHO SET
Ti+II
Ti
Ti
R
R
Ti IV
O=Ti=O



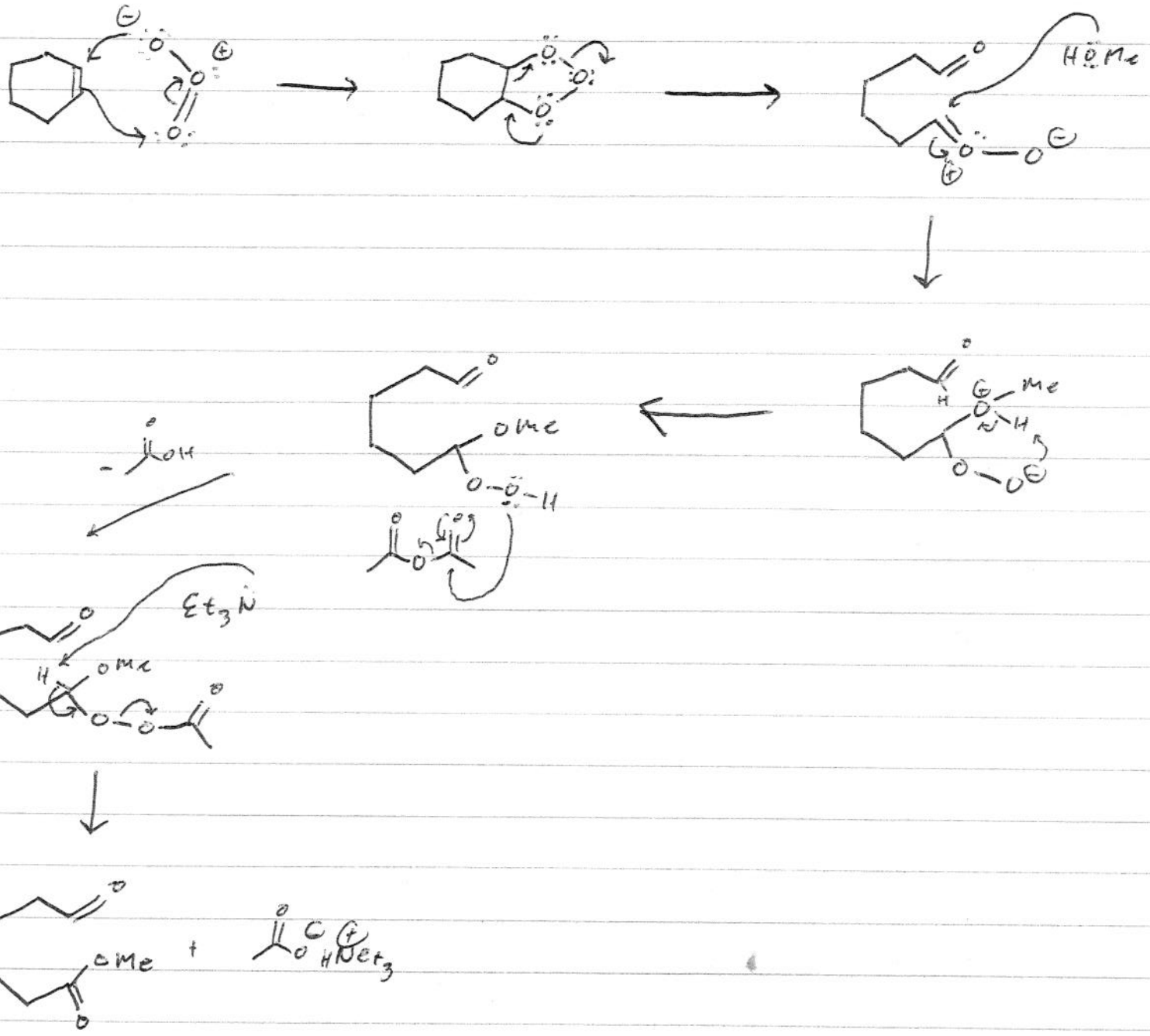
mech

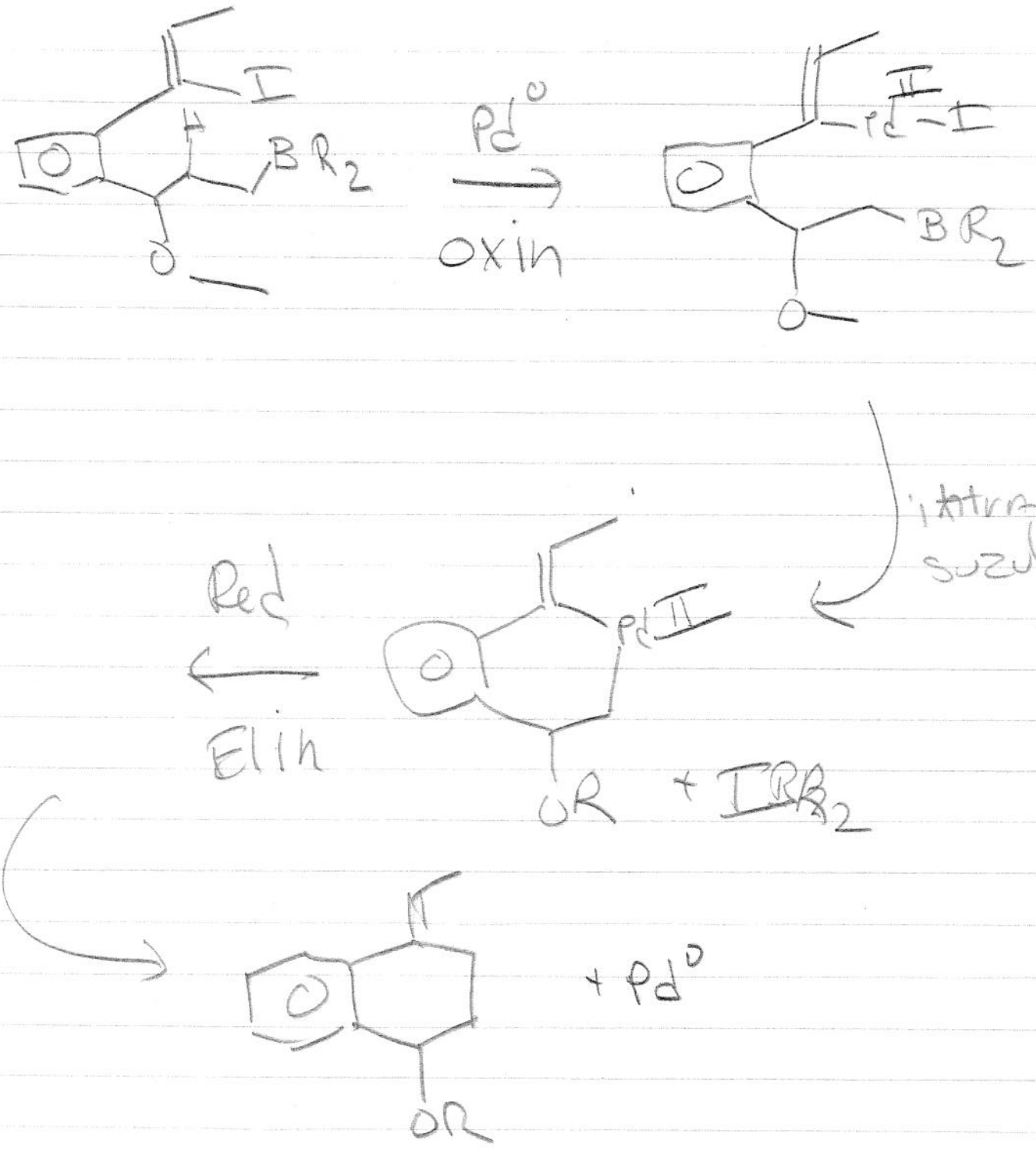


Ozone



mech




I
H
BR_2
O
Pd^0
oxin
II
Pd
I
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BR_2
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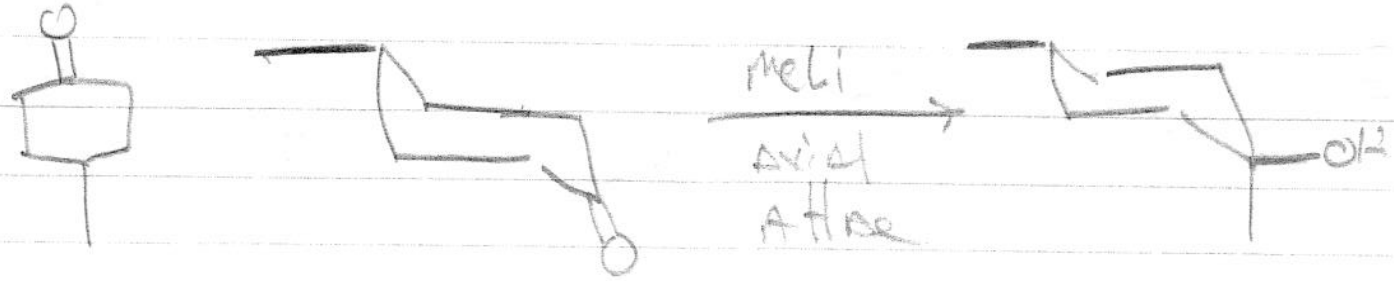
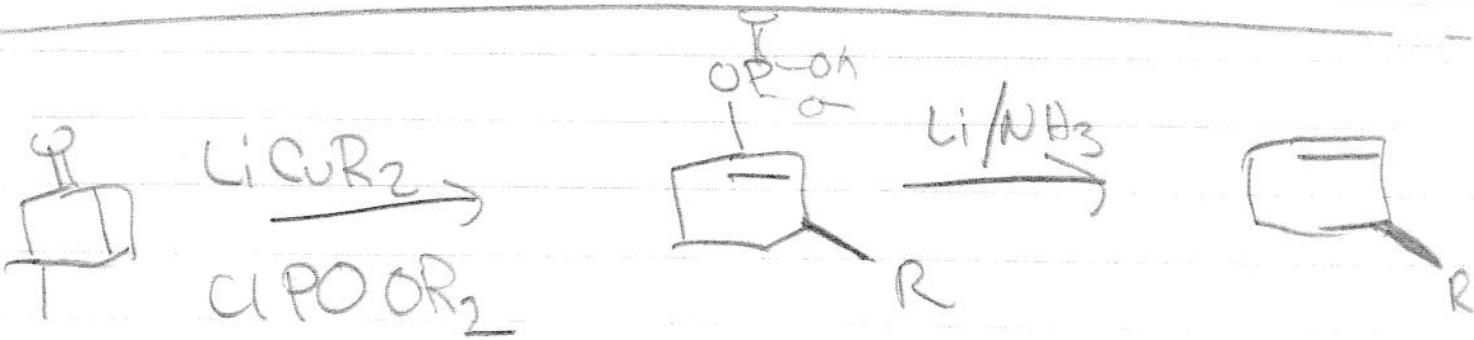
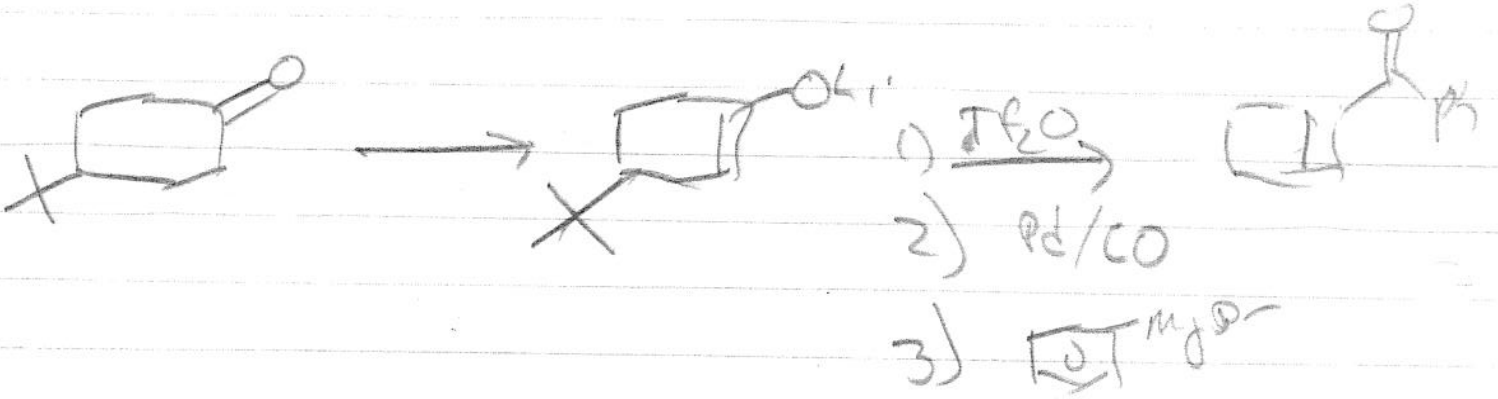
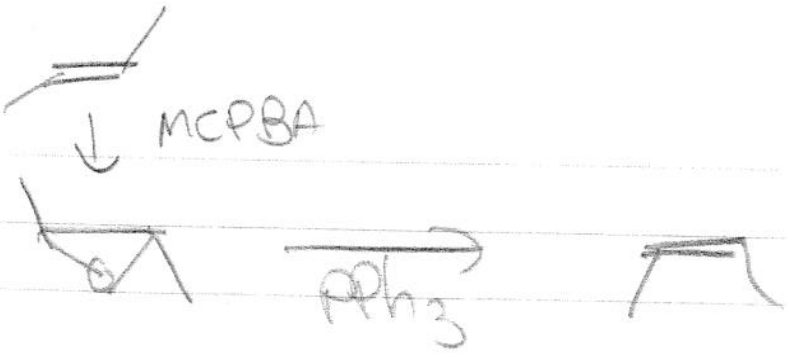
ittrm
suzuki
Red
Elin
II
Pd
O
OR
+ IRR_2
O
OR
+ Pd^0

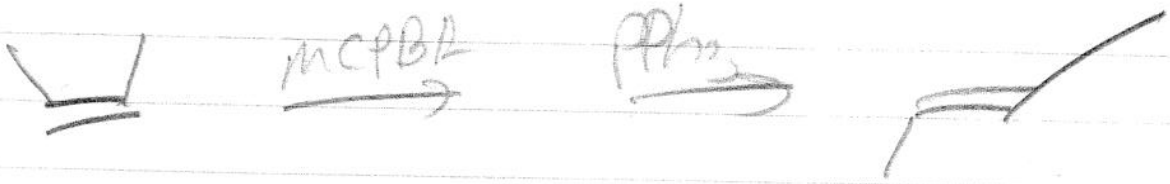

MeLi
Axial
Attack

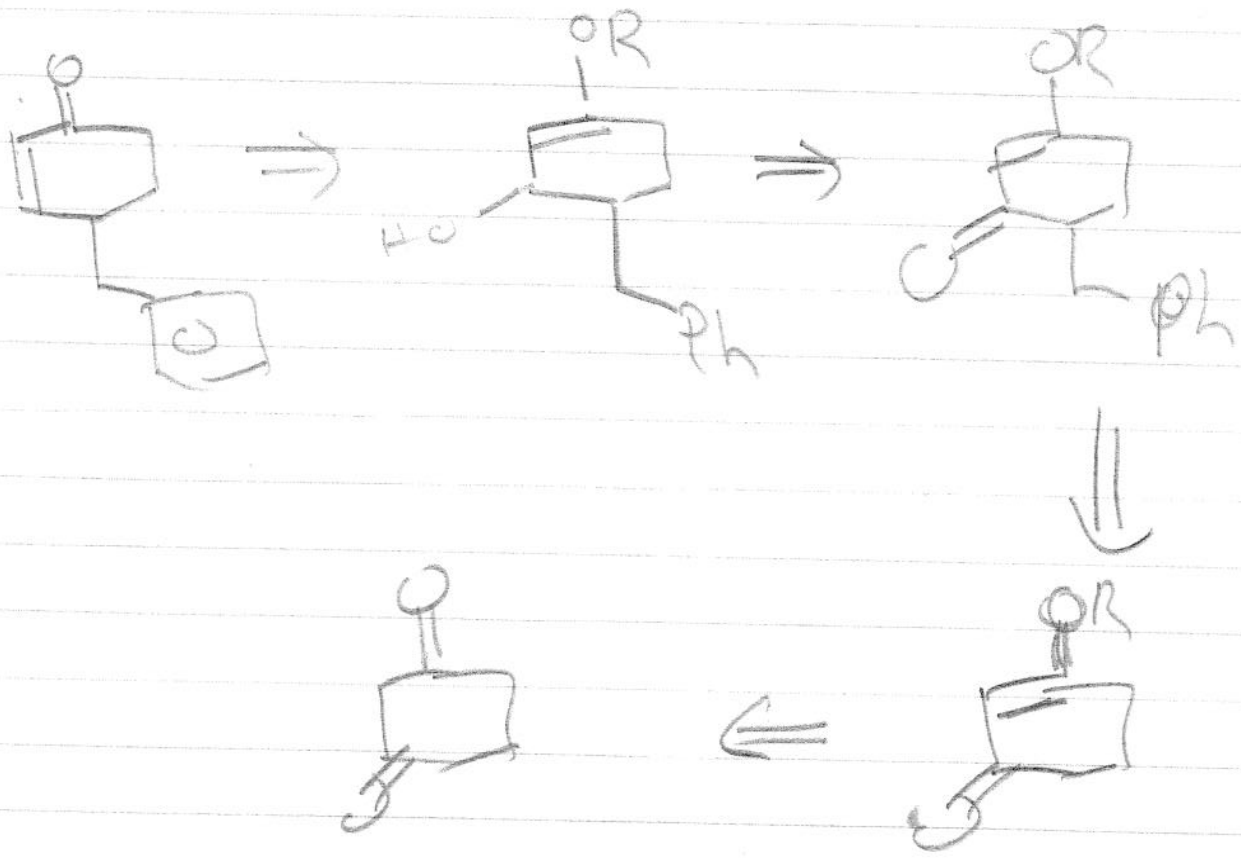

O3


LiCuR2
ClPOOR2
Li/NH3
R
R


1) Tf2O
2) Pd/CO
3) MgBr


MCPBA
PPh3


MCPBA
PPh3


OR
HO
Ph
OR
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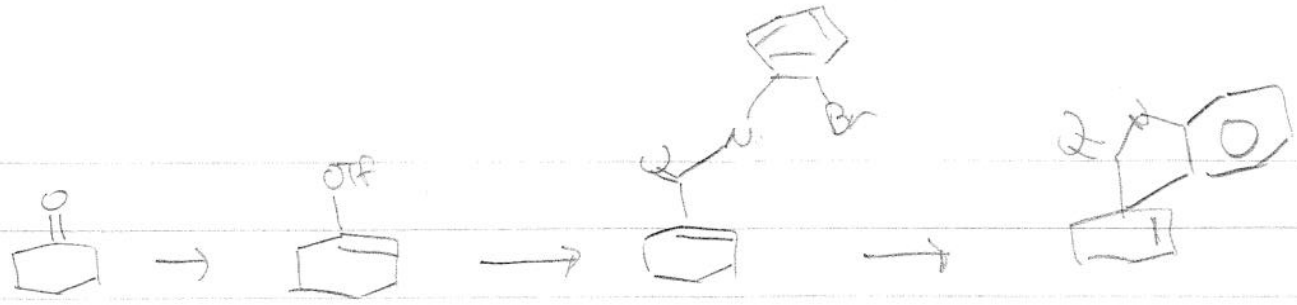
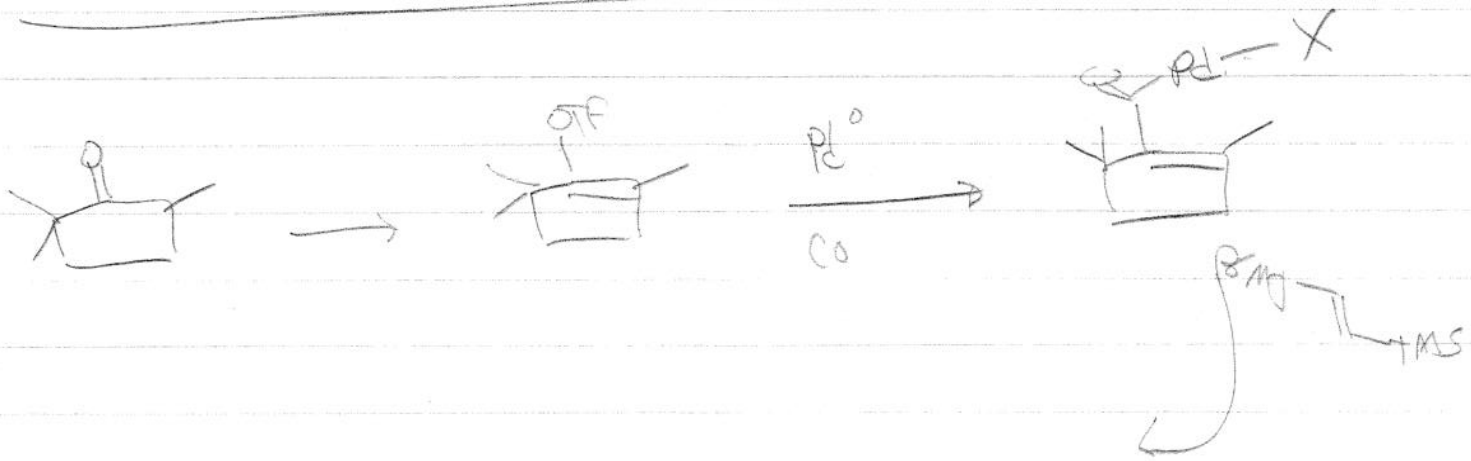
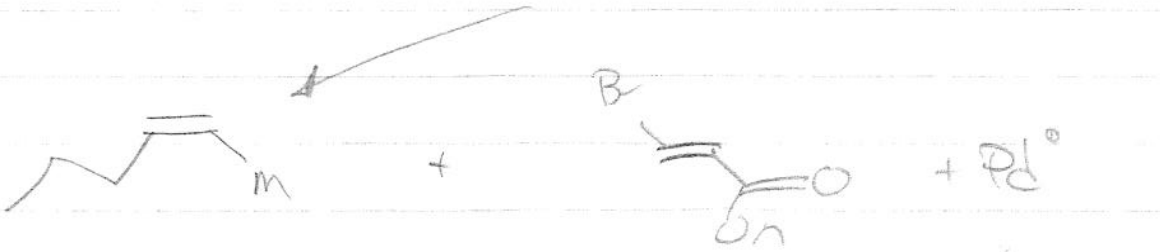
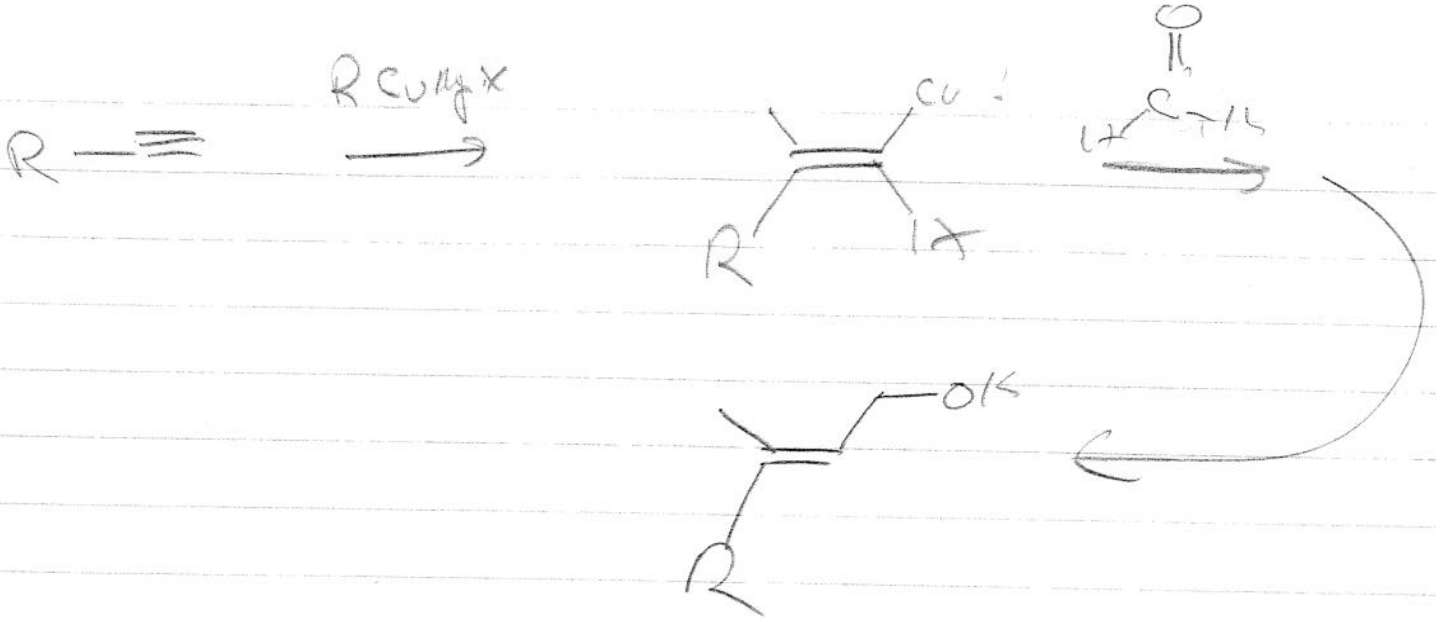
OR

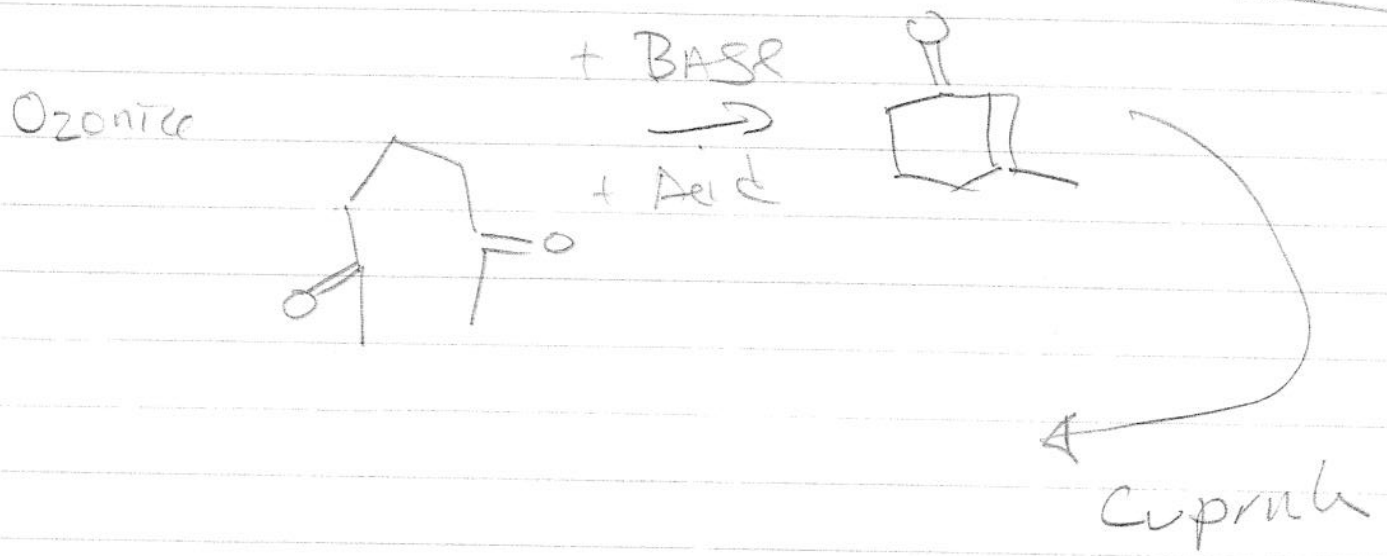




Robinson Annulation + Cuprate Addition

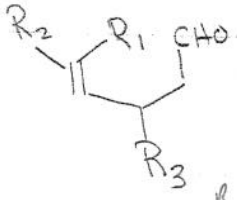
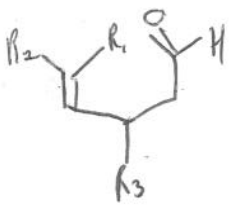
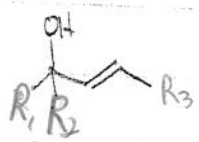
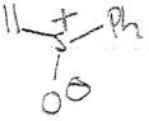




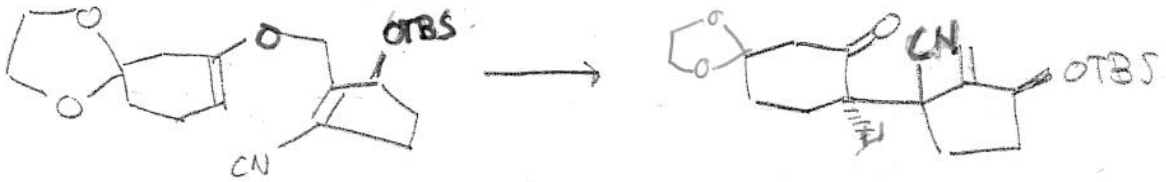


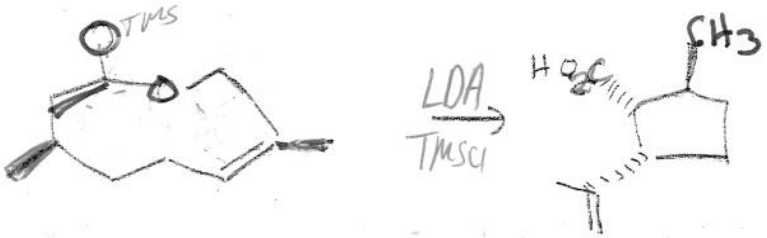
Grob

Due Oct 9

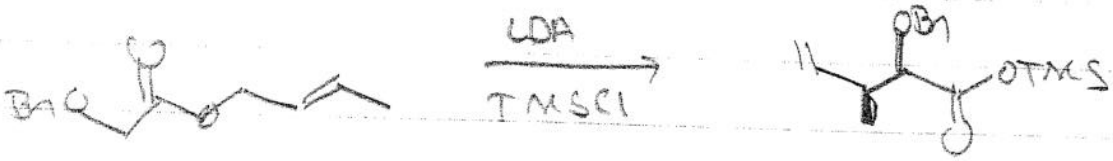
Prepare  From  and  

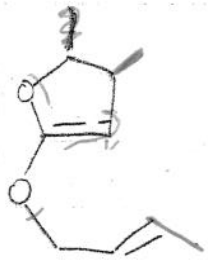
Using 3d pictures explain the following result

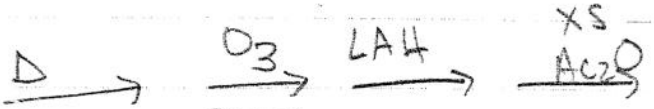




IN some cases chelation effects override the Ireland paradigm! explain the following

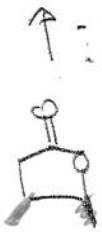




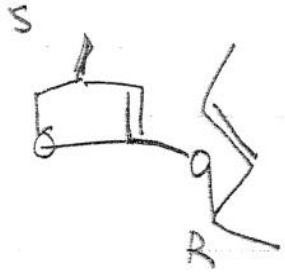


A

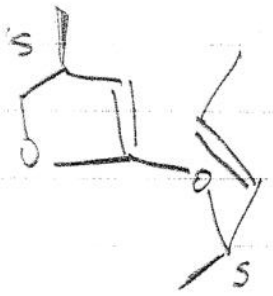
9 ^{13}C peaks



Explain the following observation with pictures



100%



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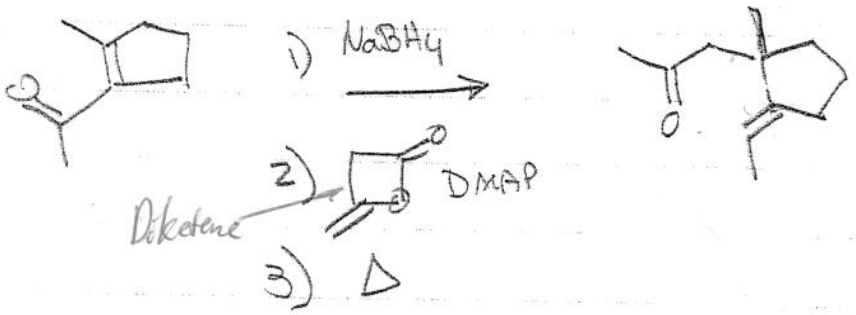
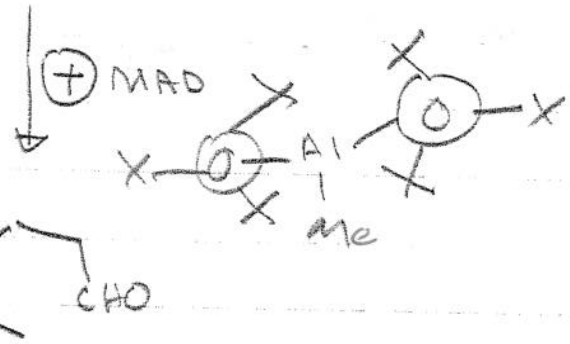


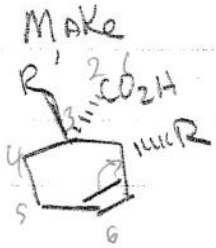
Provide arrow pushing mech for all steps

Explain why?

but



Make



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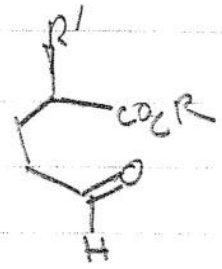

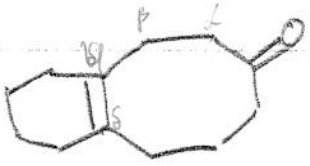

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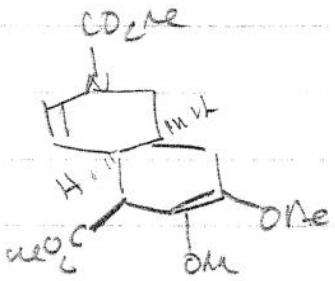

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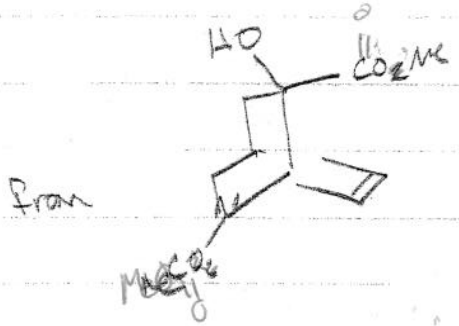

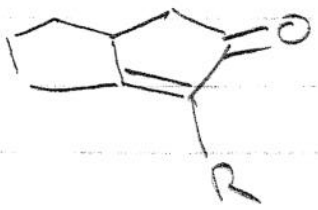

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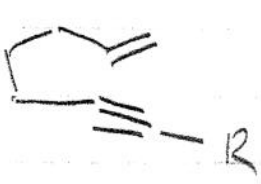
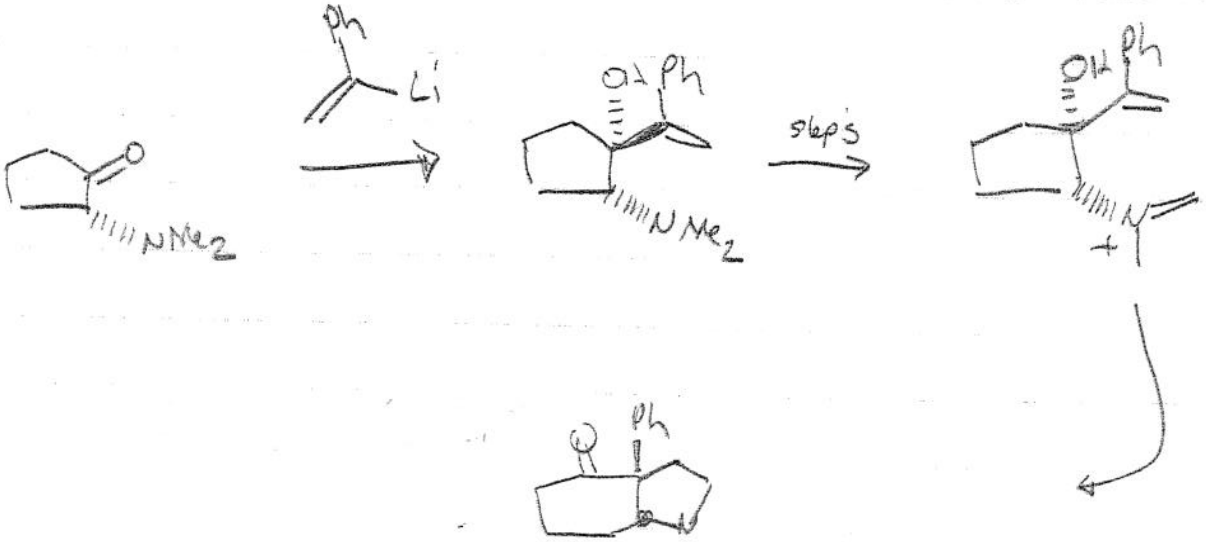
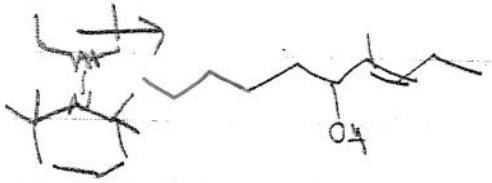


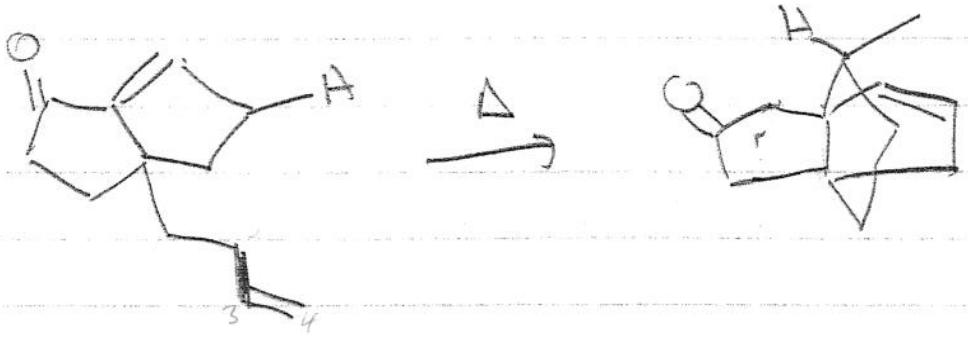
Explain all stereochemistry with TS≠

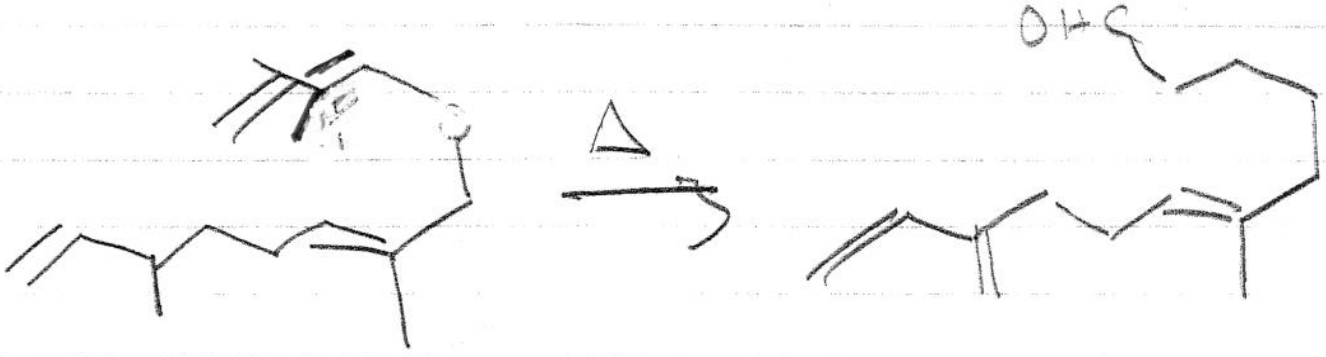


Explain why

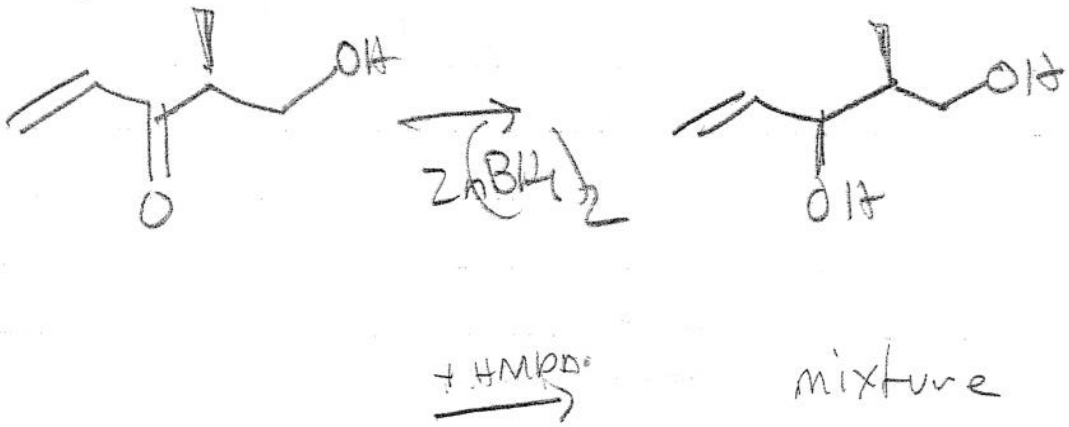


Provide a mechanism



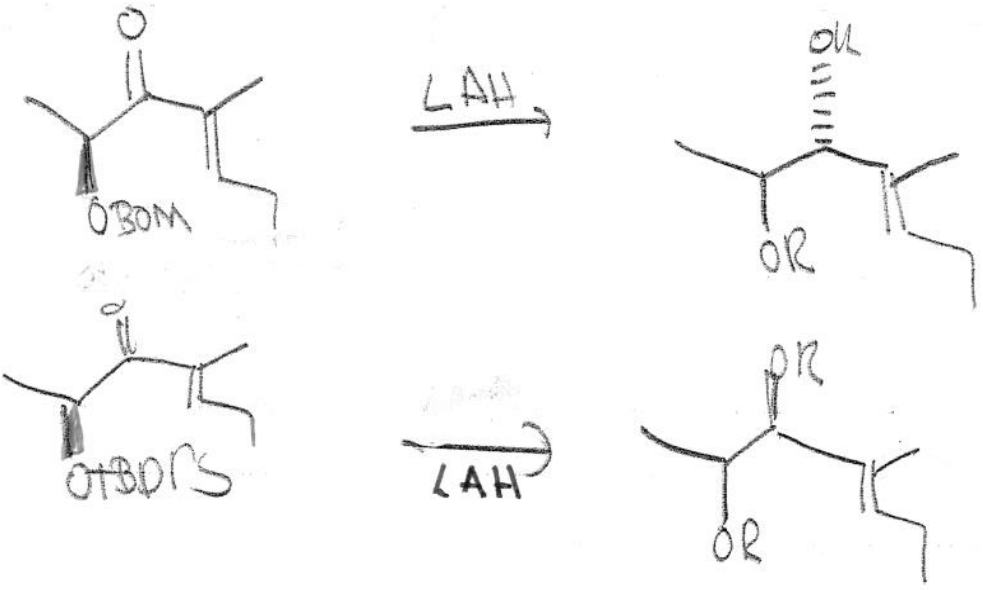


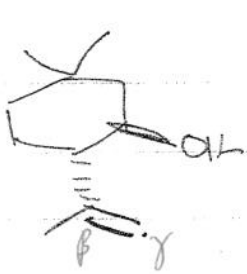
Explain the following observation



+ HMPA

mixture





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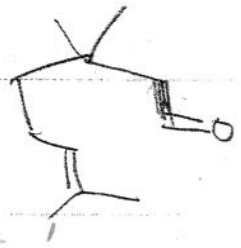

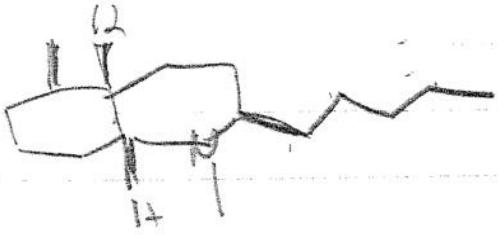

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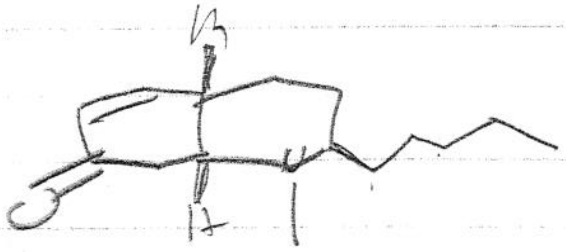
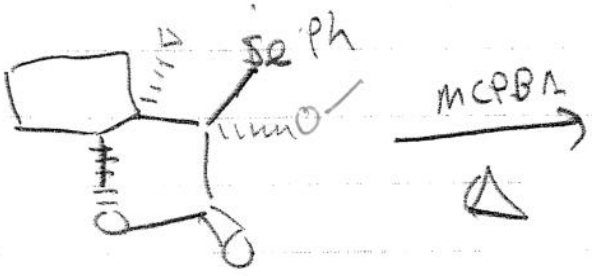
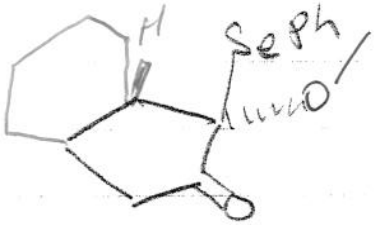


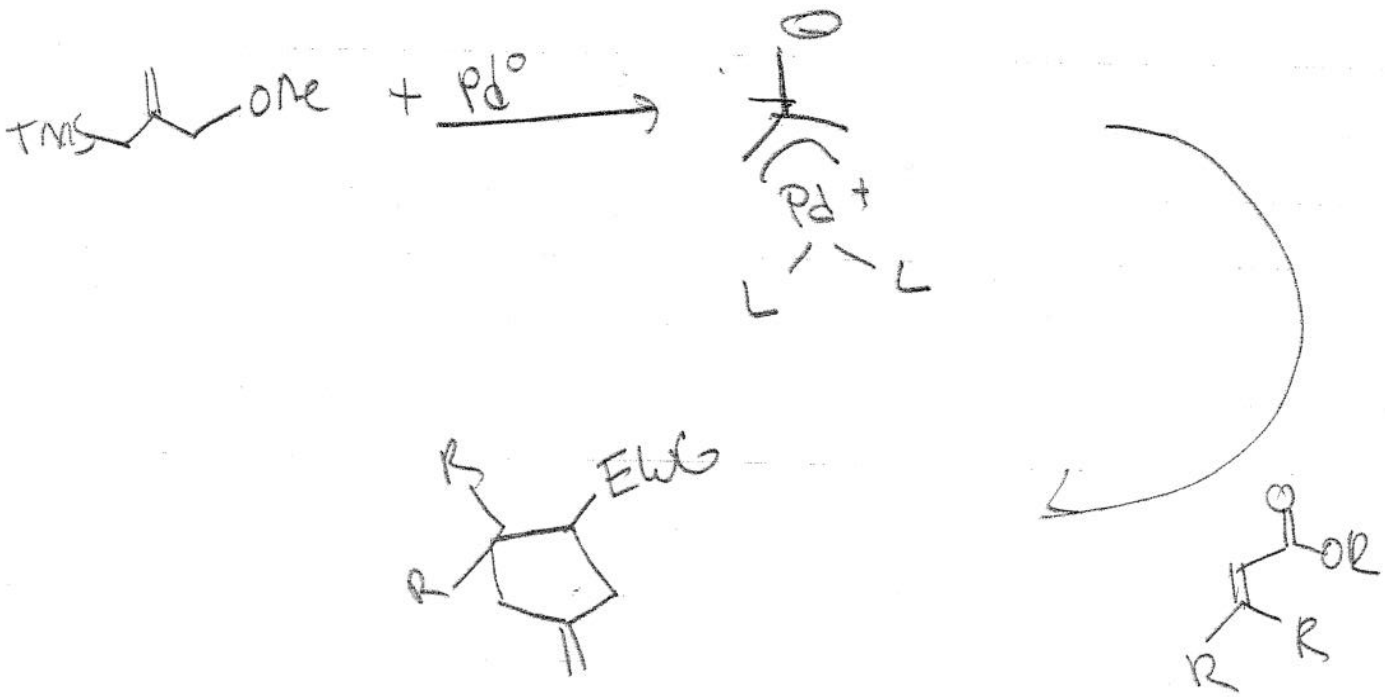
In the case of



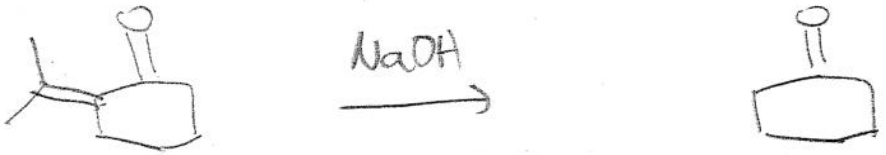
good



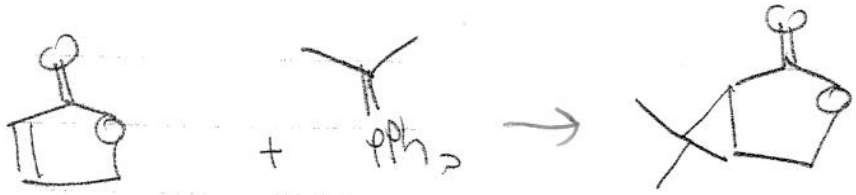
bad



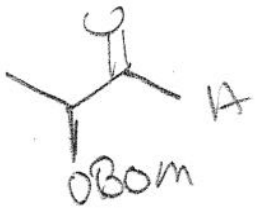
Proline enLine mechanism



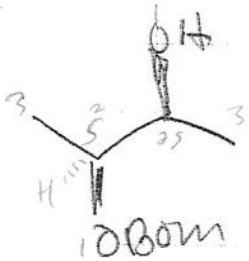
how?



Exp 1

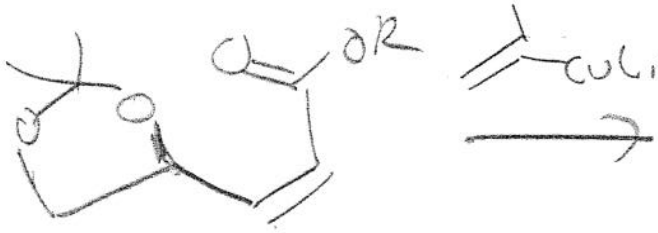


Me_2CuLi →

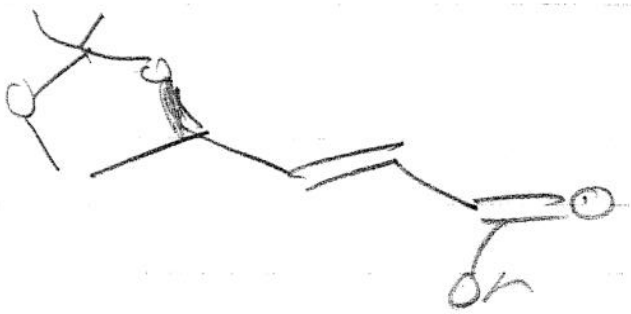


2 : 1

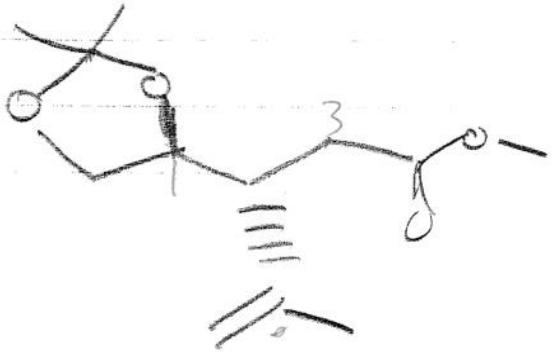
MeMgBr 10 : 1

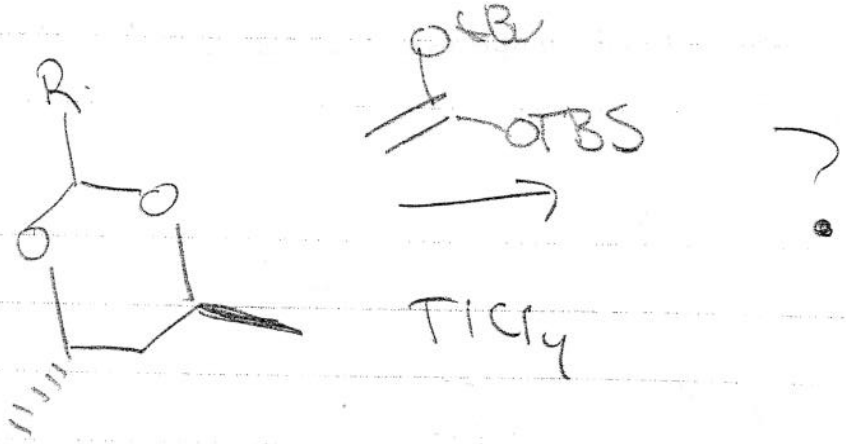


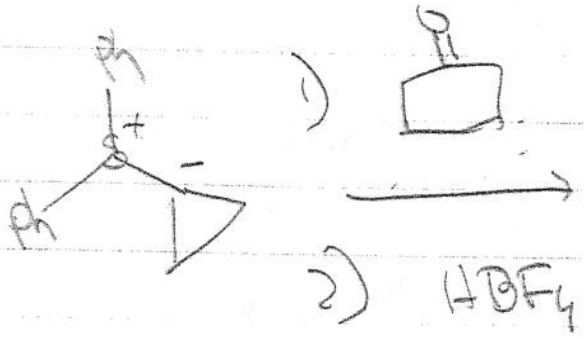
8 : 1



5 : 1

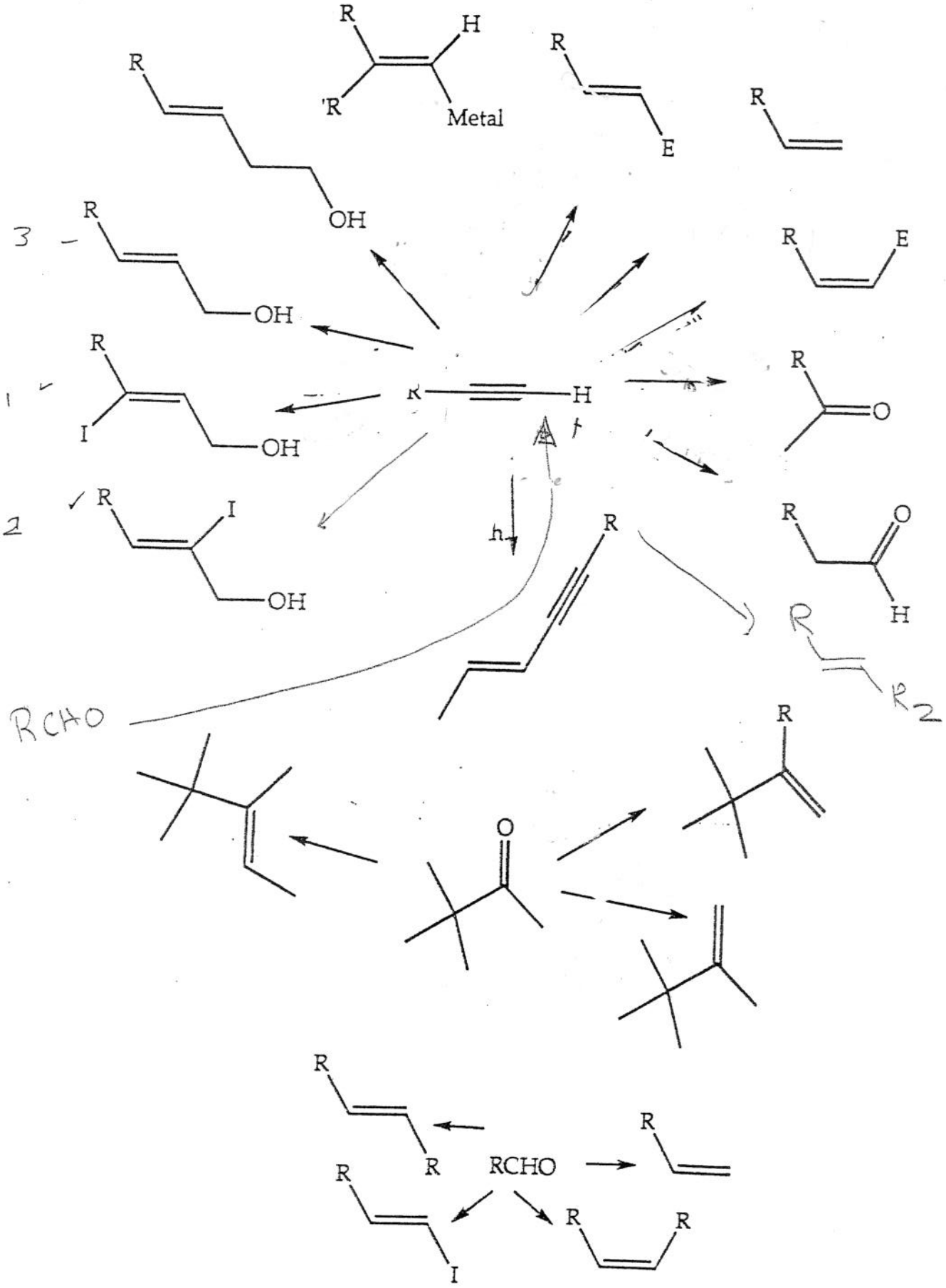



R
OTBS
TiCl4
?


1)
2) HBF4

Review of Alkene Synthesis

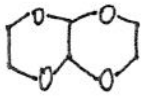
Write the reagent(s) over the arrow which most readily completes each conversion

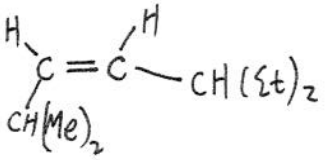


Problem Set

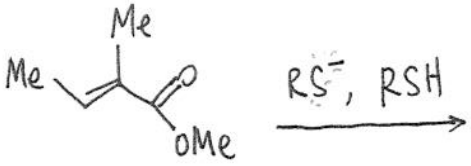
I) Draw the Likely conformation of the following Compounds.

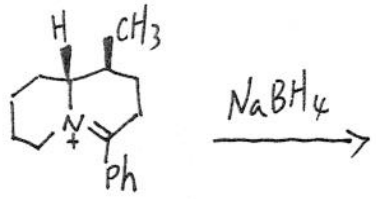
$CH_3CO_2CH_2CH_3$

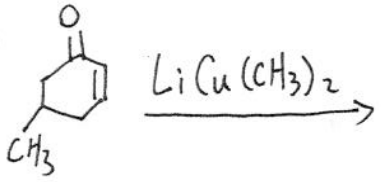


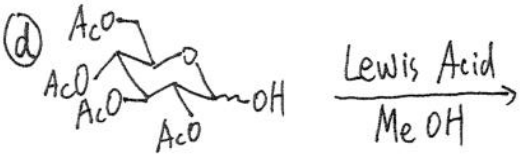


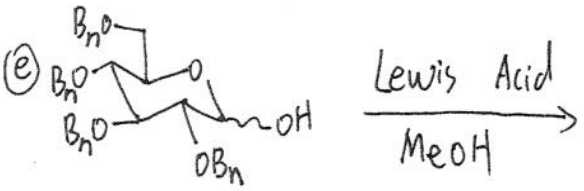
II) Predict stereo chemistry of following reaction. Give a brief explaination.

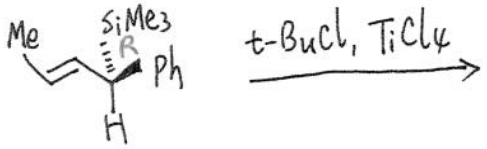
ⓐ 

ⓑ 

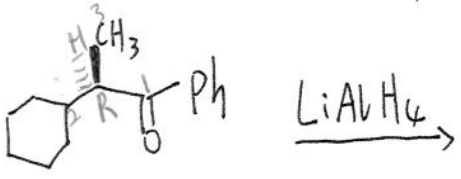
(c) 

(d) 

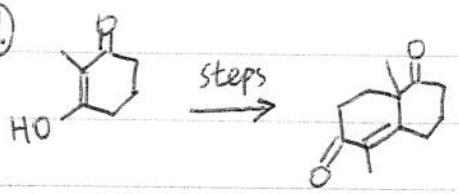
(e) 

(f) 

III) Predict Stereochemistry with appropriate model

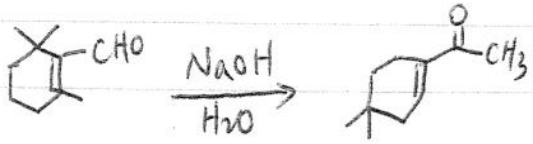
(a) 

I).

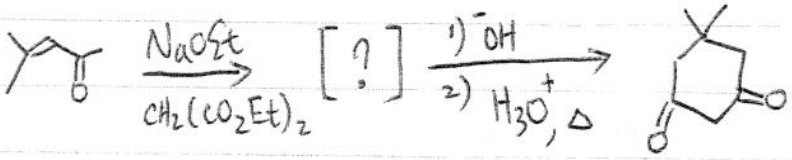


II). Suggest possible mechanism for following reactions.

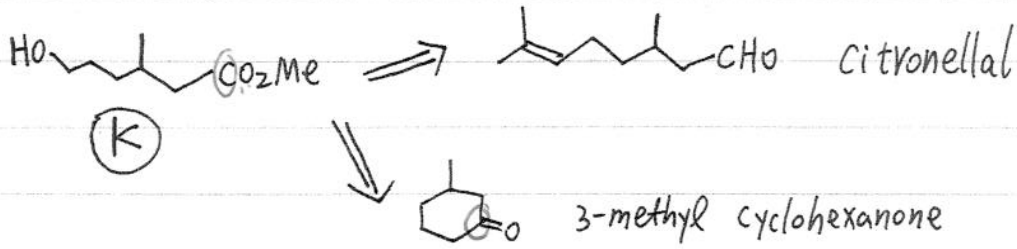
(a)

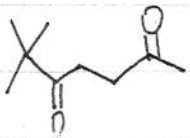


(b)

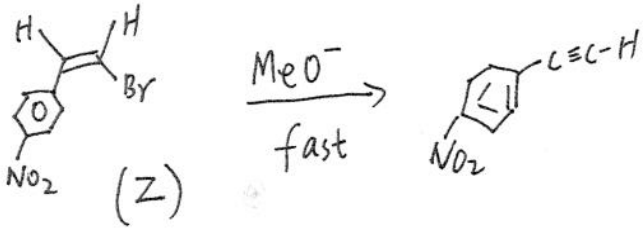


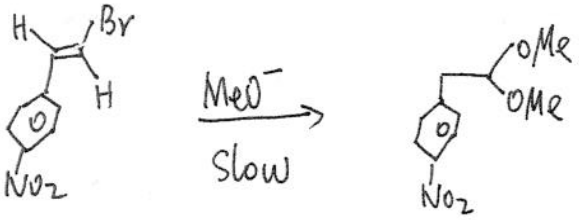
III). propose two synthetic routes to target molecule K, one starting from citronellal, the other from 3-methyl cyclohexanone.



IV) Using Aldrich material, Suggest a synthetic route to  in no more than 5 steps.

(b) The elimination of bromide from Z-isomer is 2000 times faster than the E-isomer, also provides different product. Why?

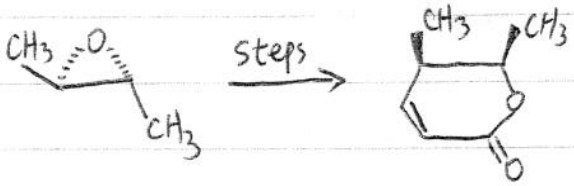




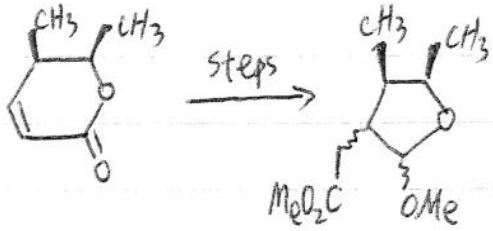
Problem Set

I). Starting from the given precursor, Synthesize the following material.

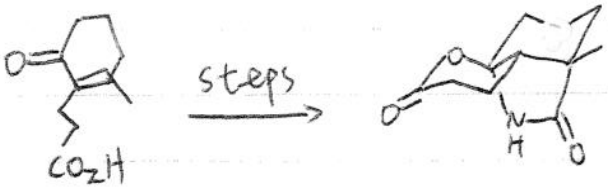
(a)

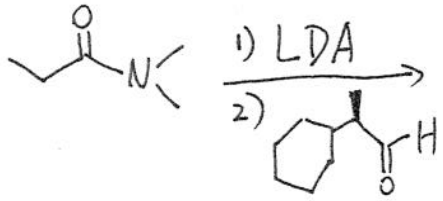


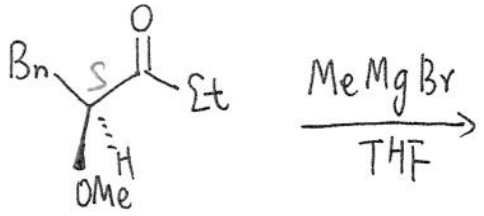
(b)



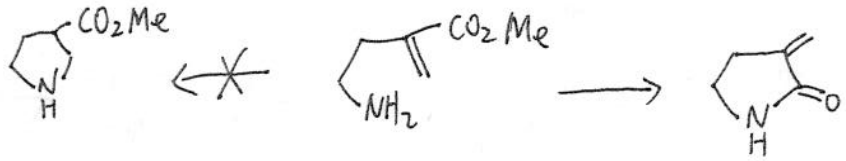
(c)



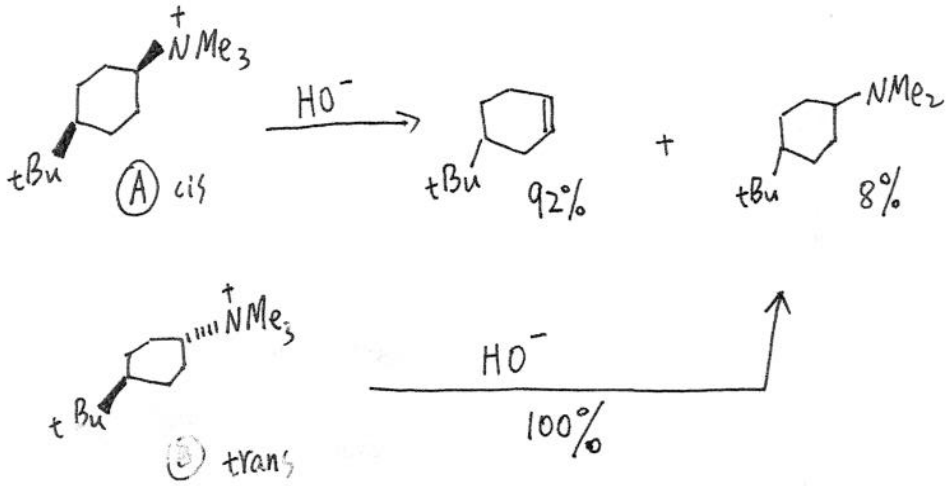
(b) 

(c) 

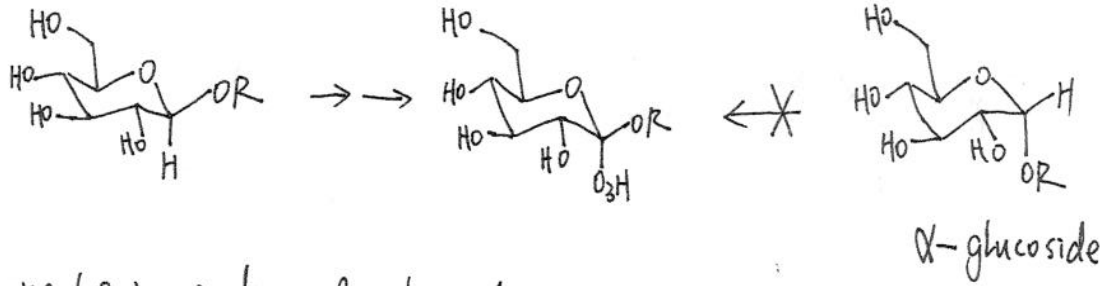
IV). Explain why primary amine cyclizes to form the lactam rather than adds to the c=c of acrylate ester.



V). Explain why the cis (A) and trans (B) isomers react so differently with HO^-. (scheme in next page)



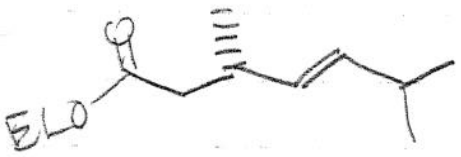
VII. (a)



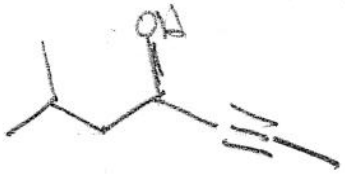
Pg 70

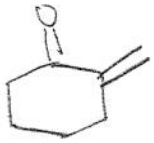
Ozone (O_3) oxidizes β-glucoside to form initially a hydrotrioxide as shown above. Why doesn't α-glucoside react with O_3 in a similar way?

Make

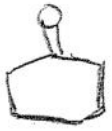


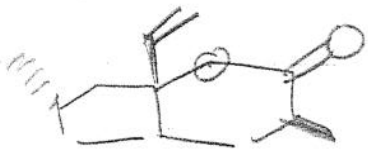
from



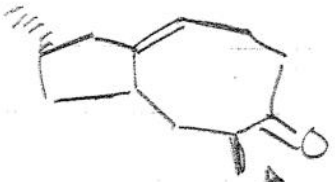


from





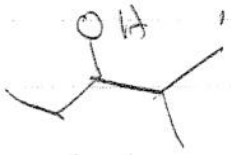
from



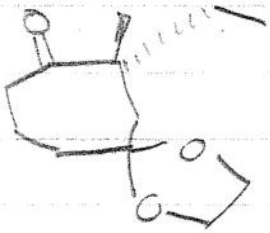
Make

what is Martin Sulfurane
Burgess Reagent

when you use the reagents with

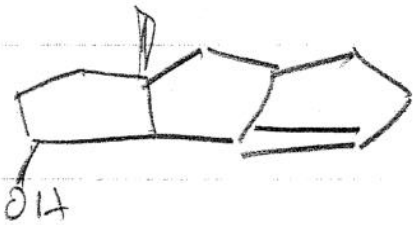


will they give similar major product with



1) LDA
TF_2NPh
2) Pd^0

A ?



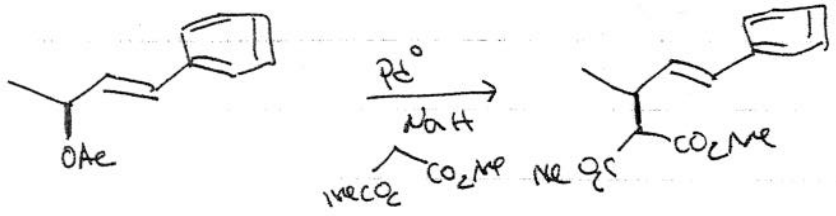
$RhCl_3$
no H_2

?

Keep careful track of the metal oxidation states!

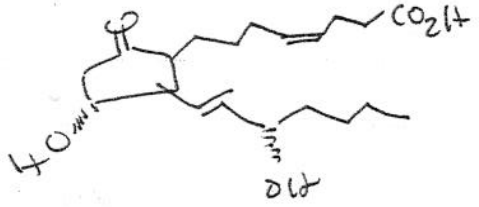
Problem Set IV

1) Propose a mechanism for



your mech. should include 1) oxidn
2) electrophilic species
3) nucleophilic addition
4) reduct elim

2) propose ~~of~~ mech for Wilkinson Reduction of

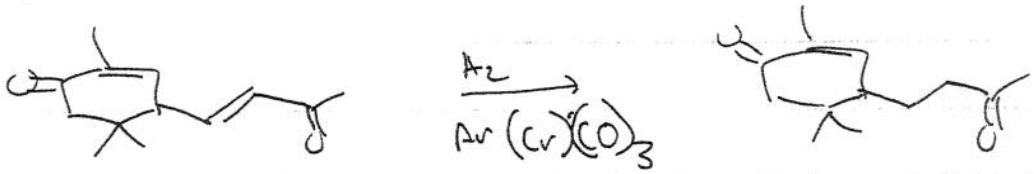


why does cis reduce faster

3) Propose a mechanism for Crabtree Reduction of

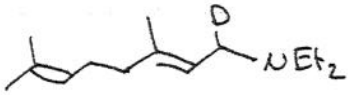
TL 38 3867

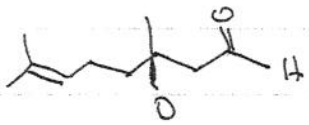
Propose a mechanism



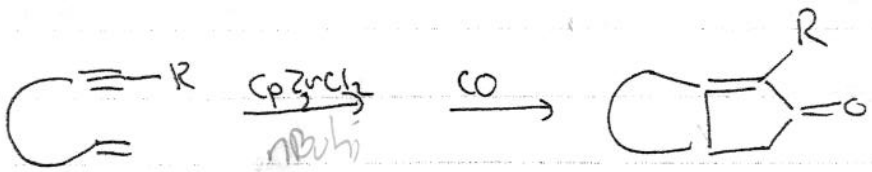
why only one enone?

Propose a mechanism for:

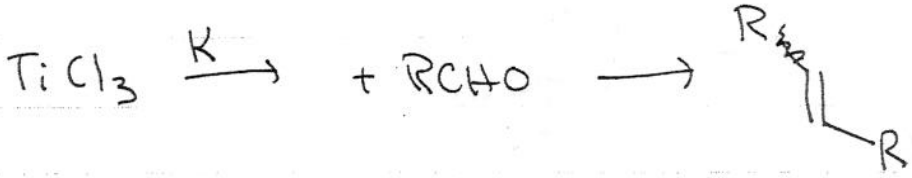


citronellal 

Propose a mechanism for



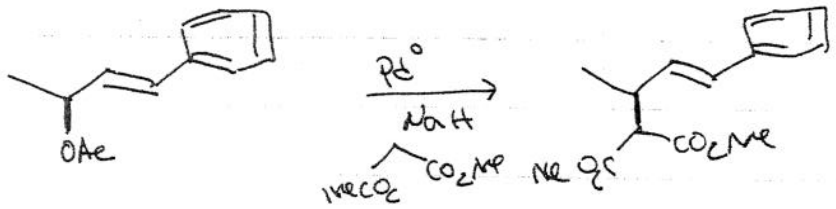
Propose a mechanism for



Keep careful track of the metal oxidation states!

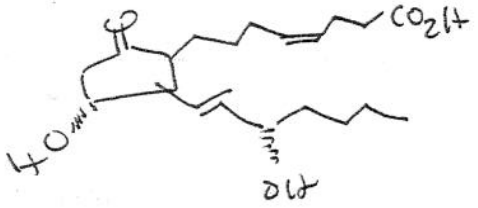
Problem Set IV

1) Propose a mechanism for



your mech. should include 1) oxidn
2) electrophilic species
3) nucleophilic addition
4) reduct elim

2) propose ~~of~~ mech for Wilkinson Reduction of

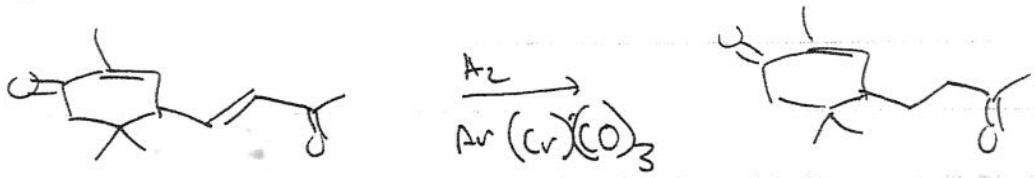


why does cis reduce faster

3) Propose a mechanism for Crabtree Reduction of

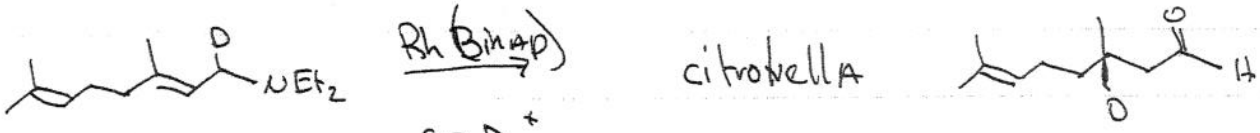
TL 38 3867

Propose a mechanism

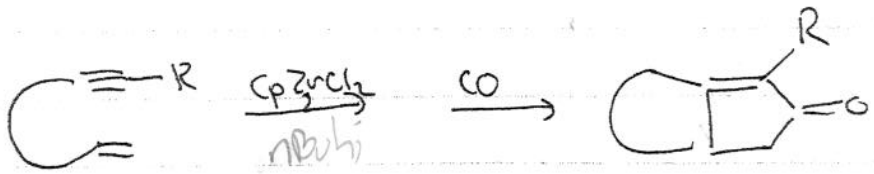


why only one enone?

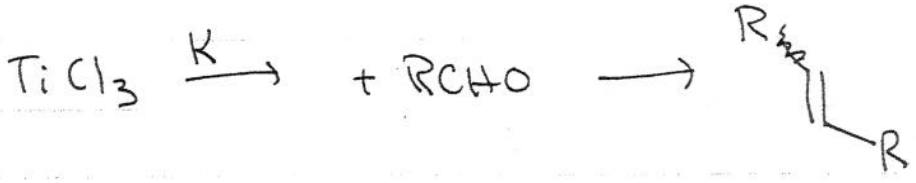
Propose a mechanism for:



Propose a mechanism for

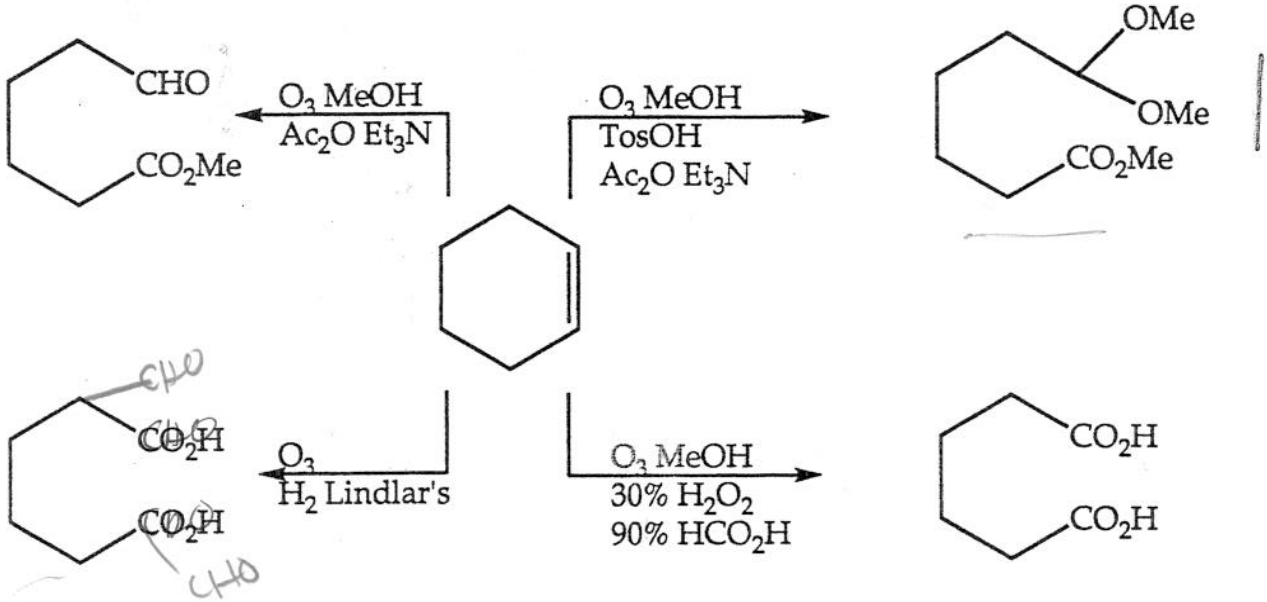


Propose a mechanism for

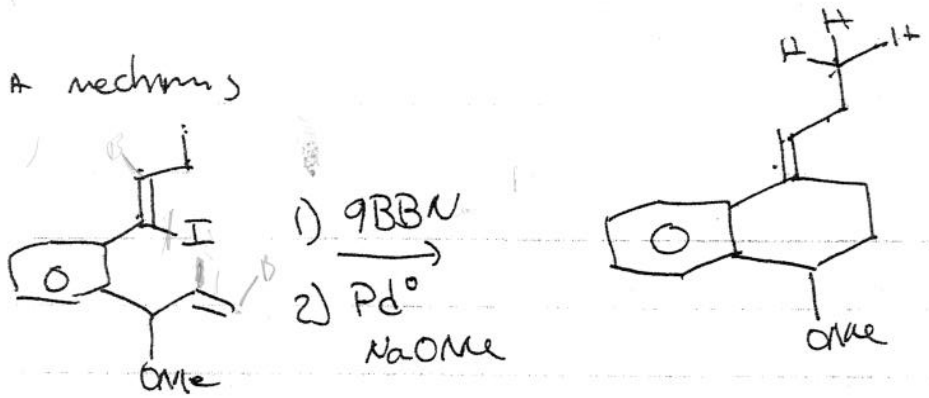


Propose a mechanism for the following transformations

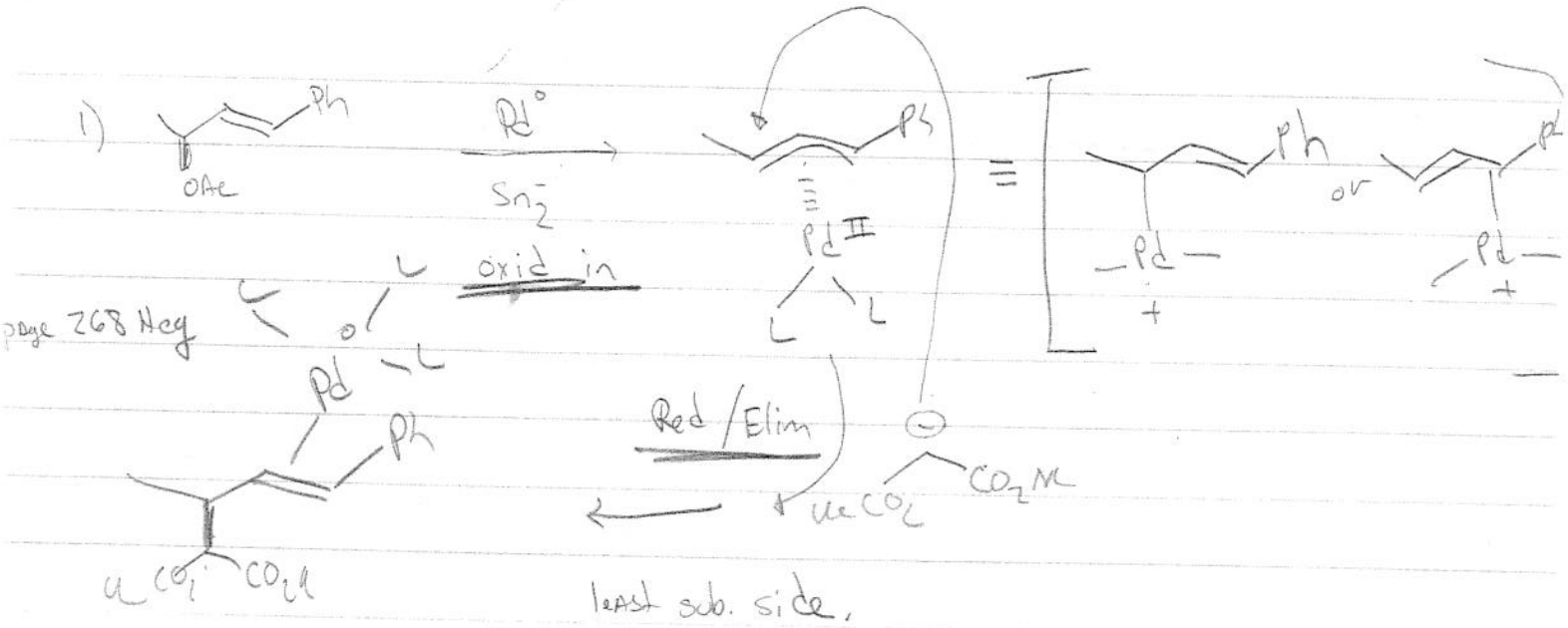
What's the mechanism

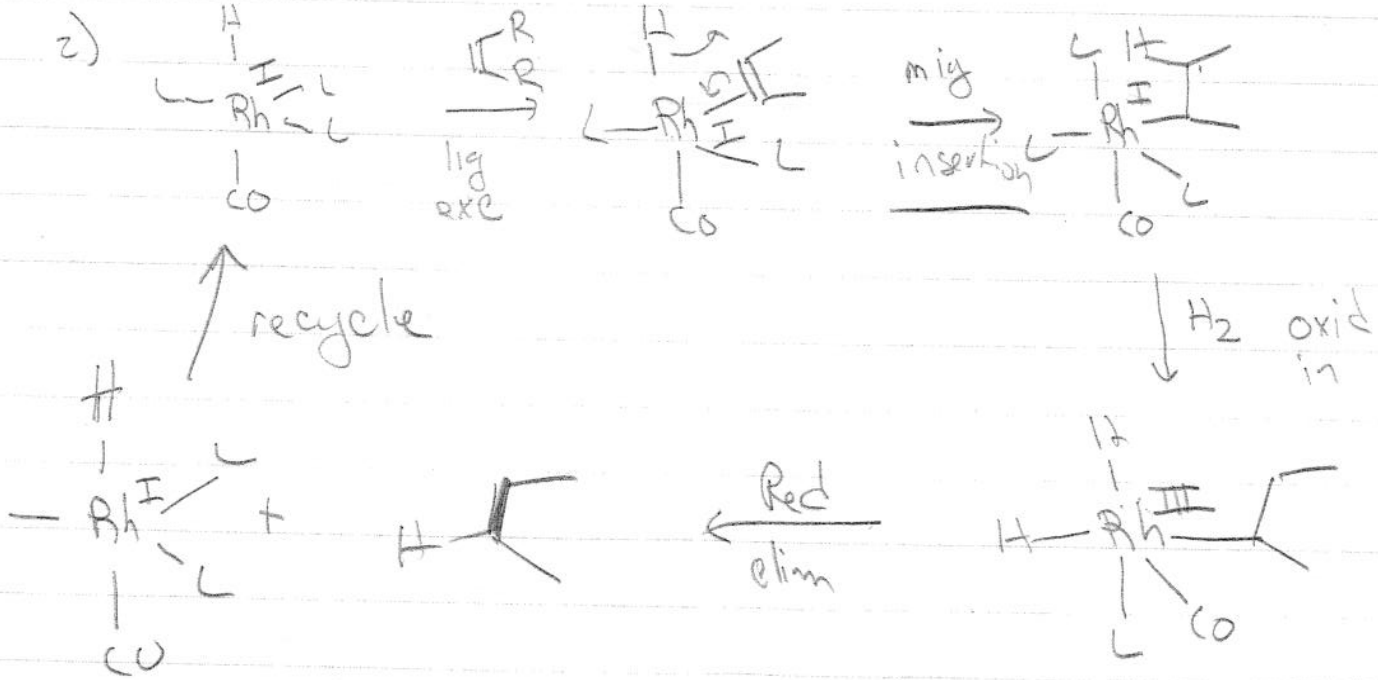


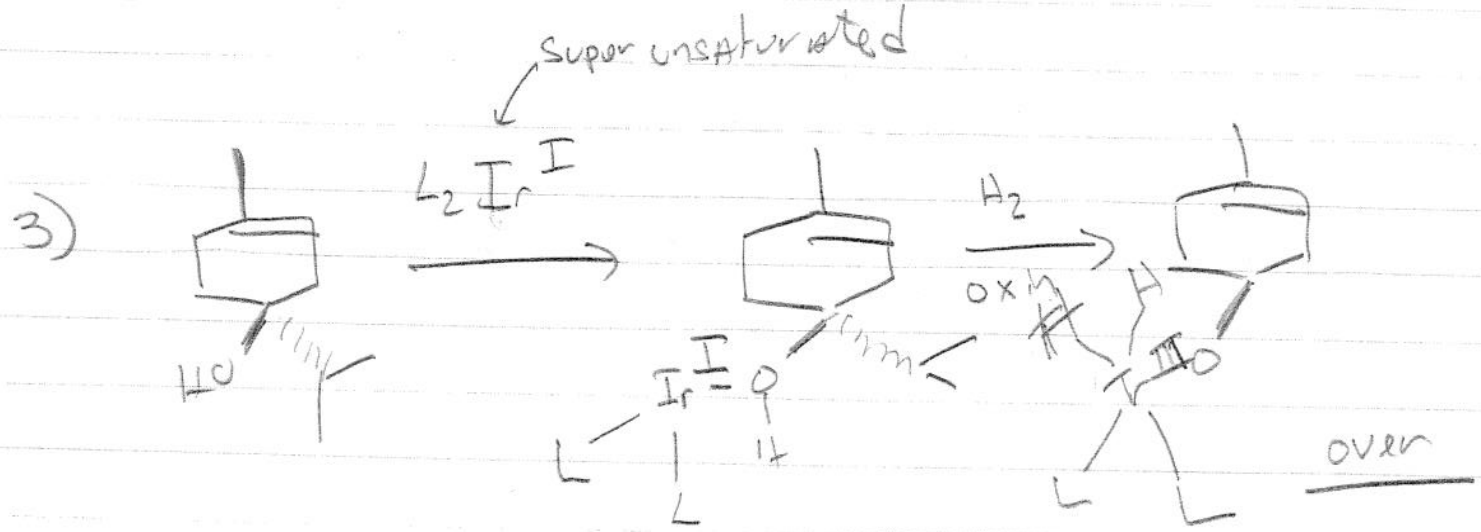
Propose a mechanism

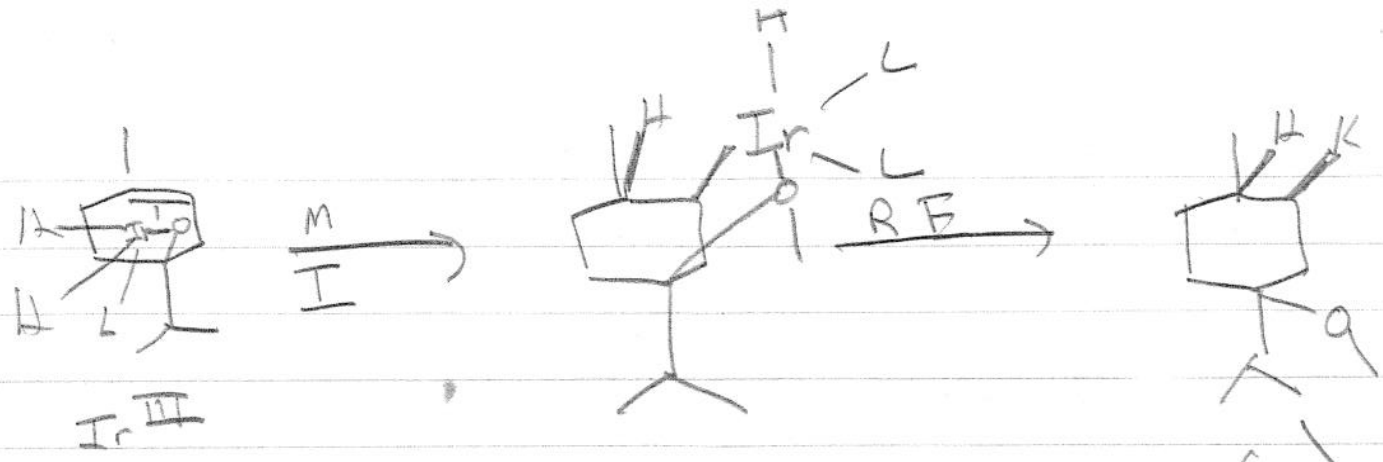


Problem Set IV

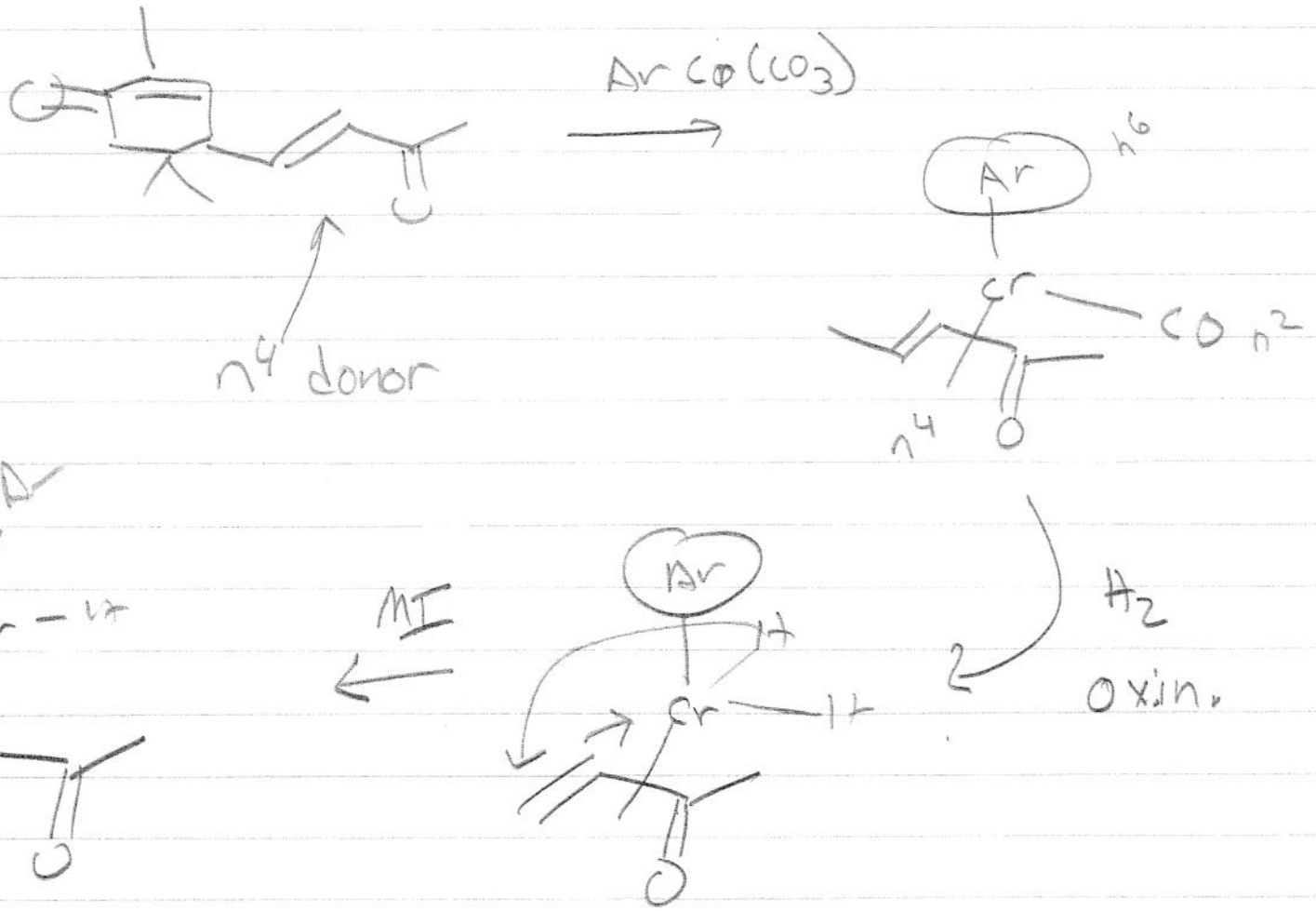


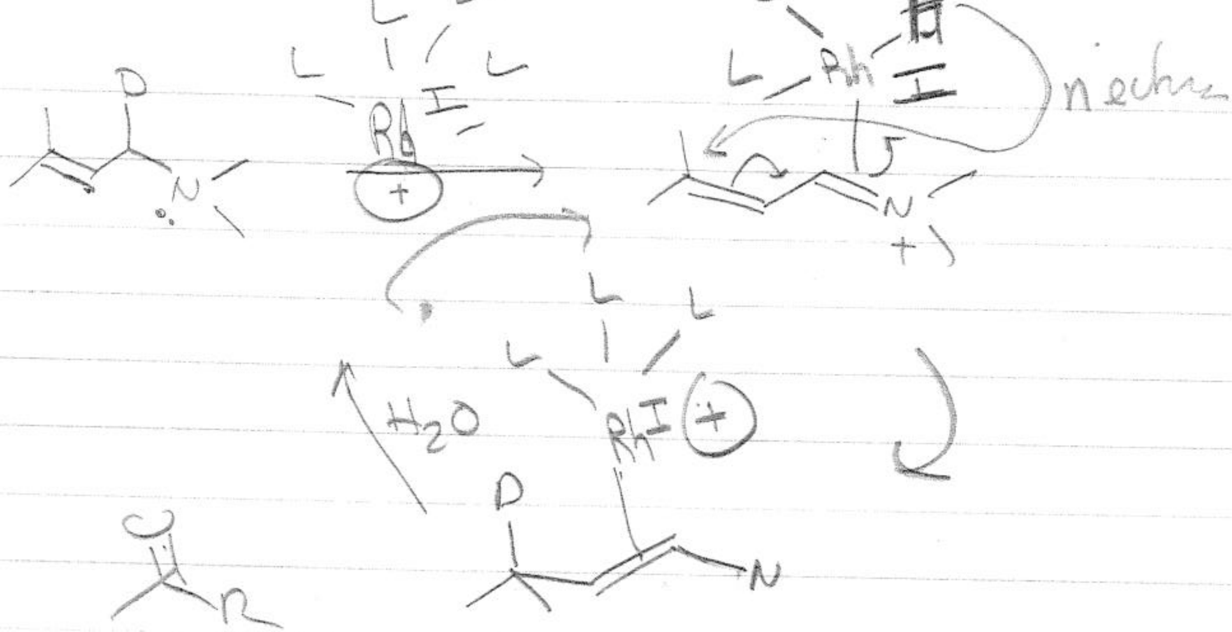


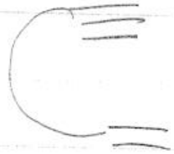


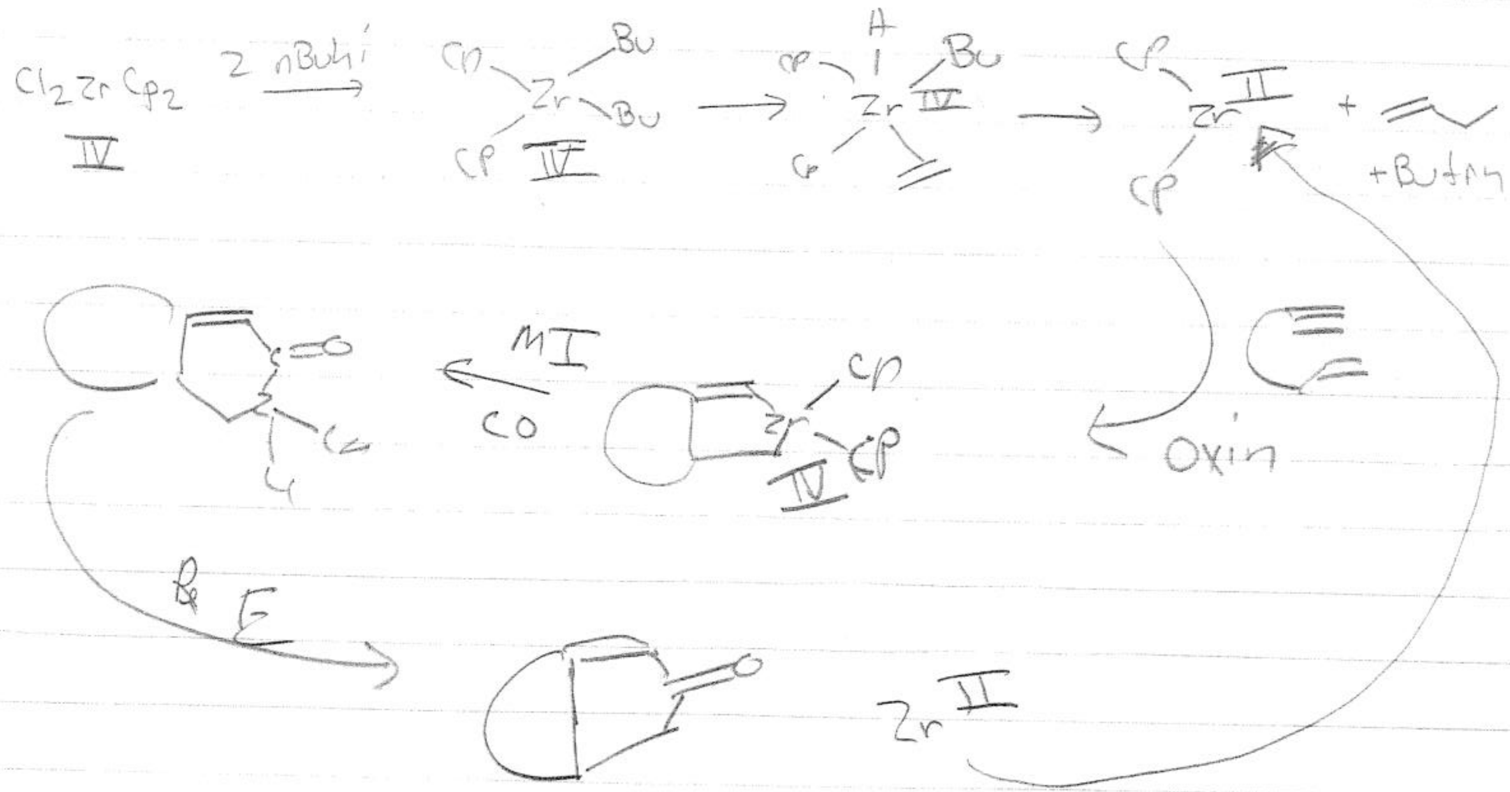

I
Ir III
MI
RE
Super unsaturated
d⁸
12 e⁻
I
Ir L₂

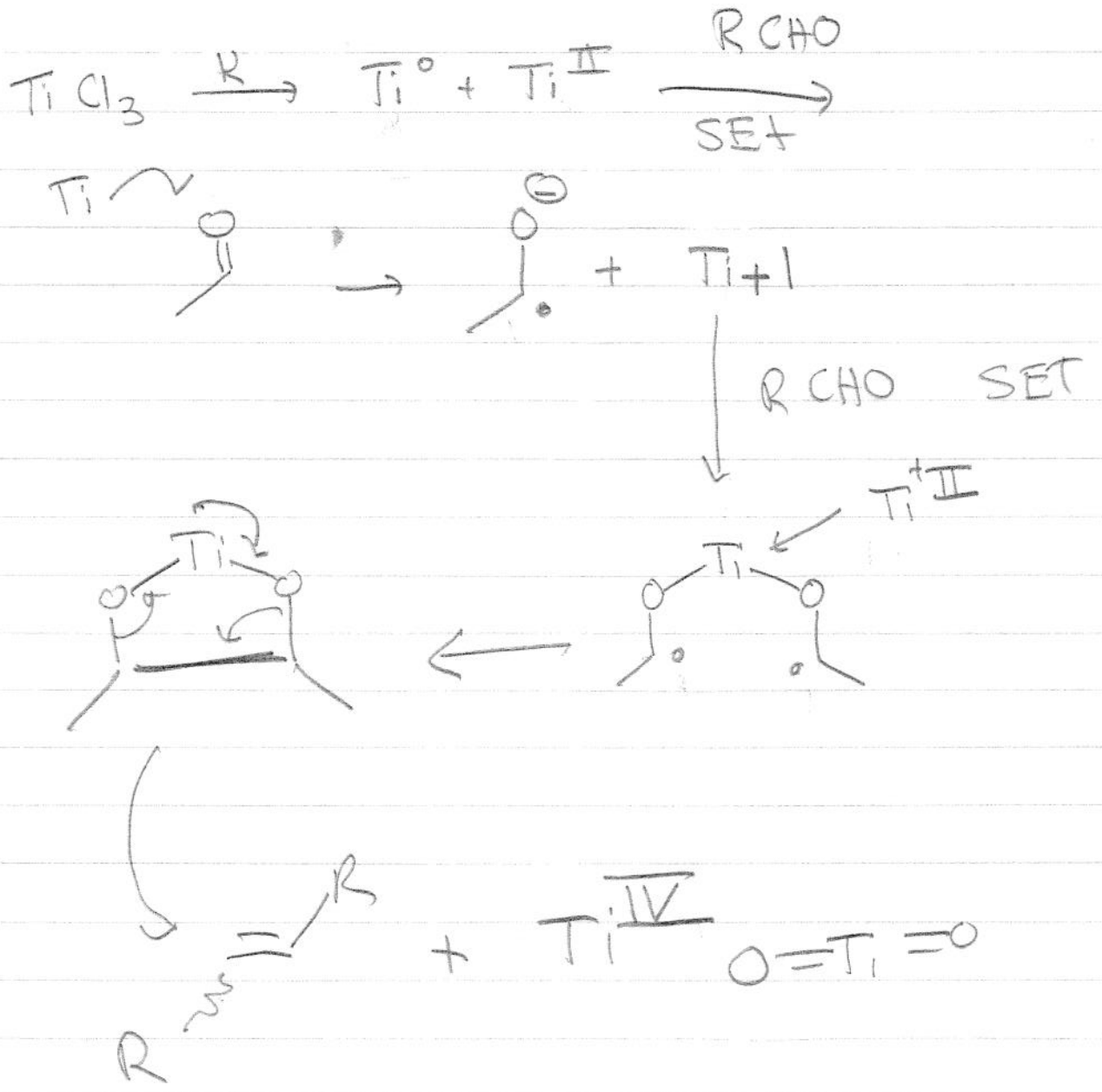
IV

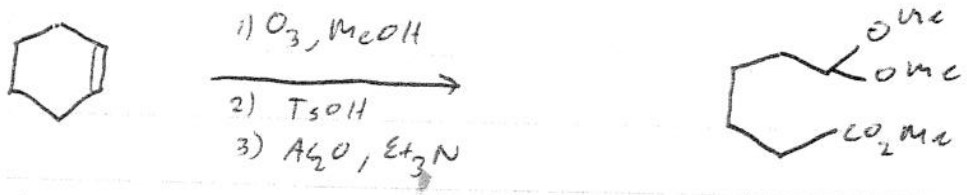

Ar Co(CO)₃
η⁴ donor
Ar
η⁶
Cr
CO
η²
η⁴
O
H₂
oxin.
MI
Ar
Cr
H
CO
red
elim
Ar
Cr
CO


L
Rh
I
mechn
H_2O
N
R

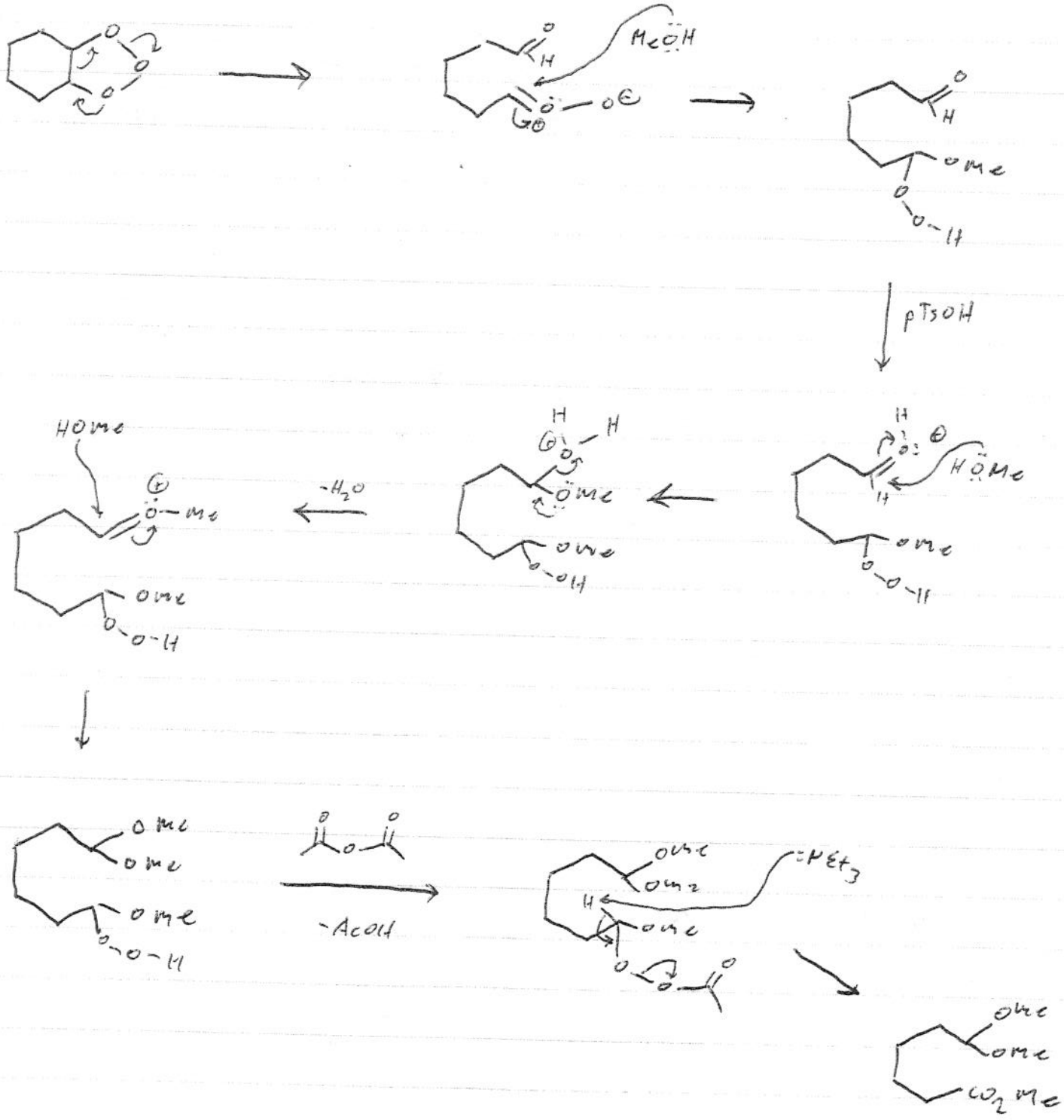



Cl_2ZrCp_2
IV
2 nBuLi
Cp
Zr
Bu
IV
II
+ Butan
Oxin
MI
CO
Zr II

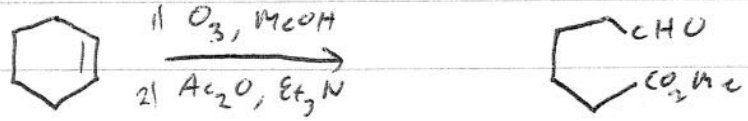

TiCl3
K
Ti° + Ti II
RCHO
SET
Ti
Ti+1
RCHO SET
Ti II
Ti
Ti
R
R
+ Ti IV
O=Ti=O


1) O_3, MeOH
2) TsOH
3) Ac_2O, Et_3N
OMe
OMe
CO_2Me

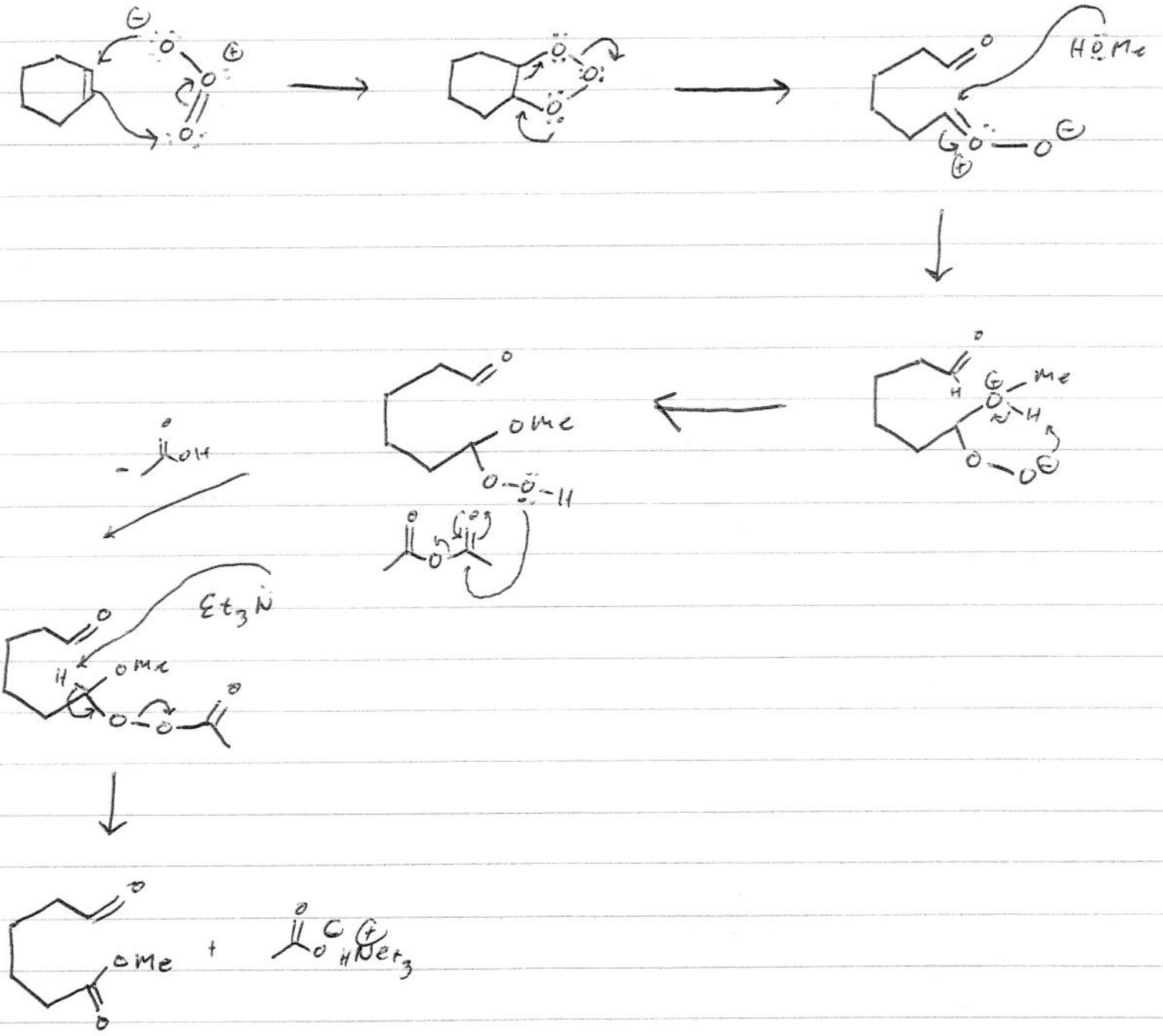
mech

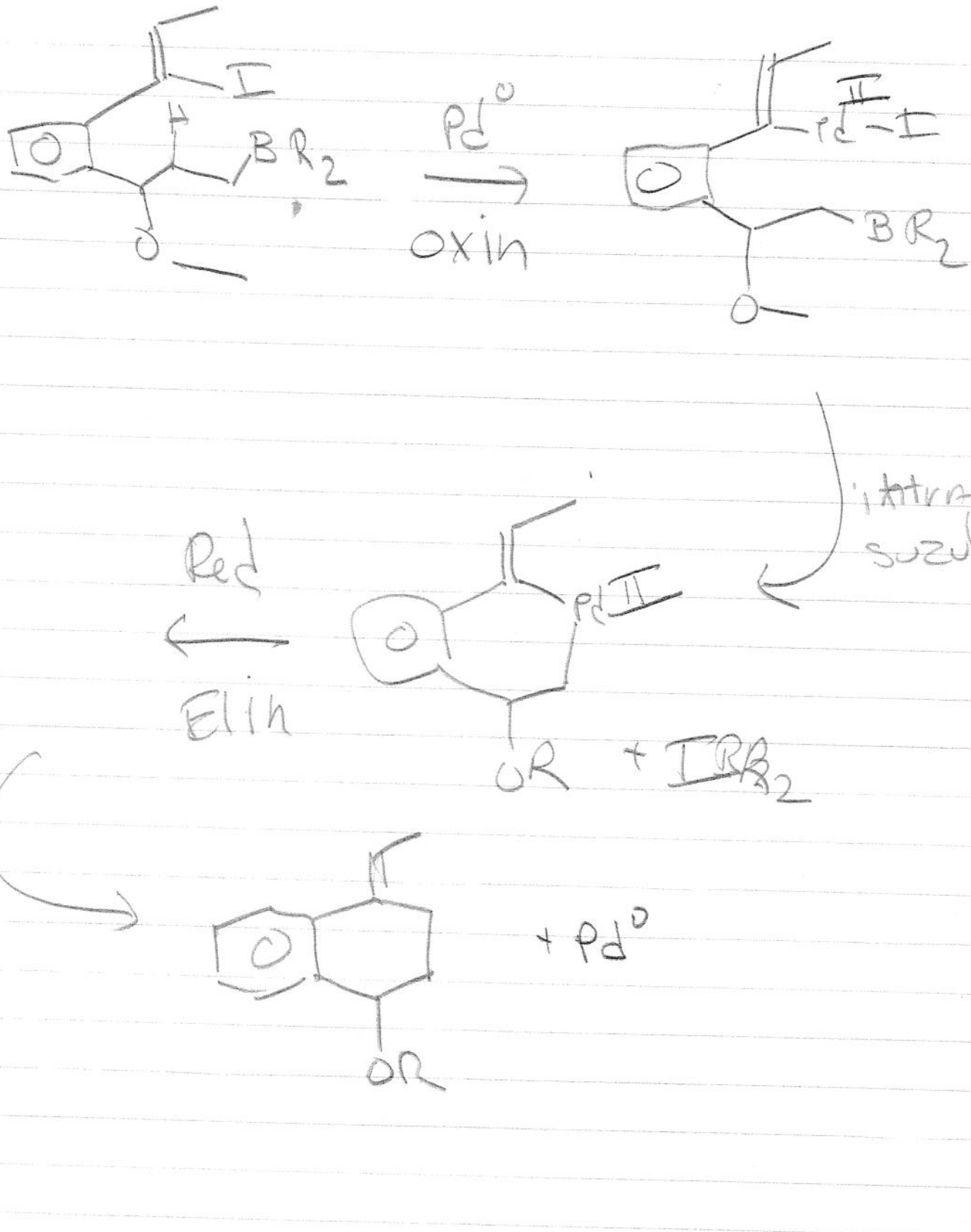

MeOH
pTsOH
$-H_2O$
HOMe
$-AcOH$
$:NEt_3$
OMe
CO_2Me

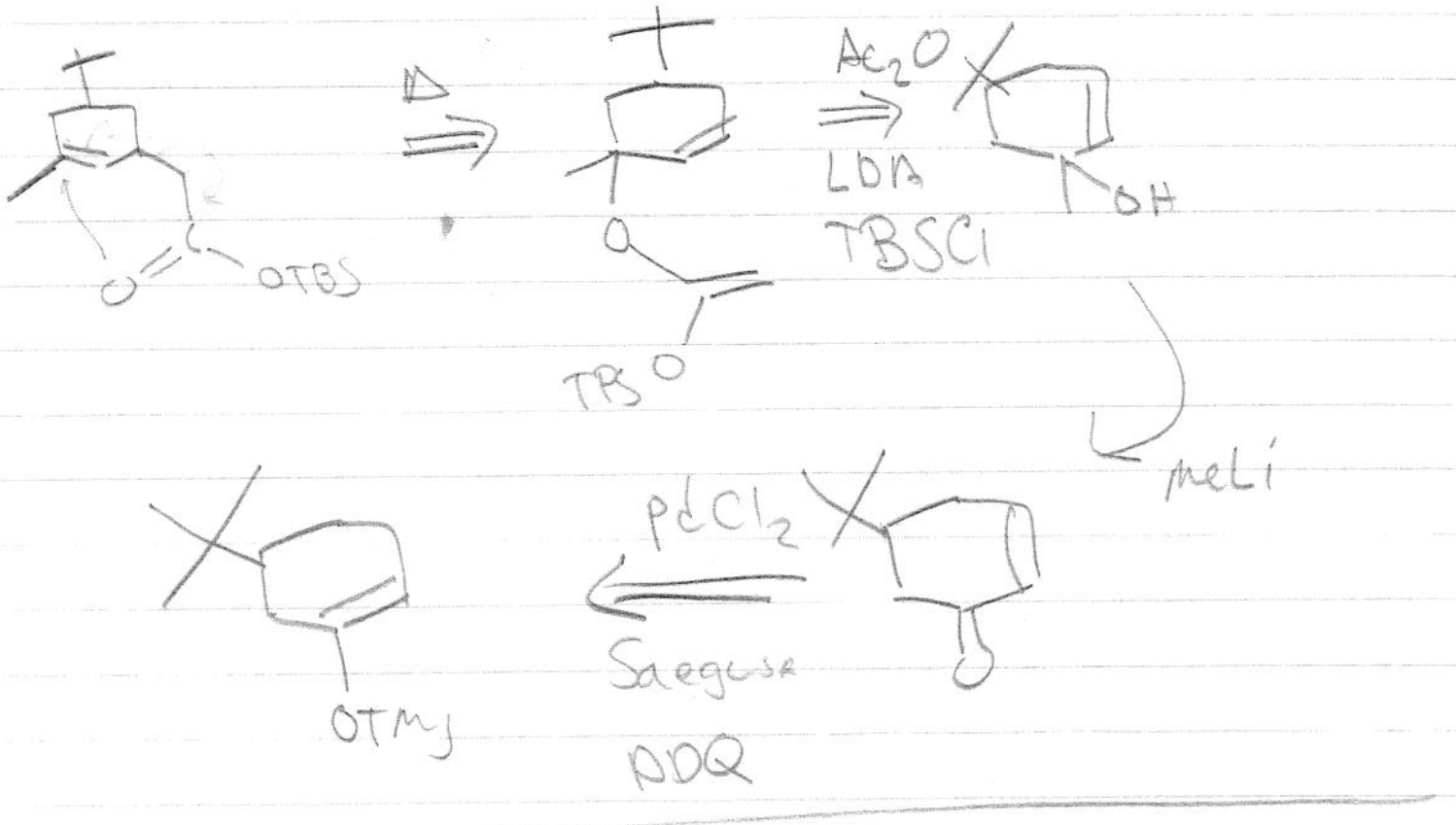
Ozonz

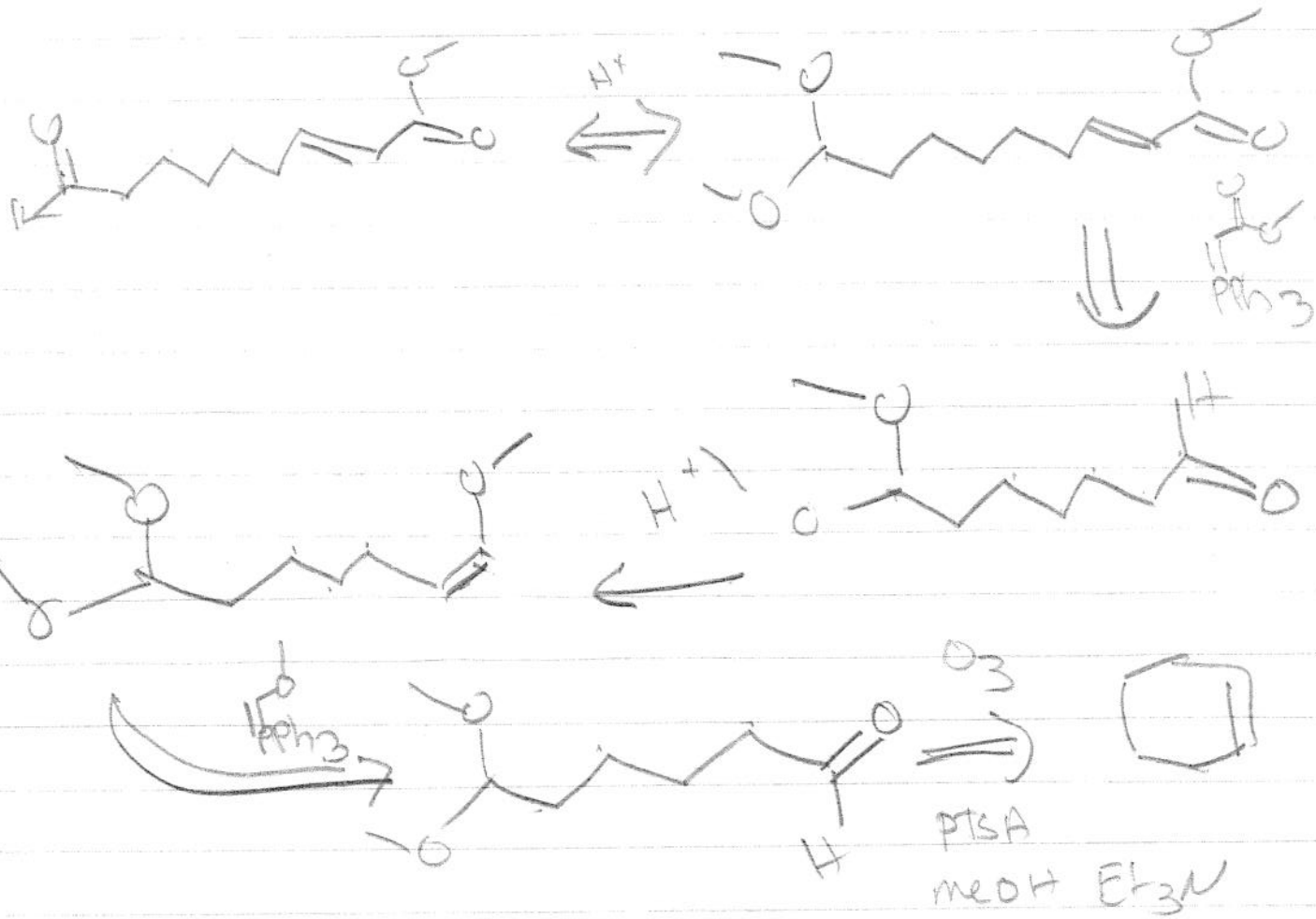


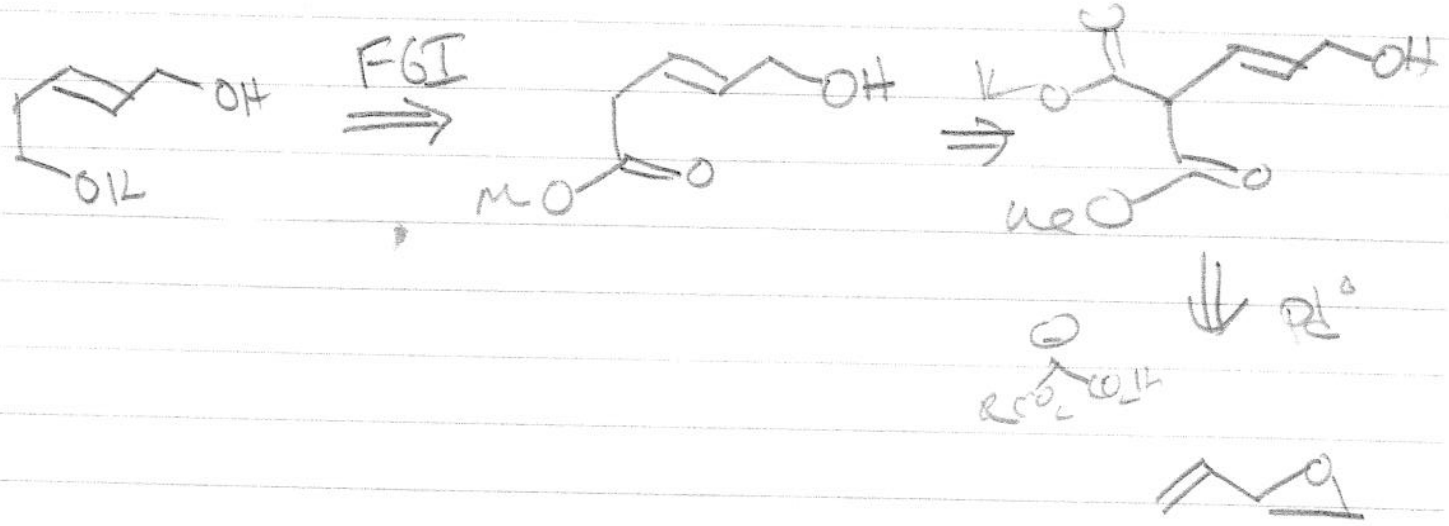
mech

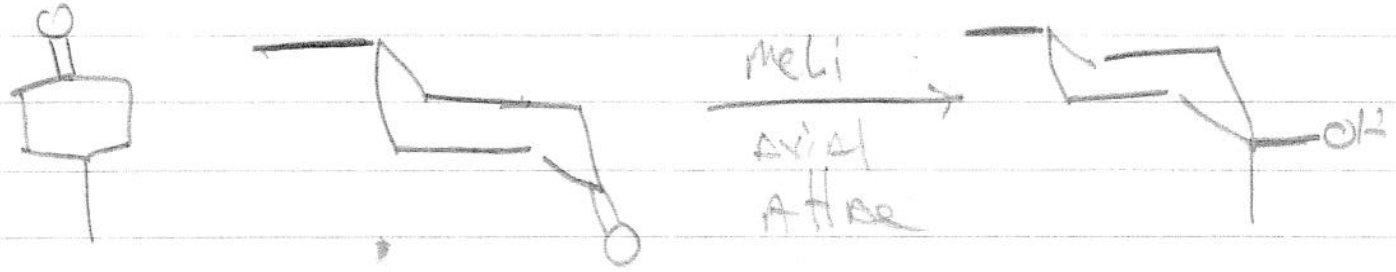



I
H
BR_2
O
Pd^0
oxin
II
Pd
I
O
BR_2
O
Red
Elih
II
Pd
O
OR
+ IBR_2
itirm
suzuki
O
OR
+ Pd^0

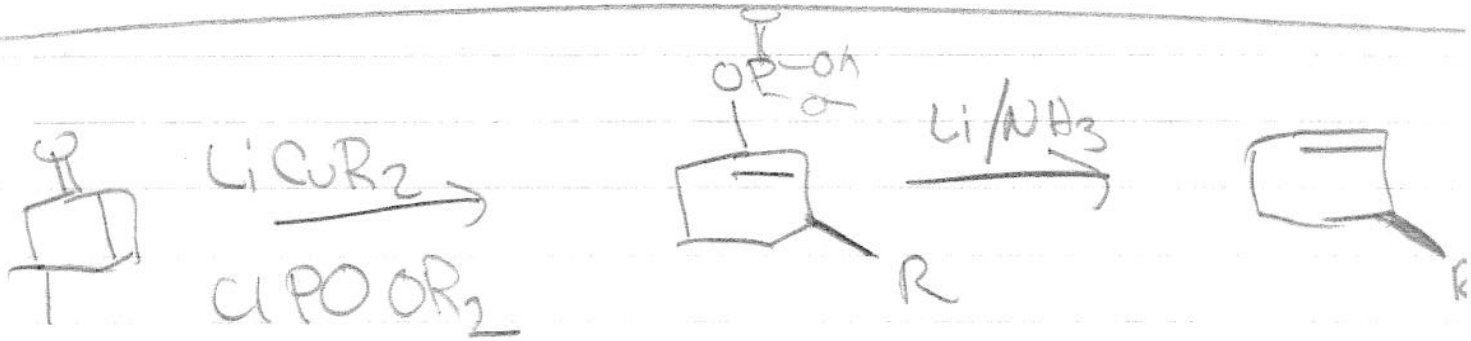

OTBS
Δ
Ac2O
LDA
TBSCl
OH
TBSO
MeLi
PdCl2
Saegusa
DDQ
OTMy

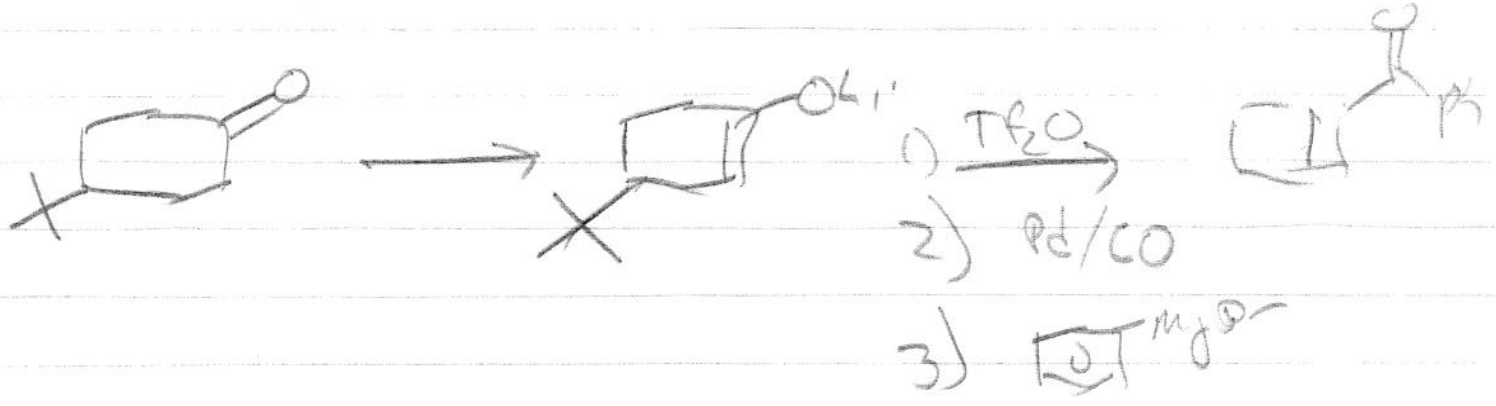

H+
PPh3
H+
PPh3
O3
PTSA
MeOH
Et3N

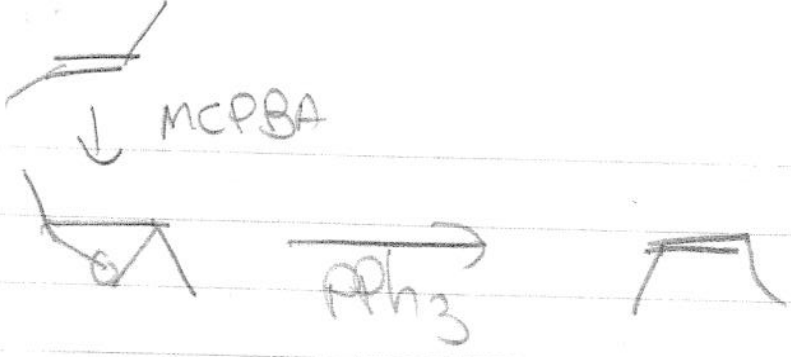

FGI
OH
OH
MeO
OH
MeO
Δ
OH

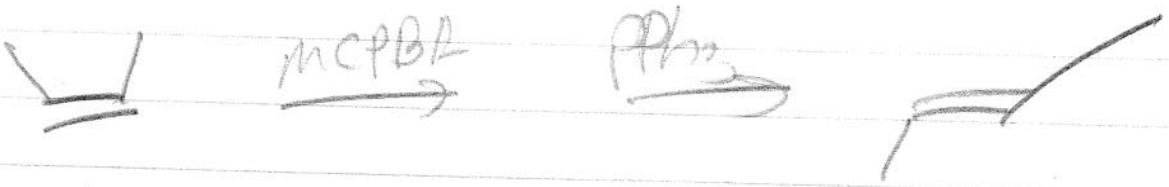

MeLi
axial
Attack

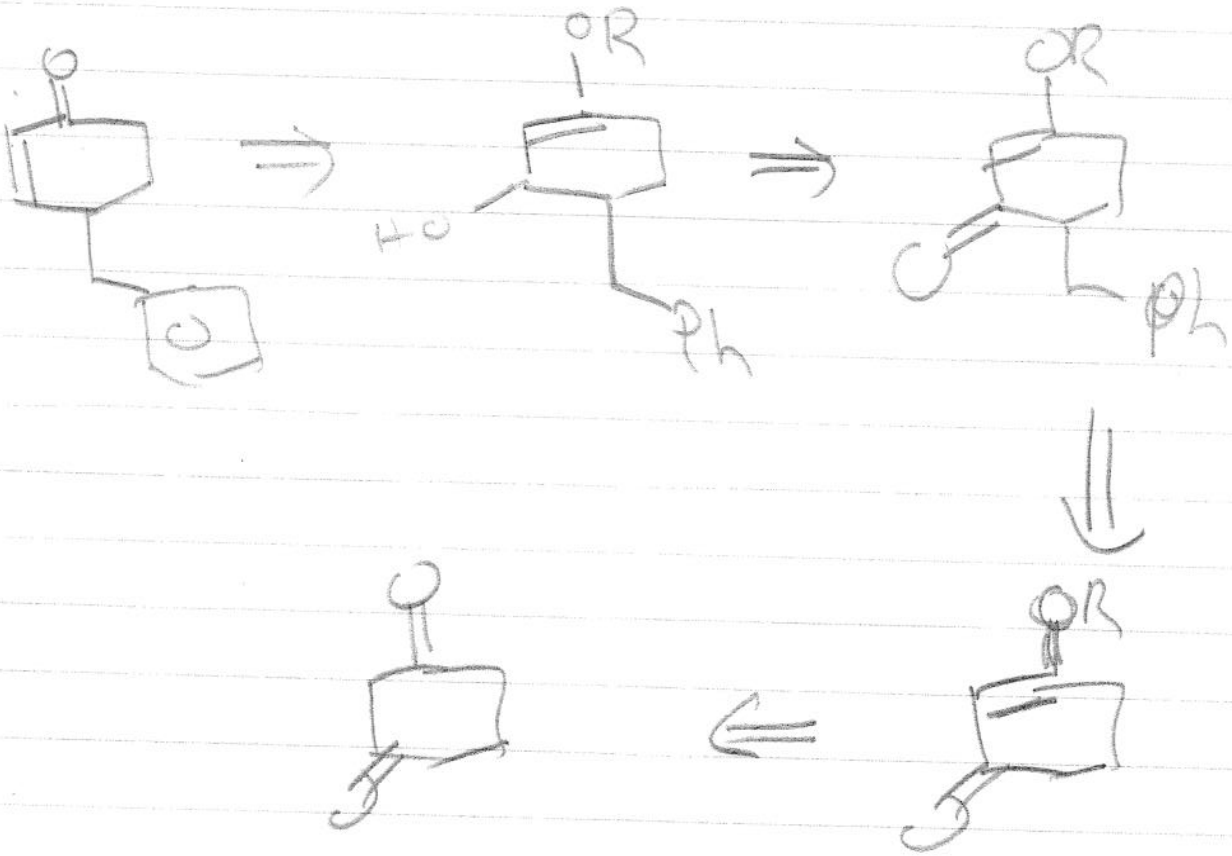

O3

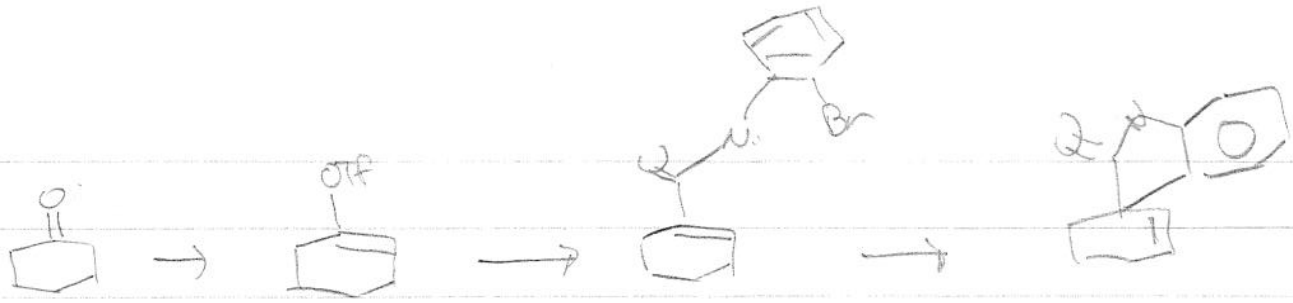

LiCuR2
ClPOOR2
Li/NH3
R

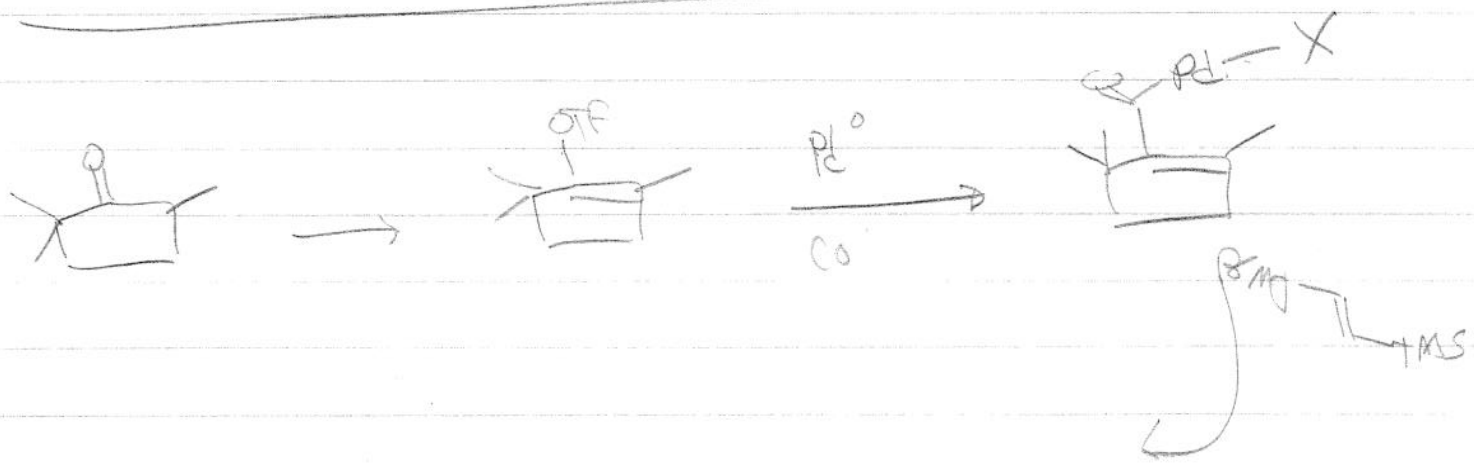

1) Tf2O
2) Pd/CO
3) MgO


MCPBA
PPh3

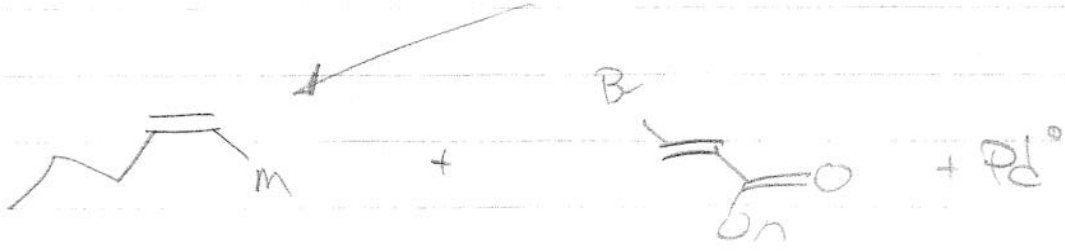

MCPBA
PPh3

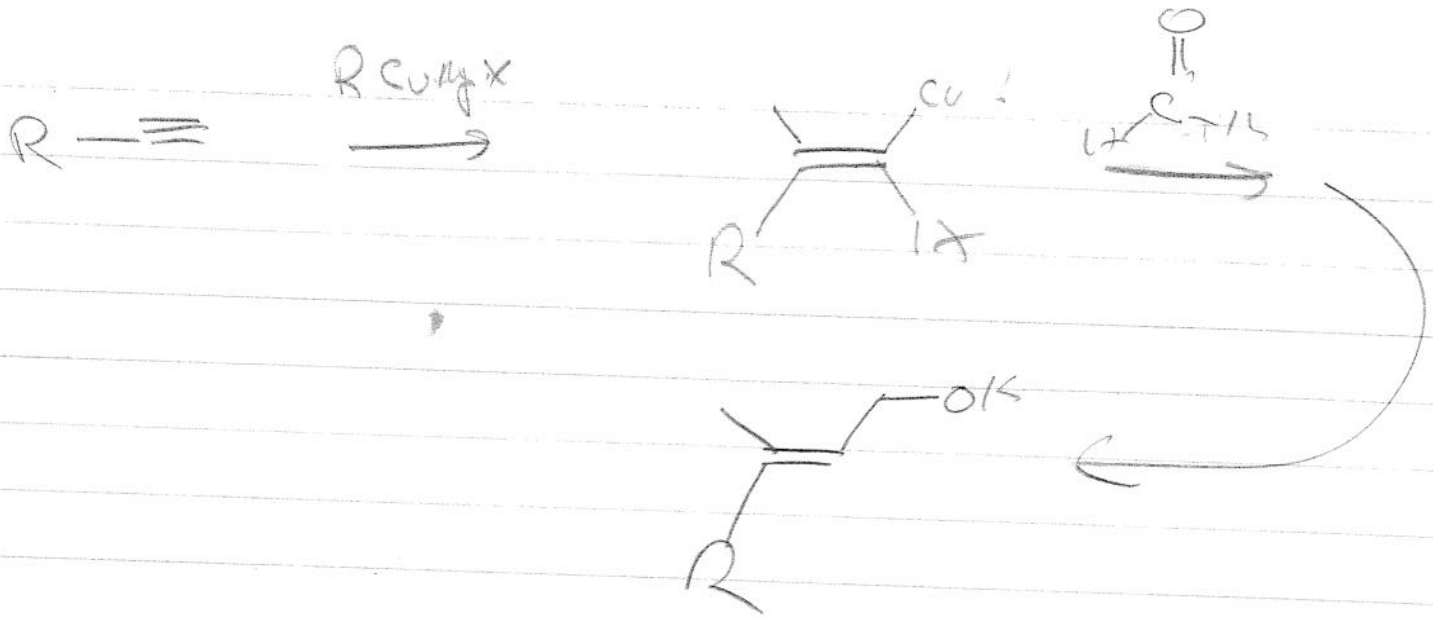

OR
HO
Ph
OR
Ph
OR

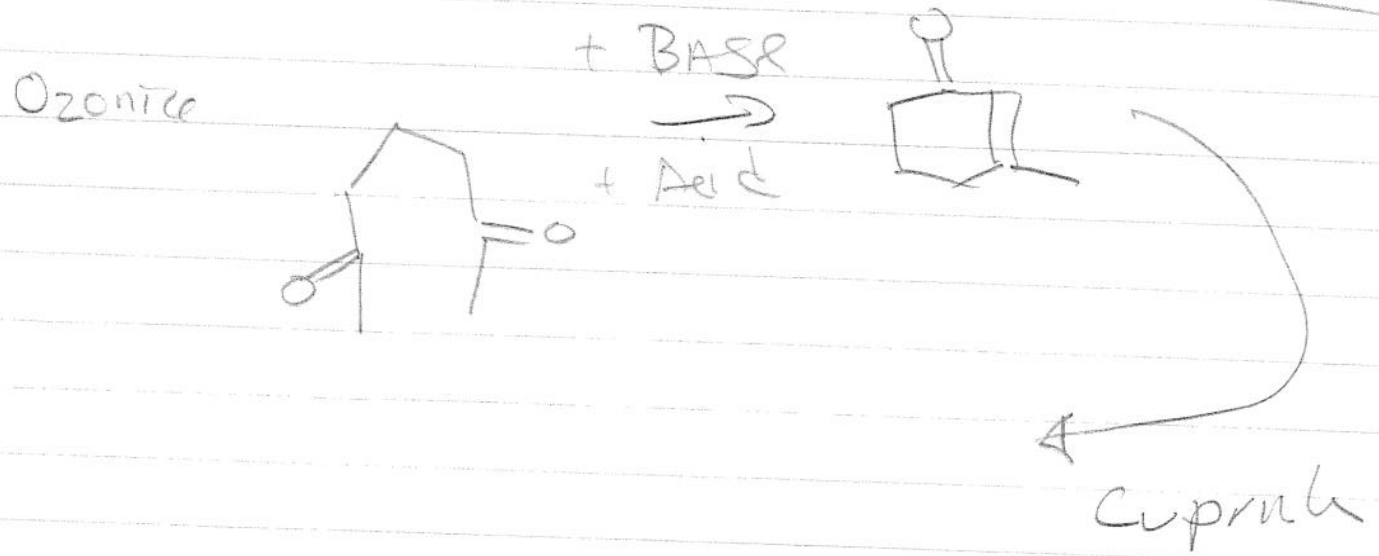




Robinson Annulation + Cuprate Addition







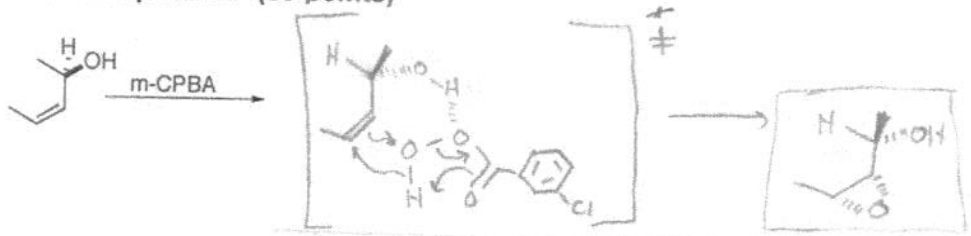
Grob

CHEM 233 WINTER 2005 TEST 1

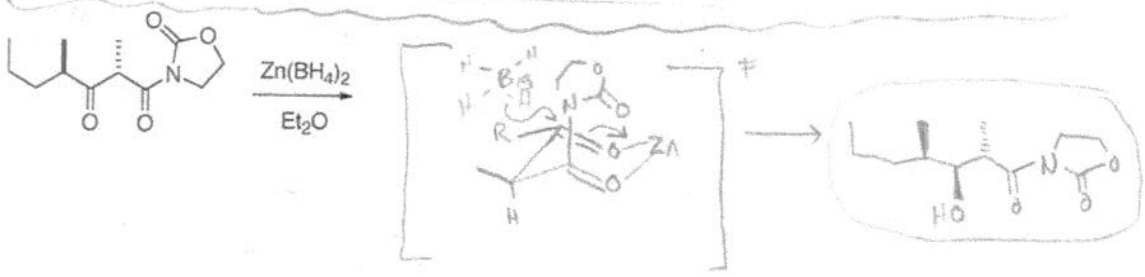
Your name: _____

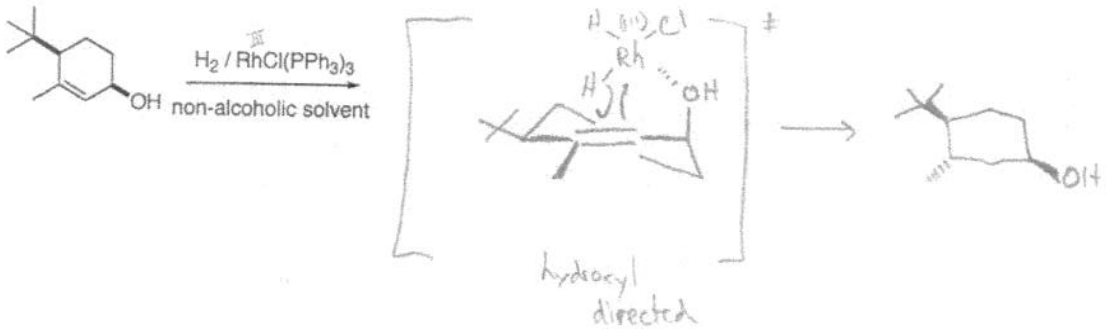
Date: _____

STEREOELECTRONIC EFFECTS. **Given below are pairs of reactants. Carefully draw the product with the correct stereochemistry and the model that predicts the preferred diastereomer or regioisomer. The right answer only gets you ¼ of the points. Use nice 3D pictures or Newman projections please! Some answers require more than one picture. (80 points)**

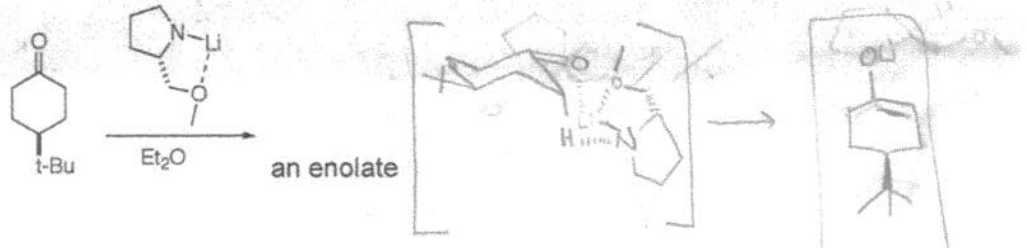


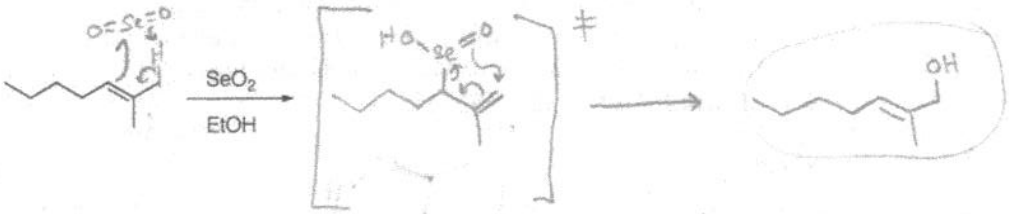
↳ 1,3-allylic strain, hydroxyl directed



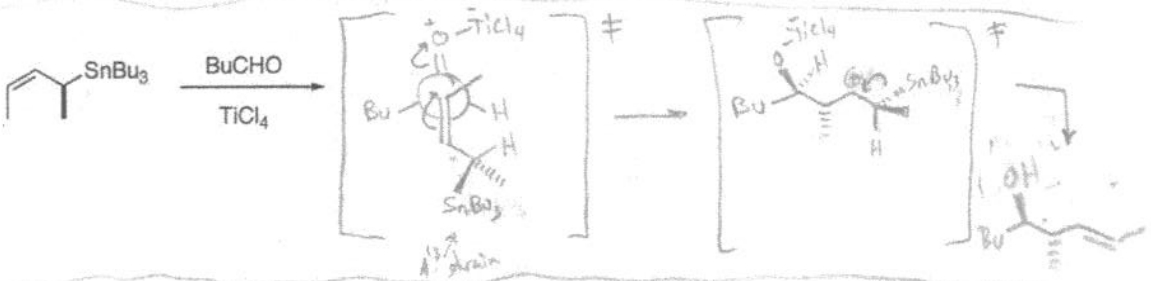


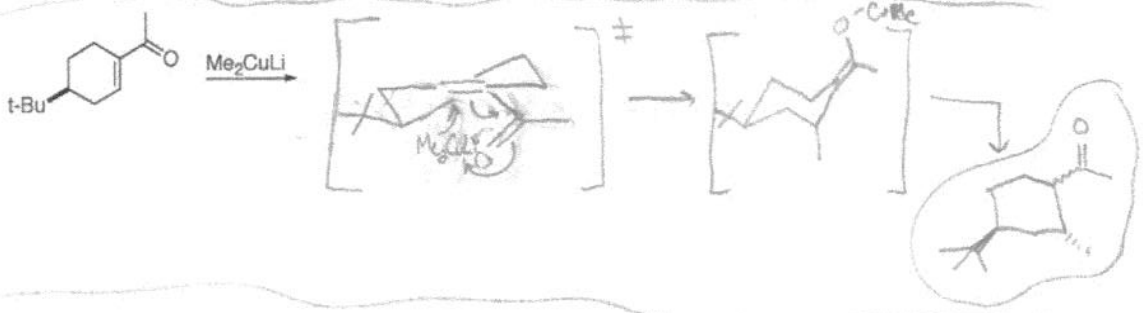
hydroxyl directed



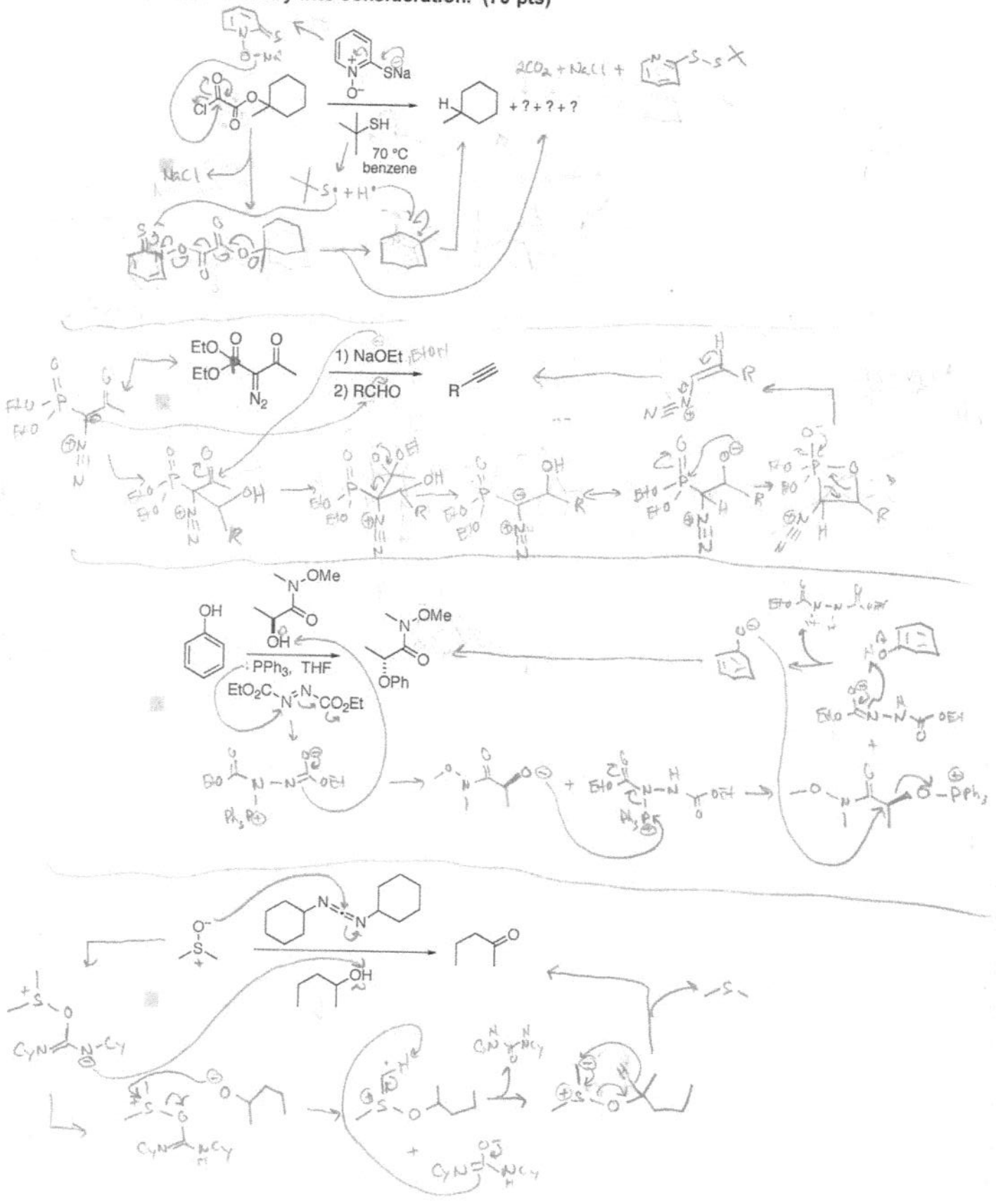


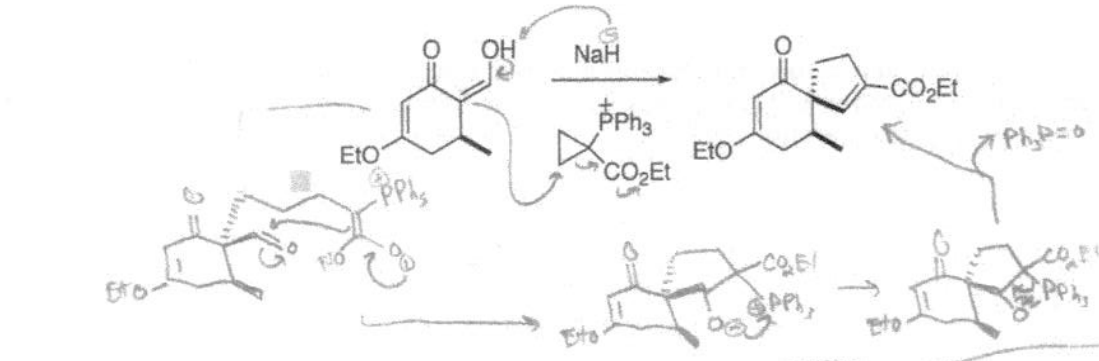
↳ goes to least substituted, least hindered side

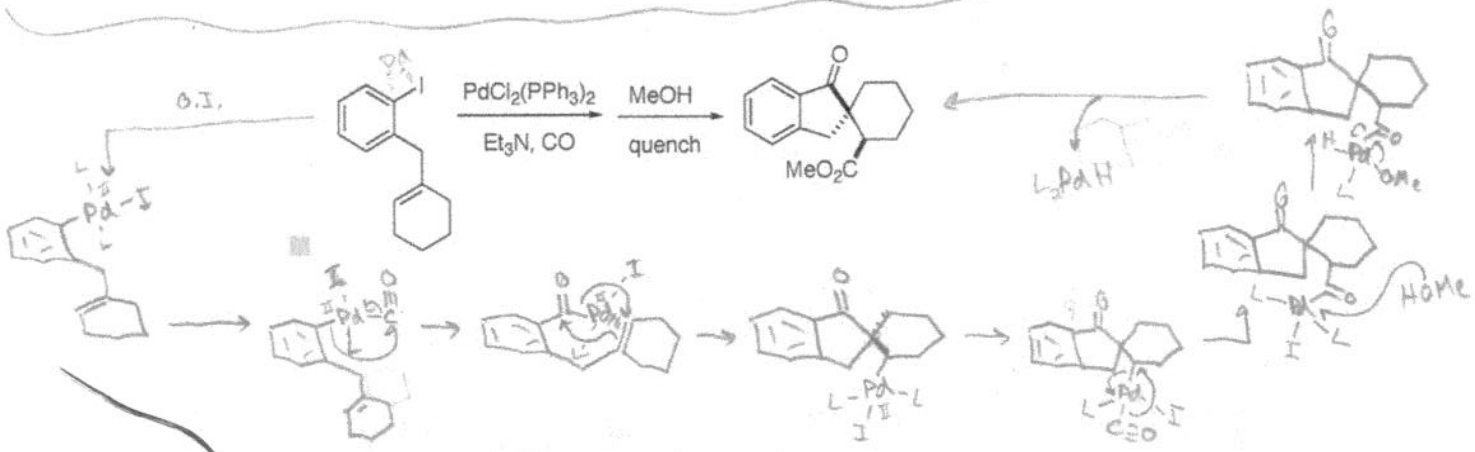


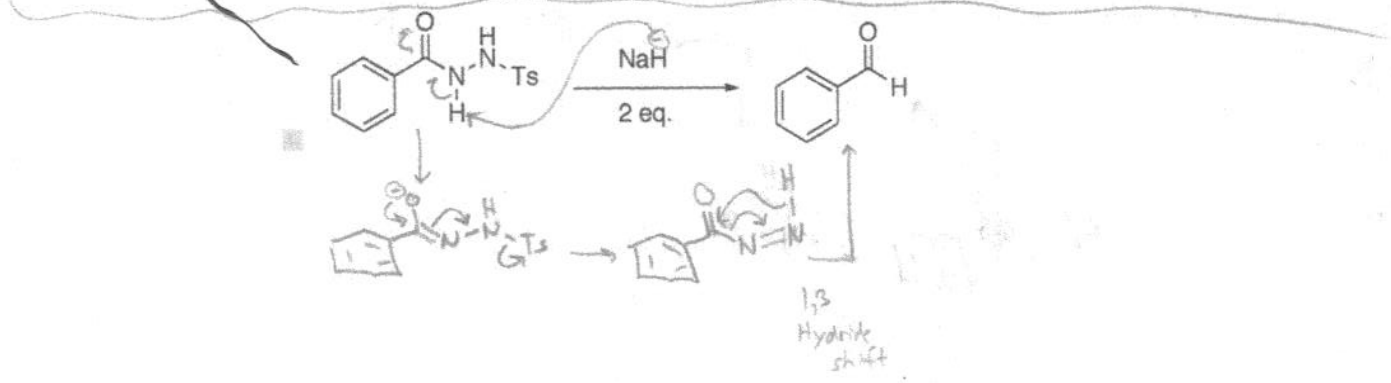


II ARROW PUSHING. **Given below is a starting material and a product. Provide an mechanism that accounts for its formation taking regiochemistry and stereochemistry into consideration. (70 pts)**



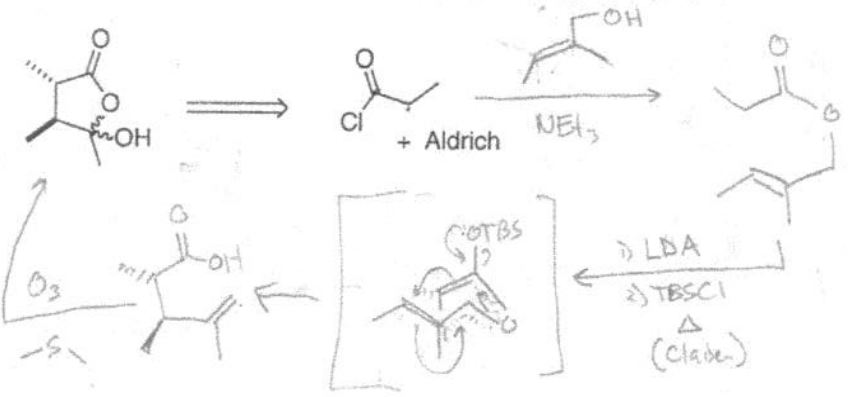

NaH
EtO
CO2Et
Ph3P=O

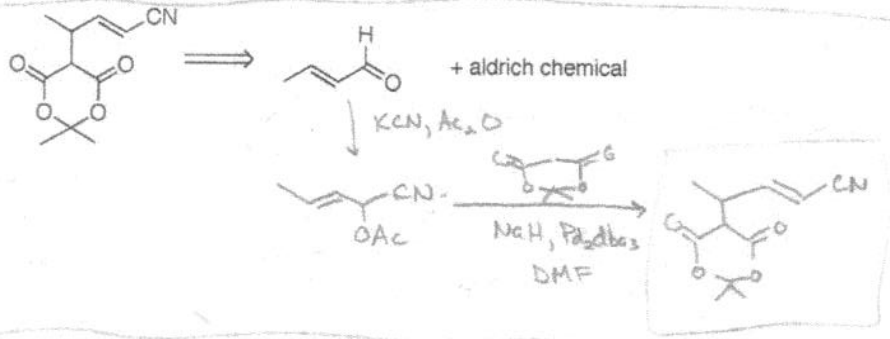

O.I.
PdCl2(PPh3)2
Et3N, CO
MeOH
quench
MeO2C
L2PdH
HOMe

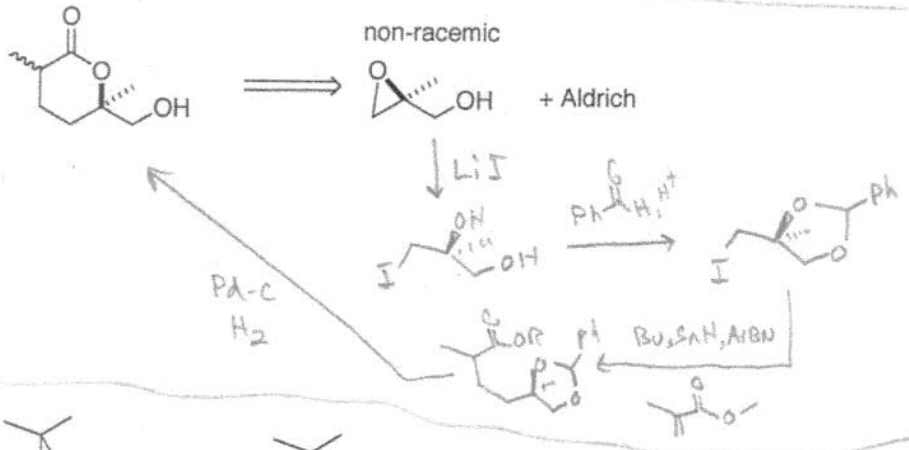

NaH
2 eq.
Ts
1,3
Hydride
shift

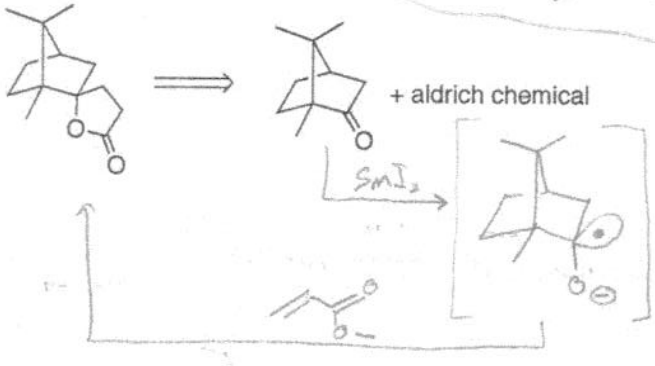

OAc
Ph

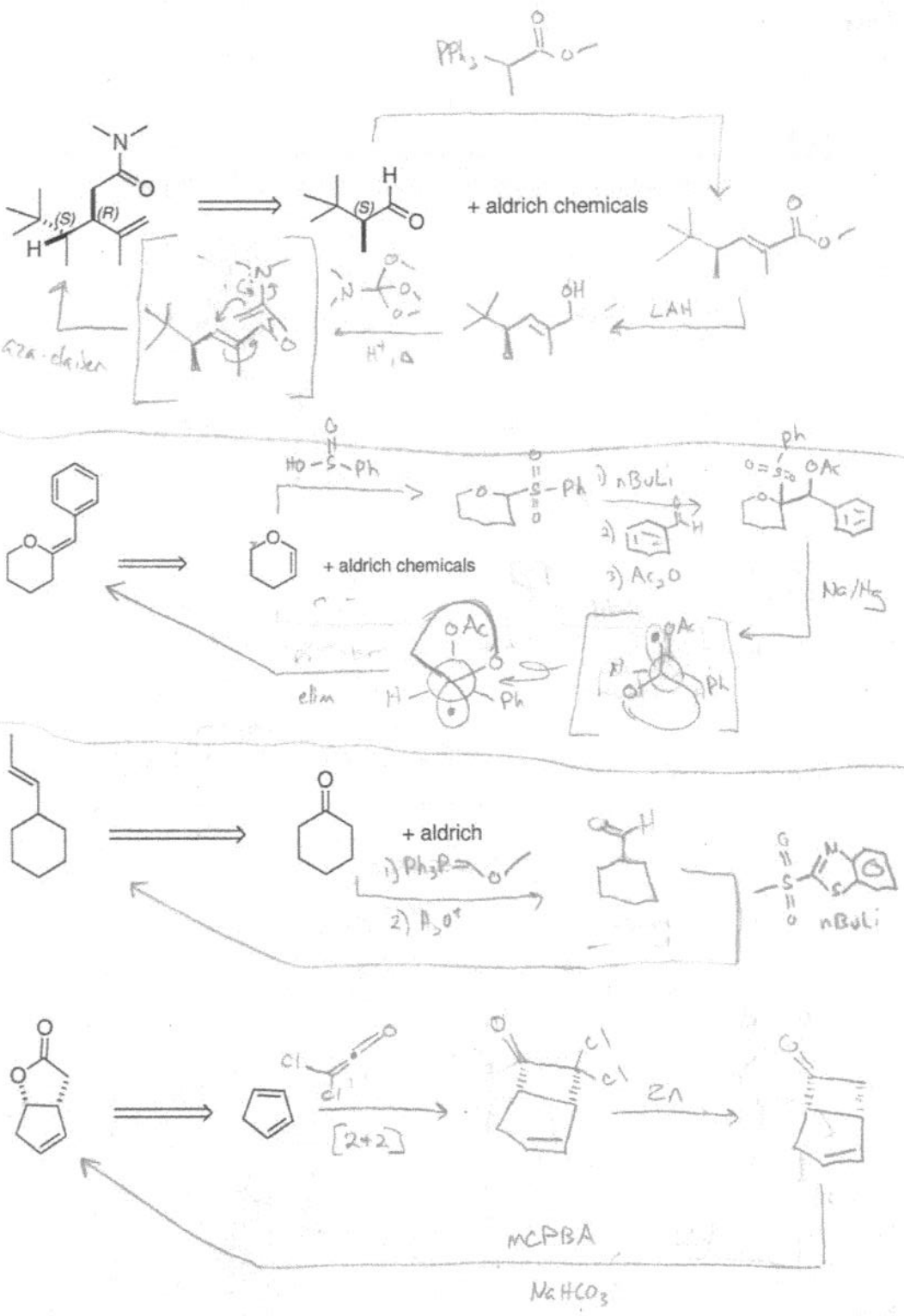
III SYNTHESIS. **All compounds are racemic unless otherwise stated, and your synthesis must address relative stereochemistry. (80 pts)**










+ aldrich chemicals
LAH
Claisen
+ aldrich chemicals
nBuLi
Na/Hg
elim
+ aldrich
nBuLi
[2+2]
Zn
mCPBA
NaHCO3