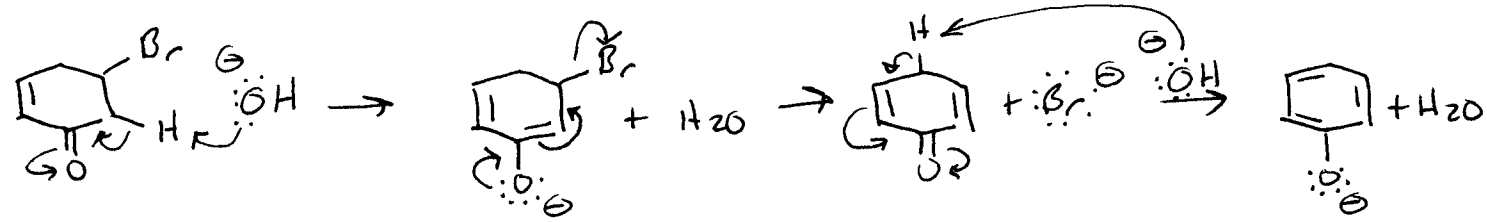
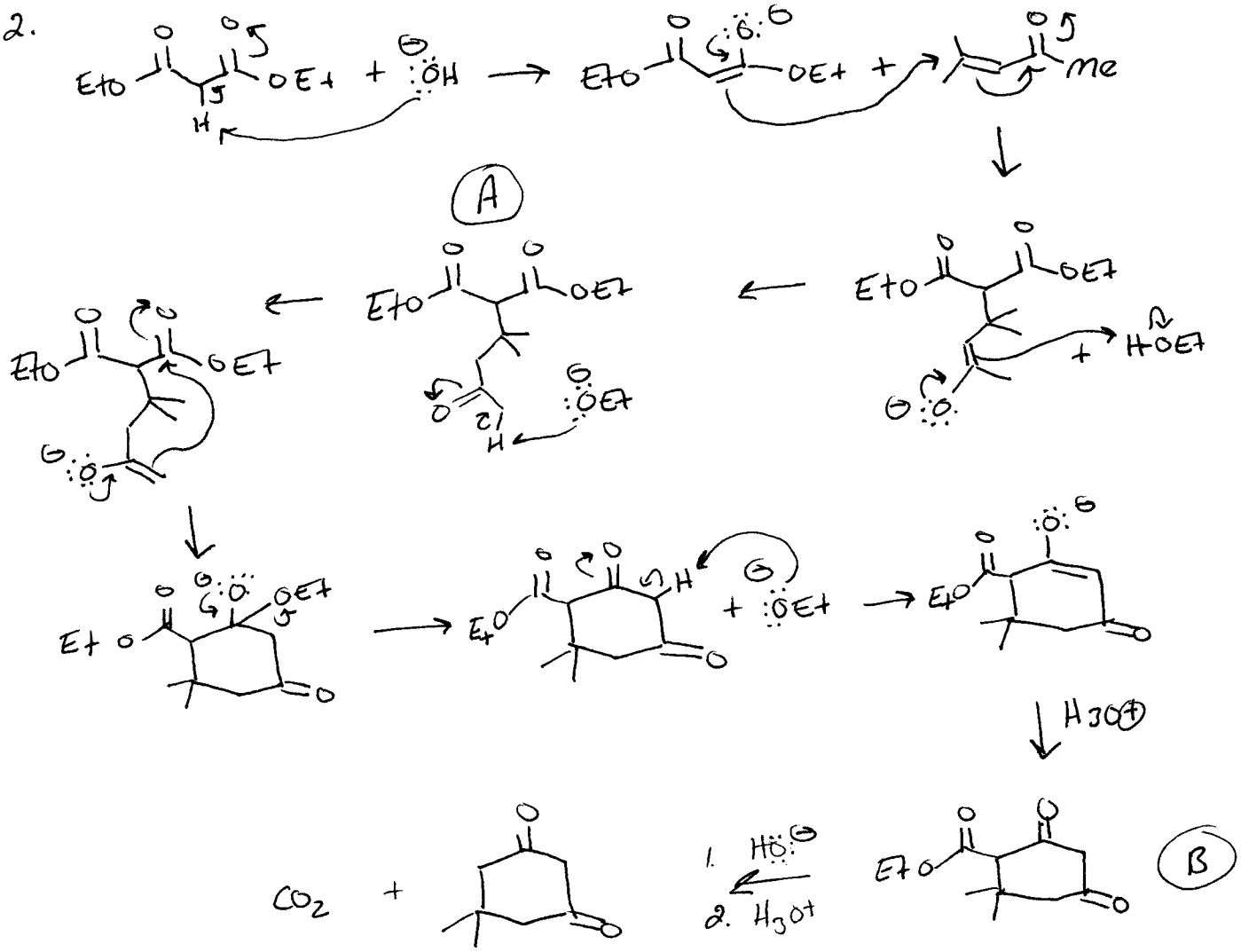
Exam 4 - Extra Problems - Key

1.

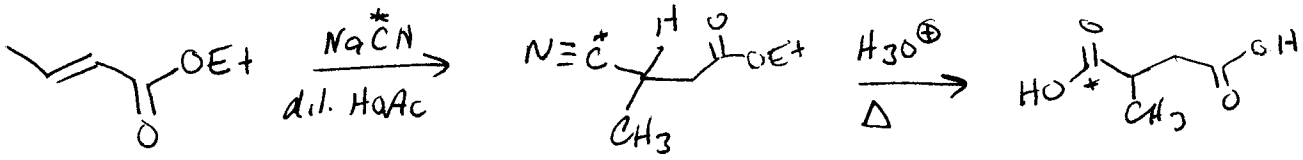


2.

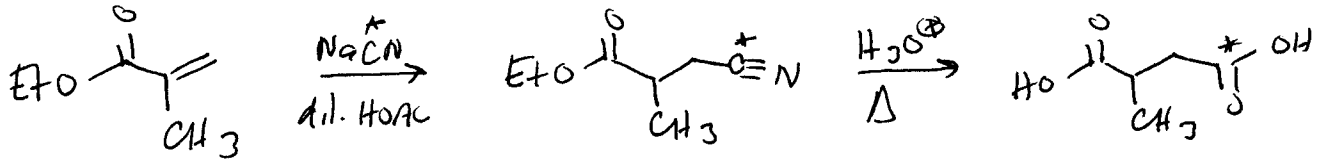


3.

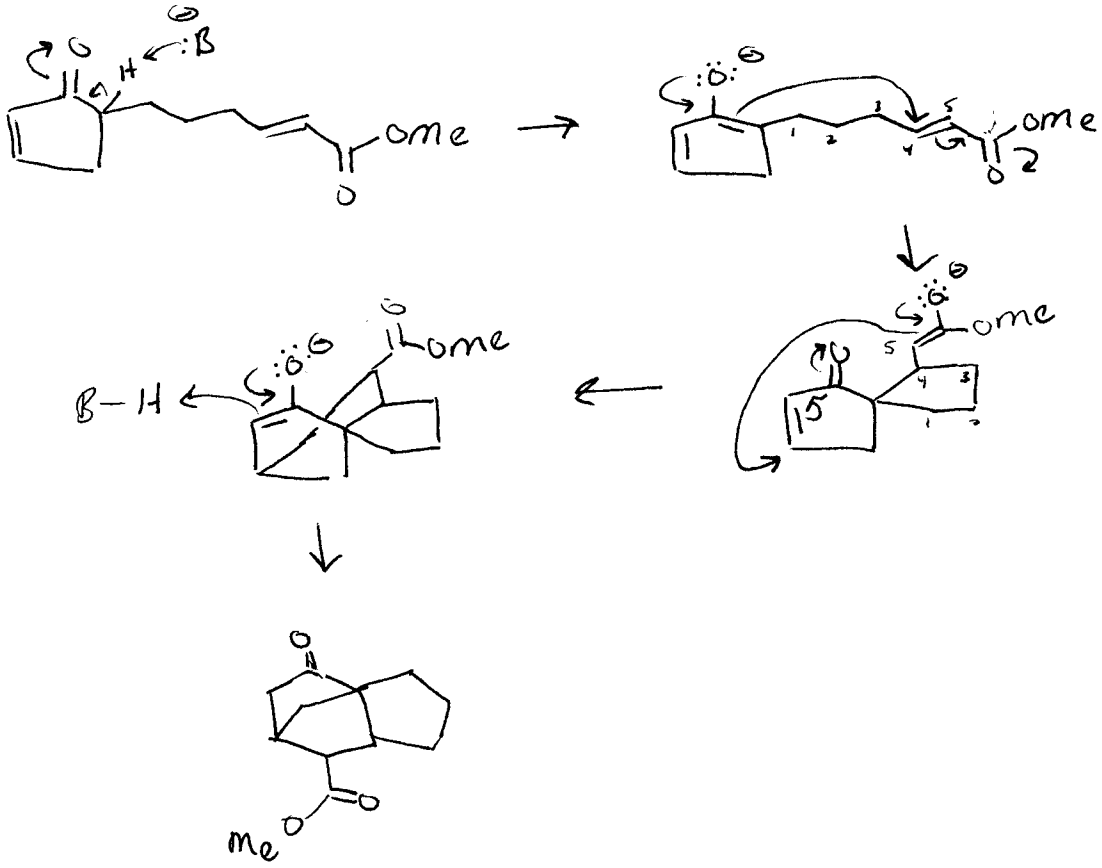
a)


OEt
NaCN
dil. HOAc
N≡C
H
O
OEt
CH3
H3O⊕
Δ
HO
O
OH
CH3
O

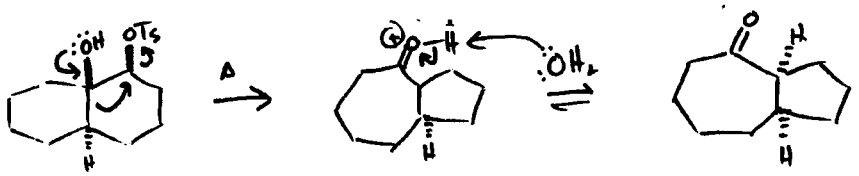
b)


EtO
O
CH3
NaCN
dil. HOAc
EtO
N
CH3
H3O⊕
Δ
HO
OH
CH3
O

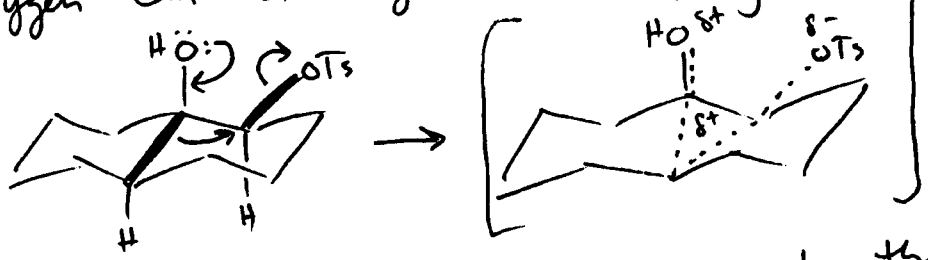
4.


B
H
OMe
O
1
2
3
4
5
B–H
Me

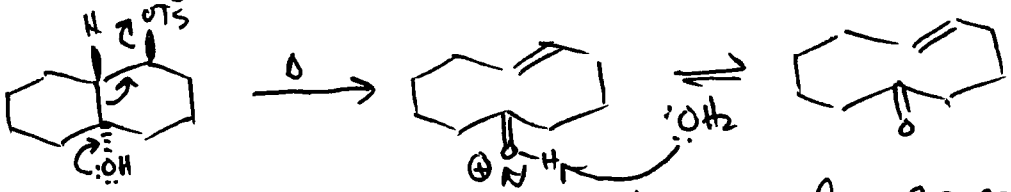
5.



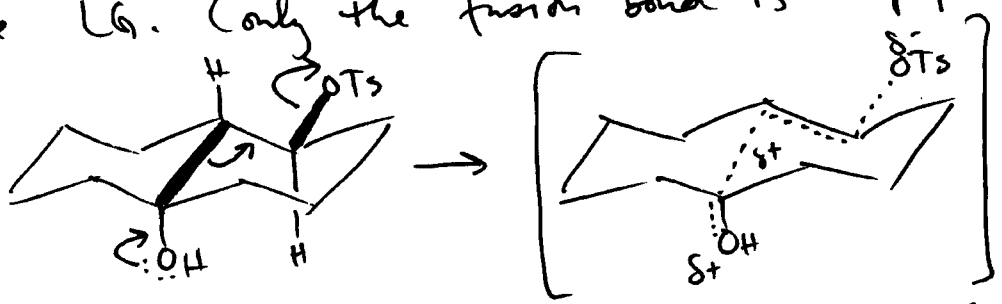
In this "Pinacol-like" concerted process, the migrating bond must be antiperiplanar to the LG so that the oxygen can stabilize the developing charge in the TS.



Only the ring fusion bond is a.p.p. to the LG.

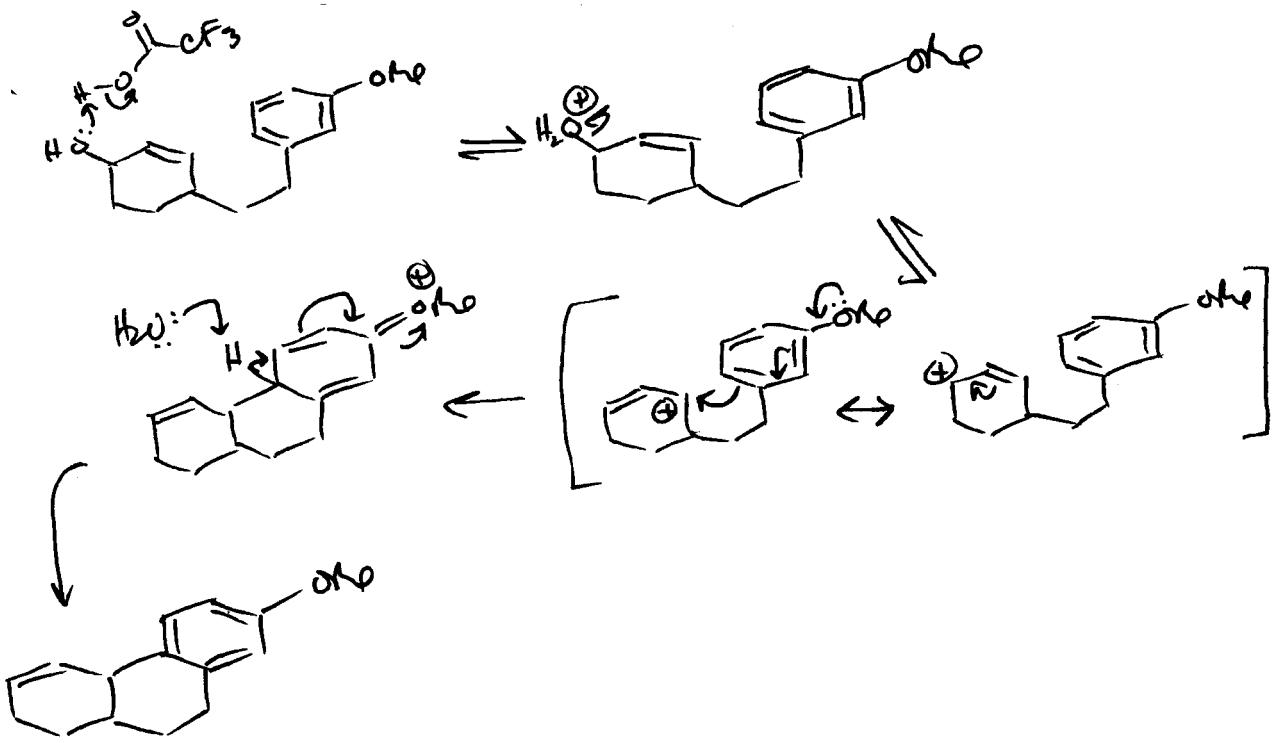


This Grob fragmentation is also concerted, so the bond that is cleaved must be antiperiplanar to the LG. (Only the fusion bond is a.p.p.)

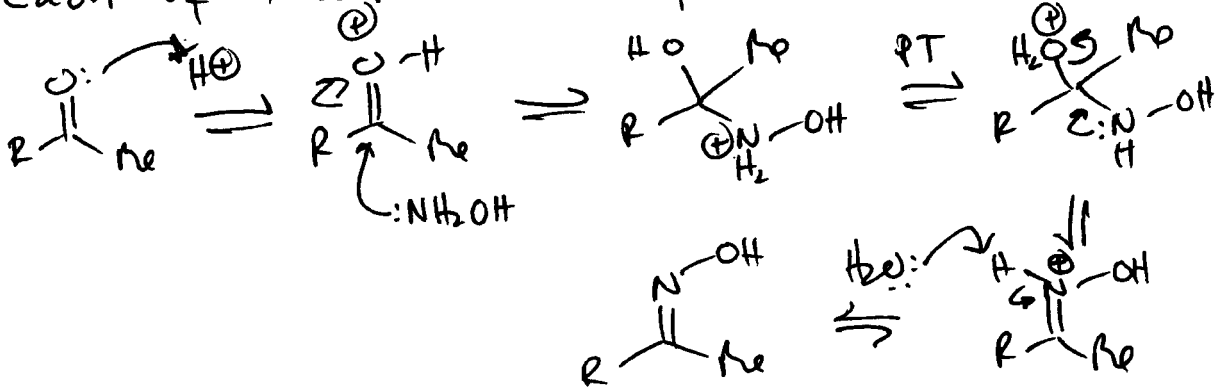


Only the bond a.p.p. to the LG is involved in these processes. The position of the oxygen determines which product will be formed.

6.

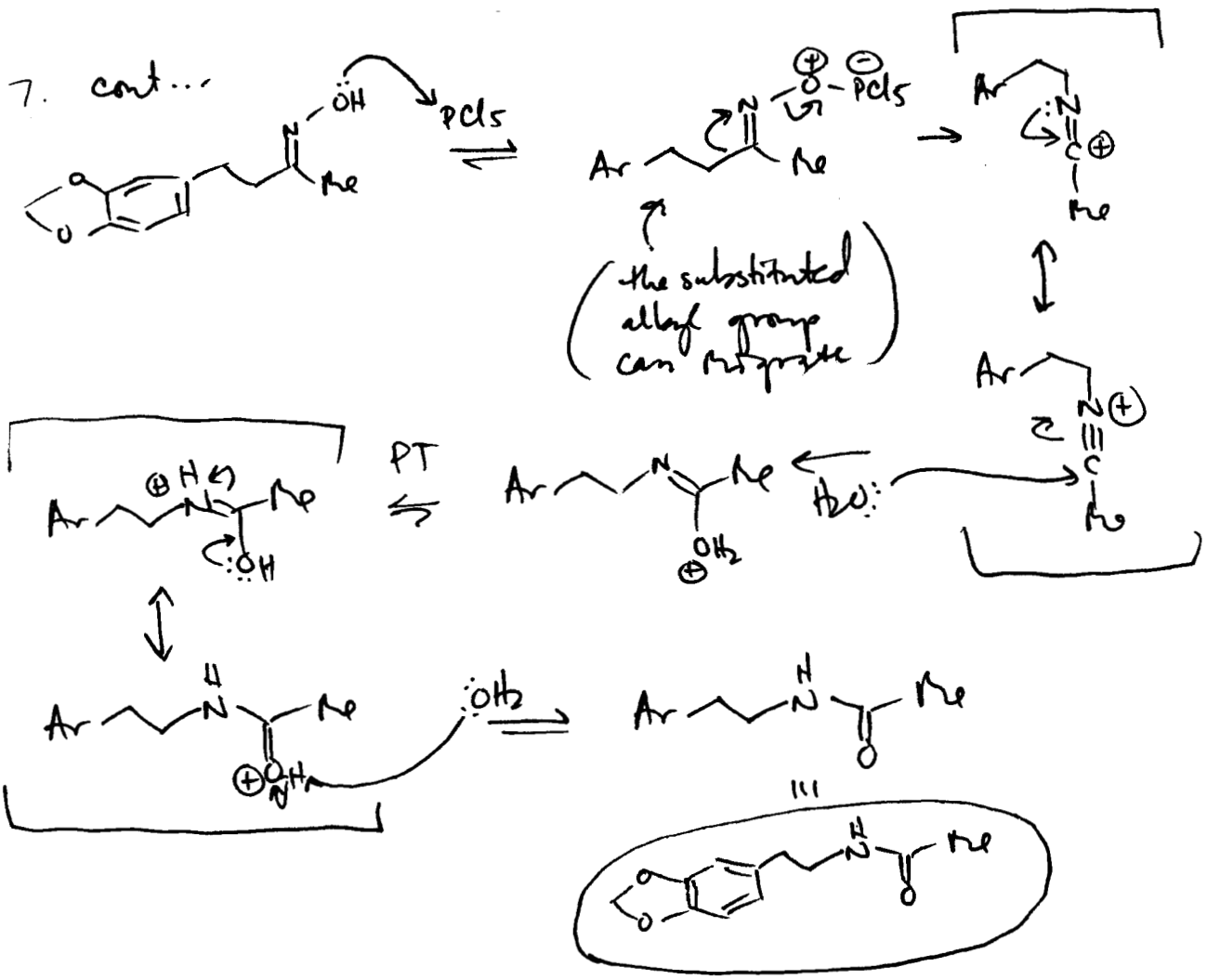


7. Each of these mechanisms proceeds through an oxime.

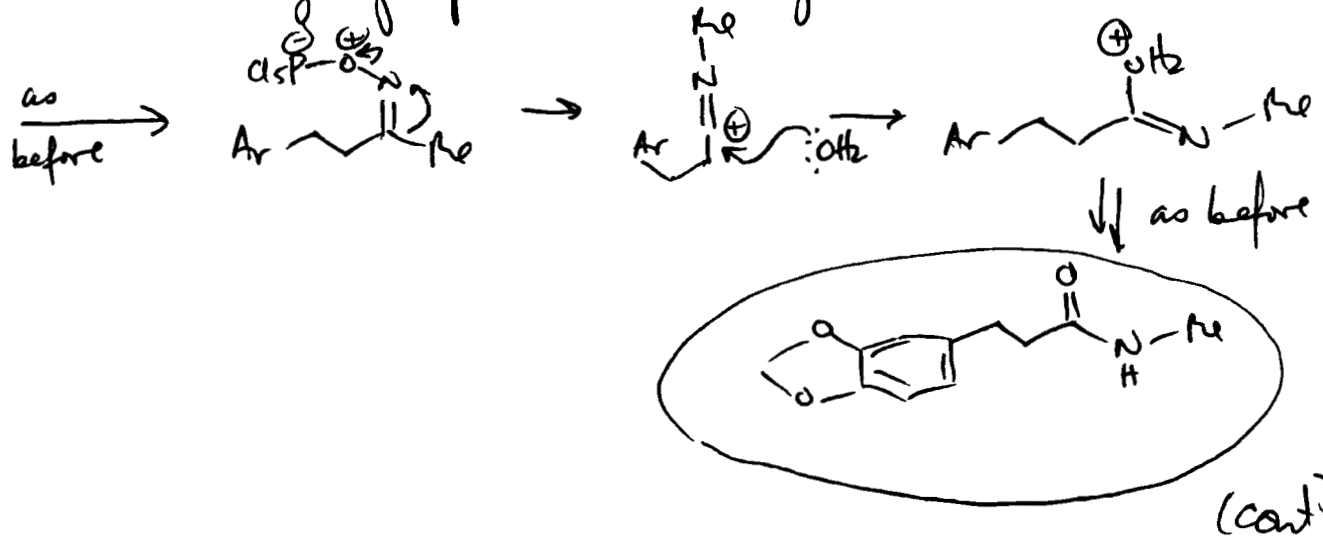


≠ Would likely form mixture of

(cont.)

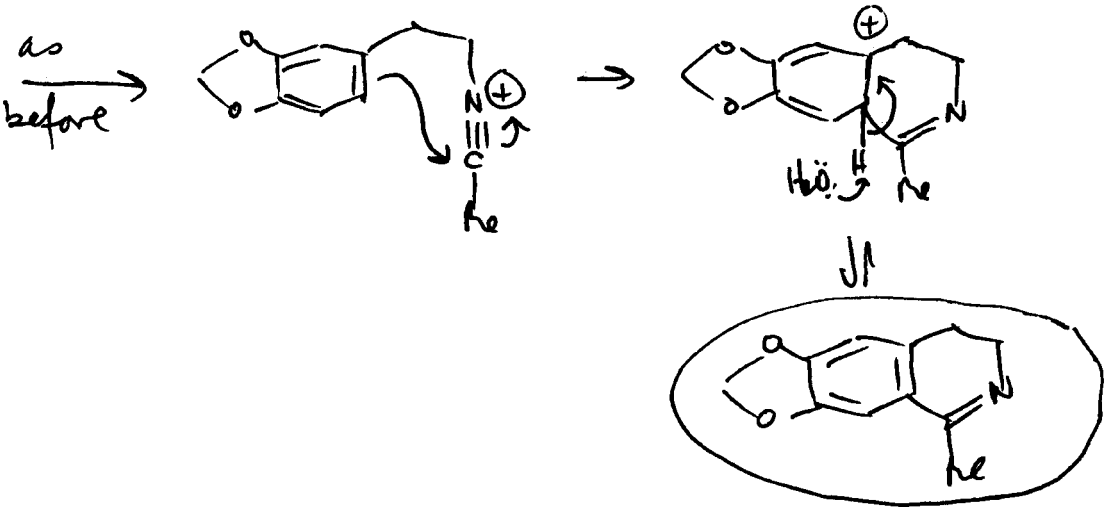


... the methyl group can also migrate.

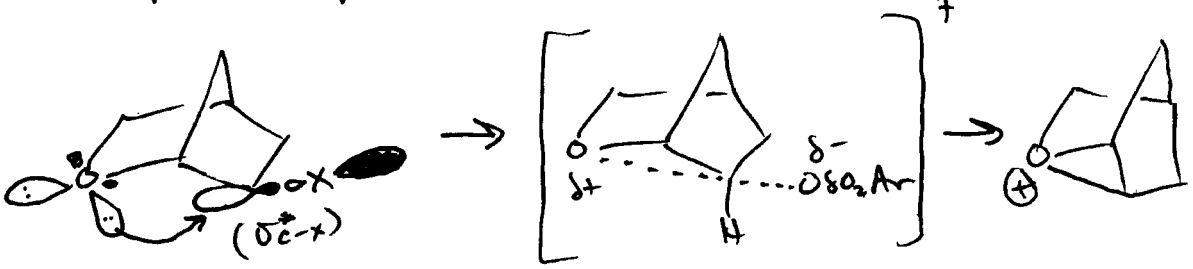


(cont)

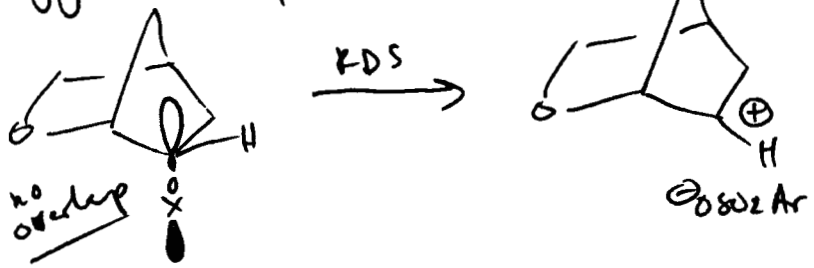
7. cont... The nitrilium ion formed after migration is very electrophilic & the aryl group is electron-rich → electrophilic aromatic substitution.



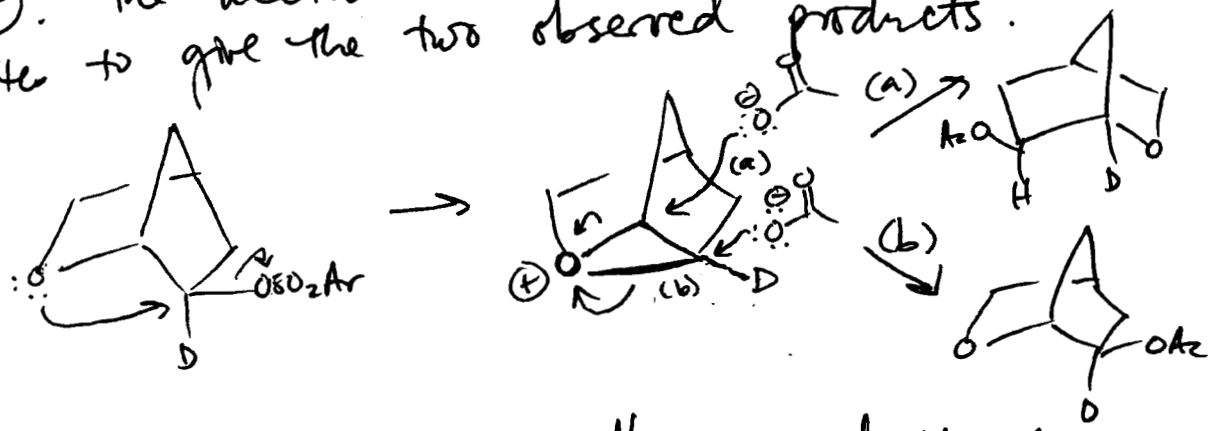
8. a) Both of the substitution reactions must go through a cationic species. Formation of this intermediate is the RDS. In the first reaction, the oxygen can facilitate ionization by donating its lone pair into the C–LG antibonding orbital. This speeds up the reaction. (NGP!)



In the second reaction, neighboring group participation is not possible because there is no overlap between the oxygen lone pair & σ^*_{CX}. The ionization step is slower.

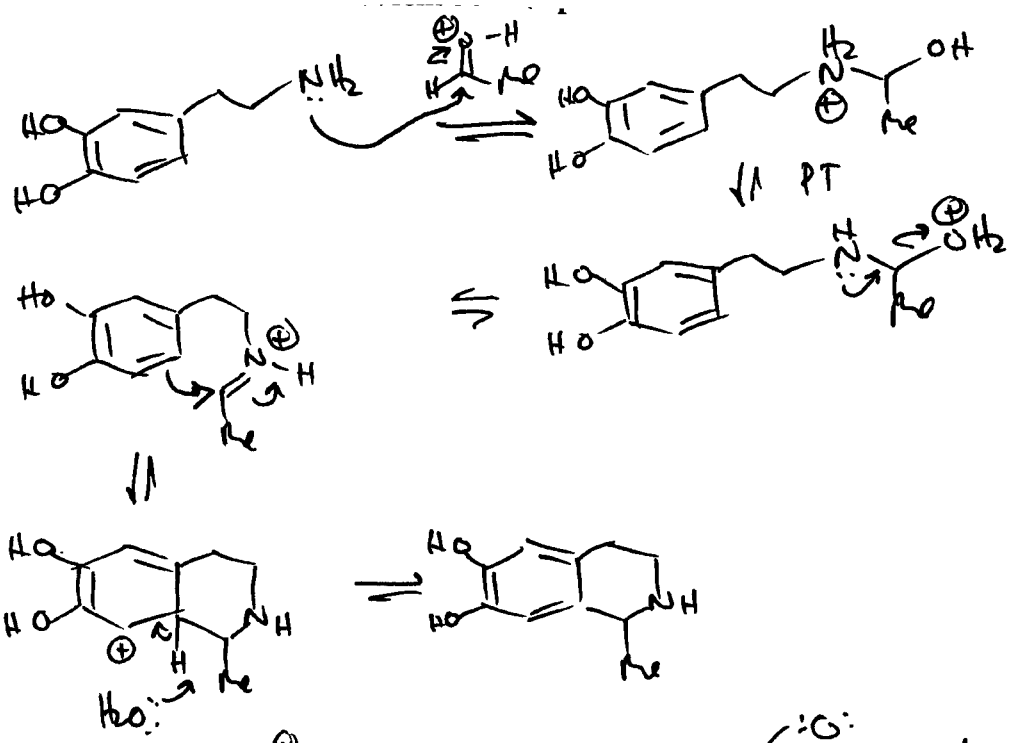


b) Both rxns proceed through the following intermediate (A). The acetate ion can attack two possible site to give the two observed products.

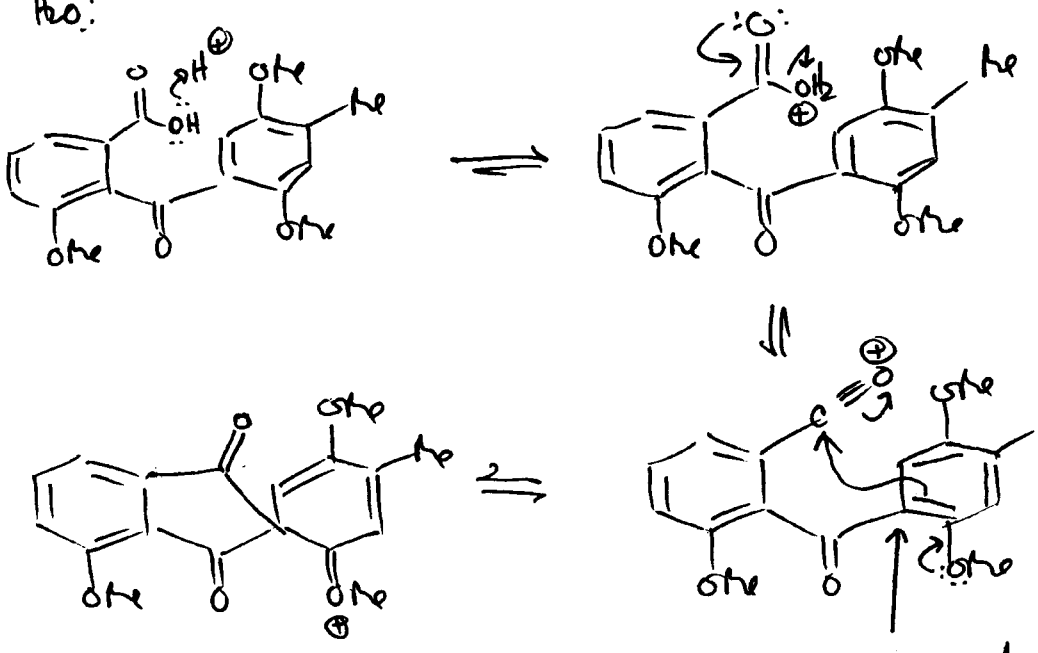


The rxns essentially proceed through an "SN2-like" pathway because of the NGP. → No other stereoisomers are formed.

9.



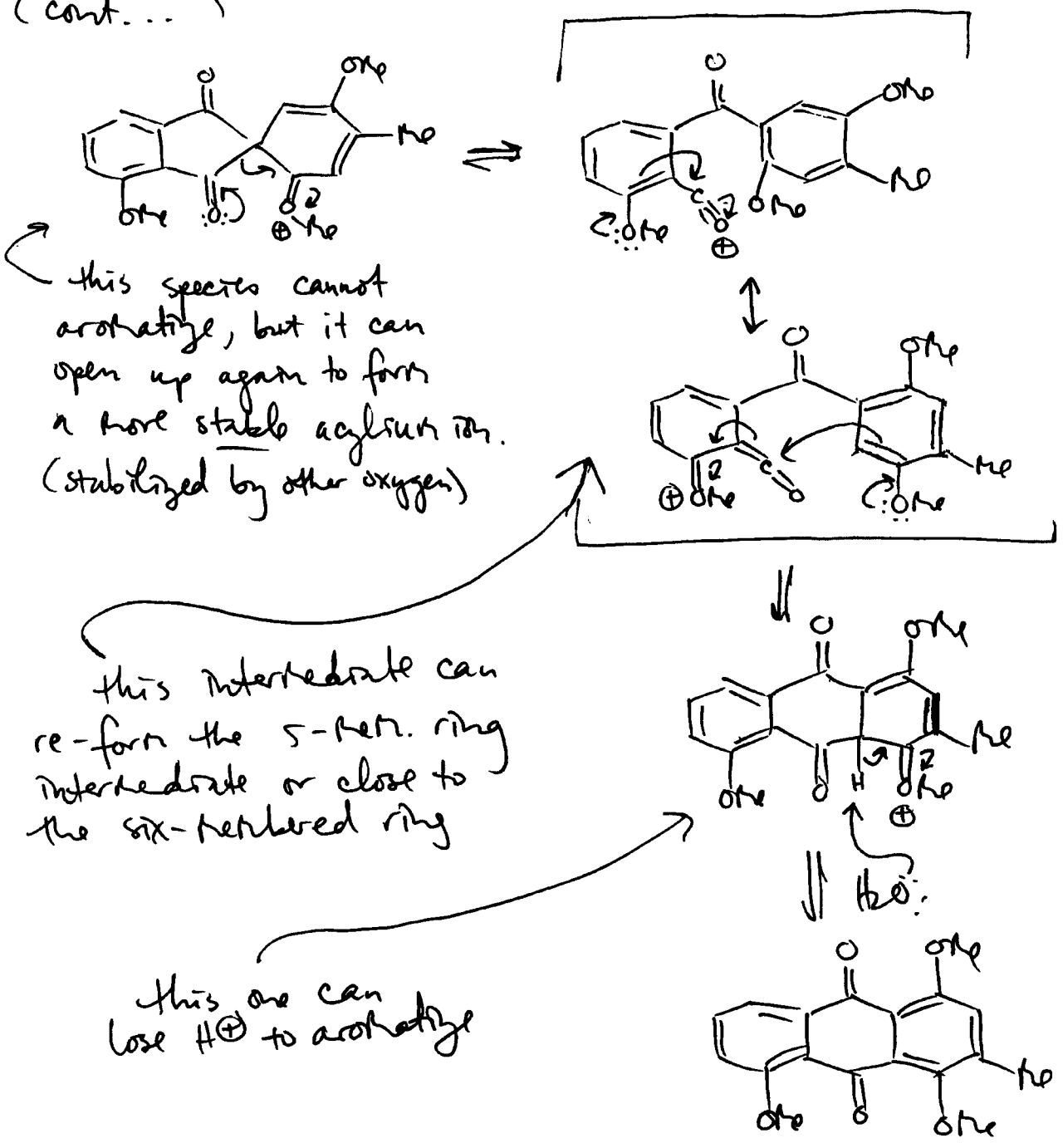
10.



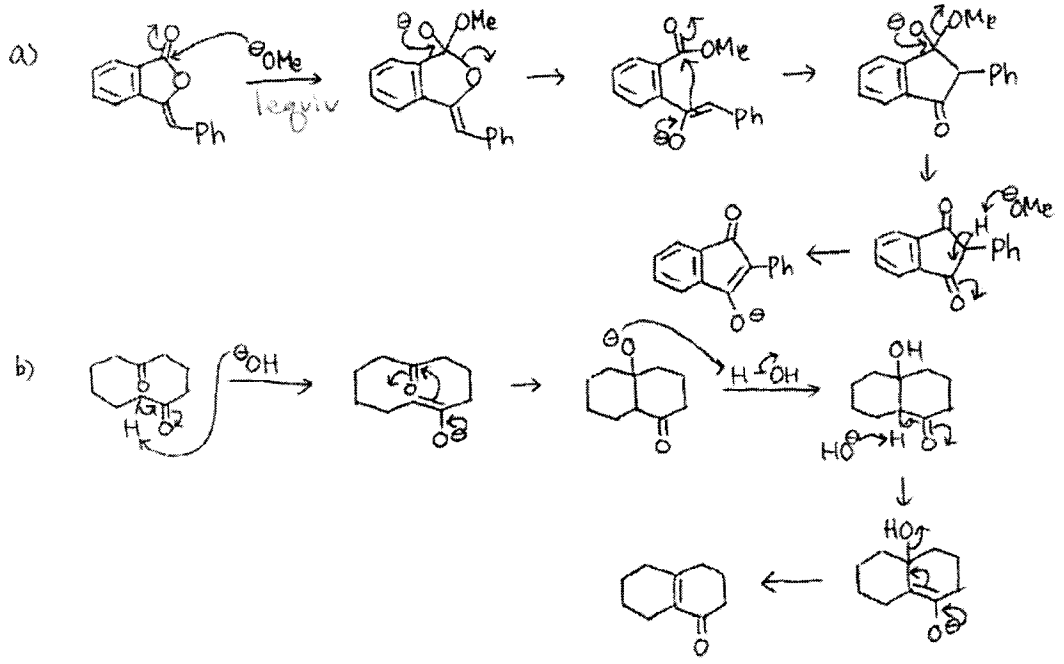
(cont. on next page)

This carbon more nucleophilic because cation formed stabilized by ortho Me ; not destabilized by ortho-acyl group

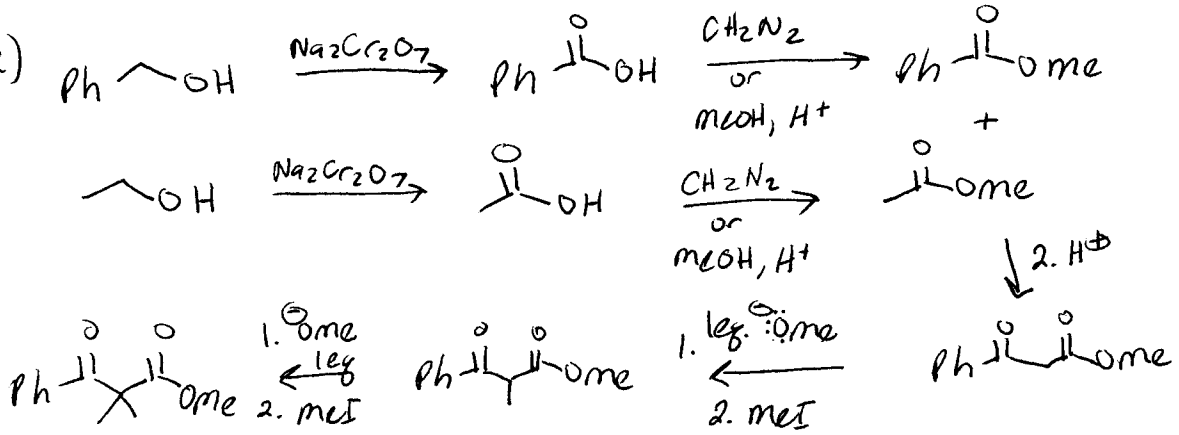
16. (cont...)


this species cannot aromatize, but it can open up again to form a more stable acylium ion. (stabilized by other oxygen)
this intermediate can re-form the 5-mem. ring intermediate or close to the six-membered ring
this one can lose H⊕ to aromatize

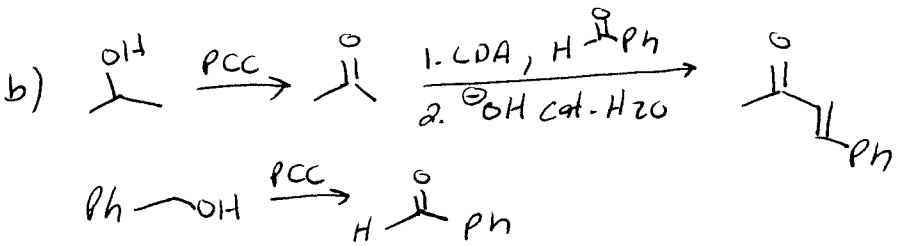
11.


a)
OMe
Ph
b)
OH
H

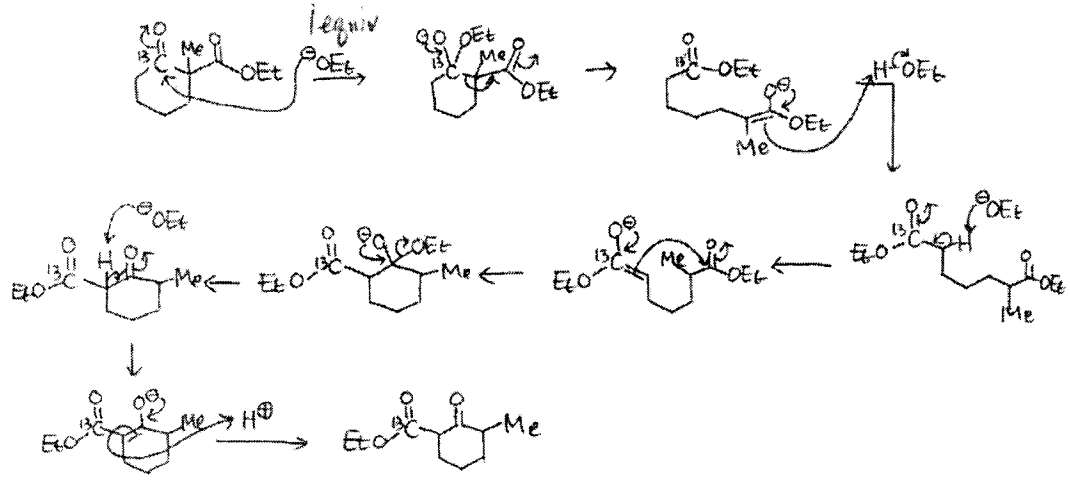
12. a)


Ph
OH
$Na_2Cr_2O_7$
CH_2N_2
or
MeOH, H^+
OMe
2. $H^\oplus$
1. LDA
2. MeI

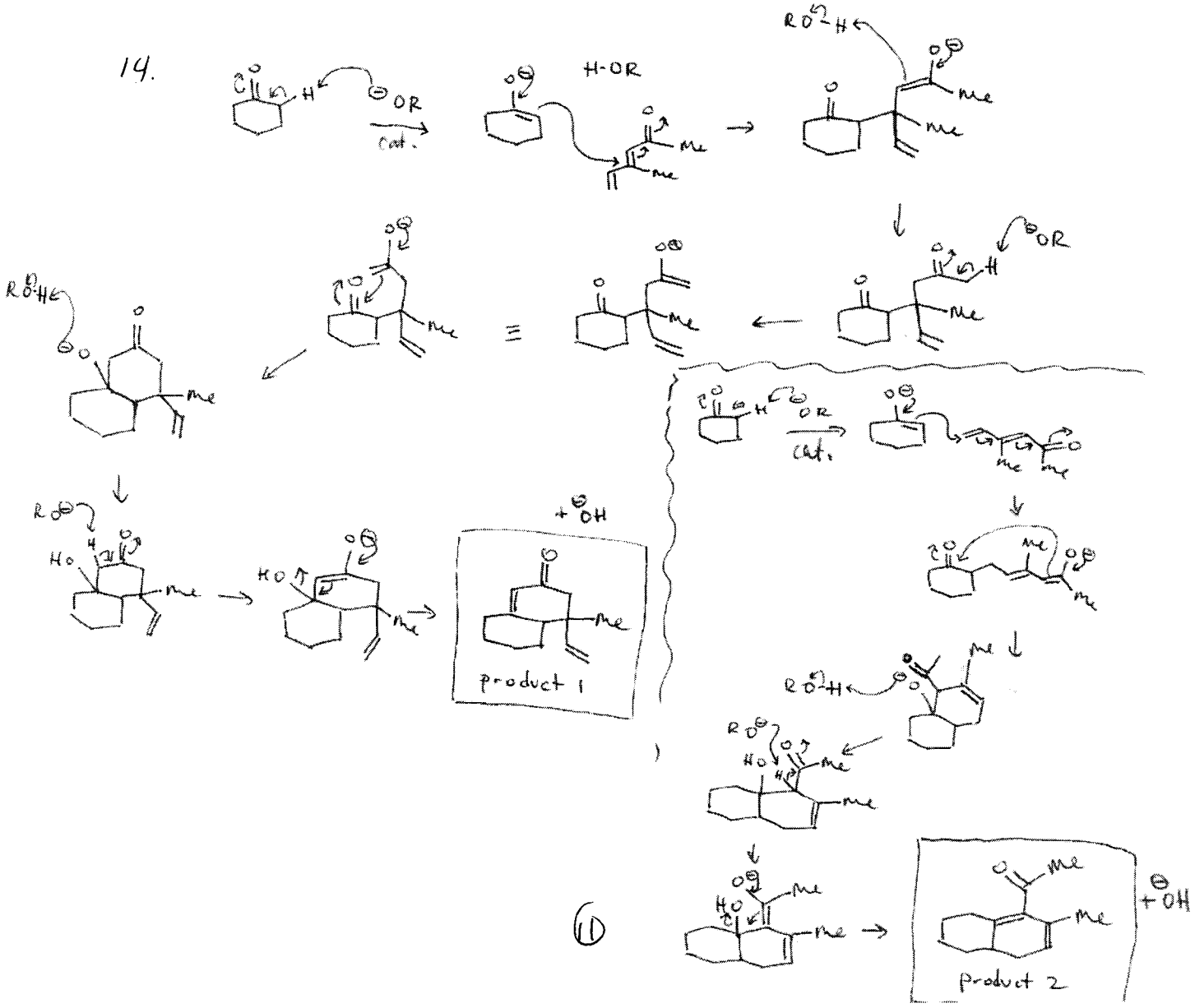
b)


PCC
1. LDA, H
Ph
2. $^\ominus$OH cat. H_2O

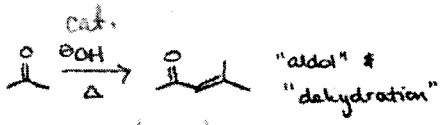
13.

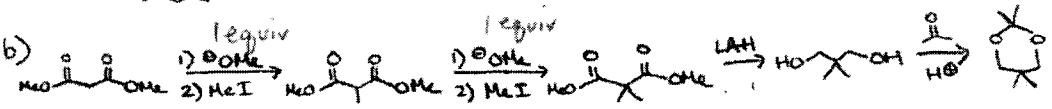


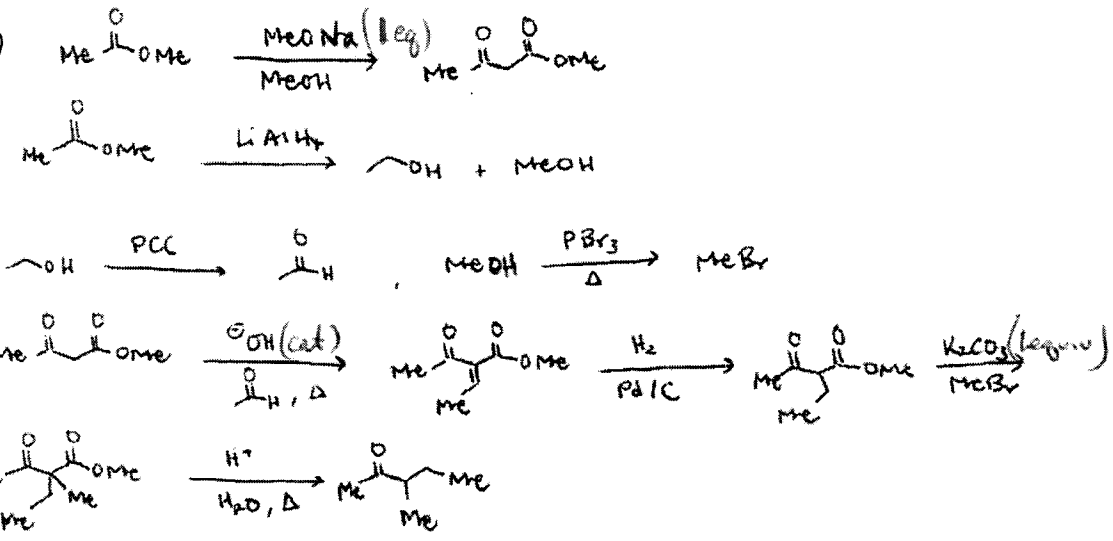
14.



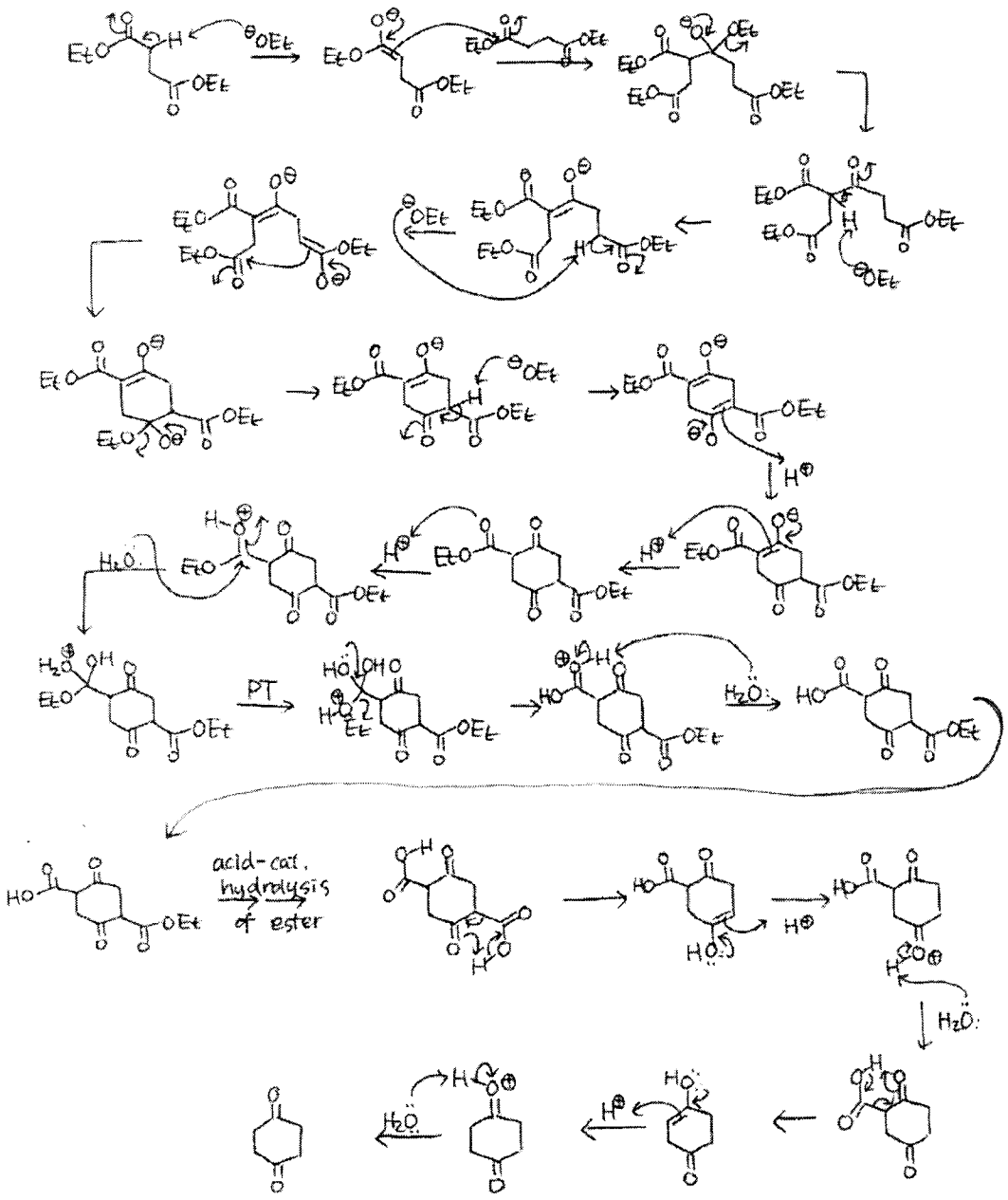
15.

a) 
cat.
⊖OH
Δ
"aldol" +
"dehydration"
1) LDA (1 equiv)
2)

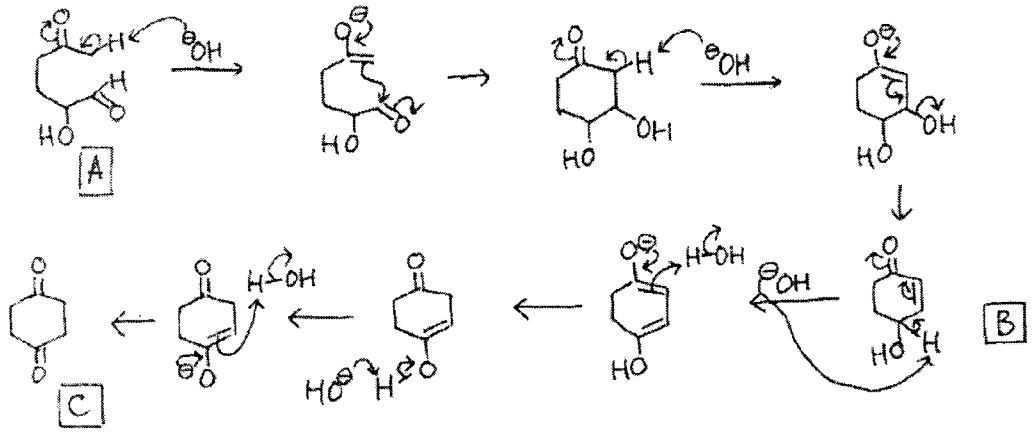
b) 
1 equiv
1) ⊖OMe
2) MeI
1 equiv
1) ⊖OMe
2) MeI
LAH
H⊕

c) 
MeONa (1 eq)
MeOH
LiAlH4
+ MeOH
PCC
MeOH
PBr3
Δ
MeBr
⊖OH (cat)
H, Δ
H2
Pd/C
K2CO3 (1 equiv)
MeBr
H+
H2O, Δ

16.



17.



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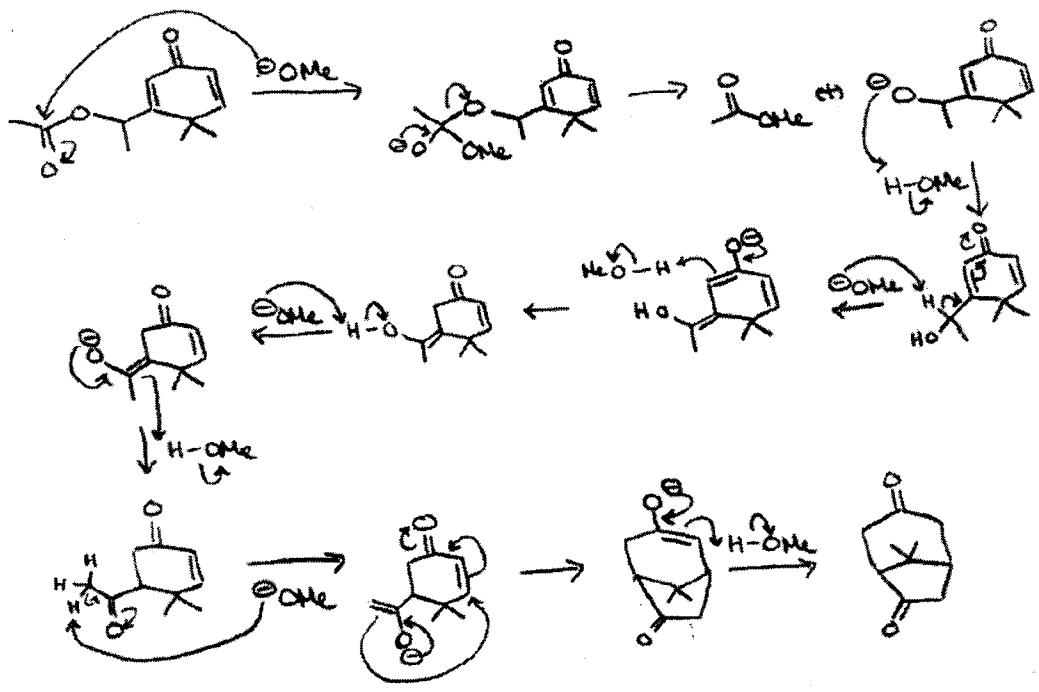
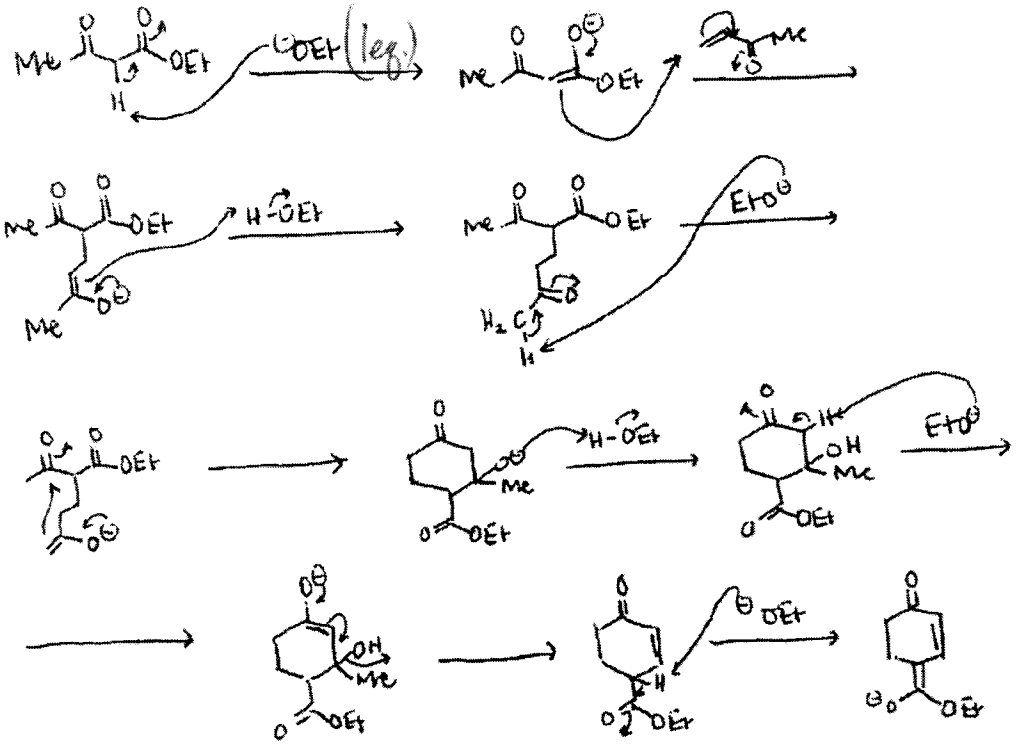
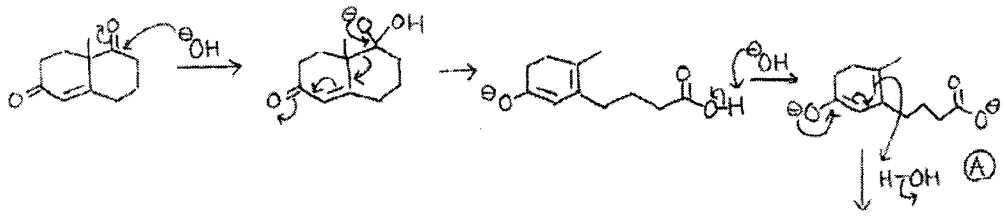


19.

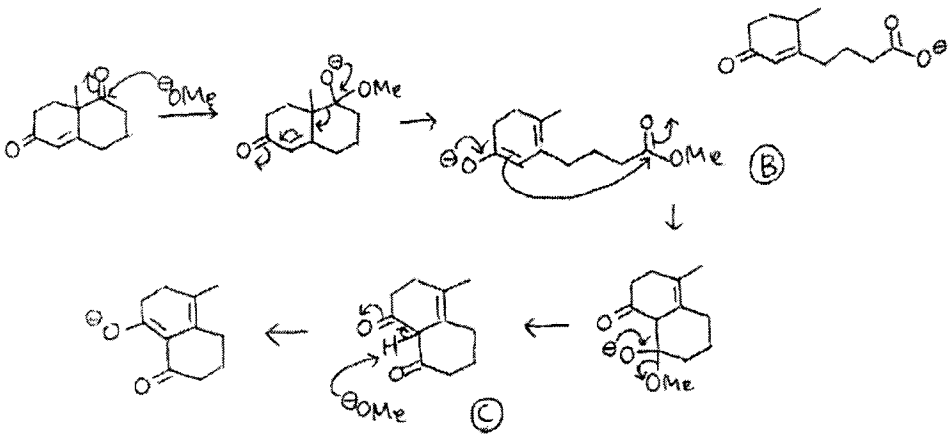

Me
OEt
H
⊖OEt (leg.)
Me
OEt
Me
H-OEt
Me
OEt
Me
OEt
H₂C
H
EtO⊖
OEt
H-OEt
Me
OEt
OH
Me
OEt
EtO⊖
OH
Me
OEt
⊖OEt
OEt

20.

a)

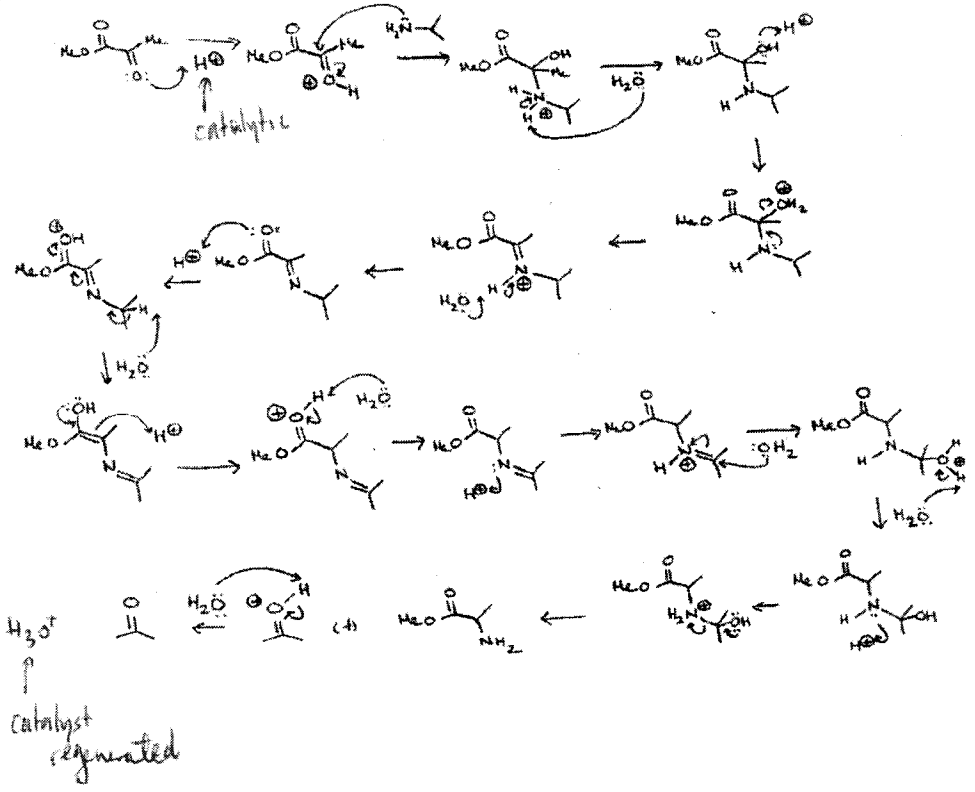


b)

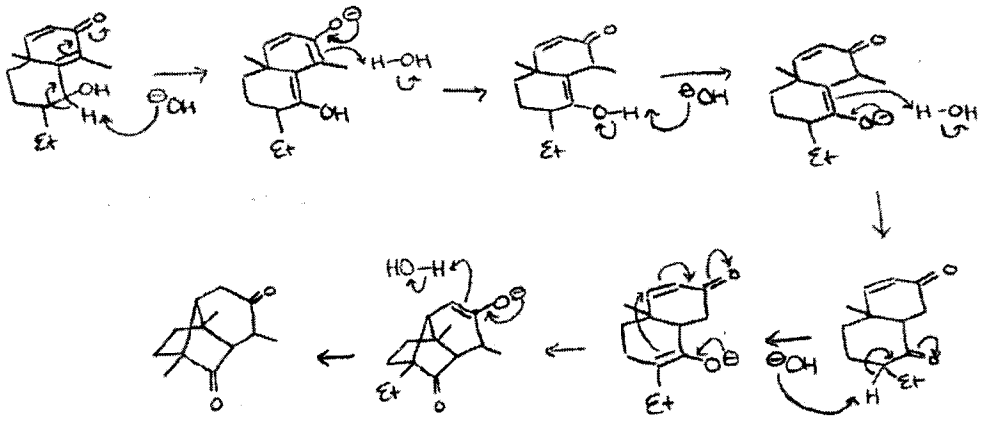


c) carboxylate (A) generated from rapid deprotonation is not reactive toward nucleophilic attack by enolates. In contrast, (B) can do further condensation generating (C), which can be deprotonated under rxn condition.

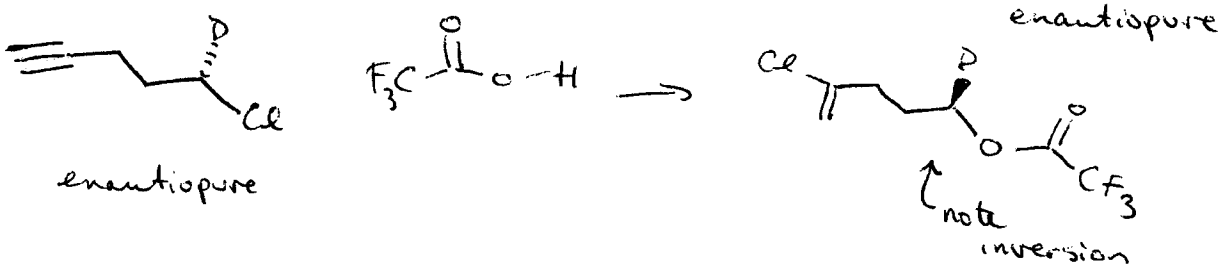
21.



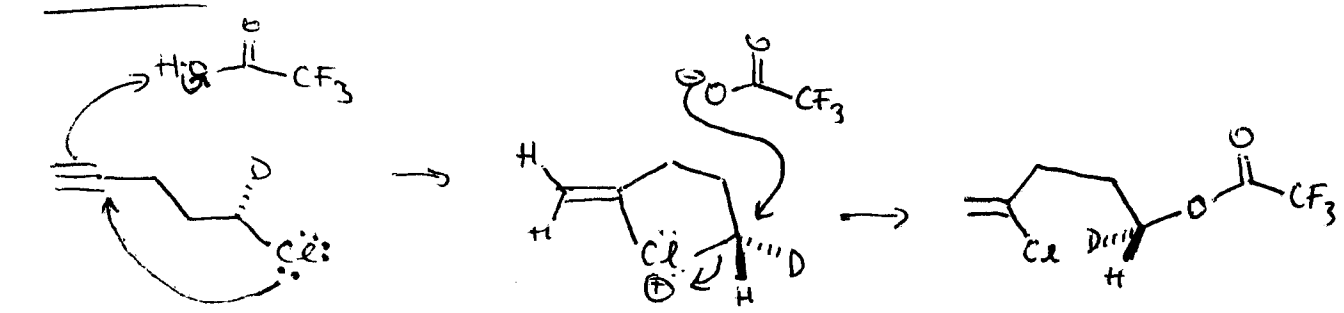
22.



23.



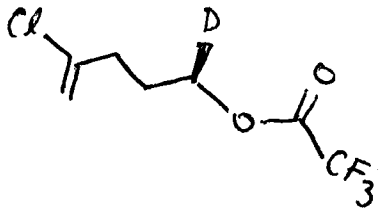
Mechanism



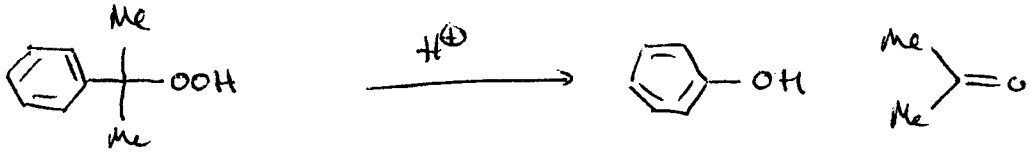
neighboring group participation avoids a high energy carbocation

S_N2 backside attack inverts the stereocenter

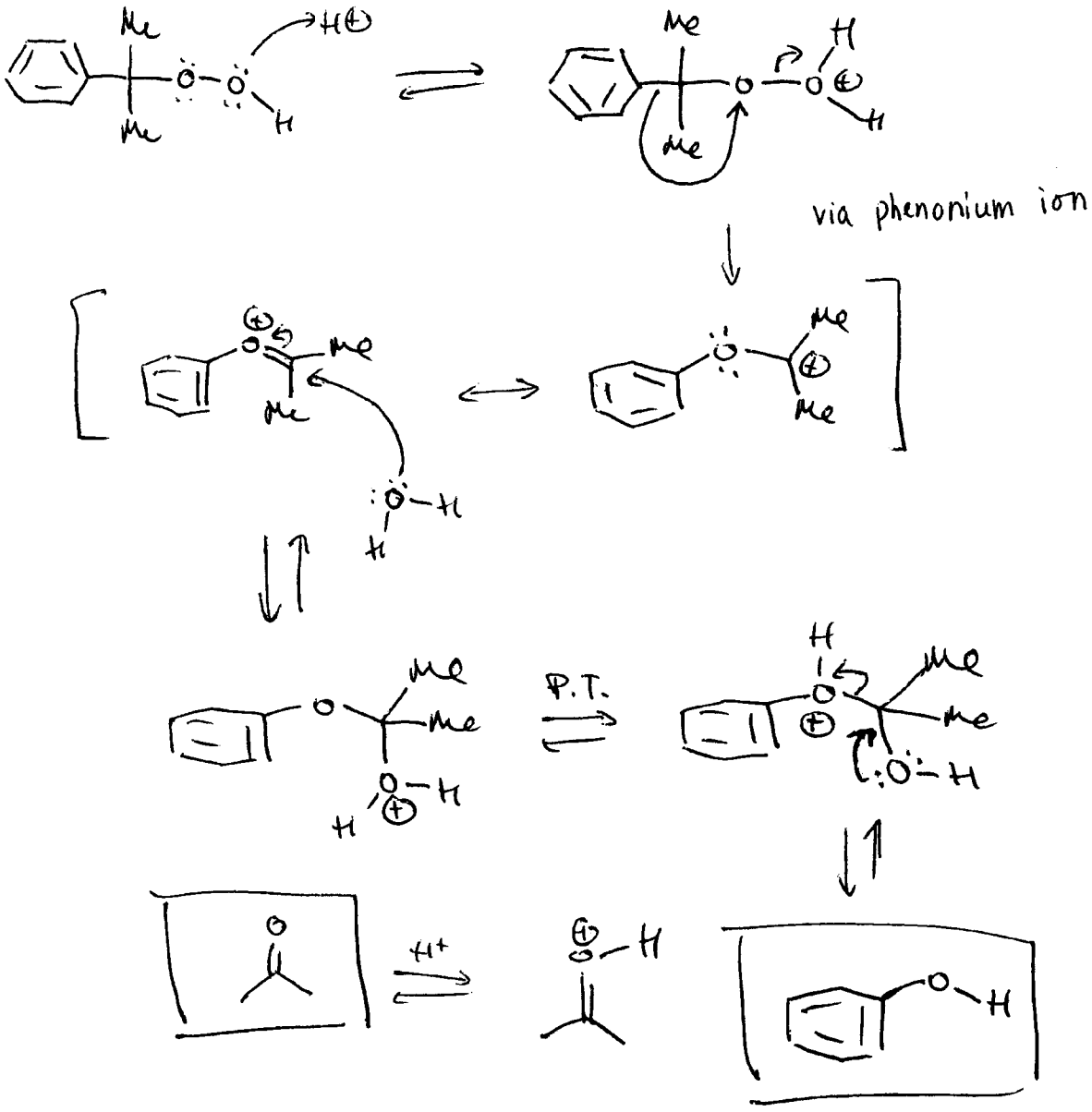
III



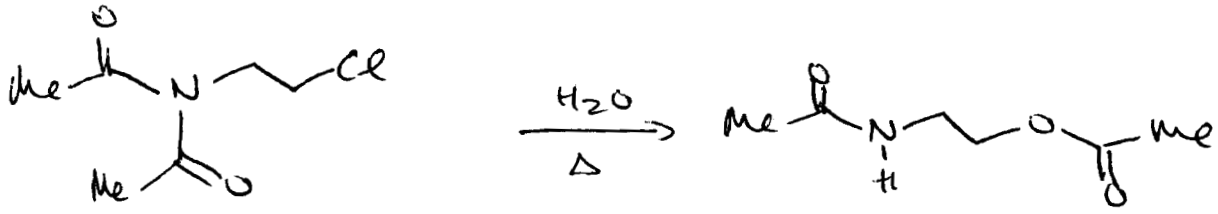
24.



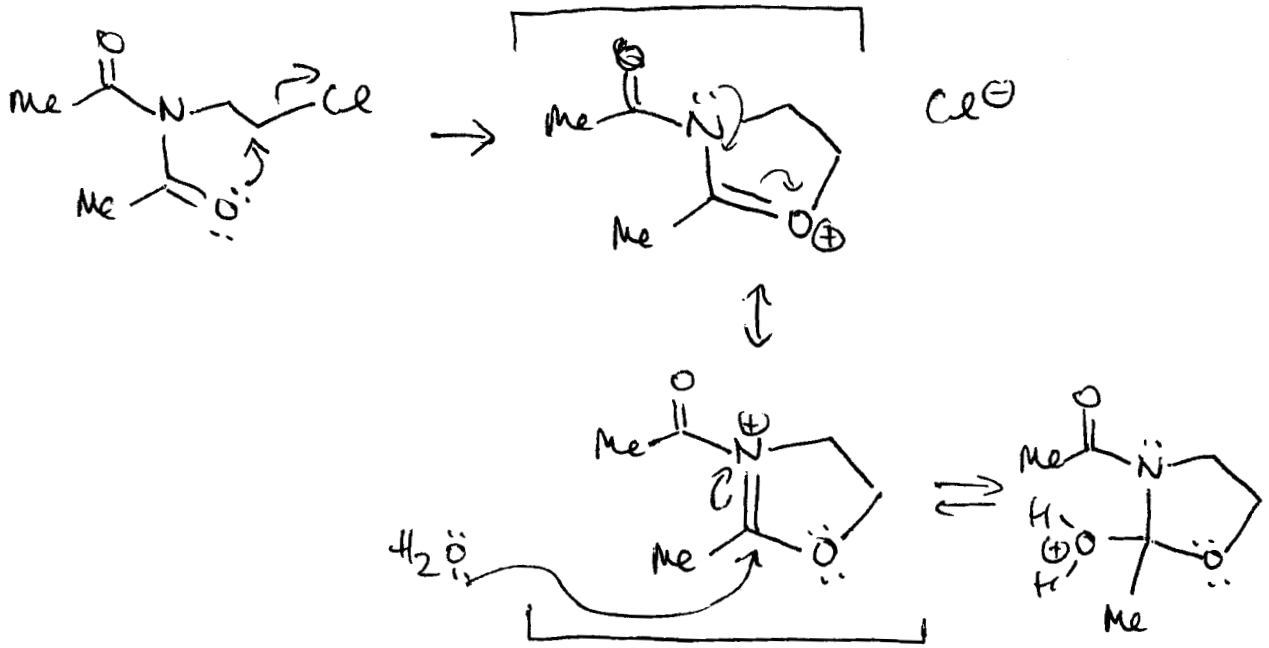
Mechanism

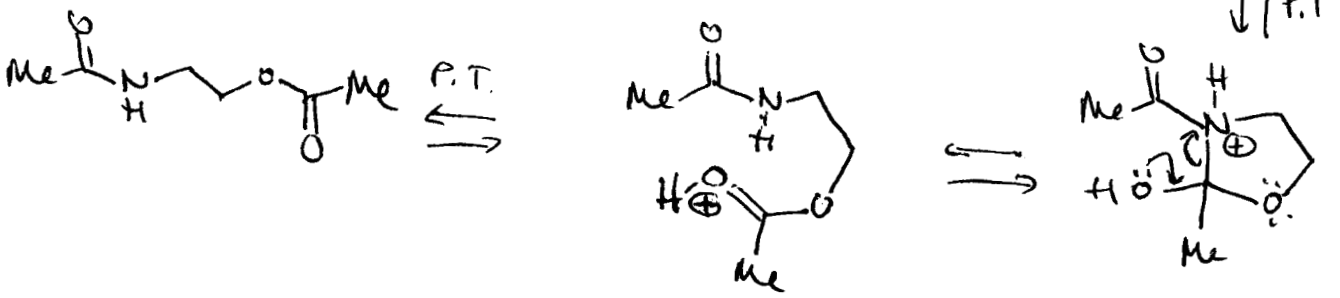


25.

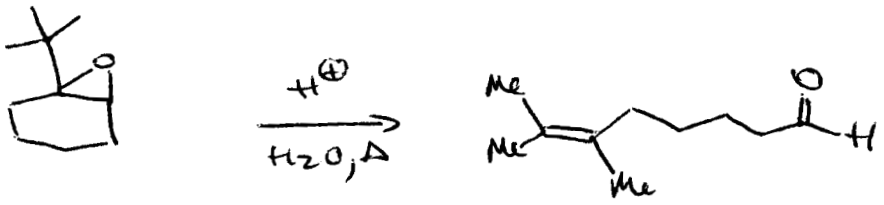


Mechanism

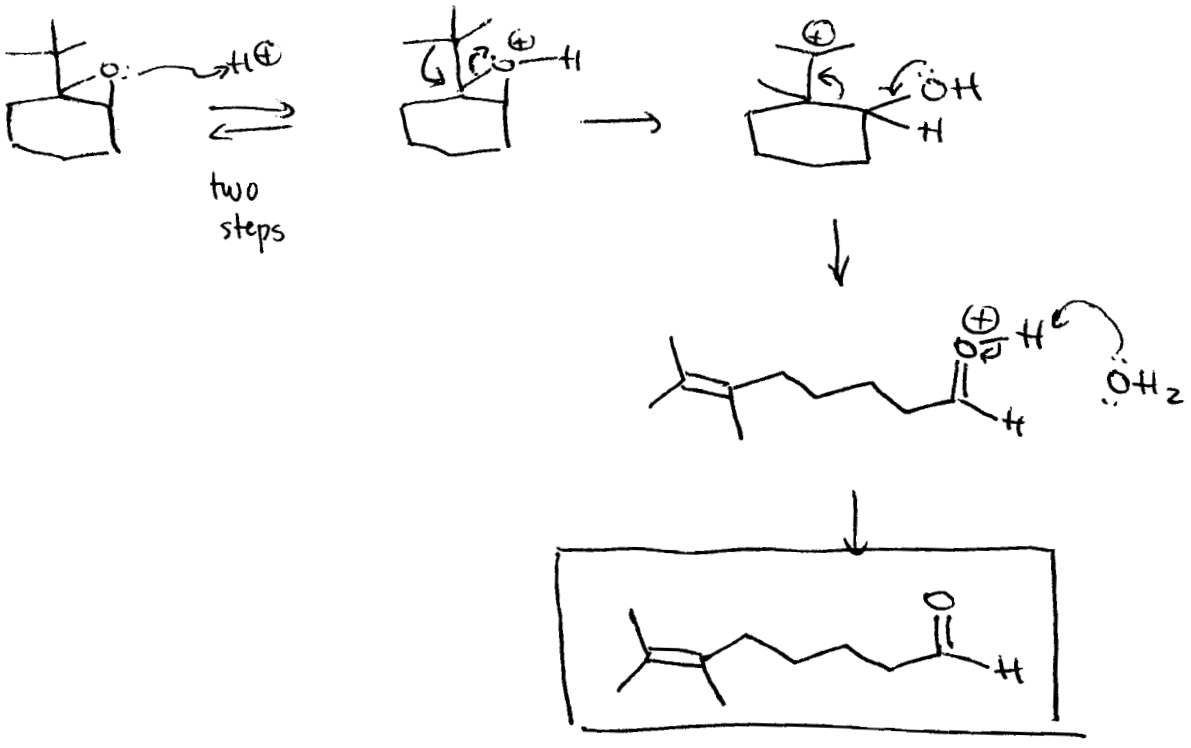




26.



Mechanism



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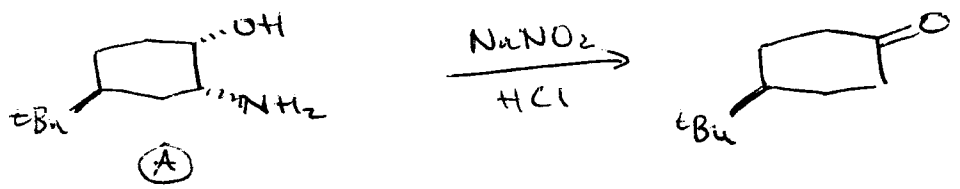
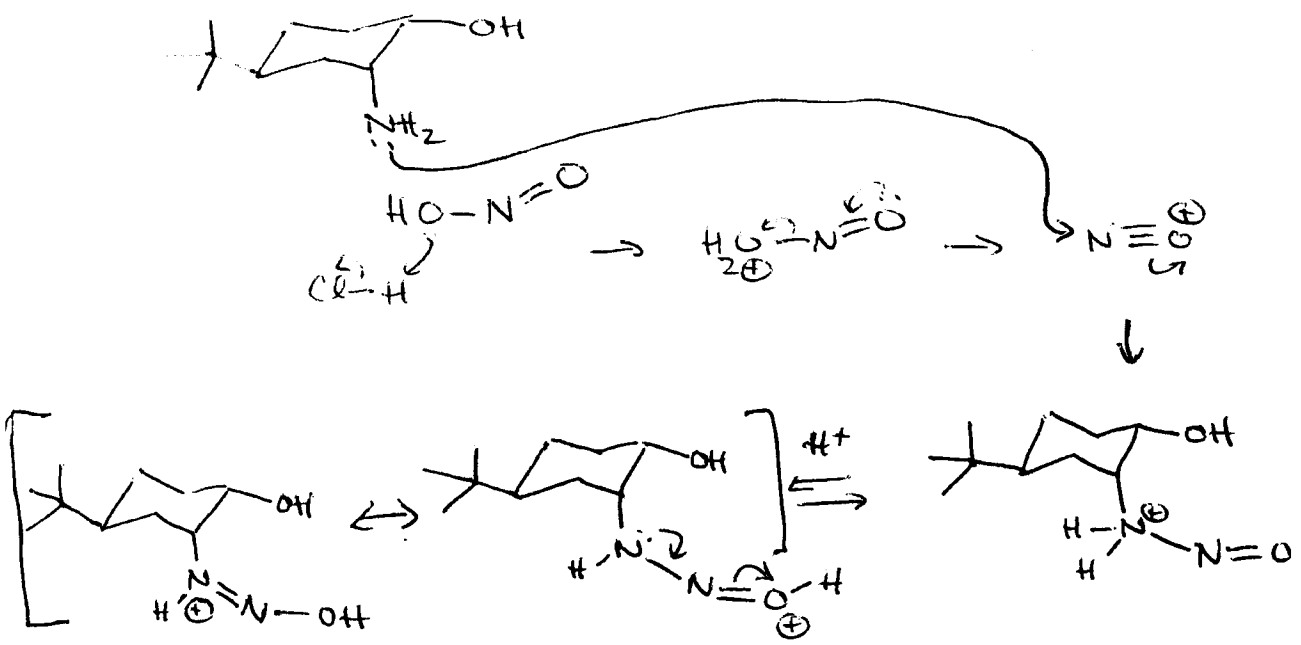
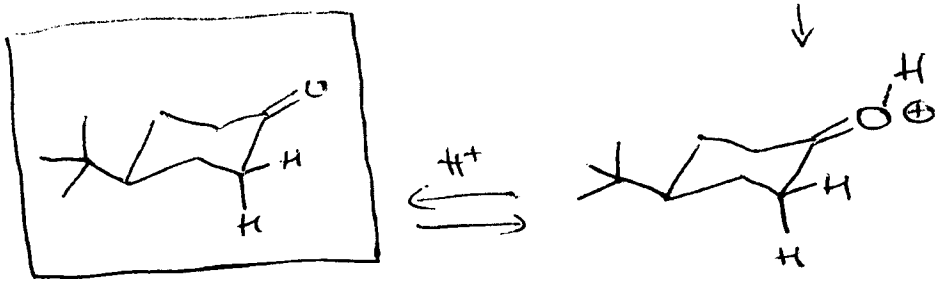


(A)

Mechanism

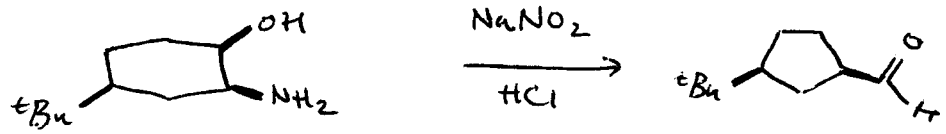


★Note: Migrating group is antiperiplanar to Leaving group

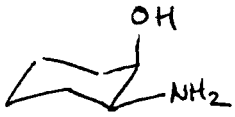


Next page for (B)

#27 part B

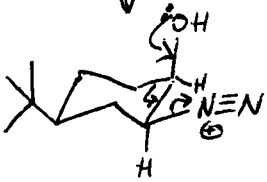


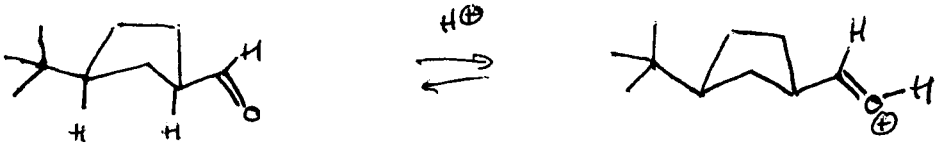
Mechanism



(for diazonium formation, see part A)

★ Once again: the migrating group is anti-periplanar to the leaving group.





III