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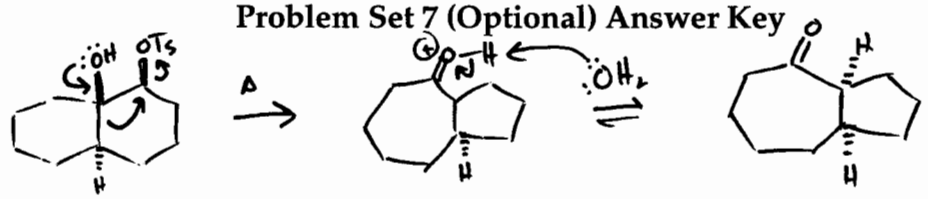
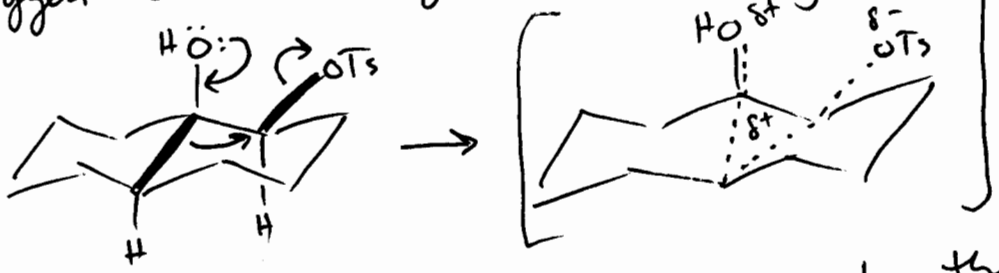
5.13: Organic Chemistry II *Fall 2003, S. Tabacco*

Problem Set 7 (Optional) Answer Key

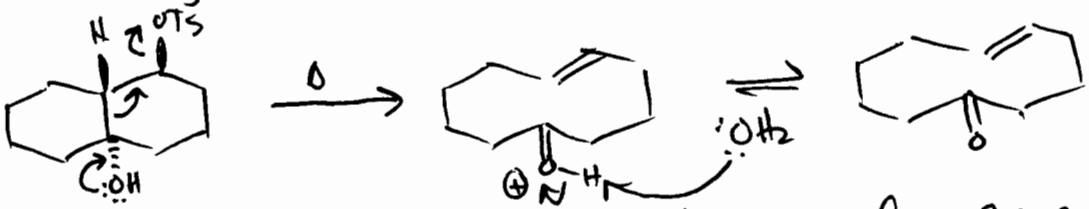
(1)



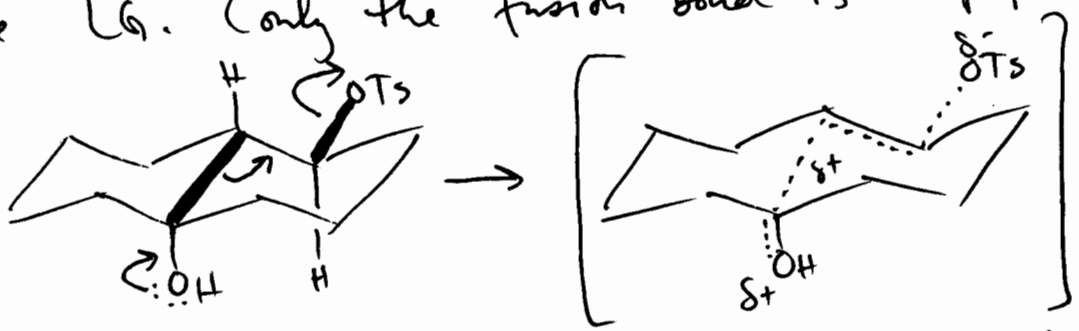
In this "Pinacol-like" concerted process, the migrating bond must be antiperiplanar to the LG so that the oxygen can stabilize the developing charge in the TS.



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



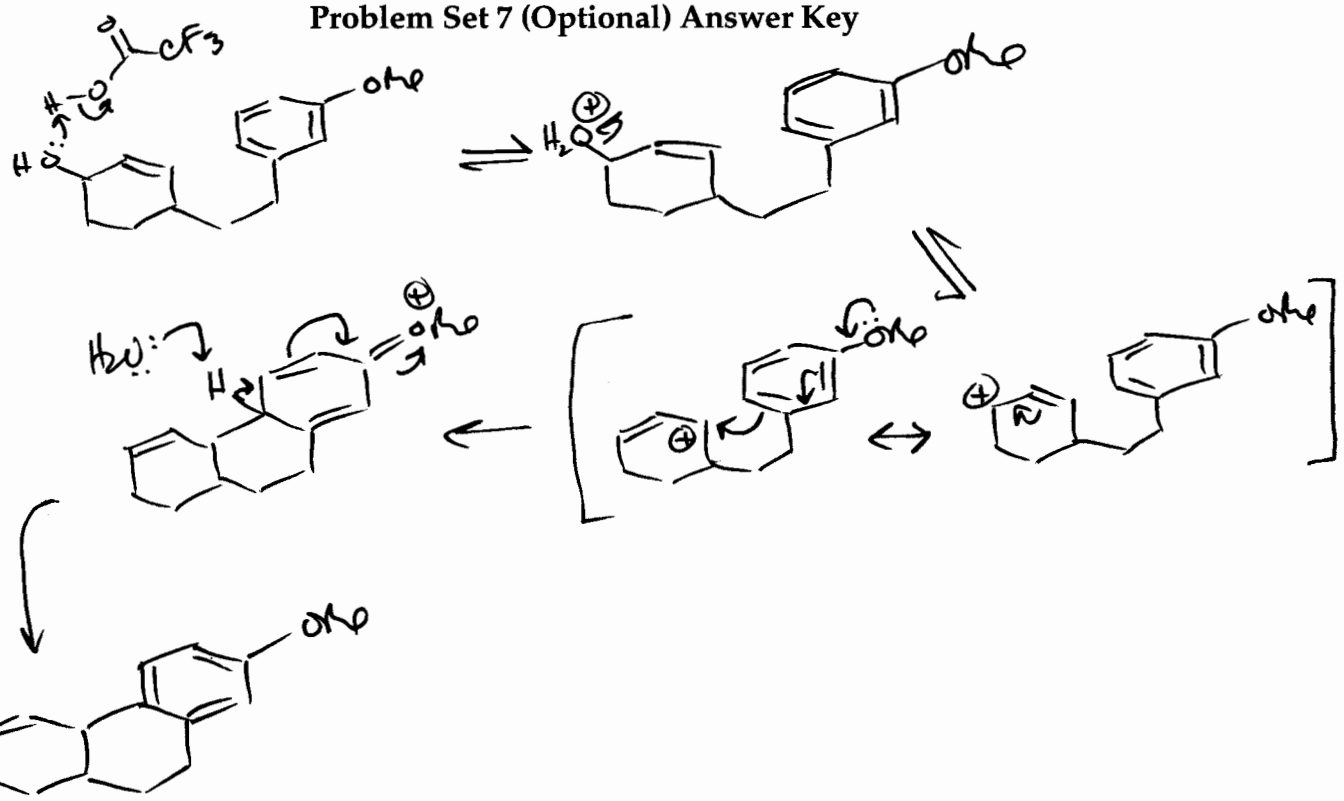
This concerted Grob fragmentation is also concerted, so the bond that is cleaved must be antiperiplanar to the LG. (Only the fusion bond is a.p.p.)



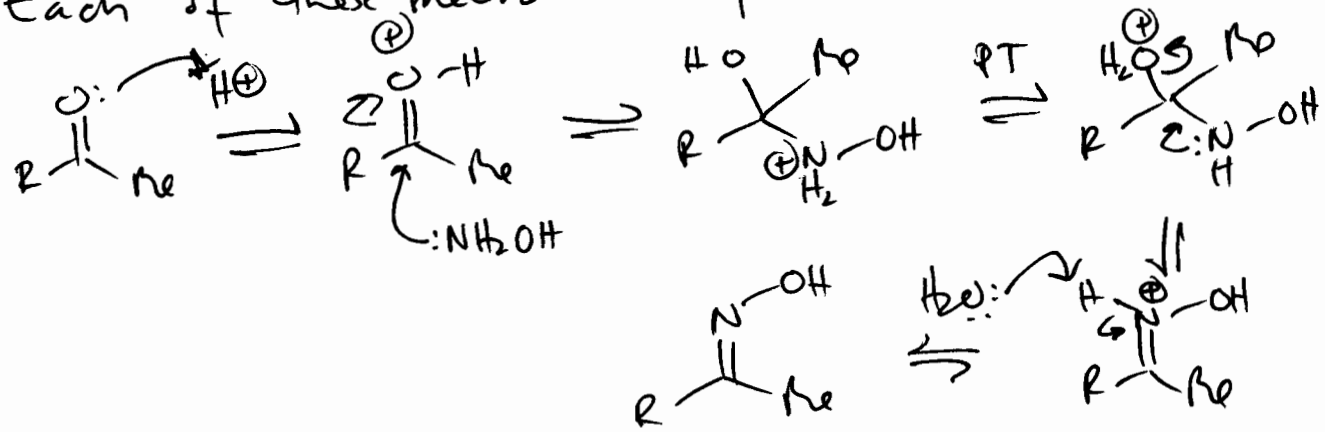
Only the bond a.p.p. to the LG is involved in these processes. The position of the oxygen determines which product will be formed.

Problem Set 7 (Optional) Answer Key

(2)



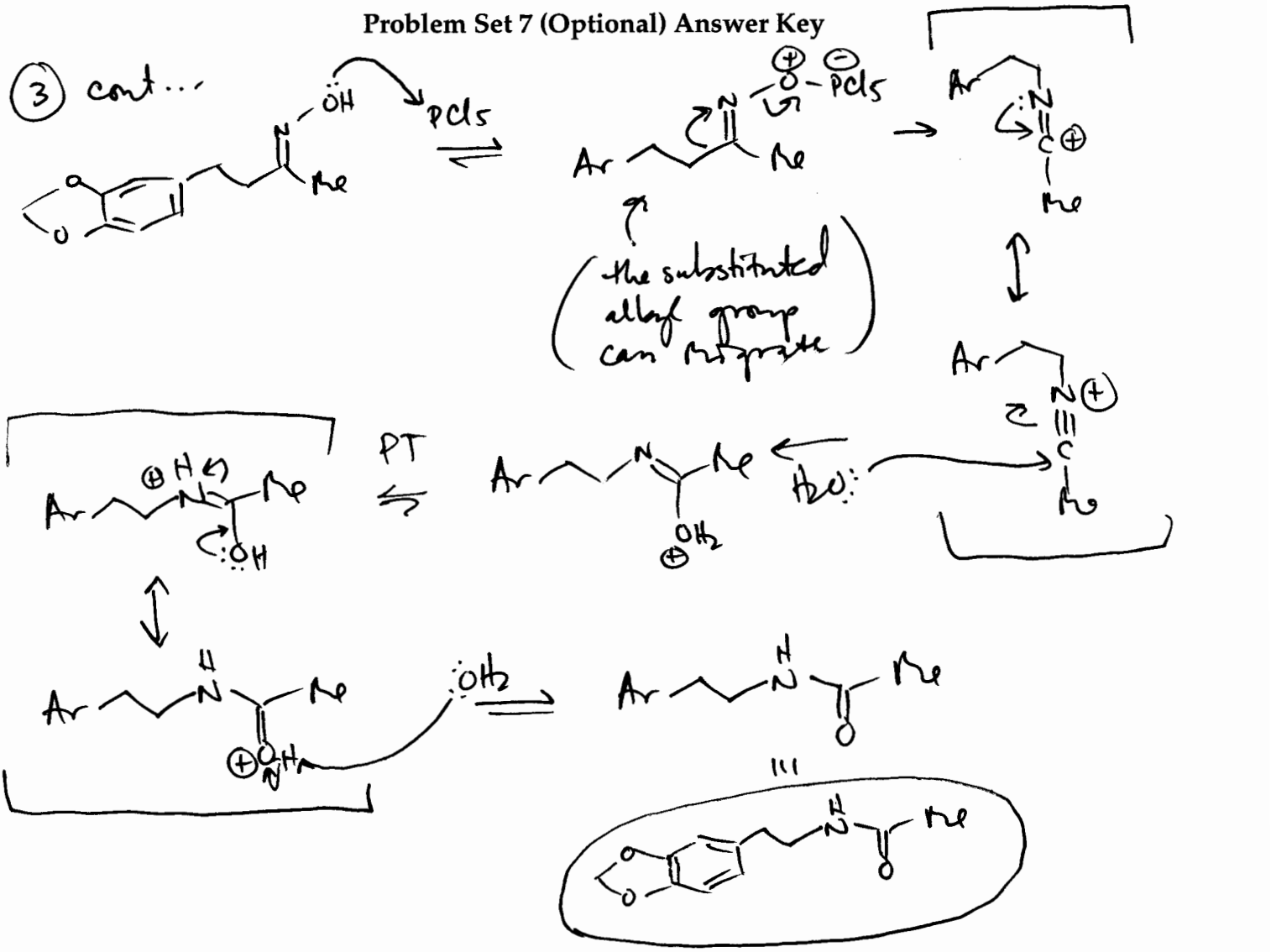
(3) Each of these mechanisms proceeds through an oxime.



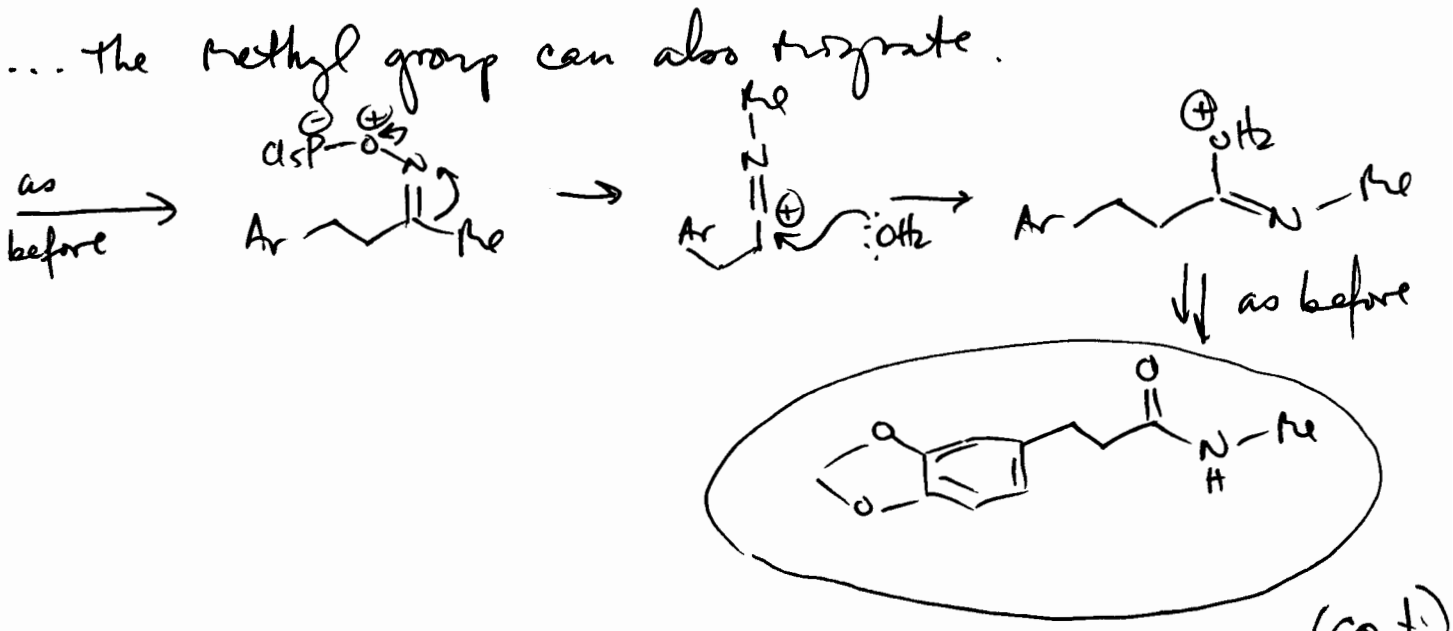
≠ Would likely form mixture of

(cont.)

Problem Set 7 (Optional) Answer Key



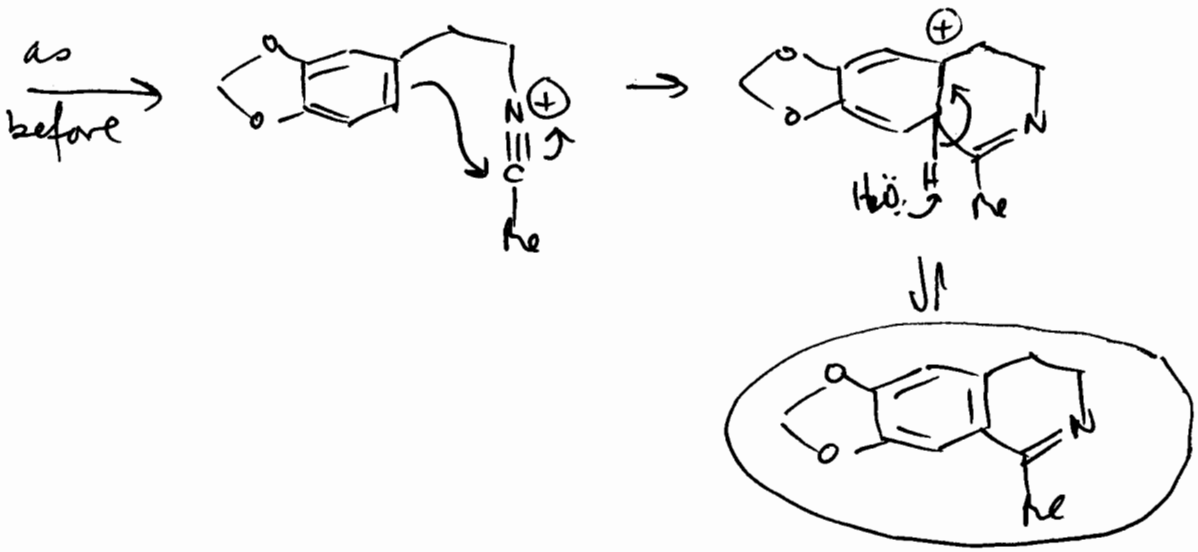
...the methyl group can also migrate.



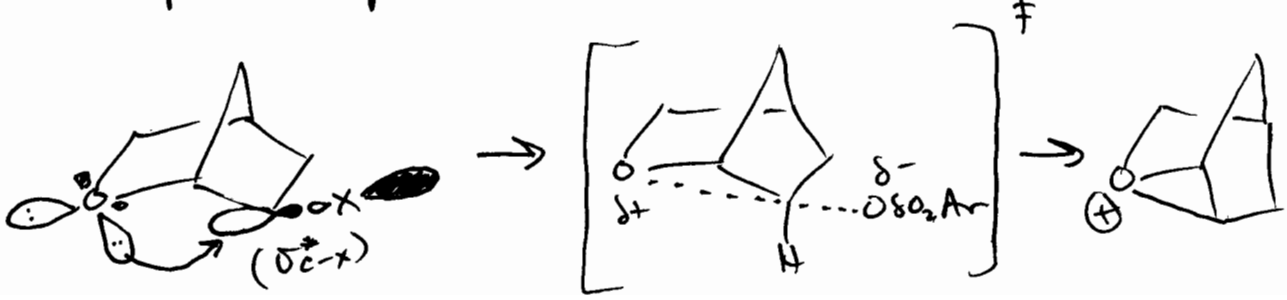
(cont.)

Problem Set 7 (Optional) Answer Key

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



(4) 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!)



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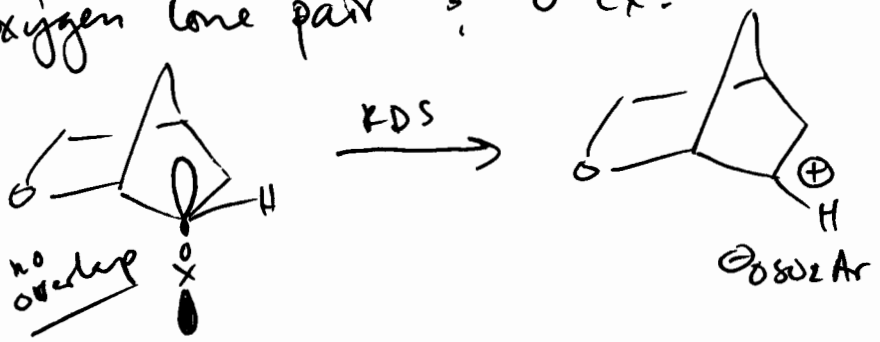
In the second reaction, neighboring group participation is not possible because there is no overlap between the oxygen lone pair & σ^*_{CX}. The ionization step is slower.



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

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

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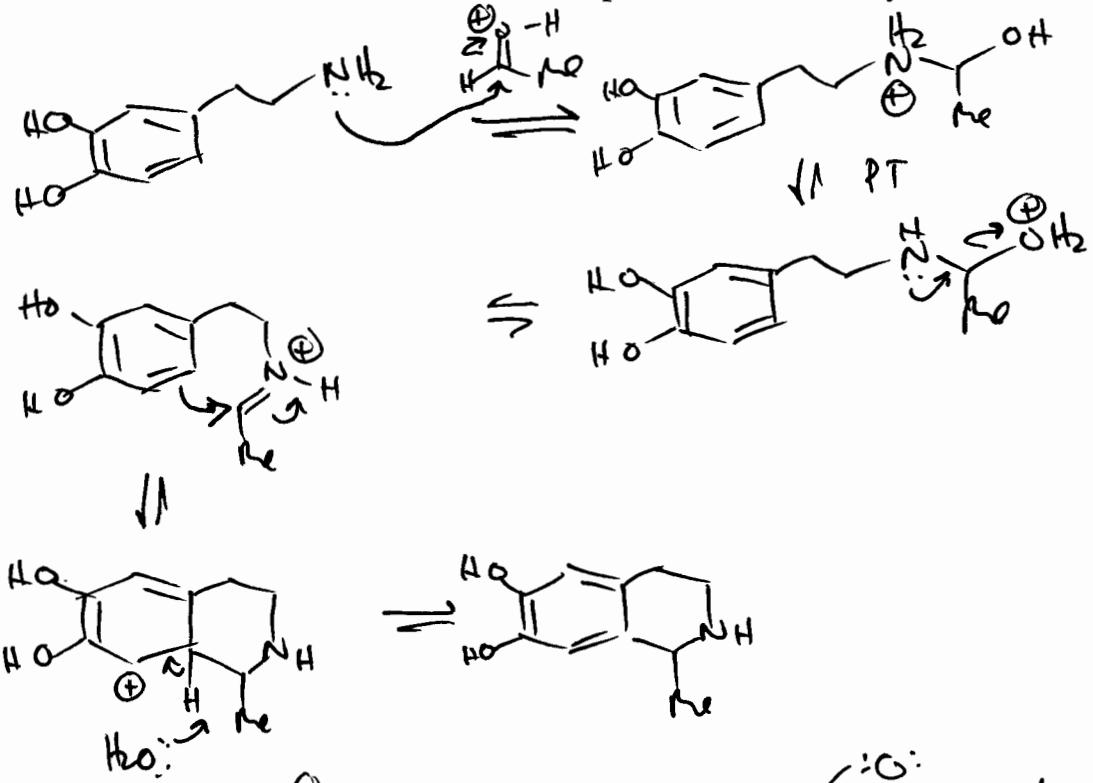
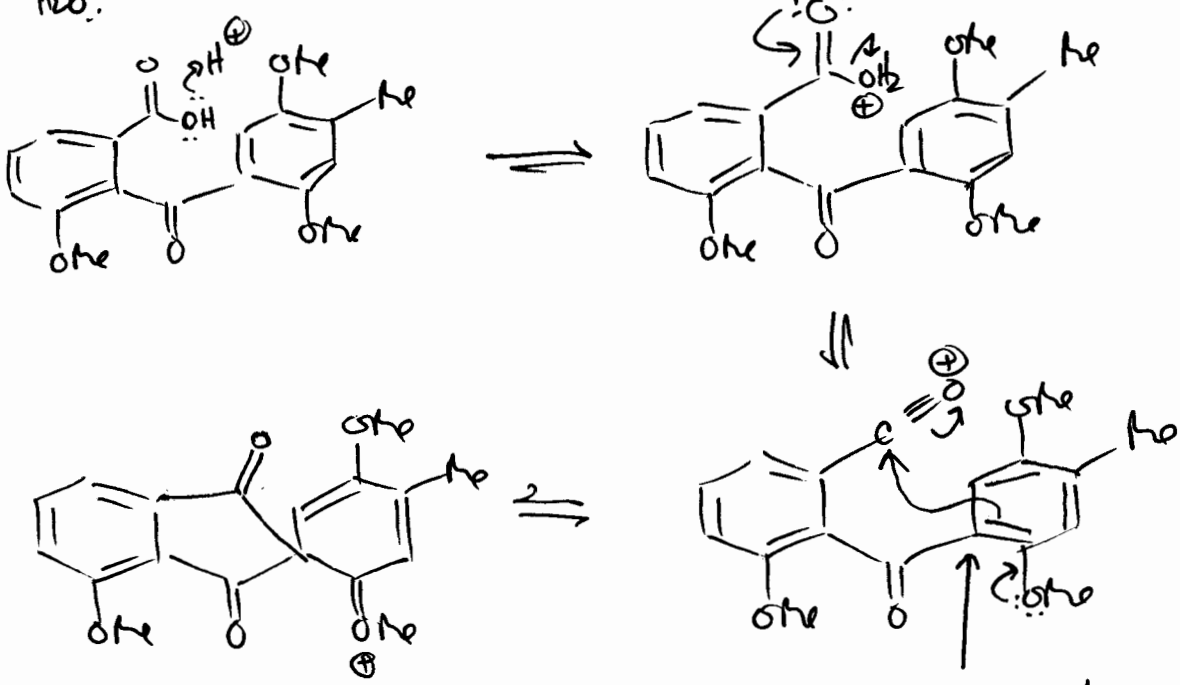
Problem Set 7 (Optional) Answer Key

(5)



(6)



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

(cont. on next page)

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Problem Set 7 (Optional) Answer Key