

# SOLUTIONS TO PSET #9,

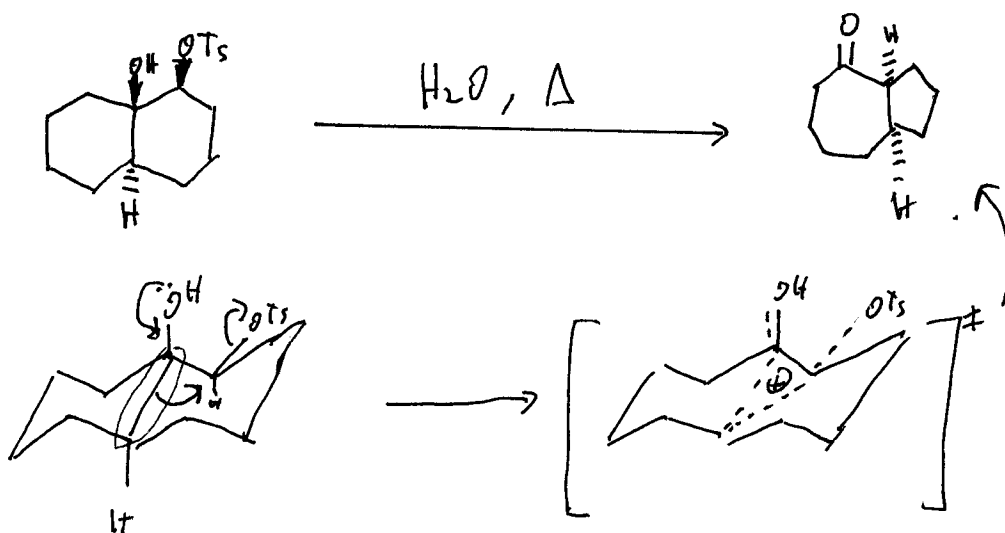
ES 1

5.13 Org. Chem. II

Spring 2003

①

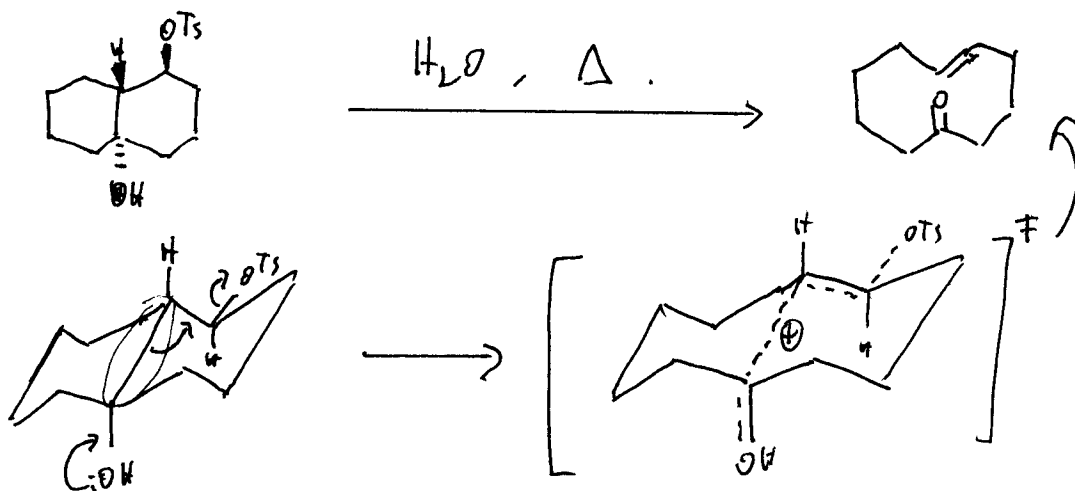
a)



F is stabilized by delocalization of +ve charge onto Oxygen.

Process is concerted so the attack must occur from behind ( $S_N2$ ) hence the circled bond is the one to migrate.

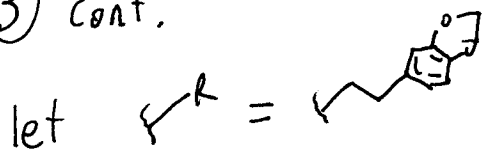
b)



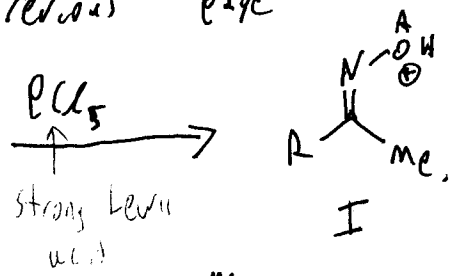
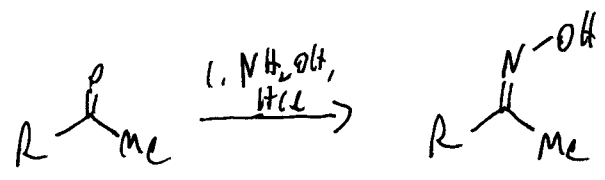
Again, the reaction is concerted so the elimination must be (anti)-periplanar. Hence the circled bond is the one which is cleaved.



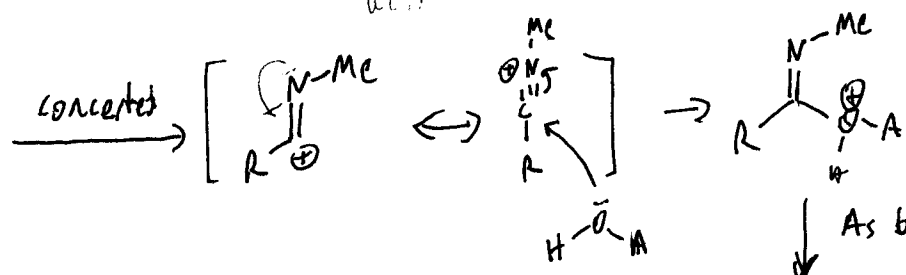
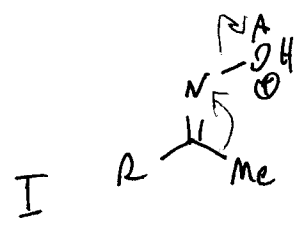
(3) cont.



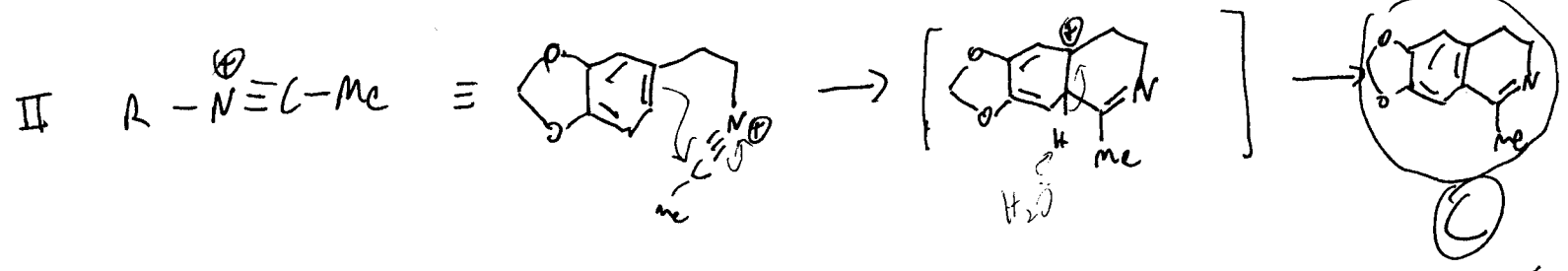
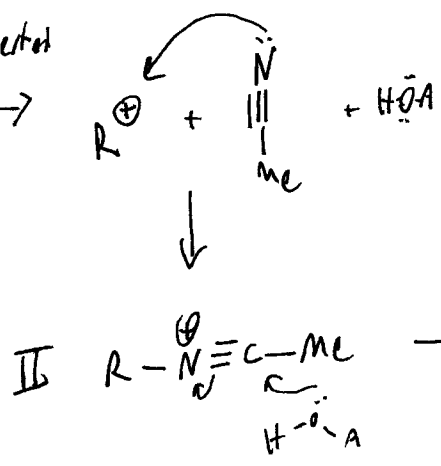
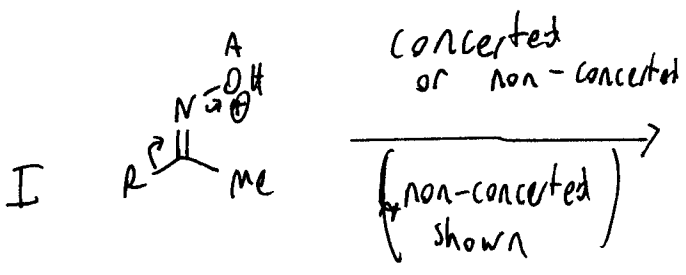
then from the <sup>generic</sup> mechanisms from the previous page



Let A = Lewis acid OR  $H^+$



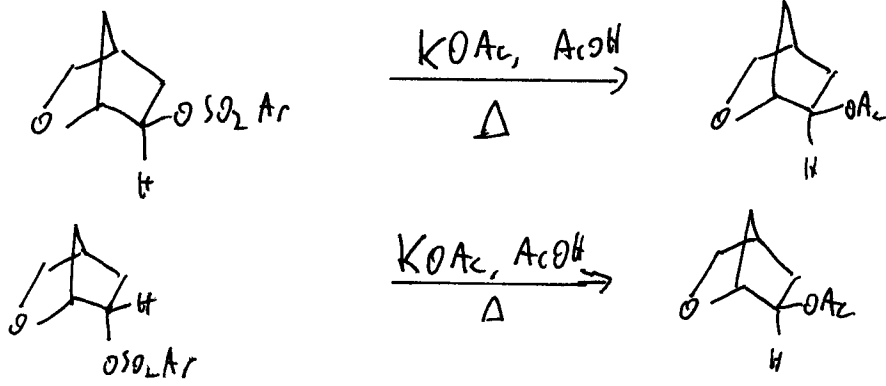
As before (previous page)



$\rho_{SET} \neq \rho_{cont}$

pg 4.

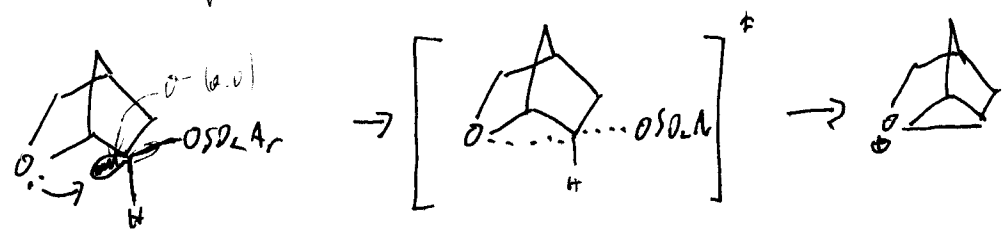
(4) a)



$k_{rel}$   
 $7 \times 10^7$

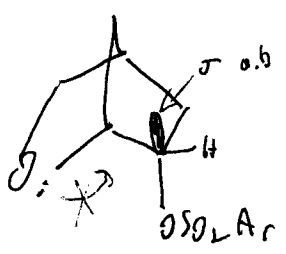
The rate difference is a result of neighboring group participation (NGP). Both reactions proceed through a high energy cationic intermediate (shown as resonance structures of a bicyclic carbocation) the formation of which is the rate determining step (RDS). In the upper case NGP facilitates the formation of the <sup>cationic</sup> intermediate by helping to kick off the LG by donating the oxygen lone pairs into the  $\sigma^*_{C-O}$  as shown. (figure 1)

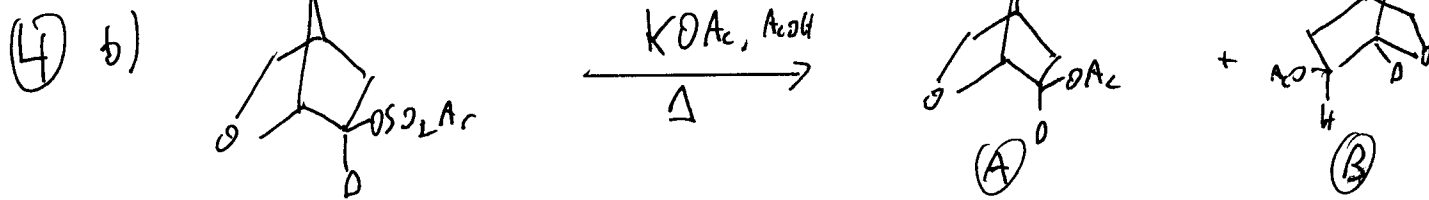
Figure 1




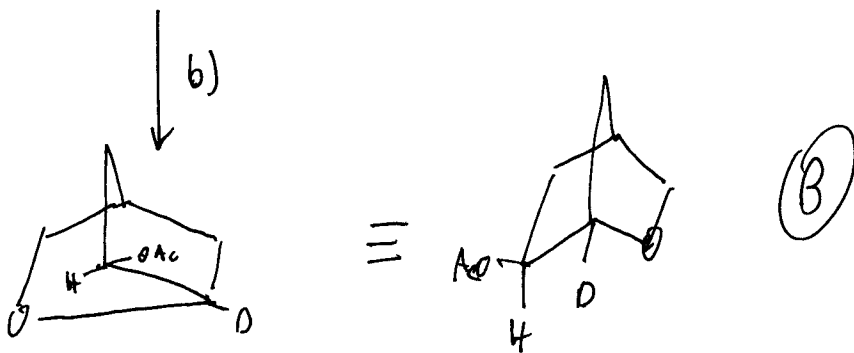
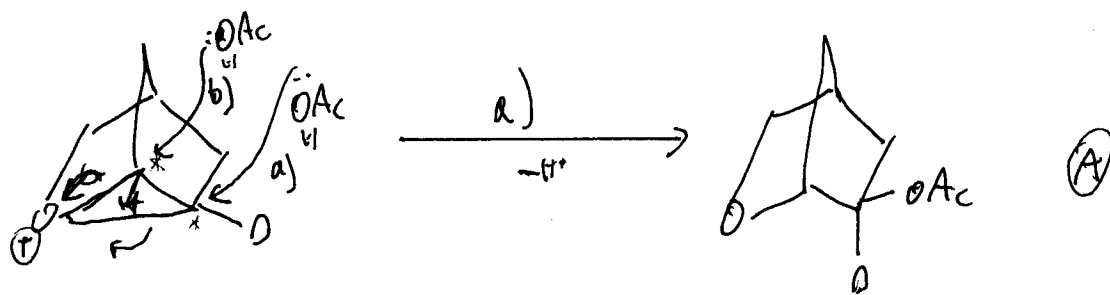
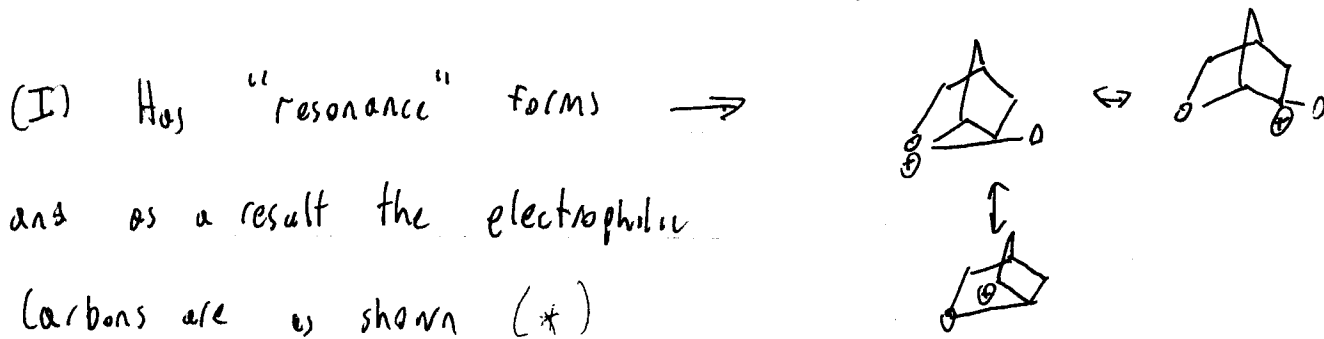
In the lower case no such NGP is possible because ~~of~~ the orientation of the  $\sigma^*_{C-O}$  (anti bond) as shown below (figure 2)

Figure 2



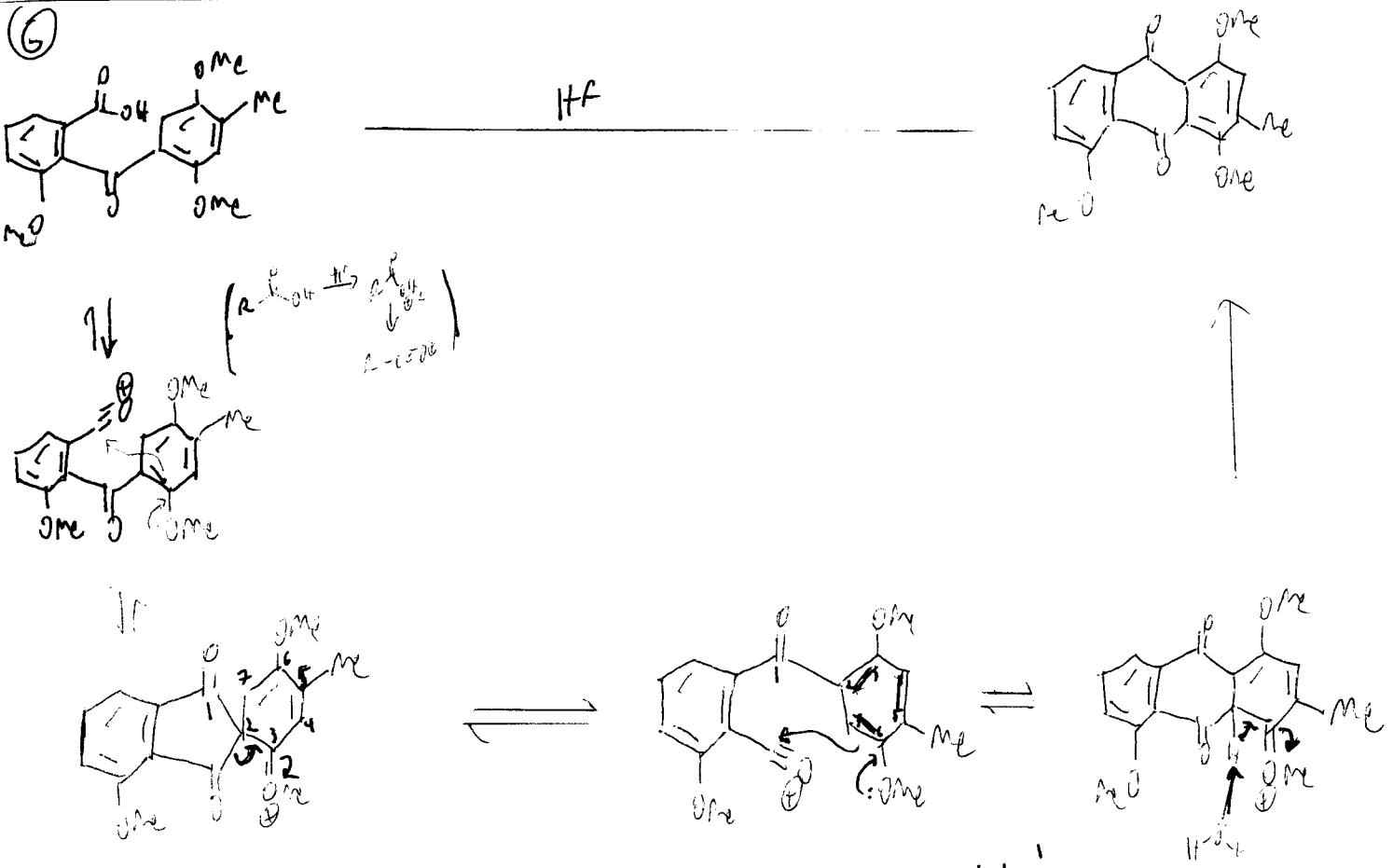
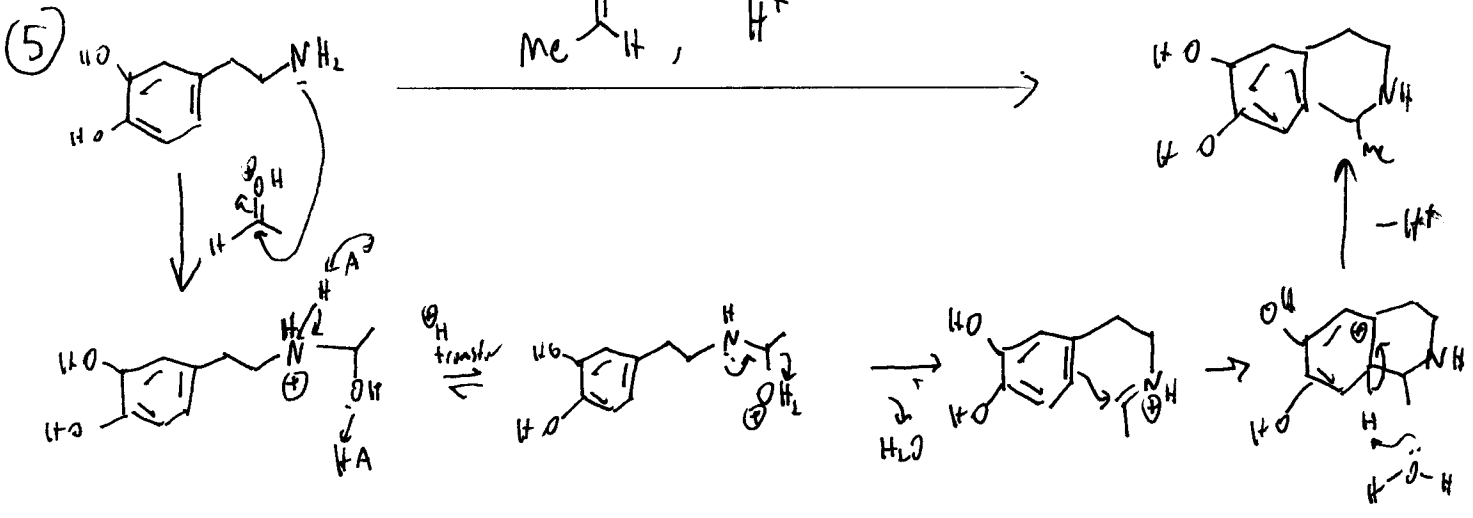


Both reactions proceed through  (I) as illustrated in 4a)



P<sub>5</sub>ET #d (cont)

pg 6



Important things to note:

