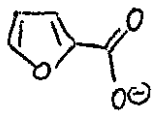
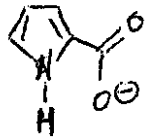
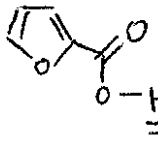
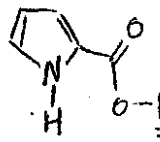
PROBLEM SET #11 SOLUTIONS CHEM 3231

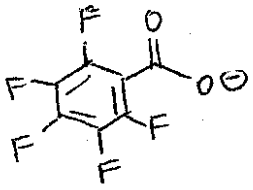
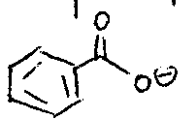
1. For all of these, compare the conjugate bases in each pair. Remember that a stronger acid will necessarily have the more stable (i.e., less reactive) conjugate base.

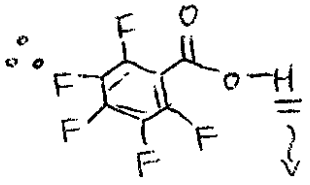
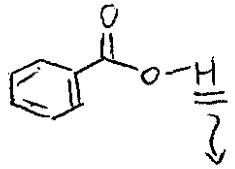
(a)  vs. 

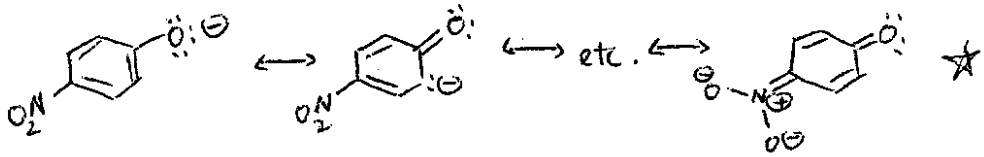
better stabilized by more electronegative oxygen

nitrogen is less electronegative — stabilizes carboxylate to a lesser extent

∴  $pK_a = 3.2$ more acidic than  $pK_a = 4.4$

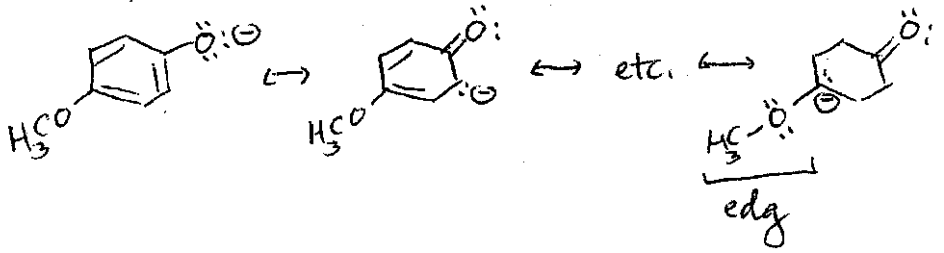
(b)  The pentafluorobenzoate is more stable than  due to electron-withdrawing F's.

∴  $pK_a = 3.4$ more acidic than  $pK_a = 4.2$

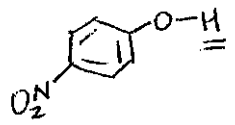
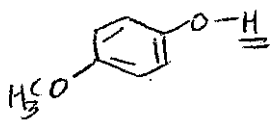
(c) 

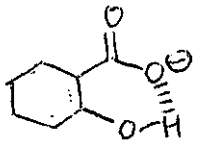
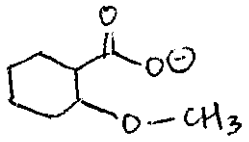
NO_2 is ewg; can stabilize ⊖ charge both inductively and by resonance

#1 (cont)



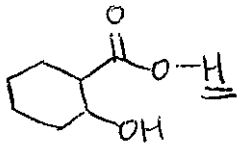
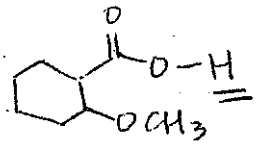
OCH_3 is edg; will destabilize ⊖ charge

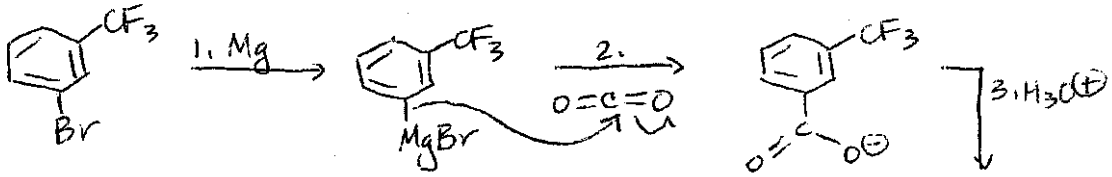
∴  more acidic than 

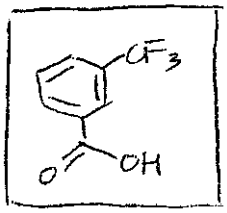
(d)  vs. 

carboxylate stabilized by a good intramolecular hydrogen bond

no hydrogen bond possible

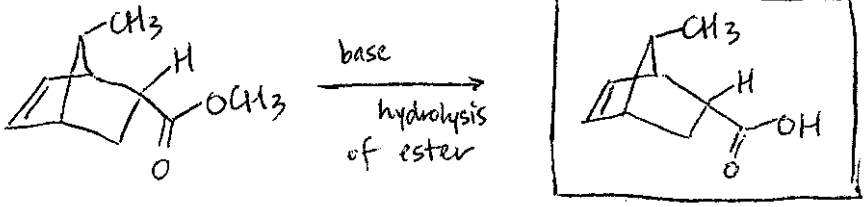
∴  more acidic than 

2. (a) 

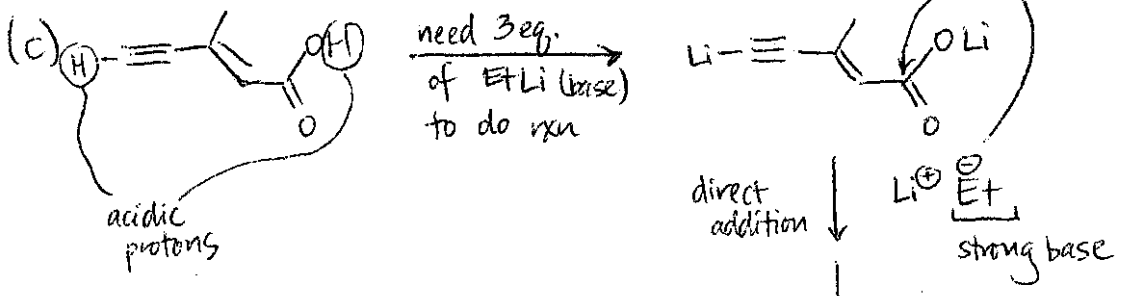


#2 (con't)

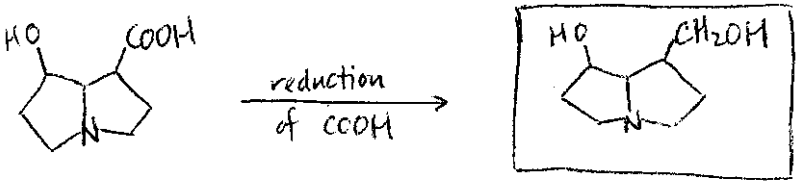
(b)



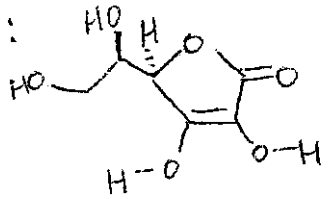
(c)



(d)



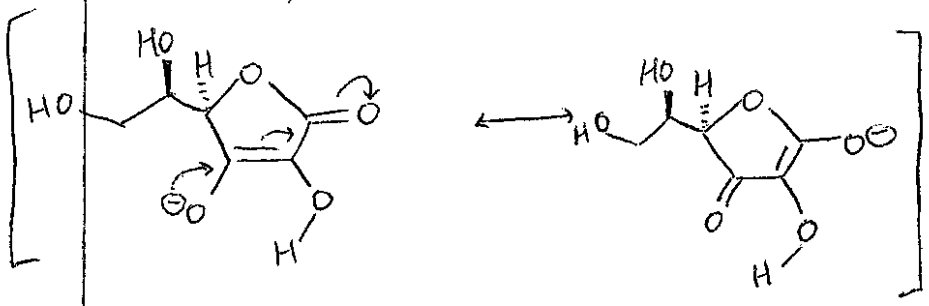
3. Vitamin C:



this is the most acidic H

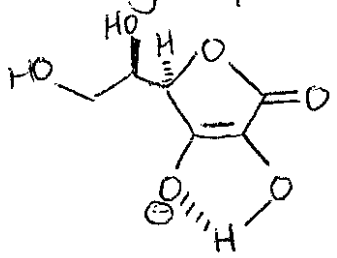
To see why, look at conjugate base — see over

#3 (con't)

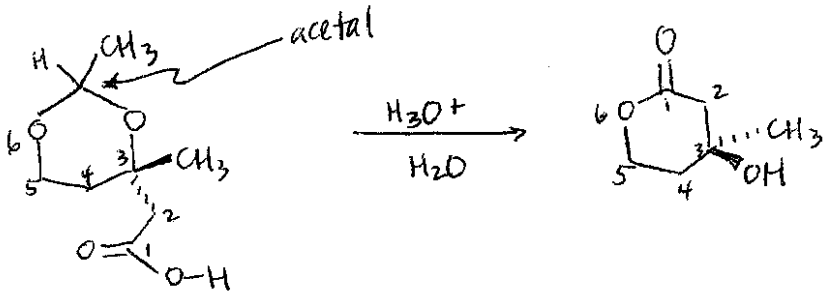


resonance delocalization of ⊖ charge

Also, H-bonding may stabilize conjugate base:



4.

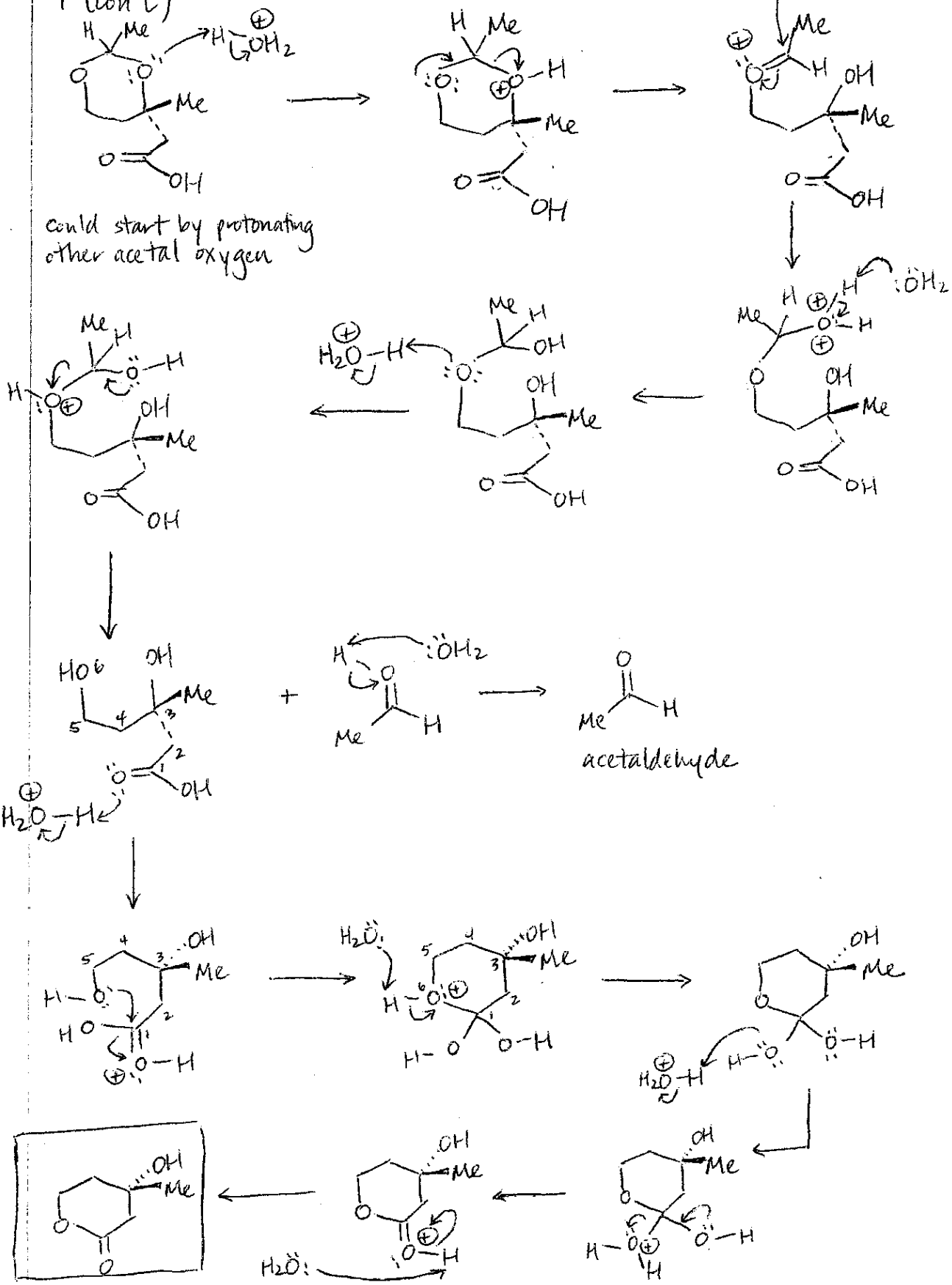


$C_8H_{14}O_4$ $C_6H_{10}O_3$

Note the presence of the acetal in the starting material. In acid, we will hydrolyze the acetal first (liberating acetaldehyde C_2H_4O), then we'll use Fischer esterification to close the lactone.

These are two <u>very</u> <u>important</u> mechanisms — be sure to practice this problem.

#4 (con't)


could start by protonating other acetal oxygen
acetaldehyde
!!

5. The two mechanisms can be distinguished by labeling the singly-bonded oxygen with ^{18}O, and then examining the subsequent saponification products.

If the carboxylate anion (or carboxylic acid, formed on protonation) contains the label, then mechanism (A) is the correct path.

If the carboxylate anion / carboxylic acid does NOT contain the label, then mechanism (B) is the correct mechanism.