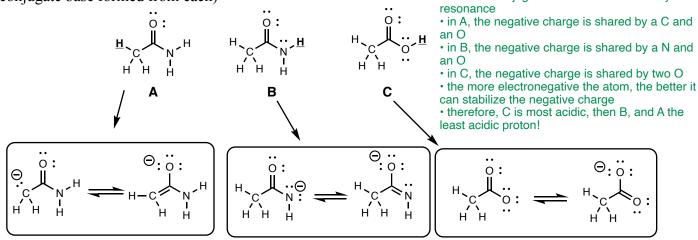
## Problem Set Chapter 3

Organic Chemistry for Life Sciences: CHM 223 Section A

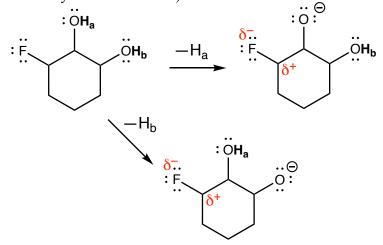
Name\_

## **DUE: Monday October 4**

1. Rank the bold hydrogen atoms according to their acidity (most acidic >> least): (HINT: draw the conjugate base formed from each) • all three conjugate bases are stabilized by



2. Which of the two protons is expected to be most acidic,  $H_a$  or  $H_b$ ? Explain (HINT: draw the conjugate bases formed by removal of each).

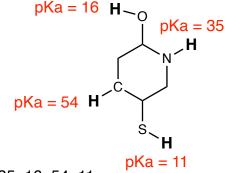


 removal of the indicated protons in both cases lead to placement of a negative charge on an O atom in the conjugate base, hence, the "Atom" is the same

• The C–F bond is polarized and places a  $\delta^{\scriptscriptstyle +}$  on the carbon in the ring

• The negative charge on the O of the conjugate base resulting from removal of  $H_a$  is closer to the  $\delta^+$  and therefore experiences greater stabilization than does the negative charge on the O of the conjugate base resulting from removal of  $H_b$ . • Therefore, the conjugate base resulting from removal of  $H_a$  is more stable, and  $H_a$  will be the more acidic proton.

3. pKa's for each of the bold hydrogen atoms below are provided. Assign them to the proper hydrogen atom in the molecule.



pKa values = 35, 16, 54, 11

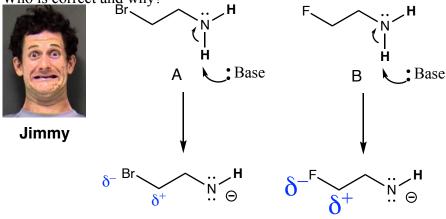
• there are 4 bond types to consider:

CH, NH, OH and SH • between CH, NH, and OH, the OH will be most acidic, followed by NH and CH. This follows the rule that when comparing Atoms in the same row, the hydrogen attached the more electronegative atom will be more acidic • SH is just below OH in the periodic table. SH will be more acidic than OH because the S is larger than the O and therefore better delocalizes (spreads out) the negative charge, making it more stable.

• therefore the order is SH > OH > NH > CH

• the most acidic = lowest pKa, the least acidic = highest pKa

4. Jimmy said that the NH protons on compound A will be more acidic than those on compound B because of the 'atom effect' that Breton "blabbered on about in class". Sally, however, disagreed and said that compound B will be more acidic due to the 'inductive effect' that Breton "eloquently presented in class". Who is correct and why?



• in both cases, removal of one of the NH protons puts a negative charge onto the SAME atom, a nitrogen atom, of the conjugate base. Hence the atom effect is not relevant, despite what Jimmy said!

• because the C-F bond is much more polar than the C-Br bond because of the greater difference in electronegativies, the carbon of the C-F bond has a much larger partial positive charge

• the partial positive charge stabilizes the negative charge of the conjugate base. This is the inductive effect.

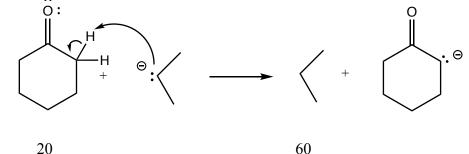
• since the partial positive charge on the conjutage base of compound B is larger, it is the most stabilizing

• Therefore, compound B is the more acidic compound

рКа

• Sorry Jimmy, but Sally is correct and the reason is the inductive effect.

5. The pKa's of relevant compounds are provided below. Fill in any missing lone pairs and draw the curved arrows that describe this acid-base reaction. Does the reaction proceed to the right or to the left as drawn? Explain.



• acid-base reactions always proceed in the direction that lead to the weaker acid

• the acid on the right side of the equation has a much higher pKa than the acid on the left side of the equation, thus it is much less acidic

• the reaction, therefore, will proceed towards the right as drawn