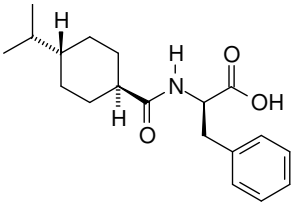
I have fallen *waaay* behind in the production of study guides. We may never see another one this semester, but I have been looking through the Study Guide that comes with your Solutions Manual and it is simply excellent. I was overjoyed when I caught sight of Fig. SG5.1 (p. 73). I have always talked about flash cards in *my* study guides, but your author has saved me. I also appreciated the encouraging words under **Review Frequently** (p. 72-74). Notice that it contains advice for *instructors*, as well as students.

#1. (from 50 minute exam #2, Fall 2000)

Nateglinide is an amino acid derivative that was marketed in Japan in 1998 as a treatment for type-2 diabetes mellitus (the compound stimulates insulin secretion from beta-cells in the pancreas).



Nateglinide

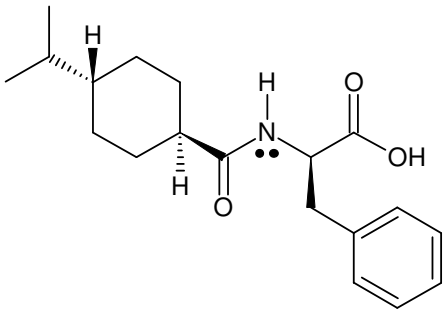
a. *(6 pts)* What is the molecular formula of nateglinide?

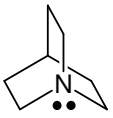
b. *(4 pts)* Draw the form of nateglinide present in the blood stream.

c. *(6 pts)* Label the configuration of each chirality center. How many stereoisomers of nateglinide are possible?

d. *(6 pts)* Nateglinide is marketed as a *racemic mixture*. Draw the compounds in this mixture

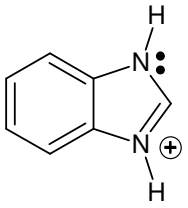
#2. Nitrogen can sometimes act as an asymmetric atom, but only if it is "tetrahedral" (and not always then, see Section 6.10B). "Planar" nitrogen is never asymmetric. Which N in the following molecules are planar and why? (Don't explain with words. Just draw two good resonance structures for each planar N showing what happens to the lone pair.)





$C_7H_{13}N$

(a model might help)



#3. Loudon problems from chapter 6: 30G, 32, 38, 40, 44, 47B

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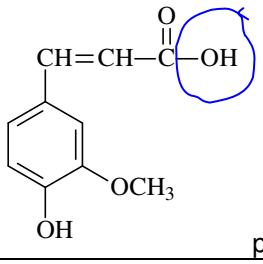
ANSWERS

#1. (last page from 50 minute exam #1, Fall 2000)[1,2]

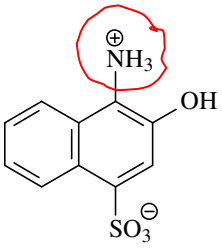
(14 points) Circle the most acidic hydrogen in each acid and estimate its pK_a. Be as precise as you can be. Full credit will only be given for acids that are placed within ±2 pK_a units of the correct (or most reasonable) value.

a. Ferulic acid (found in cell walls and also used as a food preservative)



pK_a = 5

b. A starting point for the manufacture of several chemical dyes



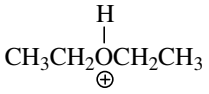
pK_a = 5

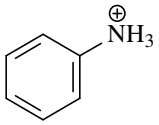
(20 points) Identify the most and least acidic molecules in each group.

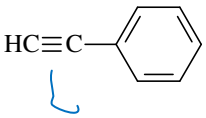
a. $CH_3CH_2NH_3^+$ M $CH_3CH_2NH_2$ L CH_3CH_2OH

b. $FCH_2CH_2CO_2H$ L CH_3CHFCO_2H $CH_3CF_2CO_2H$ M

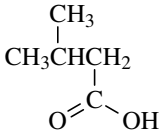
c.



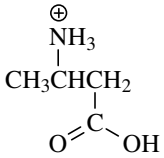




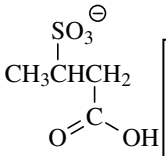
d.



L



M



I accepted L for this one b/c of "-"charge on 503 group. If student re-drew formula w/ S +2, I accepted M.

#2. (second page from 50 minute exam #1, Fall 2005)

www.pherobase.net contains an information database on pheromones (chemicals that act as signals between organisms). The database lists these compounds as pheromones for the speckled cockroach:

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[1] Try to work these problems at least once as exam problems, i.e., without referring to your book or notes, but feel free to consult your book and notes before deciding on a final answer (books and notes won't be available during the exam).

[2] The exam's value was 100 points and lasted 50 minutes. Since the total value assigned to problem #1 was 34 points, my expectation is that you can solve all of these pieces and draw all your answers in one-third of the exam time, 17 minutes.

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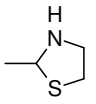
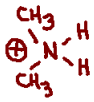
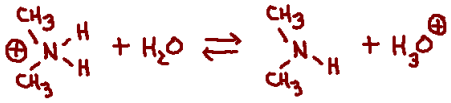
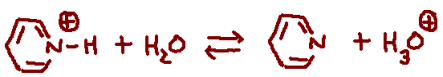


2-methylthiazolidine

4,5-dihydro-2-methylthiazole

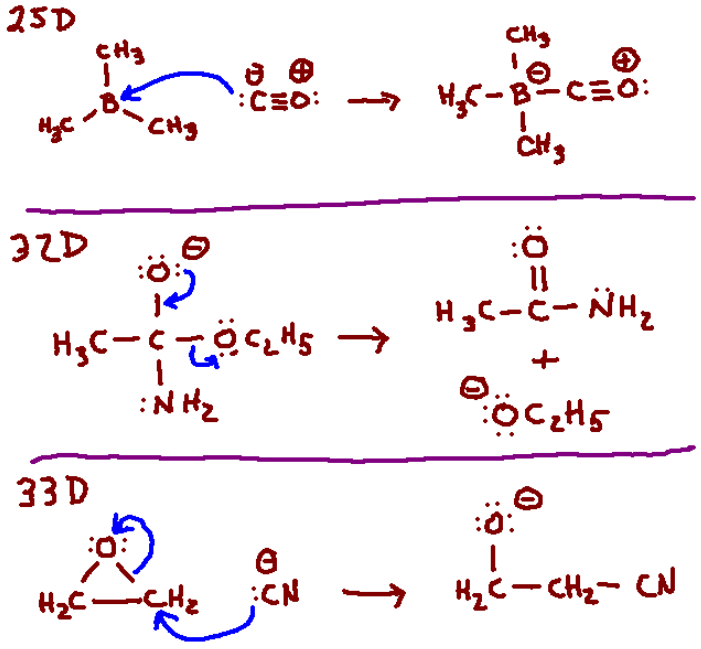
(*16 points*) Predict the pK_a of each pheromone's conjugate acid. Your answer must be based on a close structural analogy, i.e, I want you to identify the acidic functional group in each compound (call this group a "model" acid) and use the model to estimate the compound's pK_a. Also, draw the chemical equilibrium used to define the model acid's pK_a.

Compound	predicted pK_a	chemical equilibrium used to define pK_a of model acid
thiazolidine		
thiazole		

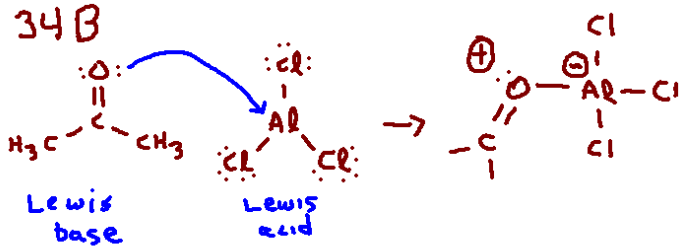
(*6 points*) Over what pH ranges would you expect the thiazolidine to carry a positive charge? A negative charge?

+1 charge < 10 -1 charge > 35

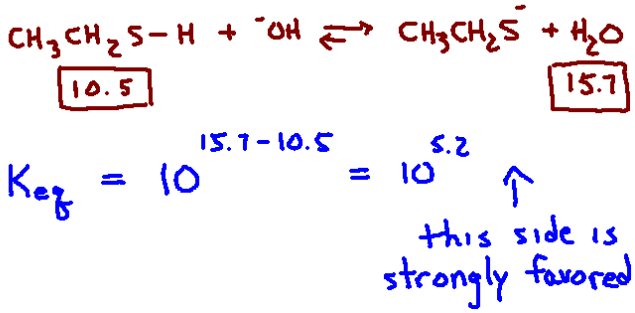
#3. Loudon problems from chapter 3: 25D, 32D, 33D, 34B, 38B, 40B, 45



34 B



40B



45

Let **HA** be an acid that is *destabilized* by some structural effect. Assume too that $\mathbf{A^-}$, its conjugate base is *not* destabilized. Let $\mathbf{HA_{no}}$ be another acid that is identical to **HA** in all respects, except that it (and its conjugate base) are not destabilized by this effect. We can investigate an acid-base equilibrium between **HA** and $\mathbf{HA_{no}}$ easily by constructing an energy diagram in two steps:

1. Assume a purely hypothetical situation in which **HA** no longer experiences any structural effects. In this case, $K_{eq} = 1$ for its acid-base reaction with $\mathbf{HA_{no}}$. $\Delta G^o = 0$. This is shown as "hypothetical" in the reaction energy diagram below.
2. Introduce the actual *destabilization* of **HA** into the energy diagram. This reveals that the favored (lower free energy) side of the equation is the *right-hand* side, $\mathbf{A^- + HA_{no}}$. Since the weaker acid is always favored, we must conclude that **HA** is a stronger acid than $\mathbf{HA_{no}}$, i.e., the structural effect makes **HA** more acidic.

First, the equilibrium

Second, the reaction energy diagram