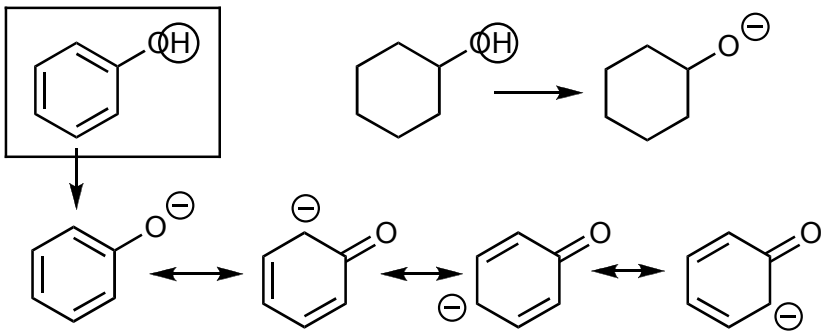
Exam 2 SOLUTION

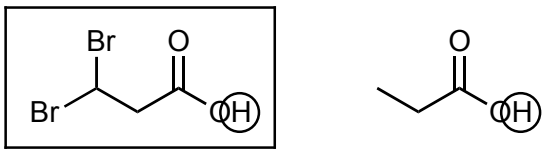
1. For each molecule below, ***circle* the most acidic hydrogen** (draw it in if necessary). For each pair, **put a *box* around the more acidic molecule**. For each pair, explain your choice in 15 words or less. [18]

***The most acidic hydrogen is the one that is attached to the most electronegative atom!!

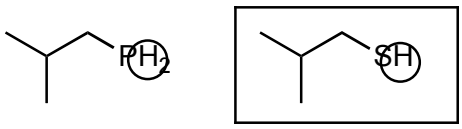
Explanation



The anion/conjugate base of the first molecule can be delocalized through resonance.

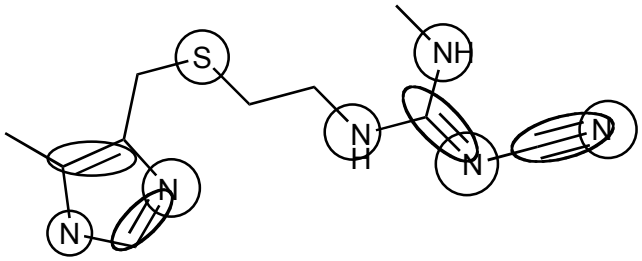


Both molecules exhibit resonance in the conjugate base. The bromides on the first molecule also withdraw electron density through induction.



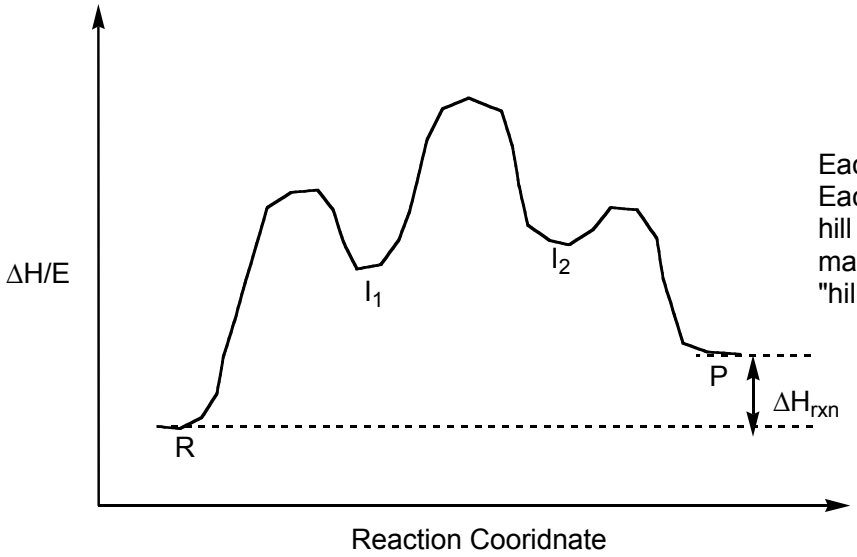
Sulfur is more electronegative than phosphorus, so the anionic conjugate for sulfur is more stable. Since sulfur and phosphorus are in the same row, and adjacent to each other on the periodic table, they are about the same size.

2. Circle or label all sites on the molecule below (cimetidine, or Tagamet®) that can behave at a Lewis base in a reaction. [8]



Any pi bond or pair of electrons can behave as a Lewis base.

3. Answer the questions regarding the reaction energy diagram below. [10]



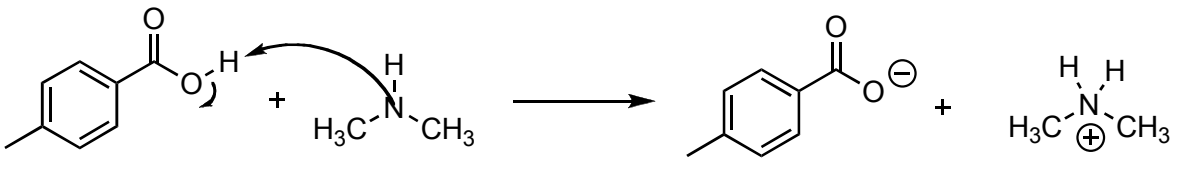
Each local minimum is an intermediate. Each "hill" is a step, and the top of each hill is a transition state, where bond making and breaking occur. The highest "hill" represents the rate-determining step.

a. Label the axes.
b. Label the reactants, intermediates and products.
c. Label ΔH_{rxn}
d. How many steps are in the mechanism of this reaction?
e. Which step is the rate-determining step?
f. Is this reaction endothermic or exothermic?

3 steps
Step 2
Products are higher E than the reactants → Endothermic!

4. Determine the products for the following reaction. Label each species as either Acid (A), Base (B), Conjugate Acid (CA) or Conjugate Base (CB). Draw the "mechanism" for the reaction using curved arrows. Determine K_{eq}, using estimated values from the pK_a table attached. [16]

a.



Acid Base Conjugate Base Conjugate Acid

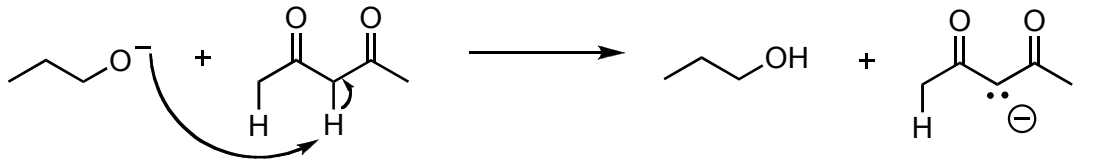
pK_a = 4 9

pK_{eq} = 4-9 = -5

K_{eq} = 10^{+5}

**From your last homework, the middle proton is the most acidic proton on the molecule, so that is the one that should come off!

b.



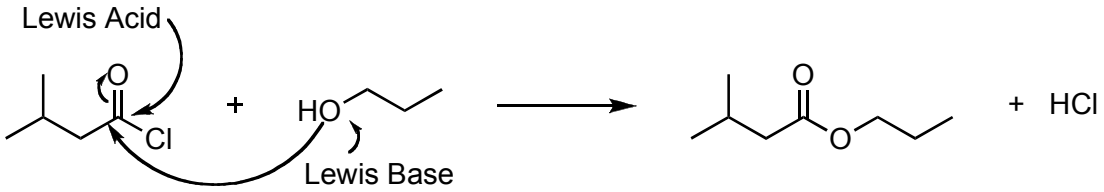
Base Acid Conjugate Acid Conjugate Base

pK_a = 10 16

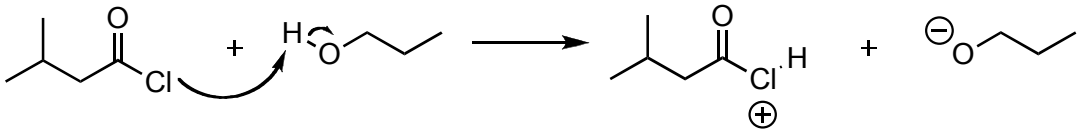
pK_{eq} = 10-16 = -6

K_{eq} = 10^{+6}

5. Analyze the reaction below. For the reaction, indicate which atom is behaving as the Lewis base and which atom is behaving as the Lewis Acid. Explain your choice for the acid – what makes it a good Lewis acid? [6]



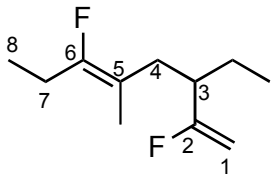
A new bond forms between the carbonyl carbon and the alcohol oxygen, so that is one choice for a Lewis Acid/Base pair. Also, a new bond forms between H and Cl, so that can be another choice. If we consider the second possibility, a positive charge forms on the chlorine, which is *highly* unlikely! This is not the pair we should consider.



On the other hand, the carbonyl carbon is a great Lewis acid in this reaction, as it has a large partial-positive charge, caused by the induction of electron density from both the chlorine and the oxygen.

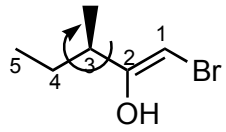
6. Nomenclature. [10]

a. Provide complete IUPAC names for the following molecules.



Z-3-ethyl-2,6-difluoro-5-methyl-1,5-octadiene

*Alphabetize based on the "f" in fluoro.
*Only one alkene has stereochemistry, so no number is used!

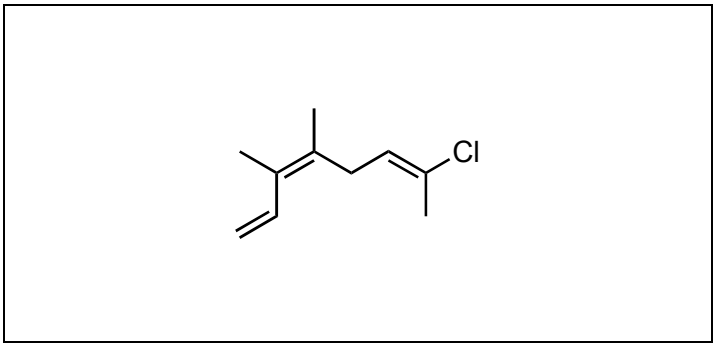


(1Z, 3R)-1-bromo-3-methylpenten-2-ol

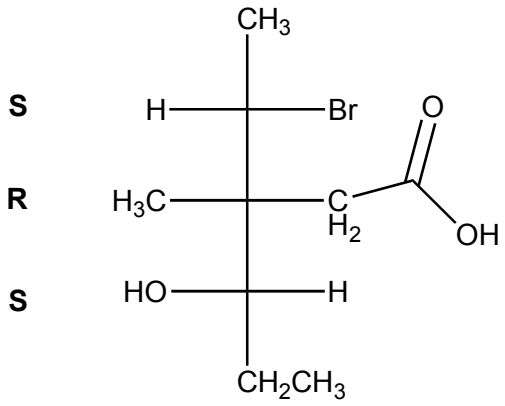
*Remember to start numbering at the *carbon*.
*The position of the alcohol *must* go in front of the -ol, if it goes in front of the pentene part the number then refers to the ene.

b. Provide the structure for the following molecule from its IUPAC name.

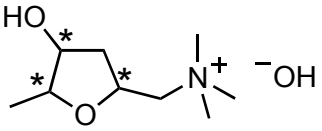
(*3Z, 6E)*-7-chloro-3,4-dimethyl-1,3,6-octatriene



7. Assign absolute configuration to every stereocenter in the following molecule. [6]



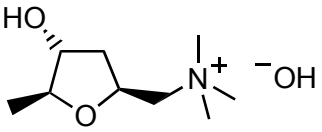
7. The following structure corresponds to muscarine, a poisonous compound found in some mushrooms. [6]



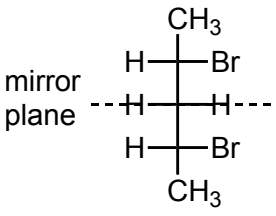
a. Label all stereocenters with a * star. How many possible isomers can form?

2^3 isomers = 8 isomers

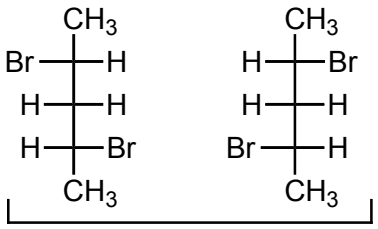
b. The actual compound has the absolute configuration of *2S, 3R, 5S.* Redraw the molecule, and using wedge-dash notation, provide the structure that corresponds to muscarine.



8. Use Fisher projections to draw all *unique* molecules of 2,4-dibromopentane. Label all stereochemical relationships between the molecules. [8]



#1 meso



#2 and #3, enantiomers

#1 and #2, and #1 and #3 are diastereomers.

9. Which molecule below can behave as a Lewis acid but *not* as a Brønsted-Lowry acid? [4]

a. CH_3COOH

b. H_2O

c. AlH_3 Hydrogen is more electronegative than Al, so it is an H^-, not an H^+!

d. CH_3OH

10. Which of the following is the weakest acid? [4]

Be sure to consider which atom the proton comes off of for this one! Always consider the conj. base!

a. CH_3SH **(remove the S-H proton)**

b. CH_3OH **(remove the O-H proton)**

c. CH_3NH_2 **(remove an N-H range)**

d. CH_3F ***There are only C-H protons! This is the weakest base!***

11. The index of hydrogen deficiency for $C_{22}H_{23}N_2O_2Cl$, loratadine, the active ingredient in Claritin®, is: [4]

a. 11

b. 12

c. 13

d. 14

$H_{max} = 2 \bullet 22 + 2 = 46$

$H_{molec} = 23 + 1(Cl) - 2\ (N) = 22$

$H_{def} = (46-22)/2 = 12$