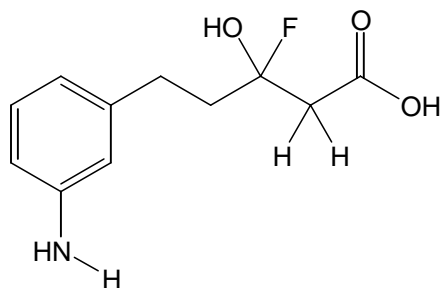
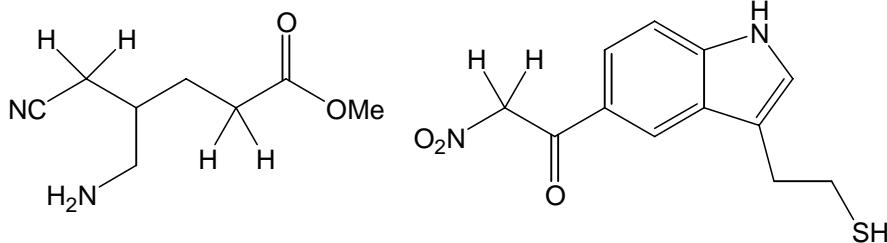
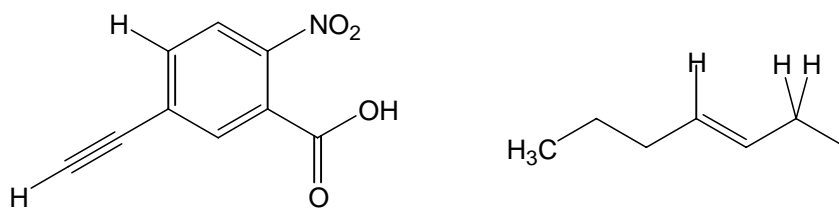
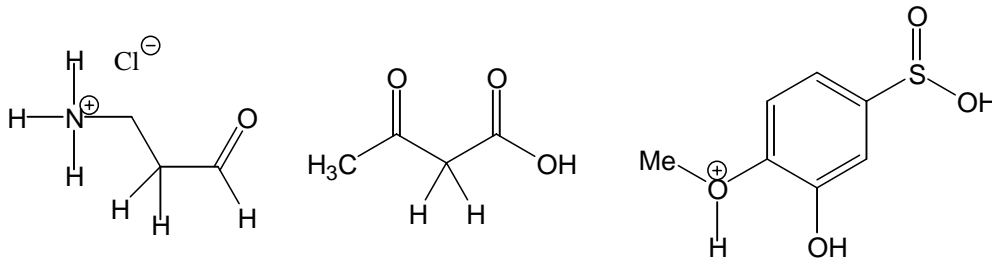


Fall Workshop #7

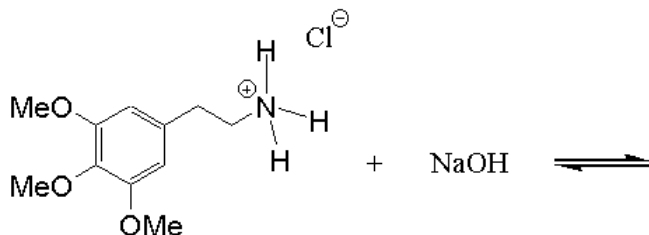
Problem #1

Using the tables on pages 18-22 of "SAM" and the table **inside the back cover** of Jones, report an estimated pKa value for each hydrogen atom shown in each structure. Circle the most acidic hydrogen on each molecule. Find examples of the **formal charge**, **electronegativity**, **inductive**, and **resonance** effects in the various structures below.



Problem #2

Often times, amines are converted to their acid salts in order that they can be stored for long periods of time without degrading. One such example is shown below in which mescaline exists as a hydrochloride salt. Consider the reaction shown below between the protonated form of mescaline and NaOH.



Using the pair problem solving method (as explained by your workshop leader), answer the following directives. Note: each directive has been labeled with an A or B to indicate the task of each person in the pair.

A: Show all hydrogen atoms in protonated mescaline and report the pK_a values (from the tables in “SAM”). Circle the most acidic hydrogen and explain your choice.

B: Realizing that NaOH dissociates into ions, draw the Lewis structure for hydroxide anion.

A: The hydroxide anion exists as a major reactive species in solution and functions as the Bronsted-Lowry base in the forward direction. Use the curved-arrow formalism to show the flow of electrons as the reaction proceeds from reactants to products (forward direction)

A: Draw the structures for the expected products of this reaction based upon the mechanism you derived.

B: Which species is your nucleophile (Lewis base) and which is your electrophile (Lewis acid) in the forward direction? Which species will donate electrons via its HOMO and which will use its LUMO to accept the electron pair? Briefly explain your choices.

A: Report the appropriate pK_a value to use for the “other acid” (on the product side of the of your equilibrium reaction.

B: Designate each of the species in your reaction as a strong acid (SA), strong base (SB), weak acid (WA), or weak base (WB). Explain your rationale.

B: Show the conjugate acid-base pairs.

A: Calculate the overall pK_a (from the individual pK_a's) and convert to the K_a.

$$\text{pK}_a(\text{overall}) = \text{pK}_a(\text{forward rxn}) - \text{pK}_a(\text{reverse rxn})$$

B: Use the K_a from the previous answer to find $\Delta G^\circ_{\text{rxn}}$ at room temperature (23 °C).

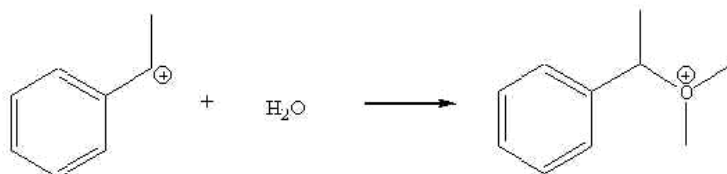
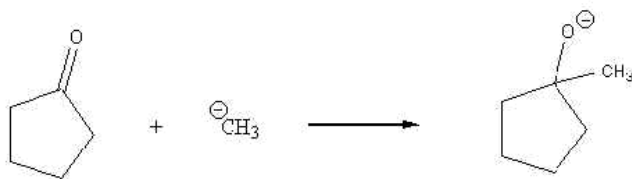
B: Which species (products or reactants) are favored at equilibrium? Explain.

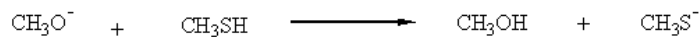
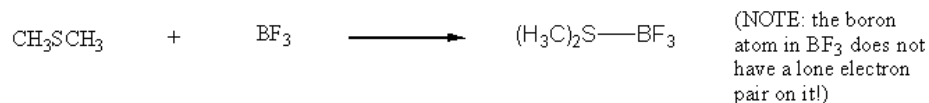
Writing Reaction Mechanisms. A reaction mechanism is a detailed description of the way a reaction occurs and is based on the known experimental data (usually kinetic and spectroscopic data) about the reaction. Some reaction mechanisms are well established, while others may be speculative and are likely to change as more data becomes available. When composing a mechanism, we use the curved-arrow formalism to demonstrate the process by which reactants are converted into products by showing the movement of electrons as bonds are broken and formed. You should recall that the full-headed arrow represents the movement of 2 electrons while the half arrow (fishhook) shows the movement of 1 electron. Therefore, we can use these arrow formalisms to show both heterolytic and homolytic bond breakage. In some cases, the reaction occurs in a concerted fashion without the formation of intermediates. In other cases, distinct reaction intermediates (carbocations, for example) are formed during the course of reaction

Problem #3

For each of the following reactions:

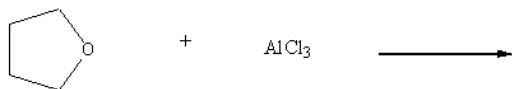
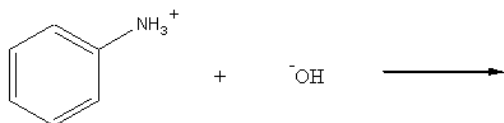
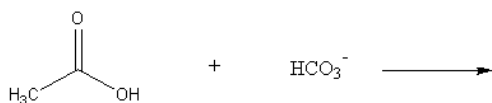
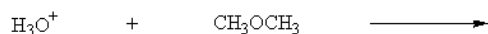
- Draw each structure as a **complete Lewis structure** showing all bonding and non-bonding electron pairs before you proceed.
- Verify formal charges by using the formal charge calculation.
- Identify the Lewis acid and Lewis base in each reaction. (In other words, identify the electrophile and the nucleophile, respectively.)
- Use curved arrows to show the flow of electrons as the reaction proceeds from the left to the right. *Be sure to initiate at the electron rich (Lewis Base/nucleophile) site.*





Problem #4

Predict the products for each of the following reactions based upon the ideas developed in the previous question. I would recommend **drawing out Lewis structures first!** Discuss your answers. Perform formal charge calculations on your product structures to verify that the charges balance on both sides of the reaction.



Problem #5

For the following pair of reactions, predict which one will occur at the faster rate. Develop a reasonable explanation (and be prepared to back it up) to explain your choices. You should begin by (a) completing Lewis structures, (b) determining the direction of any polar covalent bonds, (c) identifying the "electrophile" and nucleophile", and (d) drawing in the expected curved-arrow formalism to show which bonds are broken and which bonds are made. You should also consider the *basicity* (stability) of the anion released on the product side of the reaction. Can you envision a **general theme** occurring throughout these examples?

