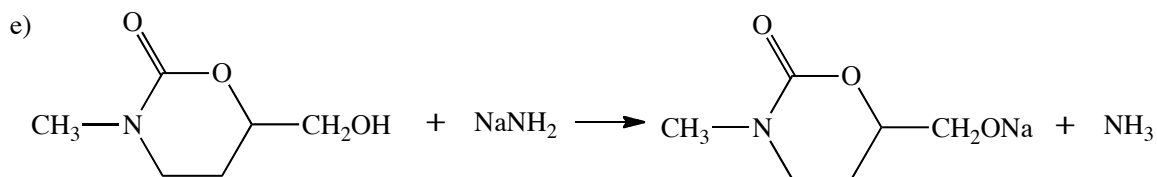
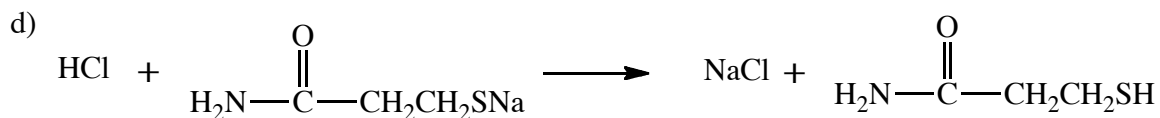
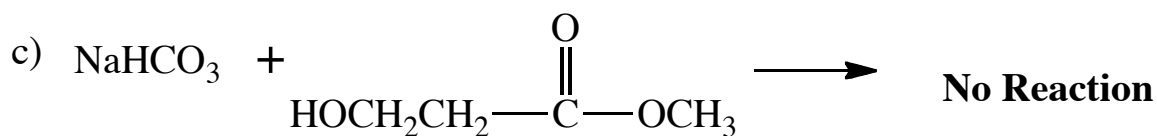
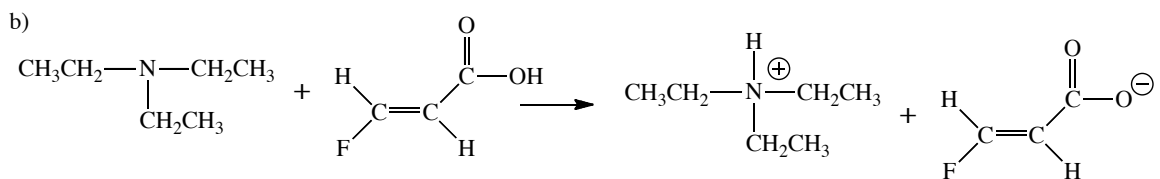
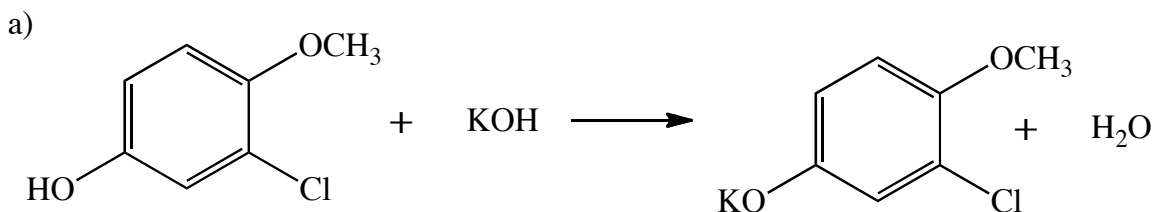


Chemistry 250A -- Exam #1 Answer Key -- September 22, 2009

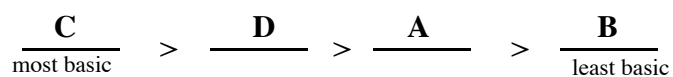
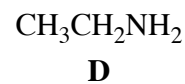
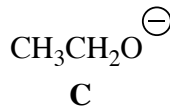
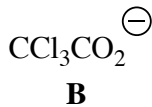
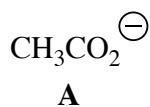
(There are 5 pages.)

1. (15 pts) Show the major product(s) from the following acid-base reactions. If there is no reaction then say "No Reaction". Assume the two reactants are present in equimolar amounts.

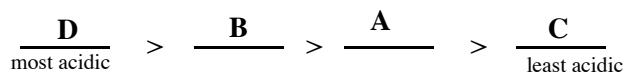
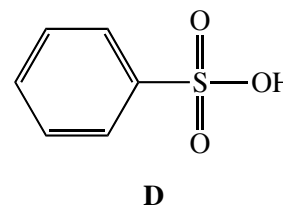
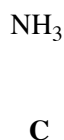
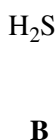
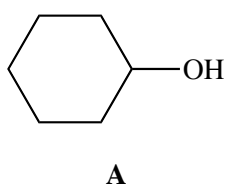


3. (20 pts) Order the following compounds according to the indicated property.

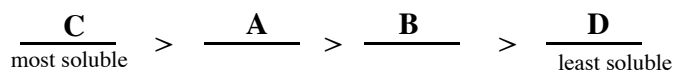
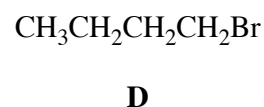
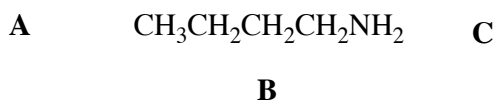
a) basicity



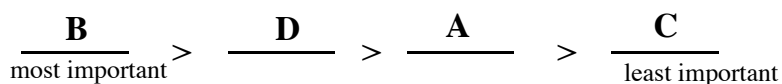
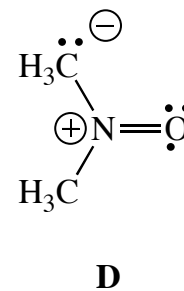
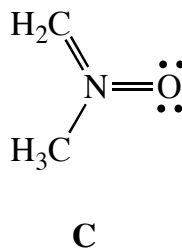
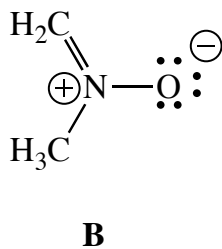
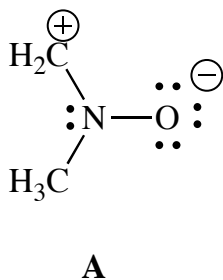
b) acidity



c) solubility in water

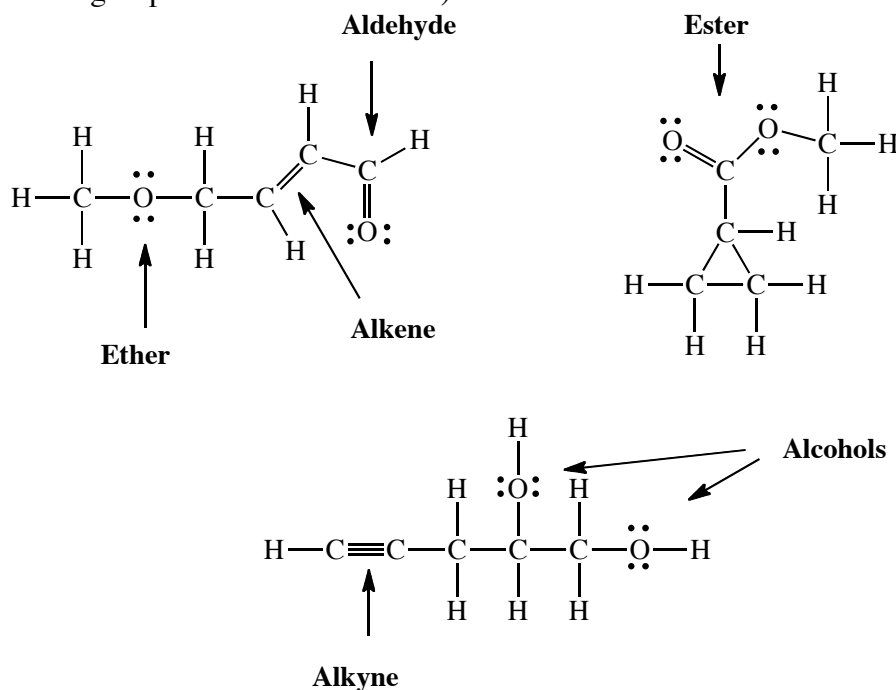


d) relative importance of resonance structures



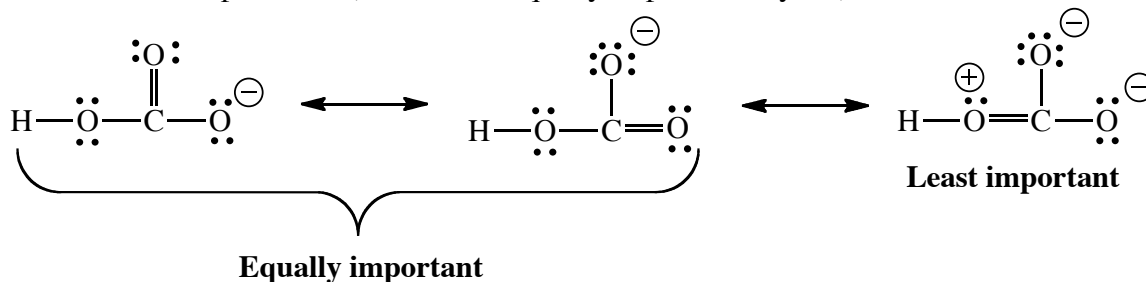
4. (23 pts) For the problems below **draw complete Lewis structures** (showing all atoms, lone pairs, and non-zero formal charges).

a) Draw three stable isomers with the formula $C_5H_8O_2$. One of these isomers must contain an **aldehyde** and an **ether**. Another isomer must contain an **ester**, but **NOT an alkene**. The final isomer may **NOT contain an aldehyde, ether, or ester**. Identify all the functional groups in these molecules. (Note that the molecules you draw may contain other functional groups besides those listed.)

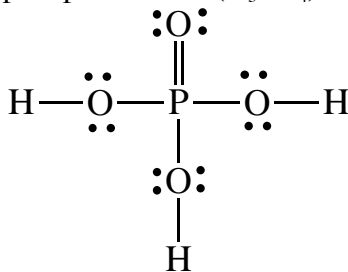


These are other correct answers. These are just examples.

b) Draw the three most important resonance forms for sodium bicarbonate ($NaHCO_3$). Rank them in importance. (If some are equally important, say so.)

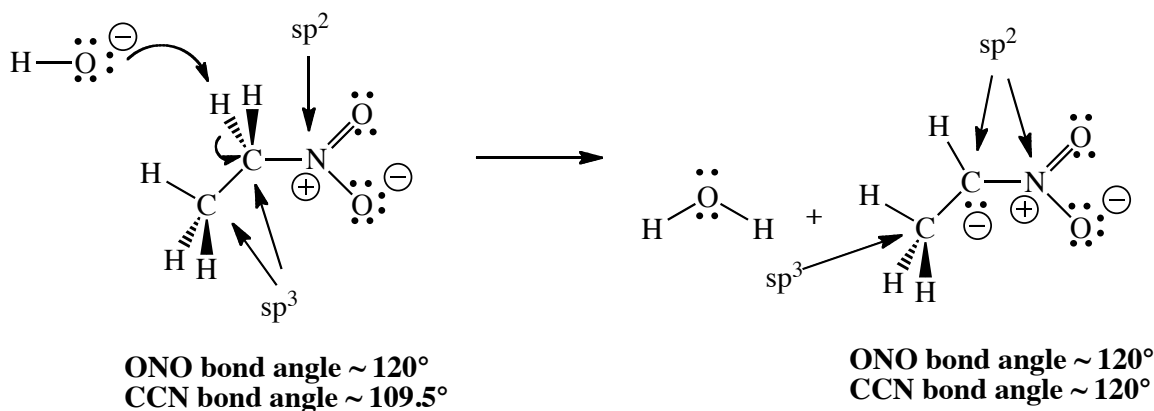


c) Draw the Lewis structure of phosphoric acid (H_3PO_4).

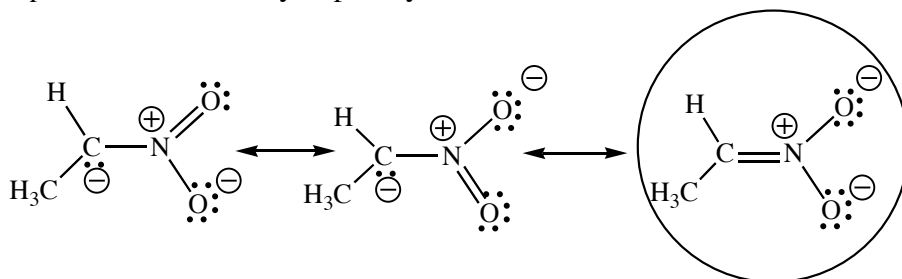


5. (25 pts) The condensed structural formula for nitroethane is $\text{CH}_3\text{CH}_2\text{NO}_2$. (Note: Both oxygen atoms are bonded to the nitrogen, they are not bonded to each other.)

a) Nitroethane has a pK_a of 8.5. Write the reaction that occurs when nitroethane and NaOH are mixed together. Draw full Lewis structures (showing all lone pairs and non-zero formal charges) for all the reactants and products. Also indicate the mechanism by drawing curved arrows.



b) Draw all the important resonance forms for the conjugate base of nitroethane. Circle the most important one. Briefly explain your choice.



Oxygen is more electronegative than carbon. Consequently, it is more favorable to have a negative charge on an oxygen, rather than on a carbon.

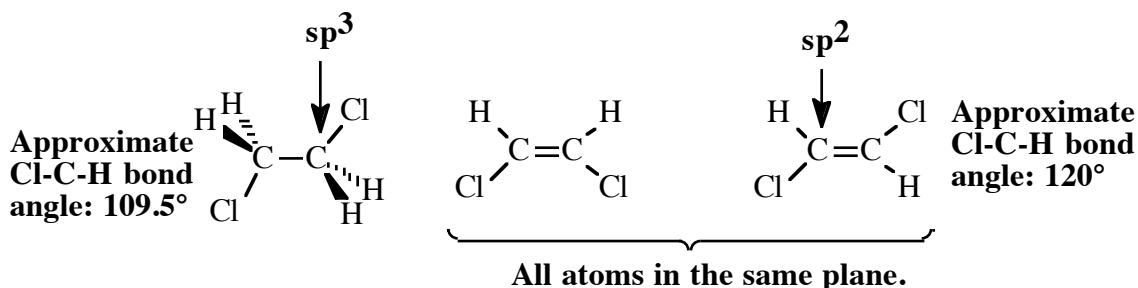
c) Indicate the hybridization on both carbons and the nitrogen in both nitroethane and its conjugate base. Also estimate the ONO and CCN bond angles in both nitroethane and its conjugate base.

d) In a 1982 paper in the *Journal of Biological Chemistry* 1-chloronitroethane ($\text{CH}_3\text{CHClNO}_2$) was reported to be a suicide inactivator of D-amino acid oxidase. Would you expect the pK_a of 1-chloronitroethane to be higher or lower than that of nitroethane. Briefly explain.

The pK_a for 1-chloronitroethane should be lower than that of nitroethane. (Actual pK_a is approximately 7.) Since the chlorine atom is more electronegative than hydrogen it will stabilize the adjacent negative charge on the conjugate base (by pulling electron density away from the site, minimizing the charge). Stabilizing the conjugate base form means that the acid is more acidic, i.e., lower pK_a .

6. (17 pts) Aldrich Chemical Company sells two isomers of 1,2-dichloroethylene ($\text{ClCH}=\text{CHCl}$), but only one isomer of 1,2-dichloroethane ($\text{ClCH}_2\text{CH}_2\text{Cl}$).

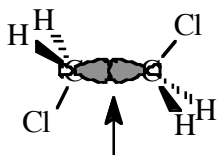
a) Draw accurate 3-dimensional representations of 1,2-dichloroethane and the two isomers of 1,2-dichloroethylene. On your drawings indicate the approximate Cl-C-H bond angle in each molecule and the hybridization on each carbon atom.



b) Explain why there are two isomers of 1,2-dichloroethylene, but only one isomer of 1,2-dichloroethane. As part of your explanation, draw the relevant atomic orbitals and clearly explain how bonding with these orbitals leads to the difference in the number of isomers.

The sigma bond (from overlap of two sp^3 orbitals pointing at each other) between the two carbons in 1,2-dichloroethane is (like all sigma bonds) symmetric about the bonding axis, which means that rotation around the carbon-carbon bond can occur without breaking the bond. At room temperature there is rapid rotation around the bond and it is not possible to isolate separate isomers that differ only by rotation about this bond.

In contrast the pi bond that makes up the second of the two bonds between the carbons in 1,2-dichloroethylene is dependent on the rotation angle. Efficient pi bonding can only occur when the p-orbitals on each carbon are lined up with each other (so they can overlap). Rotation about the carbon-carbon axis would require breaking the pi bond. There is not enough energy at room temperature for this to happen at any significant rate, and therefore it is possible to isolate two different isomers that differ only in the rotation about the double bond.



Two sp^3 hybrid orbitals pointing at each other overlap to form a sigma bond between the two carbons in 1,2-dichloroethane.



Two sp^2 hybrid orbitals pointing at each other overlap to form a sigma bond between the two carbons in 1,2-dichloroethylene.



The "leftover" p-orbitals must be aligned with each other for overlap to occur leading to a pi bond. Rotation about the C-C bond requires breaking the pi bond.

c) One of the isomers of 1,2-dichloroethylene has a boiling point of 48°C, the other has a boiling point of 60°C. Which isomer corresponds to each boiling point? Briefly explain the rationale for your answer.

The isomer with the two chlorines on the same side of the double bond will have a net dipole moment, whereas the other isomer has no net dipole. The dipole-dipole interaction in the isomer with both chlorines on the same side will lead to stronger intermolecular interactions and hence to a higher boiling point.