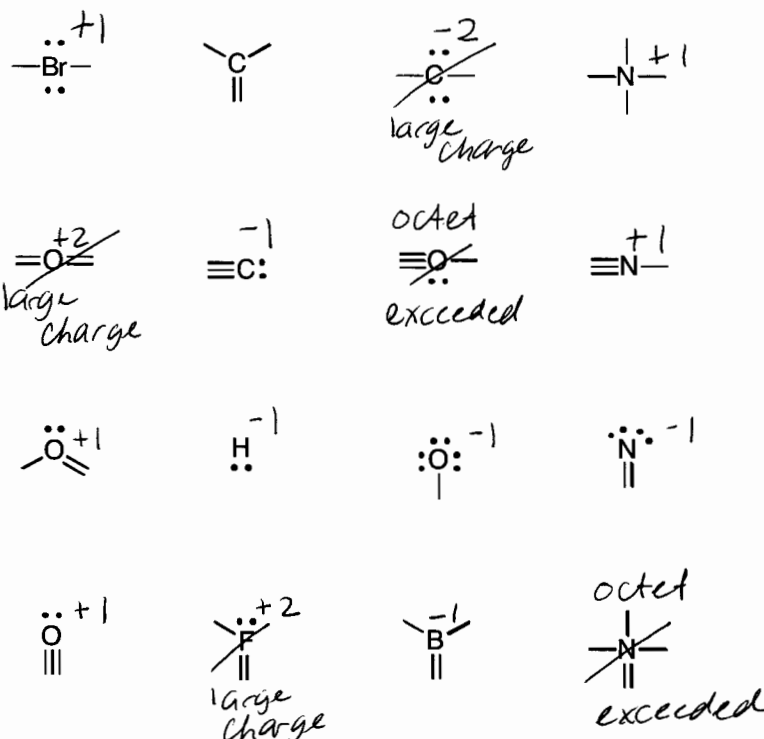


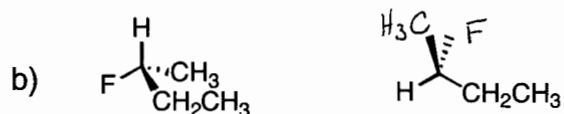
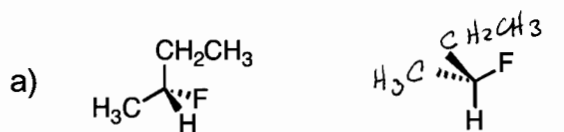
Problem Set #1

Due: February 10, 4:00 pm

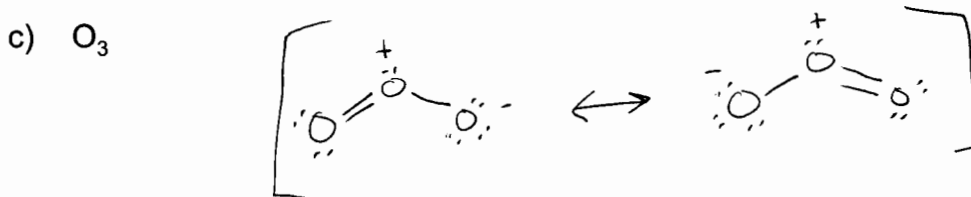
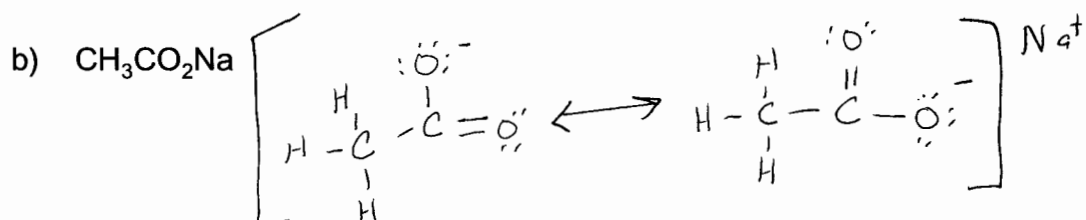
1. Assign formal charges to each atom below (a formal charge of zero is assumed if no charge is indicated). Cross out the configurations that are not reasonable, and provide an explanation (large charge - greater than +/- 1, incomplete octet, octet exceeded).



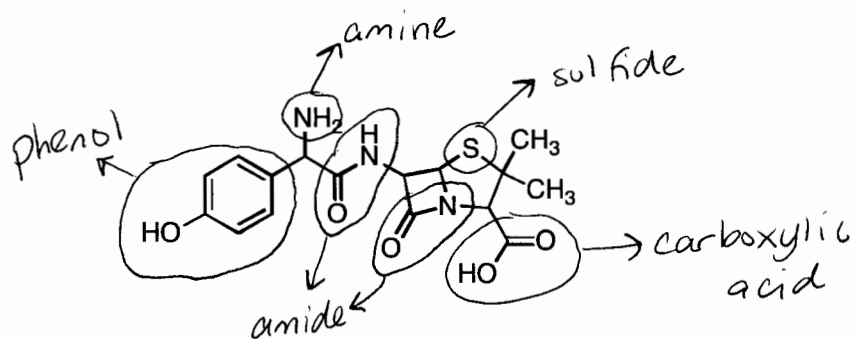
2. Reorient the molecule at the left to match the partially drawn perspective at the right. Complete the drawing at the right by adding the two missing substituents at their correct positions. Build a model if necessary.



3. Provide the Lewis structures for the following molecules, including all major resonance contributors (no more than 2 formal charges, no formal charge greater than +/- 1).

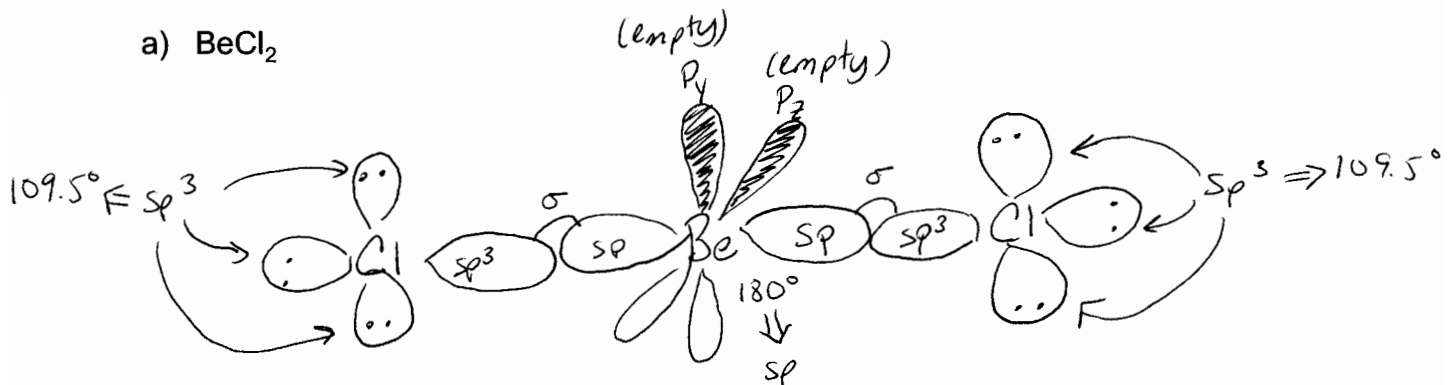


4. Label all of the functional groups in amoxicillin, an antibiotic from the penicillin family.

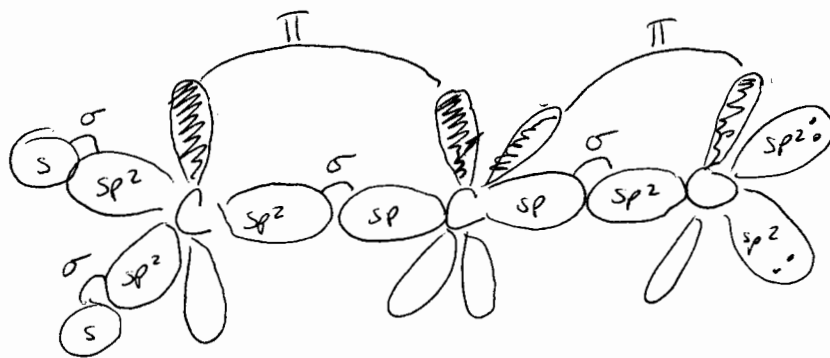


5. Provide orbital drawings of the following molecules. (Don't forget to shade the p orbitals appropriately!) Indicate the hybridization and bond angle at each non-hydrogen atom. Indicate the sigma and pi bonds and all lone pairs of electrons.

a) BeCl_2



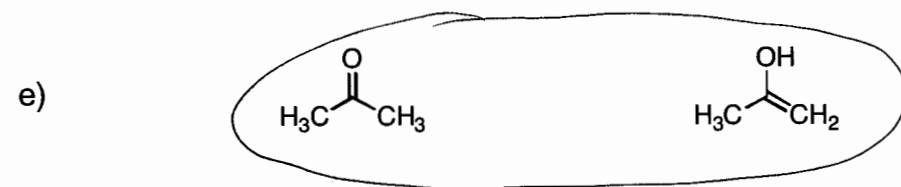
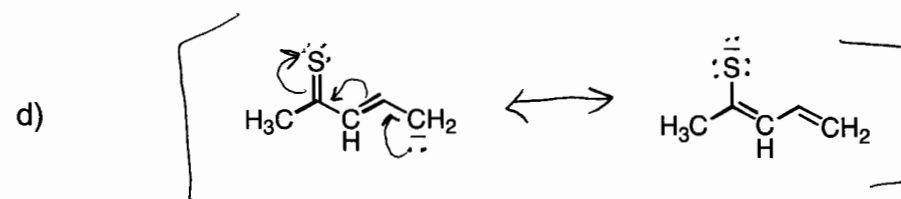
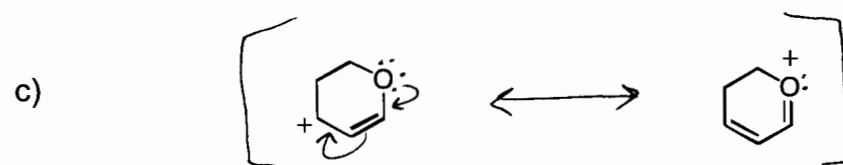
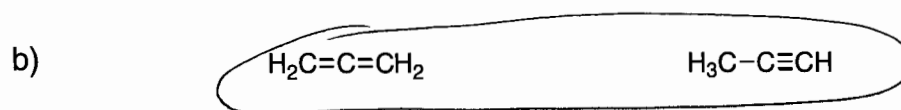
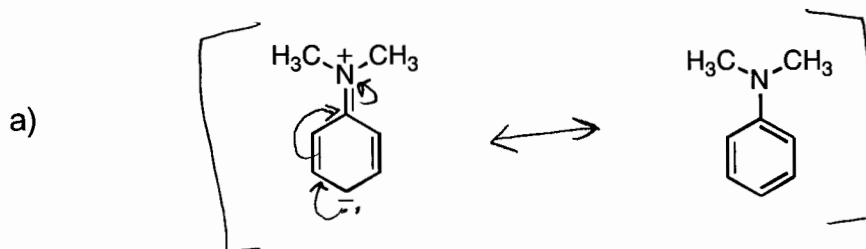
b) $\text{H}_2\text{C}=\text{C}=\text{O}$



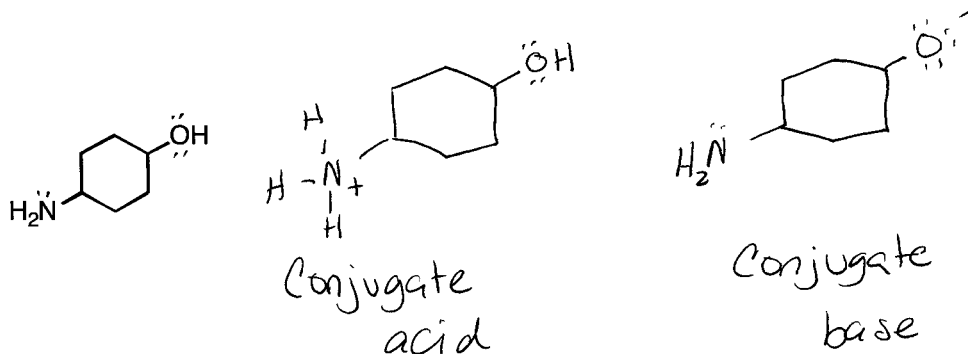
$sp^2 = 120^\circ$ bond \angle

$sp = 180^\circ$ bond \angle

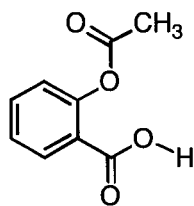
6. Circle the following pairs of structures that do not constitute resonance structures. For the proper resonance pairs, draw curved arrows to convert the first structure to the second. Draw in all lone pairs of electrons.



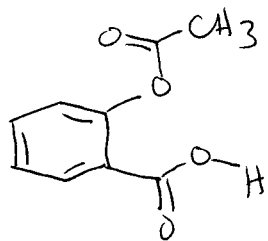
7. a) Draw the conjugate acid of the following molecule.
b) Draw the conjugate base.



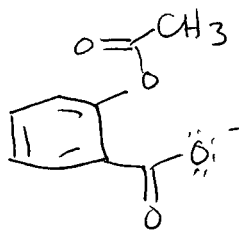
8. When you ingest aspirin, it passes through your stomach, which has an acidic pH, before traveling through the basic environment of your intestine. Provide the correct structure of aspirin **a)** as it exists in the stomach and **b)** as it exists in the intestine.



aspirin

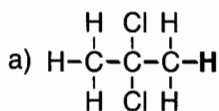


stomach

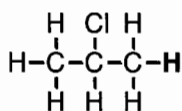


intestine

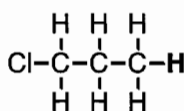
9. Rank the following sets of molecules according to acidity (1 = most acidic). Explain your choices.



1

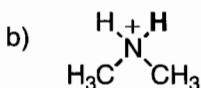


2

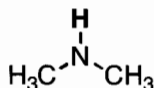


3

Inductive effects
Cl is e⁻ withdrawing

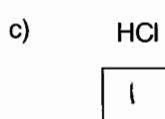


1



2

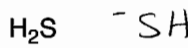
Charged more acidic
than noncharged (if comparing same atom)



1



3

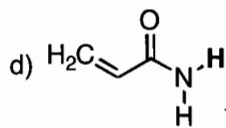


2



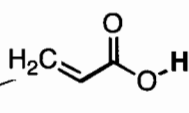
1) -OH vs -SH
S bigger than O, e⁻ more spread out, less dense

2) -SH vs -Cl
Cl more electronegative (EN) than S, better at stabilizing (-) charge

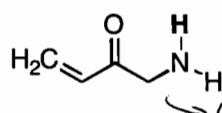


2

O more EN than N

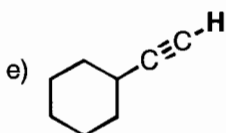


1

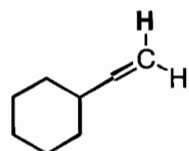


3

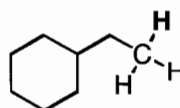
(e⁻ delocalization)
conjugate base has no resonance less stable b/c charge is localized instead of spread out



1



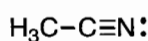
2



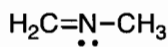
3

sp orbitals have greatest amount of s character, electrons held closer to nucleus, more stable
sp³ orbitals have least amount of s character, electrons not held as tightly to nucleus, less stable

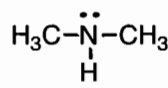
10. Rank the following molecules according to basicity (1 = most basic). Explain.



3



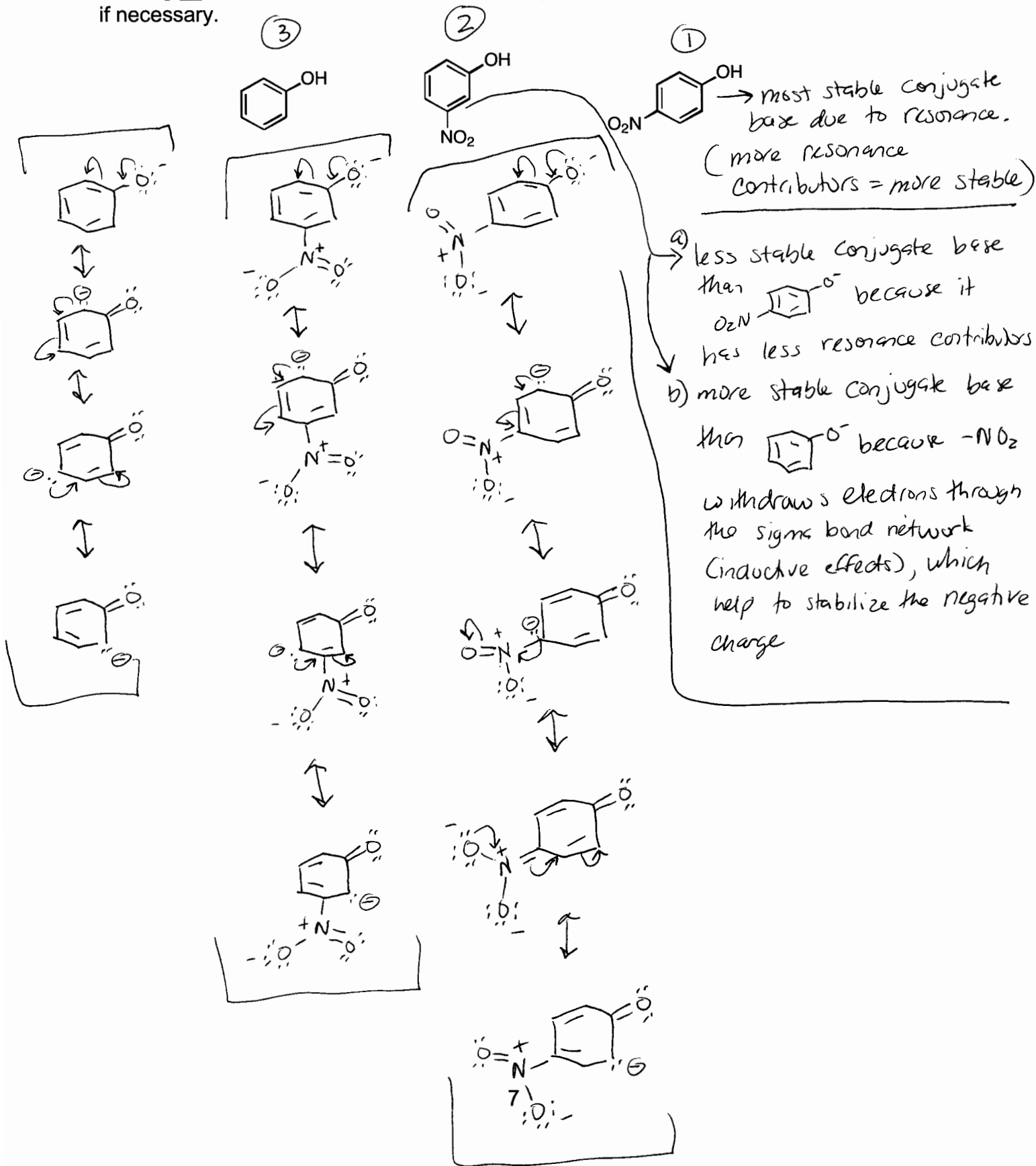
2



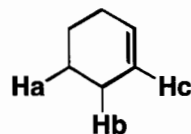
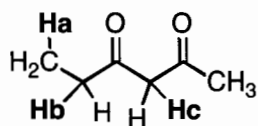
1

sp orbitals have greatest amount of s character, electrons are held closer to nucleus & are less available to a proton
sp³ orbitals have the least amount of s character, electrons are further from the nucleus & more available to a proton

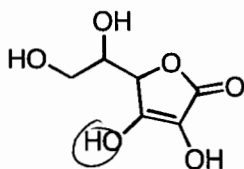
11. Rank the molecules in order of acidity (1 = most acidic). Explain your answer by drawing all resonance contributors of each conjugate base. Use the back of this page, if necessary.



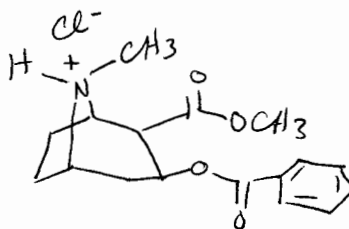
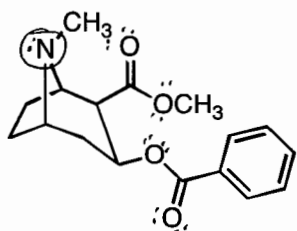
12. Rank the hydrogen atoms (H_a , H_b , H_c) in the following molecules according to acidity.



13. Circle the most acidic H atom in ascorbic acid (vitamin C).



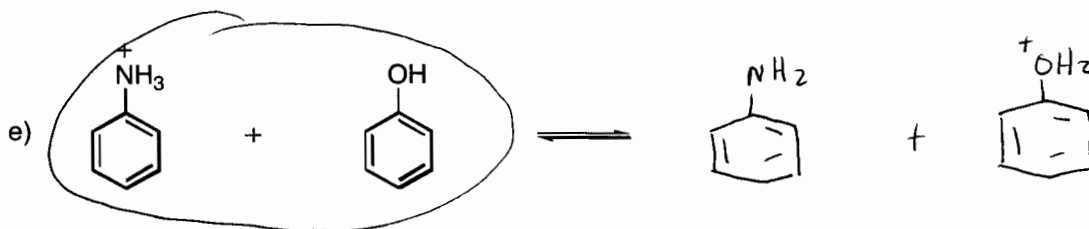
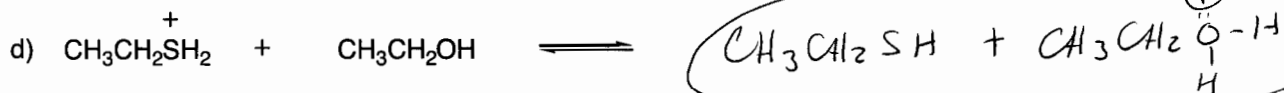
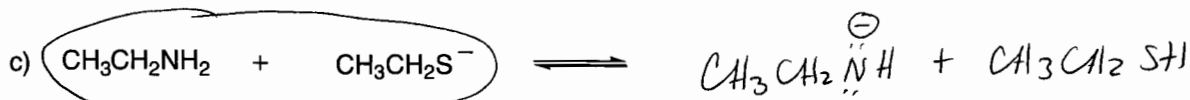
14. Cocaine is usually obtained in a protonated form as its hydrochloride salt (cocaine hydrochloride). However, it can be converted to crack by treatment with a base. The structure of crack is shown below. Circle the atom that is protonated in the hydrochloride form (i.e. the most basic atom) and draw the resulting salt. Considering the solubilities of both these molecules, why is crack usually smoked but cocaine injected directly into the bloodstream?



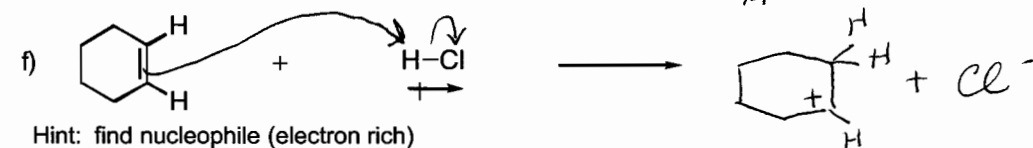
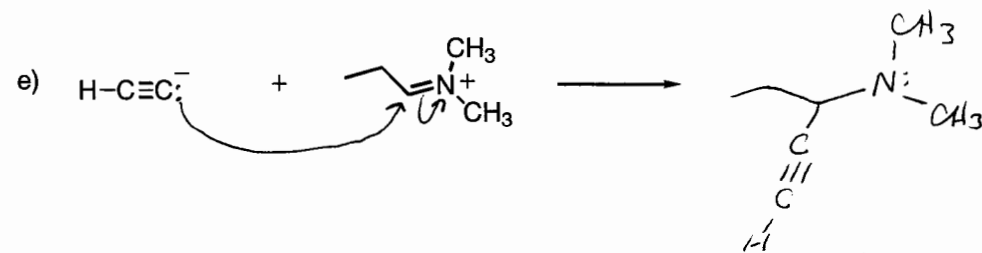
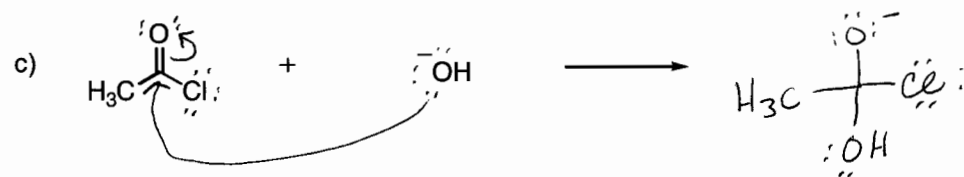
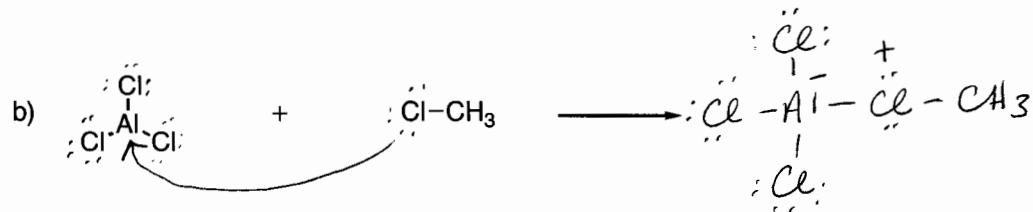
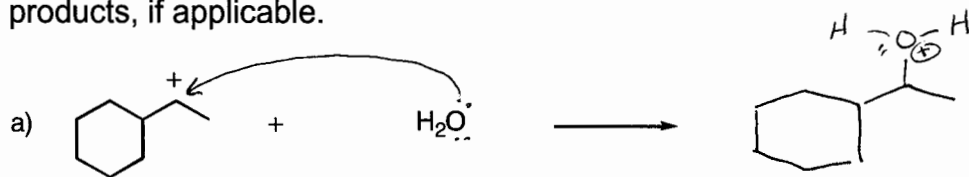
Crack is a neutral, organic molecule & not H_2O soluble.
Cocaine hydrochloride is charged & thus, H_2O soluble.

$\sim 70\%$ of the body is composed of H_2O & fluids, such as blood, contain a lot of H_2O .

15. Draw the products of each reaction. Show all lone pairs in reactants and products. Circle the side of the reaction that is favored at equilibrium.



16. Draw in all lone pairs and provide the product of each reaction. Use curved arrow notation to show the mechanism. Show all resonance contributors of reactants and products, if applicable.



Hint: find nucleophile (electron rich) and electrophile (electron poor).

