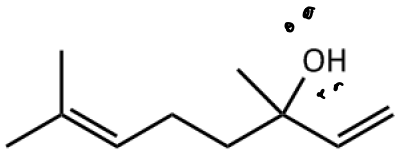
Answer Key

1. The natural product linalool is found in many fragrant plants and spices. It smells like citrus mixed with roses. (10 points)



a. What is the *molecular formula* for linalool?

$C_{10}H_{18}O$

b. How many valence electrons does linalool have? Are they all shown in the structure above? If not, what's missing?

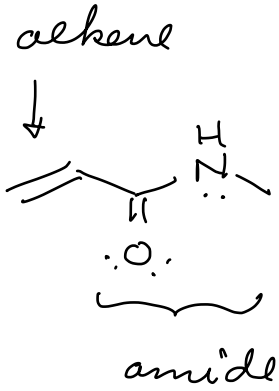
two lone pairs of e⁻ on oxygen are not shown

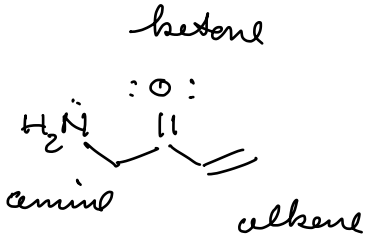
10 C — 40
18 H — 18
1 O — 6

= 64 valence electrons

2. Draw a molecule that has the molecular formula C_4H_7NO. The structure must contain only the "common" functional groups discussed in Chapter 2 (it could have more than one!) and should be shown using *bond-line* structures *with lone pairs of electrons clearly shown*.

Also, name the *functional groups* shown in your structure. (20 points)
(If you draw multiple structure, only one will be graded so just circle the single one you want graded!)

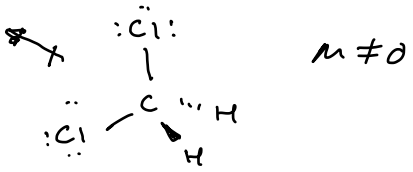




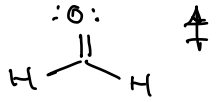
3. For the following molecules,

   a. Draw *bond-line* drawings that show the expected *geometry* (use dashes and wedges where necessary). (Note that C. has three possible structures, just choose one and answer b. and c.)
   b. In your structures, show all of the lone pairs of electrons.
   c. Indicate whether the molecule has a permanent dipole moment ($\mu \neq 0$ D), if it does, then indicate the direction of the overall dipole, or if it doesn't have a permanent dipole moment ($\mu = 0$ D) (15 points)

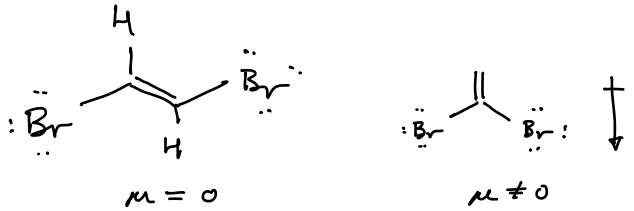
A. **CH_2Cl_2**



B. **CH_2O**

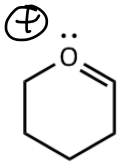


C. **$C_2H_2Br_2$**

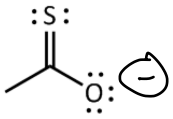


4. Assign formal charges (if non-zero) to the appropriate atoms in the following molecules (or ions). (Note that *all* lone pairs of electrons are shown in each structure) (10 points)

a.

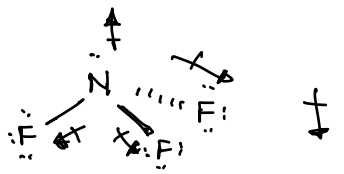


b.



5. Ammonia (NH_3) has a dipole moment (μ) of 1.42 D, whereas nitrogen trifluoride (NF_3) has a value of 0.234 D. Since the two compounds have eseentially the same structure, suggest a reason for the dramatic difference in their polarities. (Hint: carefully consider the structure, polarity, and geometry) (10 points)

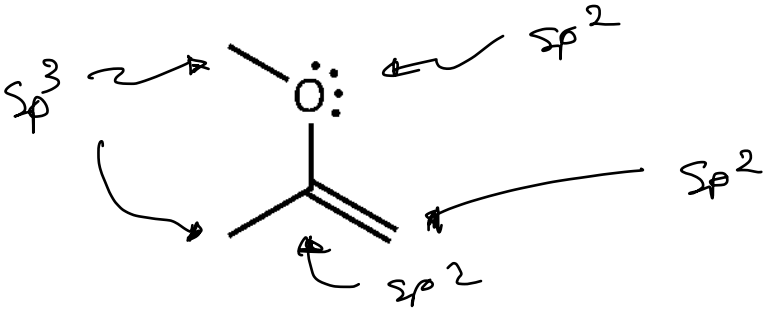
all bond dipoles constribute to overall dipole - in the same direction - this includes the lone pair



N-F bonds dipoles constribute in opposite direction as lone pair so the partially cancel

Note the geometry of both molecules is trigonal pyramidal (neither are planar)

6. Consider the structure shown below. (20 points)

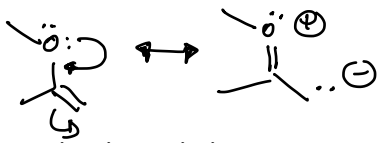


a. Label the hybridization for each of the atoms (except hydrogen).

b. What type of atomic orbital(s) do both lone pairs on the oxygen occupy?

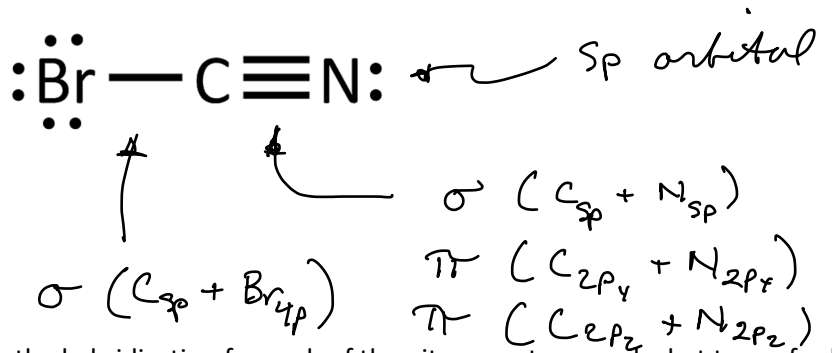
one pair is in a 2p orbital, the other is in an sp^2

c. Is there a resonance structure for this compound? If so, show it using electron pushing.

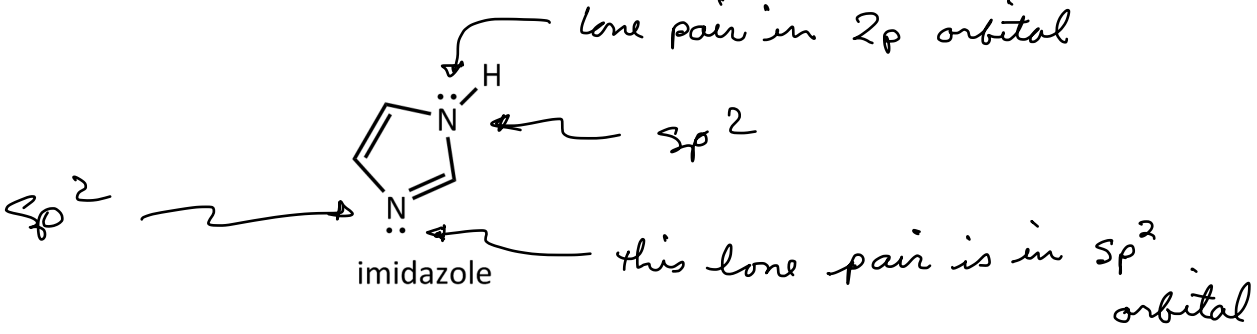


this resonance is only possible because the oxygen atom is hybridized sp^2

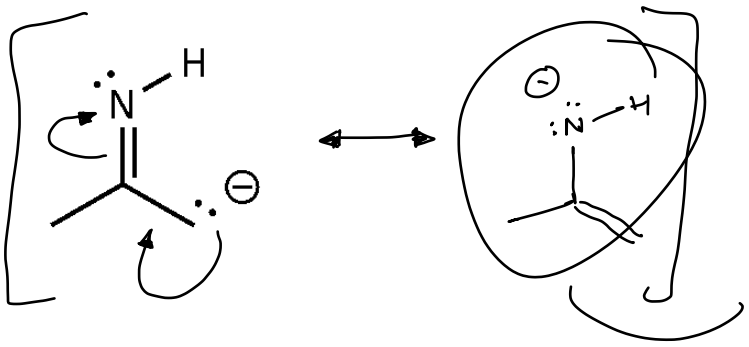
7. Cyanogen bromide, shown below, is a reagent used for cleaving proteins at specific locations and is useful for protein sequencing. For every bond in the molecule, indicate which *type* of bond it is (π or σ) and what atomic orbitals are used to form them (hybridized orbitals are considered atomic orbitals). Also, what type of orbital is the *nitrogen* lone pair of electrons in. (note: there are 4 unique bonds that need identifying). (20 points)



8. Imidazole is shown below. Indicate the hybridization for each of the nitrogen atoms and what type of orbital each of the lone pair of electrons is in. (10 points)

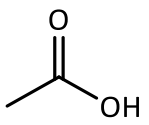


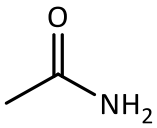
9. Push electrons to show the other resonance form for the ion shown below. Circle the *major* resonance form and provide the reason for your choice. (10 points)

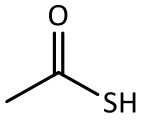


major because N is more electronegative

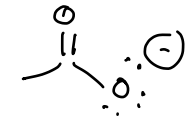
10. Consider the three compounds below. Indicate which compound is the most acidic and which is the least acidic. Use ARIO to justify your answers (don't forget about the conj. bases) (20 points)

a. 

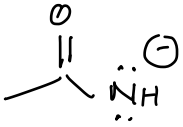
b. 

c. 

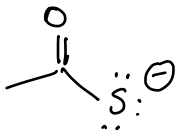
most acidic, since conj. base is most stable due to size of atom w/ ⊖ charge



less stable than c.



least stable

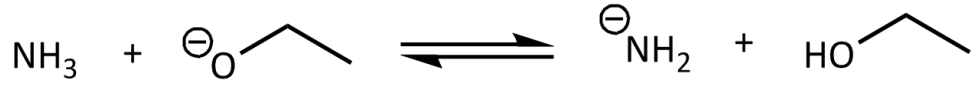


Atom effect for all three

11. Given the pK_a of the acid and conjugate acid are 16 and 38 (which one is which?), indicate which side of the equilibrium is favored (i.e., right or left). Also, explain why the data indicate this – be clear about this. Calculate the equilibrium constant (K_{eq}) – show your calculation. (15 points)

larger pKa means weaker acid!

K_{eq}



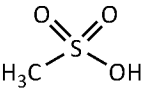
pK_a 38 pK_a 16

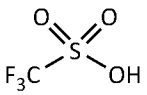
Equilibrium always favors the weakest acid, so in this case the left side is favored.

$$K_{eq} = 10^{16-38} = 10^{-22}$$

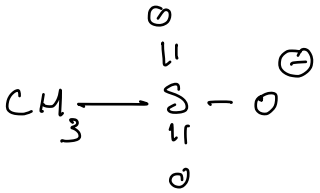
12. Trifluoromethanesulfonic acid (aka *triflic* acid) is one of the strongest known acids. Use ARIO to explain the difference in acidity between methanesulfonic acid and trifluoromethanesulfonic acid (don't forget about the conjugate base). (10 points)

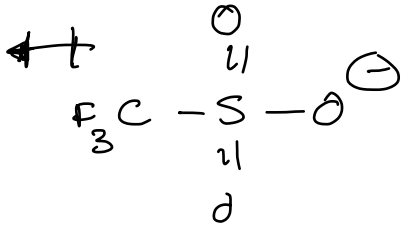
Atom 1
Resonance effects in both conj. bases is same





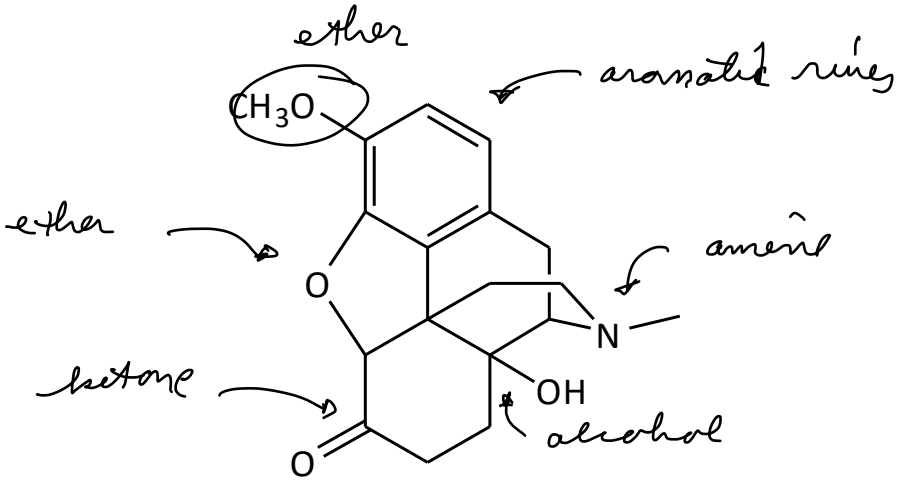
	methanesulfonic acid	trifluoromethanesulfonic acid
pK_a	-2.6	-12





inductive effect of the CF_3 group stabilizes the conj. base, so the acid is stronger

13. Oxycodone is a "semi-synthetic" product derived from opium poppy extracts. It is a widely prescribed (and abused) narcotic pain killer that is the active ingredient in OxyContin®. Circle and identify as many of the common functional groups as you can. (30 points)



oxycodone