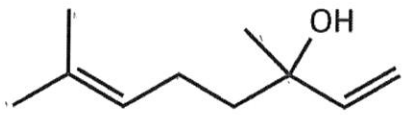
1. The natural product linalool is found in many fragrant plants and spices. It smells like citrus mixed with roses. (10 points)



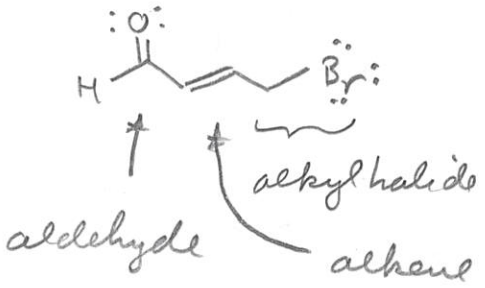
a. What is the *molecular formula* for linalool? $C_{10}H_{18}O$

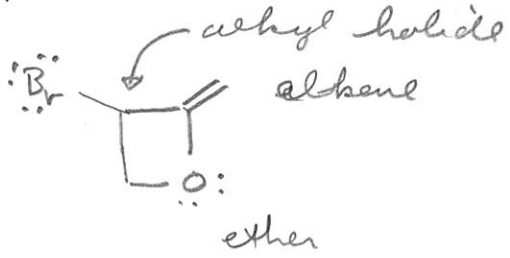
b. How many degrees of unsaturation are there in the compound?

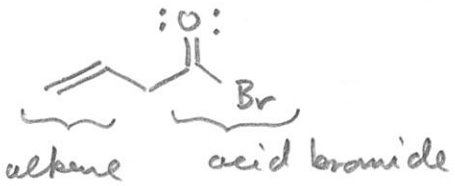
2° – there are two double bonds

2. Draw a molecule that has the molecular formula C_4H_5BrO. 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)



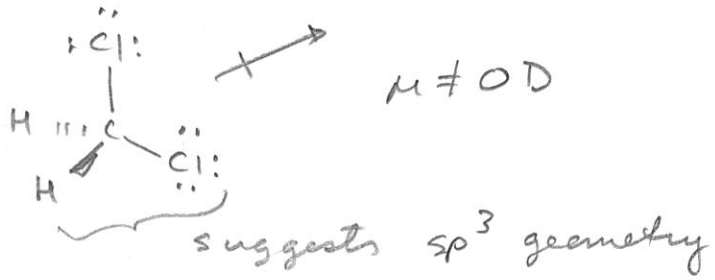




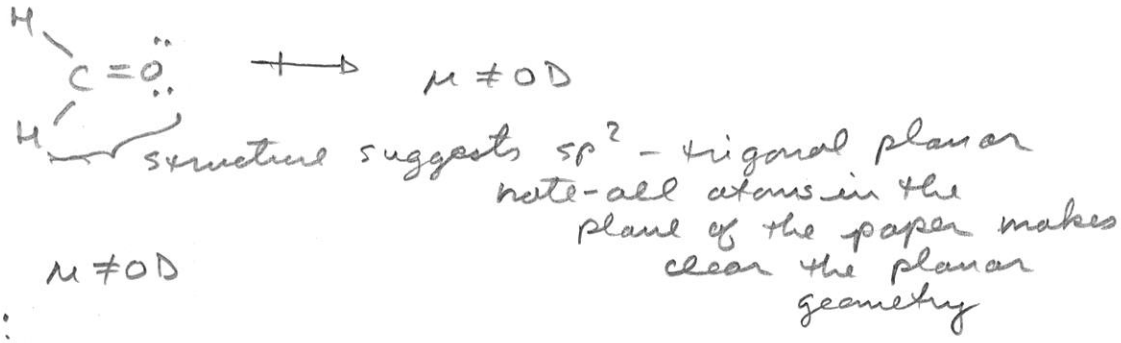
3. For the following molecules,

   a. Draw *bond-line* drawings that show the expected *geometry* (use dashes and wedges where necessary).
   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)

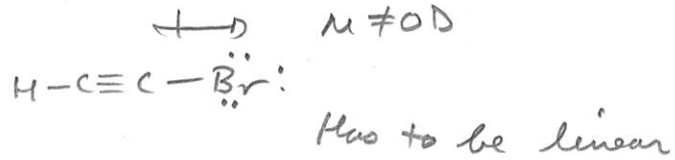
CH_2Cl_2



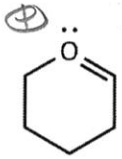
CH_2O

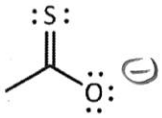


C_2HBr

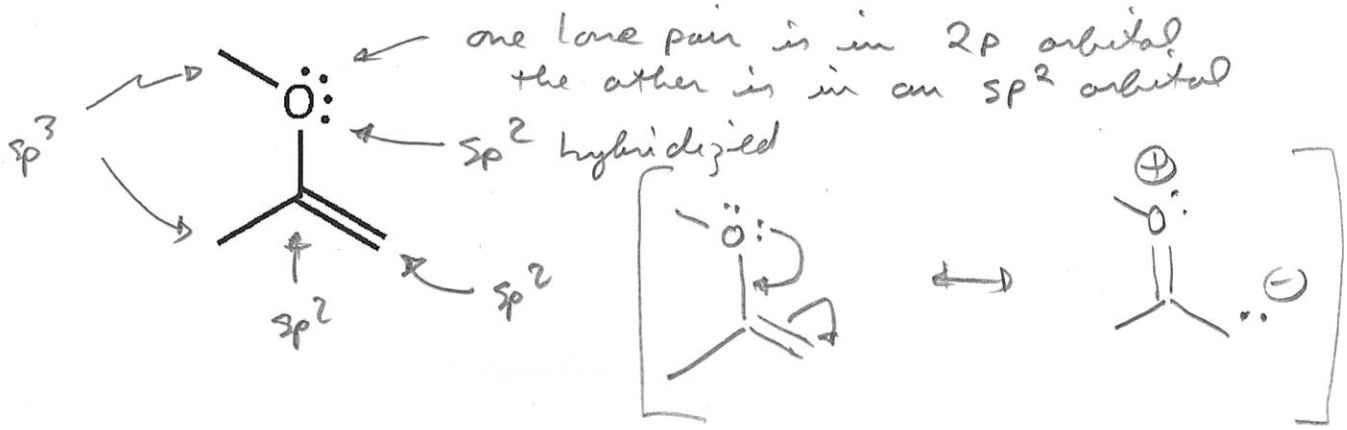


4. Assign formal charges (if non-zero) to the appropriate atoms in the following molecules (or ions). (Note that *all* lone pairs of electrons are shown in each structure) (10 points)

a. 

b. 

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



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

See above

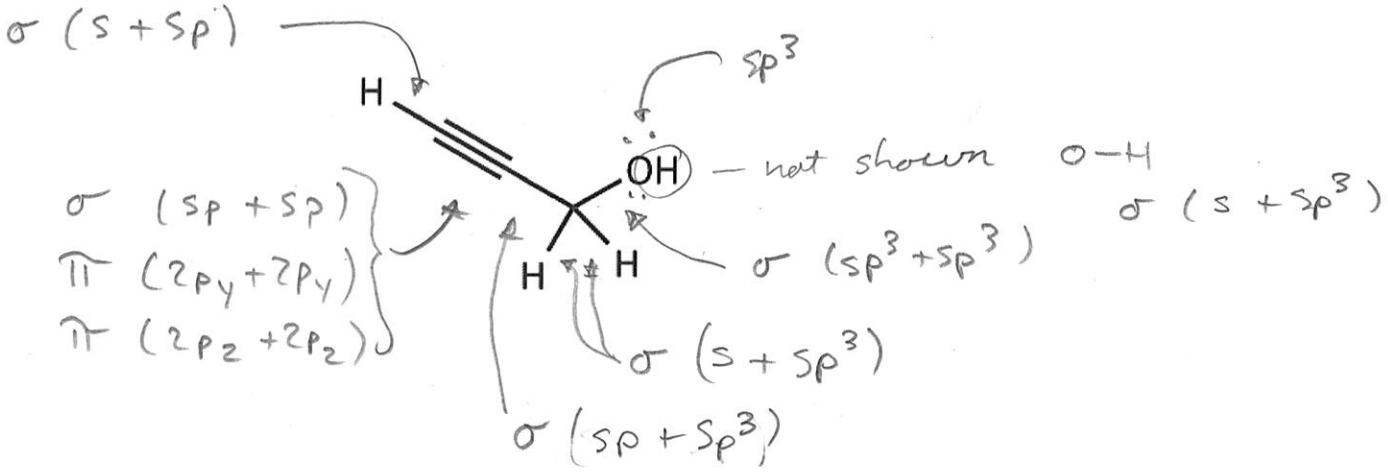
b. What type of atomic orbital(s) do the lone pairs on the oxygen occupy?

$2p$ & sp^2

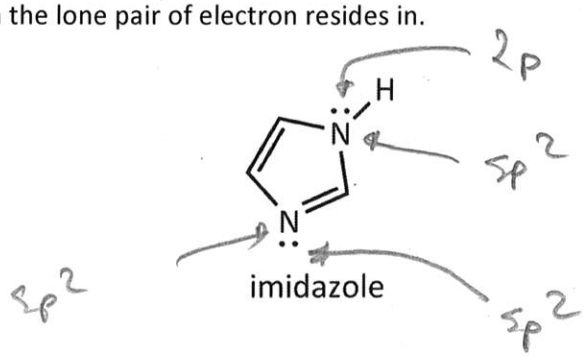
c. Is there a resonance structure for this compound? If so, show it using electron pushing.

Yes

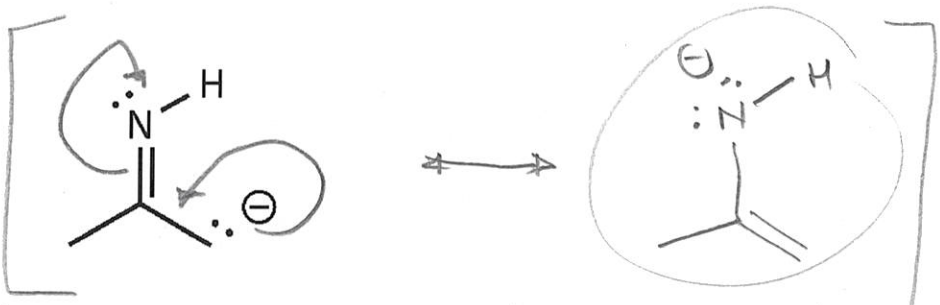
6. For every bond in the molecule, indicate which *type* of bond it is (π or σ) and what atomic orbitals are used to form them (hybridized orbitals are considered atomic orbitals). Also, what type of orbital is the lone pair of electrons in. (note: there are seven bonds that need identifying). (20 points)



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



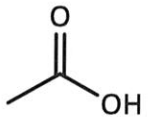
8. By "pushing" electrons, show the other resonance form for the ion shown below. Circle the *major* resonance form and provide the reason for your choice. (20 points)

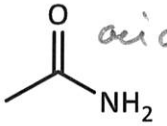


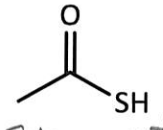
nitrogen is more electronegative so better to hold the negative charge

9. Consider the three compounds below.

a. Indicate which compound is the most acidic and which is the least acidic.
b. Use ARIO to justify your answers (don't forget about the conj. bases) (20 points)

a. 

b. 

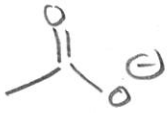
c. 

weakest acid

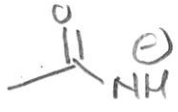
This is the A-atom effect

strongest acid

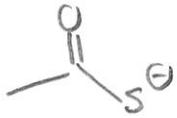
consider the conj. bases



more stable since oxygen is more electronegative



least stable



most stable since S is largest - can stabilize charge better than 2nd row O & N

10. 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)

Equilibrium (Nature) favors weakest acid

$pK_a = 38$

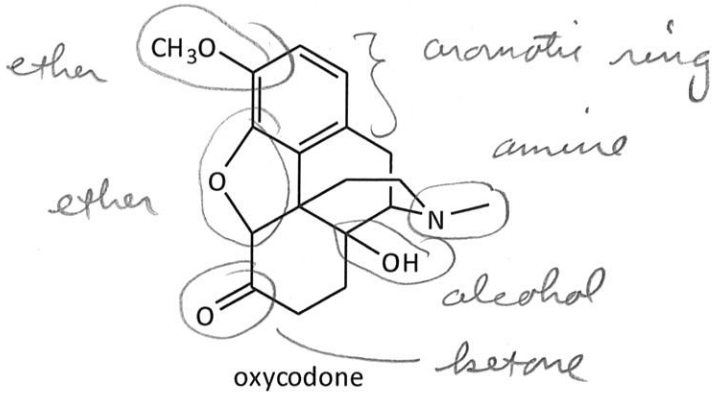
weakest acid - highest pKa

$pK_a = 16$

Reactants favors as written!

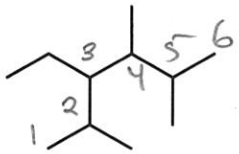
$K_{eq} = 10^{16-38} = 10^{-22}$

11. 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 Oxicontin®. Circle and identify as many of the common functional groups as you can. (10 points)



oxycodone

12. Name each of the following compounds using IUPAC (systematic) names. (20 points)

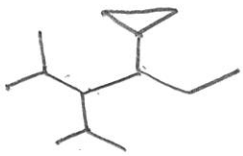
a. 

b. 

bicyclo[5.3.0]decane

3-ethyl-2,4,5-trimethylhexane

13. Draw structures for the following compounds. (20 points)

a. 4-cyclopropyl-2-methyl-3-(1-methylethyl)hexane 

b. *trans*-1,4-dibutylcyclooctane 

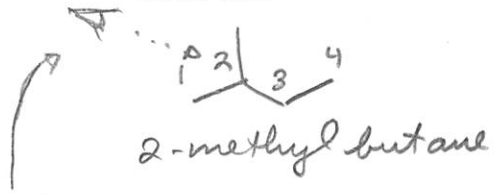
14. The boiling points for octane and isooctane (2,2,4-trimethylpentane) are 98°C and 125°C, *irrespectively*. Which one is which? Provide an explanation for your choice. (5 points)

bp = 125°C

less surface area, less London dispersion, lower bp = 98°C

octane has greater surface area thus more London dispersion forces so higher bp.

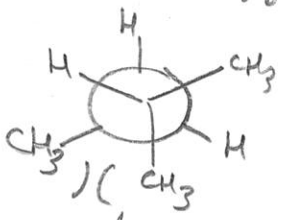
15. Consider the molecule, 2-methylbutane (C_5H_{12}). Using Newman projections, draw the lowest energy and the highest energy conformations around the C2-C3 bond. In each conformation, label it as staggered or eclipsed, and indicate what type of strain is present – torsional, steric, angle, or some combination of them – be specific about this. (25 points)



2-methyl butane

view "with" eye down the C2-C3 axis

Lowest energy

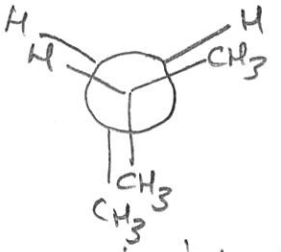


gauche

steric strain

- staggered

Highest energy



steric & torsional strain

- eclipsed

16. Draw both chair forms, and provide an IUPAC name for the structure shown below of the compound *cis*-1-ethyl-1-methylcyclohexane. Calculate the equilibrium constant (K_{eq}) between the two chairs at 25°C from the least to the most stable chair (least stable chair on left of equilibrium – most stable on the right). Given the following formulas and data (25 points)

$K_{eq} = e^{-\Delta G/RT}$

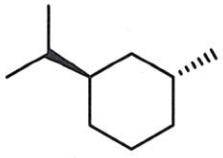
$R = 8.314$ J/mol · K

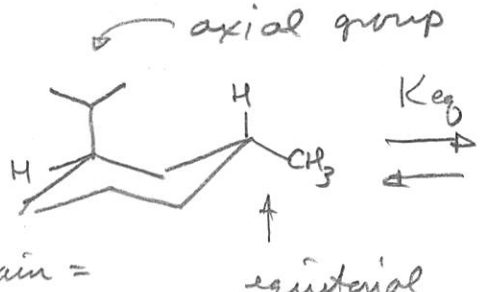
K = °C + 273.15

1,3-Diaxial Interactions	
$-CH_3$	7.6 kJ/mol
$-CH(CH_3)_2$	9.2 kJ/mol

T = 25°C = 298.15 K

$R = 8.314 \frac{J}{mol \cdot K}$





strain = 9.2 kJ/mol (equatorial group)

strain = 7.6 kJ/mol

$\Delta G = (7.6 - 9.2)$ kJ/mol

$= -1.6$ kJ/mol

$= -1600$ J/mol

$K_{eq} = e^{-(-1600\ J/mol)/(8.314\ J/mol \cdot K)(298.15\ K)}$

$K_{eq} = 1.9$