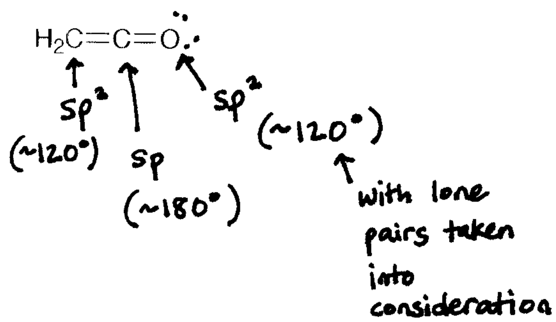
Massachusetts Institute of Technology

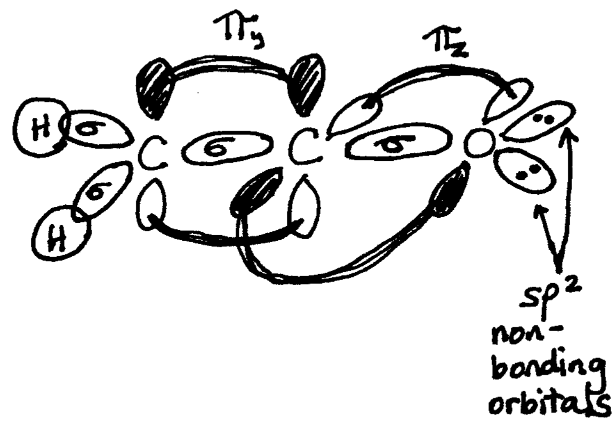
5.12: Organic Chemistry I *Fall 2008, S. O'Connor*

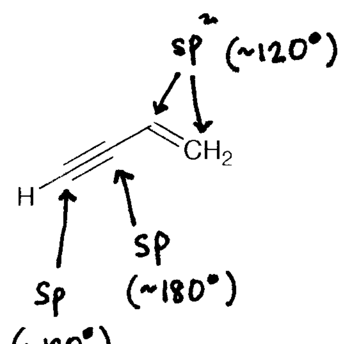
Problem Set 1
Posted Wednesday September 3
Key Posted Monday September 8 at 4 pm

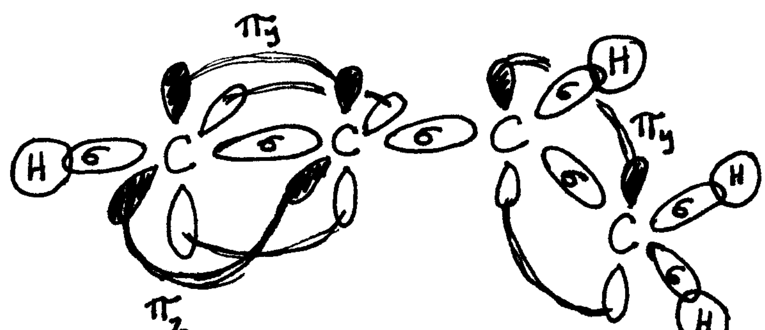
attempt ***ALL*** *problems* ***BEFORE*** *looking at the key*

1. a) Draw a molecular orbital bonding picture for each of the following. Include all bonding and non-bonding orbitals, and label each clearly.
b) Label the hybridization of each non-hydrogen atom.
c) Assign all bond angles.

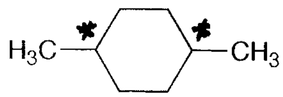




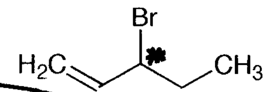


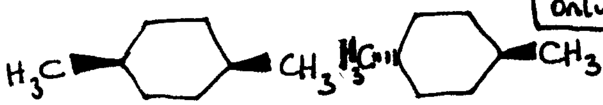


2. Using dashes and wedges, draw two **different** 3-D structures for each molecule. Only indicate 3-D structure for the **relevant** bonds in the structures.

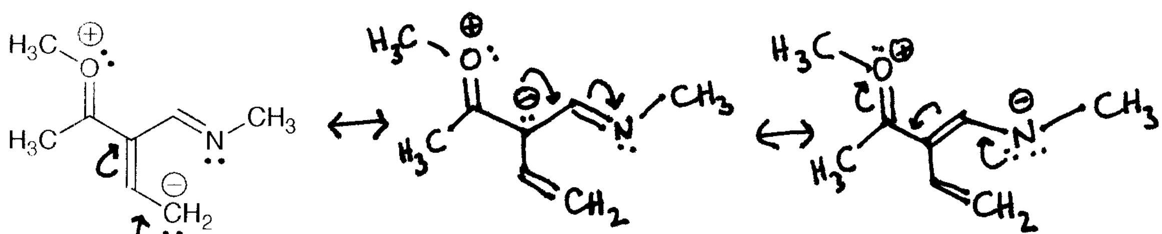


note: * denotes the only stereocenters in the molecules, which is why these are the only relevant bonds.

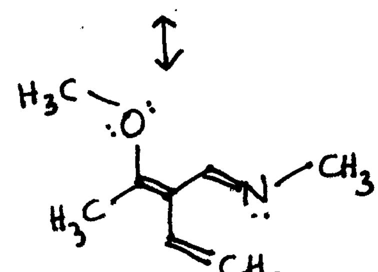




3. A **high energy** resonance structure of the following compound is shown.
a) Briefly explain why the resonance structure is unfavorable, and provide **three lower energy resonance structures**. (Use curved arrows to interconvert structures, and show all lone pairs and formal charges.)
b) Rank the stability of the four resonance structures, and briefly explain your reasoning.



A B C



D

a) A is unfavorable because it has 2 formal charges, one of which is a ⊖ on carbon. Also, there's a large charge separation.

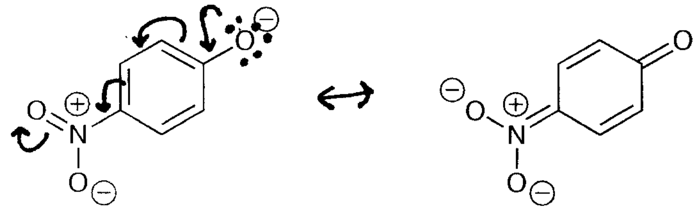
b) Stability ranking:

D > C > B > A

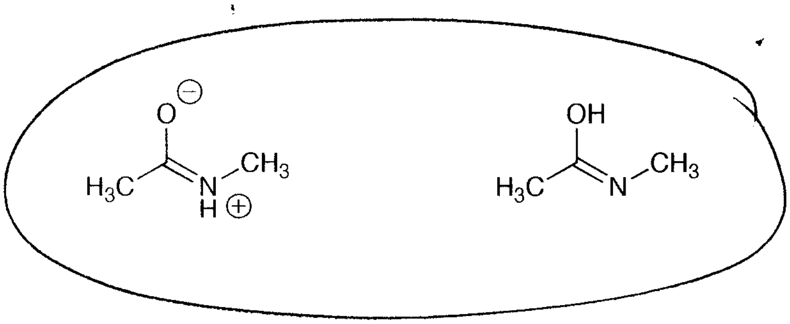
B → less charge separation than A
C → ⊖ charge on electronegative N atom (better than on C)
D → follows all the rules

4. 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 any lone pairs that you move.**

a)

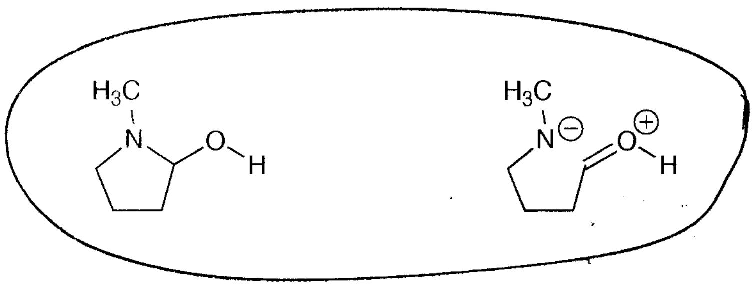


b)



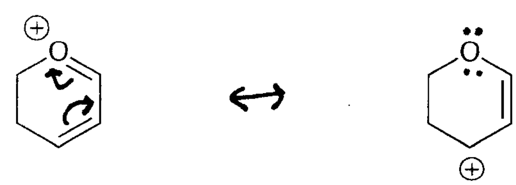
why?
H atom moves from N to O ; atom connectivity cannot change.

c)

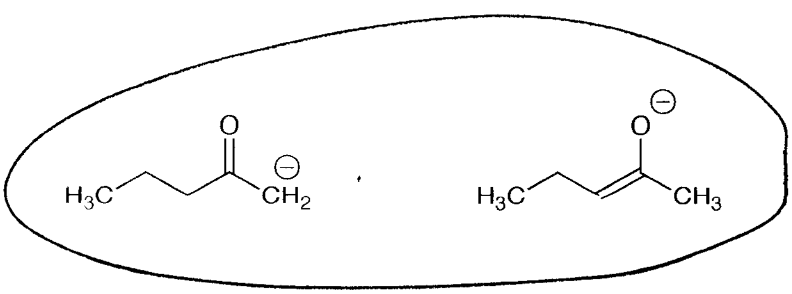


σ - bond is broken. only π - bonds can be broken/changed, not σ - bonds.

d)



e)

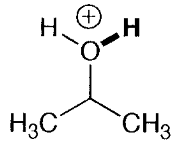


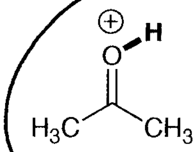
H is attached to different C atoms in each structure. Again, atom connectivity cannot change.

5. For each pair, circle the molecule with the **lowest pK_a** and give a brief explanation.

Why?

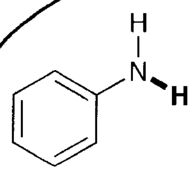
a)

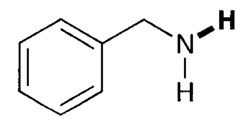




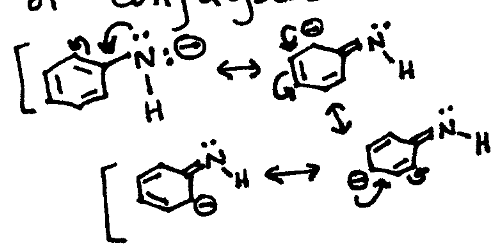
*hybridization.
sp^2 O atom is more electronegative than sp^3 O atom.

b)





*resonance stabilization of conjugate base:



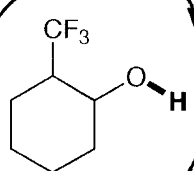
c)

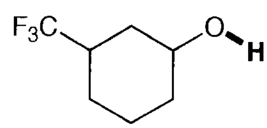
$HS—H$

$Cl—H$

*Cl is more electronegative than S atom.

d)





* inductive effects: electron withdrawing group ($-CF_3$) is closer to the acidic proton.

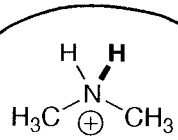
e)

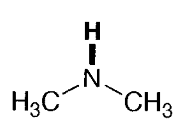
$Br—H$

$F—H$

* $Br^{\ominus}$ is more diffuse/larger than $F^{\ominus}$.
i.e. look at the stabilization of the conjugate base.

f)



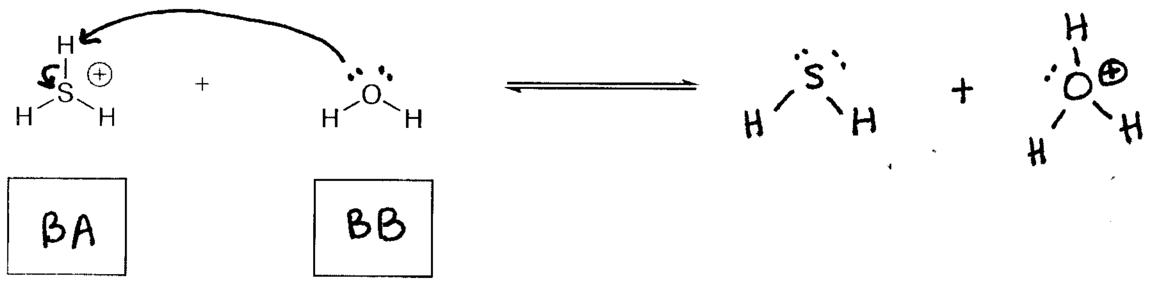


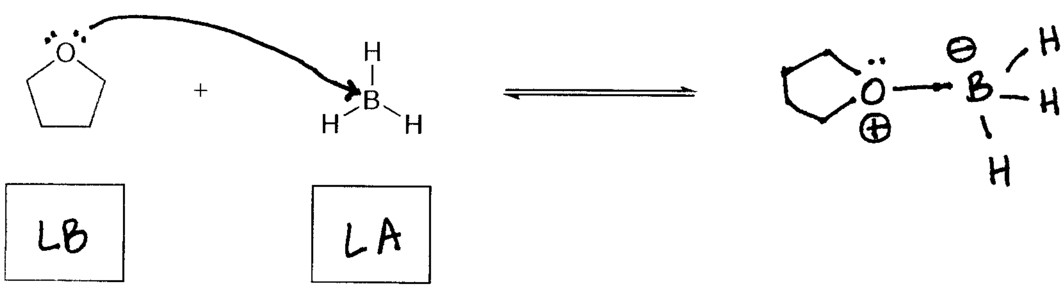
* charge: $\oplus$N-H is more acidic than neutral N-H. Conjugate base of the charged one is neutral.

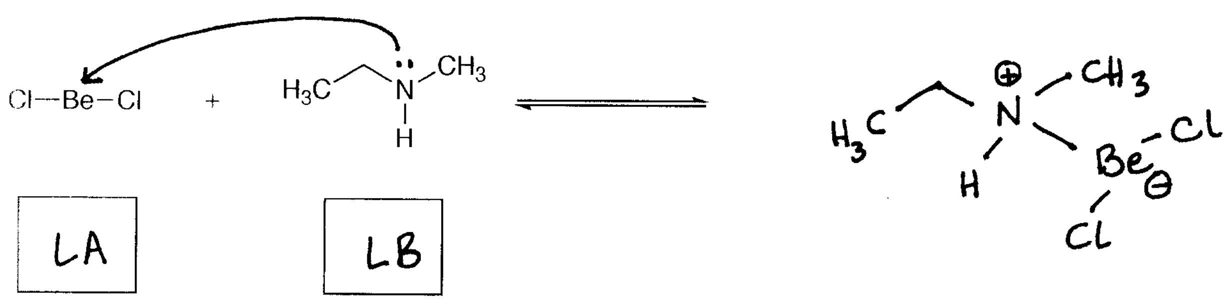
6. a) Provide the products for each of the following acid-base reactions.

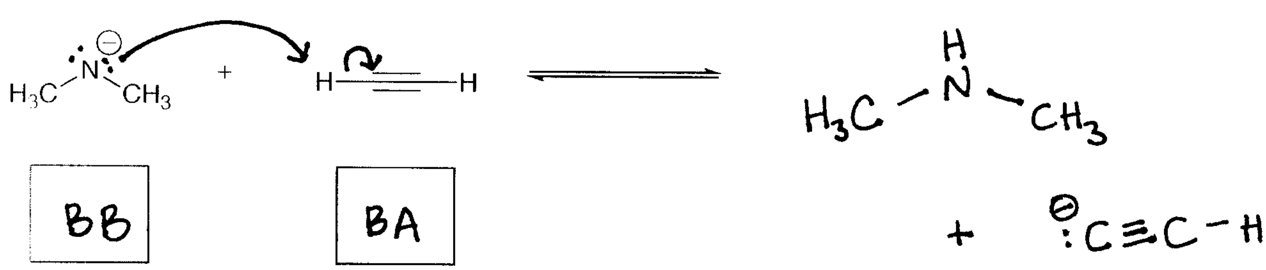
b) Provide the mechanism for each reaction. **Don't forget lone pairs and formal charges!**

c) Label each reactant as a Lewis acid (**LA**), Lewis base (**LB**), Brønsted acid (**BA**), or Brønsted base (**BB**).

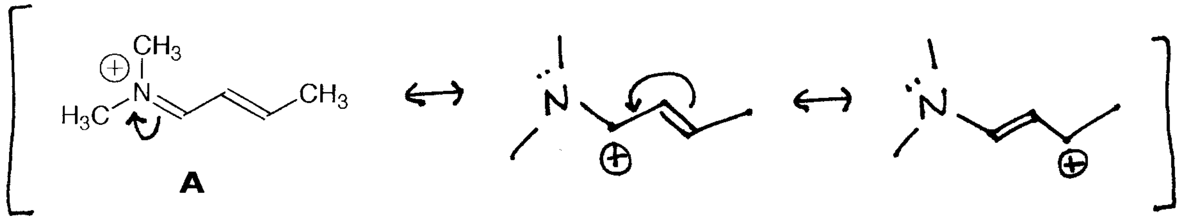


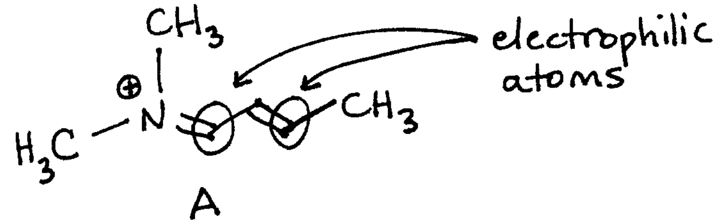




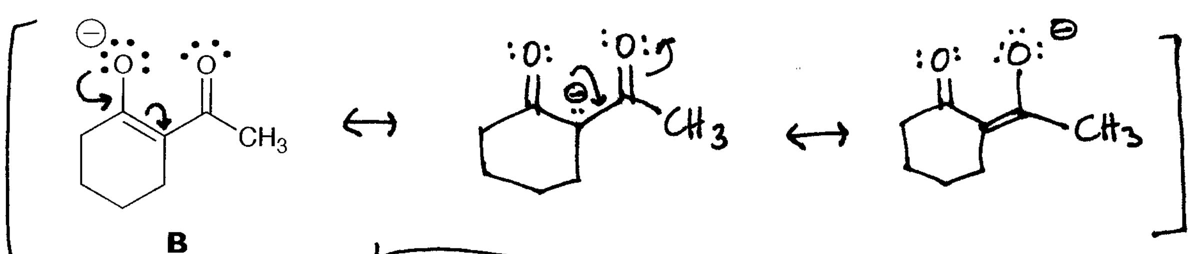


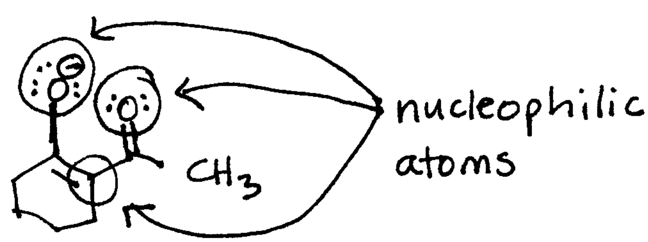
7. a) Use resonance to determine which of the atoms in **A** are **electrophilic**, and circle the electrophilic atoms. **Draw all relevant resonance structures.**





b) Use resonance to determine which of the atoms in **B** are **nucleophilic**, and circle the nucleophilic atoms. **Draw all relevant resonance structures.**





B