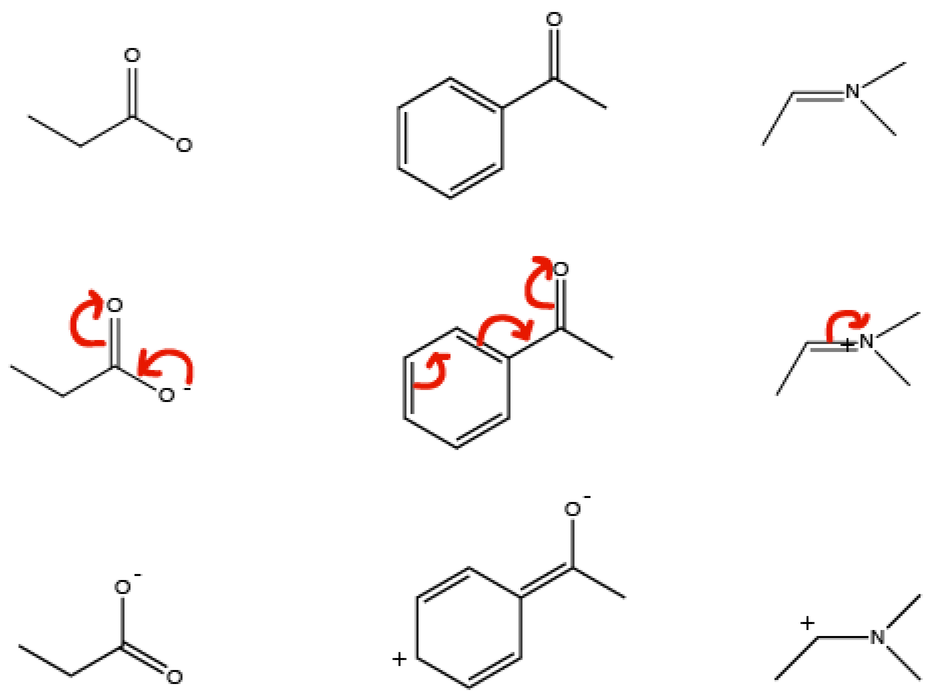
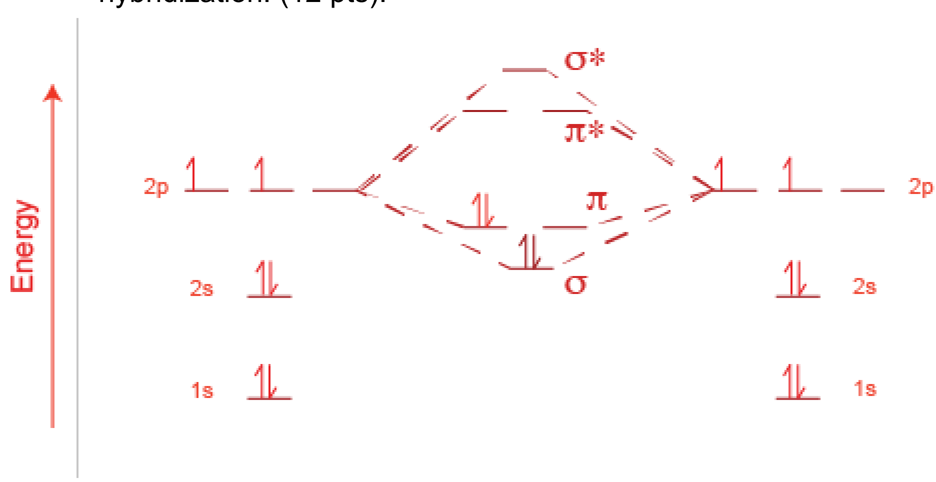
Orgo Midterm S2018 Answer Key

1. Draw the resonance forms for the following structures showing arrow-pushing mechanisms. Make sure to include where the electrons are mostly likely to flow to and end up. (9 pts).



2. What is the bond order of the diatom C2? Explain how you derived your answer by drawing a molecular orbital diagram (i.e., energy diagram). Assume there is no hybridization. (12 pts).

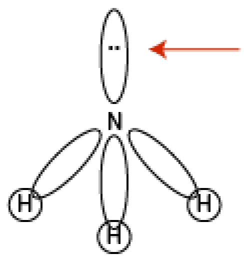


If not including 1s: Bonding Order = (4-0)/2 = 2
If including 1s: Bonding Order = (6-2)/2 = 2

3. A) Draw NH_3 with the hybridization state you expect for the nitrogen. Your drawing should show the approximate geometry of this molecule and the orbital shapes (5 pts).

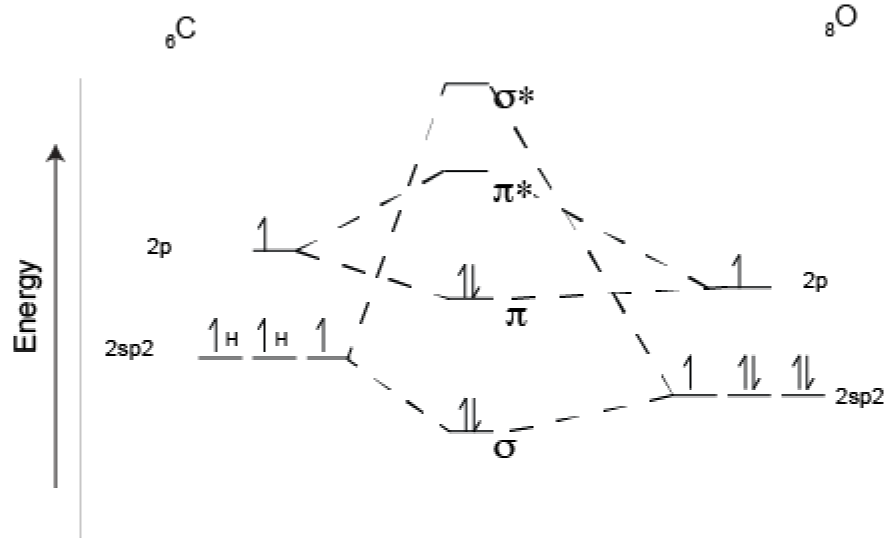
   tetrahedral geometry
   one pair in one of the four orbitals

   B) Put an arrow next to the orbital that will act as the HOMO when NH_3 behaves as a nucleophile. (3 pts).

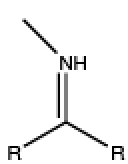


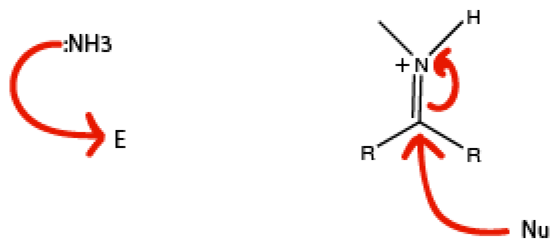
   arrow pointing to the lone pair in the molecule.

4. Draw a molecular orbital diagram (i.e., energy diagram) between the carbon and oxygen of the carbonyl CH2O (methanal, aka formaldehyde). (10 pts).



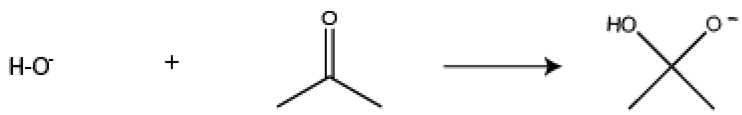
5. Identify if the below molecules are nucleophilic or electrophilic and where the electrons would originate or attack. (6 pts).
   NH3





A. nucleophile
   electrons from lone pair attack an electrophile.
B. electrophile
   nucleophile attacks the imine carbon and electrons flow to nitrogen.

6. For the following reaction, identify the HOMO and LUMO: (8 pts).



The HOMO is the negative charge (extra pair of electrons) on the oxygen of the hydroxyl. The LUMO is the pi * (pi antibonding) of the carbonyl

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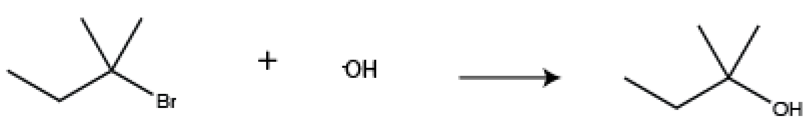
7. Write an equation describing the rate for both of the below reactions: (4, 4 pts).

A)

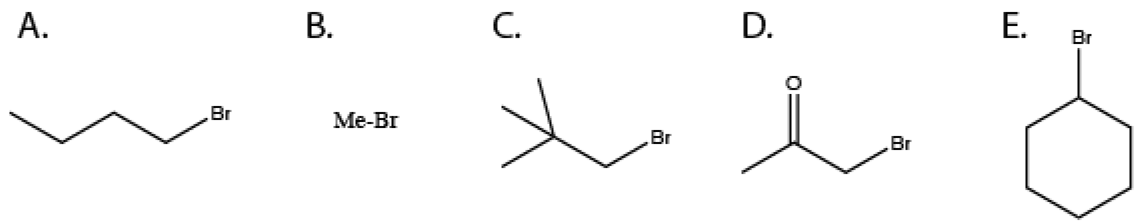
B)



A) SN2, rate proportional to the concentration of both the electrophile and nucleophile.
Rate = k[electrophile][$^{-}$OH]

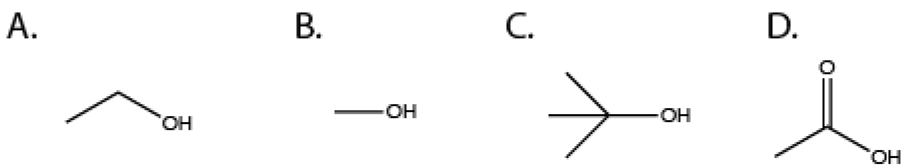
B) SN1, rate proportional to only the concentration of the electrophile.
Rate = k[electrophile]

8. Arrange the following in order from greatest to least reactivity towards a strong nucleophile. Give a brief comment for each compound to explain what factor influences its place in the reactivity scale. (8 pts).



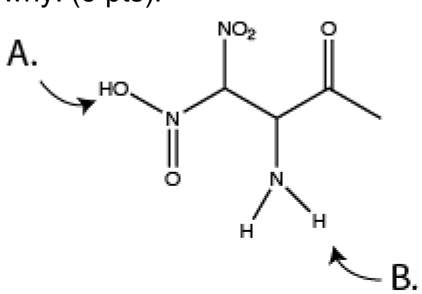
D - resonance/conjugation with carbonyl group
B - increasing steric hindrance B<A<C<E
A
C
E - secondary with strong nucleophile so SN2 but poor with steric hindrance

9. List the following molecules in order of lowest to highest pKa. (6 pts).



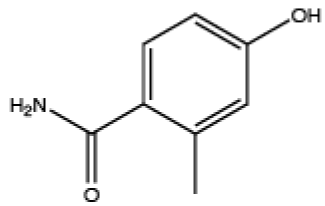
D - resonance/displacement
B - only a methyl, least electron donating
A - primary
C - 3 carbon, most electron donating

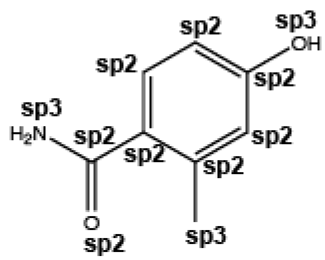
10. Compare the two hydrogens identified below. Which is more acidic (A. or B.)? Explain why. (5 pts).



A is more acidic because of resonance stabilizing the anion on oxygen.

11. Identify the hybridization state and geometry of every carbon and oxygen atom in the following molecule: (6 pts).

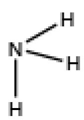




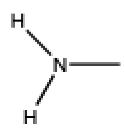
sp2=trigonal planar, sp3=tetrahedral

12. Put these molecules in the order of lowest to highest pKa. (6 pts).

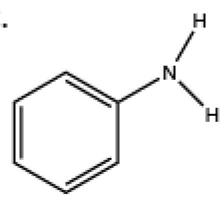
A.



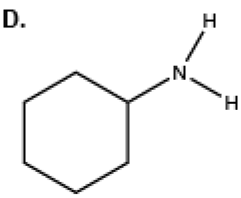
B.



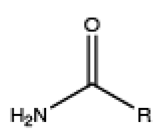
C.



D.



C. resonance/displacement
A. no carbon electron donating
B. 1 carbon electron donating
D. most carbons for electron donating

13. The peptide bond (an amide - 

) is extremely stable with a t1/2 of 7 years. There is resonance providing rigidity to this bond (which is very impactful for protein structures). Briefly explain the main reason this N-C bond is so stable (hint: the reason is not resonance). (8 pts).

-NH2 is a terrible leaving group.