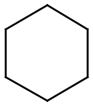
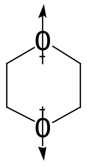
Chemistry 304B, Spring 1999 Key to Problem Set 1

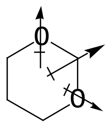
Question 1.



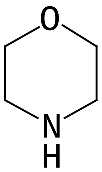
Molecule 3 has the lowest boiling point. It does not have any polar bonds and therefore no dipole moment or H-bonding. The only type of molecular interactions that holds these molecules together is Van der Waals.



Molecule 4 has a higher bp due to the presence of the polar bonds which participate in the local dipole-dipole interactions. Also oxygen atoms have lone pairs which are more easily polarizable leading to the stronger Van der Waals interactions. Please note that the whole molecule is symmetrical and the two dipoles drawn on the oxygen exactly cancel each other.



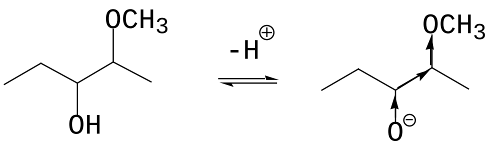
Molecule 2 is not symmetrical and the dipole moments add up. These molecules can interact by dipole-dipole type interactions. The bp is therefore higher then for 4.



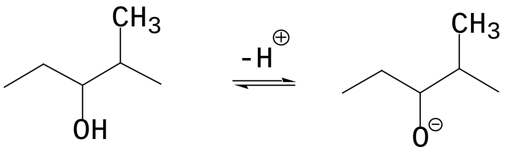
Molecule 1 has a hydrogen atom that can participate in H-boding (it is attached to a heteroatom, N in this case). It also has two heteroatoms with lone pair that can participate as H-bond acceptors. Therefore this molecule will have the highest bp.

Question 2.

A. Both molecules dissociate a proton attached to the oxygen.

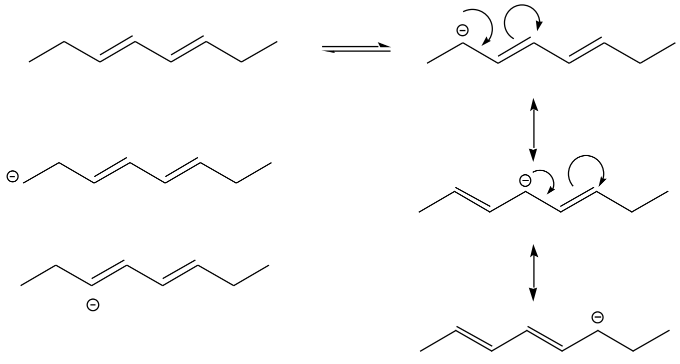


The conjugate base of the methoxy substituted compound is stabilized by the inductive electron withdrawing effect of the oxygen (see above).

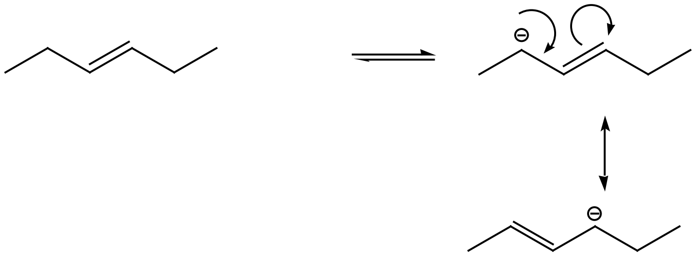


This type of stabilization is not available to the methyl substituted compound and it is therefore less acidic.

B. Several hydrogens can in principle be removed.

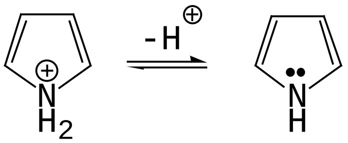


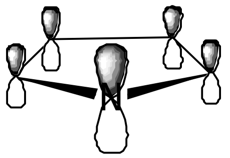
The resulting carbanions differ in stability. Allylic anion is more stable due to resonance delocalization as shown above. The conjugate base of the compound shown above has more resonance sturctures then the one below.



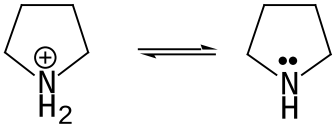
Therefore the diene is more acidic.

C. Acidic protons are obviously ones attached to the nitrogen.
The protonated form of pyrrole (shown immediately below) is more acidic due to the

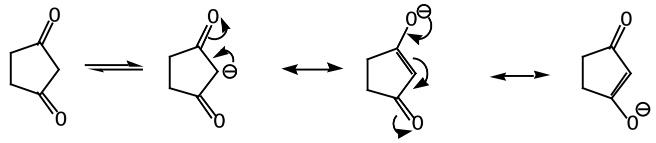




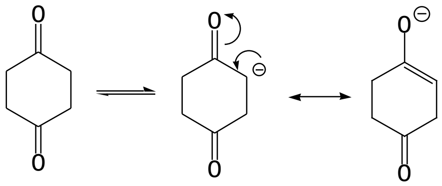
stabilization present in its conjugate base. The lone pair of the nitrogen overlaps with p-orbitals in the ring creating an aromatic system (like benzene). Another way of thinking about this stabilization is by drawing resonance structures (problem 4 D).
Pyrrolidine lacks this special stability and therefore its protonated form is less acidic.



D. Again several protons can be removed. The most acidic one will be delocalized over the carbonyl.

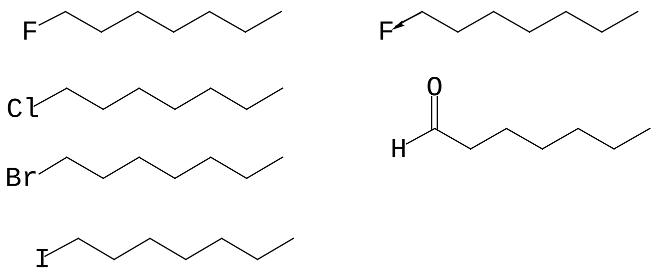


As you can see the conjugate base of the 1,3-diketone has more resonance forms then the one for 1,4-diketone. It is thefore more stable and thus 1,3 diketone is more acidic.



Question 3

A.The order of boiling points suggests that the dipole-dipole interactions in the series of halohexanes are overshadowed by some other type of interactions. The trend for dipole-dipole interactions is exactly opposite to the one observed (fluorohexane has a larger dipole moment due to its higher electronegativity then a chlorohexane).



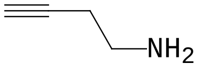
In Van der Waals interactions it’s the size of the molecule (its polarizability) that is of major importance. Iodine is bigger then bromine that is bigger then chlorine that is bigger then fluorine. The observed trend is therefore consistent with Van der Waals interactions as the major contriutor to molecular association in halohexanes series.

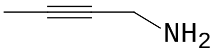
Hexanal has a strong dipole moment because of the double bond to the oxygen. It makes this compound comparable to chlorohexane in terms of its bp.

B. The strongest molecular association (leaving aside ionic compounds that are not very common among neutral organic molecules) is H-bonding (hydrogen bonding). The strenght of the H-bond depends on both H-bond donor and acceptor. The more acidic the H-bond donor is the more willing it will be to donate the H to the H-bond acceptor. Similarly the more basic the H-bond acceptor is the stornger will be the H-bond.

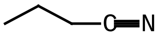
This suggest the NH2 group as a functional group responsible for the H-bonding.

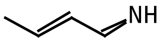
Molecular formula C4H7N corresponds to the index of unsaturation of 2 (remember you first calculate the number of hydrogens in the corresponding alkane 2n+2 then deduct the number of H’s present, accounting for one extra H present due to the N in the molecule, and divide the resulting number by 2 since each unsaturation unit corresponds to the absence of 2 H’s). Therefore we will have 2 double bonds / 1 triple bond / 1 doulbe bond and a ring or two rings. The Van der Waals interactions are going to be maximized if the molecule is linear, the suggested molecules are:



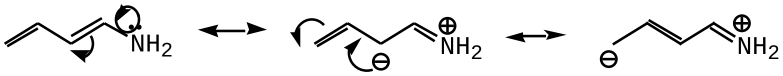


Please note that we want an sp3 hybridized nitrogen as it is the most basic in the sp3>sp2>sp series. The following molecules are not going to be particularly good:



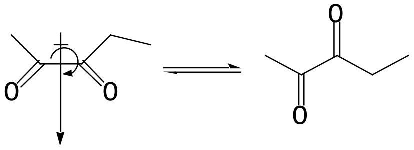


Another bad choice is the cojugated molecule shown below

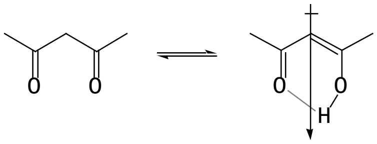


In this case it is again less basic because the starting material is stabilized by resonance while the protonated form is not.

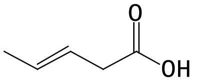
C. The IOU is 2. In order to generate a high dipole we need two carbonyl groups pointing in the same direction.

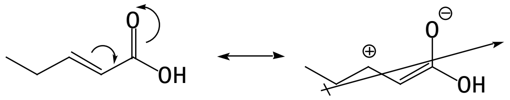


Moreover we would like for this molecule to be frozen in one conformation with bond dipoles reinforcing each other.



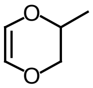
The molecule above exists predominantly as an internally H-bound enol locked in the desired conformation.
Other possibilities include the unsaturated carobylic acids:

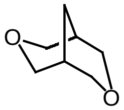


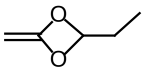


In the second case the dipole moment is enhanced by the charge separated resonance form contribution.

D. IOU is 2. In this case we want to minimize all the dipoles and H-bonding properties. Some examples are:

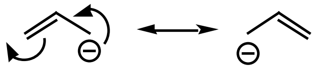




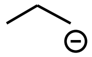


Question 4.

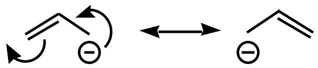
More basic molecule is the one in wich a lone pair is more available for bonding.
B. The lone pir in the allylic anion is delocalized through resonance over the double bond making the molecule less basic:

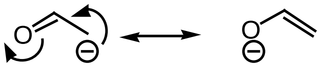


In the normal alkane case the lone pair on the carbon is localized, making this molecule a stronger base.



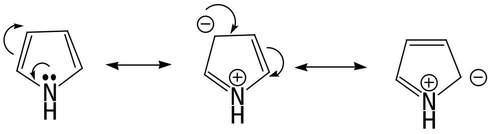
C. Here the delocalization over oxygen is more favourable due to its higher elecronegativity. Another explanation would be the stabilizing effect of the partially positive carbonyl carbon that is adjacent to the negative charge.



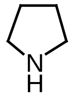


Therefore the lone pair in the carbonyl compound is less available to bind proton making it a weaker base.

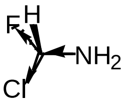
D. In these molecules nitrogen is obviously the most basic atom, therefore we should inspect the availability of the nitrogen lone pair:

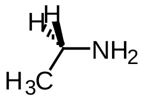


as you can see in pyrrole the nitrogen lone pair is involved in the resonance. It is terefore less basic then in pyrrolidine:

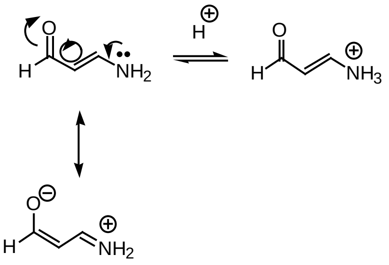


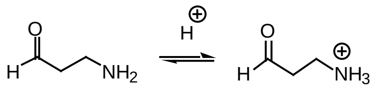
E. The electronegative halogens will pool electron density off the nitrogen lone pair thus making a fluoro- chloro- compound less basic:





F. Again nitrogen is the most basic heteroatom in the molecule. Resonance is present in the α,β unsaturated compound making it less basic.

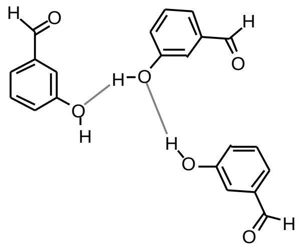




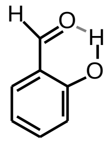
Another way of explaining the same result is by saying that the starting material is stabilized by resonance while the product is not. The equilibrium is therefore unfavourable for the unsaturated compund.

Question 5.

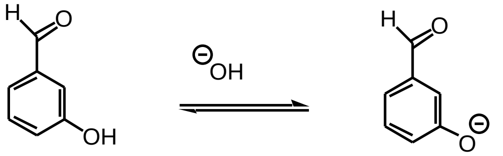
A. Compound B can form H-bonds through its OH groups. Aldehyde hydrogens are not acidic.



B. o-oxybenzaldehyde has a possibility of internal H-bonding. This will decrease its external H-bonding capabilities lowring its melting point (mp. trends parallel bp. trends).

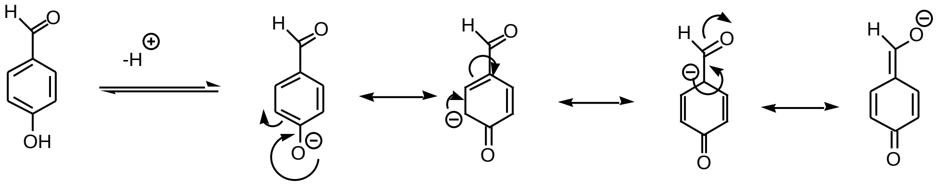


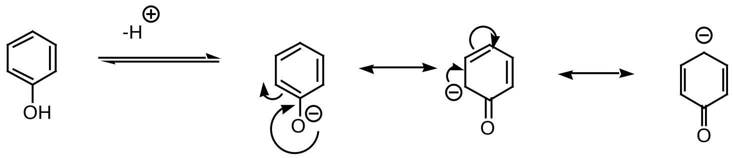
C. Compounds A-C are weak acids. They can get deprotonated by hydroxide ion which is a strong base:



The resulting anion is much more polar and therefore soluble in water.

D. The acidity is related to the stability of the conjugate base. The more stable it is the stronger is the acid.





Apparently in compound C the substituent can participate in the resonance stabilization making C more acidic then a simple phenol.