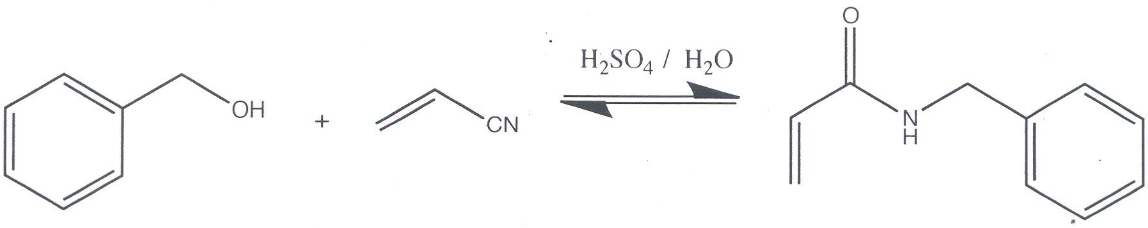
Chemistry 386J
Anslyn
29 September 2012
Exam 1

Name: ______________________

1. ________ (6 points)
2. ________ (9 points)
3. ________ (10 points)
4. ________ (10 points)
5. ________ (8 points)
6. ________ (15 points)
7. ________ (9 points)
8. ________ (4 points)
9. ________ (4 points)
10. ________ (6.5 points)
11. ________ (4 points)
12. ________ (8 points)
13. ________ (7 points)
14. ________ (11.5 points)
15. ________ (5 points)

Total. __________ (117 points)

1) Write the mechanism for this variation on the Ritter reaction. Show the movement of all electrons and atoms as well as any charges generated in the mechanism. All atoms should come from the starting material or reagents listed. (6 pts)

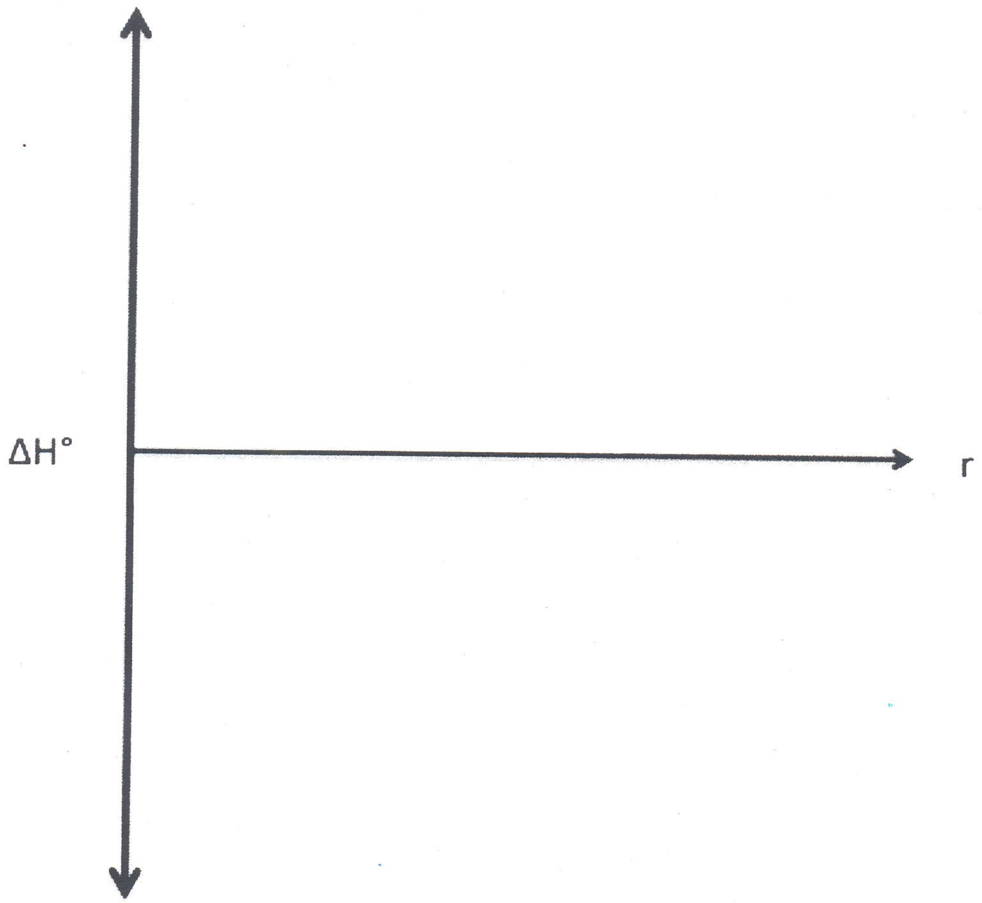


2) Draw a qualitative Morse potential for each of the following bonds. Label the r_0, bond dissociation energy (BDE), and draw the curves on the same plot showing the proper relative shapes. Label which graphs represent each bond. (9 pts)

A. A C-Cl bond (IR frequency - 600-800 cm^{-1})

B. A C-C single bond (IR frequency – 1160-1210 cm^{-1})

C. An O-H bond (IR frequency - 3500-3700 cm^{-1})

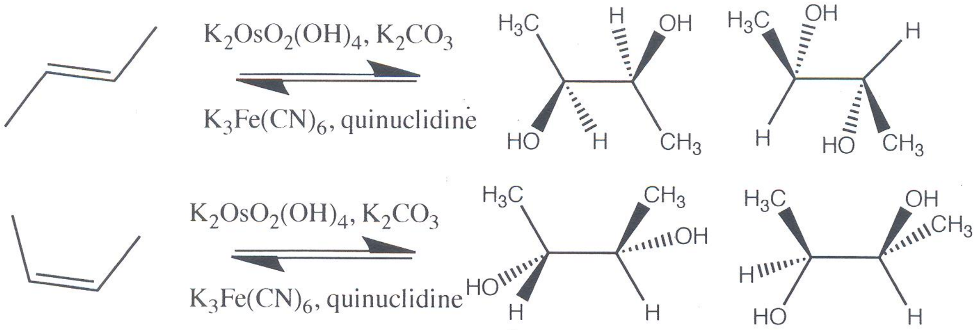


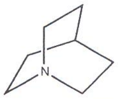
3) A. Draw the Walsh diagram for CH_2 that we discussed in class and is in the book. Show orbitals for linear H-C-H, bent H-C-H, and additional mixing that occurs upon bending. (5 pts)

B. Populate the diagram with the number of electrons for water, and using the diagram predict the geometry of H_2O. Also, circle which two orbitals would be best considered lone pairs. (2 pts)

C. The bond angle in H_2S is 92°. Which populated orbital in the Walsh diagram changes the most in energy leading to this geometry? Thinking about the electronegativity differences between "O" and "S", explain why the orbital you choose changes in energy. (3 pts)

4) The following dihydroxylation reactions give the products shown using the catalyst quinuclidine shown below.





Quinuclidine

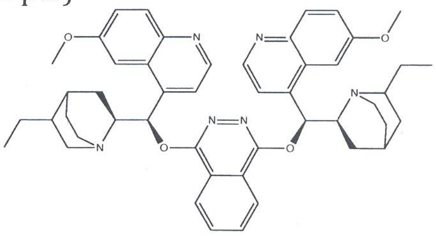
A. Which reaction gives a racemic mix or do both? (2 pts)

B. Circle any set of enantiomers and put a box around any set of diastereomers. (2 pts)

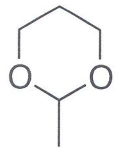
C. Are the dihydroxylation reactions of the alkenes stereoselective? (2 pts)

D. Is the dihydroxylation reaction stereospecific? (2 pts)

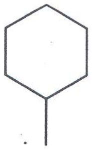
E. Which reaction above would give a different product ratio if the quinuclidine were replaced with the chiral ligand shown below? (2 pts)



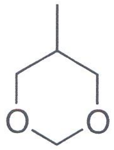
6) Below we list the A-values for methyl groups in 3 ring systems.



4.0 kcal/mol

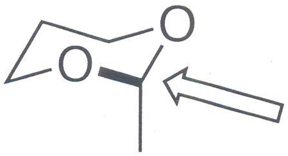


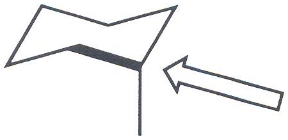
1.7 kcal/mol

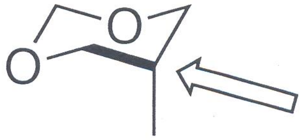


0.8 kcal/mol

A. Draw the Newman projections down the indicated bonds. (6 pts)





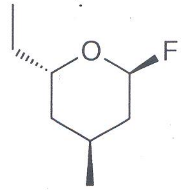


B. In the second structure, show on your Newman projection the strain that leads to destabilization of the methyl being axial. (2 pts)

C. Using the Newman projections and any other topic, explain the differences in A-values between cyclohexane and the other two rings. (5 pts)

D. What is the correct Klyne-Prelog terminology for the arrangement of the methyl group on the front carbon and the alkyl group on the rear atom of the first two Newman projections you drew in part A. (2 pts)

5) A. Draw the two chair conformations of the following molecule. (4 pts)



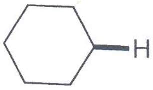
B. The A-value of methyl is 1.7 kcal/mol, ethyl is 1.8 kcal/mol, and a F is 0.4 kcal/mol. Using these values, calculate the energy difference between the two conformers. (2 pts)

C. Using further insights you may have about the conformers, how would you expect to adjust the energy difference? Explain your reasoning. (2 pts)

7) Consider the following molecules and their C-H BDEs.

106.3 Kcal/mol

96.5 Kcal/mol



94.5 Kcal/mol

a) Explain the trend in bond dissociation energies (3 pts).

b) If the Benson group increment for a methylene group is -4.9 Kcal/mol, calculate the heat of formation of the hydrocarbons above assuming no strain (2 pts).

c) Clearly we know cyclopropane is strained. How can this be if the CH bonds are actually stronger than in the other hydrocarbons? (1 pt)

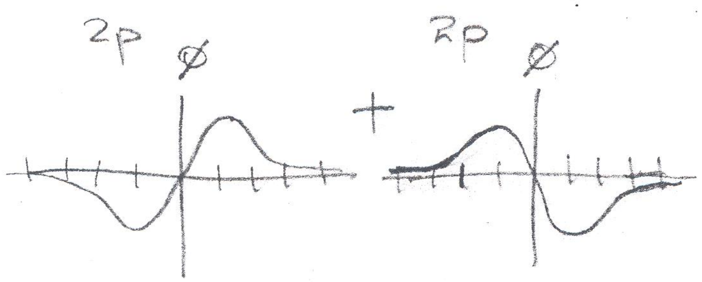
d) The heats of combustion for propane and cyclopropane are -500 Kcal/mol and -530 Kcal/mol respectively. Ignoring the fact that when you burn propane there is one more water created than when you burn cyclopropane, calculate the strain energy in cyclopropane (2 pts).

e) Finally, estimate the real heat of formation of cyclopropane (1 pt).

8) Keeping in mind the definition of hydride ion affinity, explain the following trend in HIAs (4 pts):

$NH_2\underset{\oplus}{C}H_2$	$HO\underset{\oplus}{C}H_2$	$CH_3\underset{\oplus}{C}H_2$	$F\underset{\oplus}{C}H_2$
218 Kcal/mol	243 Kcal/mol	273 Kcal/mol	290 Kcal/mol

9) Considering the differences in kinetic and potential energies between isolated atoms and bonded atoms, let's develop an explanation for why bonds form. Using the graphics of p orbitals such as shown here, explain and draw what happens to the kinetic energy (K.E.) of the p orbitals upon forming a bond and explain how potential energy (P.E.) changes. (4 pts)



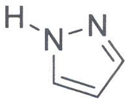
⇒ A sigma bond formed from the overlap of two 2p orbitals.

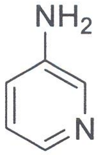
10) For the following molecules,

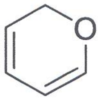
a) Indicate the hybridization of each heteroatom (N & O). Write your answer by that atom preceded by "a)" (2.5 pts).

b) Indicate which orbital(s) contain the lone pairs in those heteroatoms (N & O). Write your answer by that atom preceded by "b)" (2.5 pts).

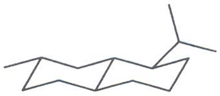
c) Label each species as aromatic, non-aromatic or antiaromatic (1.5 pts).

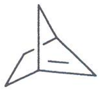


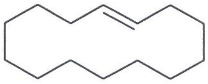


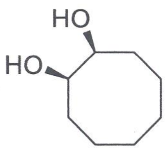


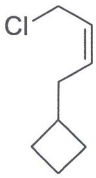
11) Identify the strain(s) in the following molecules as drawn (4pts).



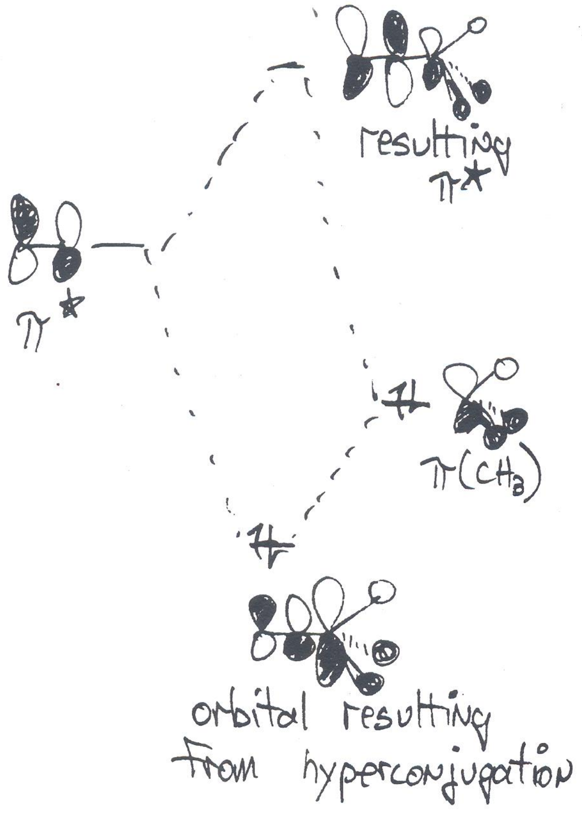








12) Here is the orbital mixing diagram creating the π* antibonding orbital of propene showing with the cartoon molecular orbitals, showing a donor acceptor mixing we call hyperconjugation.



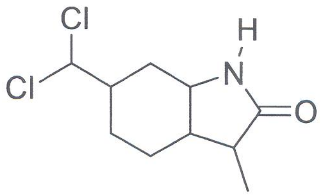
a) Using it as a starting point, draw a qualitative representation of the equivalent MOs corresponding to the analogous orbital mixing of CF_3-$CH=CH_2$ next to the original diagram above and point out the differences (For simplicity model the F atoms as spheres just like H atoms) (5 pts).

b) The heat of hydrogenation for propene is roughly -30 Kcal/mol, whereas the one for CF_3-$CH=CH_2$ is about -40 Kcal/mol. Which alkene is more stable given these values? (1 pt)

c) Using the orbital mixing diagrams from the previous page, devise an explanation that lends credibility to your answer to part b (2 pts).

THIS QUESTION BROUGHT TO YOU BY NABISCO

13) Use the following structure to answer the questions below.



a) Label the face of the carbonyl group that you can see as either Re or Si (1 pt).

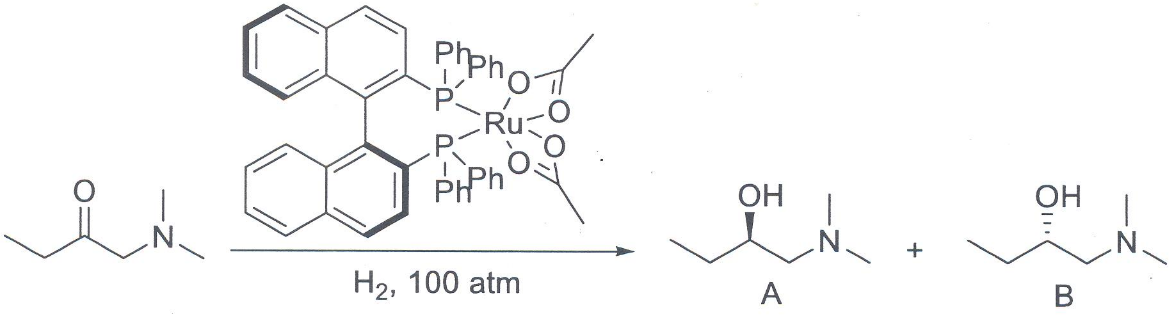
b) Identify all prochiral centers by circling them (2 pts).

c) Identify all stereocenters by drawing a star by them (2 pts).

d) Is the carbonyl group enantiotopic, diastereotopic or homotopic? (1 pt)

e) Are the two chlorine atoms enantiotopic, diastereotopic or homotopic? (1 pt)

14) The following reaction is catalyzed by a chiral BINAP derivative.



When the reaction takes place as shown the ratio of A to B is 1 to 89, whereas the other enantiomer of the catalyst leads to an 89 to 1 ratio of A to B.

a) Estimate the energy difference between A and B (2 pts).

b) Estimate the energy difference between the transition state for the reactions that set the stereochemistry leading to A and B (2 pts).

c) Circle the stereocenter(s) in said catalyst (1.5 pts).

d) Is the reaction stereoselective? (2 pts)

e) Is the reaction stereospecific? (2 pts)

f) Is the ketone homotopic, enantiotopic or diastereotopic? (2 pts)

15) Are the faces of the following carbonyls homotopic, enantiotopic or diastereotopic? (5 pts)