**Chemistry 386J**
**Anslyn**
**Oct 12, 2013**
**Exam 1**

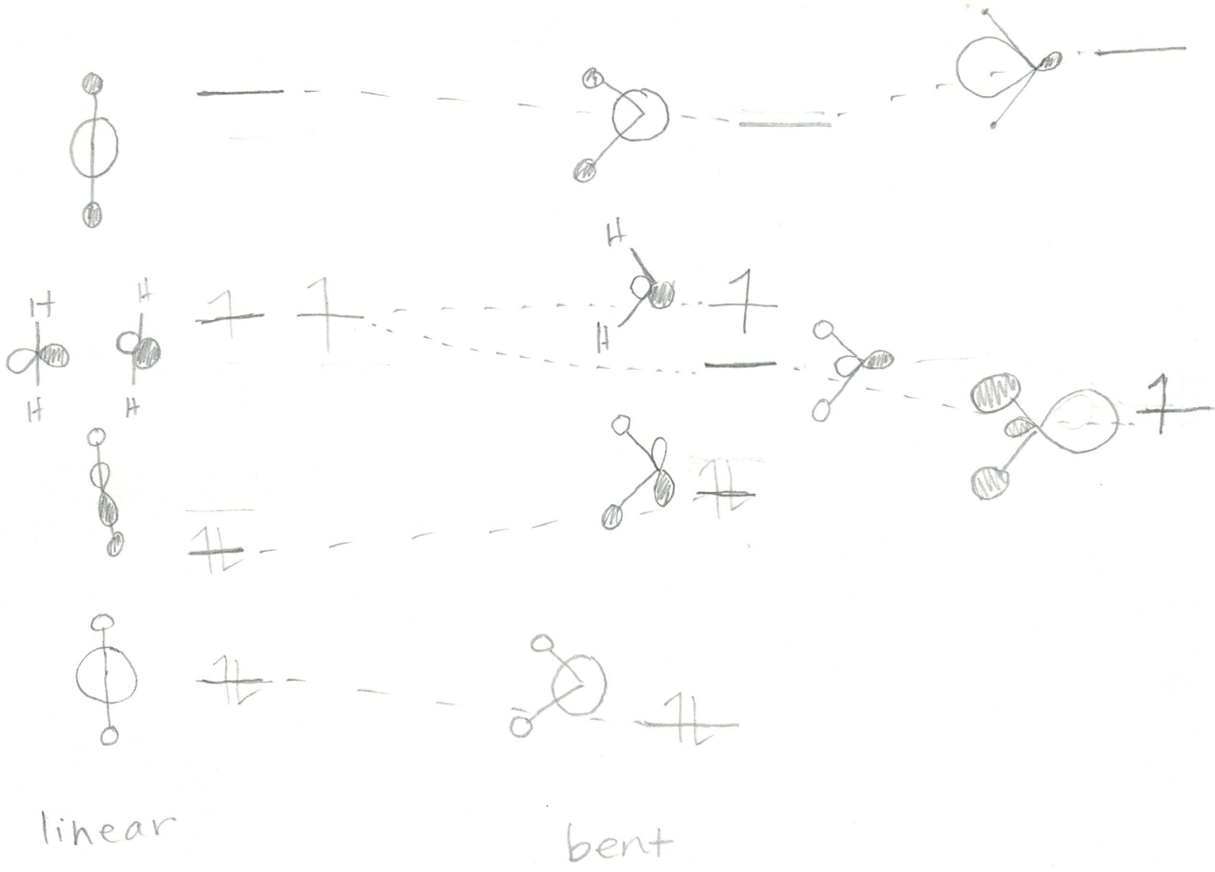
**Name:** Key

1. ___________ (15 pts)
2. ___________ (6 pts)
3. ___________ (8 pts)
4. ___________ (10 pts)
5. ___________ (9 pts)
6. ___________ (8 pts)
7. ___________ (20 pts)
8. ___________ (6 pts)
9. ___________ (10 pts)
10. ___________ (11 pts)
11. ___________ (18 pts)
12. ___________ (15 pts)
13. ___________ (8 pts)
14. ___________ (7 pts)

**TOTAL (151 pts)** ___________

1. (15pts)

a) Draw the Walsh diagram of linear :$CH_2$. Next, distort the geometry to be bent and draw the resulting orbitals. (6 pts)

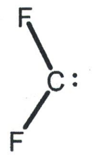


b) Experimental electron paramagnetic spectrum (EPR) measurements show that singlet carbene adopts an H-C-H angle of 102° while triplet carbene adopts an H-C-H angle of 140°. Using the MO diagram you drew above, explain why triplet carbene has a larger H-C-H bond angle compared to singlet carbene. (3 pts)

larger bond angle = less bent character
Triplet is spin unpaired so need to occupy two separate orbitals. Only one $e^-$ is stabilized by becoming bent, as opposed to $2e^-$ for singlet. Balanced by putting $2e^-$ in higher E,

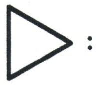
c) Usually, simple carbenes present a triplet ground state, yet this configuration can be selectively changed and stabilized by appropriate substituents. Difluorocarbene and cyclopropenylidene prefer the singlet state configuration.

i) For the first case explain using the fact the F is very electronegative and how it changes the orbital character that carbon uses for its bonding. (3 pts)



The electronegativity of F gives more p character to the C-F bond, which is more bent, thus stabilizing more the singlet state

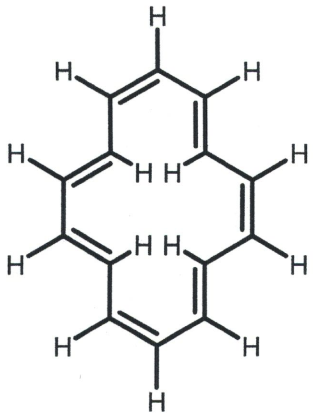
ii) For this second case, again explain the singlet ground state by considering the orbital character, but now in the C-C bonds. (3 pts)



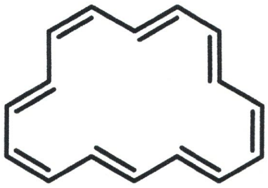
Bond angle is smaller, which gives more p character to the C-C bonds, thus stabilizing more the singlet state.

2. (6 pts)

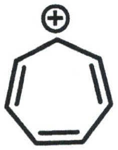
a) According to the rules of aromaticity, predict if the following annulenes are aromatic or anti-aromatic. (3 pts)



Aromatic

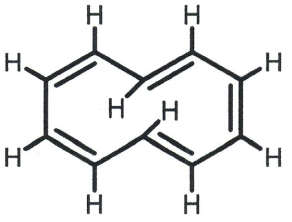


Anti-aromatic



Aromatic

b) [10]-annulene is apparently aromatic because it obeys Huckel's rule for aromaticity. However, this structure is reasonably reactive, similar to normal alkenes. Briefly explain why this molecule does not show the hallmarks of aromaticity. (3 pts)

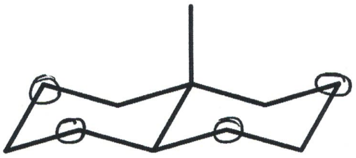


[10]-annulene

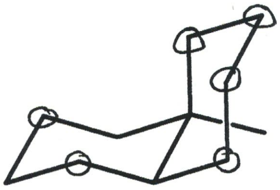
The hydrogens at the center increase the steric interaction which make the annulene non-planar, decreasing its aromaticity and increasing reactivity.

3. (8 pts)

a) Using Benson group increments provided on the previous page, calculate the ΔH°$_f$ for the following structures assuming no strain (given no strain, they are both the same). (4 pts)



**A**



**B**

• $C(H_2)(C)_2$ $-4.93(8) = -39.44$

* $C(H)(C)_3$ $-1.90$

$C(C)_4$ $0.50$

$C(H)_3(C)$ $\underline{-10.20}$

$-51.04$ kcal/mol

b) Count up how many gauche strains are present in A and B due to any axial substituents. Which stereoisomer is higher in energy and estimate by how much. (4 pts)

A

+1

0.9kcal/mol(4) =

3.6kcal/mol

B

+1

0.9kcal/mol (6) =

5.4kcal/mol

+1

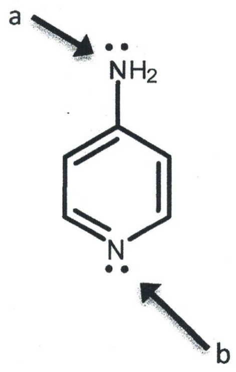
B is higher in erg by

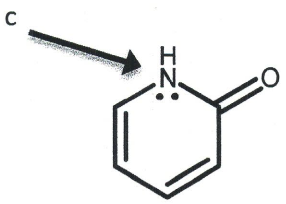
~1.8 kcal/mol

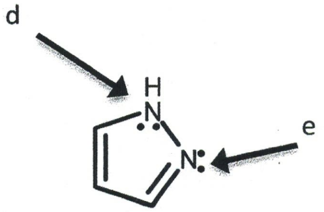
+1

4. Using the following table, assign the hybridization of each nitrogen atom, and predict the type of orbital that the lone pair resides in for each of the following structures. (10 pts)

| Hybridization of nitrogen atom | Type of orbital for nitrogen lone pairs |
|---|---|
| a $sp^2$ | p |
| b $sp^2$ | $sp^2$ |
| c $sp^2$ | p |
| d $sp^2$ | p |
| e $sp^2$ | $sp^2$ |

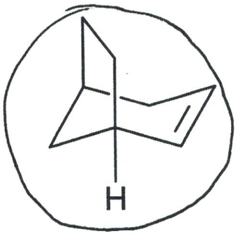


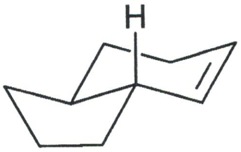




5. (9 pts)

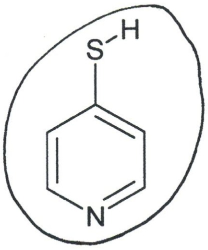
a) Circle the structure that has a higher bond dissociation energy, and explain your choice. (3 pts)

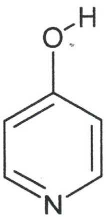




Homolytic cleavage creates a
more strain structure or formation
of Anti-Bredt olefin.
less stable

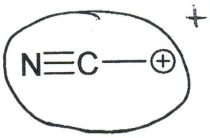
b) Circle the structure that is the most acidic, and explain your choice. (3 pts)





- S-H weaker bond than O-H
- Larger Sulfur atom can delocalized the negative charge better than O atom.

c) Circle the structure that has a higher hydride affinity value, and explain your choice. (3 pts)



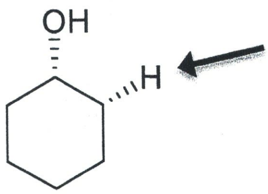
+1

(or EWgroup)

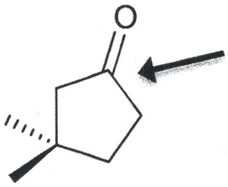
+2

Positive charge close to an sp group is
more destabilizing than sp2 that
has less s character, and is less EWG.
More unstable sp has higher HIA.

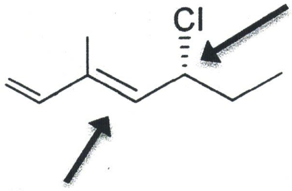
6. Circle the correct descriptor to what the arrows point at. (8 pts, 2 each)



[✓ Pro R] or Pro S



Re or [✓ Si] carbonyl face that projects out of the page.



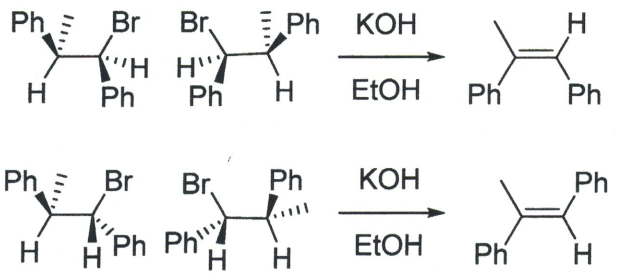
[✓ R] or S

[✓ E] or Z

7. For the following reactions indicate the answer according to the following instructions. (20 pts, 5 each)

a) Write "yes" or "no" to indicate if the reactions are stereoselective.
b) Write "yes" or "no" to indicate if the reactions are stereospecific, or "n/a" (not applicable).
c) Write the stereochemical relationship for reactants (enantiomers, diastereomers or the same).
d) Write the stereochemical relationship for products (enantiomers, diastereomers or the same).
e) Write "yes" or "no" to indicate if the reaction gives a racemic mixture, or "n/a" (not applicable).

i)



a Yes

b Yes

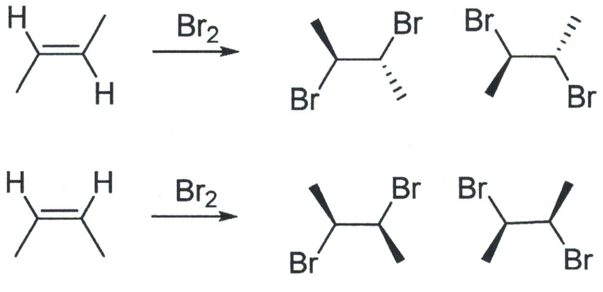
c top reaction Enantiomers

bottom reaction Enantiomers

d Diastereomers

e N.A.

ii)



a yes

b Yes

c Diastereomers

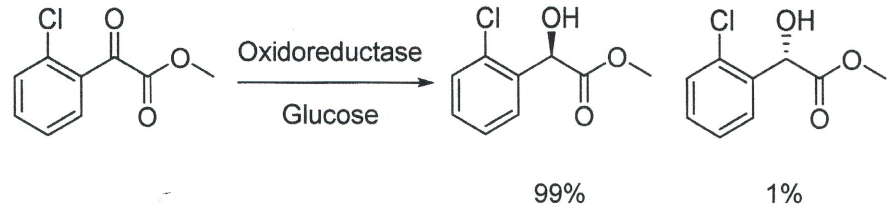
d top reaction Same

bottom reaction Enantiomers

e top reaction N.A.

bottom reaction Racemic Yes

iii) Remember from class that enzymes represent chiral environments



a Yes

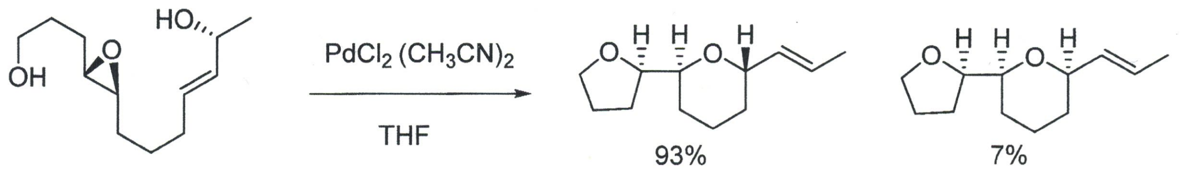
b N.A.

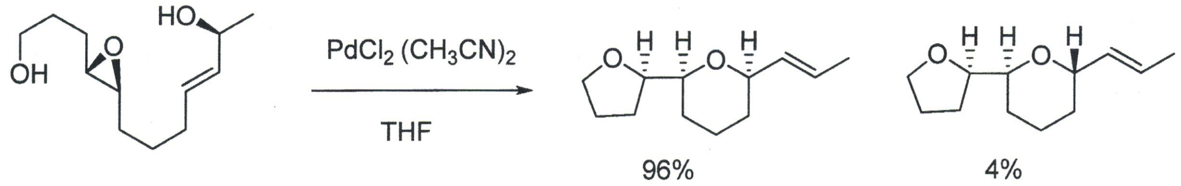
c Same

d Enantiomers

e No

iiii)





a Yes

b Yes

c Diastereomers

d top reaction Diastereomers

bottom reaction Diastereomers

e top reaction N.A.

bottom reaction N.A. or No

8. (6 pts)

a) Indicate the pKa values for the acid and the conjugate acid in the following reaction. (2 pts)

~4-5

~9-10

b) Estimate the equilibrium constant of the above reaction at 25°C. (2 pts)

$K_{eq} = 10^{\Delta pKa} = 10^5$

c) Estimate the Gibbs free energy of the above reaction at 25°C. (2 pts)

$\Delta G^\circ = -7$ kcal/mol

9. (10 pts)

a) Write the acid/base reactions of HCl in water and HCl in acetonitrile. (4 pts)

i) Circle the lyonium ions

ii) Indicate to which side each equilibrium lies

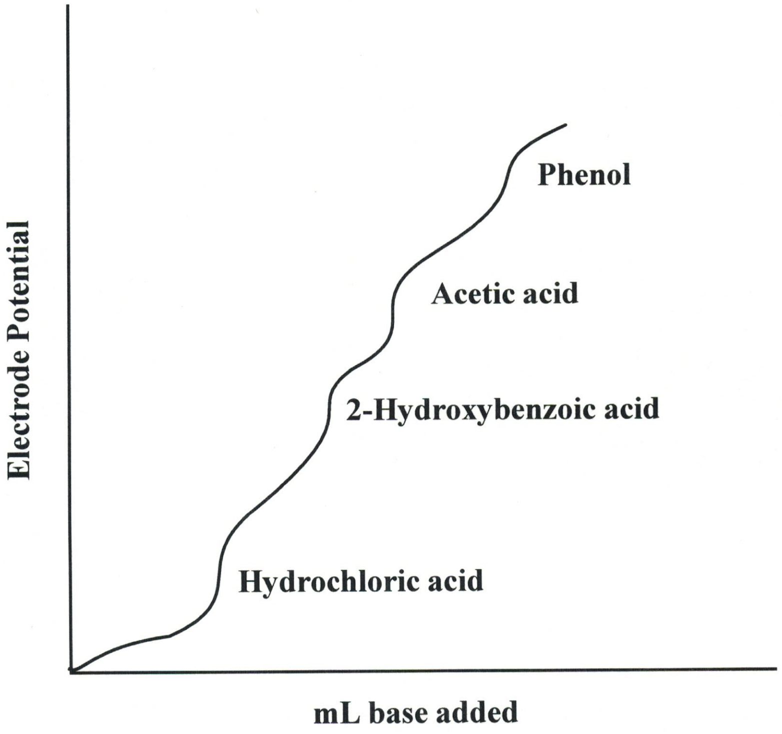
$$H-Cl + H_2O \longrightarrow \boxed{H_3O^{\oplus}} + Cl^{\ominus}$$

$$H-Cl + CH_3C\equiv N \leftrightharpoons \boxed{CH_3C\equiv \overset{\oplus}{N}-H} + Cl^{\ominus}$$

b) Is the p$K_a$ of HCl in acetonitrile higher or lower than it is in water? Explain. (2 pts)

H-Cl is less acidic in $CH_3C\equiv N$ b/c the lyonium $CH_3C\equiv \overset{\oplus}{N}H$ is a stronger acid than $H_3O^{\oplus}$ b/c N has more s-character than O. ∴ pKa is HIGHER

c) The following graph shows a pH titration in acetonitrile where several acids have been mixed together. The name of the acid is listed near its equivalence point.



i) Based on the above pH titration, write the following acids in order of increasing acidity, weakest on the left, strongest on the right: hydrochloric acid, phenol, acetonitrile, acetic acid, 2-hydroxybenzoic acid. (2 pts)

acetonitrile < phenol < acetic acid < 2-hydroxybenzoic acid < HCl

ii) Estimate between which two acids on the above curve the buffer region of hydronium would lie. (2 pts)

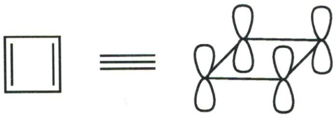
Between HCl and 2-hydroxybenzoic acid

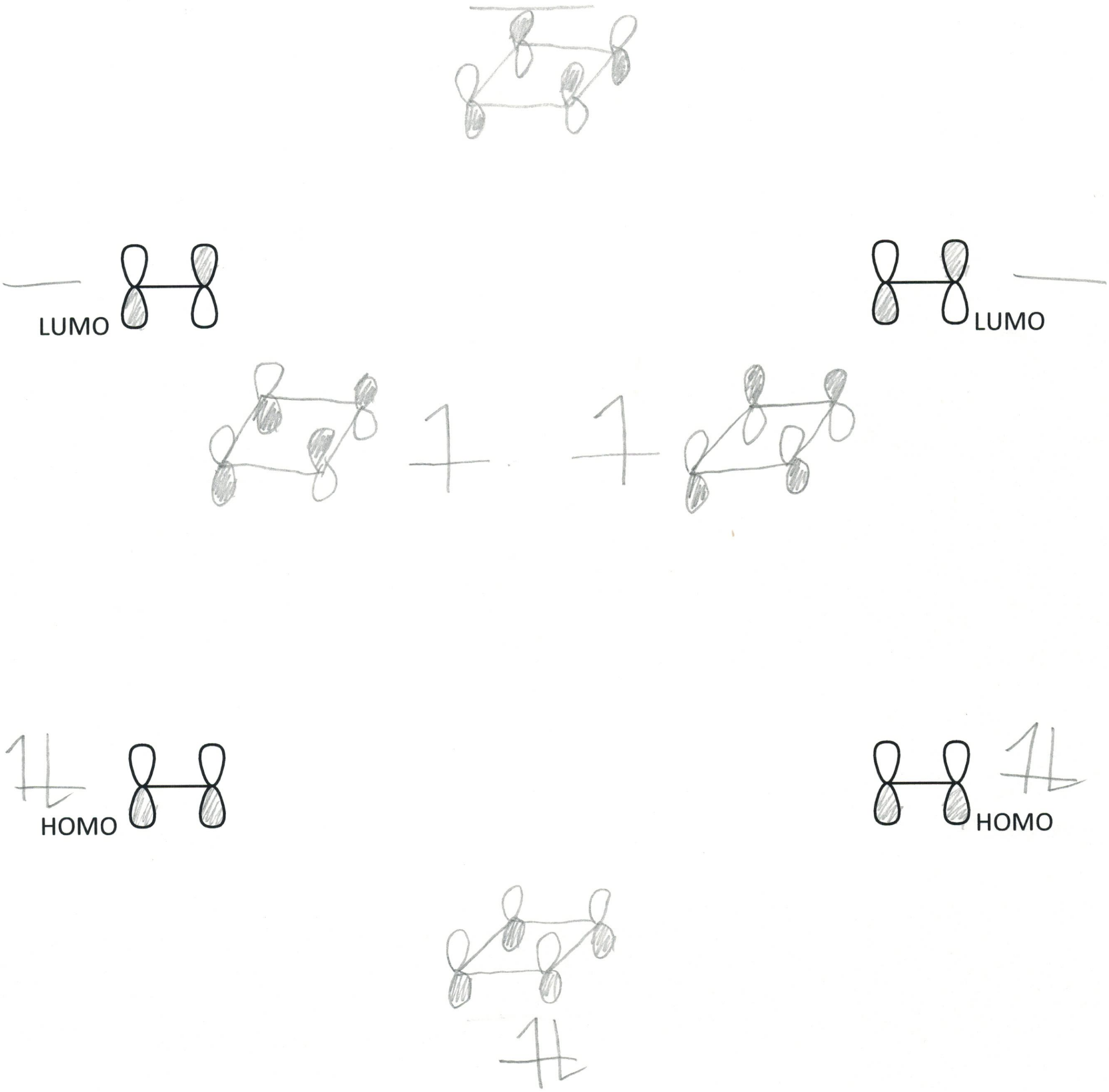
iii) Explain why the acid strength of HCl can be measured in acetonitrile but cannot be measured in water. Name the effect responsible for this. (2 pts)

H-Cl completely dissociates in $H_2O$ but not in $CH_3C\equiv N$. Can never titrate HCl in $H_2O$ b/c it's all $H_3O^+$ as HCl is stronger than $H_3O^+$. when titrating $H_3O^+$ on a pH titration curve, it is "levelled". This is the levelling effect.

10. (11 pts)

In class, Dr. Anslyn said we would learn why cyclobutadiene is best described as a diradical in Chapter 14. Luckily, you already have the tools to rationalize the diradical structure of cyclobutadiene! Create cartoons of the molecular orbitals for cyclobutadiene by mixing together the HOMOs of two ethylene molecules and also mixing together the LUMOs of two ethylene molecules. The relative energies of the mixed orbitals will be important here; be careful where you place them on the page! To make your diagrams clear, draw cyclobutadiene viewed from an angle, as drawn shown in the following structure with p-orbitals. (8 pts)





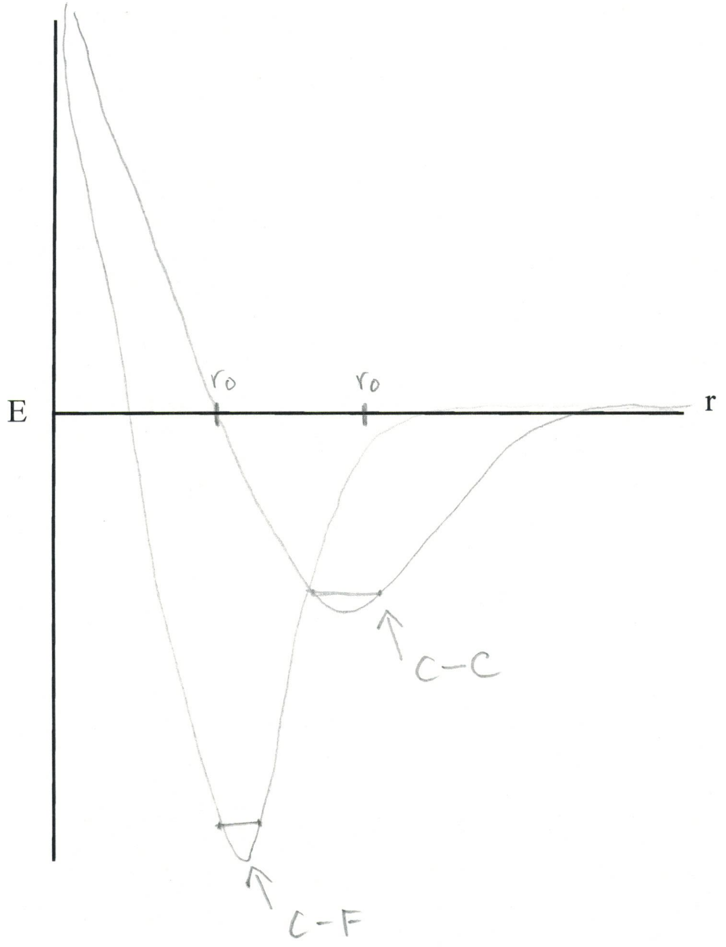
10. continued

Populate the molecular orbitals you constructed on the previous page with the appropriate amount of electrons. Based on the electron population, explain why cyclobutadiene is best described as a diradical. (3 pts)

Two degenerate orbitals created when we subtract the HOMOs and add the LUMOs. According to Hund's rule, we fill these sequentially. Therefore each orbital has 1e⁻ like a radical.

11. (18 pts)

a) Draw the Morse potentials for the C-C stretch and the C-F stretch in 1,2-difluoroethane on the diagram below. Clearly label each curve with the appropriate bond. Explain how the relative bond strengths and lengths are reflected in your drawing. (4 pts)

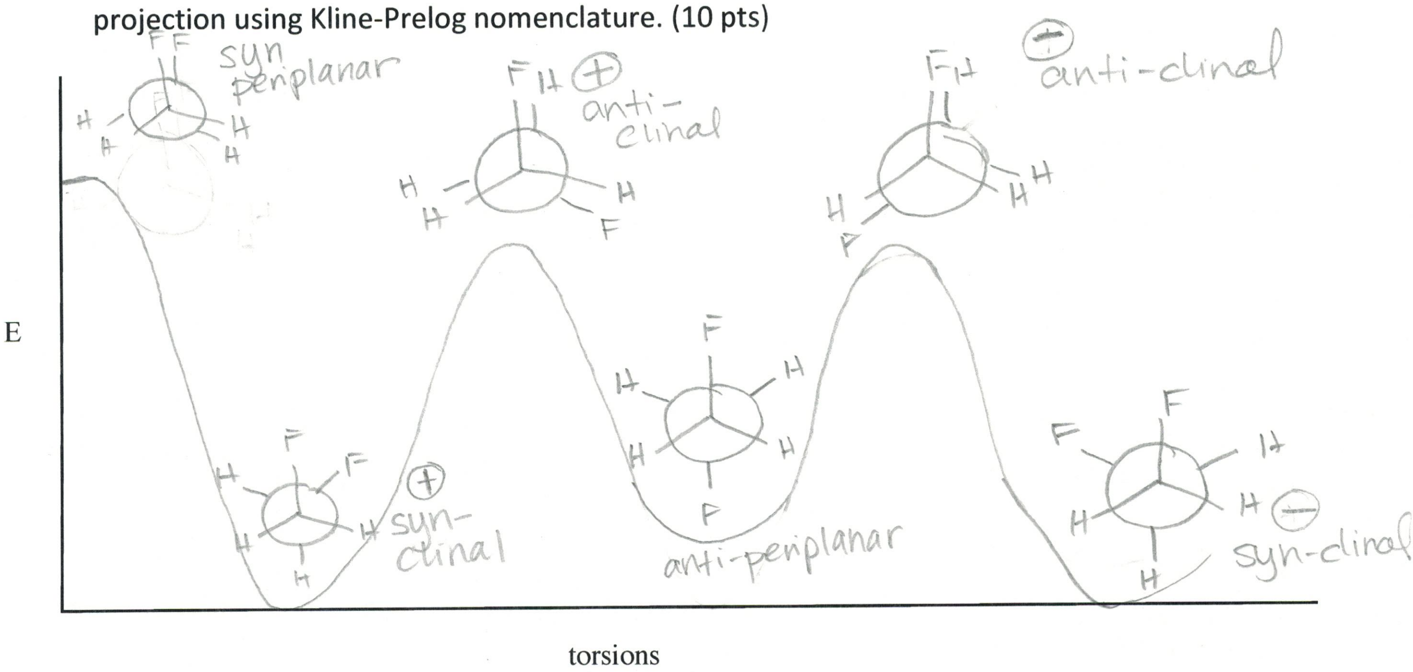


- weaker C-C bond has shallower and potential

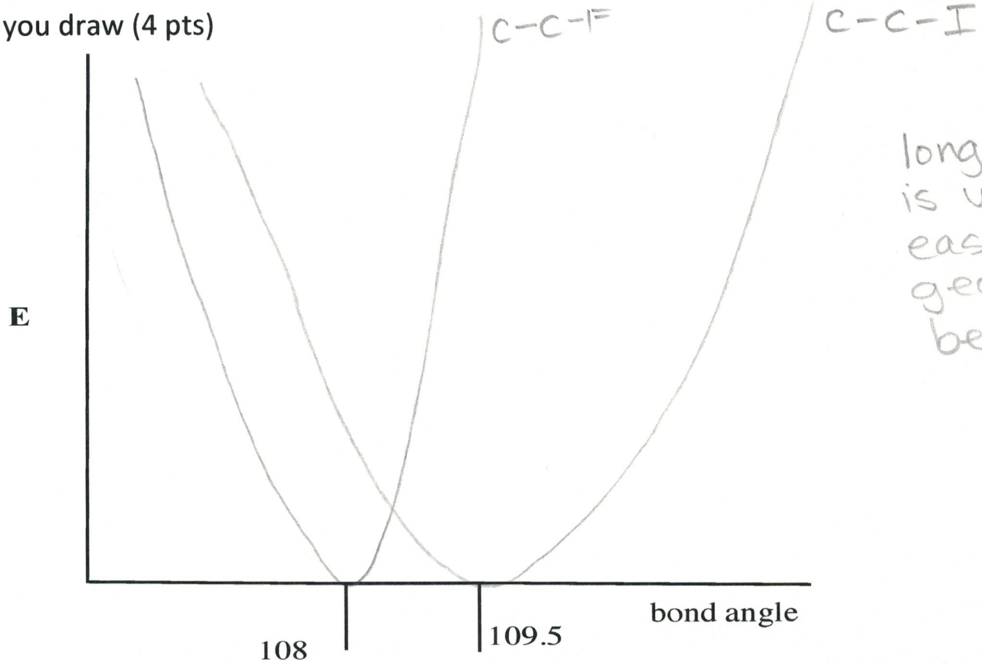
- C-C bond is longer and morse potential is wider

11. continued

b) Draw the torsional energy diagram of rotation about the C-C bond in 1,2-difluoroethane below. Write the appropriate Newman projection next to each energy minimum and maximum. Indicate the relationship between the two fluorines for each Newman projection using Kline-Prelog nomenclature. (10 pts)



c) On the diagram below, draw potential energy diagrams for both the C-C-F bend in fluoroethane and the C-C-I bend in iodoethane. The optimal C-C-F bond angle is ~108° while the optimal C-C-I bond angle is ~109.5°. Explain the relative shapes of the curves you draw (4 pts)

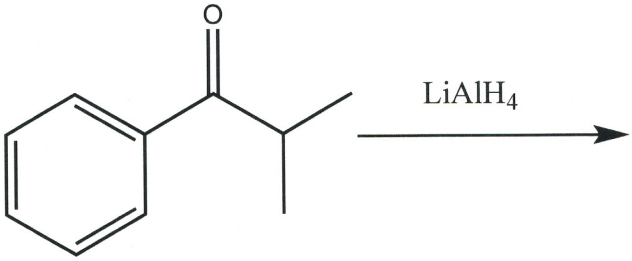


longer C-I bond
is weaker
easier to distort
geometry to
bend

12. For the following reactions it is **not** necessary to draw the products. Instead for each reaction (15 pts, 3 each):

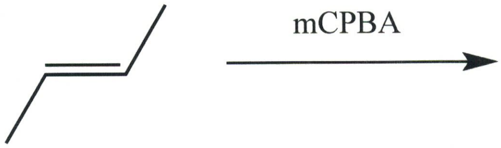
a) Identify the faces or the indicated groups as homotopic, enantiotopic, or diastereotopic
b) State whether *one* or *more than one* product is formed
c) If multiple products are formed, state whether they are formed in *equal* or *unequal* ratios. If only one product is formed write "n/a"

i)



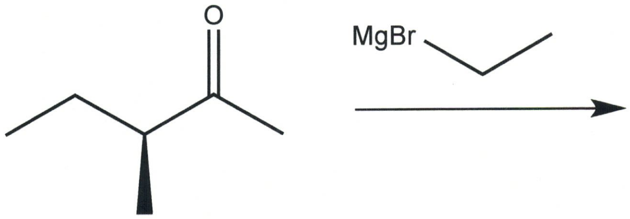
enantiotopic
more
equal

ii)



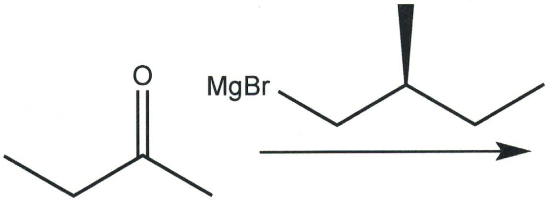
enantiotopic
more
equal

iii)



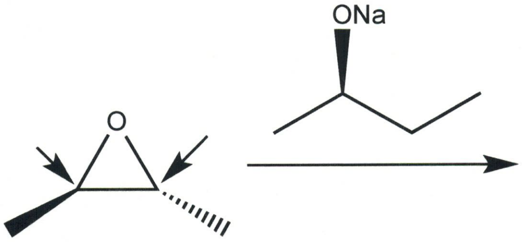
diastereotopic
more
unequal

iv)



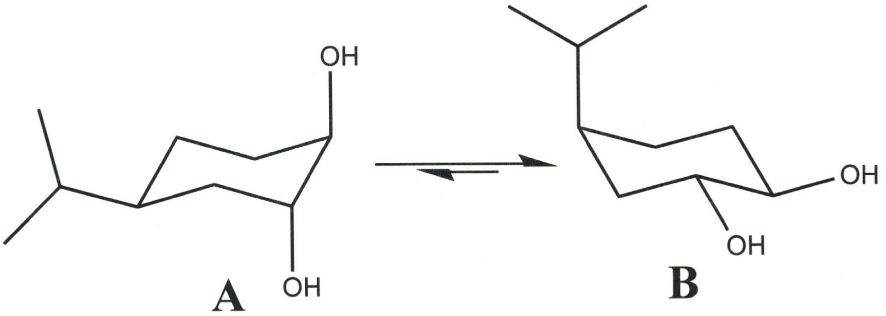
enantiotopic
more
unequal

v)



homotopic
one
n/a

13. The equilibrium of the following chair forms of 4-isopropylcyclohexane-1,2-diol lies towards the **B** form. This structure is more stable than **A** by 1.9kcal/mol. (8 pts)



a) Provide an estimate of the ratio of **A:B** at equilibrium. (2 pts)

between 0.1 and 0.01 A to 1 B

— OR —

10 – 100 B : A

b) The A value of of an isopropyl group is 2.2 kcal/mol and that of an alcohol group is 0.6 kcal/mol. Calculate the expected ΔG° based on A values and using this value provide an estimate of the ratio of **A**:**B**. (3 pts)

$2.2 - 2(0.6) = 1.0$ in favor of A

5 – 10 A : B

c) What interaction(s) exist in **B** but not in **A** that contribute to the greater stability of **B**? (3 pts)

**Hint:** The stability of **B** is magnified in the gas phase.

equatorial OH groups can H-bond
axial OH groups cannot

14. Circle any chiral molecules in the set below. (7 pts)