Professor Pete Marsden July 6, 2012

Chemistry 3A –Exam #1

Student Name: _____

Student ID Number: _____

TA or Section: _____

Point Breakdown

Problem 1	_____	/ 18
Problem 2	_____	/ 16
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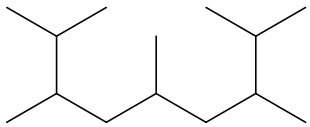
Total	_____	/ 150

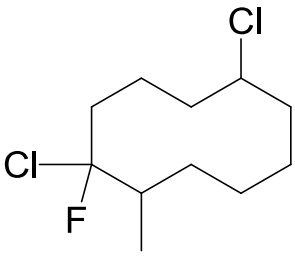
Check that you have 11 pages.

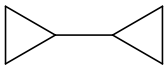
You will have 120 minutes for this exam.

REMEMBER: Opposites attract, the octet rule is super important and formal charges are necessary.

1. A. Provide systematic names for the following molecules. Use common names where appropriate. (6 pts)







1. B. Match the names with the structure by placing the letter for the structure next to the name. Note: you can solve this problem without knowledge of each functional group. (12 pts)

fluoro*neo*pentane ☐

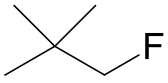
dimethylsulfoxide ☐

*tert*butylthiol ☐

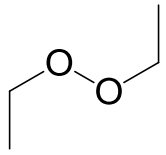
diethylperoxide ☐

*iso*butylazide ☐

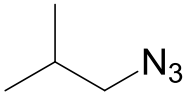
trimethyloxonium ☐



A

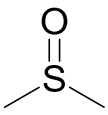


B

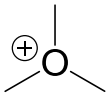


C

D



E



F

2. A. Construct the molecular orbital diagram for the neutral species CF_2. Use the following guidlines and labeling schemes. Please be sure to include everything asked for below. (12 pts)

a. Assume the carbon atom is **sp^2** hybrized and the flourine atoms are each **sp^3** hybridized
b. Indicate the relative energy levels of any atomic and hybrid orbitals on both the left and right of the diagram
c. Clearly indicate which orbitals are being combined to make MOs
d. Fill in all of the electrons
e. Label all of the levels (σ, π, π^*, non-bonding, etc.)
f. Label the HOMO and LUMO

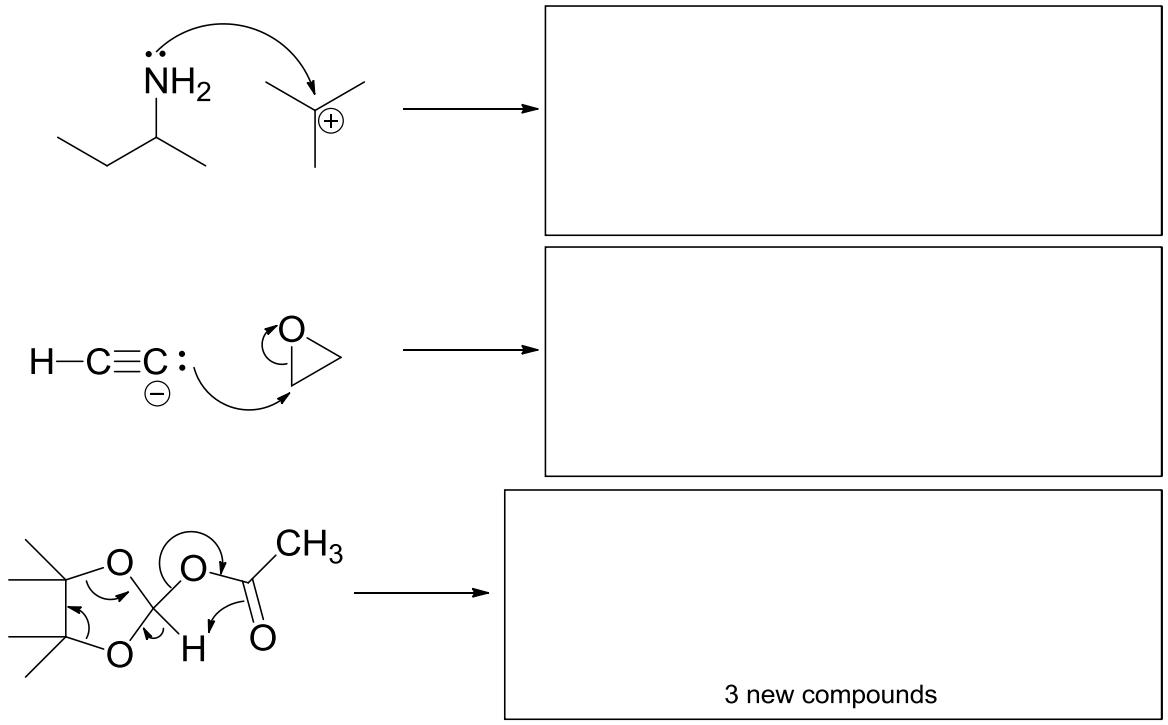
Carbon

Fluorine

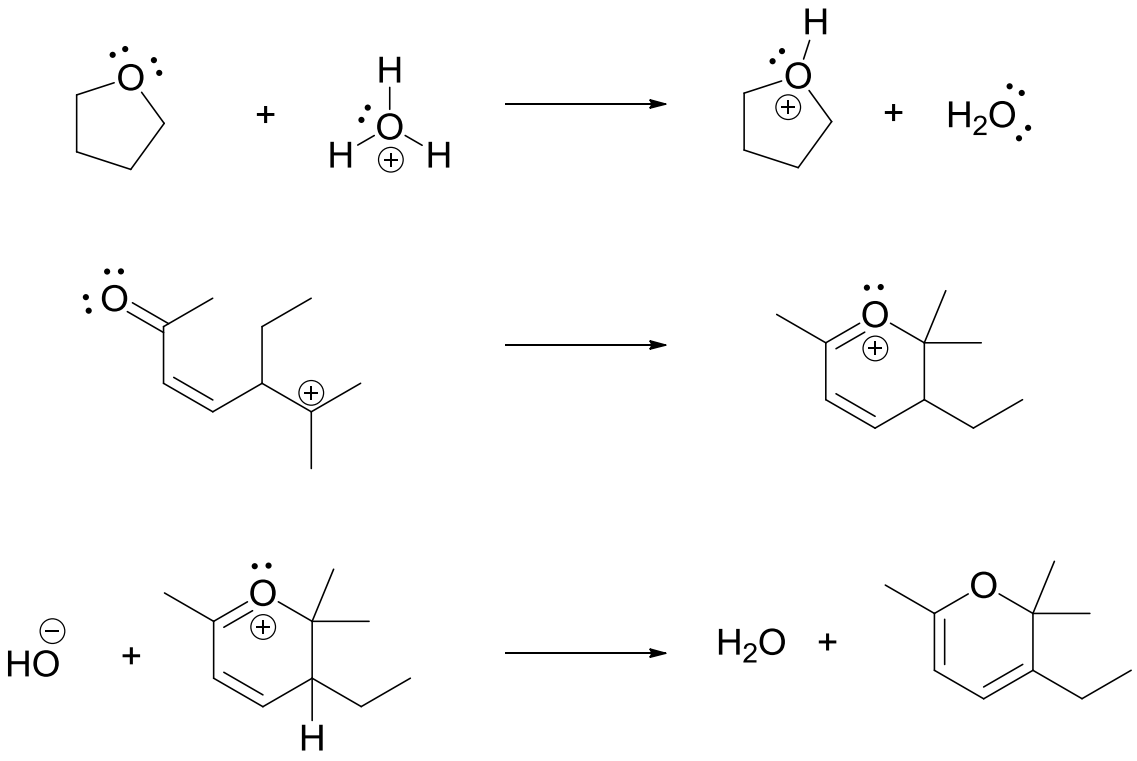
Molecular Orbital Diagram for CF_2

2. B. Draw a 3D image of CF_2, clearly showing any empty orbitals. You may use our template to show the directionality of any lone pairs of electrons on carbon. You may ignore the lone pairs on the fluorine atoms. (4 pts)

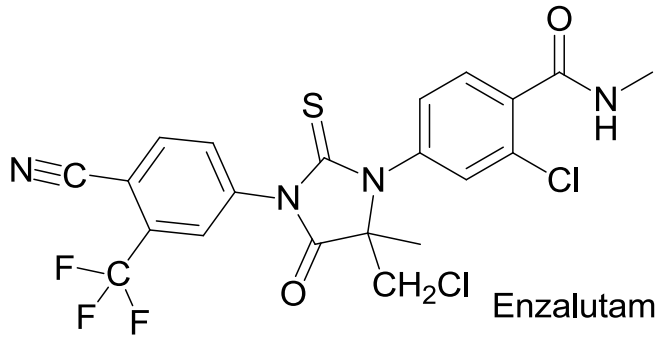
3. A. Provide the products following the electron-pushing arrows shown. (9 points)



3. B. Add appropriate electron-pushing arrows for the following reactions. (12 points)

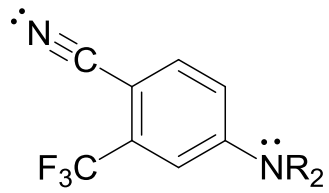


4. Enzalutamide is a recently approved prostate-cancer drug. This molecule interacts with an androgen receptor which is responsible for transporting testosterone in cells. The following questions will help you understand its reactivity. (45 points)

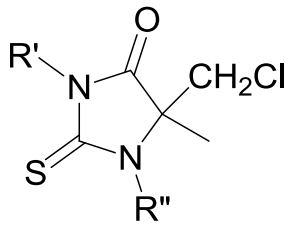


Enzalutamide

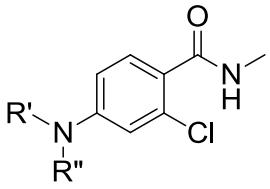
4. A. Provide resonance structures where all atoms have filled octets for the following portions of Enzalutamide. Pay special attention to directions in each box. (12 points)



One more contributor with **two charged nitrogen atoms.**

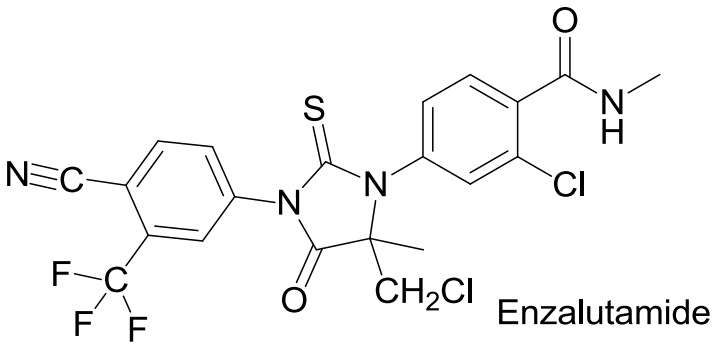


One more contributor with **two charged nitrogen atoms.**



Two more contributors, each having a **different nitrogen atom with a charge.**

4. B. Using your resonance structures from 4.A., determine which nitrogen atom in Enzalutamide has the most partial negative charge. Circle it on the structure below. (2 points)

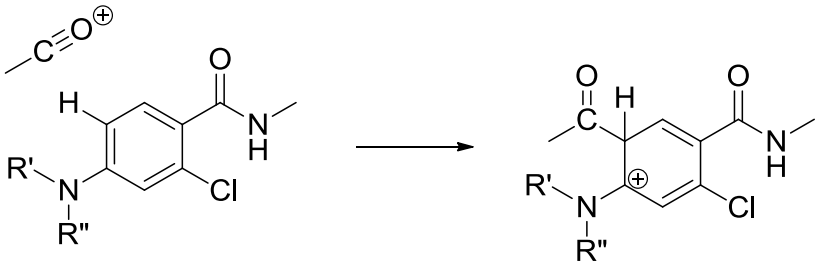


Enzalutamide

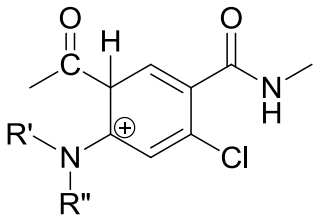
4. C. Using your resonance structures from 4.A., determine the hydrogen atom in Enzalutamide that is the most acidic. Draw a square around it on the structure above. (2 points)

4. D. How many **sp** hybridized atoms are there in Enzalutamide? _____ (2 points)

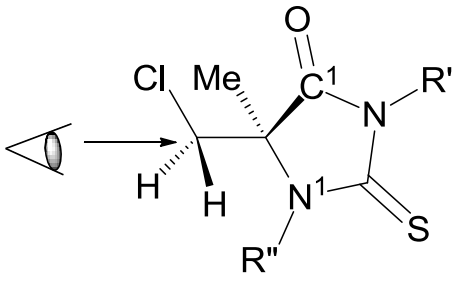
4. E. Add electron-pushing arrows to the following reaction sequence. (3 points)



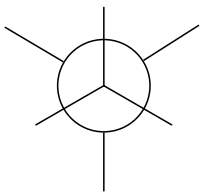
4. F. Provide 2 more resonance structures **with filled octets** for the cation below that clearly show relocation of the positive charge. (6 points)



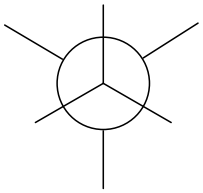
4. G. Draw a Newman Projection along the indicated bond below. (3 points)

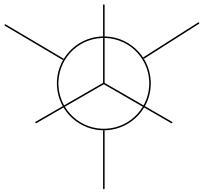


0º



4. H. Starting from the Newman Projection above as 0º, rotate the BACK CARBON COUNTER CLOCKWISE in 120º increments. (6 points)





120º 240º

4. I. For each of the three Newman Projections that you have drawn, (0º, 120º, 240º), clearly describe any steric interactions among non-hydrogen substituents in the chart below. (6 points)
Please use the abbreviations "C^1" and "N^1" when describing the interactions.

Steric Interactions

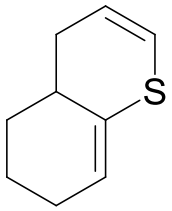
0º	
120º	
240º	

4. J. If the relative size of the groups is Cl < Me < "C^1" < "N^1" , which conformational isomer is the lowest energy? (3 points)

LOWEST ENERGY : _____º

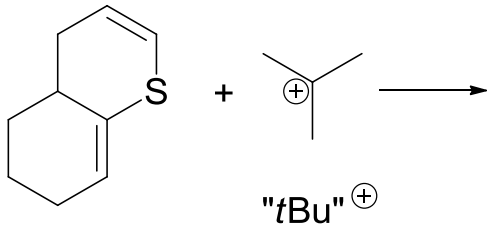
5. Sulfonium ions contain a positively charged sulfur atom. Let's play with a couple of them, below. (18 points)

5. A. Provide 2 more resonance structures of the compound shown below. (6 points)



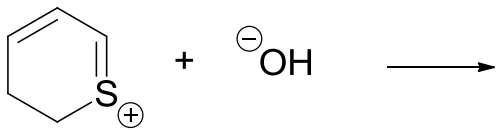
Two more contributors with **filled octets.**

5. B. Based on the resonance contributors that you drew, predict the two products where new carbon-carbon sigma bonds are formed in the reaction below. You may use the abbreviation *t*Bu when drawing the new products. Be sure to show the products such that each atom has a filled octet. (6 pts)



+

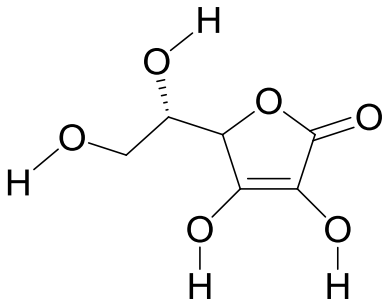
5. C. Predict the two products where new carbon-oxygen sigma bonds are formed in the reaction between the hydroxide anion and the sulfonium ion below. (6 points)



sulfonium hydroxide

+

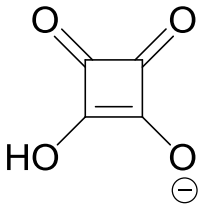
6. A. There are four different OH bonds in ascorbic acid (vitamin C). Which of those hydrogens is the most acidic? Circle it on the structure below. (3 points)



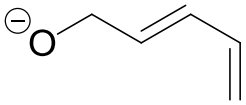
Vitamin C

6. B. Justify your answer to 6.A. using words and resonance structures. (5 points)

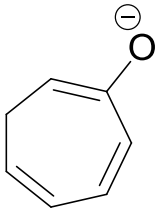
6. C. Order the following compounds from MOST BASIC (1) to LEAST BASIC (3). (3 points)



Rank : ____



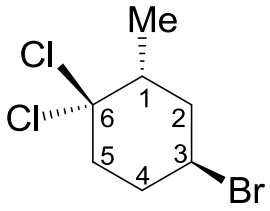
Rank : ____



Rank : ____

6. D. Explain your choice for the MOST BASIC compound. (3 points)

7. For this question, you will be analyzing the chair structure of the following molecule. (18 pts)

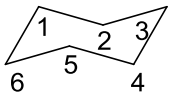


7. A. Draw the substituents in the proper orientation on the chair structure provided below. (4 pts)

7. B. Draw the chair-flipped structure in the box on the right. (4 pts)

7. C. Using the data provided on the last page of the exam, calculate the ΔG for the chair-flip and write the answer in the appropriate box. Be sure to show your work. (5 pts)

7. D. Based on your ΔG, draw in the equilibrium arrow for this chair flip in the appropriate box. (2 pts)



Chair

ΔG =

equilibrium arrow

Chair-flipped structure

Show work:

7. E. Would you expect the experimental ΔG to be higher, lower, or the same as the one you calculated? Explain. (3 pts)

You may tear out this page for your own reference.

Abbreviated Periodic Table

Valence e^-	3	4	5	6	7
	B	C	N	O	F
			P	S	Cl
					Br

Chair-flipping energies

The energies reported are from flipping the cyclohexane conformer with the indicated substituent **equatorial to the conformer with the substituent axial**.

Substituent	ΔG° (kcal/mol)	Substituent	ΔG° (kcal/mol)
H	0	F	0.25
Me	1.70	Cl	0.52
Et	1.75	Br	0.55
*i*Pr	2.20	I	0.5
*t*Bu	5	SH	1.0
NH_2	1.5	CH_3O	0.75