Professor Pete Marsden August 10, 2012

Chemistry 3A – Final Exam

Student Name: _____

SID Number: _____

TA or Section: _____

Place an X in the line if you are making up an incomplete : _____
Which semester did you receive the "I"? : _____

Point Breakdown

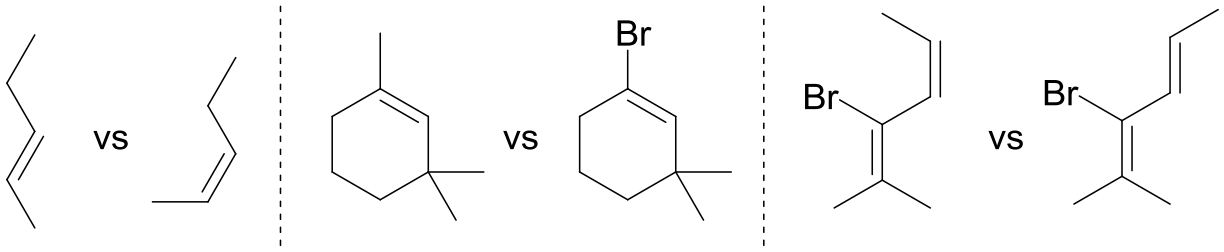
Problem 1	_____ / 20	Problem 6	_____ / 12
	_____ / 16		_____ / 14
Problem 2	_____ / 18		_____ / 11
Problem 3	_____ / 16	Problem 7	_____ / 11
	_____ / 16	Problem 8	_____ / 16
Problem 4	_____ / 10		_____ / 12
	_____ / 5		_____ / 16
Problem 5	_____ / 20		
	_____ / 12	Total	_____ / 225

Check that you have 17 pages.

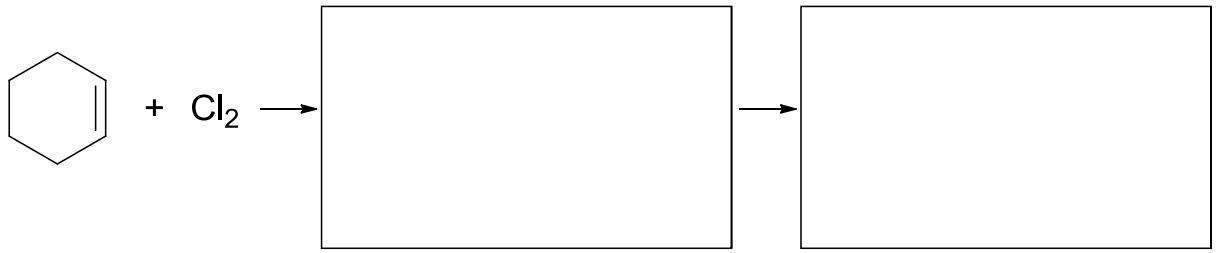
You will have 180 minutes for this exam.

Remember : CARBOCATION STABILITY IS IMPORTANT!!!!!!!!

1. A. Circle the "Z" alkene in each pair. (3 points)



1. B. Draw the key intermediate that leads to the anti addition of chlorine across the double bond below. (4 points)



Key intermediate Product

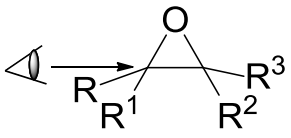
1. C. Draw the product of the above reaction in the appropriately labeled box. (3 points)

1. D. What is the generic name of the "key intermediate" from 1.B.? (2 points)

1. E. Define "reduction" of a double bond using terms learned in class. (2 points)

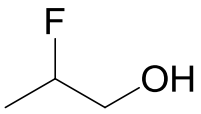
1. F. Are epoxides in the staggered or eclipsed conformation? (2 points)

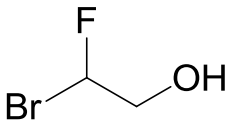
1. G. Add appropriate wedges and dashes to the "R" groups of the epoxide below and then draw the Newman Projection along the indicated bond. (4 points)

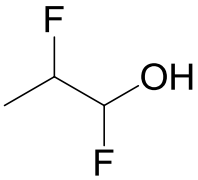


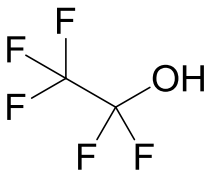
Newman Projection

1. H. Rank the following molecules from MOST ACIDIC (1) to least acidic (4). (4 points)



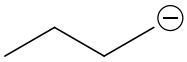


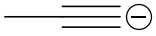


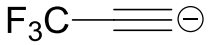


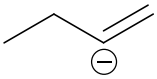
_____ _____ _____ _____

1. I. Rank the following molecules from MOST BASIC (1) to least basic (4). (4 points)



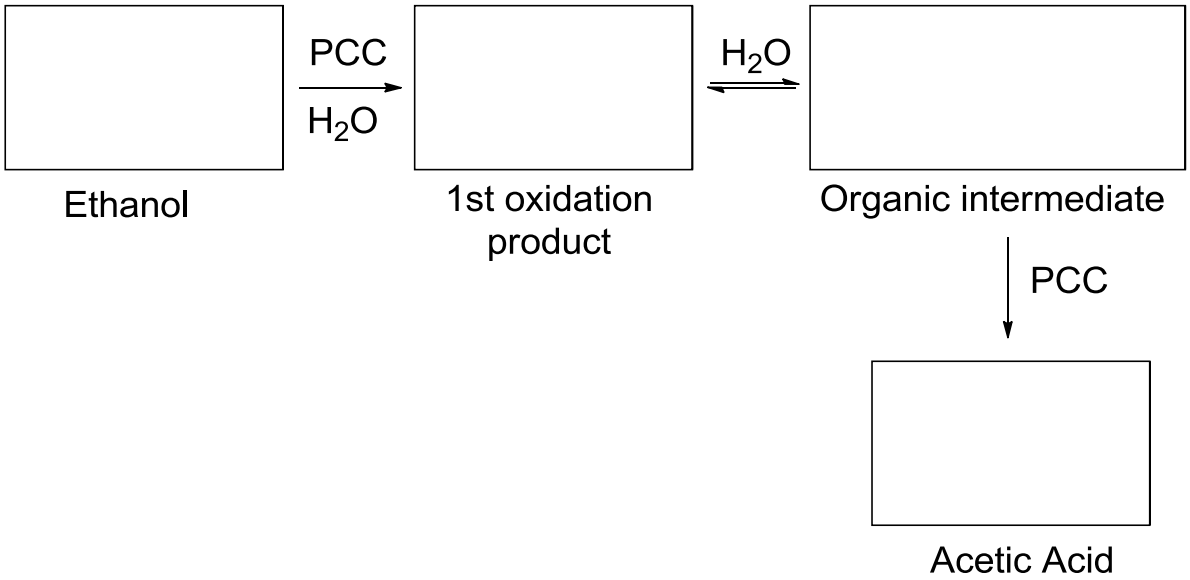




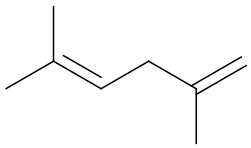


_____ _____ _____ _____

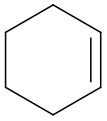
1. J. Ethanol reacts with PCC and water to yield acetic acid. In the boxes below, clearly draw : (1) ethanol, (2) the first oxidation product, (3) the organic intermediate that is ultimately oxidized to yield acetic acid, and (4) acetic acid. (8 points)



2. Predict the products of the following reactions. Pay special attention to any directions in the boxes. Be wary of stereochemistry. Repeat answers will cancel out correct answers. (18 points)

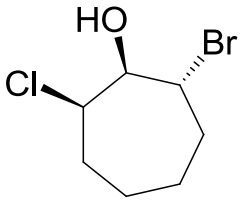


excess
H_2, Pd/C



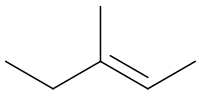
1. BD_3
2. D_2O_2, $\ominus$OD
D_2O

All organic products



NaH

Major organic product(s)

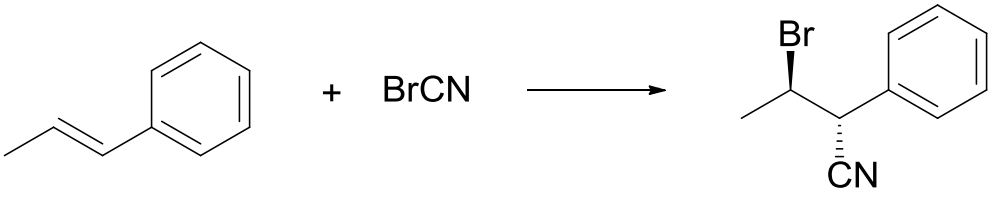


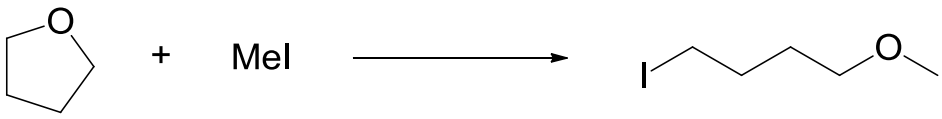
Cl_2, EtSH

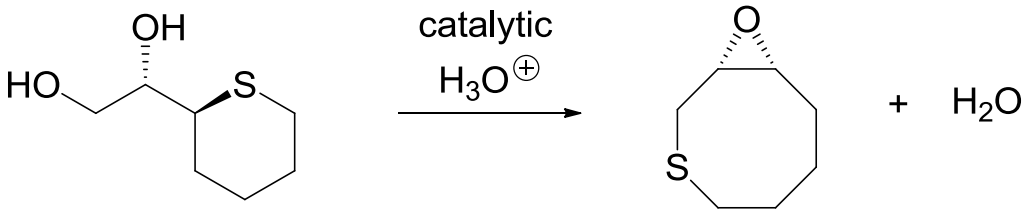
+ HCl

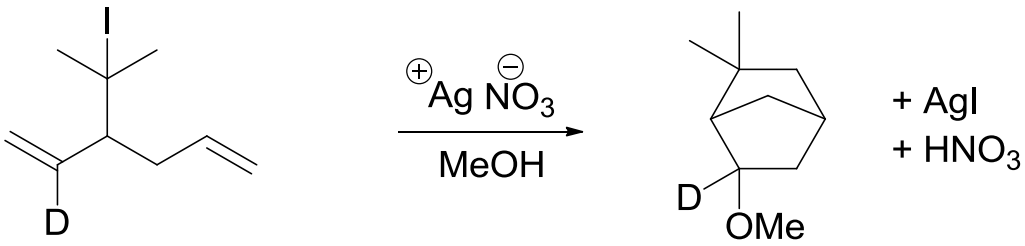
Major organic product(s)

3. Provide logical arrow pushing mechanisms for the following reactions. Be sure to show the formation of all of the products. *Show any important intermediates* that lead give specific stereochemical outcomes. (32 points)

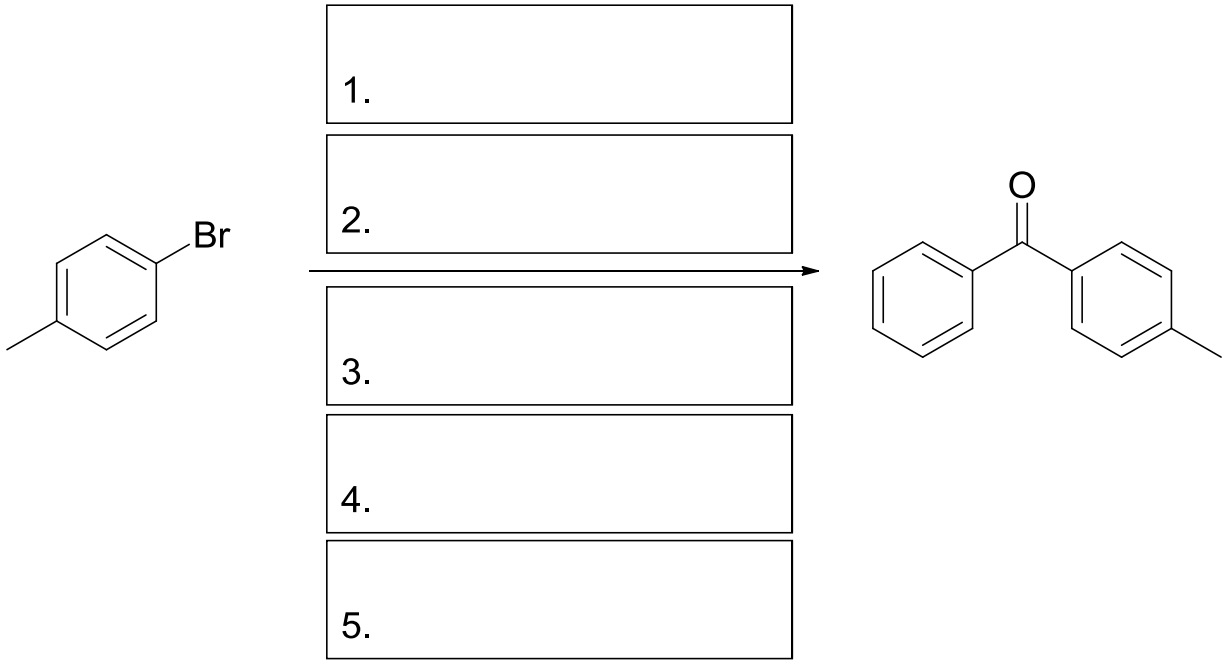


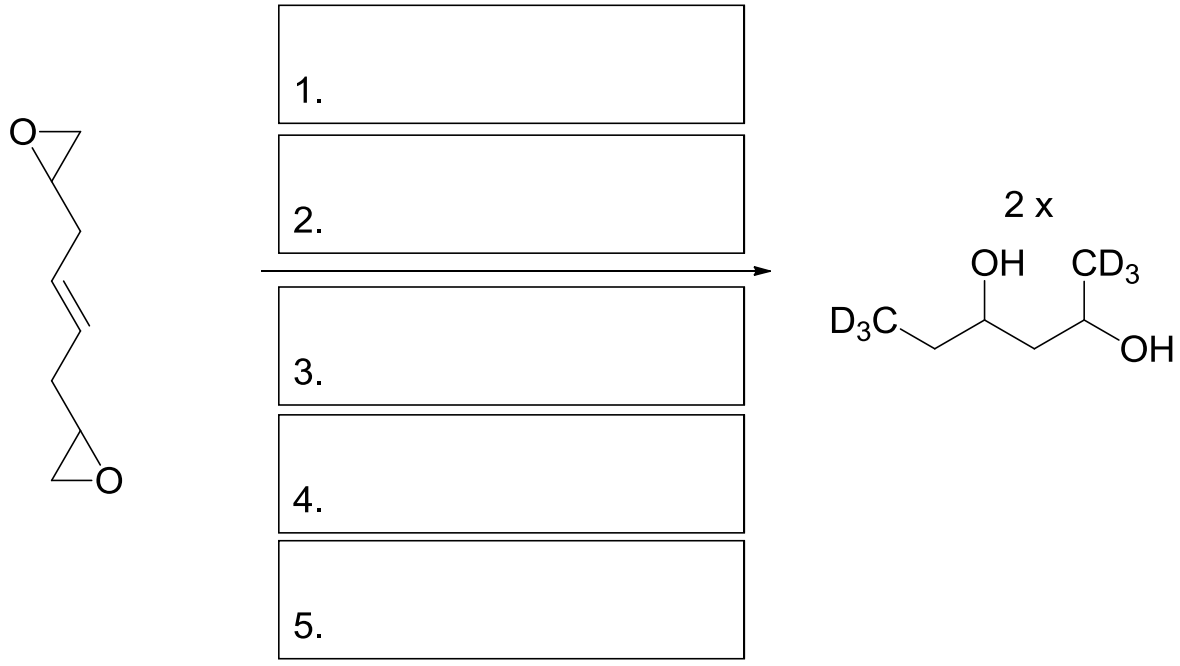


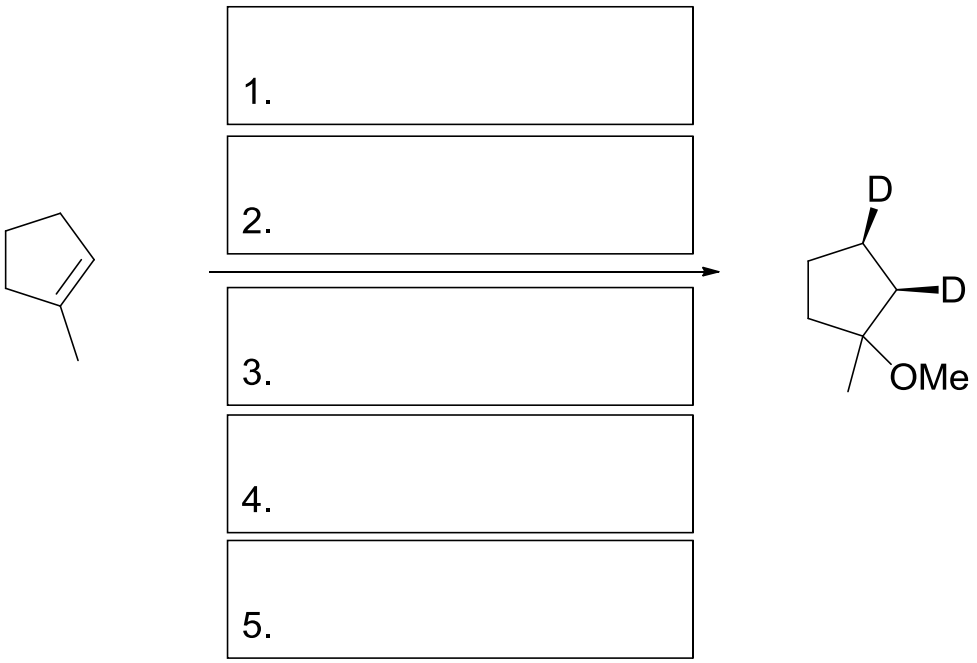

OH
HO
S
catalytic
$H_3O^{\oplus}$
O
S
+ H_2O


I
D
$^{\oplus}Ag\ NO_3^{\ominus}$
MeOH
D
OMe
+ AgI
+ HNO_3

4. Complete the following synthetic transformations by supplying the necessary reagents. You may add preformed Grignard reagents and organolithiates is they are needed. You will need five or fewer steps to complete each of these syntheses. (15 points)

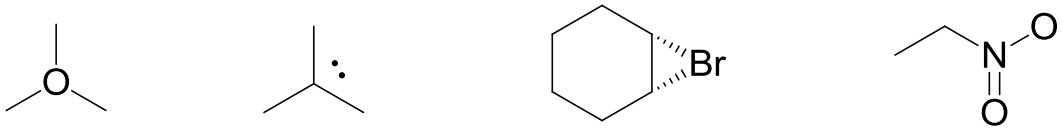





1.
2.
3.
4.
5.
D
D
OMe

5. This question will test your grasp of the basics of organic chemistry. (32 points)

5. A. Add formal charges to the appropriate atoms in the molecules below. (4 pts)



5. B. Draw *trans*-1,4-dimethylcyclohexane as a flat-ring AND in its LEAST FAVORABLE chair conformation. (4 points)

Flat-ring structure

Least Favorable Chair Conformation

5. C. Define "diastereomer". (3 points)

5. D. Say whether the following statements are True (**T**) or False (**F**). (6 points)

S_N2 reactions go through stereochemical inversion at the alpha carbon. ☐

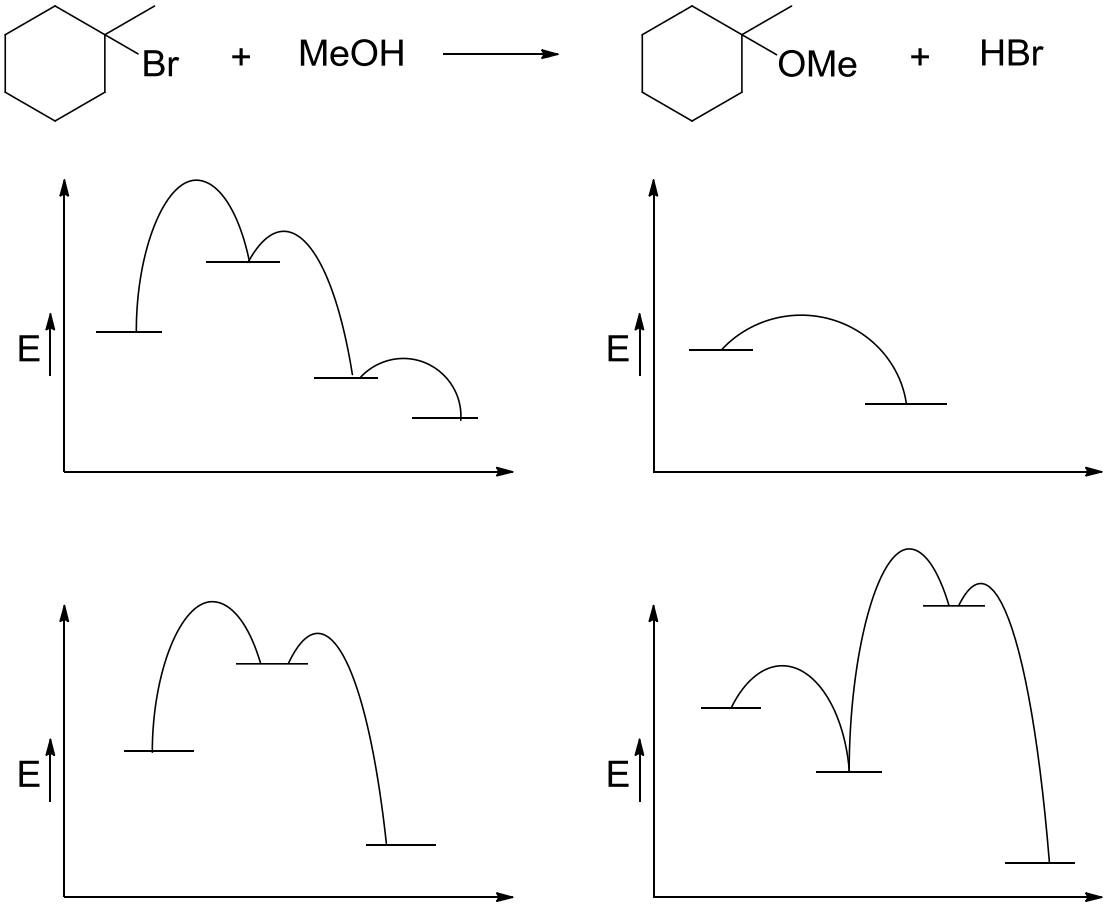
Only chiral molecules can have diastereomers. ☐

Alkynes contain at least two sp hybridized carbons. ☐

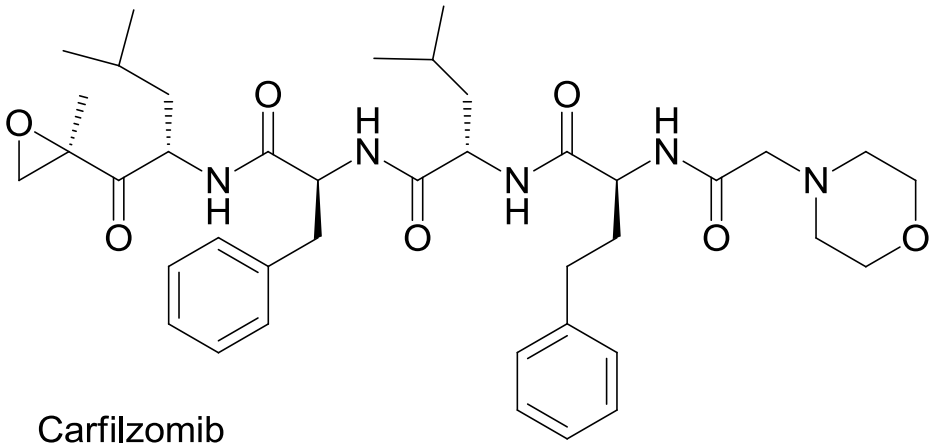
5. E. Draw the best S_N2 electrophile that has a tosylate (OTs) leaving group. (3 pts)

5. F. Draw an arrow-pushing mechanism for the first propagation step in the radical bromination of 2-methylpropane. (8 points)

5. G. Circle the energy diagram that corresponds to the S_N1 reaction shown below. (4 points)



6. Carfilzomib is (you guessed it) a late-stage cancer drug that was recently granted accelerated approval in July of 2012. (32 points)



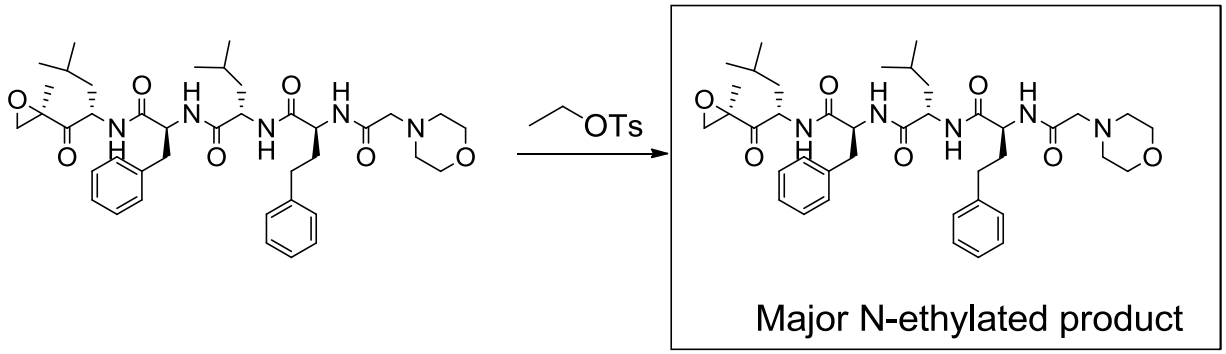
Carfilzomib

6. A. Circle an *iso*butyl group on the structure above. (2 points)

6. B. Place an asterisk on every stereocenter on the structure above. (3 points)

6. C. Choose TWO of those stereocenters and assign R or S. If more than two stereocenters are assigned, no points will be rewarded for this question. (4 points)

6. D. Using your knowledge of resonance contributors and their effects on nucleophilicity, predict the major product of the reaction between a nitrogen on Carfilzomib and EtOTs. Add the "Et" group to the appropriate atom in the box provided below. (3 points)



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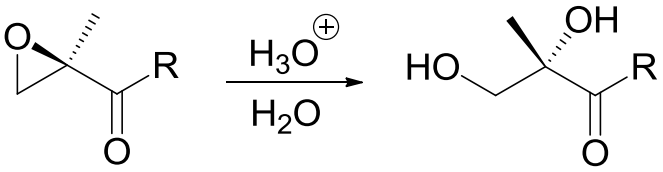
6. E. The epoxide of Carfilzomib can undergo nucleophilic attack under acidic conditions as well as under basic conditions. In the appropriate boxes, draw the transition states that lead to the products shown. (8 points)

Transition State

Transition State

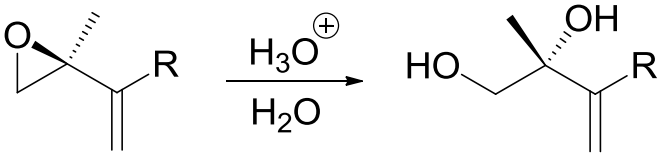
+ H_2O

6. F. Compound "X" below (an analog of Carfilzomib) undergoes acidic epoxide opening much more readily than the original molecule. Explain this result by comparing the highest energy intermediates of both compounds. Please use pictures and words. (6 points)



Requires 240 minutes for the reaction to complete

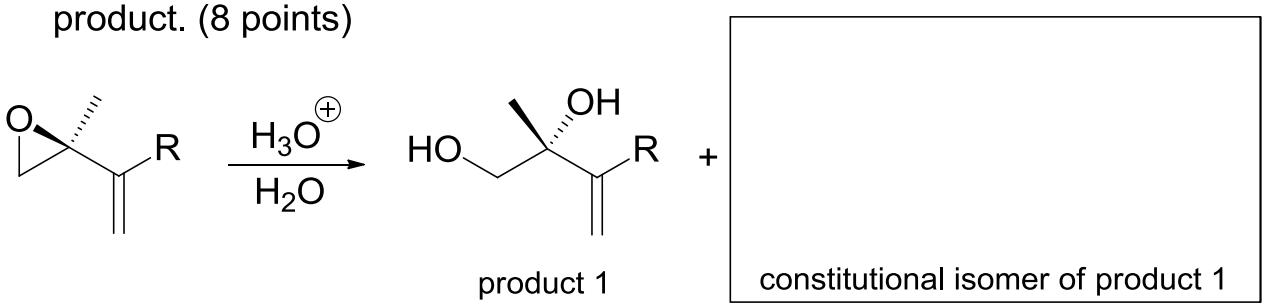
"**X**"



Requires 15 minutes for the reaction to complete

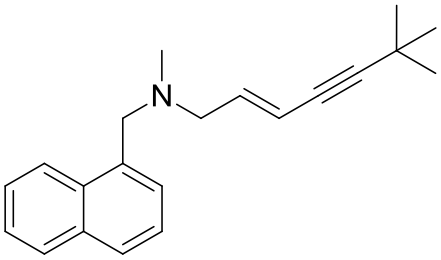
6. G. When compound "**X**" reacts with $H_3O^{\oplus}$, two constitutional isomers are formed. Provide the second isomer in the box provided. You may ignore stereochemistry. (3 points)

6. H. Provide a rational arrow-pushing mechanism that shows formation of each product. (8 points)



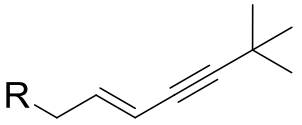
Mechanism :

7. In the spirit of the olympics, let's investigate the reactivity of Terbinafine, a drug used to treat Athlete's Foot. (11 points)



Terbinafine

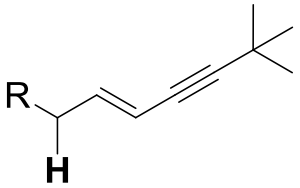
7. A. We discussed in class that the Lindlar catalyst is selective for reduction of alkynes to alkenes. Predict the product(s) of the following reaction. (3 pts)



H_2

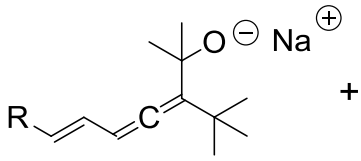
Lindlar catalyst

7. B. Reaction of Terbinafine with a strong base ($NaNH_2$) followed by reaction with an electrophile (acetone) leads to the product shown. Provide a mechanism that accounts for this product. THE FIRST STEP OF THE MECHANISM IS AN ACID BASE REACTION WITH THE HYDROGEN SHOWN. (8 points)



1. $NaNH_2$

2. 



+ NH_3

8. Allenes are compounds that have two adjacent C-C pi bonds. This question will explore the stereochemistry and reactivity of these fascinating, linear compounds. (44 points)

8. A. Draw the molecular orbital diagram for the simple allene, "**A**", shown below. Remember to (1) label each energy level (σ, π^*, etc.), (2) fill in the electrons, and (3) label the HOMO and LUMO. (12 points)

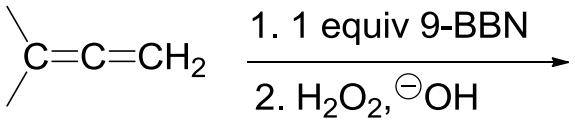
$H_2C{=}C{=}CH_2$

"**A**"

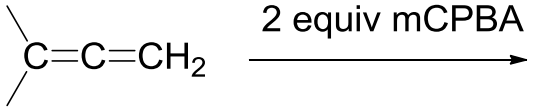
MO Diagram for "**A**"

8. B. Draw a 3D image of allene "**A**" below. Clearly show the orientation of all pi bonds as well as sigma bonds. (4 points)

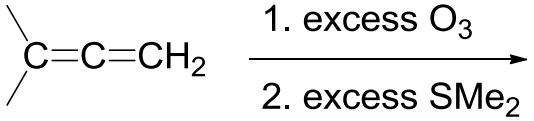
8. C. Allenes react similarly to alkenes. Predict the products of the following reactions. (12 points)



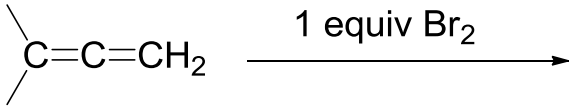
Major organic product



you may ignore stereochemistry

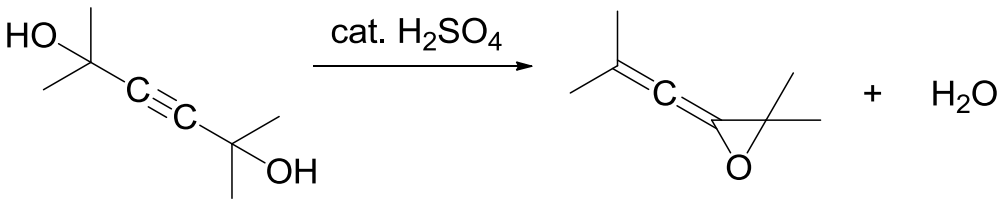


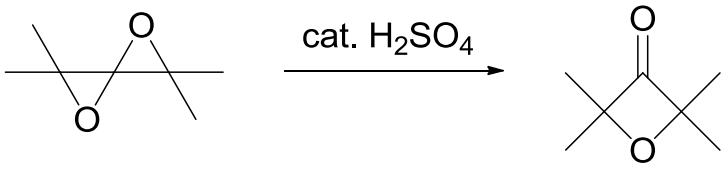
3 carbon containing compounds excluding DMSO



Major organic product

8. D. Provide rational arrow-pushing mechanisms for the following reactions. (16 points)





CONGRATULATIONS ON A SUMMER WELL SPENT!