Chemistry 3A – Final Exam

Student Name: Pete's Key

Student ID Number: _____

Place an X in the line if you are making up an incomplete : _____

Which semester did you receive the "I"? : _____

Point Breakdown Student Averages

Problem 1	3.06	/ 6	Problem 5	5 / 10
	3.95	/ 6	Problem 6	8.25 / 12
	8.3	/ 12		12.5 / 21
	11.0	/ 16		
Problem 2	6.9	/ 15	Problem 7	6.8 / 8
	9.3	/ 13		7.8 / 12
Problem 3	6.4	/ 10		7.1 / 15
	5.9	/ 11		7.1 / 11
Problem 4	13.1	/ 16		7.8 / 12
	8.3	/ 12		
	4.5	/ 12	Extra Credit	1.2 / 5

Total 144.5 / 225

Check that you have 22 pages on 11 pieces of paper.
You will have 180 minutes for this exam.

Note: There are 235 available points. It is possible to get 235/225.

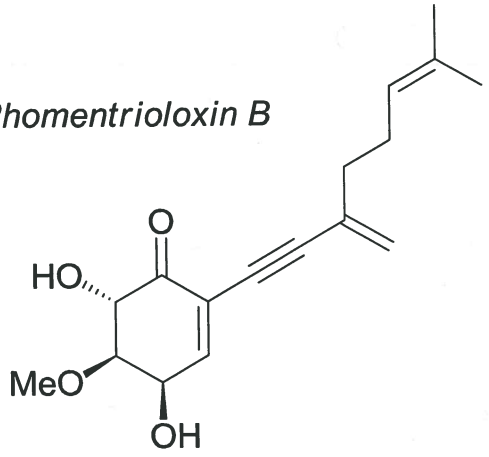
Note: This exam is long. Problem 4 is the only question that MUST be done in order

REMEMBER: CHARGES, ACID/BASE, OCTETS, MINUS GOES TO PLUS, READ THE QUESTIONS, and most importantly:
I know you can do this.

1. Phomentrioloxins are herbicides used to control Saffron Thistle in Australia. *J. Nat. Prod.*, **2015**, *78*, pp 623-629.

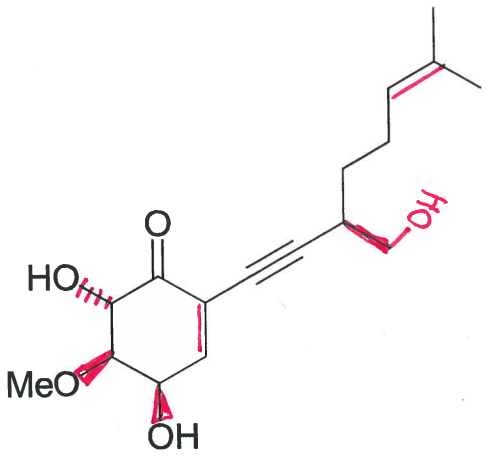
1. A. Predict the two major stereoisomeric products of the following reaction. Add the missing groups, the missing pi bonds, and add the appropriate wedges and dashes to the templates. (6 points)

Phomentrioloxin B

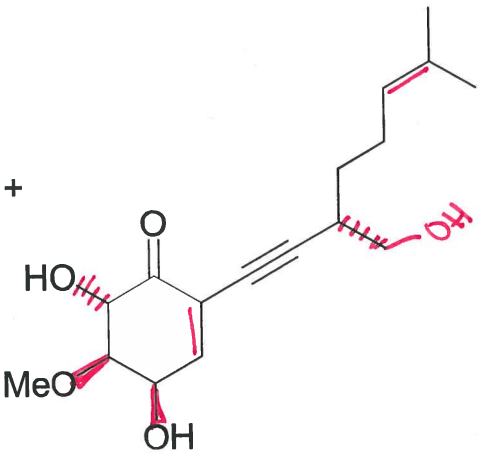


3.06
6

1. 9BBN
2. NaOH
   H_2O_2
   H_2O

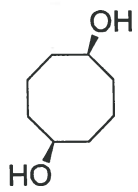


+



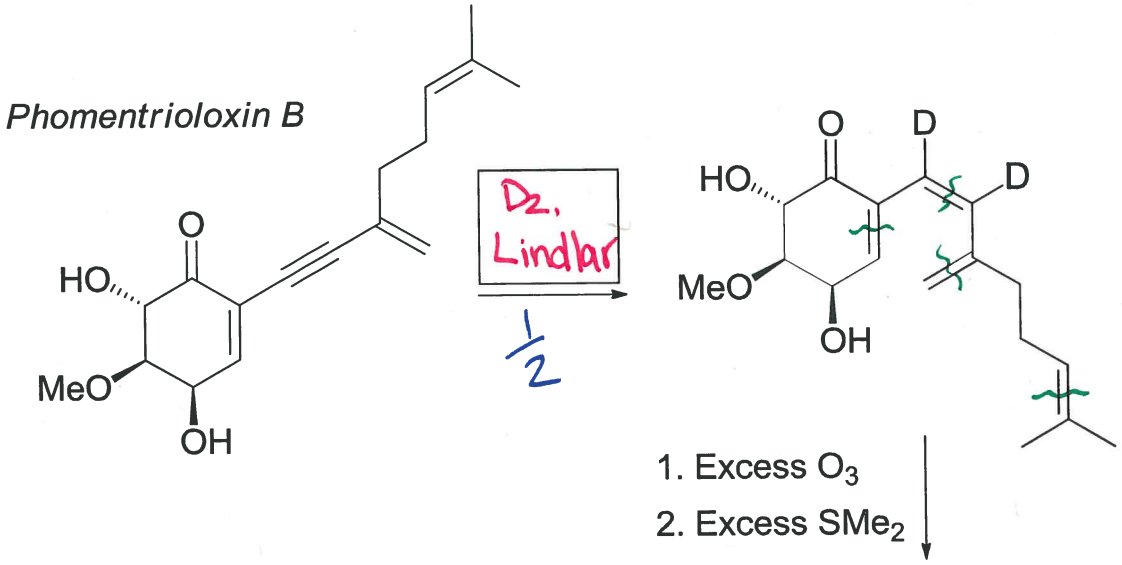
Major Stereoisomeric Products

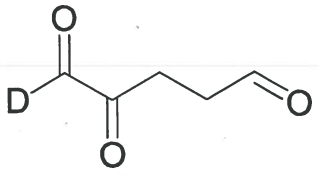
+



Add wedges, dashes, missing groups and missing pi bonds.

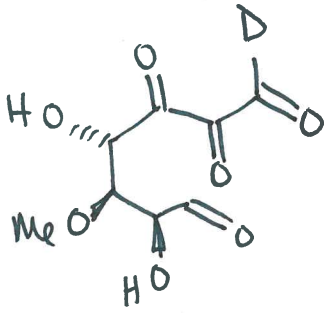
1. B. Fill in the missing reagents or products. (6 points)





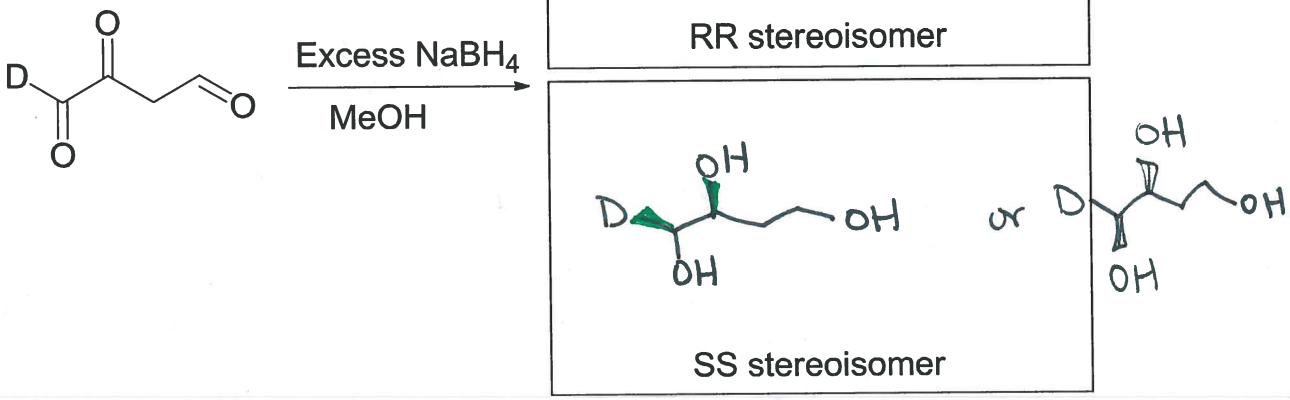
+ 4 x DMSO

2.95/4



Draw the three other products.

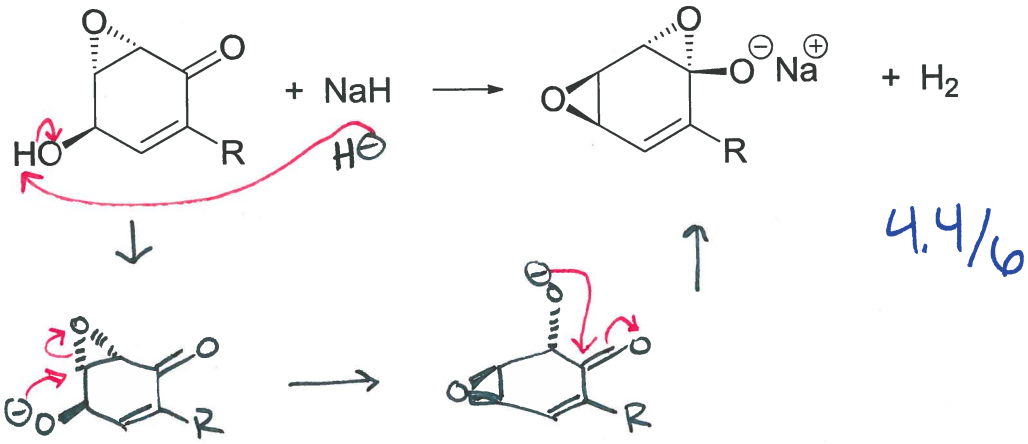
1. C. Predict the RR and the SS enantiomers of the following reaction. Place them in the appropriate answer boxes. (6 pts)



3.9/6

4 possible products. ONLY SHOW the RR and SS stereoisomers.

1. D. Show an electron pushing mechanism for each of the following chemical reactions. Do not worry about showing formation of ionic bonds. (22 pts)



4.4/6

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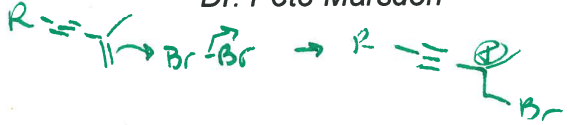
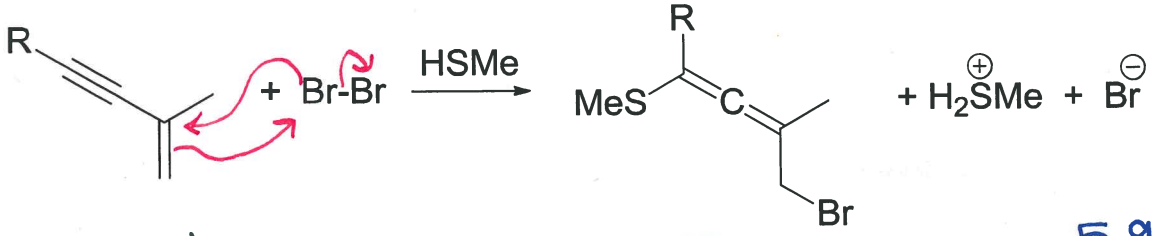
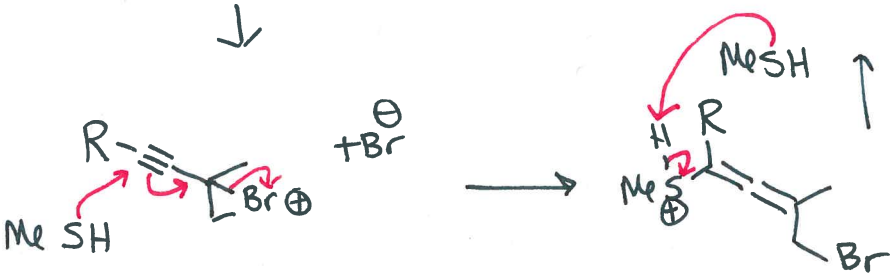




5.9/8



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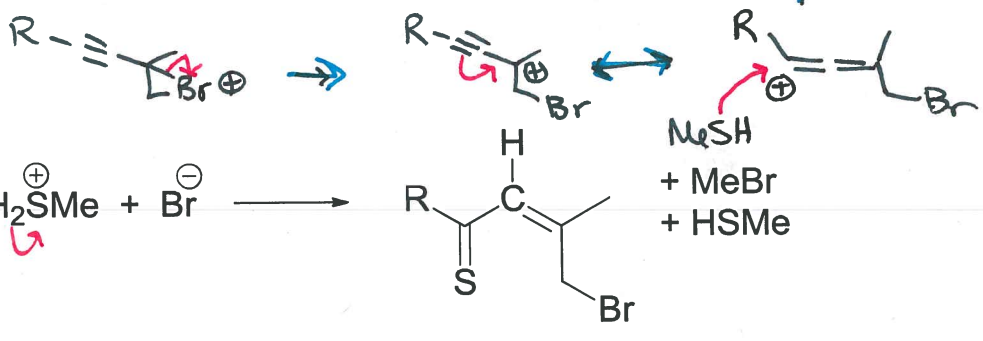
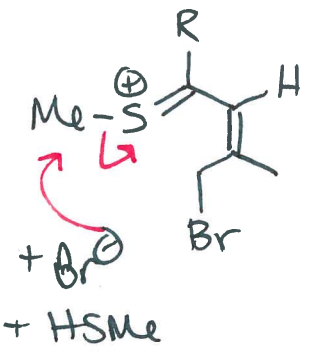
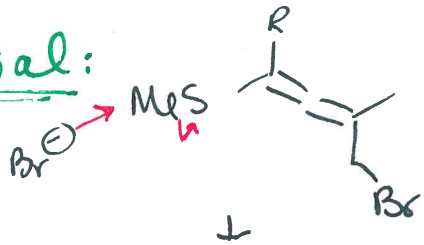


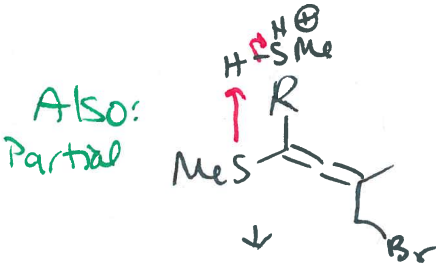
5.1/8

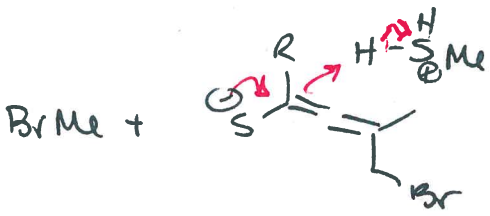


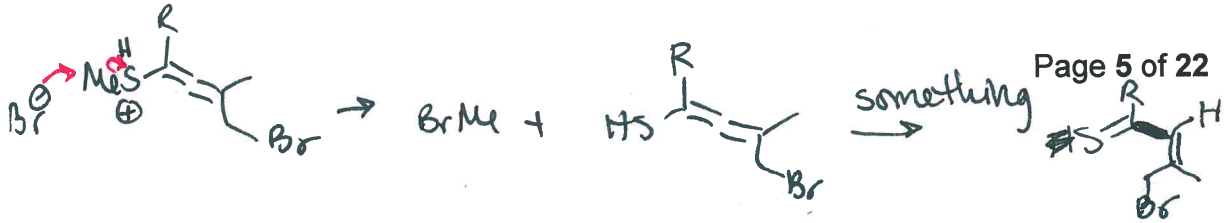
Partial:



Also:
Partial



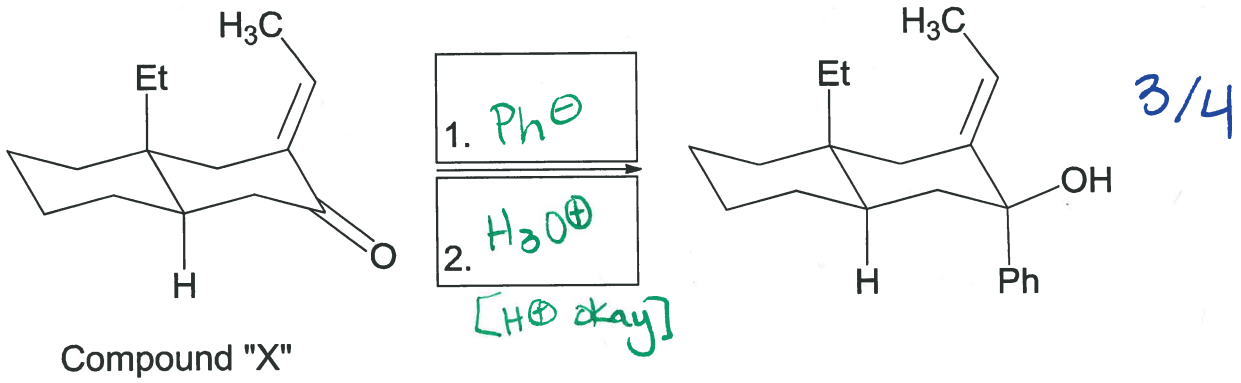




2. A. Is the alkene in compound "X" in the *E* or *Z* configuration? (2 points)

E 1.6/2

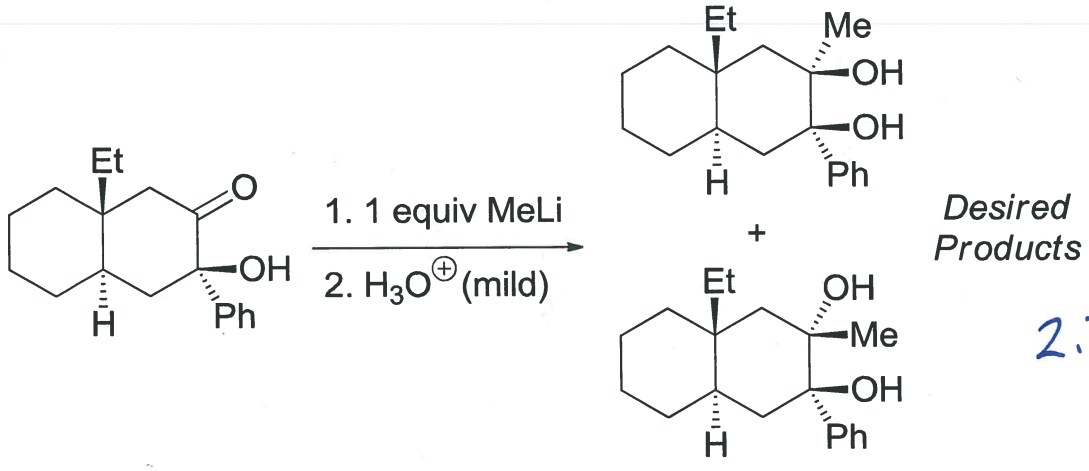
2. B. Provide the missing reagents for the following reaction. (4 points)



3/4

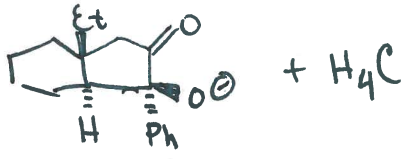
Compound "X"

2. C. A student proposes the following synthesis. It will not yield the desired product. Indicate the problem, provide the actual products, and suggest a change to the synthesis which will make it work. (9 pts)



Desired Products

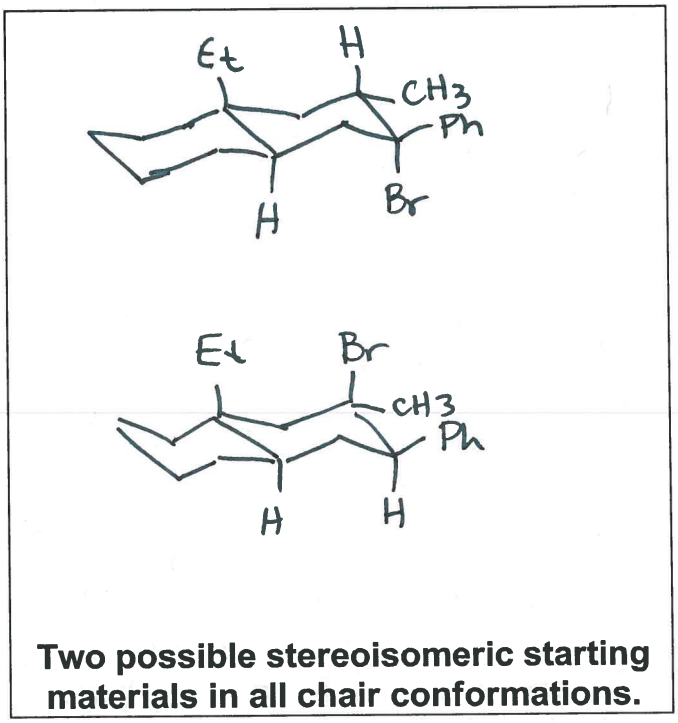
2.3/9

Problem 1:	Actual Products:	Proposed Change:
MeΘ will deprotonate before it attacks	 + H_4C	Add extra MeΘ.

2. D. For the following reaction, will a big base or a small base yield the alkene shown? Circle your choice and expalin in 10 words or fewer. (3 points)

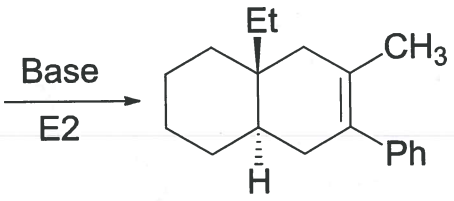
1.9/3

A Big / (Small) base because: the alkene is the most substituted.



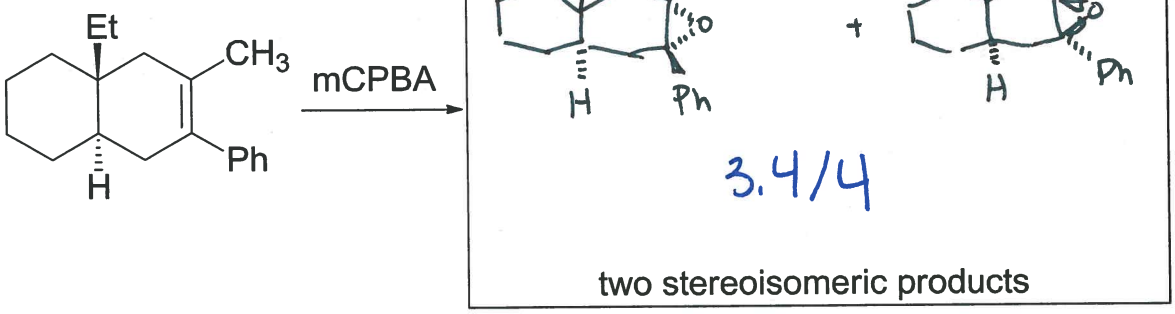
Two possible stereoisomeric starting materials in all chair conformations.

4/6



2. E. For the above reaction, provide the two possible starting materials that lead to the alkene shown following E2 elimination. Draw the starting materials in the all chair conformations (see 2.A. for a template). Use Br as the leaving group. (6 points)

2. F. Predict the products of the following reaction. (4 points)

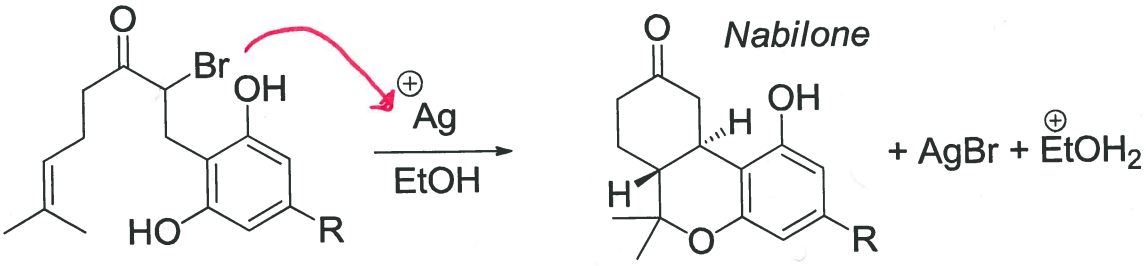


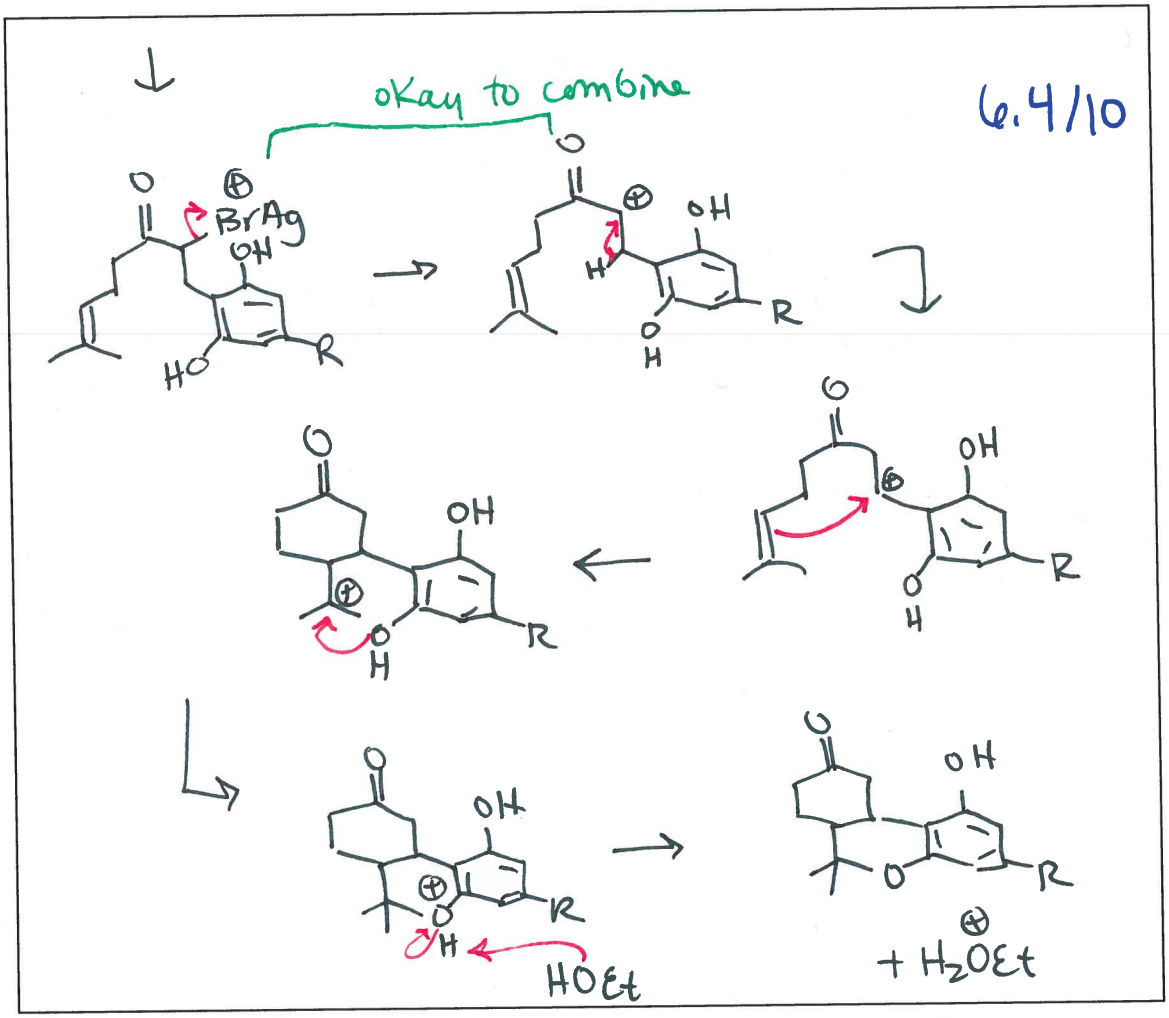
3.4/4

two stereoisomeric products

3. Nabilone is a cannabinoid used to treat neuropathic pain.

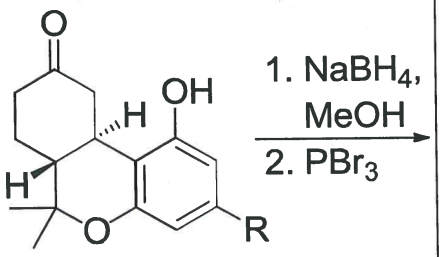
3. A. Provide a mechanism for the following transformation. (10 points)



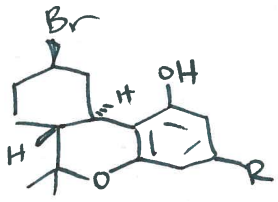


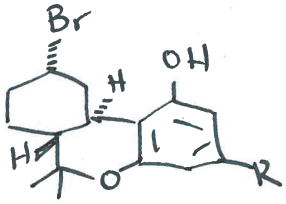
You will not need all of this space.

3. B. Predict the product(s) of the following reactions. Note that the OH group attached to the benzene ring will not react with PBr_3. (6 points)



1. $NaBH_4$, MeOH
2. PBr_3

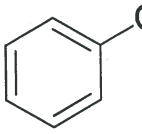




4.5/6

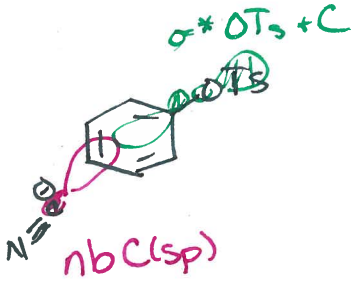
Two stereoisomeric products

3. C. Using an orbital picture, explain why PhOTs cannot undergo an S_N2 reaction with cyanide as a nucleophile. Use 10 words or fewer. (5 pts)



$+ {}^{\ominus}CN \longrightarrow$ No Reaction

1.4/5

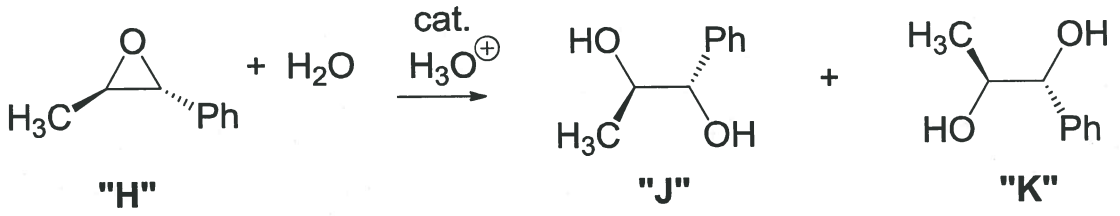


Draw the necessary orbital interaction for an S_N2 reaction.

PhOTs cannot undergo an S_N2 reaction because:

The σ* orbital is blocked by the Ph ring.

10 words or fewer.

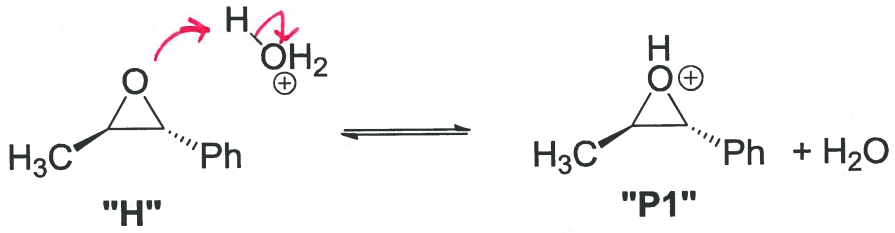


4. A. What is the stereochemical relationship between **"J"** and **"K"**? (2 points)

Enantiomers

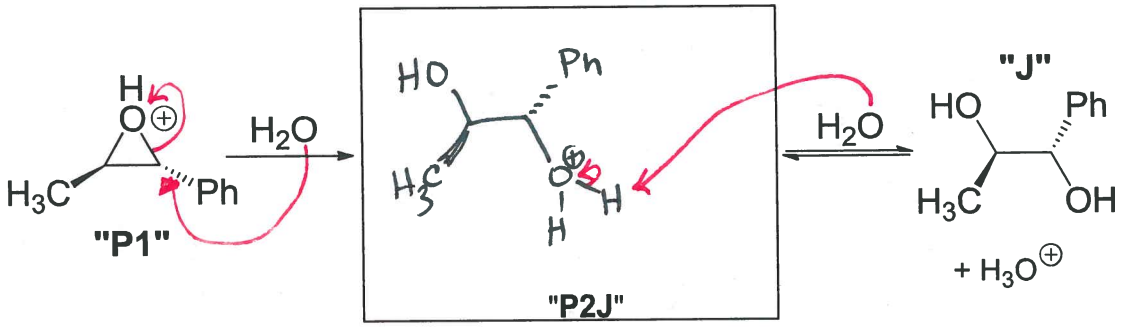
1.7/2

4.B. Add arrows to get from **"H"** to **"P1"**. (2 points)



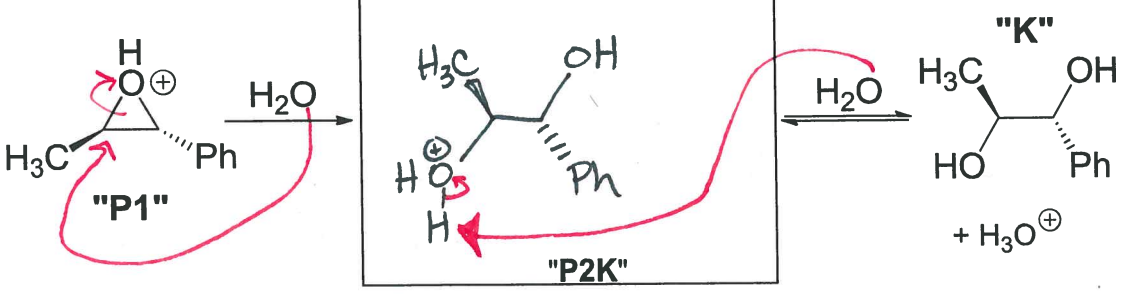
1.92/2

4.C. Finish this mechanism converting "P1" to "J" by adding necessary arrows and the missing structure **"P2J"**. (6 points)

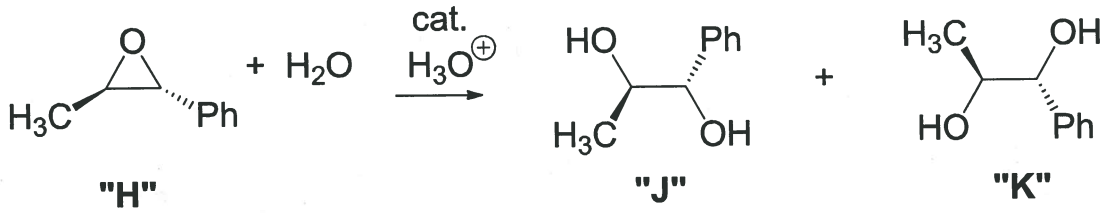


4.8/6

4.D. Finish this mechanism converting "P1" to "K" by adding necessary arrows and the missing structure **"P2K"**. (6 points)

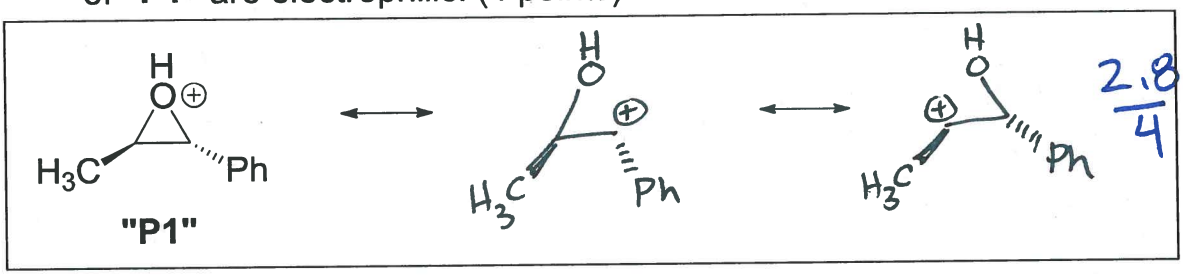


4.6/6



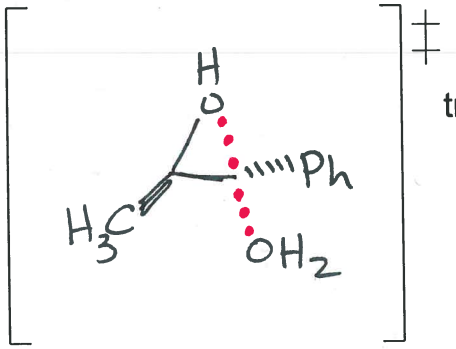
"H" **"J"** **"K"**

4.E. Draw two relevant resonance contributors that show why the carbons of **"P1"** are electrophilic. (4 points)



"P1"

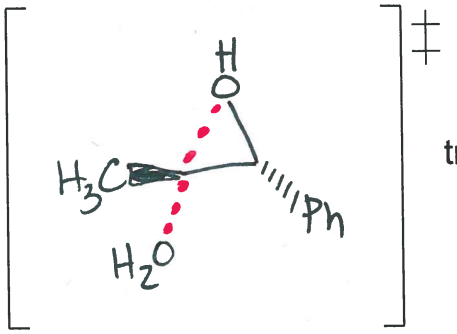
4.F. Draw the transition state for the step converting **"P1"** to **"P2J"** from question 4.C. (3 points)



transition state leading to **"P2J"**

2.5
3

4.G. Draw the transition state for the step converting **"P1"** to **"P2K"** from question 4.D. (3 points)

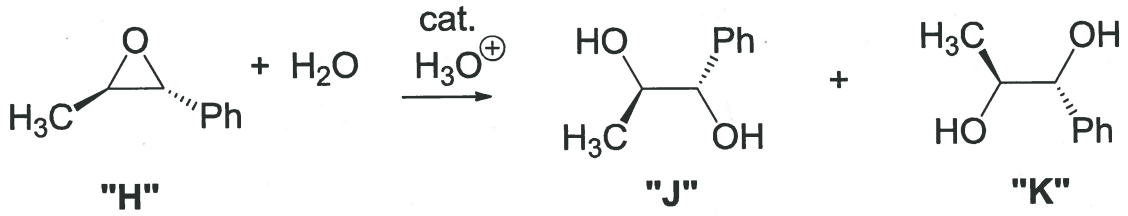


transition state leading to **"P2K"**

2.5
3

4.H. Are the transition states you drew stereochemically related? If yes, how? (2 pts)

NO 0.5/2



"H" **"J"** **"K"**

4.I. Product **"J"** is the major product of this reaction. Explain in 20 or fewer words. (4 points)

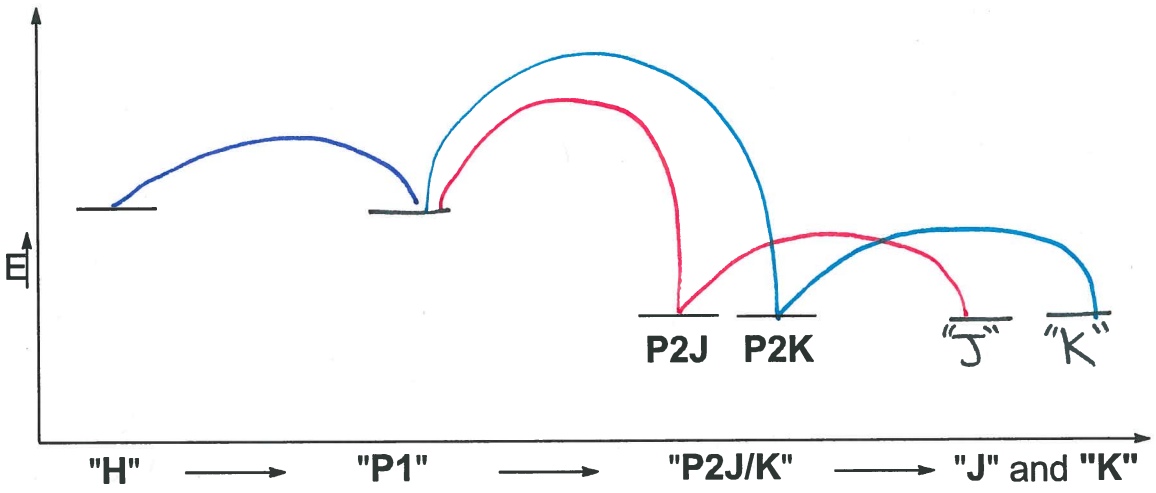
"J" is the major product because: H_2O attacks the more positive carbon. The carbon near the Ph group is resonance stabilized.

1/4

4.J. Draw the reaction coordinate diagram for the conversion of **"H"** to the di-alcohol products **"J"** and **"K"**. Use the following assumptions to help with relative energies of intermediates, products and transition states (8 points):

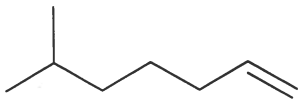
(1) Answer to 4.A.
(2) Equilibrium arrows on questions 4.B., 4.C., and 4.D.
(3) Answer to 4.H.
(4) Question 4.I.
(5) Assume formation of P2J/K is rate determining.
(6) Assume P2J and P2K are the same energy

3.5/8

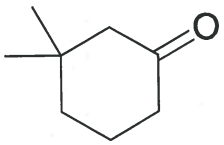


5. Provide the missing reagents. You will need to use all 5 steps. Extra space is provided as scratch paper so you can show your work. (10 points)

5/10

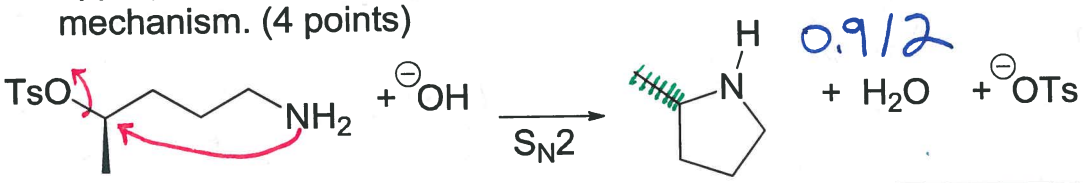


1. mCPBA
2. $Br_2, h\nu$
3. Mg
4. $H_3O^{\oplus}$
5. PCC

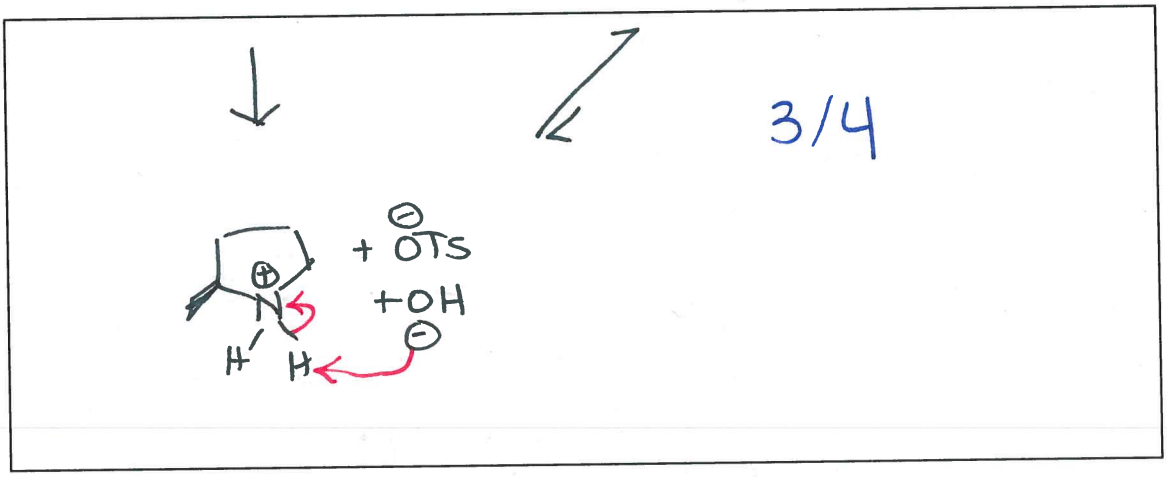


Basics and Redemption.

6. A. Provide a rational arrow-pushing mechanism for this reaction. Add appropriate equilibrium arrows for any acid/base portions of your mechanism. (4 points)



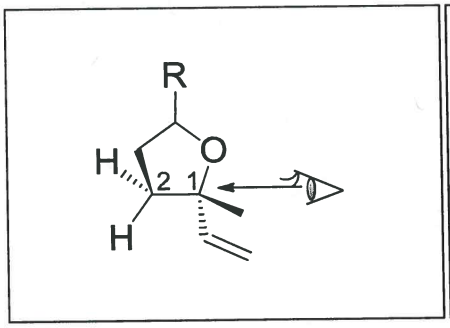
0.9/2

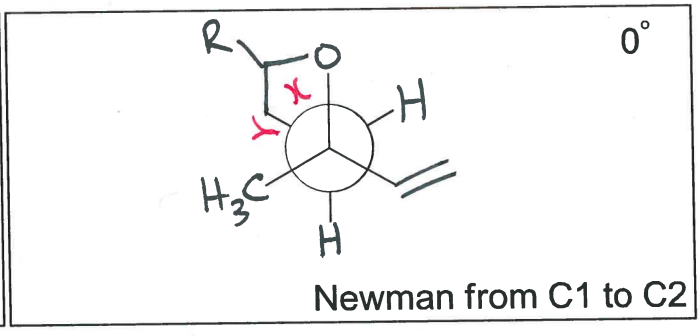


3/4

6. B. On the product above the answer box, add the appropriate stereochemistry to the methyl group (wedge or dash). (2 pts)

6. C. Draw a Newman Projection along the indicated bond of Lilac Alcohol. (3 points)





4.3/6

6. D. Describe the steric interactions at 0°. Use the abbreviations "Me" for the methyl group, "Alk" for the alkene, "O" for the oxygen, and "ring" for the oxa-cyclopentane ring. Use "E" and/or "G" for eclipsing and/or gauche interactions. (3 points)

Rotation Angle	Steric Interactions
Front Carbon 0°	G: Me-Ring G: O, ring

6. E. State whether the following statements are True or False. (6 points)

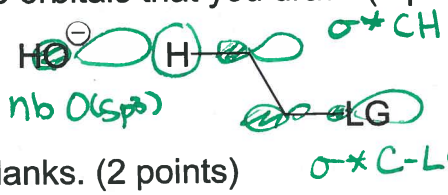
Small bases give the kinetic product in an E2 elimination **TRUE**

Large bases give the kinetic product in an E2 elimination **TRUE**

NaH is a source of nucleophilic $H^{\ominus}$. **FALSE**

3.3/6

6. F. Show the orbital overlap necessary for a successful E2 reaction. Add labels to the orbitals that you draw. (4 points)



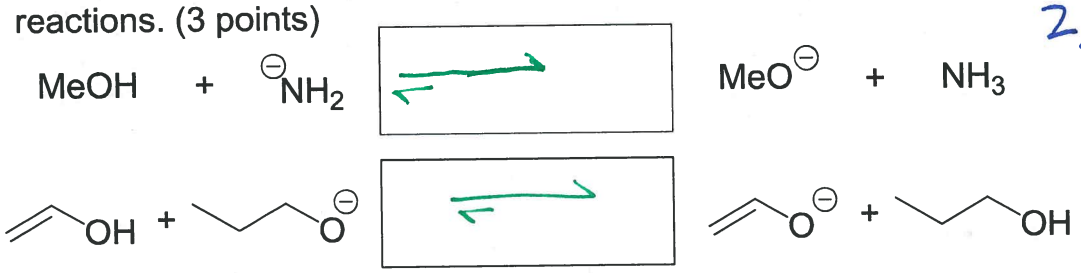
0.8/4

6. G. Fill in the Blanks. (2 points)

Hammond's Postulate states that the Transition State of an endothermic reaction will more resemble the products.

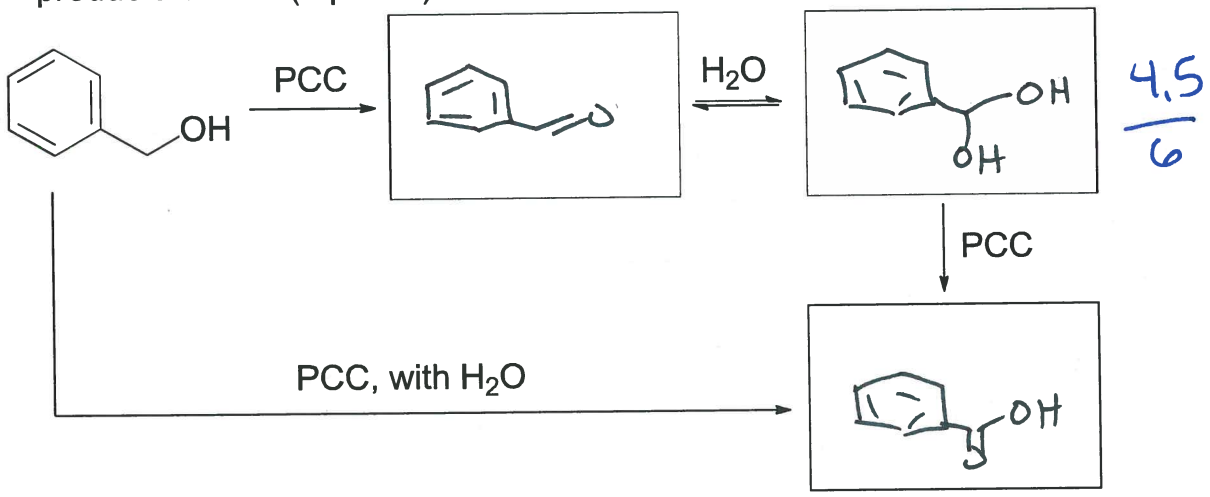
1.8/2

6. H. Add appropriate equilibrium arrows for the following acid / base reactions. (3 points)



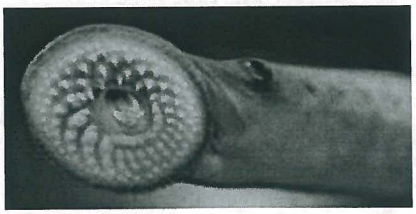
2/3

6. I. Primary alcohols can be oxidized to carboxylic acids. Fill in the missing products below. (6 points)

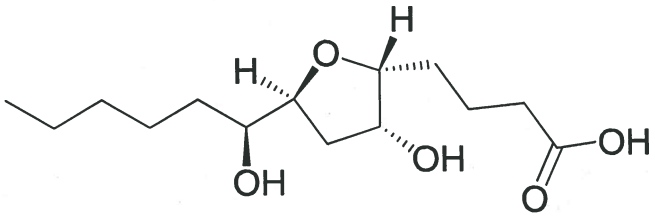


4.5/6

7. Sea lampreys are currently terrorizing the Great Lakes. Researchers are investigating a pheromone, petromyroxol, to help control the infestation. *J. Org. Chem.*, **2015**, *ASAP. Author: Alistair Boyer.*

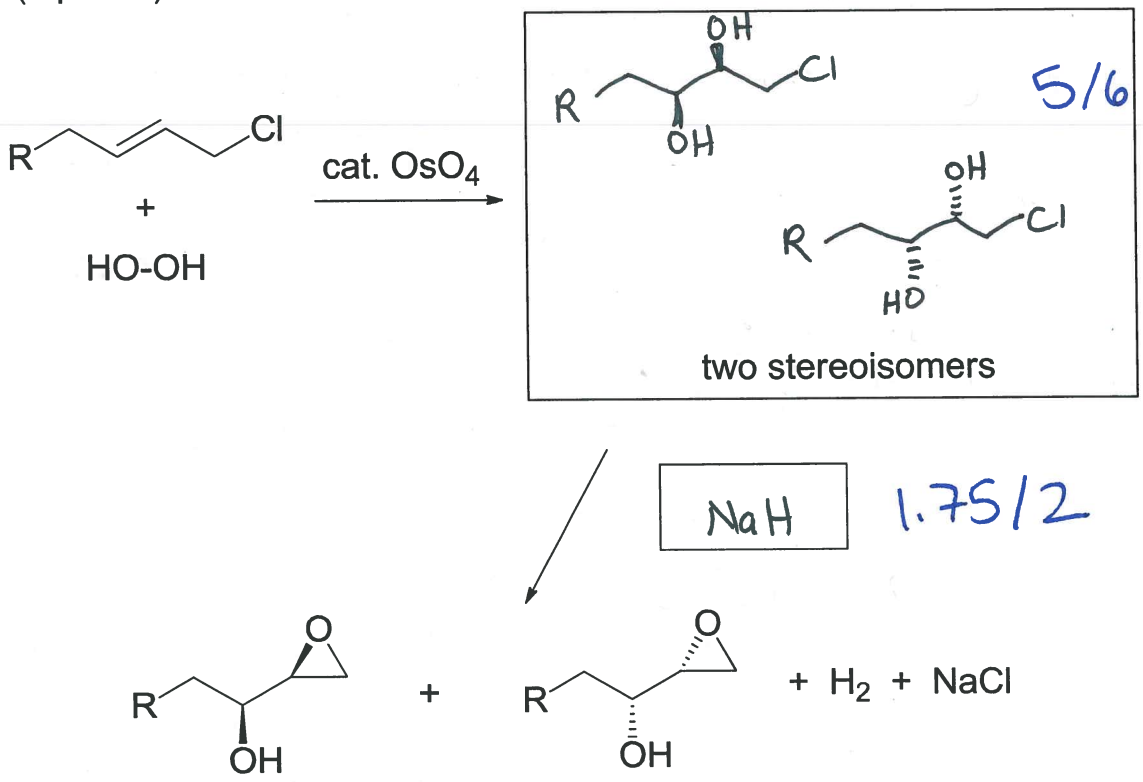


Sea Lamprey

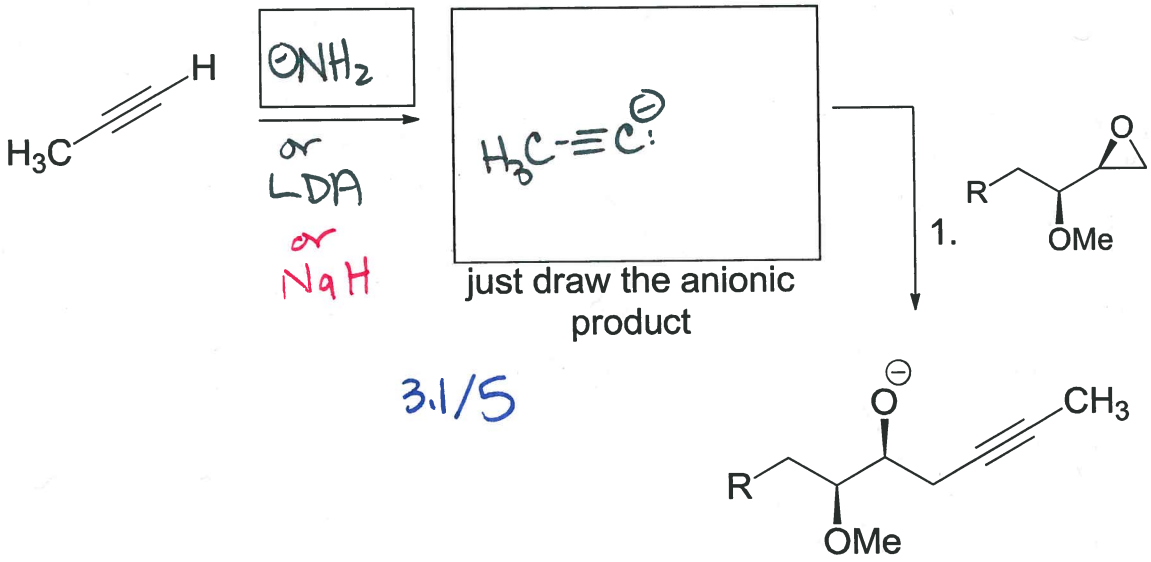


Petromyroxol

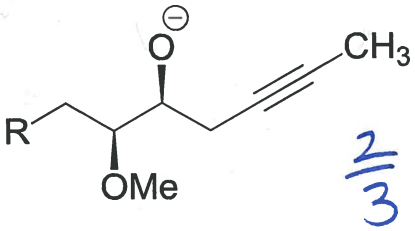
7. A. Please fill in the missing starting material, reagents, or products. (8 points)



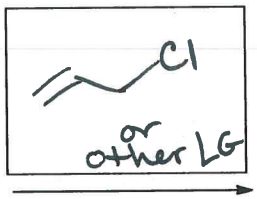
7. B. Please fill in the missing reagents or products. (12 points)

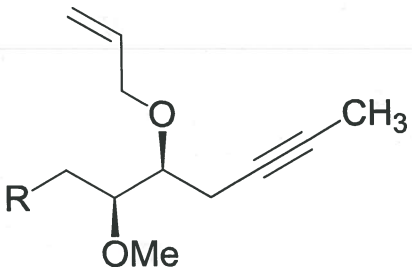


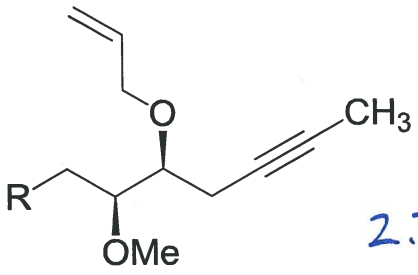
3.1/5

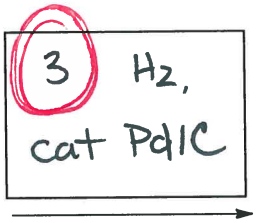


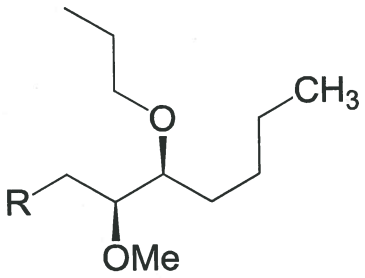
2/3











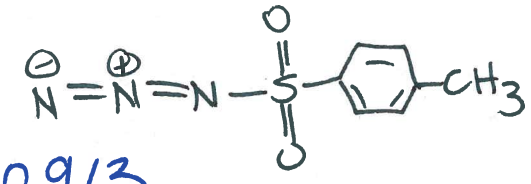
2.7/4

Specify exact quantities of reagents for this last transformation. For example, 2 equivalents and/or catalytic.

7. C. Draw the structure of the following molecule. Be sure to show any formal charges. (3 points)

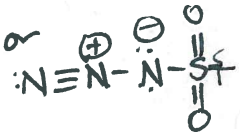
TsN_3 ⟹

Tosyl Azide

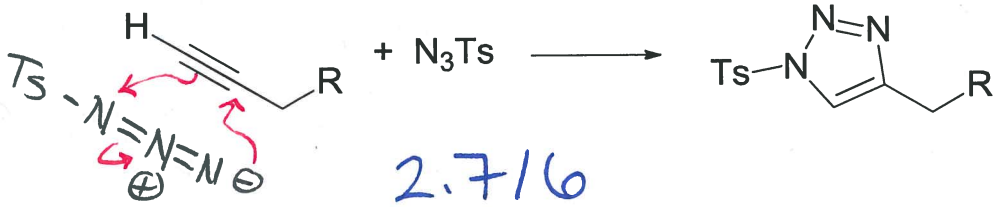


0.9/3

Lewis Structure of Tosyl Azide

or 

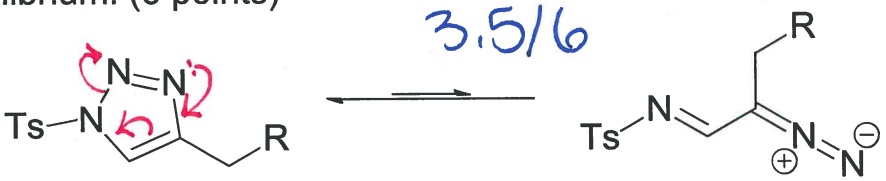
7. D. Provide a rational electron pushing mechanism for the following reaction. *Hint: It is very similar to the first step of ozonolysis.* (6 points)



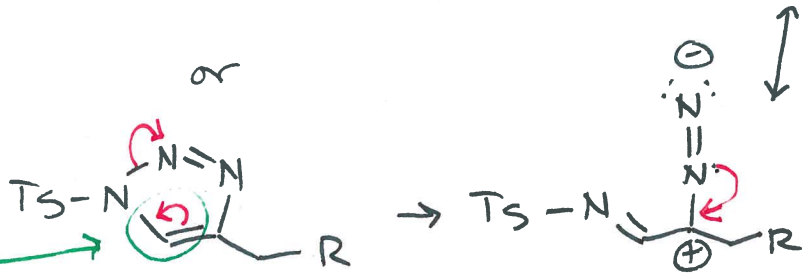
2.7/6

7. E. Provide a rational electron pushing mechanism for the following equilibrium. (6 points)

3.5/6

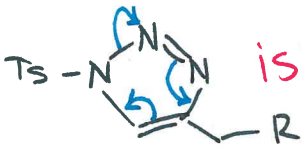


or



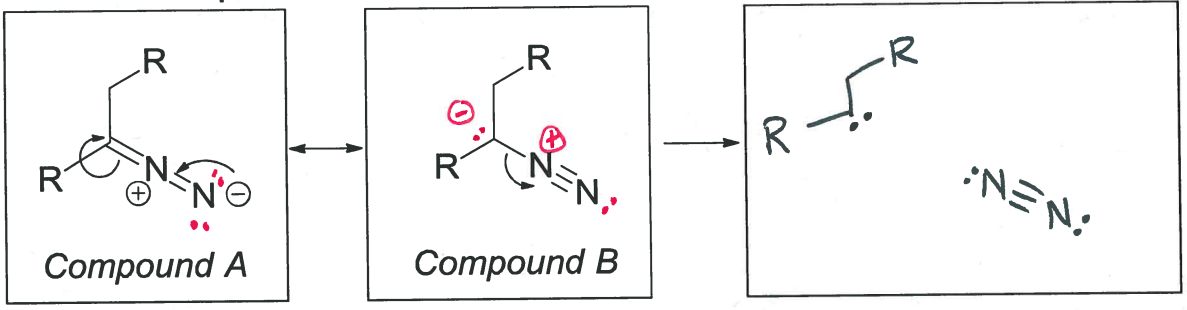
if they do this arrow in a separate step, 3/6

BE AWARE:



is worth 4/6.

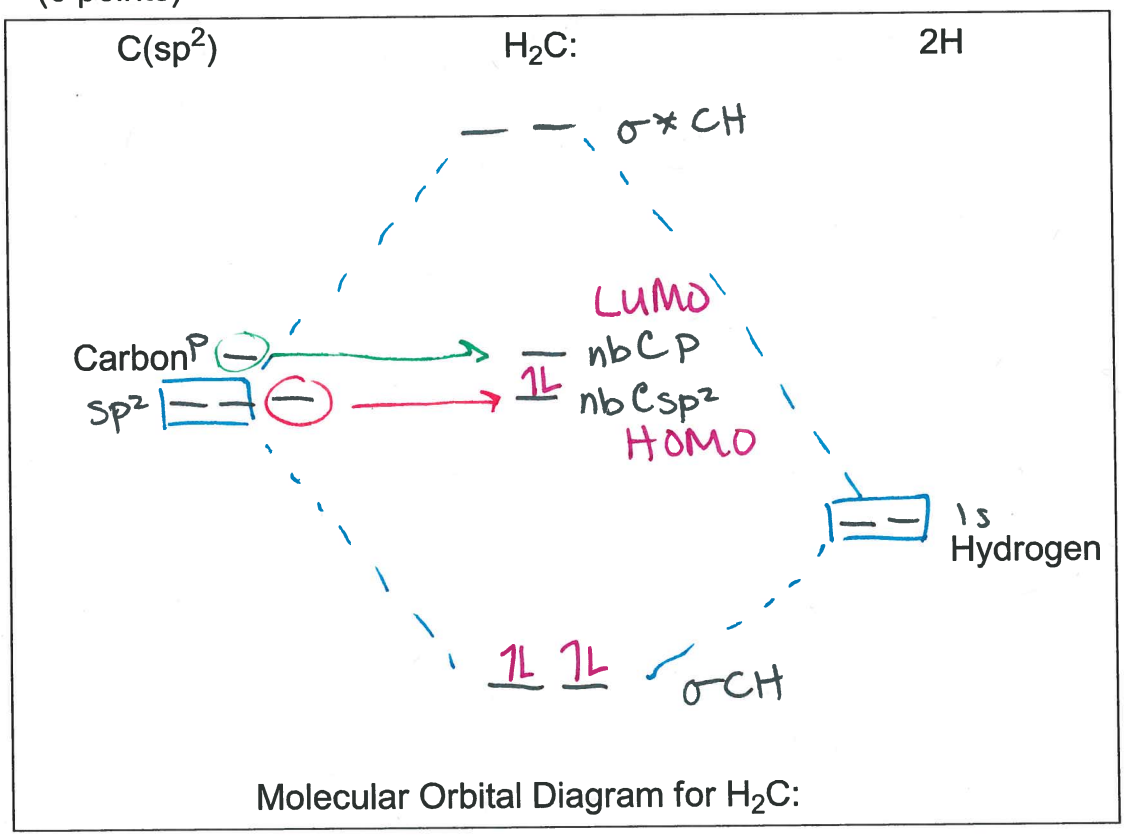
7. F. Add missing lone pairs to compound A below. (1 point)
7. G. Add charges **AND** missing lone pairs to the resonance contributor, B, below. (2 points)
7. H. Show the product(s) of the arrow on compound B. Be sure to show all lone pairs and formal charges. (2 points)



Add lone pairs. **Add lone pairs and charges.** **Show product(s) with lone pairs and charges.**

3.1/5

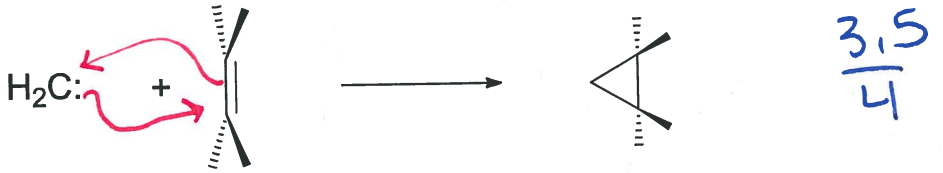
7. I. Construct the MO diagram for H_2C:, where the carbon is sp^2hybridized. Remember to (1) label the atomic orbitals and molecular orbitals, (2) add electrons to the proper MO levels and (3) label the HOMO and LUMO. (6 points)



Molecular Orbital Diagram for H_2C:

4/6

7. J. H_2C: is known as a carbene. It is electron deficient, but neutral. It reacts with alkenes similarly to Br_2 to create a 3-membered ring. Provide a mechanism for the following transformation. (4 points)



3.5/4

7. K. Which orbital of H_2C: has the correct symmetry to overlap with the pi orbital of the alkene? Draw the pictures of the orbitals and label them. (3 points)

1.5/3

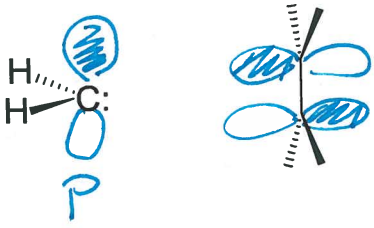
Add the orbital that matches the pi bond's symmetry

Add the pi-bonding orbital

7. L. Which orbital of H_2C: has the correct symmetry to overlap with the pi anti-bonding orbital of the alkene? Draw the pictures of the orbitals and label them. (3 points)

1.4/3

Add the orbital that matches the pi anti-bond's symmetry



Add the pi anti-bonding orbital

7. M. Based on questions 7.K. and 7.L., which orbital on the carbene H_2C: do the two electrons reside? Circle the answer below. (2 points)
Remember: Filled orbitals ineract with unfilled orbitals to create new bonds

1.2/2

(Carbon P orbital)

Carbon sp^2 hybrid orbital

EXTRA CREDIT:

The orbitals of 7.M. should not match your HOMO/LUMO assignment in your MO diagram. Using the arrows drawn in 7.F. and 7.G., rationalize how the electrons on the carbene end up in the orbitals necessary for reaction with an alkene. (5 points)

The C-N bond that breaks to release N_2 leaves the sp^2 orbital on carbon empty.

The lone pair resides in a p-orbital.

$\frac{1.2}{5}$

30 words or fewer

Y'ALL HAVE BEEN AMAZING. IT WAS AN HONOR TEACHING YOU THIS SEMESTER. REMEMBER TO HAVE FUN THIS SUMMER WHEN YOU HAVE THE TIME.

Abbreviated Periodic Table

3	4	5	6	7
B	C	N	O	F
		P	S	Cl
				Br

You can use this space as scratch paper. It will not be graded.