

## Chemistry 3A – Final Exam

Student Name: \_\_\_\_\_

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

Problem 1	_____ / 6	Problem 5	_____ / 10
	_____ / 6		
	_____ / 12	Problem 6	_____ / 12
	_____ / 16		_____ / 21
Problem 2	_____ / 15		
	_____ / 13	Problem 7	_____ / 8
Problem 3	_____ / 10		_____ / 12
	_____ / 11		_____ / 15
			_____ / 11
Problem 4	_____ / 16		_____ / 12
	_____ / 12		
	_____ / 12	Extra Credit	_____ / 5

Total \_\_\_\_\_ / 225

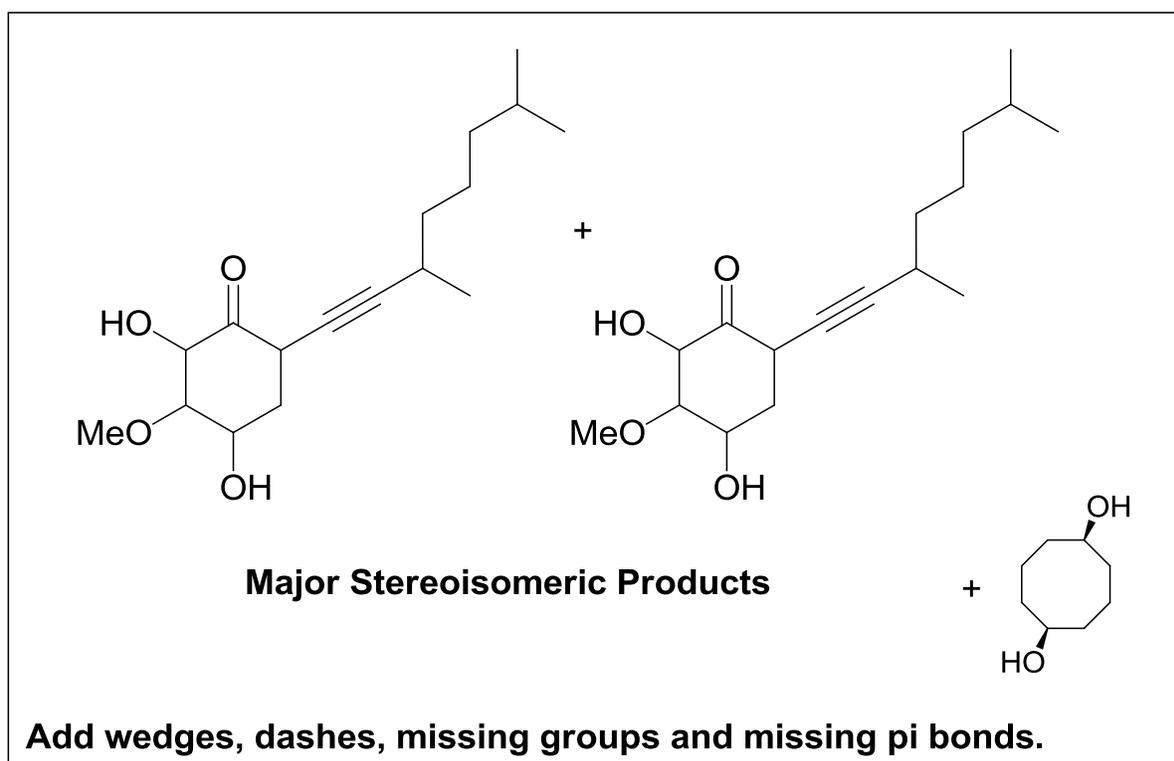
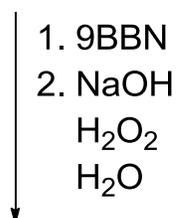
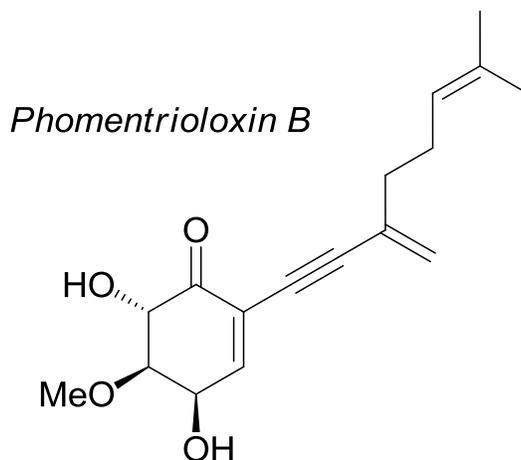
Check that you have 22 pages on 11 pieces of paper.  
You will have 180 minutes for this exam.

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

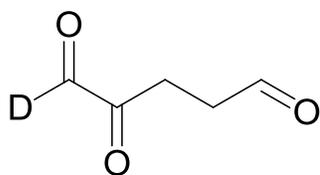
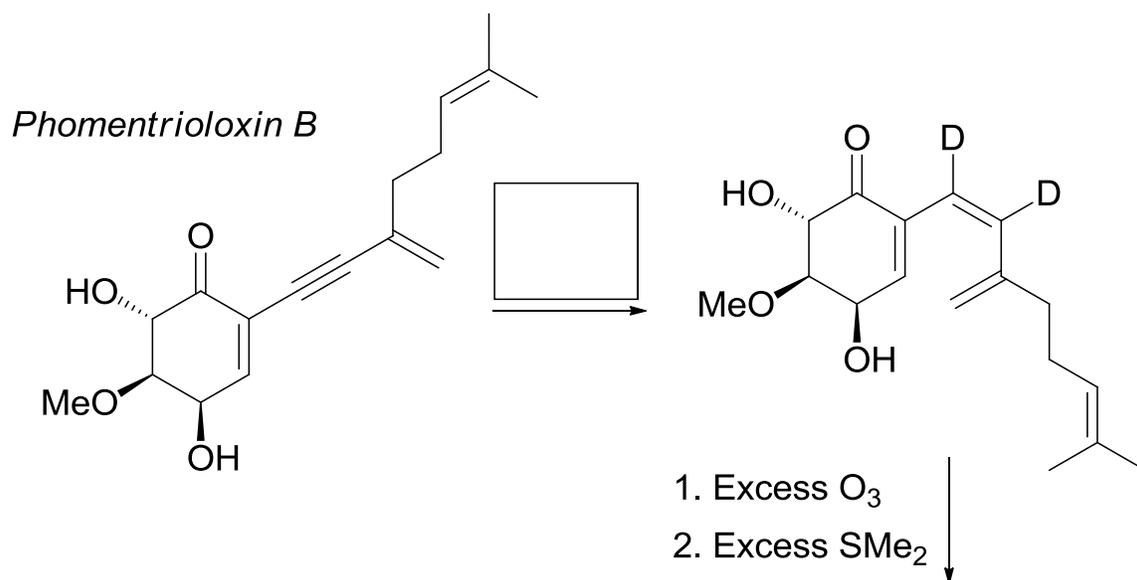
**Note: This exam is long. Problem 4 is the only question that MUST be done in order**

**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)



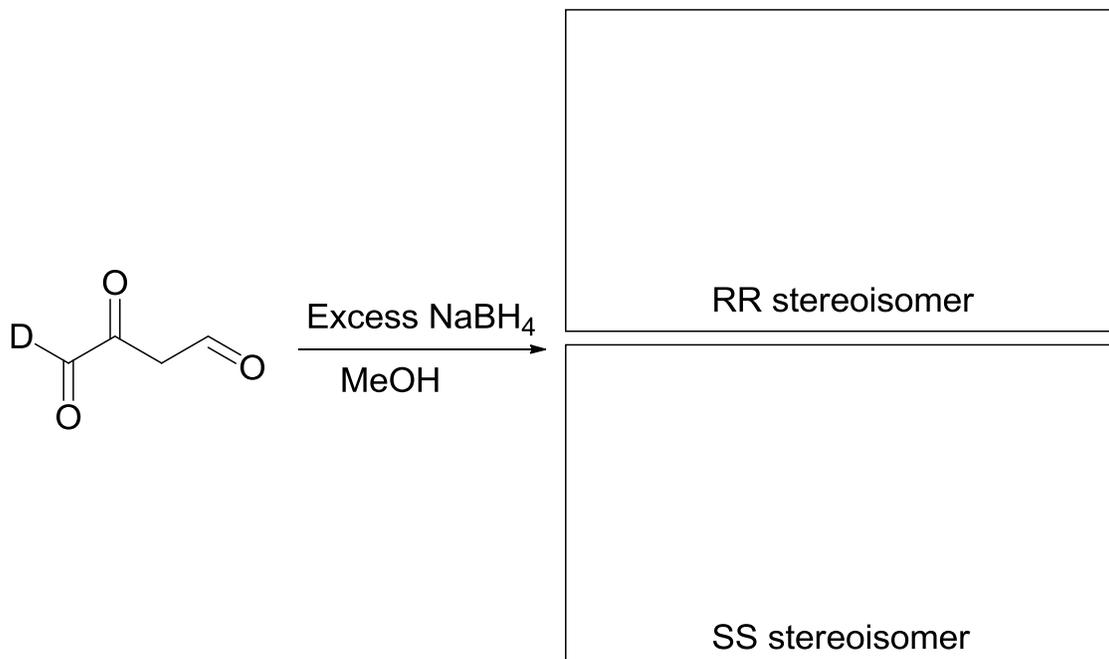
1. B. Fill in the missing reagents or products. (6 points)



+ 4 x DMSO

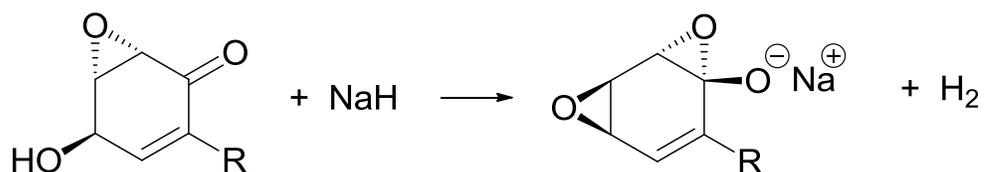
**Draw the three other products.**

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

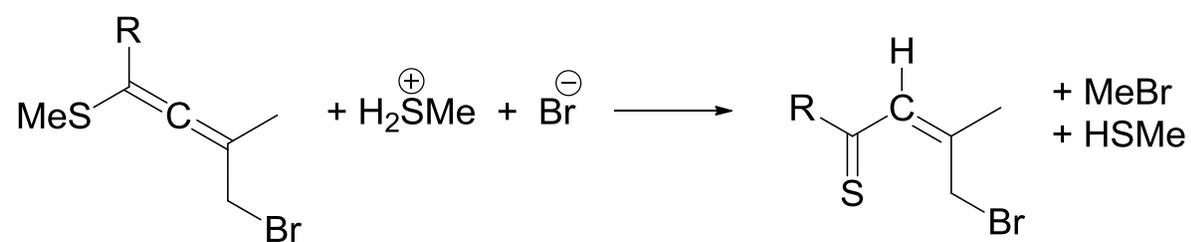
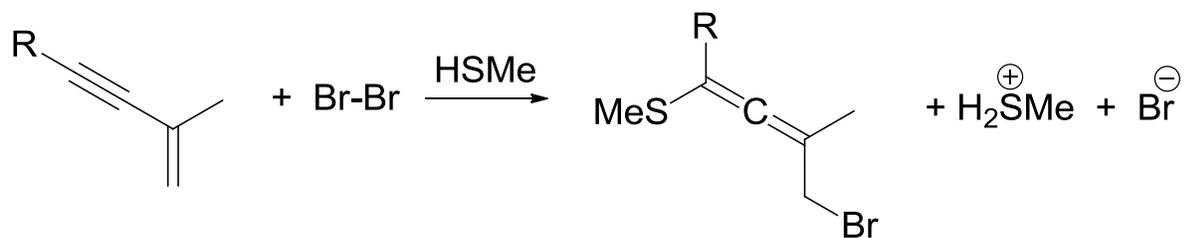


**4 possible products. ONLY SHOW the RR and SS stereoisomers.**

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)

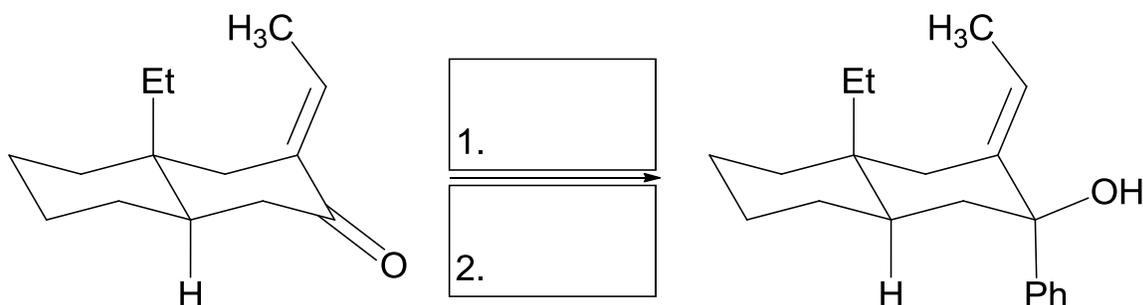


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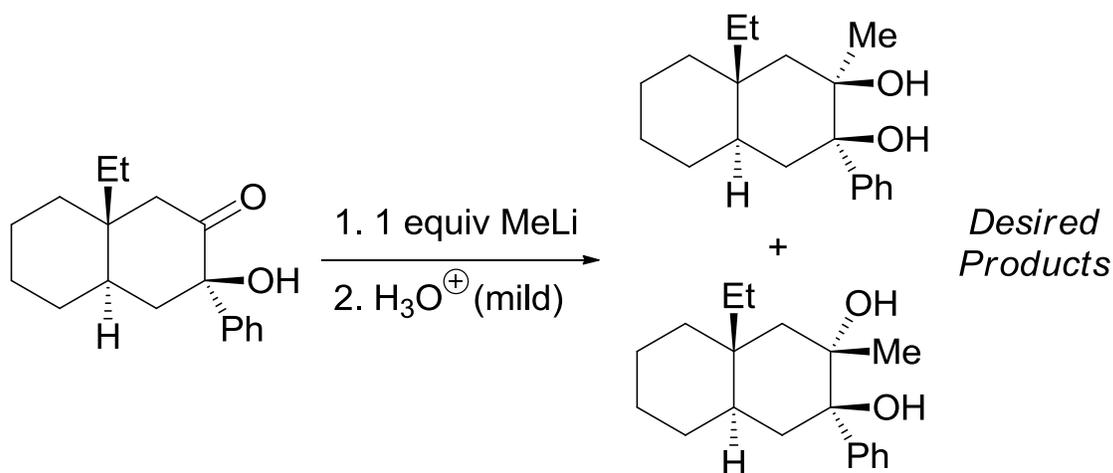
2. A. Is the alkene in compound "X" in the *E* or *Z* configuration?  (2 points)

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



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)

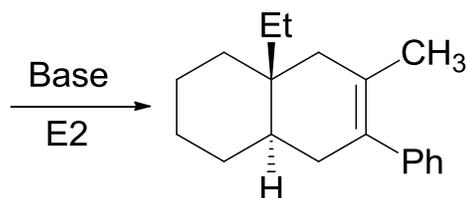


Problem 1:	Actual Products:	Proposed Change:

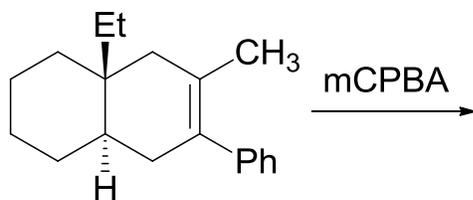
2. D. For the following reaction, will a big base or a small base yield the alkene shown? Circle your choice and explain in 10 words or fewer. (3 points)

A Big / Small base because:

**Two possible stereoisomeric starting materials in all chair conformations.**



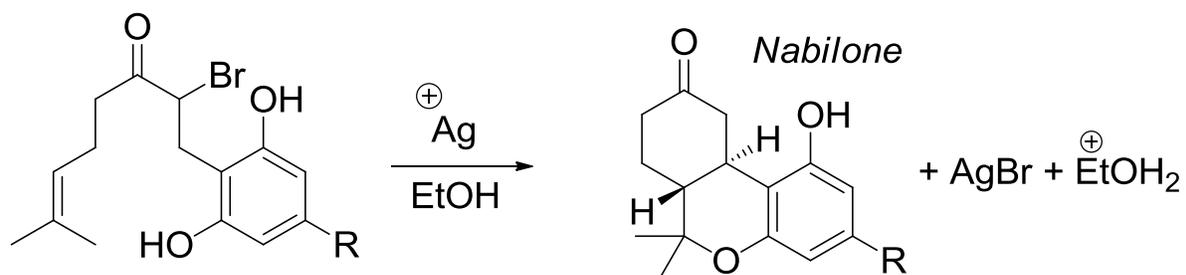
2. E. For the above reaction, provide the two possible starting materials that lead to the alkene shown following E2 elimination. Draw the starting materials in the all chair conformations (see 2.A. for a template). Use Br as the leaving group. (6 points)
2. F. Predict the products of the following reaction. (4 points)



two stereoisomeric products

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

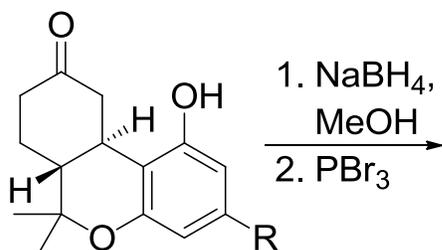
3. A. Provide a mechanism for the following transformation. (10 points)



Blank space for providing the mechanism.

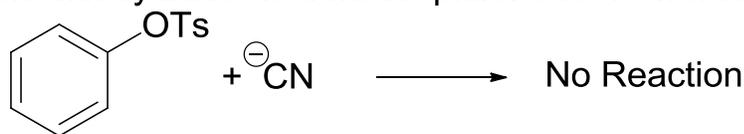
You will not need all of this space.

3. B. Predict the product(s) of the following reactions. Note that the OH group attached to the benzene ring will not react with  $\text{PBr}_3$ . (6 points)



Two stereoisomeric products

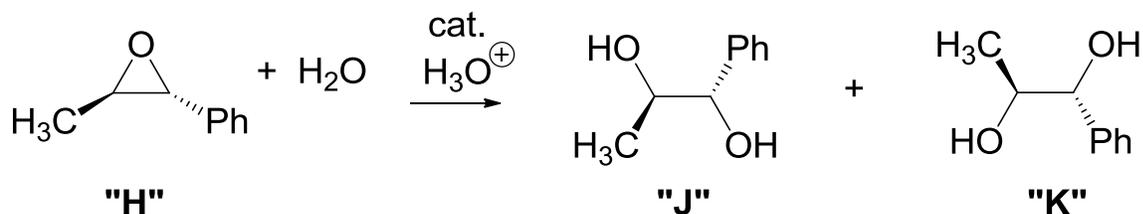
3. C. Using an orbital picture, explain why PhOTs cannot undergo an  $\text{S}_{\text{N}}2$  reaction with cyanide as a nucleophile. Use 10 words or fewer. (5 pts)



Draw the necessary orbital interaction for an  $\text{S}_{\text{N}}2$  reaction.

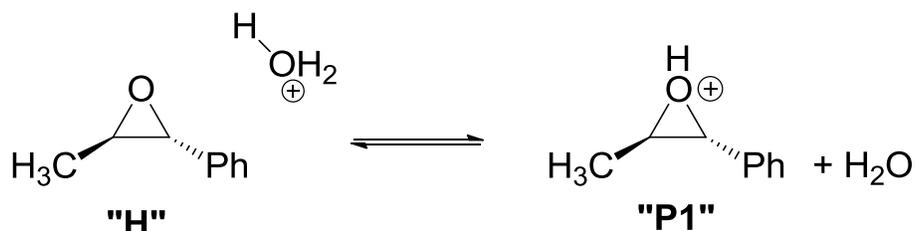
PhOTs cannot undergo an  $\text{S}_{\text{N}}2$  reaction because:

10 words or fewer.

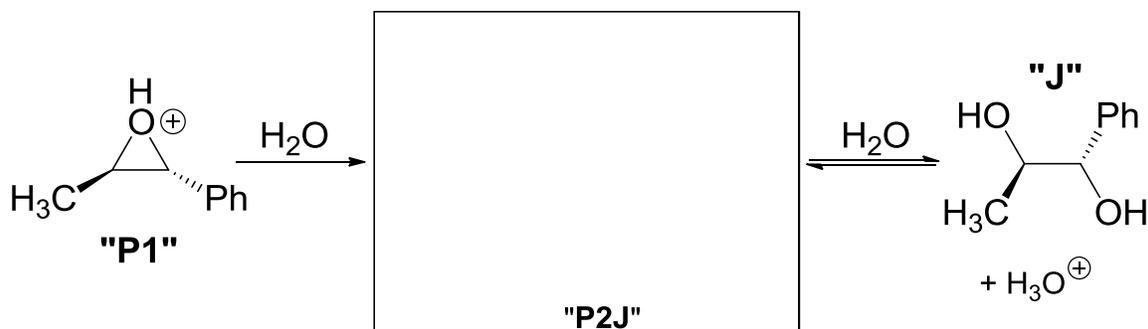


4. A. What is the stereochemical relationship between **"J"** and **"K"**? (2 points)

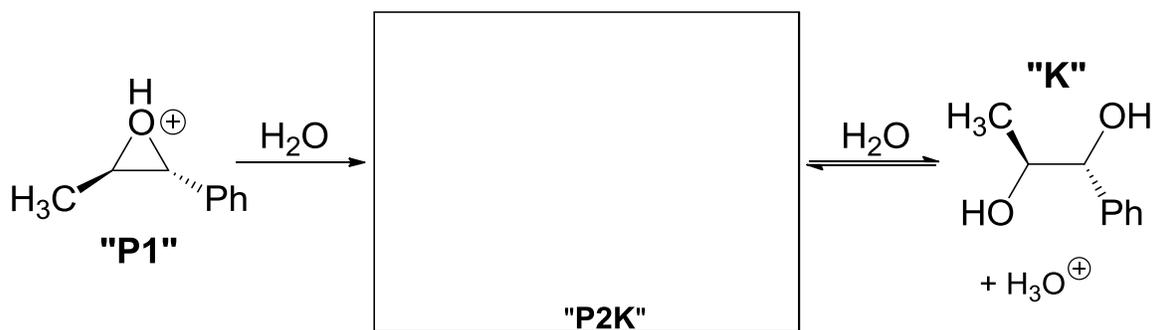
4.B. Add arrows to get from **"H"** to **"P1"**. (2 points)

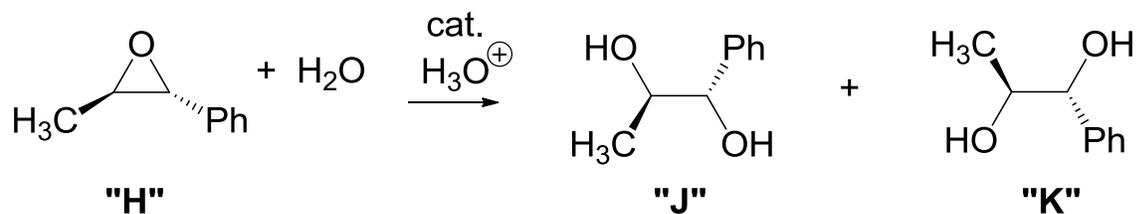


4.C. Finish this mechanism converting **"P1"** to **"J"** by adding necessary arrows and the missing structure **"P2J"**. (6 points)



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

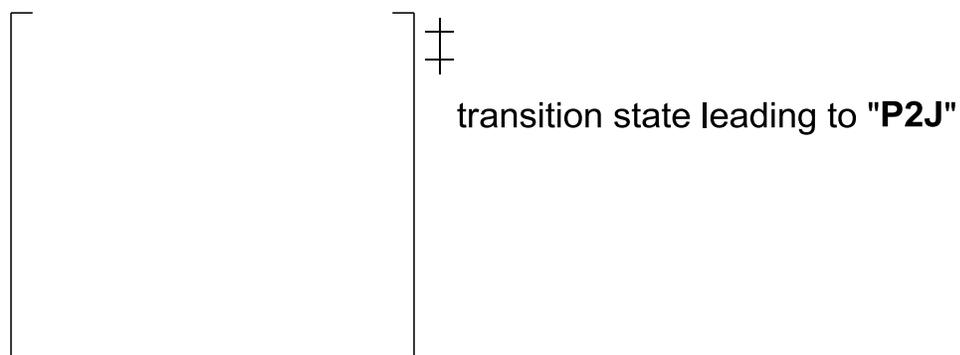




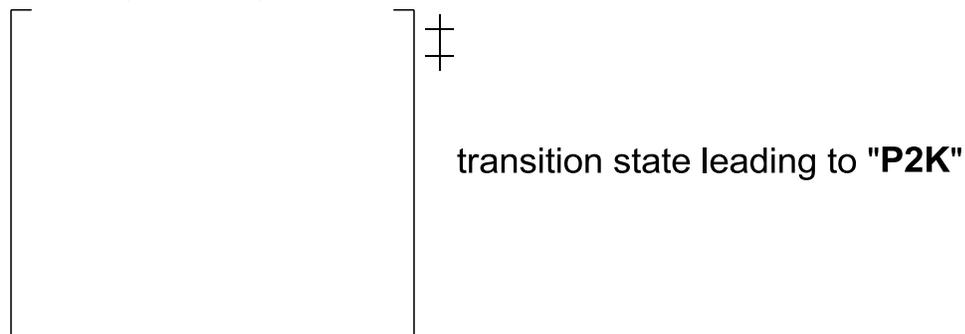
4.E. Draw two relevant resonance contributors that show why the carbons of **"P1"** are electrophilic. (4 points)



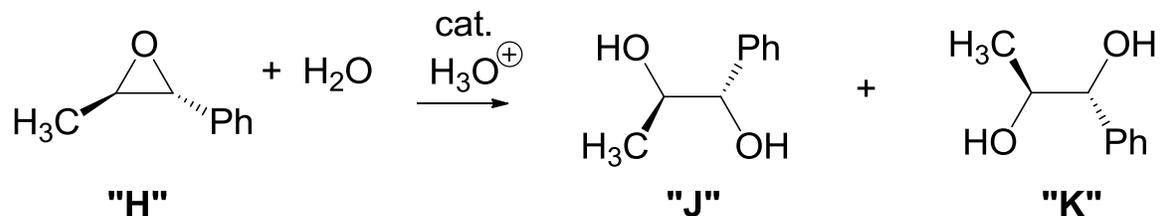
4.F. Draw the transition state for the step converting **"P1"** to **"P2J"** from question 4.C. (3 points)



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



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

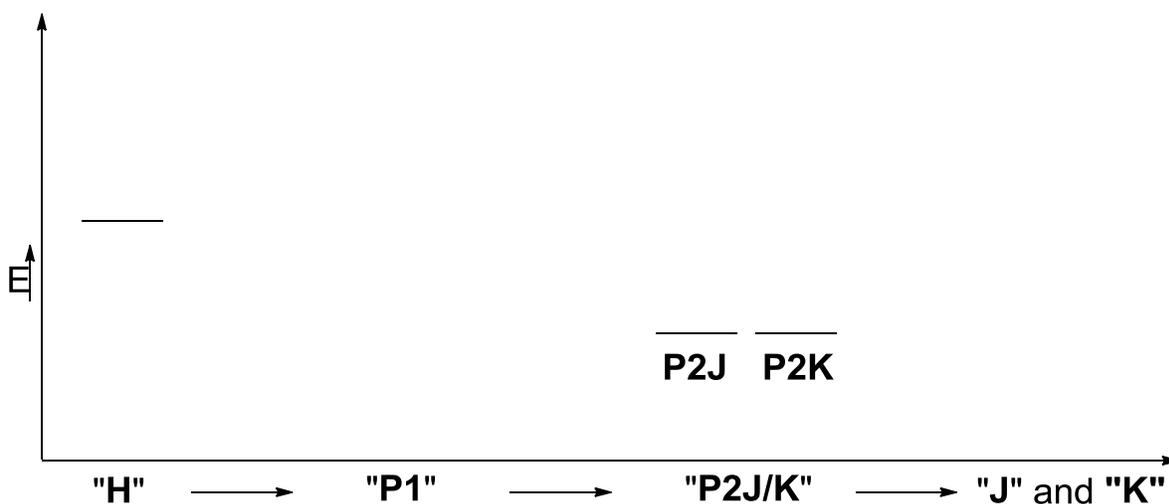


4.I. Product **"J"** is the major product of this reaction. Explain in 20 or fewer words. (4 points)

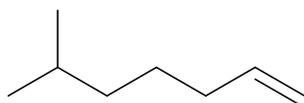
**"J"** is the major product because:

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



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)



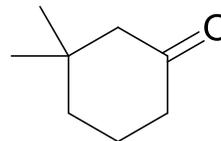
1.

2.

3.

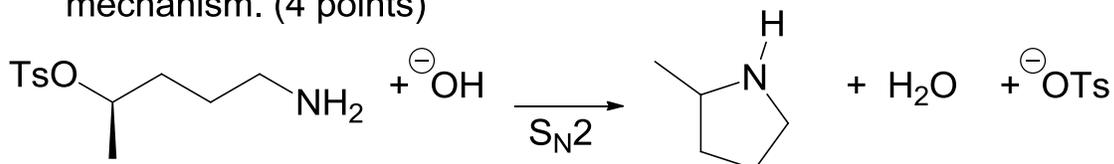
4.

5.

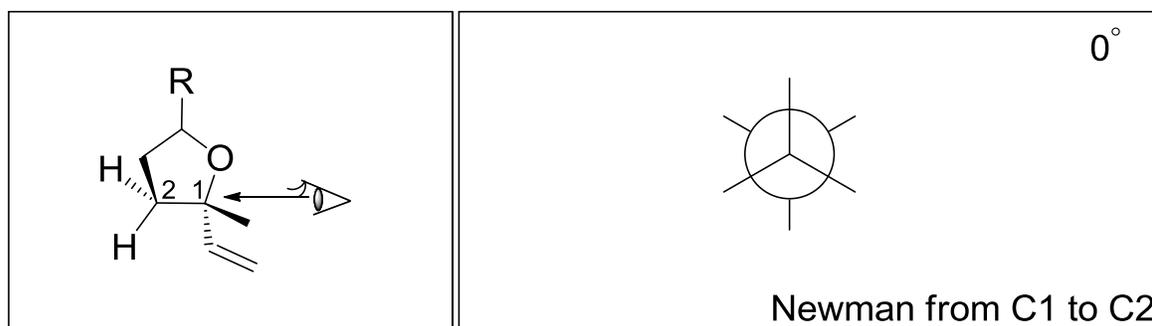


## Basics and Redemption.

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)



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)



6. D. Describe the steric interactions at  $0^\circ$ . 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 $0^\circ$	

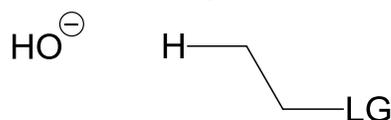
6. E. State whether the following statements are True or False. (6 points)

Small bases give the kinetic product in an E2 elimination

Large bases give the kinetic product in an E2 elimination

NaH is a source of nucleophilic  $\text{H}^-$ .

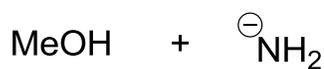
6. F. Show the orbital overlap necessary for a successful E2 reaction. Add labels to the orbitals that you draw. (4 points)

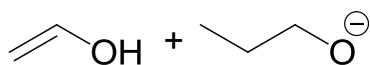
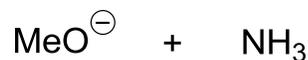


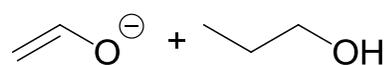
6. G. Fill in the Blanks. (2 points)

Hammond's Postulate states that the \_\_\_\_\_ of an \_\_\_\_\_ will more resemble the products.

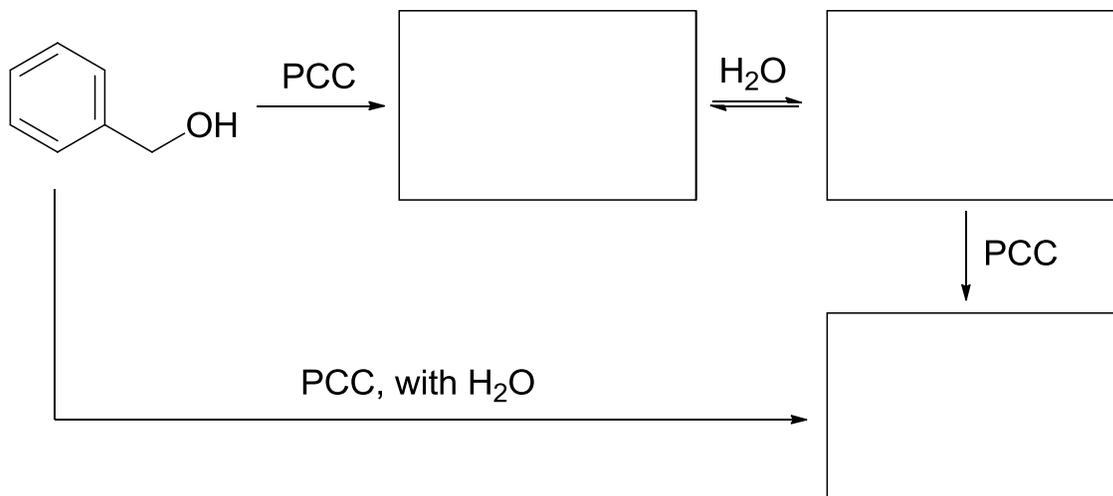
6. H. Add appropriate equilibrium arrows for the following acid / base reactions. (3 points)







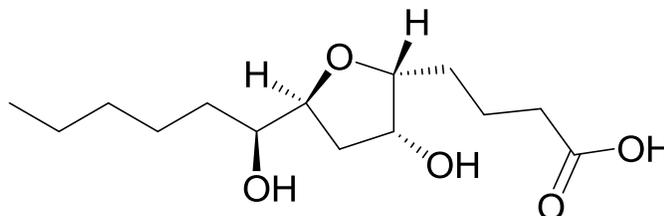
6. I. Primary alcohols can be oxidized to carboxylic acids. Fill in the missing products below. (6 points)



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.

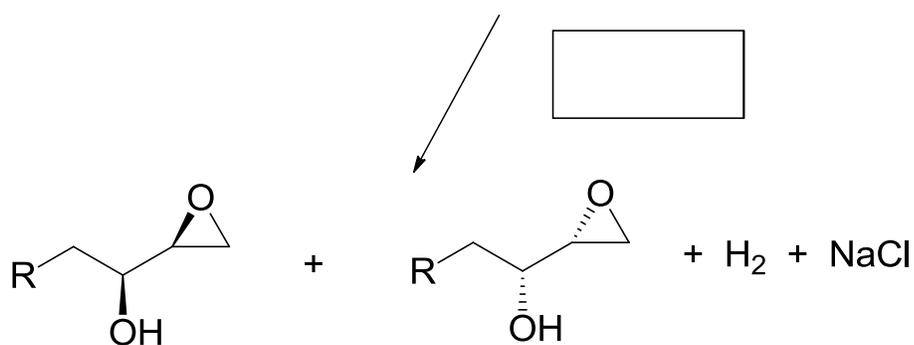
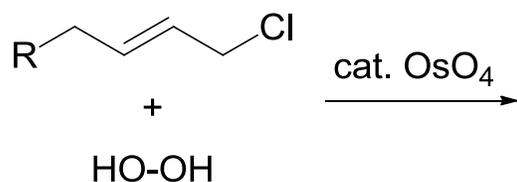


Sea Lamprey

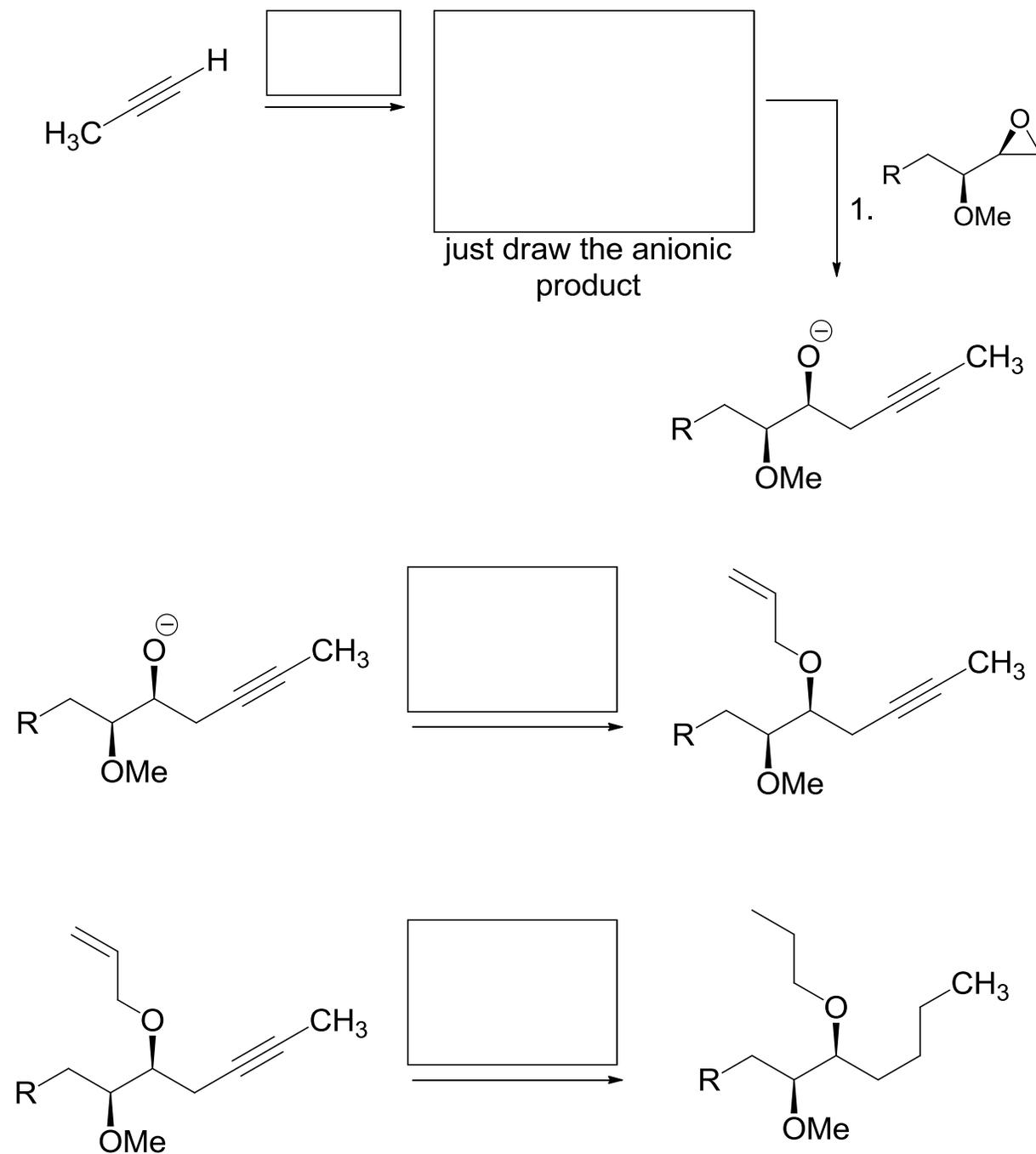


Petromyroxol

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

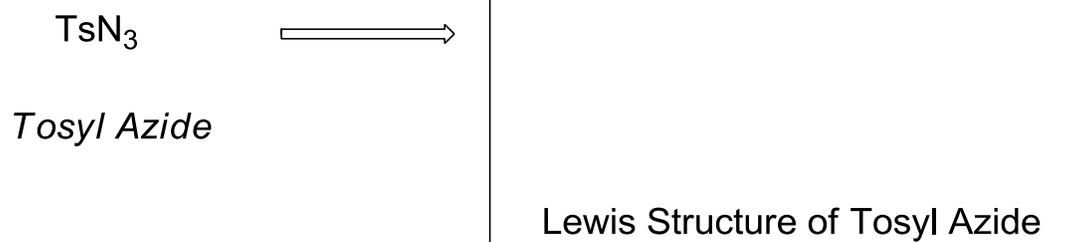


7. B. Please fill in the missing reagents or products. (12 points)

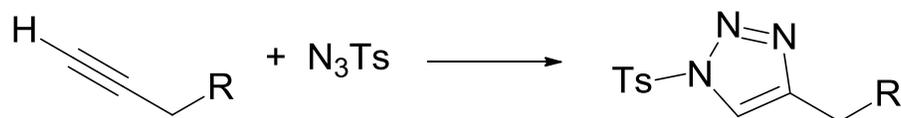


Specify exact quantities of reagents for this last transformation. For example, 2 equivalents and/or catalytic.

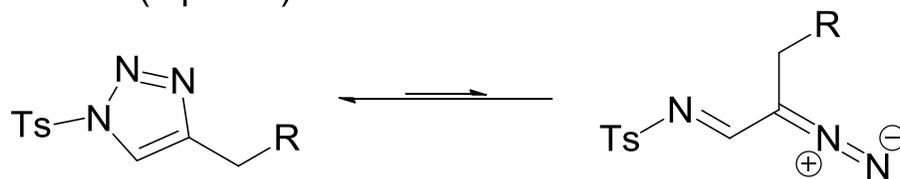
7. C. Draw the structure of the following molecule. Be sure to show any formal charges. (3 points)



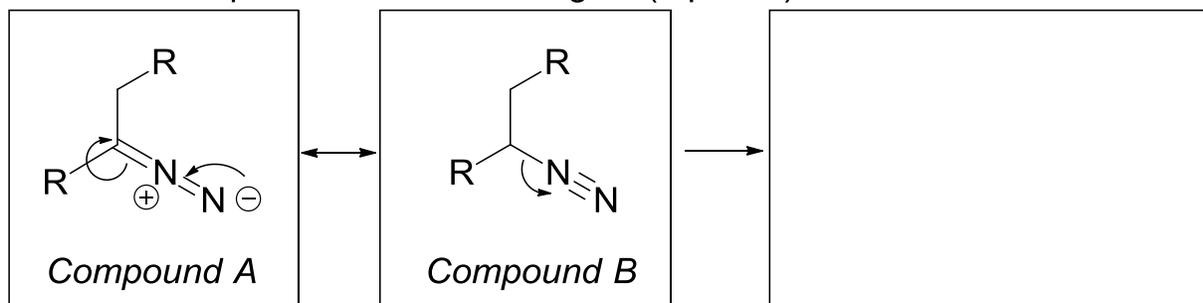
7. D. Provide a rational electron pushing mechanism for the following reaction. *Hint: It is very similar to the first step of ozonolysis.* (6 points)



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



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)

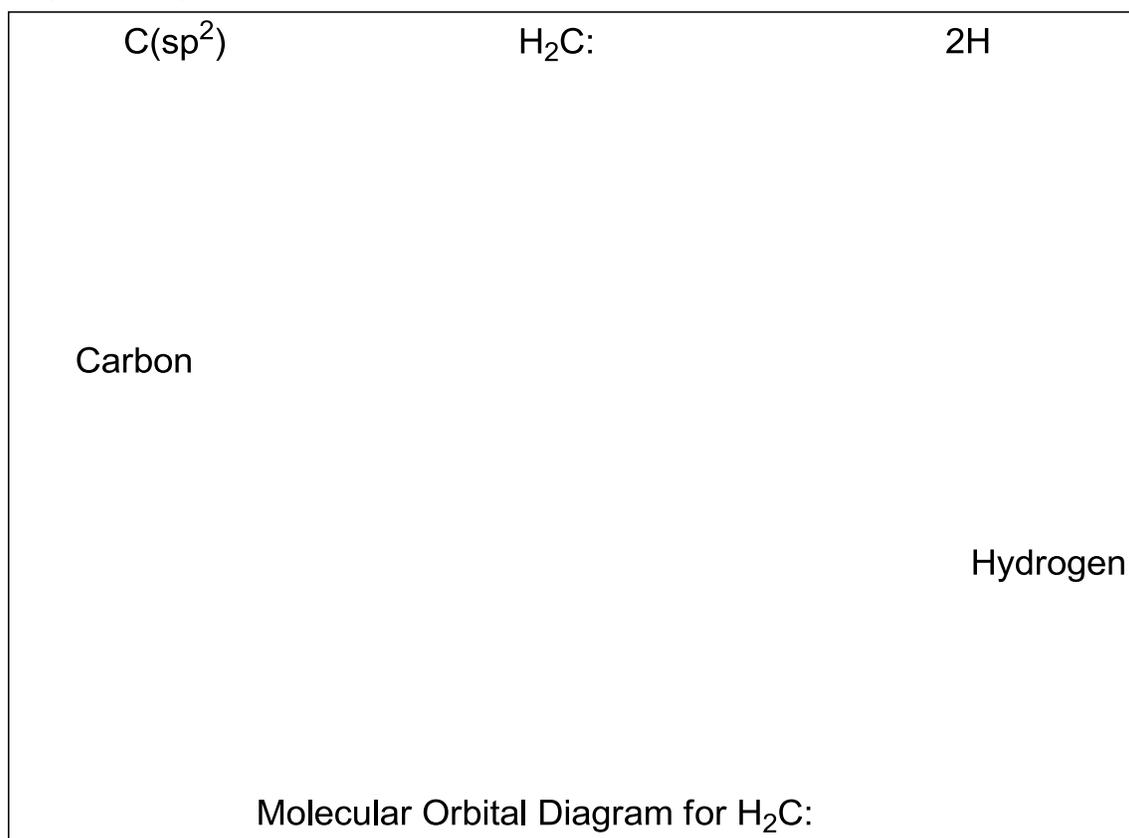


**Add lone pairs.**

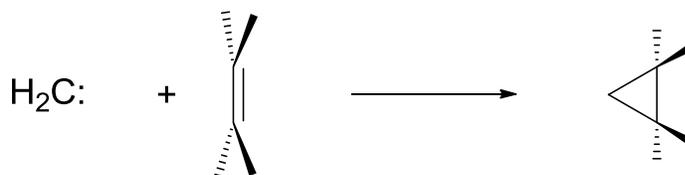
**Add lone pairs and charges.**

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

7. I. Construct the MO diagram for  $\text{H}_2\text{C:}$ , where the carbon is  $\text{sp}^2$  hybridized. 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)



7. J.  $\text{H}_2\text{C:}$  is known as a carbene. It is electron deficient, but neutral. It reacts with alkenes similarly to  $\text{Br}_2$  to create a 3-membered ring. Provide a mechanism for the following transformation. (4 points)



7. K. Which orbital of  $\text{H}_2\text{C:}$  has the correct symmetry to overlap with the pi orbital of the alkene? Draw the pictures of the orbitals and label them. (3 points)

Add the orbital  
that matches  
the pi bond's  
symmetry



Add the pi-  
bonding orbital

7. L. Which orbital of  $\text{H}_2\text{C:}$  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)

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  $\text{H}_2\text{C:}$  do the two electrons reside? Circle the answer below. (2 points)  
*Remember: Filled orbitals interact with unfilled orbitals to create new bonds*

Carbon P orbital

Carbon  $\text{sp}^2$  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)

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.