NAME (Print): _____

EID _____

SIGNATURE: _____

Chemistry 320M/328M
Dr. Brent Iverson
3rd Midterm
November 17, 2022

Please print the first three letters of your last name in the three boxes

Please Note: Please take your time. We are giving you three hours to take this exam. The idea is to give you enough time to show us what you know, not how fast you can draw structures. Please take all the time you need to draw the best possible structures that you can! Do not be surprised if you are comfortable leaving the exam before 9 PM.

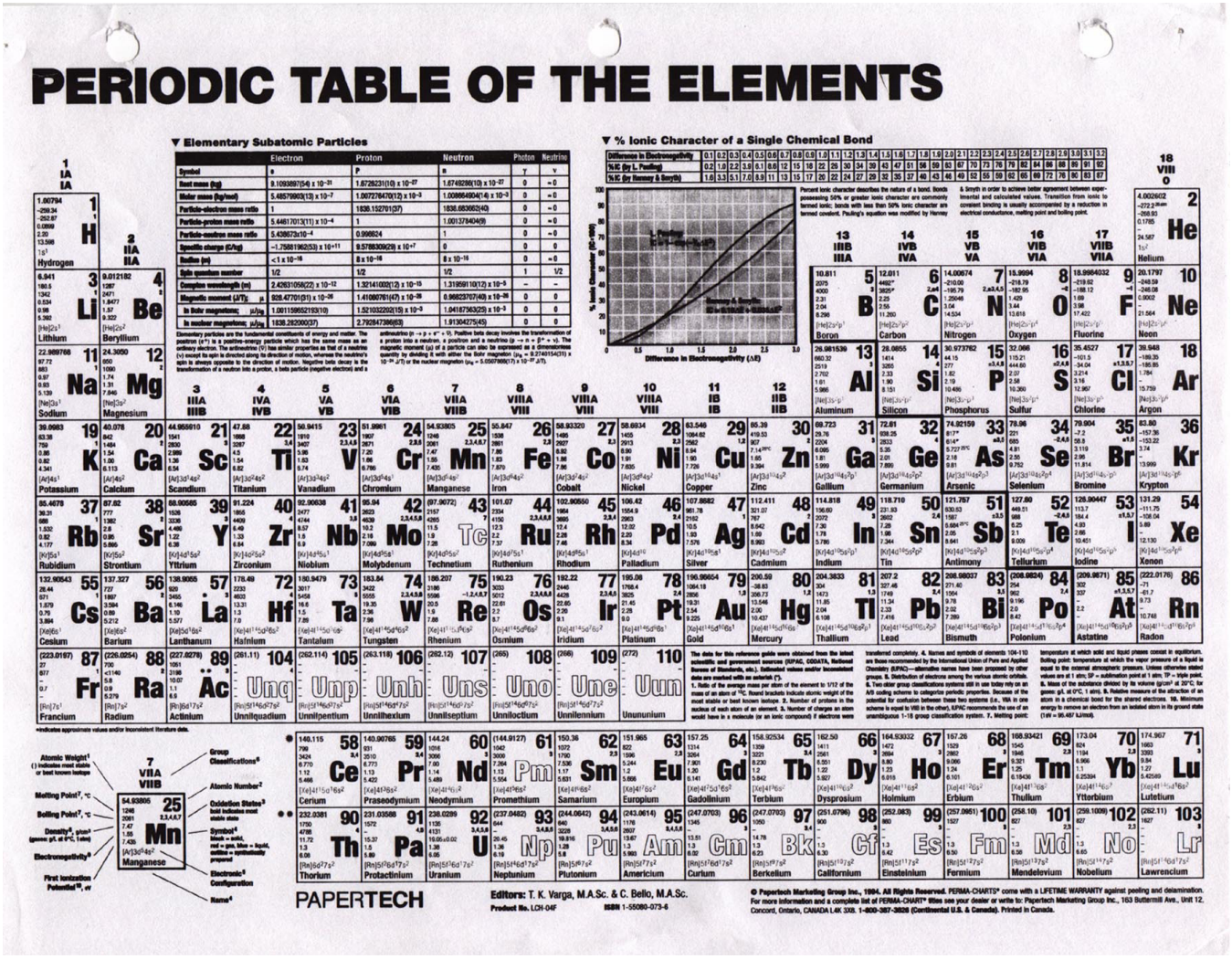
FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

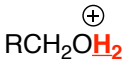
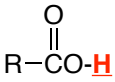
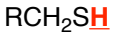
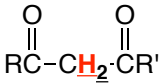
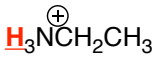
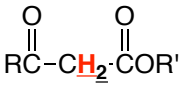
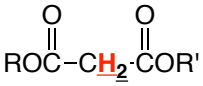
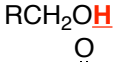
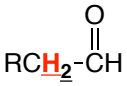
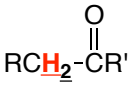
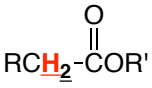
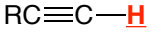
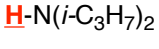
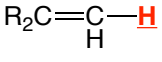
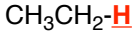
Student Honor Code

“As a student of The University of Texas at Austin, I shall abide by the core values of the University and uphold academic integrity.”

_____

(Your signature)



Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Carboxylic acids		3-5
Thiols		8-9
Ammonium ion		9.2
β-Dicarbonyls		10
Primary ammonium		10.5
β-Ketoesters		11
β-Diesters		13
Water		15.7
Alcohols		15-19
Acid chlorides		16
Aldehydes		18-20
Ketones		18-20
Esters		23-25
Terminal alkynes		25
LDA		40
Terminal alkenes		44
Alkanes		51

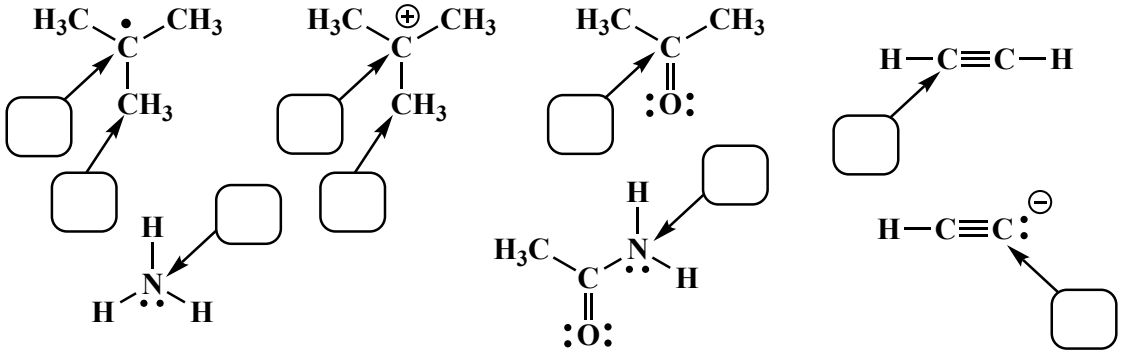
Here is a blank page to write down your roadmap if you wish.

Signature_____ Pg 1 _____(33)

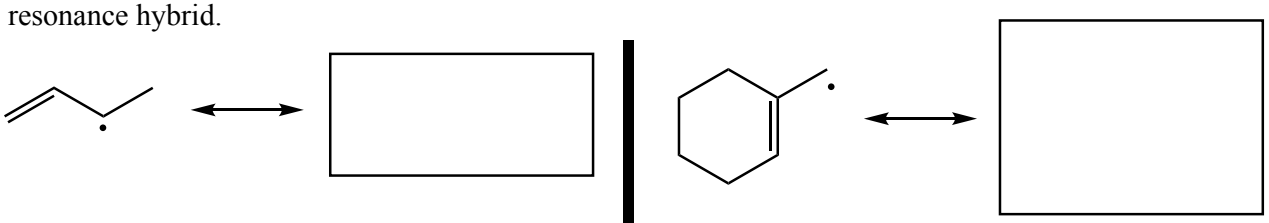
1. (2 pts) What is the most important question in organic chemistry?

2. (6 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges. For the two structures on the left in each problem, use arrows to indicate the movement of electrons to give the structures you drew. There is no need to draw any circles around any of these contributing structures. You might want to read these directions again to make sure you know what we want

3. (9 pts.) For the following structures, write the hybridization state of each atom that is indicated with an arrow.



4. (16 pts total) Draw the other important contributing structure for the following two allylic radicals. Under each structure, fill in the apprорpriate circle to indicate major and minor contributors to the overall resonance hybrid.



○ Major Contributor
○ Minor Contributor

○ Major Contributor
○ Minor Contributor

○ Major Contributor
○ Minor Contributor

○ Major Contributor
○ Minor Contributor

5. (4 pts each) For the following lists of structures, fill in the circles to indicate which structure is the most stable or most reactive/reactive and which is the least stable or least/not reactive. You do not have to fill in any circles for molecules of intermediate stability or intermediate reactivity.

Radical Stability

○ Most Stable ○ Least Stable	○ Most Stable ○ Least Stable	○ Most Stable ○ Least Stable	○ Most Stable ○ Least Stable

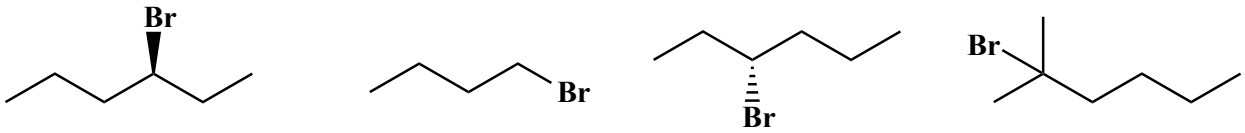
Carbocation Stability

○ Most Stable ○ Least Stable	○ Most Stable ○ Least Stable	○ Most Stable ○ Least Stable	○ Most Stable ○ Least Stable

Alkene Stability

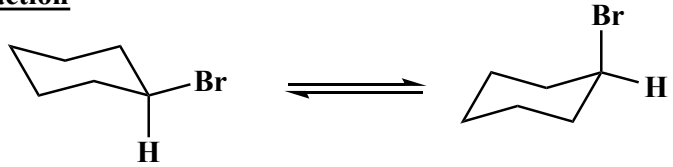
○ Most Stable ○ Least Stable	○ Most Stable ○ Least Stable	○ Most Stable ○ Least Stable	○ Most Stable ○ Least Stable

Reactivity in an S_N2 Reaction



○ Most Reactive ○ Least Reactive	○ Most Reactive ○ Least Reactive	○ Most Reactive ○ Least Reactive	○ Most Reactive ○ Least Reactive

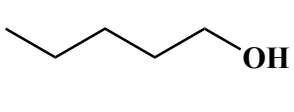
Reactivity in an E2 Reaction



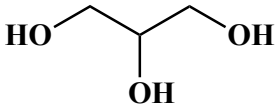
○ Reactive ○ Not Reactive	○ Reactive ○ Not Reactive

6. (4 pts) For the following list of structures, fill in the circles to indicate which structure has the highest boiling point, and which one has the lowest boiling point. You do not have to fill in any circles for molecules of intermediate boiling point.

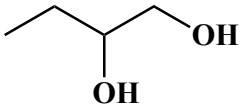
Boiling Point



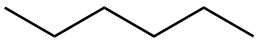
◯ **Highest Boiling Point**
◯ **Lowest Boiling Point**



◯ **Highest Boiling Point**
◯ **Lowest Boiling Point**



◯ **Highest Boiling Point**
◯ **Lowest Boiling Point**



◯ **Highest Boiling Point**
◯ **Lowest Boiling Point**

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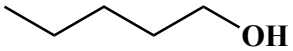
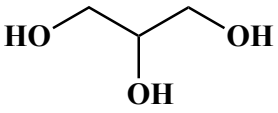
7. (4 pts) For the following list of structures, fill in the circles to indicate which structure has the highest solubility in water, and which one has the lowest solubility in water. You do not have to fill in any circles for molecules of intermediate solubility.

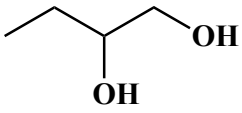
Water Solubility



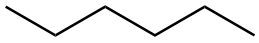
◯ **Most Soluble in Water**
◯ **Least Soluble in Water**



◯ **Most Soluble in Water**
◯ **Least Soluble in Water**



◯ **Most Soluble in Water**
◯ **Least Soluble in Water**



◯ **Most Soluble in Water**
◯ **Least Soluble in Water**

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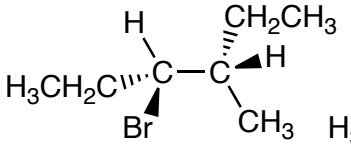
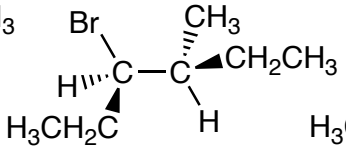
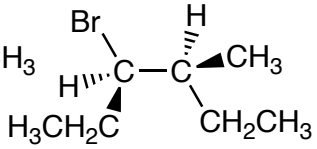
8. (8 pts) Drawn below are four conformations of the molecule (3*R,4S*)-3-bromo-4-methylhexane. Indicate any of the conformations that, **as drawn**, would be able to react through an E2 mechanism with a strong base.



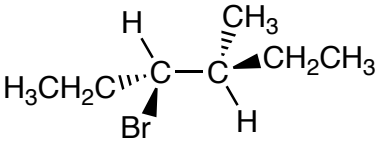
◯ **Reacts by E2**
◯ **Cannot react by E2**



◯ **Reacts by E2**
◯ **Cannot react by E2**



◯ **Reacts by E2**
◯ **Cannot react by E2**



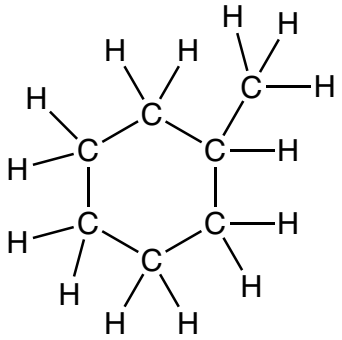
◯ **Reacts by E2**
◯ **Cannot react by E2**

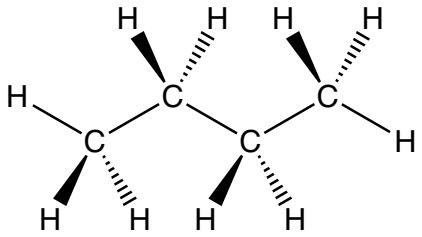
In the box, draw the product of the E2 reaction of (3*R,4S*)-3-bromo-4-methylhexane with strong base.

9. (20 pts) Consider the following statements that refer **S_N1, S_N2, E1, E2**, or a **radical chain reaction** mechanism. Fill in the circles to indicate to which mechanism(s) each statement applies.

A. A reaction that involves "scrambling" of stereochemistry at the site of reaction.	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**
B. A reaction that involves initiation, propagation and termination steps.	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**
C. A reaction that involves an anti-periplanar transition state.	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**
D. A reaction observed when tertiary haloalkanes react with any nucleophile that is not a very weak base.	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**
E. A reaction in which the predominant product is predicted by Zaitsev's rule.	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**
F. A reaction that will occur when Br_2 and light are used with an alkane.	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**
G. A reaction obeserved when secondary haloalkanes react with a nucleophile that is a very weak base (as solvent).	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**
H. A reaction observed when primary haloalkanes react with any nucleophile.	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**
I. A reaction that causes InVERSiON of sterechemistry at the site of reaction.	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**
J. A reaction that is favored for secondary haloalkanes when a nucleophile that is NOT a strong base and is also NOT a very weak base is used	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**
K. A reaction mechanism that involves a carbocation intermediate.	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**
L. A reaction mechanism that involves a radical intermediate.	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**
M. A reaction mechanism that involves only a transition state, no intermediate.	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**
N. A reaction mechanism that is seen when 2° and 3° alcohols react with H-X.	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**
O. A reaction mechanism that is seen when 2° and 3° alcohols react with H_2SO_4 (no added water).	○ **S_N2** ○ **S_N1**	○ **E2** ○ **E1**	○ **Radical chain reaction**

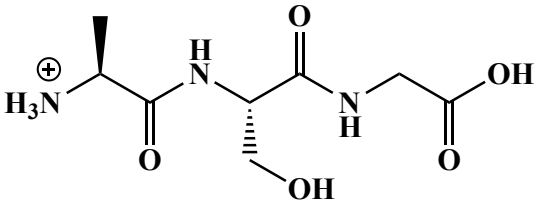
10. (5 pts) For the following molecules**, circle the H atom(s) that are most likely to react during a free radical halogenation reaction using Br_2 and light. If more than one H atom ties as the most reactive on the molecule, circle all of the most reactive ones.**





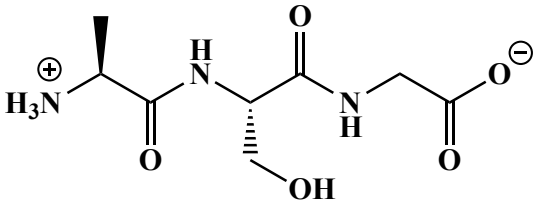
11. (8 pts.) Fill in the circle to indicate the pH at which the species shown will be the prodominant one. Fill in the circle next to the "X" under a species that cannot predominant at any pH.

The pKa of a carboxylic acid (RCO_2H) is generally in the 4-5 range. The pKa of ammonium ions ($RNH_3^{\oplus}$) is in the 9-10 range and that of -OH groups is in the 15-16 range.



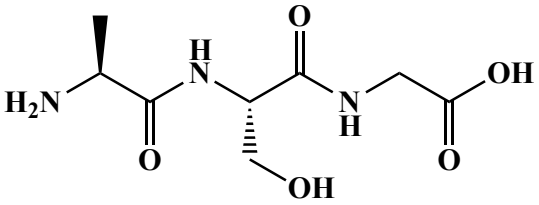
○ **pH 2.0** ○ **pH 12.0**

○ **pH 7.0** ○ **X**



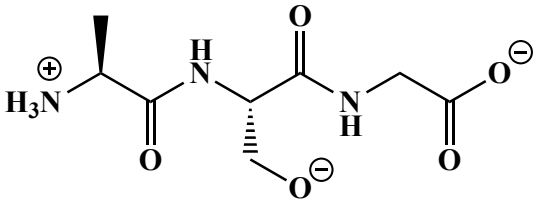
○ **pH 2.0** ○ **pH 12.0**

○ **pH 7.0** ○ **X**



○ **pH 2.0** ○ **pH 12.0**

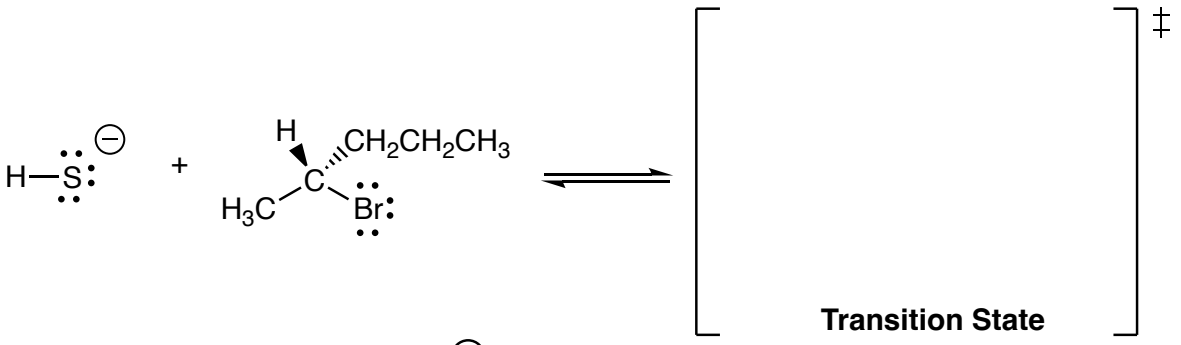
○ **pH 7.0** ○ **X**



○ **pH 2.0** ○ **pH 12.0**

○ **pH 7.0** ○ **X**

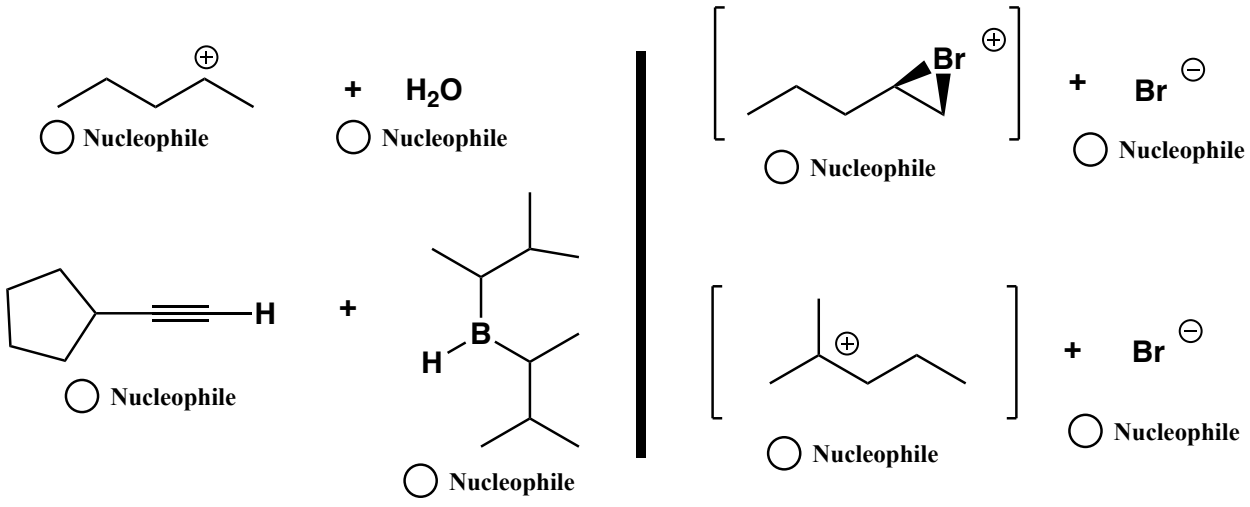
12. (17 pts total) For the S_N2 reaction below, **draw the key transition state that leads to the product. Also draw the product(s). In the transition state, use dotted/dashed lines to indicate bonds that are in the process of being broken or made. Write all lone pairs and all formal charges. On the starting structures, draw all appropriate arrows to indicate the flow of electrons. Use wedges and dashes to indicate stereochemistry as appropriate and write "racemic" if that term applies.**



Is the starting material *R* or *S*? ○ ***R*** ○ ***S***

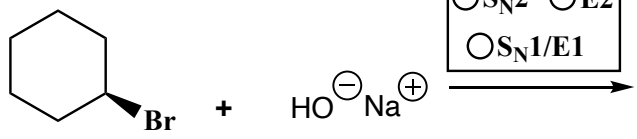
Is the product *R* or *S*? ○ ***R*** ○ ***S***

13. (8 pts) For the following four sets of reagents you have seen in various bond-making steps in mechanisms, **fill in the circle to inidicate which of the two species is the nucleophile.** DO NOT WRITE THE PRODUCTS OF THESE STEPS, we only want to see circles filled-in here!!

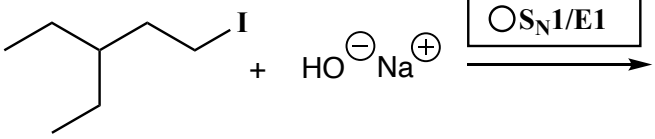


14. (5 or 6 pts each) The following reactions all involve chemistry of haloalkanes. **Fill in the circle above the arrow to indicate the mechanism that will be followed (S_N2, E2, etc.)**. **Then draw only the predominant product or products** and please remember that **you must draw the correct stereoisomers**. For S_N1/E1 reactions you must draw all significant products (including all stereoisomers).

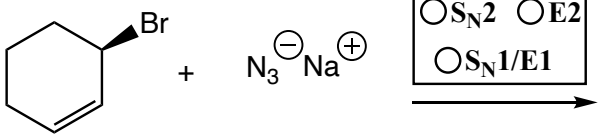
A.



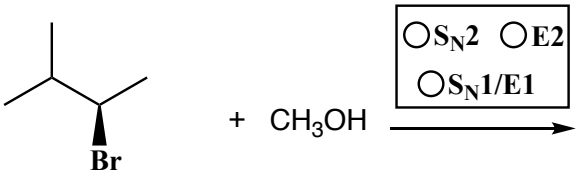
B.



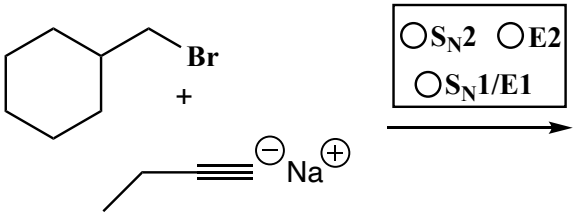
C.



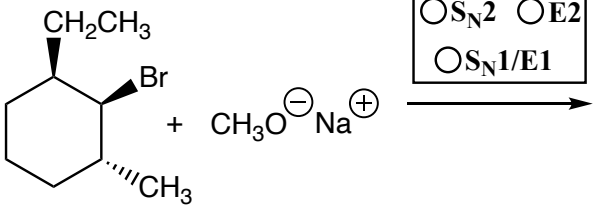
D.



E.

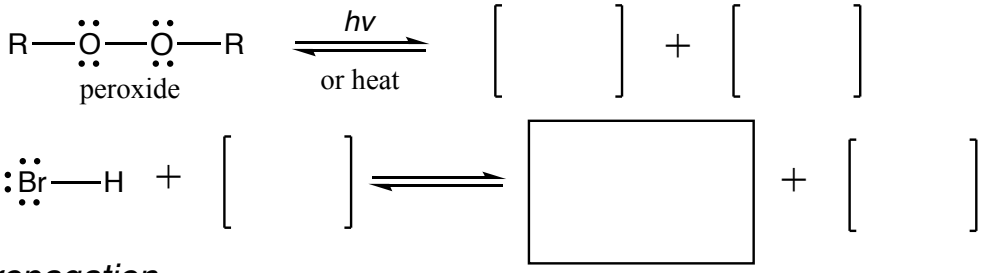


F.

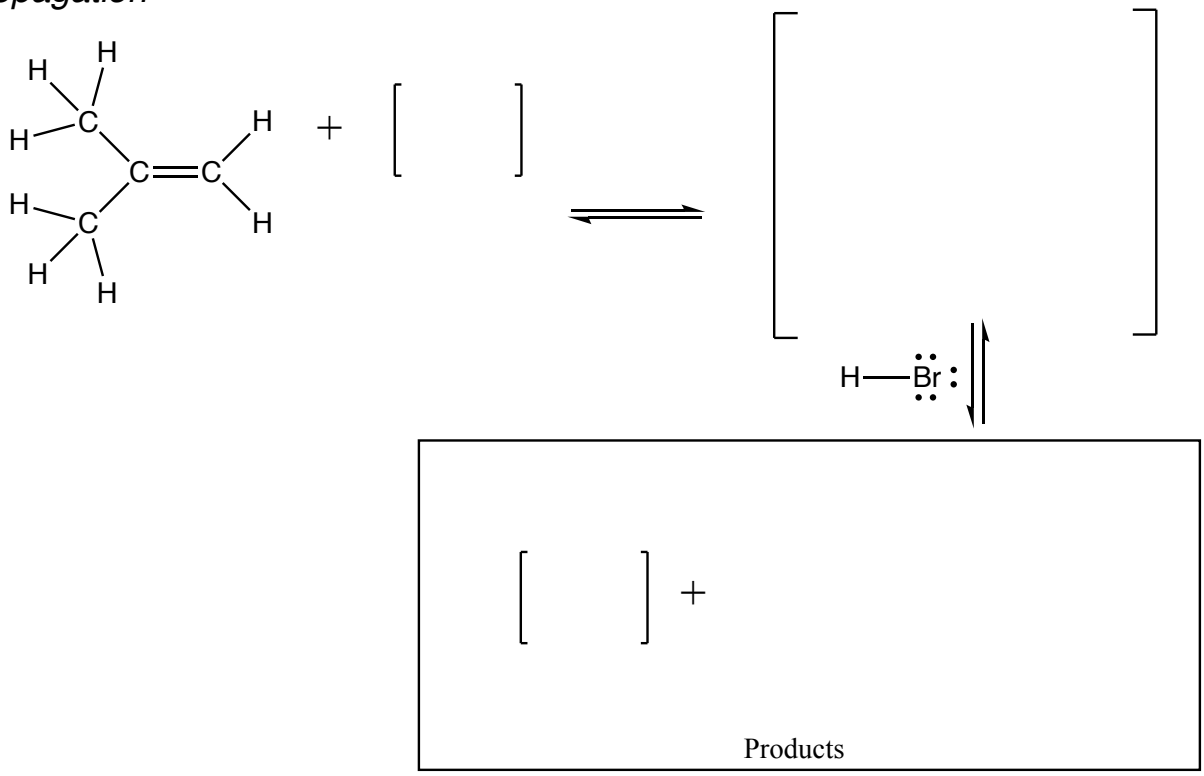


15. (34 pts total) Complete the following mechanism for the free radical addition of HBr to an alkene. Use appropriate arrows to show movement of electron density, and show all non-bonding electrons as dots and show any formal charges. **If any of the species are really a racemic mixtures of enantiomers, you only need to draw one stereoisomer and write "racemic". Note that for the termination step, you only need to draw one of the three possible examples of termination.**

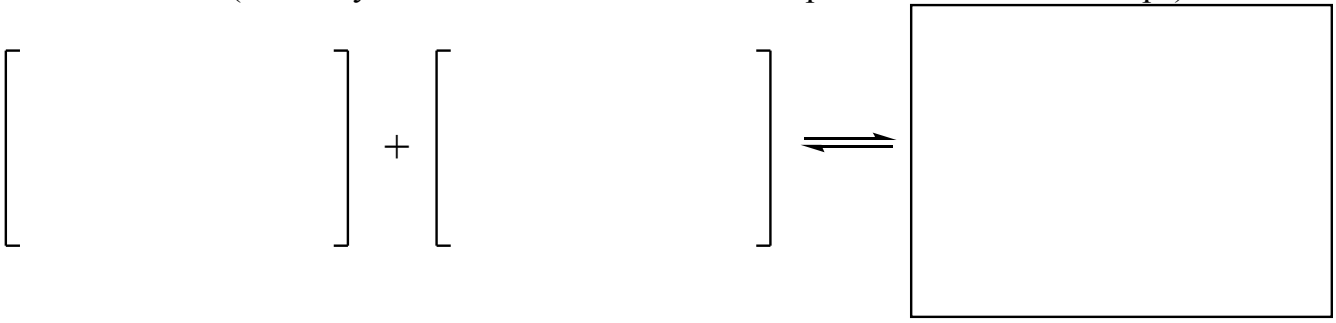
Initiation



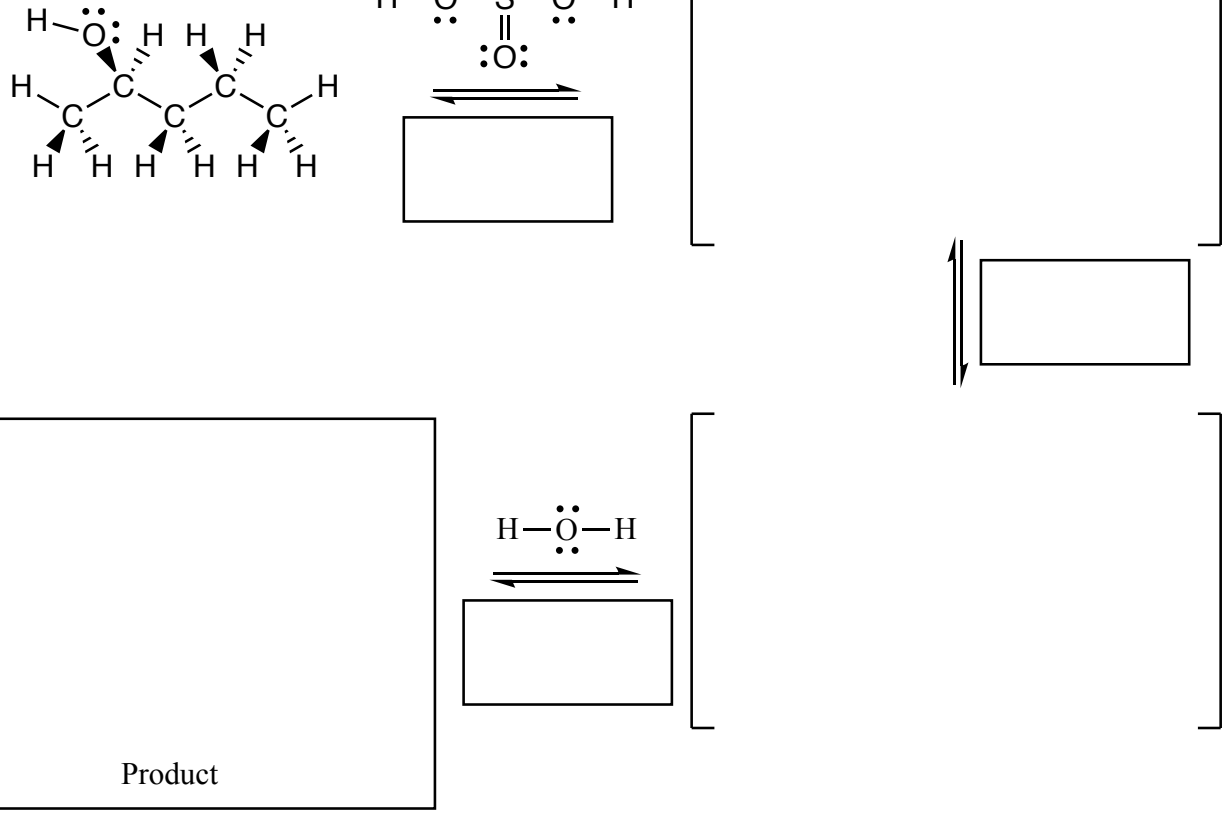
Propagation



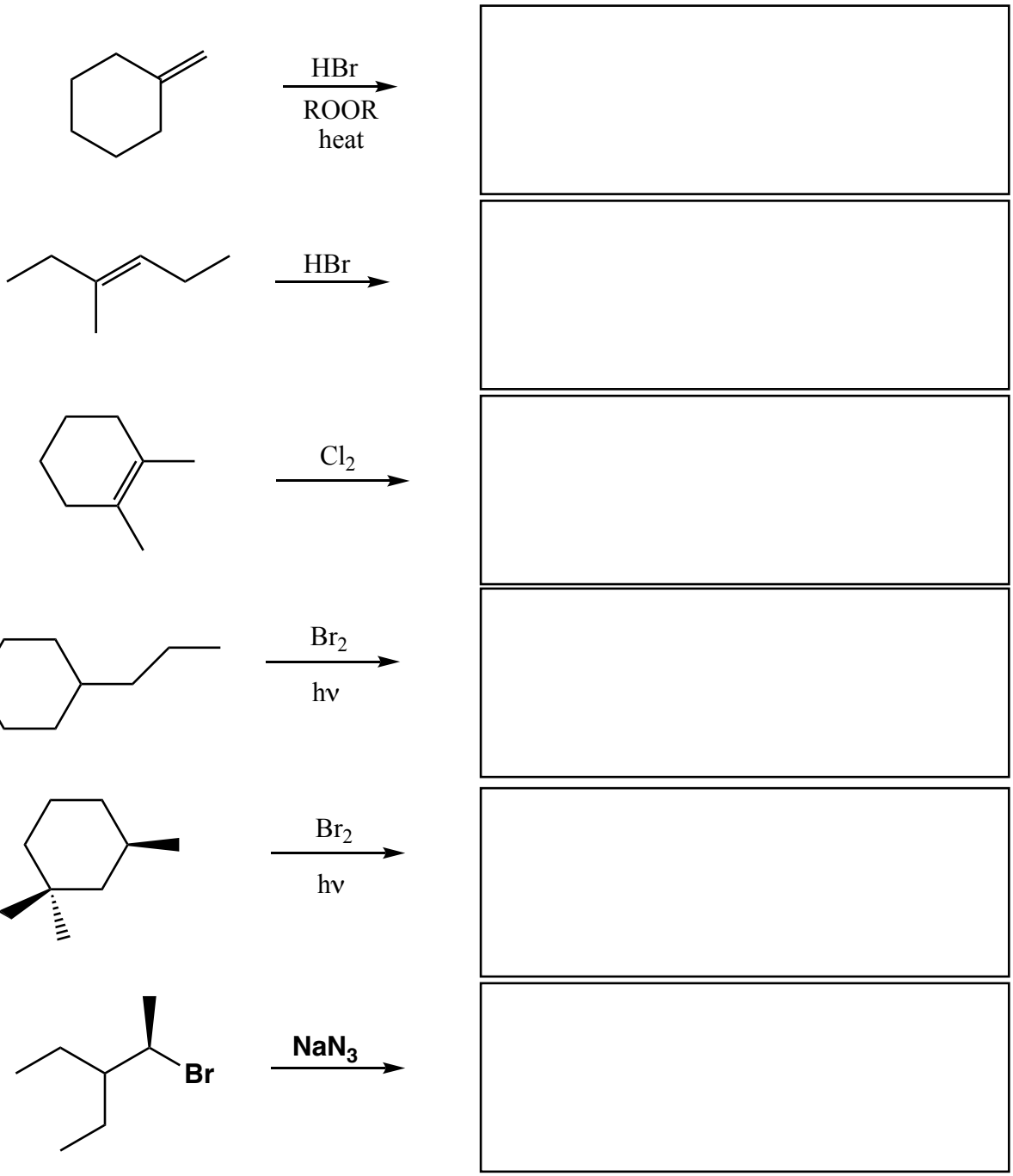
Termination (You only need to show one of the three possible termination steps)



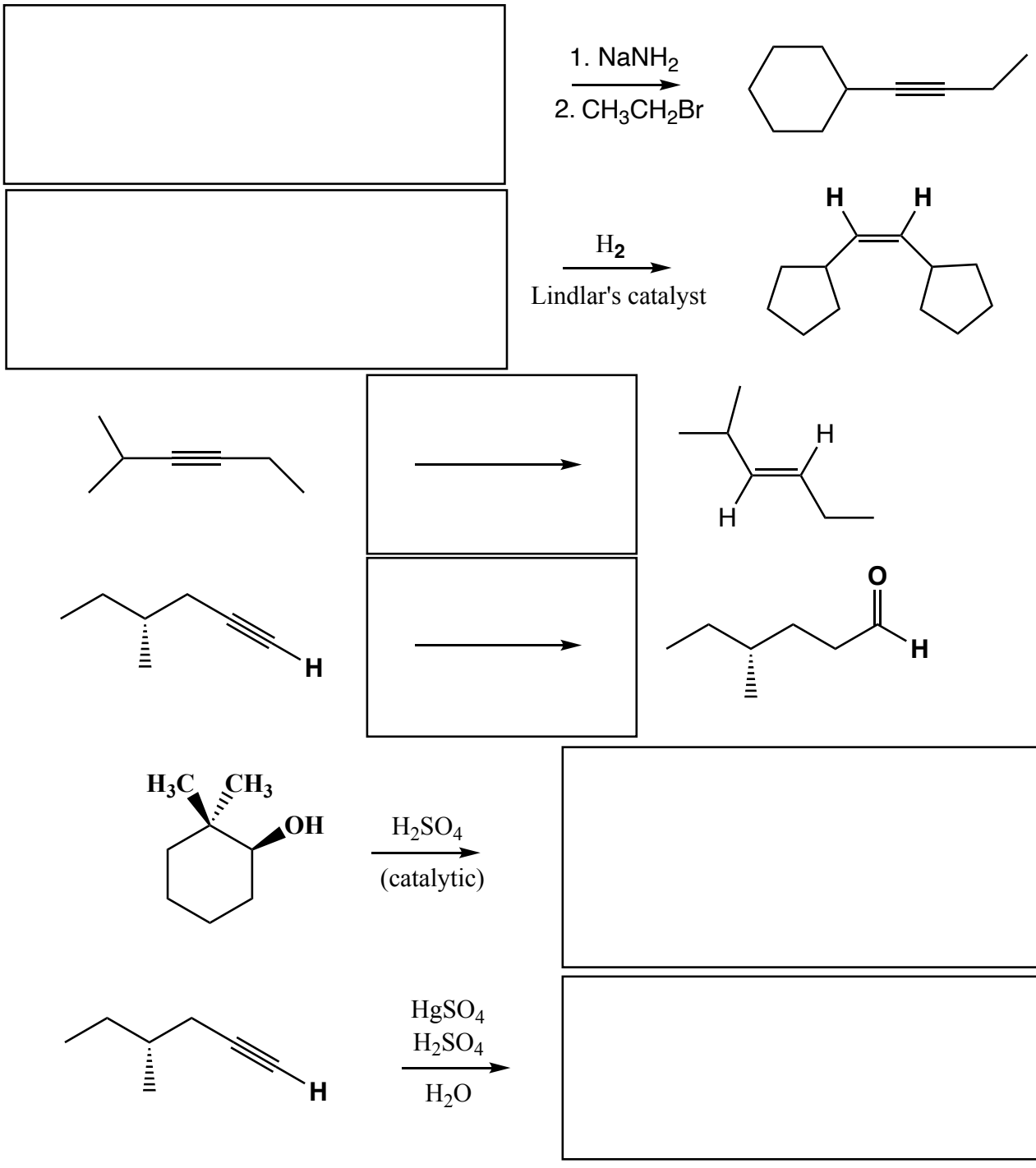
16. (20 pts) Complete the mechanism for the following acid-catalyzed alcohol dehydration reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. YOU ONLY NEED TO DRAW ONE STEREOISOMER OF A CHIRAL INTERMEDIATE OR PRODUCT (using wedges and dashes as appropriate) IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. In the three boxes provided, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).



17. (24 pts) Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov, etc.) and please remember that you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry. When a racemic mixture is formed, you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES.

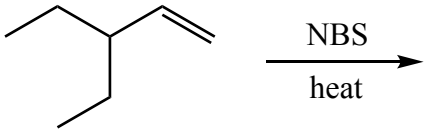


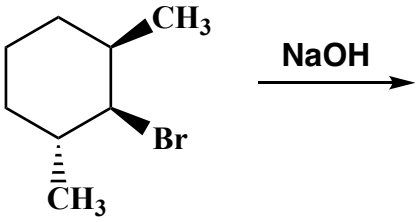
18. (18 pts) For the following reactions, fill in the box with the predominant starting materials, product(s) or reagent(s) necessary to complete the following syntheses. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate.



19. (6 pts) The following two reactions take a little more thought. Fill in the box with **only the predominant regioisomer product or products** and please remember that **you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry**. When a racemic mixture is formed, **you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES**.

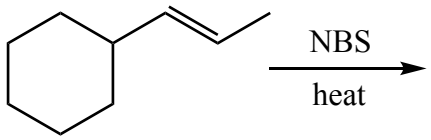
I am giving you some extra room to work through these



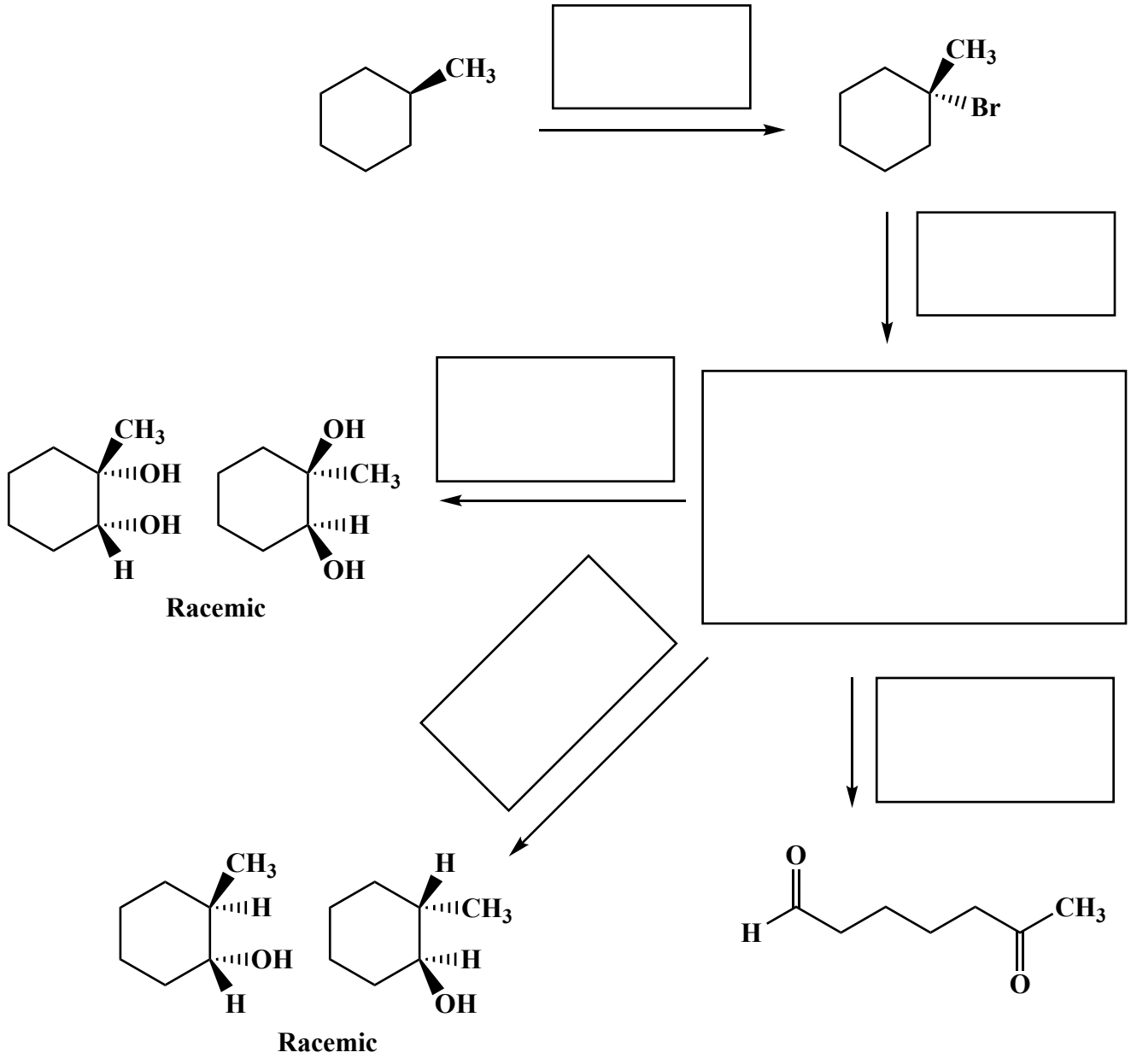


19. (6 pts) The following two reactions take a little more thought. Fill in the box with **only the predominant regioisomer product or products** and please remember that **you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry**. When a racemic mixture is formed, **you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES**.

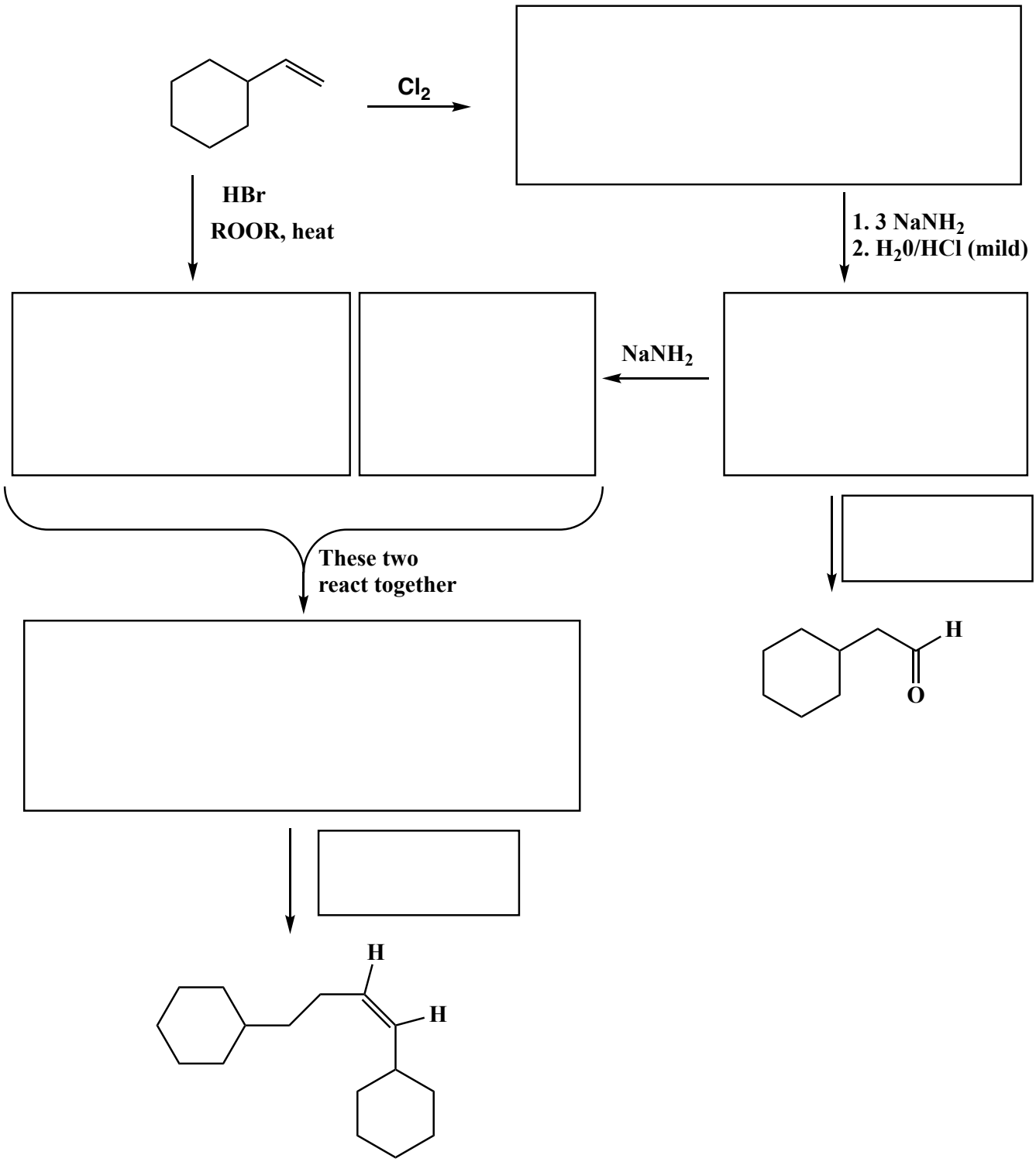
I am giving you some extra room to work through these



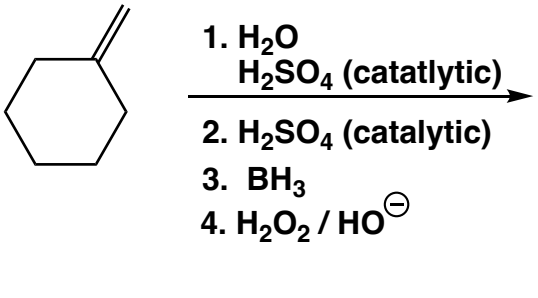
20. (13 pts) For the following reactions, fill in the box with the **predominant product(s)** or **reagent(s)** necessary to complete the following syntheses. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate.



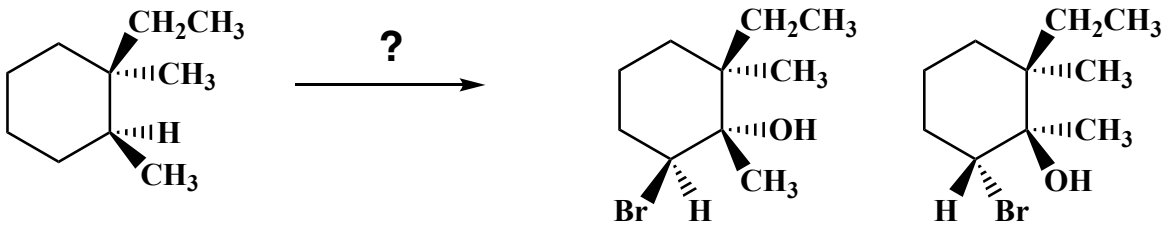
21. (21 pts) For the following reactions, fill in the box with the **predominant product(s)** or **reagent(s)** necessary to complete the following syntheses. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate.



22. (8 pts) For the following sequence of reactions, **draw the final product(s)**. You only need to draw **the very last product(s) in the box provided**, although feel free to draw any other structures in the empty space provided. We will only grade the structure(s) in the box. As always, if a racemic mixture is created you need to draw both enantiomers using wedges and dashes and write "racemic".



23. (7 pts) This is your first synthesis problem. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting materials. Do not be intimidated by the complicated nature of these molecules. Recognize the product as something you have seen. You can do this! Seriously, I would not BS you!**



Not racemic, these are diasteromers

Here is a blank page to use as scratch paper. Have a fantastic Thanksgiving break, and remember to run every chance you get! Don't forget to watch the NMR lecture I recorded yesterday!