NAME (Print): _____

EID _____

SIGNATURE: _____

Chemistry 320M/328M
Dr. Brent Iverson
3rd Midterm
November 21, 2024

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 for the University of Texas at Austin

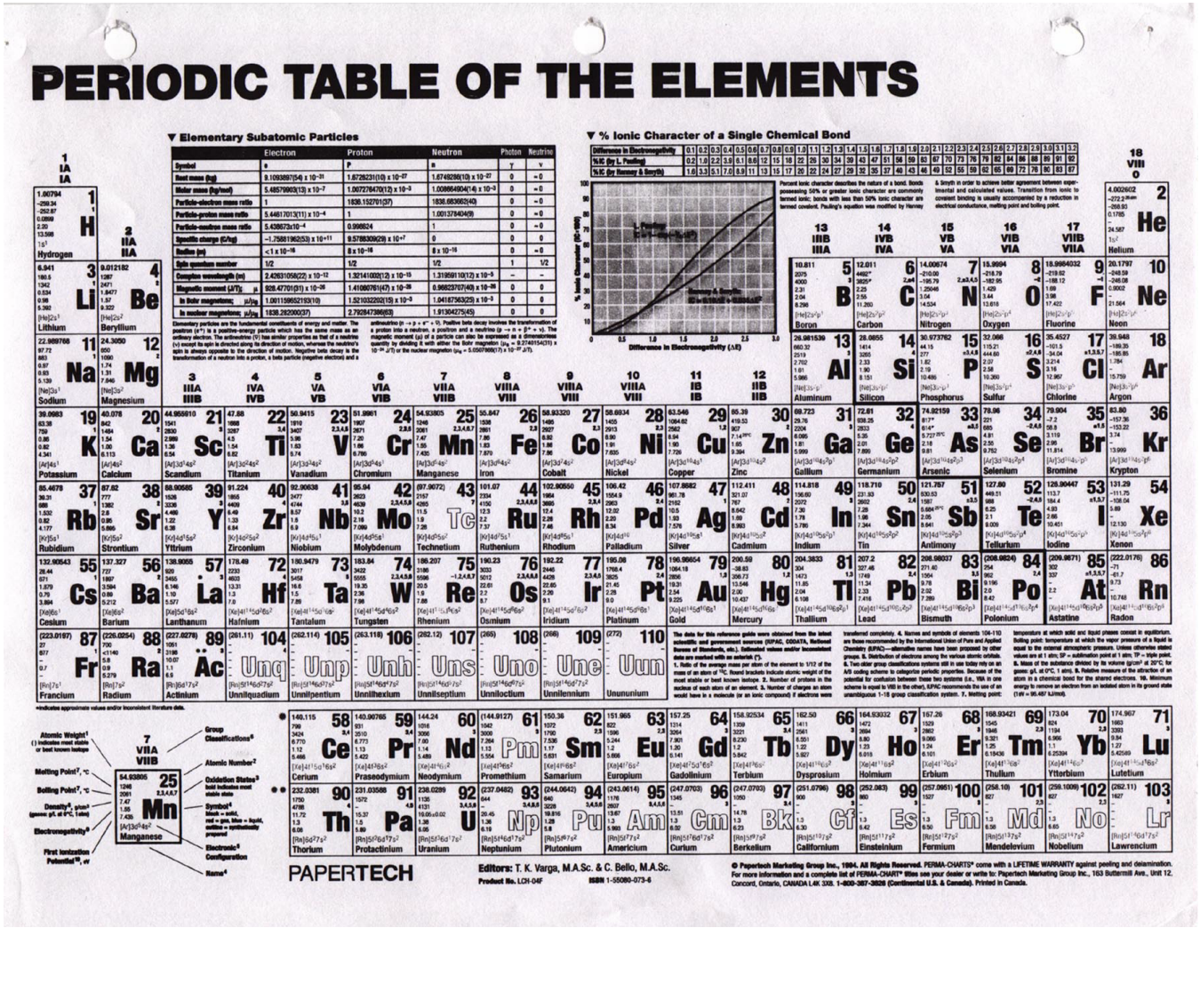
"I pledge, as a member of The University of Texas at Austin community, to do my work honestly, respectfully, and through the intentional pursuit of learning and scholarship."

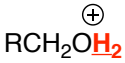
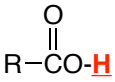
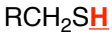
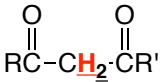
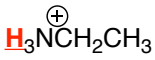
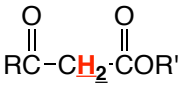
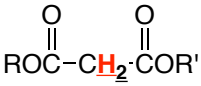
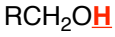
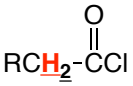
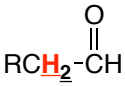
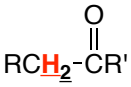
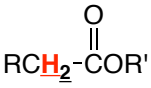
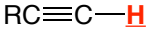
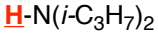
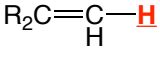
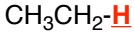
Elaboration

1. I pledge to be honest about what I create and to acknowledge what I use that belongs to others.
2. I pledge to value the process of learning in addition to the outcome, while celebrating and learning from mistakes.
3. This code encompasses all of the academic and scholarly endeavors of the university community.

_____

(Your signature)



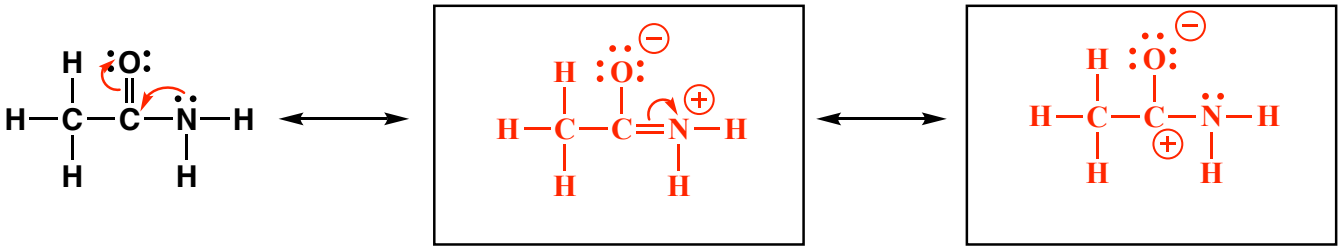
Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Carboxylic acids		3-5
Thiols		8-9
Ammonium ion		9.2
β-Dicarbonyls		10
Primary ammonium		10.5
β-Ketoesters		11
β-Diesters		13
Water		15.7
Alcohols		15-19
Acid chlorides		16
Aldehydes		18-20
Ketones		18-20
Esters		23-25
Terminal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

Signature_____ Pg 1 _____(33)

1. (5 pts) What is the most important question in organic chemistry?

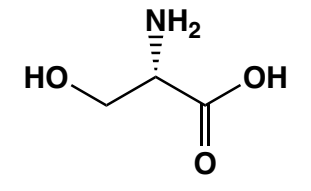
Where are the electrons?

2. (10 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, use arrows to indicate the movement of electrons to give the structures you drew.

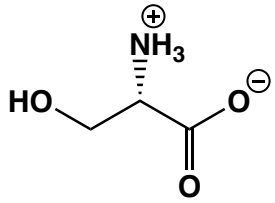


3. (8 pts.) Fill in the circle next to the pH value that coresponds the pH at which the structure drawn would be present. If the structure drawn cannot exist at any pH, fill in the circle next to the "pH = X"

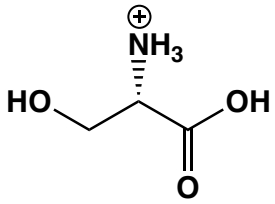
The pK_a of a carboxylic acid (RCO_2H) is generally in the 4-5 range. The pK_a of ammonium ions ($RNH_3^{\oplus}$) is in the 9-10 range.



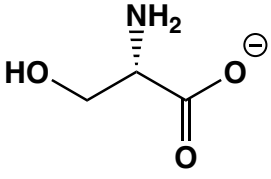
○ pH = 2 ○ pH = 12
○ pH = 7 ● pH = X



○ pH = 2 ○ pH = 12
● pH = 7 ○ pH = X

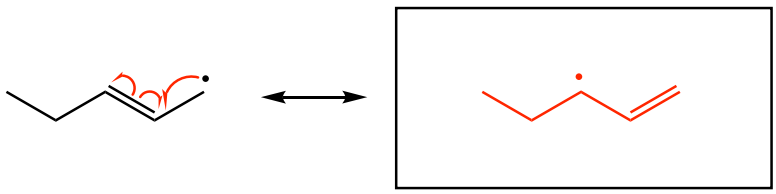


● pH = 2 ○ pH = 12
○ pH = 7 ○ pH = X



○ pH = 2 ● pH = 12
○ pH = 7 ○ pH = X

4. (10 pts.) Draw the other important contributing structure for this allyl radical. Draw arrows on the structure given that leads to the contributing structure you drew. Remember to include all formal charges and unpaired electrons.



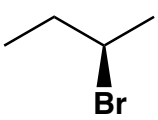
Fill in the circle to indicate how many pi electrons are in the delocalized pi system ("pi-way") indicated by the two contributing structures

○ 0
○ 2
● 3
○ 4

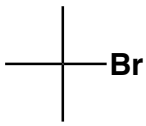
5. (11 pts) Consider the following statements that refer to **S_N1, S_N2, E1, E2**, or a **radical chain reaction** mechanisms. Fill in the circles to indicate to which mechanism(s) each statement applies. You may need to fill in more then one circle for some of these.

A. A reaction mechanism that involves a radical intermediate.	○ 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 will occur when Br_2 and light (hν) are used with an alkane.	○ S_N2 ○ S_N1	○ E2 ○ E1	● Radical chain reaction
D. A reaction mechanism that involves only a transition state, no intermediate.	● S_N2 ○ S_N1	● E2 ○ E1	○ Radical chain reaction
E. A reaction that causes only InVERSiON of sterechemistry at the site of reaction.	● S_N2 ○ S_N1	○ E2 ○ E1	○ Radical chain reaction
F. The mechanism that occurs when a secondary alcohol reacts with catalytic H_2SO_4 to give an alkene product.	○ S_N2 ○ S_N1	○ E2 ● E1	○ Radical chain reaction
G. A reaction mechanism that involves a carbocation intermediate.	○ S_N2 ● S_N1	○ E2 ● E1	○ Radical chain reaction
H. A reaction mechanism that involves "scrambling" of stereochemistry at the site of reaction.	○ S_N2 ● S_N1	○ E2 ○ E1	○ Radical chain reaction
I. A reaction mechanism that happens when NBS and light or heat are used with an alkene.	○ S_N2 ○ S_N1	○ E2 ○ E1	● Radical chain reaction

6. (4 pts) Rank the following four molecules with respect to their ability to react according to an S_N2 mechanism. **Put a 1 under the most reactive and a 4 under the least reactive molecule.**



3



4

CH_3Br

1

CH_3CH_2Br

2

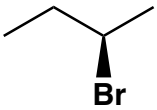
7. (4 pts) Rank the following four molecules with respect to their ability to react according to an S_N1/ E1 mechanism. **Put a 1 under the most reactive and a 4 under the least reactive molecule.**

CH_3CH_2F

4

CH_3CH_2Br

3



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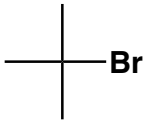
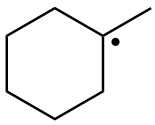


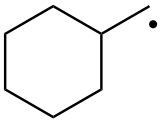
1

8. (4 pts each) For the following lists of structures, fill in the circles as appropriate to indicate which molecules of the four listed correspond to the parameter listed. **You will only fill in two circles per four molecules listed.**

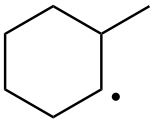
Radical Stability



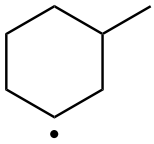
● Most Stable
○ Least Stable



○ Most Stable
● Least Stable

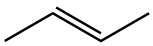


○ Most Stable
○ Least Stable

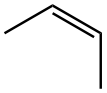


○ Most Stable
○ Least Stable

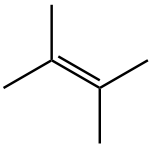
Alkene Stability



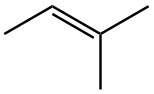
○ Most Stable
○ Least Stable



○ Most Stable
● Least Stable

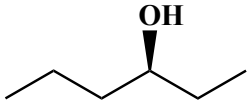


● Most Stable
○ Least Stable

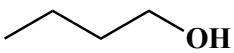


○ Most Stable
○ Least Stable

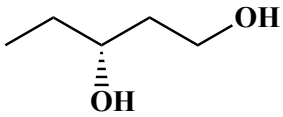
Solubility in water



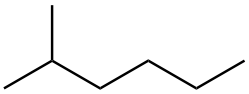
○ Most Soluble
○ Least Soluble



○ Most Soluble
○ Least Soluble

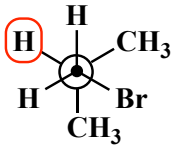


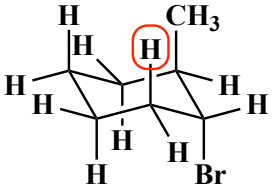
● Most Soluble
○ Least Soluble

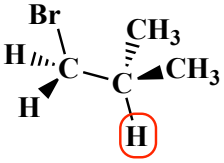


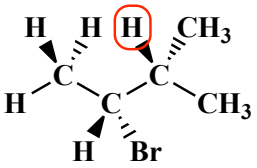
○ Most Soluble
● Least Soluble

9. (3 pts each) In each case, circle the one H atom that will react during an E2 reaction in strong base to give the predominant product.

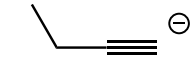






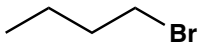


10. (2 pts each) For the following four pairs of reagents you have seen in various bond-making steps in mechanisms, **fill in the circle to indicate which structure is acting as a nucleophile.**

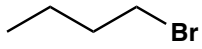


● nucleophile

+



○ nucleophile



○ nucleophile

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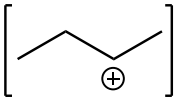
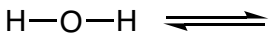
● nucleophile

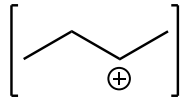


○ nucleophile

+

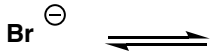


● nucleophile



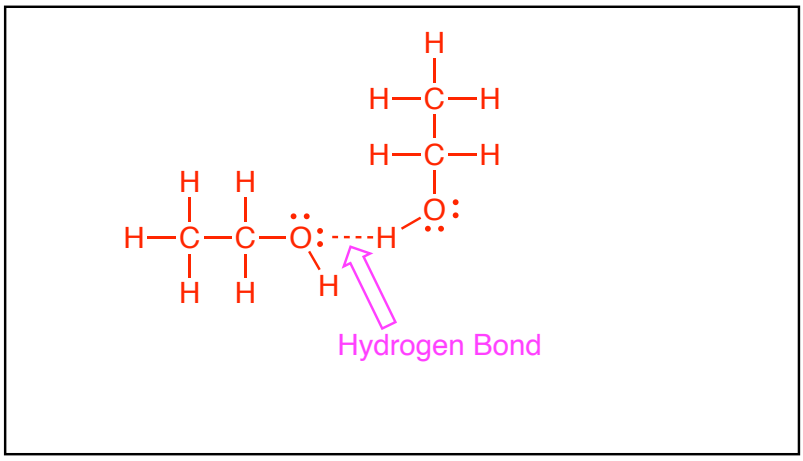
○ nucleophile

+

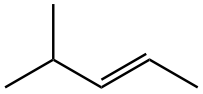


● nucleophile

11. (7 pts) In the space provided, draw Lewis structures for two ethanol molecules (CH_3CH_2OH) wih one hydrogen bond between them indicated by a dashed line. Make sure to include all appropriate lone pairs of electrons in your answer.



12. (8 pts) Consider what happens when (*E*)-4-methyl-2-pentene is reacted with NBS and heat.

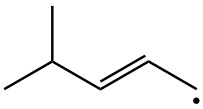


NBS
heat

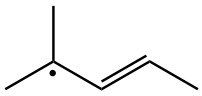
You will draw the product of this reaction in the box at the bottom of the page

(*E*)-4-methyl-2-pentene

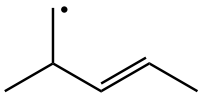
Fill in the circles to indicate which allyl radical contributing structures are relevant and therefore must be considered when predicting the predominant product of the reaction



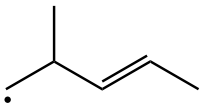
● This contributing structure should be considered



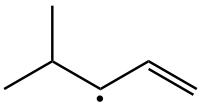
● This contributing structure should be considered



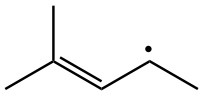
○ This contributing structure should be considered



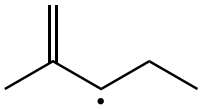
○ This contributing structure should be considered



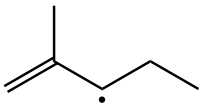
● This contributing structure should be considered



● This contributing structure should be considered

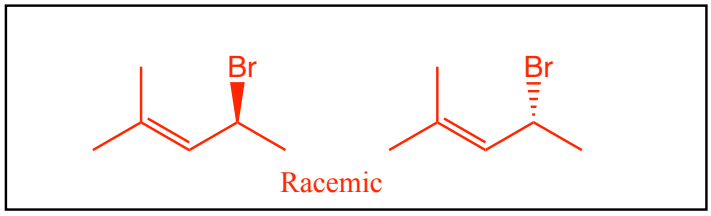


○ This contributing structure should be considered



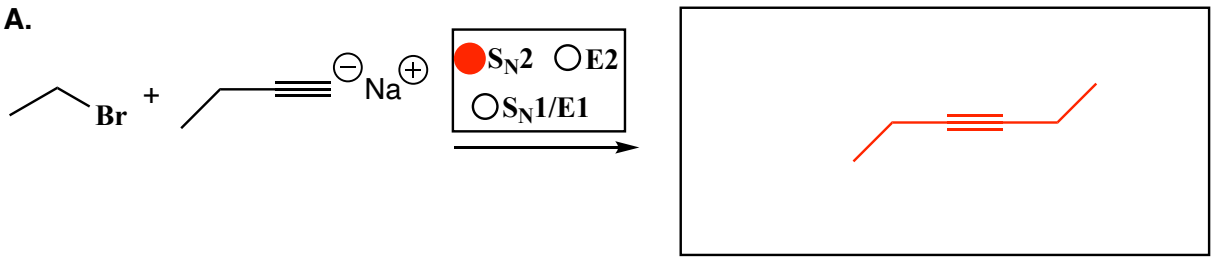
○ This contributing structure should be considered

(6 pts) Given your analysis of the above contributing structures, in the box provided, draw the product of the reaction of (*E*)-4-methyl-2-pentene with NBS and heat. Use wedges and dashes to indicate sterochemistry, and draw all relevant stereoisomers, indicating the product is racemic if appropriate.

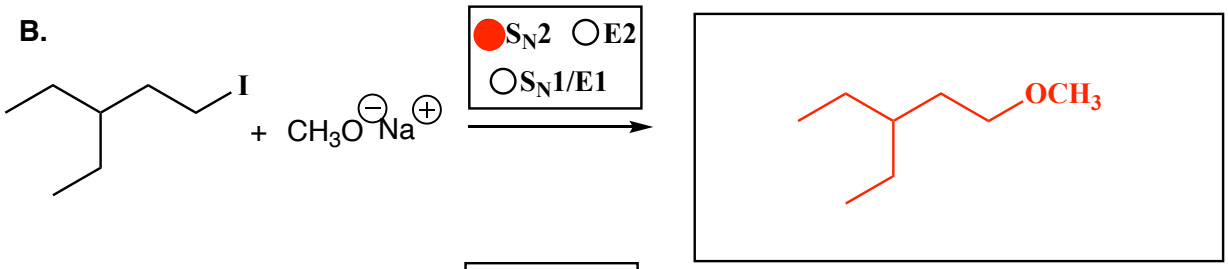


14. (5 or 6 pts each) The following reactions all involve the chemistry of haloalkanes. **Fill in the circle above the arrow to indicate the mechanism that will be followed (S_N2, E2, etc.). Then draw only the predominant product or products** and please remember that **you must draw the correct stereoisomers**.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

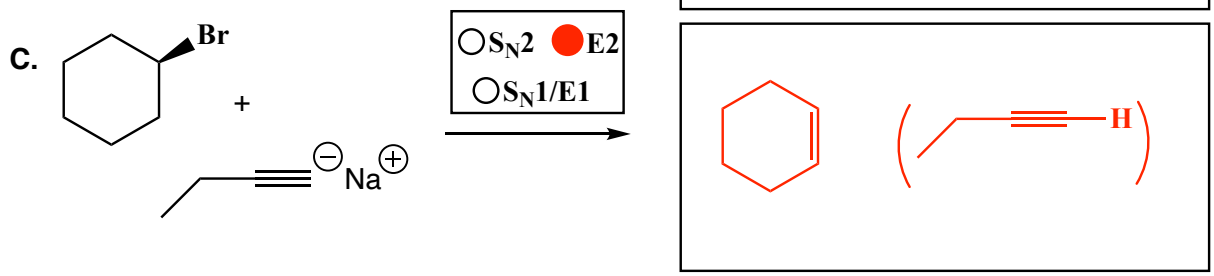
A.



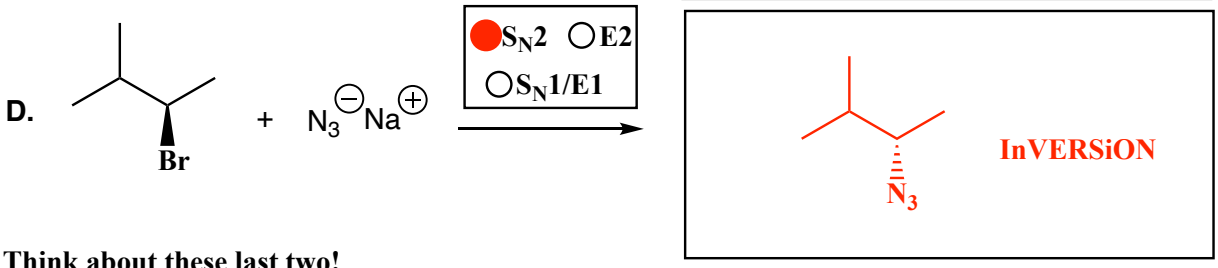
B.



C.

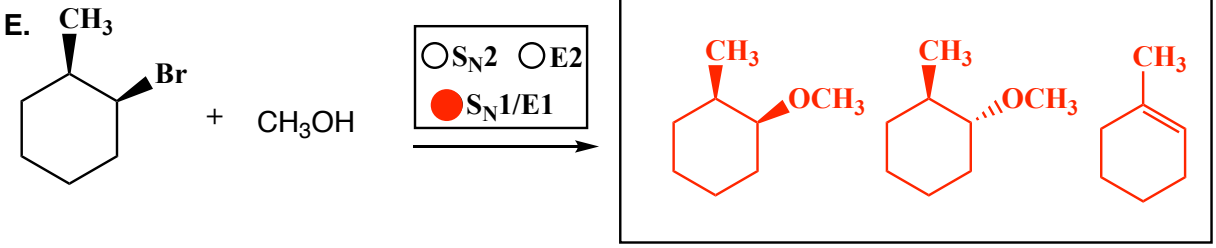


D.

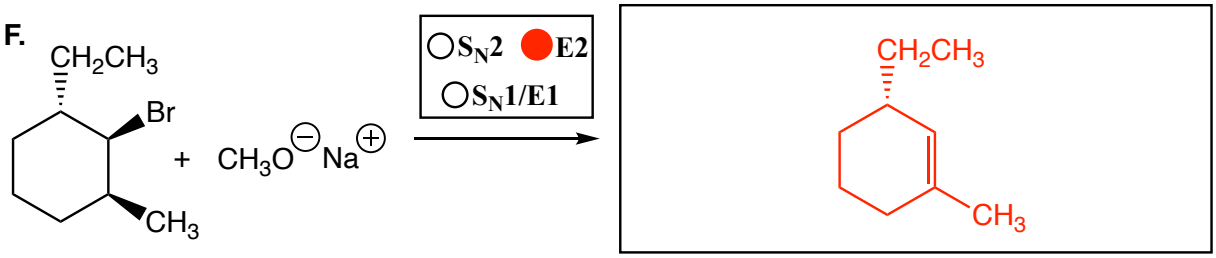


Think about these last two!

E.

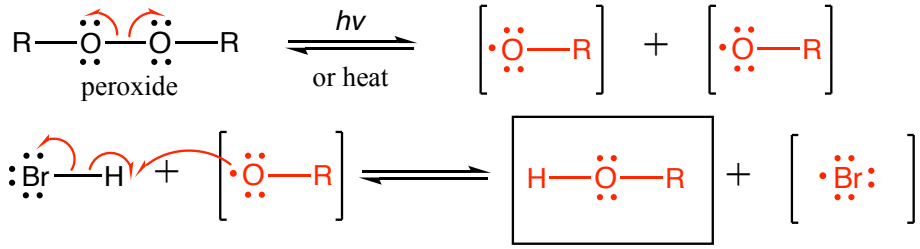


F.

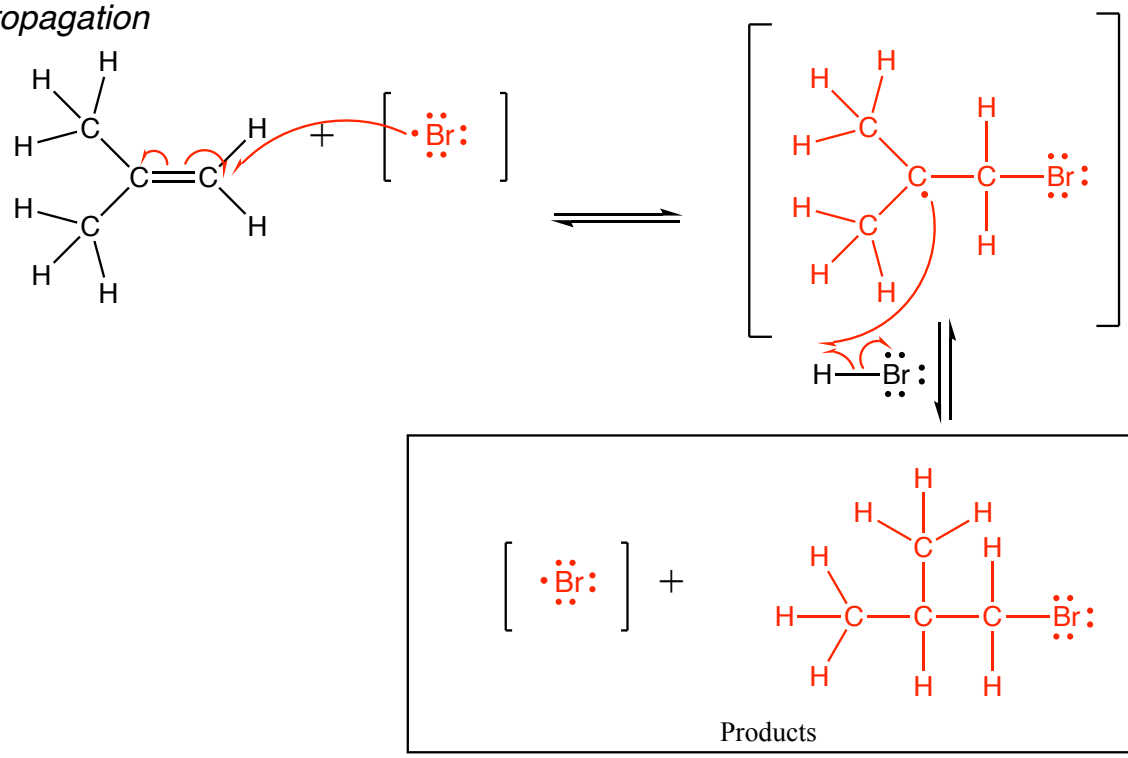


15. (34 pts total) Complete the following mechanism for the free radical addition of HBr to an alkene. Use appropriate arrows to show movement of electron density, and show all non-bonding electrons as dots and show any formal charges. **If any of the species are really a racemic mixtures of enantiomers,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

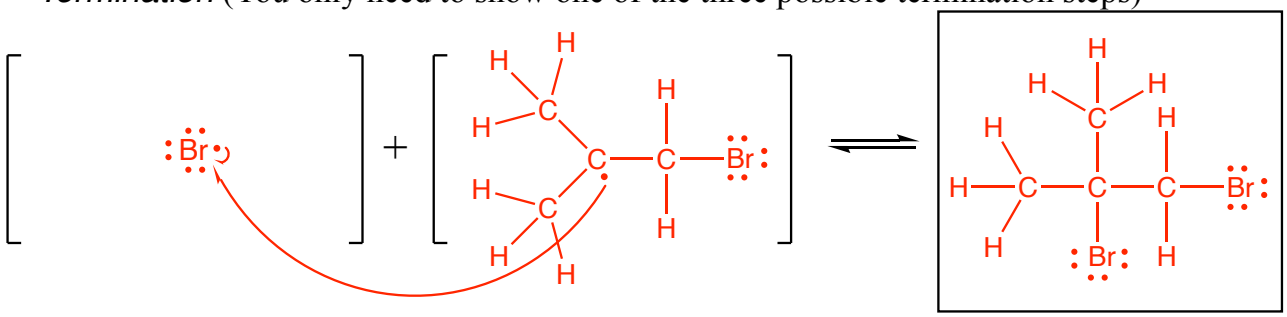
Initiation



Propagation



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



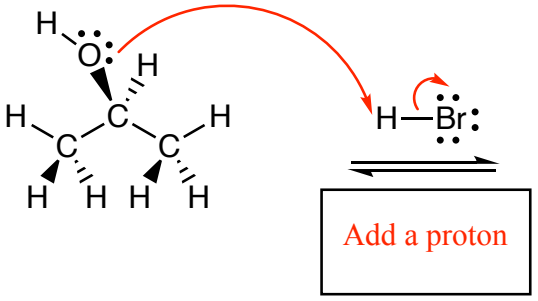
Any combination of these two radicals is correct for an example of a termination step

16. (18 pts) Complete the mechanism for the following reaction of an alcohol with H-Br. Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step. Remember, I said <u>all</u> the products for each step. **If any of the species are really a racemic mixtures of enantiomers, you only need to draw one stereoisomer using wedges and dashes, indicating the chiral center with an asterisk (*) and write "racemic".** In the three boxes provided, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).

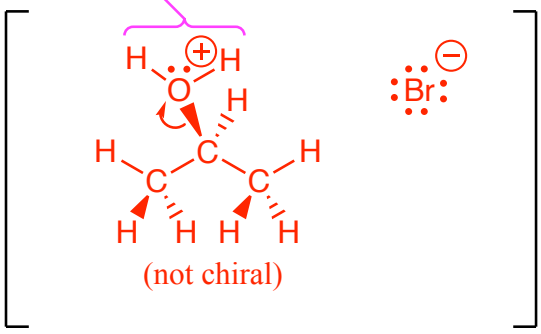
There is a strong acid present (HBr) and there are no electrophiles so the only choice is to "add a proton" to the only lone pairs on the alcohol, namely the O atom of the alcohol group.

This is a great leaving group.

Taking a proton away goes back to where we started so not productive. Noting the presence of a really great leaving group (H_2O) and the fact this is secondary that hinders S_N2, "Break a bond" is the only reasonable choice.

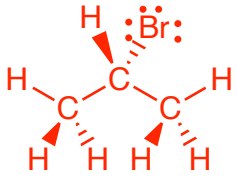


Add a proton



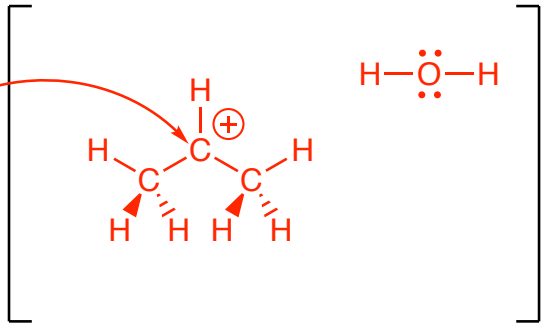
Break a bond

Note the overall similarity to an S_N1 reaction mechanism here.



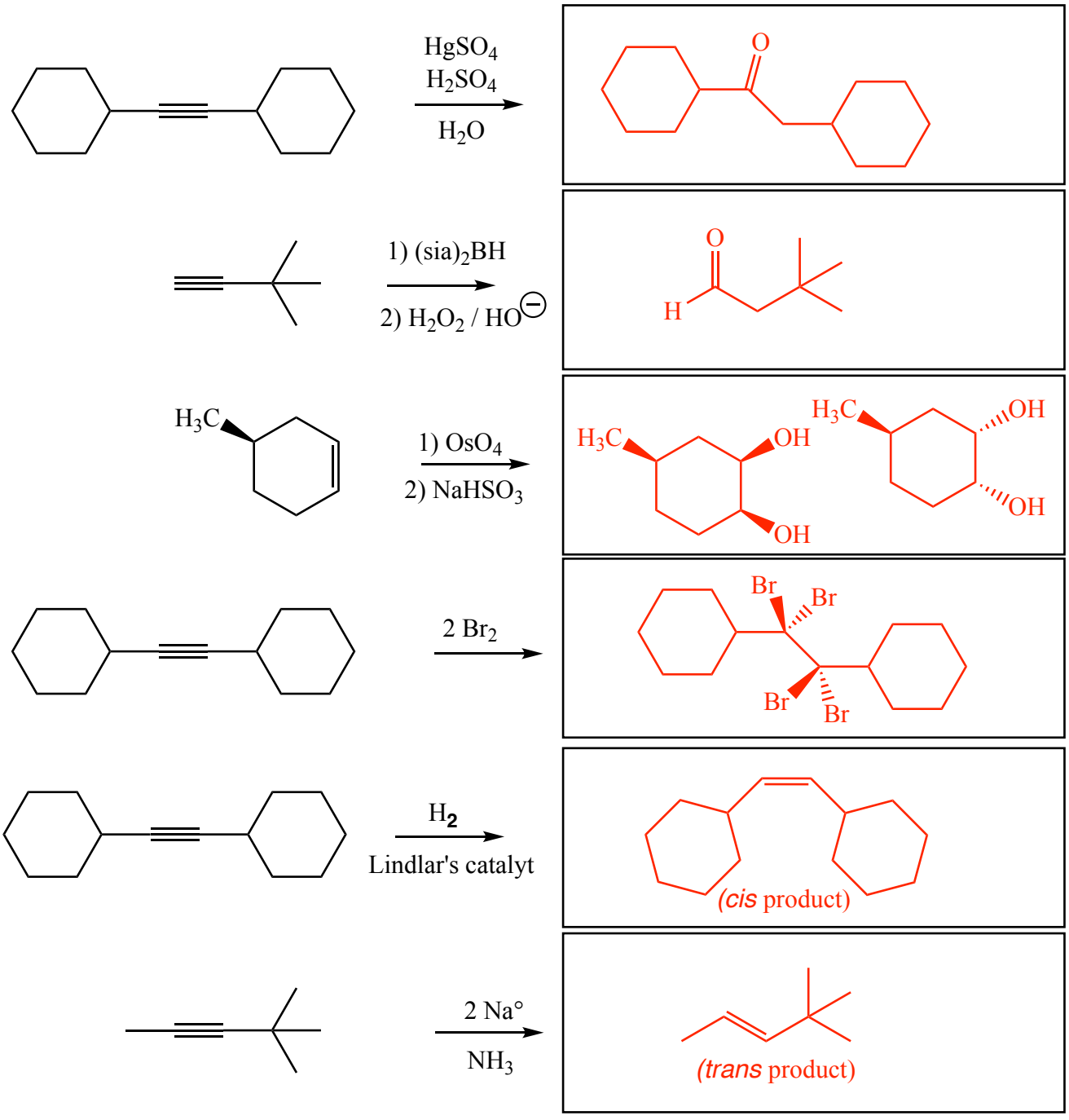
Product

Make a bond

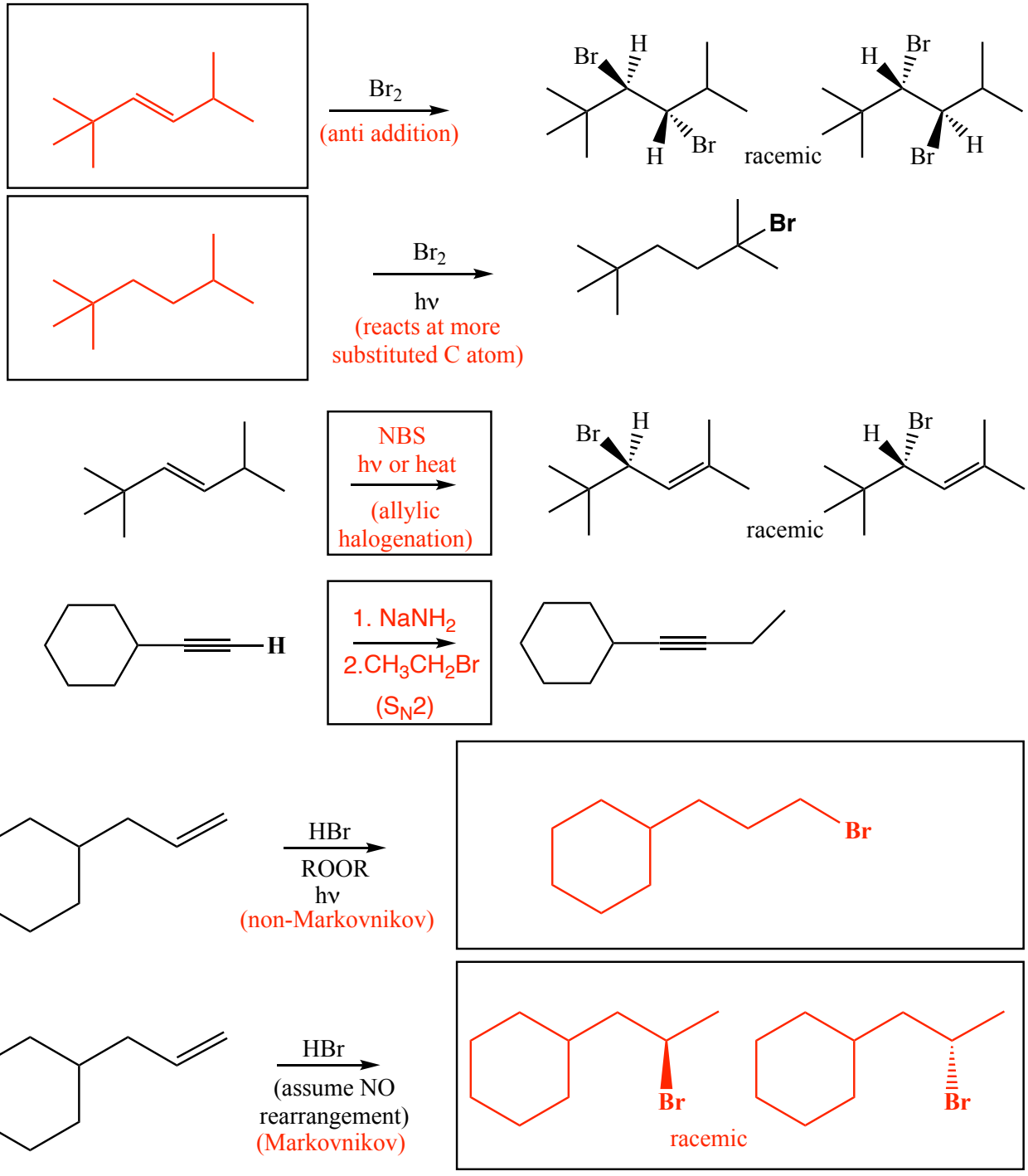


There is a great electrophile, the carbocation, and a great nucleophile ($Br^{\ominus}$), make a bond is the logical choice

17. (3 or 5 pts each) 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 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**.

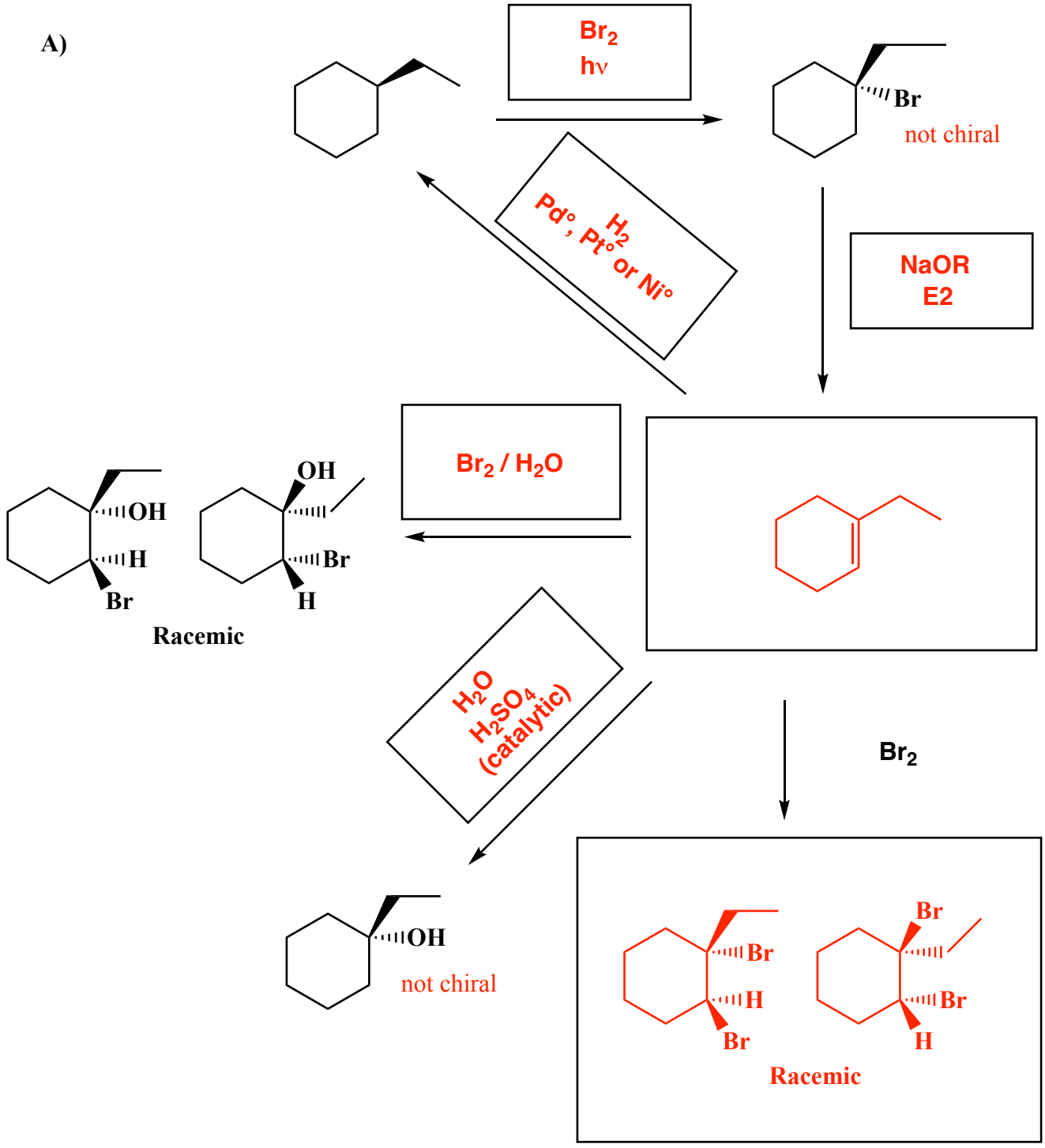


18. (3 or 5 pts each) Fill in the boxes with the starting material, reagents or product(s) that are missing from the chemical reaction equations. **Once again, for the products draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products)** and please remember 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**.



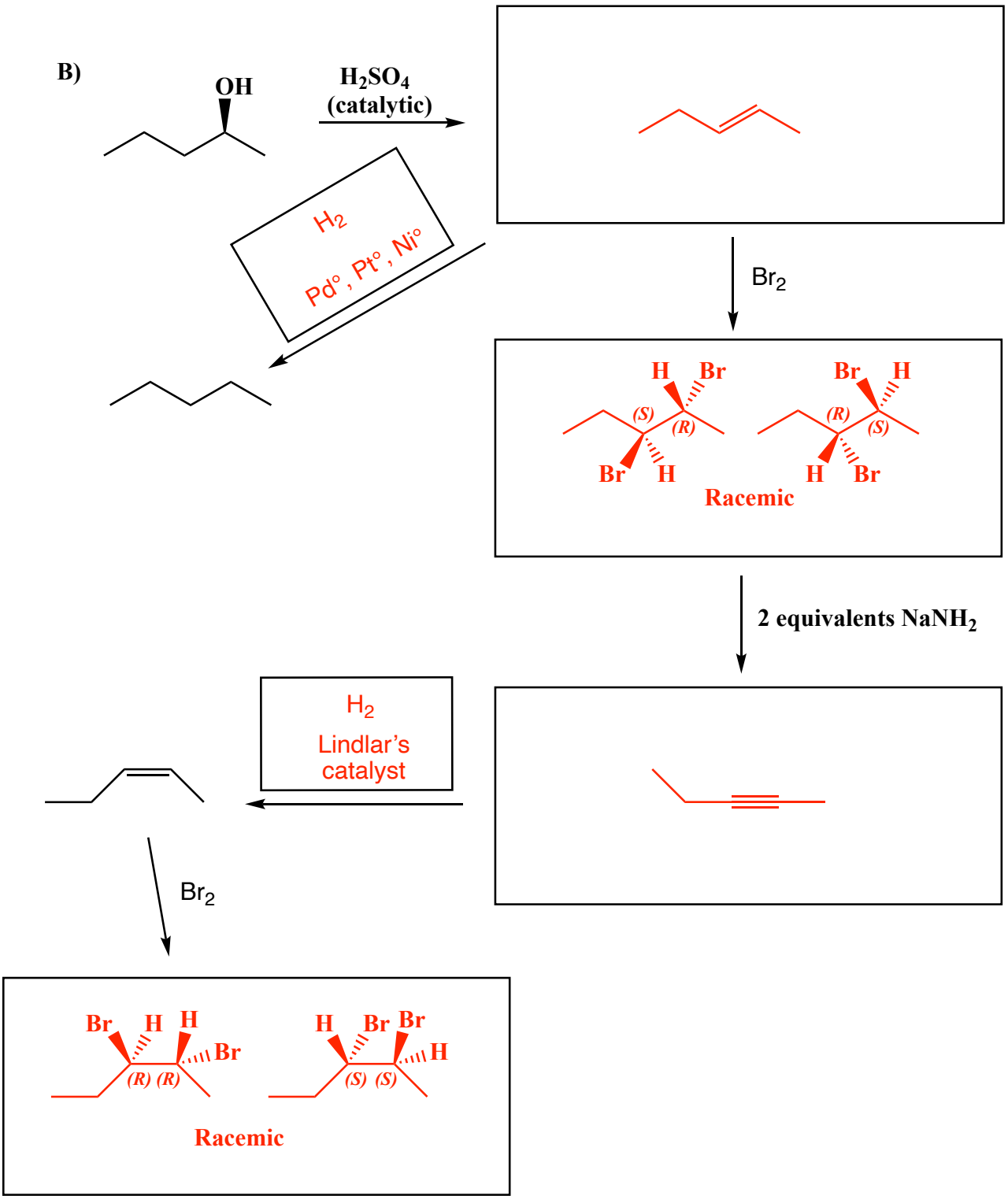
19. (18 pts) For the following reactions, fill in the box with the **predominant product(s)** or **reagent(s)** necessary to complete the following syntheses. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate.

A)



19 (cont.). (20 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.

B)

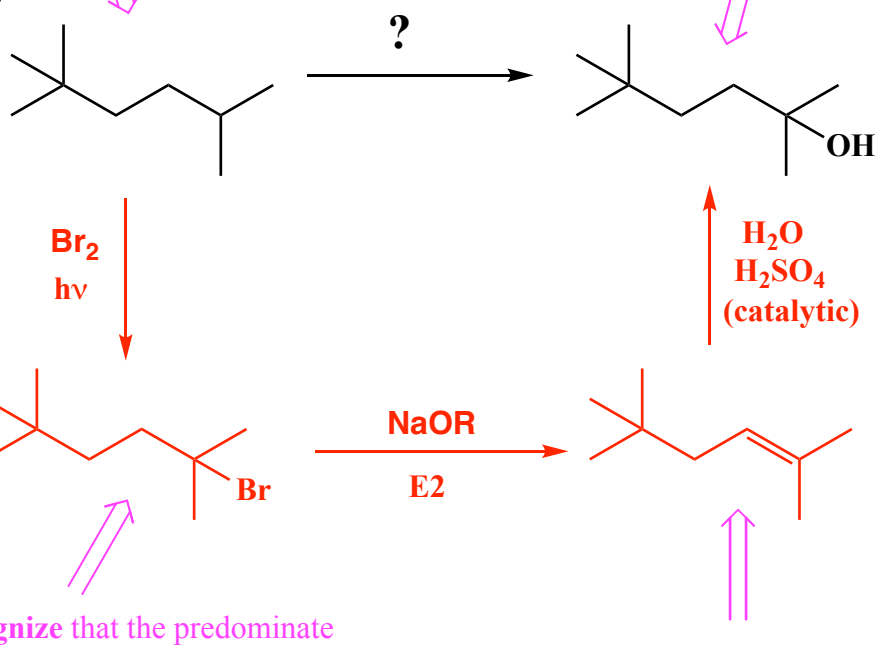


20. (7 pts) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction because only predominant products can be used. All the carbon atoms of the product(s) must come from the starting material(s) shown.

Recognize the starting material is an alkane and the only reaction you know that uses an alkane as a starting material is the free radical halogenation reaction using Br_2 and light (hν).

Recognize the product as a tertiary alcohol. Because it is tertiary, it cannot be made from and S_N2 reaction (the haloalkane would have to be terriary!), but the product alcohol could be a Markovnikov product of an acid catalyzed hydration of an alkene. Therefore propose that the last step involves reacting the alkene shown with H_2O and catalytic H_2SO_4.

A) 7 pts

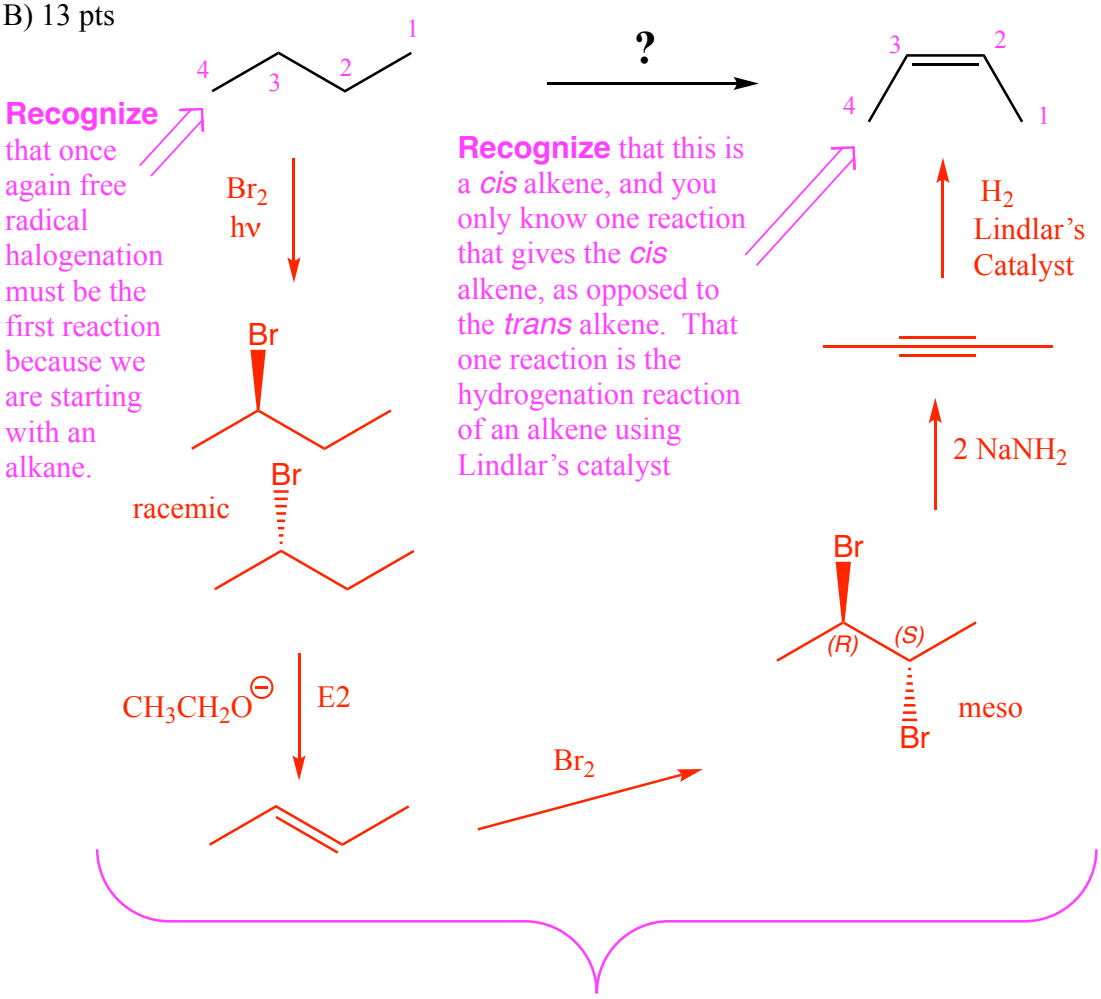


Recognize that the predominate product of the free radical halogenation reaction with Br_2 and hν is the tertiary haloalkane shown. When reacted with strong base, the Zaitsev product will be precisely the alkene needed to deliver the product tertiary alcohol when reacted with H_2O and catalytic H_2SO_4.

Recognize this alkene as the Zaitsev (most substituted) alkene in the molecule, so assume it is made through an E2 reaction as shown.

20 (cont.). (13 pts) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. 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 because only predominant products can be used. All the carbon atoms of the product(s) must come from the starting material(s) shown.

B) 13 pts



Recognize that the rest of the process is just taking the alkane to an alkyne, which is the set of reactions we refer to as "I-35" on your roadmap. You should be very familiar with all of these reactions, because they show up quite often in synthesis problems.