

NAME (Print): _____

Chemistry 320M/328M
Dr. Brent Iverson
3rd Midterm
November 14, 2019

SIGNATURE: _____

EID: _____

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

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Please Note: This test may be a bit long, but there is a reason. I would like to give you a lot of little questions, so you can find ones you can answer and show me what you know, rather than just a few questions that may be testing the one thing you forgot. **I recommend you look the exam over and answer the questions you are sure of first**, then go back and try to figure out the rest. Also make sure to **look at the point totals** on the questions as a guide to help budget your time.

You cannot use a red pen to take the exam. You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK will be regraded.

Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.

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!!!

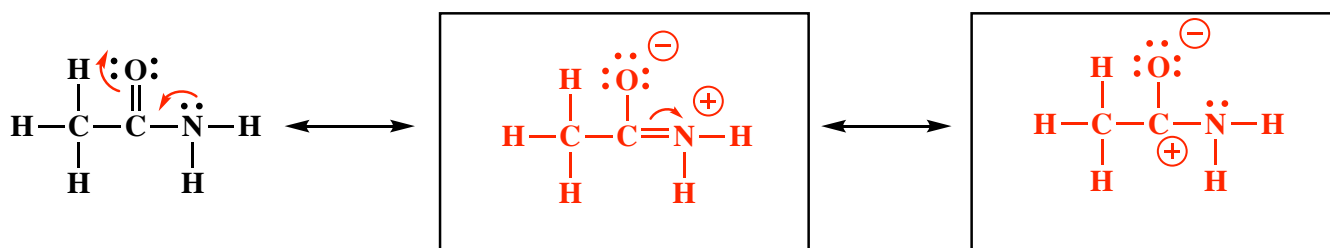
Page	Points
1	(25)
2	(25)
3	(14)
4	(20)
5	(30)
6	(18)
7	(27)
8	(26)
9	(27)
10	(24)
11	(18)
12	(8)
13	(21)
14	(18)
15	(12)
Total	(313)

Compound		pK _a
Hydrochloric acid	$\text{H}-\text{Cl}$	-7
Protonated alcohol	$\text{RCH}_2\text{OH}_2^{\oplus}$	-2
Hydronium ion	$\text{H}_3\text{O}^{\oplus}$	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-5
Thiols	RCH_2SH	8-9
Ammonium ion	$\text{H}_4\text{N}^{\oplus}$	9.2
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CR}'$	10
Primary ammonium	$\text{H}_3\text{N}^{\oplus}\text{CH}_2\text{CH}_3$	10.5
β-Ketoesters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	11
β-Diesters	$\text{ROC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	16
Aldehydes	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	18-20
Ketones	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CR}'$	18-20
Esters	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\text{H}$	25
LDA	$\text{H}-\text{N}(\text{i}-\text{C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{H}$	44
Alkanes	$\text{CH}_3\text{CH}_2-\text{H}$	51

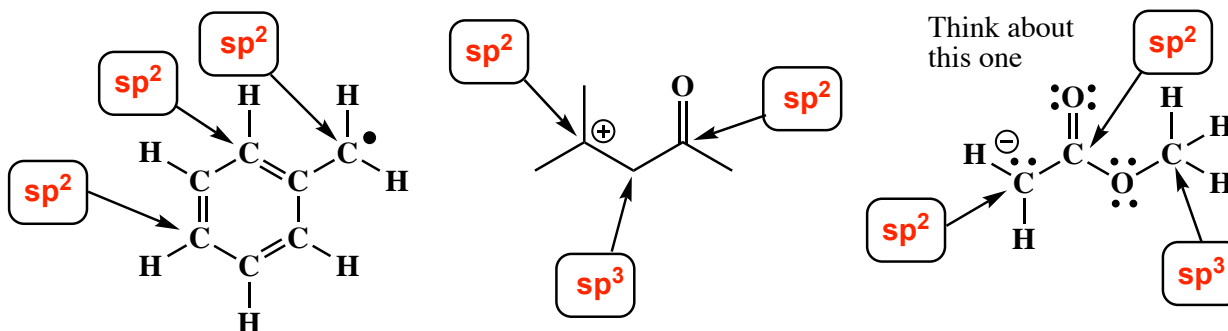
1. (2 pts) What is the most important question in organic chemistry?

Where are the electrons?

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

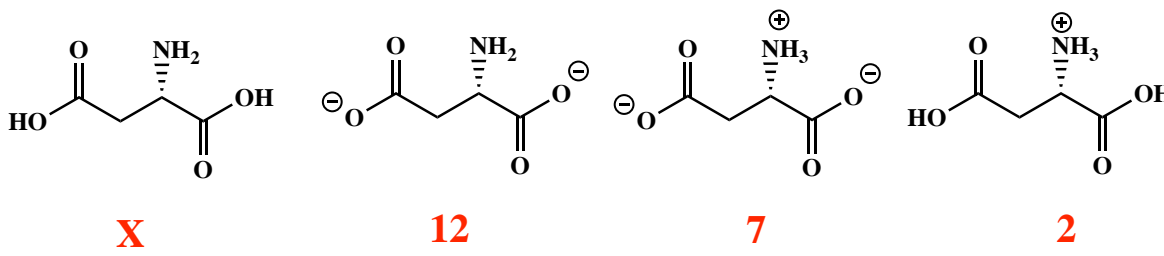


3. (9 pts.) On the following structures, indicate the hybridization state of each atom indicated with an arrow

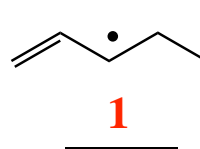
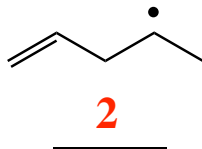
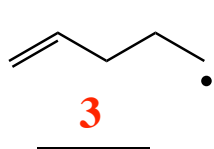
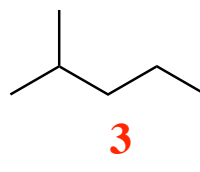
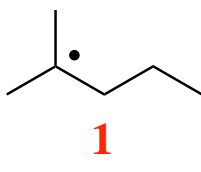
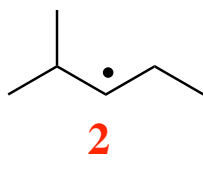
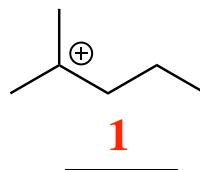
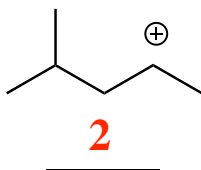
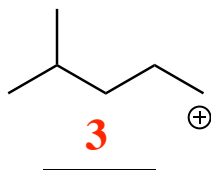


4. (8 pts.) Put a 2 under the species that will be the predominant one present at pH 2.0, put a 7 under the species that will be the predominant one present at pH 7.0, put a 12 under the species that will be the predominant one present at pH 12.0 and **put an "X" under a species that cannot predominant at any pH.**

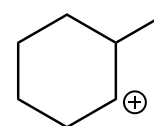
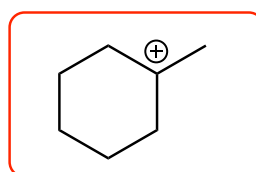
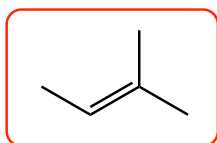
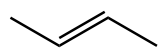
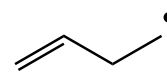
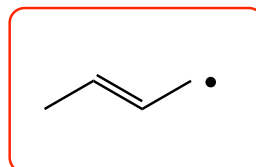
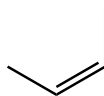
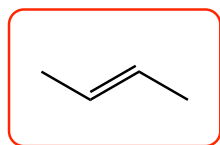
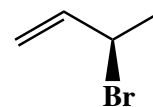
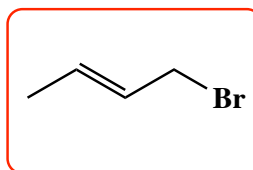
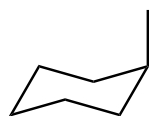
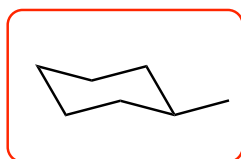
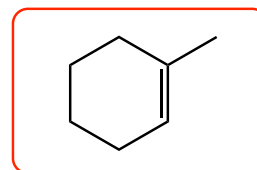
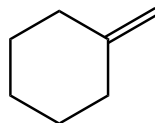
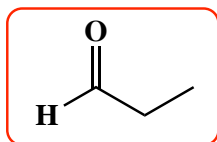
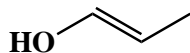
The pKa of a carboxylic acid (RCO_2H) is generally in the 4-5 range. The pKa of ammonium ions (RNH_3^+) is in the 9-10 range.



5. (9 pts) Rank the following sets of three molecules with respect to stability, **putting a 1 under the most stable and a 3 under the least stable in the series.**



6. (16 pts) For the following pairs of molecules or species, circle the one that is more stable (i.e. lower in energy).



7. (14 pts) Consider the following statements that refer S_N1 , S_N2 , E1, E2, or a **radical chain reaction** mechanism. To which mechanism(s), if any, does each statement apply?

A. The reaction that involves an InVERSiON of stereochemistry at the site of reaction.

Mechanism(s)

S_N2

B. The reaction that involves a carbocation intermediate.

$S_N1, E1$

C. The reaction that involves an anti-periplanar transition state.

E2

D. Favored for tertiary haloalkanes when weak nucleophiles/weak bases are used

$S_N1, E1$

E. The reaction in which the predominant product is predicted by Zaitsev's rule

E2, E1

F. The reaction mechanism that will occur when NBS and light are used.

radical chain reaction

G. Favored for secondary haloalkanes when a nucleophile that is also a strong base is used

E2

H. Favored for primary haloalkanes when any nucleophile is used

S_N2

I. The reaction mechanism that will occur when HBr, peroxides and heat are used.

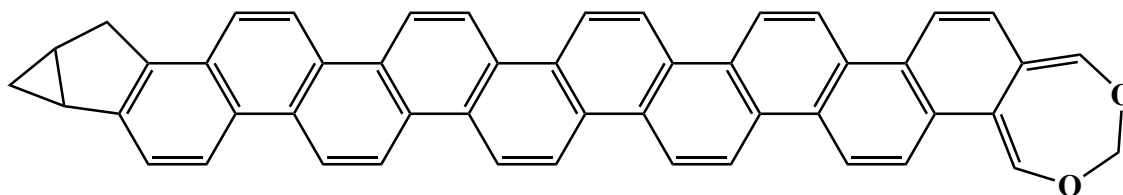
radical chain reaction

J. The reaction mechanism that starts with one pure enantiomer starting material and produces two enantiomer products, but not a racemic mixture.

S_N1

K. Favored for secondary haloalkanes when a nucleophile that is NOT a strong base and is also NOT a very weak base is used

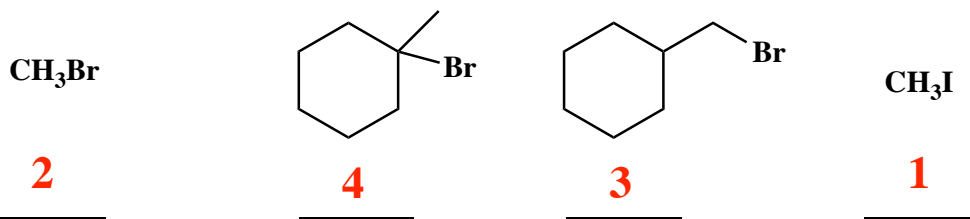
S_N2



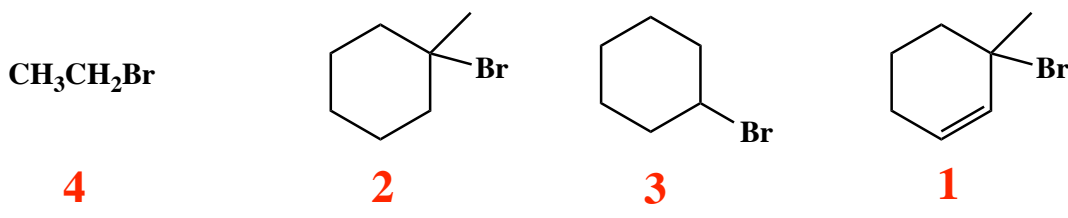
25b,26,26a,27-tetrahydrocyclopropa[3'',4'']cyclopenta[1'',2'':9',10']piceno[3',4':9,10]piceno[3,4-e][1,3]dioxepine

AKA "Snakene"

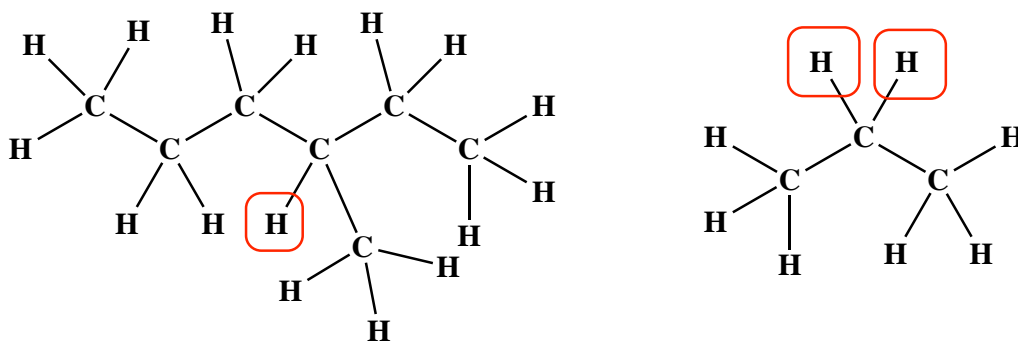
8. (4 pts) Rank the following four molecules with respect to their ability to react according to an S_N2 mechanism. Put a 1 under the most reactive and a 4 under the least reactive molecule.



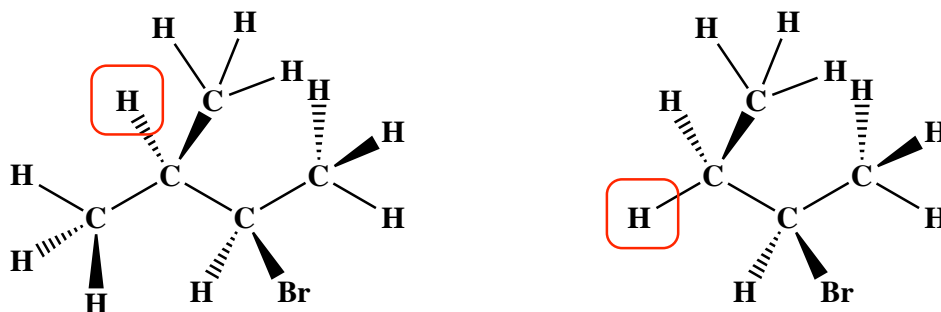
9. (4 pts) Rank the following four molecules with respect to their ability to react according to an $S_N1/E1$ mechanism. Put a 1 under the most reactive and a 4 under the least reactive molecule.



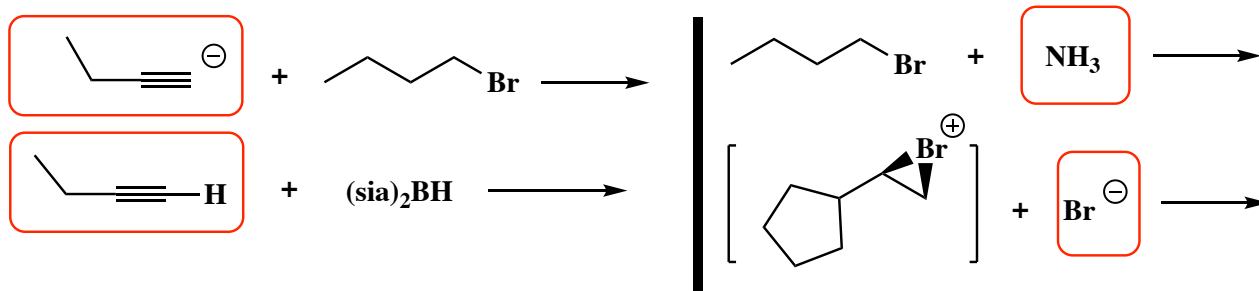
10. (6 pts) For the following molecules, circle the H atom(s) that are most likely to react during a free radical halogenation reaction using Br_2 and light. If more than one H atom ties as the most reactive on the molecule, circle all of the most reactive ones.



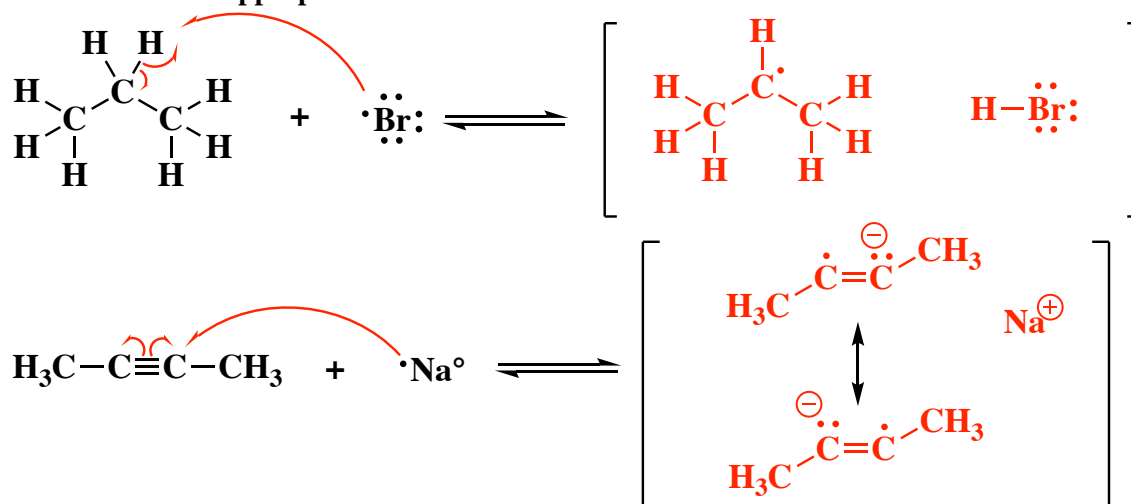
11. (6 pts) For the following molecule, circle the H atom(s) that are most likely to react during an $E2$ reaction. If more than one H atom ties as the most reactive on the molecule, circle all of the most reactive ones.



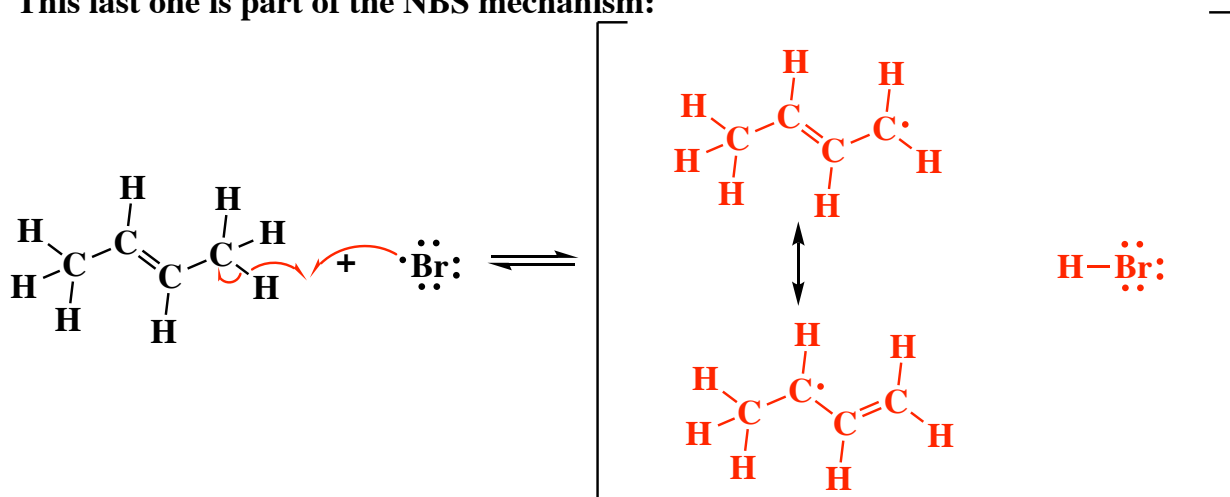
12. (2 pts each) For the following four pairs of reagents you have seen in various bond-making steps in mechanisms, **circle the nucleophile**. Do not make any marks on the electrophiles. DO NOT WRITE THE PRODUCTS OF THESE STEPS, we only want to see four circles on this problem!!



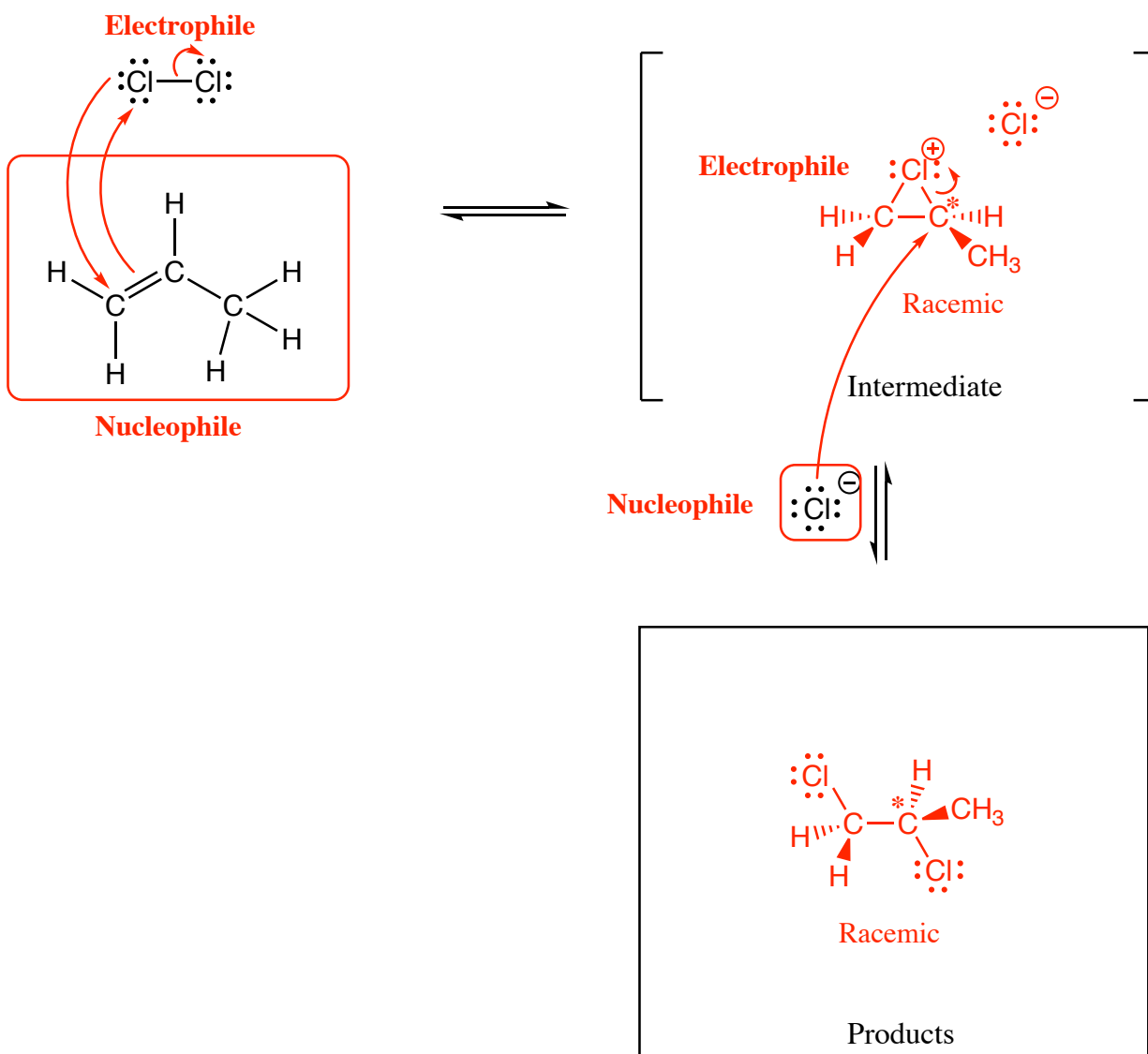
13. (22 pts) For the following sets of reagents use arrows to indicate the flow of electrons in the first step of each mechanism. Then draw only the first intermediate as indicated. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. For the last two intermediates, draw the two most important contributing structures as indicated by the \longleftrightarrow . No need to draw any arrows on a contributing structure. As always, if the intermediate is chiral, only draw one enantiomer using wedges and dashes, then write "racemic" if appropriate.



This last one is part of the NBS mechanism:



14. (12 pts) This is from a while ago. Complete the mechanism for the following alkene 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.**



(4 pts) **For any step** in the mechanism on this page that involves a nucleophile reacting with an electrophile to make a bond, **draw a circle around the nucleophile**

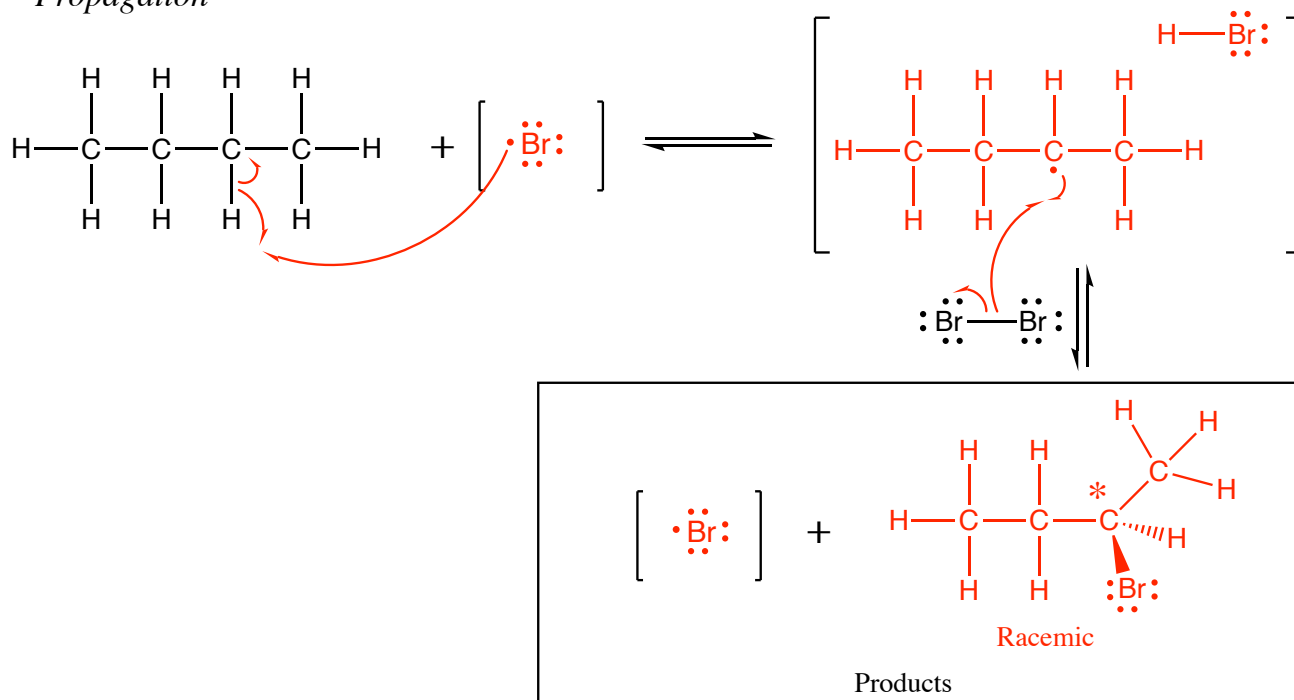
(2 pts) How many total stereoisomers are created as the final products? 2

15. (27 pts) Complete the mechanism for the halogenation of an alkane. **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.** Note that for the termination step, you only need to draw one of the three possible examples of termination.

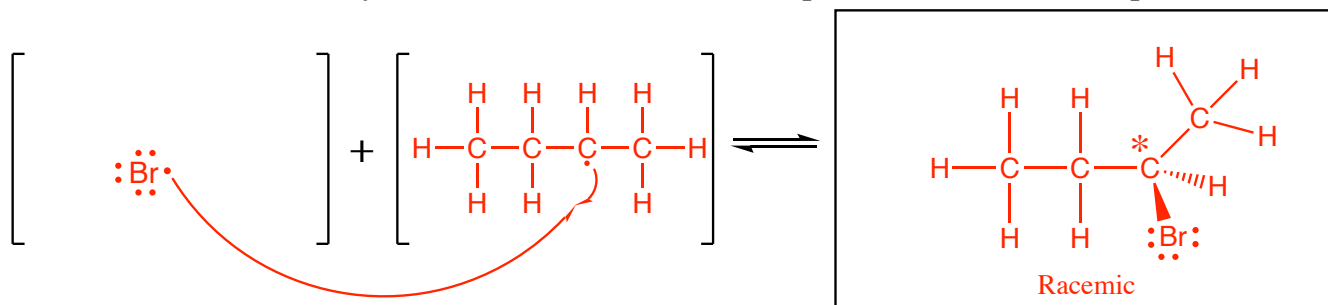
Initiation



Propagation

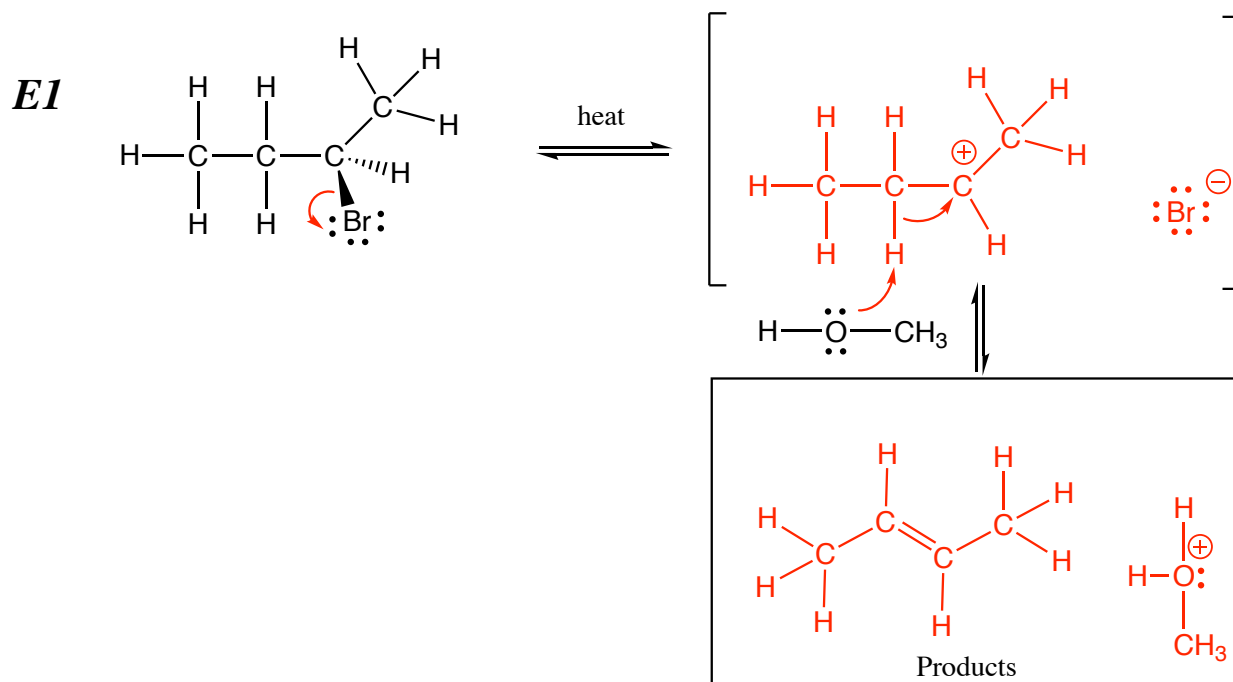
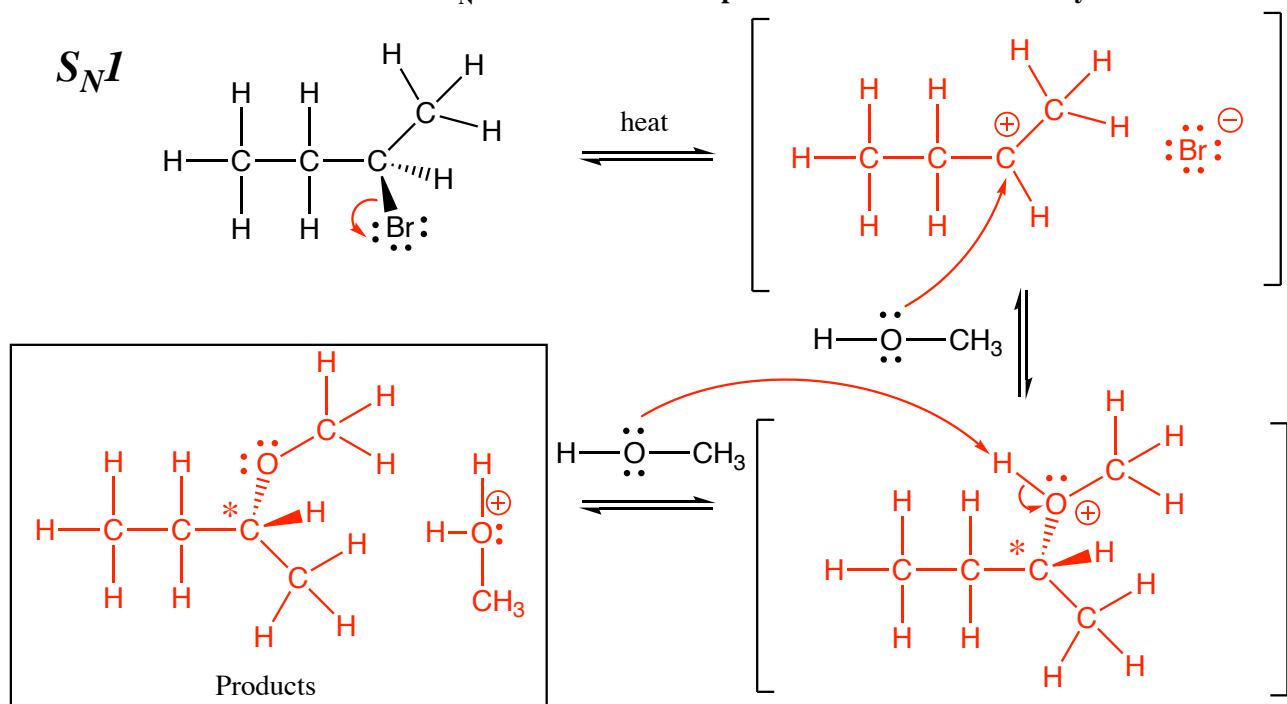


Termination (You only need to show one of the three possible termination steps)



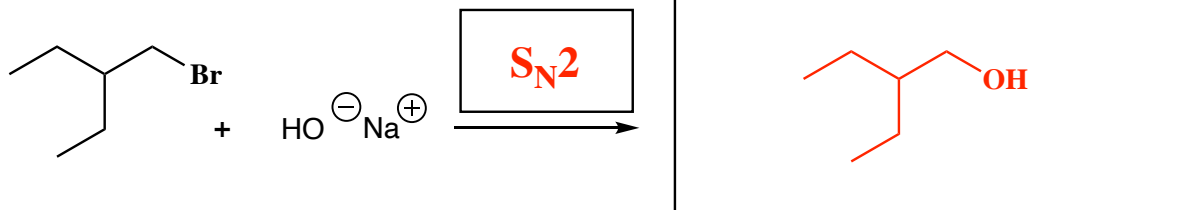
Any combination of these two radicals is correct for an example of a termination step

16. (26 pts total) Complete the following mechanism for substitution and elimination of a haloalkane. 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. Note we break S_N1 and $E1$ into two separate mechanisms for clarity.

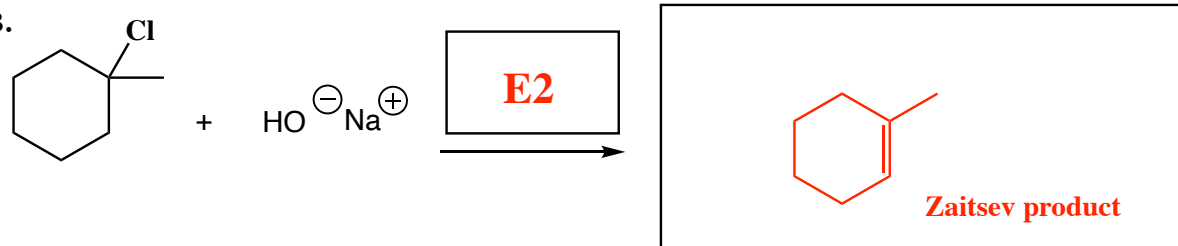


17. (27 pts) The following reactions all involve chemistry of haloalkanes. **Fill in the box above the arrow with the mechanism that will be followed (S_N2 , E2, etc.). Then draw only the predominant product or products** and please remember that **you must draw the correct stereoisomers**. For $S_N1/E1$ reactions you must draw all significant products (including all stereoisomers).

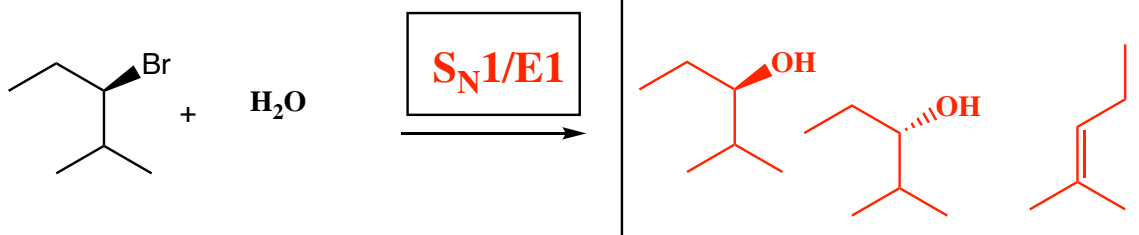
A.



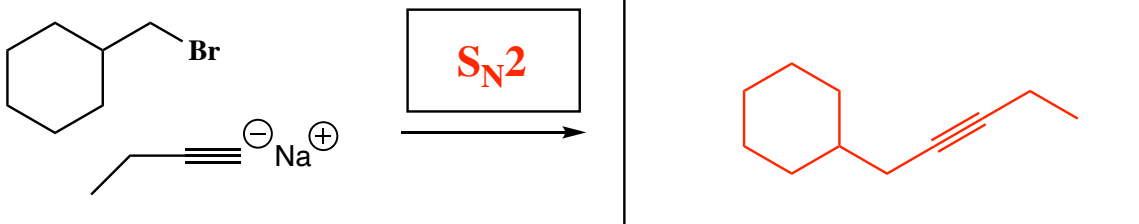
B.



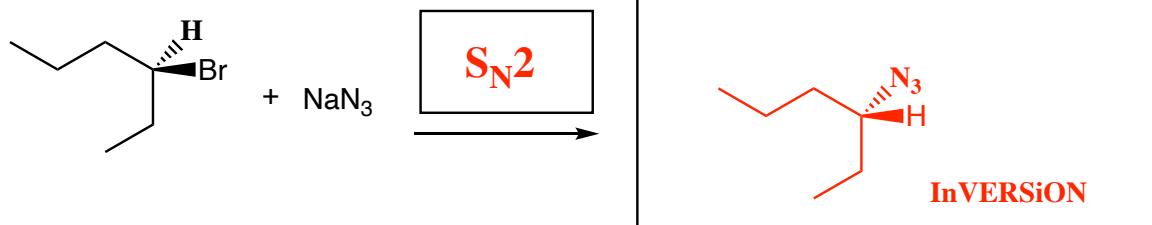
C.



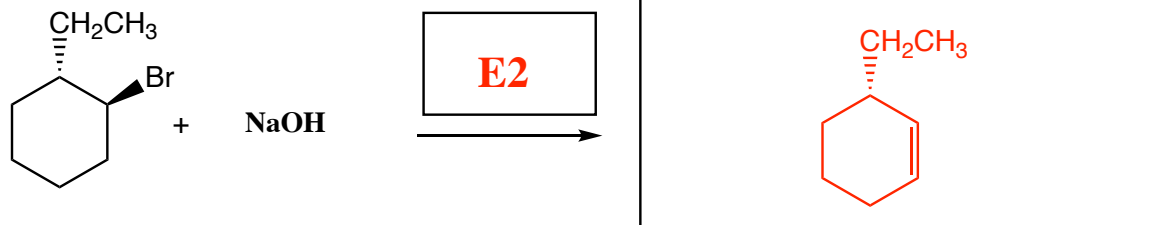
D.



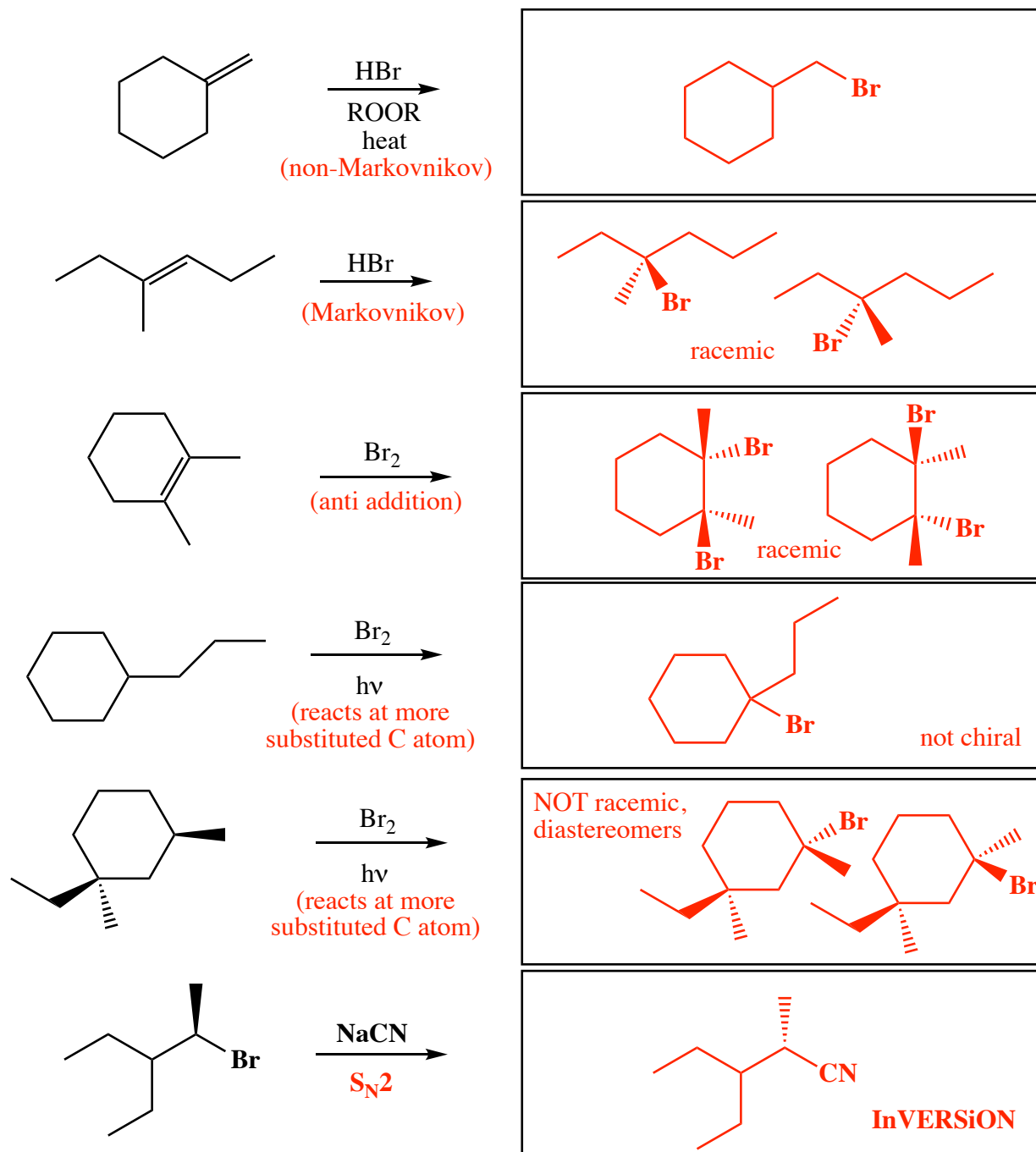
E.



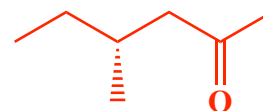
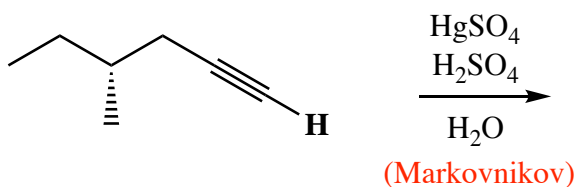
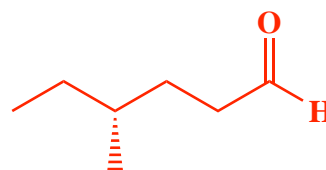
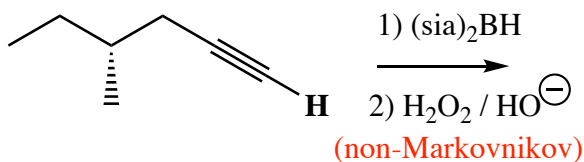
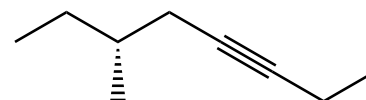
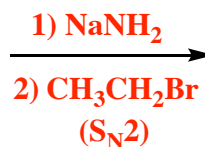
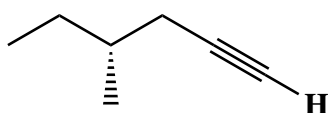
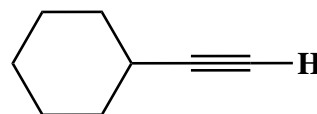
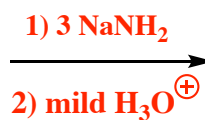
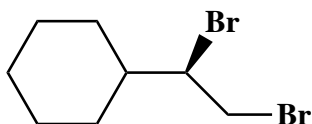
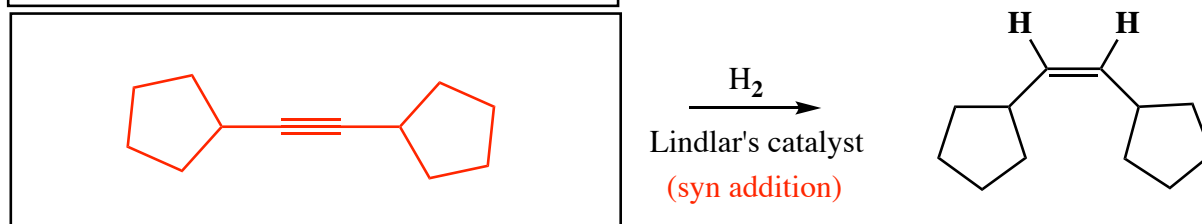
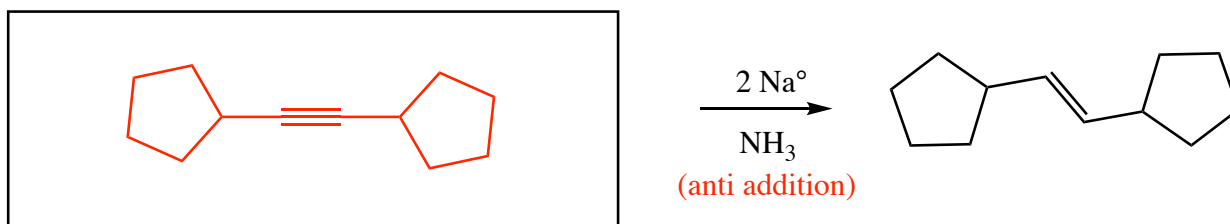
F.



18. (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**.

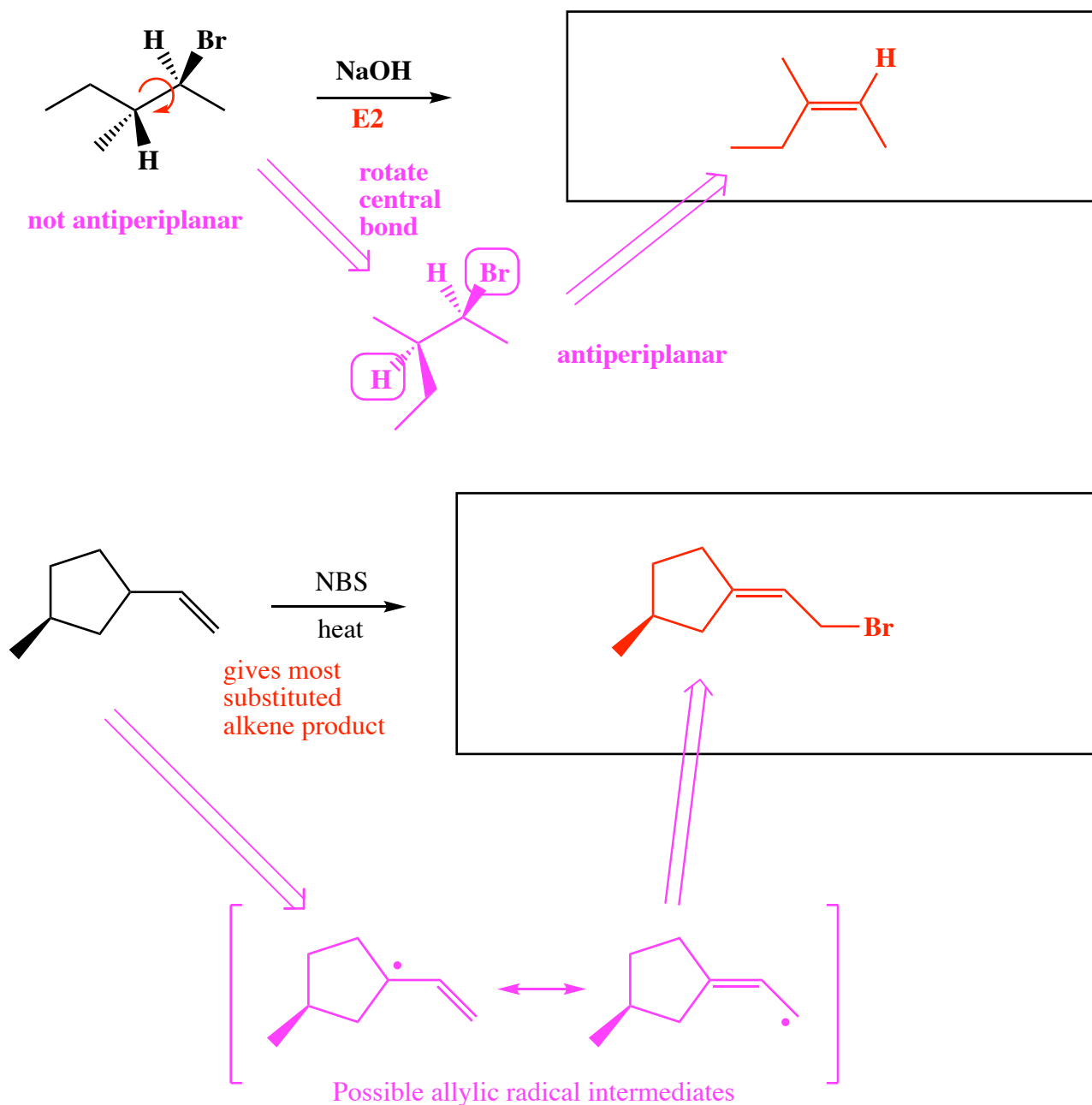


19 (18 pts) For the following reactions, fill in the box with the predominant **starting materials**, **product(s)** or **reagent(s)** necessary to complete the following syntheses. **You must indicate stereochemistry with wedges and dashes.** **You must draw all stereoisomers** produced as predominant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

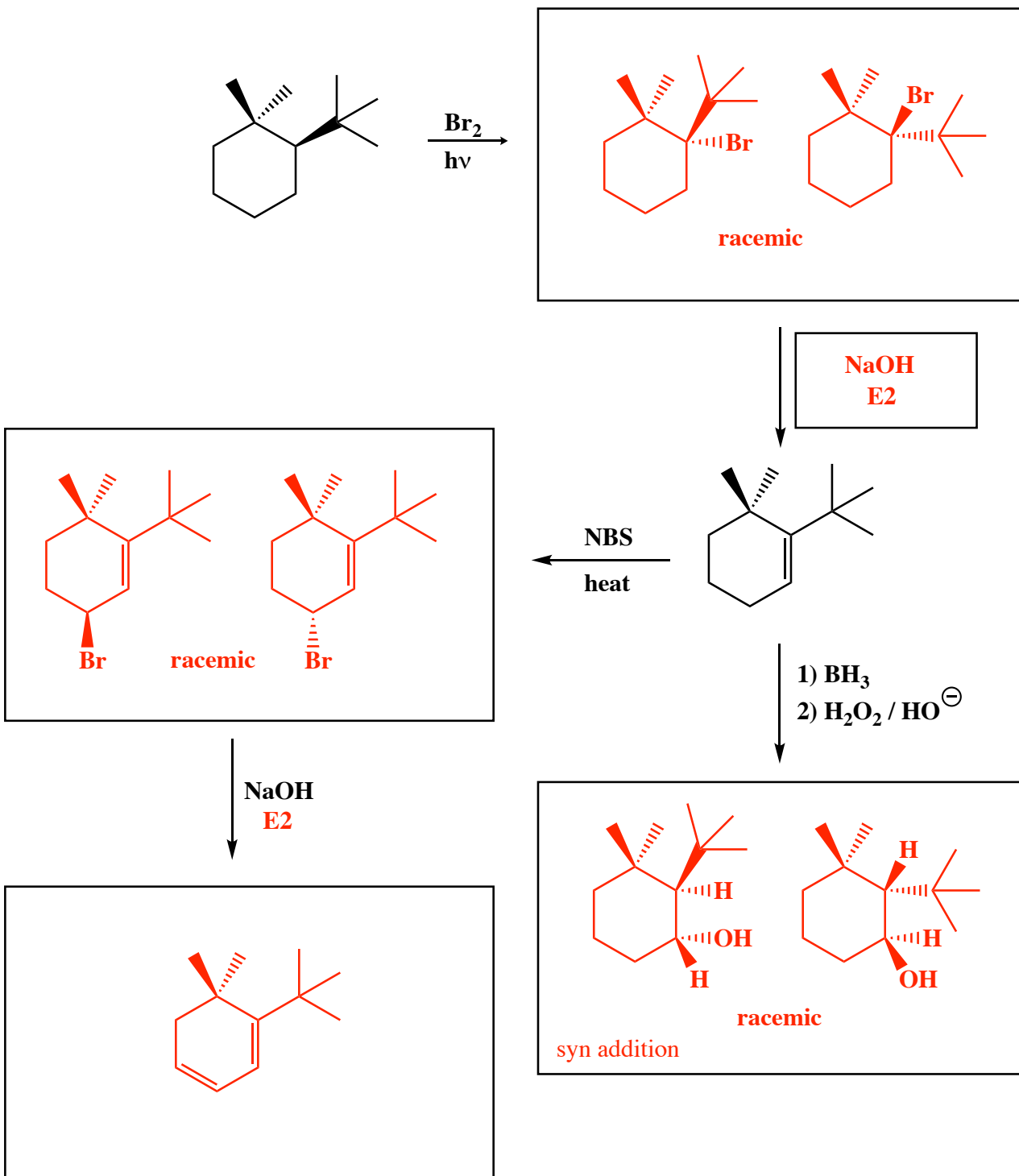


20. (8 pts) The following two reactions take a little more thought. Fill in the box with **only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products)** and please remember that **you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry**. When a racemic mixture is formed, you must write "racemic" under both structures **EVEN THOUGH YOU DREW BOTH STRUCTURES**.

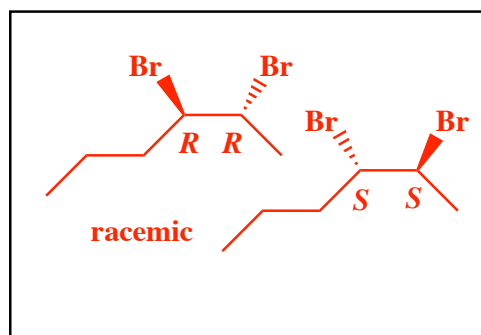
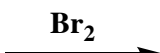
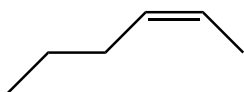
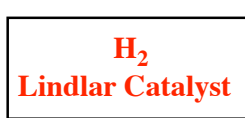
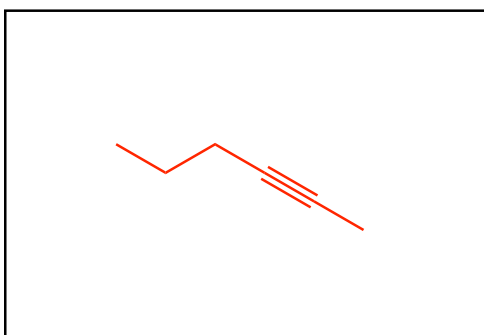
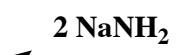
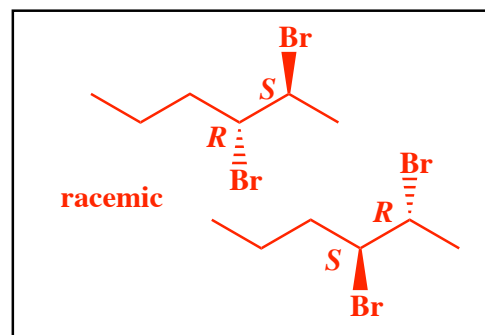
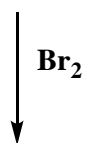
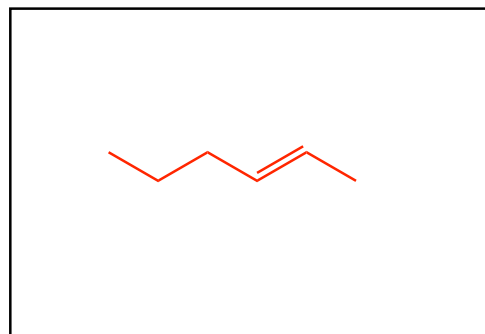
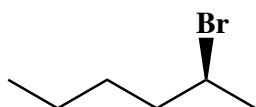
I am giving you some extra room to work through these



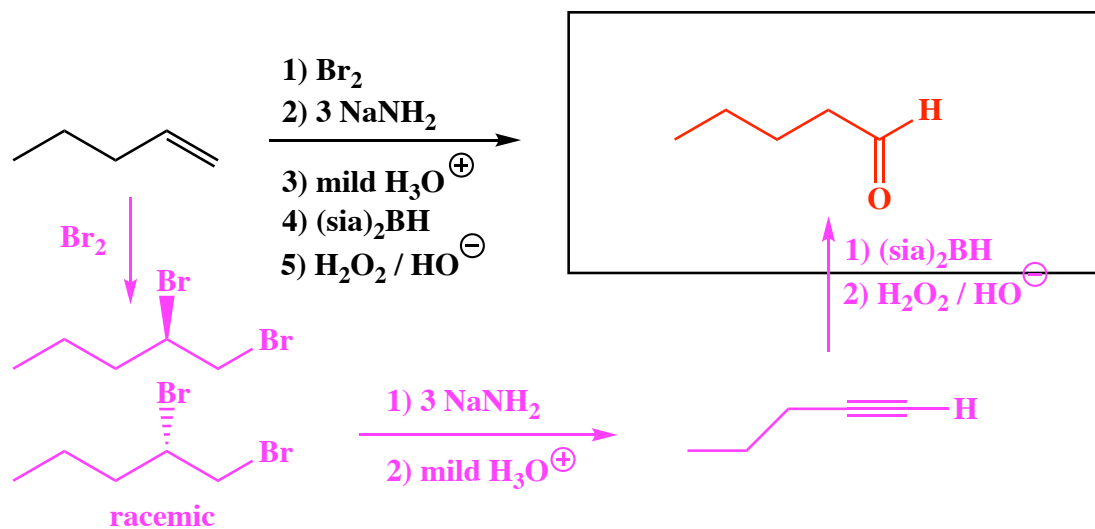
21. (21 pts) For the following reactions, fill in the box with the predominant **product(s)** or **reagent(s)** necessary to complete the following syntheses. **You must indicate stereochemistry with wedges and dashes.** **You must draw all stereoisomers** produced as predominant products and **write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



22. (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.



23. (6 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".



24. (6 pts) Fill in the missing reagents, next to the 3) and 4) in the box, required to make the product. You can use the space to work things out, but we will only grade the reagents shown in the box.

