

NAME (Print): _____

Chemistry 320M/328M

Dr. Brent Iverson

3rd Midterm

November 16, 2017

SIGNATURE: _____

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	(33)
2	(27)
3	(24)
4	(19)
5	(28)
6	(19)
7	(26)
8	(23)
9	(20)
10	(21)
11	(25)
12	(24)
13	(10)
Total	(299)

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)

PERIODIC TABLE OF THE ELEMENTS

Elementary Subatomic Particles																	
Symbol	Electron	Proton	Neutron	Photon	Neutrino												
Mass (kg)	$9.10938954 \times 10^{-31}$	$1.6726231 \times 10^{-27}$	$1.6749273 \times 10^{-27}$	$1.4959789 \times 10^{-27}$	$1.6749273 \times 10^{-27}$												
Relative mass (m _e)	1	1836.152673(43)	1838.683661(43)	1838.683661(43)	1838.683661(43)												
Charge (C)	$-1.602176634 \times 10^{-19}$	$1.602176634 \times 10^{-19}$	0	0	0												
Spin (h)	1/2	1/2	1/2	1	1/2												
Compton wavelength (m)	$2.42631024 \times 10^{-12}$	$1.3214085 \times 10^{-15}$	$1.3195911 \times 10^{-15}$	$1.3195911 \times 10^{-15}$	$1.3195911 \times 10^{-15}$												
Magnetic moment (J/T)	$9.28476377 \times 10^{-24}$	$1.4106076 \times 10^{-26}$	$0.966237074 \times 10^{-26}$	$0.966237074 \times 10^{-26}$	$0.966237074 \times 10^{-26}$												
In Bohr magneton (μ _B)	$1.83614796 \times 10^{-11}$	$1.4106076 \times 10^{-26}$	$0.966237074 \times 10^{-26}$	$0.966237074 \times 10^{-26}$	$0.966237074 \times 10^{-26}$												
In nuclear magneton (μ _N)	$1.83614796 \times 10^{-11}$	$1.4106076 \times 10^{-26}$	$0.966237074 \times 10^{-26}$	$0.966237074 \times 10^{-26}$	$0.966237074 \times 10^{-26}$												

% Ionic Character of a Single Chemical Bond																	
Electronegativity (Pauling)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7
% Ionic Character (Pauling)	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4
% Ionic Character (Mulliken)	1.6	3.3	5.1	7.0	9.1	11.3	13.5	15.7	17.9	20.1	22.3	24.5	26.7	28.9	31.1	33.3	35.5

possessing 50% or greater ionic character are commonly termed ionic, bonds with less than 50% ionic character are termed covalent. Pauling's equation was modified by Huggins.

PAPERTECH

Editors: T. K. Varga, M.A.Sc. & C. Bello, M.A.Sc.
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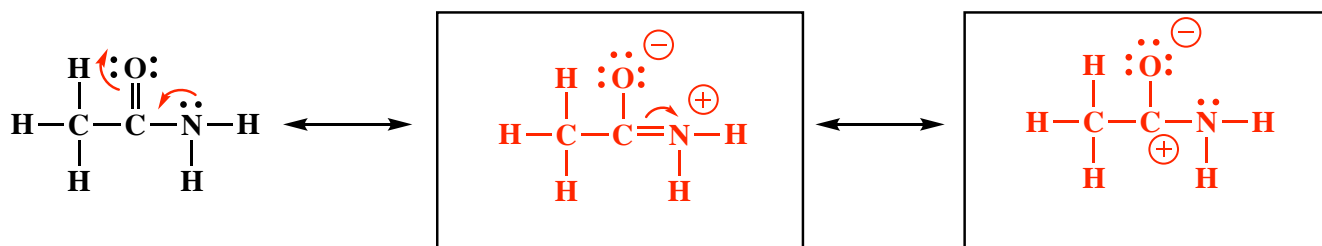
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Compound		pK _a
Hydrochloric acid	H-Cl	-7
Protonated alcohol	$\text{RCH}_2\text{O}^+\text{H}_2$	-2
Hydronium ion	H_3O^+	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-5
Thiols	RCH_2SH	8-9
Ammonium ion	H_4N^+	9.2
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	10
Primary ammonium	$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_3$	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	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	16
Aldehydes	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	18-20
Ketones	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	18-20
Esters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\text{H}$	25
LDA	$\text{H}-\text{N}(\text{i-C}_3\text{H}_7)_2$	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

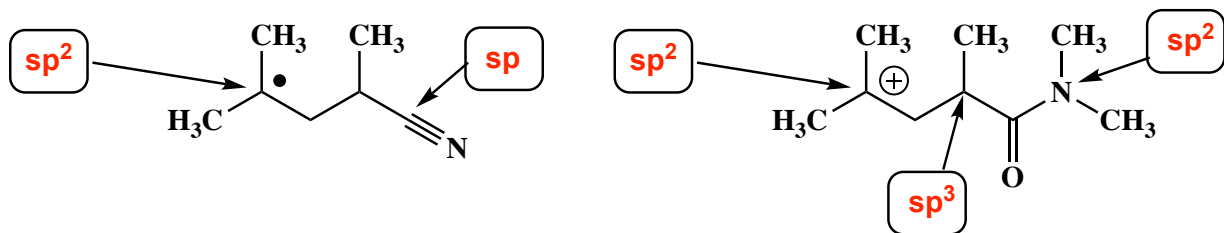
1. (5 pts) What is the most important question in organic chemistry?

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 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

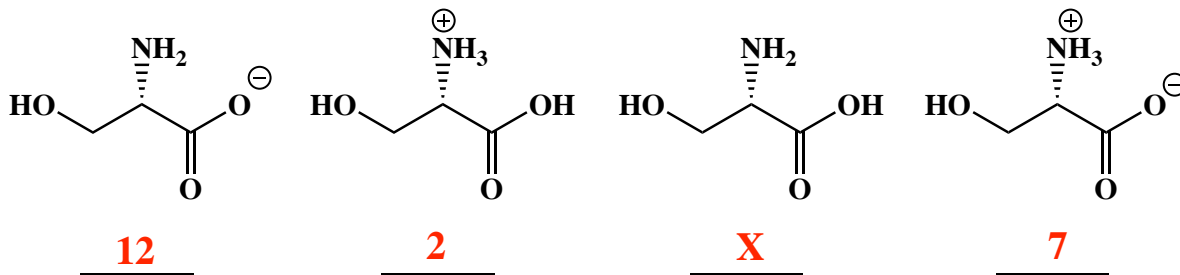


3. (10 pts.) On the following structures, indicate the hybridization state of each atom indicated with an arrow



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 be 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. (16 pts) Fill in each blank with the word that best completes each sentence

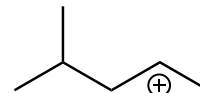
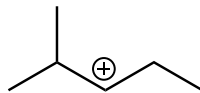
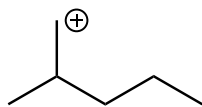
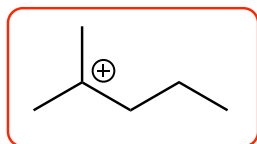
The Hammond postulate, i.e. transition states resemble more closely the structures of the species they are closest to in energy, explains why bromination is more selective than chlorination. Bottom line: Always use Br₂ and light when reacting alkanes to give haloalkanes.

The enol form of a compound rapidly tautomerizes to the more stable keto form. The keto form is more stable because the C=O pi bond is stronger than the C=C pi bond

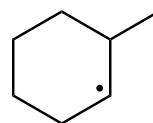
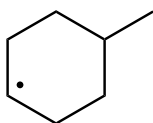
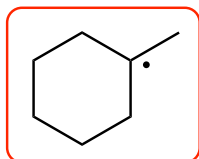
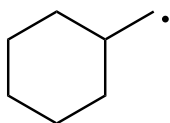
6. (11 pts) Consider the following statements that refer S_N1, S_N2, E1, E2, or a radical chain reaction mechanism. To which mechanism(s), if any, does each statement apply?

	<i>Mechanism(s)</i>
A. The reaction(s) that involves an InVERSiON of stereochemistry at the site of reaction.	<u>S_N2</u>
B. The reaction(s) that involves a carbocation intermediate.	<u>S_N1, E1</u>
C. The reaction(s) that involves an anti-periplanar transition state.	<u>E2</u>
D. This reaction mechanism can be triggered by using light of the appropriate wavelength or heat.	<u>radical chain reaction</u>
E. Favored for tertiary haloalkanes when weak nucleophiles/weak bases are used.	<u>S_N1, E1</u>
F. Favored for primary haloalkanes when any nucleophile is used.	<u>S_N2</u>
G. Favored for secondary haloalkanes when a nucleophile that is also a strong base is used.	<u>E2</u>
H. The reaction(s) in which the predominant product is predicted by Zaitsev's rule.	<u>E2, E1</u>

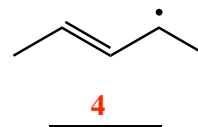
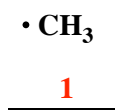
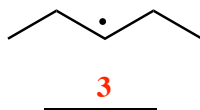
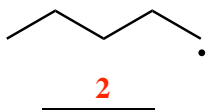
7. (4 pts) For the following series of carbocations, **circle the most stable carbocation.**



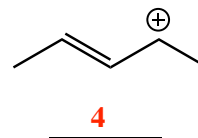
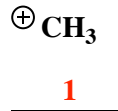
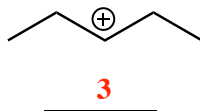
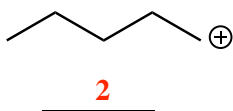
8. (4 pts) For the following series of radicals, **circle the most stable radical.**



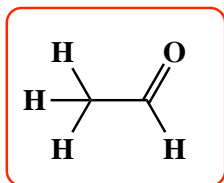
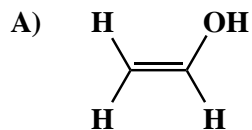
9A. (4 pts) **Rank the following from 1-4** with respect to radical stability, with the **1** under the least stable radical and the **4** under the most stable radical.



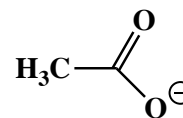
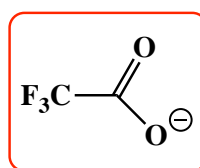
9B. (4 pts) **Rank the following from 1-4** with respect to carbocation stability, with the **1** under the least stable carbocation and the **4** under the most stable carbocation.



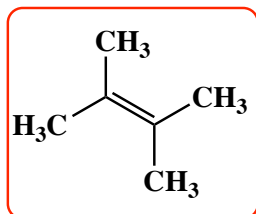
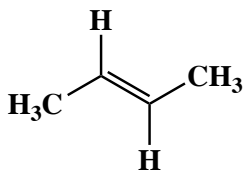
10. (8 pts) For each pair of molecules, **circle the one that is more stable** (lower in energy)



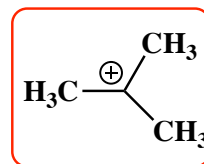
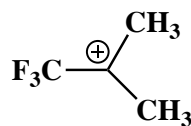
B)



C)



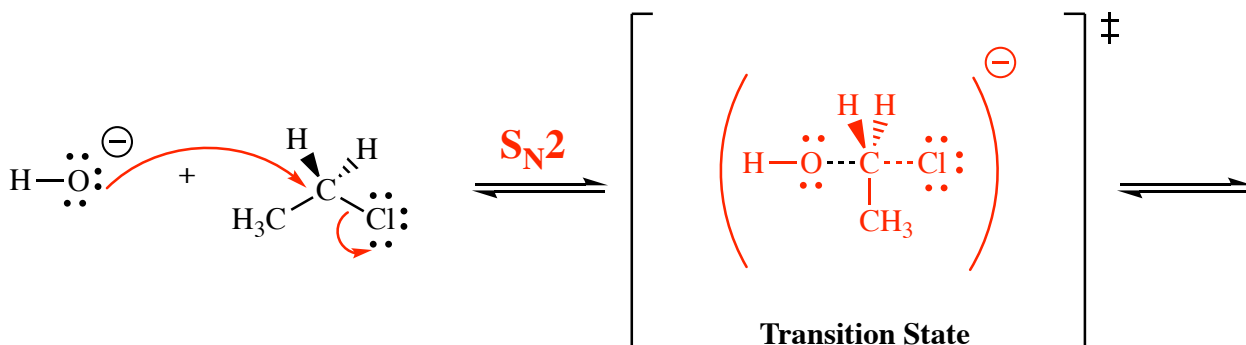
D)



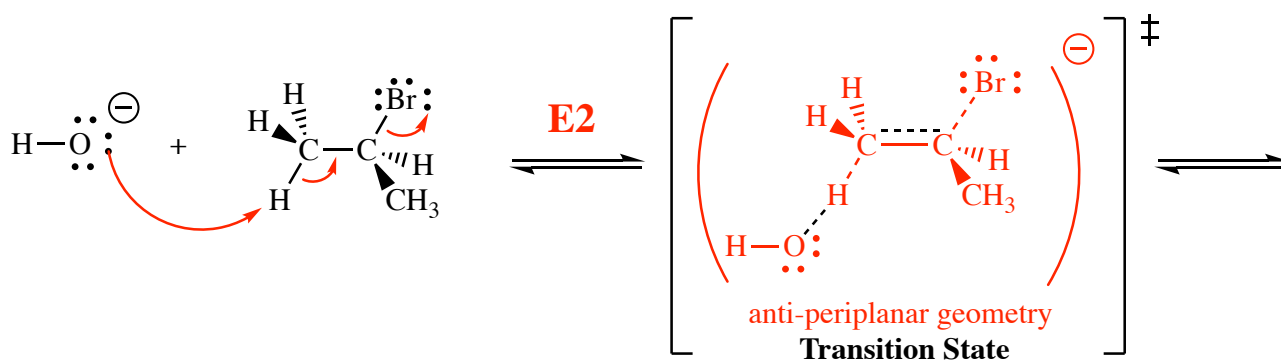
11. (13 pts total) For each reaction below, draw the indicated **key transition state**. We do not want the entire mechanism or products, just the first key transition state. Use dotted lines to indicate bonds that are in the process of being broken or made. Write all formal charges. On the starting structures, draw all appropriate arrows to indicate the flow of electrons.

----- Bond being formed
----- Bond being broken

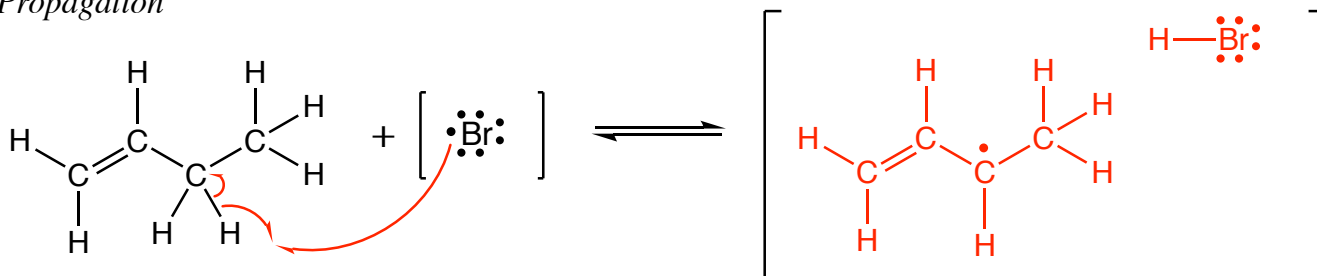
A.



B.



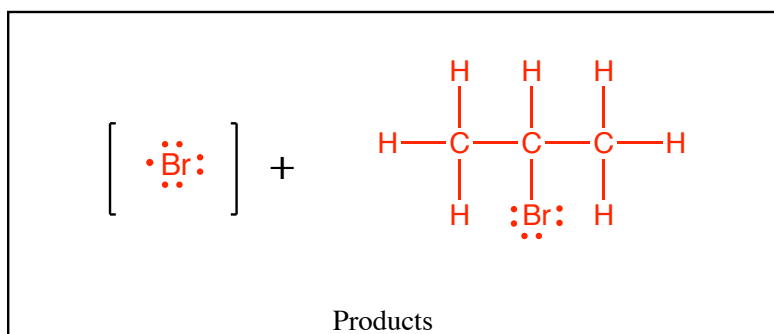
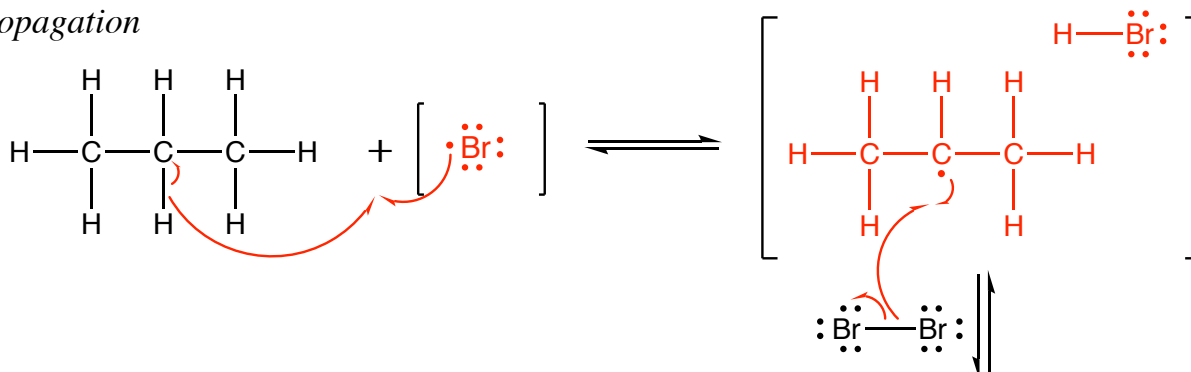
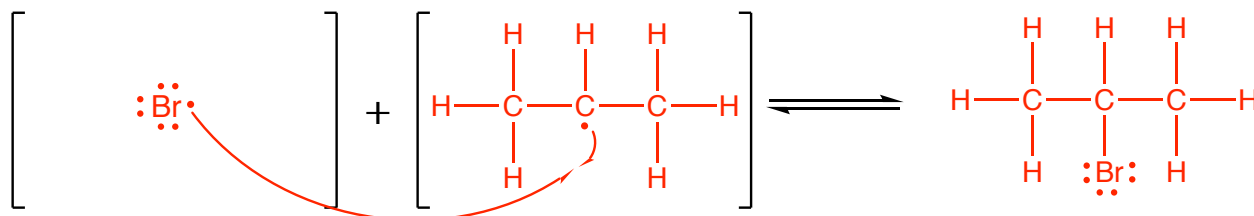
12. (6 pts total) For the reagents below, draw the **first key intermediate** that occurs during the allylic halogenation of an alkene reaction that uses NBS and light. We do not want the entire mechanism or products, just the first key intermediate in the propagation step. Write all formal charges. On the starting structures, draw all appropriate arrows to indicate the flow of electrons.

Propagation

Signature _____

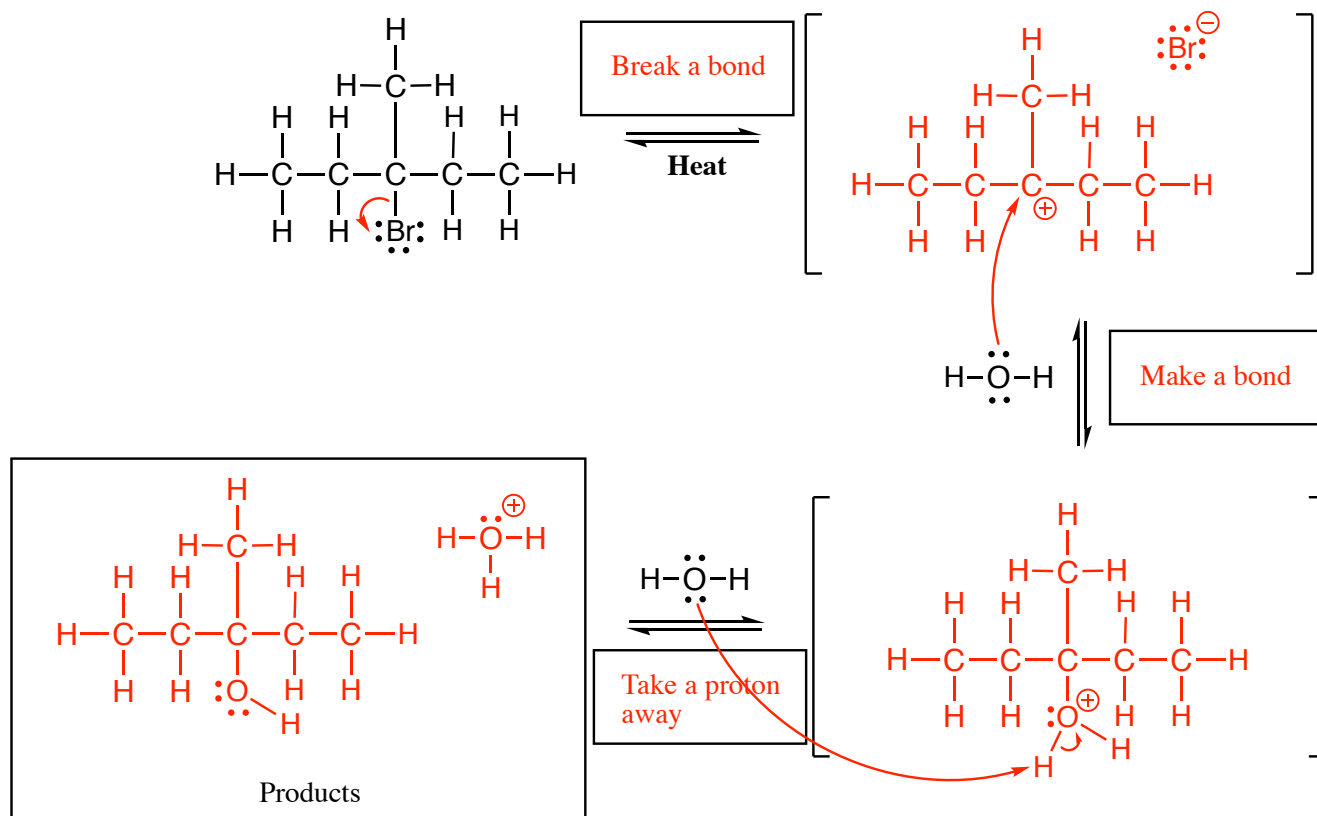
Pg 5 _____(28)

13. (28 pts total) Complete the following mechanism for the halogenation of an alkane. 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)

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

14. (19 pts total) Complete the following mechanism for an S_N1 reaction. Note that to keep this simple, you do NOT have to show the $E1$ reaction that would accompany this one. 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". In the boxes provided next to the arrows, list the mechanistic element that best describes each step ("make a bond", "break a bond", etc.) NOTICE THE QUESTIONS AT THE BOTTOM.**



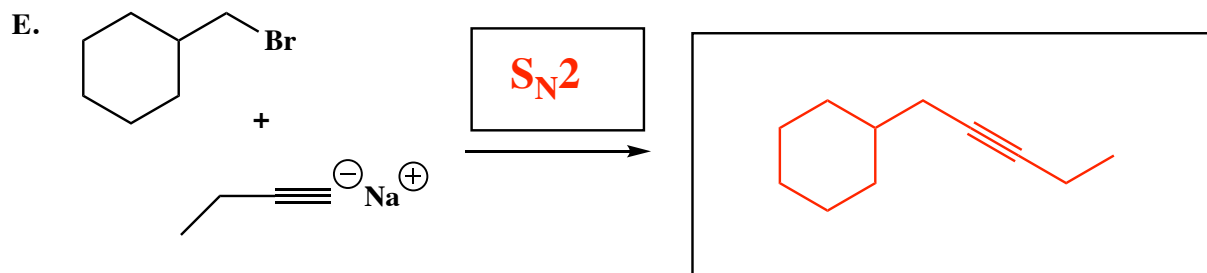
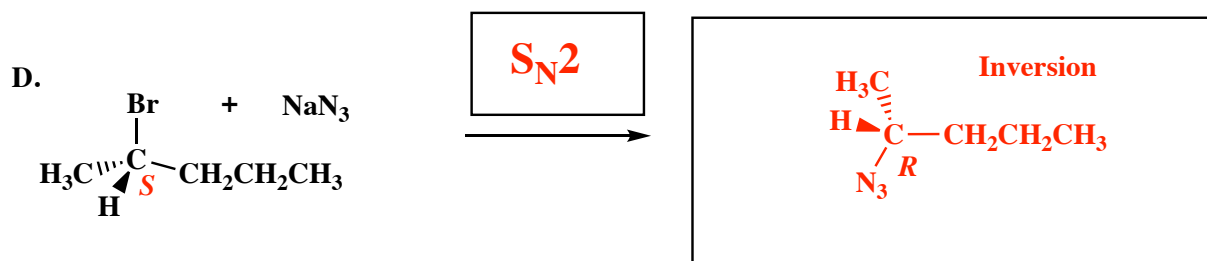
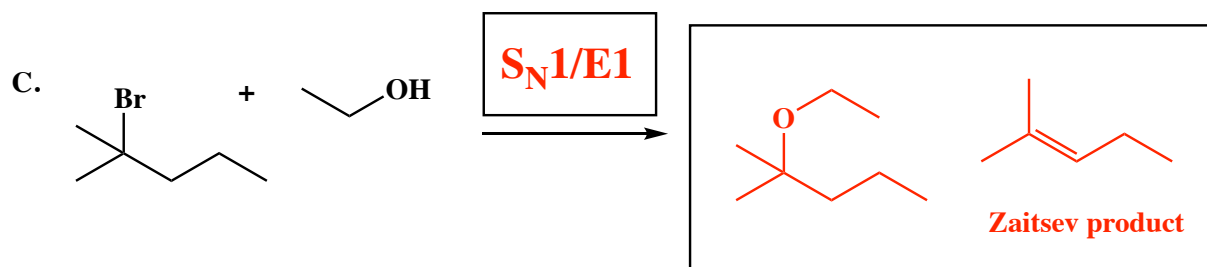
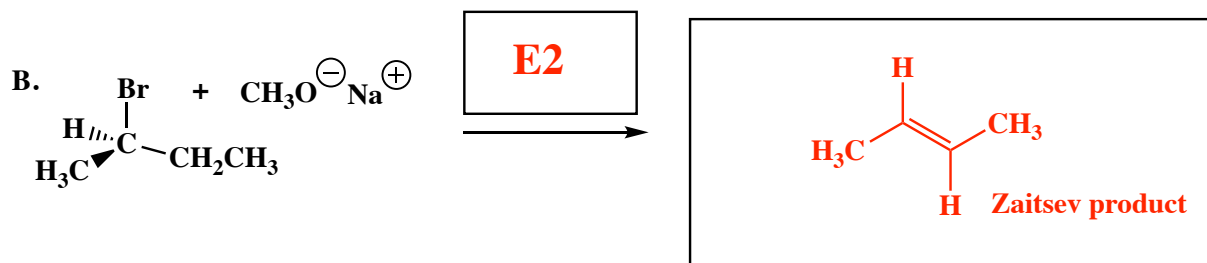
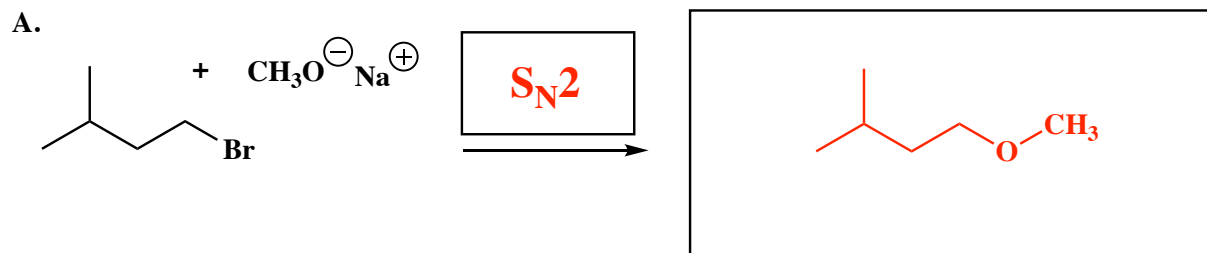
As the reaction shown above proceeds, does the pH remain the same, get lower or get higher with time?

It gets lower (acid is produced)

Does the rate-limiting step of this reaction involve only the haloalkane, or both the haloalkane and the H_2O ?

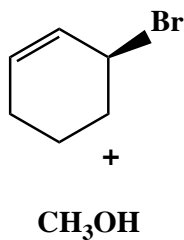
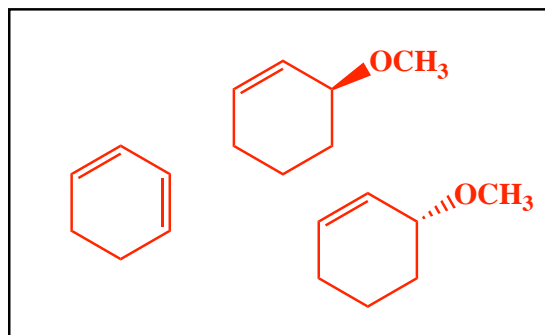
Only the haloalkane (the bond breaking step is slowest and therefore rate-limiting)

16. (5 or 6 pts each) 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).**

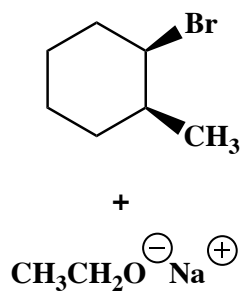


15. (5,7 or 9 pts each) The following reactions all involve chemistry of haloalkanes. Fill in the box above the arrow with the mechanism that will be followed (S_N2 , E2, etc.). Then draw only the predominant product or products and please remember that you must draw the correct stereoisomers. For $S_N1/E1$ reactions you must draw all significant products (including all stereoisomers).

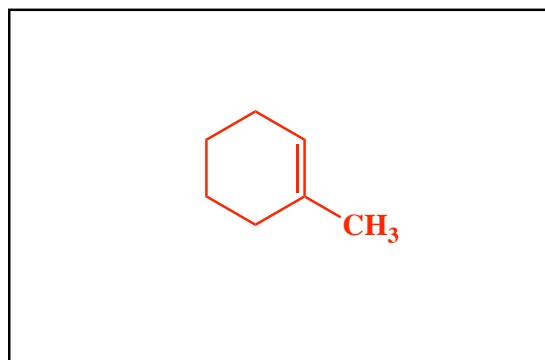
F.

 $S_N1/E1$ 

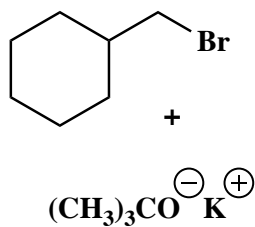
G.



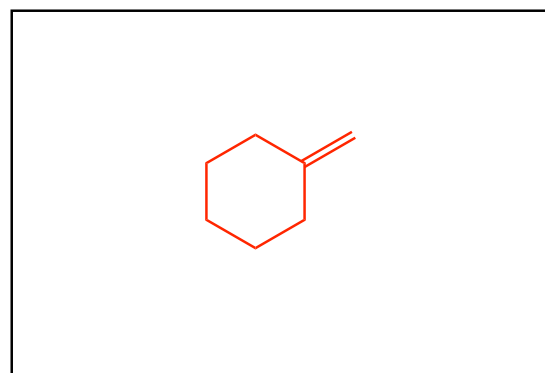
E2



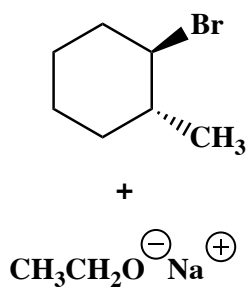
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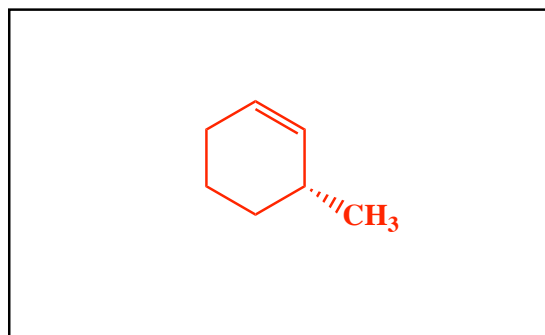
E2



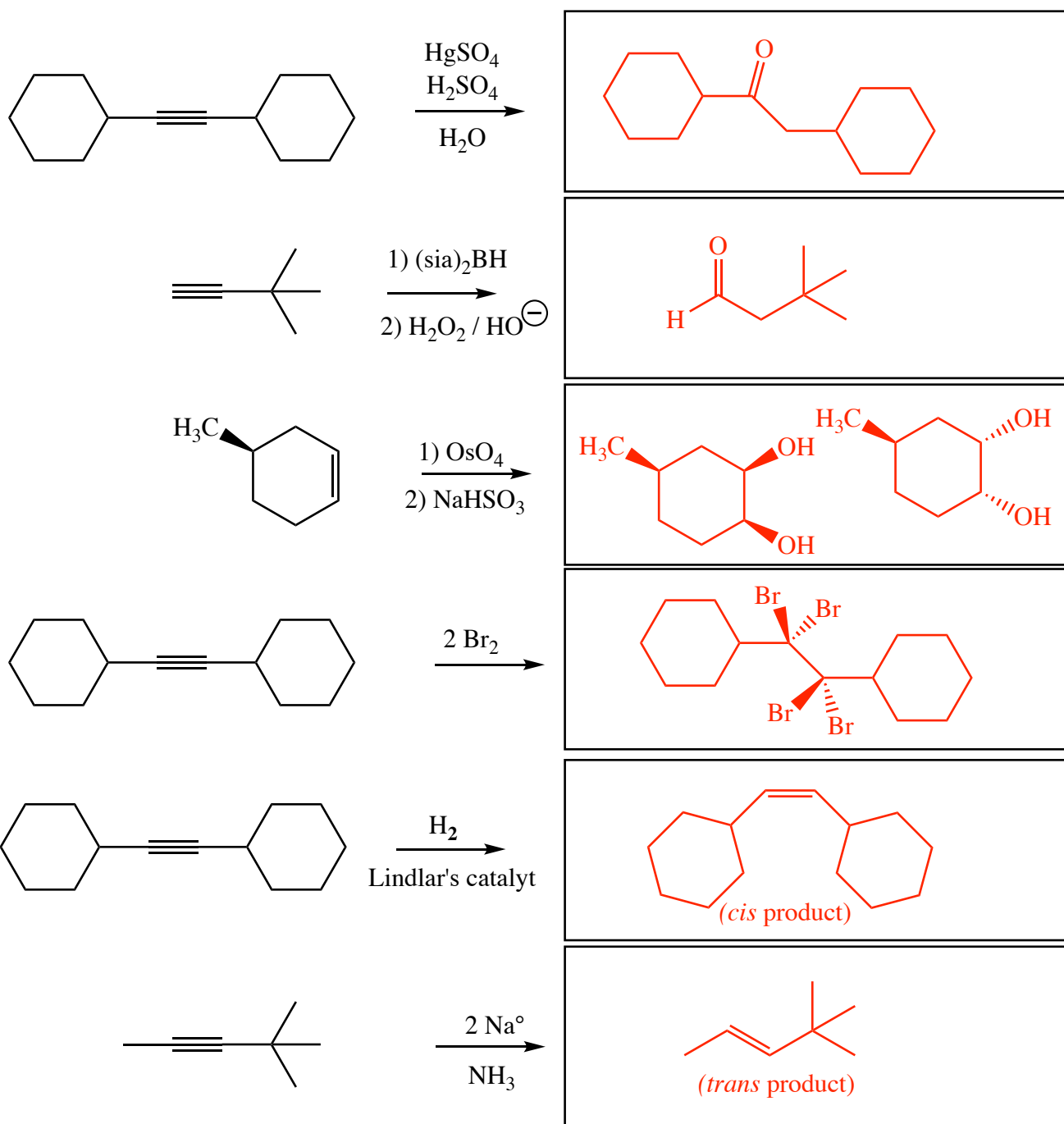
I.



E2



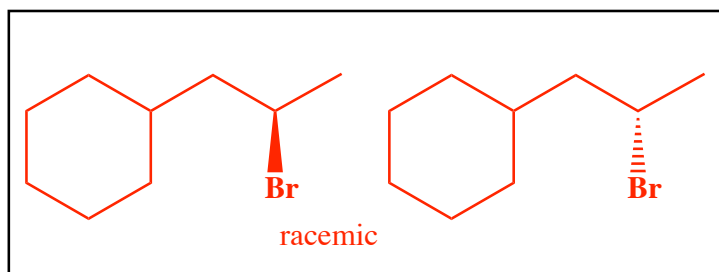
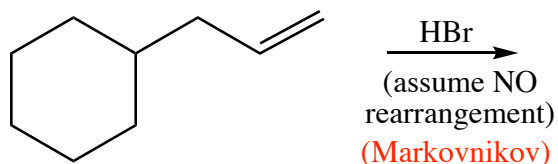
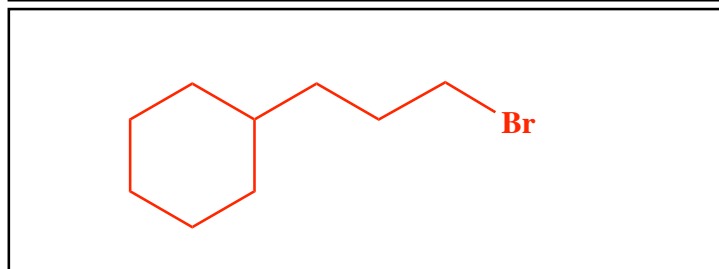
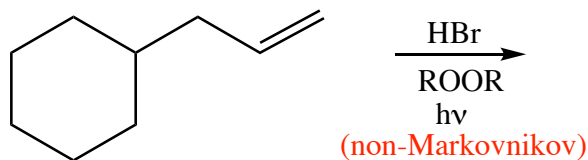
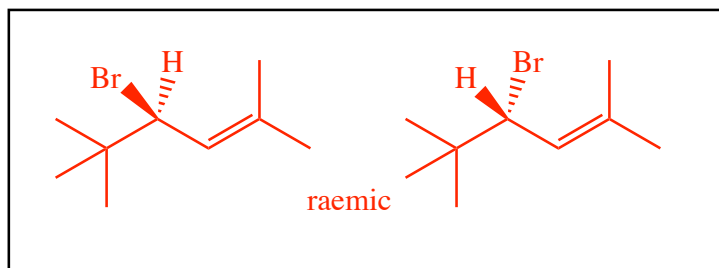
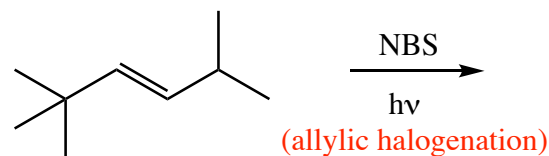
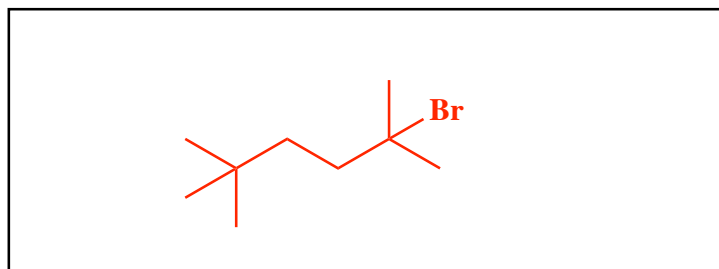
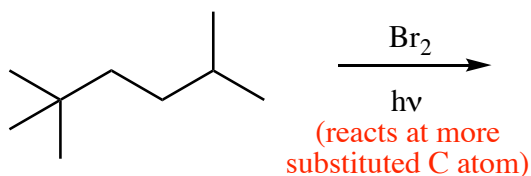
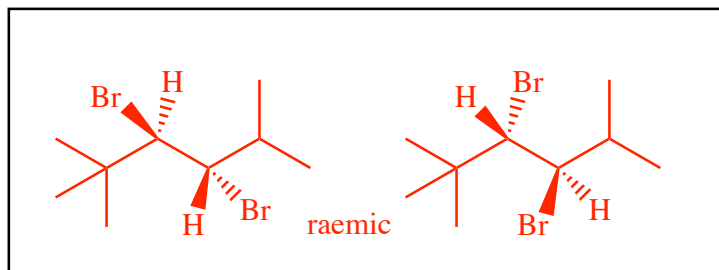
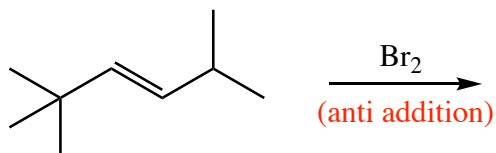
16. (3 or 5 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products)** and please remember that **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**.



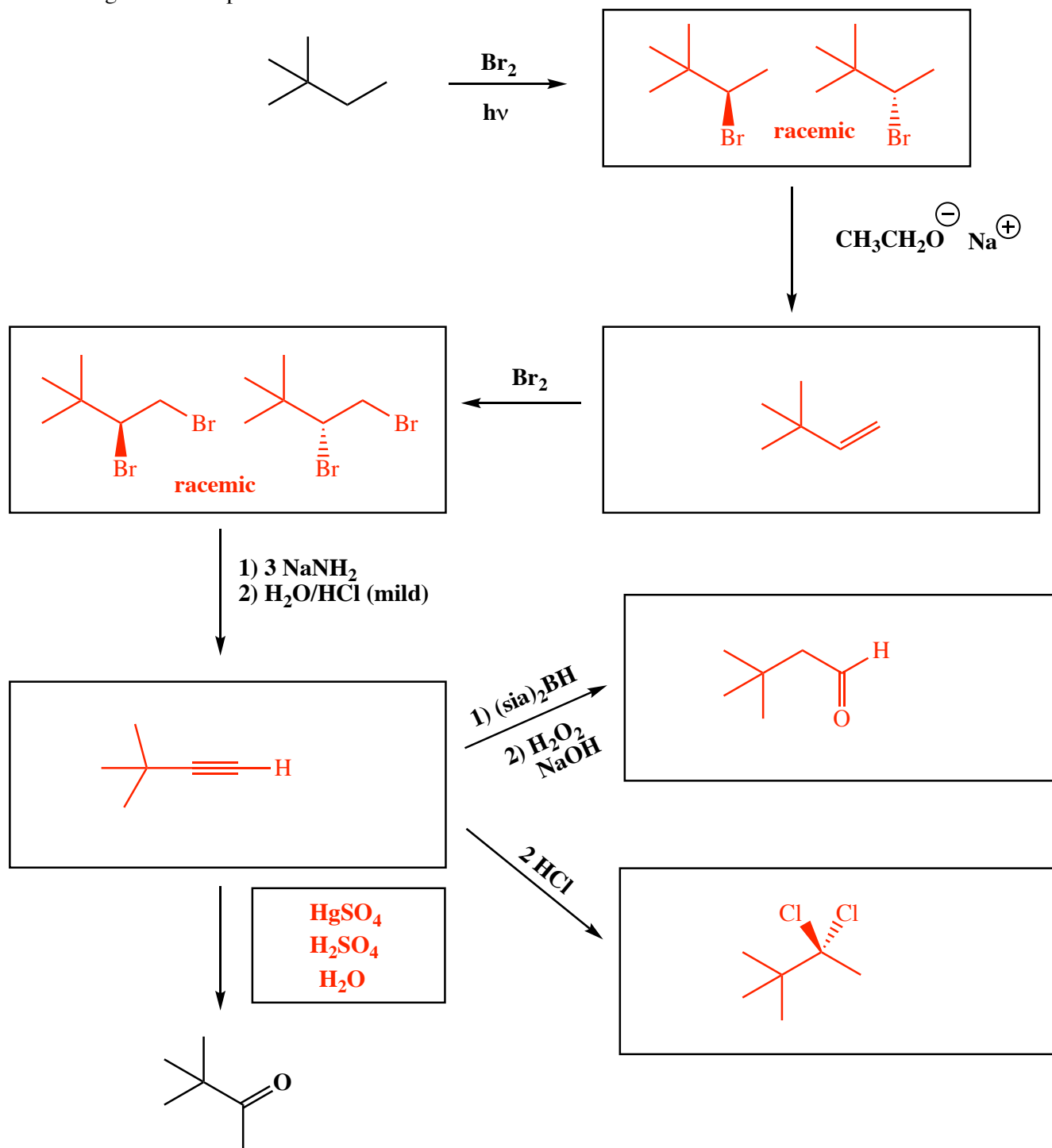
Signature _____

Pg 10 _____(21)

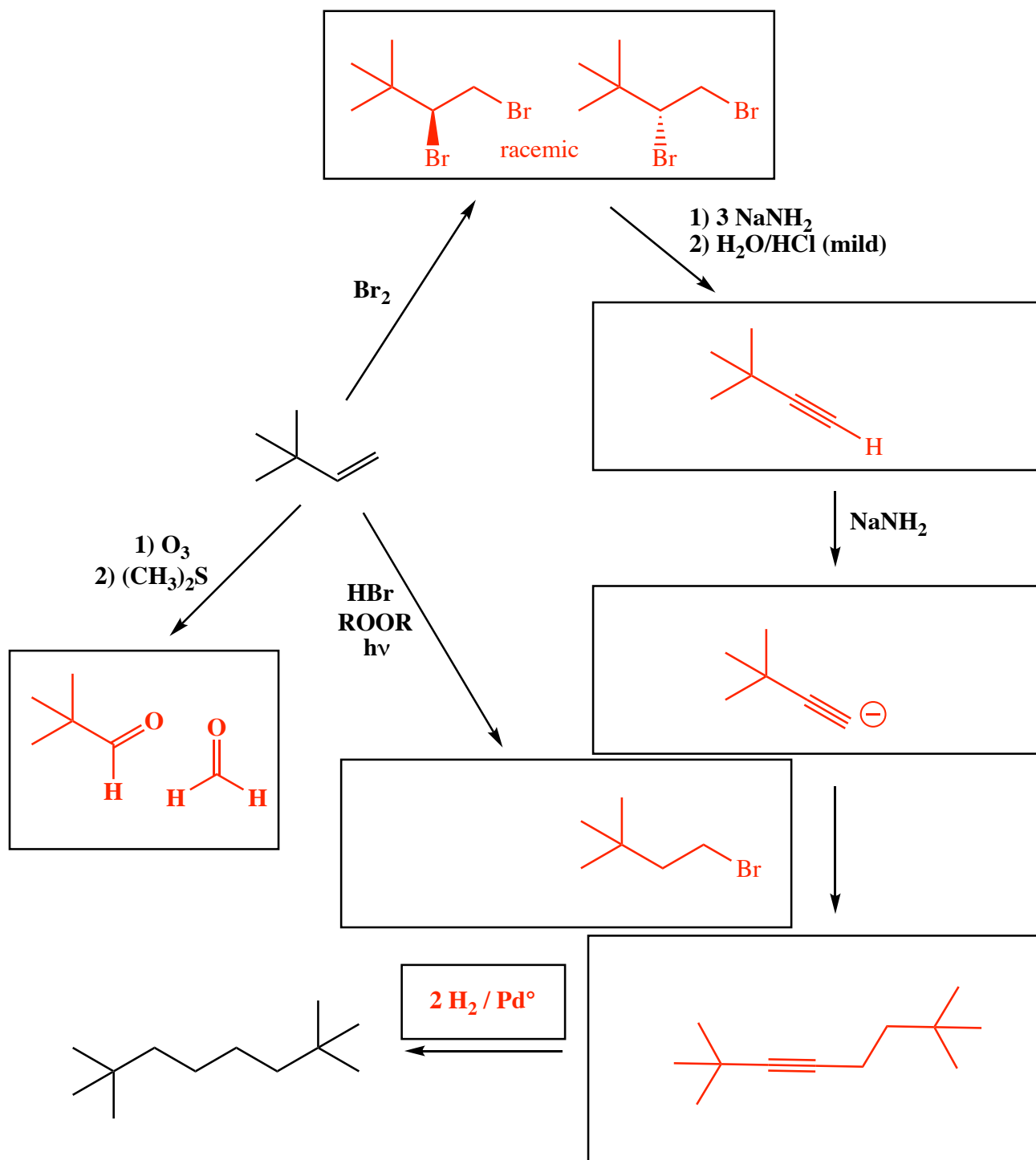
17. (3 or 5 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products)** and please remember that **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) For the following reactions, fill in the box with the predominant **products** or **reagents** 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. Assume no rearrangements take place.



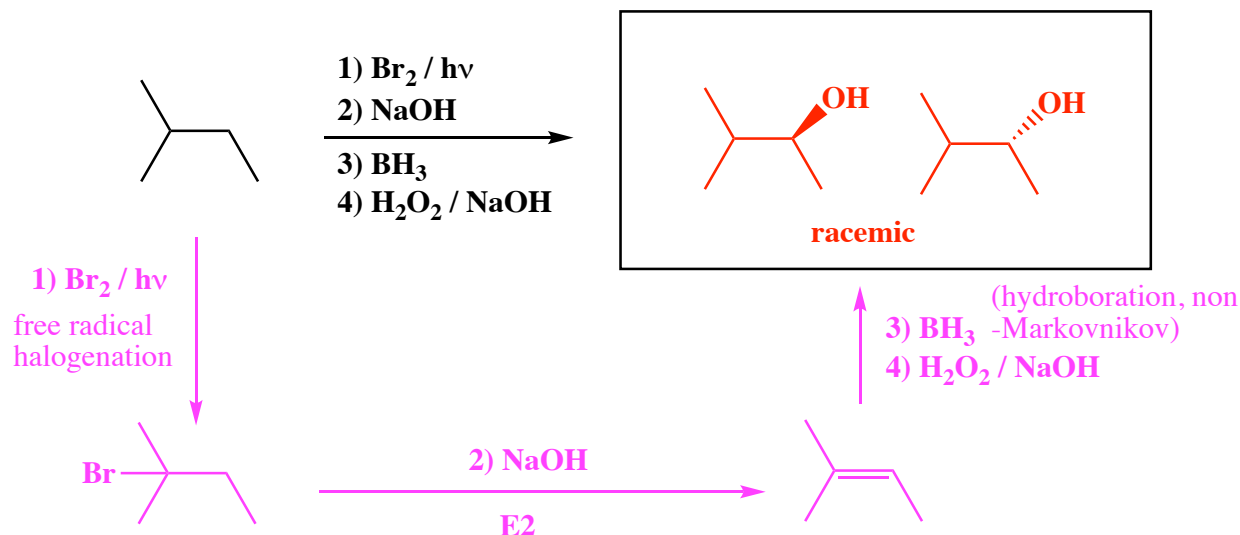
18. (3, 4 or 5 pts each) For the following reactions, fill in the box with the predominant **products** or **reagents** necessary to complete the following syntheses. **You must indicate stereochemistry with wedges and dashes.** **You must draw all stereoisomers** produced as predominant products and **write "racemic"** under the structures when appropriate. Assume no rearrangements take place.



Signature _____

Pg 13 _____(10)

19. (5 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”.



20. (5 pts) Save this until last. Super challenge problem. In the box provided, **draw the starting material** that leads to the product shown. Feel free to draw any other structures in the empty space provided. We will only grade the structure in the box.

