NAME (Print): _____

SIGNATURE: _____

Chemistry 320M/328M
Dr. Brent Iverson
3rd Midterm
November 15, 2018

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

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 INCIDENCTS 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!!!

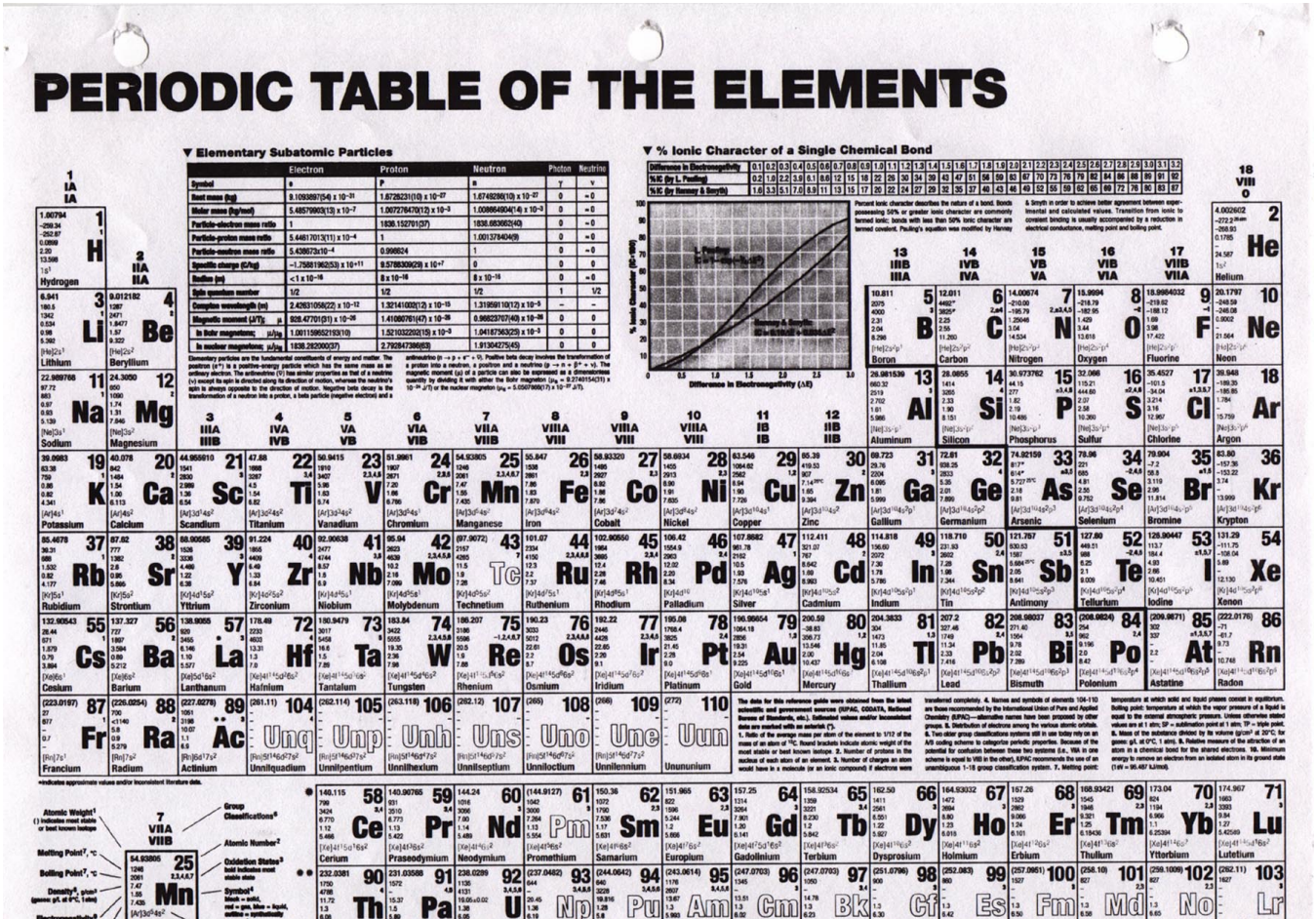
Page	Points	
1		(29)
2		(24)
3		(19)
4		(16)
5		(25)
6		(38)
7		(25)
8		(31)
9		(22)
10		(18)
11		(8)
12		(23)
13		(20)
14		(12)
Total		(310)

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

	Electron	Proton	Neutron	Photon	Neutrino
Symbol	e	P	n	γ	ν
Rest mass (kg)	9.1093897(54) x 10^{-31}	1.6726231(10) x 10^{-27}	1.6749286(10) x 10^{-27}	0	= 0
Molar mass (kg/mol)	5.4857990(13) x 10^{-7}	1.00727647(12) x 10^{-3}	1.00866404(14) x 10^{-3}	0	= 0
Particle-electron mass ratio	1	1836.1527071(37)	1838.6830(62)	0	= 0
Particle-proton mass ratio	5.44617013(11) x 10^{-4}	1	1.0013784004(9)	0	= 0
Particle-neutron mass ratio	5.43807a10−4	0.998624	1	0	= 0
Specific charge (C/kg)	−1.75881962(53) x 10^{+11}	9.5788309(29) x 10^{+7}	0	0	0
Radius (m)	<1 x 10^{-18}	8 x 10^{-16}	8 x 10^{-16}	0	= 0
Spin quantum number	1/2	1/2	1/2	1	1/2
Compton wavelength (m)	2.42631058(22) x 10^{-12}	1.32141002(12) x 10^{-15}	1.3195911O(12) x 10^{-5}	–	–
Magnetic moment (J/T); μ	928.47701(31) x 10^{-26}	1.4106076(47) x 10^{-26}	0.9662370(40) x 10^{-26}	0	0
In Bohr magnetons; μ/μ_B	1.001159652193(10)	1.521032202(15) x 10^{-3}	1.041875630(25) x 10^{-3}	0	0
In nuclear magnetons; μ/μ_N	1838.282000(37)	2.792847396(63)	1.91304275(45)	0	0

Elementary particles are the fundamental constituents of energy and matter. The positron (e^+) is a positive-energy particle which has the same mass as an ordinary electron. The antineutrino ($\bar{\nu}$) has similar properties as that of a neutrino (ν) except its spin is directed along its direction of motion, whereas the neutrino's spin is always opposite to the direction of motion. Negative beta decay is the transformation of a neutron into a proton, a beta particle (negative electron) and a antineutrino ($n \rightarrow p + e^- + \bar{\nu}$). Positive beta decay involves the transformation of a proton into a neutron, a positron and a neutrino ($p \rightarrow n + \beta^+ + \nu$). The magnetic moment ($\mu$) of a particle can also be expressed as a dimensionless quantity by dividing it with either the Bohr magneton (μ_B = 9.2740154(31) x 10^{-24} J/T) or the nuclear magneton (μ_N = 5.0507800(17) x 10^{-27} J/T).

▼ % Ionic Character of a Single Chemical Bond

Difference in Electronegativity	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	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2
%IC (by L. Pauling)	0.2	1.0	2.2	3.9	6.1	8.6	12	15	18	22	26	30	34	39	43	47	51	56	59	63	67	70	73	76	79	82	84	86	88	89	91	92
%IC (by Hanney & Smyth)	1.6	3.3	5.1	7.0	8.9	11	13	15	17	20	22	24	27	29	32	35	37	40	43	46	49	52	55	59	62	65	68	72	76	78	80	83	87

Percent ionic character describes the nature of a bond. Bonds 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 Hanney & Smyth in order to achieve better agreement between experimental and calculated values. Transition from ionic to covalent binding is usually accompanied by a reduction in electrical conductance, melting point and boiling point.

Atomic Weight[1] () indicates most stable or best known isotope
Melting Point[2], °C
Boiling Point[2], °C
Density[3], g/cm³ (gases: g/L at 0°C, 1 atm)
Electronegativity[4]
First Ionization Potential[4], eV
Group Classifications[5]
Atomic Number[2]
Oxidation States[3] bold indicates most stable state
Symbol[2] Black = solid, red = gas, blue = liquid, outline = synthetically prepared
Electronic[5] Configuration
Name[2]

Mn — 25 — 54.93805 — 1246 — 2061 — 7.47 — 1.55 — 7.435 — [Ar]3d⁵4s² — 2,13,15,7 — Manganese

PAPERTECH

Editors: T. K. Varga, M.A.Sc. & C. Bello, M.A.Sc.

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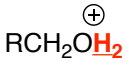
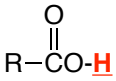
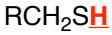
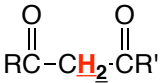
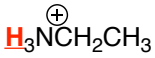
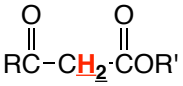
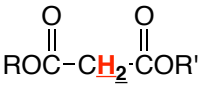
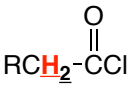
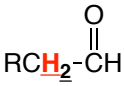
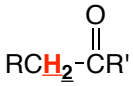
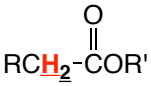
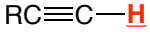
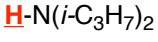
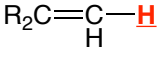
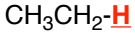
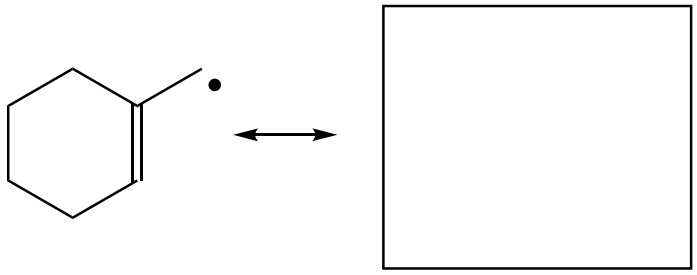
Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Carboxylic acids		3-5
Thiols		8-9
Ammonium ion		9.2
β-Dicarbonyls		10
Primary ammonium		10.5
β-Ketoesters		11
β-Diesters		13
Water		15.7
Alcohols		15-19
Acid chlorides		16
Aldehydes		18-20
Ketones		18-20
Esters		23-25
Terminal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

Signature_____ Pg 1 _____(29)

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

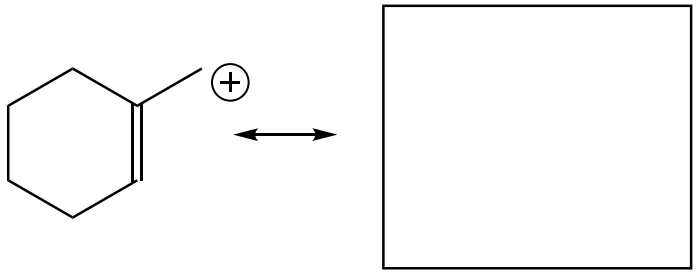
2. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges. For the two structures on the left in each problem, use arrows to indicate the movement of electrons to give the structures you drew. There is no need to draw any circles around any of these contributing strucures. You might want to read these directions again to make sure you know what we want.

3. (14 pts.) For the following molecules, draw the other important contributing structure. Draw arrows on the structure given to indicate the flow of electrons leading to the contributing structure you drew in the box.



(2 pts) How many electrons are in the delocalized pi system ("pi-way") of the species to the left?

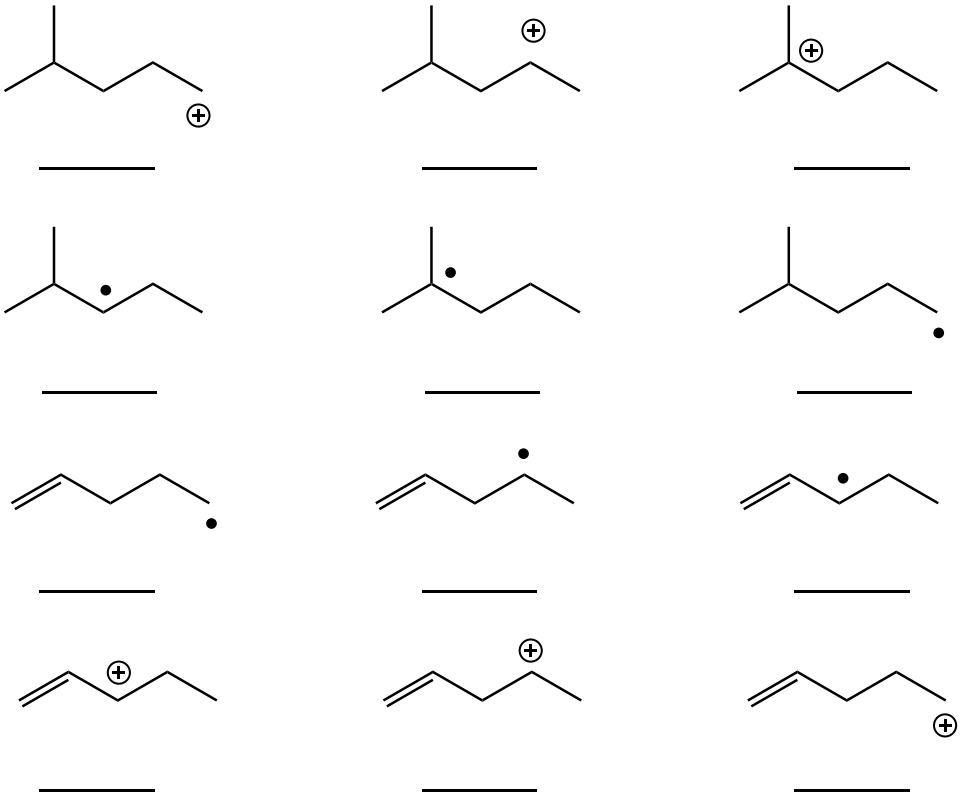
_____



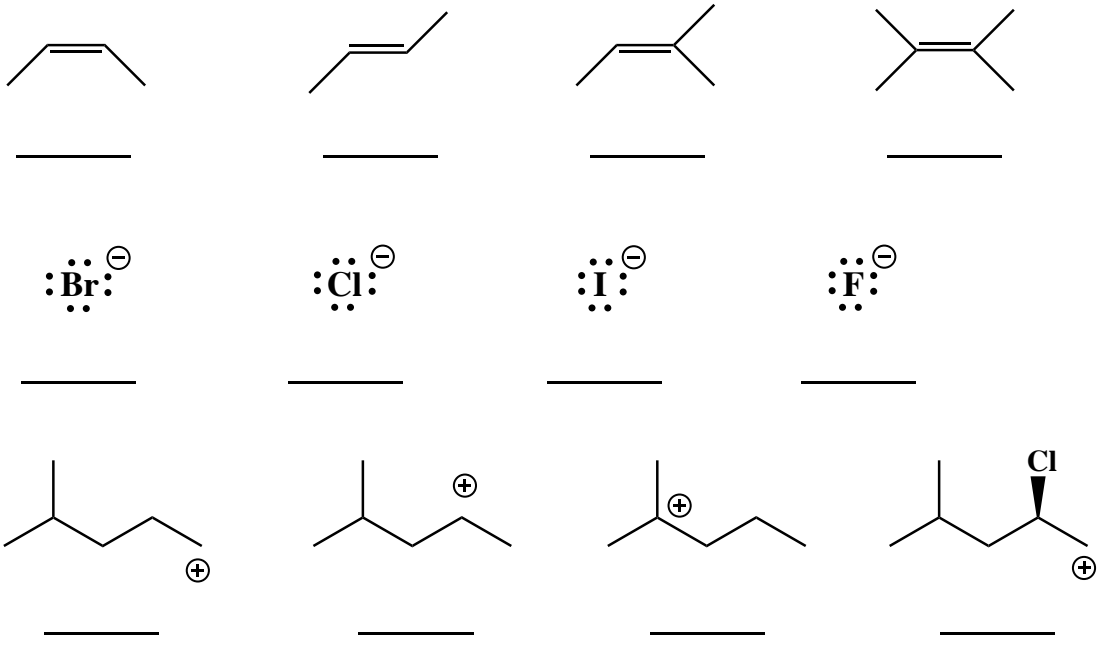
(2 pts) How many electrons are in the delocalized pi system ("pi-way") of the species to the left?

_____

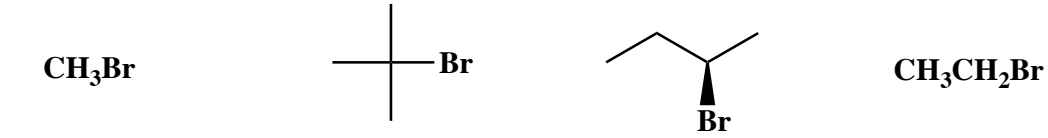
4. (12 pts) Rank the following sets of three molecules with respect to stability, **putting a 1 under the most stable and a 3 under the least stable in the series.**



5. (12 pts) Rank the following sets of four molecules with respect to stability, **putting a 1 under the most stable and a 4 under the least stable in the series.**



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.**

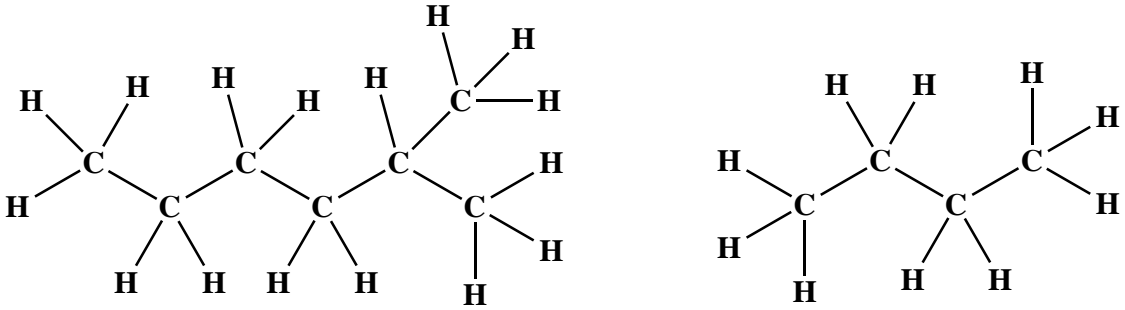


_____ _____ _____ _____

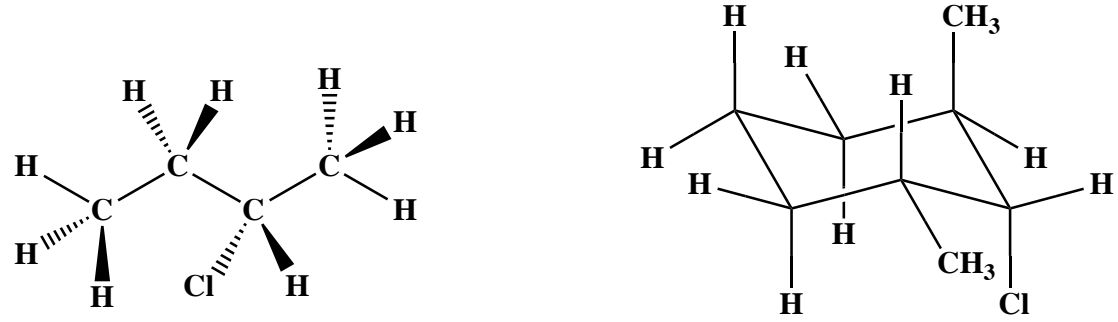
7. (4 pts) Rank the following four molecules with respect to their ability to react according to an S_N1/E1 mechanism. **Put a 1 under the most reactive and a 4 under the least reactive molecule.**

_____ _____ _____ _____

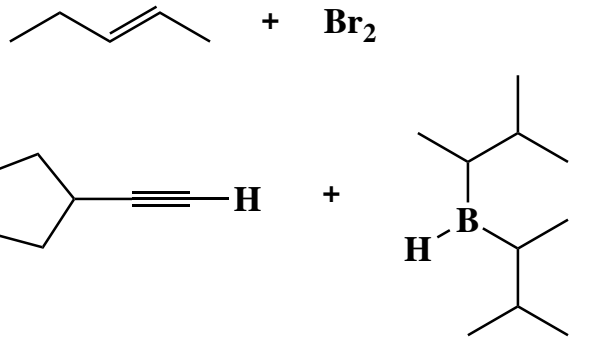
8. (5 pts) For the following molecules, **circle the H atom(s) that are most likely to react during a free radical halogenation reaction using Br_2 and light. If more than one H atom ties as the most reactive on the molecule, circle all of the most reactive ones.**



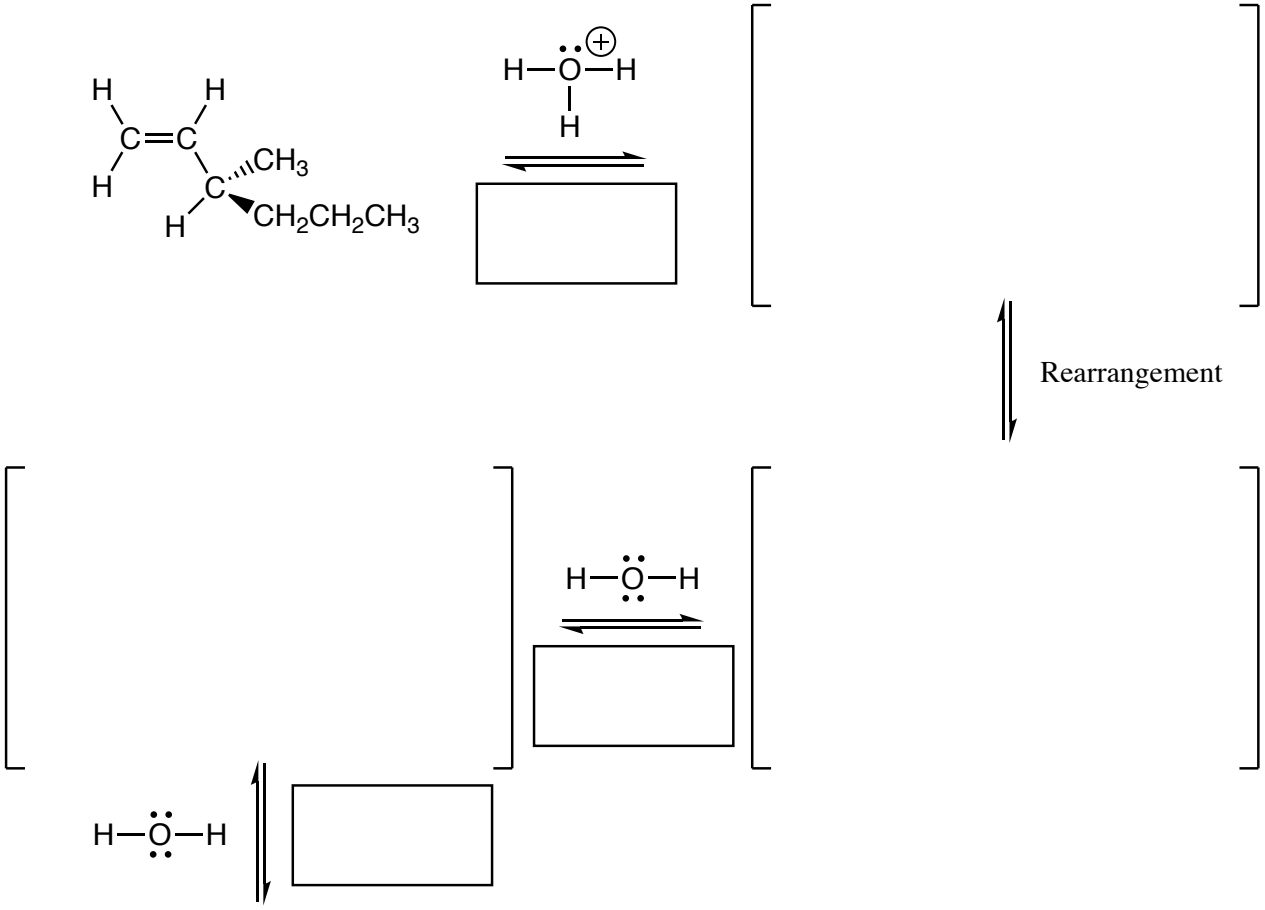
9. (6 pts) For the following molecules, **circle the H atom(s) that are most likely to react during an E2 reaction. If more than one H atom ties as the most reactive on the molecule, circle all of the most reactive ones.**



10. (2 pts each) For the following sets 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 circles on this page!!



11. (25 pts) This will look familiar. It was on the last exam and your homework. Complete the mechanism for the following acid-catalyzed alkene hydration reaction with a rearrangement. **For this mechanism we will ONLY consider the rearranged product. 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. **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.). Be sure to notice the question at the end.**



Product

(2 pts) Does the starting material rotate the plane of plane polarized light?

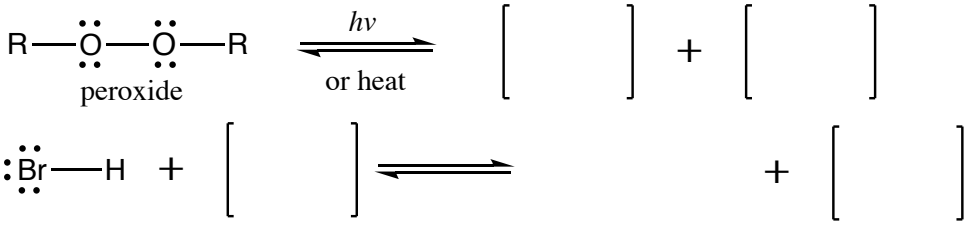
_____

(2 pts) Do(es) the product(s) rotate the plane of plane polarized light?

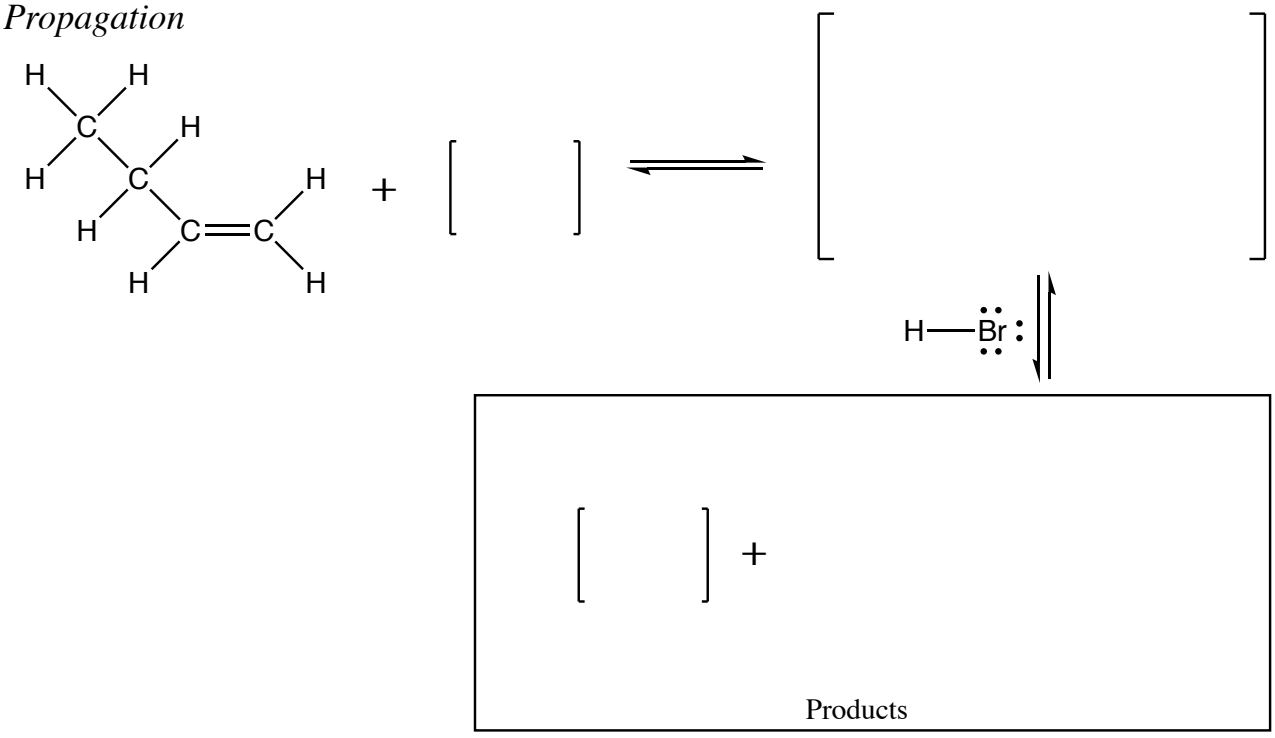
_____

12. (38 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 use wedges and dashes 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.**

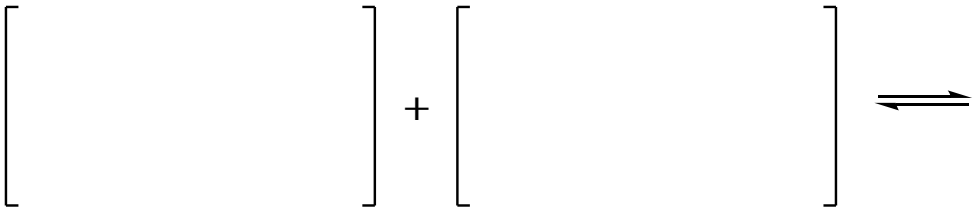
Initiation



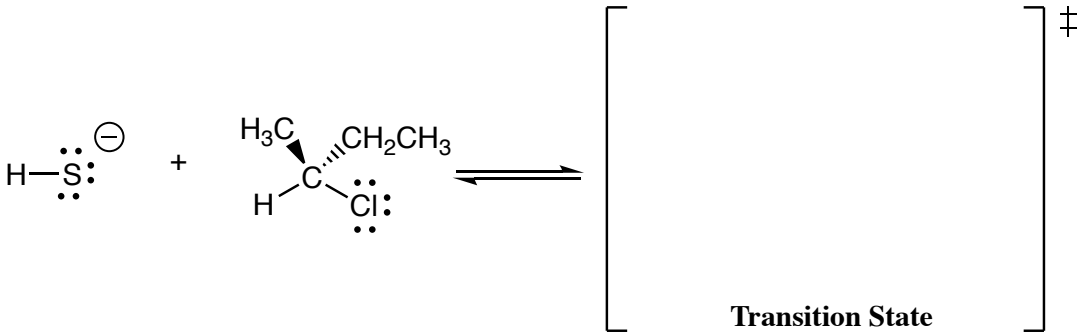
Propagation



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



13. (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.**



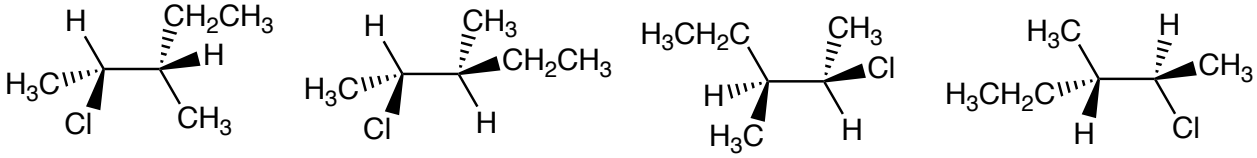
Transition State

Is the starting material R or S? _____

Is the product R or S? _____

Products

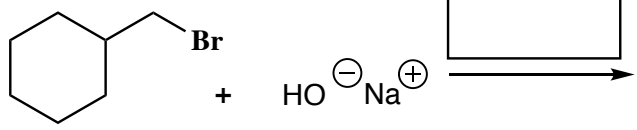
14. (8 pts) Drawn below are four conformations of the molecule (2*R*,*3S*)-2-chloro-3-methylpentane. Circle any of the conformations that, **as drawn**, would be able to react through an E2 mechanism with a strong base.



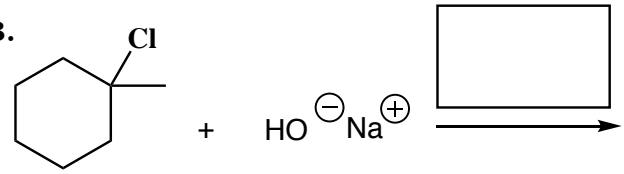
In the box, draw the product of the E2 reaction of (2*R*,*3S*)-2-chloro-3-methylpentane with strong base.

15. (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).

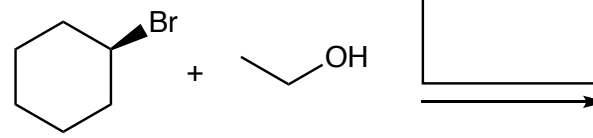
A.



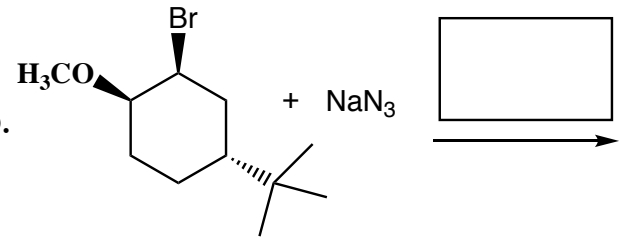
B.



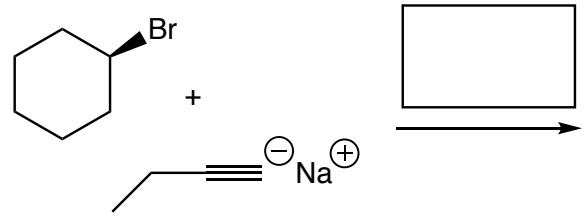
C.



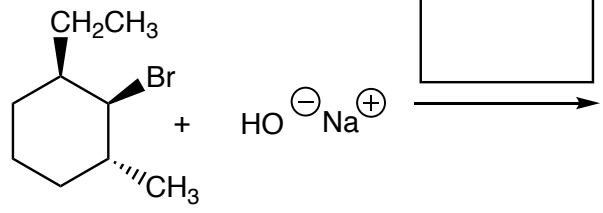
D.



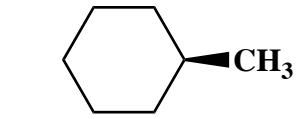
E.



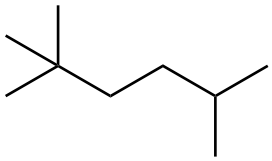
F.



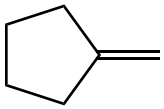
16. (3 or 5 pts each) Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov, etc.)** and please remember that **you must draw the structures of all the product stereoisomers 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**.



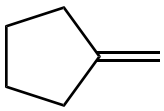
Br_2 / hν →



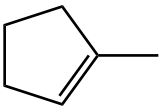
Br_2 / hν →



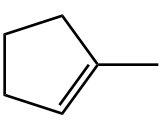
HBr / ROOR / hν →



HBr →

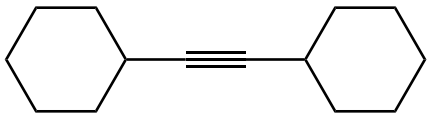


Br_2 →

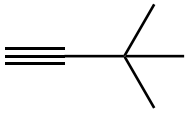


1) OsO_4 / 2) $NaHSO_3$ / H_2O →

16. (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, 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**.

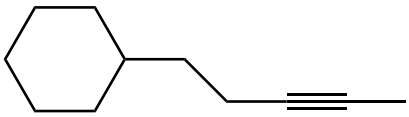


$HgSO_4$, H_2SO_4, H_2O

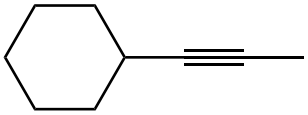


1) $(sia)_2BH$

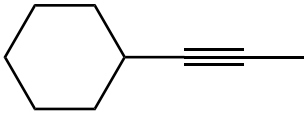
2) H_2O_2 / $HO^{\ominus}$



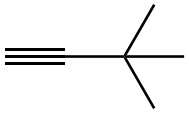
2 Na°, NH_3



2 Br_2



H_2, Lindlar's catalyt

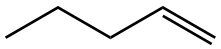


1) $NaNH_2$

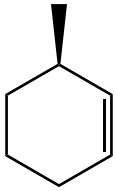
2) CH_3CH_2Br

16. (3 or 5 pts each) The following two reactions involve allylic halogenation. 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**.

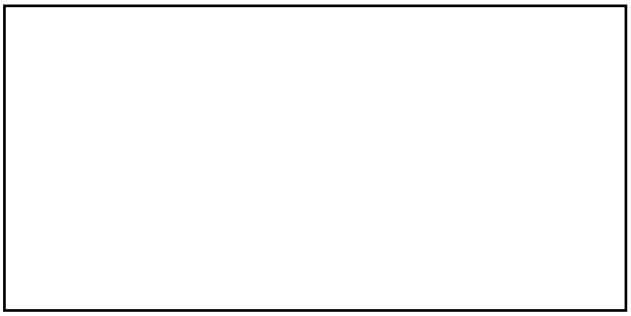
I am giving you some extra room to work through these



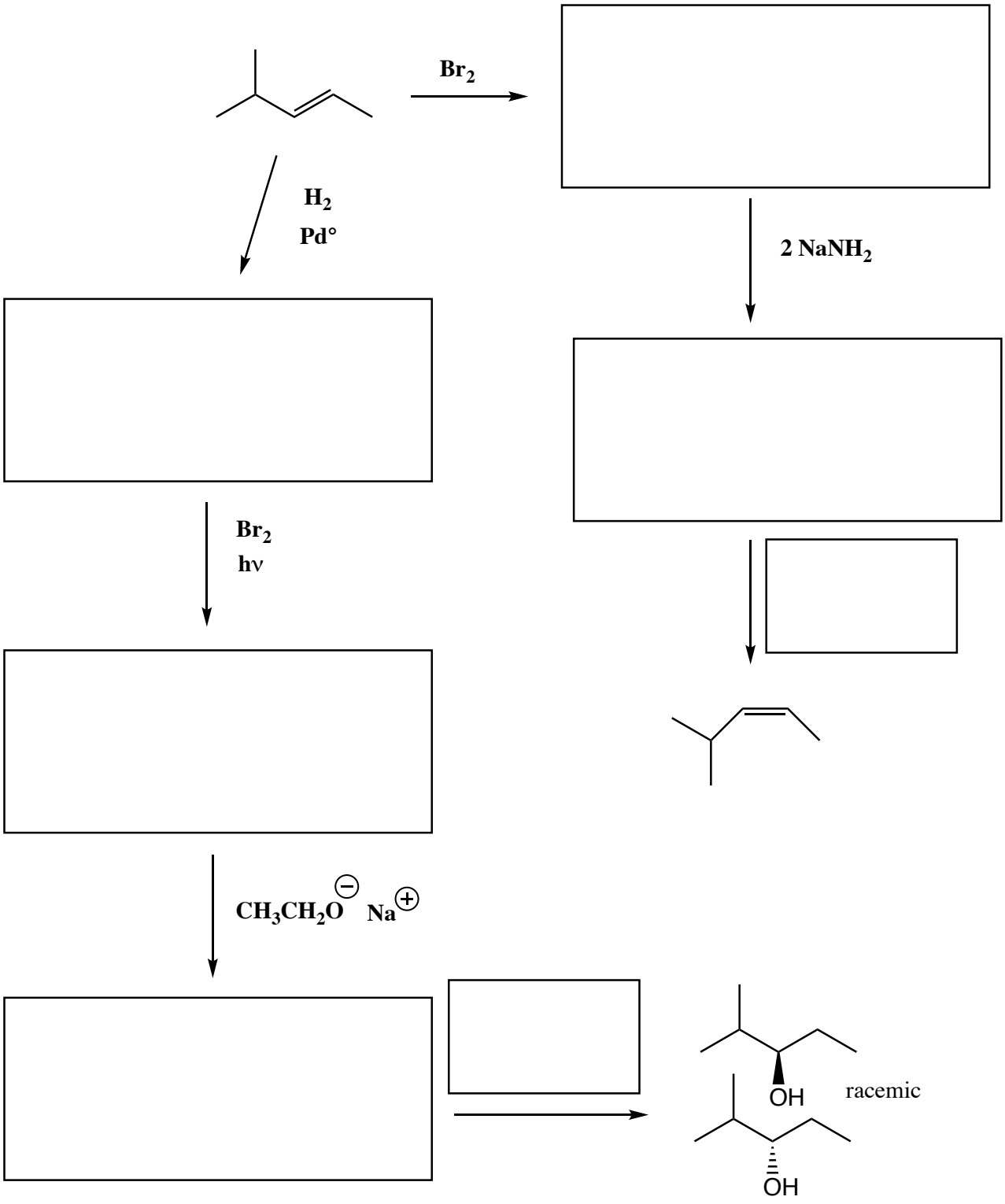
NBS
heat



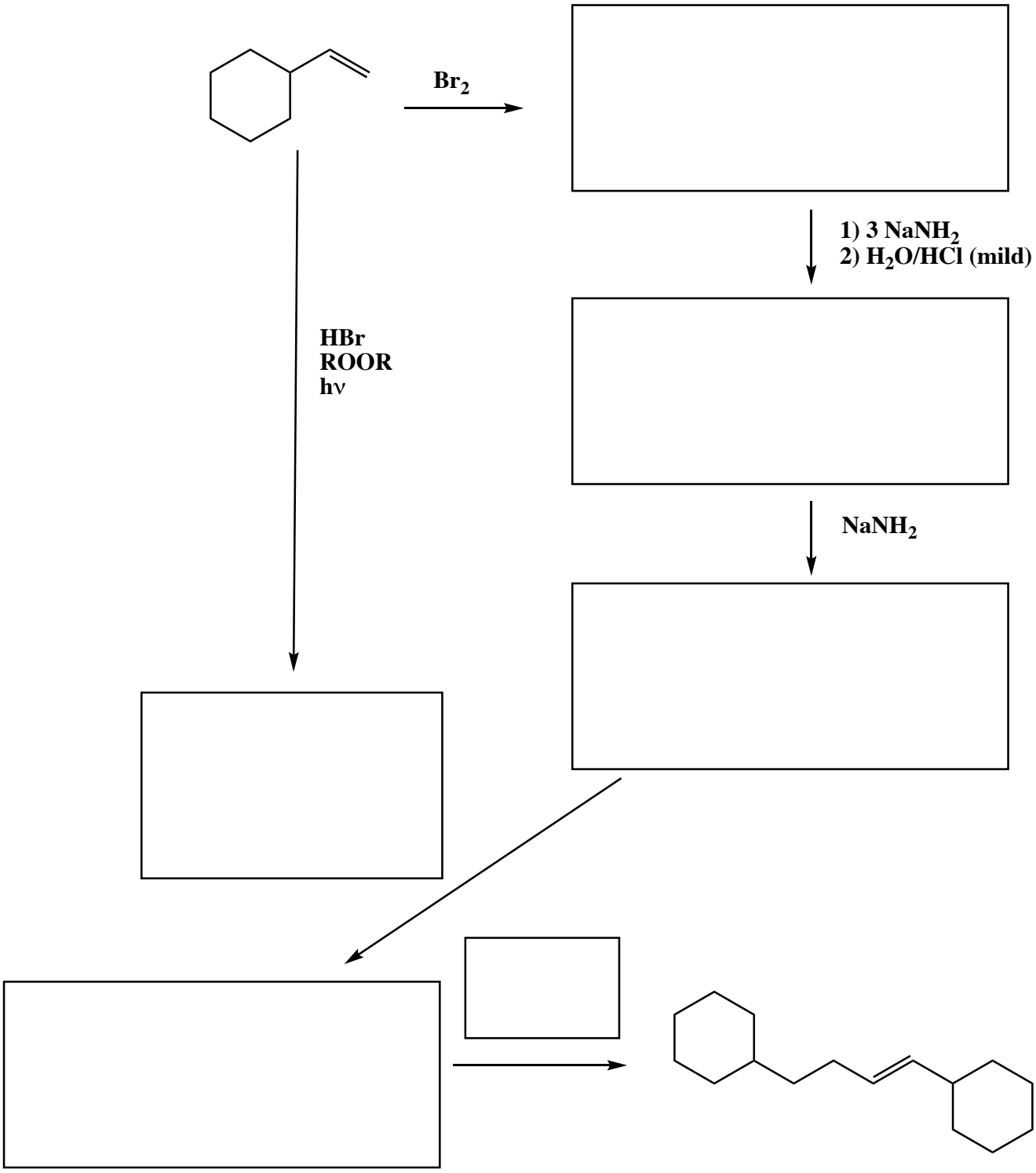
NBS
heat



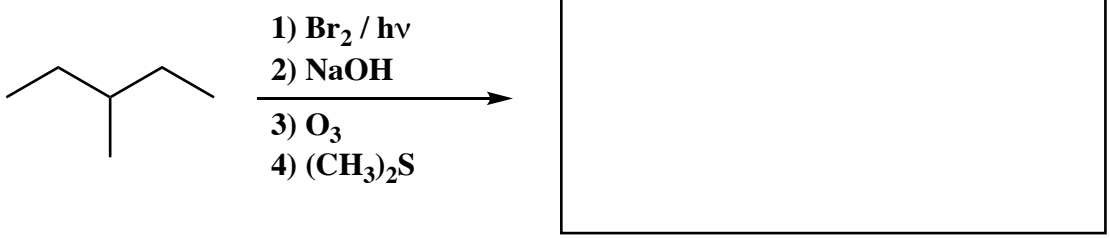
17. (3 or 5 pts each) For the following reactions, fill in the box with the predominant **product(s)** or **reagent(s)** necessary to complete the following syntheses. **You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers** produced as predominant products and **write "racemic"** under the structures when appropriate.



18. (3 or 5 pts each) 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.



19. (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".



20. (6 pts) Fill in the missing reagents, next to the 3) and 4) in the box, required to make the 2-butyne product. You can use the space to work things out, but we will only grade the reagents shown in the box.