

NAME (Print): _____

Chemistry 320M/328M
Dr. Brent Iverson
2nd Midterm
October 26, 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	(23)
2	(30)
3	(28)
4	(18)
5	(12)
6	(24)
7	(22)
8	(30)
9	(-)
10	(21)
11	(21)
12	(15)
13	(16)
14	(13)
Total	(273)

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

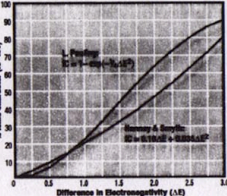
V Elementary Subatomic Particles

	Electron	Proton	Neutron	Positron	Neutrino
Symbol	e	p	n	p ⁺	ν
Rest mass (kg)	9.1093897(54) × 10 ⁻³¹	1.6726231(10) × 10 ⁻²⁷	1.6749286(10) × 10 ⁻²⁷	0	0
Rest mass (eV/c ²)	0.5109989461(12)	938.272088(4)	939.56542(12)	0	0
Relative charge (e)	-1	+1	0	+1	0
Spin quantum number	1/2	1/2	1/2	1/2	1/2
Compton wavelength (m)	2.42631024(22) × 10 ⁻¹²	1.3214002(12) × 10 ⁻¹⁵	1.31959110(12) × 10 ⁻¹⁵	—	—
Magnetic moment (N/A)	9.2847637(5) × 10 ⁻²⁴	1.4106076(47) × 10 ⁻²⁶	0.966237(7)(10) × 10 ⁻²⁶	0	0
In Bohr magneton (μ _B)	1.836152673(49) × 10 ⁻⁴	1.836152673(49) × 10 ⁻⁴	0.5282287(14) × 10 ⁻⁴	0	0
In nuclear magneton (μ _N)	1.836152673(49) × 10 ⁻⁴	1.836152673(49) × 10 ⁻⁴	0.5282287(14) × 10 ⁻⁴	0	0

Summary particles are the fundamental constituents of energy and matter. The electron (e⁻) is a negatively charged particle which has the same mass as an antiparticle, the positron (e⁺). The neutrino (ν) has a rest mass that is less than 1 eV/c² and is electrically neutral. The proton (p) and neutron (n) are baryons, which are made up of three quarks. The proton (p) is made up of two up quarks and one down quark, while the neutron (n) is made up of one up quark and two down quarks. The positron (e⁺) is the antiparticle of the electron (e⁻). The neutrino (ν) is a fermion, which means it has a half-integer spin. The proton (p) and neutron (n) are baryons, which means they have a baryon number of 1. The positron (e⁺) has a baryon number of 0. The neutrino (ν) has a baryon number of 0.

V % 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
% ionic L. Pauling	0.2	1.0	2.2	3.9	5.6	7.4	9.1	11.0	12.8	14.6	16.4	18.2	20.0	21.8	23.6	25.4	27.2	29.0	30.8	32.6	34.4	36.2	38.0	39.8	41.6	43.4	45.2	47.0	48.8	50.6
% ionic G. Hammett & Smith	1.6	3.3	5.1	7.0	8.9	11.1	13.1	15.1	17.1	19.1	21.1	23.1	25.1	27.1	29.1	31.1	33.1	35.1	37.1	39.1	41.1	43.1	45.1	47.1	49.1	51.1	53.1	55.1	57.1	59.1



Percent ionic character describes the nature of a bond. Each element is placed in a box according to its electronegativity value. The electronegativity values are given in the boxes. The electronegativity values are given in the boxes. The electronegativity values are given in the boxes.

13 IIIA	14 IIIB	15 VA	16 VIA	17 VIIA	18 VIII
Aluminum	Germanium	Antimony	Tellurium	Iodine	Xenon
13.0	2.0	2.5	2.0	2.5	2.0

1 IA	2 IIA	3 IIIA	4 IIIB	5 VA	6 VIA	7 VIIA	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB
Hydrogen	Lithium	Sodium	Potassium	Rubidium	Cesium	Francium					
1.0	0.8	0.9	0.8	0.7	0.7	0.7					

19 IIB	20 IIB	21 IIB	22 IIB	23 IIB	24 IIB	25 IIB	26 IIB	27 IIB	28 IIB	29 IIB	30 IIB	31 IIB	32 IIB	33 IIB	34 IIB	35 IIB	36 IIB
Copper	Zinc	Nickel	Cobalt	Nickel	Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine	Krypton					
1.9	1.9	1.8	1.8	1.8	1.9	1.9	1.9	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0

7 VIIA	8 VIIIB
Manganese	
1.5	

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Cerium	Praseodymium	Neodymium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium		
1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	

Compound		pK _a
Hydrochloric acid	H-Cl	-7
Protonated alcohol	$\text{RCH}_2\text{OH}_2^+$	-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	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CR}'$	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	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	16
Aldehydes	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	18-20
Ketones	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	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	$\text{H}-\text{N}(\text{i-C}_3\text{H}_7)_2$	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

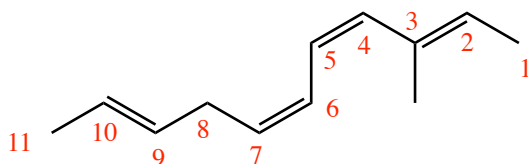
Signature _____

Pg 1 _____(23)

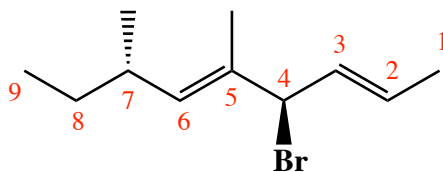
1. (5 pts) What is the most important question in organic chemistry?

Where are the electrons?

2. (12 pts) Write an acceptable IUPAC name for the following two molecules. Where appropriate, use E and Z or R and S.



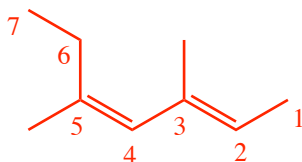
(2E,4Z,6Z,9E)-3-methyl-2,4,6,9-undecatetraene



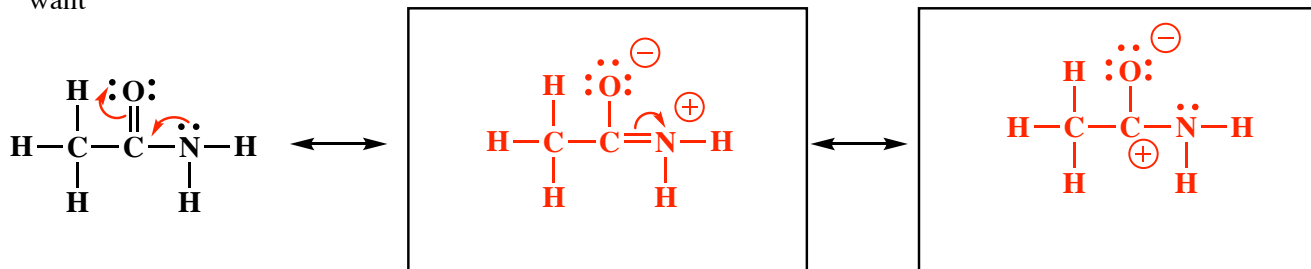
(2E,4R,5E,7S)-4-bromo-5,7-dimethyl-2,5-nonadiene

3. (6 pts) Draw the structure that corresponds to the following name:

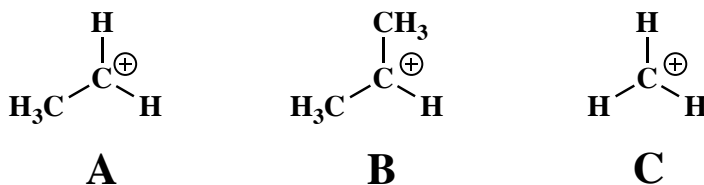
(2E,4Z)-3,5-dimethyl-2,4-heptadiene



4. (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



5. (2 pts each) Consider the three structures below, then fill in each space with the letter, word or number that best completes each of the following sentences.

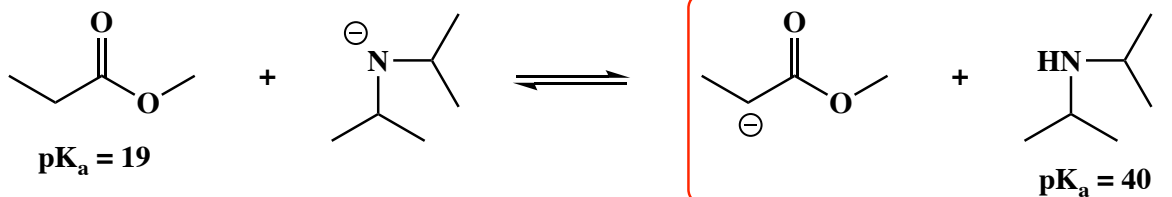
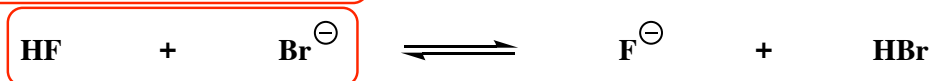
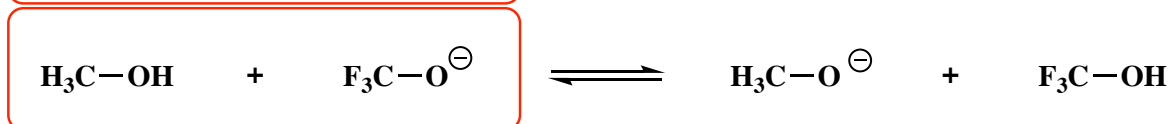
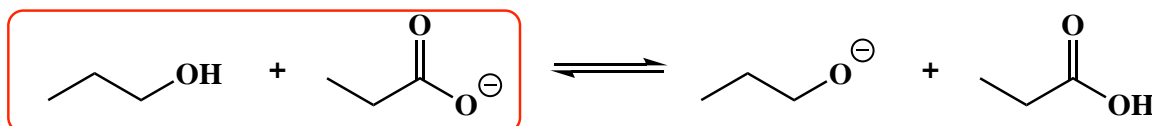


The letter that corresponds to the most stable of the three carbocations shown above is B .

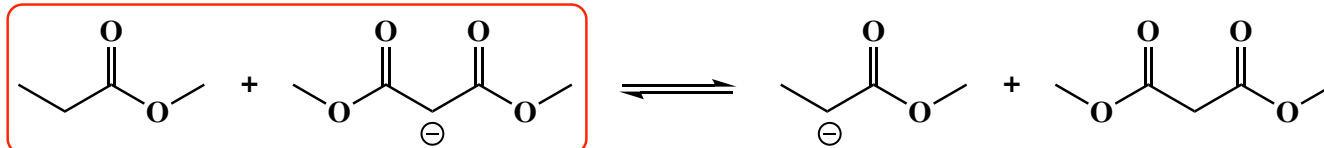
The most stable carbocation is the one that is lowest (lowest or highest) in energy. The hybridization state of the positively-charged carbon atom in the most stable carbocation is sp^2 . For the most stable carbocation, there are 6 (a number) total C-H sigma bonds that overlap with the empty 2p orbital of the positively-charged C atom, providing stabilization via an interaction called hyperconjugation .

The most stable carbocation is stabilized by a second effect called the inductive effect. For this second interaction on the most stable carbocation, electron density is drawn to the positively-charged carbon atom from 2 (a number) other carbon atom(s). This happens because of the fact that the positively-charged carbon atom is more (more or less) electronegative than a carbon atom with no full positive charge. The most stable carbocation above is referred to as a secondary (methyl, primary, secondary or tertiary) carbocation.

6. (10 pts) For each acid-base reaction, circle the side of the equation that predominates at equilibrium. In each case identify the stronger and weaker acids by comparing relative stabilities of the anions which are the conjugate bases of the two acids. Equilibrium favors formation of the weaker acid. You will notice this means you circled the side with the more stable anion.



Think about this last one!



7. (2 or 4 pts each) For the following, circle the capitalized word that best completes the statement.

In general, it is best to think of alkenes as **NUCLEOPHILES** or **ELECTROPHILES** that react with **NUCLEOPHILES** or **ELECTROPHILES** such as Br_2 .

In general, **NUCLEOPHILES** or **ELECTROPHILES** serve as electron sources and **NUCLEOPHILES** or **ELECTROPHILES** serve as electron sinks for the arrows used to indicate bond-making steps in reactions.

A pi bond or lone pair will serve as an **ELECTRON SOURCE** or **ELECTRON SINK** for an arrow that indicates the making of a new bond.

An atom that can accommodate a new bond can serve as an **ELECTRON SOURCE** or **ELECTRON SINK** for an arrow that indicates the making of a new bond.

A reaction that occurs slower generally has a **LOWER** or **HIGHER** activation energy.

A reaction that has a strong thermodynamic driving force (a strong motive) is **FAVORABLE** or **UNFAVORABLE** as written.

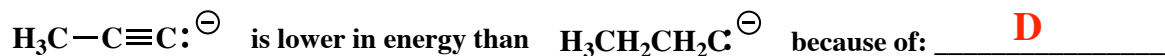
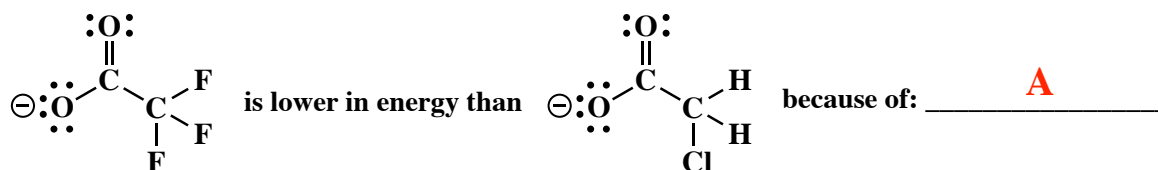
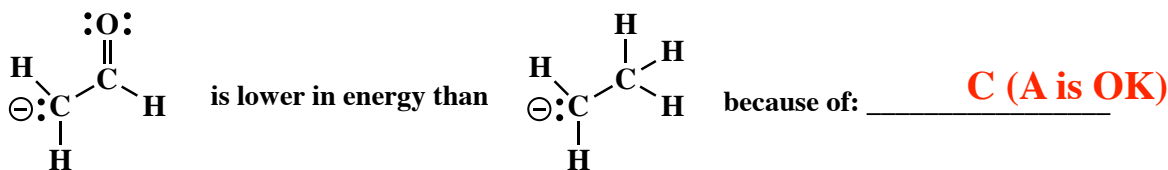
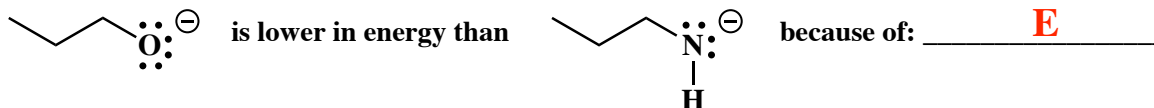
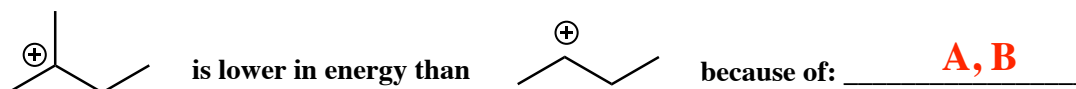
A reaction will have a strong motive (thermodynamic driving force) if the bonds made are **STRONGER** or **WEAKER** than the bonds that are broken.

8. (2 pts each) Write the mechanistic element (of the four) that is appropriate when you see the following species in a mechanism:

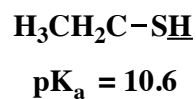
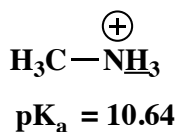
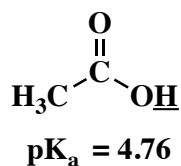
A nucleophile and an electrophile are present	Make a bond between a nucleophile and an electrophile
The carbon containing species is a weak base and there is a strong acid present	Add a proton
The carbon containing species is a strong acid and a base is present	Take a proton away
The carbon containing species can fragment to make water and a tertiary carbocation	Break a bond to give stable molecules or ions

9. (2 pts each no partial credit) The following statements are true. Choose from among the following five possibilities and in the space provided, write the letter of the one *or more* phenomena that best explain the true statement.

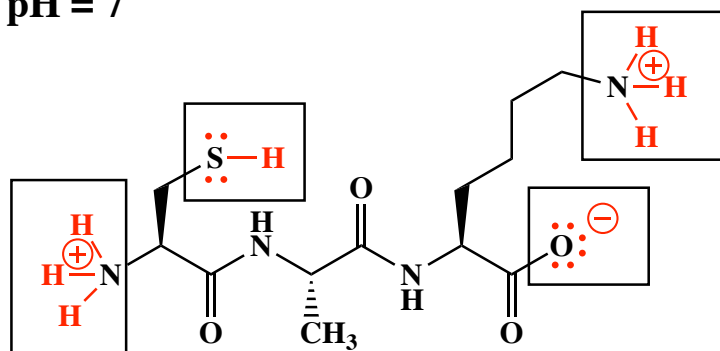
- A. The inductive effect B. Hyperconjugation C. Resonance delocalization of a charged species
 D. Greater s character of the orbital containing an electron pair on a negatively-charged atom E. The negative charge is on a more electronegative element



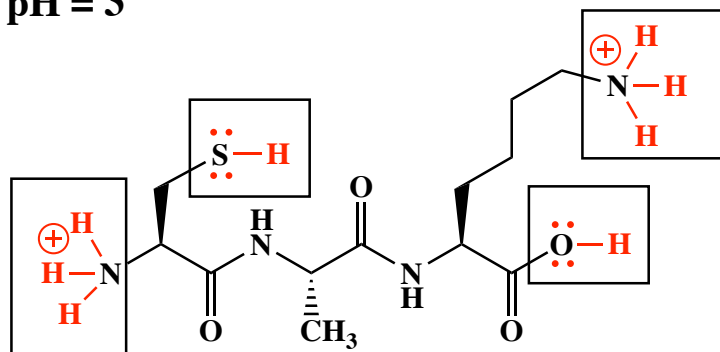
10. (12 pts) Complete the following two structures by adding appropriate numbers of lone pair electrons, H atoms, and formal charges to the atoms in the boxes. You must adjust your answers to indicate the predominant species at each indicated pH value. (You do not have to add anything such as H atoms to atoms not drawn in the boxes.) This problem is testing your understanding of the relationship of protonation state to pH to pKa values for certain functional groups we have discussed. Next, in the space provided, write the overall charge on each structure at the indicated pH. For your reference, here are the relevant pK_a values:



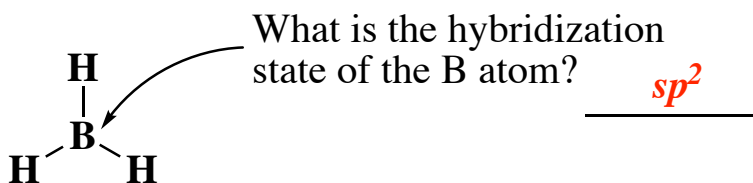
pH = 7

Total charge on molecule: +1

pH = 3

Total charge on molecule: +2

11. (2 pts each) **Complete** the following set of questions related to derivatives of boron.



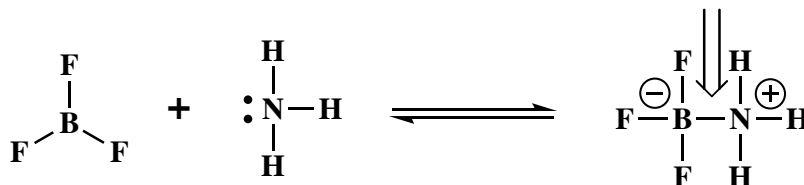
The BH₃ molecule has 6 valence electrons around the B atom.

The BH₃ molecule is best considered a Lewis acid.

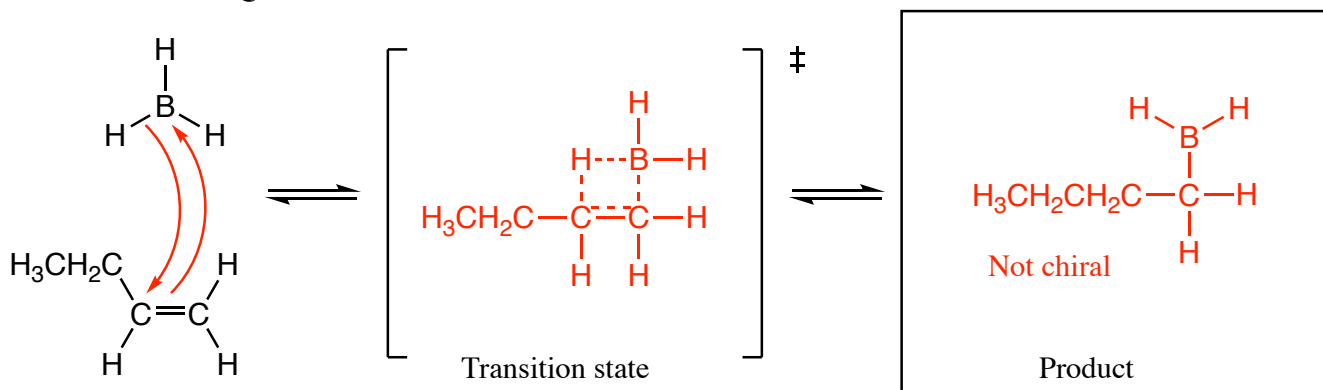
In the BH₃ molecule, there is an empty 2p orbital on the B atom.

Related molecules such as BF₃ react with ammonia to create a special type of bond known as a coordinate covalent or dative bond that is

illustrated in the following equation and indicated by the arrow:



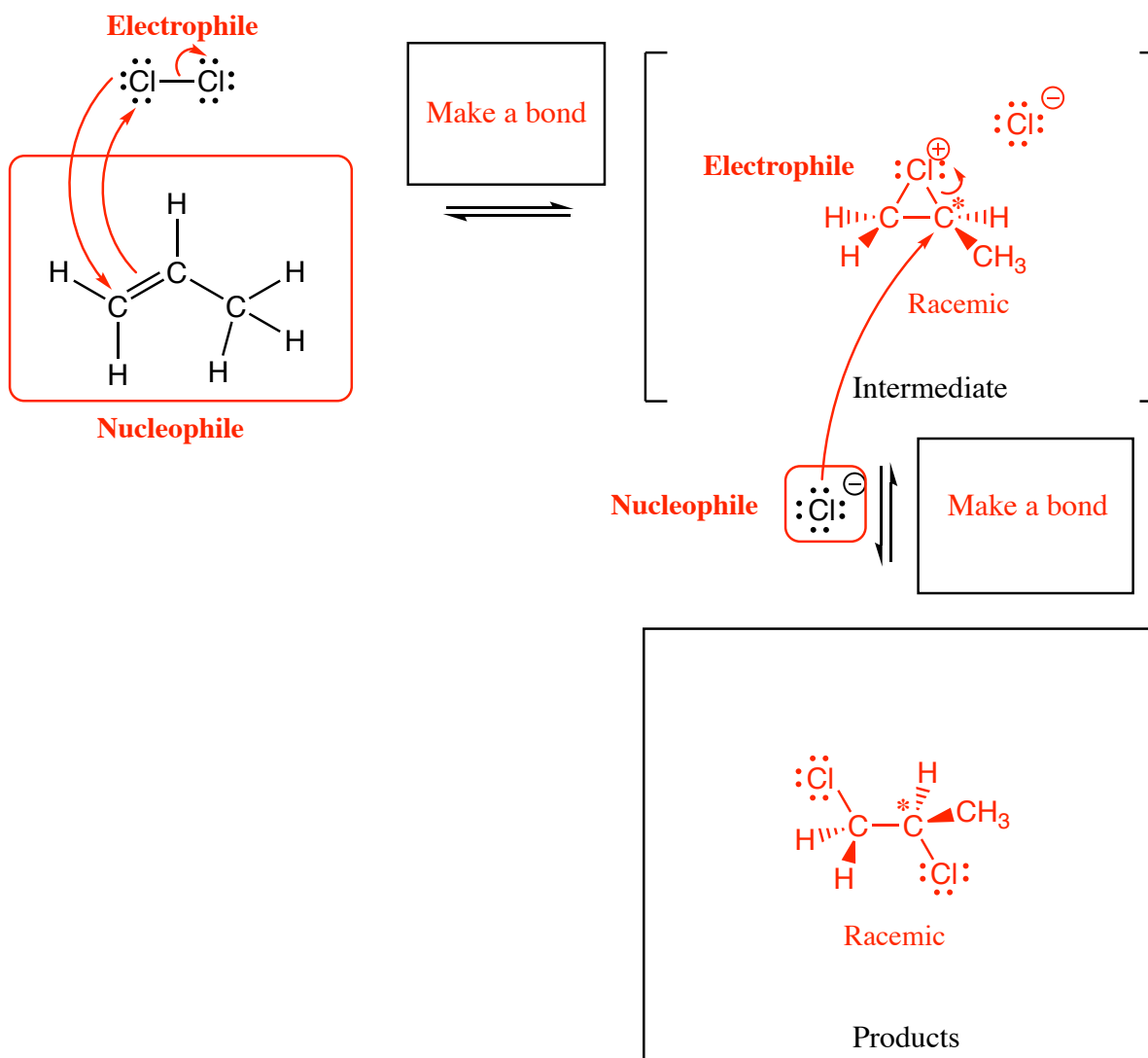
12. (10 pts) Complete the following mechanism for the first step of the hydroboration reaction. Use arrows to indicate the movement of all electrons and be sure to show all electron pairs and formal charges. For this one, we are asking you to draw a transition state. Used dotted lines to indicated any bonds that are being made or broken in the transition state. Indicate any chiral centers with an asterisk (*) and write ‘racemic’ if appropriate. You only need to draw one stereoisomer of any chiral species. **Note that you should only draw arrows on the structure to the left, not the transition state.** **NOTICE THE QUESTION AT THE END.**



(4 pts) Look at the energy diagrams on page 9. Write the letter of the one that best describes the mechanism of this reaction.

A

13. (12 pts) Complete the mechanism for the following alkene halogenation reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **YOU ONLY NEED TO DRAW ONE STEREOISOMER OF A CHIRAL INTERMEDIATE OR PRODUCT (using wedges and dashes as appropriate) IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE.** In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.). Be sure to notice the questions at the end.

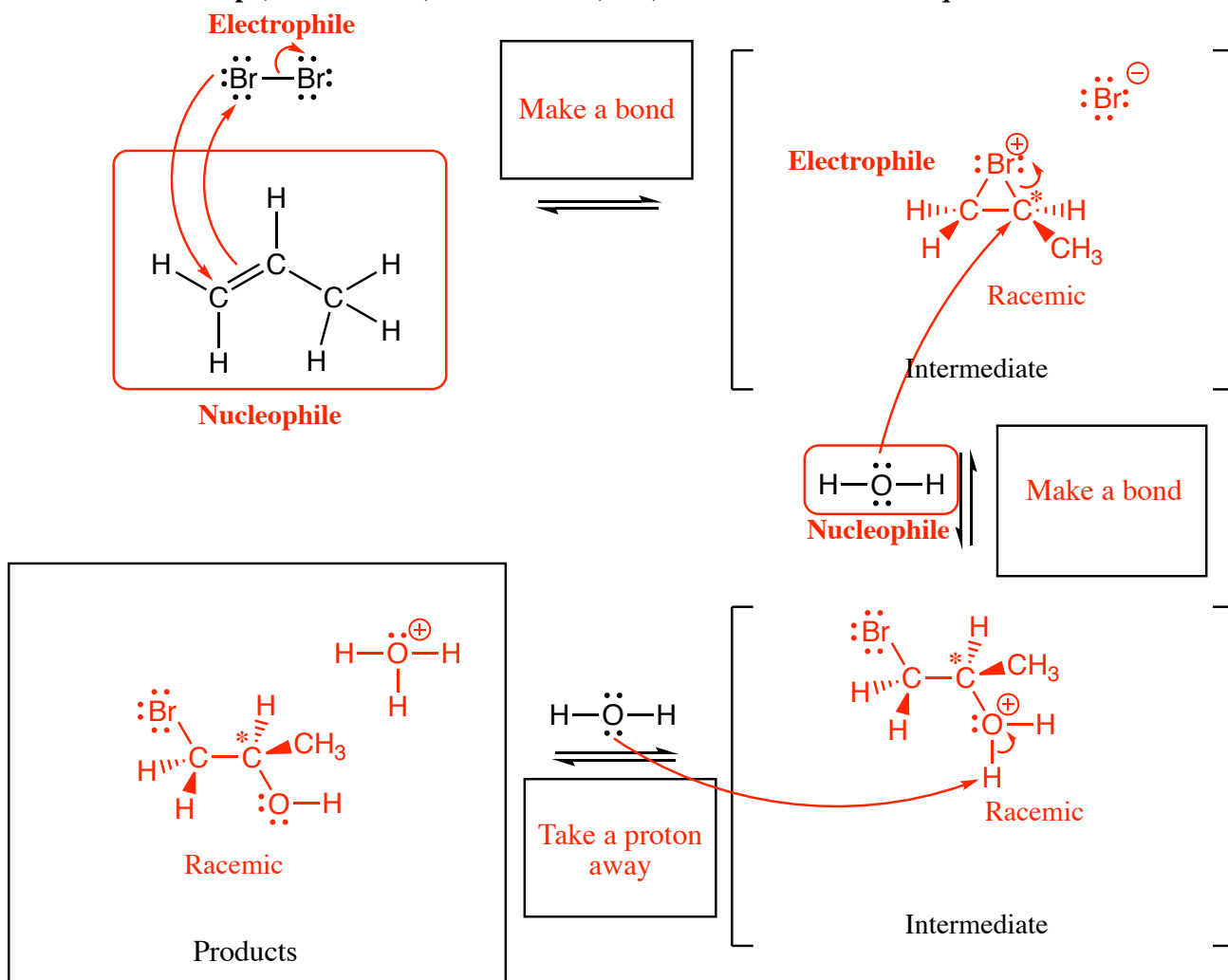


(4 pts) **For any step** in the mechanism on this page that involves a nucleophile reacting with an electrophile to make a bond, **draw a circle around the nucleophile**

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

(4 pts) Look at the energy diagrams on page 9. Write the letter of the one that best describes this reaction. B

14. (19 pts) Complete the mechanism for the following alkene hydrohalogenation reaction. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **YOU ONLY NEED TO DRAW ONE STEREOISOMER OF A CHIRAL INTERMEDIATE OR PRODUCT (using wedges and dashes as appropriate) IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE.** In the boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.). Be sure to notice the questions at the end.



(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**

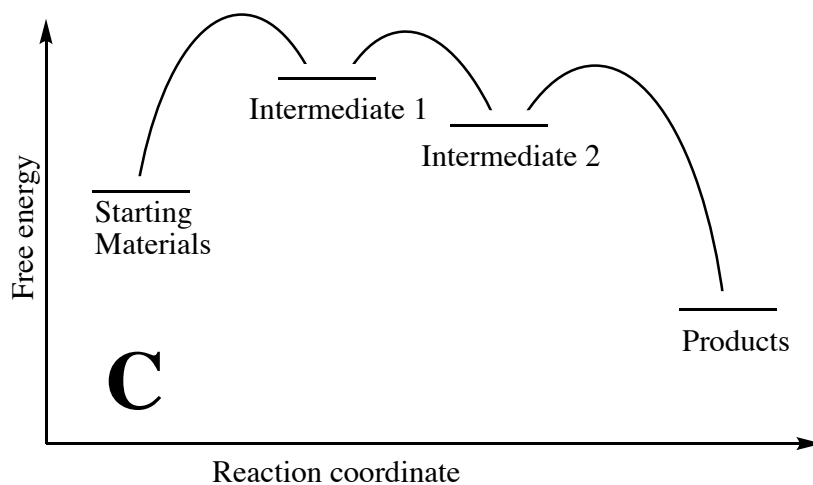
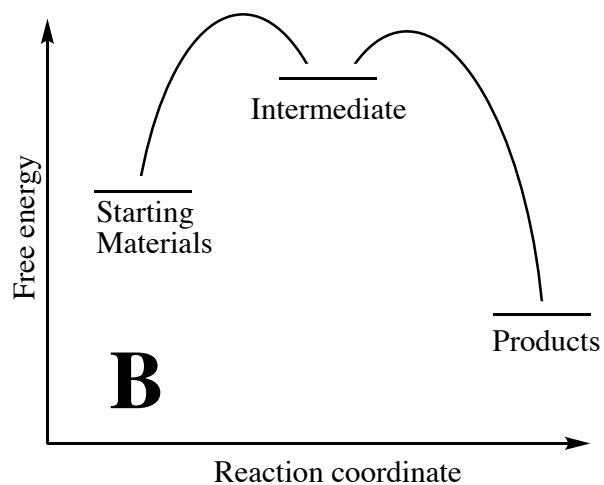
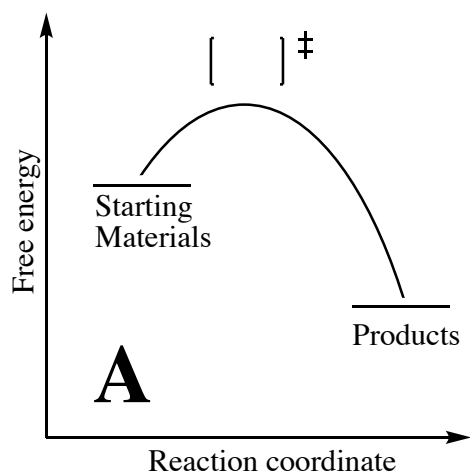
(2 pts) **How many total stereoisomers** are created as the final **products**? 2

(4 pts) **Look as the energy diagrams on page 9. Write the letter of the one that best describes this reaction.** C

(2 pts) Think about this! As the reaction progresses, does the pH get **higher, lower, or stay the same?**

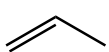
it gets lower (acid is created)

These energy diagrams refer to the mechanisms you completed in problems 12-14 on pages 6-8.



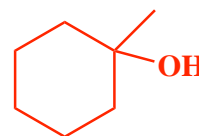
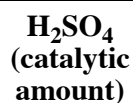
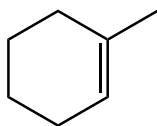
15. (3 or 5 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products)** and please remember that **you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry as appropriate**. When a racemic mixture is formed, **you must write "racemic"** under both structures **EVEN THOUGH YOU DREW BOTH STRUCTURES**.

A.

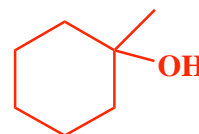
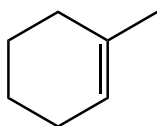


Racemic

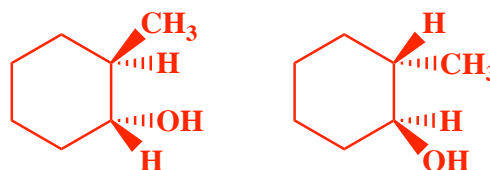
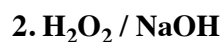
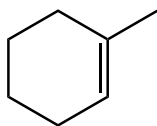
B.



C.

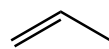


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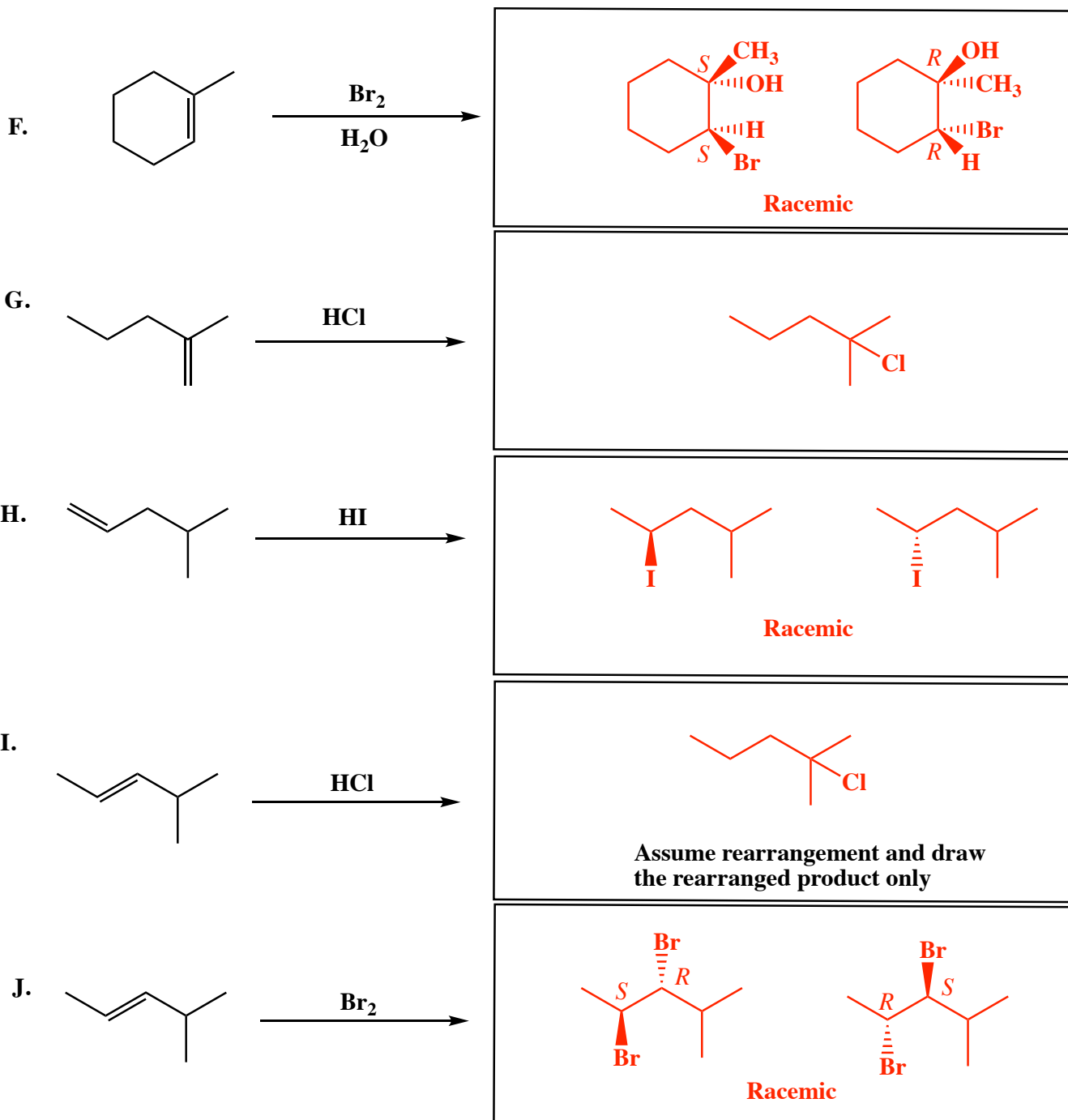
Racemic

E.



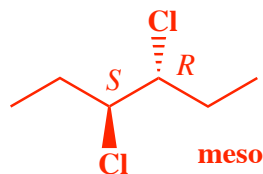
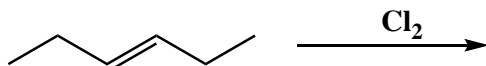
Racemic

15. (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 appropriate**. When a racemic mixture is formed, you must write "racemic" under both structures **EVEN THOUGH YOU DREW BOTH STRUCTURES**.

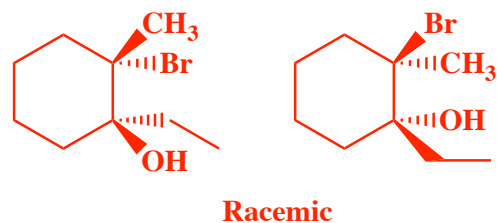
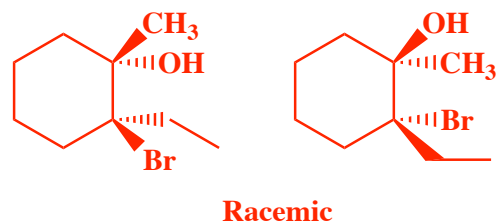
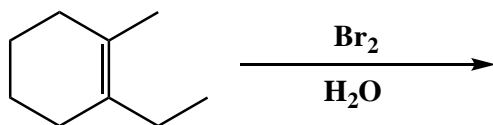


15. (5 or 10 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products)** and please remember that **you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry as appropriate**. When a racemic mixture is formed, **you must write "racemic"** under both structures **EVEN THOUGH YOU DREW BOTH STRUCTURES**.

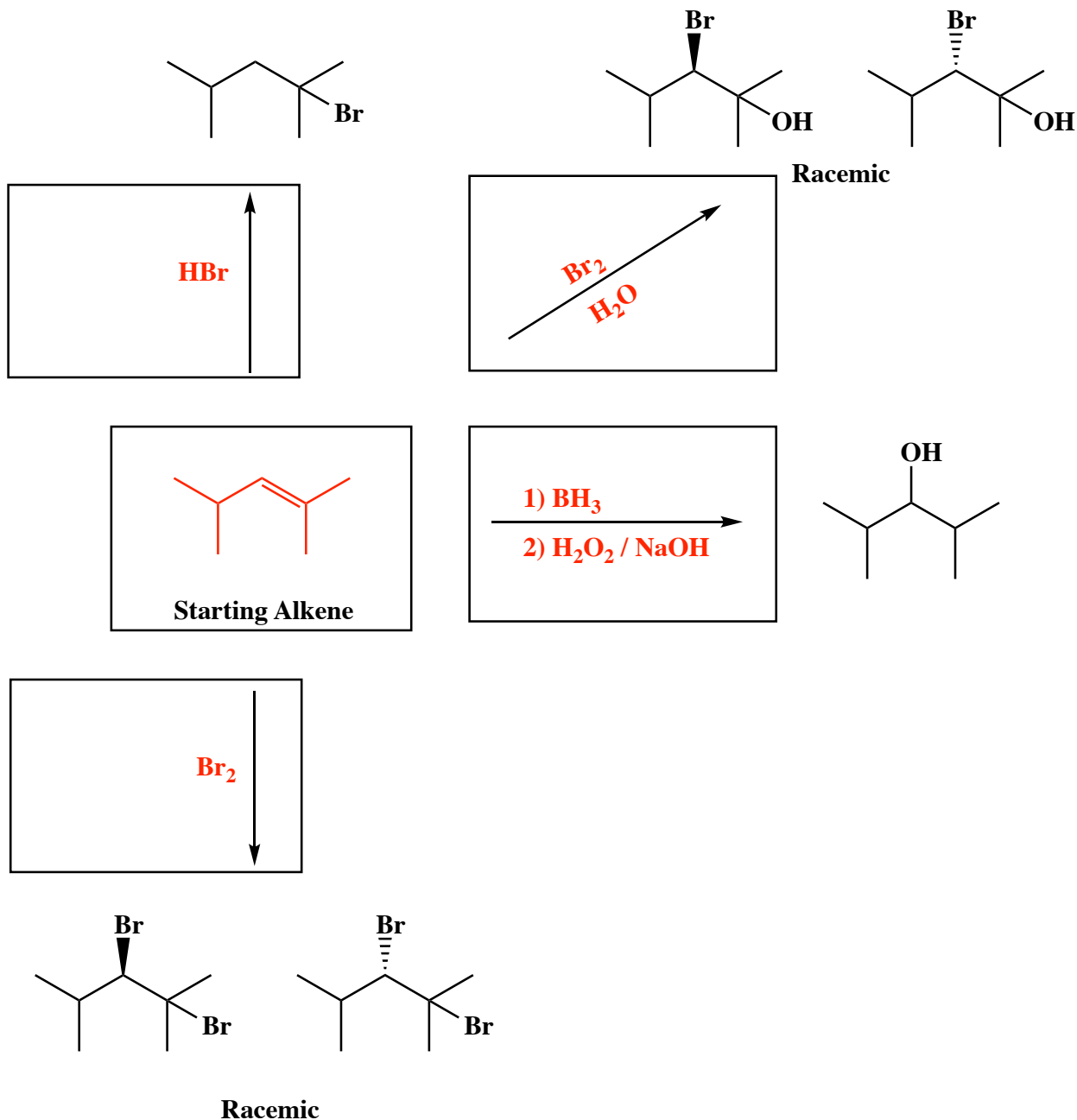
K.



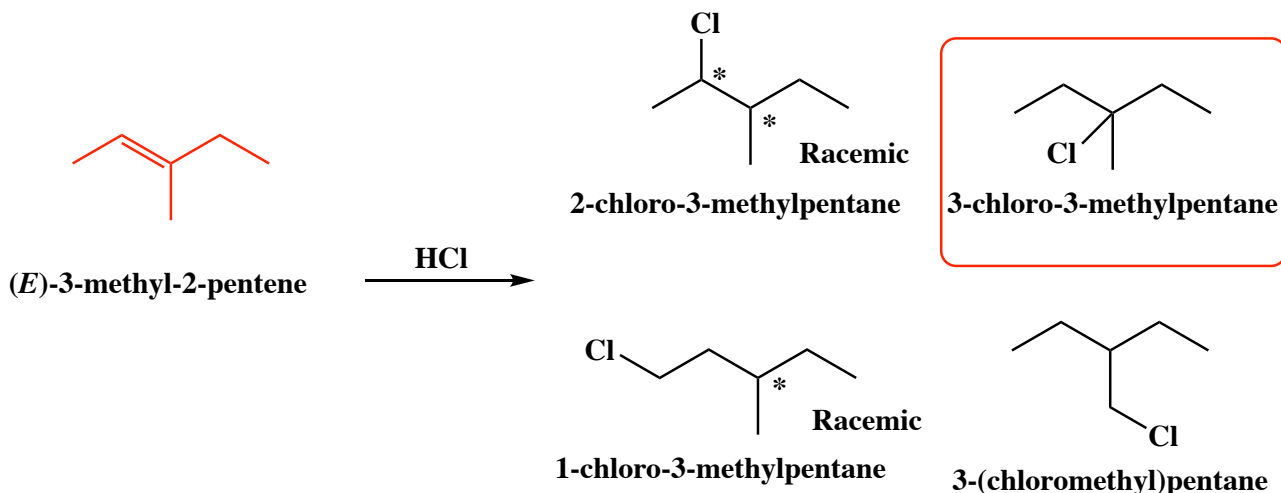
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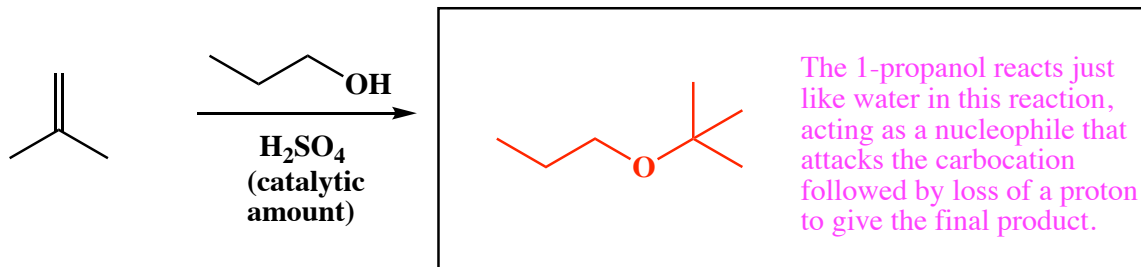
16. (16 pts total) Organic chemistry is a very creative science because there are so many different reactions known that often we are only limited by our imaginations. For example, the same starting alkene can be converted to the different products listed. **Deduce the identity of the starting alkene, and write its structure in the box labeled "Starting Alkene".** Fill in the boxes containing arrows with the reagents required to produce the given products.



17. (5 pts) The MCAT and other standard exams are famous for using IUPAC names instead of structures. From the following list, **circle the product of the following reaction**. To make this simpler, we have not used wedges and dashes, but simply designated chiral centers with an asterisk. (Note you are **NOT** allowed to write products in this format on pages 10-12 of this exam, you must use wedges and dashes on those!)



18. (8 pts total) Here is an “apply what you know” question. The reactions we teach in this class are representative examples of entire classes of reactions. Alkenes react with a variety of reagents that are similar to the ones we have discussed. You have not seen the following two reactions, but use your growing chemical intuition to predict the products for the reactions shown. My only hint is for you to not overthink this, but rely on your understanding of mechanisms to make educated guesses. **The products should be drawn in the same format as for pages 10-12 of this exam.**



Save this one until last! I have given you the products, you need to draw the starting material

