NAME (Print): _____

SIGNATURE: _____

Chemistry 320M/328M
Dr. Brent Iverson
2nd Midterm
October 25, 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!!!

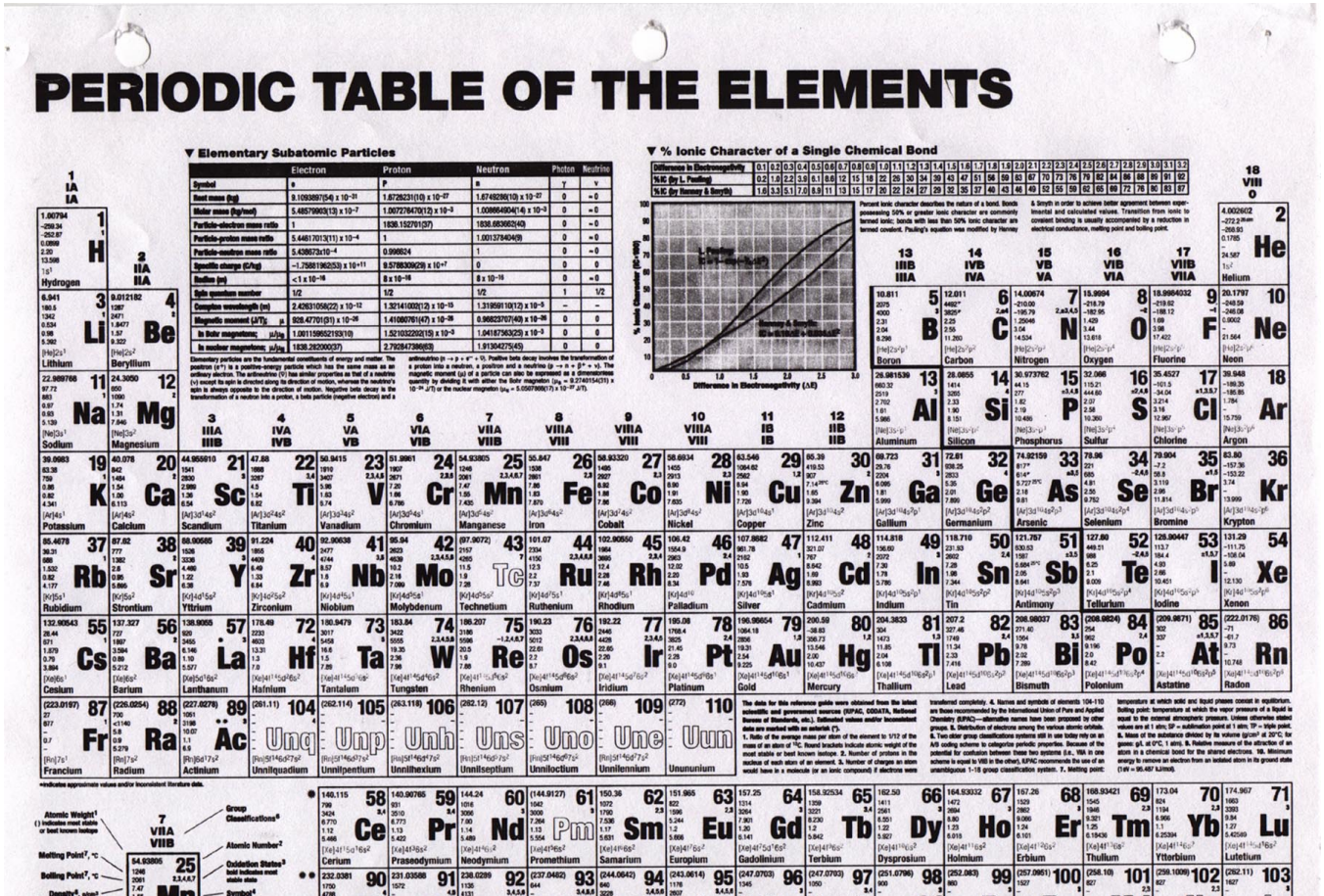
Page	Points	
1		(23)
2		(29)
3		(22)
4		(21)
5		(18)
6		(28)
7		(28)
8		(29)
9		(-)
10		(23)
11		(24)
12		(18)
13		(21)
14		(18)
Total		(302)

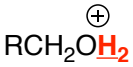
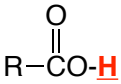
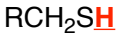
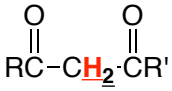
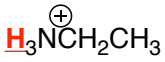
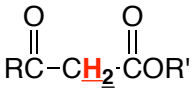
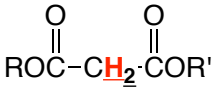
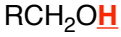
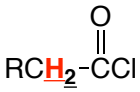
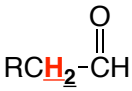
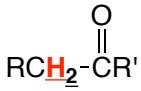
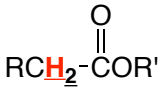
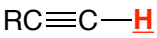
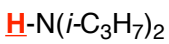
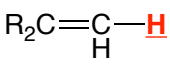
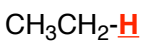
Student Honor Code

“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)



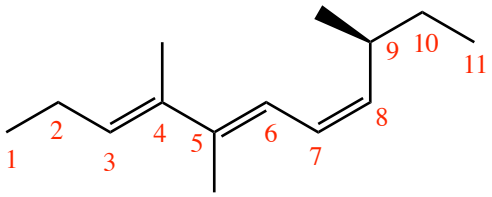
Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Carboxylic acids		3-5
Thiols		8-9
Ammonium ion		9.2
β-Dicarbonyls		10
Primary ammonium		10.5
β-Ketoesters		11
β-Diesters		13
Water		15.7
Alcohols		15-19
Acid chlorides		16
Aldehydes		18-20
Ketones		18-20
Esters		23-25
Terminal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

Signature_____ Pg 1 _____(23)

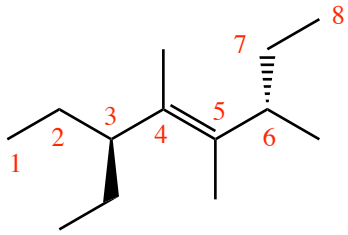
1. (5 pts) What is the most important question in organic chemistry?

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.



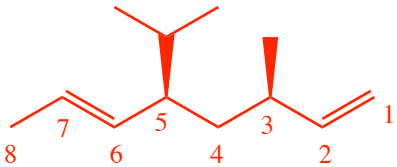
(*S*,3*E*,5*E*,7*Z*)-4,5,9-trimethyl-3,5,7-undecatriene



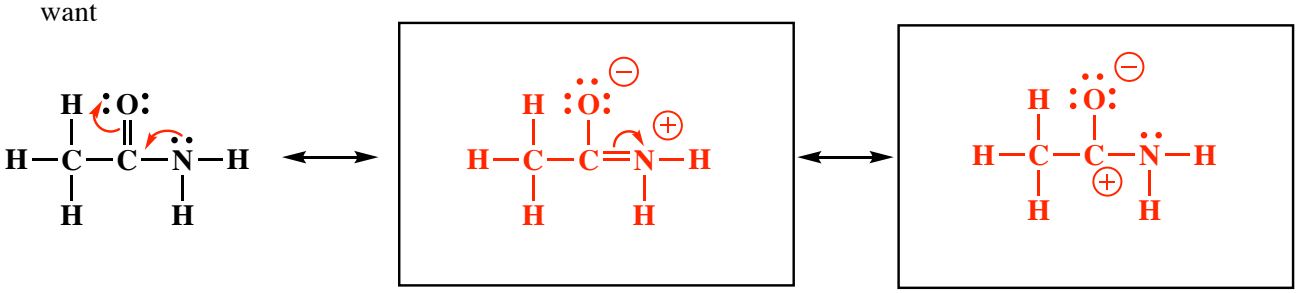
(*S*,*E*)-3-ethyl-4,5,6-trimethyl-4-octene

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

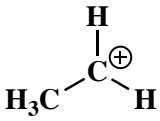
(3*R*,5*R*,*E*)-5-isopropyl-3-methyl-1,6-octadiene



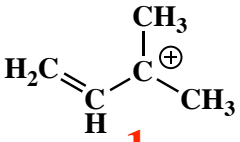
4. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges. For the two structures on the left in each problem, use arrows to indicate the movement of electrons to give the structures you drew. There is no need to draw any circles around any of these contributing strucures. You might want to read these directions again to make sure you know what we want



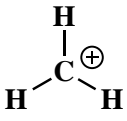
5. (1 pt each answer) Rank the following species with respect to stability. Put a 1 under the most stable, and a 4 under the least stable molecule or ion.



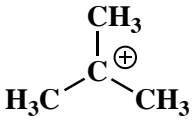
3



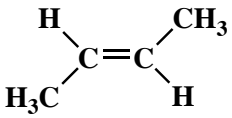
1



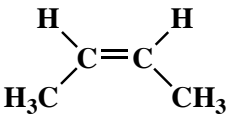
4



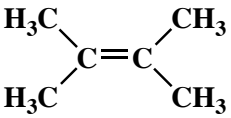
2



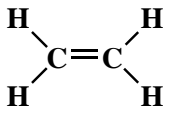
2



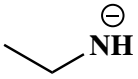
3



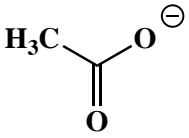
1



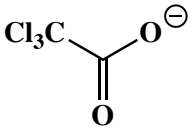
4



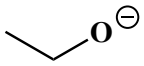
4



2

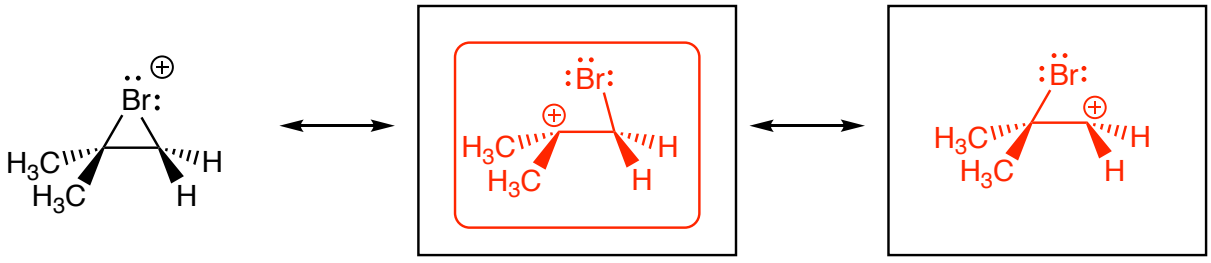


1



3

6. (7 pts) Draw the two other most important contributing structures for the bromonium ion. Draw a circle around the contributing structure you drew that makes the largest constribution to the overall resonance hybrid. You do NOT need to draw arrows on any of the structures for this problem. **Because this is a mechanism type question, use wedges and dashes to indicate stereochemistry, write "racemic" if appropriate, draw all lone pairs and formal charges.**



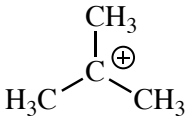
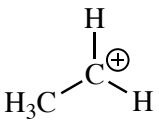
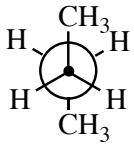
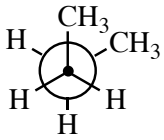
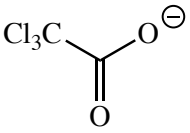
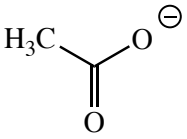
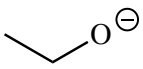
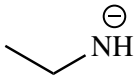
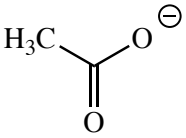
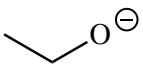
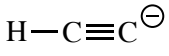
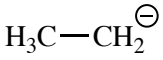
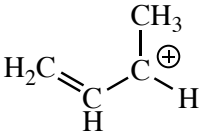
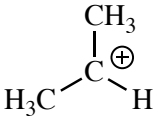
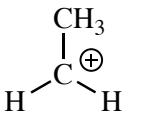
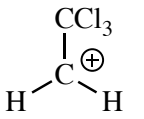
7. (**22 pts**) For each pair of molecules, the one drawn on the left is more stable (lower in energy) because of one or more principles we have discussed. **In the space provided, write the letter corresponding to the principle or principles (yes there can be more than one!) that explain why the molecule on the left is more stable. Note the wording this year is slightly different than last year.**

A. Steric Strain **B.** Angle Strain **C.** Torsional Strain **D.** The inductive effect

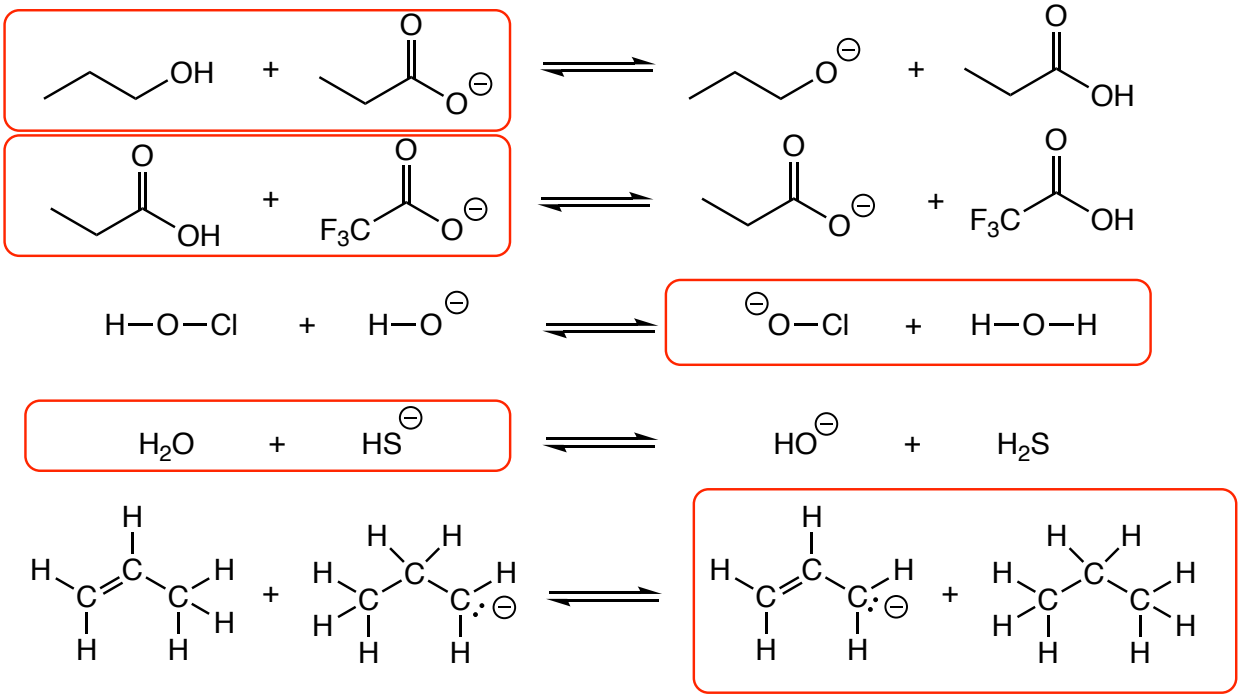
E. Hyperconjugation **F.** Delocalization of a charge **G.** Delocalization of pi electron density over more than two atoms (pi-way)

H. Greater s-character of the orbital containing an electron pair on a negatively-charged atom **I.** The negative charge is on a more electronegative element **J.** The negative charge is on a larger atom

---

More stable molecule	**Less stable molecule**	The molecule on the left is more stable primarily because of:
		**D, E**
		**A**
		**D**
		**I**
		**F, G**
		**H**
		**F, G**
		**D**

8. (**10 pts**) For each acid-base reaction, **circle the side of the equation that predominates at equilibrium.** **In the first four, 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.**



9. (**1 or 2 pts each**) For the following, **circle the capitalized word or molecule** 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 are analogous to Lewis bases and NUCLEOPHILES or ELECTROPHILES are analogous to Lewis acids.

The molecule CH_2=CH_2 or CH_3CH_3 would be a better nucleophile.

The molecule CH_4 or NH_3 would be a better nucleophile.

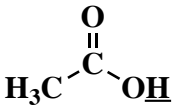
In the second step of the halogenation reaction, the CARBOCATION or the HALIDE ANION is the electrophile and the CARBOCATION or the HALIDE ANION is the nucleophile.

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

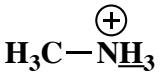
When reaction products are lower in energy than the starting materials, the reaction is FAVORABLE or UNFAVORABLE as written.

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

10. (18 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:**

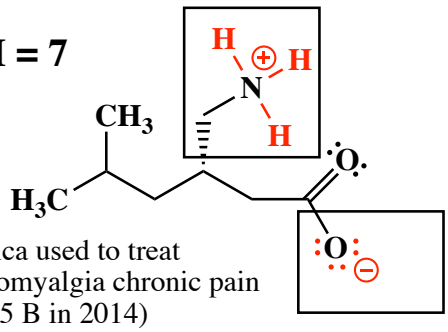


pK_a = 4.76



pK_a = 10.64

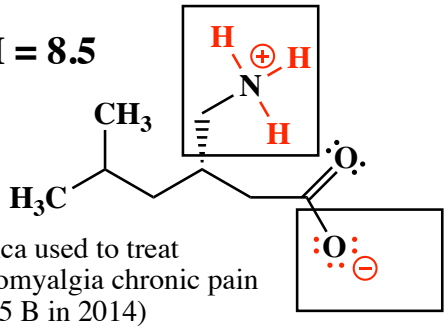
pH = 7



Lyrica used to treat fibromyalgia chronic pain ($4.5 B in 2014)

Total charge on molecule: 0

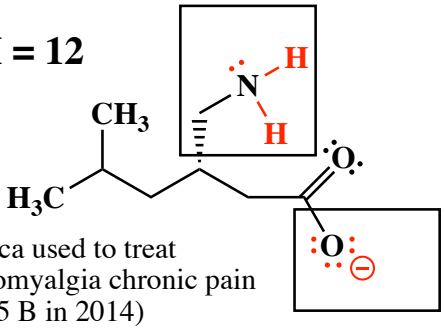
pH = 8.5



Lyrica used to treat fibromyalgia chronic pain ($4.5 B in 2014)

Total charge on molecule: 0

pH = 12



Lyrica used to treat fibromyalgia chronic pain ($4.5 B in 2014)

Total charge on molecule: -1

11. (8 points) Fill in the blanks with the words that best complete the sentences.

It is helpful to think of organic chemistry mechanisms in terms of distinct mechanistic elements. We have learned four of these so far. For example, if in a reaction we are examining you see both a good nucleophile and electrophile present, you know the most likely step is to Make a bond between a nucleophile and an electrophile .

When the carbon containing piece is a strong acid or there is a base present, the most likely step is to Take a proton away .

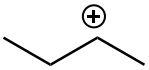
When the carbon containing piece is a base or there is an acid present, the most likely step is to Add a proton .

When none of the above are true and you can see how the carbon containing piece can fragment to create stable molecules or ions, the most likely step is to Break a bond to give stable molecules or ions .

Rarely, in the mechanisms we see, none of these fit, but in those cases we will tell you what to expect.

12. (2 points each) Below are various species we have seen in mechanisms so far. In the context of mechanisms we have seen, in the space provided, tell us whether it is best to consider these as **a nucleophile, an electrophile, a <u>strong</u> base, or a <u>strong</u> acid.** Those are your only four choices for this problem and remember this is in the context of the mechanisms we have seen so far. Write the single best answer of the four next to each species.

Nucleophile

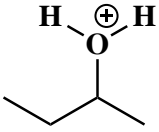


Electrophile

BH_3 Electrophile

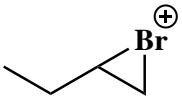
$Br^{\oplus}$ Nucleophile

HBr Strong Acid



Strong Acid

H_2O Nucleophile

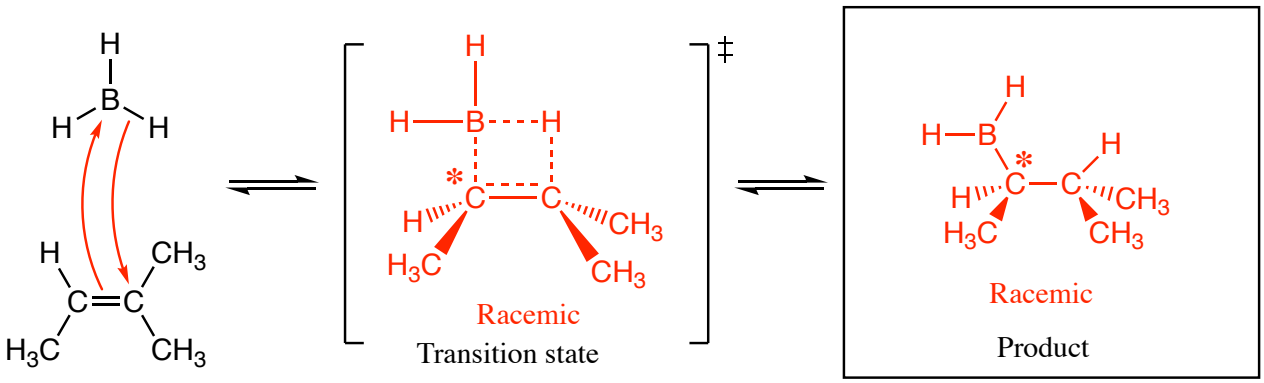


Br_2 Electrophile

$H_3O^{\oplus}$ Strong Acid

Electrophile

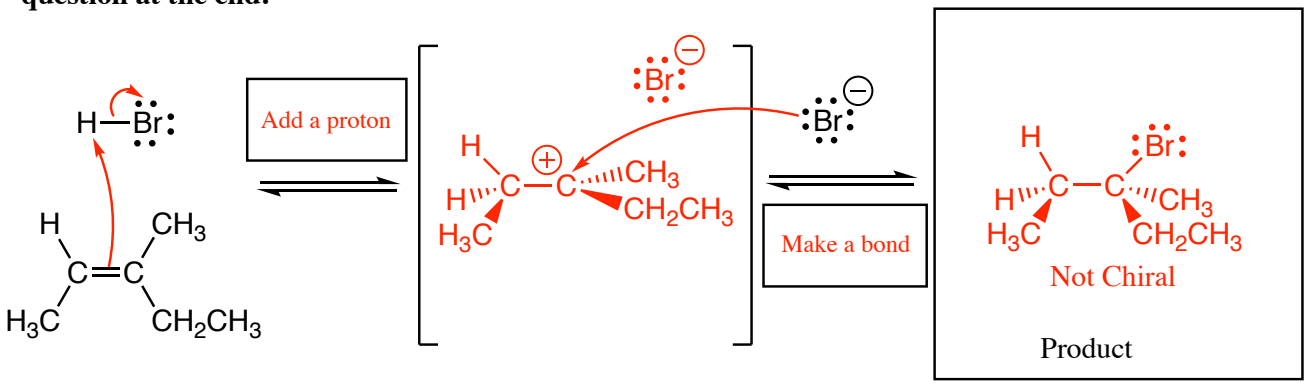
13. (14 pts) Complete the following mechanism for the first step of the hydroboration reaction. Use arrows to indicate the movement of all electrons and be sure to show all electron pairs and formal charges. For this one, we are asking you to draw a transition state. Used dotted lines to indicated any bonds that are being made or broken in the transition state. **Note that you should only draw arrows on the structure to the left, not the transition state. YOU ONLY NEED TO DRAW ONE STEREOISOMER OF A CHIRAL TRANSITION STATE 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. Be sure to notice the questions at the end.**



(4 pts) Look as the energy diagrams on page 9. Write the letter of the one that best describes the above mechanistic step.

A

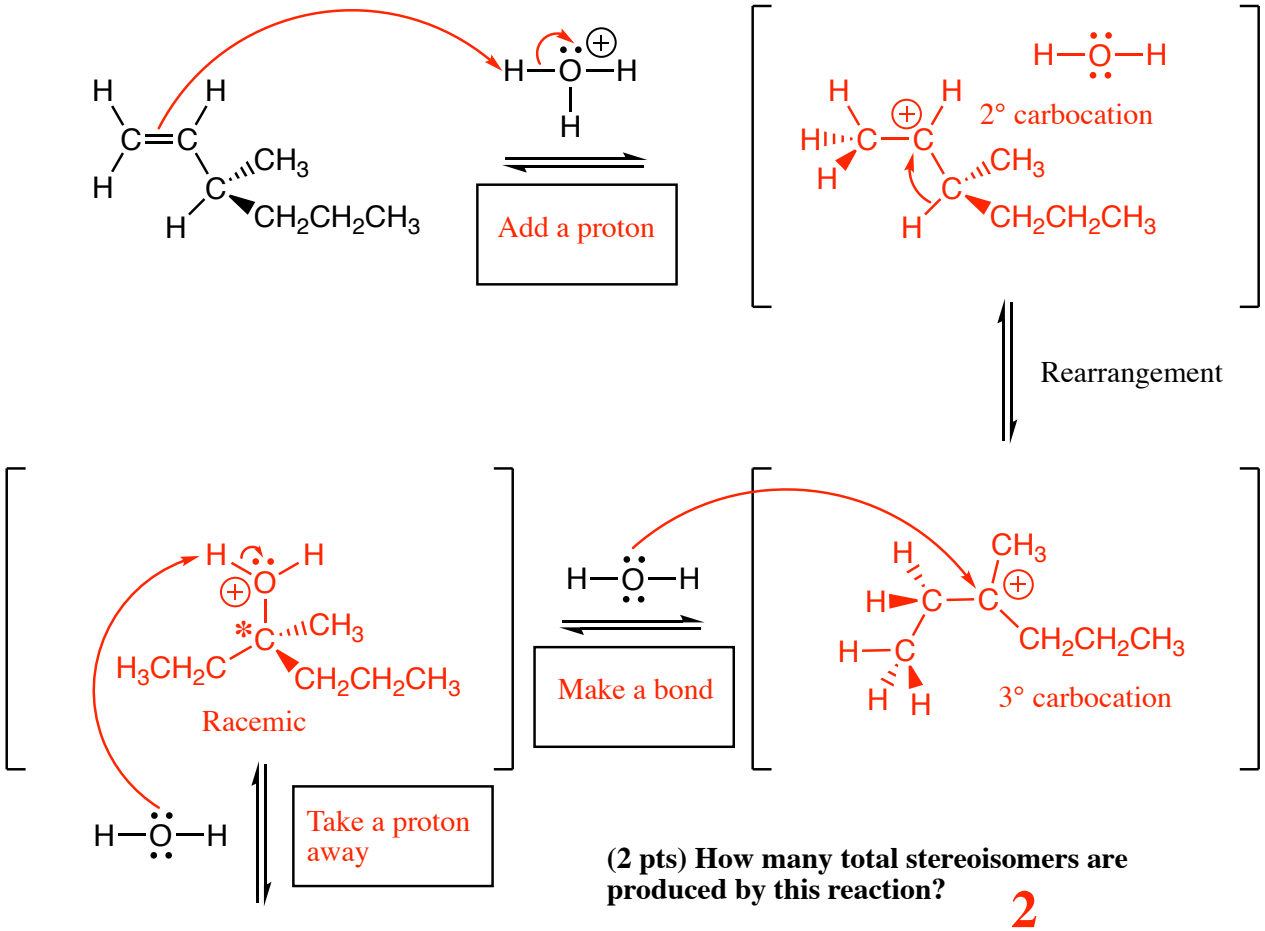
14. (14 pts) Complete the mechanism for the following alkene HX addition reaction. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each 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 boxes provided, write which of the 4 mechanistic elements describes each step (make a bond, break a bond, etc.). Be sure to notice the question at the end.**



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

B

15. (29 pts) 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.**



(2 pts) How many total stereoisomers are produced by this reaction?

2

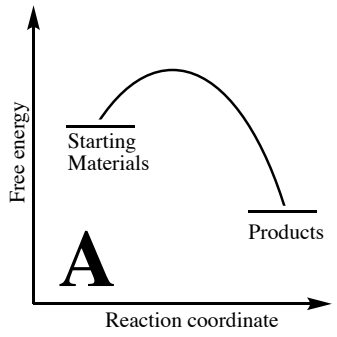
(4 pts) Look as the energy diagrams on page 9. Write the letter of the one that best describes the above mechanism.

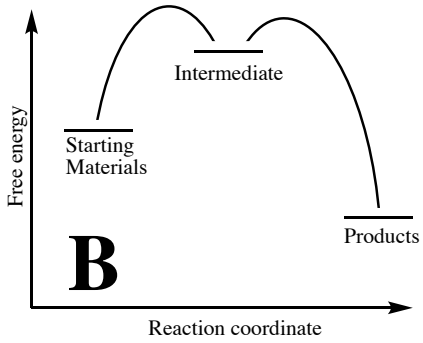
E

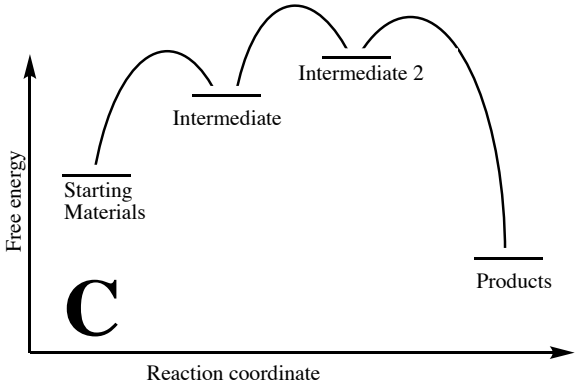
(2 pts) As the reaction proceeds, does the pH of the soluition rise, decrease or stay the same?

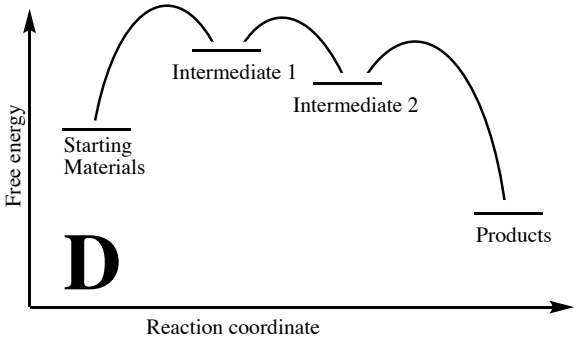
Stays the same

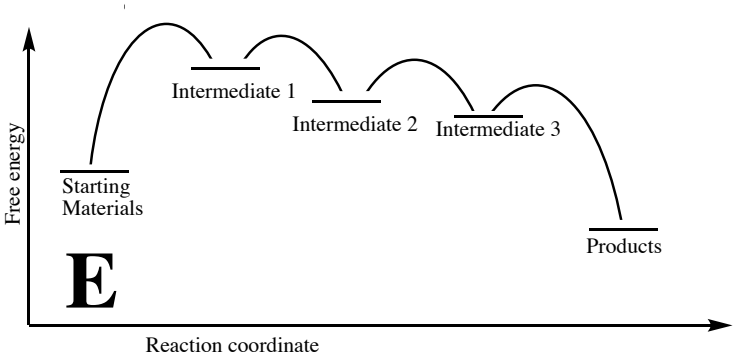
These energy diagrams refer to the mechanisms your completed in problems 13-15 on pages 7-8. This page is not graded.



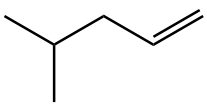


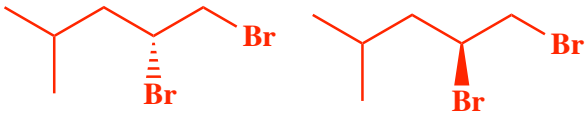




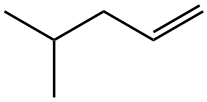


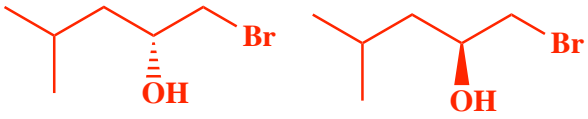
16. (3 or 5 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products)** and please remember that **you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry as appropriate**. When a racemic mixture is formed, **you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES**.

A.  Br_2 →

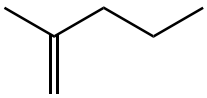


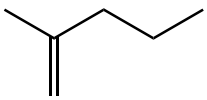
Racemic

B.  Br_2, H_2O →

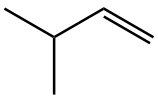


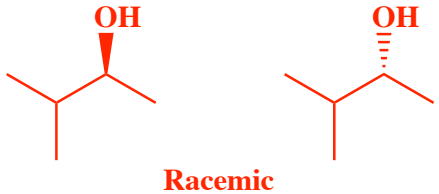
Racemic

C.  H_2O, H_2SO_4 (catalytic amount) →

D.  1. BH_3; 2. H_2O_2 / NaOH →

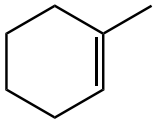
Racemic

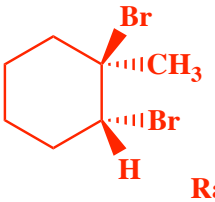
E.  1. $Hg(OAc)_2$ / H_2O; 2. $NaBH_4$ →



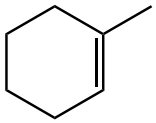
Racemic

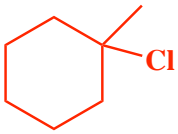
16. (3 or 5 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products)** and please remember that **you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry when appropriate**. When a racemic mixture is formed, **you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES**.

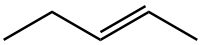
F.  Br_2 →



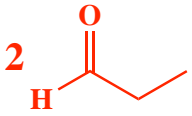
Racemic

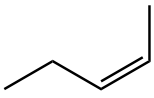
G.  HCl →

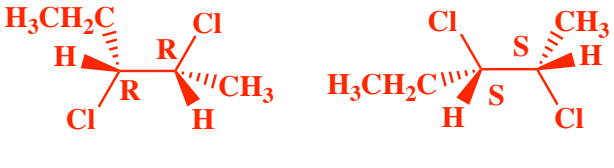


H.  H_2 / Pd° →

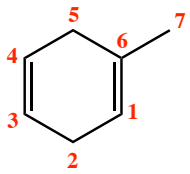
I.  1. O_3 2. $(CH_3)_2S$ →



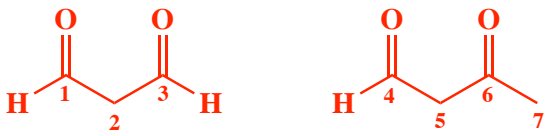
J.  Cl_2 →



Racemic

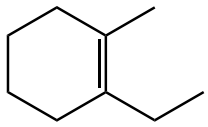
K. 

1. O_3 2. $(CH_3)_2S$ →



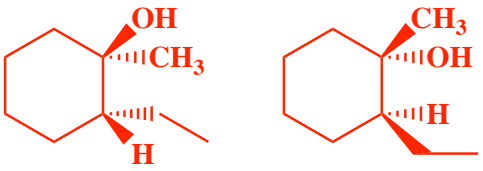
16. (7 or 11 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products)** and please remember 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**.

L

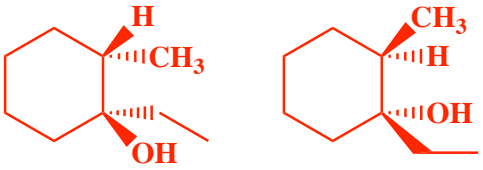


1. BH_3

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



Racemic



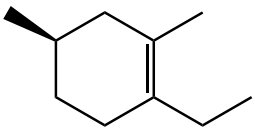
Racemic

(2 pts) Will the product mixture you drew to the right rotate the plane of plane polarized light?

No

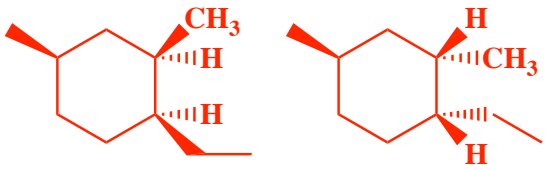
Think about this last one:

M



H_2

Pt°

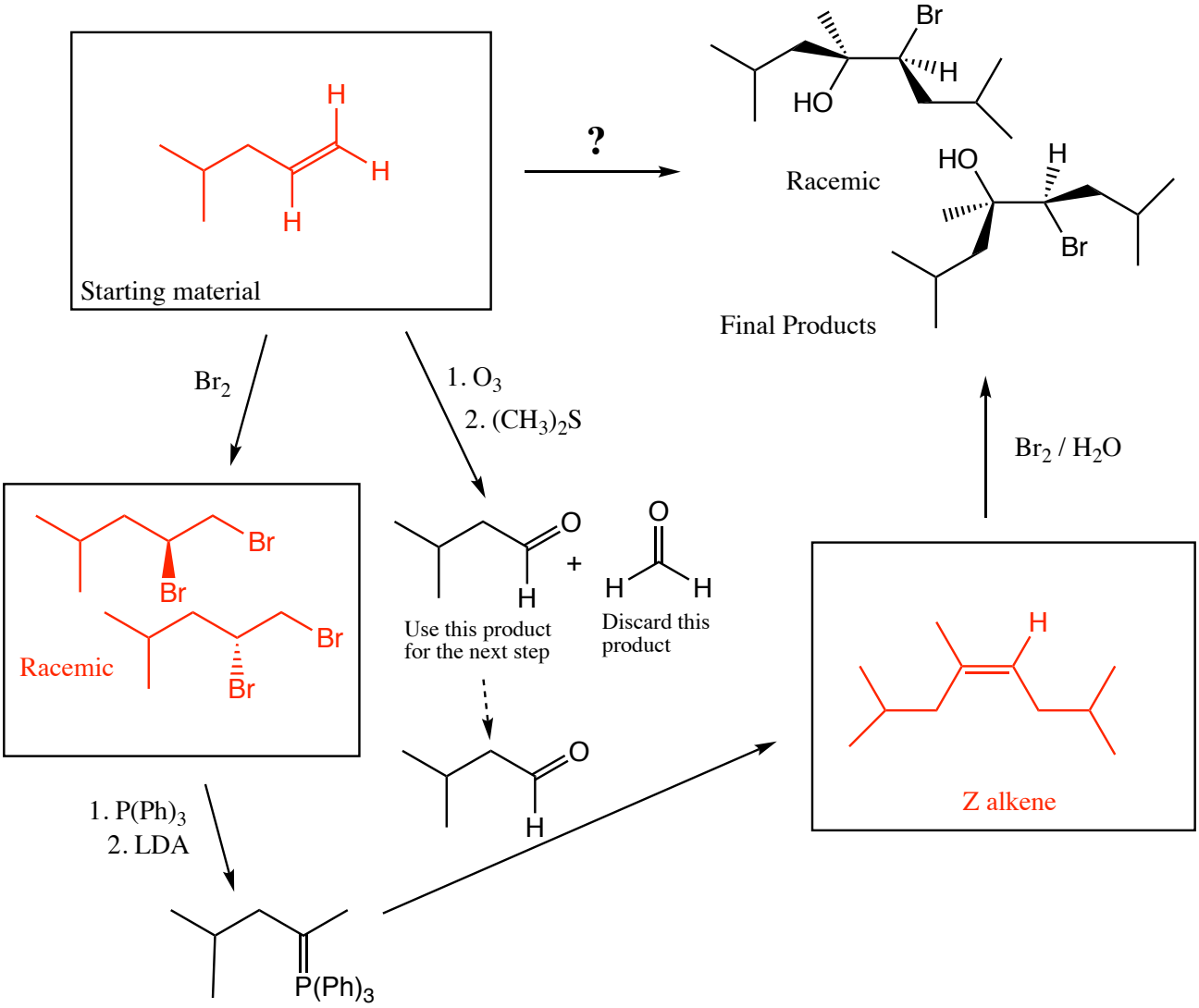


NOT racemic, these are diastereomers.

(2 pts) Will the product mixture you drew to the right rotate the plane of plane polarized light?

Yes

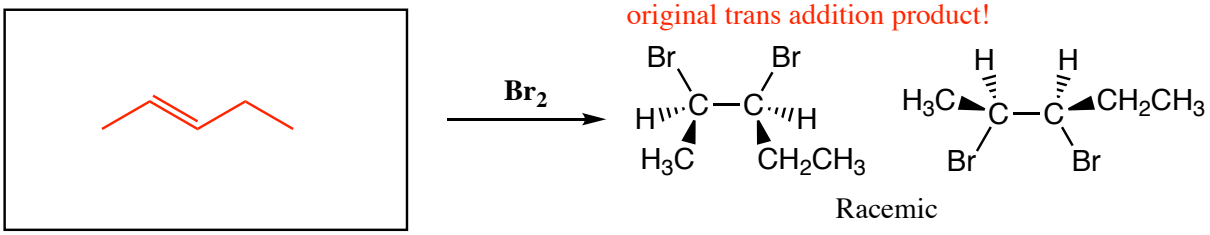
17. (17 pts total) **The point of organic chemistry is synthesis**, the conversion of simpler molecules to more complicated ones with enhanced structure and function. Each reaction you are learning should be thought of as a "tool" that allows you to create a desired type of molecule. These tools can be used in an almost infinite number of combinations to create truly interesting molecules. **In the boxes provided, draw the structures of the molecule indicated in this synthesis scheme.** FOR THIS ONE, IF STEREOISOMERS ARE CREATED YOU MUST DRAW THEM ALL USING WEDGES AND DASHES. And you must write "racemic" when appropriate. You will not recognize all of this chemistry, but by the time you finish O Chem II next spring you will!!



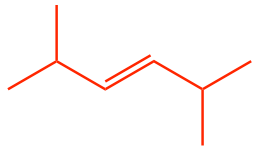
---

18. (4 pts) **Fill in the box with the appropriate starting alkene** Think about his one!!

You need to rotate the central C-C bond to find the original trans addition product!



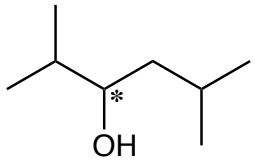
19. (8 pts) The MCAT and other standard exams are famous for using IUPAC names instead of structures. From the following list, **circle the products of the following reaction. This reaction REARRANGES, so you must circle BOTH the rearranged AND unrearranged products.** To make this simpler, we have not 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!)



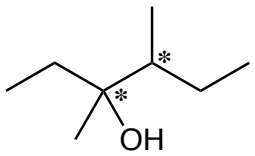
(*E*)-2,5-dimethyl-3-hexene

H_2O

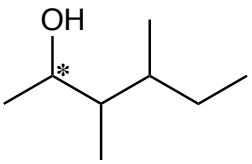
H_2SO_4
(catalytic amount)



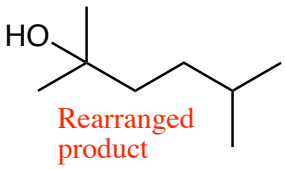
Racemic



Racemic



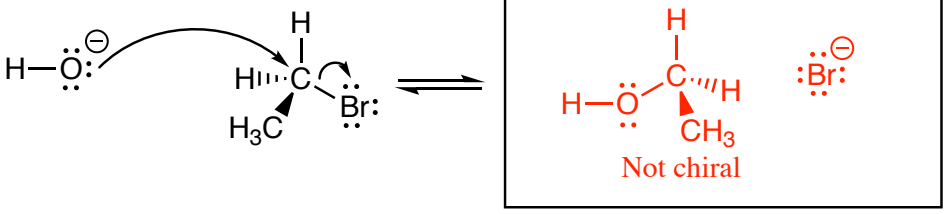
Racemic



Rearranged product

20. (10 pts total) Below are two reactions you have not learned yet, but will soon. While you have not yet learned the chemistry behind the transformations, you should be able to understand the arrows. Follow the arrows and write the products in the boxes. **Because this is a mechanism type question, use wedges and dashes to indicate stereochemistry, write "racemic" if appropriate, draw all lone pairs and formal charges and remember to draw all products of the step.** Then answer the question below each reaction

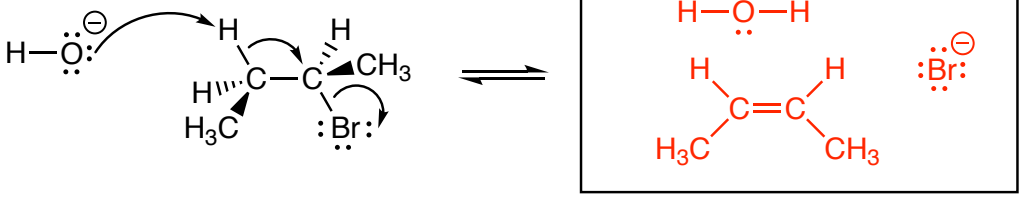
A)



Circle the correct word in all capital letters:

In the above reaction, the $HO^{\ominus}$ is acting as a NUCLEOPHILE or BASE?

B)



Circle the correct word in all capital letters:

In the above reaction, the $HO^{\ominus}$ is acting as a NUCLEOPHILE or BASE?