NAME (Print): _____

EID _____

SIGNATURE: _____

Chemistry 320M/328M
Dr. Brent Iverson
2nd Midterm
October 24, 2024

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

Please Note: Please take your time. We are giving you three hours to take this exam even though it is really a one hour exam. The idea is to give you enough time to show us what you know, not how fast you can draw structures. Please take all the time you need to draw the best possible structures that you can! Do not be surprised if you are comfortable leaving the exam long before 9 PM. That is to be expected!

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!!!

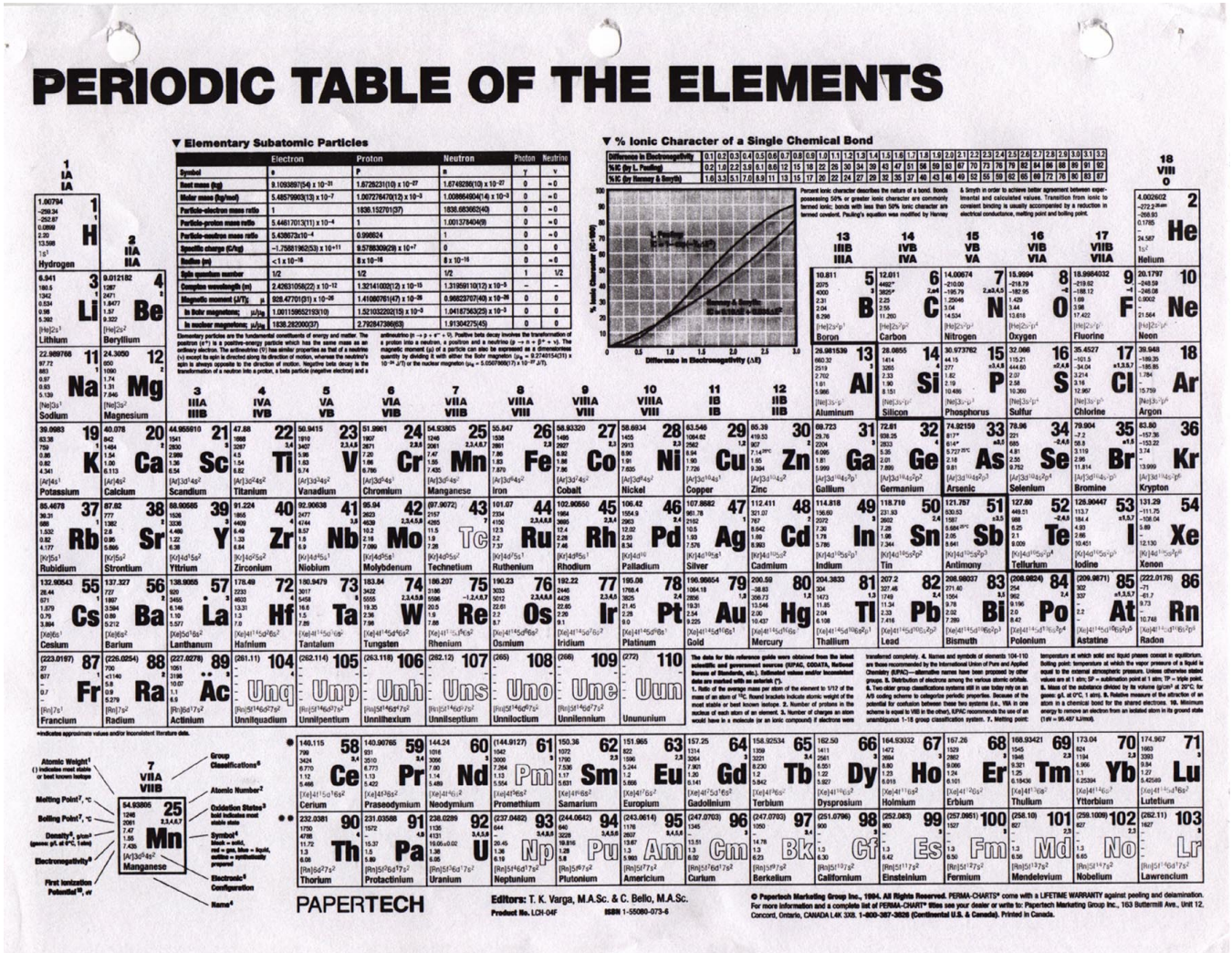
Student Honor Code for the University of Texas at Austin

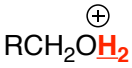
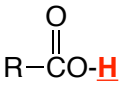
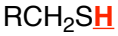
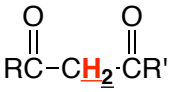
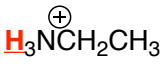
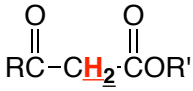
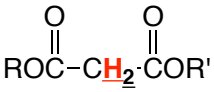
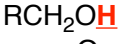
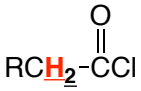
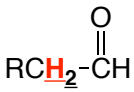
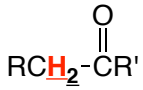
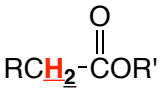
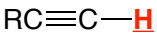
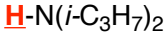
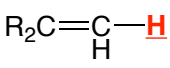
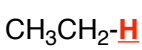
"I pledge, as a member of The University of Texas at Austin community, to do my work honestly, respectfully, and through the intentional pursuit of learning and scholarship."

Elaboration

1. I pledge to be honest about what I create and to acknowledge what I use that belongs to others.
2. I pledge to value the process of learning in addition to the outcome, while celebrating and learning from mistakes.
3. This code encompasses all of the academic and scholarly endeavors of the university community.

(Your signature)

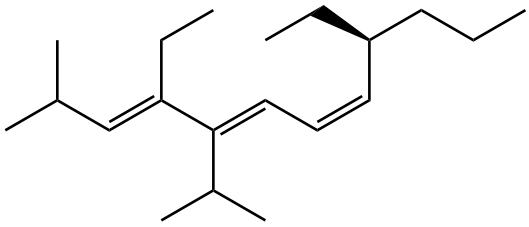


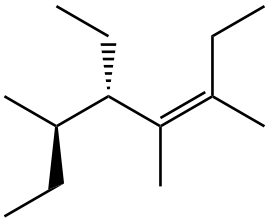
Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Carboxylic acids		3-5
Thiols		8-9
Ammonium ion		9.2
β-Dicarbonyls		10
Primary ammonium		10.5
β-Ketoesters		11
β-Diesters		13
Water		15.7
Alcohols		15-19
Acid chlorides		16
Aldehydes		18-20
Ketones		18-20
Esters		23-25
Terminal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

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

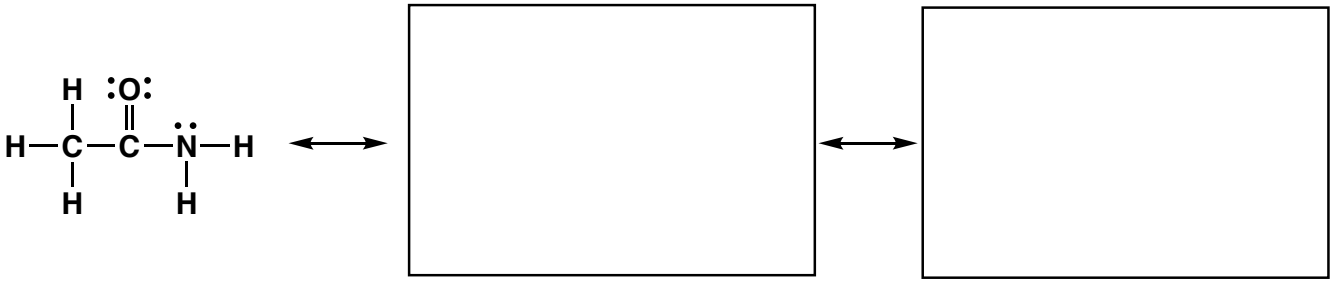




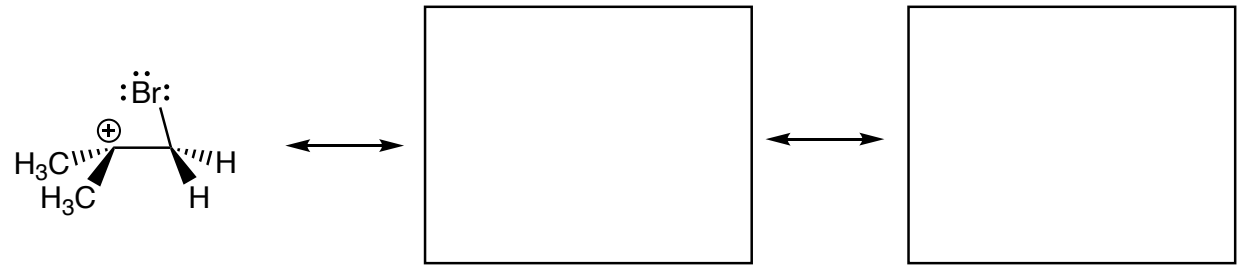
3. (6 pts) Draw the structure that corresponds to the following name:

(3*R*,5*R*,6*E*)-5-(2-bromoethyl)-3-chloro-1,6-octadiene

4. (9 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, 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



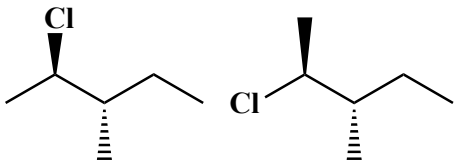
5. (7 pts) Draw the two other most important contributing structures for the bromonium ion. Fill in the circle next to "Most important" under the contributing structure of the three that makes the largest constribution to the overall resonance hybrid. You do NOT need to draw arrows on any of the structures for this problem. **Use wedges and dashes to indicate stereochemistry, write "racemic" if appropriate, draw all lone pairs and formal charges.**



◯ **Most important** ◯ **Most important** ◯ **Most important**

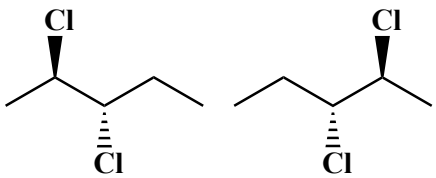
6. (6 pts) Fill in the circle to indicate the appropriate relationship between the following pairs of molecules.

A.



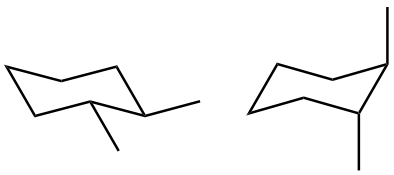
◯ Enantiomers ◯ Same Molecule
◯ Diastereomers ◯ Different constitutional isomers

B.



◯ Enantiomers ◯ Same Molecule
◯ Diastereomers ◯ Different constitutional isomers

C.



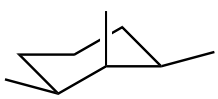
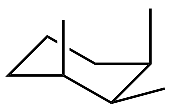
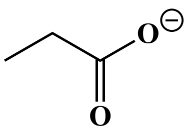
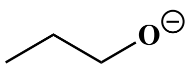
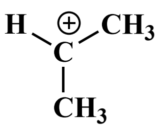
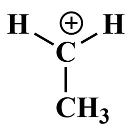
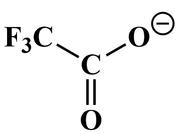
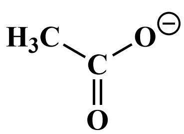
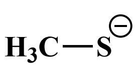
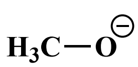
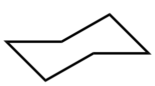
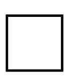
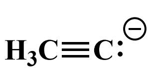
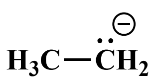
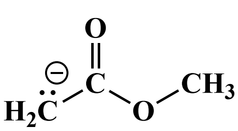
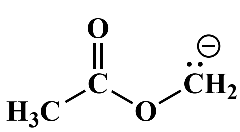
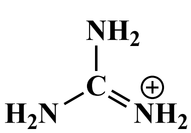
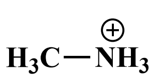
◯ Enantiomers ◯ Same Molecule
◯ Diastereomers ◯ Different constitutional isomers

7. (**28 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 boxes 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.**

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:
		
		
		
		
		
		
		
		
		

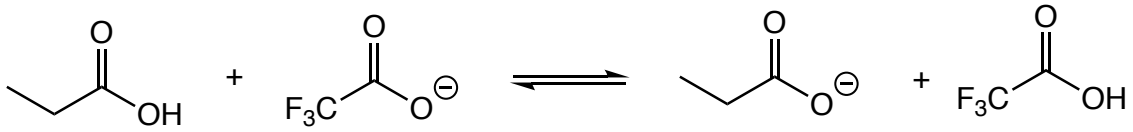
8. (**2 pts each**) **Fill in the circle** that best completes each statement..

A. In general, it is best to think of alkenes as ◯ **nucleophiles** ◯ **electrophiles** **that react with** ◯ **nucleophiles** ◯ **electrophiles** **such as Br_2.**

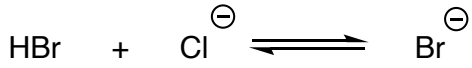
B. In general, ◯ **nucleophiles** ◯ **electrophiles** **are analogous to Lewis bases and** ◯ **nucleophiles** ◯ **electrophiles** **are analogous to Lewis acids.**

C. In the second step of the halogenation reaction, the ◯ **nucleophile** ◯ **electrophile** **is the carbocation and the** ◯ **nucleophile** ◯ **electrophile** **is the halide ion.**

9. (**2 pts each**) For the following equilibria, **fill in the circle** that is appropriate.

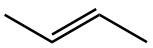


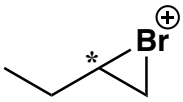
◯ **This side favored at equilibrium** ◯ **This side favored at equilibrium**



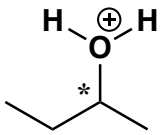
◯ **This side favored at equilibrium** ◯ **This side favored at equilibrium**

10. (**3 pts each**) For the following species we have seen in mechanisms, **fill in the circle** that is appropriate.



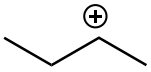


racemic



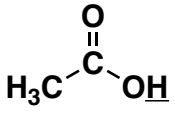
racemic

Br_2

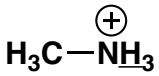


◯ **nucleophile**	◯ **nucleophile**	◯ **nucleophile**	◯ **nucleophile**	◯ **nucleophile**
◯ **electrophile**	◯ **electrophile**	◯ **electrophile**	◯ **electrophile**	◯ **electrophile**
◯ **strong acid**	◯ **strong acid**	◯ **strong acid**	◯ **strong acid**	◯ **strong acid**

11. (18 pts) **Complete the following three 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:**

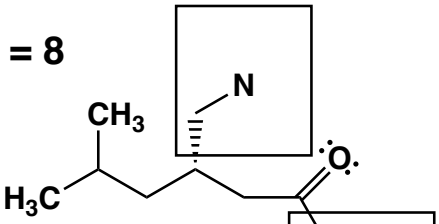


pK_a = 4.76



pK_a = 10.64

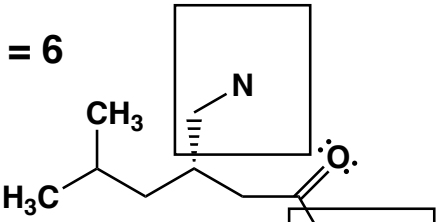
pH = 8



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

Total charge on molecule: ☐

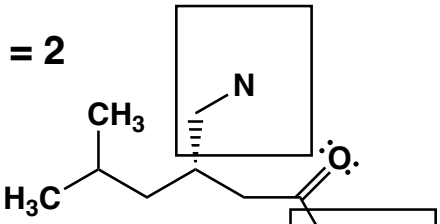
pH = 6



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

Total charge on molecule: ☐

pH = 2



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

Total charge on molecule: ☐

12. (8 points) **It is helpful to think of organic chemistry mechanisms in terms of distinct mechanistic elements. We have learned four of these so far. Fill in the circle that indicates the appropriate mechanistic element to choose if you see the following:**

A. You see both a good nucleophile and electrophile present

- ◯ **Make a bond between a nucleophile and an electrophile**
- ◯ **Break a bond to give stable molecules or ions**
- ◯ **Add a proton**
- ◯ **Take a proton away**

B. When the carbon containing piece is a strong acid or there is a base present

- ◯ **Make a bond between a nucleophile and an electrophile**
- ◯ **Break a bond to give stable molecules or ions**
- ◯ **Add a proton**
- ◯ **Take a proton away**

C. When the carbon containing piece is a base or there is a strong acid present

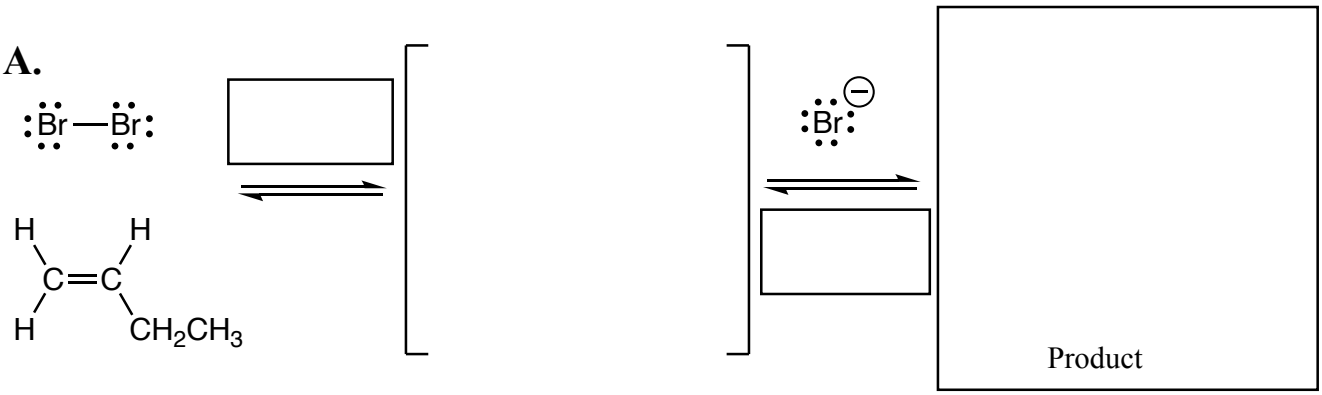
- ◯ **Make a bond between a nucleophile and an electrophile**
- ◯ **Break a bond to give stable molecules or ions**
- ◯ **Add a proton**
- ◯ **Take a proton away**

D. When none of the above are true and you can see how the carbon containing piece can fragment to create stable molecules or ions.

- ◯ **Make a bond between a nucleophile and an electrophile**
- ◯ **Break a bond to give stable molecules or ions**
- ◯ **Add a proton**
- ◯ **Take a proton away**

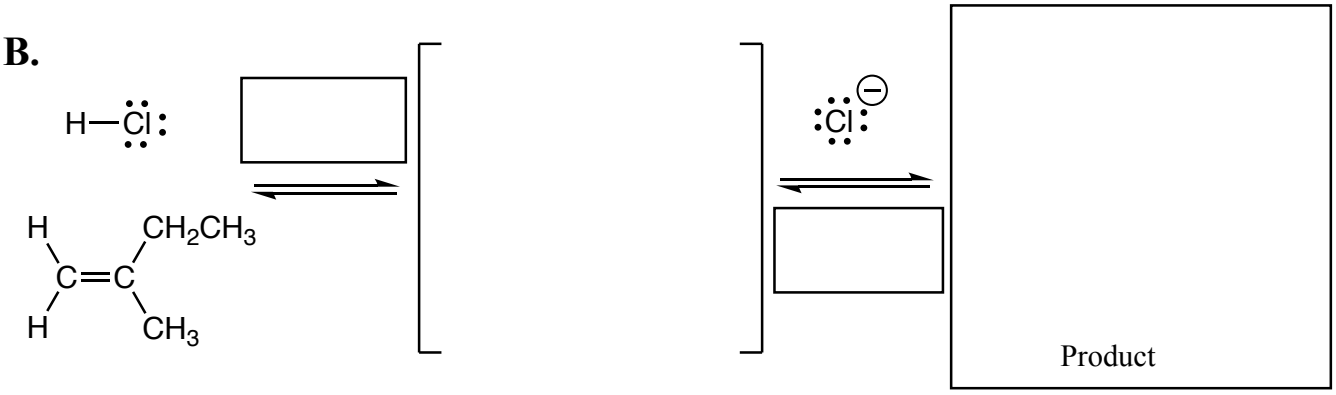
13. (30 pts) Complete the following mechanisms. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. YOU ONLY NEED TO DRAW ONE STEREOISOMER OF A CHIRAL INTERMEDIATE 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 just above or below the equilibria arrows, 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.

A.



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

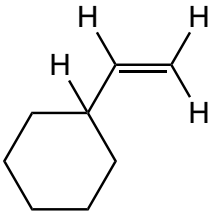
B.

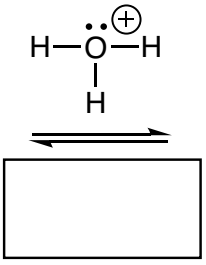


(3 pts) Look at the energy diagrams on page 9. Write the letter of the one that best describes the above mechanism. ☐

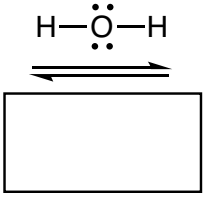
Signature_____ Pg 8 _____(31)

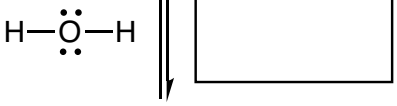
14. (31 pts) Complete the mechanism for the following acid-catalyzed alkene hydration reaction with a rearrangement. For this mechanism we will ONLY consider the rearranged product. Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, 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.





Rearrangement
(1,2 Shift)





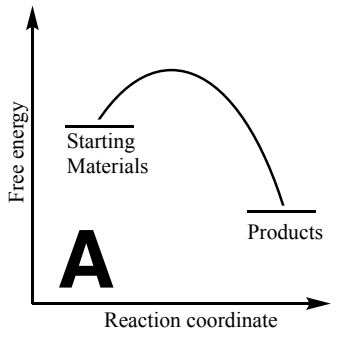
Product

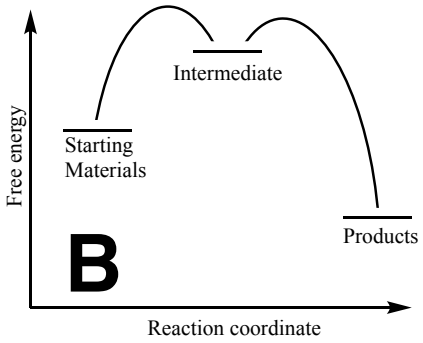
(2 pts) How many total stereoisomers are produced by this reaction?

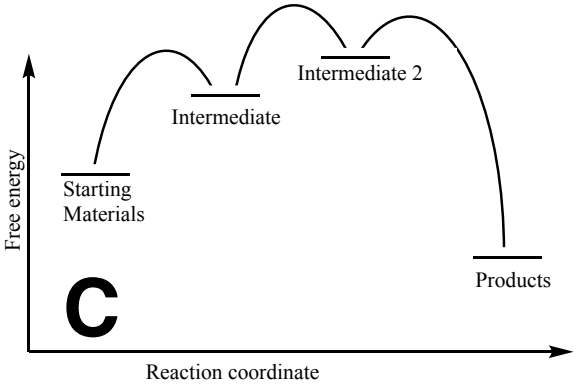
(4 pts) Look as the energy diagrams on page 9. Write the letter of the one that best describes the above mechanism.

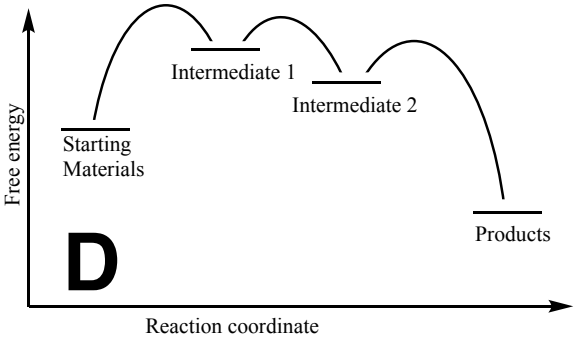
(2 pts) As the reaction proceeds, does the pH of the soluition rise, decrease or stay the same?

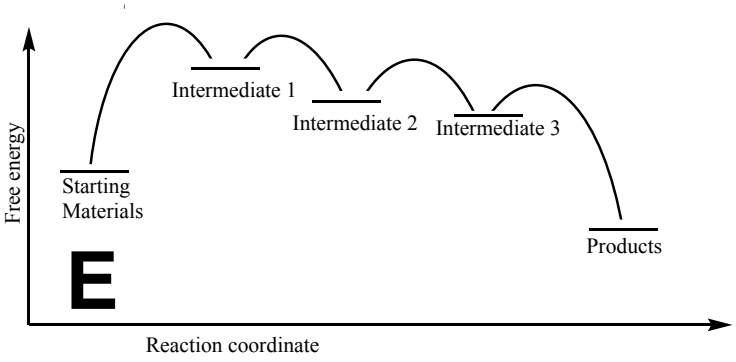
These energy diagrams refer to the mechanisms your completed in problems 13-14 on pages 7-8. This page is not graded.





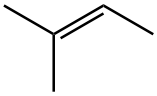


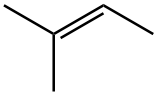


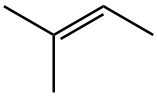


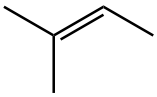
15. (3 or 5 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products)** and please remember that **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.  Cl_2 →

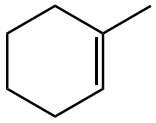
B.  Cl_2 / H_2O →

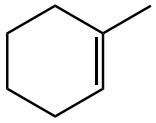
C.  H_2O / H_2SO_4 (catalytic amount) →

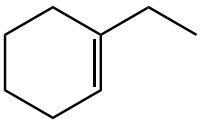
D.  1. BH_3 2. H_2O_2 / NaOH →

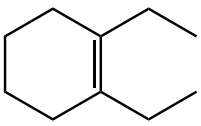
E.  1. OsO_4 2. $NaHSO_3$ / H_2O →

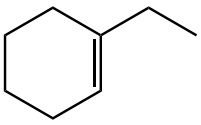
15. (3 or 5 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products) and please remember that 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.

F.  $\xrightarrow{Br_2}$

G.  $\xrightarrow{HCl}$

H.  $\xrightarrow[2.\ H_2O_2\ /\ NaOH]{1.\ BH_3}$

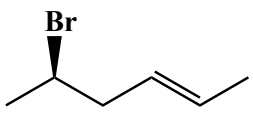
I.  $\xrightarrow[2.\ NaHSO_3\ /\ H_2O]{1.\ OsO_4}$

J.  $\xrightarrow[H_2O]{Br_2}$

15. (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.

Think about these last two:

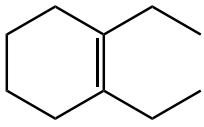
K.



Cl_2 →

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

L.

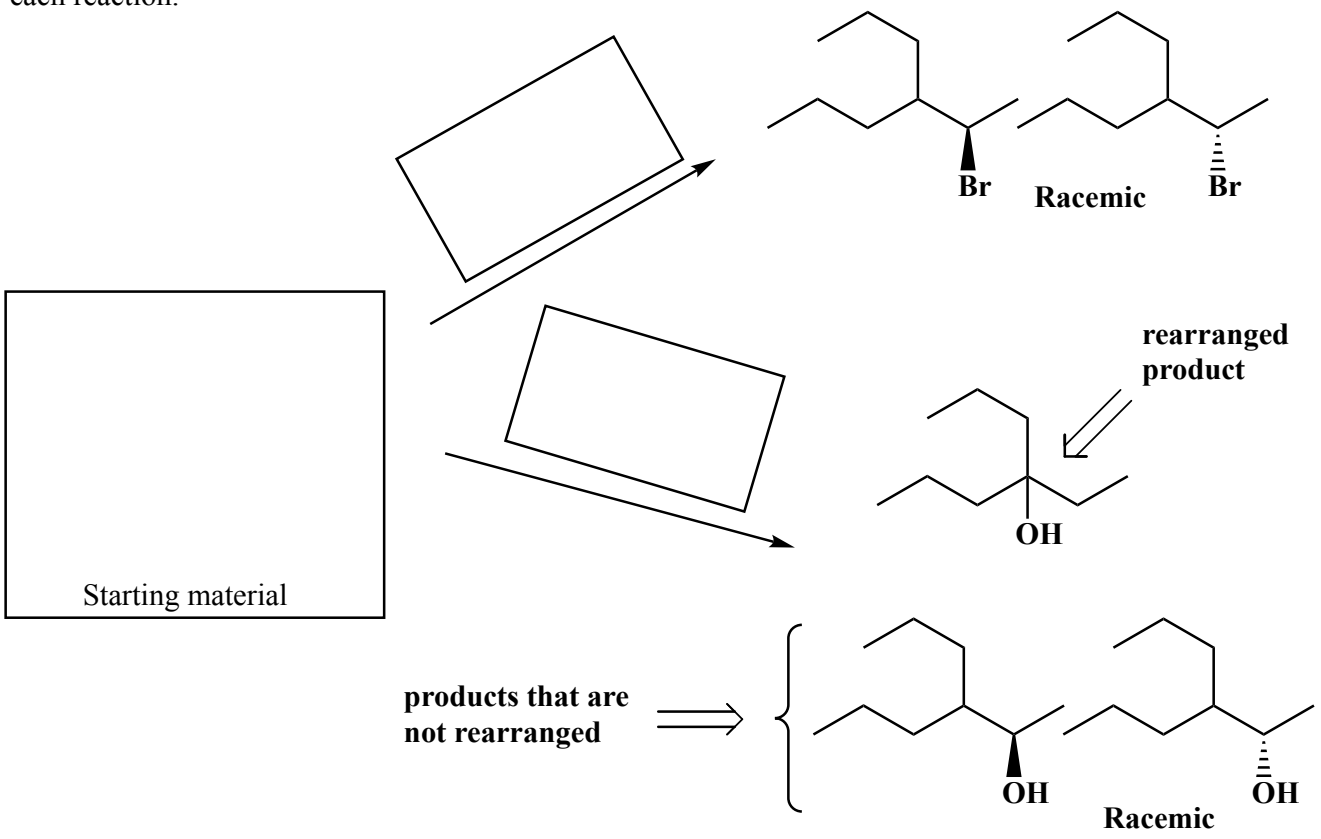


H_2O

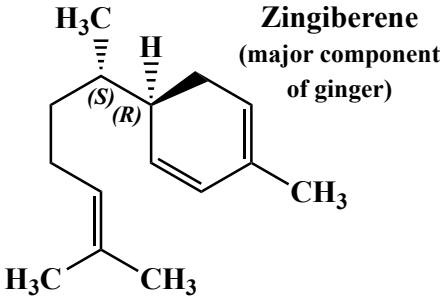
H_2SO_4 (catalytic) →

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

16. (7 pts total) It is important to think about reactions in both directions. To solve synthesis questions you will need to work backwards from a target molecule. Both reactions shown below use the same starting material. **Write the structure of that starting material in the box provided on the left, then write the appropriate reagents in the boxes over each arrow. All** observed products are shown for each reaction.

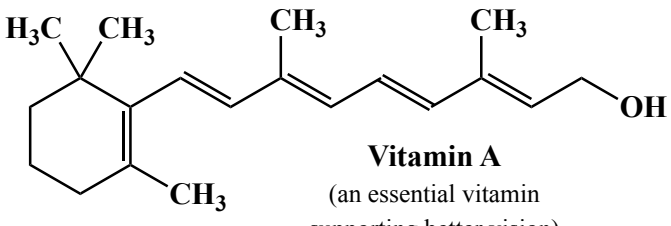


17. (6 pts total) If you understand terpenes this one is not hard. Fill in the circle to designate how many isoprene units are present in each terpene molecule.



Zingiberene
(major component of ginger)

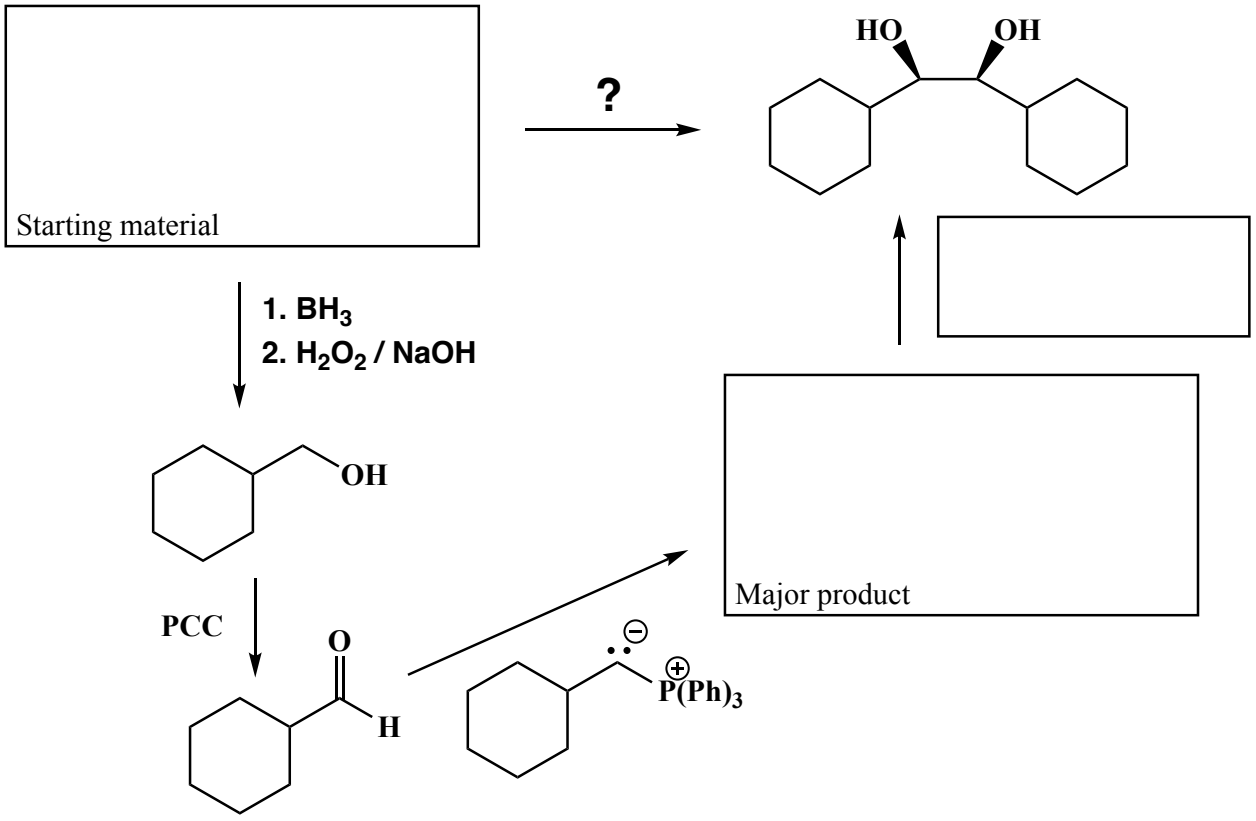
- ◯ **2 Isoprene units**
- ◯ **3 Isoprene units**
- ◯ **4 Isoprene units**
- ◯ **5 Isoprene units**



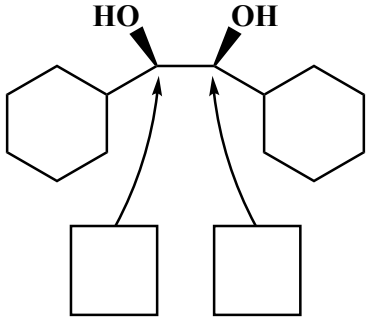
Vitamin A
(an essential vitamin supporting better vision)

- ◯ **3 Isoprene units**
- ◯ **4 Isoprene units**
- ◯ **5 Isoprene units**
- ◯ **6 Isoprene units**

18. (8 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!!



(6 pts**) Notice that the product is a single stereoisomer although it has two chiral centers.** In the boxes, write R or S as appropriate. In the third larger box, in one short sentence indicate why there is only one stereoisomer product.



Why is there only one stereoisomer final product?