**NAME (Print):** _____

**SIGNATURE:** _____

**EID:** _____

**Chemistry 320M/328M**
**Dr. Brent Iverson**
**2nd Midterm**
**October 24, 2019**

**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!!!**

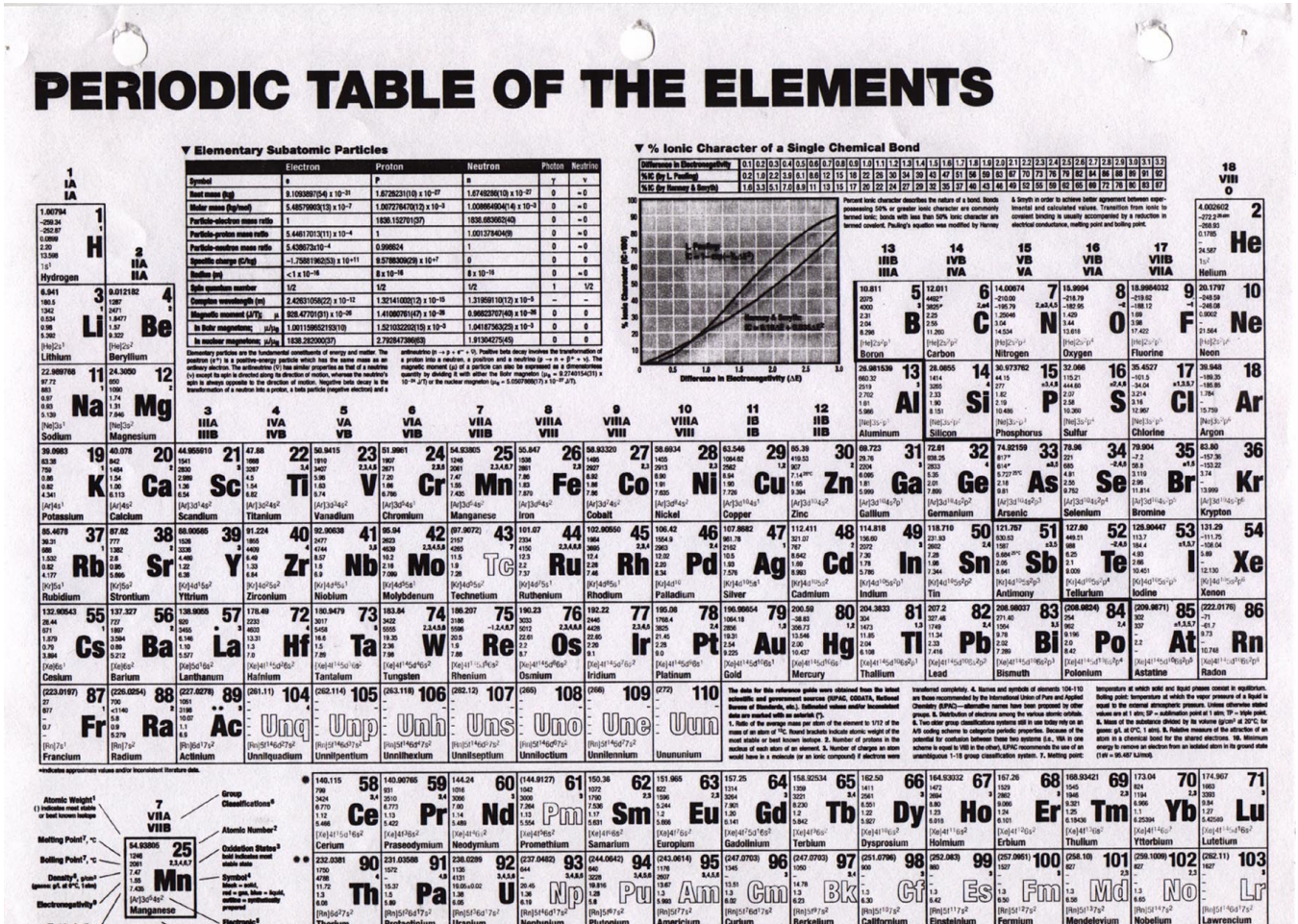
| Page | Points | |
|---|---|---|
| **1** | | **(20)** |
| **2** | | **(*27*)** |
| **3** | | **(24)** |
| **4** | | **(22)** |
| **5** | | **(24)** |
| **6** | | **(20)** |
| **7** | | **(25)** |
| **8** | | **(24)** |
| **9** | | **(-)** |
| **10** | | **(23)** |
| **11** | | **(25)** |
| **12** | | **(18)** |
| **13** | | **(15)** |
| **14** | | **(15)** |
| **15** | | **(16)** |
| **16** | | **(23)** |
| **Total** | | **(321)** |

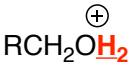
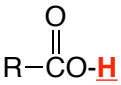
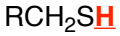
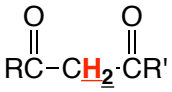
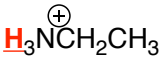
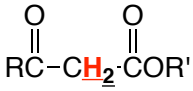
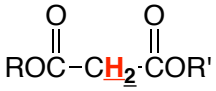
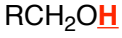
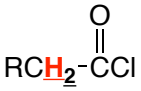
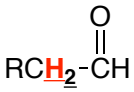
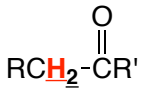
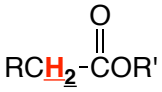
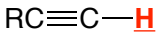
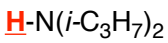
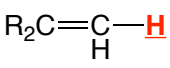
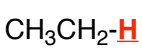
# Student Honor Code

**"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)



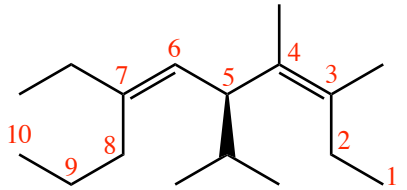
| Compound | | $pK_a$ |
|---|---|---|
| Hydrochloric acid |  | -7 |
| Protonated alcohol |  | -2 |
| Hydronium ion |  | -1.7 |
| Carboxylic acids |  | 3-5 |
| Thiols |  | 8-9 |
| Ammonium ion |  | 9.2 |
| β-Dicarbonyls |  | 10 |
| Primary ammonium |  | 10.5 |
| β-Ketoesters |  | 11 |
| β-Diesters |  | 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 _____(20)

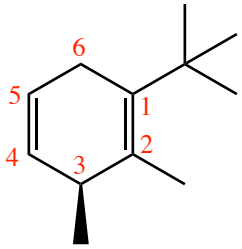
**1.** (2 pts) What is the most important question in organic chemistry?

**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.



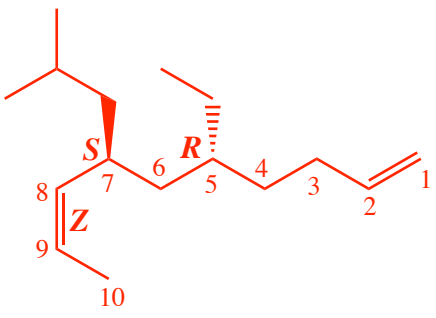

**(5*S*,3*Z*,6*Z*)-7-ethyl-5-isopropyl-3,4-dimethyl-3,6-decadiene**
**or**
**(5*S*,3*Z*,6*Z*)-7-ethyl-3,4-dimethyl-5-(1–methylethyl)-3,6-decadiene**



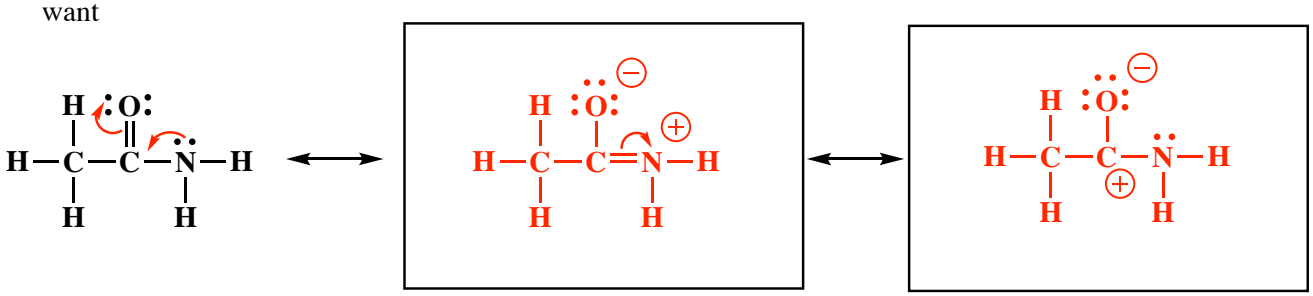

**(3*S*)-1-*tert*-butyl-2,3-dimethyl-1,4-cyclohexadiene**
**or**
**(3*S*)-2,3-dimethyl-1-(1,1-dimethylethyl)-1,4-cyclohexadiene**

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

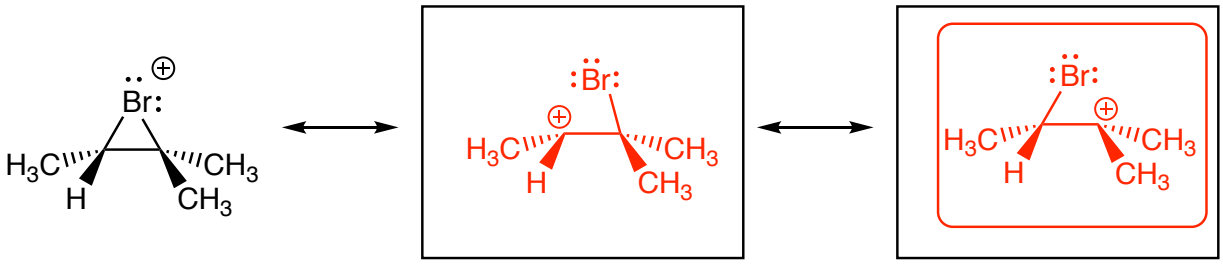
**(5*R*,7*S*,*Z*)-5-ethyl-7-isobutyl-1,8-decadiene**



**4.** (6 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

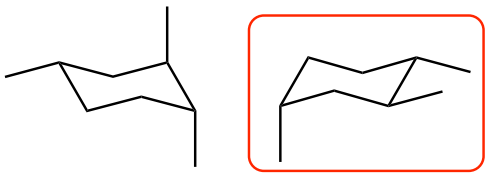


**5.** (7 pts) Draw the two other most important contributing structures for the bromonium ion. Draw a circle around the contributing structure you drew that makes the largest constribution to the overall resonance hybrid. You do NOT need to draw arrows on any of the structures for this problem. **Because this is a mechanism type question, use wedges and dashes to indicate stereochemistry, write "racemic" if appropriate, draw all lone pairs and formal charges.**

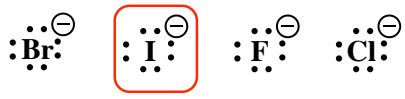


**6.** (14 pts) For each set of molecules or ions drawn below, circle the one that is the MOST stable.

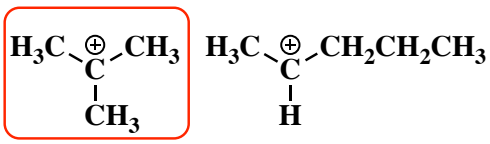
**A.**



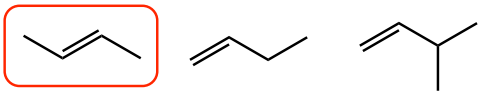
**B.**



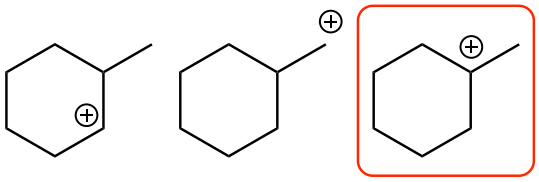
**C.**



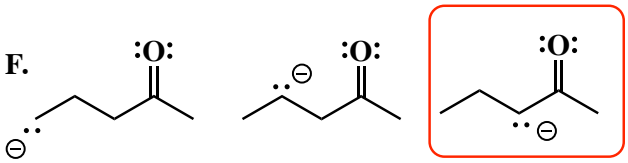
**D.**



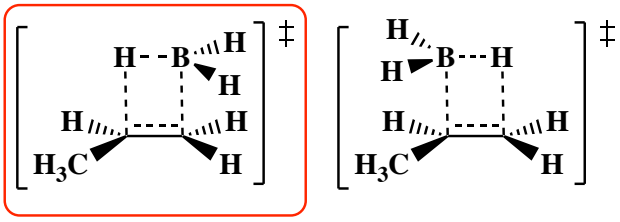
**E.**



**F.**



**G.**



**7.** (**24 pts**) For each pair of molecules, one is more stable (lower in energy) because of one or more principles we have discussed. **Circle the more stable molecule. Then, 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 you circled 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 over more atoms **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

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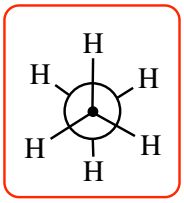
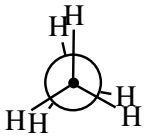
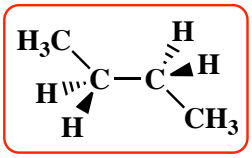
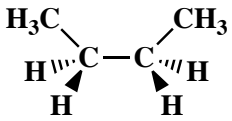
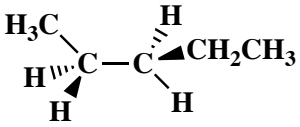
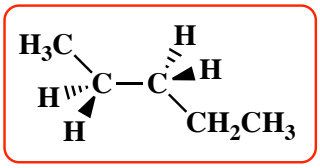
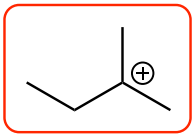
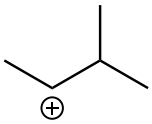
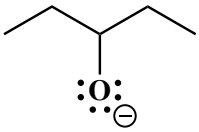
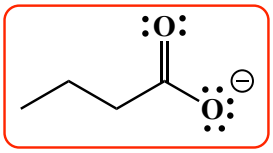
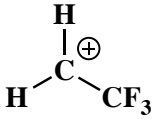
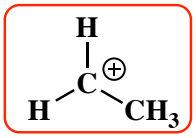
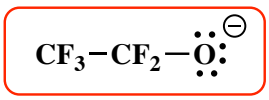
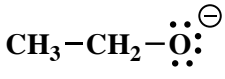
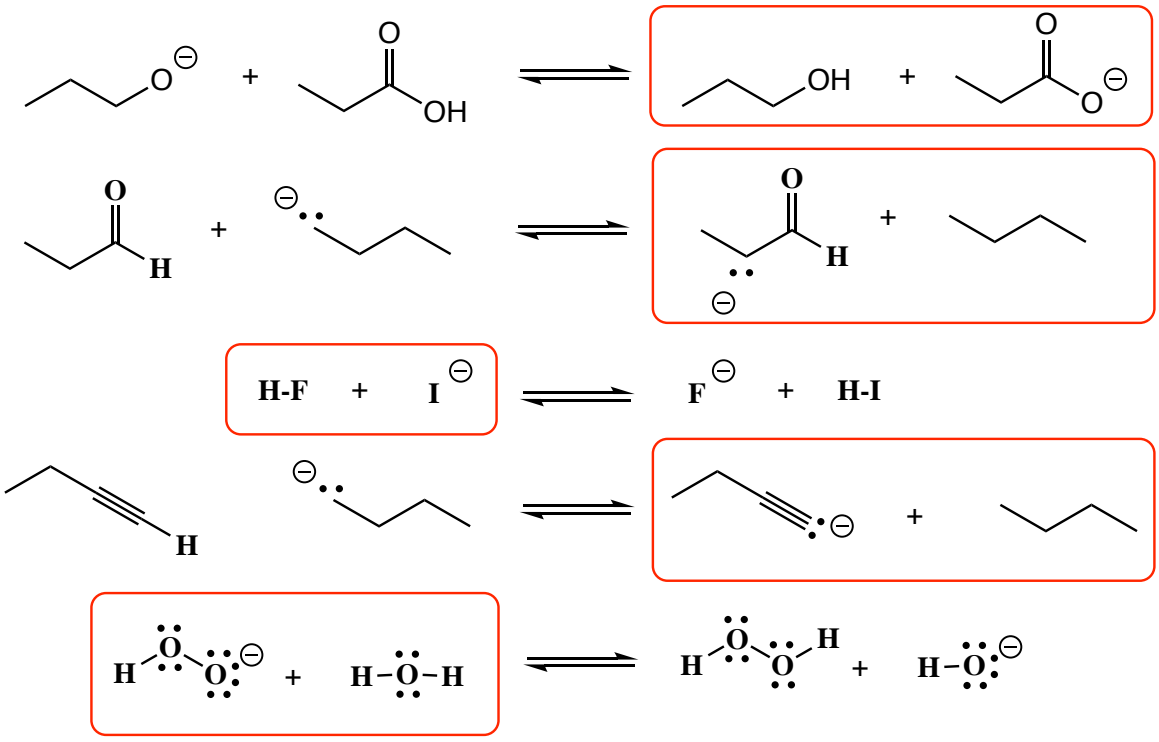
| | The molecule your circled is more stable upon considering: |
|---|---|
|   | **C** |
|   | **A, C** |
|   | **A** |
|   | **D, E** |
|   | **F, G** |
|   | **D** |
|   | **D** |

**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.** (**2 pts each**) List the four mechanistic elements that make up most of the steps of the reactions we will present in the first two semesters of Organic Chemistry:

**1.** **Make a bond between a nucleophile and an electrophile.**

**2.** **Break a bond to give stable molecules or ions.**

**3.** **Add a proton**

**4.** **Take a proton away**

**10.** (**2 pts each**) List the two most common electron **sources** for mechanism arrows that we have seen so far this semster:

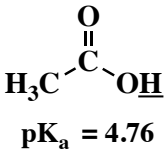
**Pi bonds and lone pairs on atoms.**

**11.** (**2 pts each**) Below are a series of definitions. From the list at the bottom of the page, write the letter, i.e. (A), (C), etc., of the word that corresponds to the following definitions (note you will not use all the letters from down below, there are more words than definitions) I filled in the first one for you.

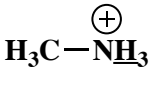
| **Letter of the word best fitting the definition** | |
|---|---|
| **T** | Is a great way to stay healthy and deal with the stress of midterms. |
| **R** | Complex natural molecules that are built from 5 carbon "isoprene" units in Nature, |
| **K** | Contains an electron rich source for a bond forming process. Analogous to a Lewis base |
| **E** | Contains an electron deficient atom that serves as the electron sink in a bond forming process (Analogous to a Lewis acid) or possesses a weak bond that breaks to make a stable ion or fragment. |
| **G** | Adjacent sigma bonds from attached alkyl groups overlap and share electron density with empty 2p orbital. |
| **N** | The analysis of which of the possible constitutional isomes (also called regioisomers) are made in a reaction. |
| **B** | Means that the atoms add to either side of a C=C double bond during a chemical reaction. |
| **Q** | Means that the atoms add to the same side of a C=C double bond during a chemical reaction. |
| **L** | Involves a net loss of electrons and replaces C-H bonds with C-O bonds or pi bonds. |
| **M** | Involves a net gain of electrons and replaces C-O or pi bonds with C-H bonds. |
| **F** | A molecule that cannot be superimposed on its mirror image (it does not have a plane or center of symmetry). |
| **D** | Molecules that are stereoisomers but not enantiomers; a situation that arises when there is more than one chiral center in the same molecule. |
| **J** | A molecule with two or more chiral centers yet is not chiral because it contains a symmetry element, usually a plane of symmetry. |

| | | | | | |
|---|---|---|---|---|---|
| **Addition reaction (A)** | **Anti (B)** | **Cis (C)** | **Diastereomers (D)** | **Electrophile (E)** | **Enantiomer (F)** |
| **Hyperconjugation (G)** | **Inductive effect (H)** | **Lipid (I)** | **Meso compound (J)** | **Nucleophile (K)** | |
| **Oxidation reaction (L)** | **Reduction reaction (M)** | **Regiochemistry (N)** | **Stereochemistry (O)** | **Steroid (P)** | |
| **Syn (Q)** | **Terpene (R)** | **Trans (S)** | **Running (T)** | | |

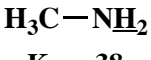
**12.** (20 pts) **Complete the following four structures by adding appropriate numbers of lone pair electrons, H atoms, and formal charges to the atoms in the boxes.** You must adjust your answers to indicate the predominant species at each indicated pH value. (You do not have to add anything such as 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**

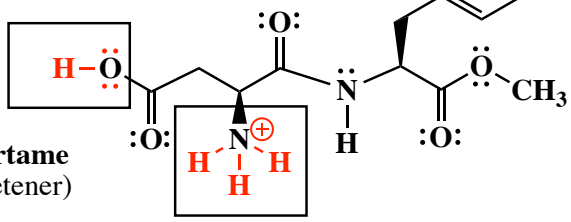



**$pK_a$ = 10.64**




**$pK_a$ = 38**

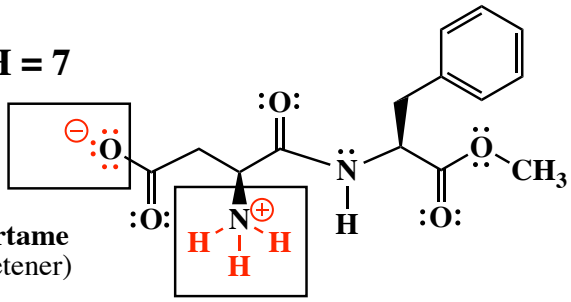
**pH = 3**



**Aspartame**
(Sweetener)

**Total charge on molecule:** 1

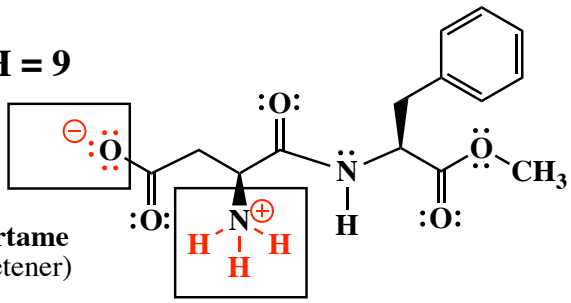
**pH = 7**



**Aspartame**
(Sweetener)

**Total charge on molecule:** 0

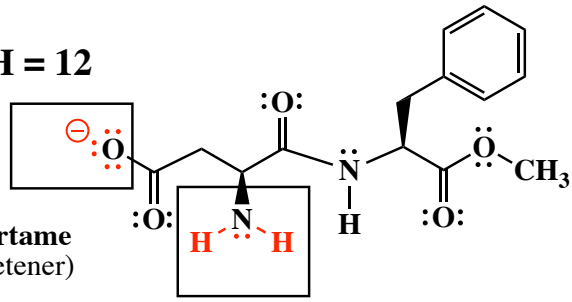
**pH = 9**



**Aspartame**
(Sweetener)

**Total charge on molecule:** 0

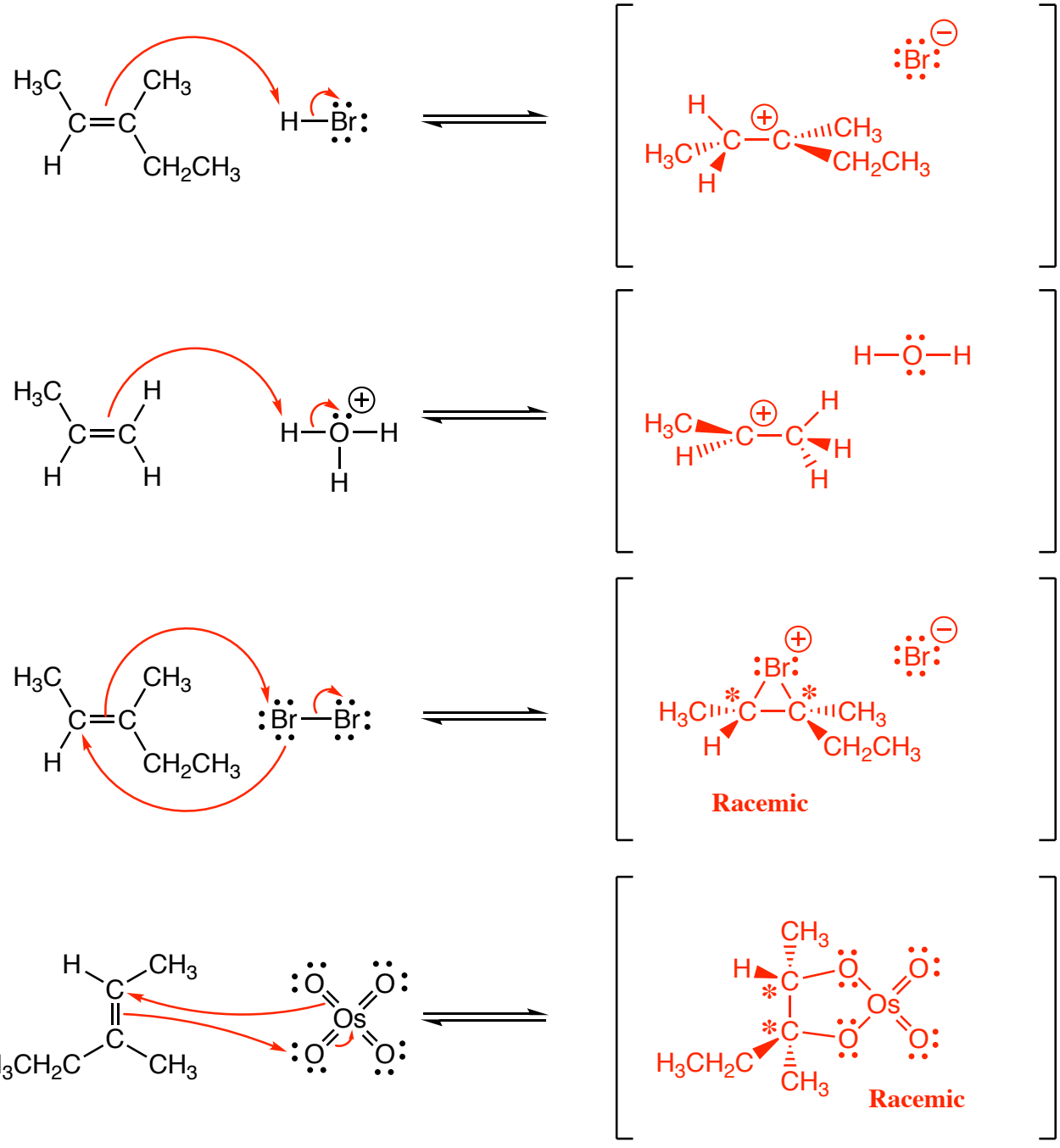
**pH = 12**



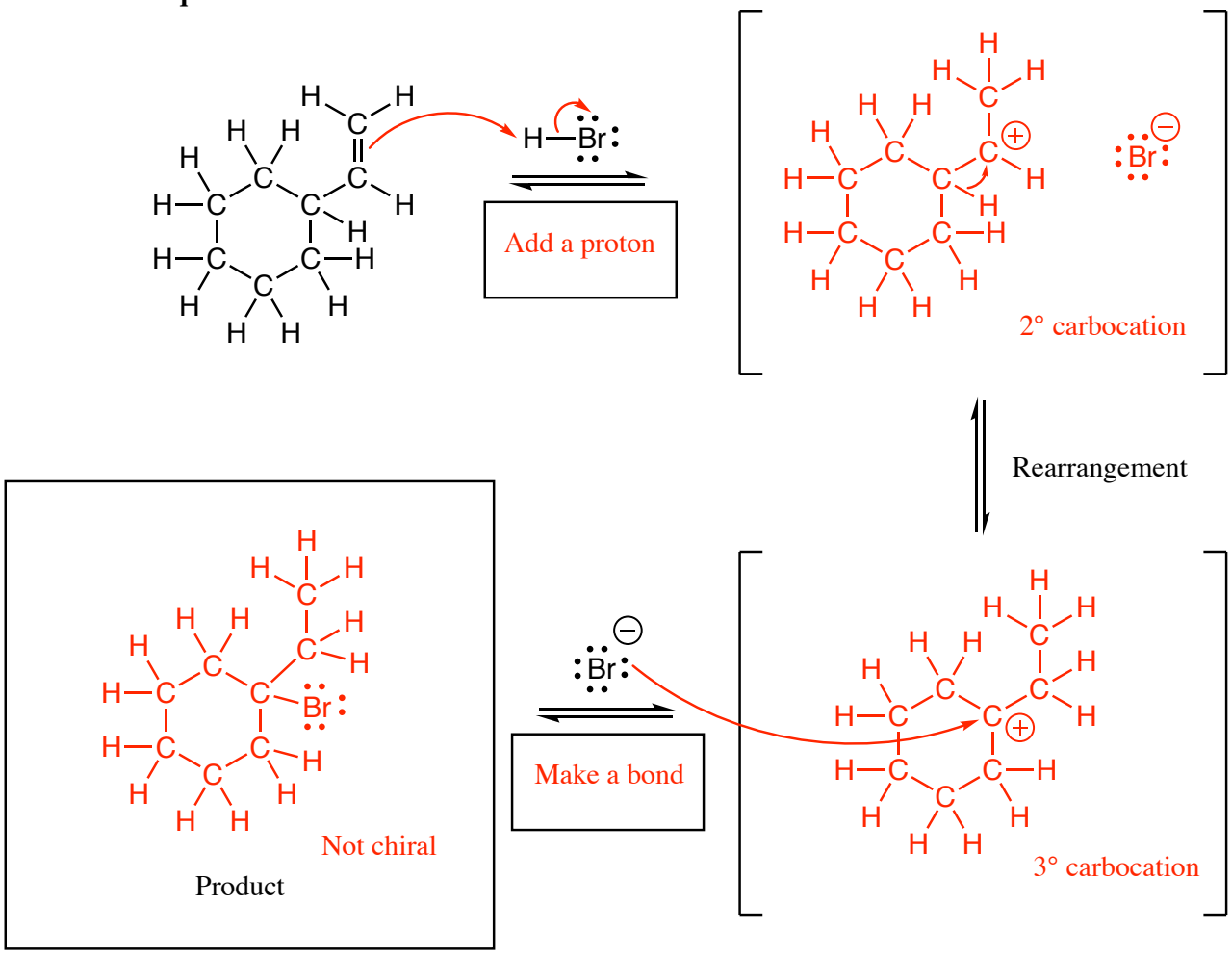
**Aspartame**
(Sweetener)

**Total charge on molecule:** - 1

**13.** (29 pts) Complete the following mechanism for the first step of each reaction. You are only completeing the first step, not the entire reaction here. Use arrows to indicate the movement of all electrons and be sure to show all electron pairs and formal charges. **Note that you should only draw arrows on the structure to the left, not the intermediate. YOU ONLY NEED TO DRAW ONE STEREOISOMER OF A CHIRAL INTERMEDIATE. 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.**



**14**. (29 pts) Complete the mechanism for the following H-Br 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 two boxes provided under the 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 questions at the end.**

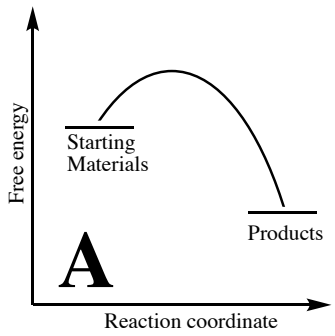


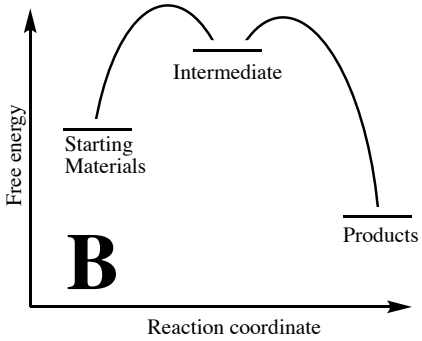

**(2 pts) How many total stereoisomers are produced by this reaction?** **1**

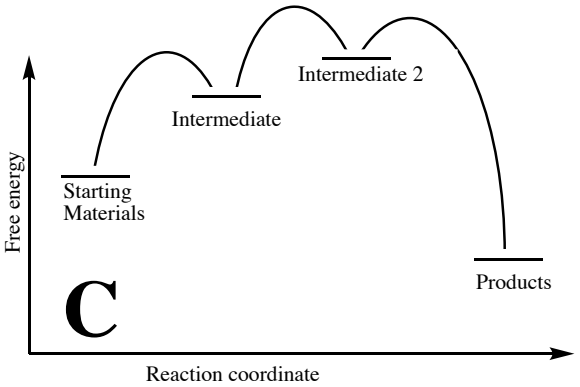
**(4 pts) Look as the energy diagrams on page 9. Write the letter of the one that best describes the above mechanism.** **D**

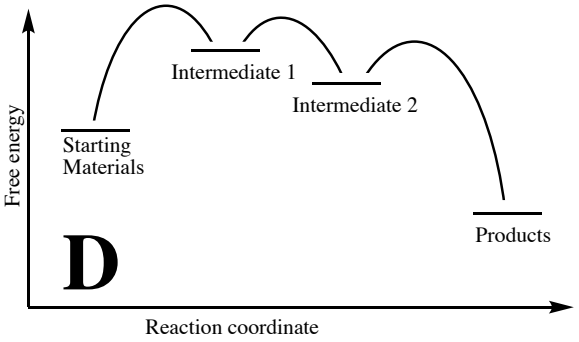
**(2 pts) As the reaction proceeds, does the pH of the solution increase, decrease, or stay the same?** **Increase (as we use up HBr)**

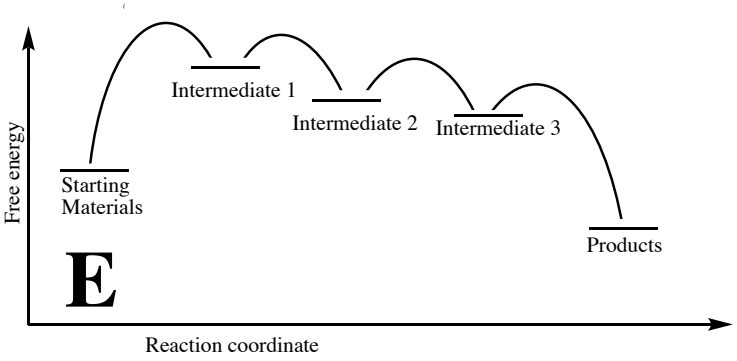
These energy diagrams refer to the mechanism your completed in problem 14 on pages 8. This page is not graded.



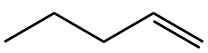



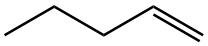
**15.** (3 or 5 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products** and please remember that **you must draw the structures of all the 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.** 

$H_2O$

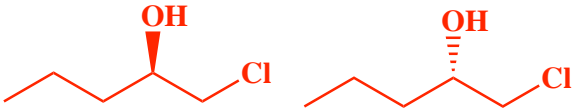
$H_2SO_4$ (catalytic amount)


Racemic

**B.** 

$Cl_2$

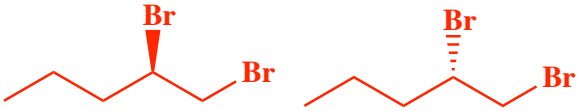
$H_2O$



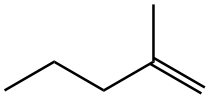

Racemic

**C.** 

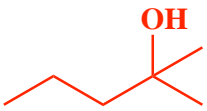
$Br_2$



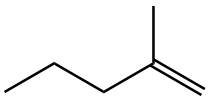

Racemic

**D.** 

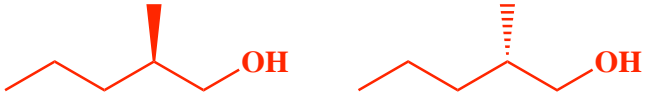
1. $Hg(OAc)_2$ / $H_2O$
2. $NaBH_4$




(Not chiral)

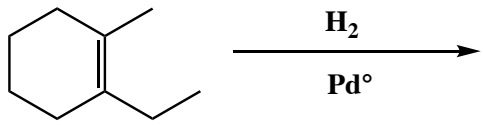
**E.** 

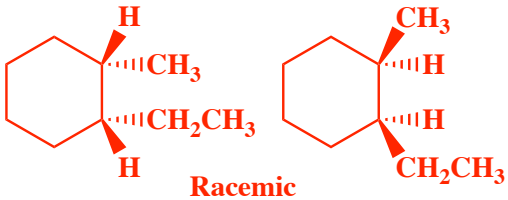
1. $BH_3$
2. $H_2O_2$ / NaOH

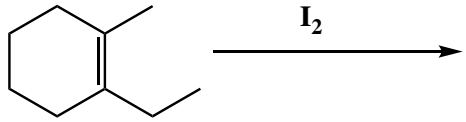



Racemic

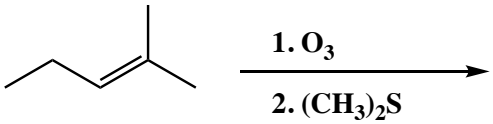
**15.** (3,4, or 5 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. **Draw only the predominant regioisomer product or products** and please remember that **you must draw the structures of all 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**.

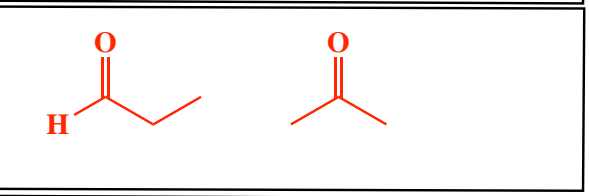
**F.** 

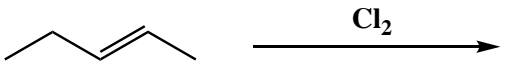



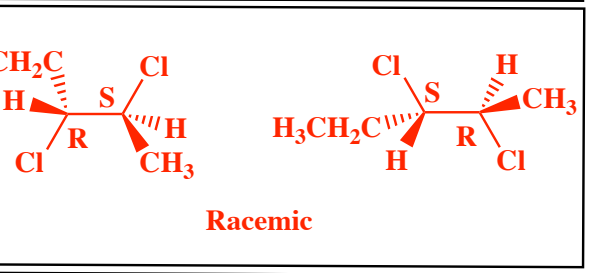

**G.** 

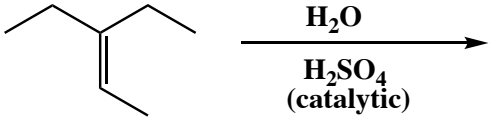


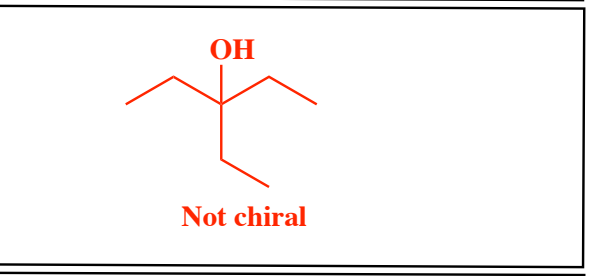
**H.** 

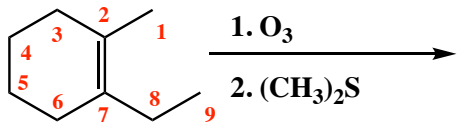



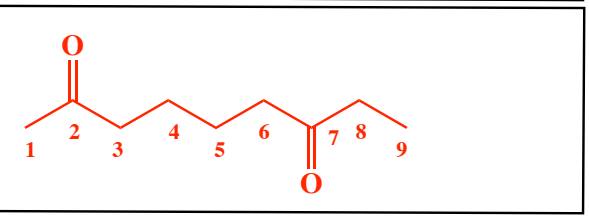

**I.** 


**J.** 

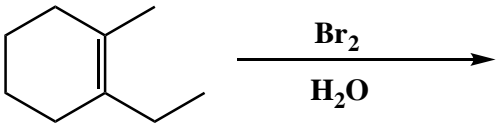



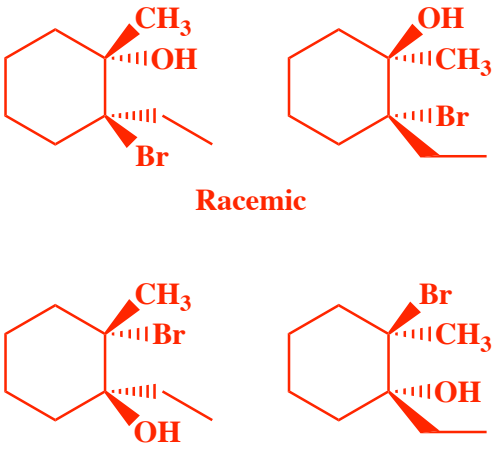

**K.** 

**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 if relevant** 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.**

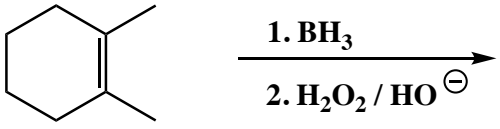


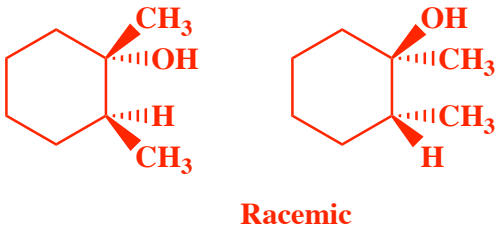




**(2 pts) Will the product mixture you drew to the right rotate the plane of plane polarized light?**

**No**

**M.**



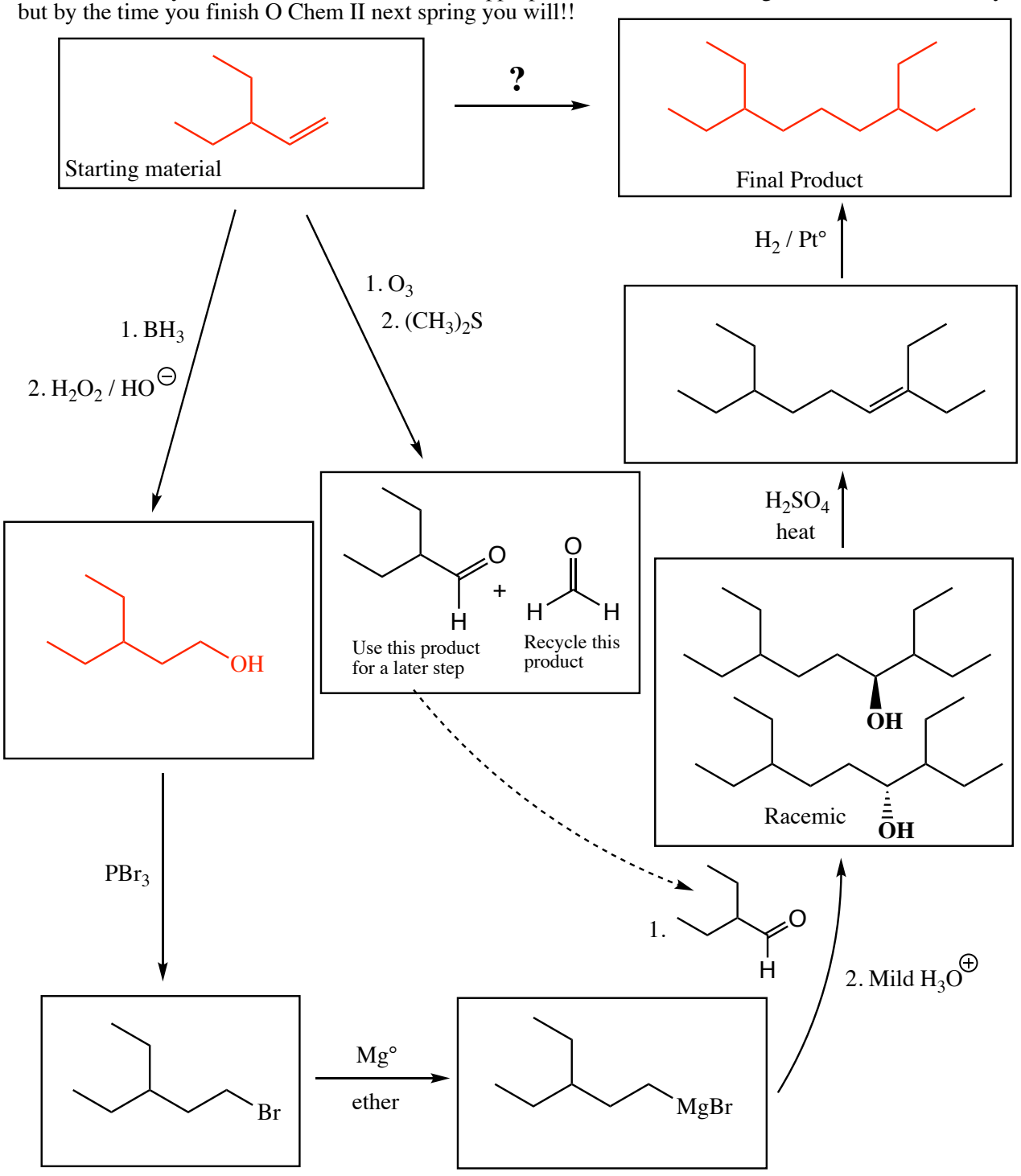




**Because of symmetry there are only two products.**

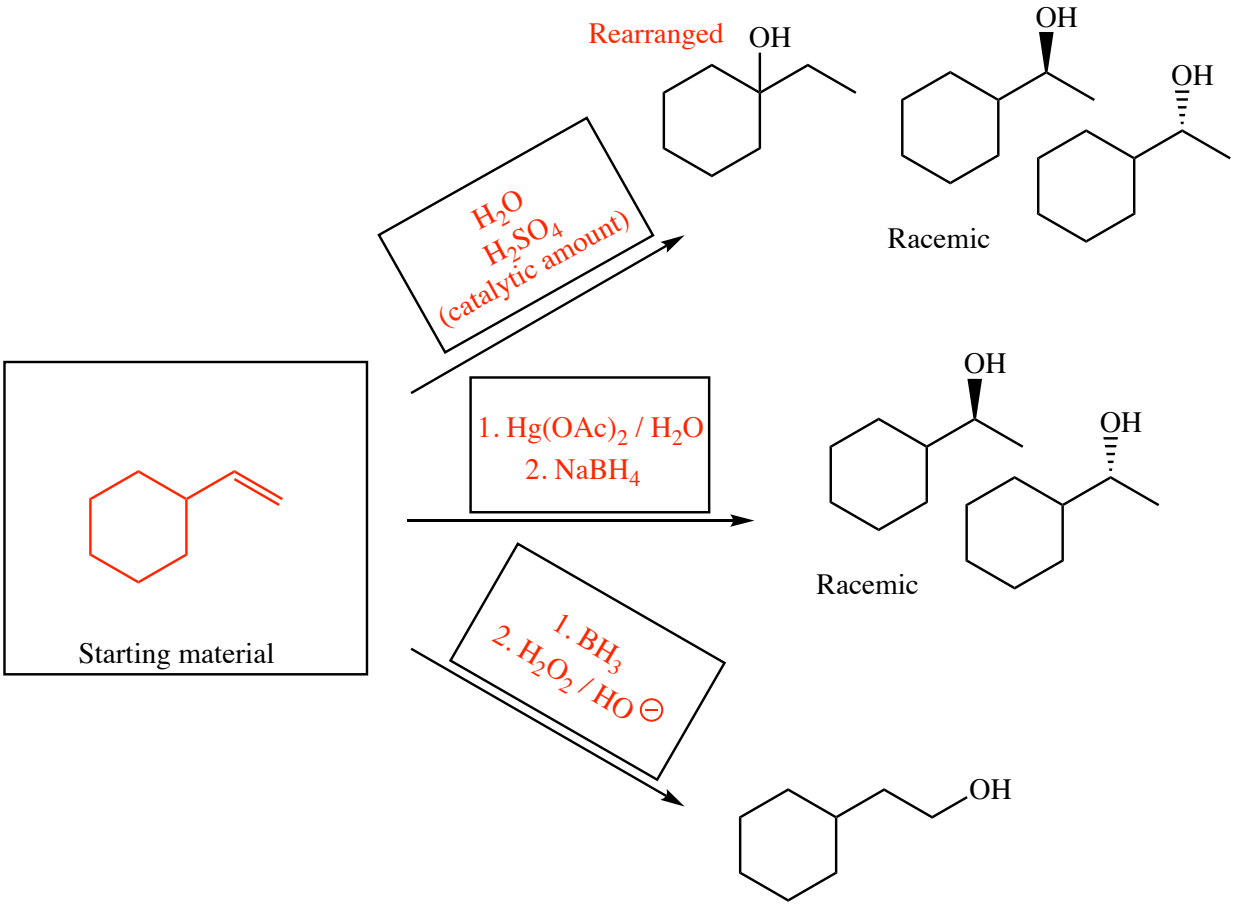
**(2 pts) Will the product mixture you drew to the right rotate the plane of plane polarized light?**

**No**

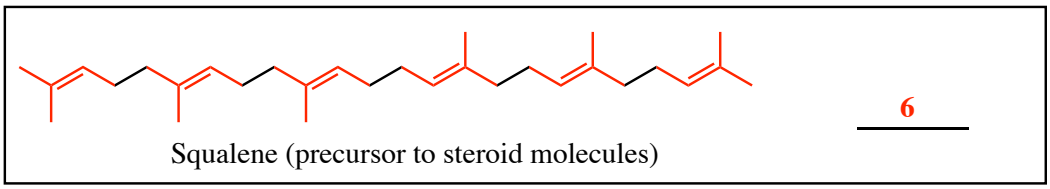
**16.** (15 pts total) **The point of organic chemistry is synthesis**, the conversion of simpler molecules to more complicated ones with enhanced structure and function. Each reaction you are learning should be thought of as a "tool" that allows you to create a desired type of molecule. These tools 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!!



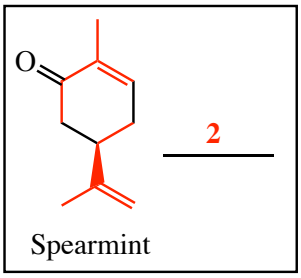
**17.** (9 pts total) It is important to think about reactions in both directions. To solve synthesis questions you will need to work backwards from a target molecule. All three reactions shown below use the same starting material. **Write the structure of that starting material in the box provided on the left, then write the appropriate reagents in the boxes over each arrow. All** observed products are shown for each reaction.



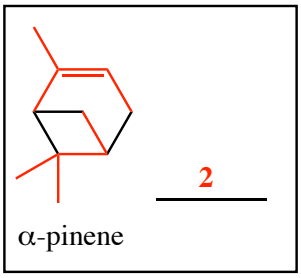

**18.** (6 pts total) On the line provided next to each terpene, **indicate the number of isoprene units contained within that structure**. You do not have to indicate where they are.



Squalene (precursor to steroid molecules) **6**

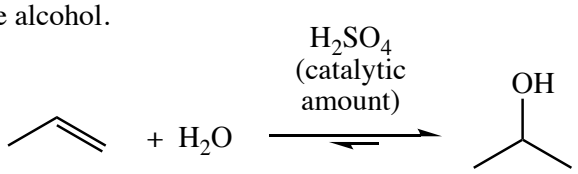



Spearmint **2**

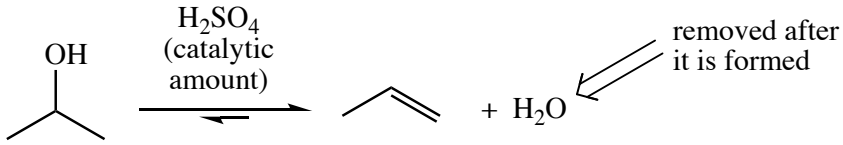


α-pinene **2**

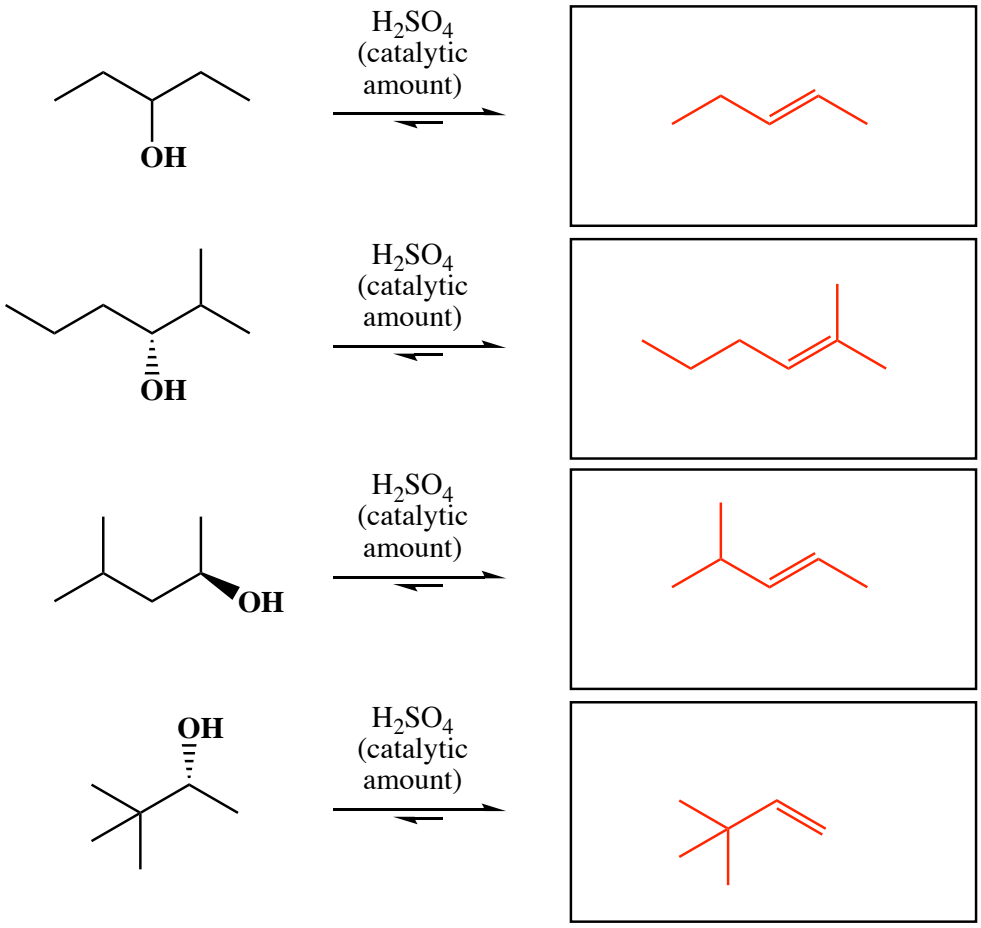
**19. (16** pts) Here is an "apply what you know" question. You already know enough to answer this, but you will have to rely on your increasing chemical intuition to get all of the answers correct. Many chemical reactions are reversible. Chemists can modify the conditions of the reaction to favor euqilibrium in either direction. You have already learned about your first useful reversible reaction, the acid-catalyzed hydration reaction of alkenes. If you place an alkene in excess water and add a catalytic amount of $H_2SO_4$, equilibrium favors formation of the alcohol.



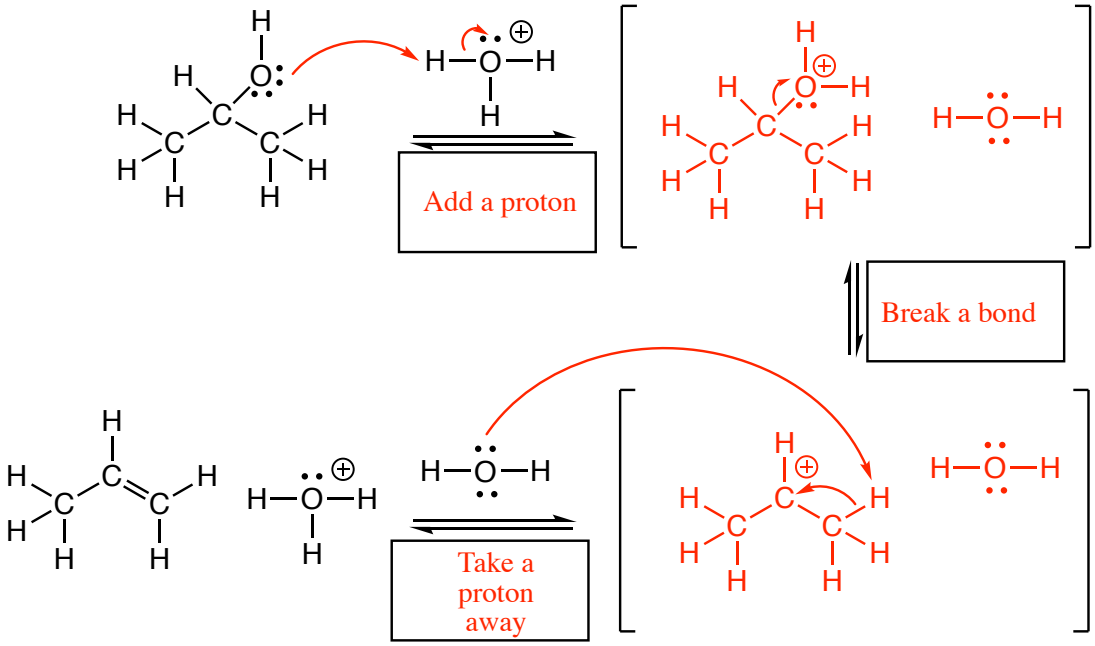

On the other hand, if you place an alcohol in the presence of a catalytic amount of $H_2SO_4$ and remove water after it forms, equilibrium favors formation of the alkene.




The key new idea is that when there is an option, the most stable possible alkene is created in this reaction. Use what you know about alkene stability to predict the predominant product of each reaction.



**20.** (15 pts) You will learn soon that reversible reactions follow the same mechanism in both directions. Think about that for a moment, then, use what you know about the acid-catalyzed hydration of alkenes to predict the mechanism of the reverse 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. The two intermediates are identical to those in the alkene hydration reaction mechanism you learned (but in reverse order), so you know there is a carbocation in one of them! In the boxes provided next to each arrow, indicate which of the four most common mechanistic elements describe that step (make a bond, etc.)




**21.** (8 pts) Challenge question, save until the end. Fill in the box with the product(s) that are missing from the chemical reaction equation. **Draw only the predominant regioisomer product or 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**.