| NAME (Print): | Chemistry 320M/328M |
|---------------|---------------------|
| | Dr. Brent Iverson |
| | 2nd Midterm |
| SIGNATURE: | October 24, 2019 |
| | |

EID: _____

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.

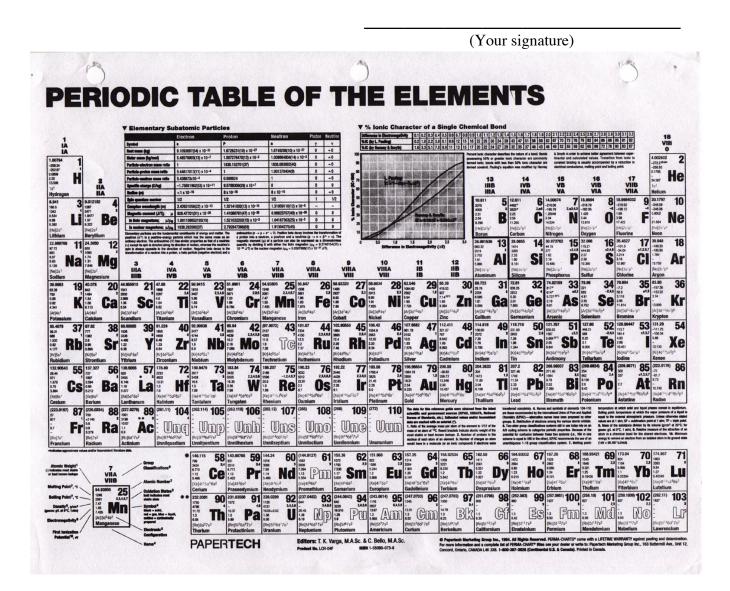
Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.

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) |
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| 11 | | (25) |
| 12 | | (18) |
| 13 | | (15) |
| 14 | | (15) |
| 15 | | (16) |
| 16 | | (23) |
| Total | | (321) |

Student Honor Code

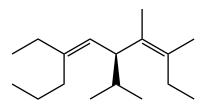
"As a student of The University of Texas at Austin, I shall abide by the core values of the University and uphold academic integrity."

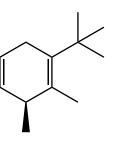


| Compo | ound | рК _а |
|----------------------|---|-----------------|
| Hydrochloric acid | H-CI | -7 |
| Protonated alcohol | ⊕ RCH₂O <mark>H₂</mark> | -2 |
| Hydronium ion | <mark>H</mark> ₃O [⊕] O | -1.7 |
| Carboxylic acids | O ∥ R−CO- <u>H</u> | 3-5 |
| Thiols | RCH₂S <mark>H</mark> | 8-9 |
| Ammonium ion | <u>H</u> ₄N [⊕] | 9.2 |
| β -Dicarbonyls | O O ∥ ∥ RC−C <mark>H₂</mark> ·CR' | 10 |
| Primary ammonium | | 10.5 |
| β-Ketoesters | 0 0 RC-C <mark>H</mark> 2 COR' | 11 |
| β-Diesters | 0 0 ROC-C <mark>H</mark> 2·COR' | 13 |
| Water | = HO <mark>H</mark> | 15.7 |
| Alcohols | RCH ₂ O <u>H</u> | 15-19 |
| Acid chlorides | RC <mark>H</mark> 2-CCI | 16 |
| Aldehydes | RC <u>H₂</u> -CH O | 18-20 |
| Ketones | ∬ RC <u>H</u> ₂-CR' | 18-20 |
| Esters | O RC <u>H</u> 2-COR' | 23-25 |
| Terminal alkynes | RC≡C— <u>H</u> | 25 |
| LDA | <u>H</u> -N(<i>i-</i> C ₃ H ₇) ₂ | 40 |
| Terminal alkenes | R₂C=C− <u>H</u> H | 44 |
| Alkanes | CH₃CH₂- <mark>H</mark> | 51 |

1. (2 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 or R and S.





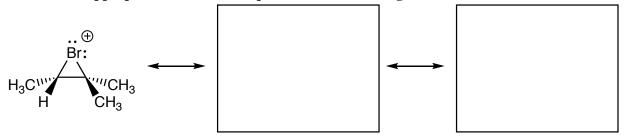
3. (6 pts) Draw the structure that corresponds to the following name:



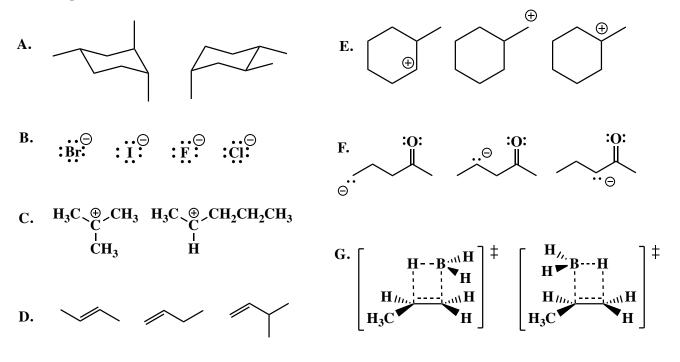
4. (6 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges. For the two structures on the left in each problem, use arrows to indicate the movement of electrons to give the structures you drew. There is no need to draw any circles around any of these contributing structures. 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 contribution 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.

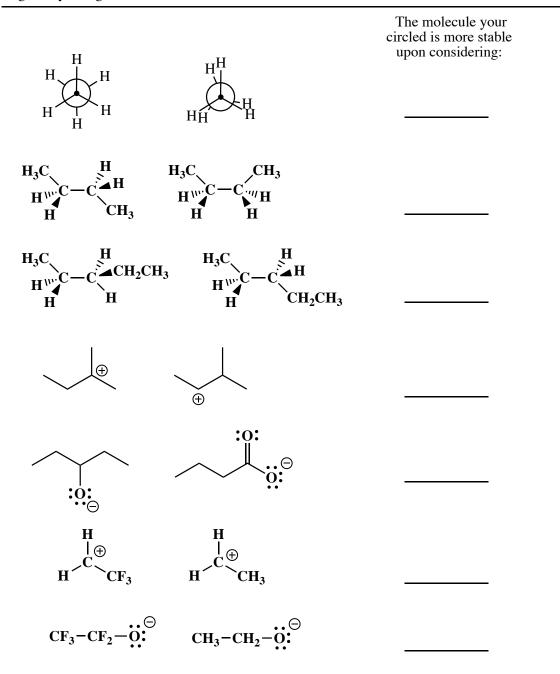


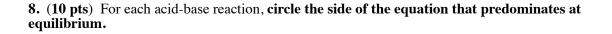
6. (14 pts) For each set of molecules or ions drawn below, circle the one that is the MOST stable.

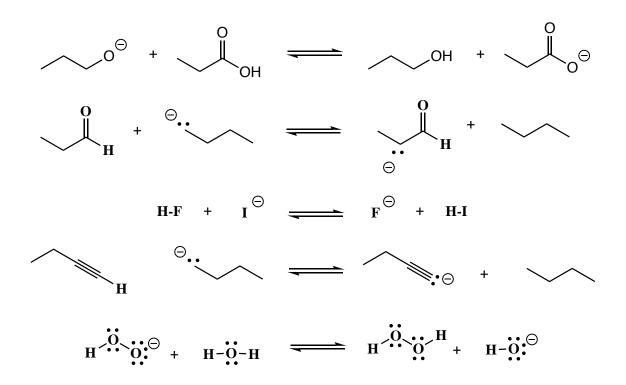


| Signature | | | | Pg 3(2 | :4) |
|---|--|-----------------------------|-----------------------------|--|-----|
| principles we have discu letter corresponding to | ssed. Circle the more the principle or princ | stable molectiples (yes the | ule. Then, i re can be m | y) because of one or more in the space provided, write the ore than one!) that explain ear is slightly different than las | |
| A. Steric Strain | B. Angle Strain | C. Torsional | Strain | D. The inductive effect | |
| E. Hyperconjugation | F. Delocalization over more atoms | of a charge | | zation of pi electron density over wo atoms ("pi-way") | r |

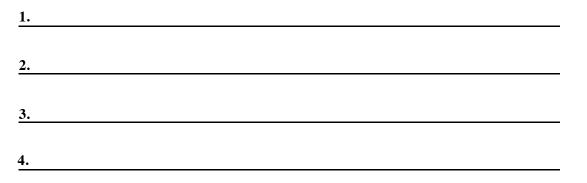
H. Greater s-character of the orbital containing an electron pair on a negatively-charged atom **I.** The negative charge is on a more electronegative element **J.** The negative charge is on a larger atom







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:



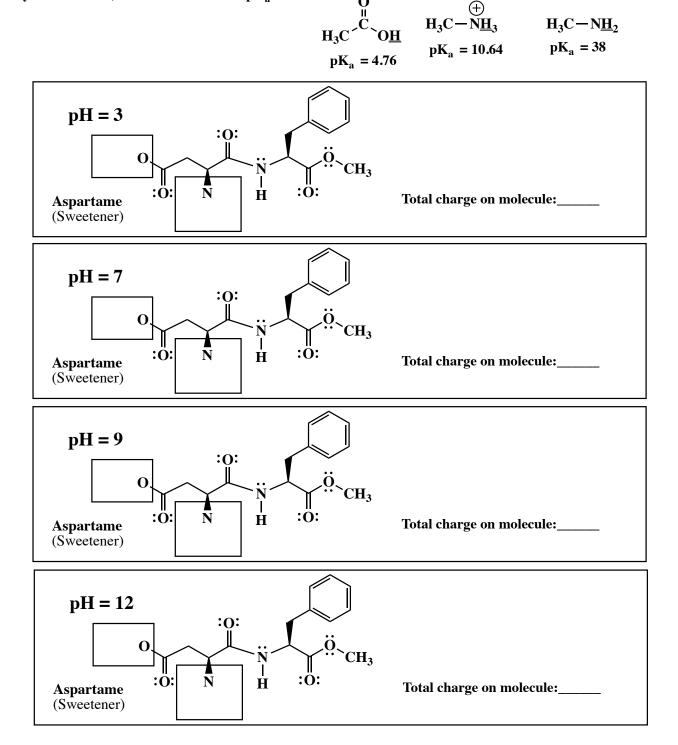
10. (**2 pts each**) List the two most common electron **sources** for mechanism arrows that we have seen so far this semster:

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.

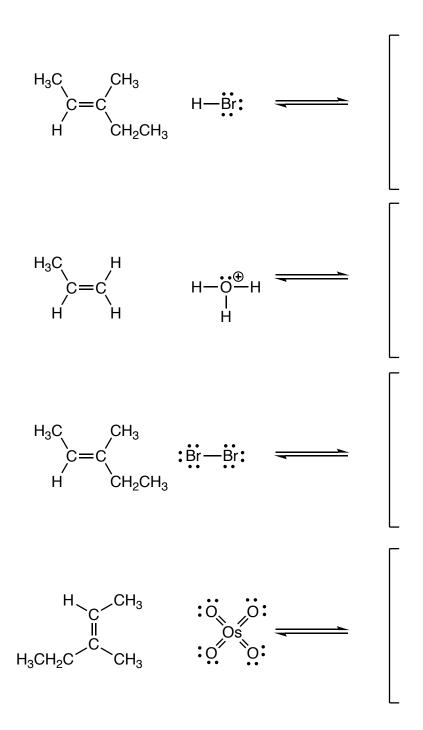
Letter of the word best fitting the definition

| | | Syn (Q) | Terpene (R) | e Trans (S) | Running (T) | |
|---|---|---------------------|----------------|--------------------|---------------------------|--------------------|
| Oxidation (L | | Reduction ro (M) | eaction | Regiochemis (N) | stry Stereochemist (O) | ry Steroid (P) |
| Hypercon (G | ijugation F) | Inductive e (H) | effect | Lipid (I) | Meso compound (J) | Nucleophile (K) |
| Addition (A | | Anti (B) | Cis 1 (C) | Diastereome (D) | rs Electrophile (E) | Enantiomer (F) |
| A molecule with two or more chiral centers yet is not chiral because it contains a symmetry element, usually a plane of symmetry. | | | | | | |
| Molecules that are stereoisomers but not enantiomers; a situation that arises when there is more than one chiral center in the same molecule. | | | | | | |
| — | A molecule that cannot be superimposed on its mirror image (it does not have a plane or center of symmetry). | | | | | |
| | Involves a ne | et gain of elect | rons and rej | places C-O or | r pi bonds with C-H bo | nds. |
| | Involves a net loss of electrons and replaces C-H bonds with C-O bonds or pi bonds. | | | | | |
| | Means that the reaction. | he atoms add t | o the same s | side of a C=C | C double bond during a | chemical |
| | Means that the | he atoms add t | o either side | e of a C=C do | ouble bond during a che | emical reaction. |
| | The analysis made in a rea | | e possible c | constitutional | isomes (also called reg | gioisomers) are |
| | Adjacent sig empty 2p ort | | n attached a | lkyl groups o | overlap and share electro | on density with |
| | 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. | | | | | |
| | Contains an electron rich source for a bond forming process. Analogous to a Lewis base | | | | | |
| | Complex natural molecules that are built from 5 carbon "isoprene" units in Nature, | | | | | |
| T | Is a great way to stay healthy and deal with the stress of midterms. | | | | | |

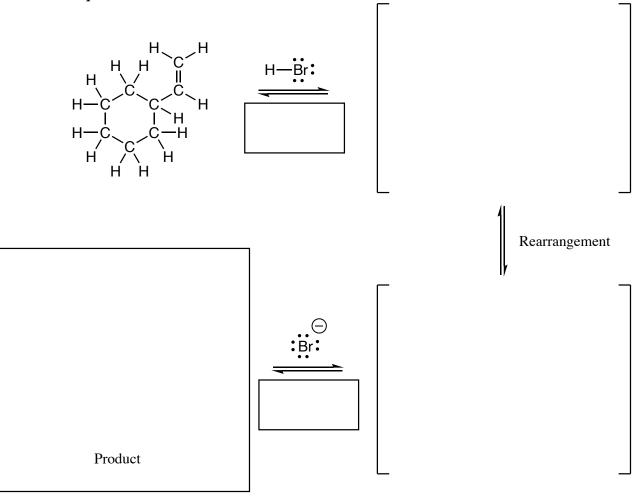
12. (20 pts) Complete the following four structures by adding appropriate numbers of lone pair electrons, H atoms, and formal charges to the atoms in the boxes. You must adjust your answers to indicate the predominant species at each indicated pH value. (You do not have to add anything such as H atoms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



13. (25 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. (16 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.

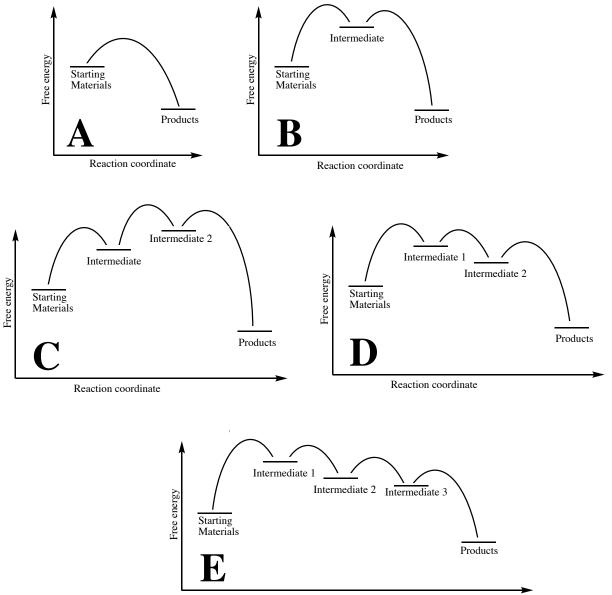


(2 pts) How many total stereoisomers are produced by this reaction?

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

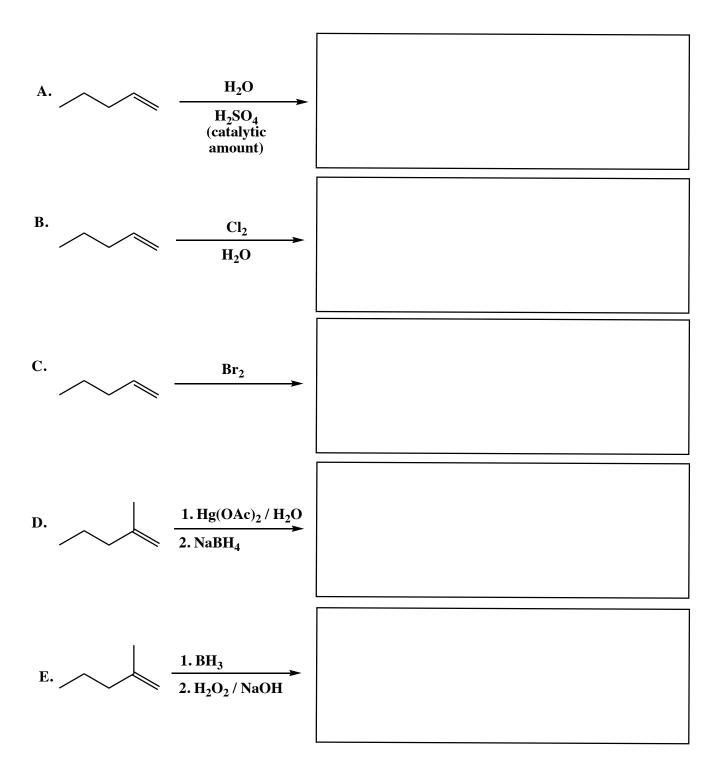
(2 pts) As the reaction proceeds, does the pH of the solution increase, decrease, or stay the same?

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

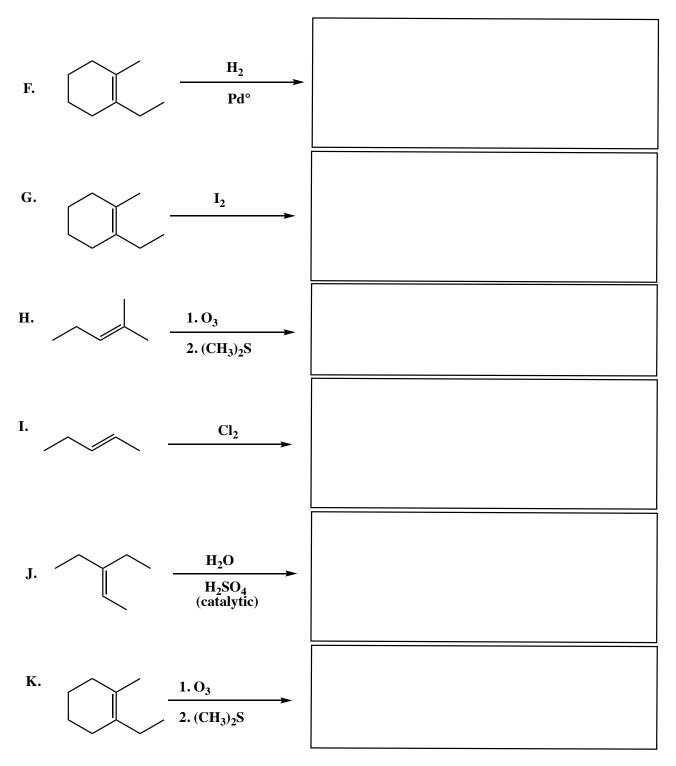


Reaction coordinate

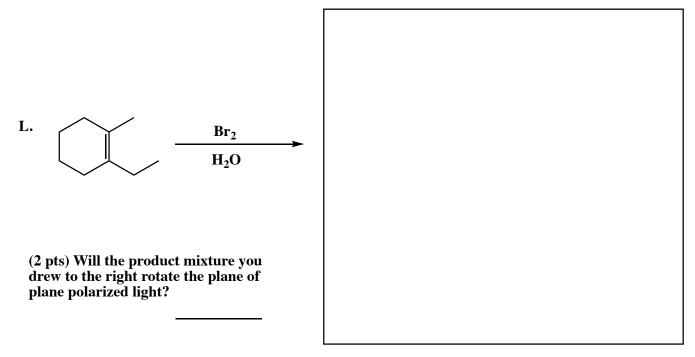
15. (23 pts) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products and please remember that you must draw the structures of all the product stereoisomers 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.

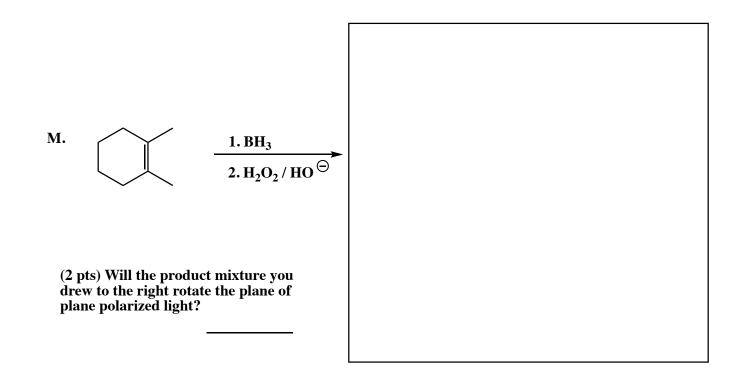


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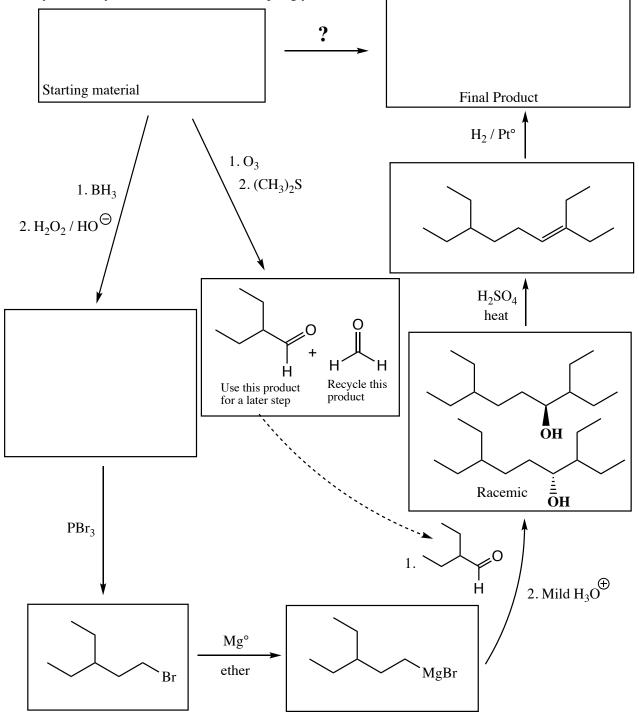


15. The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products if relevant and please remember that you must draw the structures of all the product stereoisomers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

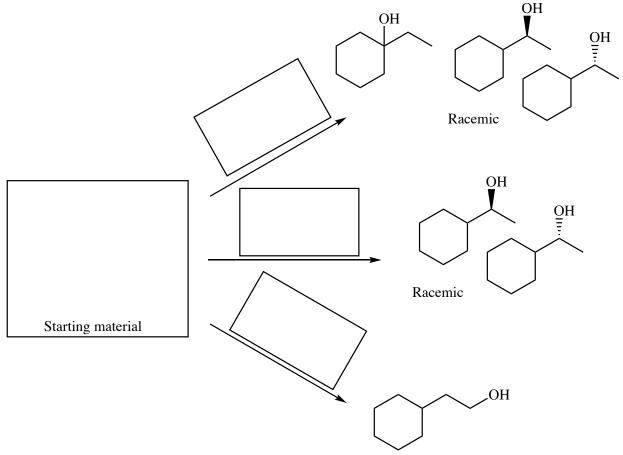




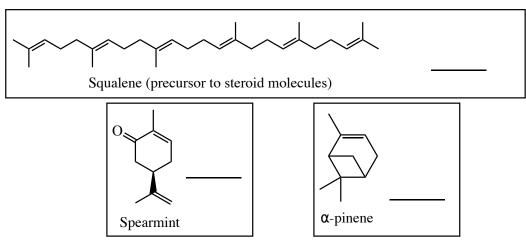
16. (15 pts total) The point of organic chemistry is synthesis, the conversion of simpler molecules to more complicated ones with enhanced structure and function. Each reaction you are learning should be thought of as a "tool" that allows you to create a desired type of molecule. These tools can be used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



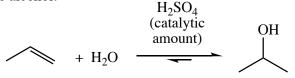
17. (9 pts total) It is important to think about reactions in both directions. To solve synthesis questions you will need to work backwards from a target molecule. All three reactions shown below use the same starting material. Write the structure of that starting material in the box provided on the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



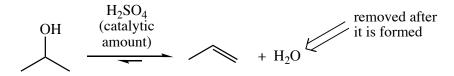
18. (6 pts total) On the line provided next to each terpene, **indicate the number of isoprene units contained within that structure**. You do not have to indicate where they are.

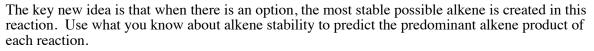


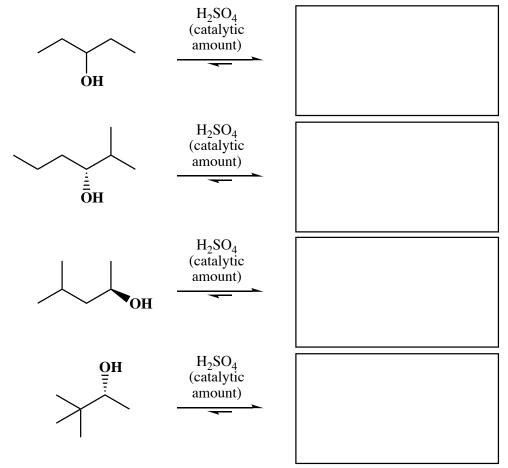
19. (16 pts) Here is an "apply what you know" question. You already know enough to answer this, but you will have to rely on your increasing chemical intuition to get all of the answers correct. Many chemical reactions are reversible. Chemists can modify the conditions of the reaction to favor euqilibrium 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.

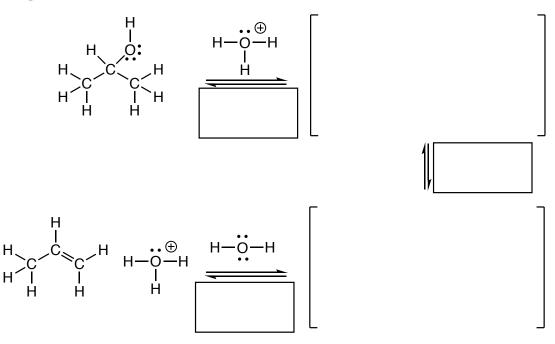






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20. (15 pts) You will learn soon that reversible reactions follow the same mechanism in both directions. Think about that for a moment, then, use what you know about the acid-catalyzed hydration of alkenes to predict the mechanism of the reverse reaction. Be sure to show arrows to indicate movement of <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. 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.

| RES. | |
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