NAME (Print): _____

EID _____

SIGNATURE: _____

Chemistry 320M/328M
Dr. Brent Iverson
2nd Midterm
October 20, 2022

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. 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 before 9 PM.

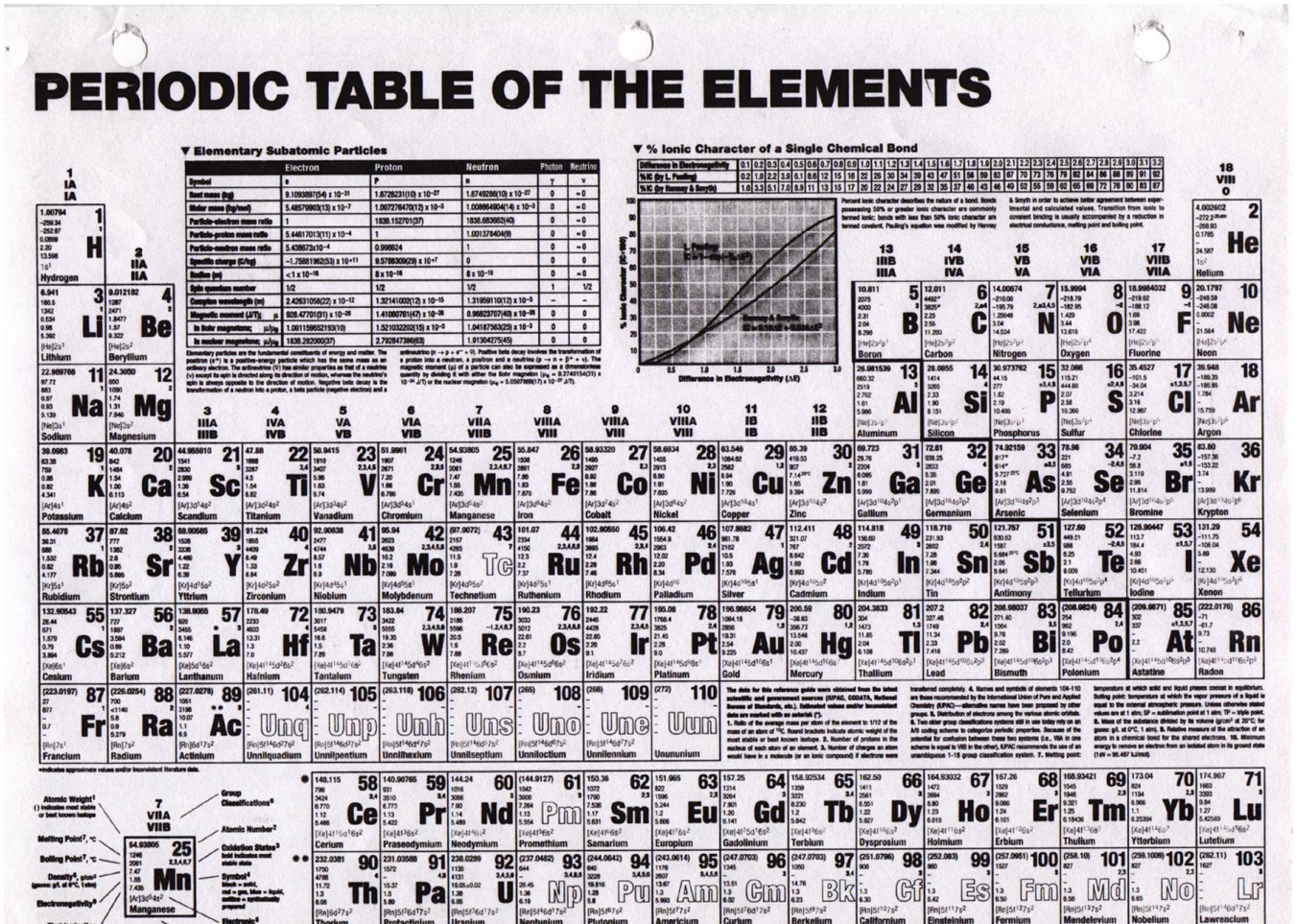
FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

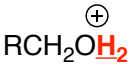
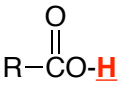
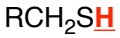
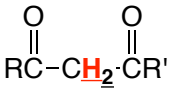
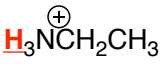
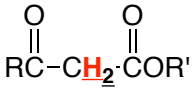
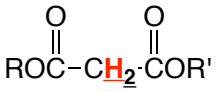
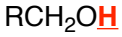
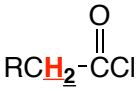
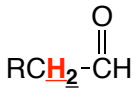
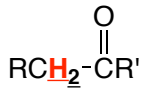
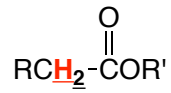
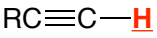
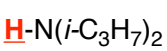
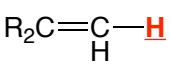
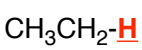
Student Honor Code

“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)



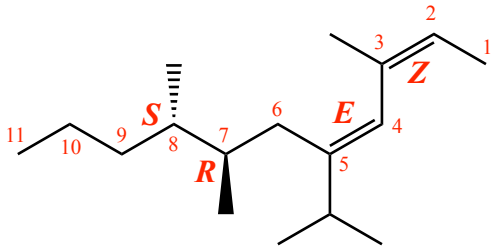
Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Carboxylic acids		3-5
Thiols		8-9
Ammonium ion		9.2
β-Dicarbonyls		10
Primary ammonium		10.5
β-Ketoesters		11
β-Diesters		13
Water		15.7
Alcohols		15-19
Acid chlorides		16
Aldehydes		18-20
Ketones		18-20
Esters		23-25
Terminal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



(2*Z*,4*E*,7*R*,8*S*)-5-isopropyl-3,7,8-trimethyl-2,4-undecadiene
(2*Z*,4*E*,7*R*,8*S*)-3,7,8-trimethyl-5-(1–methylethyl)-2,4-undecadiene

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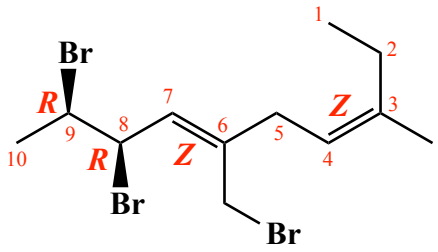

(3*Z*,6*Z*,8*R*,9*R*)-8,9-dibromo-6-(bromomethyl)-3-methyl-3,6-decadiene

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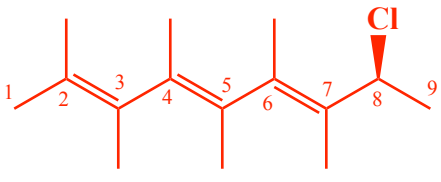
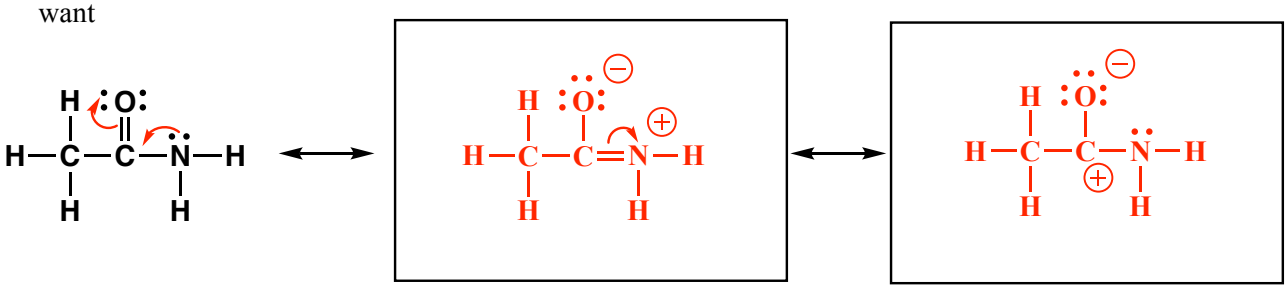
3. (6 pts) Draw the structure that corresponds to the following name:

(4*E*,6*E*,8*S*)-8-chloro-2,3,4,5,6,7-hexamethyl-2,4,6-nonatriene

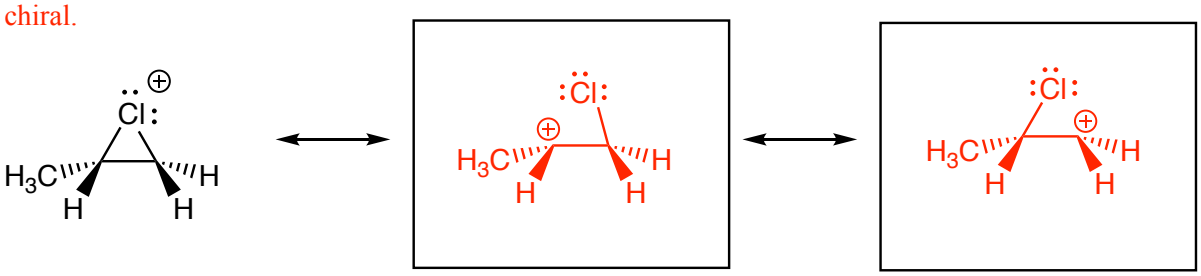


4. (9 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges. For the two structures on the left in each problem, **use arrows to indicate the movement 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



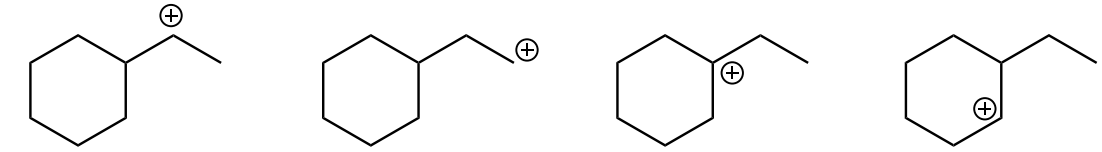
5. (7 pts) Draw the two other most important contributing structures for the chloronium ion. You do NOT need to draw arrows on any of the structures for this problem. **Because this is a mechanism type question, use wedges and dashes to indicate stereochemistry, write "racemic" if appropriate, draw all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

Note we drew only one enantiomer, so racemic is not appropriate here even though the intermediate is chiral.

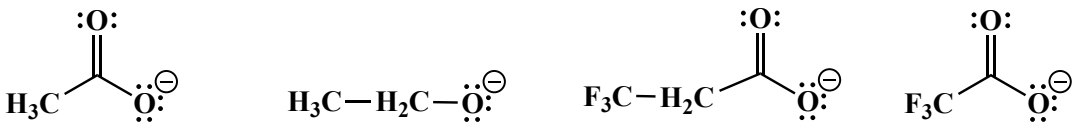


○ **Most important (major)** ● **Most important (major)** ○ **Most important (major)**

6. (4 pts each) For the following two lists of structures, fill in the circles to indicate which structure is the most stable and which is the least stable. You do not have to fill in any circles for molecules of intermediate stability.



○ **Most Stable** ○ **Least Stable** | ○ **Most Stable** ● **Least Stable** | ● **Most Stable** ○ **Least Stable** | ○ **Most Stable** ○ **Least Stable**



○ **Most Stable** ○ **Least Stable** | ○ **Most Stable** ● **Least Stable** | ○ **Most Stable** ○ **Least Stable** | ● **Most Stable** ○ **Least Stable**

7. (24 pts) For each pair of molecules, one is more stable (lower in energy) because of one or more principles we have discussed. Fill in the circle to indicate which molecule is the more or most stable. Then fill in the circle next to the letter corresponding to the principle or principles (yes there can be more than one!) that explain(s) why the molecule you circled is more stable.

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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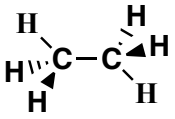
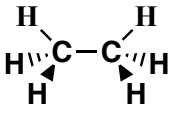


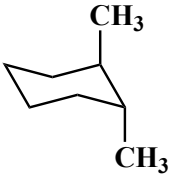
● More Stable



○ More Stable

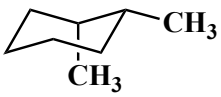
The molecule you indicated is more/ most stable upon primarily considering:

○A. ○B. ●C. ○D. ○E.
○F. ○G. ○H. ○I. ○J.



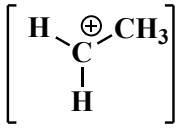
○ Most Stable

● Most Stable

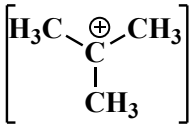


○ Most Stable

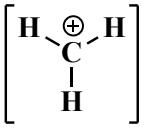
●A. ○B. ○C. ○D. ○E.
○F. ○G. ○H. ○I. ○J.



○ Most Stable

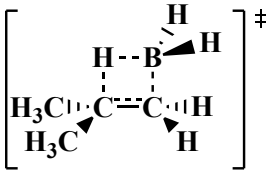


● Most Stable



○ Most Stable

○A. ○B. ○C. ●D. ●E.
○F. ○G. ○H. ○I. ○J.



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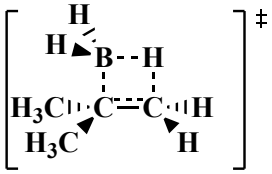
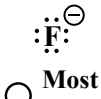


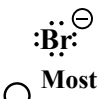
○ More Stable

●A. ○B. ○C. ○D. ○E.
○F. ○G. ○H. ○I. ○J.



○ Most Stable

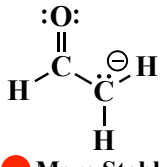
○ Most Stable



○ Most Stable

● Most Stable

○A. ○B. ○C. ○D. ○E.
○F. ○G. ○H. ○I. ●J.



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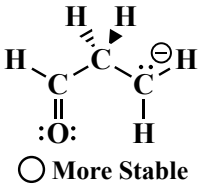


○ More Stable

○A. ○B. ○C. ○D. ○E.
●F. ●G. ○H. ○I. ○J.

8. (6 pts) Fill in the circle next to the word that best completes these sentences.

In mechanisms, arrows are used to indicate the movement of ◯ **protons** ◯ **atoms** ● **electrons**

Arrows always start at an electron ● **source** ◯ **sink** **and always point toward an electron** ◯ **source** ● **sink**.

In the mechanisms we have seen so far:

The pi bonds of alkenes have been an electron ● **source** ◯ **sink** .

Carbocations have been an electron ◯ **source** ● **sink** .

The lone pair of electrons on water have been an electron ● **source** ◯ **sink** .

9. (10 pts) The four most common mechanism elements are listed below.

A. Make a bond. B. Break a bond. C. Add a proton. D. Take a proton away.

The following statements describe the reactants you might encounter in a step of a mechanism. Based on the reactants listed, **fill in the circle next to the letter corresponding to the common mechanism element (as listed above) that would happen next in that mechanism.**

1. A strong acid is present and the carbon-containing molecule can accept a proton — ◯ **A.** ◯ **B.** ● **C.** ◯ **D.**

2. The carbon-containing molecule is a strong acid — ◯ **A.** ◯ **B.** ◯ **C.** ● **D.**

3. A strong base is present and the carbon-containing molecule has a proton that can be removed. — ◯ **A.** ◯ **B.** ◯ **C.** ● **D.**

4. There is both a nucleophile and an electrophile present — ● **A.** ◯ **B.** ◯ **C.** ◯ **D.**

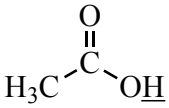
5. There is not a nucleophile and electrophile, a strong acid or strong base, the carbon-containing molecule is not a strong acid or base, but it can break a bond to give stable molecules or ions. — ◯ **A.** ● **B.** ◯ **C.** ◯ **D.**

10. (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 best 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.

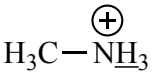
Letter of the word best fitting the definition	
U	Is a great way to stay healthy and deal with the stress of midterms.
M	Contains an electron rich source for a bond forming process. Analogous to a Lewis base
E	Contains an electron deficient atom that serves as the electron sink in a bond forming process (Analogous to a Lewis acid) or possesses a weak bond that breaks to make a stable ion or fragment.
K	Predicts that when HBr adds to an alkene, the Br atom ends up on the more highly substituted C atom.
H	Carbocations are stabilized by alkyl groups through hyperconjugation in addition to this effect.
R (C is OK)	Means that the atoms add only to the same side of a C=C double bond during a chemical reaction with an alkene.
B (T is OK)	Means that the atoms add only to the opposite sides of a C=C double bond during a chemical reaction with an alkene.
N	Involves a net loss of electrons and replaces C-H bonds with C-O bonds or pi bonds.
O	Involves a net gain of electrons and replaces C-O or pi bonds with C-H bonds.
G	A stabilizing interaction that involves the overlap of adjacent sigma bonds with an empty 2p orbital.

Addition reaction (A)	Anti (B)	Cis (C)	Diastereomers (D)	Electrophile (E)	Enantiomer (F)
Hyperconjugation (G)	Inductive effect (H)	Lewis Acid (I)	Lewis Base (J)	Markovnikov's Rule (K)	
Meso compound (L)	Nucleophile (M)	Oxidation reaction (N)	Reduction reaction (O)		
Regiochemistry (P)	Stereochemistry (Q)	Syn (R)	Terpene (S)	Trans (T)	Running (U)

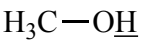
11. (15 pts) Complete the following four structures by adding appropriate numbers of lone pair electrons, H atoms, and formal charges to the atoms in the boxes. You must adjust your answers to indicate the predominant species at each indicated pH value. (You do not have to add anything such as H atoms 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

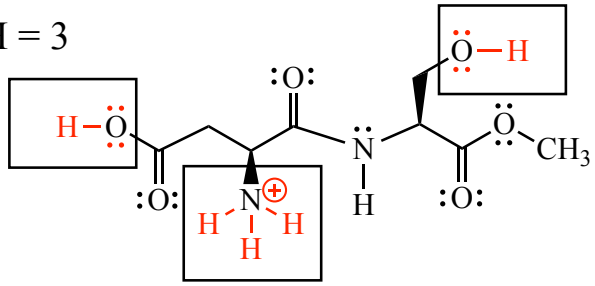


pK_a = 10.64



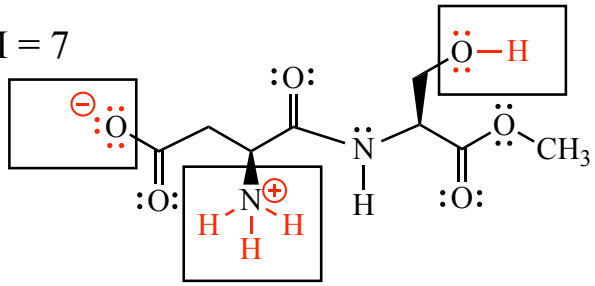
pK_a = 16

pH = 3



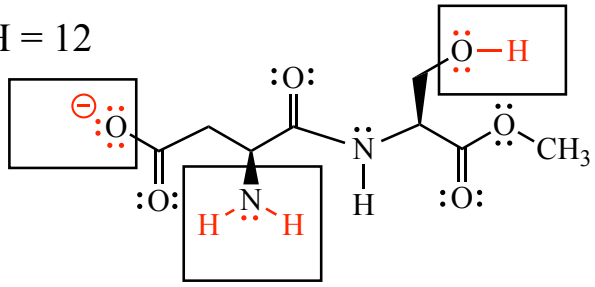
Total charge on molecule: 1

pH = 7



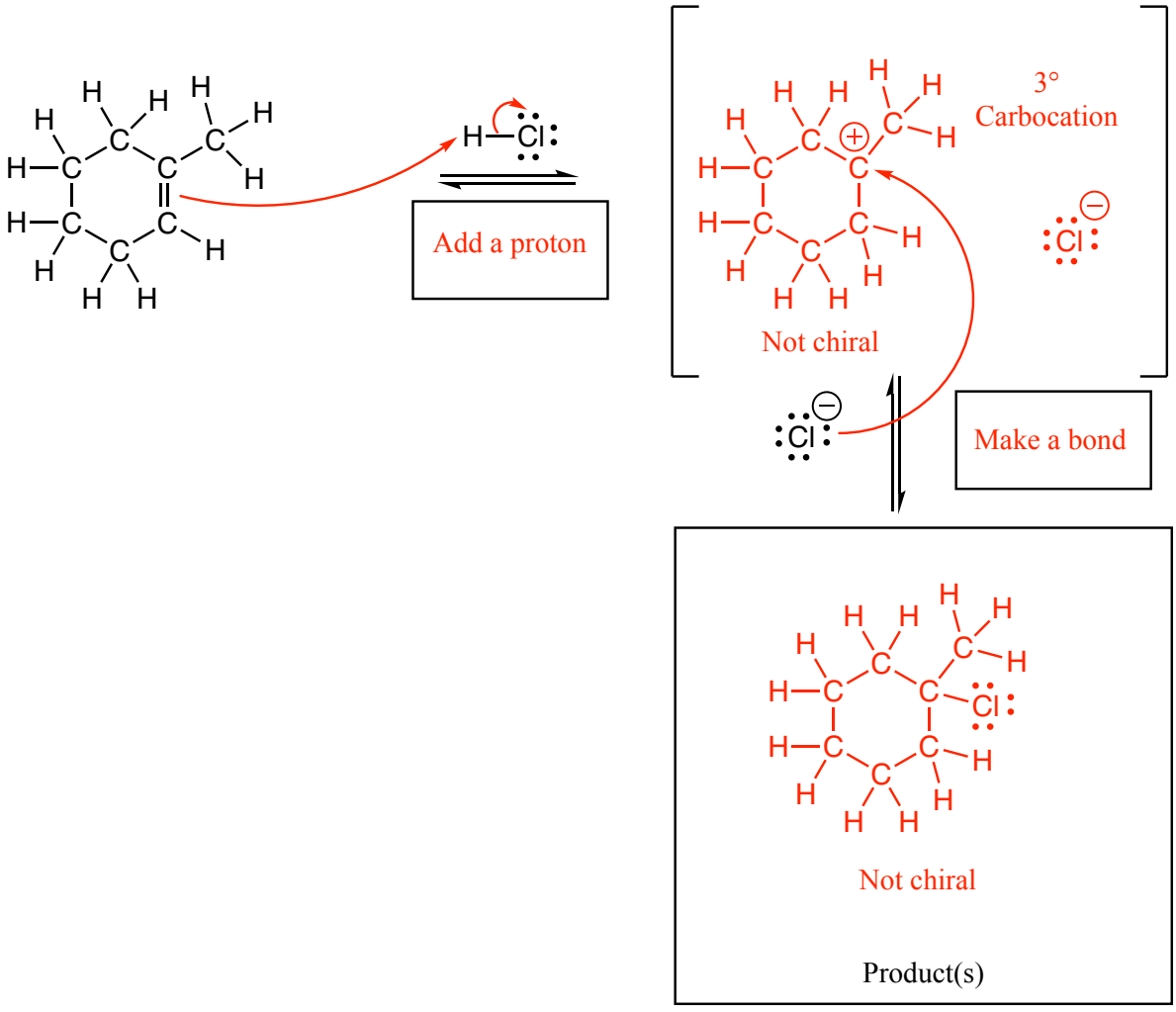
Total charge on molecule: 0

pH = 12



Total charge on molecule: - 1

12. (18 pts) Complete the mechanism for the following reaction of an alkene with HCl. **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 under/ beside 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.**

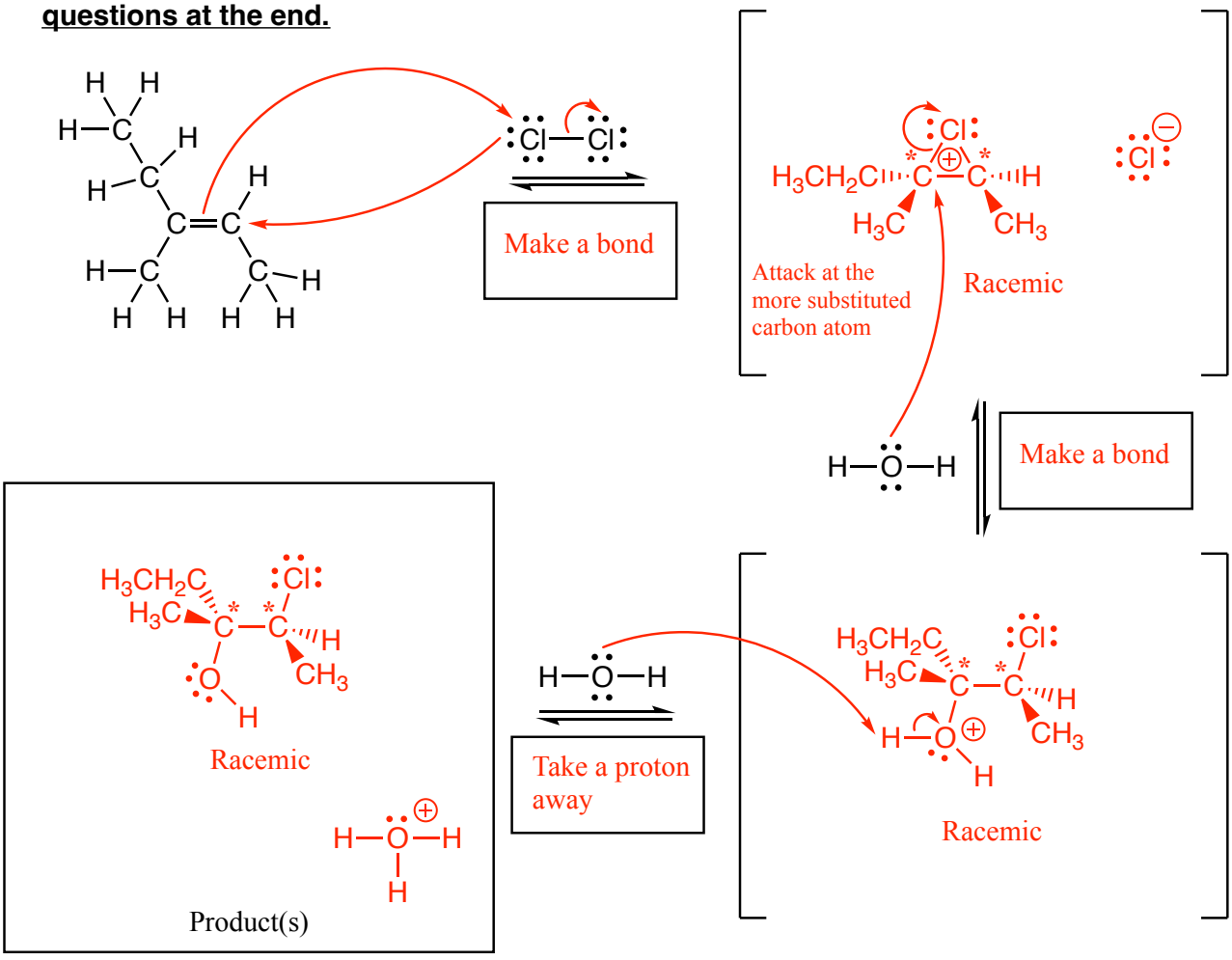


(2 pts) How many total stereoisomers are produced by this reaction? **1 (Not chiral)**

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

(2 pts) As the reaction proceeds, does the pH of the solution increase, decrease, or stay the same? **Increase (as HCl is used up)**

13. (32 pts) Complete the mechanism for the following reaction of an alkene with Cl_2 in the presence of H_2O. **Be sure to show arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **YOU ONLY NEED TO DRAW ONE STEREOISOMER OF A CHIRAL INTERMEDIATE OR PRODUCT (using wedges and dashes as appropriate) IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. In the boxes provided under/beside the arrows, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.). <u>Be sure to notice the questions at the end.</u>**

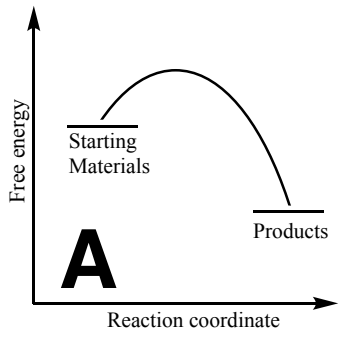


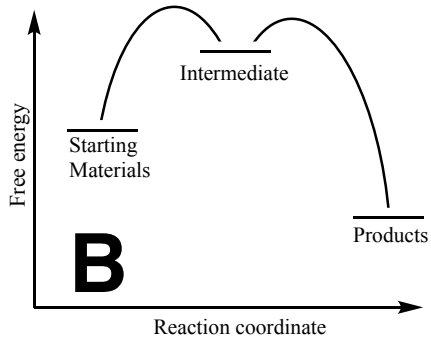
(2 pts) How many total stereoisomers are produced by this reaction? **2 (*S,R* and *R,S*)**

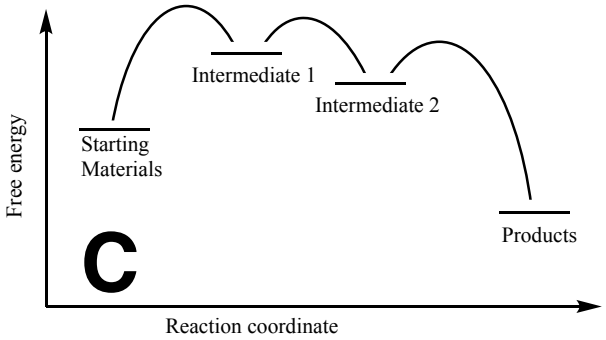
(2 pts) Look as the energy diagrams on page 9. Write the letter of the one that best describes the above mechanism. **C**

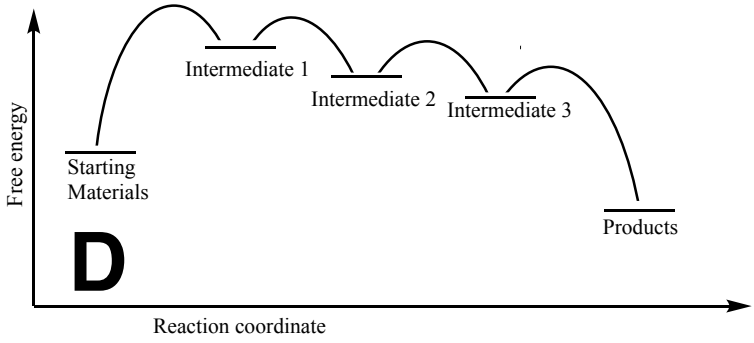
(2 pts) As the reaction proceeds, does the pH of the solution increase, decrease, or stay the same? **Decrease (as H_3O^+ is produced)**

These energy diagrams refer to the mechanism your completed in problems 12 and 13 on pages 7 and 8. This page is not graded.

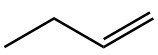








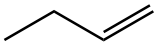
14. (3 or 5 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products and please remember that you must draw the structures of all the product 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. 

HBr

Markovnikov
Mixed

Racemic

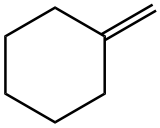
B. 

Markovnikov
Mixed

H_2O

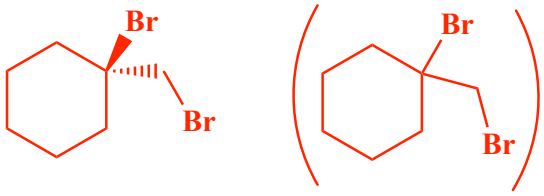
H_2SO_4
(catalytic
amount)

Racemic

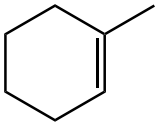
C. 

Br_2

Anti

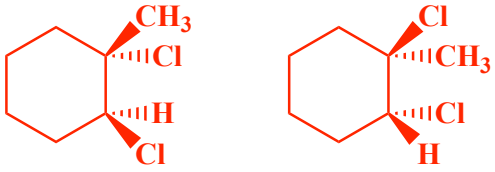


Not chiral

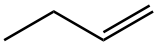
D. 

Cl_2

Anti



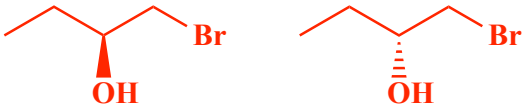
Racemic

E. 

Br_2

H_2O

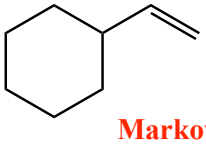
Markovnikov
Anti



Racemic

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

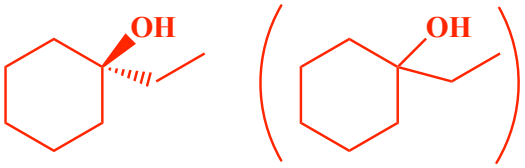
This one rearranges, draw only the rearranged product(s)

F. 

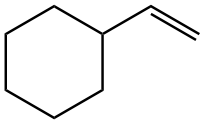
H_2O

H_2SO_4 (catalytic)

Markovnikov
Mixed



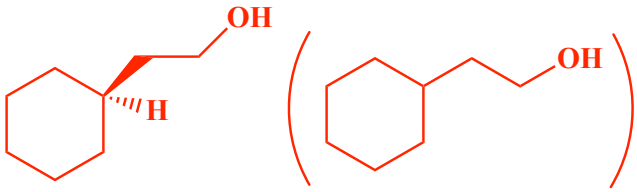
Not Chiral

G. 

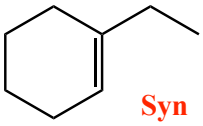
1. BH_3

2. H_2O_2 / NaOH

non-Markovnikov
Syn



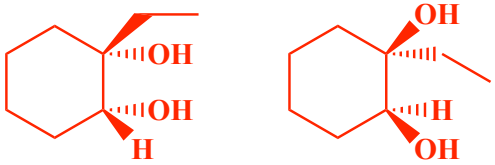
Not Chiral

H. 

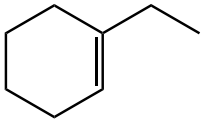
Syn

1. OsO_4

2. $NaHSO_3$ / H_2O



Racemic

I. 

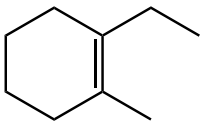
1. BH_3

2. H_2O_2 / NaOH

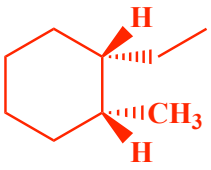
non-Markovnikov
Syn

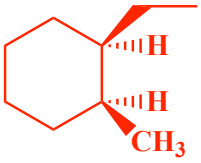
Racemic

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

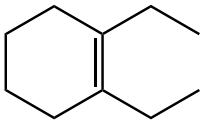
J. 

H_2 / Pt° / Syn

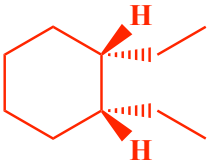




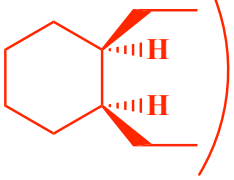
Racemic

K. 

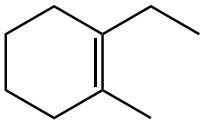
H_2 / Pt° / Syn



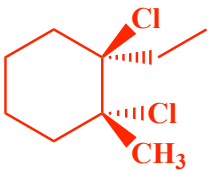
Same as

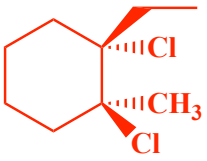


Not Chiral

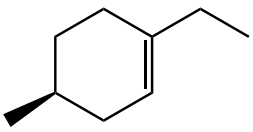
L. 

Cl_2 / Anti

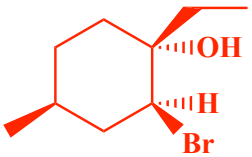


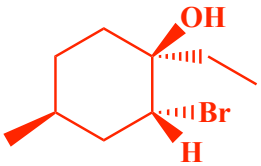


Racemic

M. 

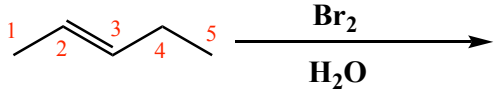
Br_2 / H_2O / Markovnikov Anti

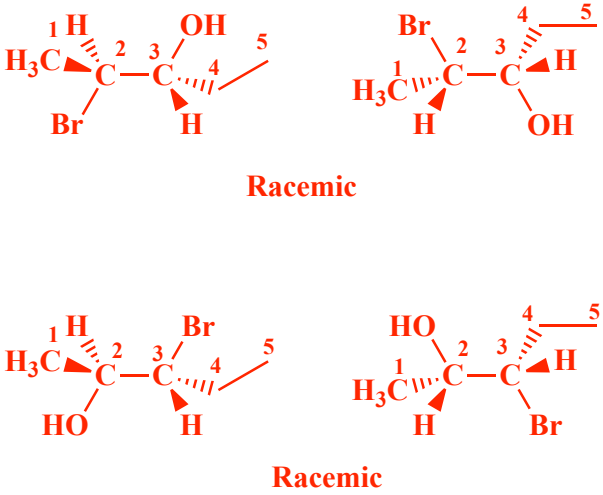




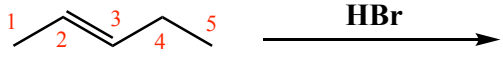
This is not racemic because these are diastereomers.

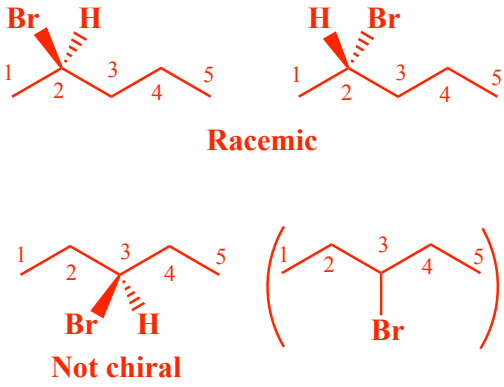
14. (9 or 11 pts each) The following reactions all involve chemistry of alkenes. Fill in the box with the product(s) that are missing from the chemical reaction equations. Draw only the predominant regioisomer product or products if relevant and please remember that you must draw the structures of all 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.

N. 



(2 pts) Will the product mixture you drew to the right rotate the plane of plane polarized light? No

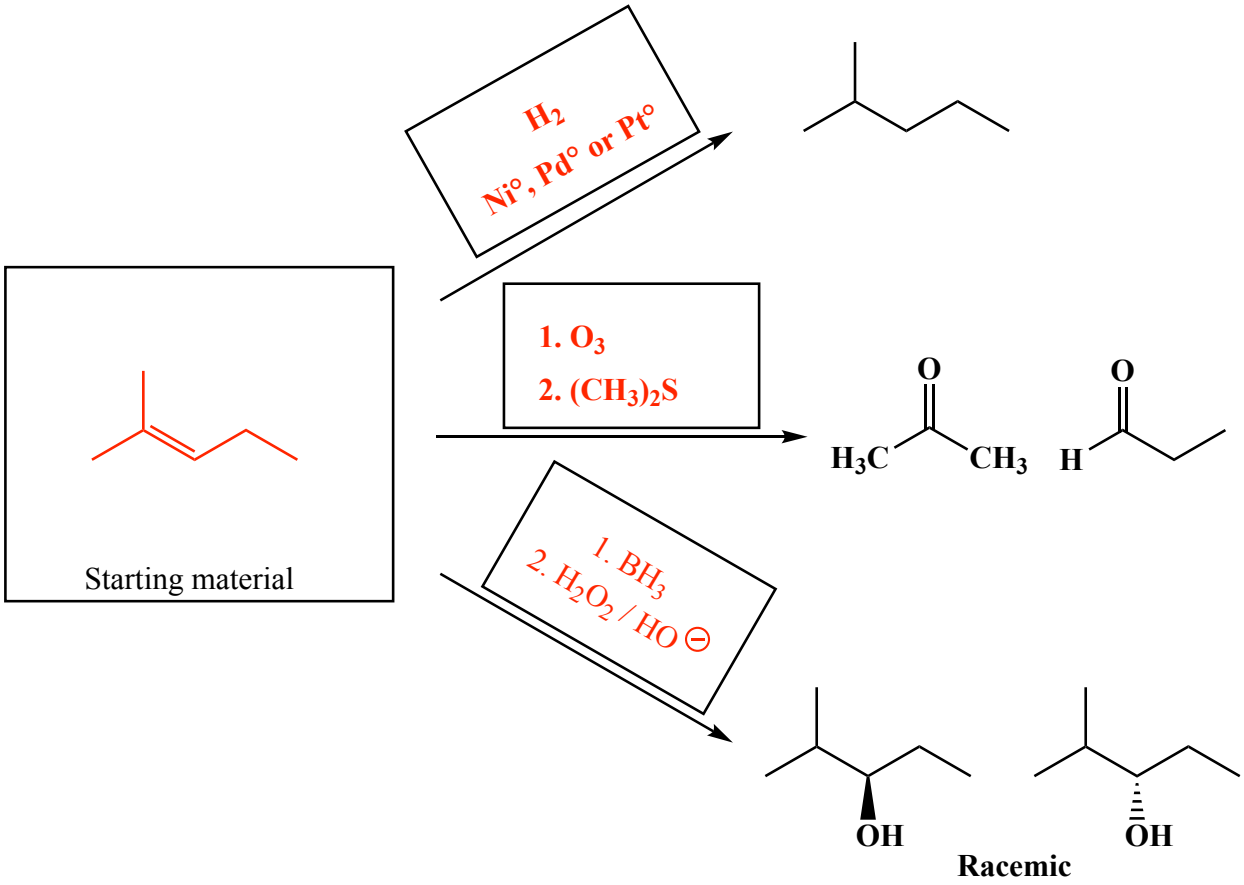
O. 



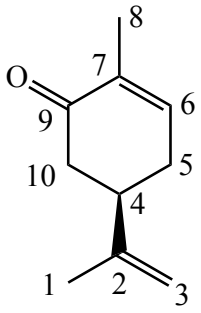
(2 pts) Will the product mixture you drew to the right rotate the plane of plane polarized light? No

Because of symmetry there are only three products.

15. (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.



16. (4 pts total) If you understand terpenes this one is not hard, but you will need to take your time to make sure you get the details correct. The terpene that produces the spearmint flavor is shown. I have added numbers to the structure. **Fill in the circle that corresponds to the sets of numbers aligned with the carbons that you expect to make up the isoprene units of spearmint.**



Spearmint

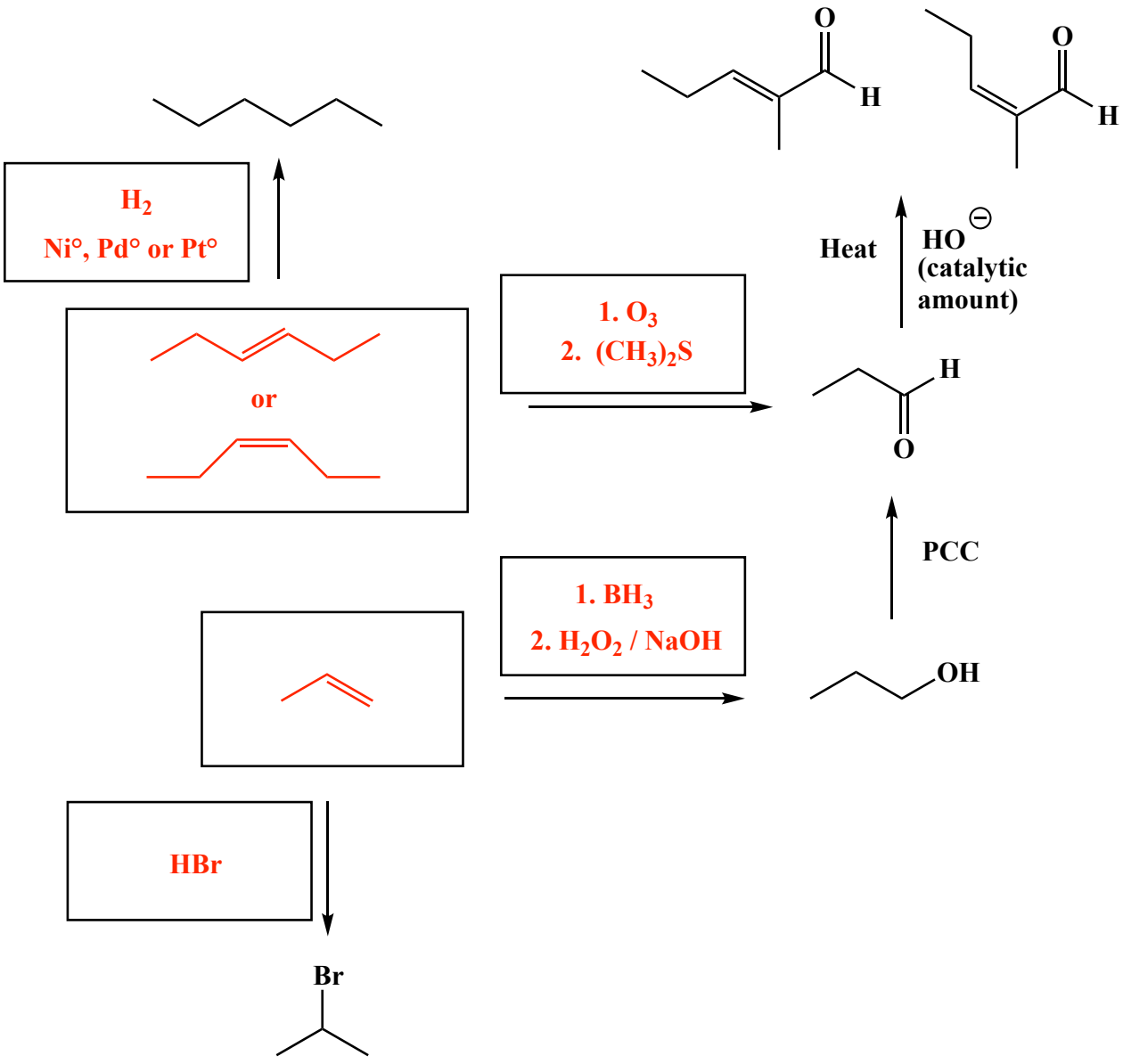
○ **Isoprene 1:** 1,2,3,9.10
Isoprene 2: 4,5,6,7,8

● **Isoprene 1:** 1,2,3,4,5
Isoprene 2: 6,7,8,9,10

○ **Isoprene 1:** 1,2,3
Isoprene 2: 4,5,6
Isoprene 3: 7, 8,9,10

○ **Isoprene 1:** 1,2,3,4
Isoprene 2: 5,6,7
Isoprene 3: 8,9,10

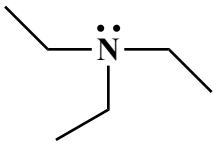
17. (16 pts total) The point of organic chemistry is synthesis, the conversion of simpler molecules to more complicated ones with enhanced structure and function. Each reaction you are learning should be thought of as a "tool" that allows you to create a desired type of molecule. These tools can be used 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. In addition, in the boxes beside the arrows, write the reagents needed to accomplish the reaction indicated.** You will not recognize all of this chemistry, but by the time you finish O Chem II next spring you will!!



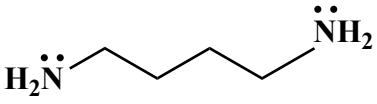
18. (12 pts total) Here is the MCAT style "apply what you know" question. This one is a true "apply what you know" in that you will likely be able to apply what you learn from this question in your personal life!

Humans are literally programmed to avoid spoiled food. In particular, our smell receptors are highly tuned to the molecules produced when bacteria break down our foods such as fish, mammal meat and eggs. In addition, we are programmed to avoid any food that has been vomitted by another human or animal. All of this makes sure we do not eat something that has a large number of bacteria that would make us sick. This is powerful stuff. A very, very small amount of these molecules will make us extremely nauseous, to the point we feel like we are going to vomit! This effectively prevents any thought of eating the tainted food, no matter how hungry we might be. You have all smelled these molecules! The problem is that sometimes we cannot avoid coming in contact with these smells, but we want to eliminate them as soon as possible.

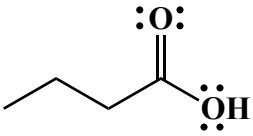
Here are some of the smelliest, most nauseating molecules we are all familiar with:



Triethylamine
Decaying fish

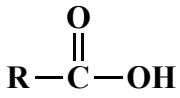


Putrescine
Decaying mammal flesh

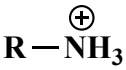


Butyric acid
Vomit smell

The neutral molecules shown above are volatile, so they evaporate and fill the air. Yuk! On the other hand, if you create the charged form of them through an acid-base reaction, they will no longer be volatile, they will not evaporate and you no longer smell them. This provides an effective strategy for a rapid cleanup using ammonia (NH_3), often found in glass cleaners, and vinegar (dilute acetic acid, CH_3CO_2H). Here are the relevant pK_a values.



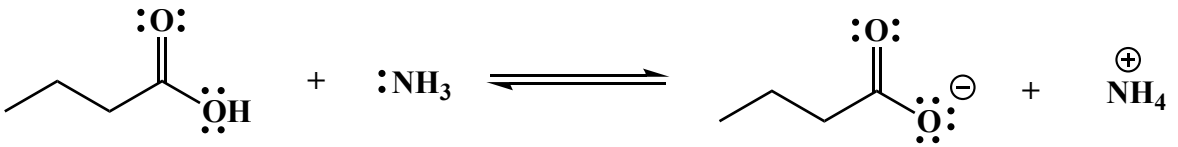
pK_a = 3-5



pK_a = 9-10.5

R = any alkyl group or a hydrogen atom

A. For the following equilibrium, indicate which side is favored by filling in the appropriate circle.



Butyric acid
Vomit smell

Ammonia
In glass cleaner

○ **This side favored at equilibrium**

● **This side favored at equilibrium**

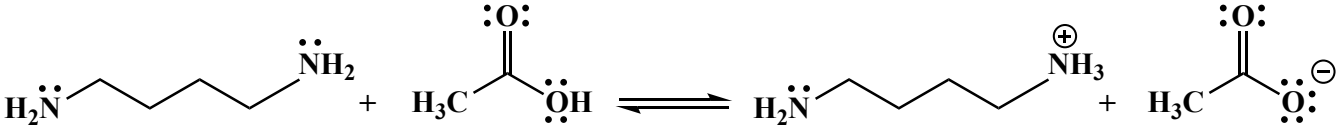
B. Based on what you decide in part A., would spraying an ammonia-based cleaner be a powerful way to eliminate that nauseating barf smell when cleaning the area of the couch affected where your roommate or pet just vomitted?

● **Yes** ○ **No**

C. Based on the pK_a values listed above, would spraying vinegar be a powerful way to eliminate that nauseating barf smell when cleaning the area of the couch affected where your roommate or pet just vomitted?

○ **Yes** ● **No**

D. For the following equilibrium, indicate which side is favored by filling in the appropriate circle.



Putrescine
Decaying mammal flesh

Acetic acid
In vinegar

○ **This side favored at equilibrium**

● **This side favored at equilibrium**

E. Based on what you decide in part D., if you discover a dead animal in your garage, and you cannot get rid of that awful dead animal smell, would it make sense to try and eliminate that dead animal smell by cleaning it up with some vinegar?

● **Yes** ○ **No**

F. Based on the pK_a values listed above, would using an ammonia-based glass cleaner be a powerful way to eliminate the dead animal smell from your garage?

○ **Yes** ● **No**

Pro tip: When cleaning up vomit or a dead animal always use soap and water first, followed by the ammonia-based glass cleaner or vinegar as appropriate. In addition, if you are out of ammonia-based glass cleaner or vinegar, dissolving some baking soda in water will work for either.

I hope everyone is thinking more about exercise and keeping in shape. Good mental health and good physical health go hand-in-hand. Getting some exercise on a continual basis is the best way to get a positive new outlook! In other words, the absolute best thing you can do for yourself is to go for a walk or run with friends. The weather is now perfect. If you have been hesitating, please give it a try. There are a growing number of neuroscience studies that are uncovering just how this works. Even as the science is advancing, please believe me, this does work.