

NAME (Print): _____

Chemistry 320M/328M
Dr. Brent Iverson
Final
December 16, 2019

SIGNATURE: _____

EID: _____

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

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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 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!!!

Page	Points
1	(29)
2	(23)
3	(24)
4	(24)
5	(-)
6	(-)
7	(-)
8	(28)
9	(21)
10	(23)
11	(26)
12	(27)
13	(32)
14	(32)
15	(33)
16	(16)
17	(11)
18	(10)
19	(19)
20	(10)
21	(14)
Total	(402)

Take a deep breath and begin working. Start with the ones worth the most points and remember that does not mean they are hard, so do not second guess yourself. You can do this!

You have been a great class and I have very much enjoyed getting to know you.

I wrote the same poem last year, but I think it is just as meaningful this year. Here is my wish for every one of you:

*“May your wishes all come true.
May you build a ladder to the stars
and climb on every rung.
May you stay forever young.*

*May you grow up to be righteous,
May you grow up to be true,
May you always know the truth
And see the lights surrounding you
May you always be courageous
Stand upright and be strong
May you stay forever young.*

*May your hands always be busy
May your feet always be swift
May you have a strong foundation
When the winds of changes shift
May your heart always be joyful
May your song always be sung.
And may you stay forever young.”* BD

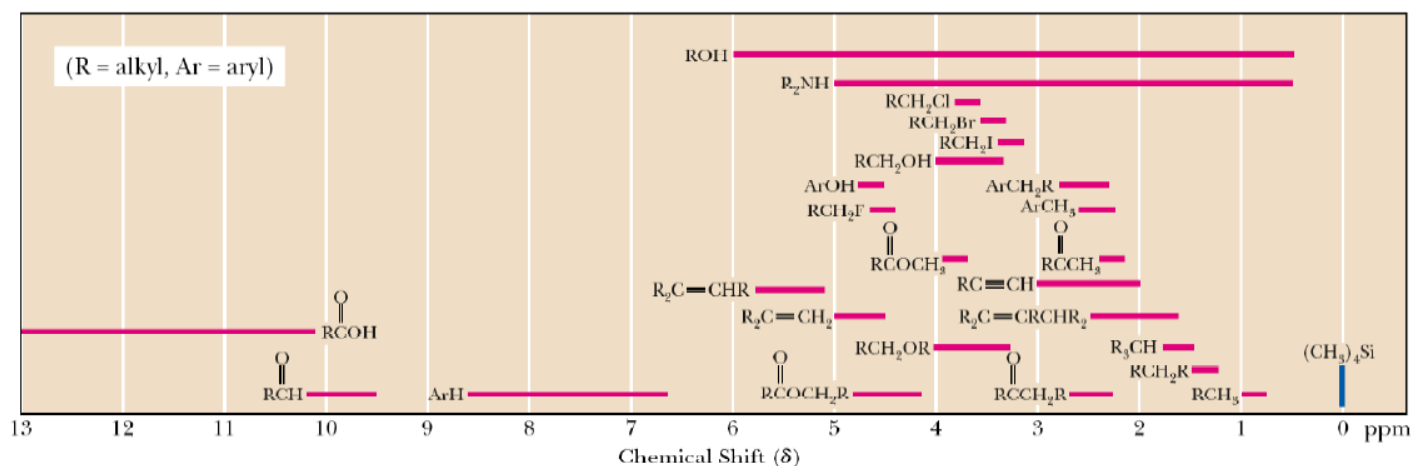
Remember to run every chance you get. Staying fit will also allow you to stay forever young. Your loved ones will be grateful.

Brent Iverson

Compound		pK _a
Hydrochloric acid	H-Cl	-7
Protonated alcohol	$\text{RCH}_2\text{OH}_2^{\oplus}$	-2
Hydronium ion	$\text{H}_3\text{O}^{\oplus}$	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-5
Thiols	RCH_2SH	8-9
Ammonium ion	$\text{H}_4\text{N}^{\oplus}$	9.2
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	10
Primary ammonium	$\text{H}_3\text{N}^{\oplus}\text{CH}_2\text{CH}_3$	10.5
β-Ketoesters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	11
β-Diesters	$\text{ROC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	16
Aldehydes	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	18-20
Ketones	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	18-20
Esters	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\text{H}$	25
LDA	$\text{H}-\text{N}(\text{i-C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{H}$	44
Alkanes	$\text{CH}_3\text{CH}_2-\text{H}$	51

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
R_2NH	0.5-5.0	RCH_2OH	3.4-4.0
ROH	0.5-6.0	RCH_2Br	3.4-3.6
RCH_3	0.8-1.0	RCH_2Cl	3.6-3.8
RCH_2R	1.2-1.4	$\begin{array}{c} O \\ \\ RCOCH_3 \end{array}$	3.7-3.9
R_3CH	1.4-1.7	$\begin{array}{c} O \\ \\ RCOCH_2R \end{array}$	4.1-4.7
$R_2C=CRCHR_2$	1.6-2.6	RCH_2F	4.4-4.5
$RC\equiv CH$	2.0-3.0	ArOH	4.5-4.7
$\begin{array}{c} O \\ \\ RCCH_3 \end{array}$	2.1-2.3	$R_2C=CH_2$	4.6-5.0
$\begin{array}{c} O \\ \\ RCCH_2R \end{array}$	2.2-2.6	$R_2C=CHR$	5.0-5.7
ArCH ₃	2.2-2.5	$\begin{array}{c} O \\ \diagup \quad \diagdown \\ H_2C \quad CH_2 \end{array}$	3.3-4.0
RCH_2NR_2	2.3-2.8	$\begin{array}{c} O \\ \\ RCH \end{array}$	9.5-10.1
RCH_2I	3.1-3.3	$\begin{array}{c} O \\ \\ RCOH \end{array}$	10-13
RCH_2OR	3.3-4.0		

* Values are relative to tetramethylsilane. Other atoms within the molecule may cause the signal to appear outside these ranges.



Use this page to write down your roadmap if you would like.

Use this page for scratch if you would like. For your reference, here are the Golden Rules of Chemistry:

A. Predicting Structure and Bonding 1. In most stable molecules, all the atoms will have filled valence shells. 2. Five- and six-membered rings are the most stable. 3. There are two possible arrangements of four different groups around a tetrahedral atom.

B. Predicting Stability and Properties 4. The most important question in organic chemistry is "Where are the electrons?" 5. Delocalization of charge over a larger area is stabilizing. 6. Delocalization of unpaired electron density over a larger area is stabilizing. 7. Delocalization of pi electron density over a larger area is stabilizing.

C. Predicting Reactions 8. Reactions will occur if the products are more stable than the reactants and the energy barrier is low enough. 9. Functional groups react the same in different molecules. 10. A reaction mechanism describes the sequence of steps occurring during a reaction. 11. Most bond-making steps in reaction mechanisms involve nucleophiles reacting with electrophiles.

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

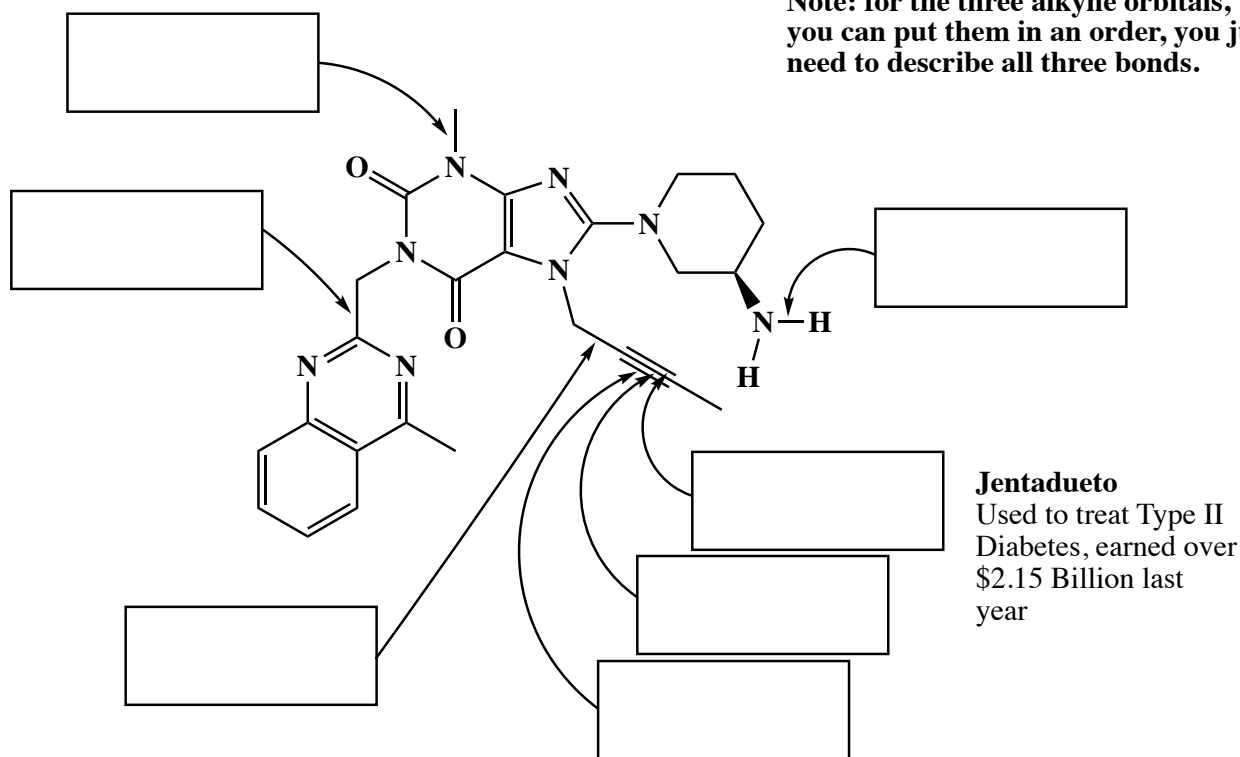
2. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges. For the two structures on the left in each problem, use arrows to indicate the movement of electrons to give the structures you drew. There is no need to draw any circles around any of these contributing structures. You might want to read these directions again to make sure you know what we want



3. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here and your answer should match a recent Rule of the Day.

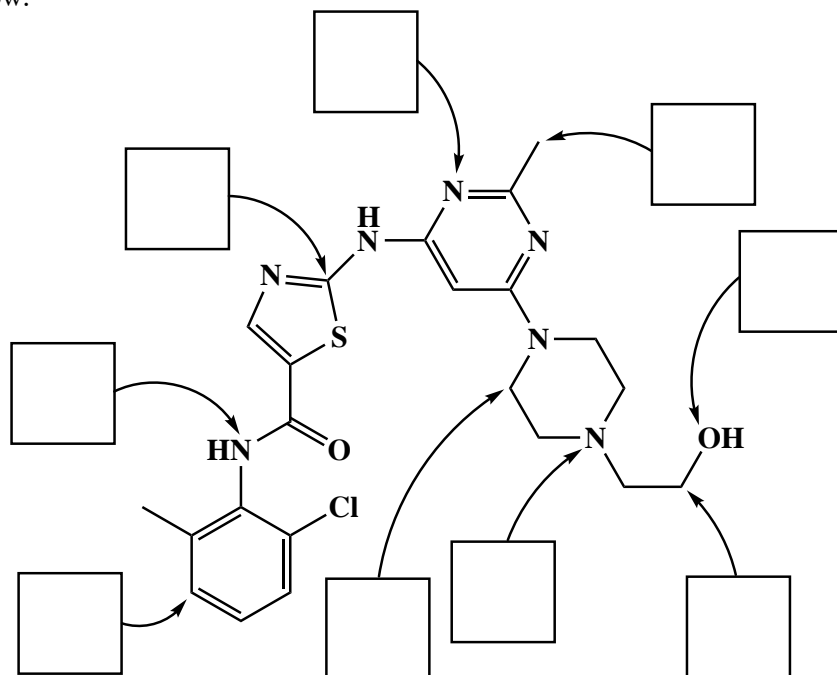
4. (2 pts each) In the spaces provided, indicate the type of bond, and the hybridized orbitals that overlap to form the bond. For example, one answer could be: σ_{Csp^3-H1s}

Note: for the three alkyne orbitals, you can put them in an order, you just need to describe all three bonds.



Jentaducto
Used to treat Type II Diabetes, earned over \$2.15 Billion last year

5. (1 pt each) In the spaces provided, write the hybridization state of the atoms indicated by the arrow.



Sprycel
An anti-cancer drug that operates by inhibiting kinase enzymes, earned over \$2.275 Billion last year

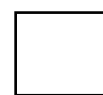
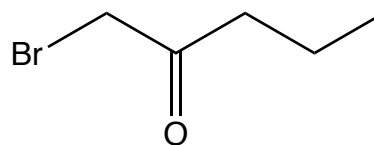
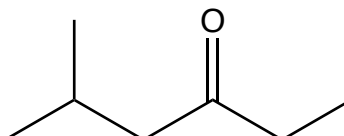
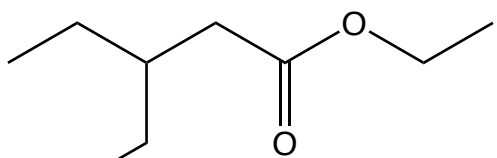
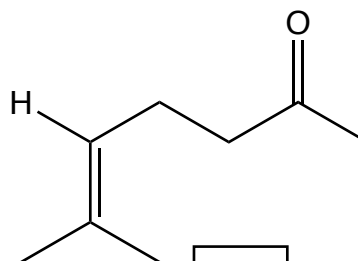
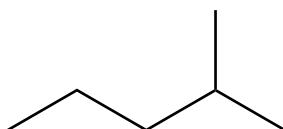
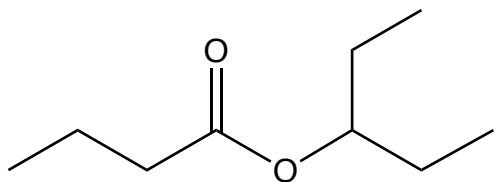
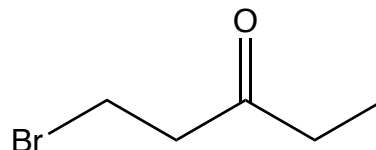
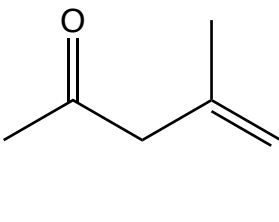
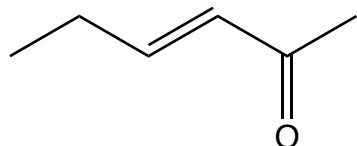
Signature _____

Pg 3 _____(24)

6. (2 pt each) **Circle whether each of the following statements is true or false.** You may notice these resemble Rules of the Day! These are worth a lot of points so please take your time and be careful. Read them carefully, but do not second guess yourself as we are not trying to trick you.

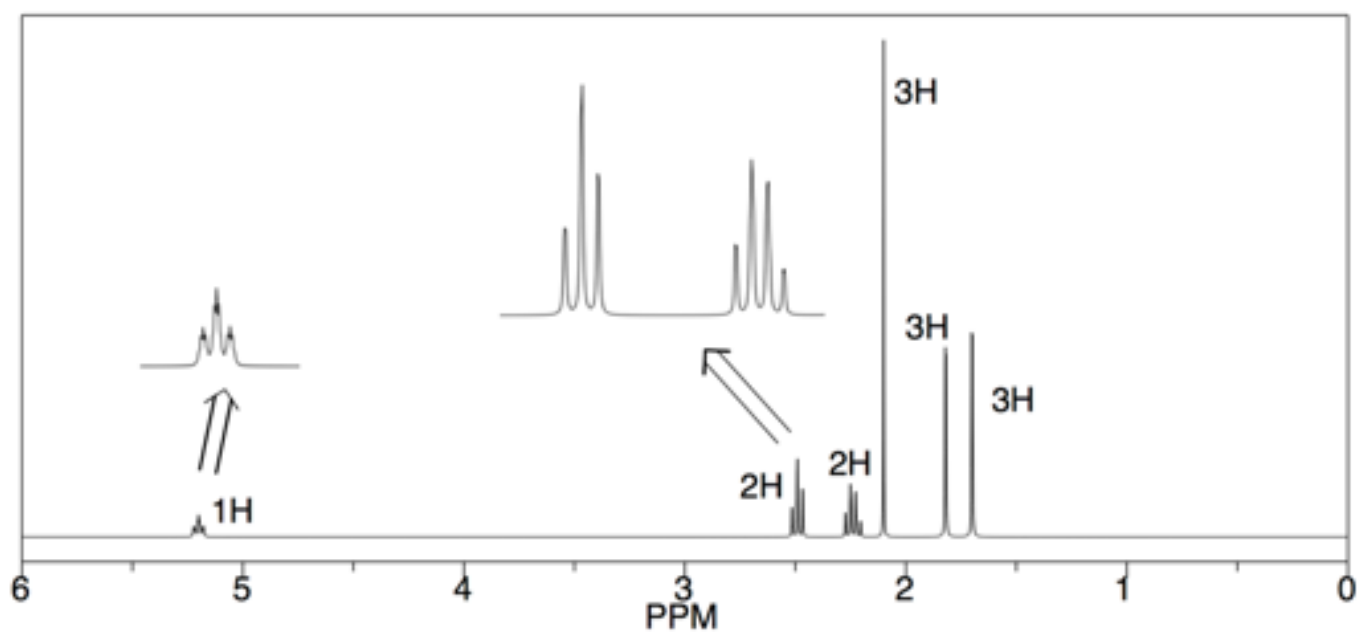
- True False** A. Resonance contributing structures are used when more than one structure are required to describe accurately how the electrons and charges are distributed in a molecule
- True False** B. Resonance contributing structures represent equilibrating molecules, rather than the hybrid (blending) of them as the true molecular representation.
- True False** C. When three parallel 2p orbitals on adjacent atoms combine, three new molecular orbitals are produced (bonding, non-bonding and antibonding).
- True False** D. When a Lewis acid and Lewis base combine, the product is referred to as a Lewis acid-Lewis base complex. The new bond is referred to as a "coordinate covalent bond" or "dative bond".
- True False** E Tetrahedral atoms such as carbon with four different substituents are chiral and are called chiral centers.
- True False** F The keto form of a compound rapidly tautomerizes to the more stable enol form.
- True False** G. The greater the electron density around a nucleus, the more shielded it is, and the lower the energy (frequency) of electromagnetic radiation required to flip its nuclear spin.
- True False** H. Nuclei with spin quantum number $1/2$ are quantized in one of two orientations, "+ $1/2$ " (lower energy) or "- $1/2$ "(higher energy) in the presence of an external magnetic field, that is, the nuclear spins are aligned with and against the external field, respectively.
- True False** I. The difference in energy between the + $1/2$ and - $1/2$ nuclear spin states is proportional to the strength of the magnetic field experienced by the nucleus.
- True False** J. The general rule of solvation is "like dissolves like", so polar, hydrogen bonding solvents dissolve non-polar molecules like hydrocarbons, and non-polar hydrocarbon solvents dissolve polar, charged, or hydrogen bonding molecules.
- True False** K. In organic synthesis, A KEY PARADIGM is the that functional groups (OH group, Pi bond of an alkene, etc.) react the same in large complex molecules as they do in simple structures.
- True False** L. Running 3-5 miles a week EVERY WEEK as an adult dramatically increases your fitness level and improves your health throughout your life. Doing this and enjoying a healthy life is even more important than this organic class!

7. (24 pts total) On the following three pages there are NMR spectra. The relative integrations are given above each signal. Each NMR spectrum has a letter on it. **In the spaces provided, write the appropriate letter underneath the molecules that would produce that spectrum.** Notice that not all of the molecules below will have letters underneath them, as there are only three spectra but nine molecules.



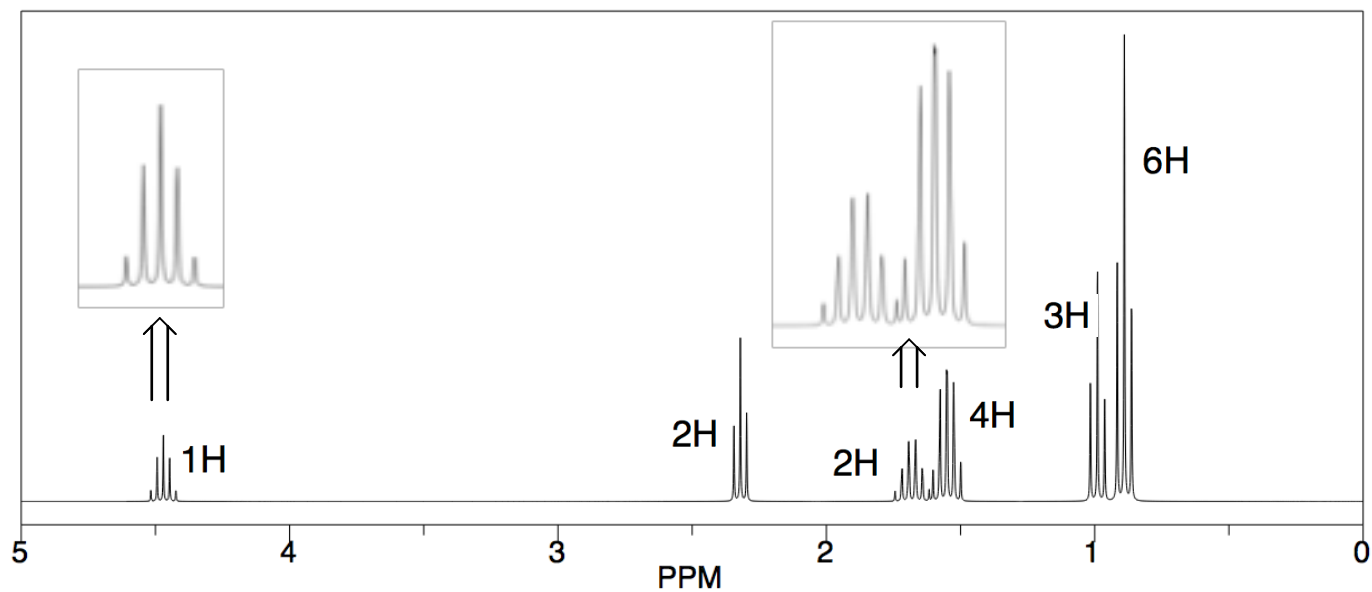
Spectrum A

This page is not graded



Spectrum B

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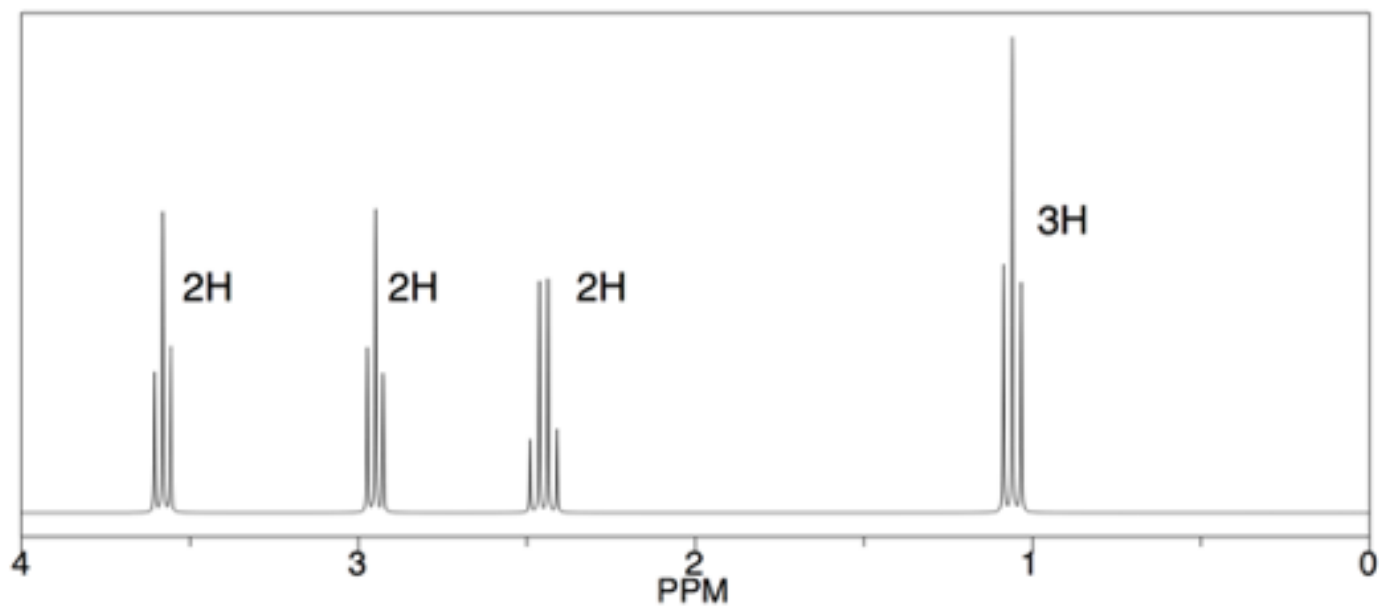


Signature _____

Pg 7

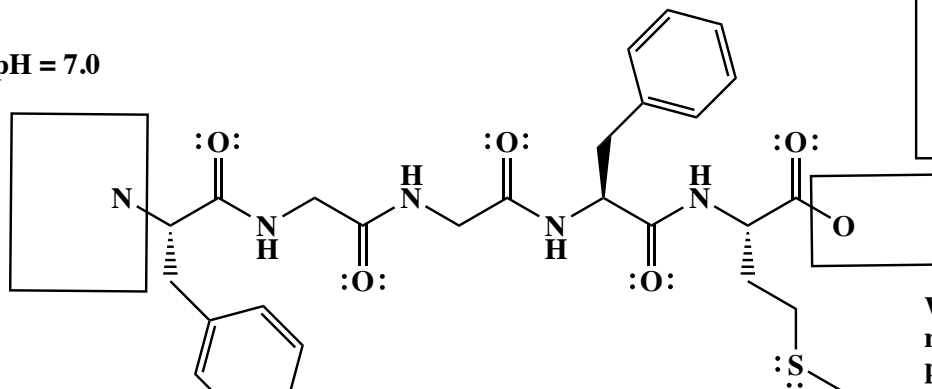
Spectrum C

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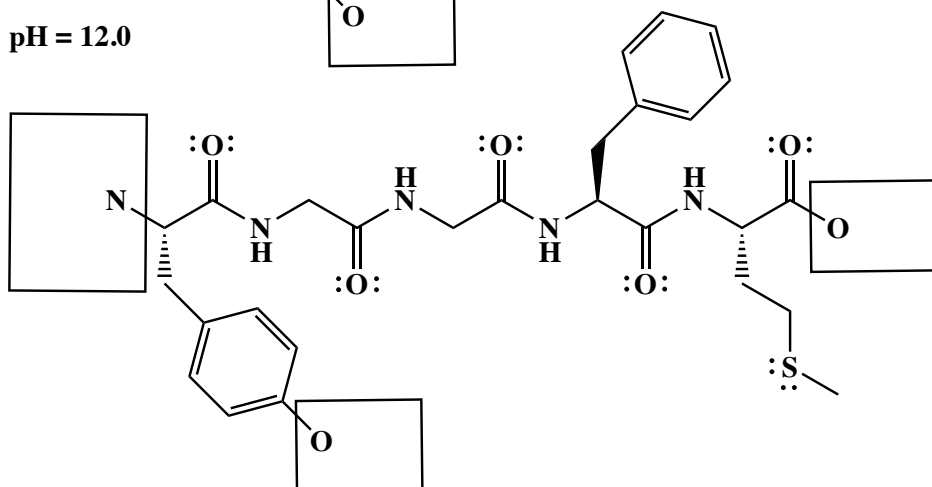
8. (16 pts) The following molecule is called Met-enkephalin. It is present in high concentration in most mammalian cells. It primarily protects cells from oxidative damage. **In the boxes, fill in the proper number of bonds to H atoms, lone pairs, and formal charges to show the protonation state of Met-enkephalin at pH 7.0, and pH 12.0.** Use the pK_a table provided at the beginning of the test for reference as well as the reference pK_a provided on the right.

pH = 7.0



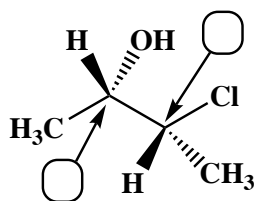
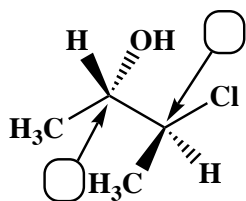
What is the total net charge of this peptide at pH 7.0? _____

pH = 12.0

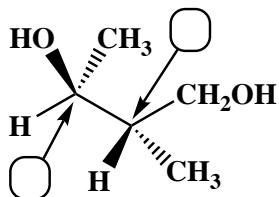
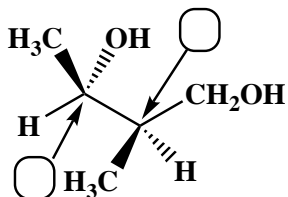


What is the total net charge of this peptide at pH 12.0? _____

9. (12 pts) For each pair of molecules, on the line provided state the relationship between the two structures. Possible answers could be **enantiomers**, **diastereomers**, **constitutional isomers**, or **same molecule**. Draw a circle around any meso compound. In the boxes provided next to each chiral center, write "R" or "S" to indicate the absolute stereochemistry present.



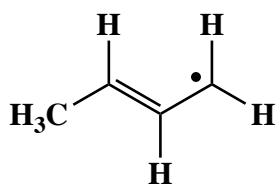
Relationship: _____



10. (5 pt) A hydrogen bond is the strongest interaction seen among neutral molecules. In the space provided, draw two molecules of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and show a hydrogen bond between them. Use a dashed line (- - - - -) to indicate any hydrogen bonds and be sure to draw all lone pairs of electrons.

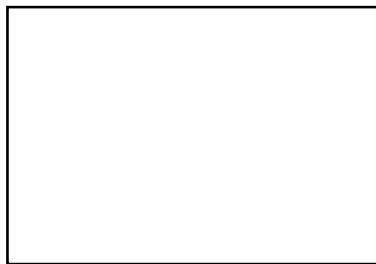
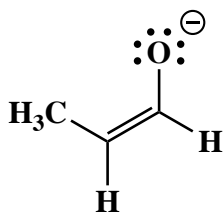
11. (16 pts total) The following are contributing structures for important resonance hybrids. Draw the other important resonance contributing structure in the box provided. Draw arrows on the structures on the left that indicate the flow of electrons that produce the contributing structures you drew to the right. Be sure to show all lone pairs and formal charges.

A.



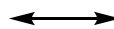
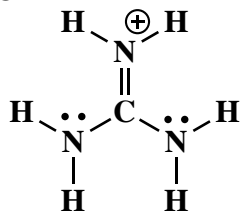
Did you remember to put arrows on the structures on the left?

B.



Yes, put arrow(s) on this structure to show how it is transformed to the structure to the far right!

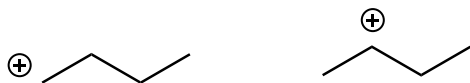
C.



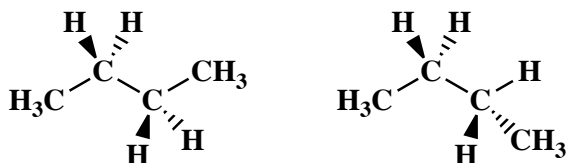
12. (23 pts) Circle the appropriate structure from each pair, then fill in the blank on the right stating the reason(s) for your answer. Possible answers for the blanks on the right are **Inductive Effect**, **Angle Strain**, **Torsional Strain**, **Steric Strain**, or **Hyperconjugation**. You might need more than one answer in some cases.

Reason(s)

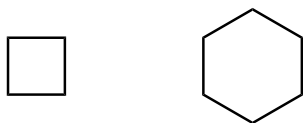
A) Circle the more stable carbocation



B) Circle the more stable conformation



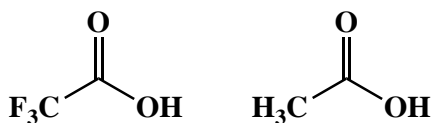
C) Circle the cycloalkane with less strain



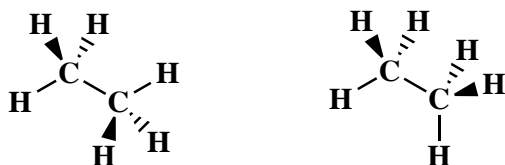
D) Circle the more stable alkene



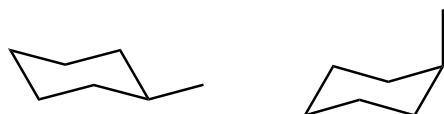
E) Circle the more acidic molecule



F) Circle the more stable conformation



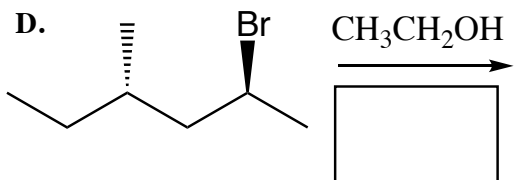
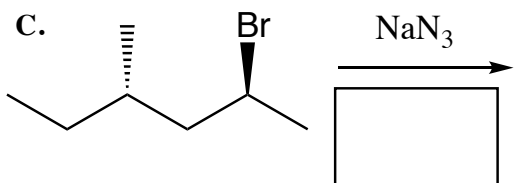
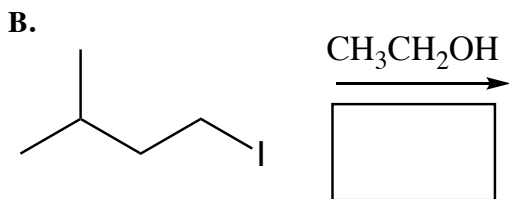
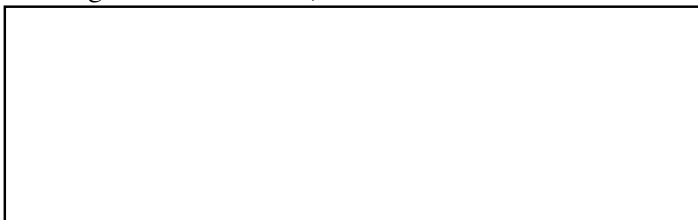
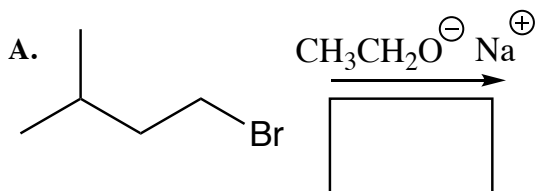
F) Circle the more stable conformation



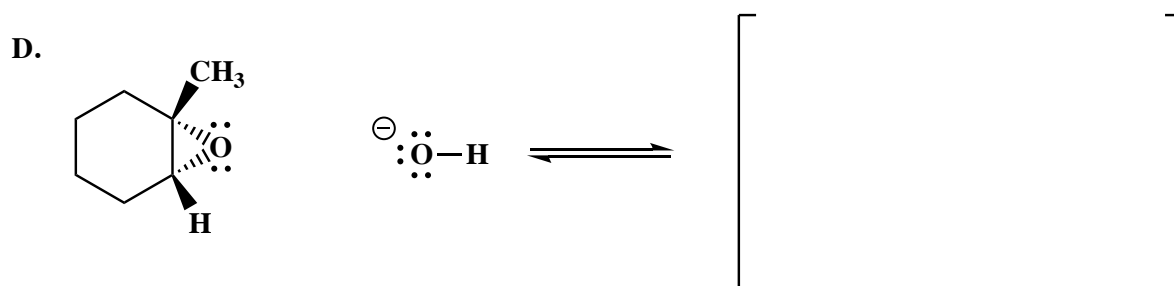
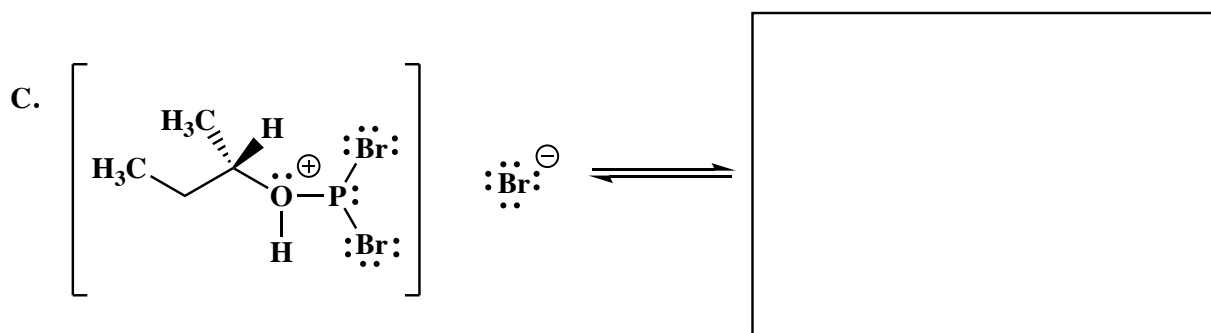
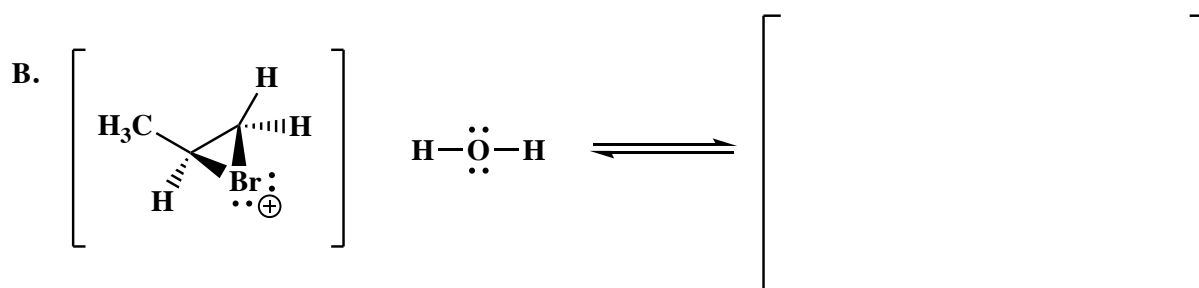
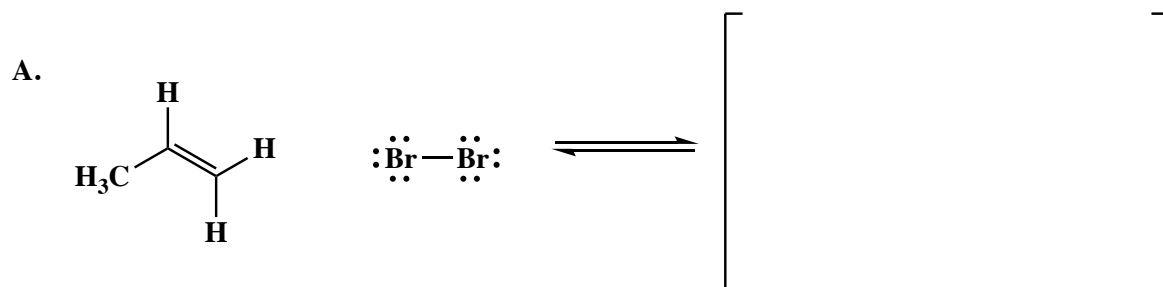
13. (7 pts total) Fill in the blanks with the word(s) that best complete(s) the sentences.

Epoxides are important because the (angle or steric) _____ strain within epoxides allows them to react with (nucleophiles or electrophiles) _____. When strong (nucleophiles or electrophiles) _____ attack epoxides at neutral or basic pH, the (more or less) _____ hindered carbon is attacked. Epoxides react with (nucleophiles or electrophiles) _____ under acid-catalysis conditions preferentially at the (more or less) _____ substituted carbon atoms that possess greater positive charge, analogous to (bromonium ion or radical) _____ intermediates.

14. (19 pts) The following reactions all involve chemistry of haloalkanes. **Fill in the box below the arrow with the mechanism that will be followed (S_N2 , E2, etc.). Then draw only the predominant product or products** and please remember that **you must draw the correct stereoisomers**. For $S_N1/E1$ reactions you must draw all significant products (including all stereoisomers).

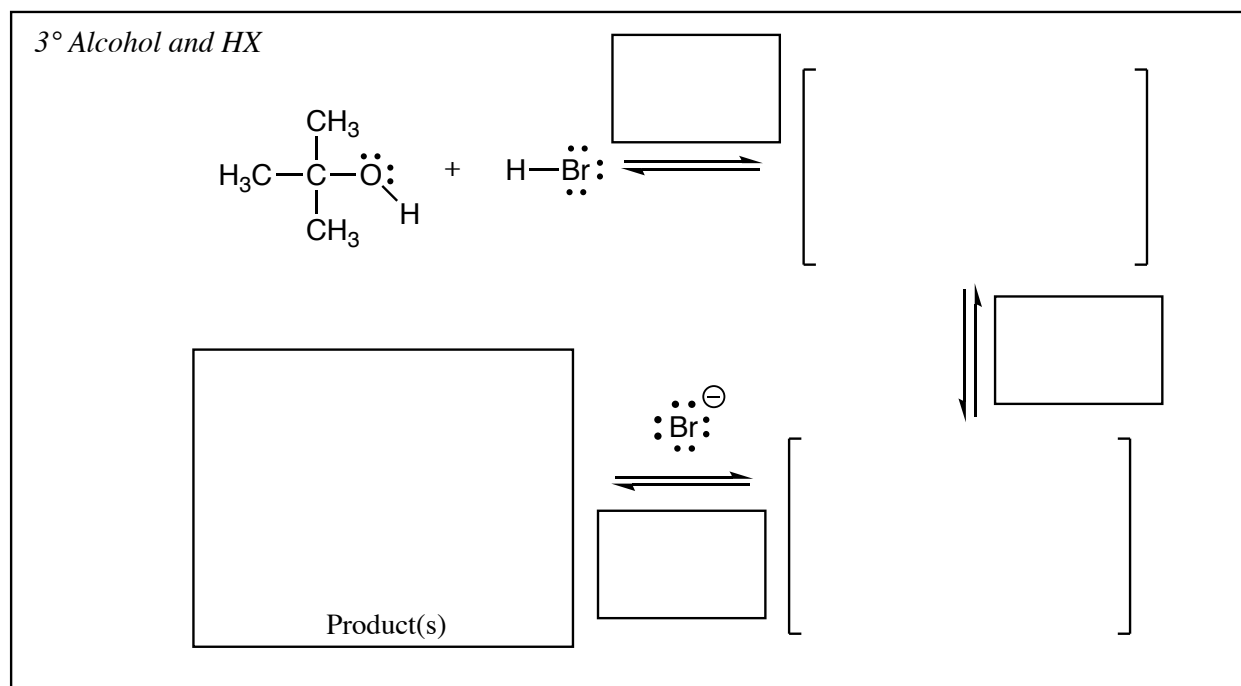
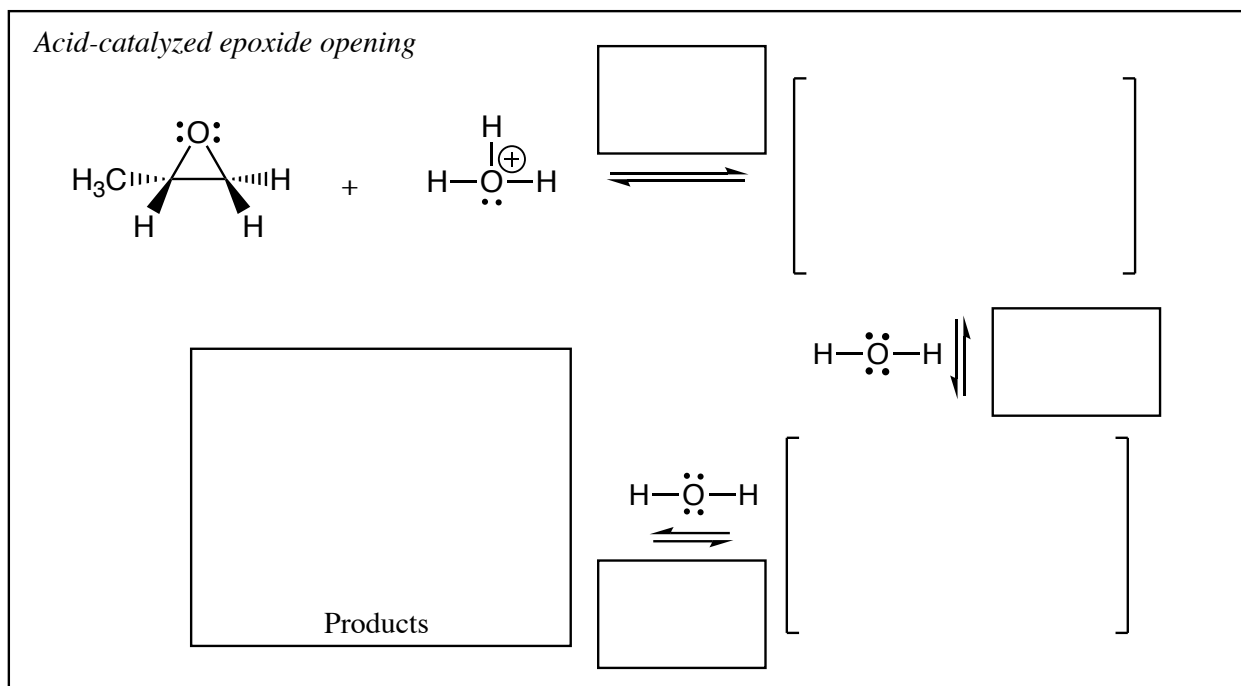


15. (27 pts) Over the semester, you have seen the following types of molecules in the context of individual mechanisms. For each pair of molecules, draw the first intermediate (or product) created in the next step of the appropriate mechanism. Do not worry about any further steps (if appropriate) in the mechanism, we are only interested in this single step. **Use arrows to indicate the movement of all electrons, draw all lone pairs and formal charges. Use wedges and dashes to indicate all stereochemistry.** Remember to draw all products of each step! If a racemic mixture is formed, you only need to draw one stereoisomer, label all chiral centers with an asterisk and write "racemic". **In each reaction draw a circle around the NUCLEOPHILE!**

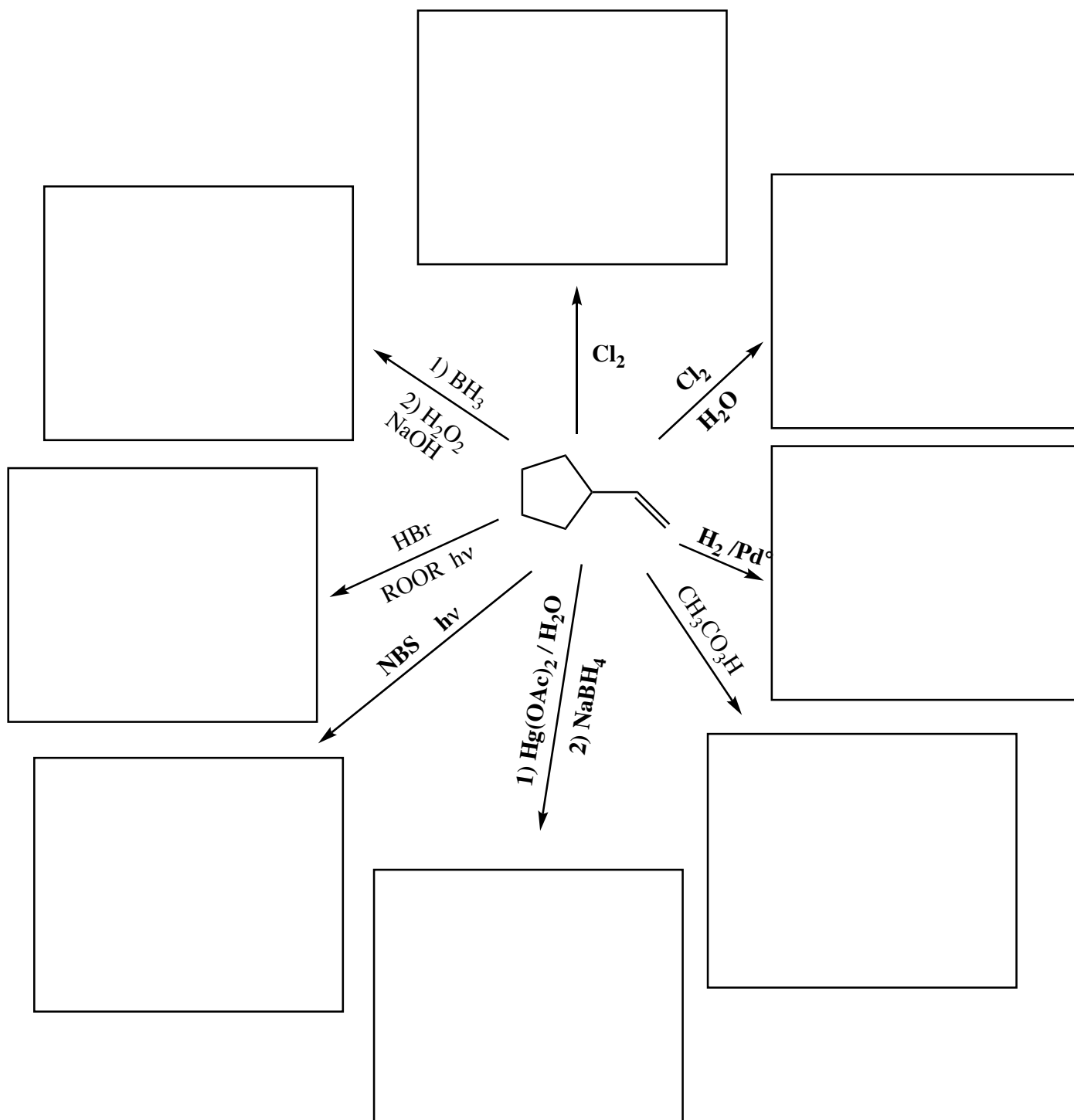


Did you remember to circle the NUCLEOPHILE in each reaction above?

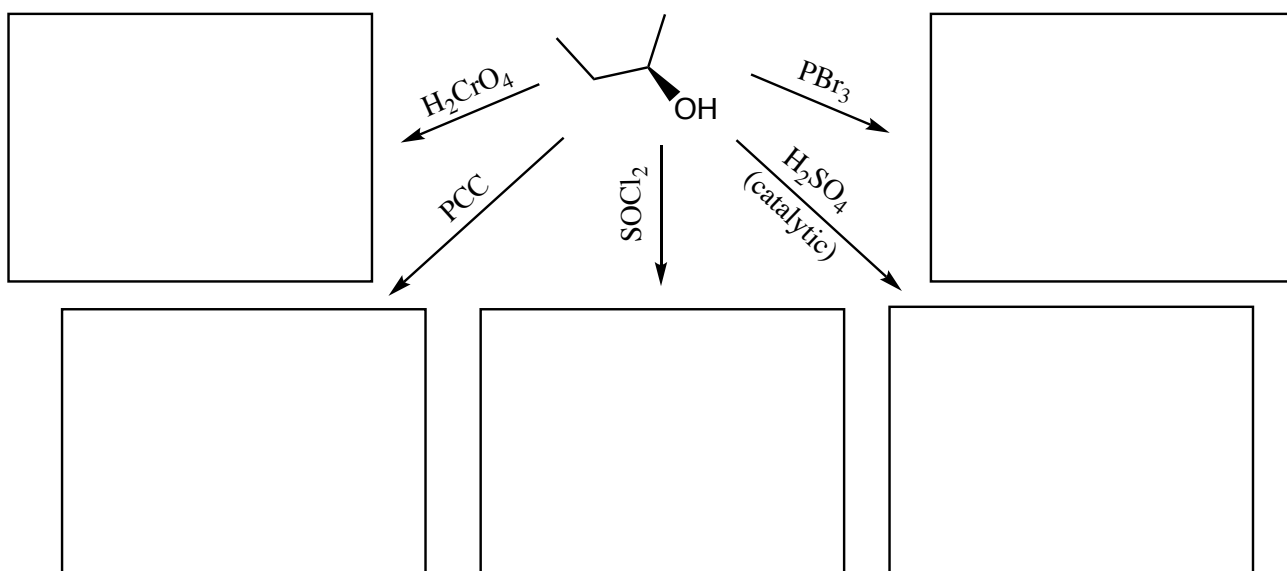
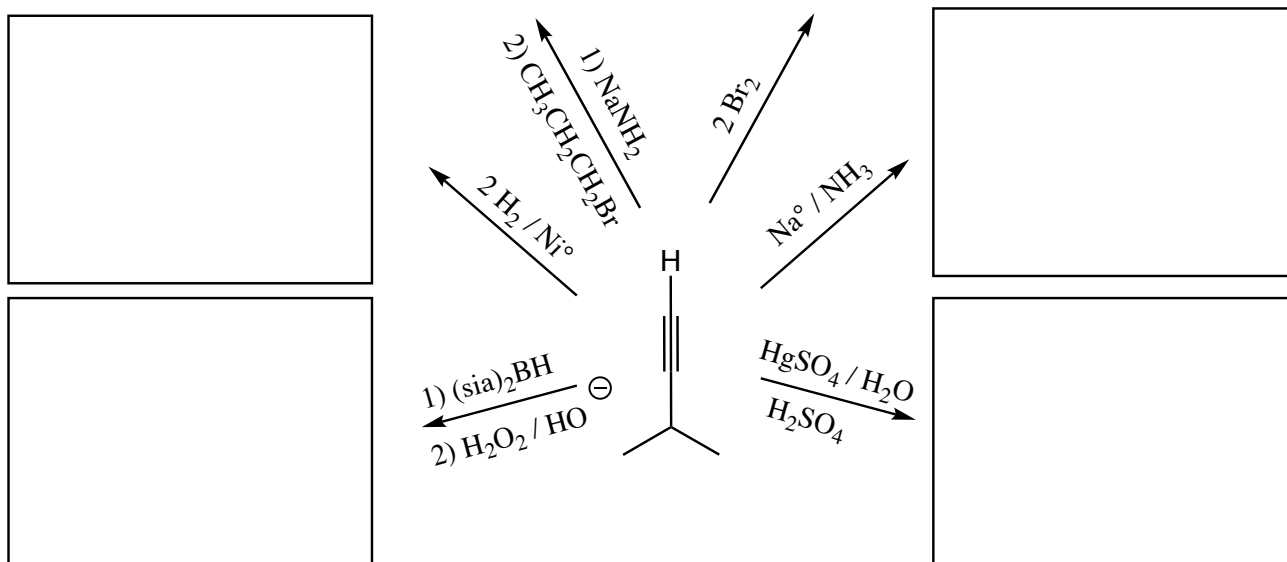
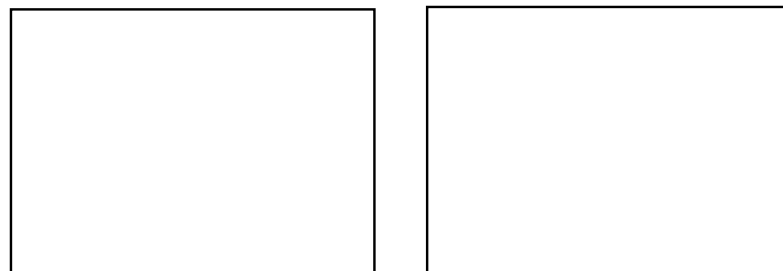
16. (32 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) **For the following reactions, fill in the details of the mechanism. Draw the appropriate chemical structures and use an arrow to show how pairs of electrons are moved to make and break bonds during the reaction. For this question, you must draw all molecules produced in each step. Finally, fill in any boxes adjacent to the arrows with the type of step involved, such as "Make a bond" or "Take a proton away". Use wedges and dashes to indicate stereochemistry where appropriate.**



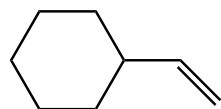
17. (32 pts) For the following, complete the reactions with the predominant carbon-containing product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



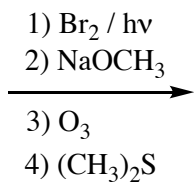
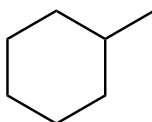
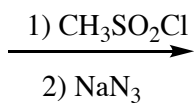
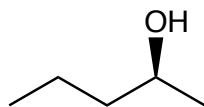
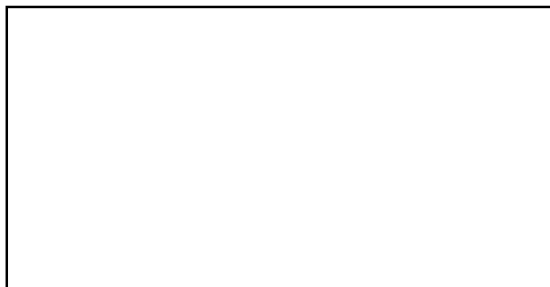
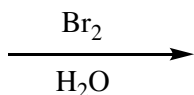
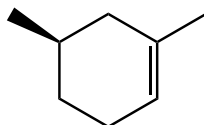
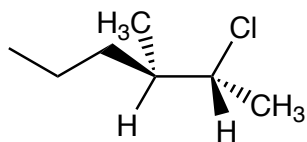
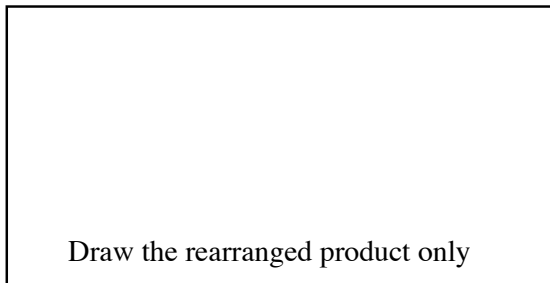
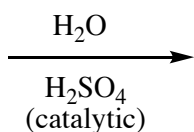
18. (33 pts) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



19. (16 pts) For the following, complete the reactions or reaction sequences with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place **except the first one in which we only want the rearranged product.**

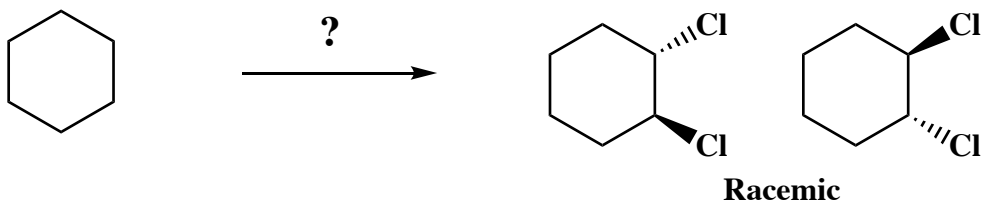


This rearranges

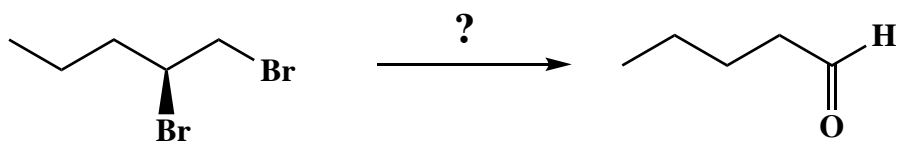


20. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

A) (7 pts)



B) (4 pts)

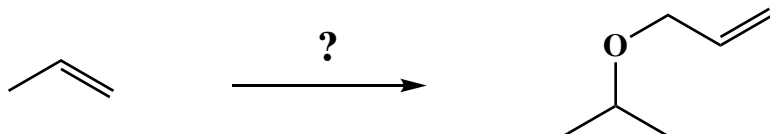


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Pg 18 _____(10)

20. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

C) (10 pts)

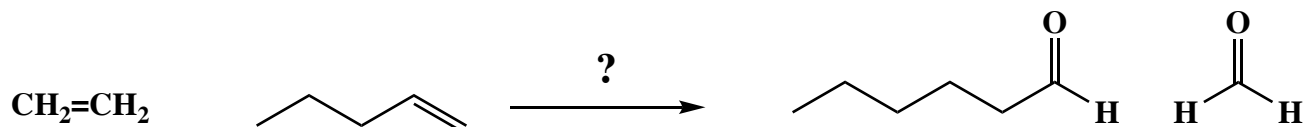


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Pg 19 _____(19)

20. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting materials.**

D (19 pts)

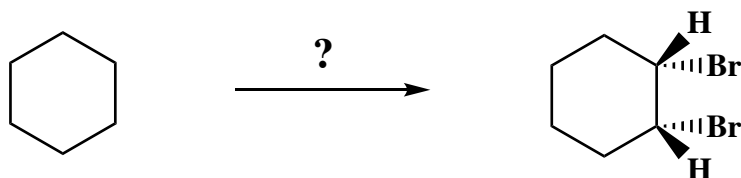


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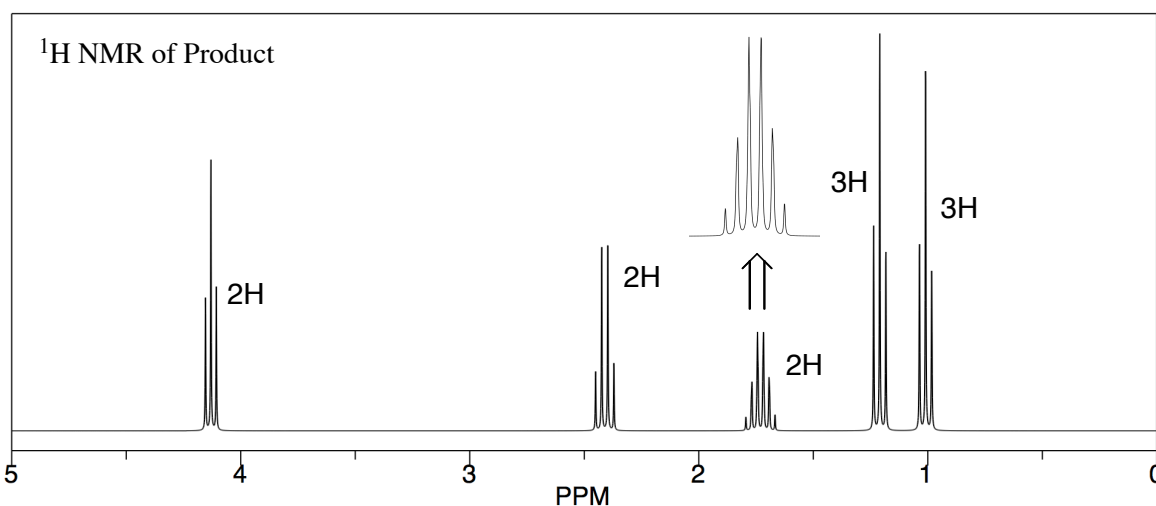
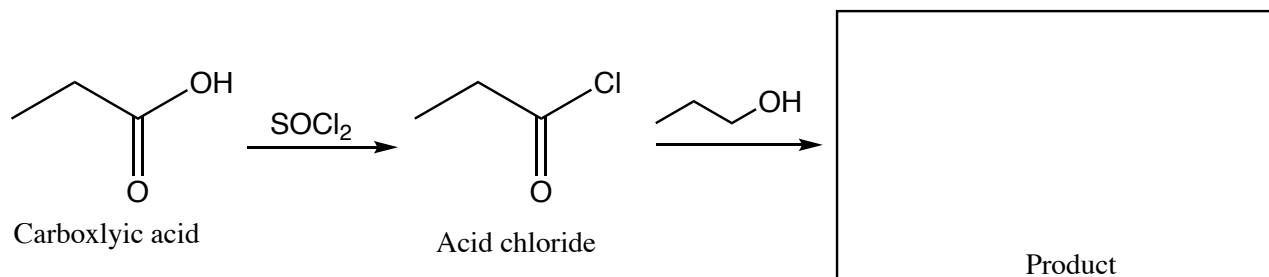
Pg 20 _____(10)

20. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting materials.**

E (10 pts)



21. (7 pts) Next semester, you will learn several new reactions involving carboxylic acids. In one reaction, carboxylic acids react with SOCl_2 to give a type of molecule called an acid chloride. Use your growing chemical intuition to predict the product formed when the acid chloride shown reacts with 1-propanol. As help, we have included the ^1H NMR of the product we want you to draw!



22. (7 points) Here is an “apply what you know” question. Fluorine is often added to pharmaceuticals to slow down metabolism of the molecule in the body, increasing potency. The following reaction is carried out during the synthesis of fluticasone, the key ingredient in the popular FlonaseTM allergy nasal spray. The molecule is a steroid, and leads to an attenuation of a local nasal immune response (it is an agonist of the glucocorticoid receptor), i.e. it slows down a runny nose. Hint: In this reaction, HF is reacting as you might expect of HBr or HCl. In other words, HF is an acid and F^- is a great nucleophile. **Draw the product of this reaction.** We have drawn the basic elements of the steroid rings to get you started.

