

NAME (Print): _____

Chemistry 320M/328M
Dr. Brent Iverson
Final
December 16, 2017

SIGNATURE: _____

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	(26)
3	(20)
4	(15)
5	(-)
6	(-)
7	(-)
8	(28)
9	(19)
10	(23)
11	(29)
12	(20)
13	(32)
14	(37)
15	(30)
16	(16)
17	(17)
18	(16)
19	(13)
20	(10)
21	(8)
Total	(388)

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)

As you go through the test, I recommend that you:

- 1) Remain as relaxed and calm as possible throughout
- 2) Work problems worth the most points first
- 3) Concentrate on finishing all the problems you are most certain about
- 4) Leave the ones you have doubts about for last
- 5) Do not second guess yourself, you got this!

What a long and wonderful road it has been this semester. We started with a review of general chemical structure and bonding then proceeded to develop an understanding of alkane conformations, relative acidities of different functional groups and stereochemistry of tetrahedral carbon. What followed was a comprehensive series of mechanisms and reactions, built around the notion that understanding the mechanisms, especially how they relate to the four common mechanistic elemental steps, provides an understanding of organic chemistry. Once you know the “personalities” of molecules, you can *predict* what they will do! The culmination of everything we have done is synthesis, that is, an ability to develop strategies to make more complex molecules from simpler ones. But this has always been about more than just Organic Chemistry. The high level thinking skills you develop while working synthesis problems for this class will be important to all of your futures, no matter what you intend to do.

I have very much enjoyed getting to know all of you. As one of my favorite poets of the 20th century put it: “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 your heart always be joyful and may your song always be sung. And may you stay forever young.” BD

Remember, run every chance you get. Being fit for your entire life is truly the best way to stay forever young.

Brent Iverson

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.

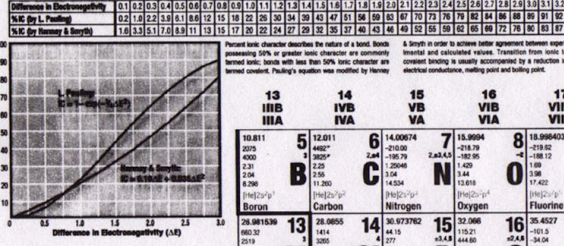
PERIODIC TABLE OF THE ELEMENTS

Elementary Subatomic Particles

	Electron	Proton	Neutron	Photon	Neutrino
Symbol	e	p	n	γ	ν
Rest mass (kg)	$9.109382(4) \times 10^{-31}$	$1.672621(9) \times 10^{-27}$	$1.674927(4) \times 10^{-27}$	0	0
Relative mass (approx)	1	1836.1526(7)	1838.6836(1)	0	0
Relative mass ratio	1	1836.1526(7)	1838.6836(1)	0	0
Relative mass ratio	1	1836.1526(7)	1838.6836(1)	0	0
Spin quantum number	1/2	1/2	1/2	1	1/2
Charge (e)	-1	+1	0	0	0
Magnetic moment (N·A)	$-9.284747(2) \times 10^{-24}$	$1.410607(6) \times 10^{-26}$	$5.788381(14) \times 10^{-27}$	0	0
In Bohr magneton, μ_B	-1.83611627(2)	0.00183611627(2)	0.00183611627(2)	0	0
In nuclear magneton, μ_N	1836.1526(7)	1	1	0	0

Summary particles are the fundamental constituents of matter and energy. The photon (γ) is a positive-energy particle which has the same mass as an electron. The neutrino (ν) has a rest mass of less than a few eV. The magnetic moment (μ) of a particle can also be expressed as a dimensionless quantity by dividing it with the Bohr magneton ($\mu_B = e\hbar/2m_e$) or the nuclear magneton ($\mu_N = e\hbar/2m_p$).

% Ionic Character of a Single Chemical Bond



1 IA		2 IIA										3 IIIA										4 IVA										5 VA										6 VIA										7 VIIA										8 VIIIA										9 VIIIA										10 VIIIA										11 IB										12 IIB										13 IIIA										14 IVA										15 VA										16 VIA										17 VIIA										18 VIII																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																			
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Atomic Weight
Boiling Point
Melting Point
Density
Electronegativity

Group Classification
Atomic Number
Oxidation States
Symbol
Name

25
Mn
Manganese

140.115 58 Ce	140.90766 59 Pr	144.24 60 Nd	144.9127 61 Pm	150.36 62 Sm	151.965 63 Eu	157.25 64 Gd	158.92534 65 Tb	162.50 66 Dy	164.93032 67 Ho	167.254 68 Er	168.93421 69 Tm	173.044 70 Yb	174.967 71 Lu
172.03391 90 Th	231.03688 91 Pa	238.02891 92 U	237.0462 93 Np	244.0642 94 Pu	244.0614 95 Am	247.0703 96 Cm	251.0796 97 Bk	252.083 98 Cf	257.0851 99 Es	258.1038 100 Fm	267 101 Md	268.1038 102 No	269 103 Lr

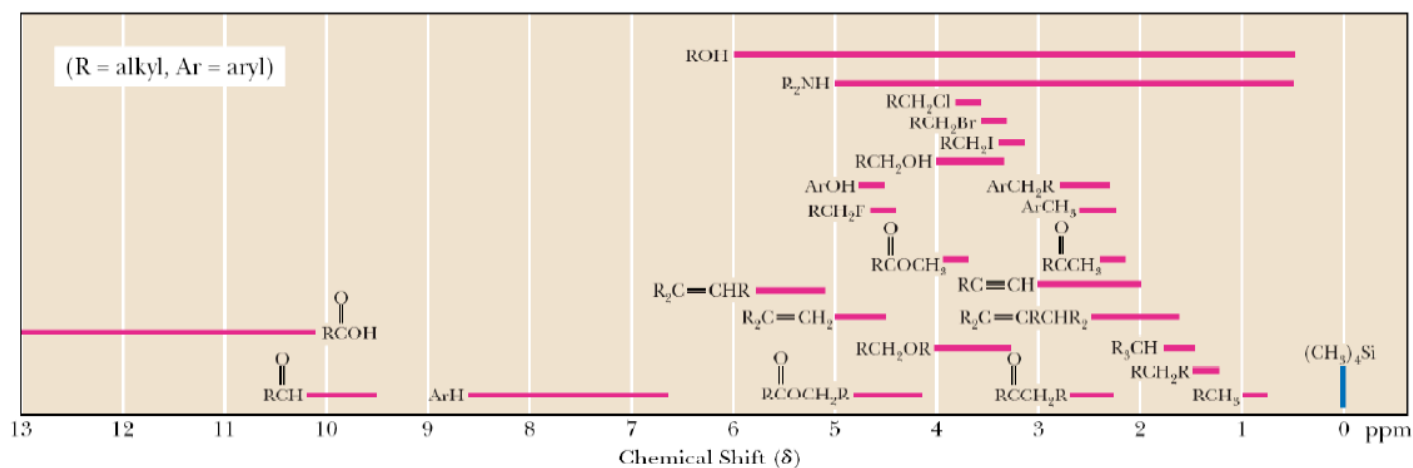
PAPERTECH

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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	$\begin{array}{c} O \\ / \backslash \\ H_2G-CH_2 \end{array}$	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.



Compound		pK _a
Hydrochloric acid	H-Cl	-7
Protonated alcohol	$\text{RCH}_2\text{OH}_2^+$	-2
Hydronium ion	H_3O^+	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-5
Thiols	RCH_2SH	8-9
Ammonium ion	H_4N^+	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	$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_3$	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

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

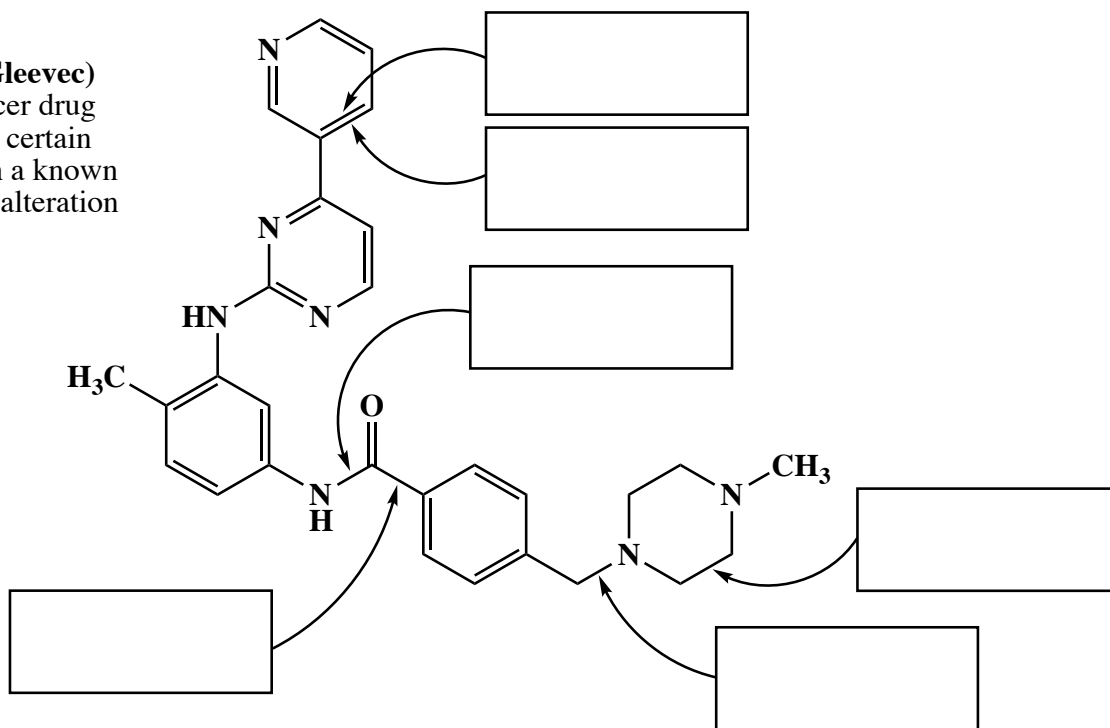
2. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges. For the two structures on the left in each problem, use arrows to indicate the movement 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



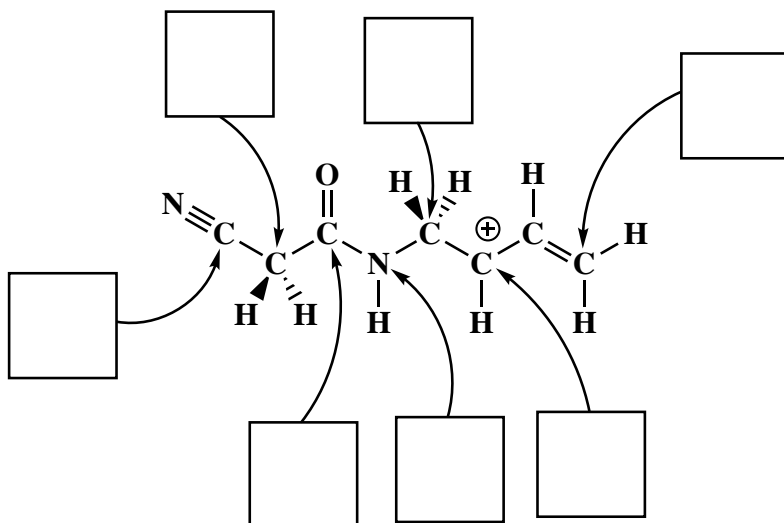
3. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here and your answer should match a recent Rule of the Day.

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}

Imatinib (Gleevec)
An anti-cancer drug used to treat certain cancers with a known kinase gene alteration



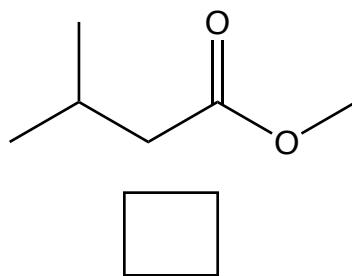
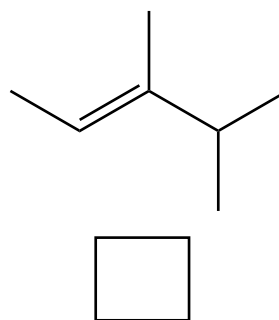
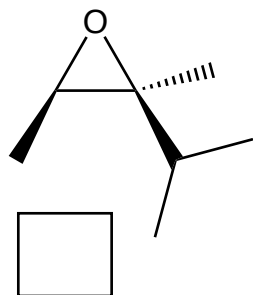
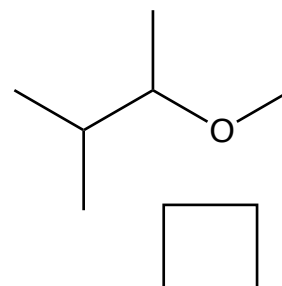
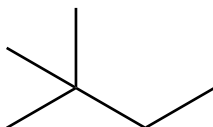
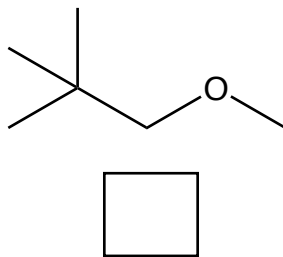
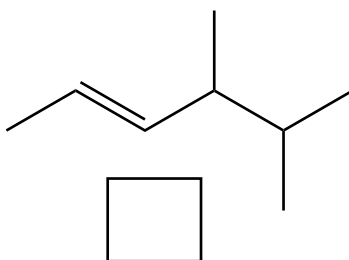
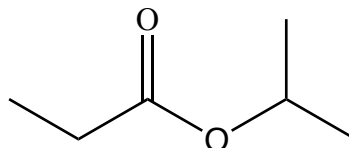
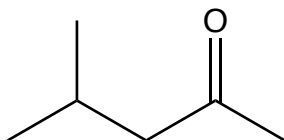
5. (2 pts each) In the spaces provided, write the hybridization state of the atoms indicated by the arrow.



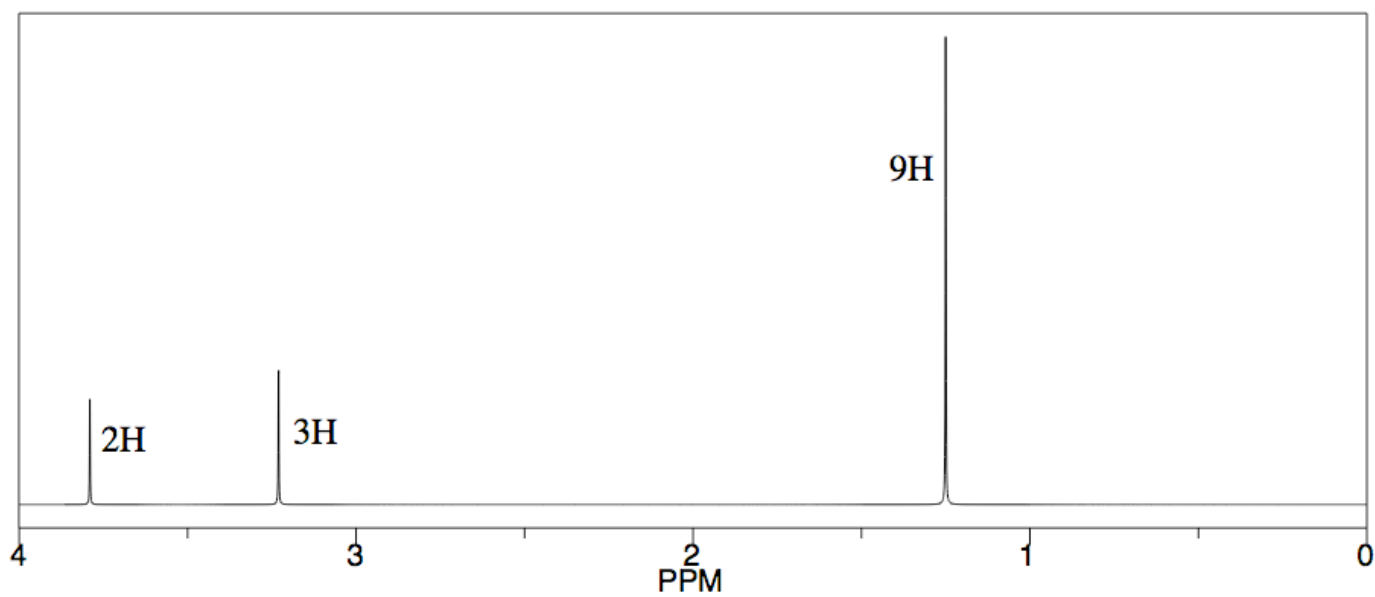
6. (2 pt each) **Circle whether each of the following statements is true or false.** You may notice these resemble Rules of the Day! These are worth a lot of points so please take your time and be careful. Read them carefully, but do not second guess yourself as we are not trying to trick you.

- True False** A. When the 2s orbital is hybridized with all three 2p orbitals, you get sp^3 hybridization that has major lobes pointed in a tetrahedral geometry.
- True False** B. When the 2s orbital is hybridized with all three 2p orbitals, you get sp^2 hybridization that has major lobes pointed in a trigonal planar geometry.
- 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 The enol form of a compound rapidly tautomerizes to the more stable keto form.
- True False** F The keto form of a compound rapidly tautomerizes to the more stable enol form.
- True False** G. Nuclei with spin quantum number 1.0 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, with and against the external field, respectively.
- 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, 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 felt by the nucleus.
- True False** J. 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 getting an A on this organic final!

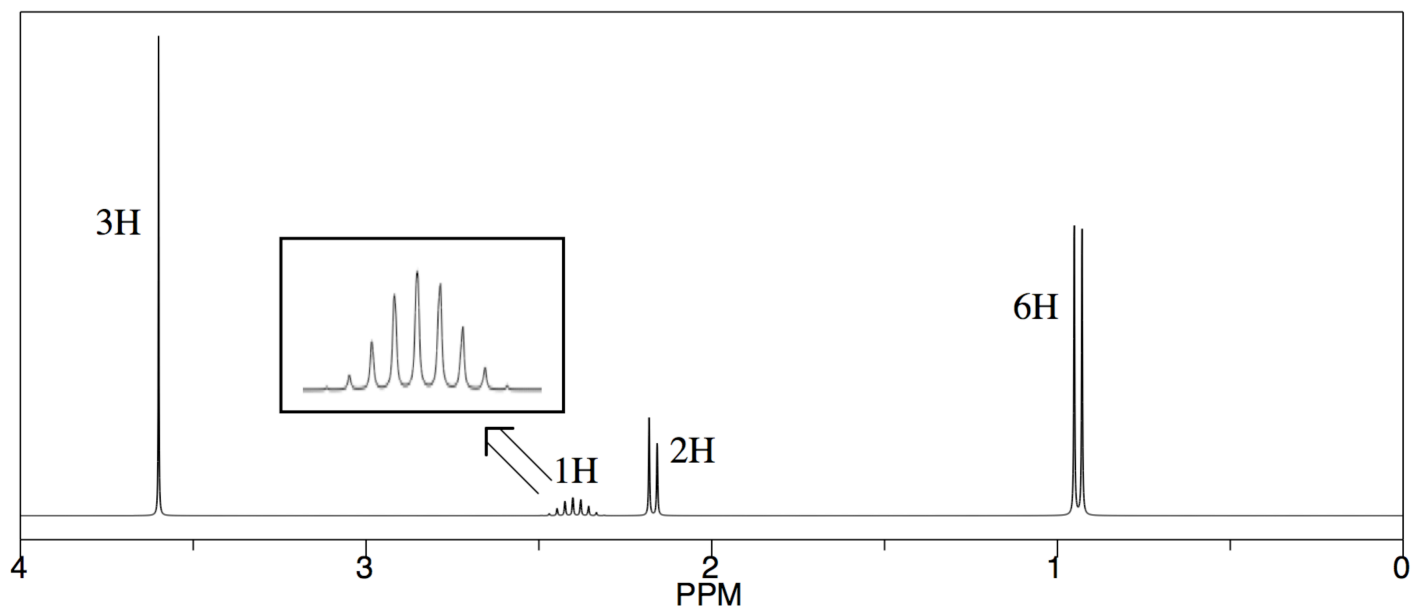
7. (15 pts total) On the following three pages there are NMR spectra. The relative integrations are given above each signal. Each NMR spectrum has a letter on it. **In the spaces provided, write the appropriate letter underneath the molecule that would produce that spectrum.** Notice that not all of the molecules below will have letters underneath them, as there are only three spectra but nine molecules.



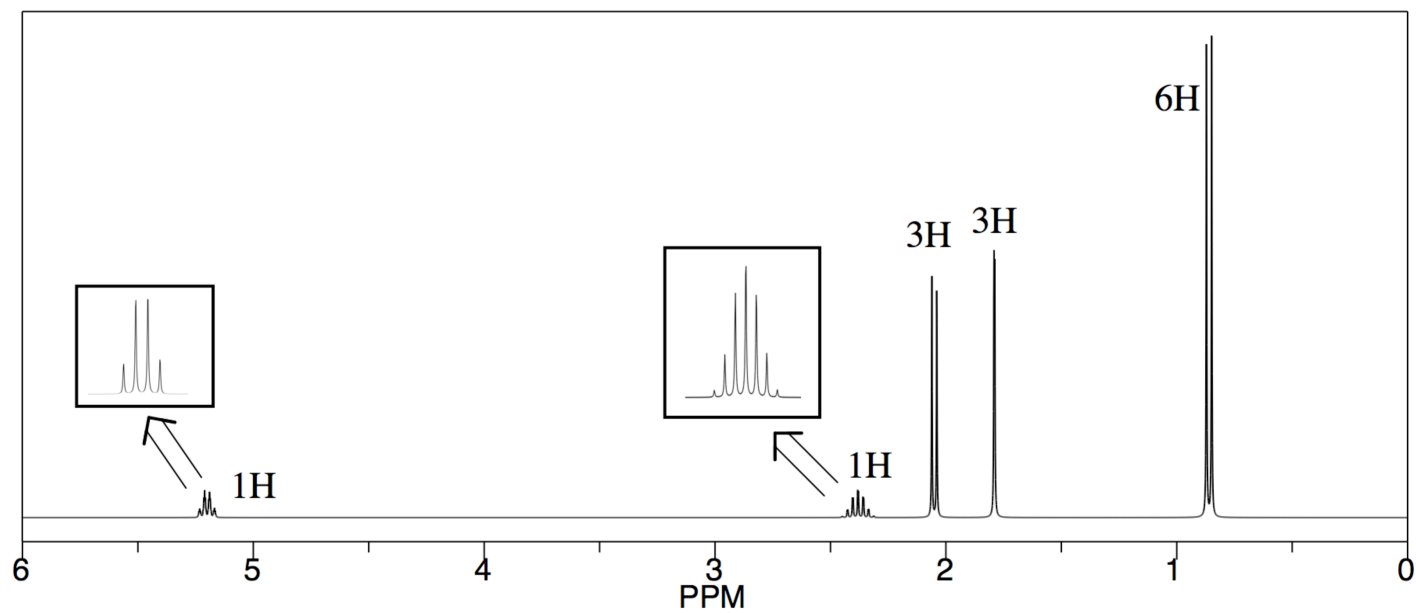
Spectrum A



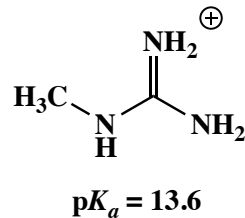
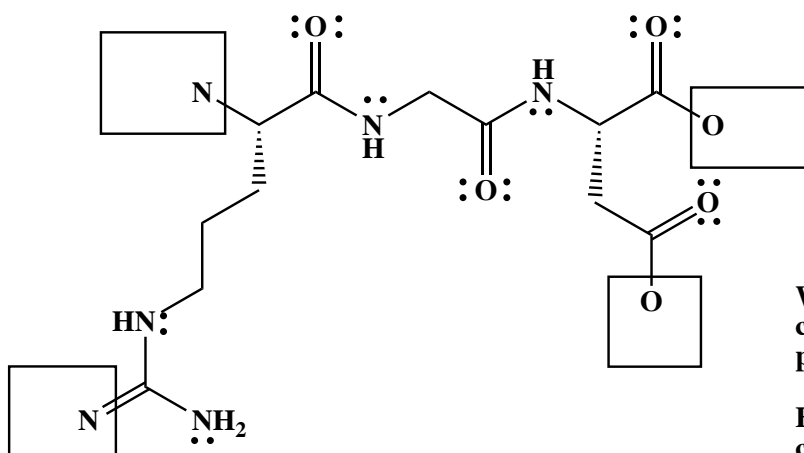
Spectrum B



Spectrum C



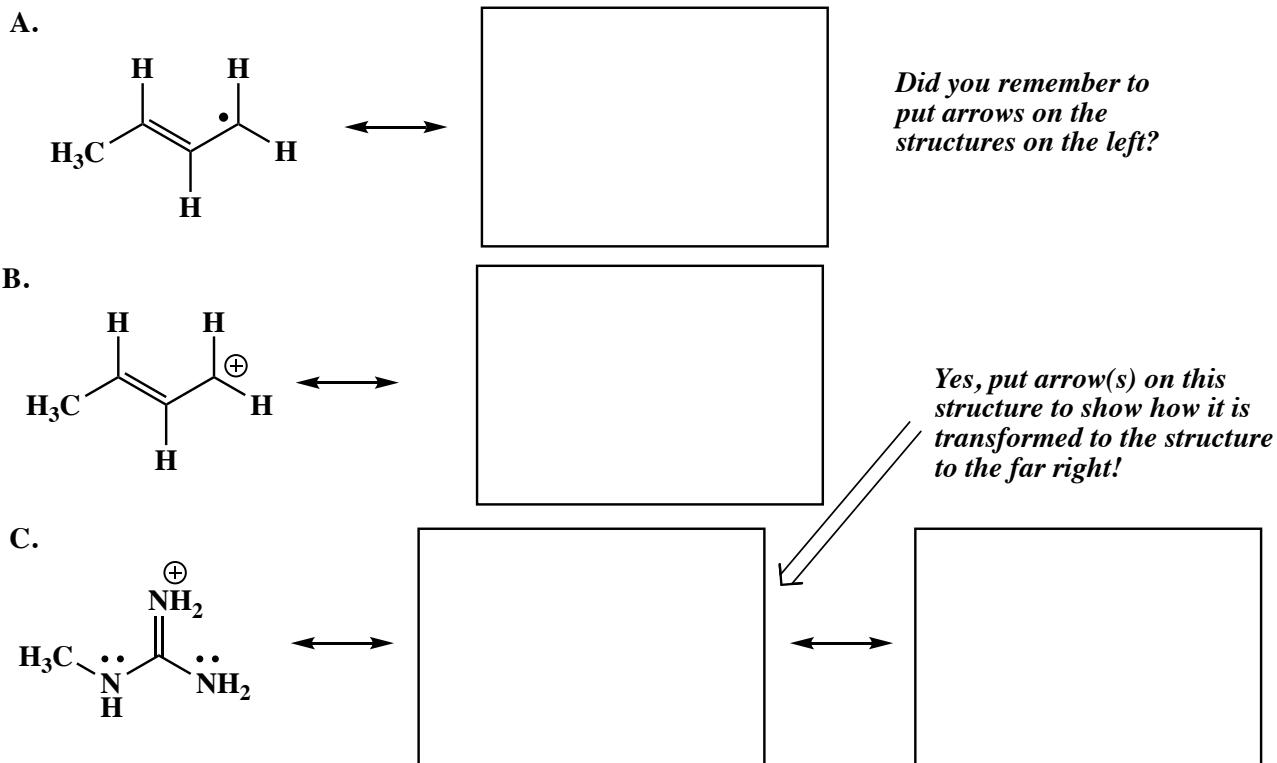
8. The following molecule is called RGD. It is the most common peptide motif responsible for cell adhesion to the extracellular matrix. Cell adhesion proteins called integrins recognize and bind the RGD sequence. **In the boxes, fill in the proper number of bonds to H atoms, lone pairs, and formal charges to show the protonation state of RGD at pH 7.0.** 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.



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

How many chiral centers are present in the RGD peptide? _____

9. (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.



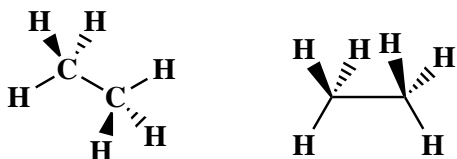
10. (19 pts) Circle the appropriate structure from each pair, then fill in the blank on the right stating the reason(s) for your answer. Possible answers for the blanks on the right are **Inductive Effect**, **Angle Strain**, **Torsional Strain**, **Ring Strain**, **Steric Strain**, or **Hyperconjugation**. You might need more than one answer in some cases.

Reason(s)

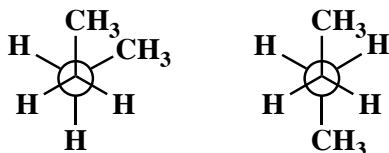
A) Circle the more stable carbocation



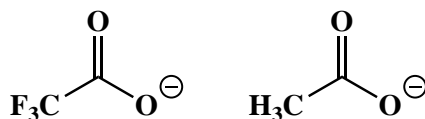
B) Circle the more stable conformation



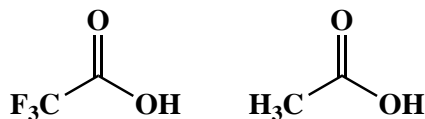
C) Circle the more stable conformation



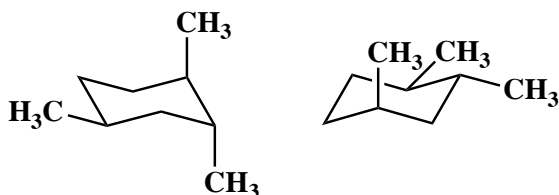
D) Circle the more stable anion



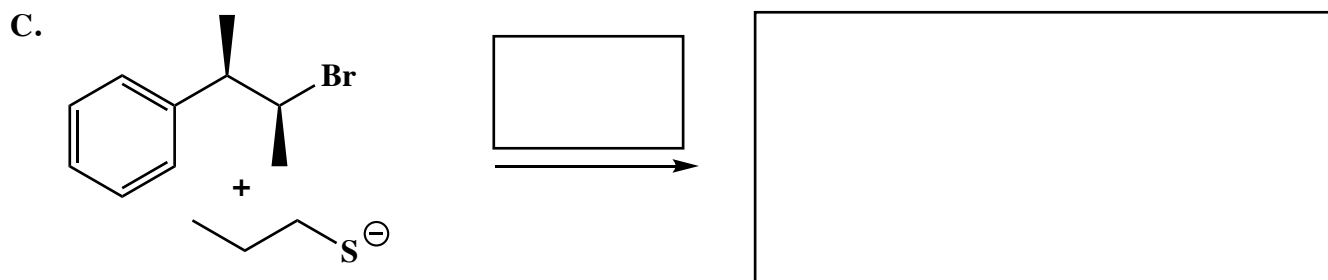
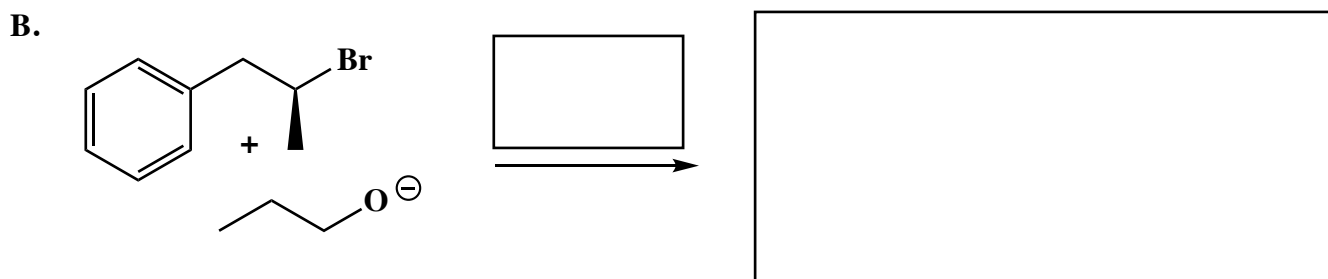
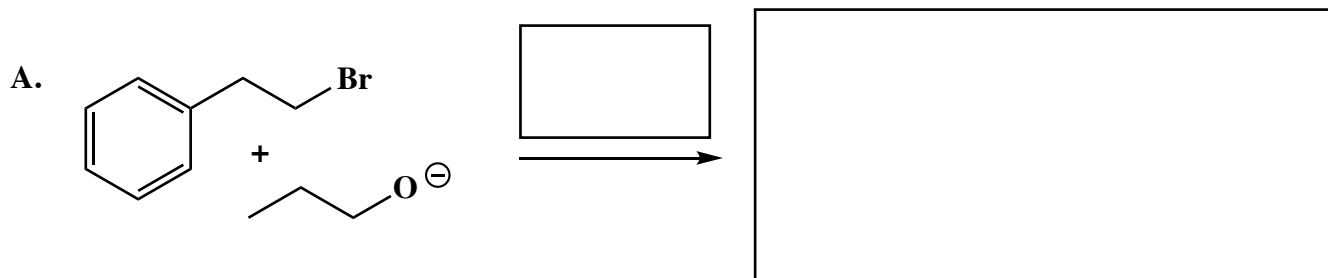
E) Circle the more acidic molecule



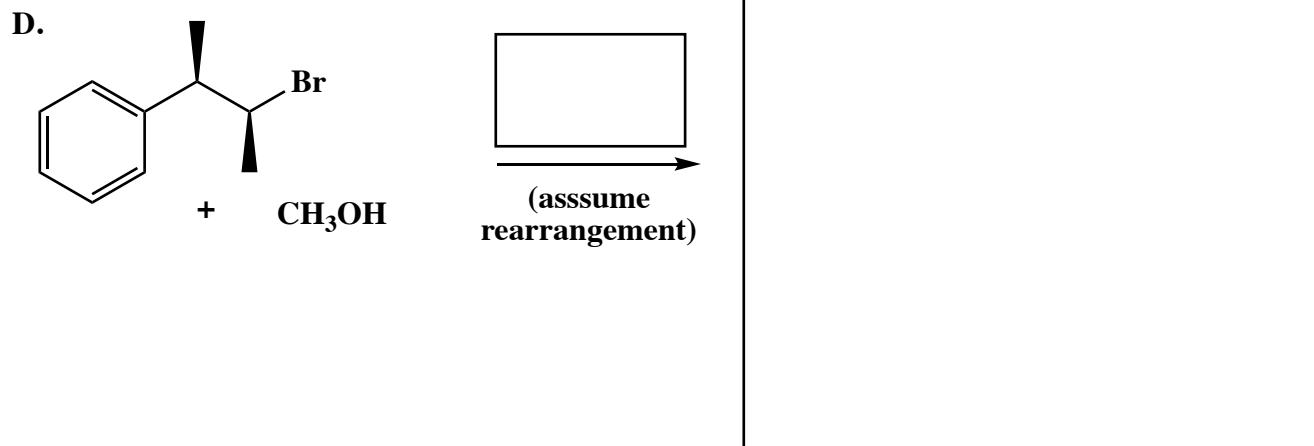
F) Circle the more stable conformation



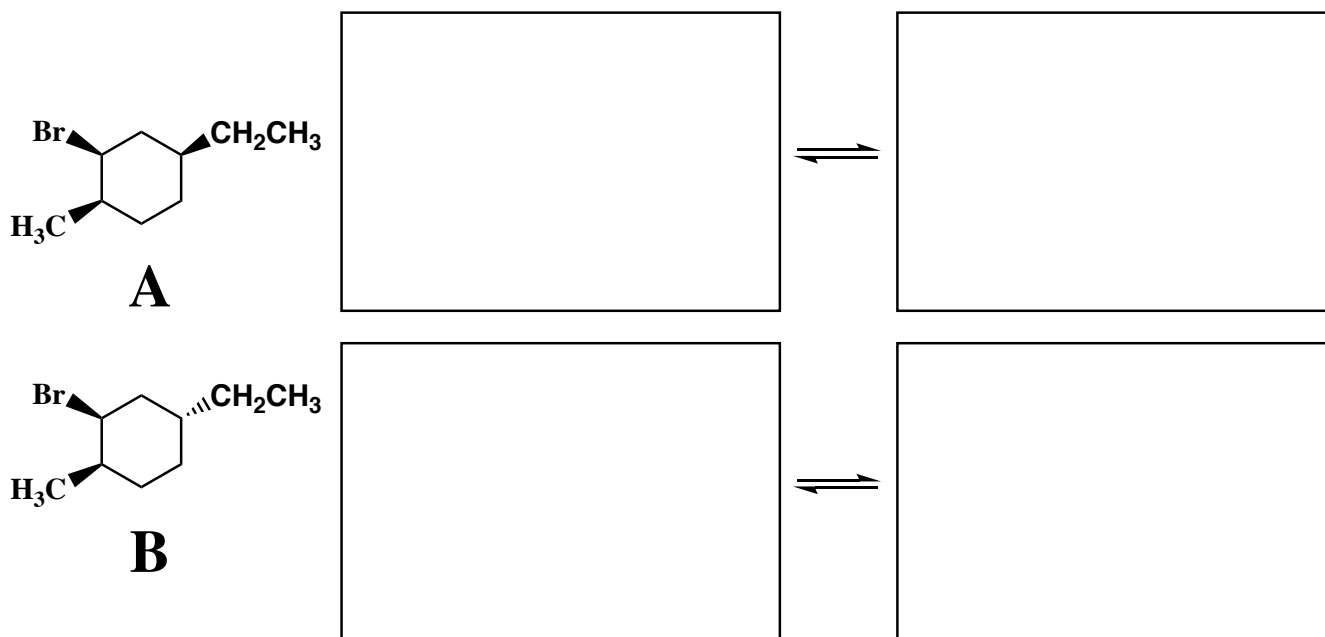
11. (5, 6 or 8 pts each) The following reactions all involve chemistry of haloalkanes. **Fill in the box above the arrow with the mechanism that will be followed (S_N2 , E2, etc.). Then draw only the predominant product or products** and please remember that **you must draw the correct stereoisomers**. For $S_N1/E1$ reactions you must draw all significant products (including all stereoisomers).



For the last one only draw rearranged products



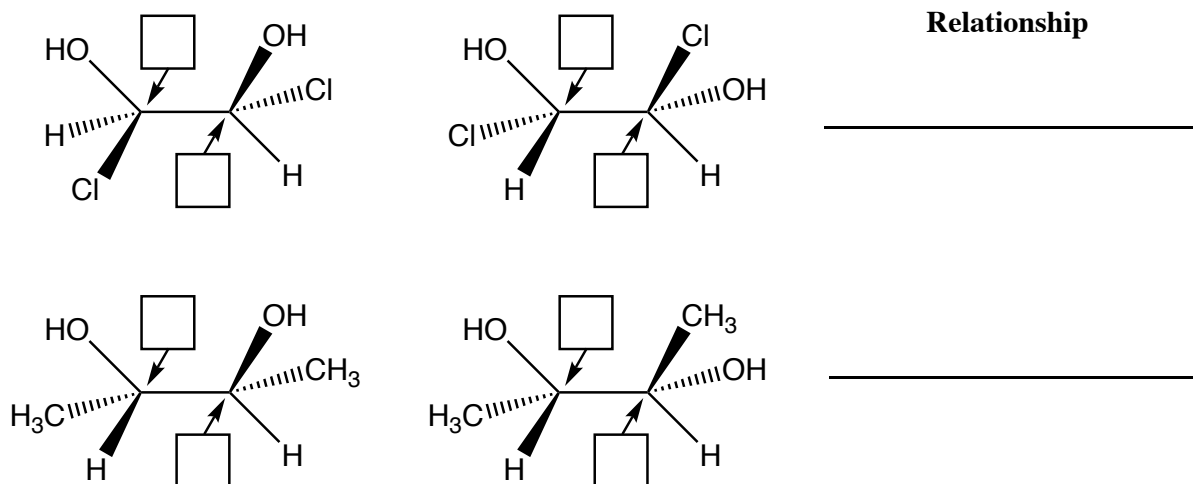
12. (10 pts) In the two spaces to the right, draw the two equilibrating chair structures for the following cyclohexane derivatives. In each case circle the one that predominates at equilibrium.



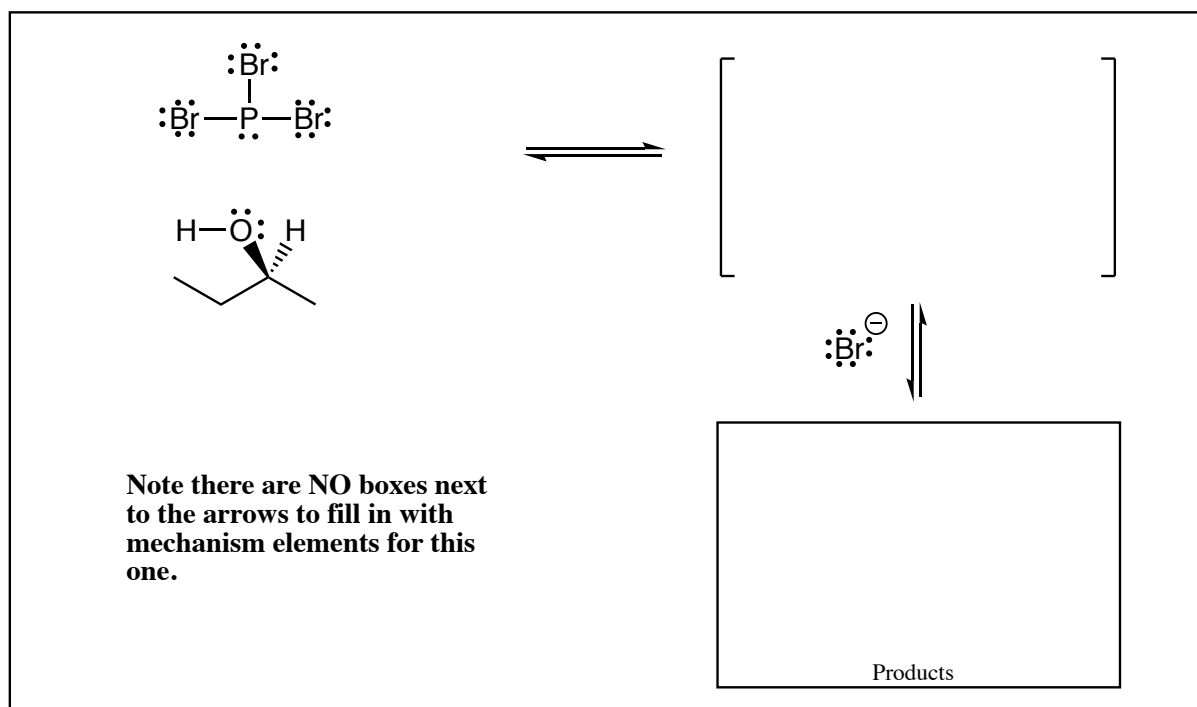
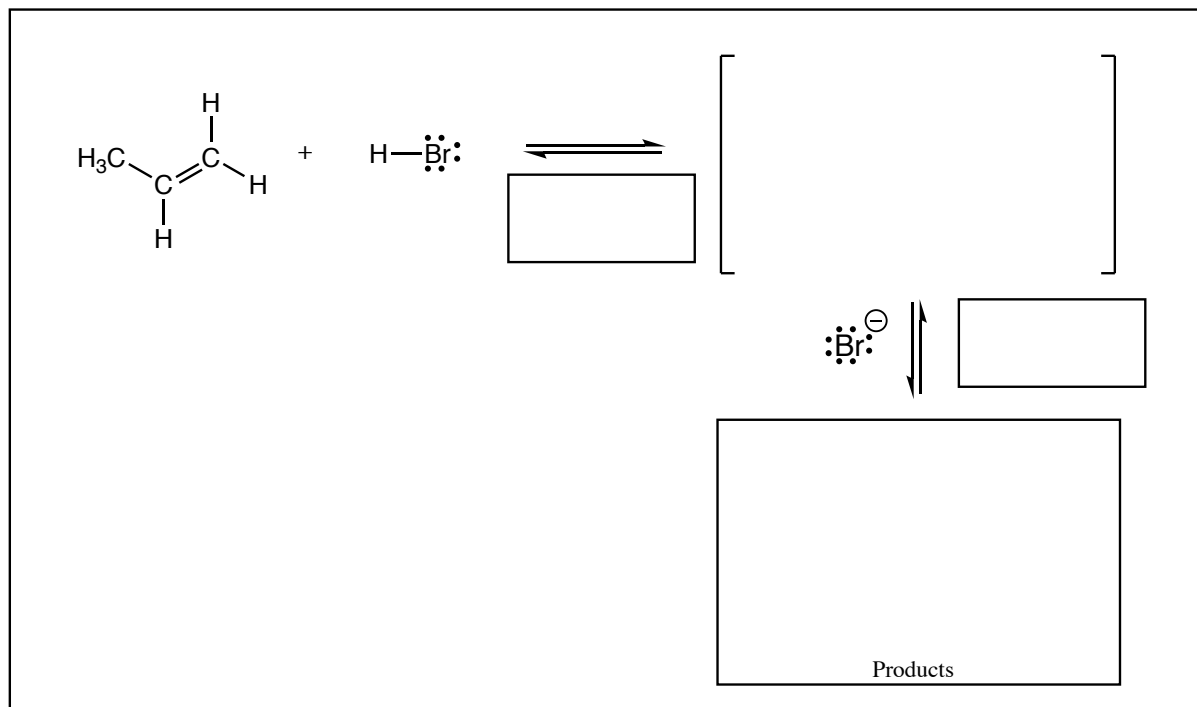
(3 pts) Which of the two structures, A or B, will react faster in an E2 reaction? _____

(3 pts) Your answer to that last question is based on noticing that for the molecule you chose, in the chair conformation that predominates, the Br atom is _____

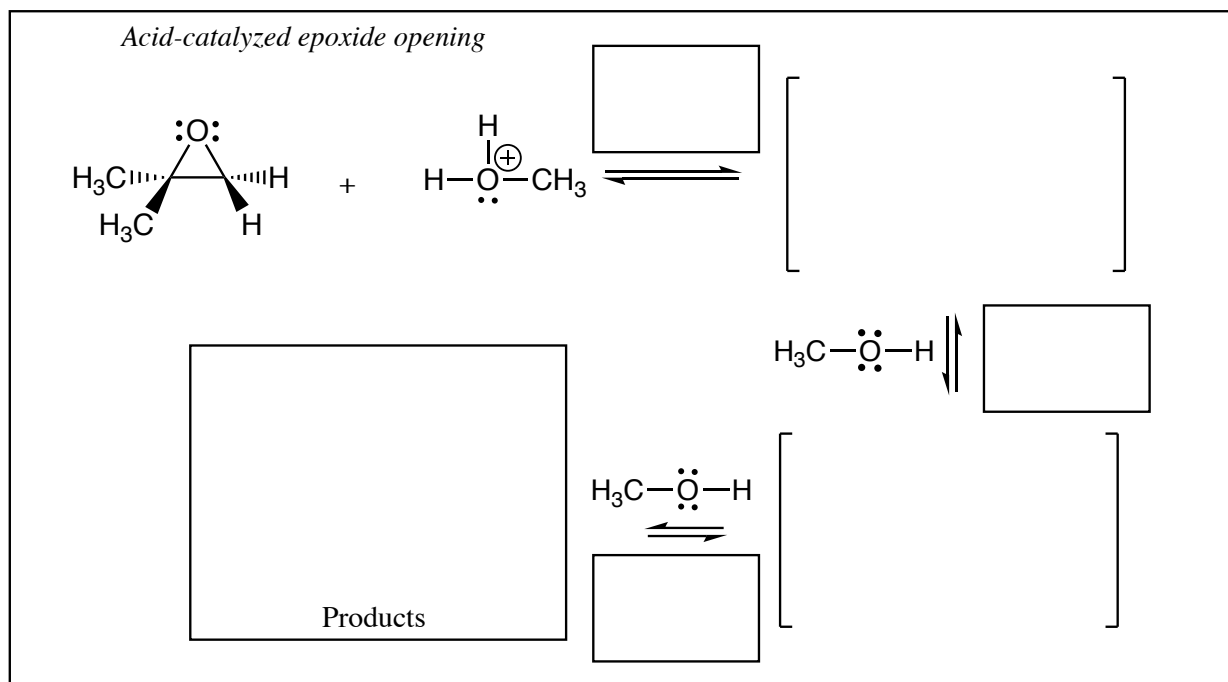
13. (13 pts total) On the line provided, state the stereochemical relationship between each pair of molecules: **enantiomers**, **diastereomers**, or **the same molecule**. In each box assign R and S to each chiral center to help answer this question. **Circle all meso compounds**.



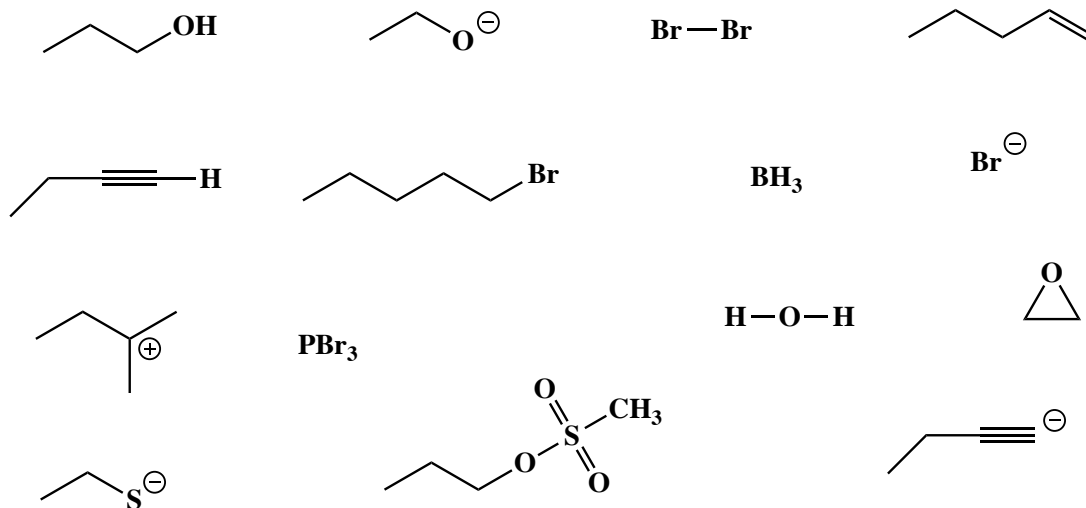
14. (20 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) For the following reactions, fill in the details of the mechanism. Draw the appropriate chemical structures and use an arrow to show how pairs of electrons are moved to make and break bonds during 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.



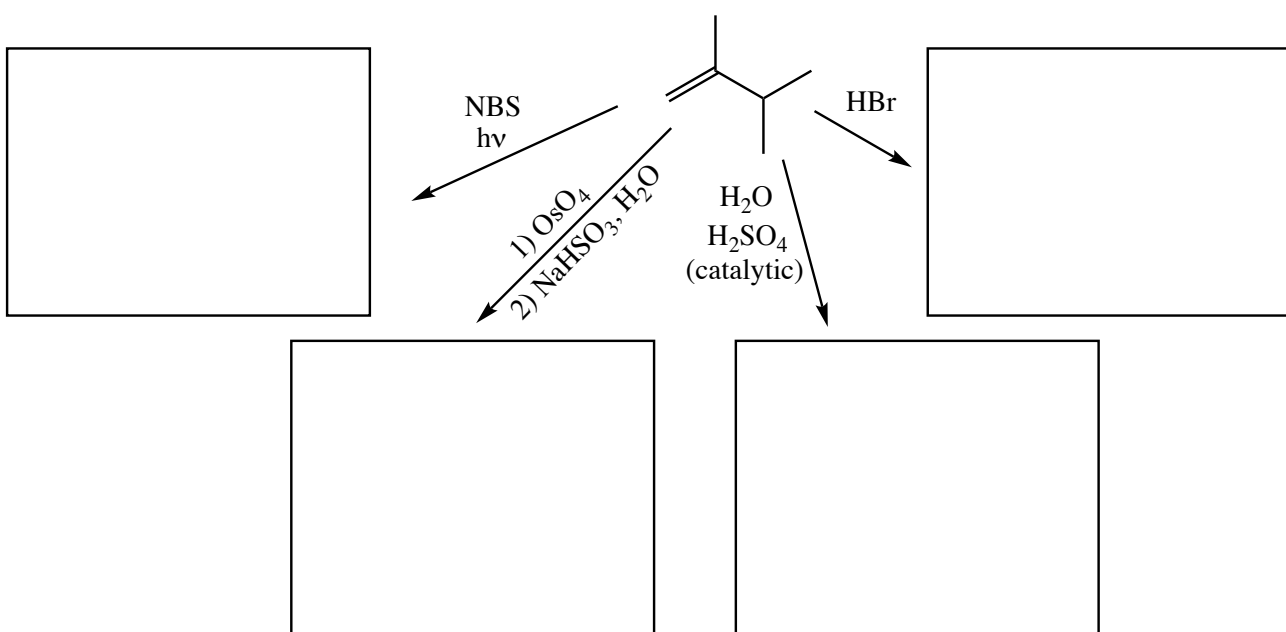
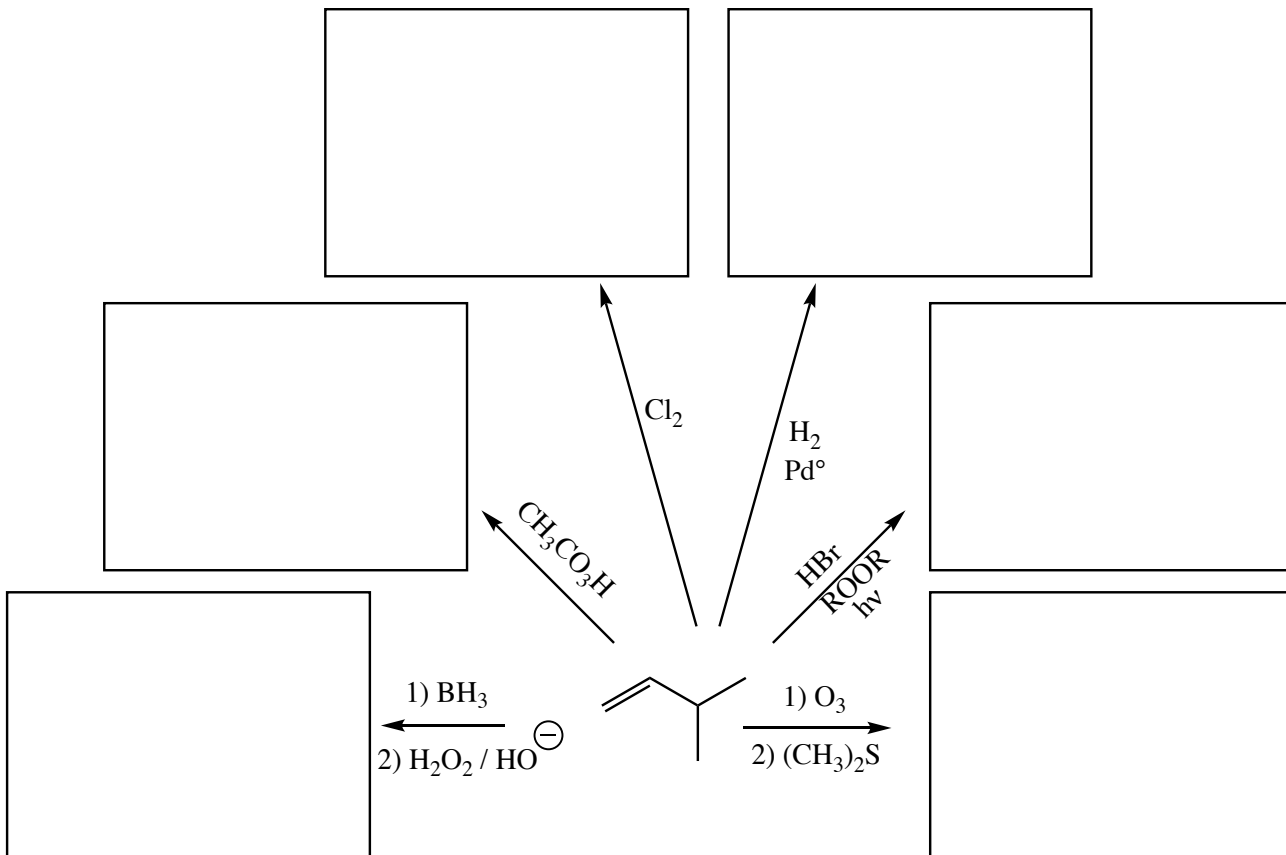
15. (17 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) For the following reaction, fill in the details of the mechanism. Draw the appropriate chemical structures and use an arrow to show how pairs of electrons are moved to make and break bonds during 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.



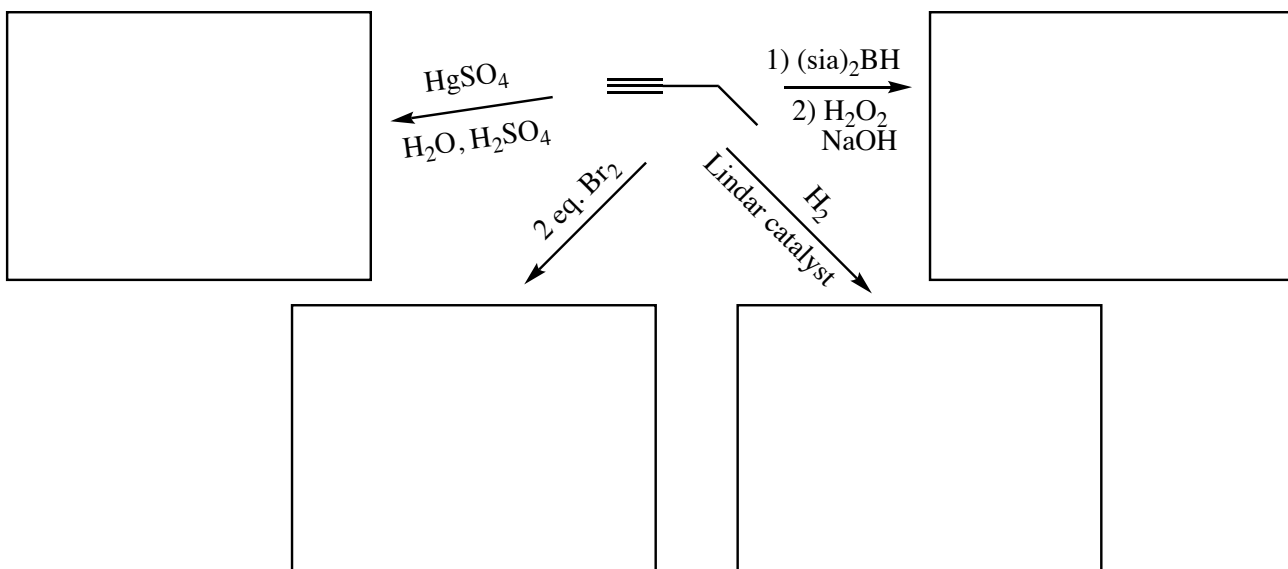
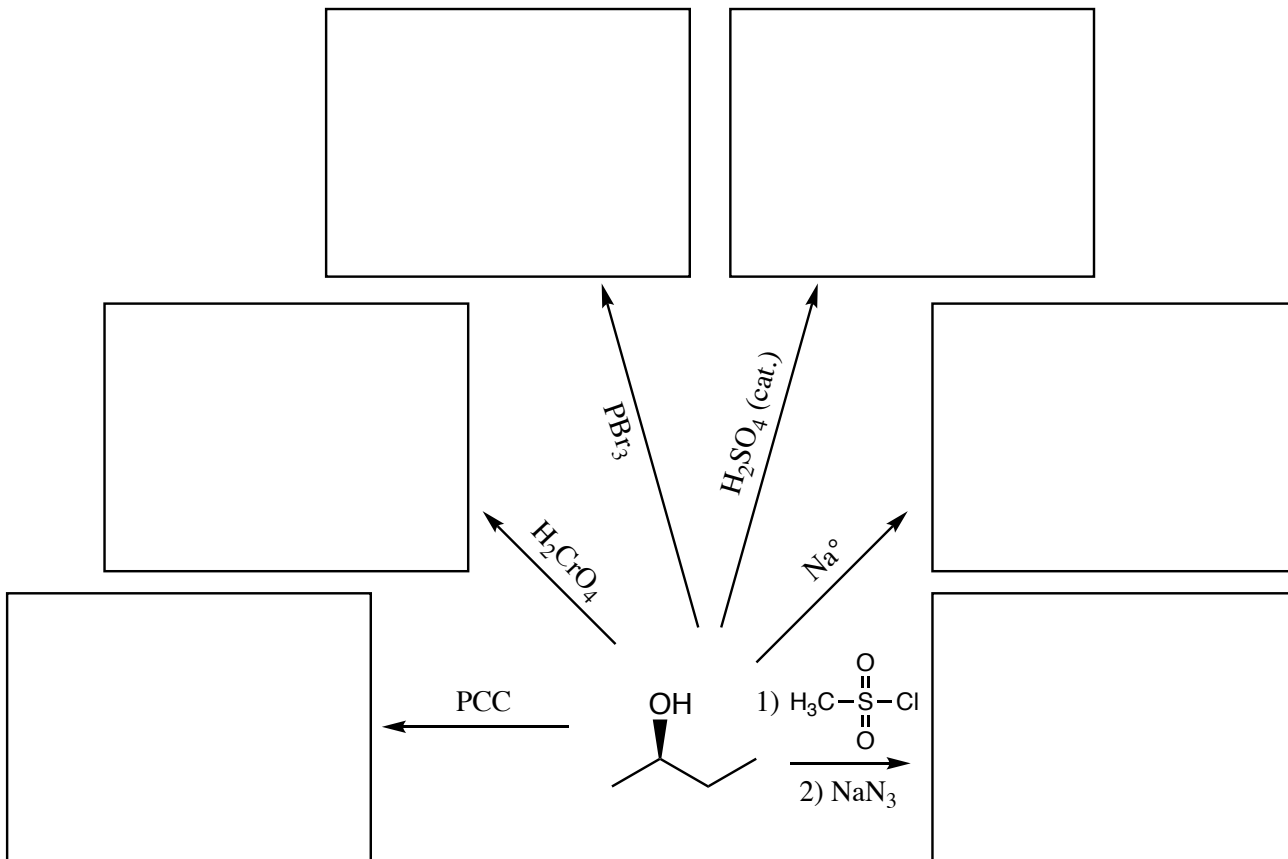
16. (15 pts) In order to predict mechanisms, it is important to understand the "personalities" of different reagents. Most important, it is essential that you can recognize **nucleophiles** and **electrophiles**. The following are either nucleophiles and electrophiles we have used in mechanisms this semester. **Draw a circle around each of the following molecules we have used as a nucleophile. Do not put any marks around the electrophiles.**



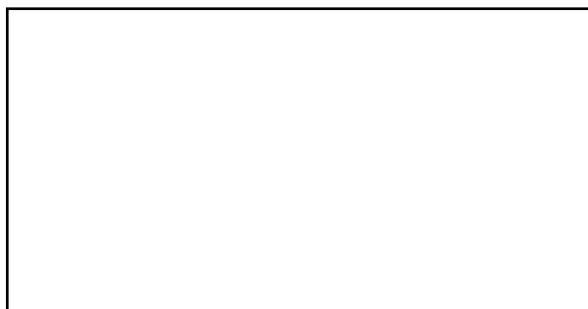
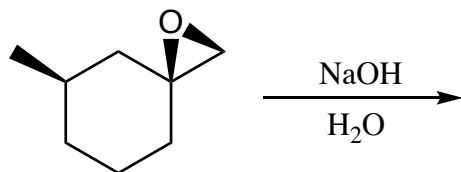
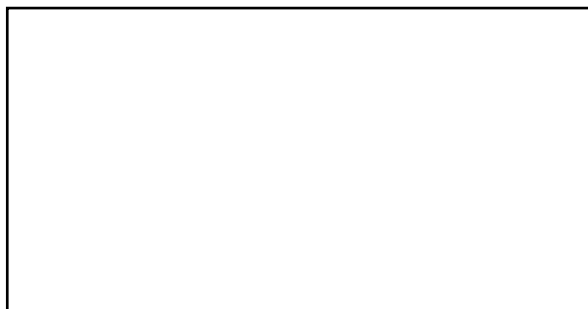
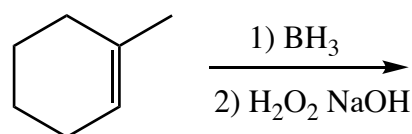
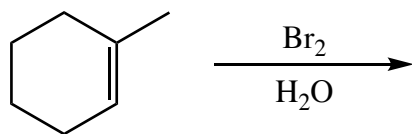
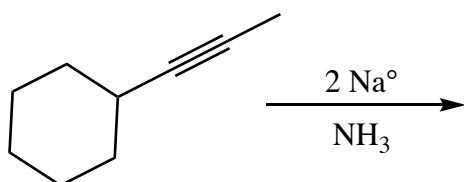
17. (3, 4 or 5 pts each) For the following, complete the reactions with the predominant carbon-containing product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



18. (3 or 5 pts each) 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. (3, 4 or 5 pts each) 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.

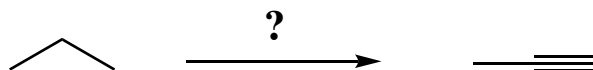


Signature _____

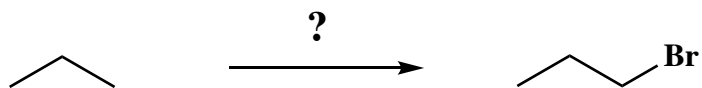
Pg 17 _____(17)

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) (10 pts)



B) (7 pts)

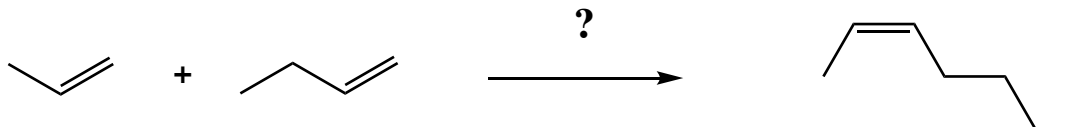


Signature _____

Pg 18 _____(16)

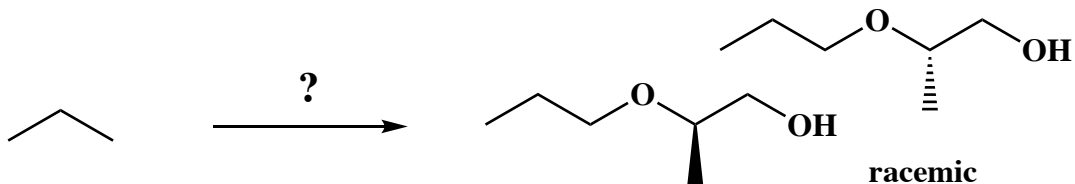
20. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule 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 material.**

C) (16 pts)

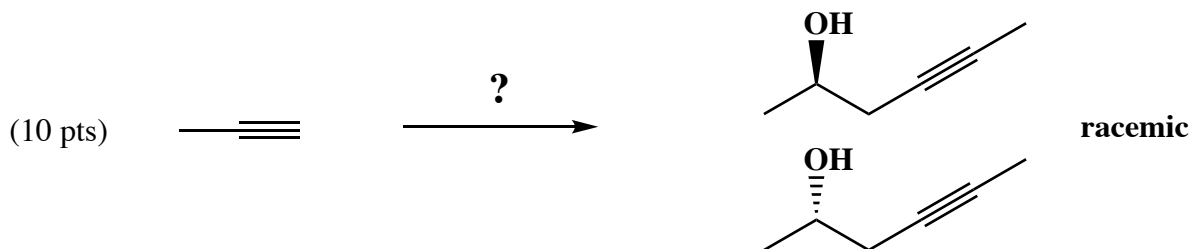


20. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule 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 material.**

D (13 pts)



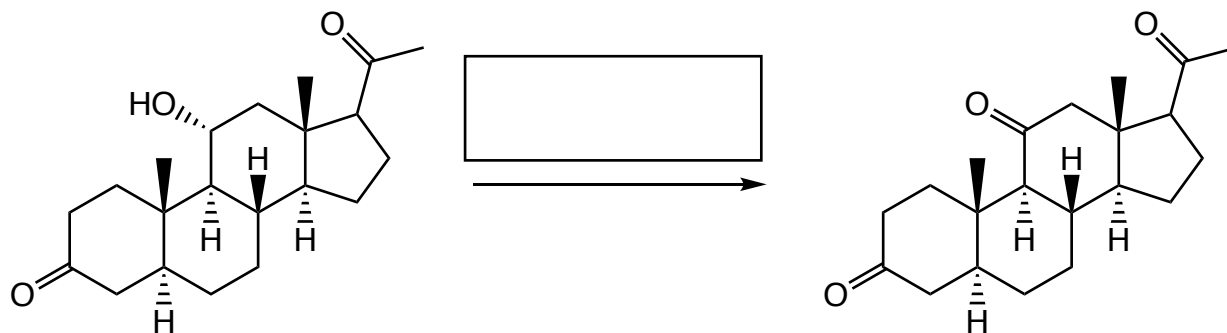
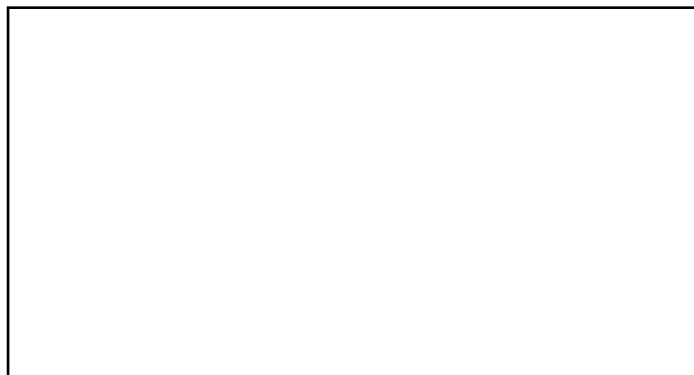
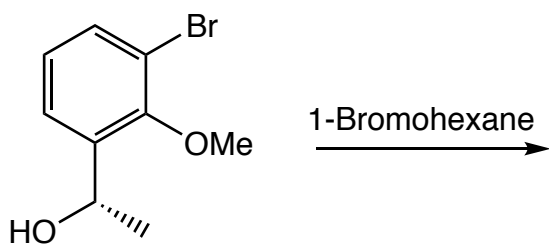
21. Here is an “apply what you know” synthesis question. You have never seen the reaction that makes the final product, but you do know enough chemistry to figure out what happens. Think about what you know about the “personalities” of the different molecules we have seen, and you will be OK. Show all 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.**



Signature _____

Pg 21 _____(8)

20. (8 pts) The chemistry you have learned this semester is used in the synthesis of important pharmaceuticals. Here are two examples. In the first, fill in the product in the space provided, in the next, fill in the reagent required to carry out the transformation indicated.



Have a great holiday break!!