

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

# 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)

# PERIODIC TABLE OF THE ELEMENTS

### Elementary Subatomic Particles

Electron	Proton	Neutron	Photon	Neutrino
Symbol	e	p	n	$\nu$
Rest mass (kg)	$9.10938291 \times 10^{-31}$	$1.67262161 \times 10^{-27}$	$1.67492716 \times 10^{-27}$	0
Relative mass (p/m)	$5.485799091 \times 10^{-4}$	$1.00727647012 \times 10^{-3}$	$1.008664914 \times 10^{-3}$	0
Particle-antiparticle mass ratio	1	1836.15270137	1838.68360140	0
Particle-antiparticle mass ratio	5.485799091	0.000544	1	0
Spin (h)	$1/2$	$1/2$	$1/2$	0
Spin quantum number	$1/2$	$1/2$	$1/2$	0
Spin quantum number (h)	$0.366255915 \times 10^{-34}$	$0.366255915 \times 10^{-34}$	$0.366255915 \times 10^{-34}$	0
Magnetic moment (J/T)	$9.274009473 \times 10^{-24}$	$1.83612463 \times 10^{-23}$	$1.83612463 \times 10^{-23}$	0
In Bohr magnetons, $\mu_B$	1.0018246903	$1.83612463 \times 10^{-23}$	$1.83612463 \times 10^{-23}$	0
In nuclear magnetons, $\mu_N$	$1836.15270137$	$1.0018246903$	$1.0018246903$	0

### % Ionic Character of a Single Chemical Bond

Percent ionic character describes the nature of a bond. Bonds possessing 50% or greater ionic character are commonly termed ionic; bonds with less than 50% ionic character are termed covalent. Pauling's equation was modified by Hershley.

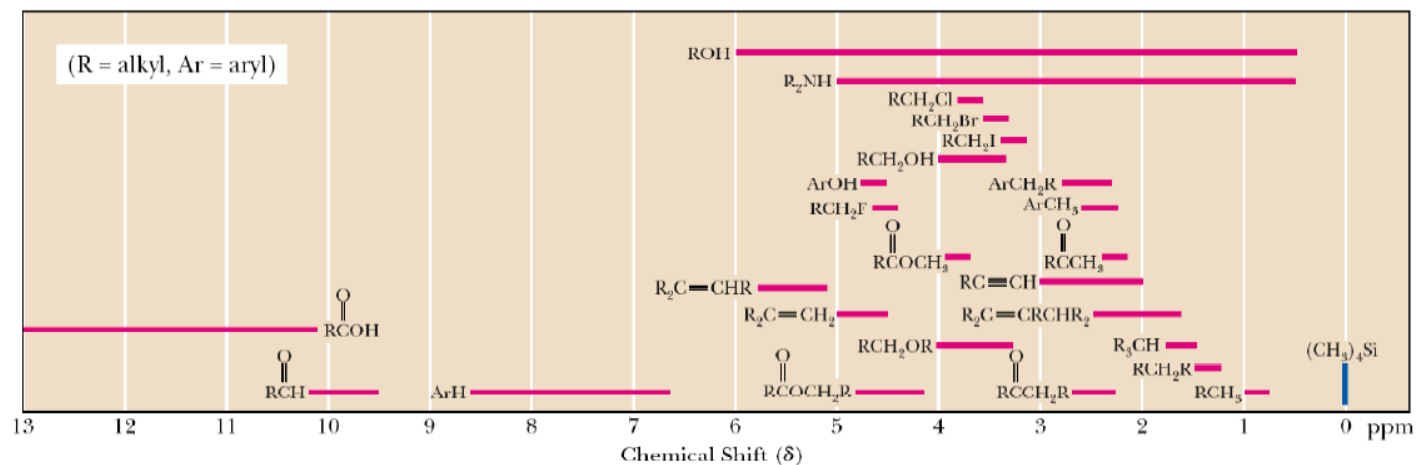
A graph in order to obtain better agreement between experimental and calculated values. Transition from covalent to ionic bonding is usually accompanied by a reduction in electron conductivity, melting point and boiling point.

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 IIIB	14 IVA	15 VA	16 VIB	17 VIIB	18 VIII O
1 H	2 He	3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Compound		pK <sub>a</sub>
Hydrochloric acid	$\text{H-Cl}$	-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	$\text{RCH}_2\text{SH}$	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	$\text{HOH}$	15.7
Alcohols	$\text{RCH}_2\text{OH}$	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 ( $\delta$ )*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift ( $\delta$ )*
$R_2NH$	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.

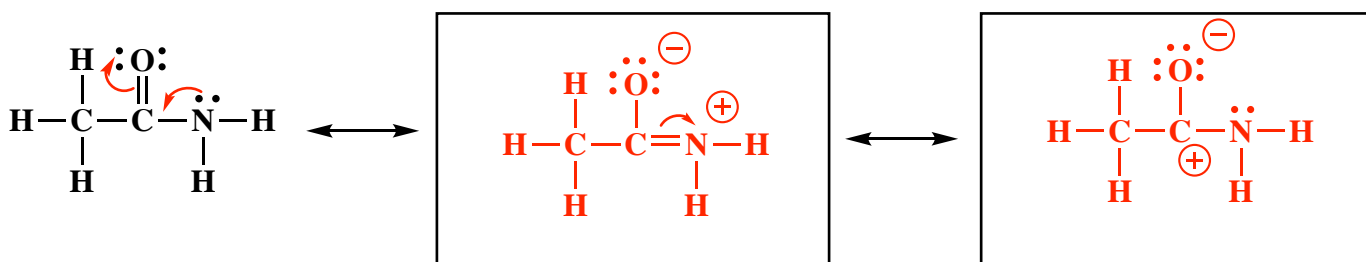
**C. Predicting Reactions** 8. Reactions will occur if the products are more stable than the reactants and the energy barrier is low enough. 9. Functional groups react the same in different molecules. 10. A reaction mechanism describes the sequence of steps occurring during a reaction. 11. Most bond-making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



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

**Where are the electrons?**

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

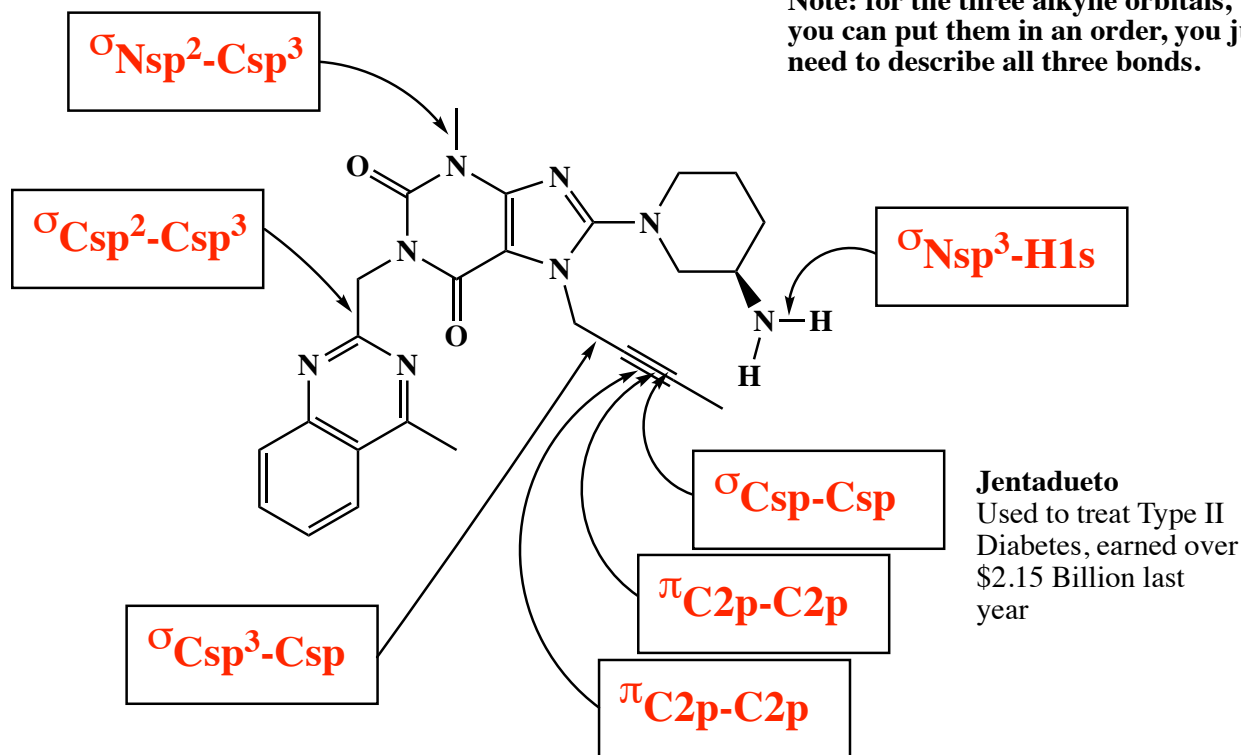


3. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here and your answer should match a recent Rule of the Day.

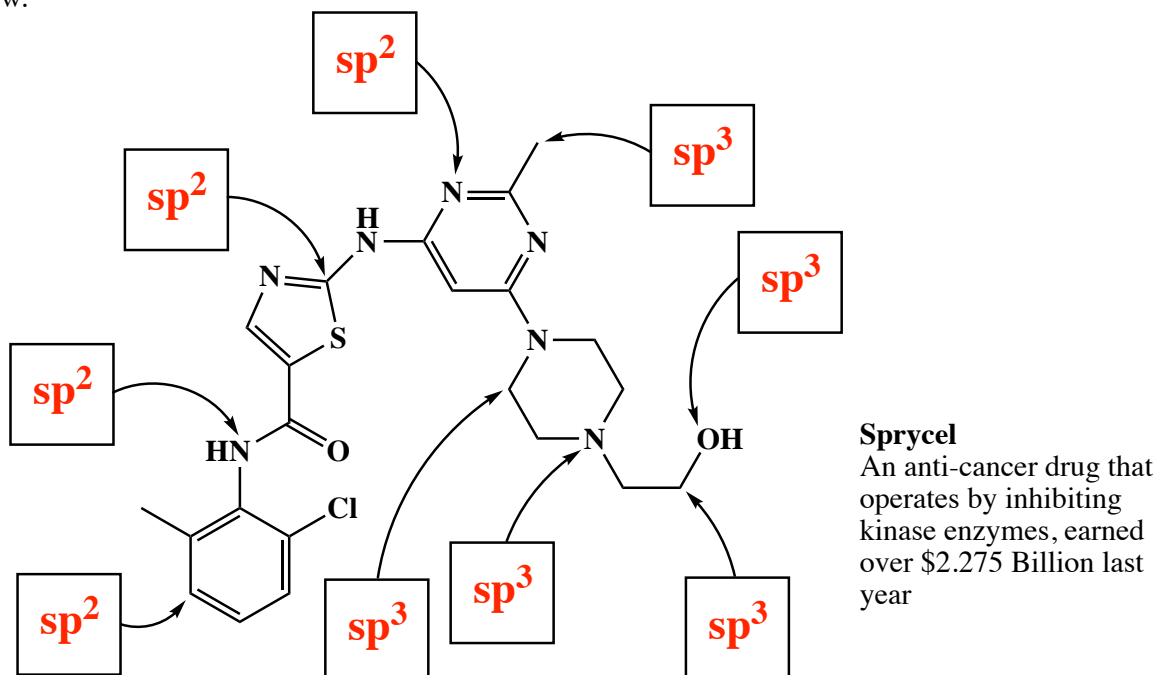
The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on the **same principles as NMR**, namely the **flipping (i.e. resonance) of nuclear spins of H atoms by radio frequency irradiation** when a patient is placed in a **strong magnetic field**. **Magnetic field gradients** are used to gain imaging information, and **rotation of the gradient around the center of the object** gives imaging in an entire plane (i.e. **slice inside patient**). In an MRI image, you are looking at **individual slices** that **when stacked make up the three-dimensional image** of relative amounts of H atoms, especially the **H atoms from water and fat, in the different tissues**.

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:  $\sigma_{\text{Csp}^3-\text{H}1\text{s}}$

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



5. (1 pt 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. 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.

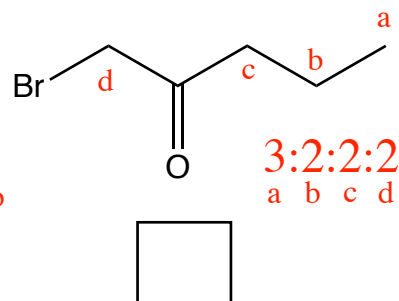
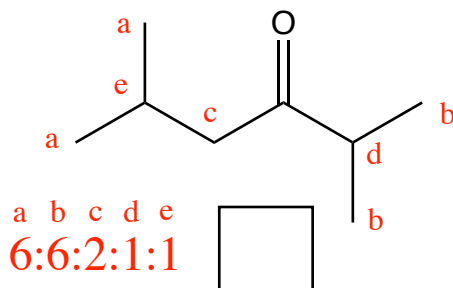
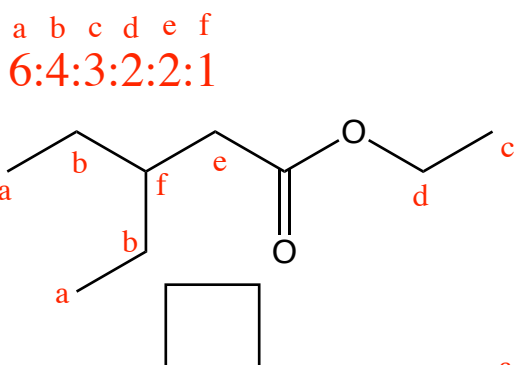
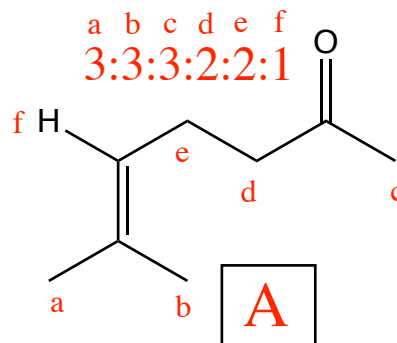
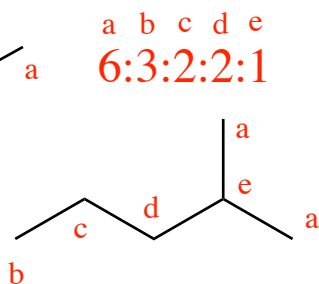
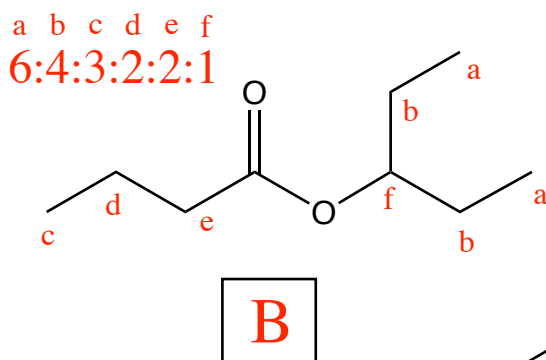
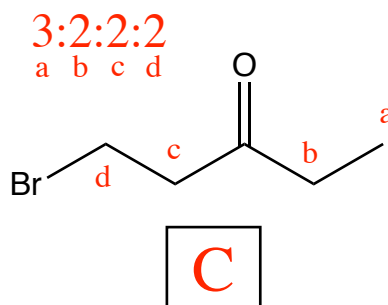
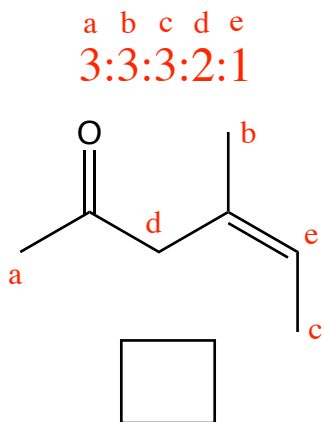
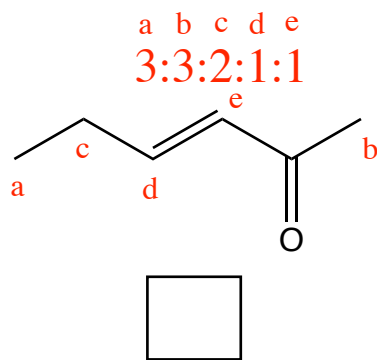
True  False

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

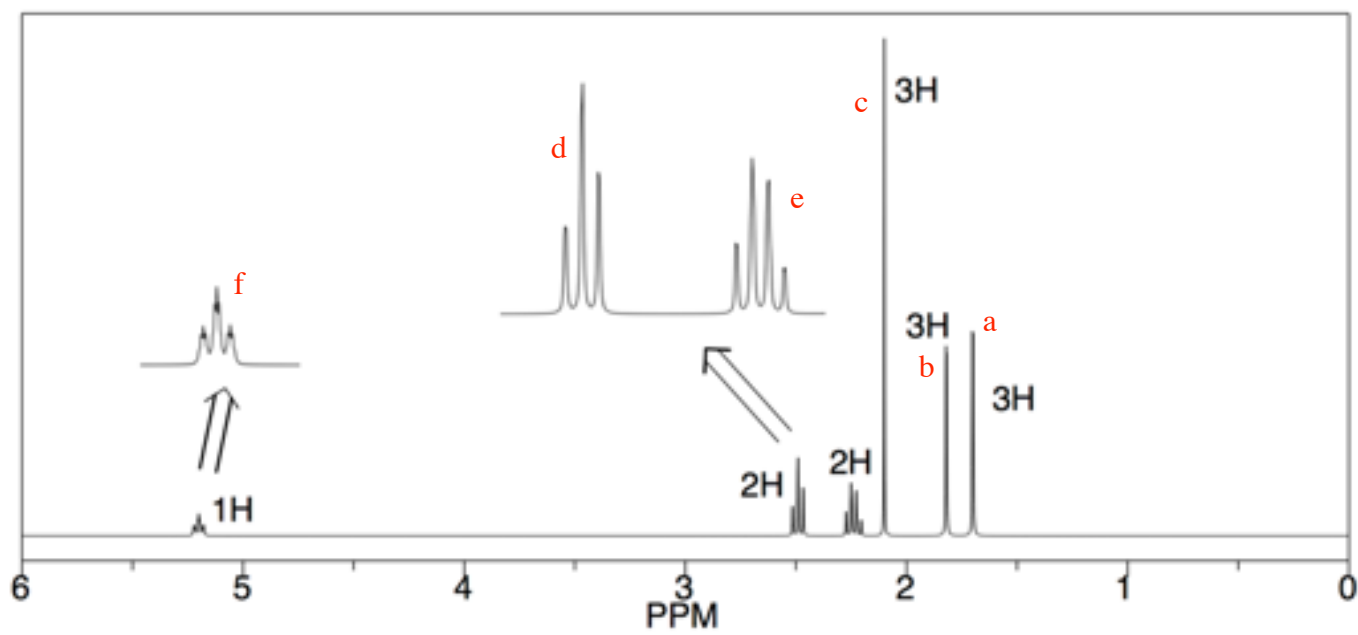
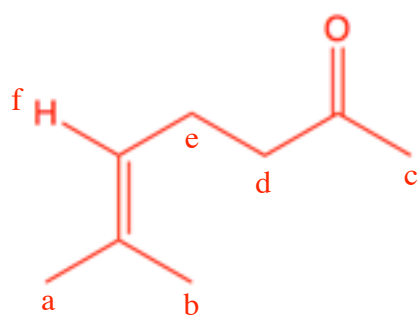
L. Running 3-5 miles a week EVERY WEEK as an adult dramatically increases your fitness level and improves your health throughout your life. Doing this and enjoying a healthy life is even more important than this organic class!

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.



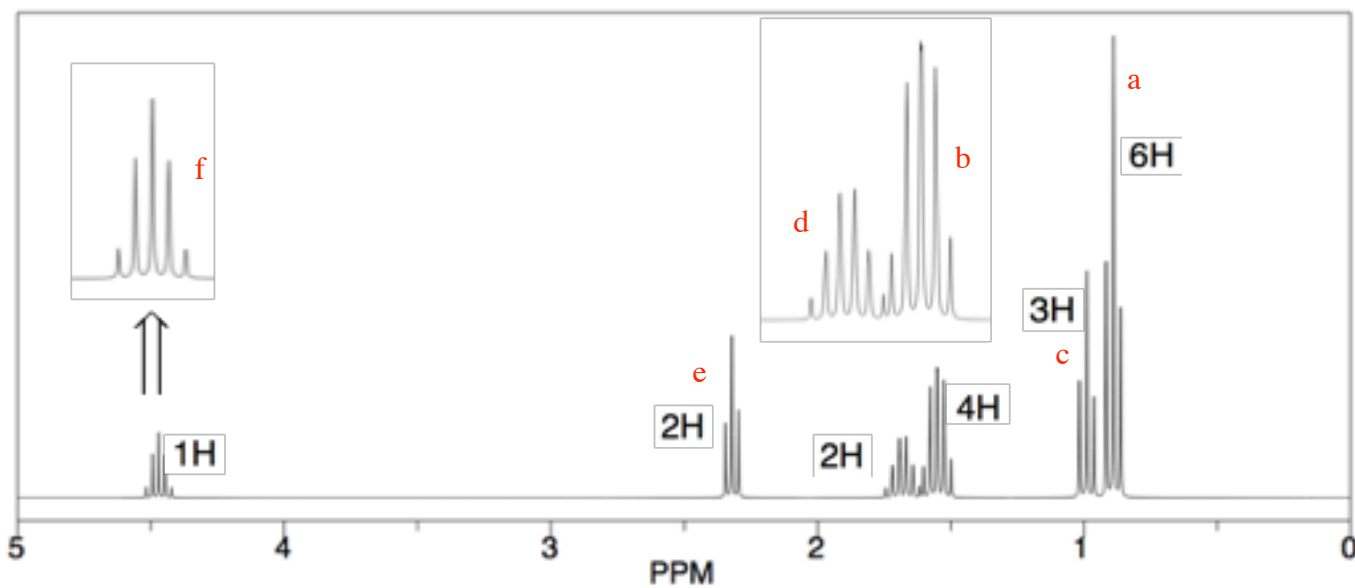
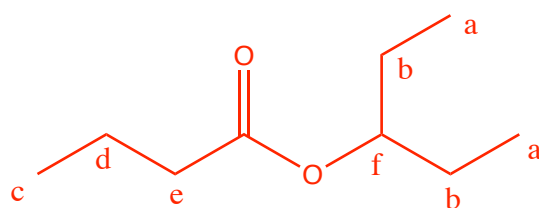
# Spectrum A

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# Spectrum B

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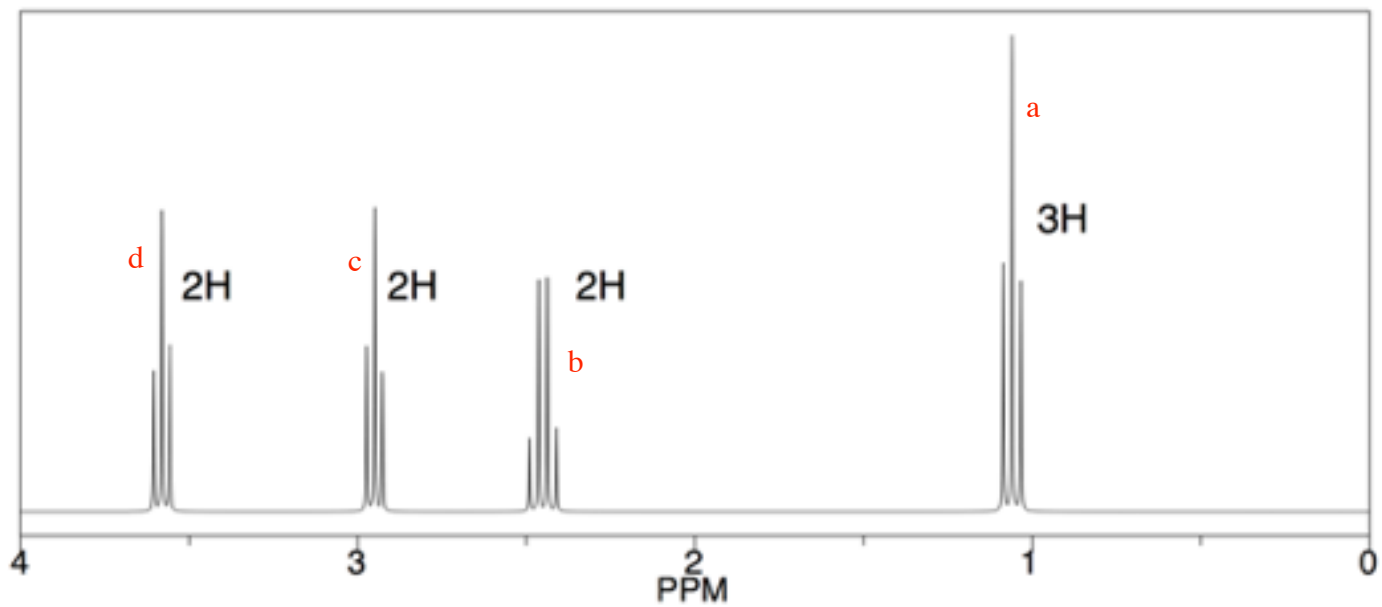
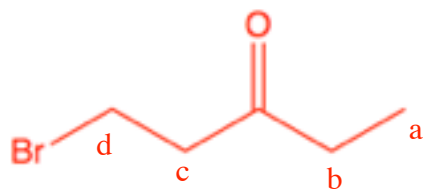


Signature \_\_\_\_\_

Pg 7

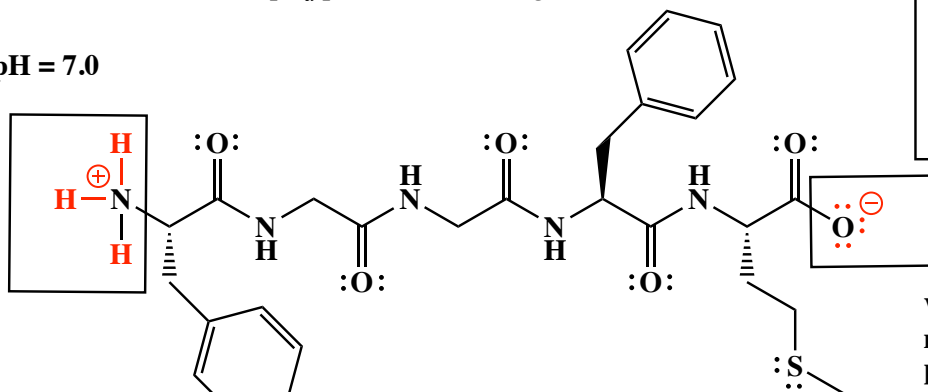
# Spectrum C

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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.

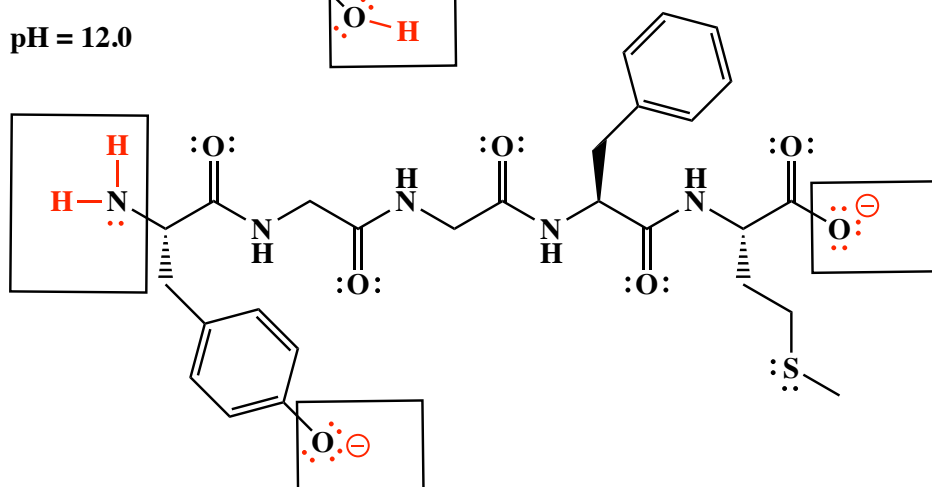
pH = 7.0



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

**0**

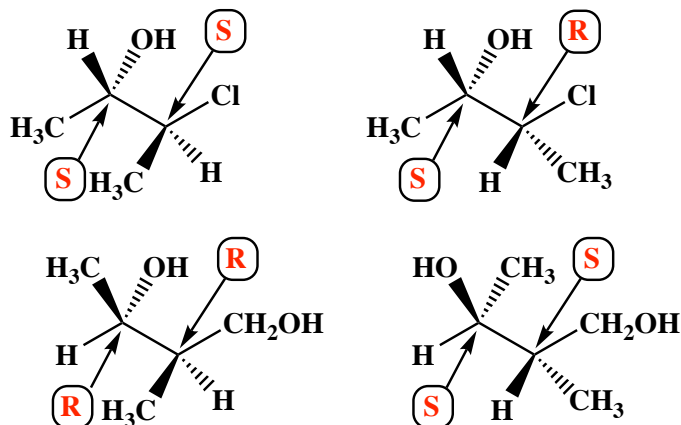
pH = 12.0



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

**-2**

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.

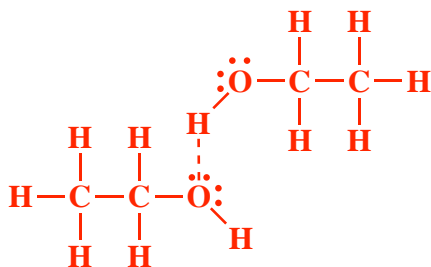


Relationship:

**diastereomers****enantiomers**

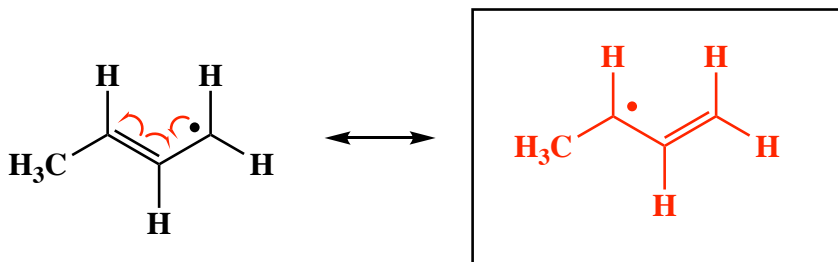


10. (5 pt) A hydrogen bond is the strongest interaction seen among neutral molecules. In the space provided, draw two molecules of ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) and show a hydrogen bond between them. Use a dashed line ( - - - - - ) to indicate any hydrogen bonds and be sure to draw all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



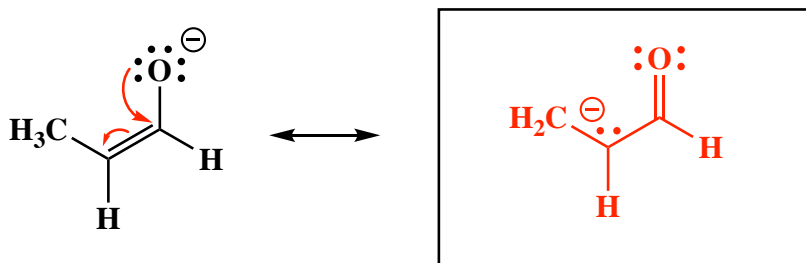
11. (16 pts total) The following are contributing structures for important resonance hybrids. Draw the other important resonance contributing structure in the box provided. Draw arrows on the structures on the left that indicate the flow of electrons that produce the contributing structures you drew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

A.



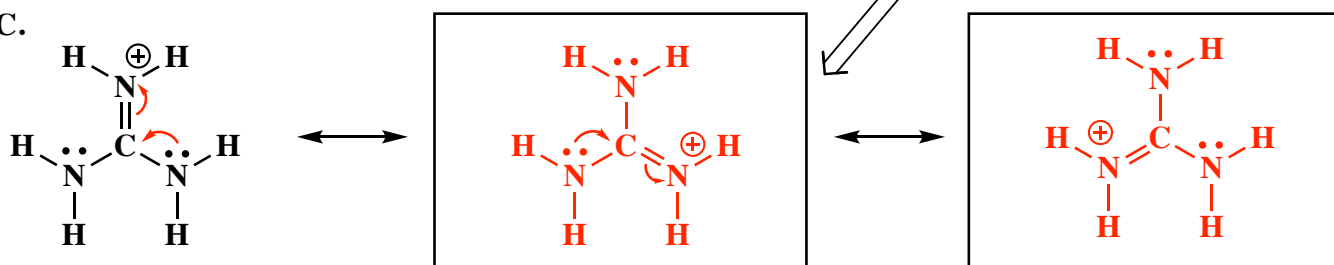
*Did you remember to put arrows on the structures on the left?*

B.



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

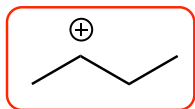
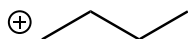
C.



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.

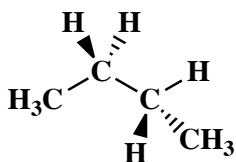
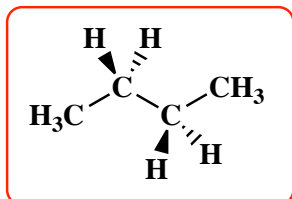
Reason(s)

A) Circle the more stable carbocation



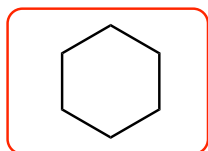
Hyperconjugation, Inductive Effect

B) Circle the more stable conformation



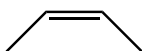
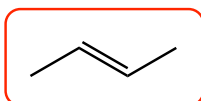
Steric Strain

C) Circle the cycloalkane with less strain



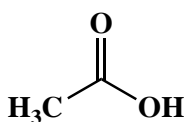
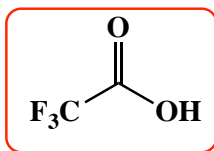
Angle Strain, Torsional Strain

D) Circle the more stable alkene



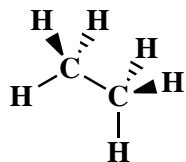
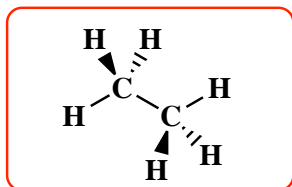
Steric Strain

E) Circle the more acidic molecule



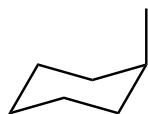
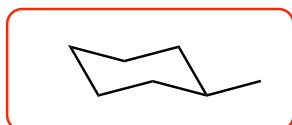
Inductive Effect

F) Circle the more stable conformation



Torsional Strain

F) Circle the more stable conformation

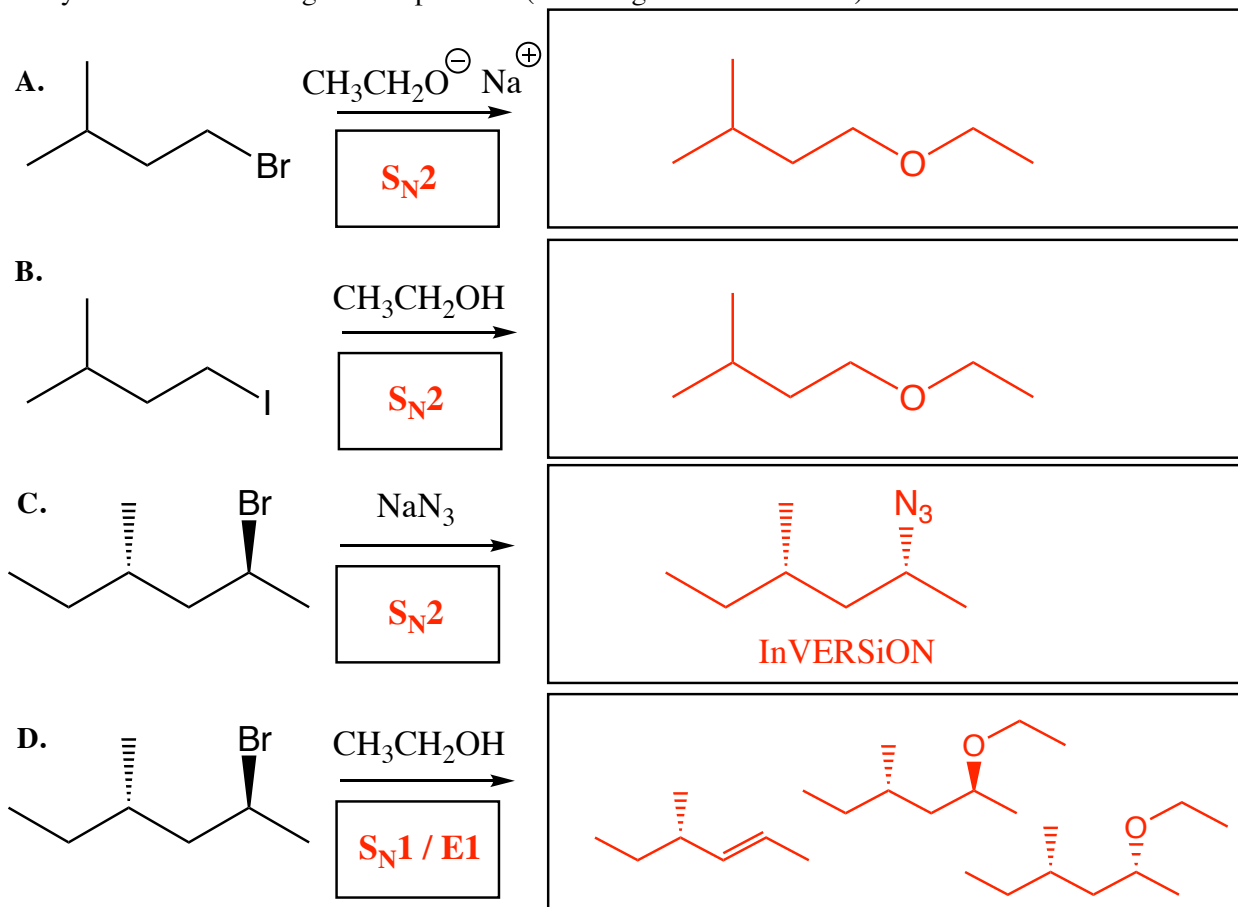


Steric Strain

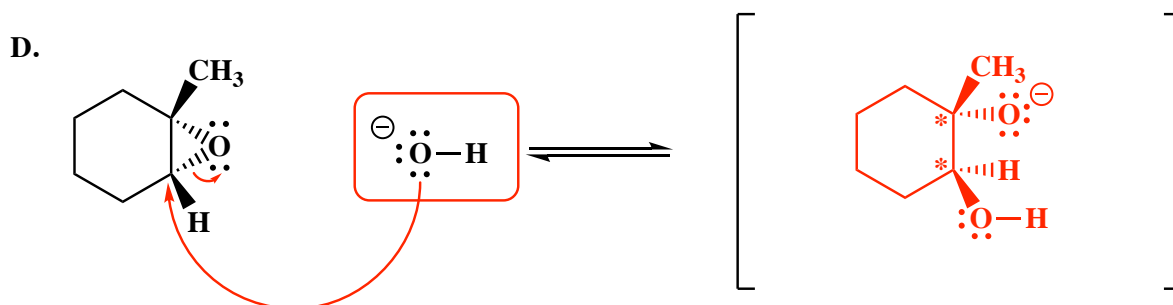
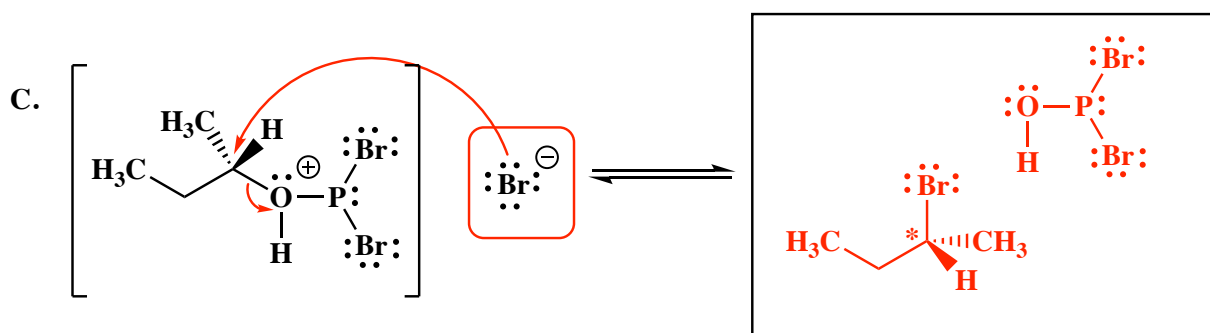
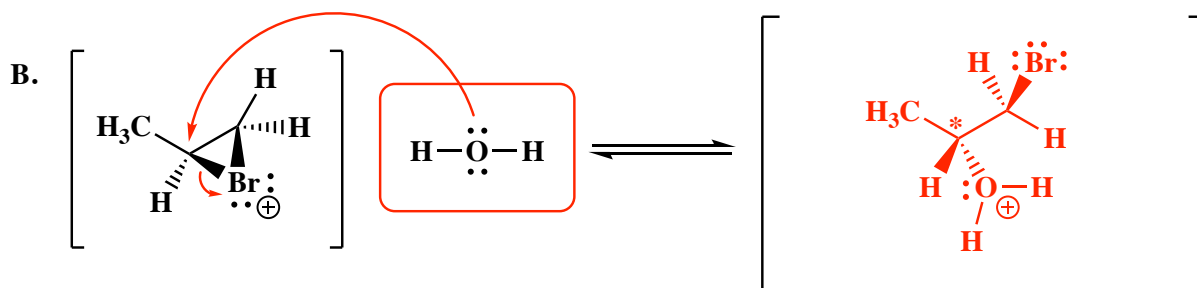
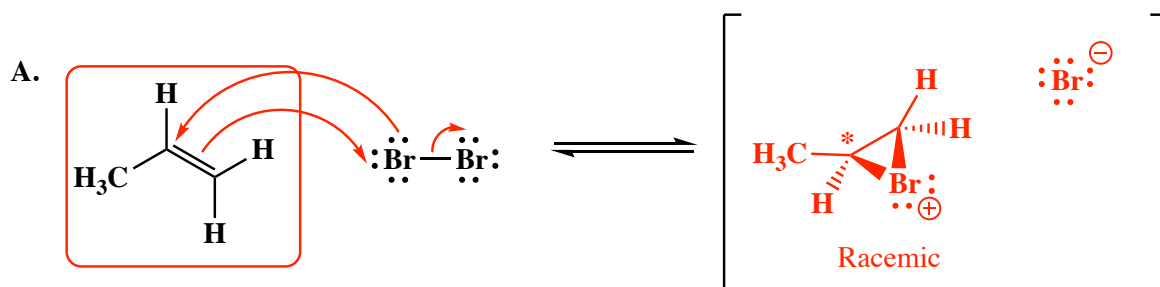
13. (7 pts total) Fill in the blanks with the word(s) that best complete(s) the sentences.

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

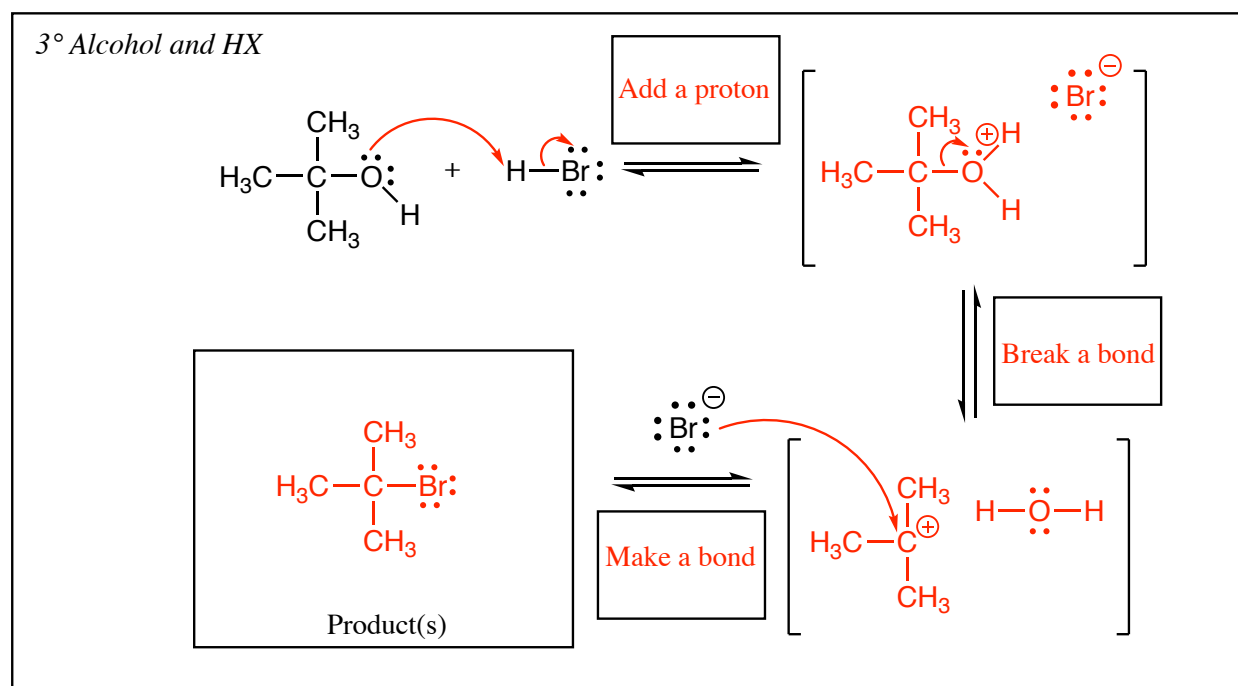
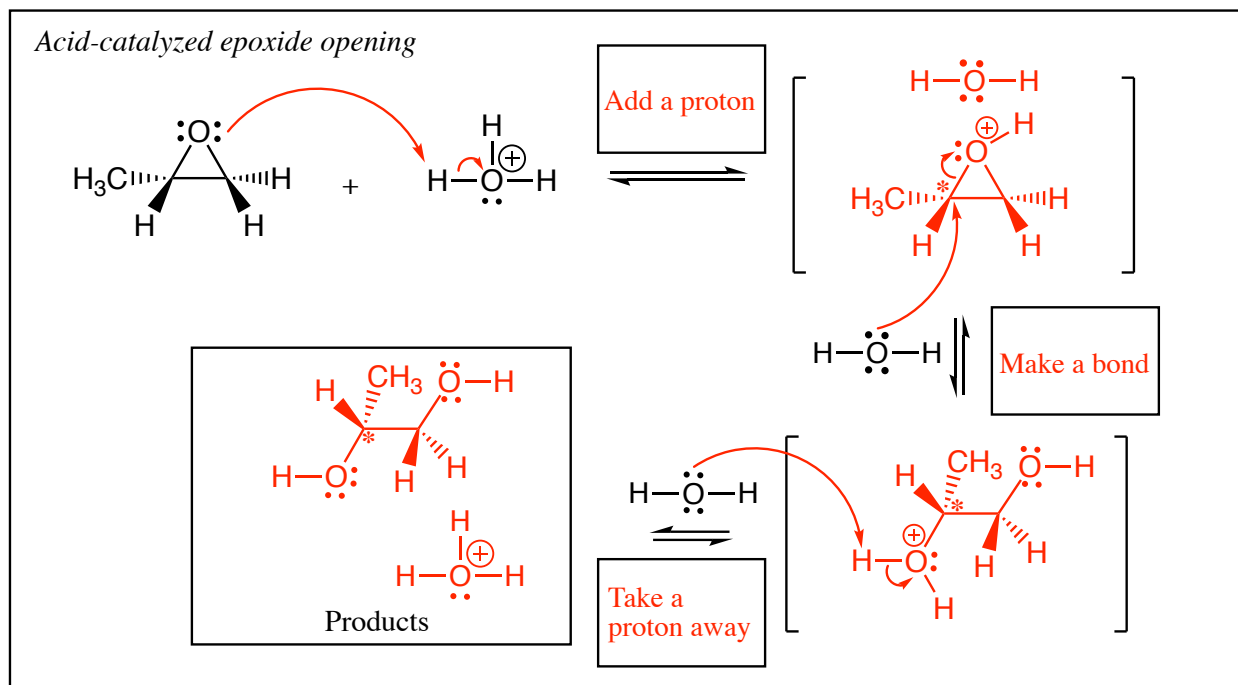


15. (27 pts) Over the semester, you have seen the following types of molecules in the context of individual mechanisms. For each pair of molecules, draw the first intermediate (or product) created in the next step of the appropriate mechanism. Do not worry about any further steps (if appropriate) in 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!**

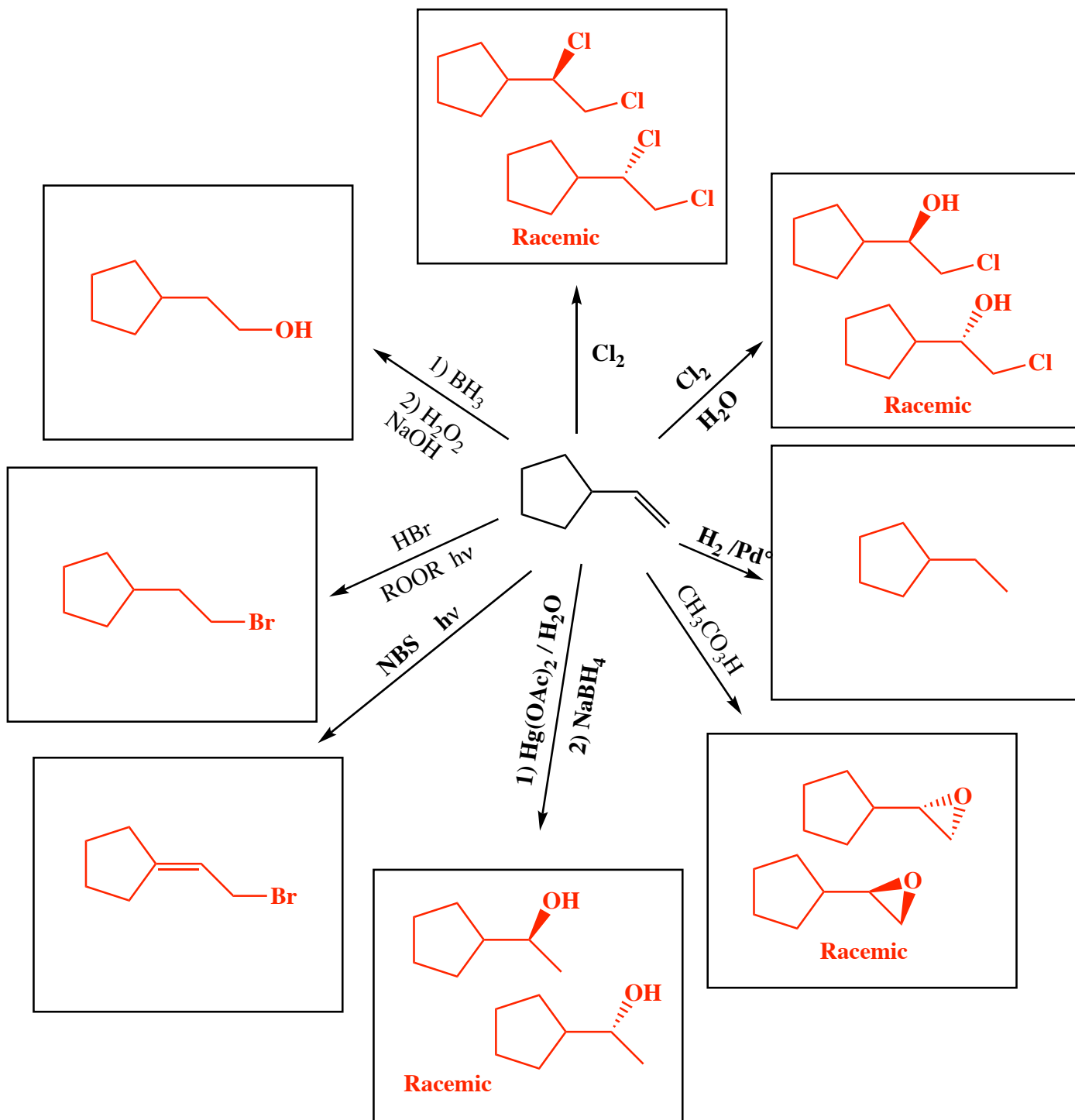


Did you remember to circle the NUCLEOPHILE in each reaction above?

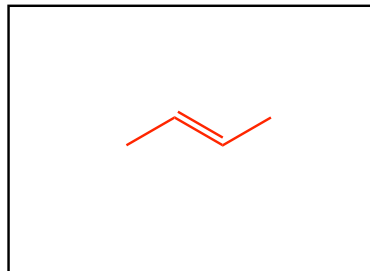
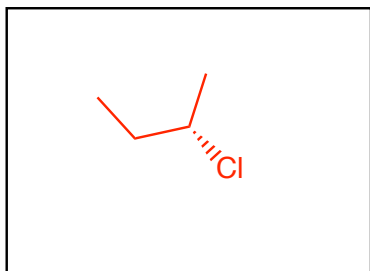
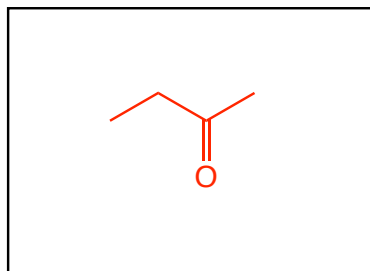
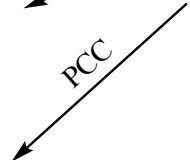
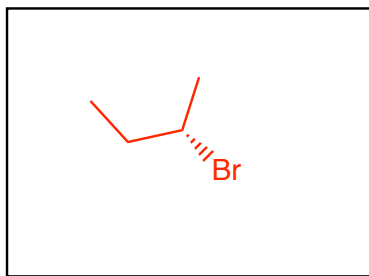
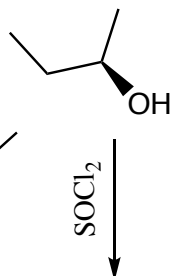
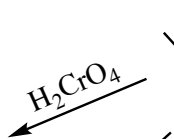
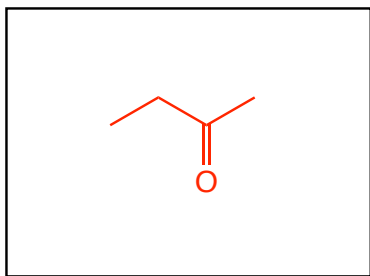
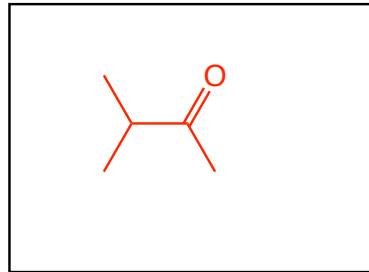
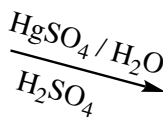
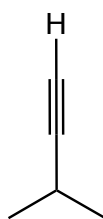
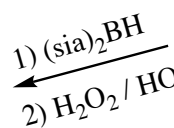
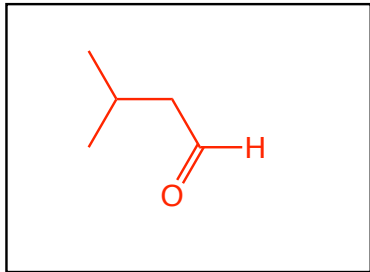
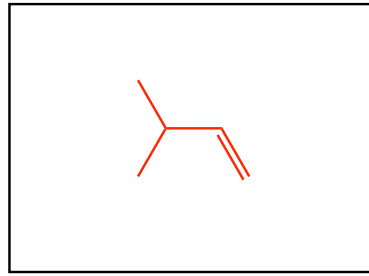
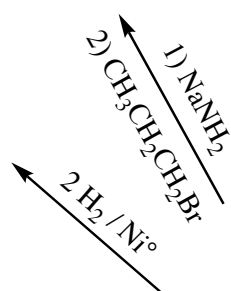
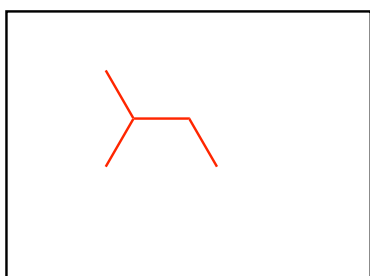
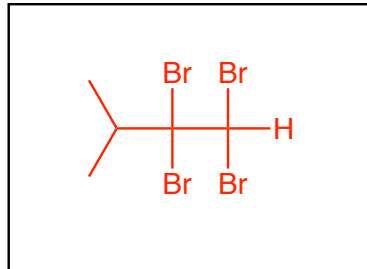
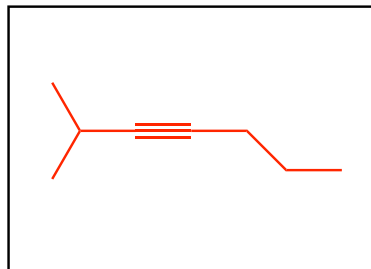
16. (32 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) **For the following reactions, fill in the details of the mechanism. Draw the appropriate chemical structures and use an arrow to show how pairs of electrons are moved to make and break bonds during 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.**



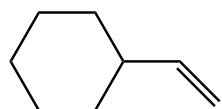
17. (32 pts) For the following, complete the reactions with the predominant carbon-containing product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume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



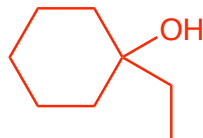
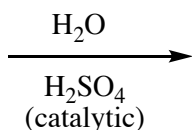
18. (33 pts) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements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



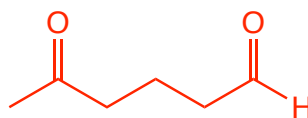
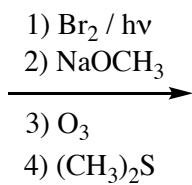
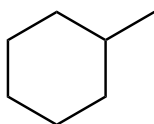
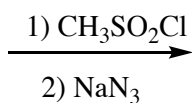
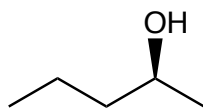
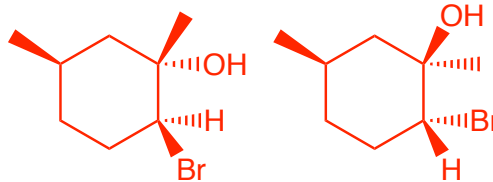
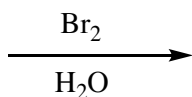
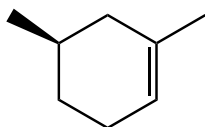
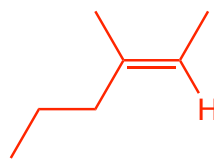
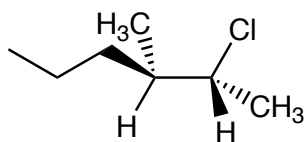
19. (16 pts) For the following, complete the reactions or reaction sequences with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate.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



This rearranges

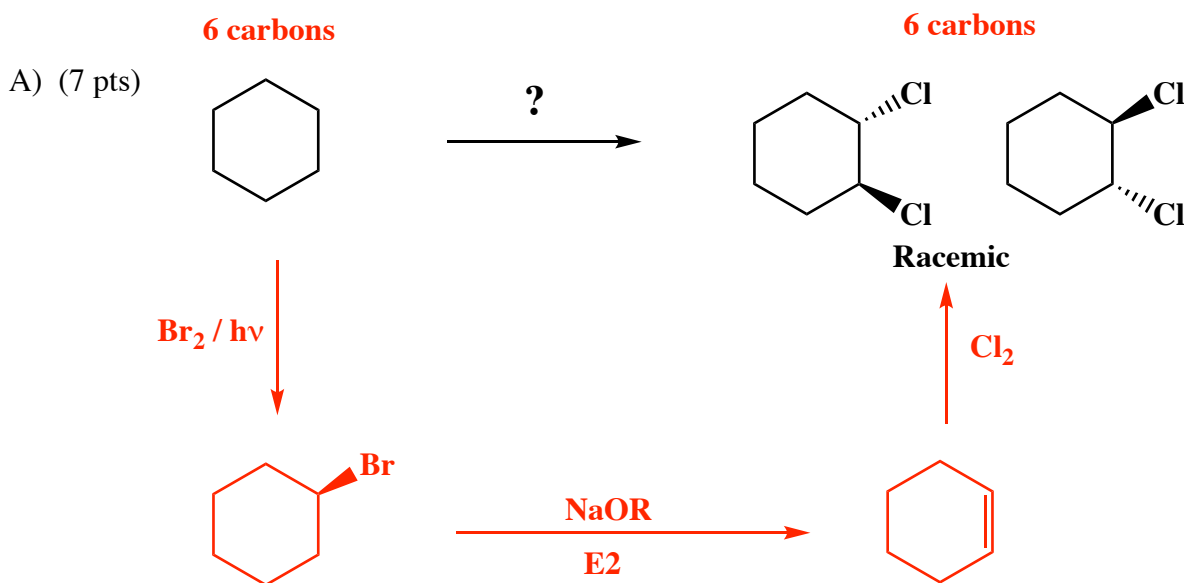


Draw the rearranged product only



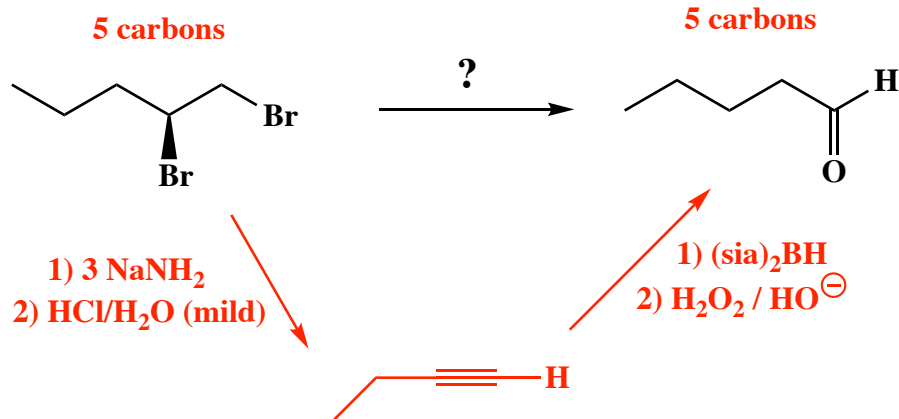


20. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized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



**Recognize:** The product is a *trans* dichlorocyclohexane that must result from the reaction of an alkene (cyclohexene) with  $\text{Cl}_2$ . **Recognize:** The cyclohexene comes from the usual "I-35" combination of halogenation of an alkane with light (the only reaction that uses an alkane starting material) followed by an E2 in strong base such as an alkoxide ( $\text{NaOR}$ ).

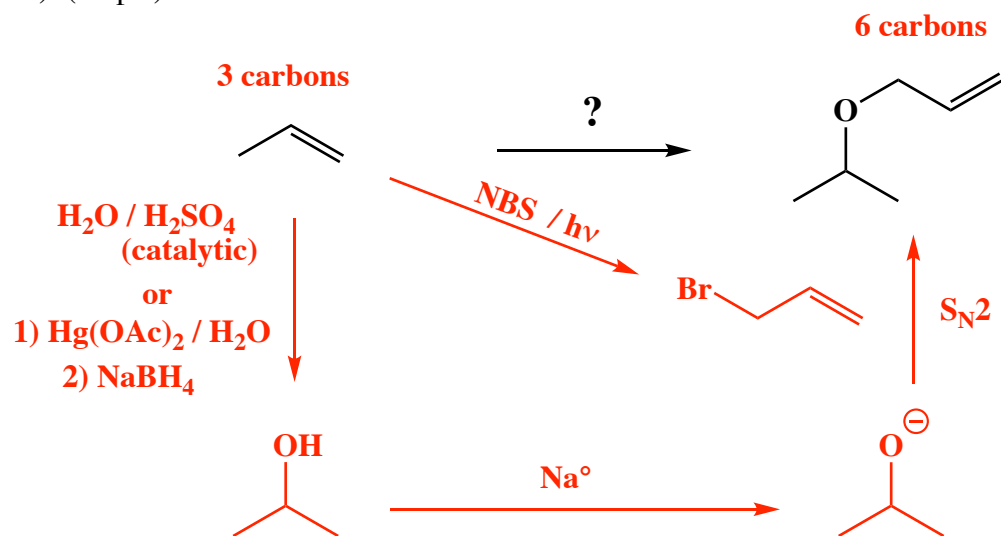
B) (4 pts)



**Recognize:** The product is an aldehyde that can be made from a primary alcohol, ozonolysis of an alkene (breaks carbon-carbon bond so not possible here) or from an alkyne. Choose the latter because an alkyne can be made from the starting vicinal dihaloalkane using base, in this case three equivalents of  $\text{NaNH}_2$  followed by mild acid workup because the product is a terminal alkyne.

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.**

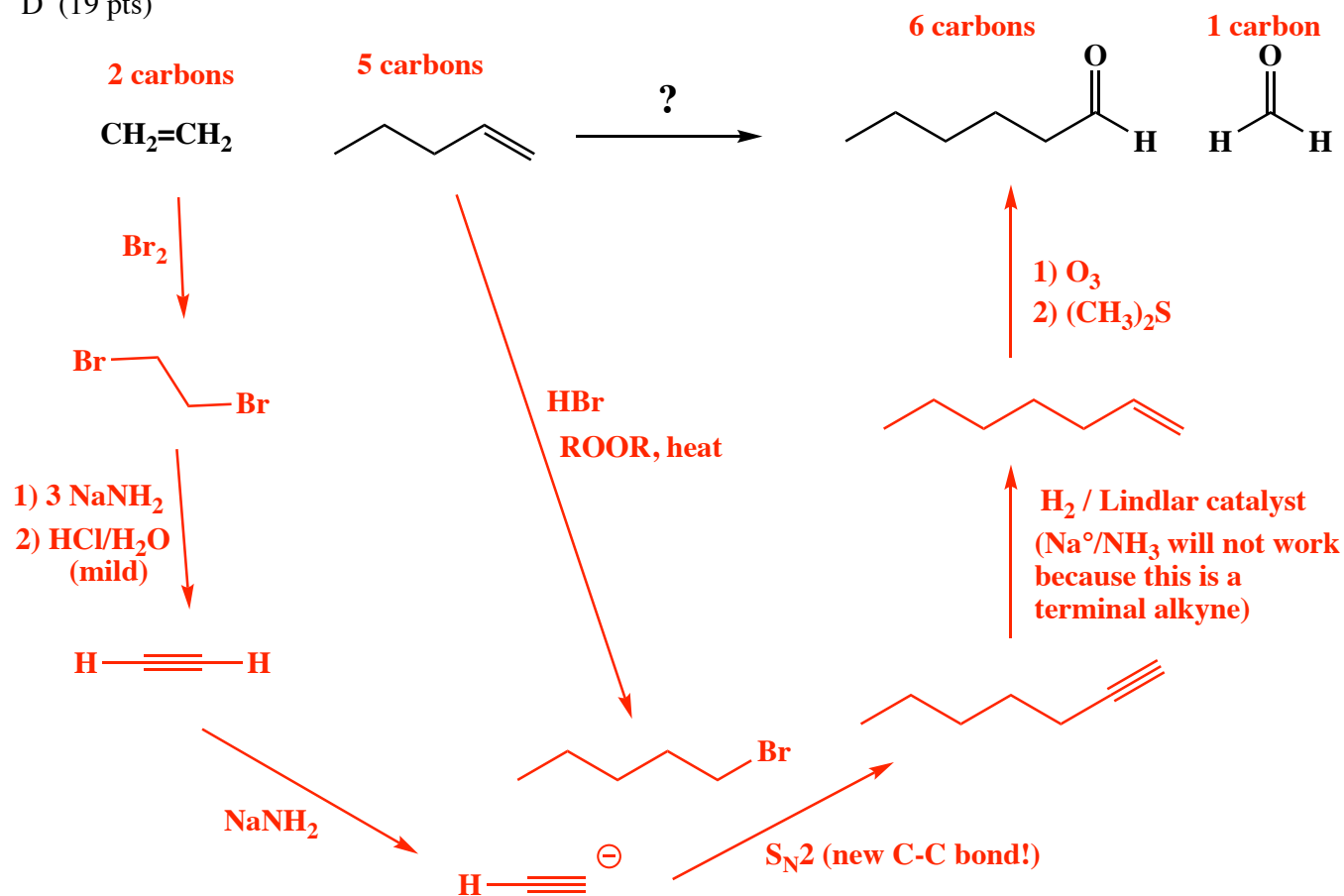
C) (10 pts)



**Recognize:** The product is an ether, so assume the last step is a Williamson ether synthesis. Given that, remember that the haloalkane (in this case a haloalkene) must be primary to avoid an E2 reaction. Therefore, the correct combination of reagents for the last step is the  $\text{S}_{\text{N}}2$  reaction of the alkoxide of isopropanol with the primary allyl bromide as shown. The isopropanol alkoxide can be derived from isopropanol reacting with a strong base or  $\text{Na}^\ominus$ . The isopropanol itself comes from Markovnikov addition using either an acid-catalyzed hydration reaction or using the two-step mercuric ion process. The allyl bromide can be made from the starting propene in one step using NBS and light.

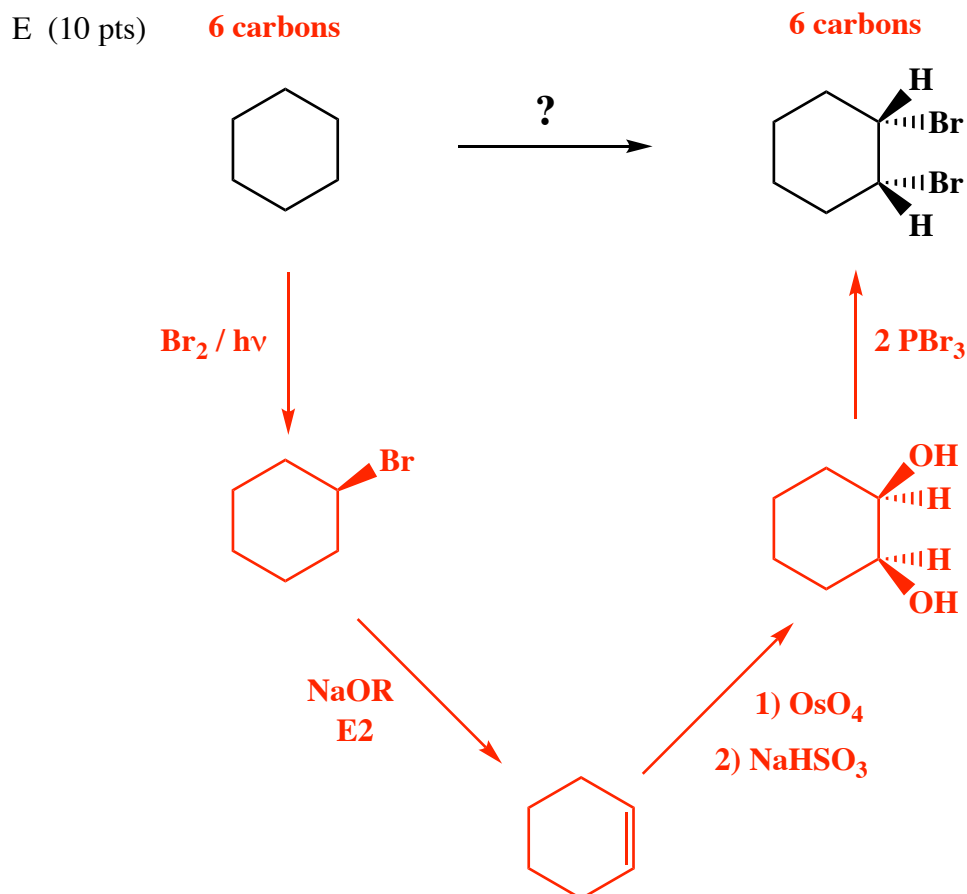
20. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule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



**Recognize:** The key to this one is counting carbons. Notice there are 6 carbons in the larger product and one in the smaller product. Notice there are two and five carbons in the starting materials. Therefore you can assume there is both a carbon-carbon bond forming reaction (alkyne anion and primary haloalkane reacting) and a carbon-carbon bond breaking reaction (ozonolysis). Because the products are two aldehydes, assume the last step is the ozonolysis reaction derived from the corresponding 1-heptene (the C=C needs to be on the end because that will make the correct aldehydes). Assume the C-C forming step must involve an alkyne, so further assume the triple bond is also on the end like the double bond is in 1-heptene. **Recognize:** Having the triple bond on the end means the C-C bond had to be made from the anion of acetylene reacting with 1-bromohexane. The anion of acetylene comes from removal of one proton from acetylene using the strong base  $\text{NaNH}_2$ . Acetylene can be derived from the starting ethene through the usual "I-35" combination of halogenation of ethene to give the corresponding dihaloalkane, followed by reaction with 3  $\text{NaNH}_2$  then mild acid workup. The 1-bromohexane can be made in one step via the non-Markovnikov addition of  $\text{HBr}$  in the presence of peroxides ( $\text{ROOR}$ ) and heat. As an alternative 1-bromohexane could be made from reacting 1-hexene with  $\text{BH}_3$  then basic hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) followed by  $\text{PBr}_3$ .

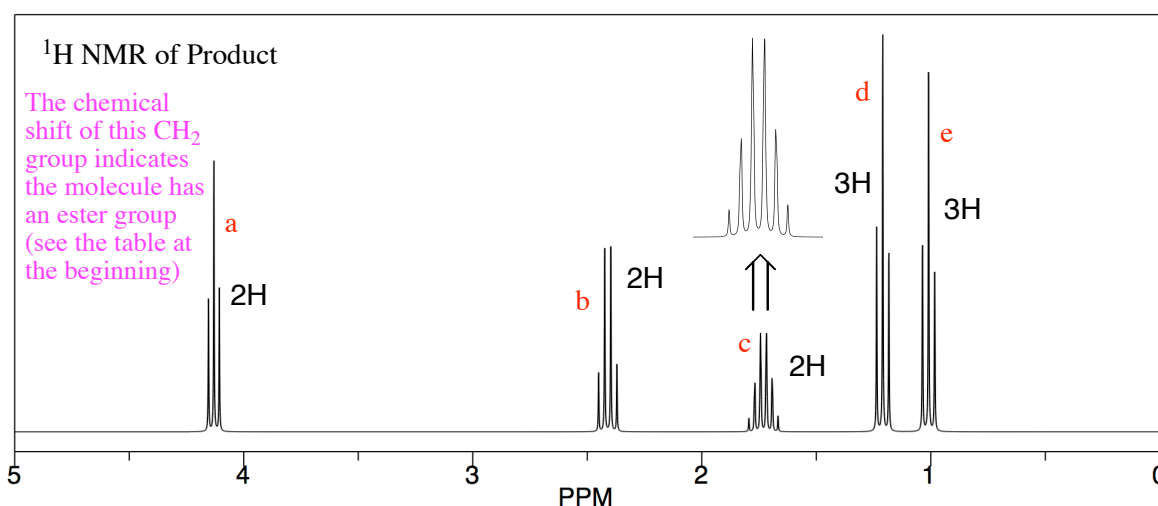
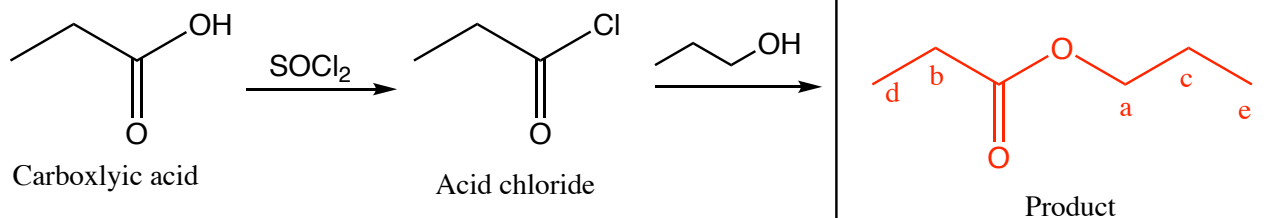
20. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule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



This one takes some creativity. **Recognize:** The last product is a *cis*-1,2-dibromocyclohexane. You do not know any reactions that can add two halogen atoms *syn* (i.e. to give the *cis* product). On the other hand, you do know how to change an OH group to a bromoalkane using PBr<sub>3</sub>, with clean **InVERSiON** of any chiral center. Further, you know about the *syn* addition of adjacent OH groups using the “Ozzy Osbourne” reaction with OsO<sub>4</sub>. Therefore, you can creatively assume the last step is a double replacement of two *cis* OH groups with 2 equivalents of PBr<sub>3</sub>. This step will retain the unique *cis* stereochemistry in the product. The *cis*-1,2-dihydroxycyclohexane can be derived from using the OsO<sub>4</sub> reaction on cyclohexene, which, in turn, is made by reacting the starting cyclohexane with Br<sub>2</sub> and light followed by an E2 in strong base just as you did in part A of this question on page 17.

21. (7 pts) Next semester, you will learn several new reactions involving carboxylic acids. In one reaction, carboxylic acids react with  $\text{SOCl}_2$  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  $^1\text{H}$  NMR of the product we want you to draw!

This reaction is analogous to an  $\text{S}_{\text{N}}2$  reaction (Cl acts as a leaving group and the ROH is a nucleophile), but there is an extra step in the mechanism due to the  $\text{C}=\text{O}$  as you will learn next semester.



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 Flonase<sup>TM</sup> 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  $\text{F}^-$  is a great nucleophile. **Draw the product of this reaction.** We have drawn the basic elements of the steroid rings to get you started.

The HF protonates the epoxide, which opens up by reaction of the fluoride anion from the backside of the more substituted epoxide carbon to give the single stereoisomer product shown

