

NAME (Print): _____

Chemistry 320M/328M
Dr. Brent Iverson
Final Exam
December 16, 2024

EID _____

SIGNATURE: _____

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

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Please Note: Please take your time. We are giving you three hours to take this exam. The idea is to give you enough time to show us what you know, not how fast you can draw structures. Please take all the time you need to draw the best possible structures that you can!

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

Student Honor Code for the University of Texas at Austin

"I pledge, as a member of The University of Texas at Austin community, to do my work honestly, respectfully, and through the intentional pursuit of learning and scholarship."

Elaboration

1. I pledge to be honest about what I create and to acknowledge what I use that belongs to others.
2. I pledge to value the process of learning in addition to the outcome, while celebrating and learning from mistakes.
3. This code encompasses all of the academic and scholarly endeavors of the university community.

(Your signature)

PERIODIC TABLE OF THE ELEMENTS

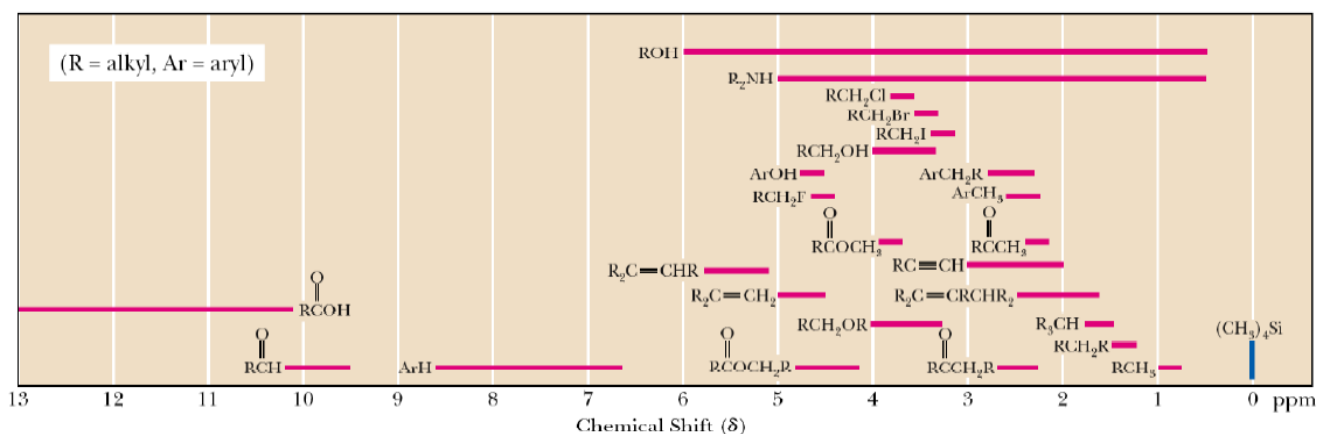
Elementary Subatomic Particles																Ionic Character of a Single Chemical Bond																																																																																															
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s	p	f	+	0	-	s	p	f	+	0	-	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	3.9	4.0	4.1	4.2	4.3	4.4	4.5	4.6	4.7	4.8	4.9	5.0	5.1	5.2	5.3	5.4	5.5	5.6	5.7	5.8	5.9	6.0	6.1	6.2	6.3	6.4	6.5	6.6	6.7	6.8	6.9	7.0	7.1	7.2	7.3	7.4	7.5	7.6	7.7	7.8	7.9	8.0	8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	8.9	9.0	9.1	9.2	9.3	9.4	9.5	9.6	9.7	9.8	9.9	10.0
1 IA Hydrogen H																18 VIIIA Helium He																																																																																															
2 IIA Helium He																17 VIIA Fluorine F																																																																																															
3 IIIA Lithium Li																16 VIA Oxygen O																																																																																															
4 IVB Beryllium Be																15 VA Nitrogen N																																																																																															
5 VA Boron B																14 IVA Carbon C																																																																																															
6 VIB Vanadium V																13 IIIA Aluminum Al																																																																																															
7 VIIB Chromium Cr																12 IIA Magnesium Mg																																																																																															
8 VIIIB Manganese Mn																11 IB Sodium Na																																																																																															
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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	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CR}'$	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	$\begin{array}{c} O \\ / \backslash \\ H_2G-CH_2 \end{array}$	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.



Wow, what a semester. You are an awesome class! I love your dedication and effort! It was a true joy and an honor to be your OChem professor this semester. I was especially inspired by your enthusiastic participation in the 3.1 mile challenge and the Run for the Water. I look forward to seeing many of you next semester as well. ***But first, do us both a favor and absolutely crush this final!***

I put the following on every final, but I think it has special meaning for all of you. You are a very strong group and you have every right to be optimistic about the bright futures in front of you. You should all be looking forward with optimism and big dreams. As one of my favorite poets of the 20th century put it, here is my truly sincere 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

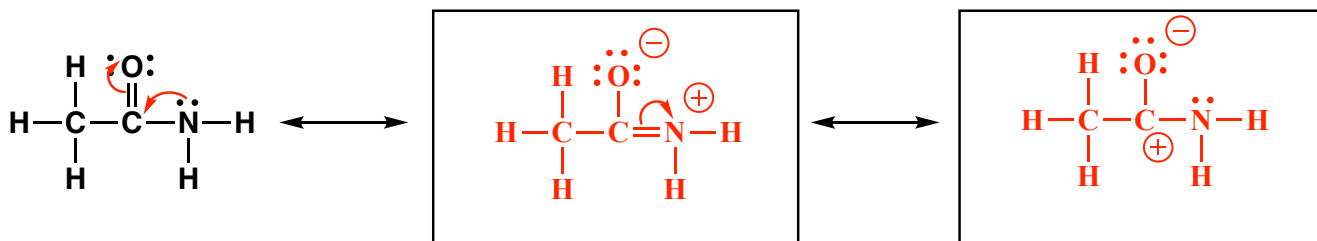
Remember, run every chance you get. Being fit for your entire life is truly the best gift you can give yourself and those you love. Staying fit will also allow you to stay forever young. Now, go get it, show me all that you have learned as you ace this final!

Brent Iverson

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

Where are the electrons?

2. (9 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges. For the two structures on the left, use arrows to indicate the movement of electrons to give the structures you drew.



3. (2 pts each) Fill in the circle to indicate whether each statement as true or false as appropriate. You might recognize these as rules of the day.

- A. The most electronegative elements are in the top right corner of the Periodic Table, the least electronegative elements are in the bottom left corner. True False
- B. The most electronegative elements are in the top left corner of the Periodic Table, the least electronegative elements are in the bottom right corner. True False
- C. Groups larger than H prefer to be equatorial because when they are axial there is steric strain with the other axial groups or atoms. True False
- D. An object or molecule is chiral if it contains a plane of symmetry. True False
- E. Enantiomers have identical properties measured in an achiral way, but diastereomers have different properties measured in any fashion. True False
- F. Sometimes the R enantiomer rotates plane polarized light in the "+" direction, and for other molecules, the S enantiomer rotates plane polarized light in the "+" direction. True False
- G. Syn stereochemistry of addition means that the atoms add to opposite sides of a C=C double bond, anti means they add to the same side. True False
- H. Allyl radicals and cations are stabilized by resonance with adjacent double bonds (pi-way). True False
- I. For E2 reactions using cyclohexane derivatives, both the H and X (leaving group) must be equatorial in order for there to be the required anti-periplanar geometry for a reaction to occur. True False
- J. Epoxides are important electrophiles because the steric strain within epoxides allows them to react with nucleophiles. True False
- K. The key paradigm of Organic Chemistry is that functional groups always react completely differently in complex molecules compared to how they react in simple molecules. True False

4. (2 pts each) Fill in the circle to indicate whether each statement is true or false as appropriate. You might recognize these as rules of the day.

A. Physics: Moving charge generates a magnetic field, and a moving magnetic field causes charges to move in a conductor. True False

B. For NMR we care about the nuclei ^1H and ^{13}C since these are commonly found in organic molecules and they have spin quantum numbers of $3/2$. True False

C. The difference in energy between the $+1/2$ and $-1/2$ nuclear spin states is never proportional to the strength of the magnetic field felt by the nucleus. True False

D. In NMR the process of absorbing energy and flipping nuclear spins from $+1/2$ to $-1/2$ is called "resonance". True False

E. For a ^1H nuclear spin to flip, it needs to be exposed to electromagnetic radiation with an energy that is exactly the same as the energy difference between the $+1/2$ and $-1/2$ nuclear spin states. True False

F. For a ^1H nuclear spin to flip, it needs to be exposed to electromagnetic radiation with an energy that is greater than or equal to the energy difference between the $+1/2$ and $-1/2$ nuclear spin states. True False

G. Electron density is induced to circulate in a strong external magnetic field, which, in turn, produces a magnetic field that opposes the external magnetic field. True False

H. The splitting of a $-\text{CH}_2-$ group adjacent to a chiral center will be "messed up", that is split into many peaks. True False

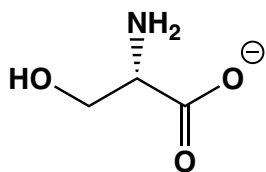
I. THEORY: When there are two sets of adjacent H atoms, the number of peaks multiply $[(N+1) \times (N'+1)]$. True False

J. WHAT YOU WILL SEE IN REALITY: For alkyl groups, complex splittings simplify to $N+1$ because coupling constants ("J") are all about the same when the C atoms can rotate freely. True False

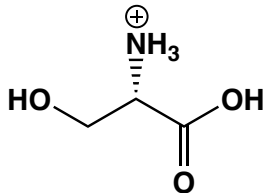
K. The H atoms of relatively acidic functional groups (alcohols, carboxylic acids, amines) exchange rapidly, so they often do not split the signals of adjacent hydrogen atoms, and they can be replaced (signal disappears) with deuterium by adding a drop of D_2O to the NMR sample. True False

5. (8 pts.) Fill in the circle next to the pH value that corresponds the pH at which the structure drawn would be dominant. If the structure drawn cannot exist at any pH, fill in the circle next to the "pH = X"

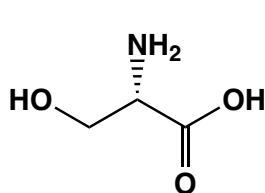
The pK_a of a carboxylic acid (RCO_2H) is generally in the 4-5 range. The pK_a of ammonium ions (RNH_3^+) is in the 9-10 range.



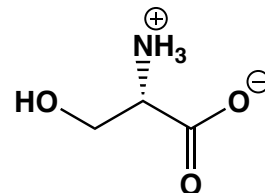
pH = 2 pH = 12
 pH = 7 pH = X



pH = 2 pH = 12
 pH = 7 pH = X



pH = 2 pH = 12
 pH = 7 pH = X

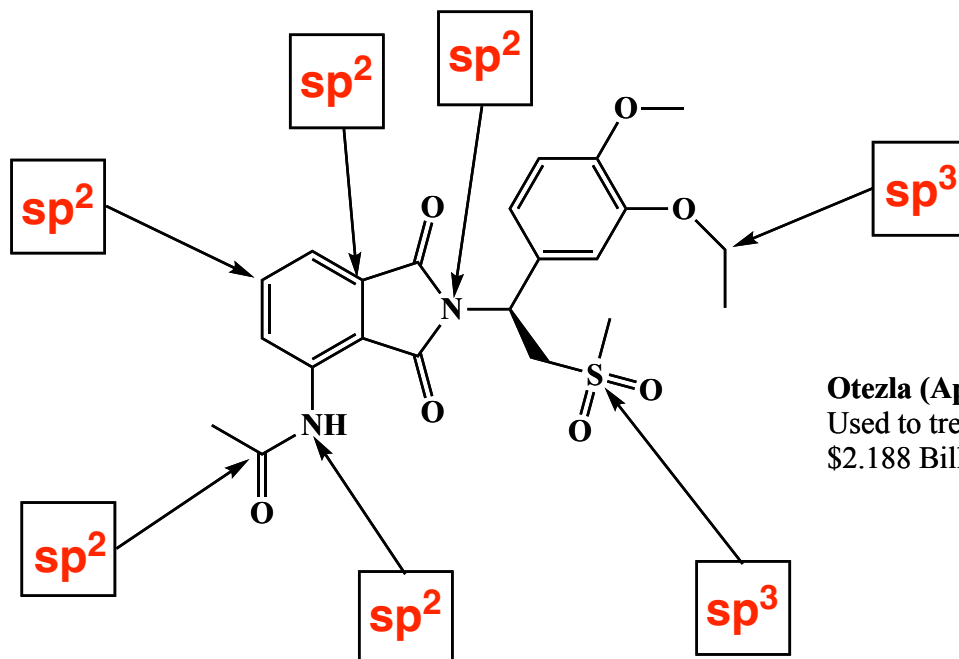


pH = 2 pH = 12
 pH = 7 pH = X

6. (1 pt each) Fill in each blank with the word that best completes the sentences. Yep, this is the MRI paragraph!

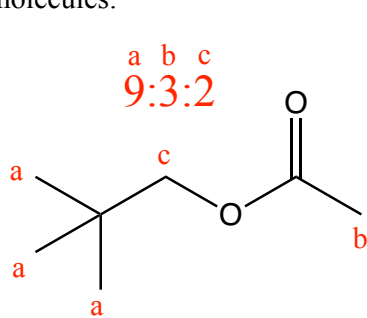
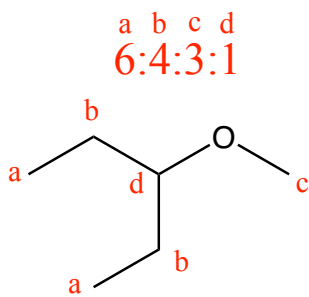
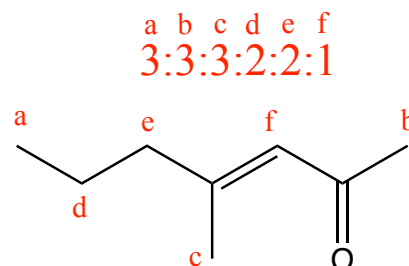
The popular medical 1. diagnostic technique of 2. magnetic
3. resonance 4. imaging (MRI) is based on the same principles
as 5. NMR, namely the 6. flipping (i.e. resonance) of 7. nuclear
spins of H atoms by radio 8. frequency 9. irradiation when a patient is
placed in a strong magnetic field. Magnetic field 10. gradients are used to
gain imaging information, and 11. rotation of the 12. gradient around the
center of the object gives imaging in an entire 13. 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
14. water and 15. fat, in the different tissues.

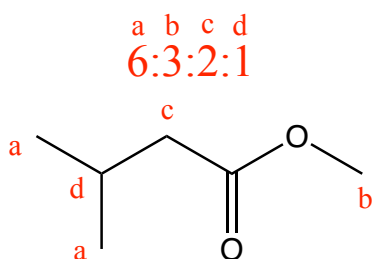
7. (1 pt each) In the boxes provided, write the hybridization state of the atoms indicated by the arrow.

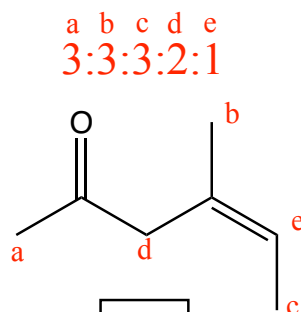


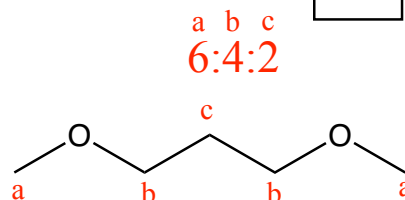
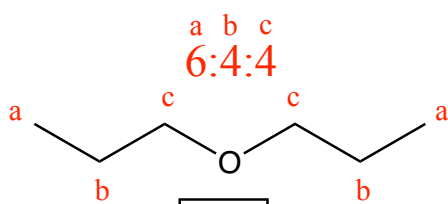
Otezla (Apremilast)
Used to treat plaque psoriasis
\$2.188 Billion in sales 2023

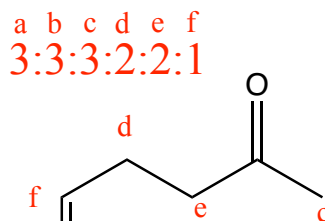
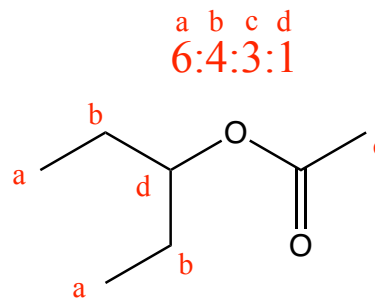
8. (24 pts total) On the following four pages there are NMR spectra. The relative integrations are given above each signal. Each NMR spectrum has a letter on it. **In the spaces provided, write the appropriate letter underneath the molecules that would produce that spectrum.** Notice that not all of the molecules below will have letters underneath them, as there are only four spectra but eleven molecules.

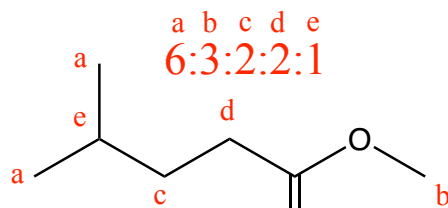

 A

 C


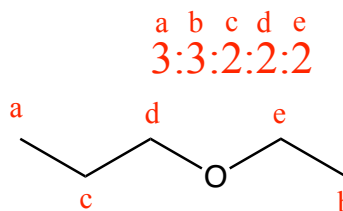





 B


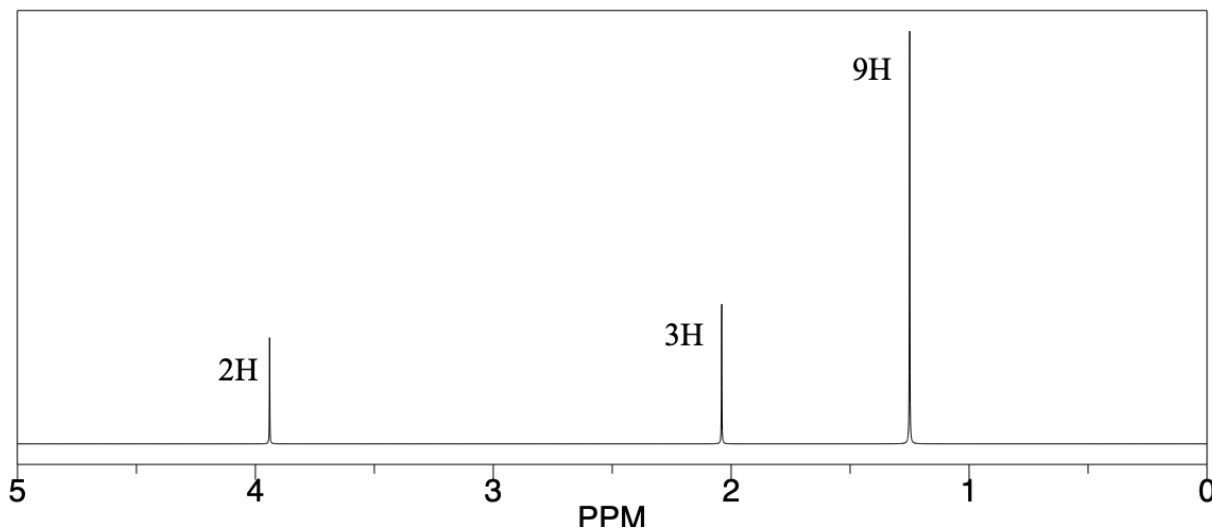
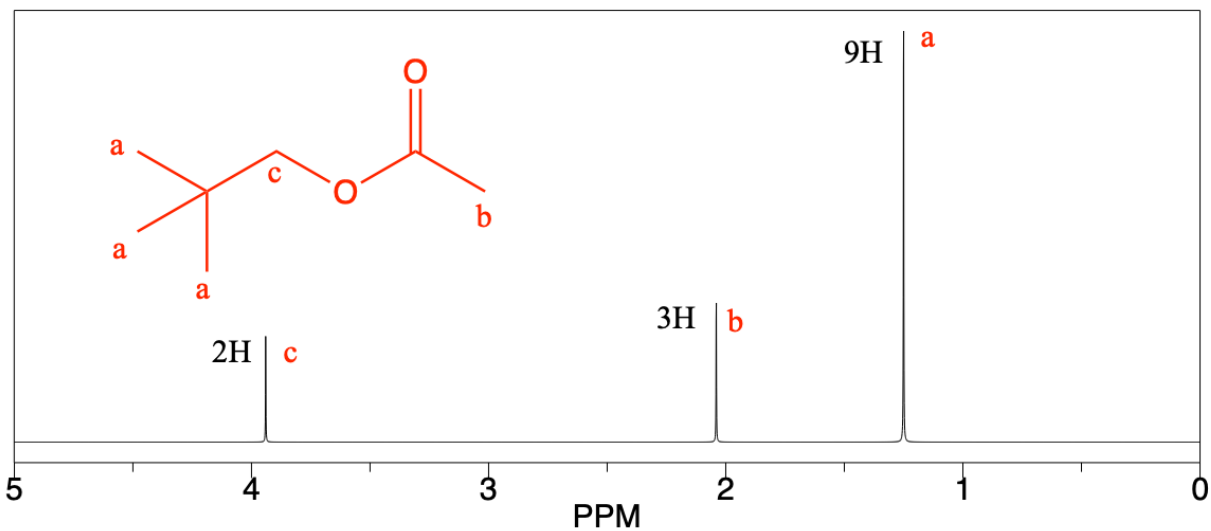

 D






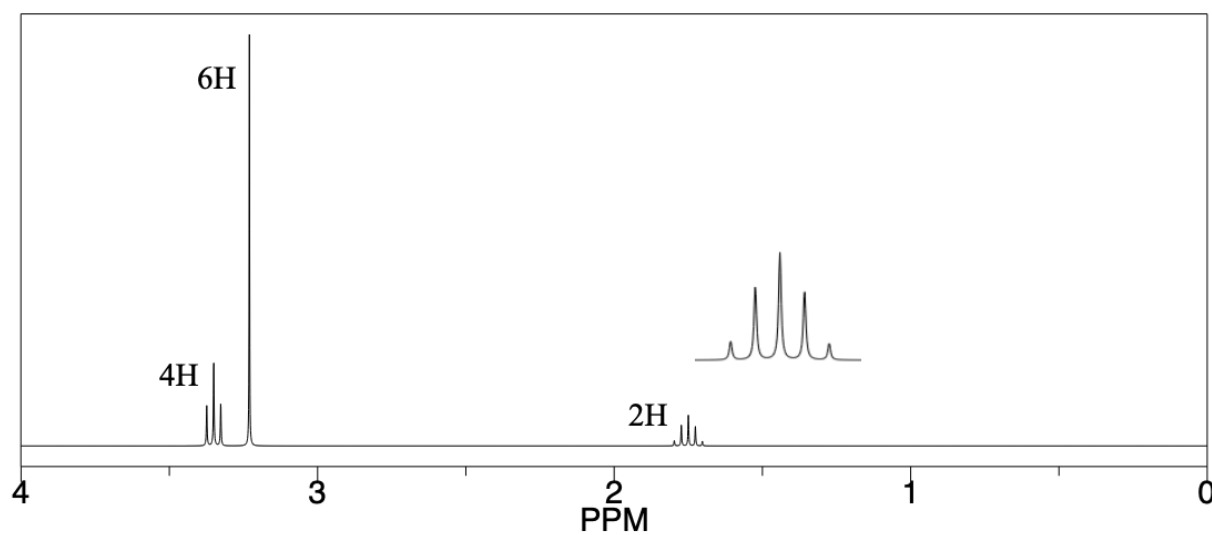
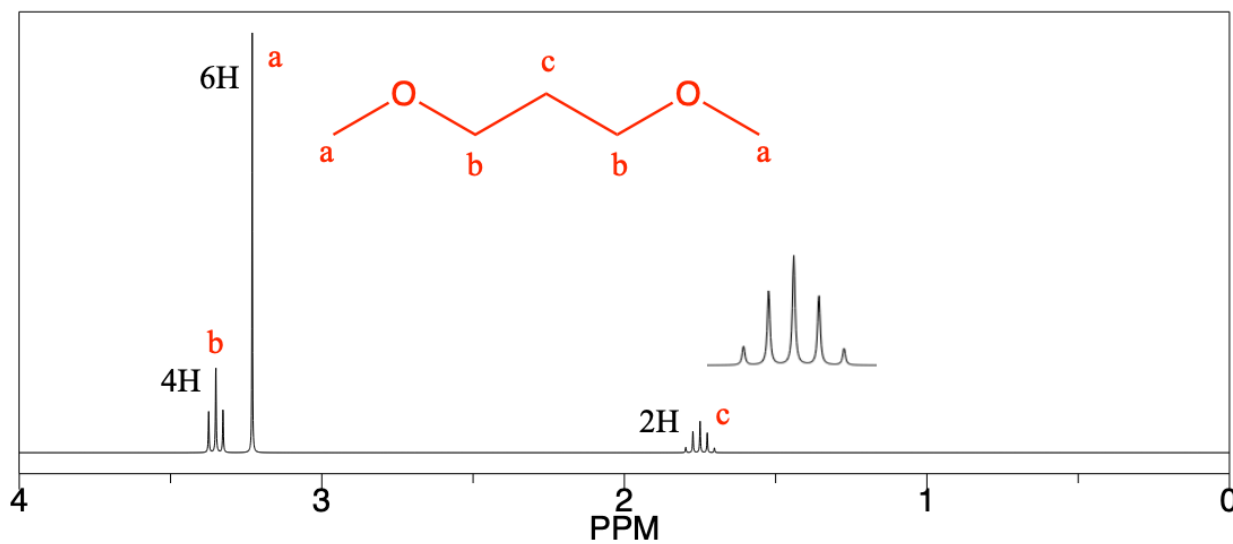
Spectrum A

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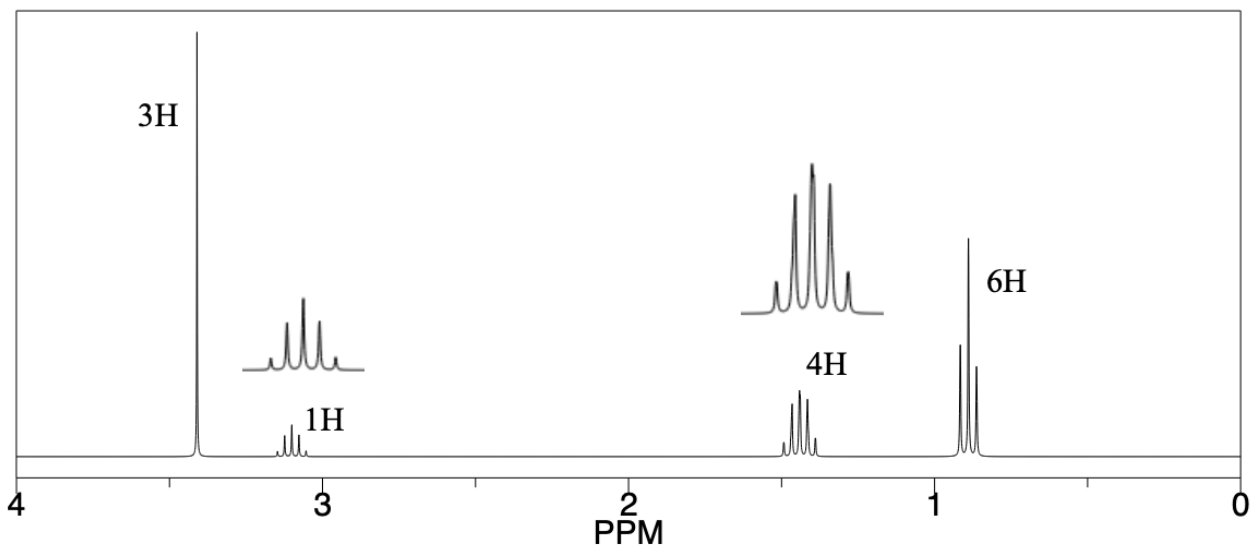
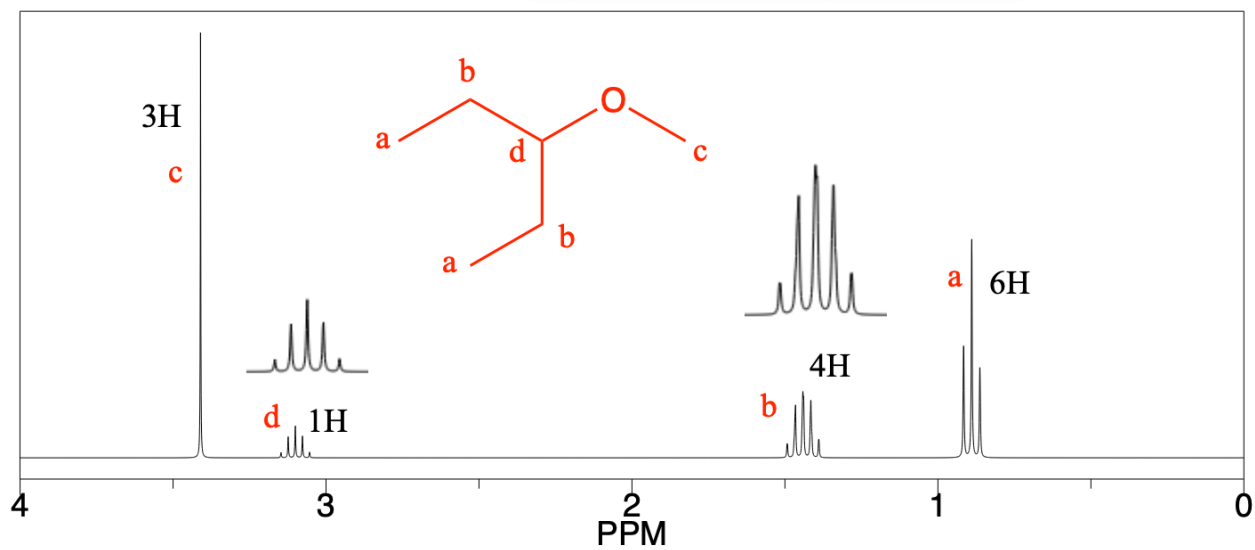
Spectrum B

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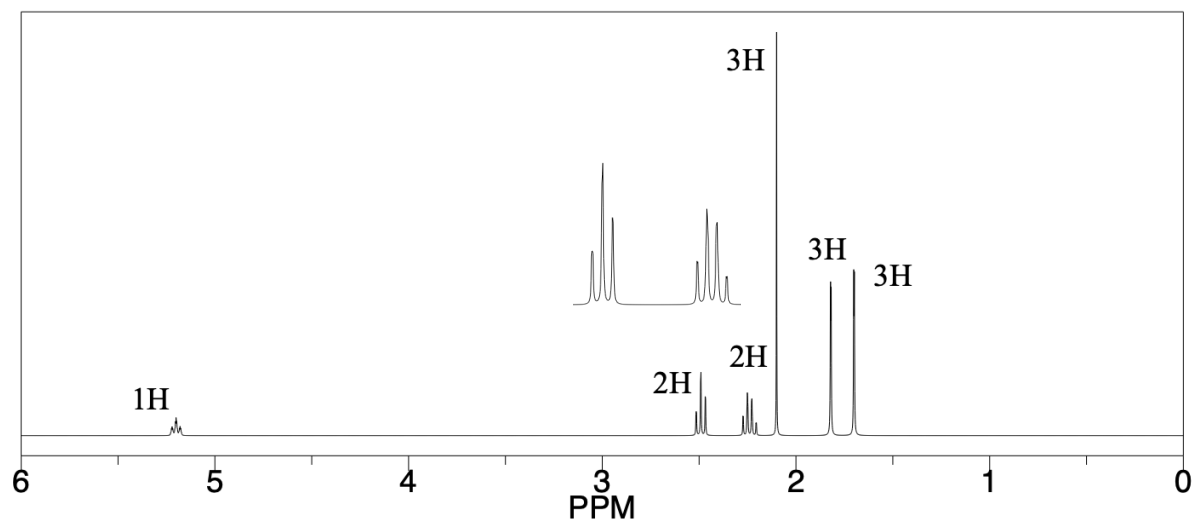
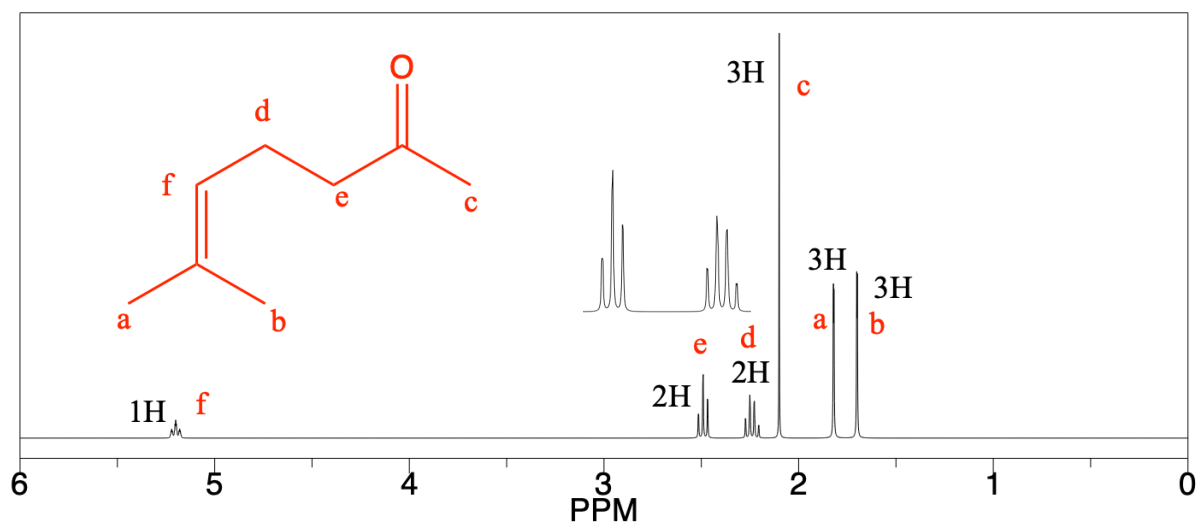
Spectrum C

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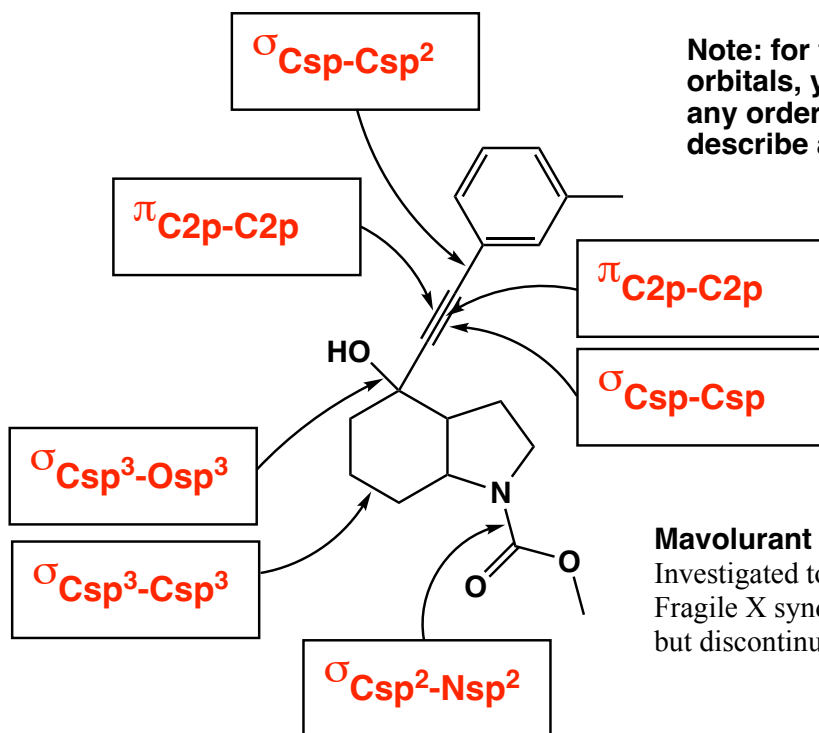


Spectrum D

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9. (2 pts each) In the boxes provided, indicate the type of bond, and the hybridized orbitals that overlap to form the bond. For example, one answer could be: $\sigma \text{Csp}^3\text{-Csp}^2$

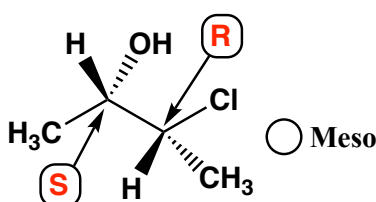
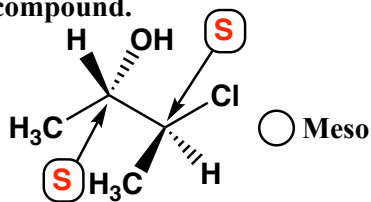


Note: for the three alkyne orbitals, you can put them in any order, you just need to describe all three bonds.

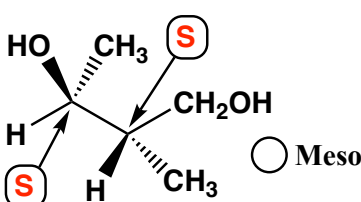
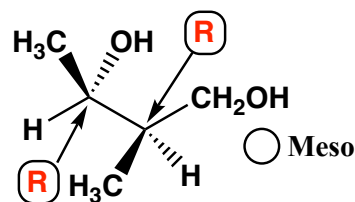
Mavolurant

Investigated to treat Fragile X syndrome but discontinued

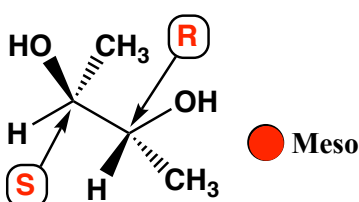
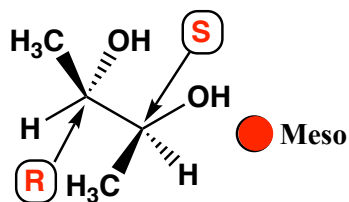
10. (24 pts) Fill in the circles to the right to indicate the correct relationship between the pairs of molecules shown. In the boxes provided next to each chiral center, write "R" or "S" to indicate the absolute stereochemistry present. Fill in the circle to the right of each structure if it is a meso compound.



- Diastereomers
- Enantiomers
- Same Molecule
- Constitutional Isomers

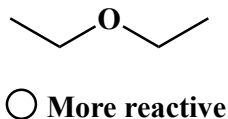
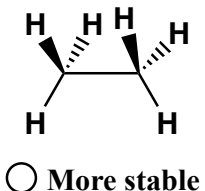
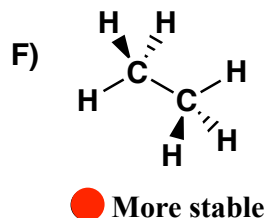
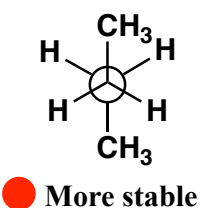
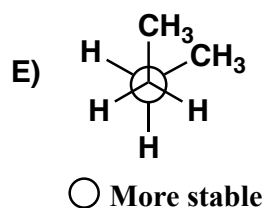
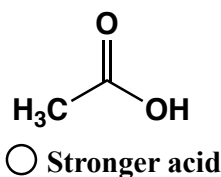
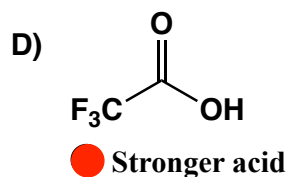
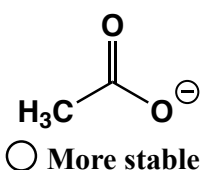
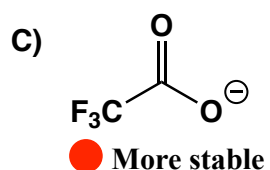
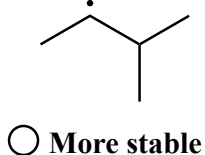
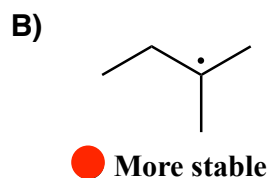
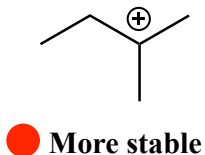
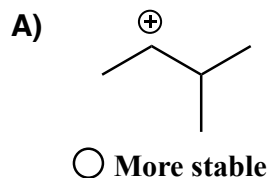


- Diastereomers
- Enantiomers
- Same Molecule
- Constitutional Isomers



- Diastereomers
- Enantiomers
- Same Molecule
- Constitutional Isomers

11. (23 pts) Fill in the circle to indicate which of each pair of molecules is more stable or in the case of E) the stronger acid or more reactive in the case of G). To the right under "Reason(s)" fill in every circle that explains which of the two molecules is more stable/stronger acid/more reactive. Notice that for some pairs of molecules the correct answer might require more than one circle filled in under "Reason(s)".



Reason(s)

- Torsional strain
 Steric strain
 Angle strain
 Hyperconjugation
 Inductive effect

- Torsional strain
 Steric strain
 Angle strain
 Hyperconjugation
 Inductive effect

- Torsional strain
 Steric strain
 Angle strain
 Hyperconjugation
 Inductive effect

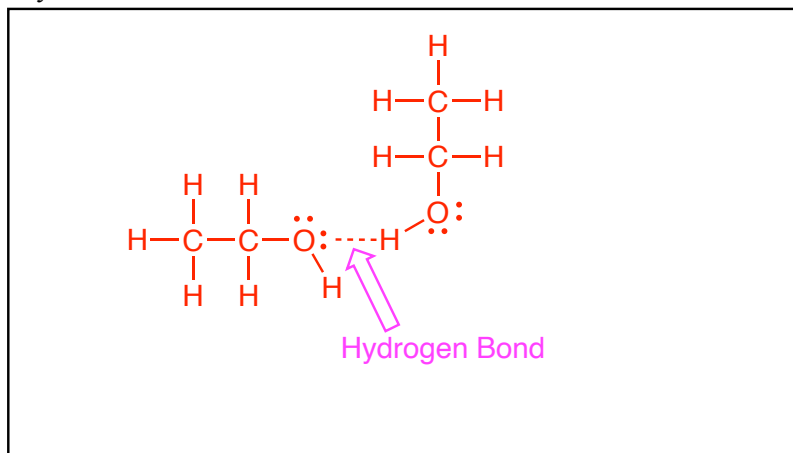
- Torsional strain
 Steric strain
 Angle strain
 Hyperconjugation
 Inductive effect

- Torsional strain
 Steric strain
 Angle strain
 Hyperconjugation
 Inductive effect

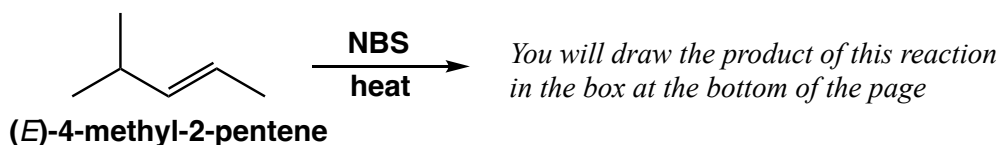
- Torsional strain
 Steric strain
 Angle strain
 Hyperconjugation
 Inductive effect

- Torsional strain
 Steric strain
 Angle strain
 Hyperconjugation
 Inductive effect

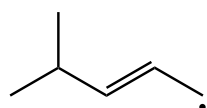
12. (7 pts) In the space provided, draw Lewis structures for two ethanol molecules ($\text{CH}_3\text{CH}_2\text{OH}$) with one hydrogen bond between them indicated by a dashed line. Make sure to include all appropriate lone pairs in your answer.



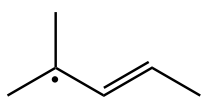
13. (8 pts) Consider what happens when (*E*)-4-methyl-2-pentene is reacted with NBS and heat.



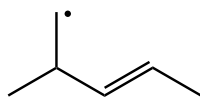
Fill in the circles to indicate which allyl radical contributing structures are relevant and therefore must be considered when predicting the predominant product of the reaction



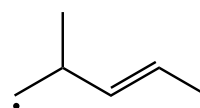
This contributing structure should be considered



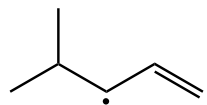
This contributing structure should be considered



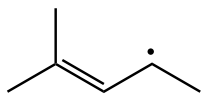
This contributing structure should be considered



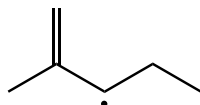
This contributing structure should be considered



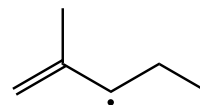
This contributing structure should be considered



This contributing structure should be considered

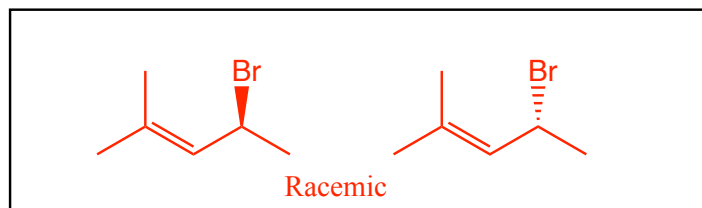


This contributing structure should be considered

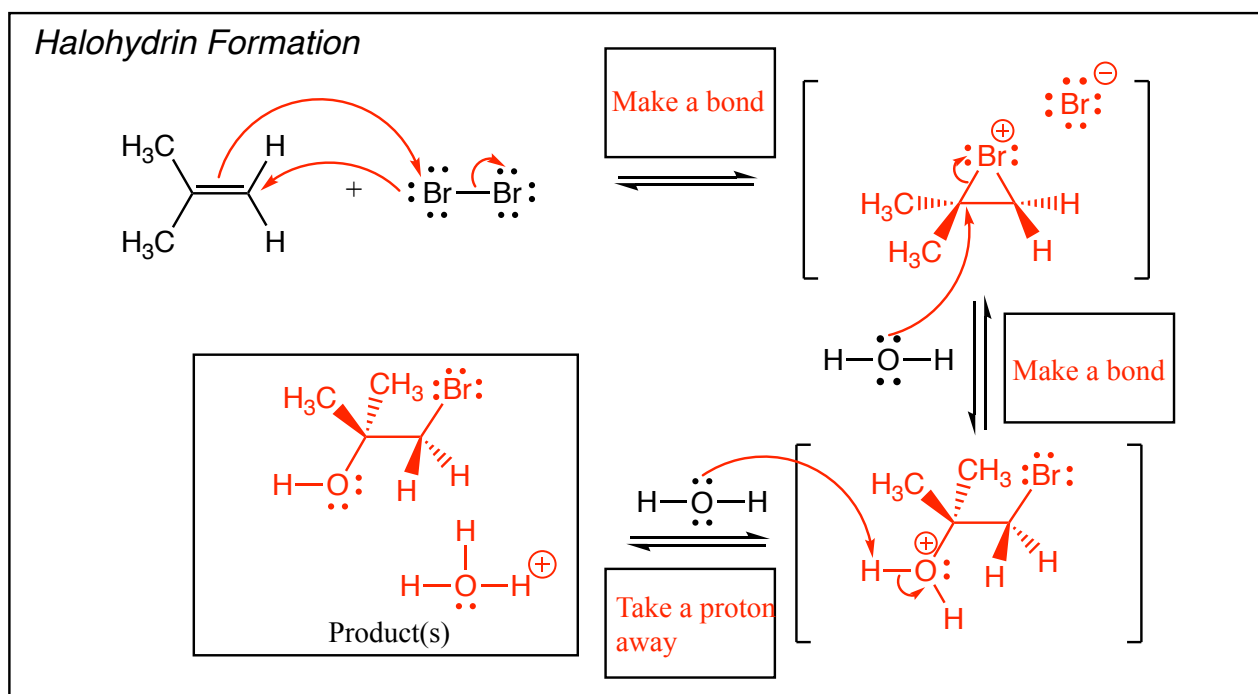
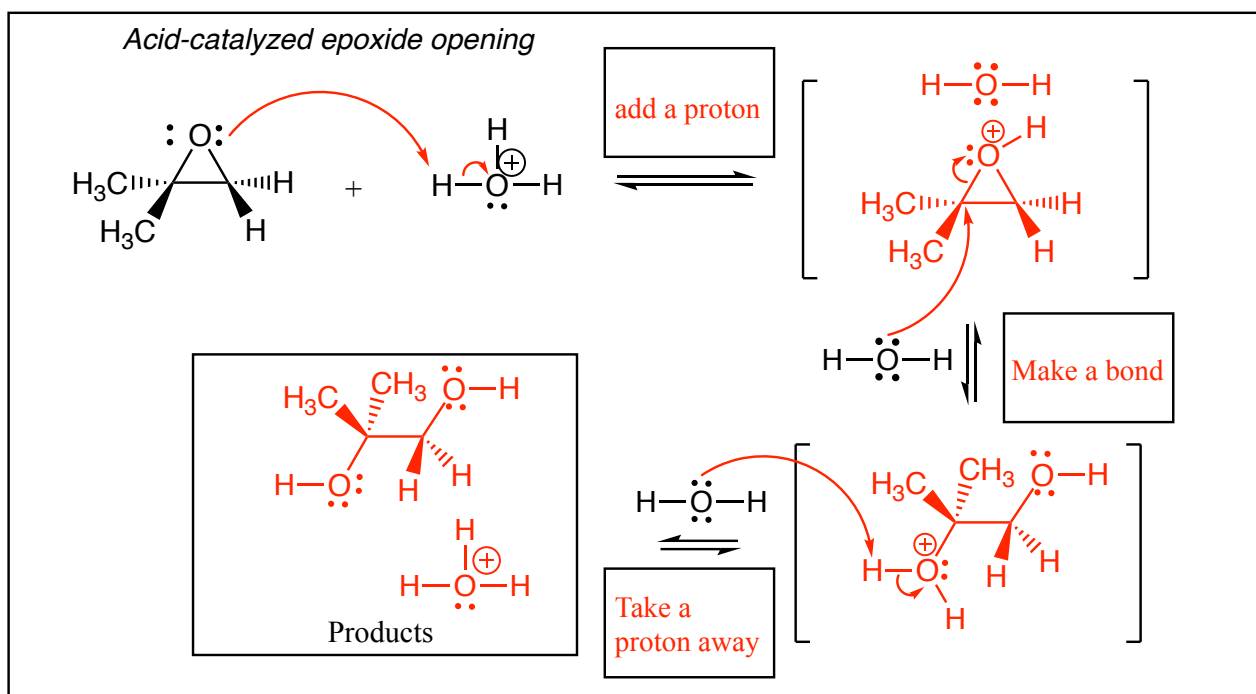


This contributing structure should be considered

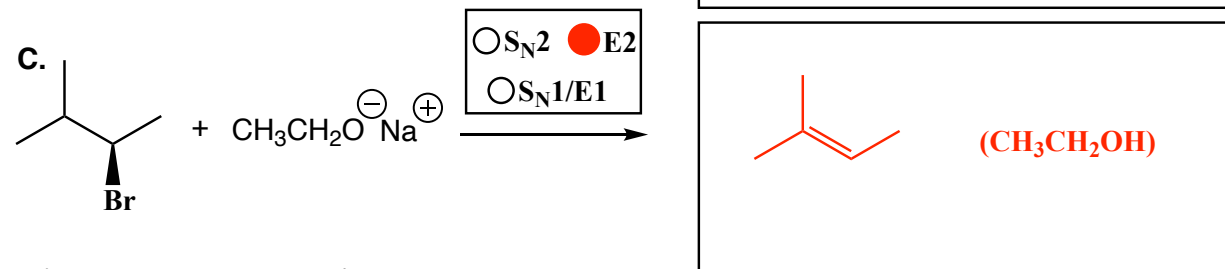
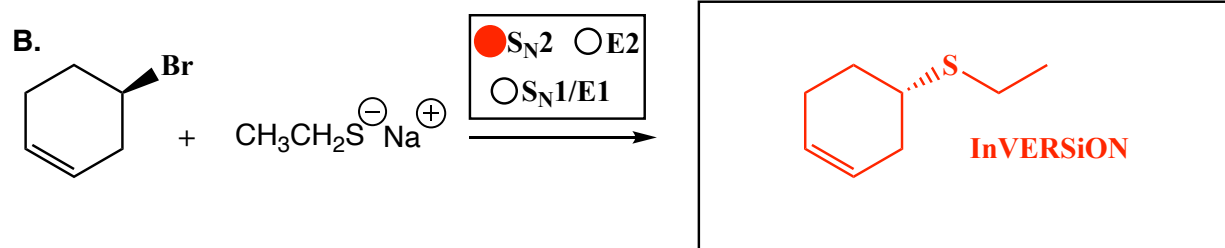
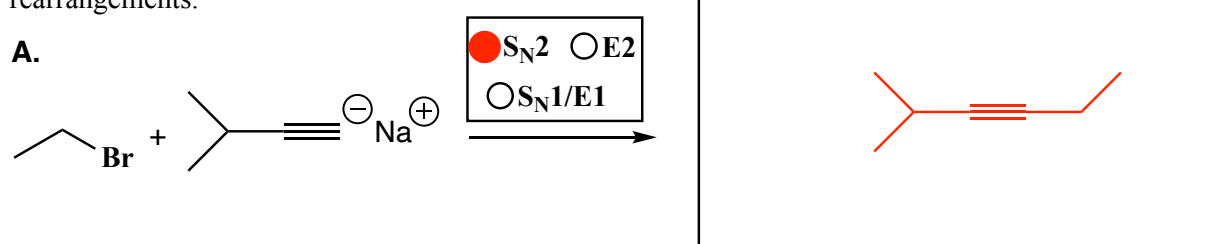
(6 pts) Given your analysis of the above contributing structures, in the box provided, draw the product of the reaction of (*E*)-4-methyl-2-pentene with NBS and heat. Use wedges and dashes to indicate stereochemistry, and draw all relevant stereoisomers, indicating the product is racemic if appropriate.



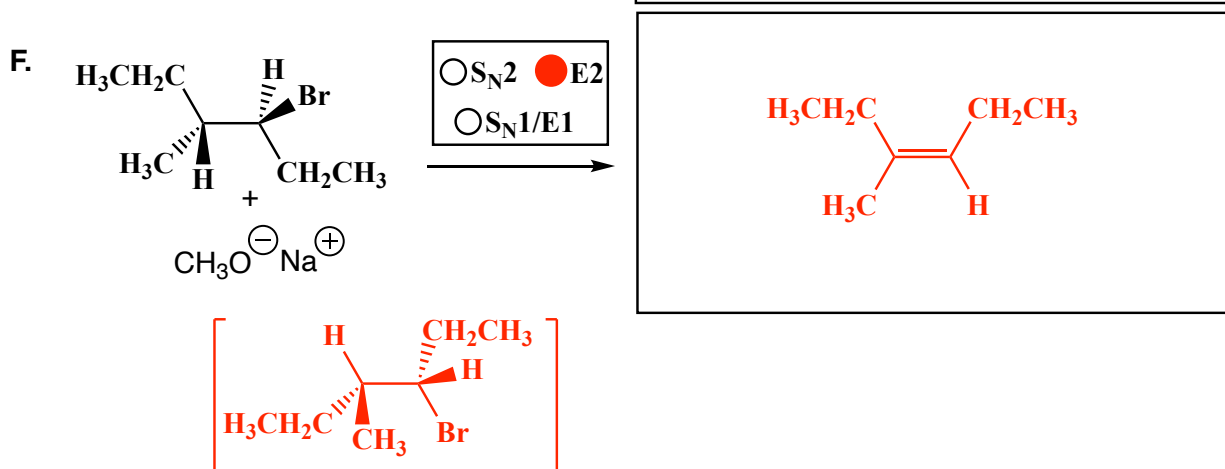
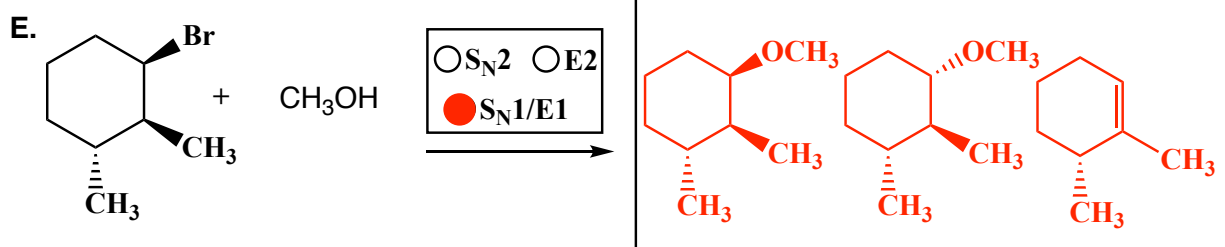
14. (35 pts) For these two mechanisms, use **arrows to indicate movement of all electrons**, write **all lone pairs**, **all formal charges**, and **all the products for each step**. Remember, I said **all** the products for each step. **YOU ONLY NEED TO DRAW ONE STEREOISOMER OF A CHIRAL INTERMEDIATE OR PRODUCT (using wedges and dashes as appropriate) IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE.** In the boxes provided, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).



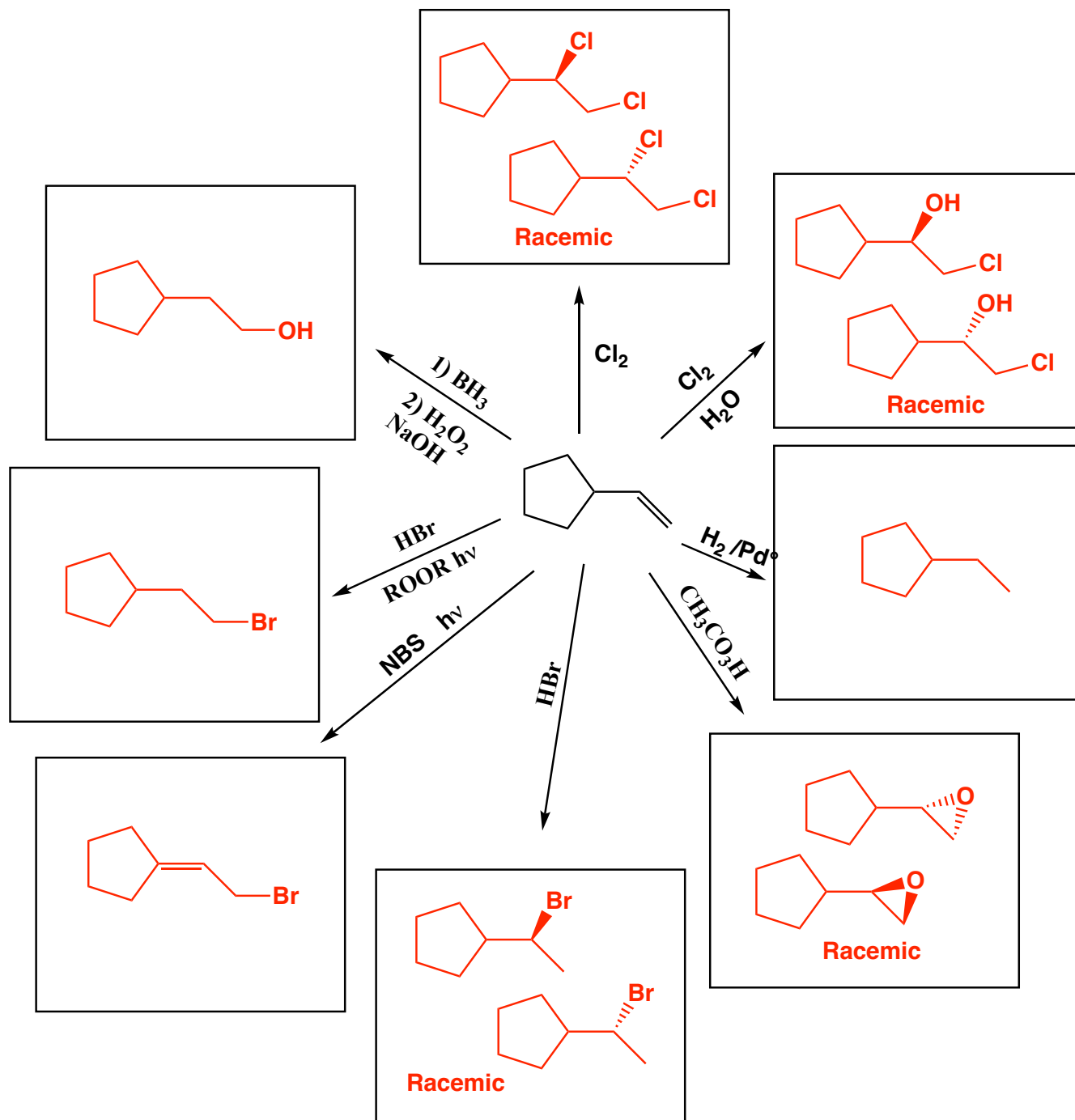
15. (5, 7 or 9 pts each) The following reactions all involve the chemistry of haloalkanes. **Fill in the circle above the arrow to indicate the mechanism that will be followed (S_N2 , E2, etc.). Then draw only the predominant product or products and please remember that you must draw the correct stereoisomers.** For $S_N1/E1$ reactions you must draw all significant products (including all stereoisomers). Assume no rearrangements.



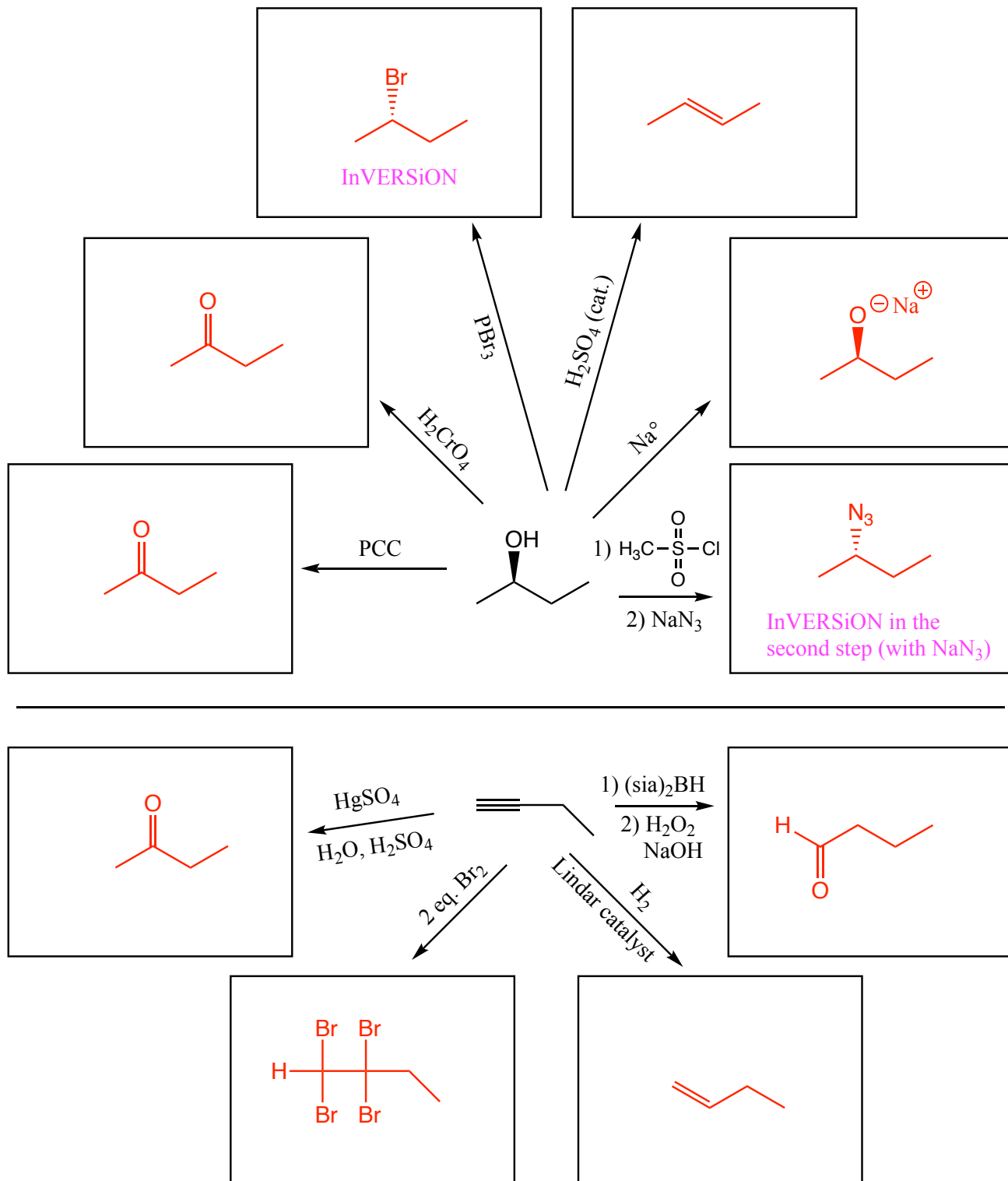
Think about these last two!



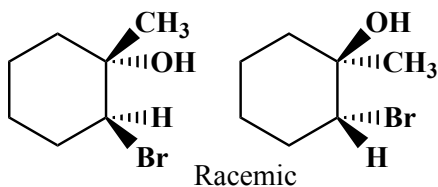
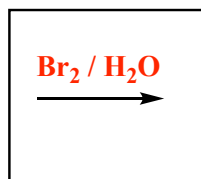
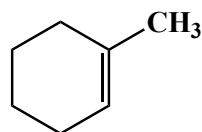
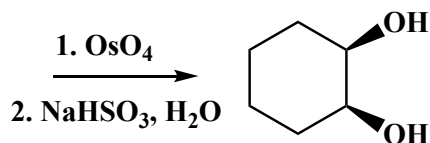
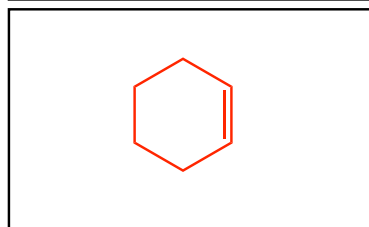
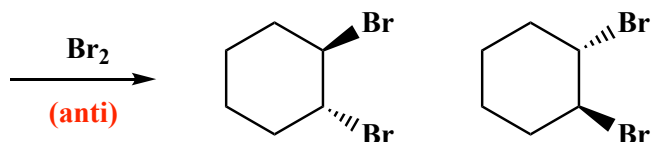
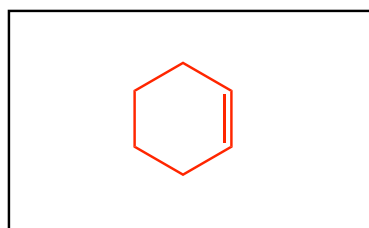
16. (3 or 5 pts) For the following, complete the reactions with the predominant carbon-containing product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



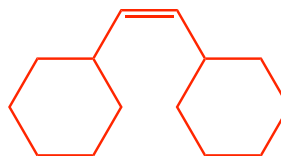
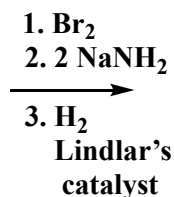
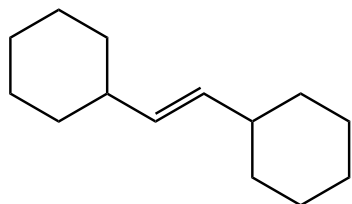
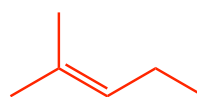
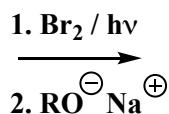
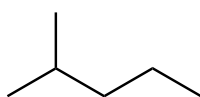
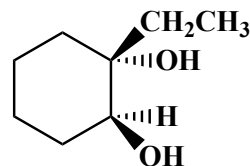
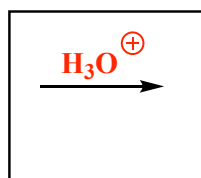
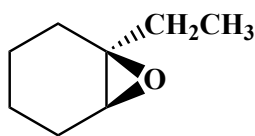
15. (3 or 5 pts each) For the following, complete the reactions with the predominant carbon-containing product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



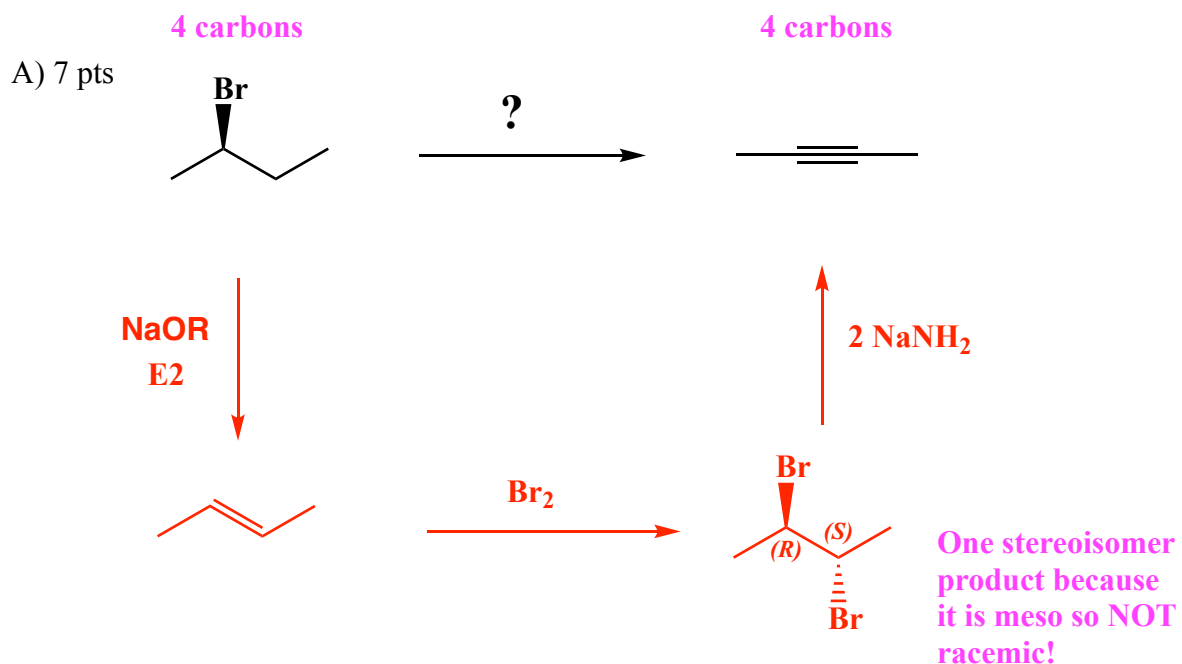
18. (3 or 5 pts each) Fill in the boxes with the starting material, reagents or product(s) that are missing from the chemical reaction equations. **Once again, for the products draw only the predominant regioisomer product or products (i.e. Markovnikov or non-Markovnikov products) and please remember that you must draw the structures of all the product stereoisomers using wedges and dashes to indicate stereochemistry. When a racemic mixture is formed, you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES.**



Think about this one!

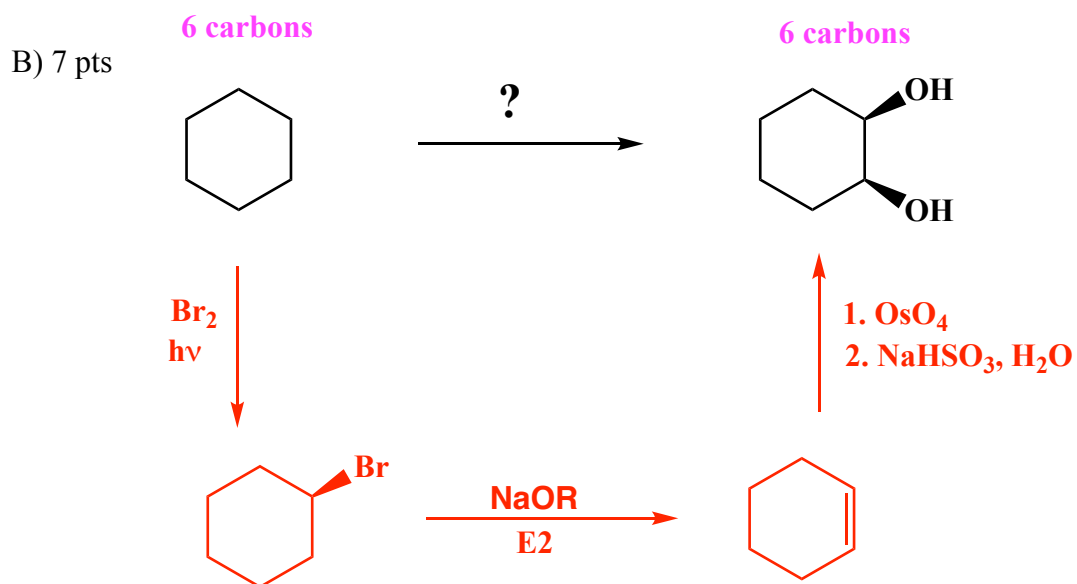


19. (7 pts) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction because only predominant products can be used. All the carbon atoms of the product(s) must come from the starting material(s) shown.



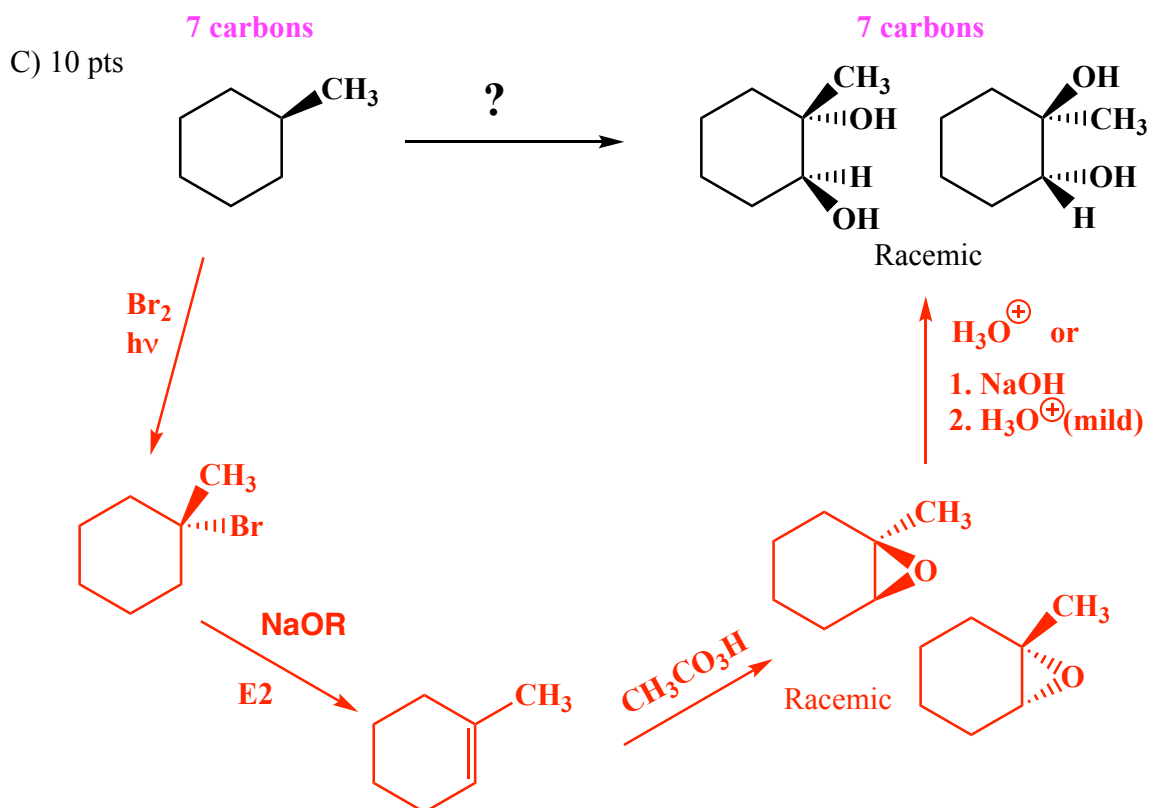
Recognize that the product is an alkyne, and the starting material is a haloalkane. Therefore, this problem follows "I-35" directly. The last step is a double E2 reaction from the appropriate vicinal dihaloalkane (i.e. Waco), that itself is the result of a halogenation reaction with X₂ from the corresponding alkene (i.e. Austin). Note that there is only one vicinal stereoisomer product, the *R,S* stereoisomer, that is meso! Note also that the alkene will be *trans*-2-butene because it is the Zaitsev product of reacting the starting haloalkane with strong base such as NaOR to give an E2 reaction.

19. (7 pts) 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. 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 because only predominant products can be used. All the carbon atoms of the product(s) must come from the starting material(s) shown.



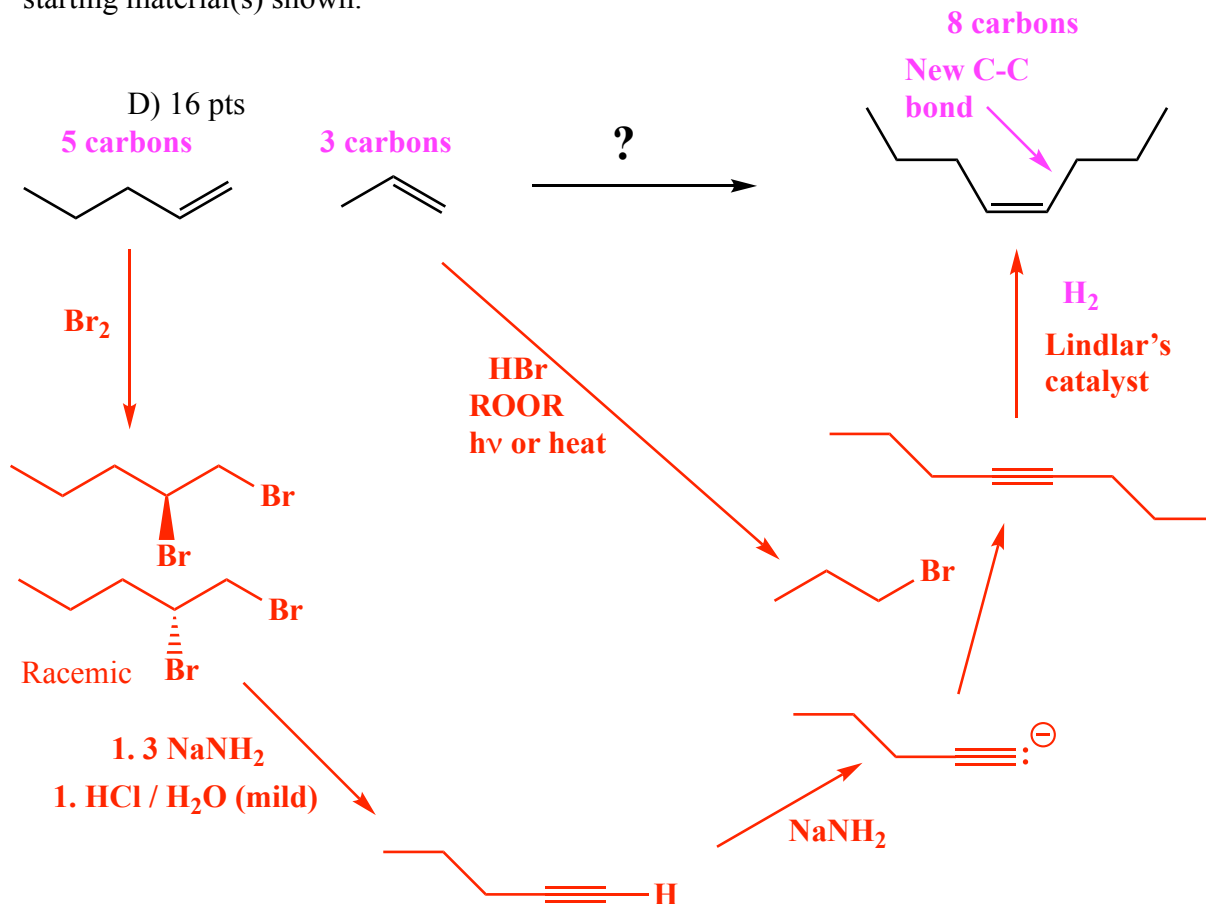
Recognize the product as a *cis* diol, the product of the Ozzy Osbourne reaction using OsO_4 followed by $\text{NaHSO}_3/\text{H}_2\text{O}$, to react with cyclohexene. The cyclohexene can be made using an E2 reaction with a bromocyclohexane as shown. **Recognize** further that the starting material is an alkane, in this case cyclohexane, so the only reaction you can use in the first step is a free radical halogenation with Br_2 and light (or heat).

19. (7 pts) 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. 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 because only predominant products can be used. All the carbon atoms of the product(s) must come from the starting material(s) shown.



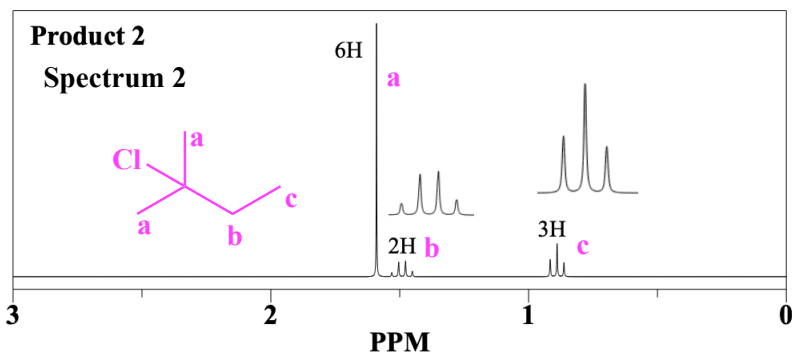
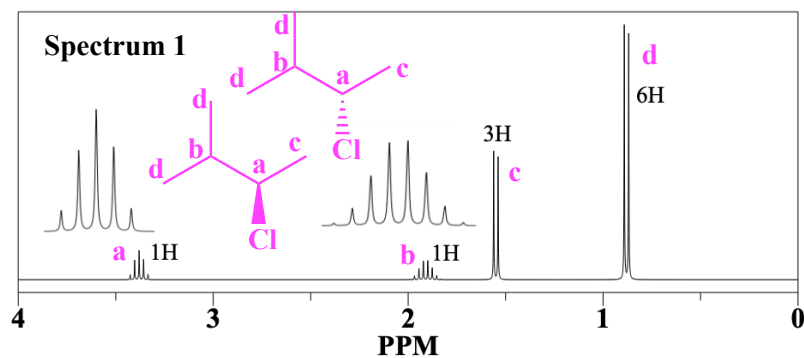
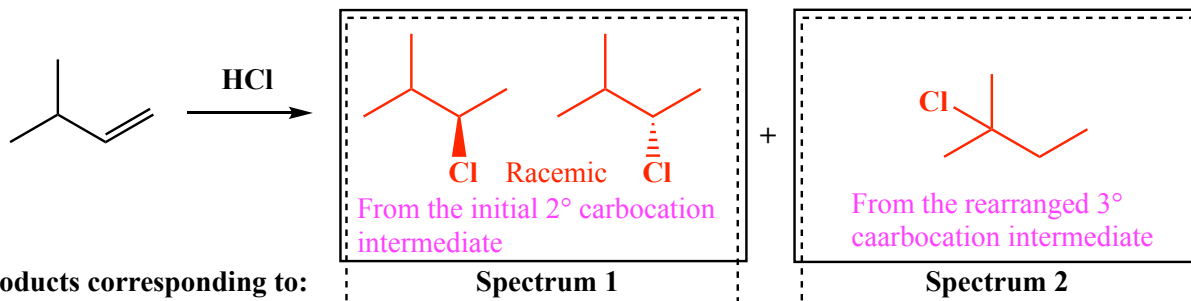
Recognize the product as a racemic *trans* vicinal diol, the product of using either aqueous acid or base conditions to react with a racemic mixture of epoxide as shown. Note that because the product is racemic, in this case the starting epoxide must be racemic as well. That is why either acidic or basic conditions could be used for this last step. The racemic epoxide is made using a peracid such as $\text{CH}_3\text{CO}_3\text{H}$ starting from the corresponding 1-methylcyclohexene as shown. **Recognize** the 1-methylcyclohexene as the Zaitsev product of an E2 reaction with the halomethylcyclohexane shown, which itself is produced by reaction of the starting methylcyclohexane with Br_2 and light (or heat). **Recognize** further that once again the starting material is an alkane, so you already knew the first step was going to be a free radical halogenation reaction! Note: You could also make the epoxide from a combination of reacting 1-methylcyclohexene with X_2 and H_2O to give the halohydrin, followed by reaction in strong base to give the racemic epoxide.

19. (7 pts) 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. 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 because only predominant products can be used. All the carbon atoms of the product(s) must come from the starting material(s) shown.



Recognize that the final product has 8 carbons, while the starting alkenes have 5 and 3 carbons, respectively. There must be a new C-C bond as shown. **Recognize** further that the new C-C bond must come from the only reaction you know that can make C-C bonds, namely reaction of an alkyne containing 5 carbons with a primary haloalkane containing 3 carbons. **Recognize** the final product is a Z alkene, only H_2 with Lindlar's catalyst can make those starting with a corresponding alkyne as shown. **Recognize** that the alkyne needed is exactly the one derived from making the new C-C bond from a 5-carbon alkyne anion with a 3-carbon primary haloalkane as shown. **Recognize** that the 5-carbon alkyne anion is made from the terminal 5-carbon alkyne by reaction with NaNH_2 as shown. The 3-carbon primary haloalkane (1-bromopropane) can be made from the starting 3-carbon alkene (propene) using HBr and peroxides and light or heat to give the non-Markovnikov addition of HBr . **Recognize** that the 5-carbon terminal alkyne can be made along "I-35" from the starting 5-carbon alkene (1-pentene) using the combination of halogenation with X_2 followed by a double E2 reaction using 1. 3 NaNH_2 then 2. $\text{HCl} / \text{H}_2\text{O}$ (mild) because it is a terminal alkyne product.

20. (11 pts) Here is a combination box problem plus NMR spectra! A chemist carries out the following reaction of 3-methyl-1-butene with HCl. She isolated the products and obtained the following two NMR spectra. Write the products that correspond to the spectra in the boxes. Make sure to indicate stereochemistry with wedges and dashes as appropriate and you need to draw all products that are appropriate for each box. Be sure to write "racemic" if appropriate.



A carbocation rearrangement (1,2 shift) of the initially formed secondary (2°) carbocation occurred to give the more stable tertiary (3°) carbocation shown in the box. The chemist saw products from both carbocation intermediates, explaining the products corresponding to both Spectrum 1 and Spectrum 2

When the chemist realized what the structures were for all the products she had made, she immediately knew what happened. **In the box provided, draw the key intermediate that must have formed to create the product that corresponds to Spectrum 2.**

