NAME (Print): _____

SIGNATURE: _____

Chemistry 320M/328M
Dr. Brent Iverson
Final
December 13, 2018

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

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 INCIDENCTS 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		(21)
3		(20)
4		(24)
5		(-)
6		(-)
7		(-)
8		(31)
9		(22)
10		(24)
11		(22)
12		(37)
13		(33)
14		(32)
15		(33)
16		(19)
17		(17)
18		(7)
19		(16)
20		(13)
21		(8)
Total		(408)

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.

As one of my favorite poets of the 20th century put it, 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, 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.

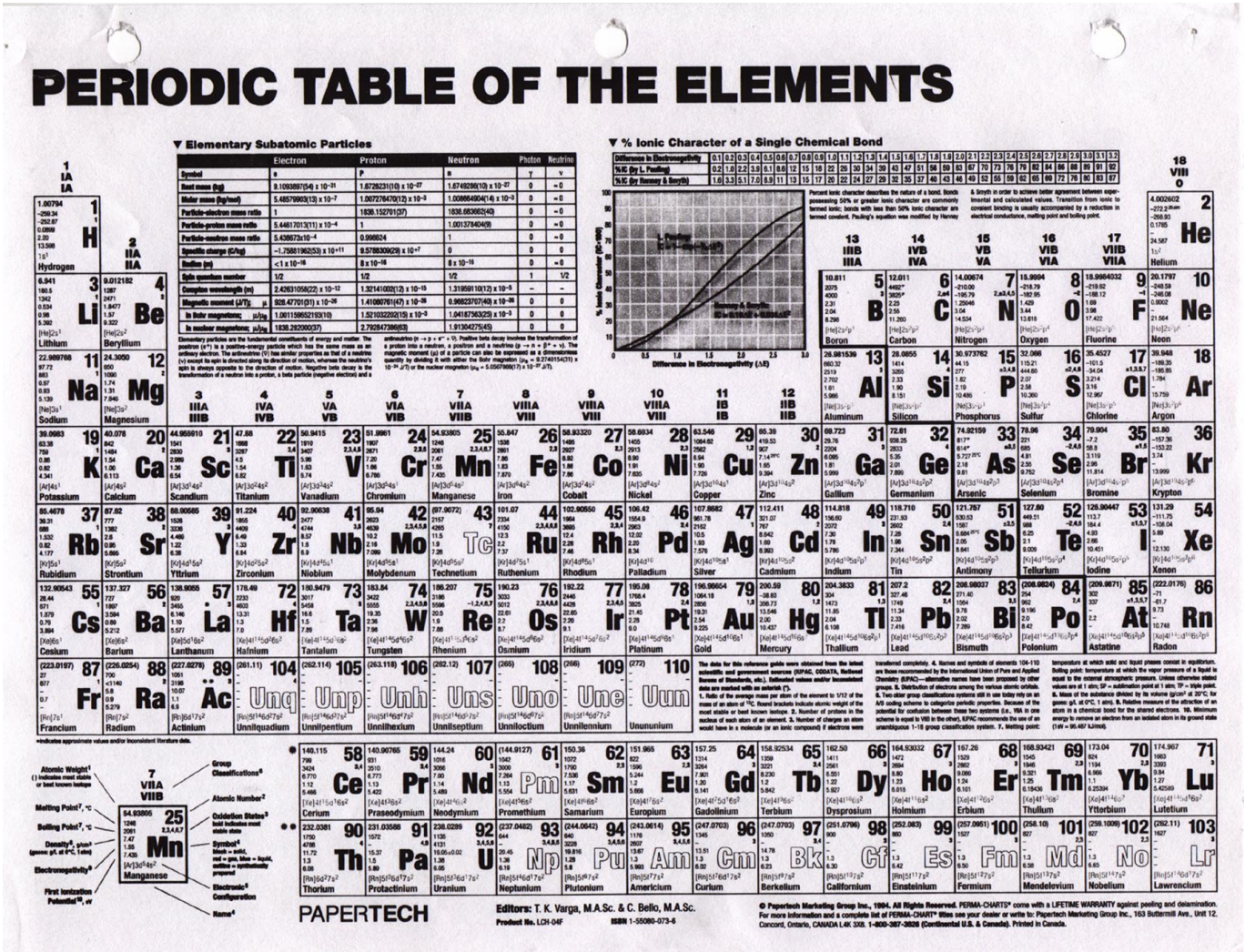
Brent Iverson

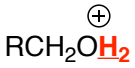
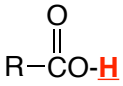
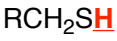
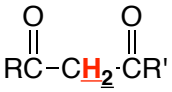
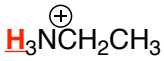
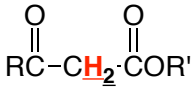
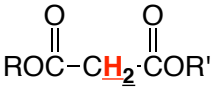
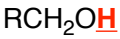
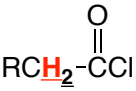
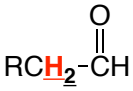
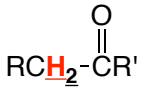
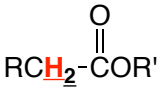
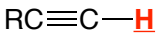
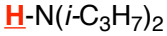
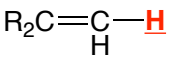
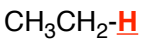
Student Honor Code

"As a student of The University of Texas at Austin, I shall abide by the core values of the University and uphold academic integrity."

_____

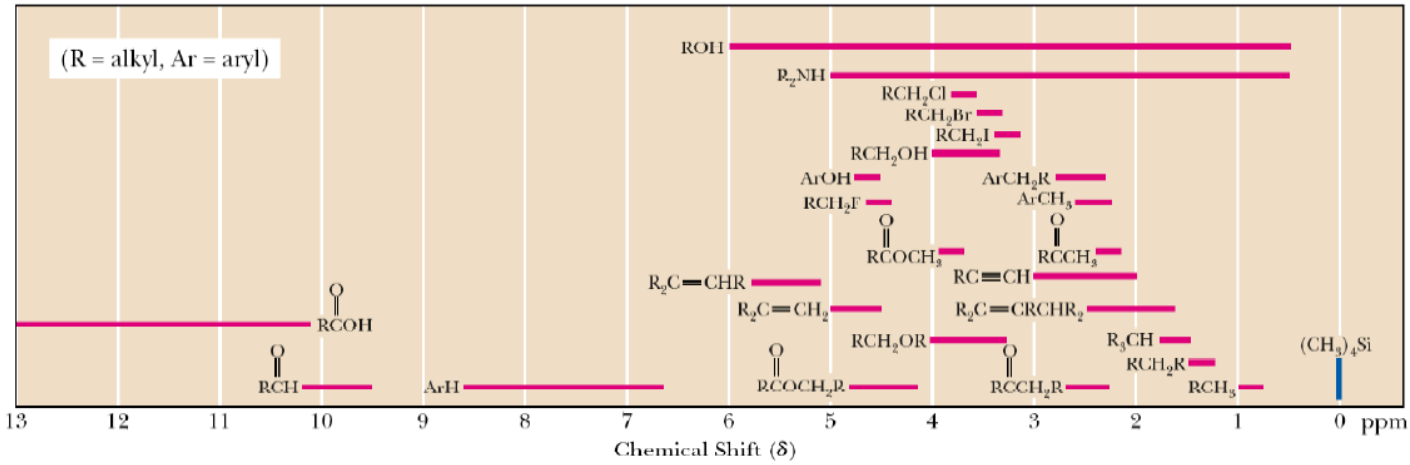
(Your signature)



Compound		pK_a
Hydrochloric acid		-7
Protonated alcohol		-2
Hydronium ion		-1.7
Carboxylic acids		3-5
Thiols		8-9
Ammonium ion		9.2
β-Dicarbonyls		10
Primary ammonium		10.5
β-Ketoesters		11
β-Diesters		13
Water		15.7
Alcohols		15-19
Acid chlorides		16
Aldehydes		18-20
Ketones		18-20
Esters		23-25
Terminal alkynes		25
LDA		40
Terminal alkenes		44
Alkanes		51

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
		RCH_2OH	3.4-4.0
R_2NH	0.5-5.0	RCH_2Br	3.4-3.6
ROH	0.5-6.0	RCH_2Cl	3.6-3.8
RCH_3	0.8-1.0	$RCOCH_3$	3.7-3.9
RCH_2R	1.2-1.4	$RCOCH_2R$	4.1-4.7
R_3CH	1.4-1.7	RCH_2F	4.4-4.5
$R_2C{=}CRCHR_2$	1.6-2.6	$ArOH$	4.5-4.7
$RC{\equiv}CH$	2.0-3.0	$R_2C{=}CH_2$	4.6-5.0
$RCCH_3$	2.1-2.3	$R_2C{=}CHR$	5.0-5.7
$RCCH_2R$	2.2-2.6	$H_2C{-}CH_2$	3.3-4.0
$ArCH_3$	2.2-2.5	RCH	9.5-10.1
RCH_2NR_2	2.3-2.8	$RCOH$	10-13
RCH_2I	3.1-3.3		
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:

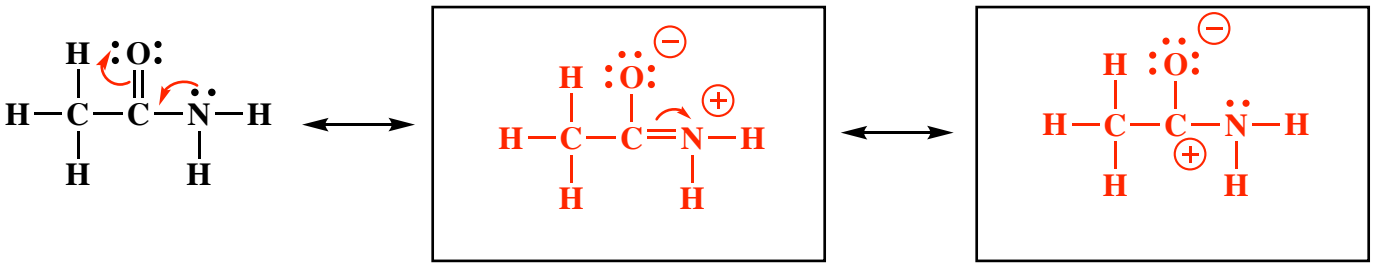
A. **Predicting Structure and Bonding** 1. In most stable molecules, all the atoms will have filled valence shells. 2. Five- and six-membered rings are the most stable. 3. There are two possible arrangements of four different groups around a tetrahedral atom.
B. **Predicting Stability and Properties**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

Signature_____ Pg 1 _____(29)

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

Where are the electrons?

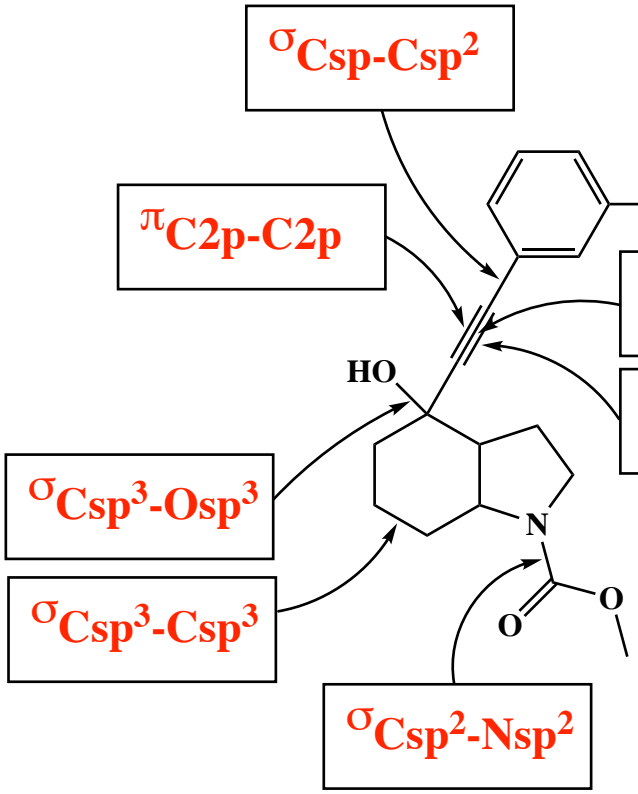
2. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges. For the two structures on the left in each problem, use arrows to indicate the movement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

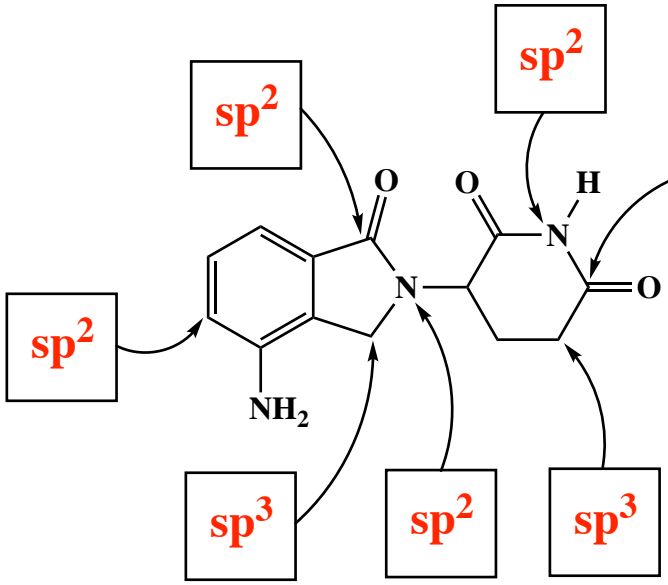
4. (2 pts each) In the spaces provided, indicate the type of bond, and the hybridized orbitals that overlap to form the bond. For example, one answer could be: $\sigma Csp^3\text{-}H1s$



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

Mavolurant
Investigated to treat Fragile X syndrome but discontinued

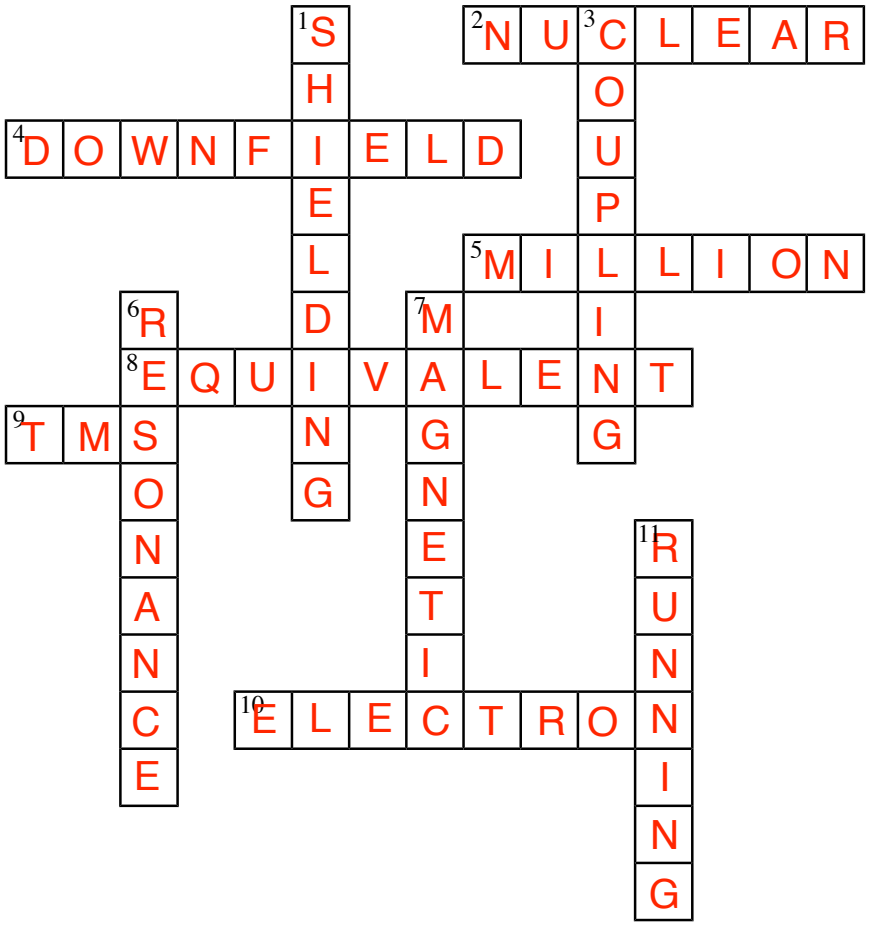
5. (1 pt each) In the spaces provided, write the hybridization state of the atoms indicated by the arrow.



Revimid (Lenalidamide)
An anti-cancer drug used to treat certain cancers such as multiple myeloma

Signature_____ Pg 3 _____(20)

6. (2 pt each) **Fill in the crossword puzzle with the best word indicated by the clues below.**



ACROSS:

2. What the "N" stands for in NMR

4. The term used to describe signals that are farther from TMS on an NMR spectrum.

5. What "m" stands for in ppm.

8. In molecules with no chiral centers, H atoms on the same freely rotating sp^3 carbon atom are _____ .

9. The three-letter acronym used for tetramethylsilane.

10. More _____ density around an H atom leads to an NMR signal at lower ppm.

DOWN:

1. Electron density around a nucleus decreases the magnetic field felt by the nucleus, an effect known as _____ .

3. The distance between peaks in an NMR signal is referred to as the _____ constant.

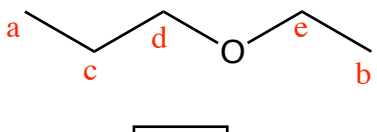
6. What the "R" stands for in NMR.

7. The energy required to flip a nuclear spin is proportional to strength of the _____ field experienced by the nucleus.

11. _____ 3-5 miles on the weekends will keep you fit for life!

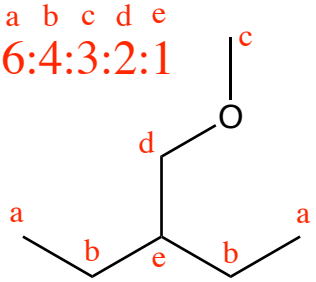
7. (24 pts total) On the following three pages there are NMR spectra. The relative integrations are given above each signal. Each NMR spectrum has a letter on it. **In the spaces provided, write the appropriate letter underneath the molecules that would produce that spectrum.** Notice that not all of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

a b c d e
3:3:2:2:2



☐

a b c d e
6:4:3:2:1



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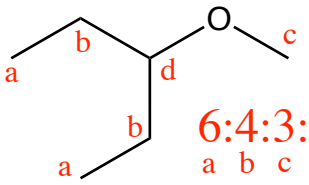
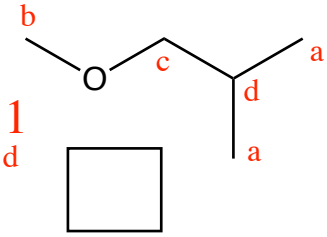


6:4:3:1
a b c d

C



6:3:2:1
a b c d

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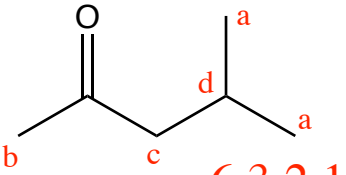
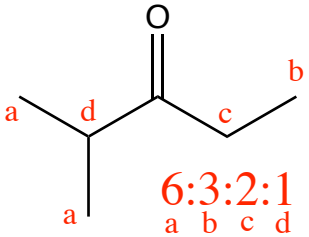


6:3:2:1
a b c d

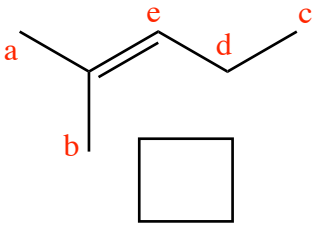
B



6:3:2:1
a b c d

☐

a b c d e
3:3:3:2:1



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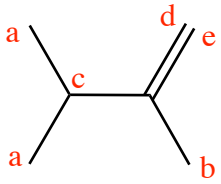
a b c d e
6:3:1:1:1



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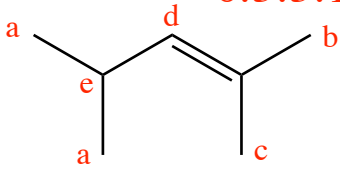
a b c d e
6:3:3:1:1



A

Spectrum A

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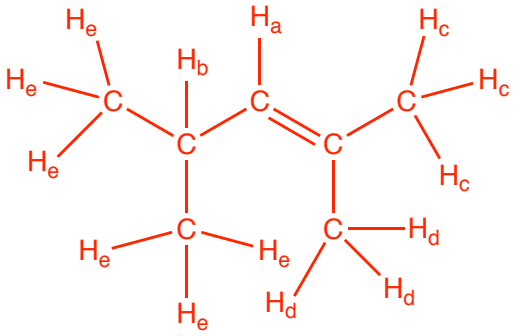

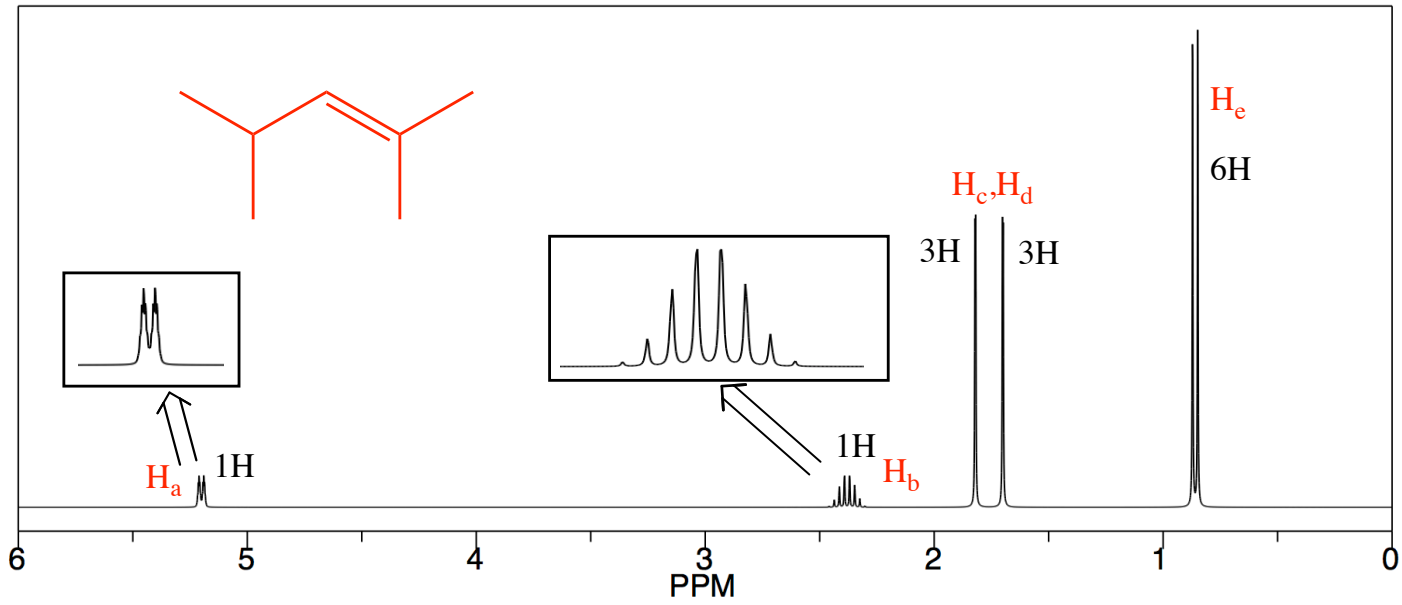

Spectrum B

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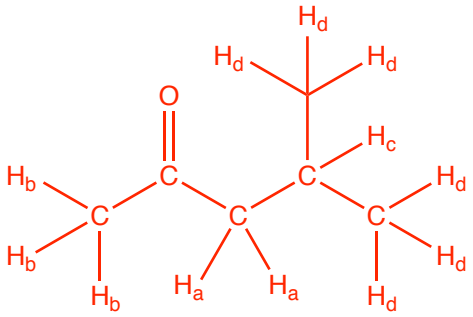

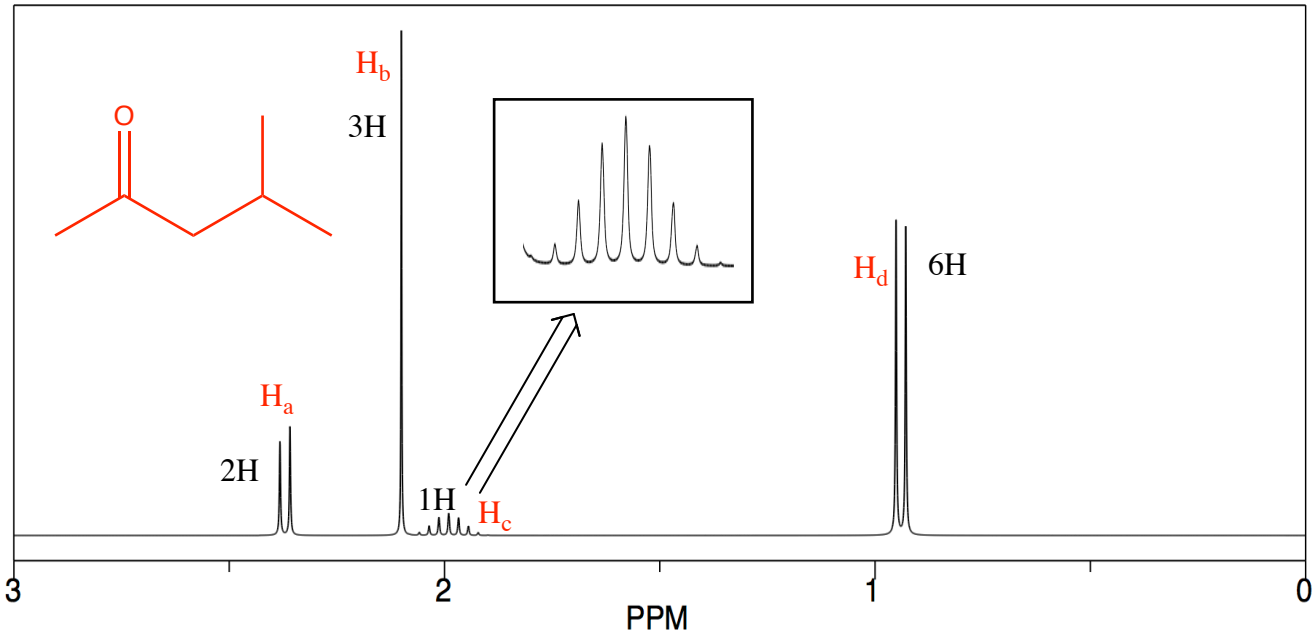

Spectrum C

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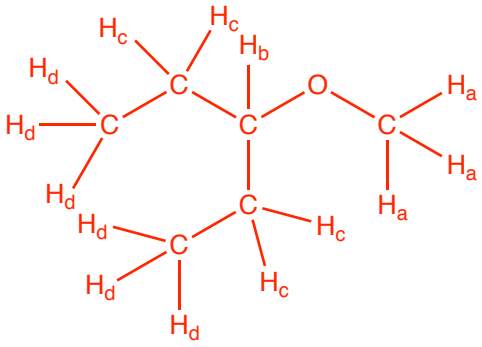
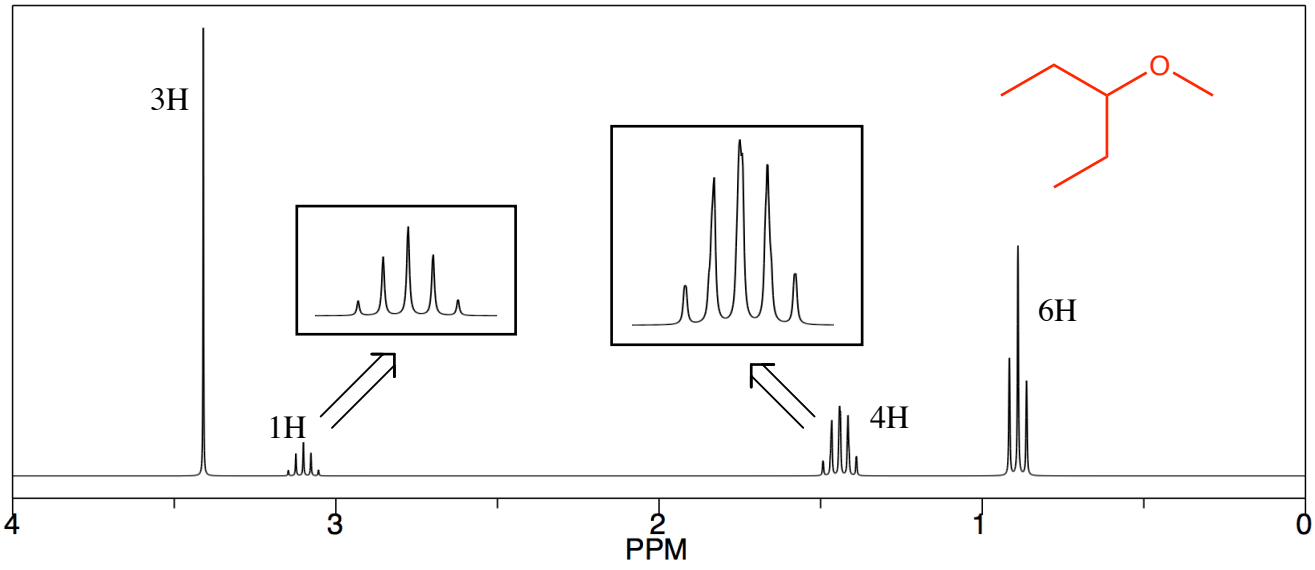
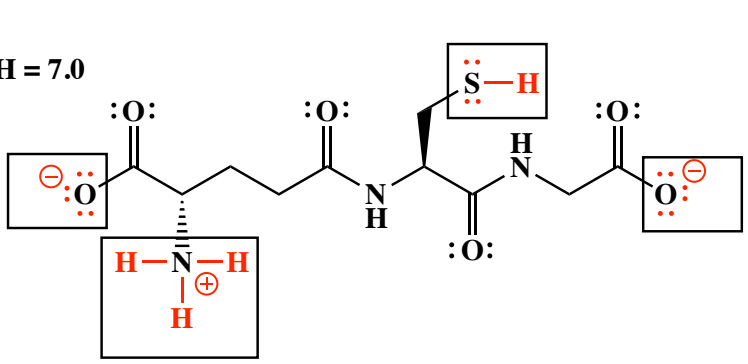




8. (19 pts) The following molecule is called glutathione. It is present in high concentration in most mamallian cells. It primarily protects cells from oxidative damage **In the boxes, fill in the proper number of bonds to H atoms, lone pairs, and formal charges to show the protonation state of glutathione 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.

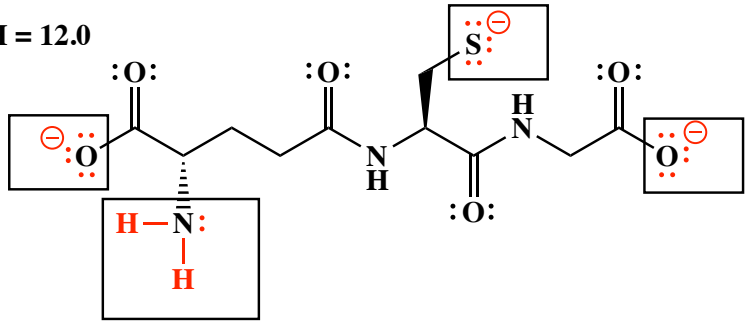


pK_a = 10.6

pH = 7.0

What is the total net charge of this peptide at pH 7.0? **-1**

pH = 12.0

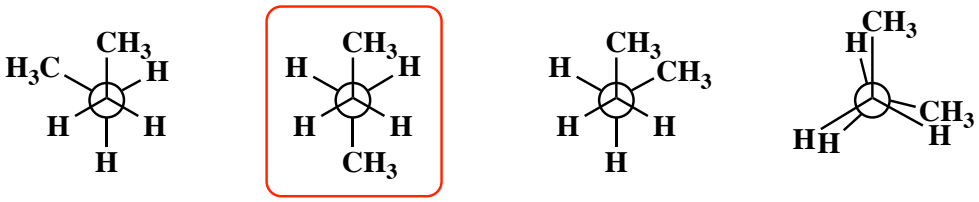


What is the total net charge of this peptide at pH 12.0? **-3**

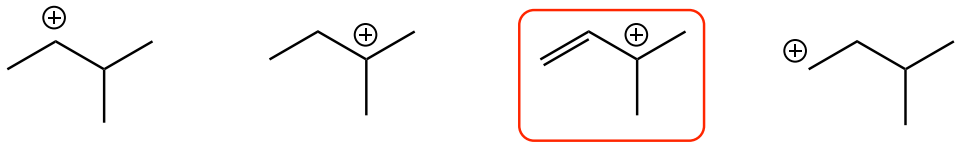
How many chiral centers are present in glutathione? **2**

9. (4 pts each) Circle the appropriate structure from each set of 4 molecules.

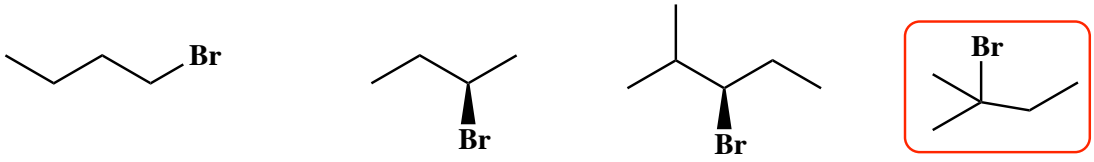
A) Circle the most stable conformation.



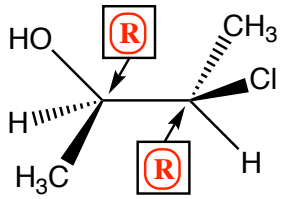
B) Circle the most stable carbocation

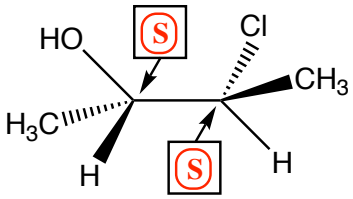


C) Circle the molecule that is most likely to react by the S_N1/E1 mechanisms.



10. (14 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. **Circle all meso compounds.**

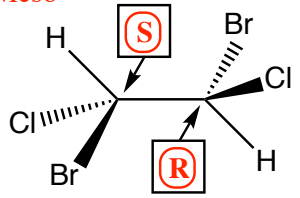




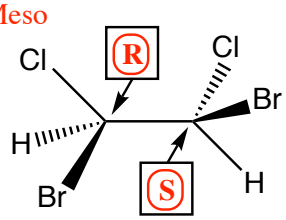
Relationship

Enantiomers

Meso



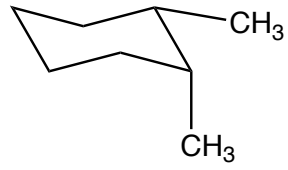
Meso



Same Molecule

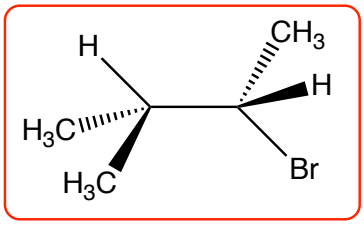
11. (4 pts) On the line provided, state the stereochemical relationship between this pair of molecules: **enantiomers, diastereomers, or the same molecule**. No need to assign R and S. **Circle all meso compounds.**

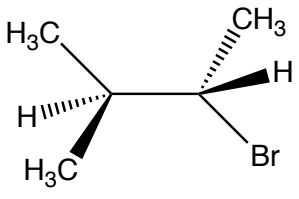
Meso

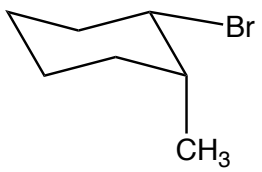


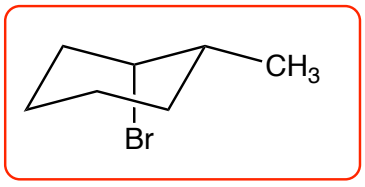
Diastereomers

12. (4 pts) For the following pairs of structures, circle the one of each pair that is in the correct conformation for an E2 reaction that gives the major product formed as predicted by Zaitsev's rule.







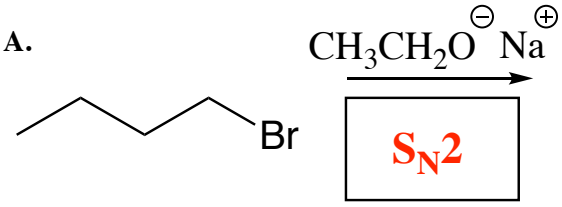


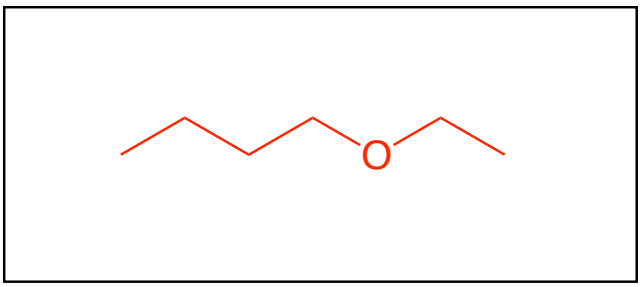
13. (6 pts total) Fill in the blanks with the word(s) that best complete(s) the sentences.

Alcohols are classified as **polar protic solvents**. This has three important consequences. First, alcohols or other polar protic solvents will (speed up or slow down) ___slow down___ S_N2 reactions because they strongly solvate (nucleophiles or electrophiles) ___nucleophiles___, (inhibiting or facilitating) ___inhibiting___ their ability to react. Second, alcohols as solvents will speed up S_N1/E1 reactions because they are good at solvating (both or neither) ___both___ cations and anions, thereby (raising or lowering) ___lowering___ the activation barriers for these reactions. Finally, alcohols are good at dissolving molecules that (can or cannot) ___can___ make hydrogen bonds.

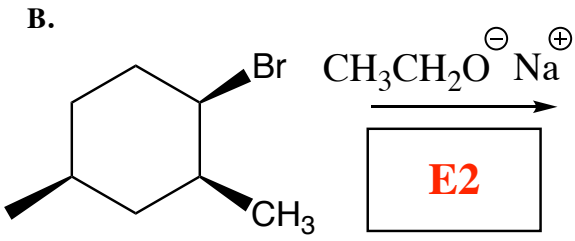
14. (18 pts) The following reactions all involve chemistry of haloalkanes. **Fill in the box below the arrow with the mechanism that will be followed (S_N2, E2, etc.). Then draw only the predominant product or products** and please remember that **you must draw the correct stereoisomers**. For S_N1/E1 reactions you must draw all significant products (including all stereoisomers).

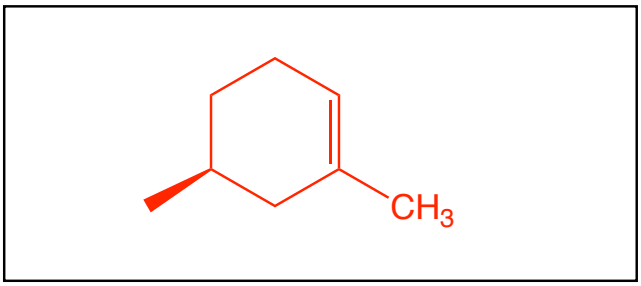
A.



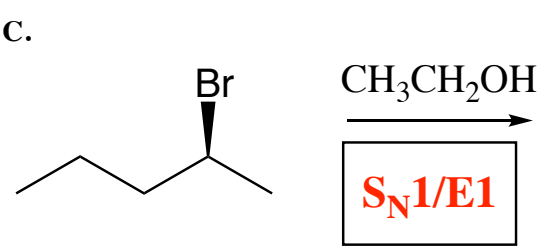


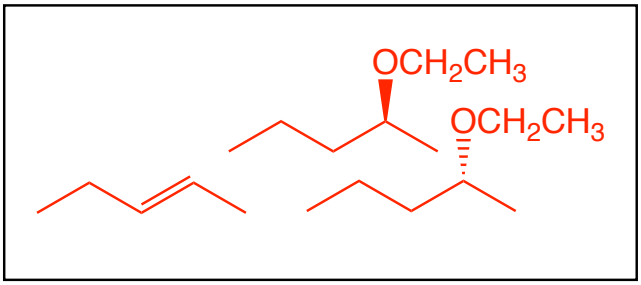
B.



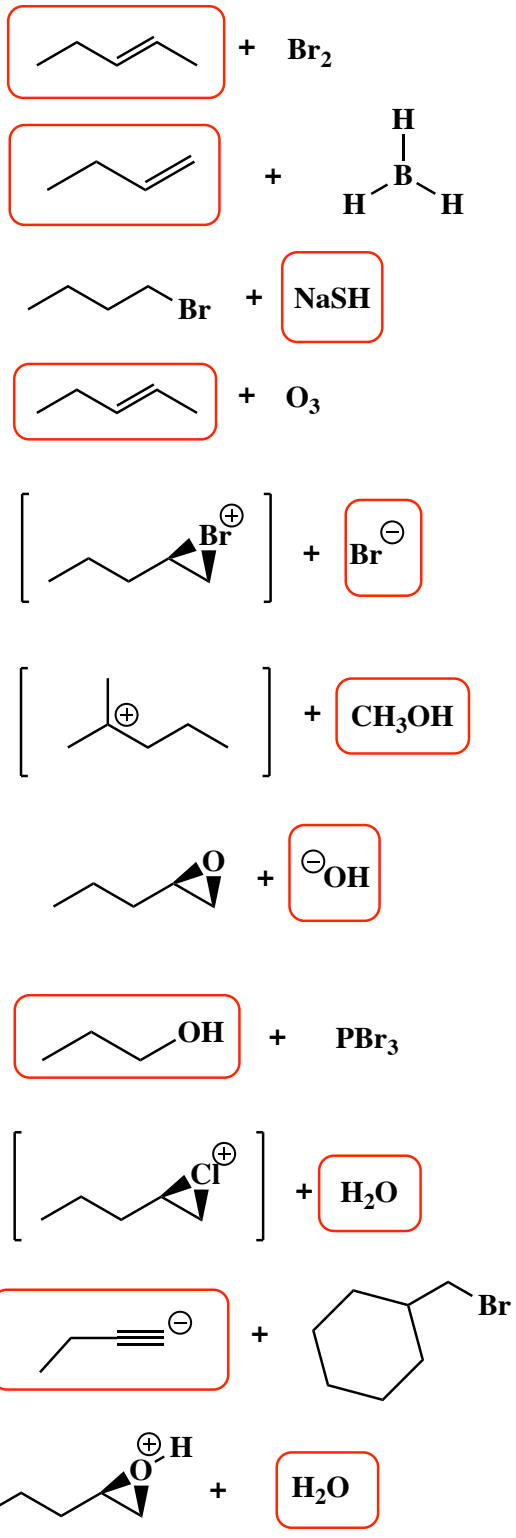


C.

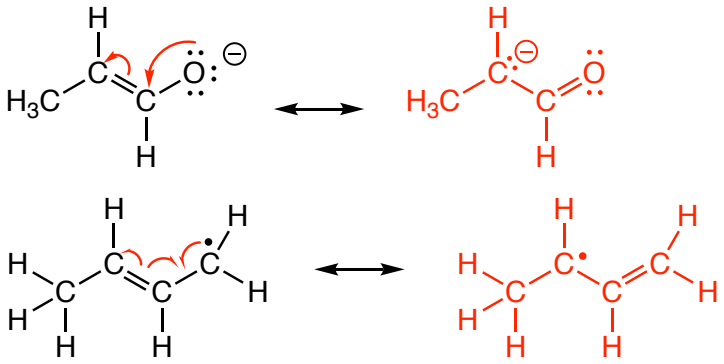




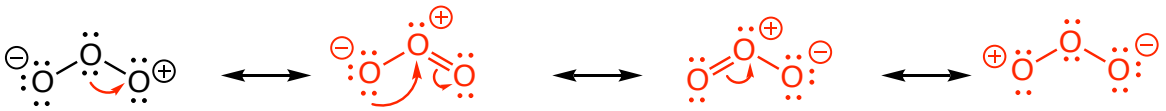
15. (2 pts each) For the following sets of reagents you have seen in various bond-making steps in mechanisms, **circle the nucleophile**. Do not make any marks on the electrophiles. DO NOT WRITE THE PRODUCTS OF THESE STEPS, we only want to see circles on this page!!



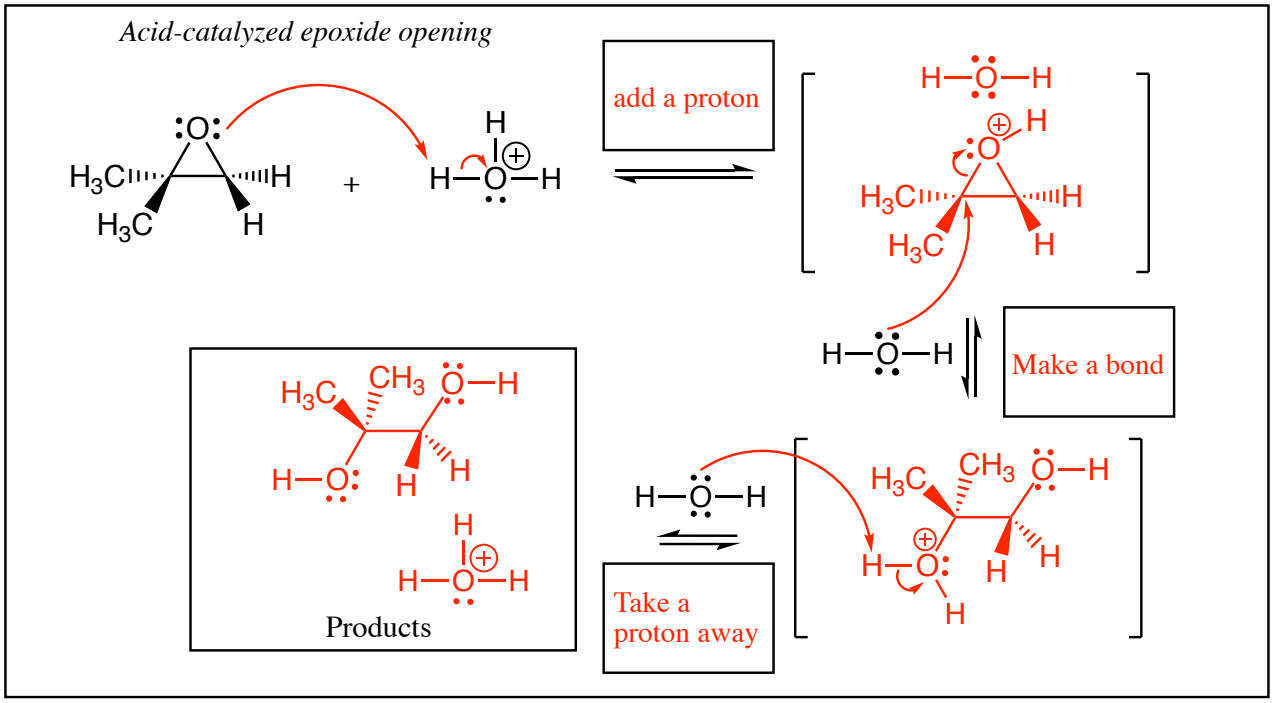
16. (20 pts) For the following, draw the indicated number of most important contributing structures. **Make sure to draw all lone pairs and formal charges. Use arrows** to indicate the movement of electrons that leads to the striucture immediately to the right. Therefore, the structure you draw farthest to the right will not have an arrows on it, but all of the others will.



This last one is hard, it was at the top of the ozonolysis mechanism sheet

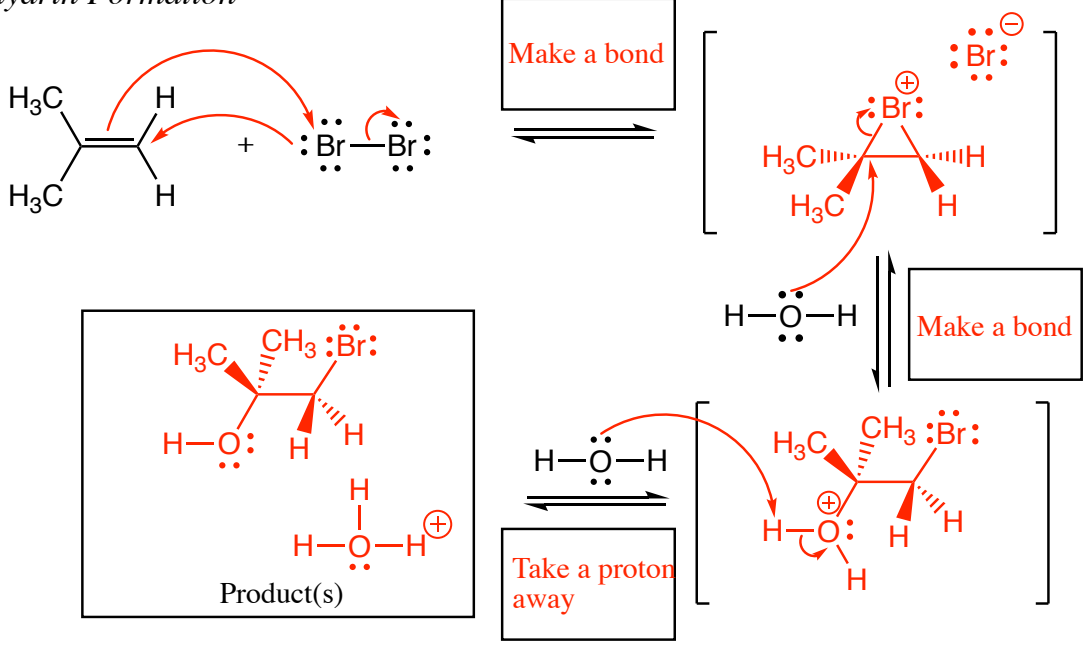


17. (17 pts) For this mechanism, use **arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **YOU ONLY NEED TO DRAW ONE STEREOISOMER OF A CHIRAL INTERMEDIATE OR PRODUCT (using wedges and dashes as appropriate) IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. In the boxes provided, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).**

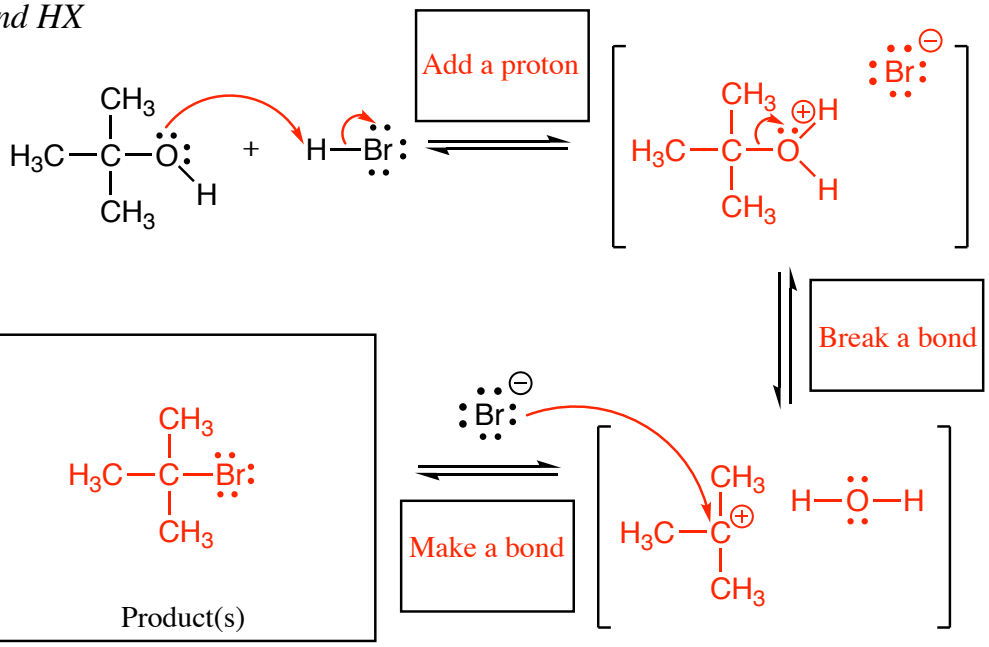


18. (33 pts) For these two mechanisms, use **arrows to indicate movement of <u>all</u> electrons, write <u>all</u> lone pairs, <u>all</u> formal charges, and <u>all</u> the products for each step.** Remember, I said <u>all</u> the products for each step. **YOU ONLY NEED TO DRAW ONE STEREOISOMER OF A CHIRAL INTERMEDIATE OR PRODUCT (using wedges and dashes as appropriate) IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR PRODUCT, MARK IT WITH AN ASTERISK AND LABEL THE MOLECULE AS "RACEMIC" IF APPROPRIATE. In the boxes provided, write which of the 4 most common mechanistic elements describes each step (make a bond, break a bond, etc.).**

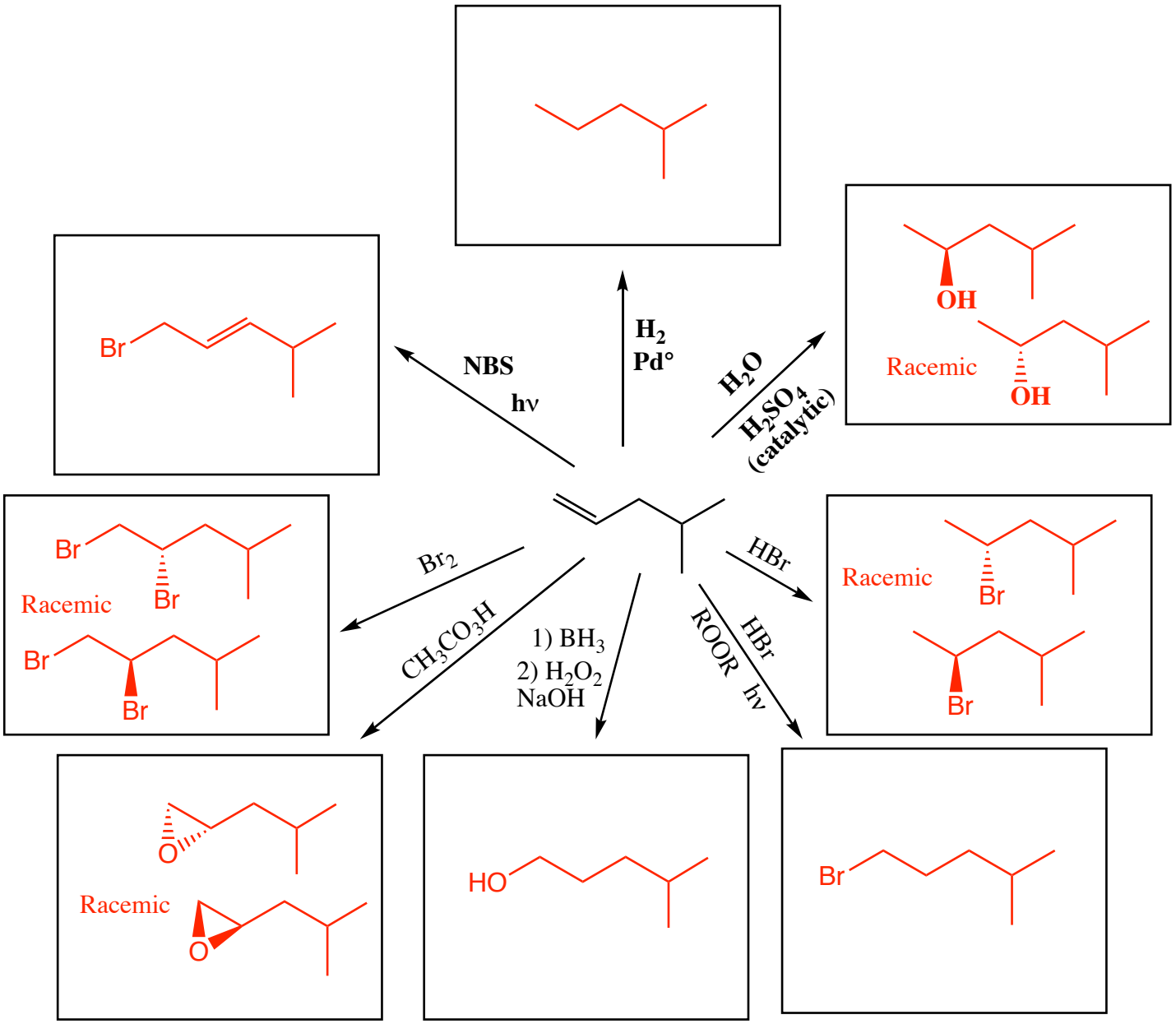
Halohydrin Formation



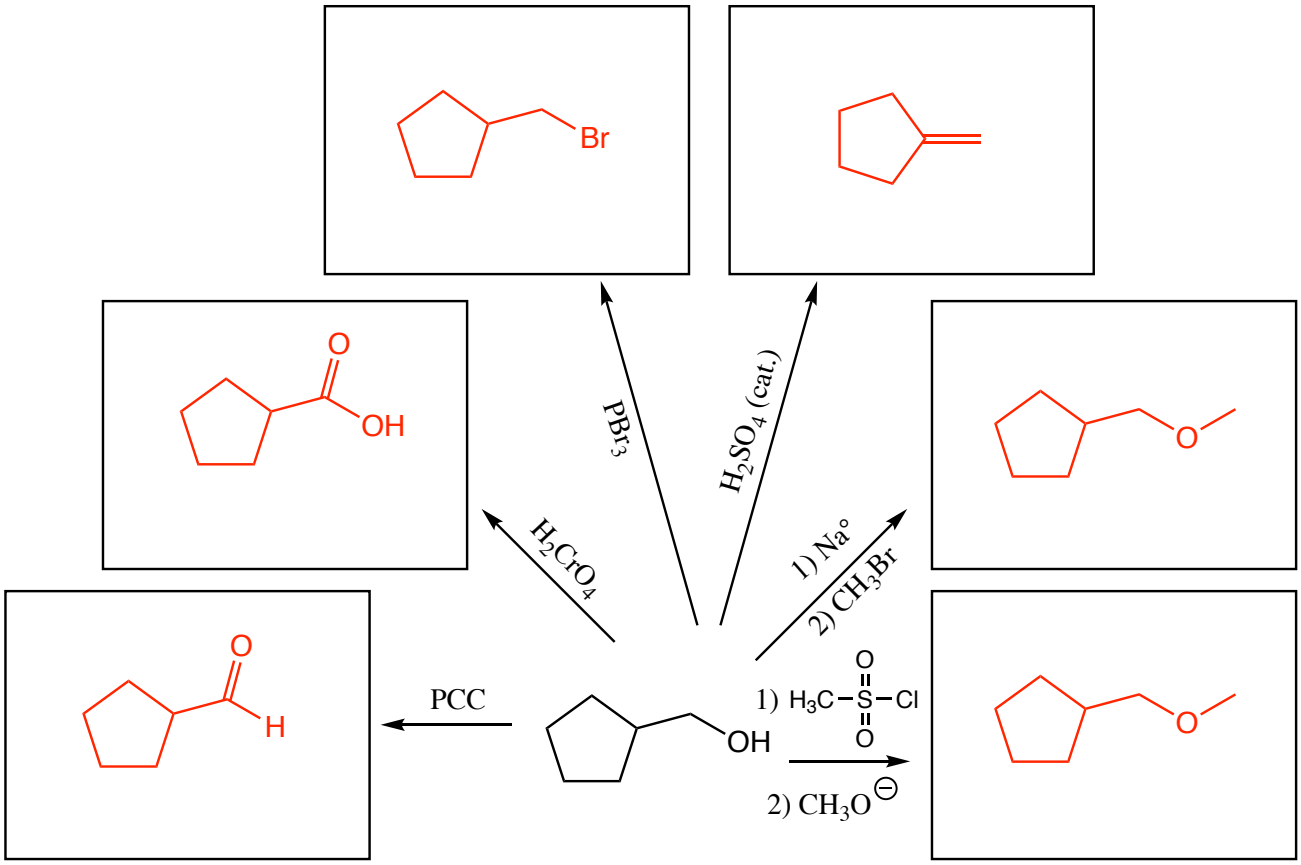
3° Alcohol and HX

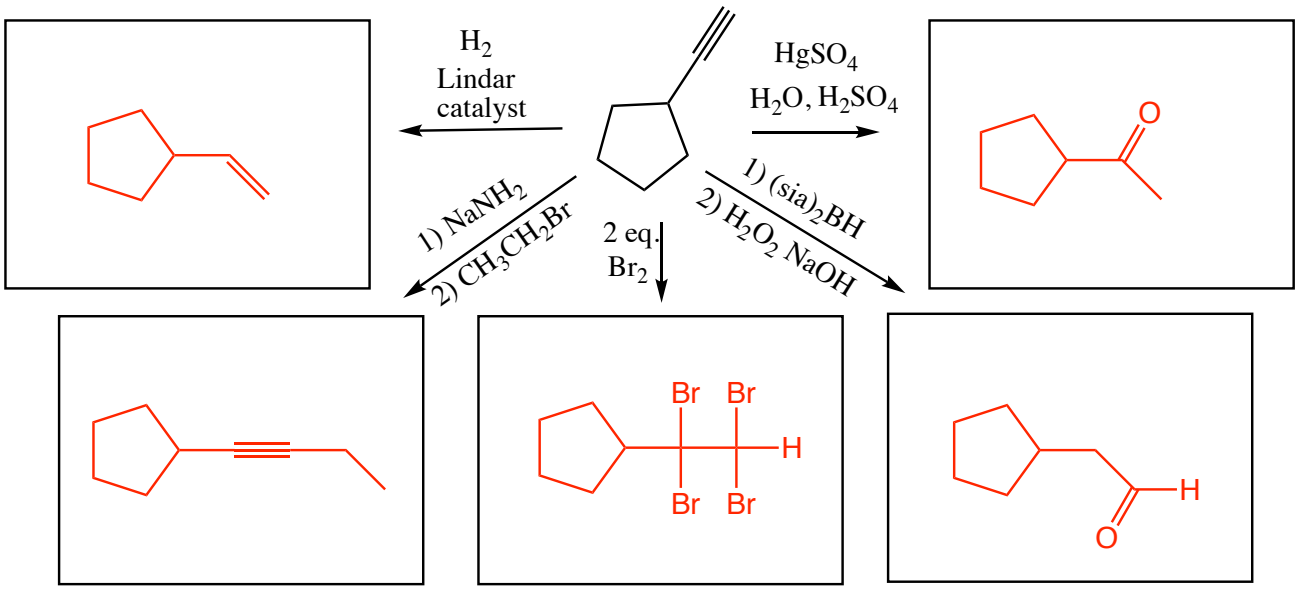


20. (3 or 5 pts each) For the following, complete the reactions with the predominant carbon-containing product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangments take place.

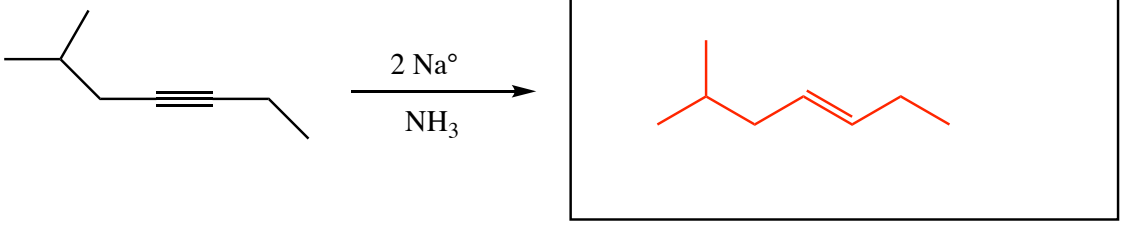


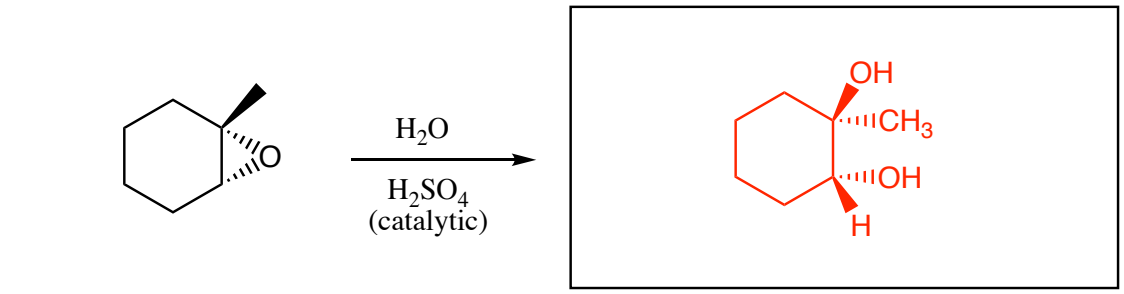
21. (3 or 5 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangments take place.

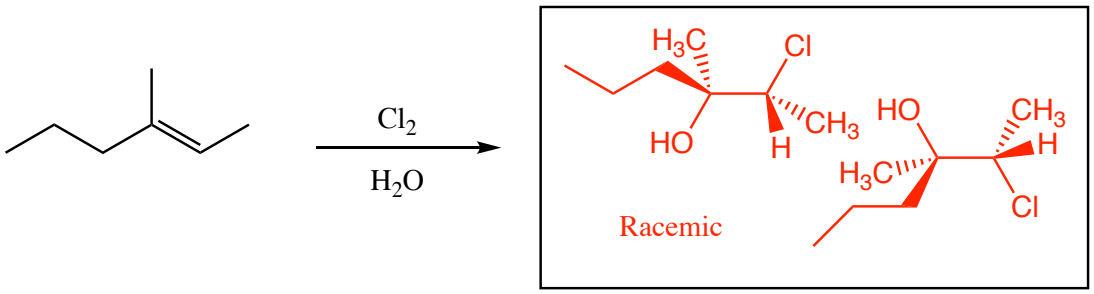


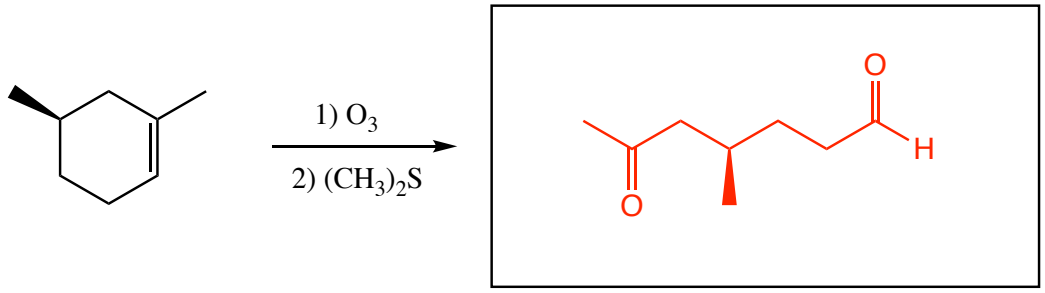


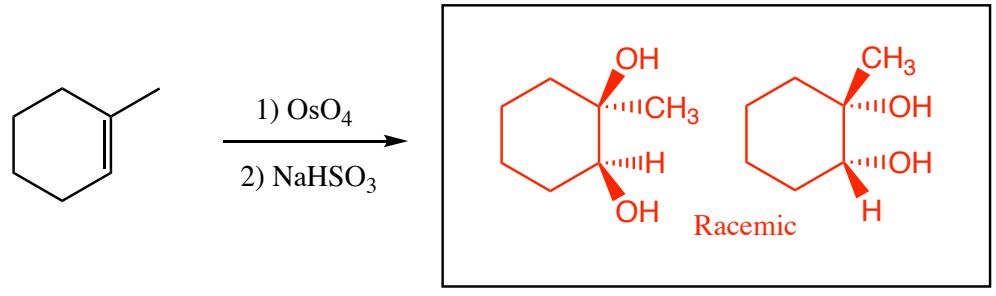
22. (3, 4 or 5 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangments take place.





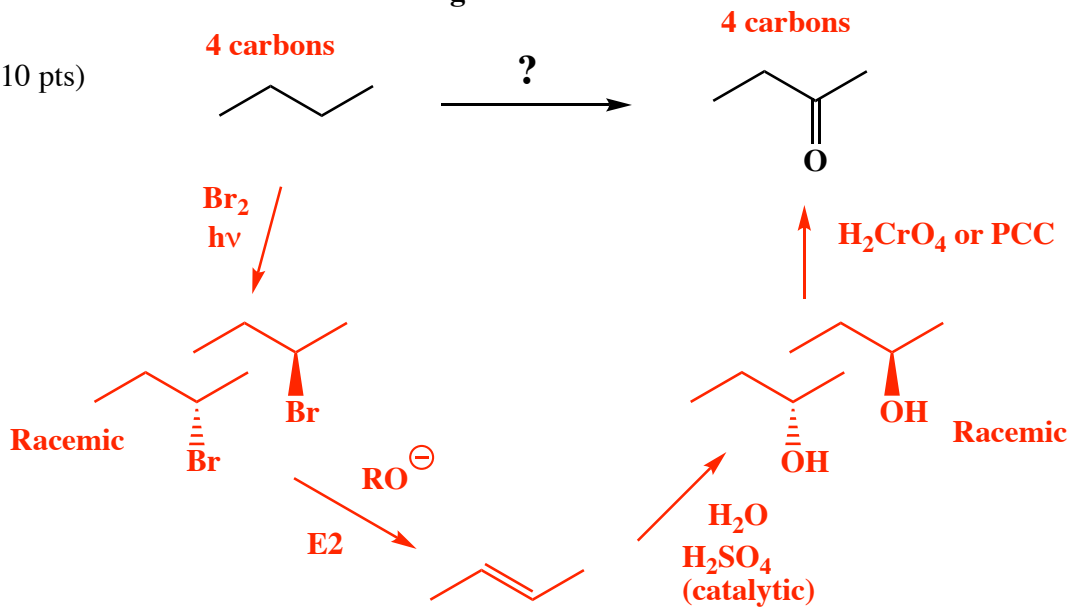






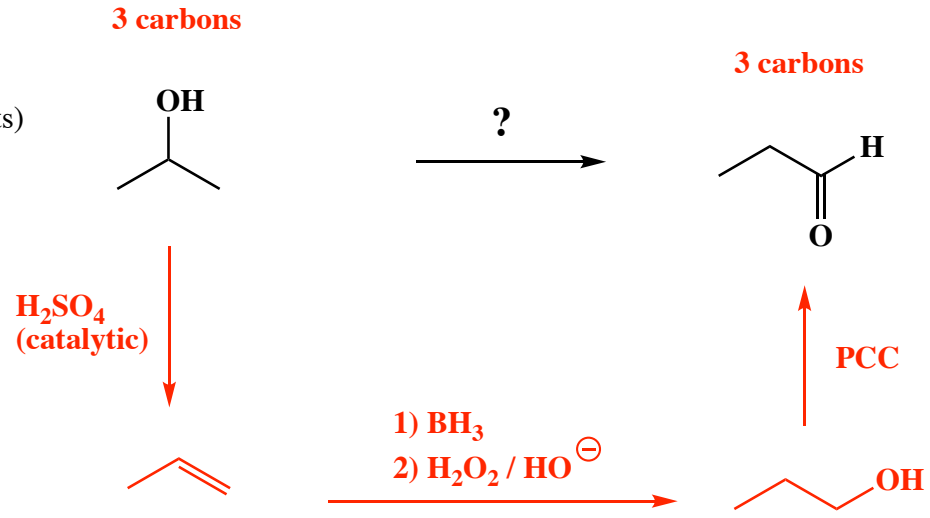
23. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized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



Alternatively, you could make this product by converting the 2-butene into 2-butyne then using either method (Hg or $(sia)_2BH$) to give the product ketone.

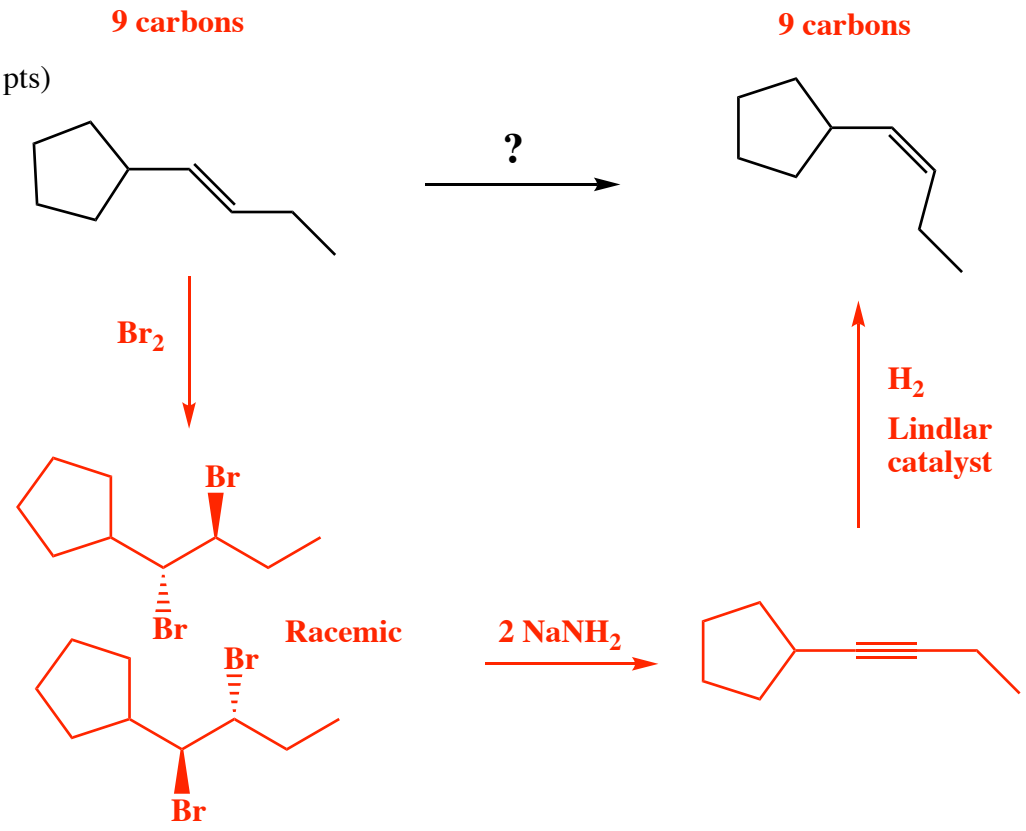
B) (7 pts)



Alternatively, you could make this product by converting the propene into propyne then using $(sia)_2BH$) to give the aldehyde product.

23. 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.**

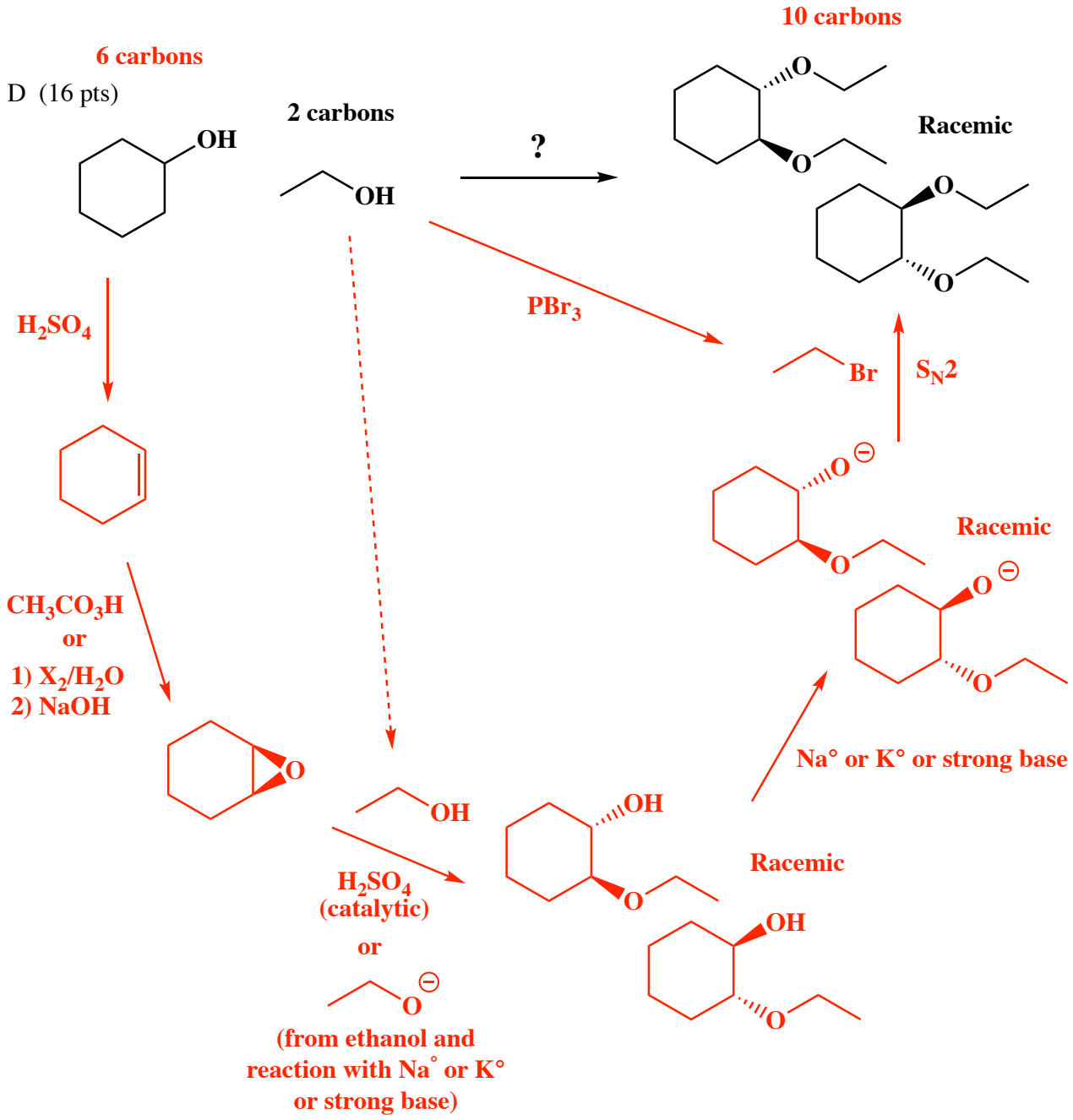
C) (7 pts)



Recognize that the product is a *Z* alkene, and the only way to make these involves using H_2 and Lindlar's catalyst. Therefore the last step must be reaction of the corresponding alkyne with those reagents. Recognize that it is then a matter of converting the starting *E* alkene into an alkyne using the standard "I-35" reactions.

23. (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.**

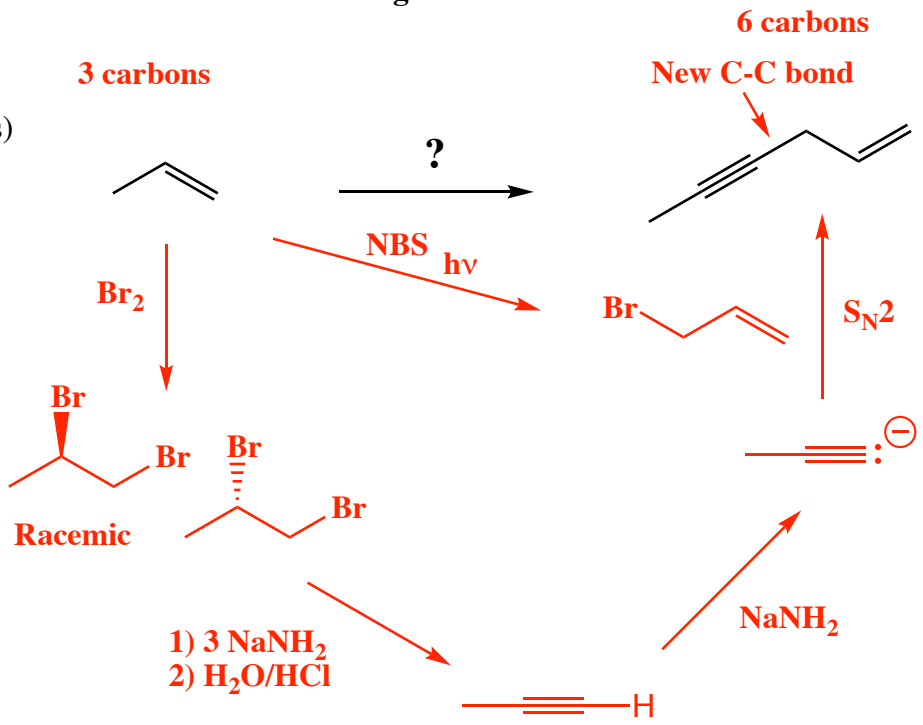
D (16 pts)



We would also accept an alternative route in which water/H_2SO_4 or HO^- is used to react with the epoxide to give the *trans* vicinal diol, that is then reacted 2X with bromoethane to give the diether final product.

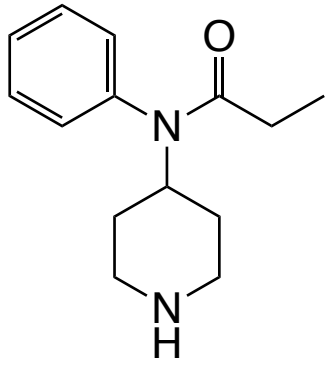
23. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule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

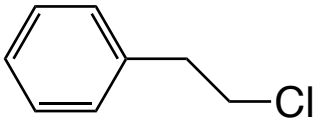
E (13 pts)



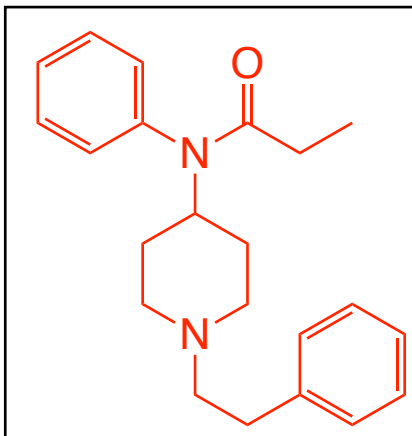
Recognize the new C-C bond is formed from and S_N2 reaction between an alkyne anion and the allyl bromide. **Recognize** the allyl halide as being the result of an NBS allylic halogenation reaction of the starting propene. **Recognize** the required alkyne as being derived from the standard "I-35" reactions to convert and alkene (propene) into a terminal alkyne.

24. (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.

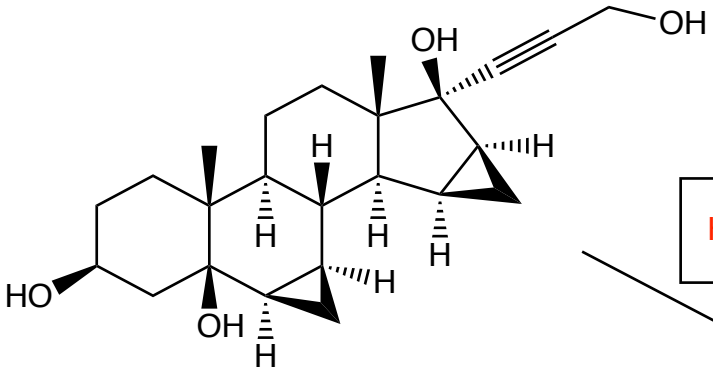




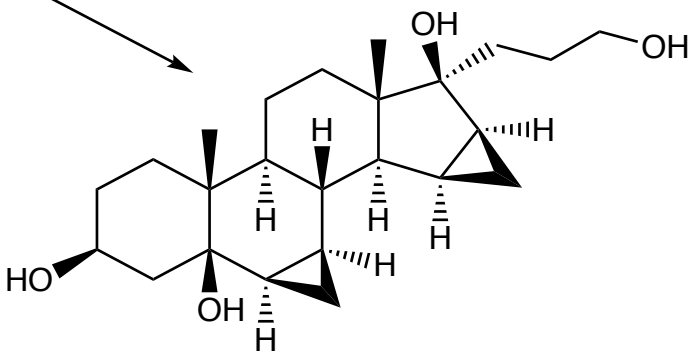
S_N2



Fentanyl an incredibly potent morphine analog that is deadly when used illegally.



H_2 Pd°, Pt° or Ni°



Have a great holiday break!!