

NAME (Print): _____

Chemistry 320M/328M

Dr. Brent Iverson

Final exam

December 15, 2012

SIGNATURE: _____

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

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Please Note: This test may be a bit long, but there is a reason. I would like to give you a lot of little questions, so you can find ones you can answer and show me what you know, rather than just a few questions that may be testing the one thing you forgot. **I recommend you look the exam over and answer the questions you are sure of first**, then go back and try to figure out the rest. Also make sure to **look at the point totals** on the questions as a guide to help budget your time.

You 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.

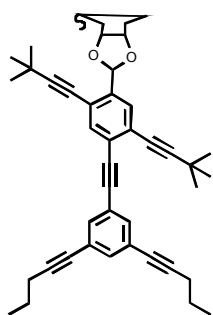
FINALLY, DUE TO SOME UNFORTUNATE RECENT INCIDENTS YOU ARE NOT ALLOWED TO INTERACT WITH YOUR CELL PHONE IN ANY WAY. IF YOU TOUCH YOUR CELL PHONE DURING THE EXAM YOU WILL GET A "0" NO MATTER WHAT YOU ARE DOING WITH THE PHONE. PUT IT AWAY AND LEAVE IT THERE!!!

Page	Points
1	(29)
2	(20)
3	(18)
4	(15)
5	(-)
6	(-)
7	(-)
8	(28)
9	(17)
10	(26)
11	(16)
12	(26)
13	(27)
14	(41)
15	(30)
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18	(15)
19	(12)
20	(11)
21	(4)
22	(12)
Total	(387)

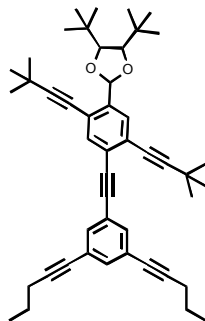
Honor Code

The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.

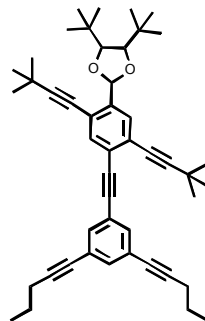
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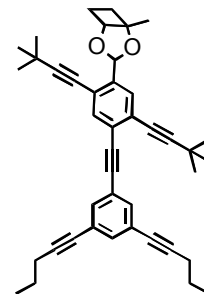
Dr. Iverson



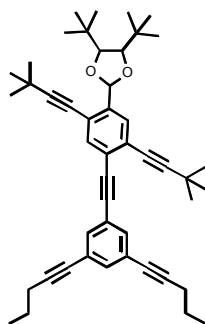
Amy



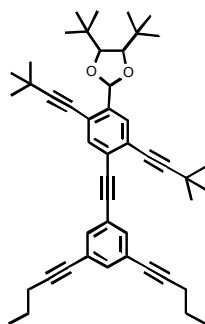
Mary



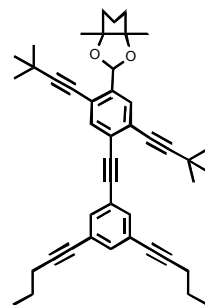
Cameron



Wenzong



Diana



Brian

The first semester of Organic Chemistry is a journey that begins with a review of material you have seen, transitions to the study of organic molecules, then settles in with a long discussion of reactions and their mechanisms. The pace accelerates through the chapters until we finish with the chemistry of epoxides. We finish with a chapter on NMR, the point of which is determining molecular structure. Solving organic synthesis problems requires not only a firm command of the many reactions and mechanisms we have presented, but also high level problem solving skills and a spark of creativity. You have all come a long way since late August when you first came to class. It is my sincere hope that this final serves to affirm that you have completed this journey successfully and caught the Organic Chemistry wave!

As you go through the test, use good test taking strategy by:

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

Have a safe holiday and remember to exercise every chance you get.

If you stay in shape throughout your life, you will thank yourself more than you can imagine!!!

Brent Iverson

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

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

1. Atoms prefer filled valence shells. 2. The most important question in chemistry is "[Where are the electrons?](#)" 3. Nature hates unpaired electrons. 4. Nature hates localized charges. 5. Most reactions involve nucleophiles (molecules with a location of particularly high electron density) attacking electrophiles (molecules with a location of particularly low electron density). 6. Steric interactions (atoms bumping into each other) can prevent reactions by keeping the reactive atoms away from each other. 7. Pi electrons prefer to be delocalized over as many adjacent sp^2 hybridized atoms (or sp^1 hybridized atoms in some cases) as possible, and aromaticity is the most stable form of pi electron delocalization.

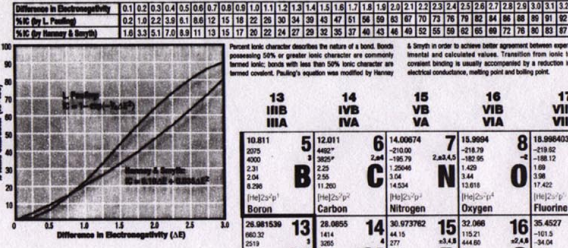
PERIODIC TABLE OF THE ELEMENTS

Elementary Subatomic Particles

	Electron	Proton	Neutron	Photon	Neutrino
Symbol	e	p	n	γ	ν
Rest mass (kg)	$9.1093897(5) \times 10^{-31}$	$1.672623(1) \times 10^{-27}$	$1.674929(1) \times 10^{-27}$	0	0
Relative atomic mass	0.00054858	1.00727647(1) $\times 10^{-3}$	1.008664916(4) $\times 10^{-3}$	0	0
Charge (e)	-1	+1	0	0	0
Spin	1/2	1/2	1/2	0	1/2
Speed of light (c)	0	0	0	1	0
Magnetic moment (N/A)	-9.2847637(5) $\times 10^{-24}$	1.836122189(4) $\times 10^{-26}$	1.818271825(4) $\times 10^{-26}$	0	0
In nuclear magnetons (μ_N)	-1.836122189(4) $\times 10^{-4}$	1.836122189(4) $\times 10^{-4}$	1.818271825(4) $\times 10^{-4}$	0	0
In nuclear magnetons (μ_N)	-1.836122189(4) $\times 10^{-4}$	1.836122189(4) $\times 10^{-4}$	1.818271825(4) $\times 10^{-4}$	0	0

Elementary particles are the fundamental constituents of matter and energy. The proton (p) is a positively charged particle which has the same mass as the neutron (n). The electron (e) is a negatively charged particle which has a mass 1/1836 that of the proton. The photon (γ) is a particle of light which has no mass and travels at the speed of light. The neutrino (ν) is a neutral particle which has a very small mass and travels at the speed of light.

% Ionic Character of a Single Chemical Bond



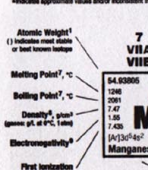
1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIB	14 IVB	15 VB	16 VIB	17 VIIB	18 VIIIB
1.00794 1.008665 1.009865 1.010708 1.011432	4.002602 6.941 9.01224 12.00783 15.00307	6.941 9.01224 12.00783 15.00307	20.1797 24.3050 28.9891 32.06 35.45	44.9559 47.88 50.9415 54.0385 57.076	58.9332 63.546 68.94 74.92159 78.94	88.90584 91.224 92.90638 95.94 98.906	101.07 102.9055 104.91 106.9055 108.9055	137.327 138.9055 140.9076 142.9051 144.9051	186.9074 188.90584 190.9076 192.9051 194.9051	223.0189 225.0189 227.0189 229.0189 231.0189	269.1015 271.1015 273.1015 275.1015 277.1015	290.01 292.01 294.01 296.01 298.01	309.07 311.07 313.07 315.07 317.07	320.07 322.07 324.07 326.07 328.07	354.5 356.5 358.5 360.5 362.5	390.9 392.9 394.9 396.9 398.9	400.15 402.15 404.15 406.15 408.15
H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar

19 IIA	20 IIIB	21 IVB	22 VB	23 VIB	24 VIIB	25 VIIIB	26 VIIIB	27 VIIIB	28 VIIIB	29 VIIIB	30 VIIIB	31 VIIIB	32 VIIIB	33 VIIIB	34 VIIIB	35 VIIIB	36 VIIIB
39.0983 39.0983 39.0983 39.0983 39.0983	40.078 40.078 40.078 40.078 40.078	44.9559 44.9559 44.9559 44.9559 44.9559	58.9332 58.9332 58.9332 58.9332 58.9332	63.546 63.546 63.546 63.546 63.546	68.94 68.94 68.94 68.94 68.94	74.92159 74.92159 74.92159 74.92159 74.92159	78.94 78.94 78.94 78.94 78.94	88.90584 88.90584 88.90584 88.90584 88.90584	91.224 91.224 91.224 91.224 91.224	92.90638 92.90638 92.90638 92.90638 92.90638	95.94 95.94 95.94 95.94 95.94	98.906 98.906 98.906 98.906 98.906	101.07 101.07 101.07 101.07 101.07	102.9055 102.9055 102.9055 102.9055 102.9055	104.91 104.91 104.91 104.91 104.91	106.9055 106.9055 106.9055 106.9055 106.9055	108.9055 108.9055 108.9055 108.9055 108.9055
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr

37 IIA	38 IIIB	39 IVB	40 VB	41 VIB	42 VIIB	43 VIIIB	44 VIIIB	45 VIIIB	46 VIIIB	47 VIIIB	48 VIIIB	49 VIIIB	50 VIIIB	51 VIIIB	52 VIIIB	53 VIIIB	54 VIIIB
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Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe

55 IIA	56 IIIB	57 IVB	58 VB	59 VIB	60 VIIB	61 VIIIB	62 VIIIB	63 VIIIB	64 VIIIB	65 VIIIB	66 VIIIB	67 VIIIB	68 VIIIB	69 VIIIB	70 VIIIB	71 VIIIB	
132.90543 132.90543 132.90543 132.90543 132.90543	137.327 137.327 137.327 137.327 137.327	174.967 174.967 174.967 174.967 174.967	180.9479 180.9479 180.9479 180.9479 180.9479	186.9074 186.9074 186.9074 186.9074 186.9074	190.23 190.23 190.23 190.23 190.23	198.22 198.22 198.22 198.22 198.22	200.59 200.59 200.59 200.59 200.59	200.59 200.59 200.59 200.59 200.59	200.59 200.59 200.59 200.59 200.59	200.59 200.59 200.59 200.59 200.59	200.59 200.59 200.59 200.59 200.59	200.59 200.59 200.59 200.59 200.59	200.59 200.59 200.59 200.59 200.59	200.59 200.59 200.59 200.59 200.59	200.59 200.59 200.59 200.59 200.59		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

72 IIA	73 IIIB	74 IVB	75 VB	76 VIB	77 VIIB	78 VIIIB	79 VIIIB	80 VIIIB	81 VIIIB	82 VIIIB	83 VIIIB	84 VIIIB	85 VIIIB	86 VIIIB
173.054 173.054 173.054 173.054 173.054	173.054 173.054 173.054 173.054 173.054	173.054 173.054 173.054 173.054 173.054	173.054 173.054 173.054 173.054 173.054	173.054 173.054 173.054 173.054 173.054	173.054 173.054 173.054 173.054 173.054	173.054 173.054 173.054 173.054 173.054	173.054 173.054 173.054 173.054 173.054	173.054 173.054 173.054 173.054 173.054	173.054 173.054 173.054 173.054 173.054	173.054 173.054 173.054 173.054 173.054	173.054 173.054 173.054 173.054 173.054	173.054 173.054 173.054 173.054 173.054	173.054 173.054 173.054 173.054 173.054	173.054 173.054 173.054 173.054 173.054
Fr	Ra	Ac	Unq	Unp	Unh	Uns	Uno	Uue	Uun					

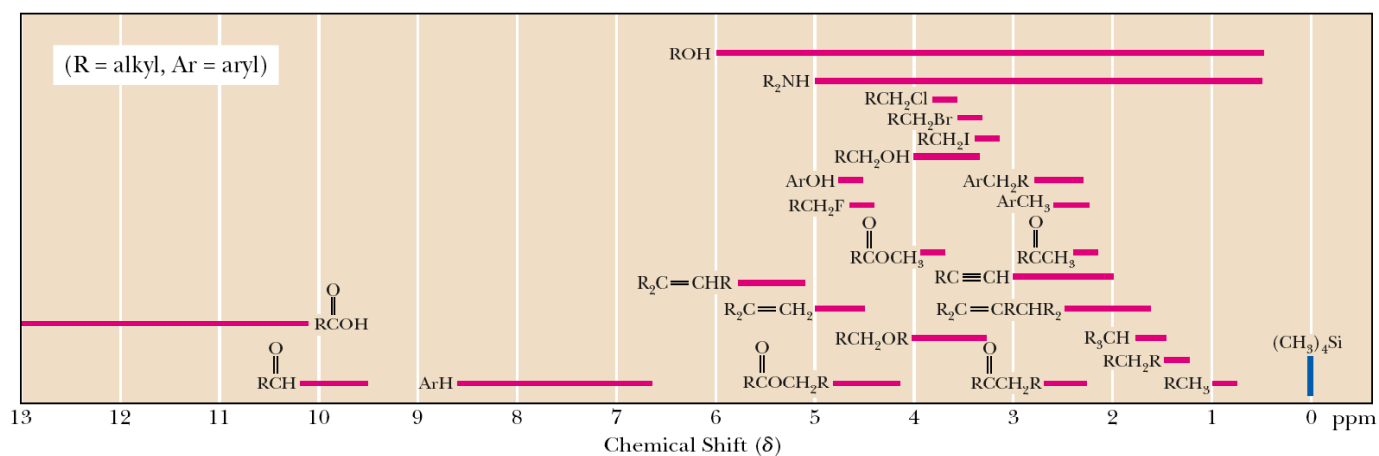


Atomic Weight: () indicates most stable or best known isotope. Melting Point, °C: () indicates most stable or best known isotope. Density, g/cm³ at 20°C: () indicates most stable or best known isotope. Electronegativity: () indicates most stable or best known isotope. First Ionization Potential, eV: () indicates most stable or best known isotope.

The data for this reference guide were obtained from the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Pure and Applied Chemistry (IUPAC). The data for this reference guide were obtained from the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Pure and Applied Chemistry (IUPAC). The data for this reference guide were obtained from the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Pure and Applied Chemistry (IUPAC).

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	$\begin{array}{c} O \\ / \backslash \\ H_2C \quad CH_2 \end{array}$	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.

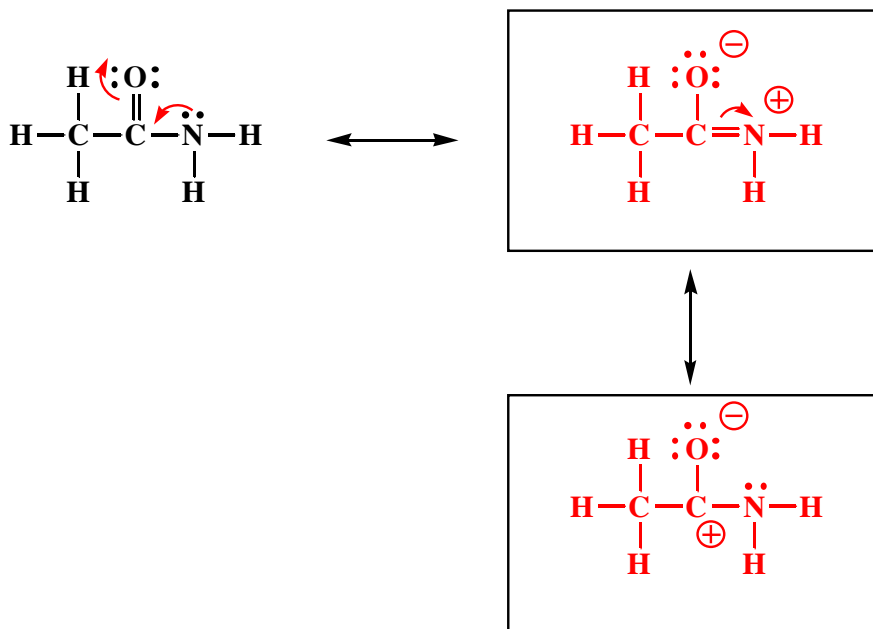


Compound		pK _a
Hydrochloric acid	$\text{H}-\text{Cl}$	-7
Protonated alcohol	$\text{RCH}_2\text{O}^+\text{H}_2$	-2
Hydronium ion	H_3O^+	-1.7
Acetic acid	$\text{CH}_3\overset{\text{O}}{\parallel}\text{C}-\text{H}$	4.8
Ammonium ion	H_4N^+	9.2
Thiols	$\text{RCH}_2\text{S}\text{H}$	10-12
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{R}'$	10
Ethyl ammonium ion	$\text{H}_3\text{N}^+-\text{CH}_2\text{CH}_3$	10.8
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	$\text{RCH}_2\text{O}\text{H}$	15-19
Acid chlorides	$\text{RC}\text{H}_2-\overset{\text{O}}{\parallel}\text{C}-\text{Cl}$	16
Aldehydes	$\text{RC}\text{H}_2-\overset{\text{O}}{\parallel}\text{C}-\text{H}$	18-20
Ketones	$\text{RC}\text{H}_2-\overset{\text{O}}{\parallel}\text{C}-\text{R}'$	18-20
Esters	$\text{RC}\text{H}_2-\overset{\text{O}}{\parallel}\text{C}-\text{OR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\text{H}$	25
LDA	$\text{H}-\text{N}(\text{i}-\text{C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{H}$	44
Alkanes	$\text{CH}_3\text{CH}_2-\text{H}$	51

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

Where are the electrons?

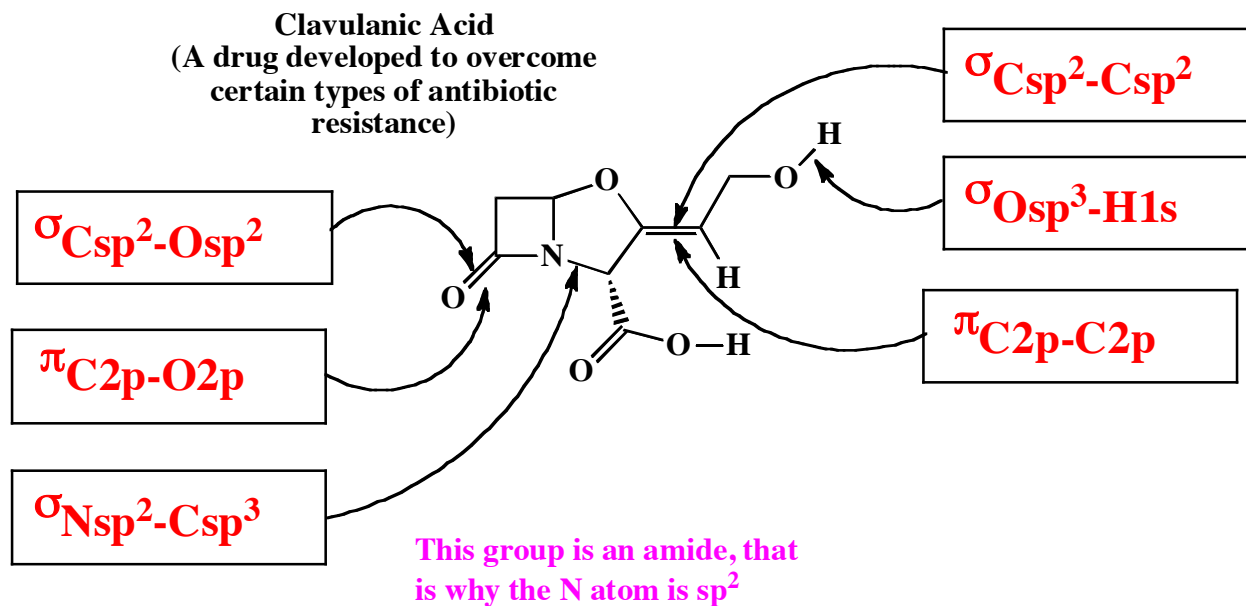
2. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges. For the two structures on the left in each problem, use arrows to indicate the movement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



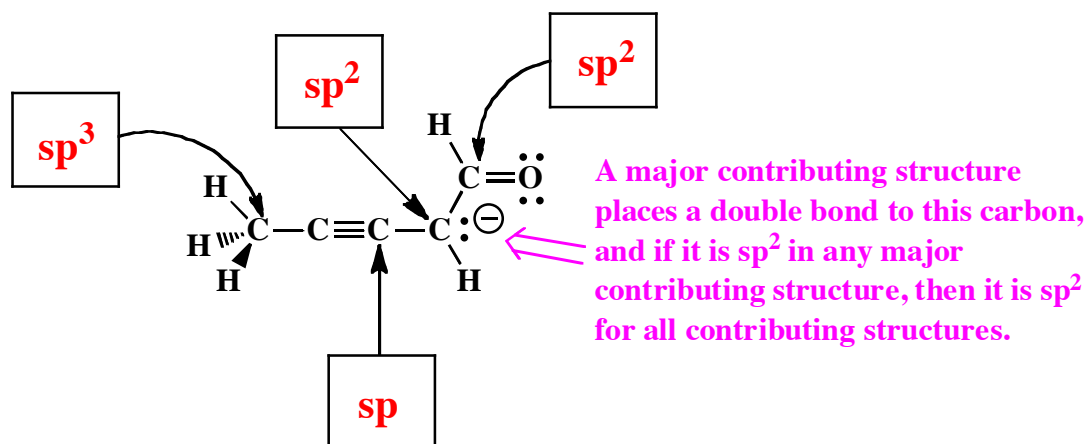
3. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here and your answer should match a recent Rule of the Day.

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 protons** 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 protons, especially the protons 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: $\sigma_{\text{Csp}^3-\text{H}1\text{s}}$



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



6. (1 pt each) **Circle all the True statements.** (Do not circle any false statements) 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.

A. More electronegative atoms attract the majority of electron density in a bond, thereby answering the most important question in chemistry.

B. A sigma bond has the majority of electron density above and below the bond axis, while a pi bond has the majority of electron density between atomic nuclei.

C. Constitutional isomers are molecules with the same molecular formula, but have the atoms connected differently.

D. The preferred staggered conformations of butane are the "gauche" conformations, rather than the "anti" conformation.

E. Stereoisomers have the same connectivity (they are the same constitutional isomer), but the atoms are arranged differently in space.

F. Dispersion forces are proportional to surface area, so the smaller the surface area of an alkane, the greater the attraction between molecules and the higher the boiling point.

G. Substituted cyclohexanes prefer to have as many substituents axial as possible, with the larger substituents dominating.

H. *Trans* alkenes are more stable than *cis* alkenes because *cis* alkenes have some non-bonded interaction strain.

I. The enol form of a compound rapidly tautomerizes to the more stable keto form.

J. The keto form of a compound rapidly tautomerizes to the more stable enol form.

K. The keto form of a compound rapidly mesmerizes to the more stable enol form.

L. In organic synthesis, A KEY PARADIGM is that functional groups (OH group, Pi bond of an alkene, etc.) react the same in large complex molecules as they do in simple structures.

M. Ethers can be synthesized using an S_N2 reaction between a primary alkyl halide and an alkoxide (called the Williamson ether synthesis)

N. Ethers are synthesized using an S_N1 reaction between a tertiary alkyl halide and an alkoxide (called the Williamson County ether synthesis)

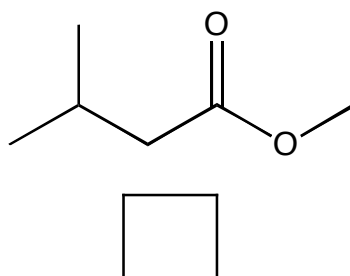
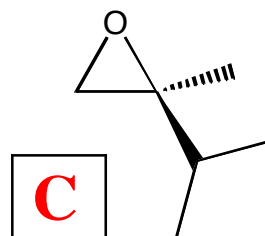
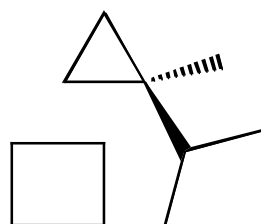
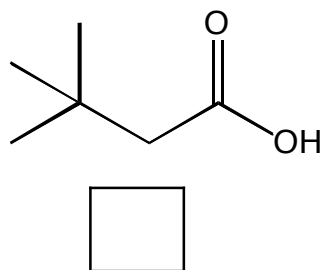
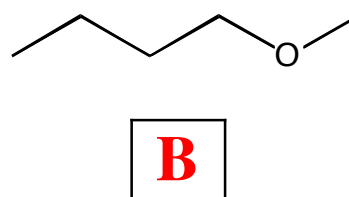
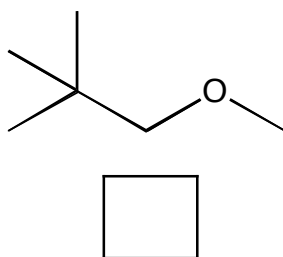
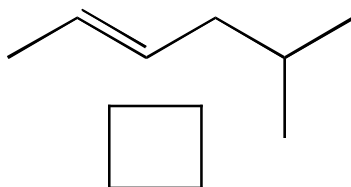
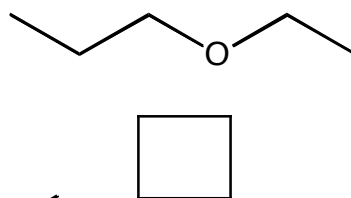
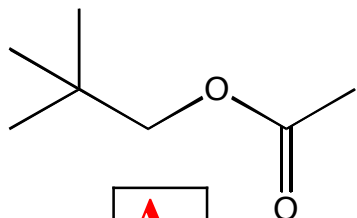
O. Epoxides are important because the ring strain within epoxides allows them to react with nucleophiles.

P. A ^1H nucleus surrounded by greater electron density is considered to be more shielded and comes into resonance (absorbs electromagnetic radiation) at a lower frequency (smaller ppm).

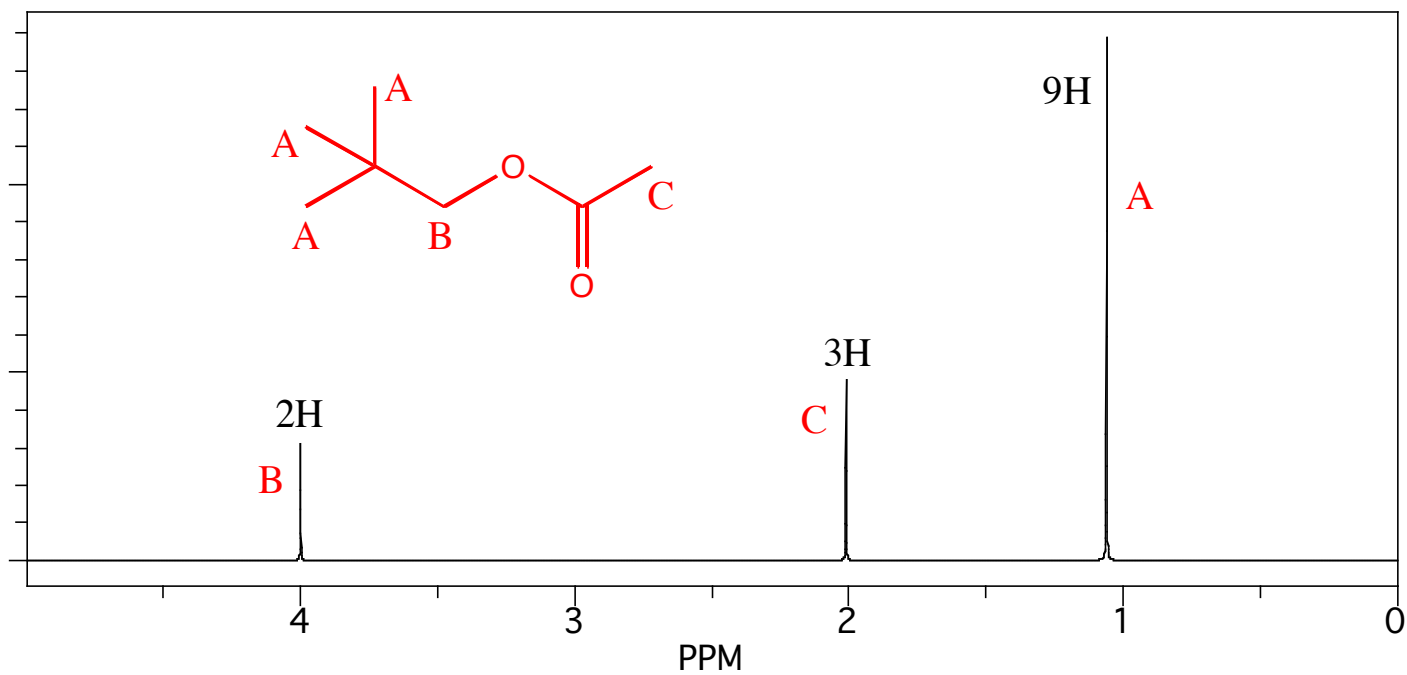
Q. "Resonance" in NMR refers to the phenomenon of absorption of energy when a nuclear spin "flips".

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

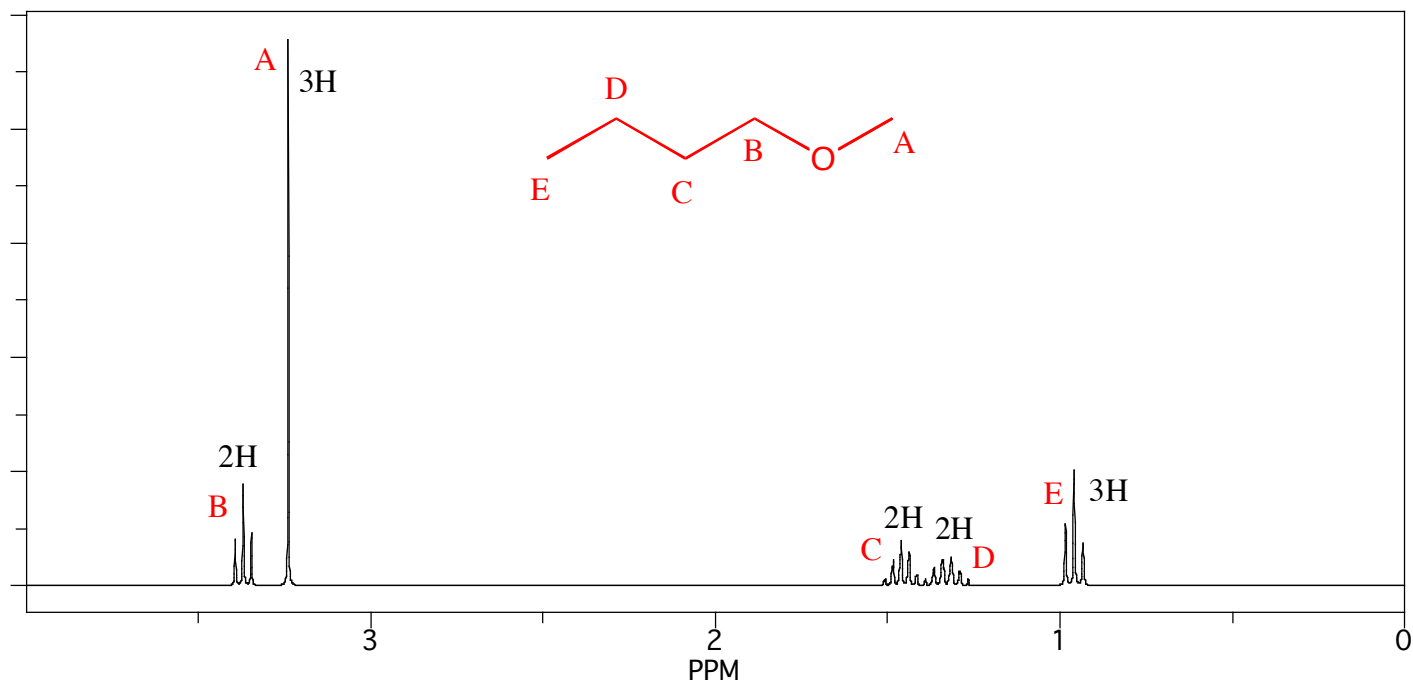
8. (15 pts total) On the following three pages there are NMR spectra. The relative integrations are given above each signal. Assign each spectra to the appropriate structure out of the following possibilities. Each NMR spectrum has a letter on it. **Write the appropriate letter underneath the molecules in the space provided.** Notice that not all of the molecules below will have letters underneath them, as there are only three spectra but seven molecules.



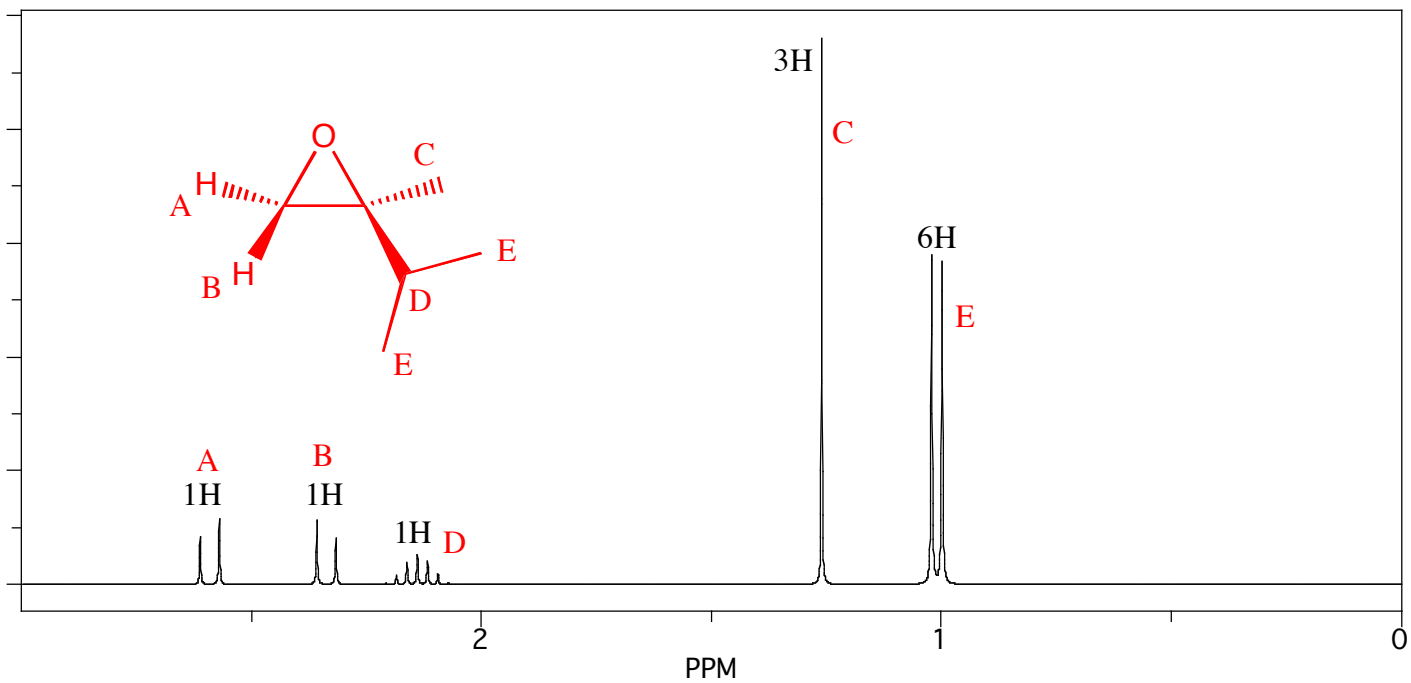
A



B

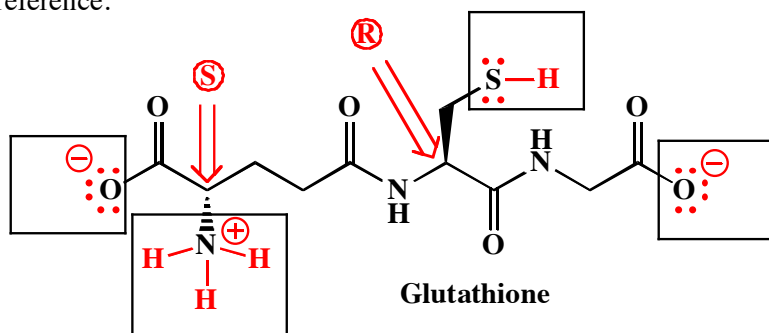


C



9. The following molecule is called glutathione. It is found in high concentration in living cells where it helps maintain the proper oxidation potential as well as providing protection from oxidants such as free radicals. **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.** Use the pK_a table provided at the beginning of the test for reference.

A.(8 pts)

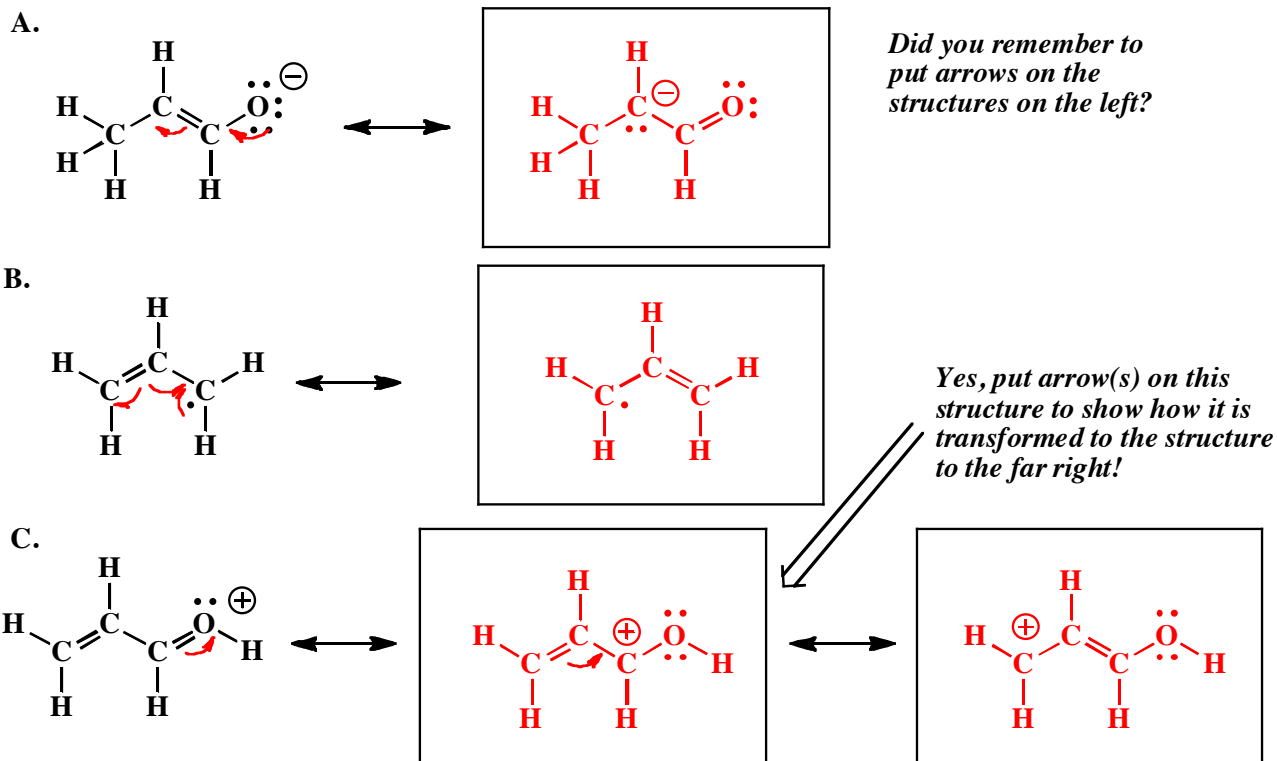


B. (1 pt) What is the total charge on glutathione at pH 7.0? -1

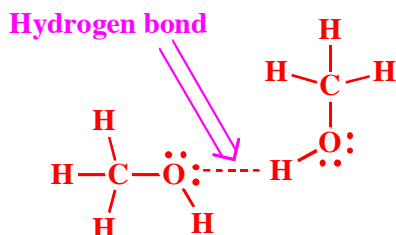
C. (1 pt) How many chiral centers does glutathione have? 2

D. (2 pt) Glutathione is found as the single stereoisomer shown. Write an "R" or "S" next to each chiral center on the structure above.

10. (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.

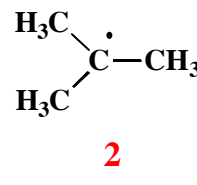
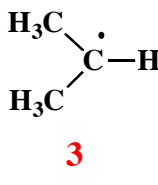
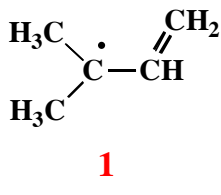
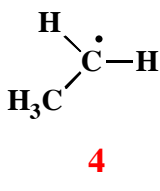


11. (5 pts) A hydrogen bond is the strongest interaction seen among neutral molecules. **In the space provided, draw two molecules of methanol (CH_3OH) and show a hydrogen bond between them. Use a dashed line (-----) to indicate the hydrogen bond. Show all lone pairs.**

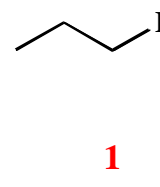
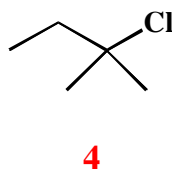
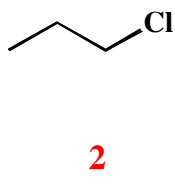
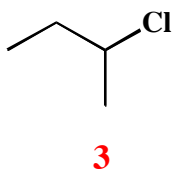


12. (12 pts. total) Rank the following species in terms of the stated property from 1 to 4 with intermediate numbers to rank the species of intermediate stability activity. **Please make sure you know what we want, as you will get no credit if you get the numbers backwards!**

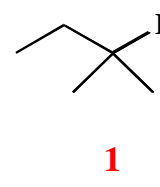
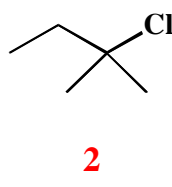
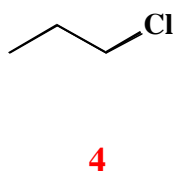
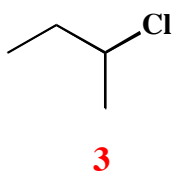
Radical Stability: Place a **1** under the most stable radical and a **4** under the least stable radical.



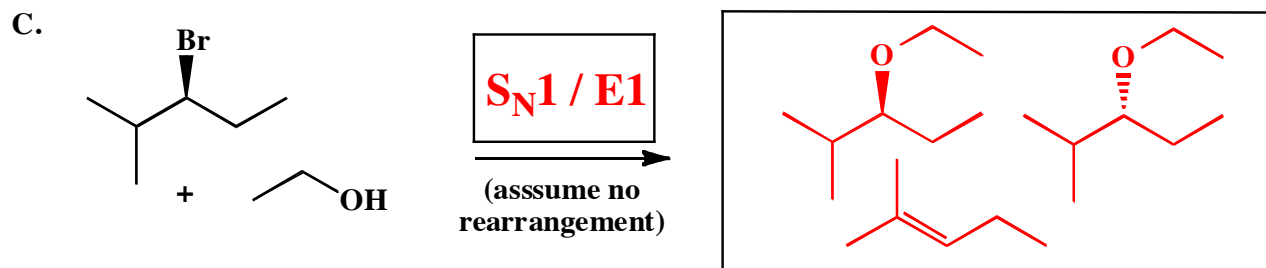
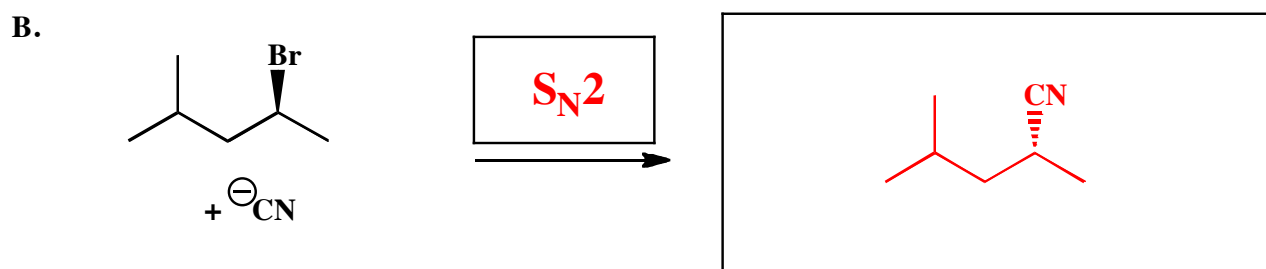
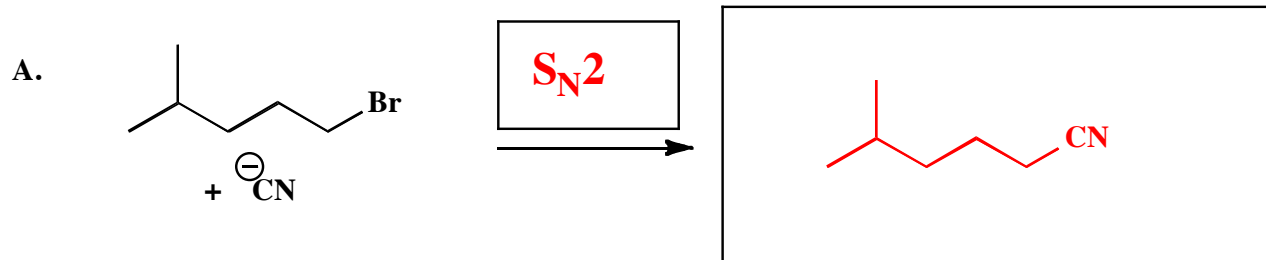
Reaction with nucleophiles: Place a **1** under the molecule that is most reactive in an $\text{S}_{\text{N}}2$ reaction and a **4** under the molecule that is least reactive in an $\text{S}_{\text{N}}2$ reaction.



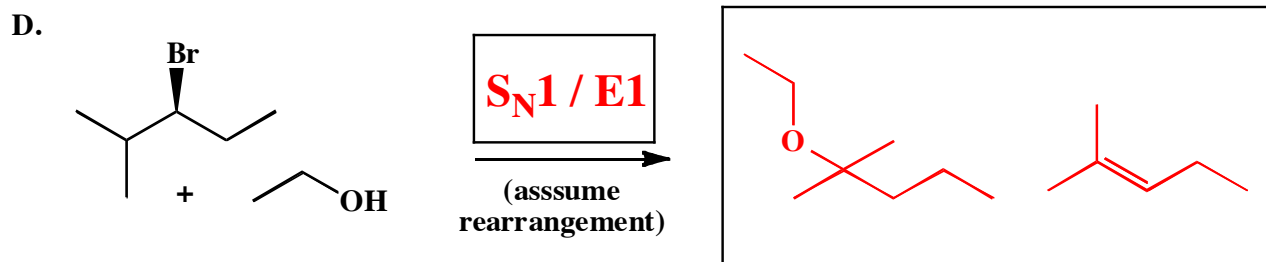
Reaction in an $\text{S}_{\text{N}}1/\text{E}1$ reaction: Place a **1** under the molecule that is most reactive in an $\text{S}_{\text{N}}1/\text{E}1$ reaction and a **4** under the molecule that is least reactive in an $\text{S}_{\text{N}}1/\text{E}1$ reaction.



13. (5, 6 or 8 pts each) The following reactions all involve chemistry of alkyl halides. **Fill in the box above the arrow with the mechanism that will be followed (S_N2 , E2, etc.). Then draw only the predominant product or products and please remember that you must draw the correct stereoisomers.** For $S_N1/E1$ reactions you must draw all significant products (including all stereoisomers).

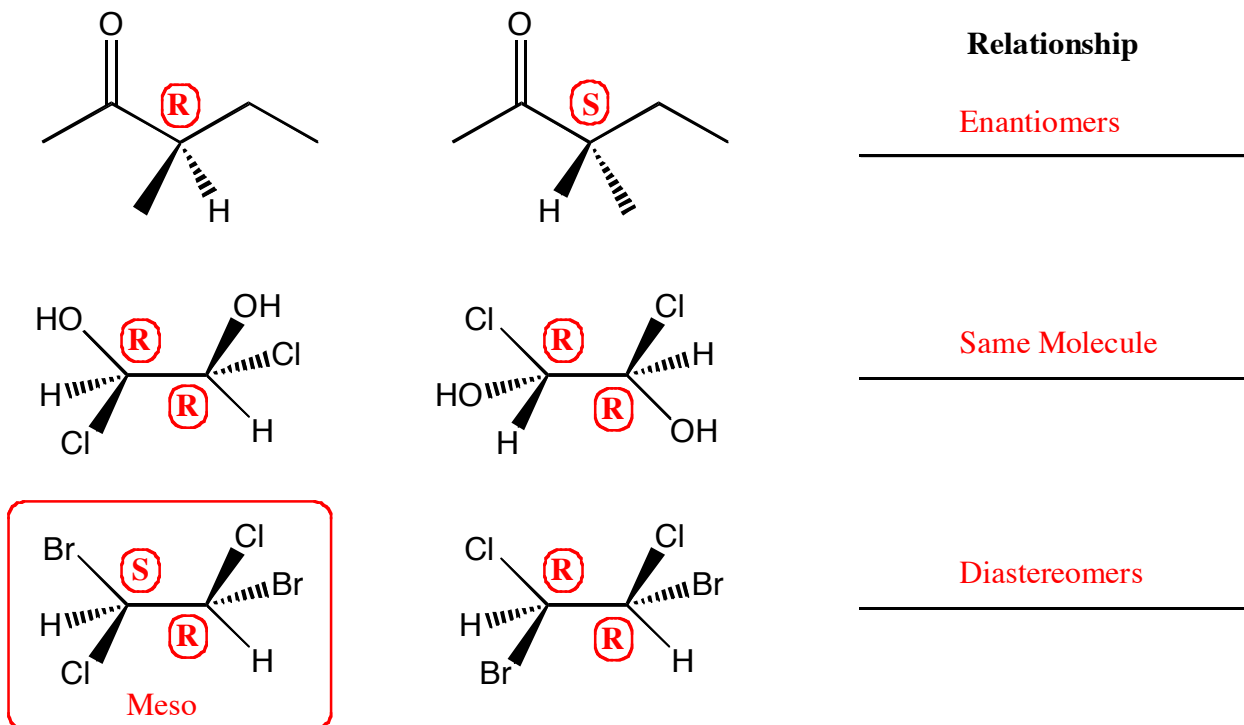


Repeat the last one, but only draw rearranged products

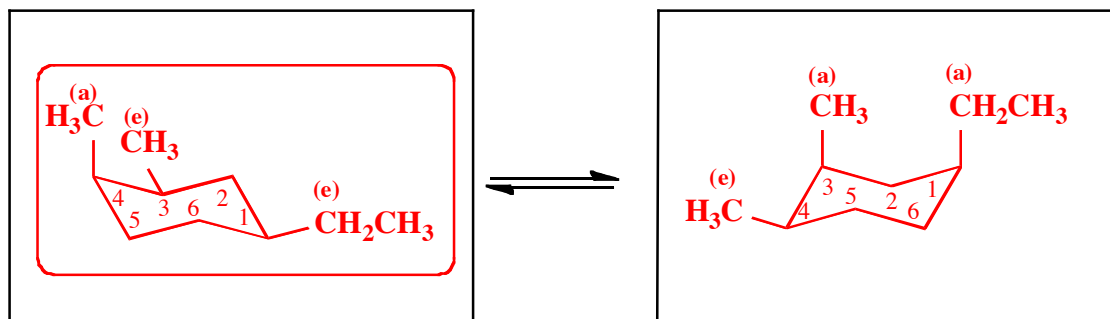
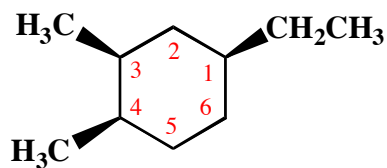


(2 pts) For the reagents listed in parts C and D, how many total *different* products will be made if the reaction proceeds both with and without rearrangement?

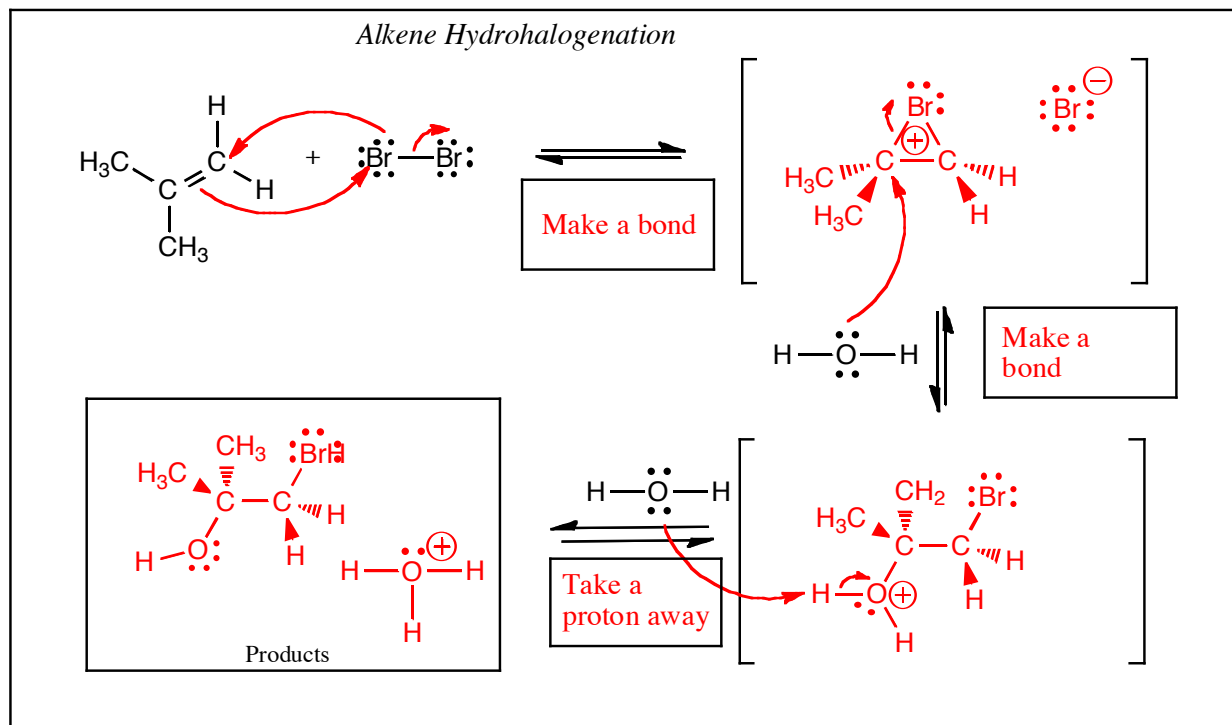
14. (8 pts total) On the line provided, state the stereochemical relationship between each pair of molecules: **enantiomers**, **diastereomers**, or **the same molecule**. I recommend you assign R and S to each chiral center to help answer this question. **Circle all meso compounds.**



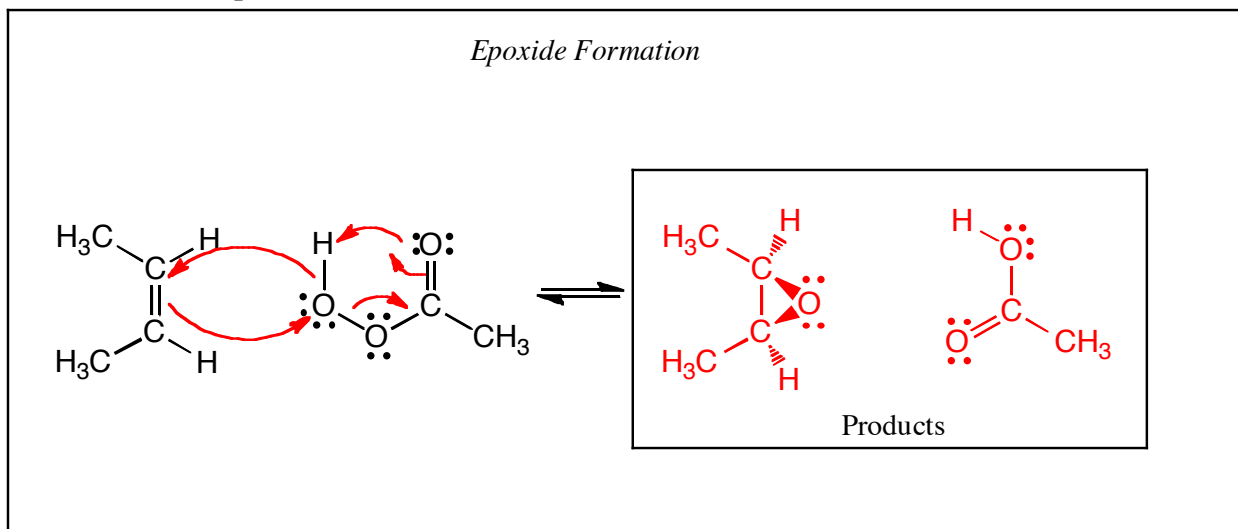
(8 pts) In the two spaces below, draw the two equilibrating chair structures for the following cyclohexane derivative. Circle the one that predominates at equilibrium.



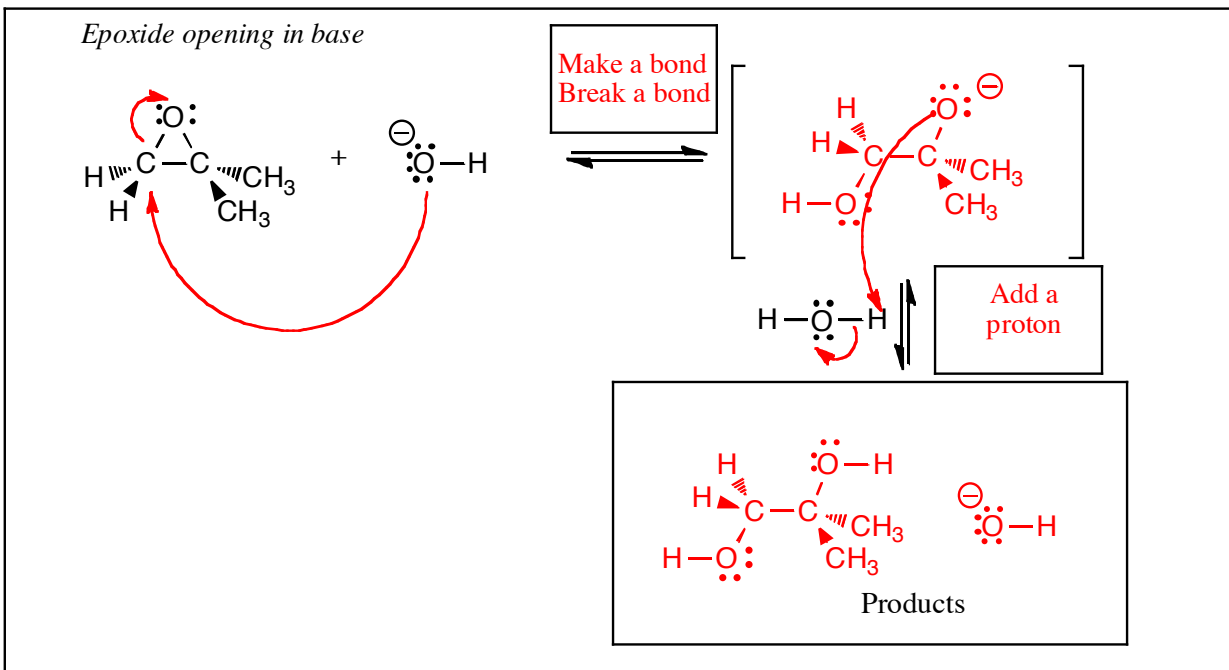
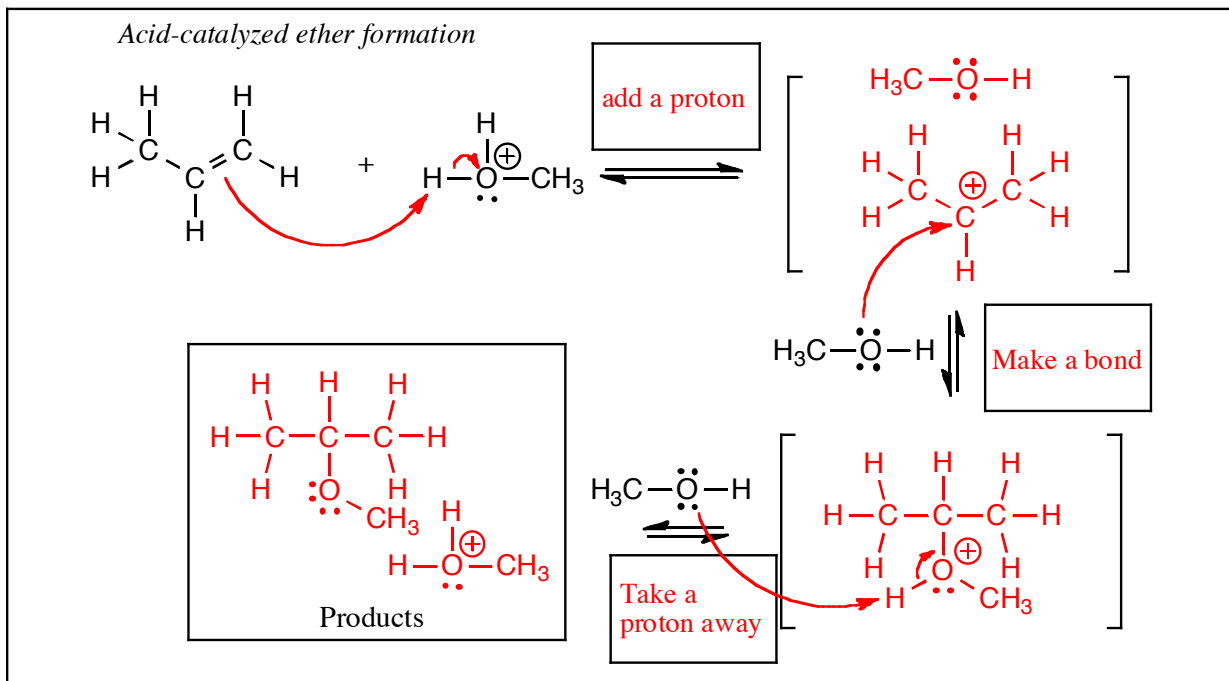
15. (26 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) For the following reactions, fill in the details of the mechanism. Draw the appropriate chemical structures and use an arrow to show how pairs of electrons are moved to make and break bonds during the reaction. For this question, you must draw all molecules produced in each step (yes, these equations need to be balanced!). Finally, fill in the 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, BUT if an intermediate or product is really a racemic mixture, you only need to draw one enantiomer and write racemic for this problem (we are making this easier for you).



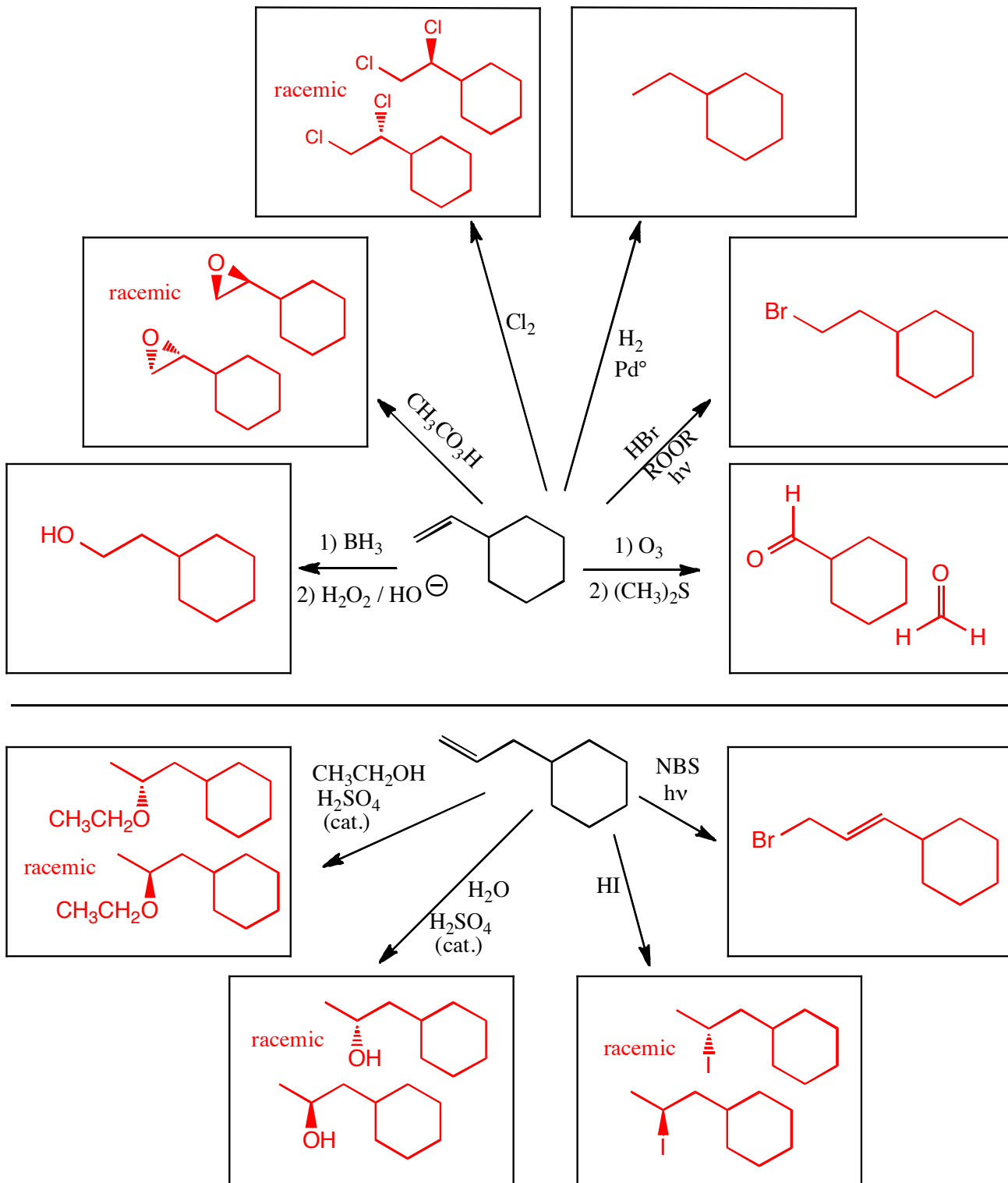
For this next one you do not need to describe the reaction using one of the four fundamental mechanistic steps ("Make a bond", etc.)



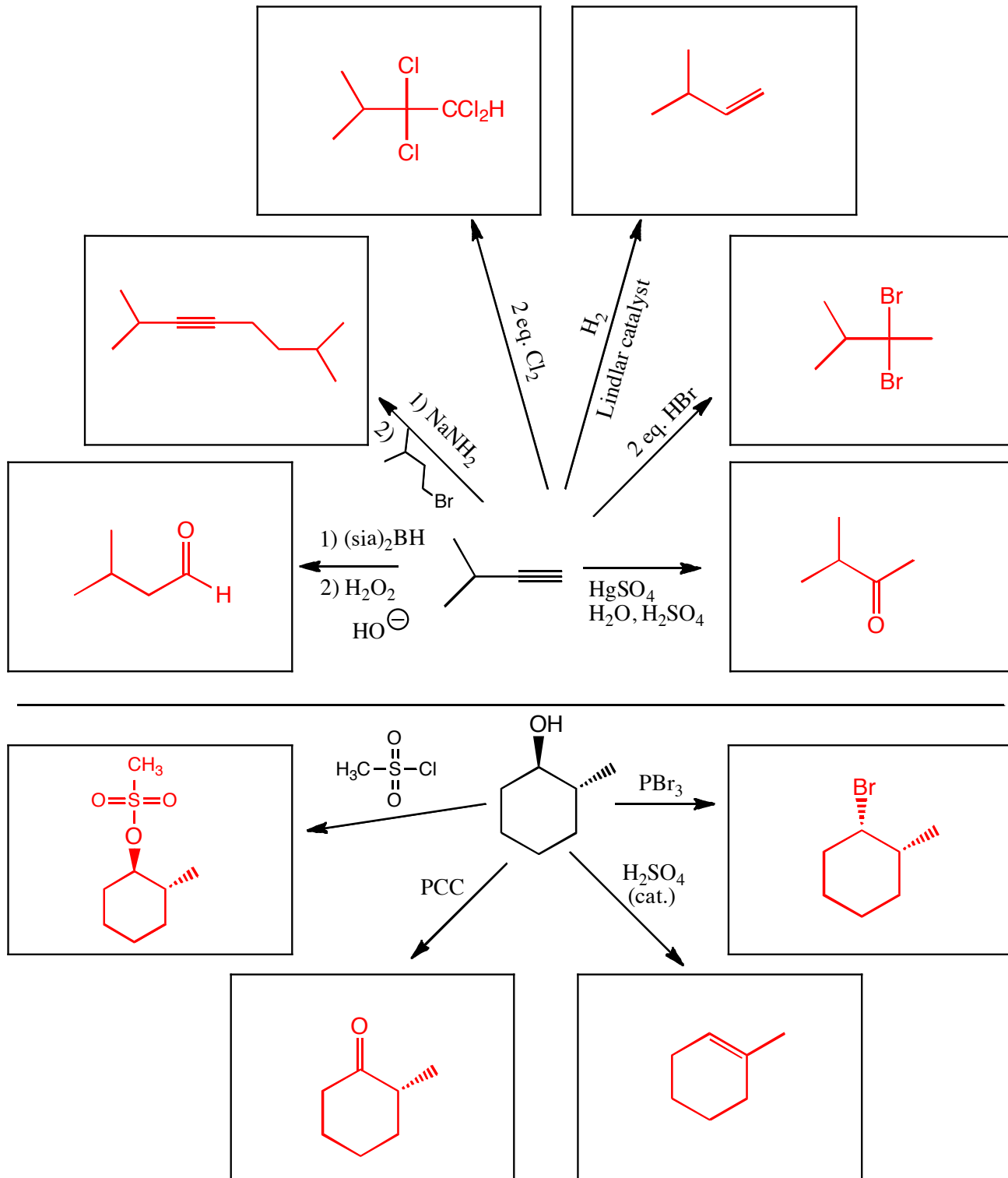
15. (22 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) For the following reactions, fill in the details of the mechanism. Draw the appropriate chemical structures and use an arrow to show how pairs of electrons are moved to make and break bonds during the reaction. For this question, you must draw all molecules produced in each step (yes, these equations need to be balanced!). Finally, fill in the 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, BUT if an intermediate or product is really a racemic mixture, you only need to draw one enantiomer then label it racemic for this problem (we are making this easier for you).



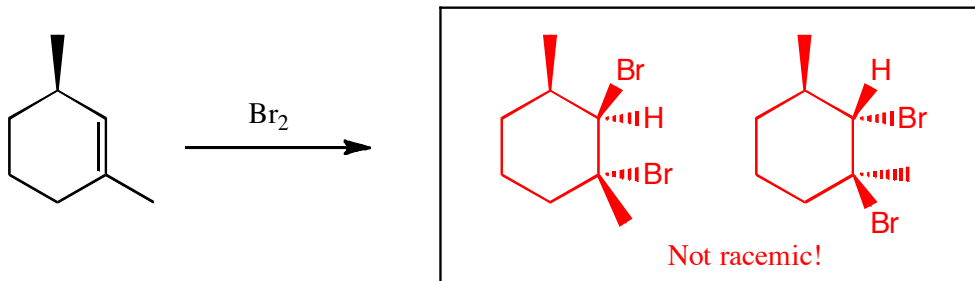
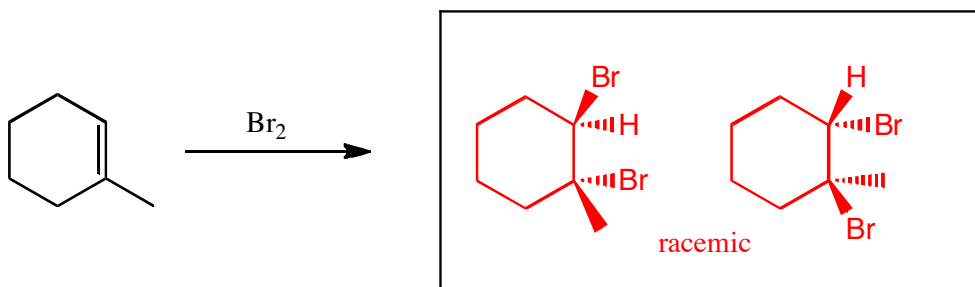
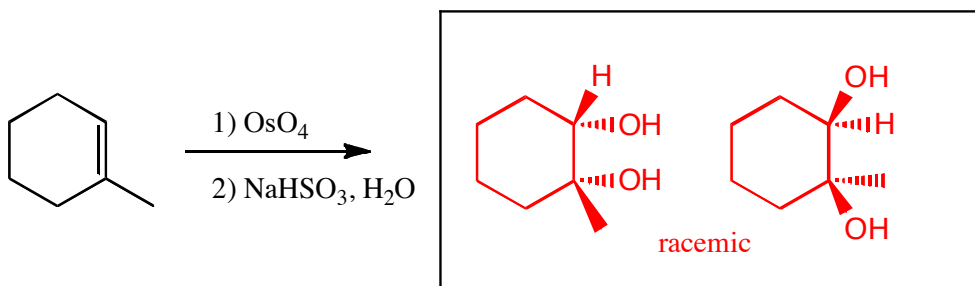
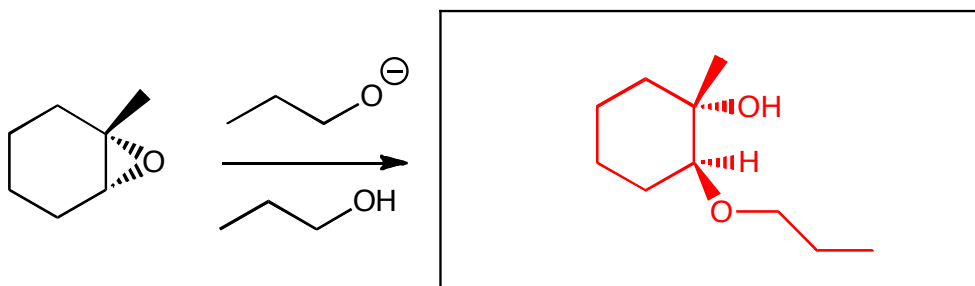
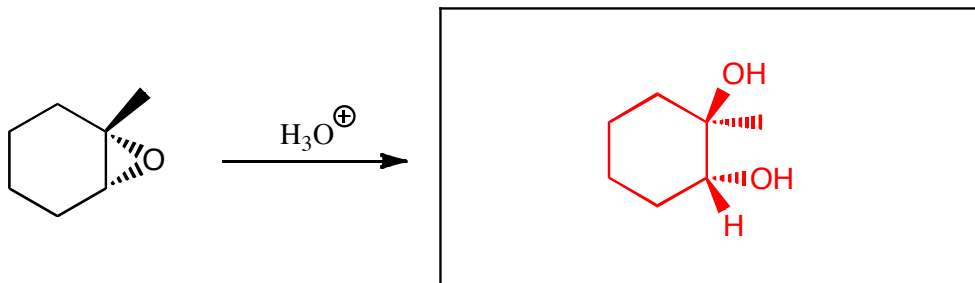
16. (3, 4 or 5 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



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

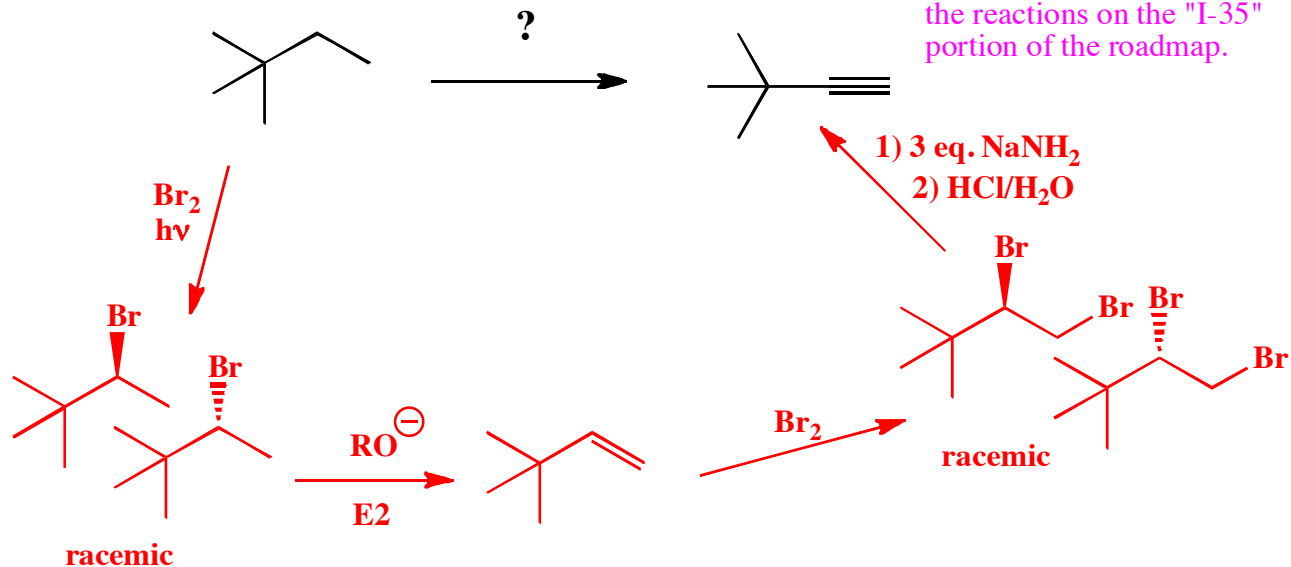


18. (3, 4 or 5 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.

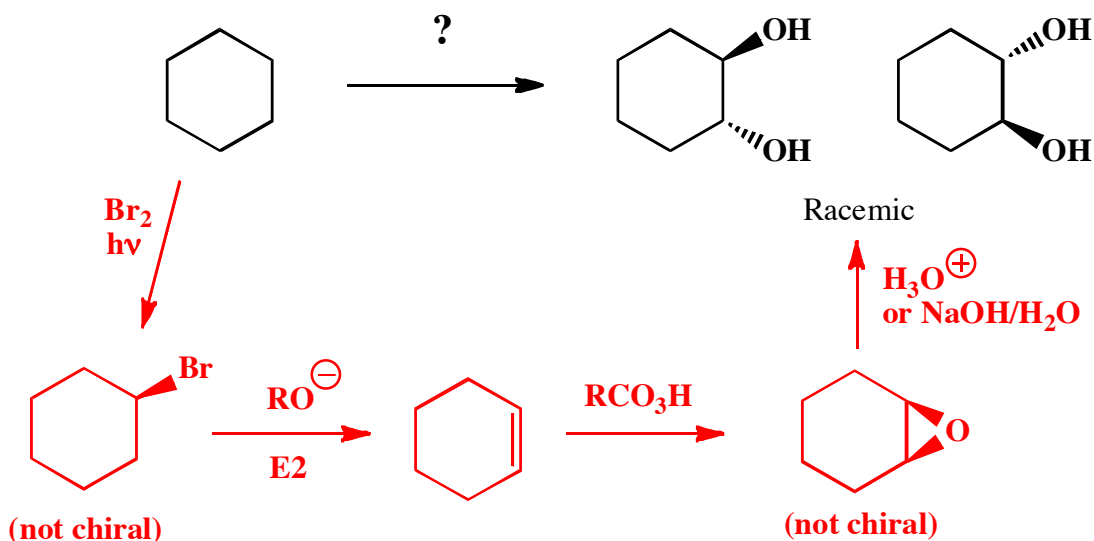


19. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized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

A) (10 pts)

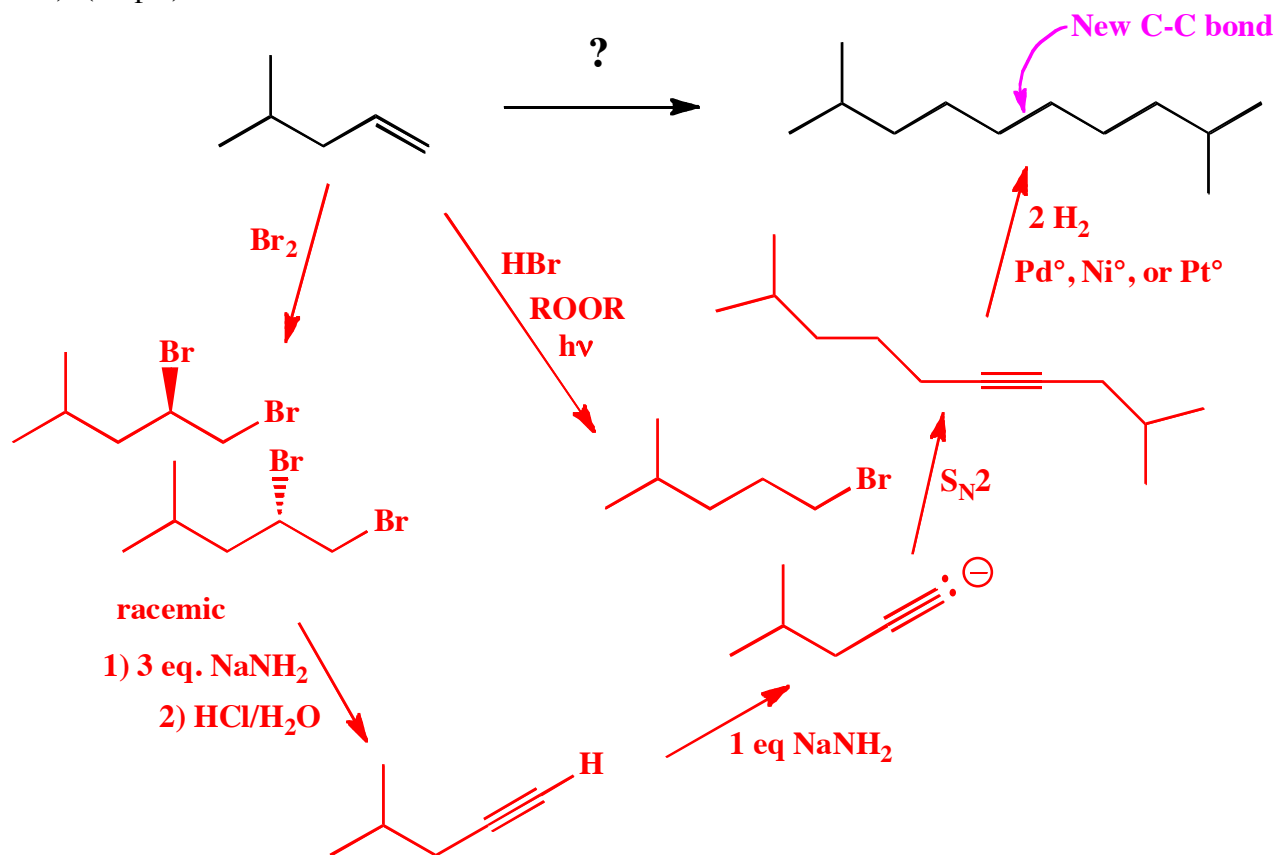


B) (10 pts)



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

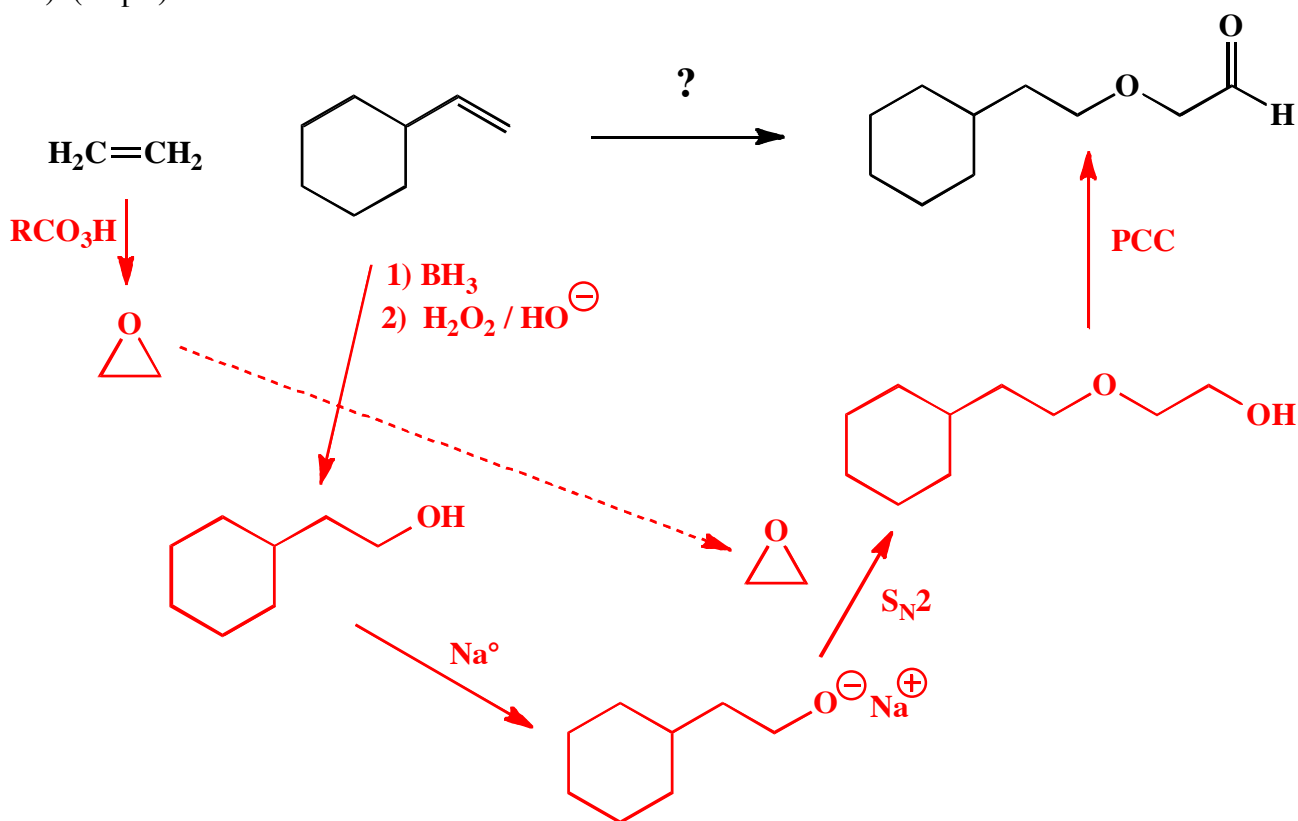
C) (15 pts)



Recognize that there are 12 carbons in the product and 6 in the starting material. Assume you need to put two starting material molecules together at the central bond as shown. The only way this can be done using the reactions you know is to react the anion of a terminal alkyne with a primary haloalkane. Therefore, assume there was once an alkyne in the molecule so predict that the last step is the hydrogenation of the alkyne to give the alkane. Continuing to work backwards, the required 12 carbon alkyne can be derived from the reaction of the 6 carbon primary haloalkane shown and the corresponding 6 carbon terminal alkyne. The primary haloalkane can be made in a single step from the starting alkene by using HBr in the presence peroxide and light. The terminal alkyne can be made using the familiar "I-35" sequence of steps involving reaction with Br_2 followed by reaction with the strong base NaNH_2 .

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

D) (12 pts)

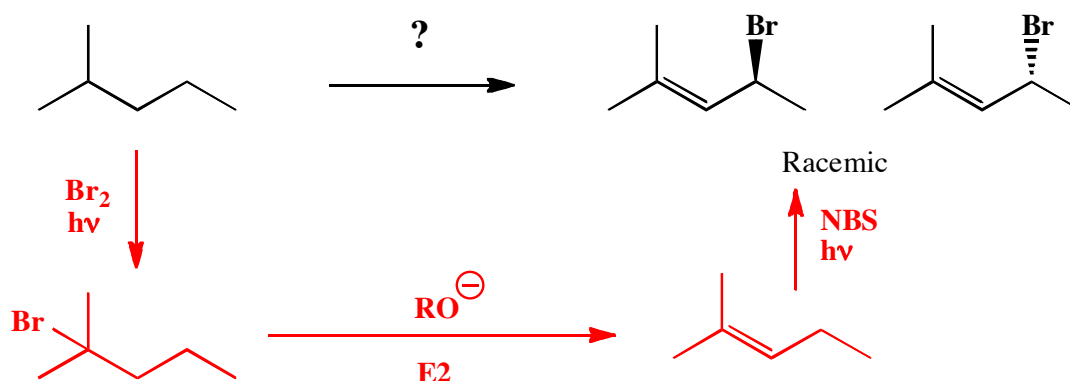


Recognize that the product has 10 carbons, and the starting materials have 8 and 2 carbons, respectively. Therefore assume the starting materials are combined at the ether oxygen functional group. **Recognize** further that the product is an aldehyde. The only way to make an aldehyde that does not break a C-C bond is using PCC. Therefore predict that reaction with PCC is the last step and draw the corresponding ether-alcohol. **Recognize** that the ether-alcohol has the same pattern as the product of an alcohol reacting with an epoxide, an alcohol function two carbons from an ether. Predict the ether-alcohol is made from the reaction of the primary alcohol shown with ethylene oxide, the two-carbon epoxide. I illustrated this in base by making the alkoxide. You could also carry out the reaction in catalytic acid and save a step. The required alcohol comes from the non-Markovnikov hydroboration of the starting alkene, and ethylene oxide can be made from the starting material ethylene through reaction with a peracid.

Alternative you could have also made the ether-alcohol by reacting the primary alcohol or alkoxide with 1,2-dibromoethane (Williamson ether synthesis) followed by conversion of the primary Br to an OH group by reaction with NaOH or H_2O . The 1,2-dibromoethane can be made by reaction of the starting ethylene with Br_2 .

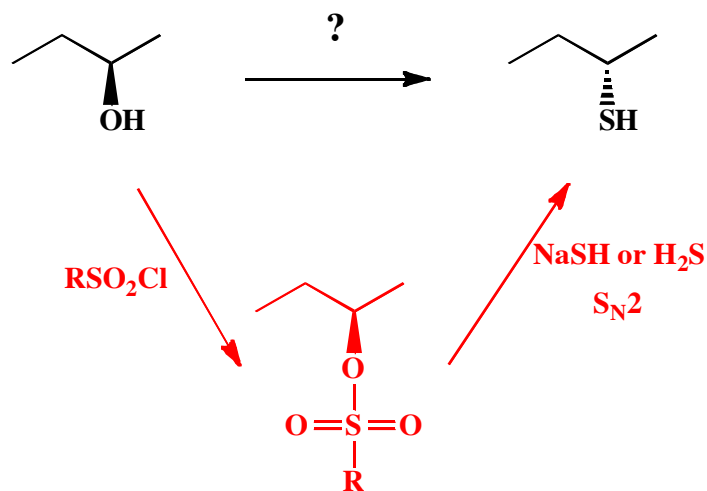
19. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule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

E) (7 pts)



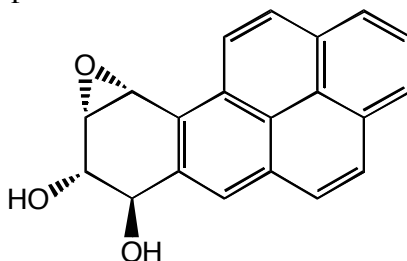
Recognize that the product is the result of the allylic halogenation of an alkene, predict therefore that the last reaction uses NBS. **Recognize** further that the required alkene for the last step is the Zaitsev product after an E2 reaction of the bromoalkane, that itself is the predominant product of free radical halogenation of the starting alkane.

F) (4 pts)



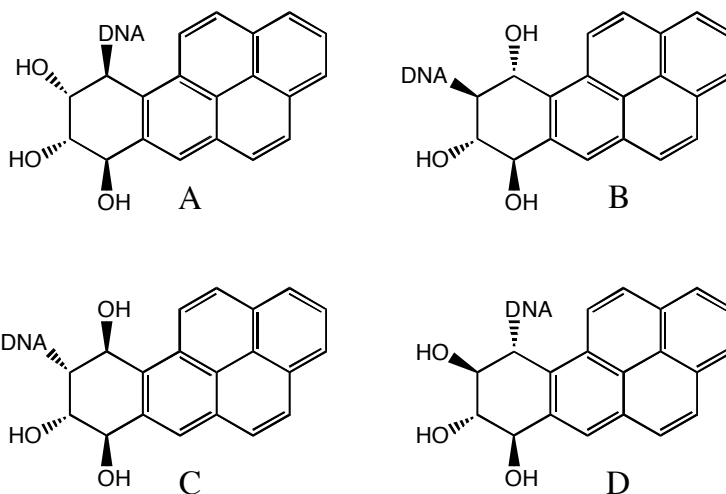
Recognize that the stereochemistry of the product is the result of a single **InVERSION** of the starting alcohol chiral center. Therefore, use the sequence of reaction with a sulfonyl chloride followed by an $\text{S}_{\text{N}}2$ reaction with either NaSH or H_2S .

20. A number of molecules are dangerous because they make a covalent bond to DNA, causing a mutation when the cell with the modified DNA divides. A characteristic of these molecules is that they are electrophiles. Often, they interact strongly with the DNA before the covalent bond forms. This so-called preassociation greatly speeds up the reaction and helps target the DNA. A potent carcinogen is the benzo[a]pyrene diol epoxide. It is a metabolized byproduct of benzo[a]pyrene, a compound found in barbecued meats cooked over an open hot flame.



Benzo[a]pyrene diol epoxide

The large flat overall structure of the molecule helps it slip between the stacked base pairs of the DNA double helix, then the DNA reacts as a nucleophile with the benzo[a]pyrene diol epoxide.



Which of these products could be produced when the benzo[a]pyrene diol epoxide stereoisomer shown above reacts with DNA?

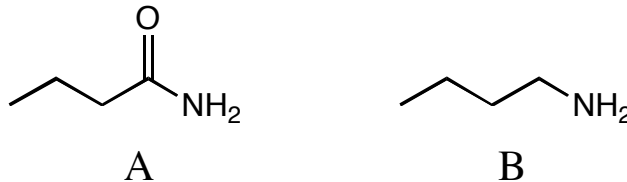
- A) Only product C could be produced
- B) Only A and B could be produced**
- C) Only C and D could be produced
- D) All four are produced.

It turns out that many other electrophiles are dangerous as well. The nerve gas Sarin as well as the chemical warfare agent mustard gas are both electrophiles. In each case, these electrophiles react with important molecules in our bodies. The new covalent bonds that form inactivate the important molecules, explaining why Sarin and mustard gas are so deadly. For protection, our bodies have catalysts called glutathione S-transferases that react with electrophiles and prevent their doing damage. It is critical that you can quickly identify nucleophiles and electrophiles in reactions. Find the answer that best describes the following reaction:



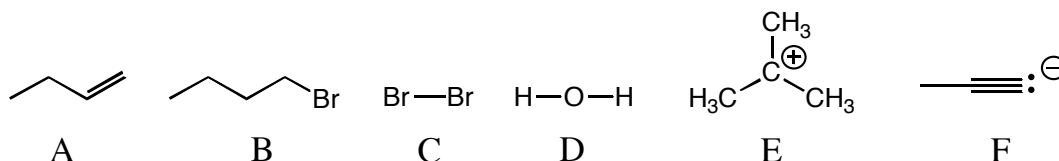
- A) In this reaction, the negatively charged S atom is the nucleophile and so is the chloroalkane
 B) **In this reaction, the negatively charged S atom is the nucleophile, and the chloroalkane is the electrophile**
 C) In this reaction, the negatively charged S atom is the electrophile, and the chloroalkane is the nucleophile
 D) In this reaction, the negatively charged S atom is the electrophile and so is the chloroalkane

It is essential that you learn to recognize nucleophiles and electrophiles. Below are two potential nucleophiles:



- A) The structure labeled A is a better nucleophile compared to B.
 B) **The structure labeled B is a better nucleophile compared to A.**
 C) The structure labeled A and the structure labeled B are equally strong nucleophiles.
 D) Neither structure is a nucleophile.

Consider the following series of molecules we have seen this semester:



- A) Structures C,D,and E are electrophiles, while structures A, B and F are nucleophiles.
 B) Structures A,B, C and E are electrophiles, while structures D and F are nucleophiles.
 C) **Structures B, C and E are electrophiles, while structures A, D and F are nucleophiles**
 D) Structures B, and E are electrophiles, while structures A, C, D and F are nucleophiles