

NAME (Print): _____

Chemistry 320M/328M

Dr. Brent Iverson

Final

December 16, 2017

SIGNATURE: _____

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

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

You cannot use a red pen to take the exam. You must have your answers written in PERMANENT ink if you want a regrade!!!! This means no test written in pencil or ERASABLE INK will be regraded.

Please note: We routinely xerox a number of exams following initial grading to guard against receiving altered answers during the regrading process.

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

Page	Points	
1		(29)
2		(26)
3		(20)
4		(15)
5		(-)
6		(-)
7		(-)
8		(28)
9		(19)
10		(23)
11		(29)
12		(20)
13		(32)
14		(37)
15		(30)
16		(16)
17		(17)
18		(16)
19		(13)
20		(10)
21		(8)
Total		(388)

Student Honor Code

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

(Your signature)

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

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

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

I have very much enjoyed getting to know all of you. As one of my favorite poets of the 20th century put it: “May your wishes all come true. May you build a ladder to the stars and climb on every rung. May you stay forever young. May your heart always be joyful and may your song always be sung. And may you stay forever young.” BD

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

Brent Iverson

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

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

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

B. Predicting Stability and Properties 4. The most important question in organic chemistry is "Where are the electrons?" 5. Delocalization of charge over a larger area is stabilizing. 6. Delocalization of unpaired electron density over a larger area is stabilizing. 7. Delocalization of pi electron density over a larger area is stabilizing.

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

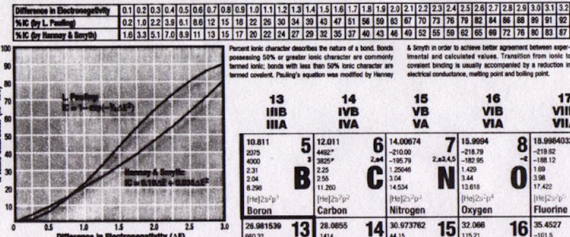
PERIODIC TABLE OF THE ELEMENTS

Elementary Subatomic Particles

Symbol	Electron	Proton	Neutron	Photon	Neutrino
Rest mass (kg)	$9.1093897(1) \times 10^{-31}$	$1.672621(1) \times 10^{-27}$	$1.674927(1) \times 10^{-27}$	0	0
Rest mass (g/mol)	$5.48579909(1) \times 10^{-4}$	$1.007276467(1) \times 10^{-3}$	$1.008664916(1) \times 10^{-3}$	0	0
Particle-electron mass ratio	1	1836.15267(25)	1838.68360(45)	0	0
Particle-proton mass ratio	$5.446170(1) \times 10^{-4}$	1	1.00137040(9)	0	0
Particle-neutron mass ratio	$5.438672(1) \times 10^{-4}$	0.99904	1	0	0
Specific charge (C/kg)	$-1.7598196(2) \times 10^{11}$	$9.578565(2) \times 10^{17}$	0	0	0
Specific charge (C/g)	$-1.7598196(2) \times 10^{11}$	$9.578565(2) \times 10^{17}$	0	0	0
Spin quantum number	1/2	1/2	1/2	1	1/2
Compton wavelength (m)	$2.42631024(2) \times 10^{-12}$	$1.3214002(1) \times 10^{-15}$	$1.31959110(1) \times 10^{-15}$	—	—
Magnetic moment (J/T)	9.2847701(2) $\times 10^{-24}$	1.4106076(1) $\times 10^{-26}$	0.9662370(1) $\times 10^{-26}$	0	0
In Bohr magneton, μ_B	1.0011586519(1)	$5.2728460(1) \times 10^{-5}$	$5.2728460(1) \times 10^{-5}$	0	0
In nuclear magneton, μ_N	1836.268600(5)	1.836268600(5)	1.836268600(5)	0	0

Summary: particles are the fundamental constituents of matter and energy. The electron (e^-) is a particle-antiparticle pair which has the same mass as an antiparticle (positron). The difference (Δ) in mass between the electron and the positron is due to the difference in their magnetic moments. The difference (Δ) in mass between the electron and the positron is due to the difference in their magnetic moments. The difference (Δ) in mass between the electron and the positron is due to the difference in their magnetic moments.

% Ionic Character of a Single Chemical Bond



Percent ionic character describes the nature of a bond. A bond is ionic to the extent that it is a polar covalent bond. A bond is ionic to the extent that it is a polar covalent bond. A bond is ionic to the extent that it is a polar covalent bond.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA	VIIIA	VIIIA	VIIIA	VIIIA	IB	IIA	IIIA	IVA	VIA	VIIA
1.00794 H 1	4.002602 He 2	6.941 Li 3	9.012182 Be 4	10.811 B 5	12.011 C 6	14.0074 N 7	15.9994 O 8	18.9984032 F 9	20.1797 Ne 10	22.989768 Na 11	24.3050 Mg 12	26.9815386 Al 13	28.0855 Si 14	30.973762 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
3.0973762 K 19	39.0983 Ca 20	44.955910 Sc 21	47.88 Ti 22	50.9415 V 23	51.9961 Cr 24	54.93805 Mn 25	55.847 Fe 26	58.93320 Co 27	58.93320 Ni 28	63.546 Cu 29	65.38 Zn 30	69.723 Ga 31	72.64 Ge 32	74.921595 As 33	78.96 Se 34	80.06 Br 35	83.80 Kr 36
85.4678 Rb 37	87.62 Sr 38	88.90585 Y 39	91.224 Zr 40	92.90638 Nb 41	95.94 Mo 42	97.9072 Tc 43	101.07 Ru 44	102.90550 Rh 45	106.42 Pd 46	107.8682 Ag 47	112.411 Cd 48	114.818 In 49	118.710 Sn 50	121.757 Sb 51	127.60 Te 52	126.90447 I 53	131.29 Xe 54
132.90545 Cs 55	137.327 Ba 56	138.905 La 57	174.967 Ce 58	175.942593 Pr 59	176.9327 Nd 60	186.90786 Pm 61	186.90786 Sm 62	186.90786 Eu 63	186.90786 Gd 64	187.9016 Tb 65	188.90584 Dy 66	190.23 Ho 67	192.22 Er 68	194.222 Tm 69	196.207 Yb 70	200.59 Lu 71	208.9804 Hf 72
223.0197 Fr 87	226.0254 Ra 88	227.0277 Ac 89	227.0277 Th 90	231.03689 Pa 91	231.03689 U 92	238.02891 Np 93	238.02891 Pu 94	244.0642 Am 95	244.0642 Cm 96	247.0703 Bk 97	247.0703 Cf 98	251.0796 Es 99	252.083 Fm 100	257.0851 Md 101	258.10 No 102	261.10 Lr 103	261.10 La 104

Atomic Weight ¹	Boiling Point ² , °C	Density ³ , g/cm ³	Electronegativity ⁴	First Ionization Potential ⁵ , eV	Group Classification ⁶	Atomic Number ⁷	Symbol	Element Name
1.00794	-252.87	0.0008	2.20	13.6	IA	1	H	Hydrogen
4.002602	-268.9	0.000178	2.20	23.72	IIA	2	He	Helium
6.941	-293.15	0.534	0.98	5.39	IIIA	3	Li	Lithium
9.012182	-279.75	0.879	1.58	9.00	IIA	4	Be	Beryllium
10.811	-252.78	2.34	2.04	5.39	IIIA	5	B	Boron
12.011	-182.962	2.07	2.55	13.61	IVA	6	C	Carbon
14.0074	-195.79	1.25	3.04	14.51	VA	7	N	Nitrogen
15.9994	-182.962	1.429	3.44	14.51	VIA	8	O	Oxygen
18.9984032	-188.94	1.497	3.98	13.81	VIIA	9	F	Fluorine
20.1797	-188.94	1.96	4.00	13.81	VIIA	10	Ne	Neon
22.989768	-29.3	0.873	0.98	5.39	IA	11	Na	Sodium
24.3050	908.4	1.738	1.31	5.14	IIA	12	Mg	Magnesium
26.9815386	2535	2.70	1.61	5.14	IIIA	13	Al	Aluminum
28.0855	2230	2.33	1.90	5.14	IIA	14	Si	Silicon
30.973762	1750	2.33	2.19	5.14	VIA	15	P	Phosphorus
32.06	1600	2.07	2.55	10.48	VIA	16	S	Sulfur
35.453	34.6	3.21	3.16	10.48	VIIA	17	Cl	Chlorine
39.948	-34.04	3.49	3.16	10.48	VIIA	18	Ar	Argon
44.955910	2835	5.02	1.31	5.14	IIIA	19	K	Potassium
47.88	2835	5.02	1.31	5.14	IIA	20	Ca	Calcium
50.9415	2835	5.02	1.31	5.14	IIIA	21	Sc	Scandium
51.9961	2835	5.02	1.31	5.14	IVA	22	Ti	Titanium
54.93805	2835	5.02	1.31	5.14	VA	23	V	Vanadium
55.847	2835	5.02	1.31	5.14	VIA	24	Cr	Chromium
58.93320	2835	5.02	1.31	5.14	VIIA	25	Mn	Manganese
58.93320	2835	5.02	1.31	5.14	VIIIA	26	Fe	Iron
58.93320	2835	5.02	1.31	5.14	VIIIA	27	Co	Cobalt
58.93320	2835	5.02	1.31	5.14	VIIIA	28	Ni	Nickel
63.546	2835	5.02	1.31	5.14	VIIIA	29	Cu	Copper
65.38	2835	5.02	1.31	5.14	VIIIA	30	Zn	Zinc
69.723	2835	5.02	1.31	5.14	VIIIA	31	Ga	Gallium
72.64	2835	5.02	1.31	5.14	VIIIA	32	Ge	Germanium
74.921595	2835	5.02	1.31	5.14	VIIIA	33	As	Arsenic
78.96	2835	5.02	1.31	5.14	VIIIA	34	Se	Selenium
80.06	2835	5.02	1.31	5.14	VIIIA	35	Br	Bromine
83.80	2835	5.02	1.31	5.14	VIIIA	36	Kr	Krypton
85.4678	2835	5.02	1.31	5.14	VIIIA	37	Rb	Rubidium
87.62	2835	5.02	1.31	5.14	VIIIA	38	Sr	Strontium
88.90585	2835	5.02	1.31	5.14	VIIIA	39	Y	Yttrium
91.224	2835	5.02	1.31	5.14	VIIIA	40	Zr	Zirconium
92.90638	2835	5.02	1.31	5.14	VIIIA	41	Nb	Niobium
95.94	2835	5.02	1.31	5.14	VIIIA	42	Mo	Molybdenum
97.9072	2835	5.02	1.31	5.14	VIIIA	43	Tc	Technetium
101.07	2835	5.02	1.31	5.14	VIIIA	44	Ru	Ruthenium
102.90550	2835	5.02	1.31	5.14	VIIIA	45	Rh	Rhodium
106.42	2835	5.02	1.31	5.14	VIIIA	46	Pd	Palladium
107.8682	2835	5.02	1.31	5.14	VIIIA	47	Ag	Silver
112.411	2835	5.02	1.31	5.14	VIIIA	48	Cd	Cadmium
114.818	2835	5.02	1.31	5.14	VIIIA	49	In	Indium
118.710	2835	5.02	1.31	5.14	VIIIA	50	Sn	Tin
121.757	2835	5.02	1.31	5.14	VIIIA	51	Sb	Antimony
127.60	2835	5.02	1.31	5.14	VIIIA	52	Te	Tellurium
126.90447	2835	5.02	1.31	5.14	VIIIA	53	I	Iodine
131.29	2835	5.02	1.31	5.14	VIIIA	54	Xe	Xenon
132.90545	2835	5.02	1.31	5.14	VIIIA	55	Cs	Cesium
137.327	2835	5.02	1.31	5.14	VIIIA	56	Ba	Barium
138.905	2835	5.02	1.31	5.14	VIIIA	57	La	Lanthanum
174.967	2835	5.02	1.31	5.14	VIIIA	72	Hf	Hafnium
175.942593	2835	5.02	1.31	5.14	VIIIA	73	Ta	Tantalum
176.9327	2835	5.02	1.31	5.14	VIIIA	74	W	Tungsten
186.90786	2835	5.02	1.31	5.14	VIIIA	75	Re	Rhenium
186.90786	2835	5.02	1.31	5.14	VIIIA	76	Os	Osmium
186.90786	2835	5.02	1.31	5.14	VIIIA	77	Ir	Iridium
186.90786	2835	5.02	1.31	5.14	VIIIA	78	Pt	Platinum
186.90786	2835	5.02	1.31	5.14	VIIIA	79	Au	Gold
186.90786	2835	5.02	1.31	5.14	VIIIA	80	Hg	Mercury
186.90786	2835	5.02	1.31	5.14	VIIIA	81	Tl	Thallium
186.90786	2835	5.02	1.31	5.14	VIIIA	82	Pb	Lead
186.90786	2835	5.02	1.31	5.14	VIIIA	83	Bi	Bismuth
186.90786	2835	5.02	1.31	5.14	VIIIA	84	Po	Polonium
186.90786	2835	5.02	1.31	5.14	VIIIA	85	At	Astatine
186.90786	2835	5.02	1.31	5.14	VIIIA	86	Rn	Radon

1. Atomic weight is the weighted average of the atomic masses of the isotopes of an element. 2. Boiling point is the temperature at which the vapor pressure of a liquid is equal to the external atmospheric pressure. 3. Density is the mass per unit volume of a substance. 4. Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. 5. First ionization potential is the energy required to remove an electron from a neutral atom in its ground state. 6. Group classification is based on the periodic table. 7. Atomic number is the number of protons in the nucleus of an atom.

PAPERTECH

Editors: T. K. Varga, M.A.Sc. & C. Bello, M.A.Sc.

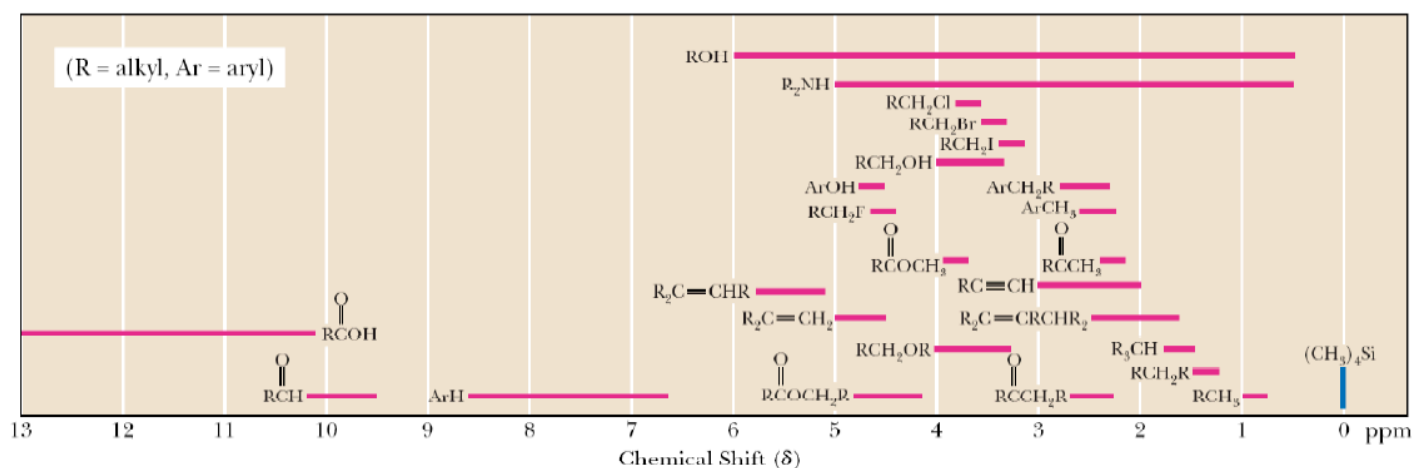
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Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
R_2NH	0.5-5.0	RCH_2OH	3.4-4.0
ROH	0.5-6.0	RCH_2Br	3.4-3.6
RCH_3	0.8-1.0	RCH_2Cl	3.6-3.8
RCH_2R	1.2-1.4	$\begin{array}{c} O \\ \\ RCOCH_3 \end{array}$	3.7-3.9
R_3CH	1.4-1.7	$\begin{array}{c} O \\ \\ RCOCH_2R \end{array}$	4.1-4.7
$R_2C=CRCHR_2$	1.6-2.6	RCH_2F	4.4-4.5
$RC\equiv CH$	2.0-3.0	$ArOH$	4.5-4.7
$\begin{array}{c} O \\ \\ RCCH_3 \end{array}$	2.1-2.3	$R_2C=CH_2$	4.6-5.0
$\begin{array}{c} O \\ \\ RCCH_2R \end{array}$	2.2-2.6	$R_2C=CHR$	5.0-5.7
$ArCH_3$	2.2-2.5	$\begin{array}{c} O \\ \diagup \quad \diagdown \\ H_2C \quad CH_2 \end{array}$	3.3-4.0
RCH_2NR_2	2.3-2.8	$\begin{array}{c} O \\ \\ RCH \end{array}$	9.5-10.1
RCH_2I	3.1-3.3	$\begin{array}{c} O \\ \\ RCOH \end{array}$	10-13
RCH_2OR	3.3-4.0		

* Values are relative to tetramethylsilane. Other atoms within the molecule may cause the signal to appear outside these ranges.

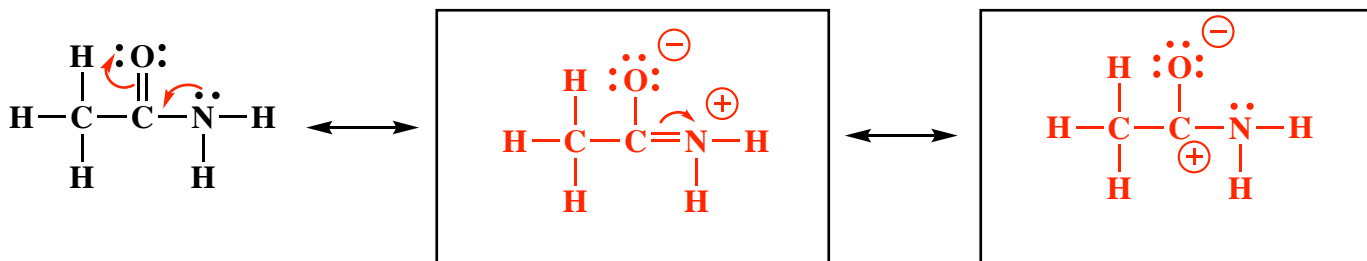


Compound		pK _a
Hydrochloric acid	H-Cl	-7
Protonated alcohol	$\text{RCH}_2\text{OH}_2^+$	-2
Hydronium ion	H_3O^+	-1.7
Carboxylic acids	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	3-5
Thiols	RCH_2SH	8-9
Ammonium ion	H_4N^+	9.2
β-Dicarbonyls	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	10
Primary ammonium	$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_3$	10.5
β-Ketoesters	$\text{RC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	11
β-Diesters	$\text{ROC}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$	16
Aldehydes	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	18-20
Ketones	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$	18-20
Esters	$\text{RCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C}-\text{H}$	25
LDA	$\text{H}-\text{N}(\text{i-C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\underset{\text{H}}{\text{C}}-\text{H}$	44
Alkanes	$\text{CH}_3\text{CH}_2-\text{H}$	51

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

Where are the electrons?

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

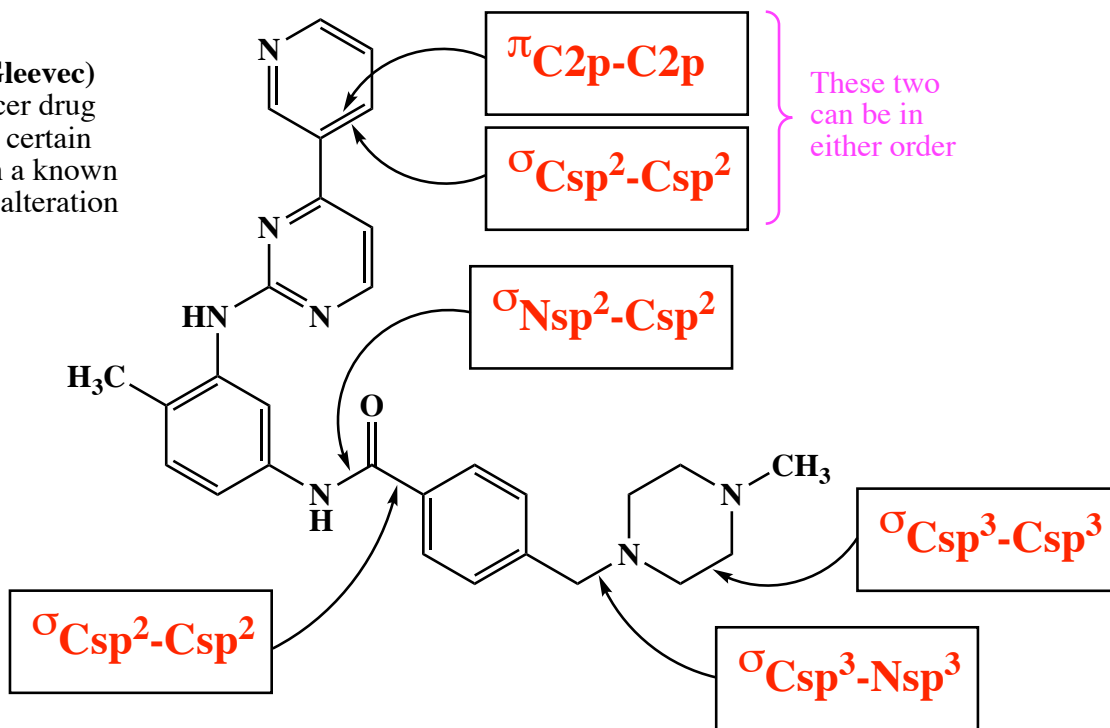


3. (14 points) Suppose a relative of yours is having an MRI. In no more than four sentences, explain to them what is happening when they have the MRI scan. We will be looking for a minimum of 7 key points here and your answer should match a recent Rule of the Day.

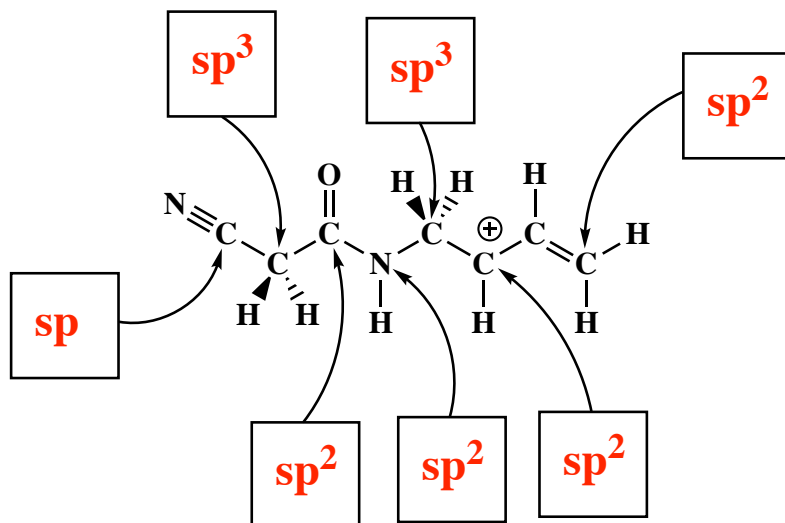
The popular medical diagnostic technique of **magnetic resonance imaging (MRI)** is based on the **same principles as NMR**, namely the **flipping (i.e. resonance) of nuclear spins of H atoms by radio frequency irradiation** when a patient is placed in a **strong magnetic field**. **Magnetic field gradients**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

4. (2 pts each) In the spaces provided, indicate the type of bond, and the hybridized orbitals that overlap to form the bond. For example, one answer could be: $\sigma_{\text{Csp}^3-\text{H}1\text{s}}$

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



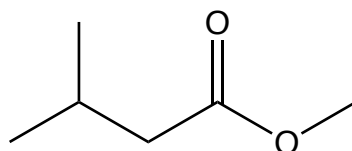
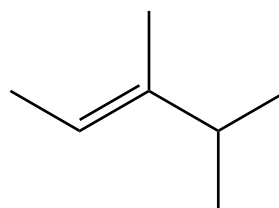
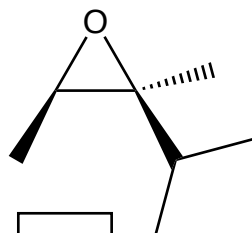
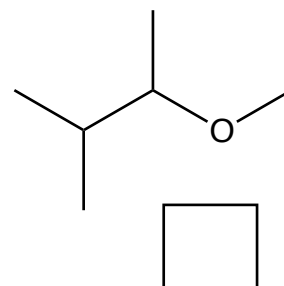
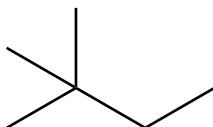
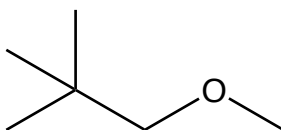
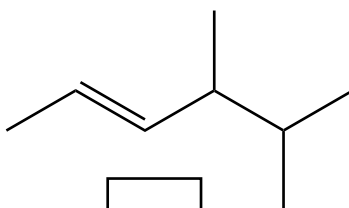
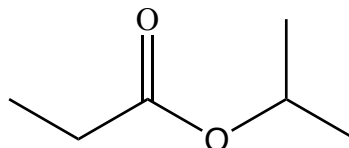
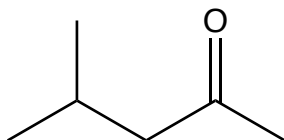
5. (2 pts each) In the spaces provided, write the hybridization state of the atoms indicated by the arrow.



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

- ☒ True ☐ False **A.** When the 2s orbital is hybridized with all three 2p orbitals, you get sp^3 hybridization that has major lobes pointed in a tetrahedral geometry.
- ☐ True ☒ False **B.** When the 2s orbital is hybridized with all three 2p orbitals, you get sp^2 hybridization that has major lobes pointed in a trigonal planar geometry.
- ☒ True ☐ False **C.** When three parallel 2p orbitals on adjacent atoms combine, three new molecular orbitals are produced (bonding, non-bonding and antibonding).
- ☒ True ☐ False **D.** When a Lewis acid and Lewis base combine, the product is referred to as a Lewis acid-Lewis base complex. The new bond is referred to as a "coordinate covalent bond" or "dative bond".
- ☒ True ☐ False **E** The enol form of a compound rapidly tautomerizes to the more stable keto form.
- ☐ True ☒ False **F** The keto form of a compound rapidly tautomerizes to the more stable enol form.
- ☐ True ☒ False **G.** Nuclei with spin quantum number 1.0 are quantized in one of two orientations, "+1/2" (lower energy) or "-1/2"(higher energy) in the presence of an external magnetic field, that is, with and against the external field, respectively.
- ☒ True ☐ False **H.** Nuclei with spin quantum number 1/2 are quantized in one of two orientations, "+1/2" (lower energy) or "-1/2"(higher energy) in the presence of an external magnetic field, that is, with and against the external field, respectively.
- ☒ True ☐ False **I.** The difference in energy between the +1/2 and -1/2 nuclear spin states is proportional to the strength of the magnetic field felt by the nucleus.
- ☒ True ☐ False **J.** Running 3-5 miles a week EVERY WEEK as an adult dramatically increases your fitness level and improves your health throughout your life. Doing this and enjoying a healthy life is even more important than getting an A on this organic final!

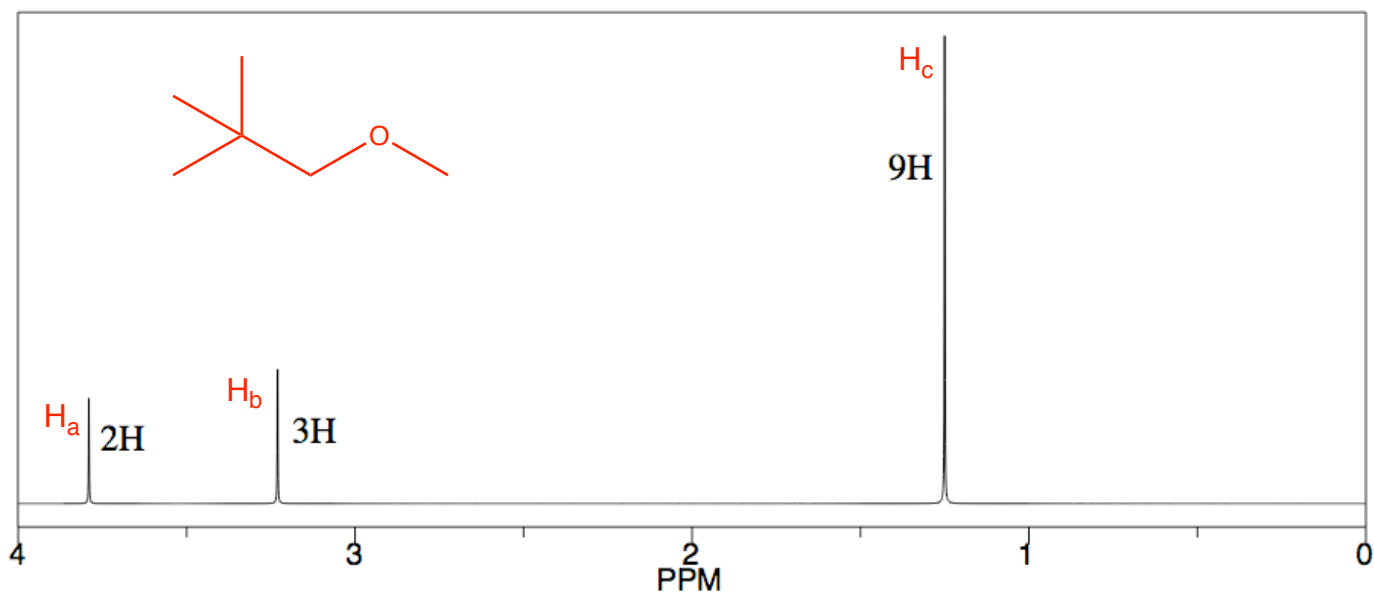
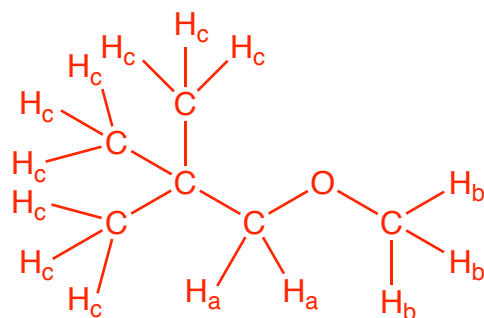
7. (15 pts total) On the following three pages there are NMR spectra. The relative integrations are given above each signal. Each NMR spectrum has a letter on it. **In the spaces provided, write the appropriate letter underneath the molecules that would produce that spectrum.** Notice that not all of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



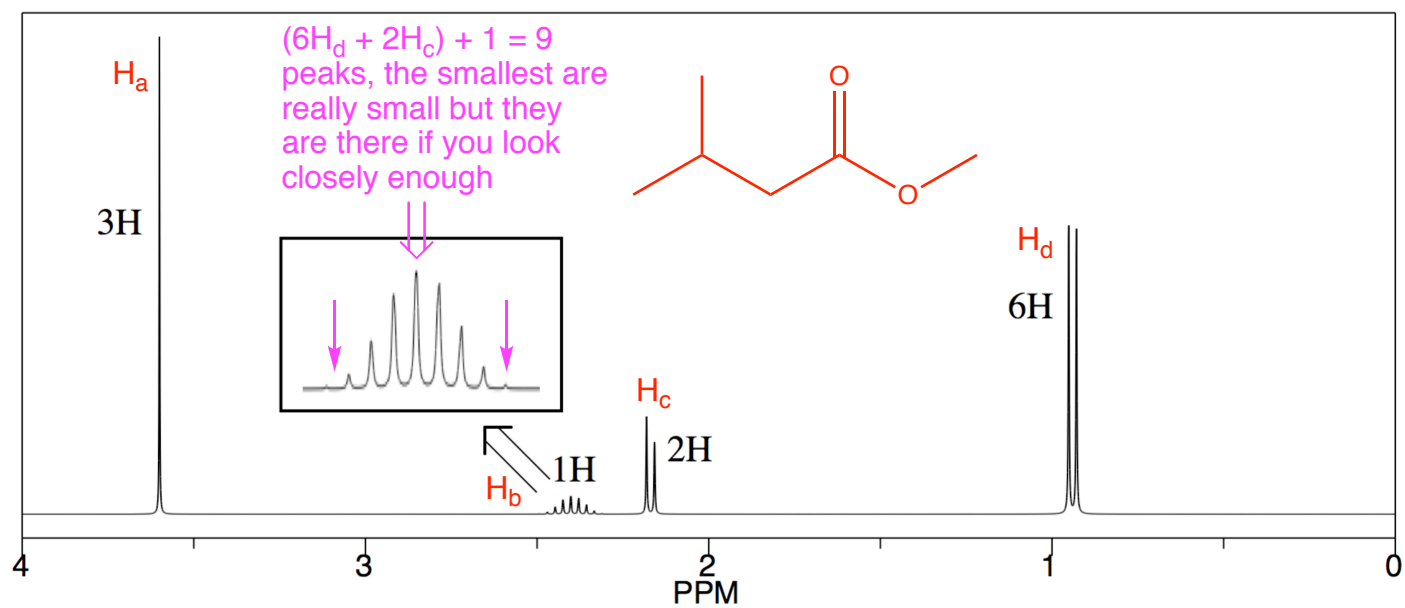
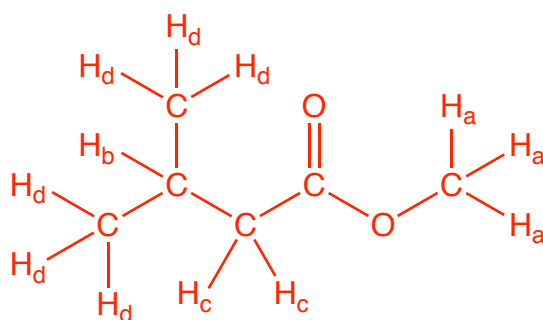
Signature_____

Pg 5

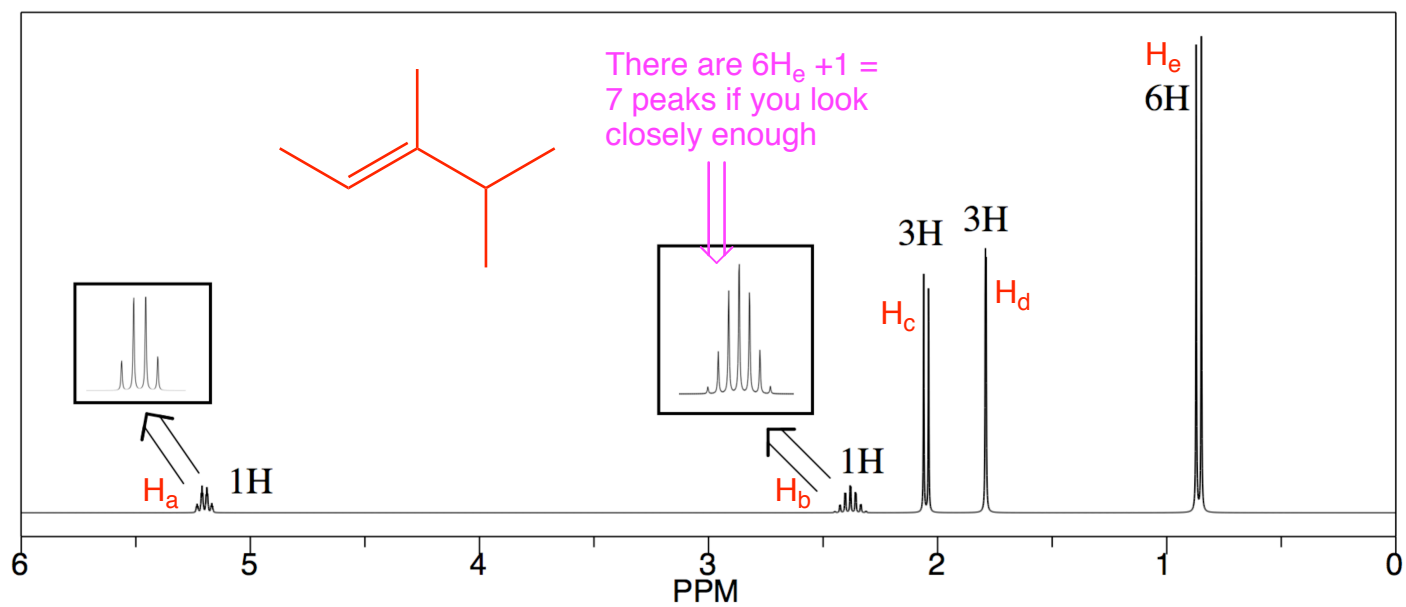
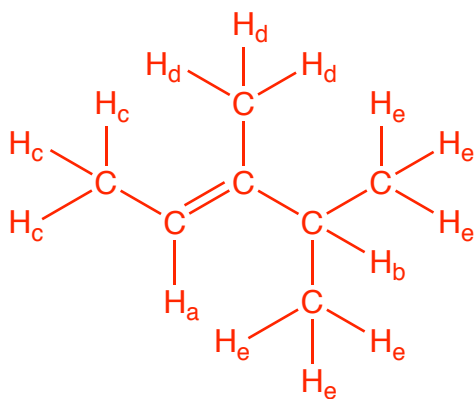
Spectrum A



Spectrum B



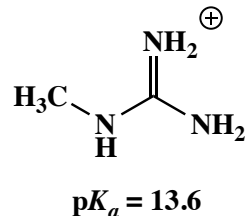
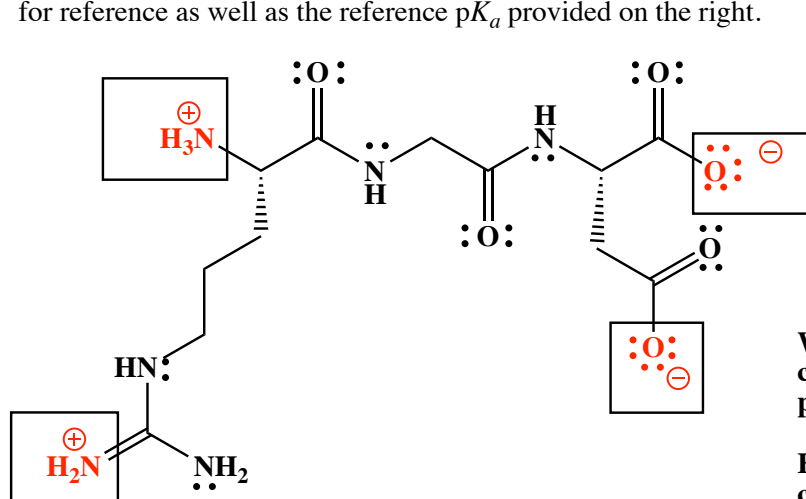
Spectrum C



Signature _____

Pg 8 _____(28)

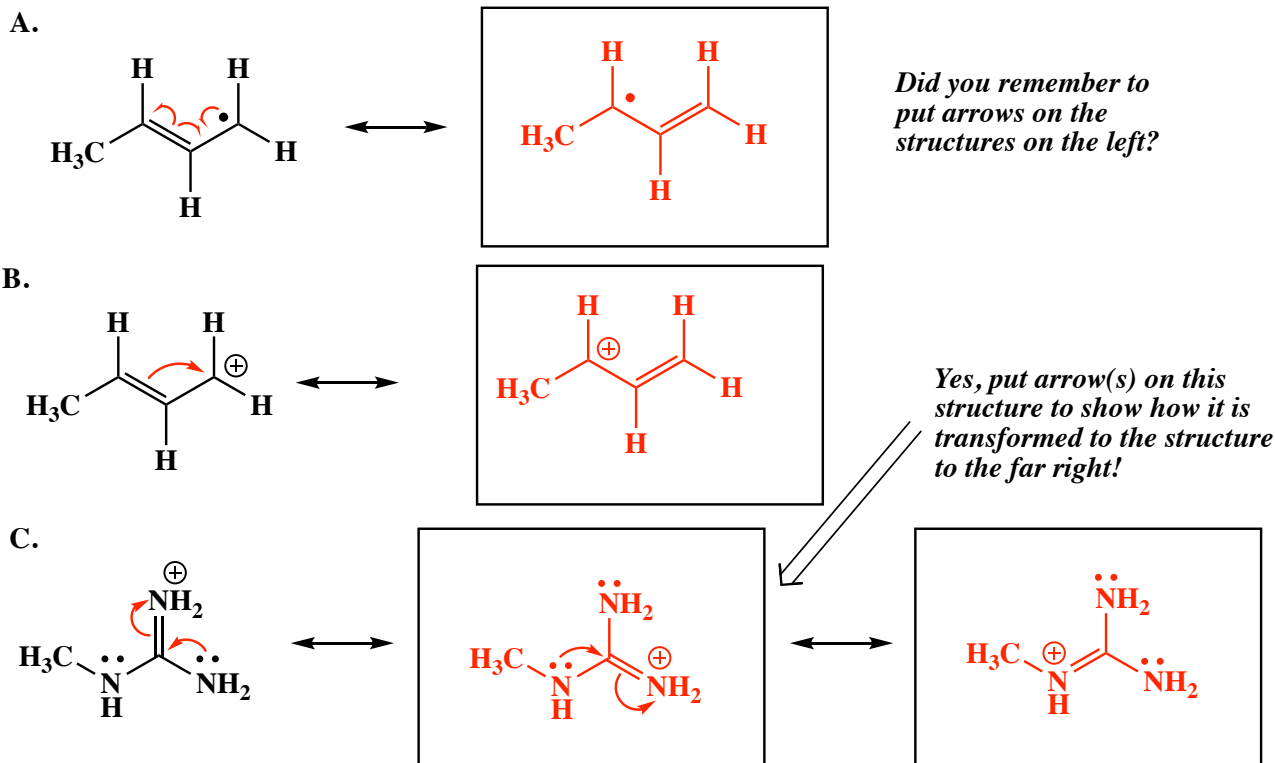
8. The following molecule is called RGD. It is the most common peptide motif responsible for cell adhesion to the extracellular matrix. Cell adhesion proteins called integrins recognize and bind the RGD sequence. **In the boxes, fill in the proper number of bonds to H atoms, lone pairs, and formal charges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



What is the total net charge of this peptide at pH 7.0? 0

How many chiral centers are present in the RGD peptide? 2

9. (16 pts total) The following are contributing structures for important resonance hybrids. Draw the other important resonance contributing structure in the box provided. Draw arrows on the structures on the left that indicate the flow of electrons that produce the contributing structures you drew to the right. Be sure to show all lone pairs and formal charges.

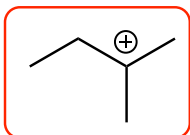
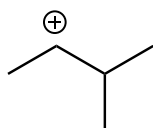


10. (19 pts) Circle the appropriate structure from each pair, then fill in the blank on the right stating the reason(s) for your answer. Possible answers for the blanks on the right are **Inductive Effect**, **Angle Strain**, **Torsional Strain**, **Ring Strain**, **Steric Strain**, or **Hyperconjugation**.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

Reason(s)

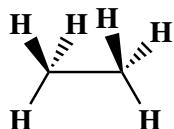
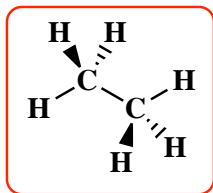
When it comes to stabilizing alkyl cations, these two go together as distinct but reinforcing stabilization mechanisms. Remember a C⁺ atom is electronegative compared to a neutral C atom

A) Circle the more stable carbocation



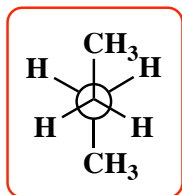
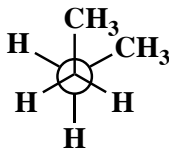
Hyperconjugation, Inductive Effect

B) Circle the more stable conformation



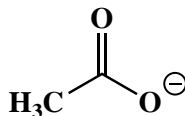
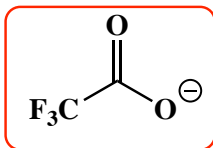
Torsional Strain

C) Circle the more stable conformation



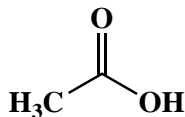
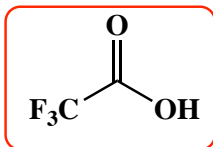
Steric Strain

D) Circle the more stable anion



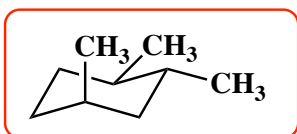
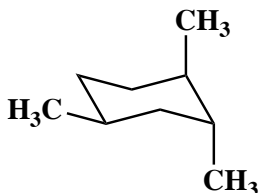
Inductive Effect

E) Circle the more acidic molecule



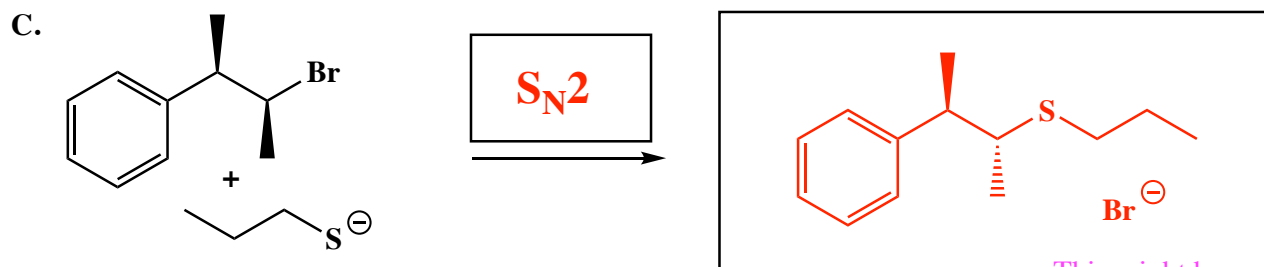
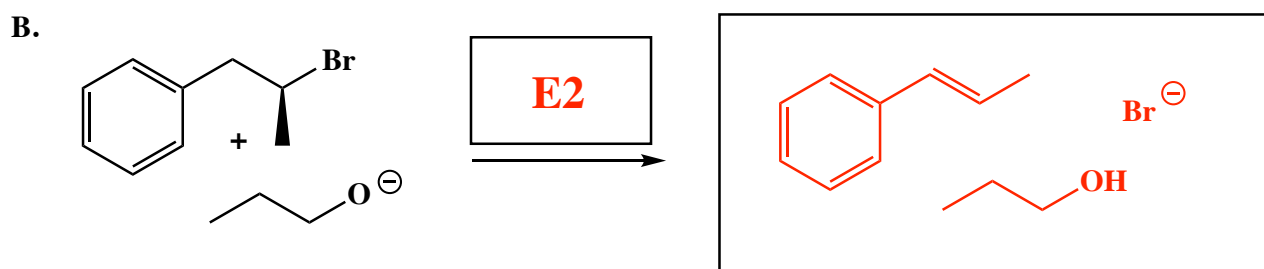
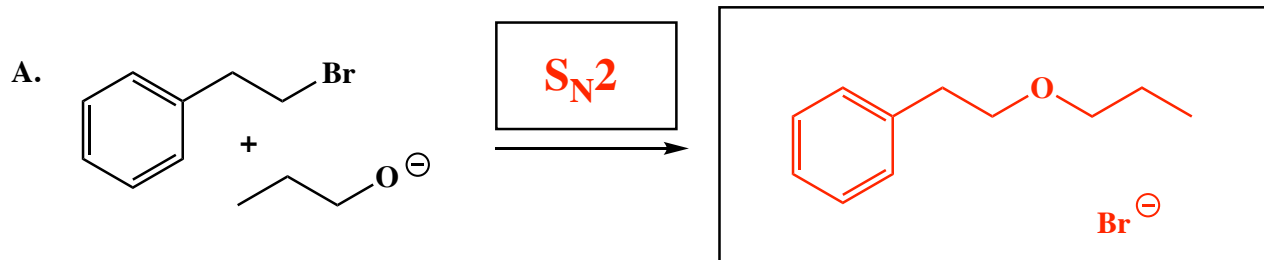
Inductive Effect

F) Circle the more stable conformation

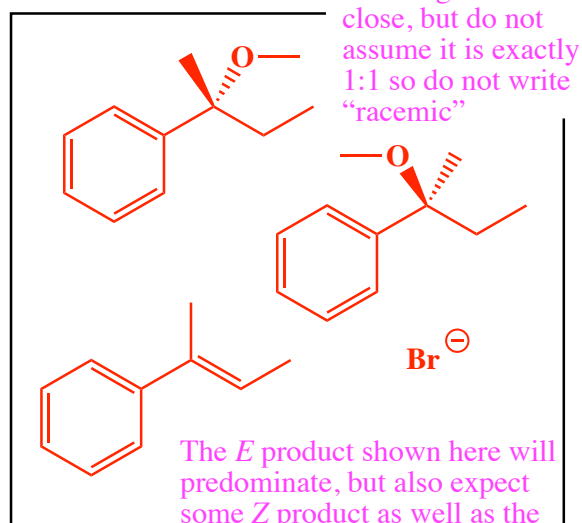
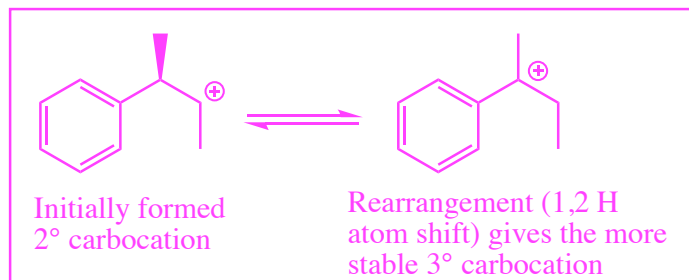
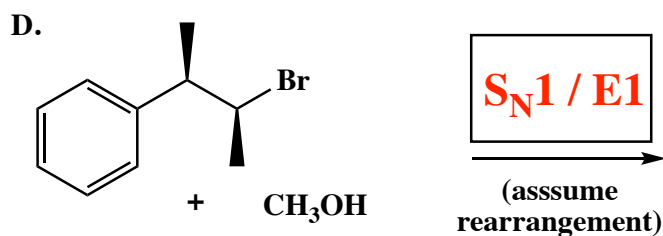


Steric Strain

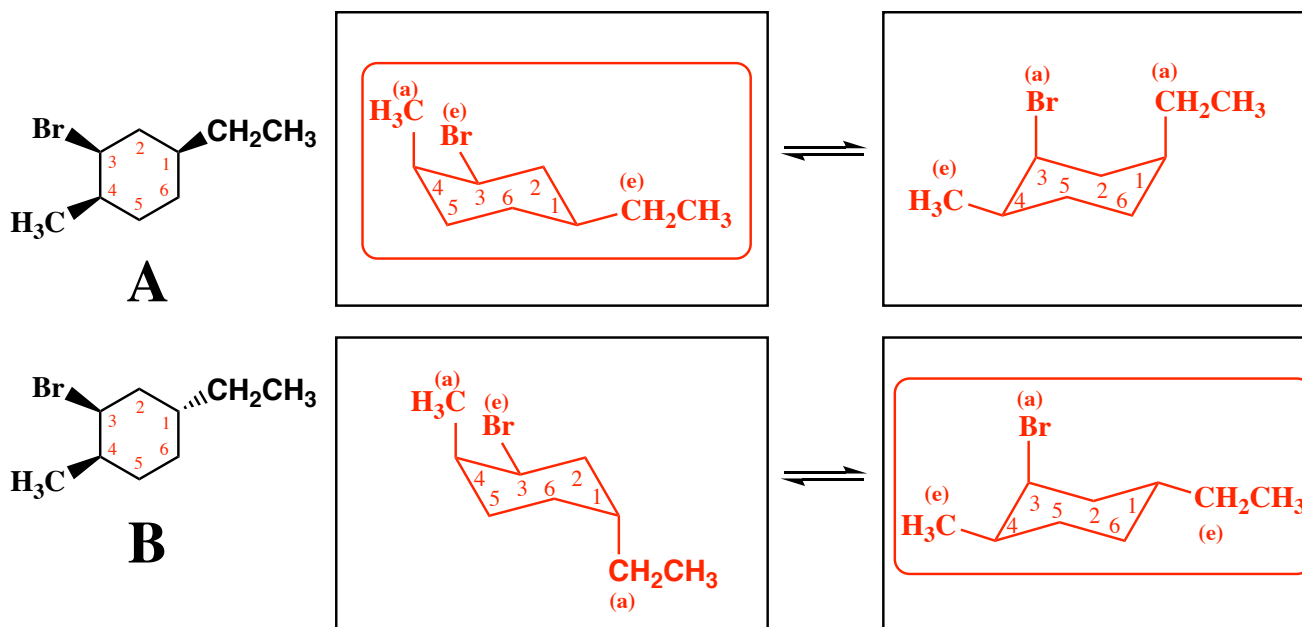
11. (5, 6 or 8 pts each) The following reactions all involve chemistry of haloalkanes. **Fill in the box above the arrow with the mechanism that will be followed (S_N2 , $E2$, etc.). Then draw only the predominant product or products** and please remember that **you must draw the correct stereoisomers**.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



For the last one only draw rearranged products



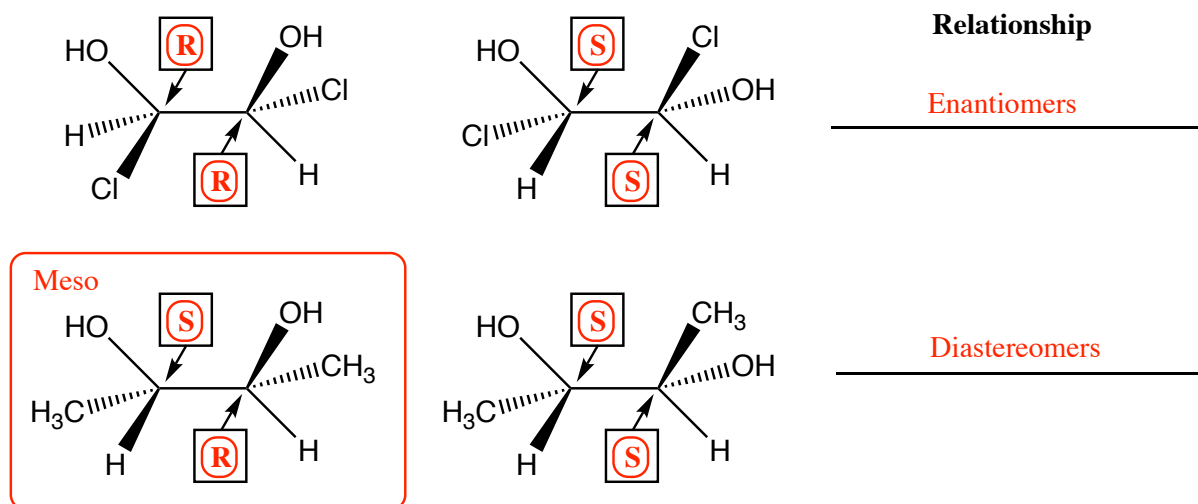
12. (10 pts) In the two spaces to the right, draw the two equilibrating chair structures for the following cyclohexane derivatives. In each case circle the one that predominates at equilibrium.



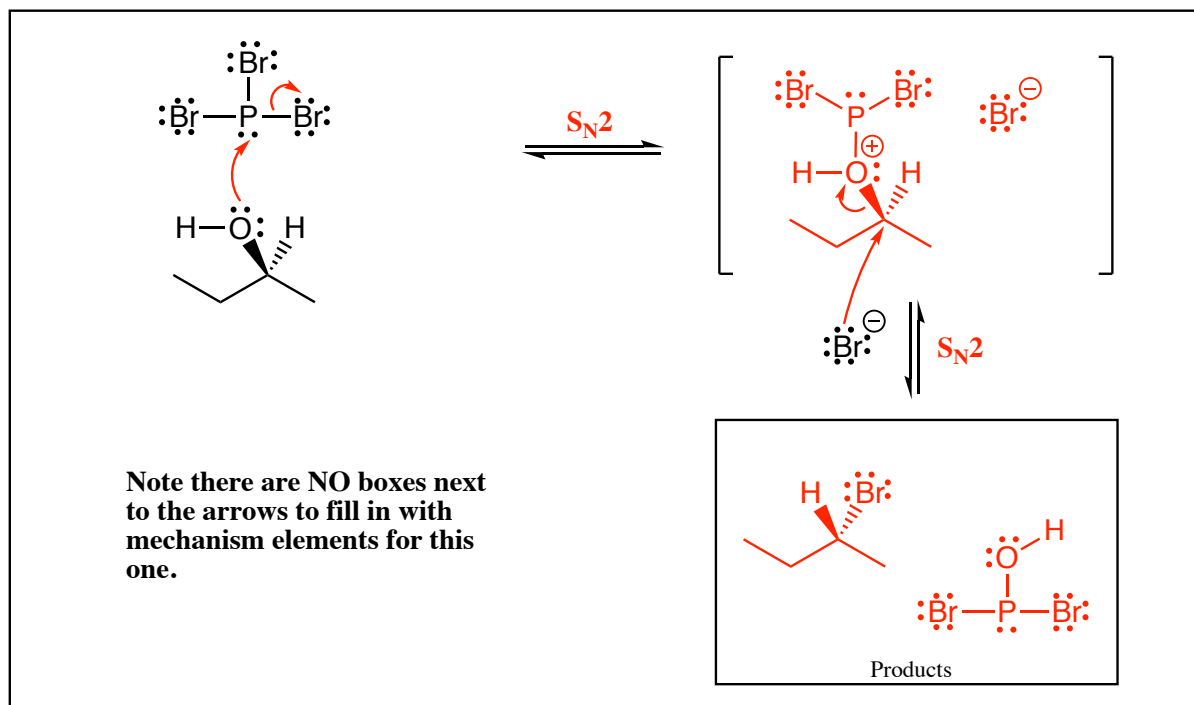
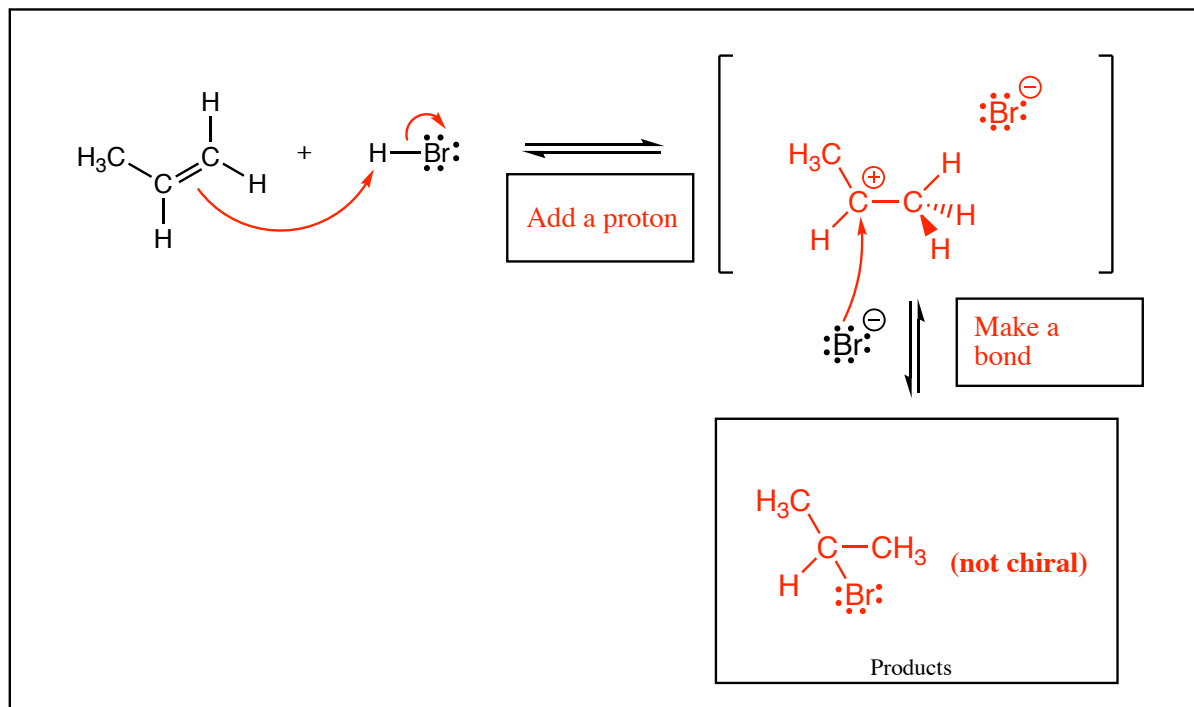
(3 pts) Which of the two structures, A or B, will react faster in an E2 reaction? **B**

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

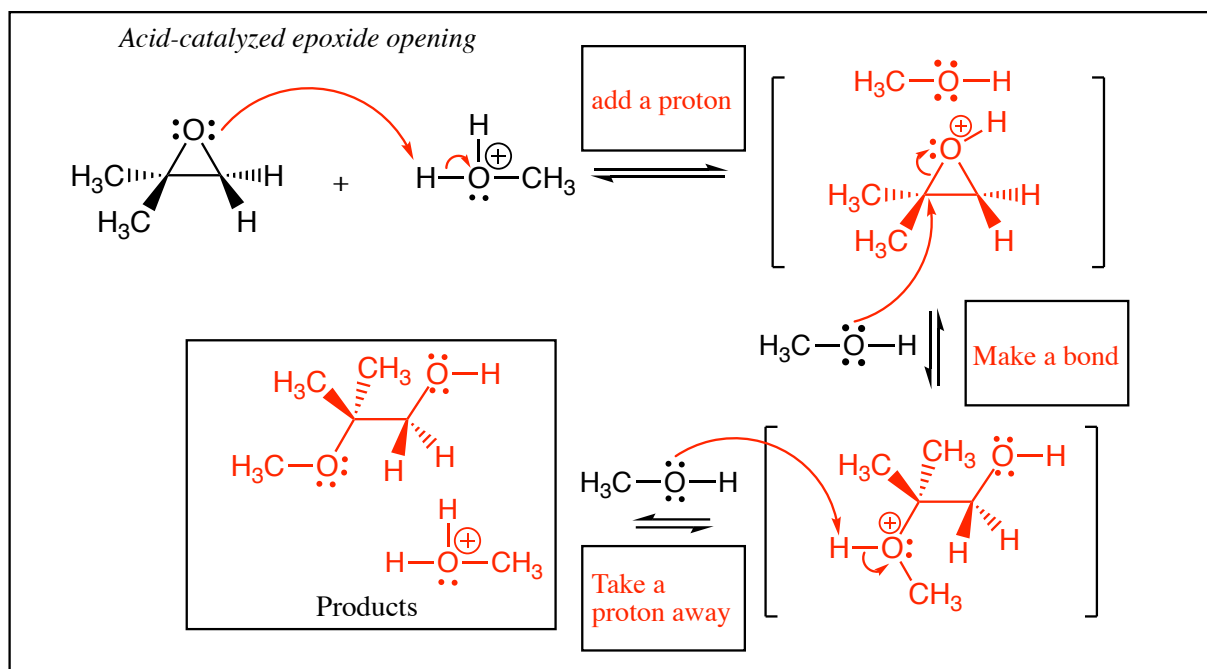
13. (13 pts total) On the line provided, state the stereochemical relationship between each pair of molecules: **enantiomers, diastereomers, or the same molecule**. In each box assign R and S to each chiral center to help answer this question. **Circle all meso compounds.**



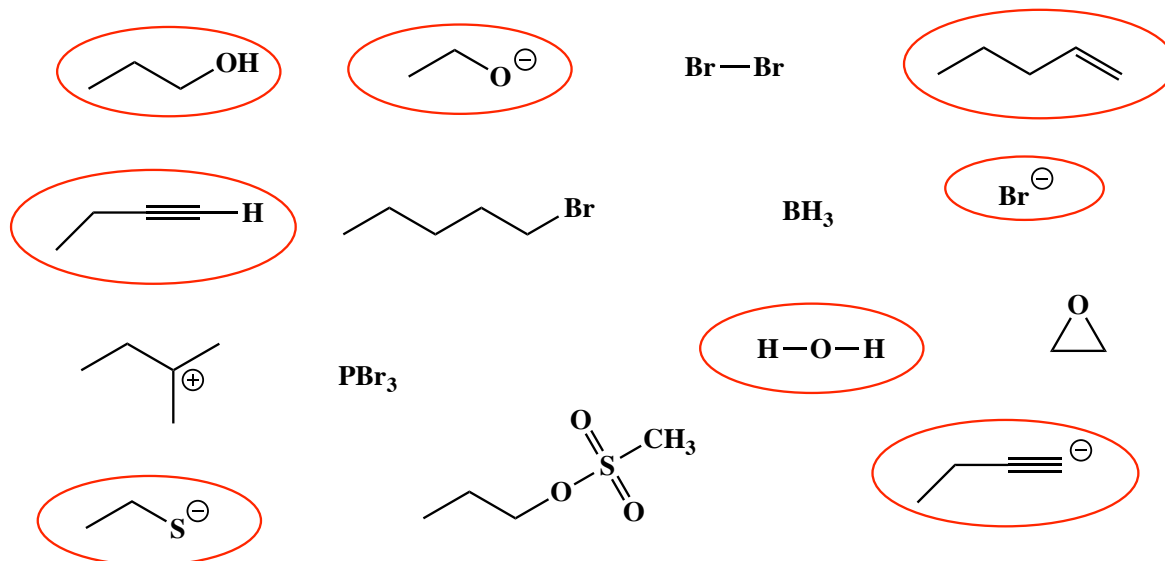
14. (20 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) For the following reactions, fill in the details of the mechanism. Draw the appropriate chemical structures and use an arrow to show how pairs of electrons are moved to make and break bonds during the reaction. For this question, you must draw all molecules produced in each step. Finally, fill in any boxes adjacent to the arrows with the type of step involved, such as "Make a bond" or "Take a proton away". Use wedges and dashes to indicate stereochemistry where appropriate.



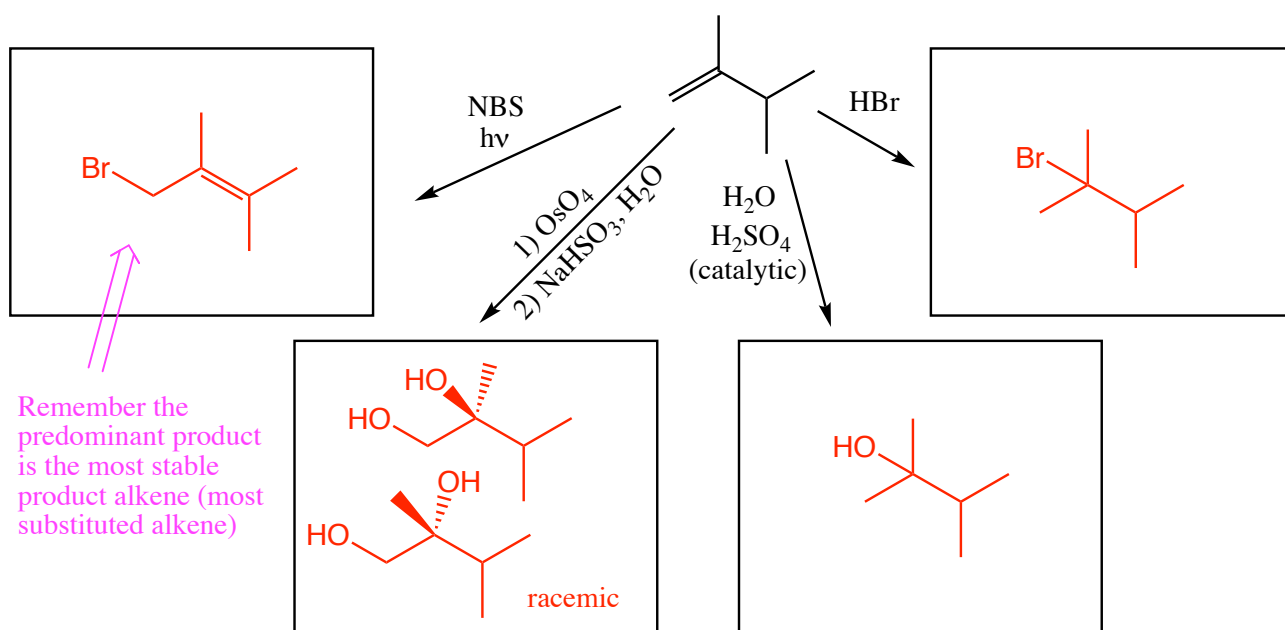
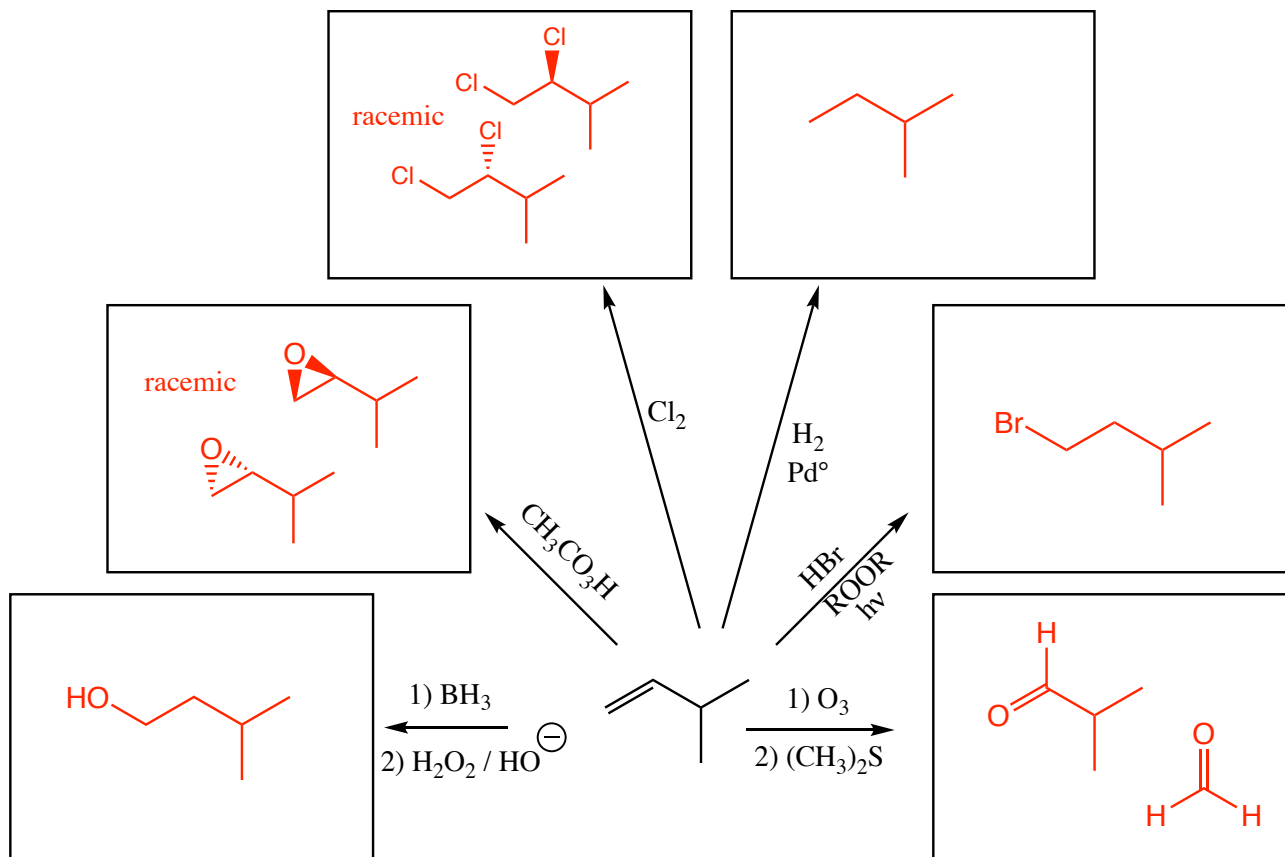
15. (17 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) For the following reactions, fill in the details of the mechanism. Draw the appropriate chemical structures and use an arrow to show how pairs of electrons are moved to make and break bonds during the reaction. For this question, you must draw all molecules produced in each step. Finally, fill in any boxes adjacent to the arrows with the type of step involved, such as "Make a bond" or "Take a proton away". Use wedges and dashes to indicate stereochemistry where appropriate.



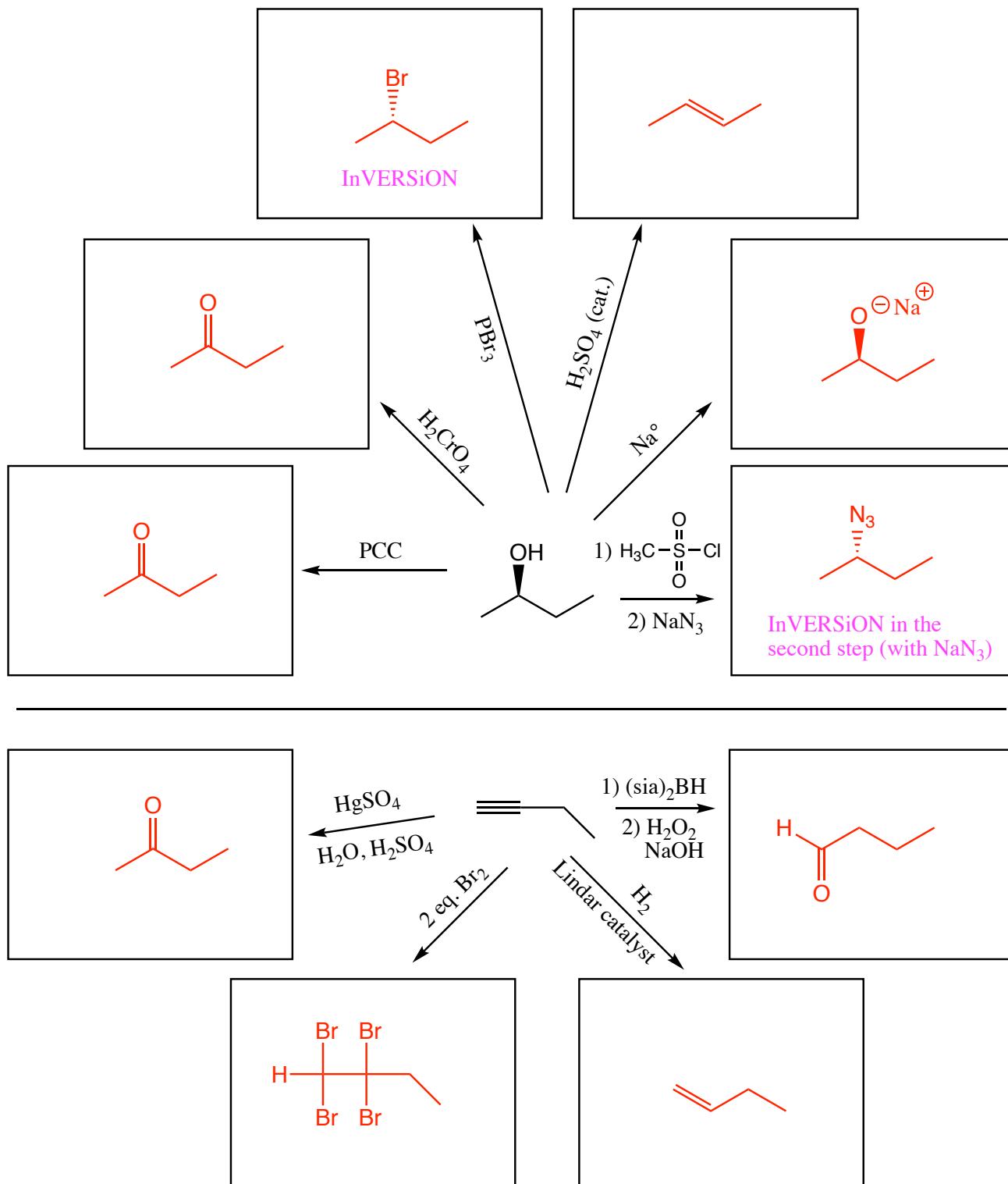
16. (15 pts) In order to predict mechanisms, it is important to understand the "personalities" of different reagents. Most important, it is essential that you can recognize **nucleophiles** and **electrophiles**. The following are either nucleophiles and electrophiles we have used in mechanisms this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



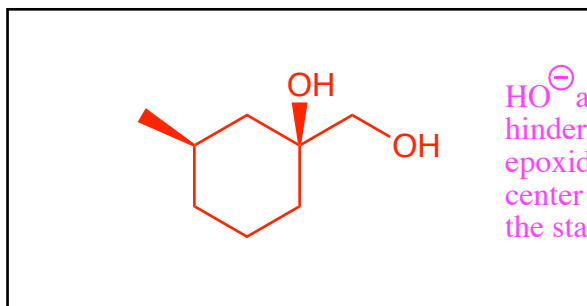
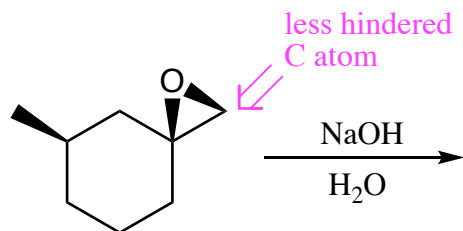
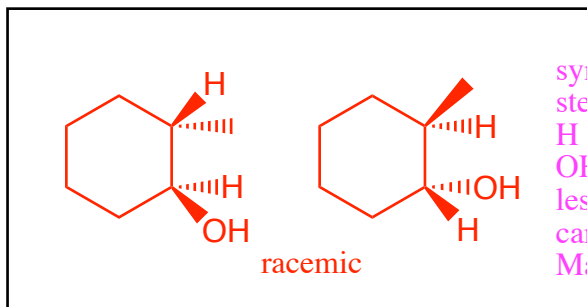
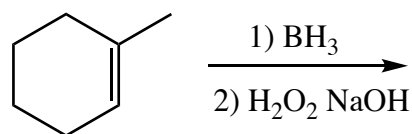
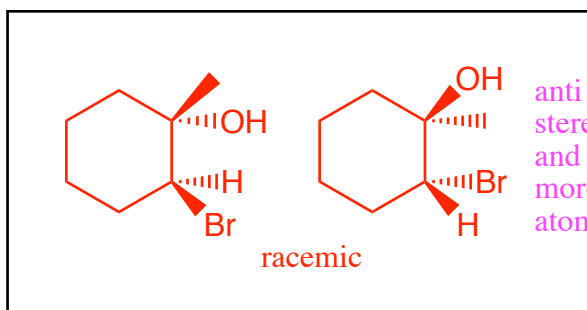
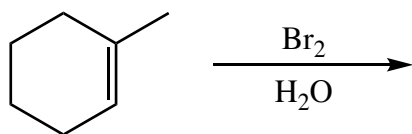
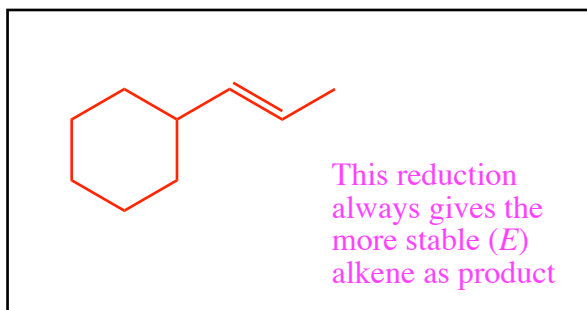
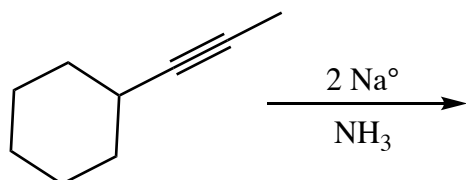
17. (3, 4 or 5 pts each) For the following, complete the reactions with the predominant carbon-containing product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate.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



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

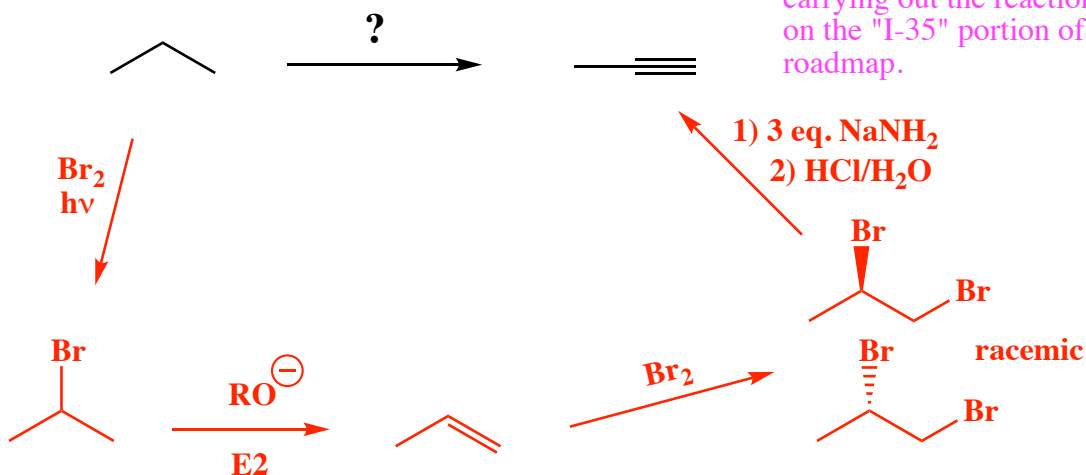


19. (3, 4 or 5 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements take place.



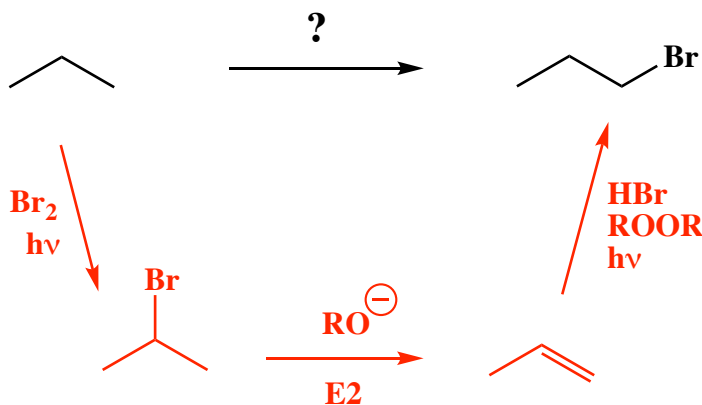
20. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized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

A) (10 pts)



Recognize that the product alkyne can be made from the starting alkane by carrying out the reactions on the "I-35" portion of the roadmap.

B) (7 pts)

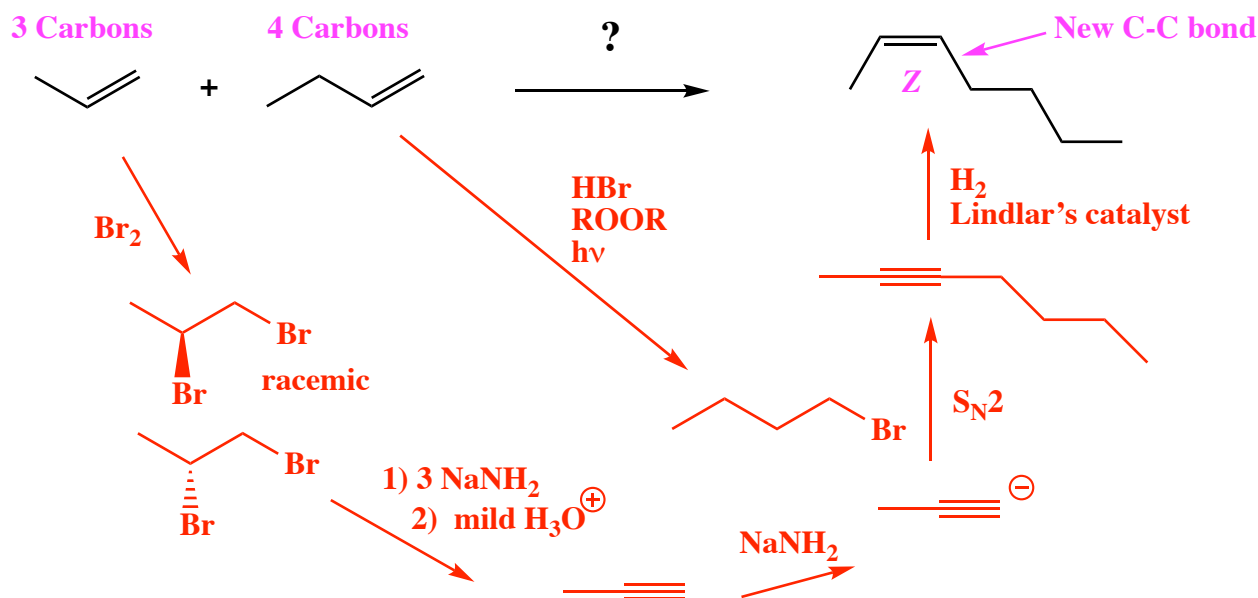


Recognize the product as NOT being the one made with a simple halogenation (that would be 2-bromopropane)
Recognize this 1-bromopropane product as being derived from the non-Markovnikov addition of HBr to an alkene in the presence of peroxide, so make the alkene like above then carry out the non-Markovnikov reaction

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

Recognize that a new C-C bond had to be made between the two starting material pieces so assume an alkyne anion needs to react with a haloalkane somewhere in the synthesis. Also, recognize that this alkene is a Z alkene, the only reaction that can make Z alkene is H_2 reduction using Lindlar's catalyst so that must be the last step

C) (16 pts)



Recognize that to put the triple bond in the correct location in the product of this step, the three carbon piece must be the alkyne anion and the four carbon piece must be the haloalkane.

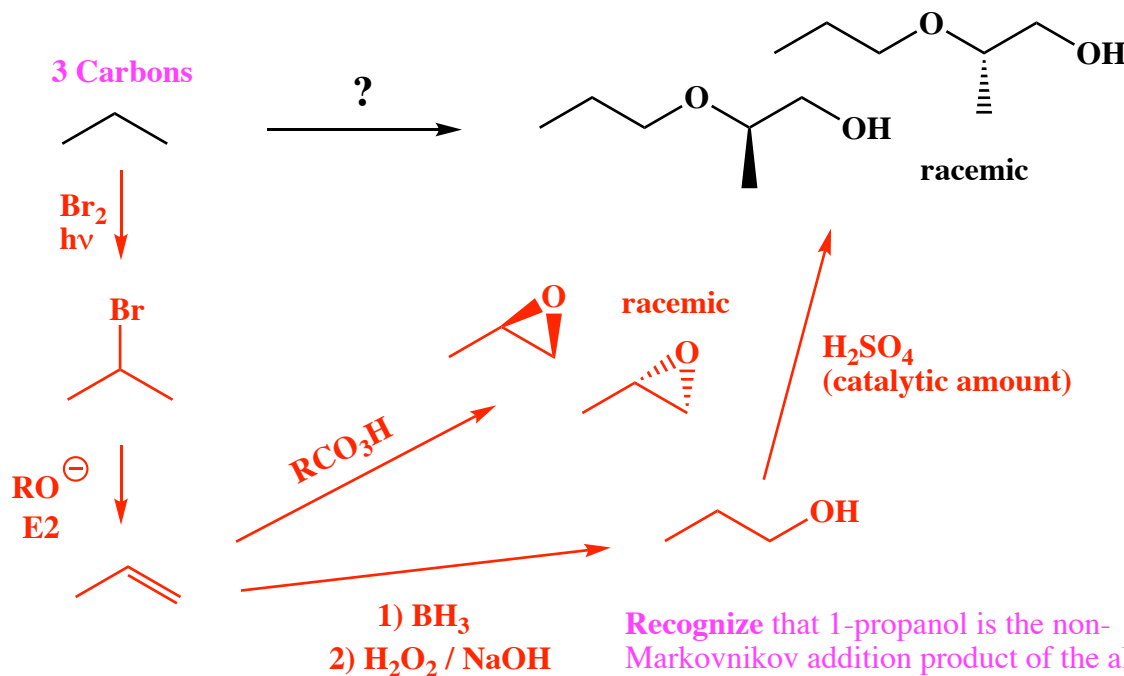
20. (cont.) These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule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

Recognize the product as resulting from an epoxide reacting at the **more hindered central carbon** atom with 1-propanol, therefore it must be an acid-catalyzed epoxide reaction as the last step.

6 Carbons

D (13 pts)

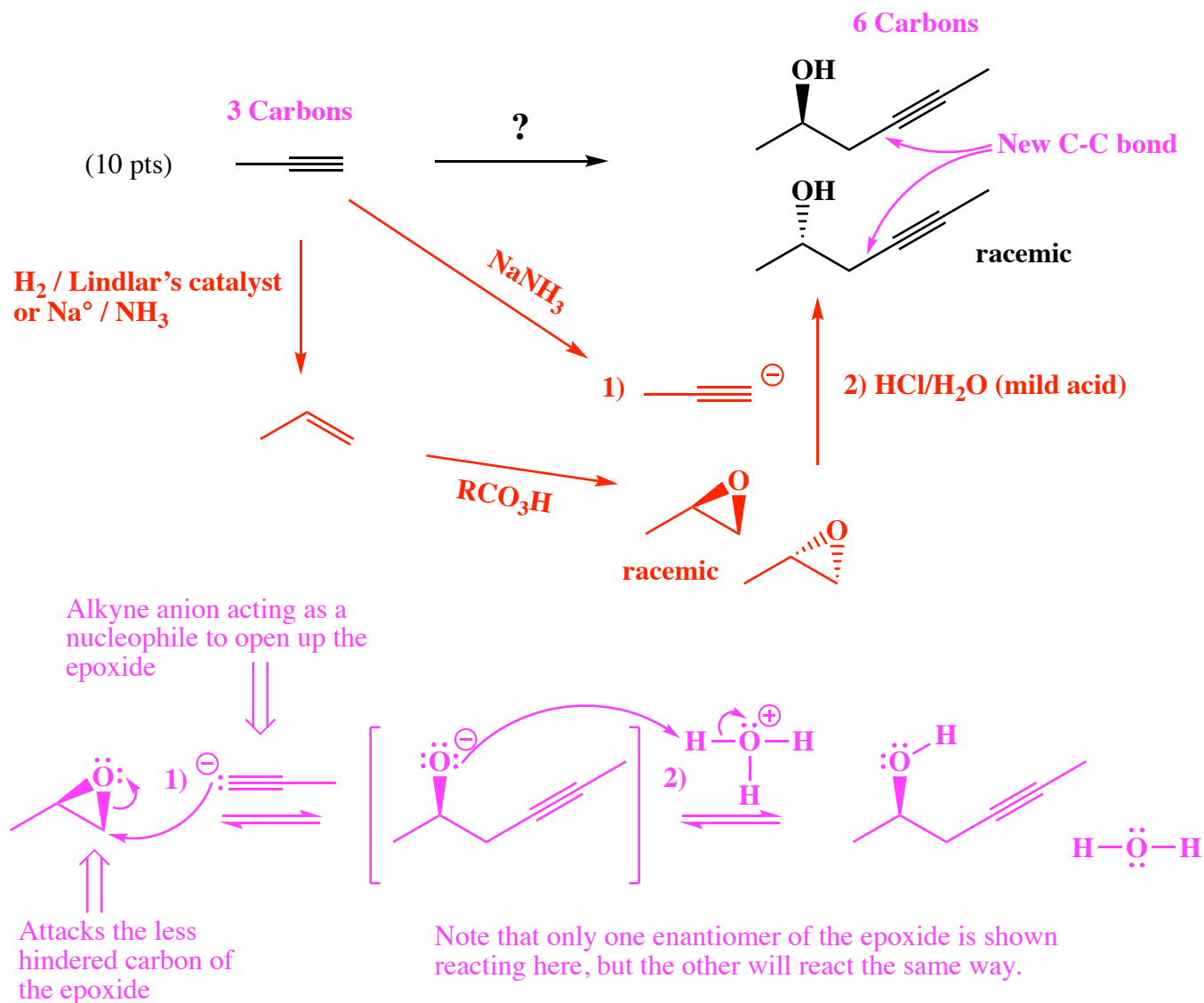
3 Carbons



Recognize that 1-propanol is the non-Markovnikov addition product of the alkene so you need to use $1) \text{BH}_3$ $2) \text{H}_2\text{O}_2 / \text{NaOH}$, not simple hydration that would have given 2-propanol

21. Here is an “apply what you know” synthesis question. You have never seen the reaction that makes the final product, but you do know enough chemistry to figure out what happens. Think about what you know about the “personalities” of the different molecules we have seen, and you will be OK. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. You must draw all stereoisomers formed, and use wedges and dashes to indicate chirality at each chiral center. Write racemic when appropriate. **All the carbons of the product must come from carbons of the starting material.**

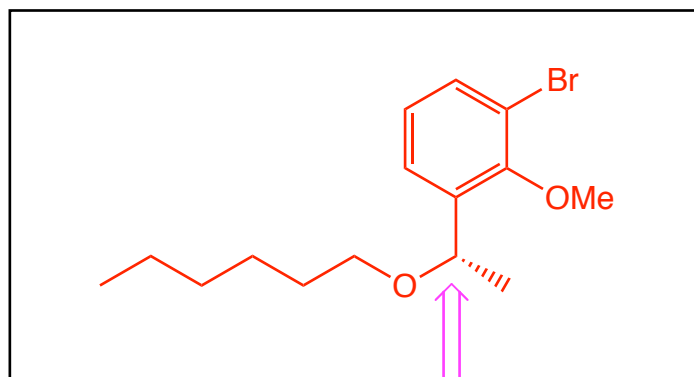
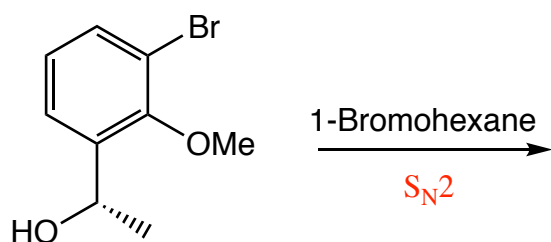
Recognize the product as having 6 carbons and the starting material has three. Therefore, there has to be a new C-C bond as shown. You have never seen this exact type of reaction before, but we wanted to you **recognize** the product as coming from an epoxide with an alkyne anion acting as a nucleophile. You have seen the alkyne anion reacting as a nucleophile with a primary haloalkane to make a new C-C bond before so this is not really an entirely new idea. Notice that as indicated below, alkyne anion will attack the less hindered carbon of the epoxide, explaining the regiochemistry of the product.



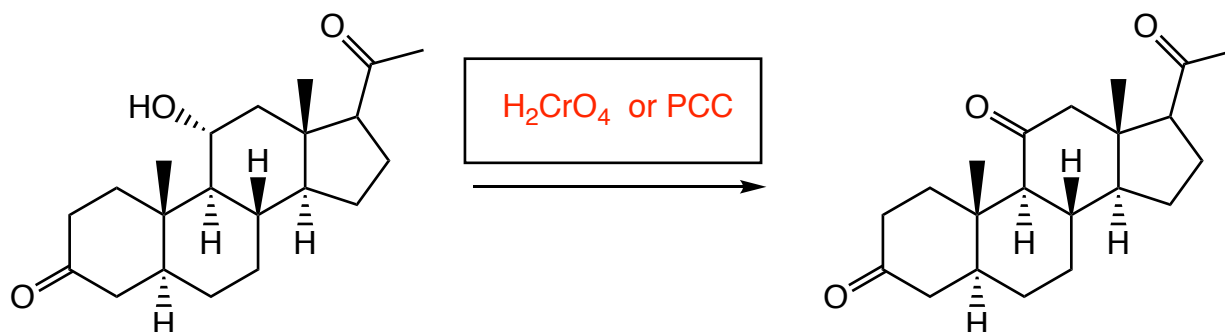
Signature _____

Pg 21 _____(8)

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



Note that this stereochemistry does not change because the alcohol is acting as the nucleophile so this chiral center is not inverted in the S_N2 step.



Have a great holiday break!!