

NAME (Print): _____

Chemistry 310M/318M

Dr. Brent Iverson

Final

December 15, 2009

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.

Page	Points	
1		(35)
2		(14)
3		(16)
4		(24)
5		(17)
6		(18)
7		(8)
8		(31)
9		(30)
10		(42)
11		(38)
12		(29)
13		(22)
14		(17)
15		(26)
16		(16)
17		(10)
18		(11)
Total		(404)
%		
T Score		
HW		
Total Grade		

(HW score + Exam Grade) \Rightarrow

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.

(Your signature)

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. 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.

		Electron		Proton		Neutron		Photon		Neutrino		Influence in Electrodynamics		0		1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18		19		20		21		22		23		24		25		26		27		28		29		30		31		32		33		34		35		36		37		38		39		40		41		42		43		44		45		46		47		48		49		50		51		52		53		54		55		56		57		58		59		60		61		62		63		64		65		66		67		68		69		70		71		72		73		74		75		76		77		78		79		80		81		82		83		84		85		86		87		88		89		90		91		92		93		94		95		96		97		98		99		100		101		102		103		104		105		106		107		108		109		110		111		112		113		114		115		116		117		118		119		120		121		122		123		124		125		126		127		128		129		130		131		132		133		134		135		136		137		138		139		140		141		142		143		144		145		146		147		148		149		150		151		152		153
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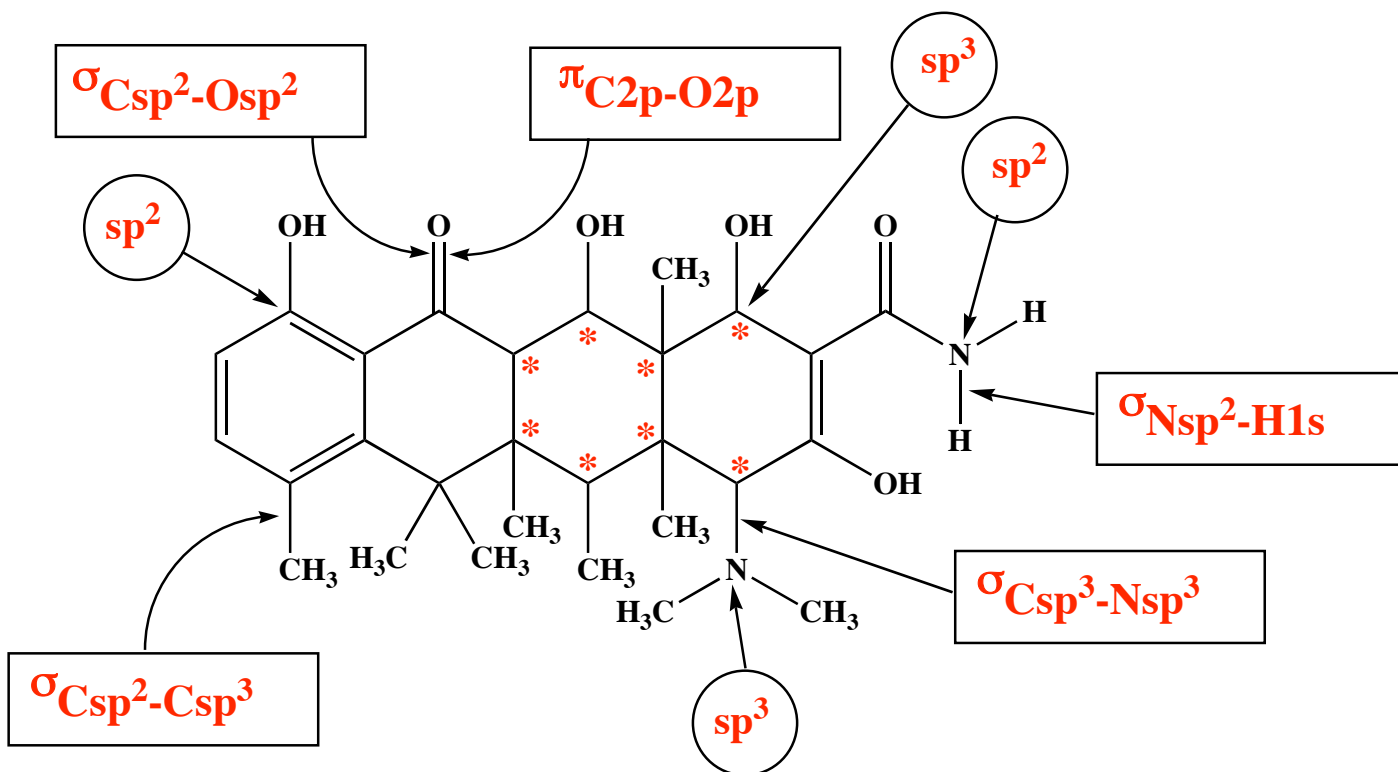
Compound		pK _a
Hydrochloric acid	H-Cl	-7
Protonated alcohol	$\text{RCH}_2\text{O}^+\text{H}_2$	-2
Hydronium ion	H_3O^+	-1.7
Acetic acid	$\text{CH}_3\text{C}(=\text{O})\text{H}$	4.8
Ammonium ion	H_4N^+	9.2
Thiols	RCH_2SH	10-12
β-Dicarbonyls	$\text{RC}(=\text{O})\text{CH}_2\text{C}(=\text{O})\text{R}'$	10
Ethyl ammonium ion	$\text{H}_3\text{N}^+\text{CH}_2\text{CH}_3$	10.8
β-Ketoesters	$\text{RC}(=\text{O})\text{CH}_2\text{C}(=\text{O})\text{OR}'$	11
β-Diesters	$\text{ROC}(=\text{O})\text{CH}_2\text{C}(=\text{O})\text{OR}'$	13
Water	HOH	15.7
Alcohols	RCH_2OH	15-19
Acid chlorides	$\text{RC}(=\text{O})\text{H}_2\text{CCl}$	16
Aldehydes	$\text{RC}(=\text{O})\text{H}_2\text{CH}$	18-20
Ketones	$\text{RC}(=\text{O})\text{H}_2\text{CR}'$	18-20
Esters	$\text{RC}(=\text{O})\text{H}_2\text{COR}'$	23-25
Terminal alkynes	$\text{RC}\equiv\text{C-H}$	25
LDA	$\text{H-N}(i\text{-C}_3\text{H}_7)_2$	40
Terminal alkenes	$\text{R}_2\text{C}=\text{CH}_2$	44
Alkanes	$\text{CH}_3\text{CH}_2\text{H}$	51

1. (5 pts) The most important question is chemistry is:

Where are the electrons?

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

Next, in the circles provided, write the hybridization state of the atoms indicated with the arrows.



3. (1 pt each) On the above structure of tetracycline, the stereochemistry is not indicated. On the above structure indicate **EACH CHIRAL CENTER WITH AN ASTERISK (*)**.

4. (5 pts). Tetracycline is sold as a single stereoisomer. How many possible stereoisomers are there for tetracycline? It is OK to leave your answer in the form of an exponential. No need to multiply it out.

$2^8 = 256$

5. (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 significant number of points, so read them carefully and do not second guess yourself. We are not trying to trick you into the wrong answer.

A. A bond dipole moment is the quantitative vector quantity that describes unequal electron distribution in a bond.

B. For organic chemistry, it is best to think of electron density as particles, described by particle equations such as Kepler's laws of motion, which were recently passed as part of the economic bailout legislation.

C. For organic chemistry, it is best to think of electron density as waves, described by wave equations (NOT discrete particles orbiting the nucleus!)

D. The preferred staggered conformation of butane is referred to as "gotcha", rather than the "anti" or "eclipsed" conformation.

E. Diastereomers are stereoisomers that are not enantiomers.

F. There is an absolute link between "R" and "S", "D" and "L" and "+" and "-", because "R" is always "+" and "S" is always "-". "D" and "L" always stand for the Duckworth-Lewis model of computing Cricket scores when the match is prematurely interrupted.

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

H. Samples of enantiomers rotate the plane of plane polarized light to an equal extent, but in opposite directions.

I. Anti stereochemistry of addition means that the atoms add to either side of a C=C double bond, syn means they add to the same side, and mixed means they add both syn and anti in the same reaction.

J. Bulky groups (who obviously used performance enhancing steroids) on the back of an alkyl halide increase non-bonded interaction strain, and thereby accelerate an S_N2 reaction.

K. Because of the electron density of the pi bond, alkenes react as nucleophiles to make new bonds with molecules containing high partial positive charge (electrophiles).

L. Alkanes react with halogens, usually Cl_2 and Br_2 , in the presence of radical initiators like peroxides, heat or light to generate alkyl halides via the radical chain reaction mechanism.

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

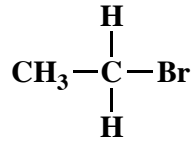
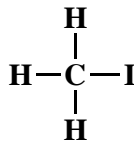
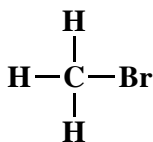
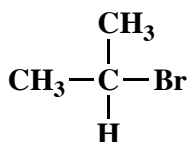
N. E2 (Elimination, Bimolecular) - anti-periplanar - involves a base reacting with the proton anti-periplanar to the leaving group (that simultaneously leaves) in a single step to give an alkene.

O. 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!

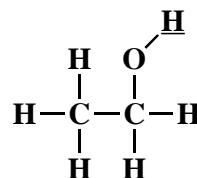
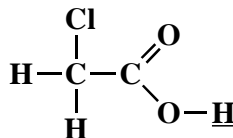
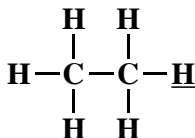
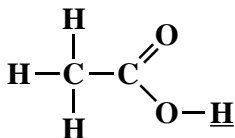
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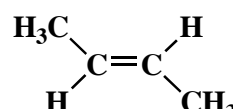
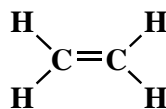
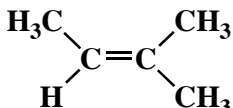
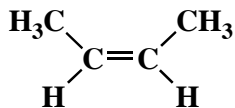
6. (4 pts total) For the following series of compounds, rank them in order of most to least reactive with nucleophiles via an S_N2 mechanism by writing a **1** under the **most reactive by an S_N2 mechanism** all the way to a **4** under the **least reactive by an S_N2 mechanism**.

relative
rank:**4****2****1****3**

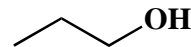
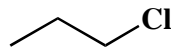
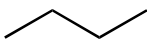
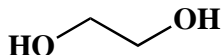
7. (4 pts) Rank the following with respect to relative acidity. Put a **1** under the molecule that is **most acidic**, and a **4** under the molecule that is **least acidic**. The acidic H atom is underlined on the structure. Make sure you know which acid gets the **1** (most acidic) as I do not want any of you to know the answer, but number them backwards!

relative
rank:**2****4****1****3**

8. (4 pts) **Stability of alkenes:** Place a **1** under the most stable (i.e. most favored Zaitzev product) and a **4** under the least stable (least stable Zaitzev product) alkene

relative
rank:**3 (cis)****1****4****2 (trans)**

9. (4 pts total) For the following compounds, rank them in order of highest to lowest boiling point, with a **1** under the molecule with the **highest boiling point** and a **4** under the molecule with the **lowest boiling point**.

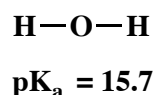
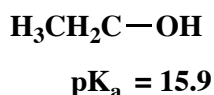
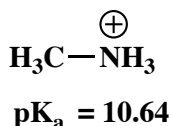
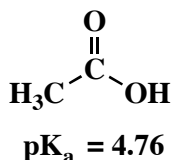
relative
rank:**1****4****3****2**

Are you sure you ranked them in the correct order according to the directions????

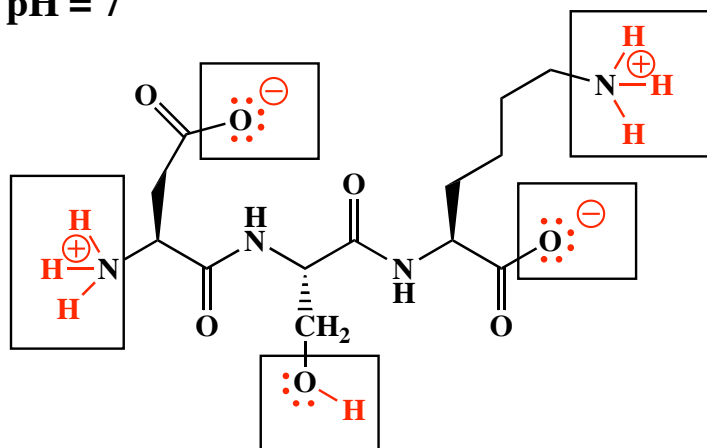
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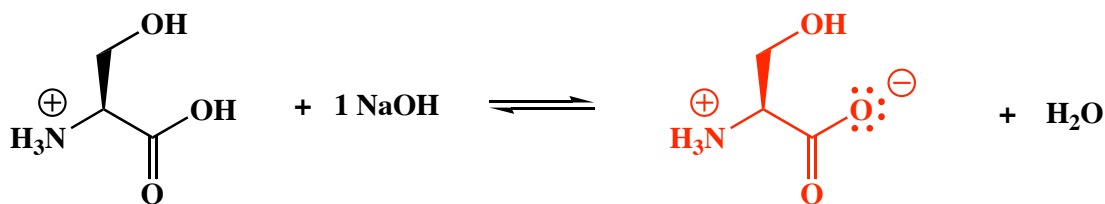
10. (12 pts) Complete the following structure by adding appropriate numbers of lone pair electrons, H atoms, and formal charges to the atoms in the boxes. You must adjust your answers to indicate the predominant species at pH 7. This problem is testing your understanding of the relationship of protonation state to pH to pKa values for certain functional groups we have discussed. Next, in the space provided, write the overall charge on the molecule at pH 7. For your reference, here are the relevant pKa values:



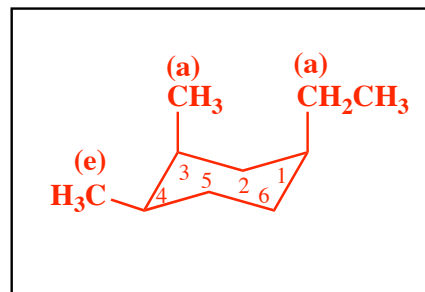
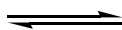
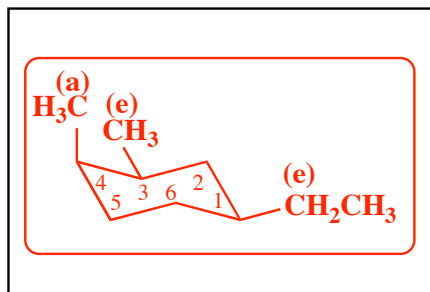
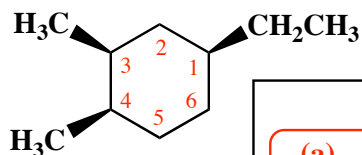
pH = 7

Total charge on molecule: 0

11. (4 pts) Using the pKa information from above (Problem 10), draw the predominant form of the following molecule (the amino acid serine) when it is mixed with exactly one equivalent of NaOH. In other words, when equal numbers of each kind of molecule are mixed.



12. (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.

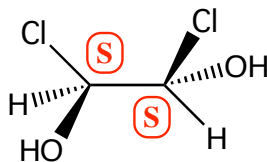
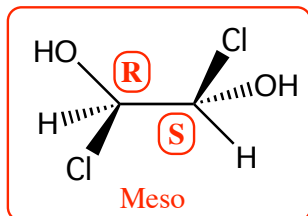


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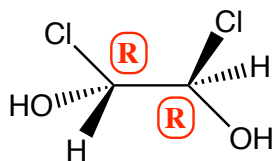
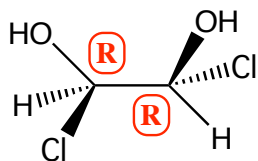
Pg 5 _____(17)

13. (8 pts) 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.**

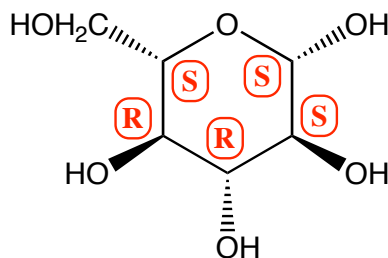
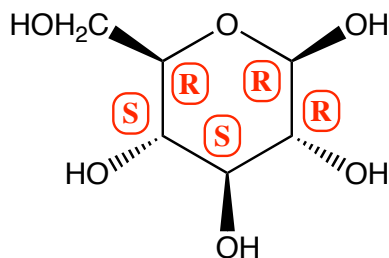
Relationship



Diastereomers



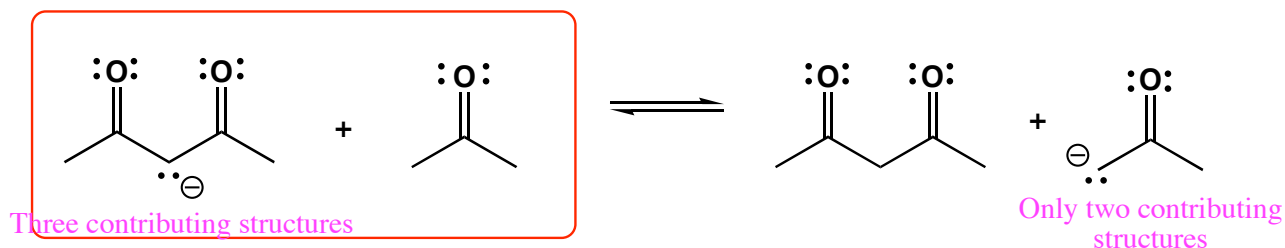
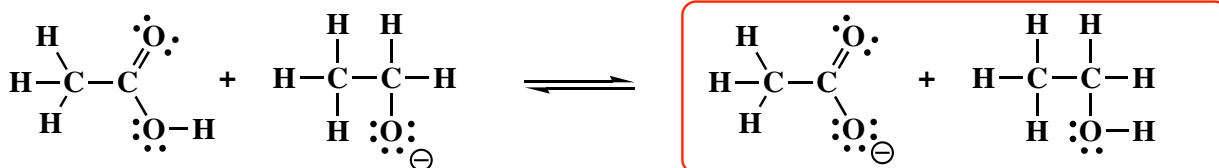
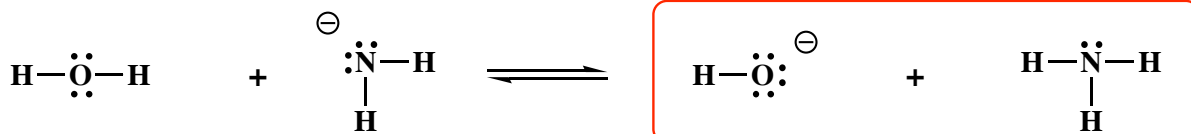
Same Molecule



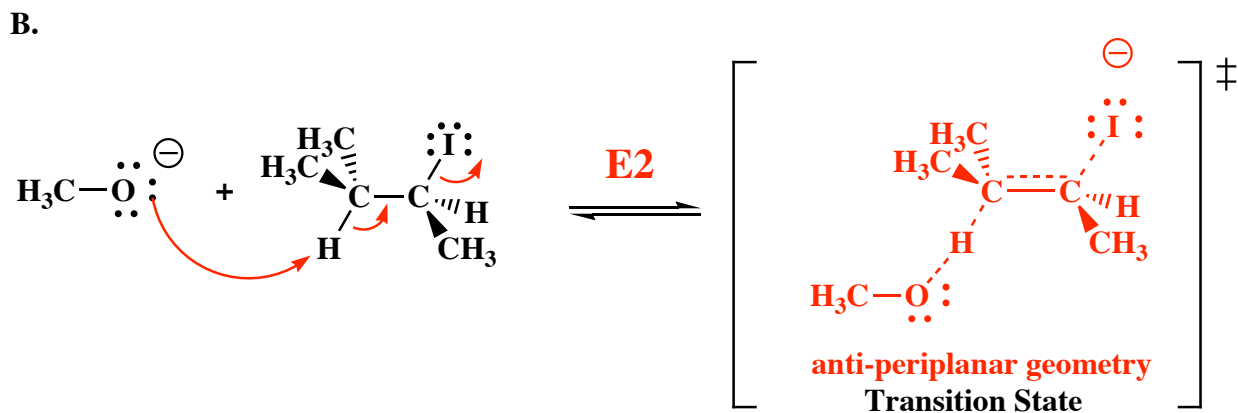
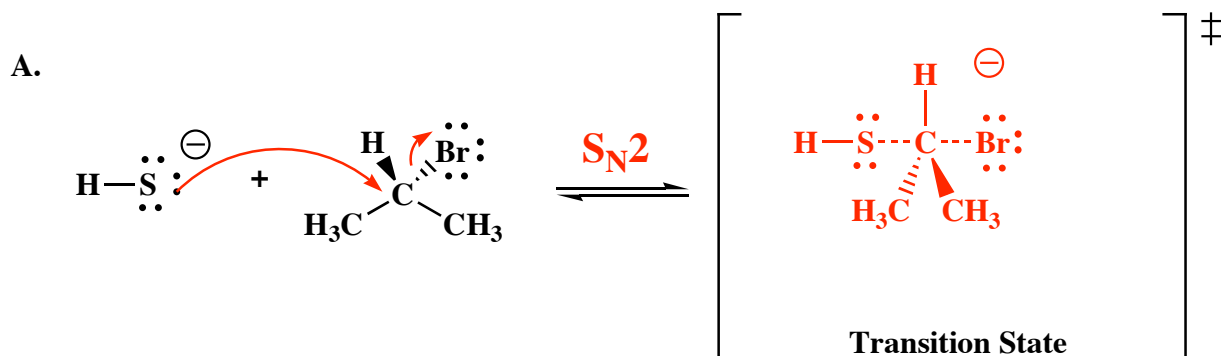
Enantiomers

14. (9 pts) For each acid-base reaction, **circle the side of the equation that predominates at equilibrium**.

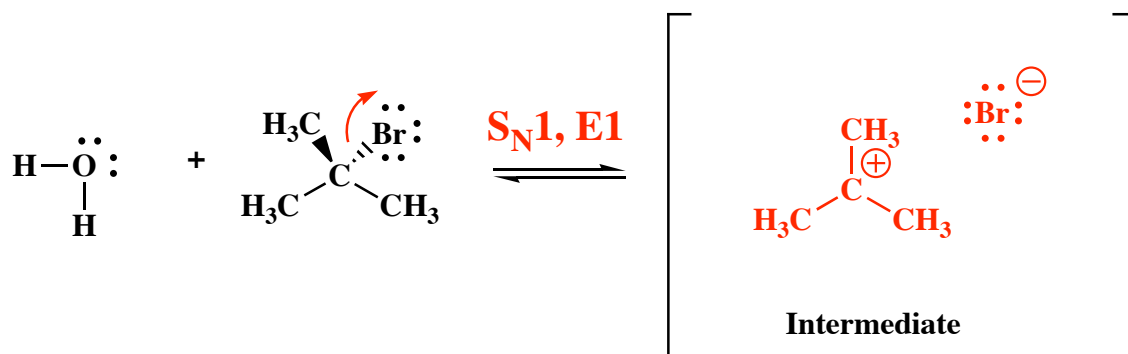
Identify the stronger and weaker acids by comparing relative stabilities of the anions which are the conjugate bases of the two acids. Equilibrium favors formation of the weaker acid. You will notice this means you circled the side with the more stable anion.



15. (13 pts total) For each set of reagents below, draw the **key transition state** that occurs during the reaction. Use dotted lines to indicate bonds that are in the process of being broken or made. Write any formal charges that you think are important. On the starting structures, draw all appropriate arrows to indicate the flow of electrons.



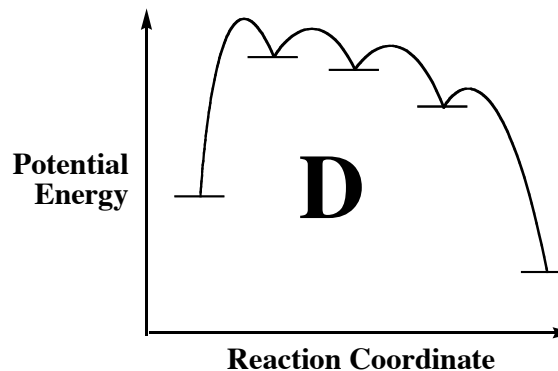
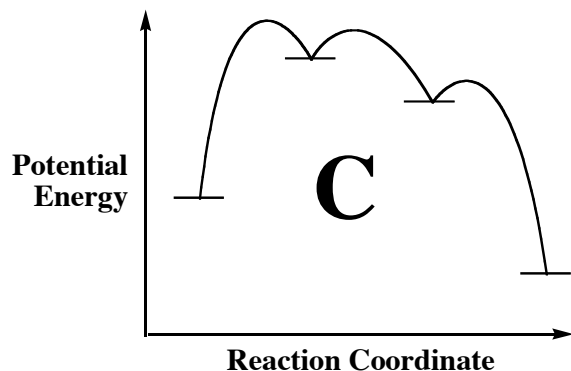
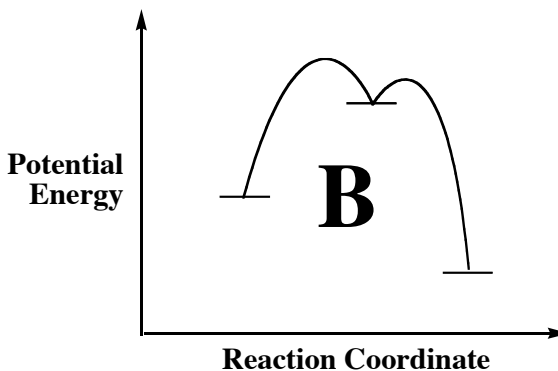
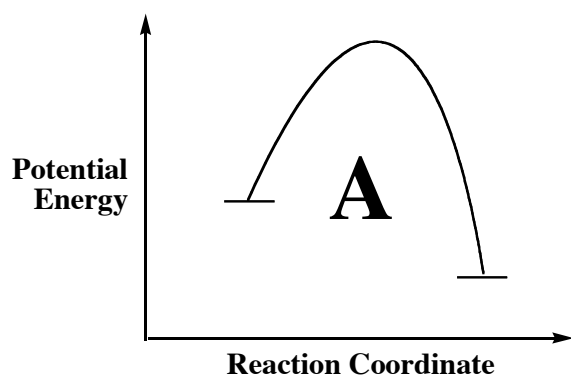
16. (5 pts total) For the set of reagents below, draw the **first key intermediate** that occurs during the indicated reaction. We do not want the entire mechanism or products, just the first key intermediate. Write any formal charges that you think are important. On the starting structures, draw all appropriate arrows to indicate the flow of electrons.



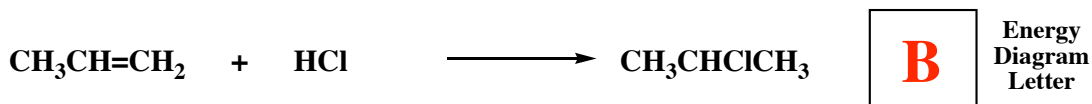
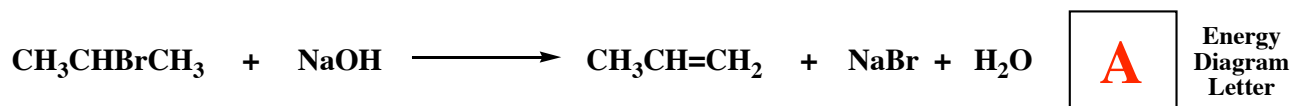
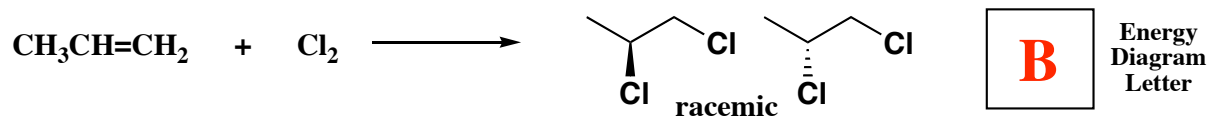
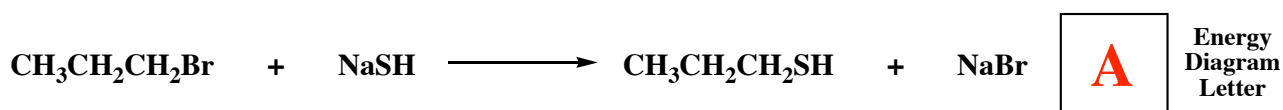
Signature _____

Pg. 7 _____ (8)

17. (8 pts.) Shown below are four different energy diagrams. Each is labeled with a letter. Use these letters to answer questions at the bottom of the page, and on the next mechanism page.



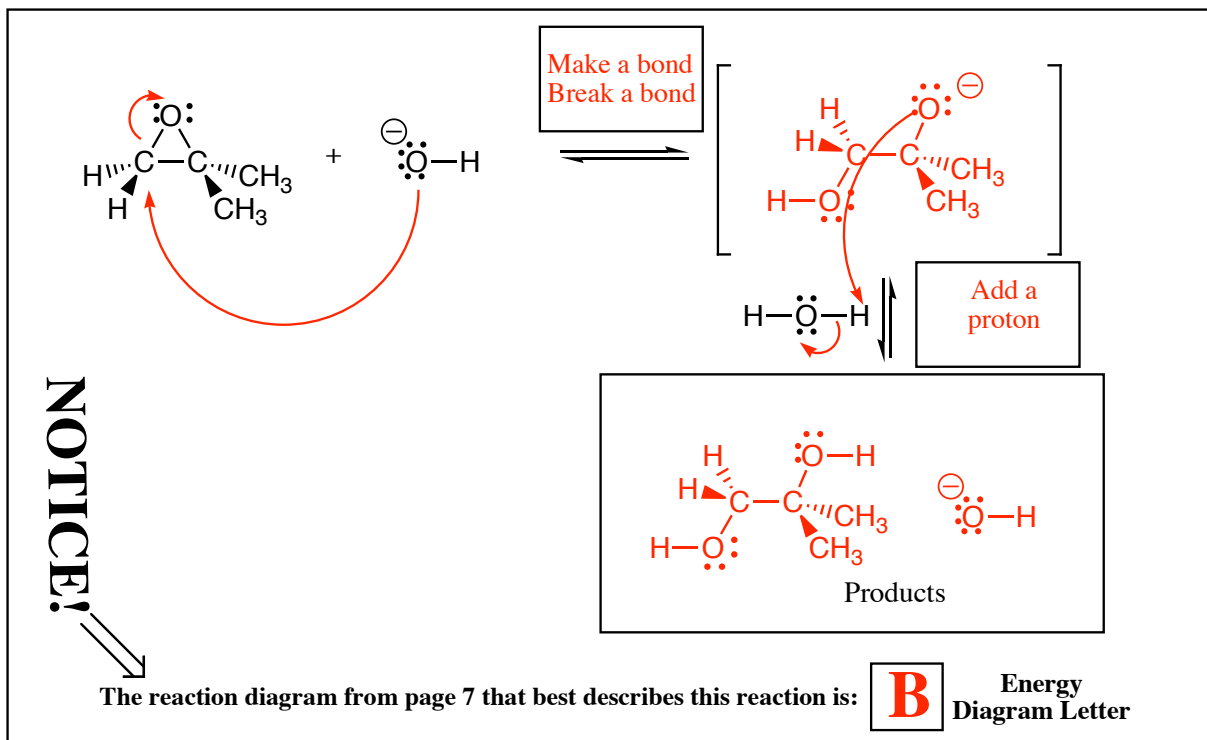
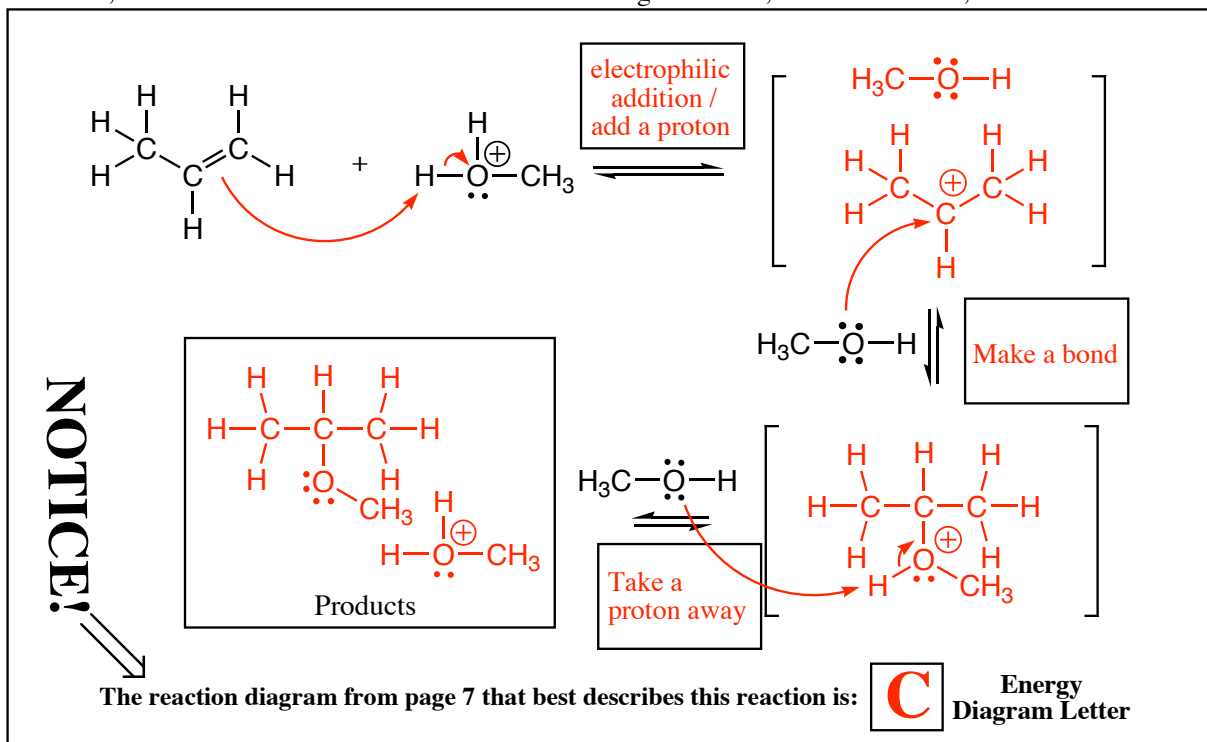
In the boxes provided, write the letter of the energy diagram that best describes the mechanism of the following reactions:



Signature _____

Pg 8 _____ (31)

14. (31 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) For the following two reactions, fill in the details of the mechanisms. Draw the appropriate chemical structures and use arrows to show how pairs of electrons are moved to make and break bonds during the reaction. Make sure to show all lone pairs and all formal charges. Indicate stereochemistry where appropriate. Draw all products of each step. In the boxes provided next to the arrows, state what kind of mechanistic element is being described, i.e. make a bond, etc.



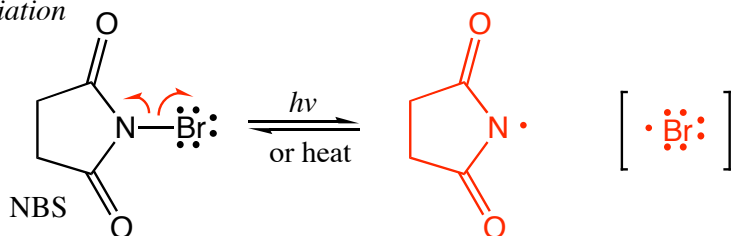
Signature _____

Pg 9 _____ (30)

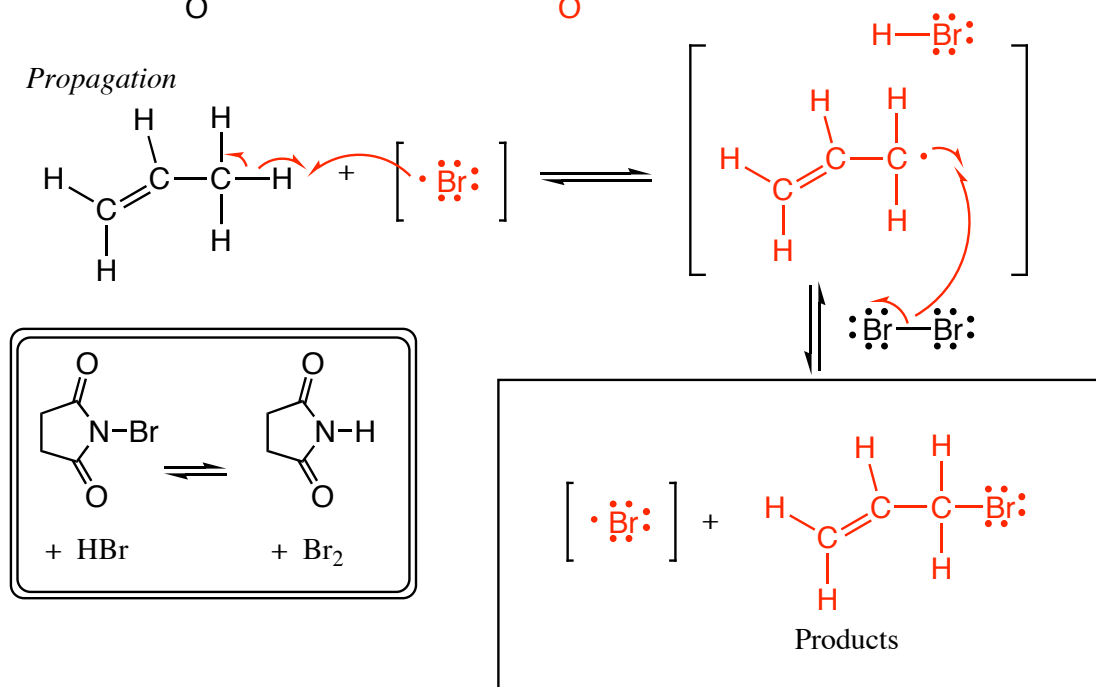
14. (30 pts.) Read these directions carefully. Read these directions carefully. (It was worth repeating) For the following reaction, fill in the details of the mechanism. Draw the appropriate chemical structures and use arrows to show how electrons are moved during the reaction. Make sure to show all electrons and all formal charges. Indicate stereochemistry where appropriate. Draw all products of each step.

Allylic Halogenation

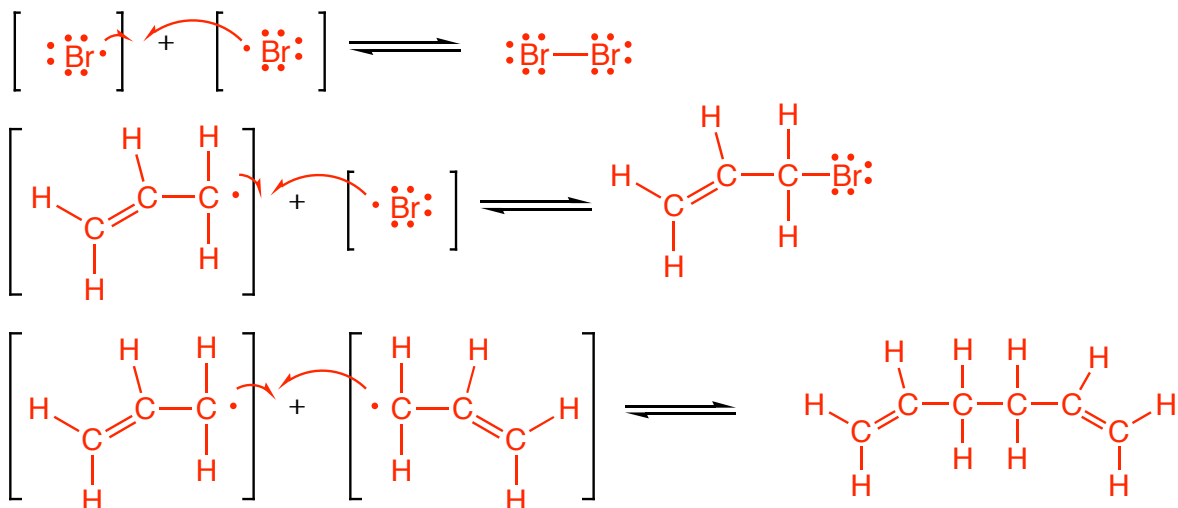
Initiation



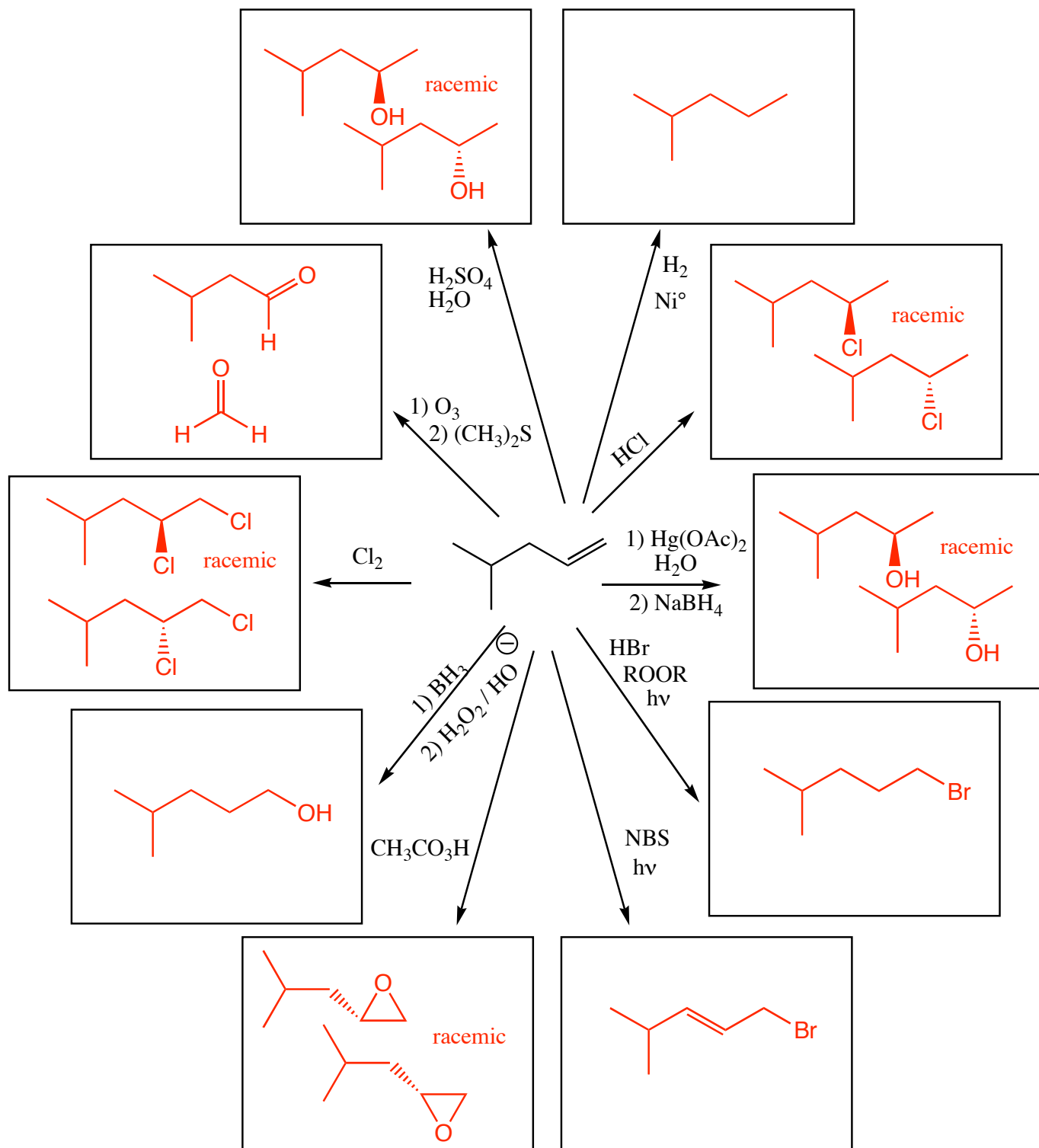
Propagation



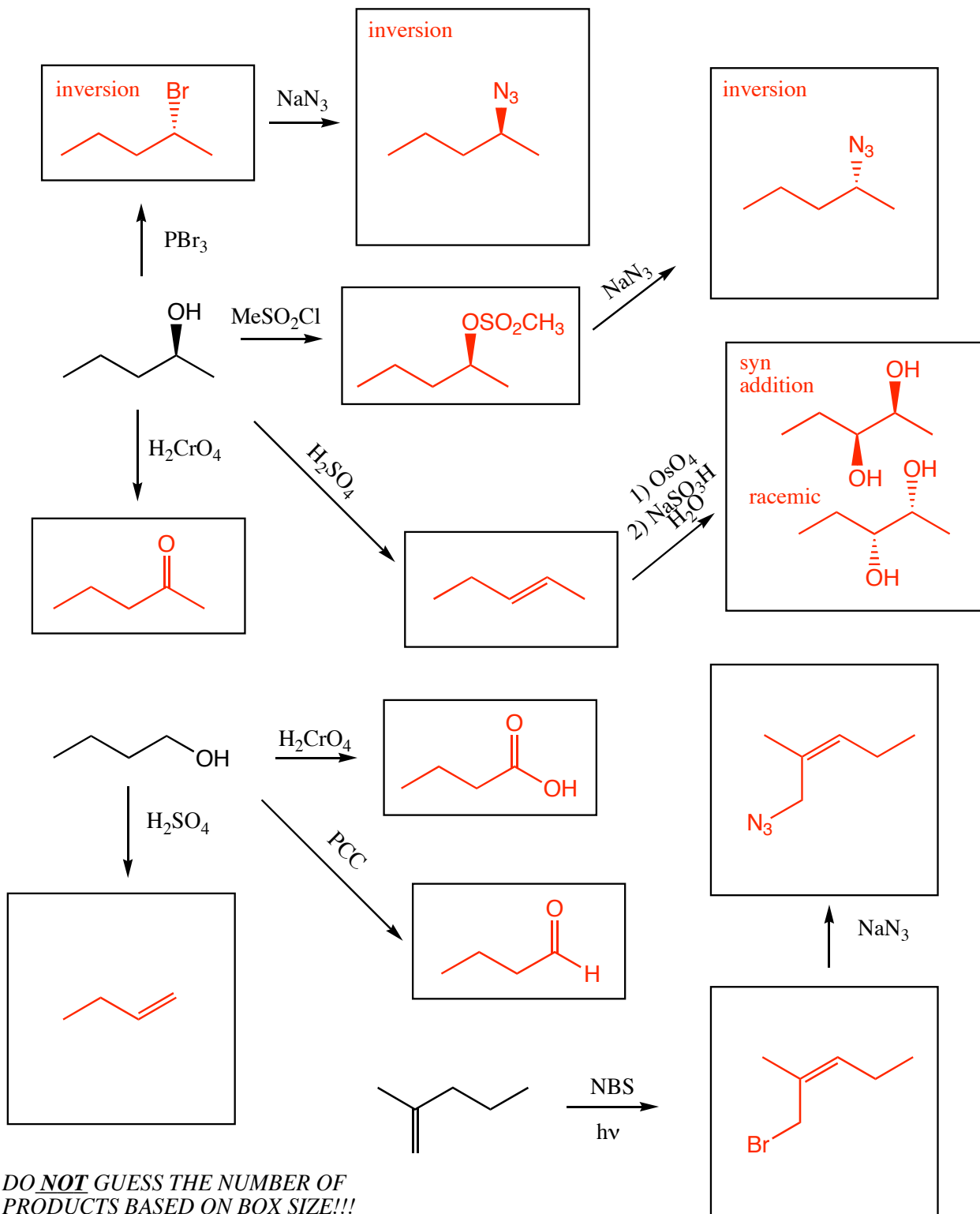
Termination



15. (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.



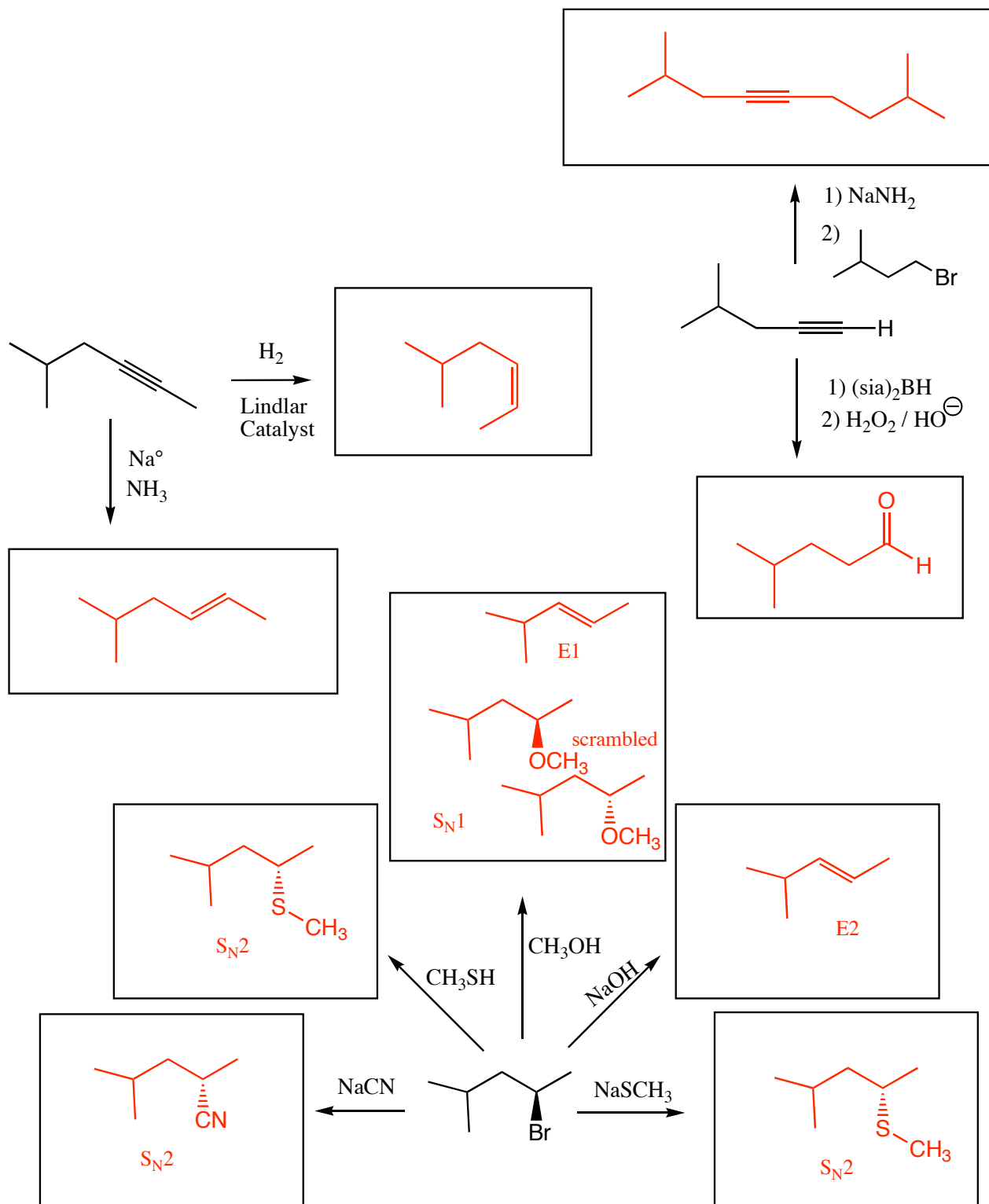
15. (3 or 5 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements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



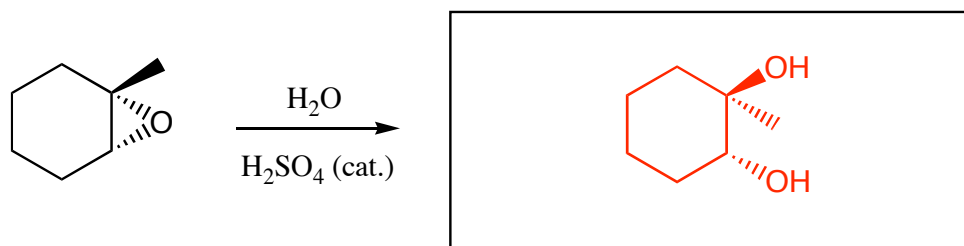
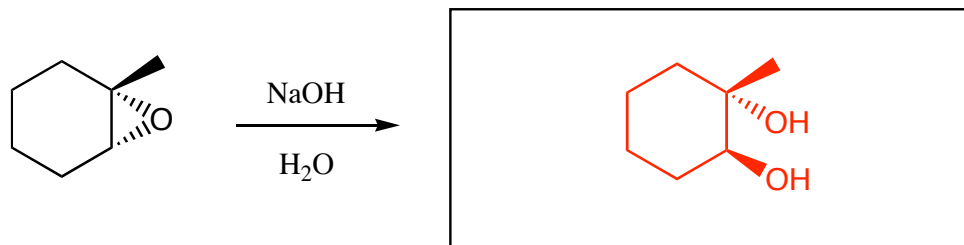
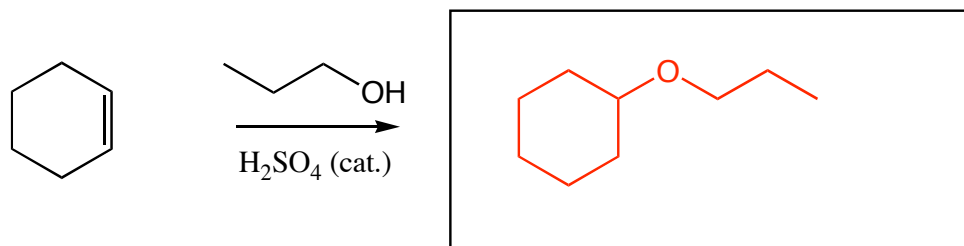
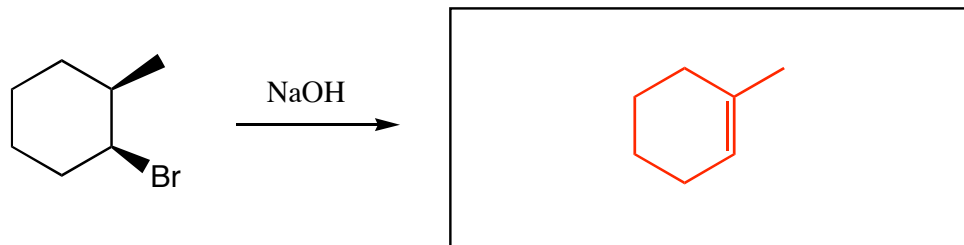
Signature _____

Pg 12 _____ (29)

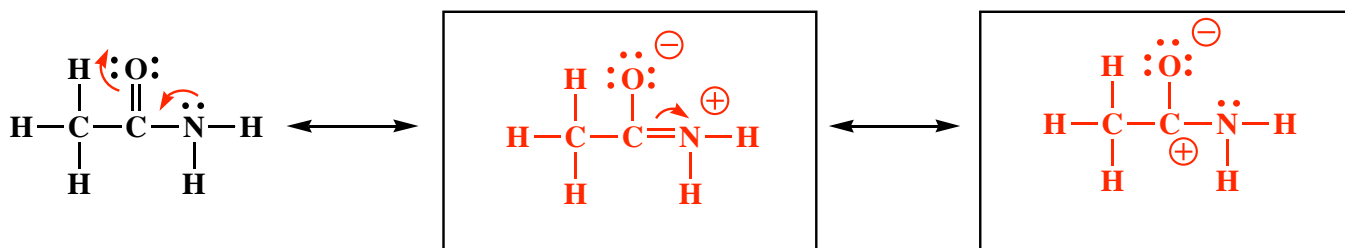
15. (3 or 5 pts each) For the following, complete the reactions with the predominant product or products. You must indicate stereochemistry with wedges and dashes. You must draw all stereoisomers produced as predominant products and write "racemic" under the structures when appropriate. Assume no rearrangements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



15. (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.

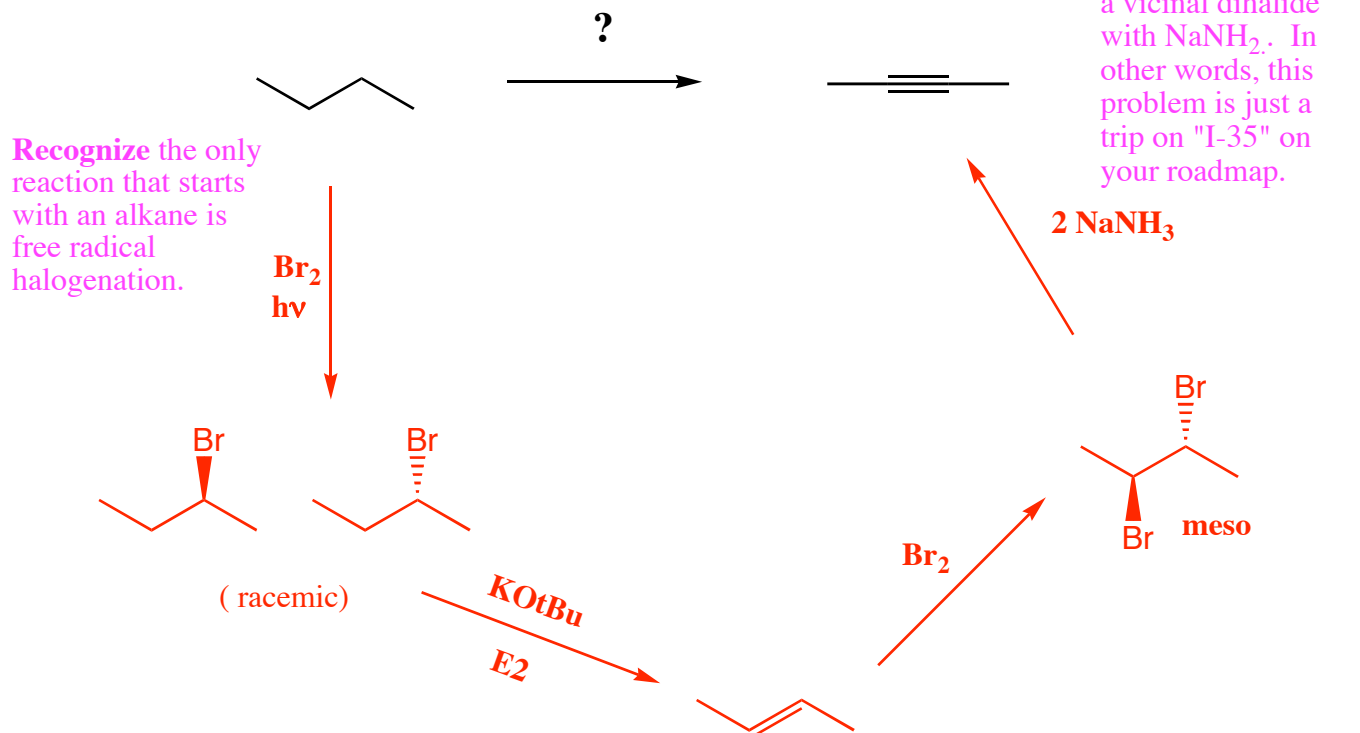


16. (10 pts) Amides are best represented as the hybrid of three contributing structures. Draw the second and third important contributing structures in the spaces provided, including all lone pairs and formal charges. For the two structures on the left, use arrows to indicate the movement of electrons to give the structures you drew.

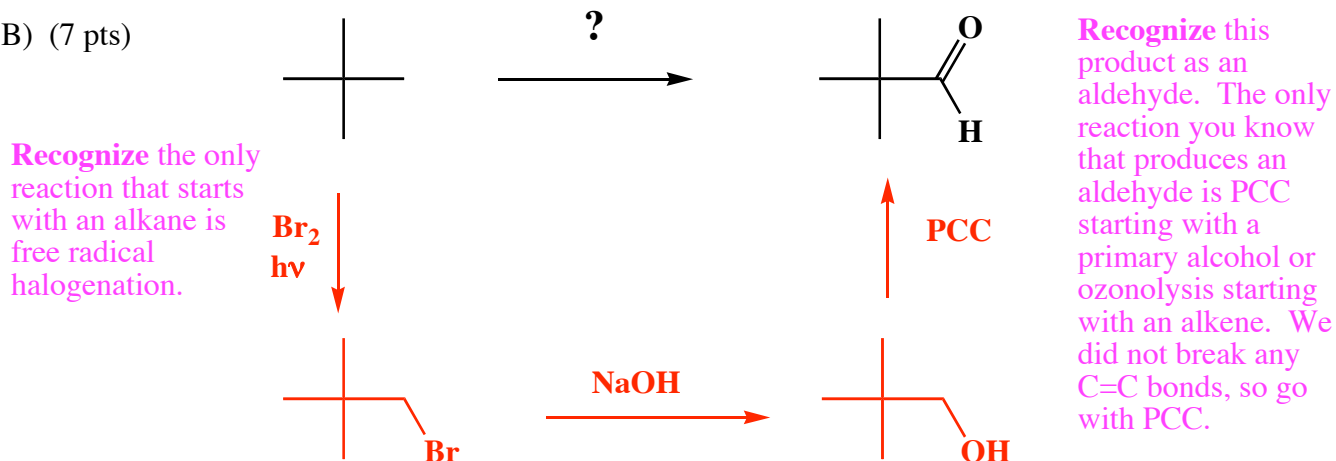


17. These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned provided that the product(s) you draw for each step is/are the predominant one(s). Show all the reagents you need. Show each molecule synthesized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

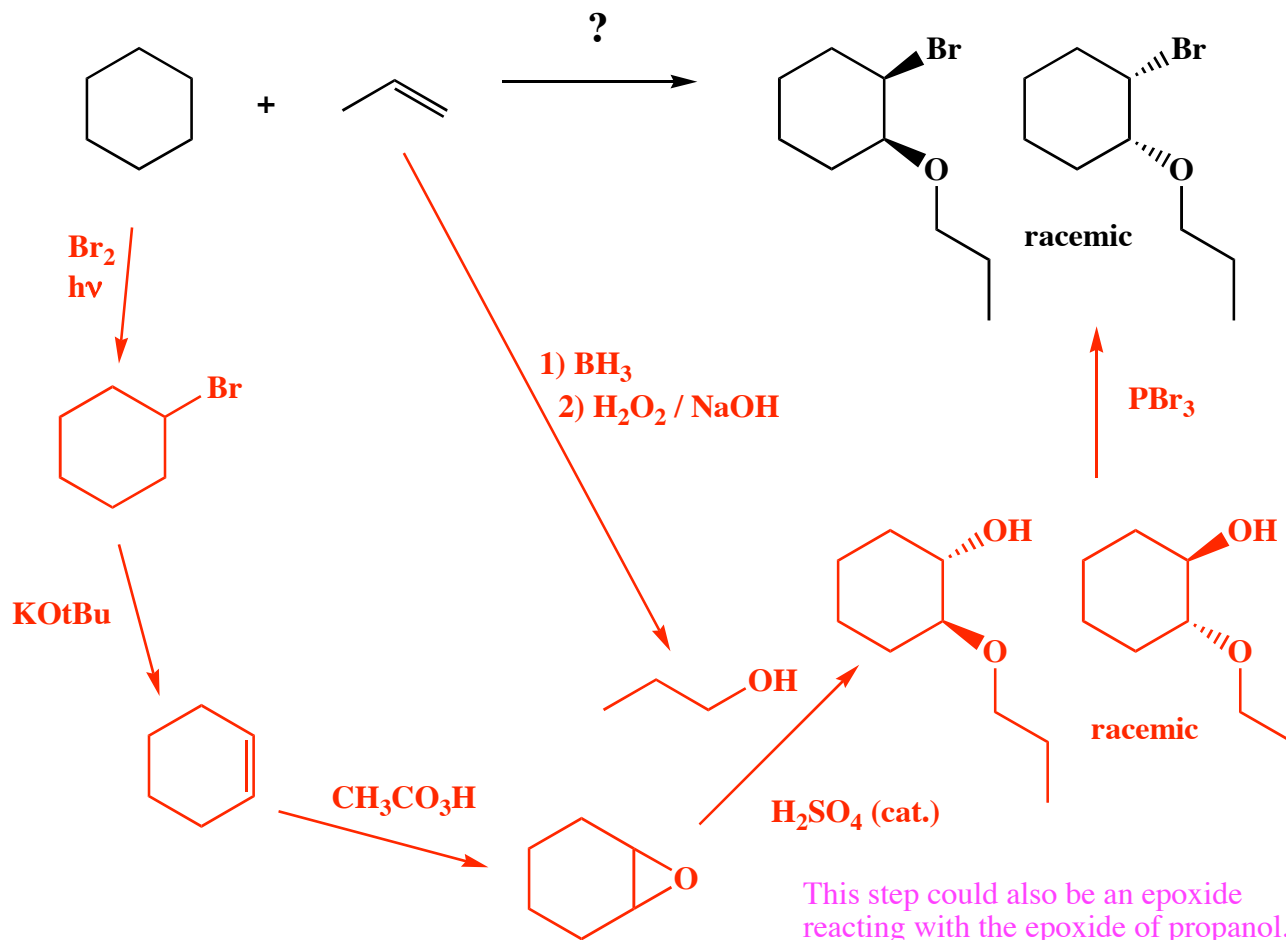


B) (7 pts)



17. 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) (16 pts)

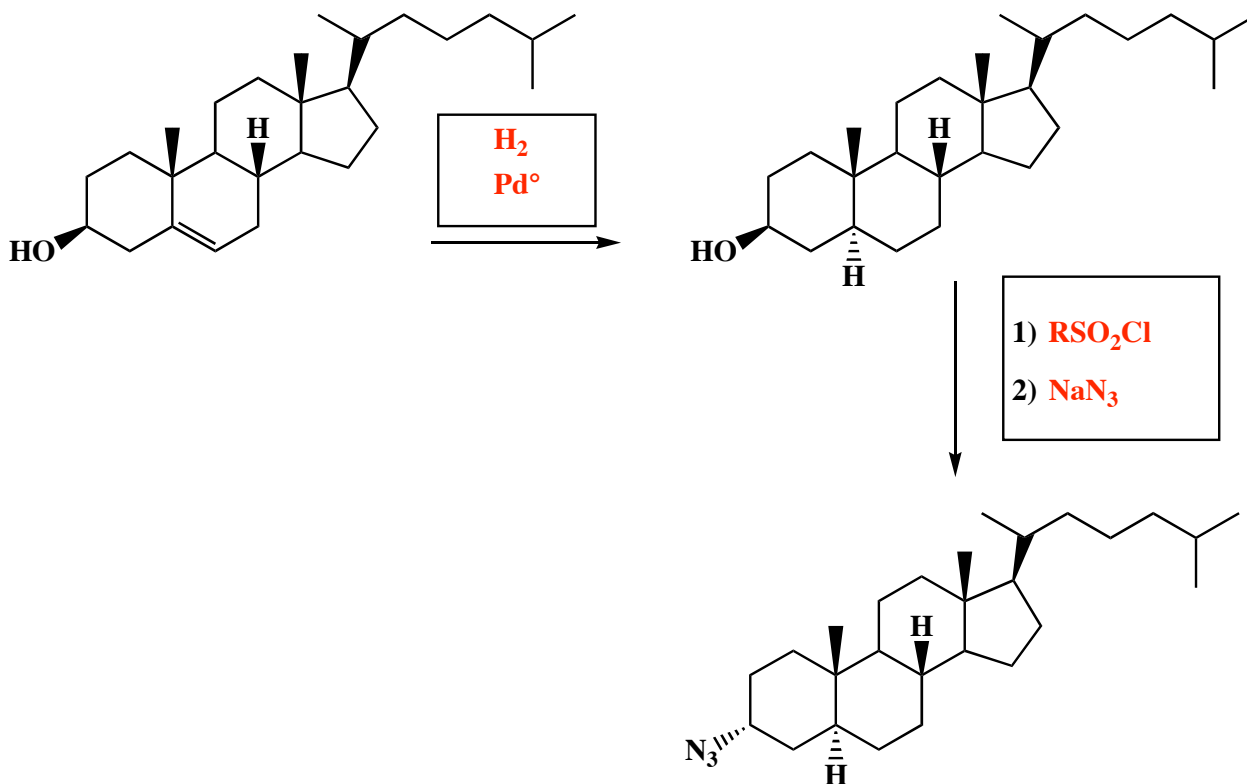
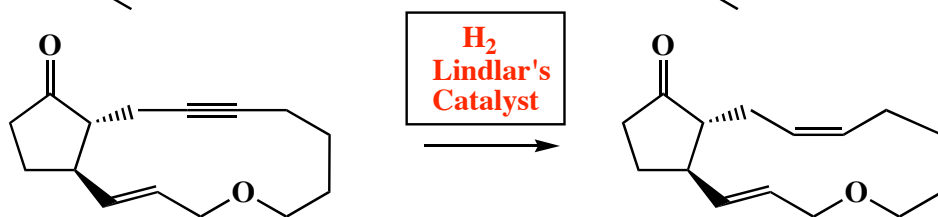
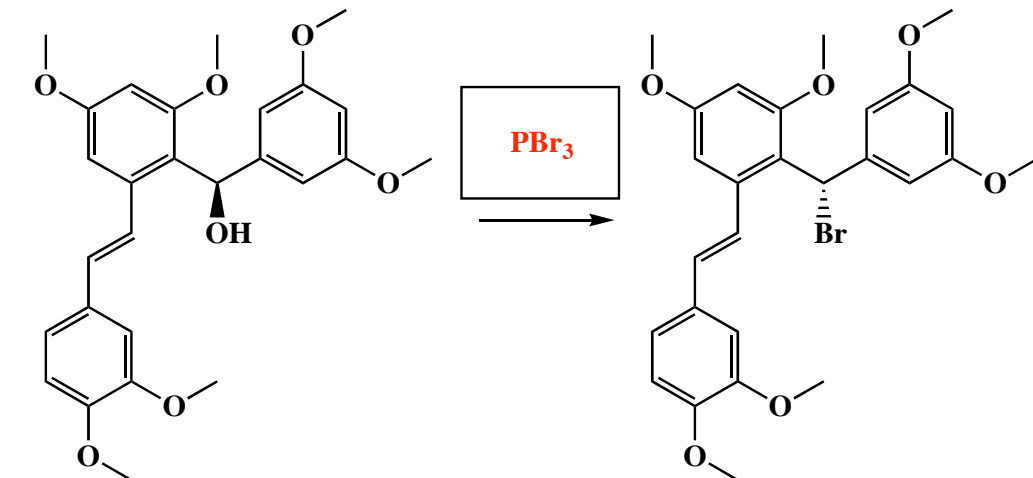


Recognize first that the product is assembled from one molecule of cyclohexane and one three-carbon piece, through formation of an ether functional group. **Recognize** also the unusual *cis* relationship of the functional groups on the cyclohexane product. You cannot make this functional arrangement directly. Hypothesize that this could come from a hydroxy-ether that is *trans*, followed by the stereochemistry inversion at the site of the $-\text{OH}$ due to a PBr_3 reaction as the last step. **Recognize** further that a *trans* hydroxy-ether is the product of an epoxide reacting with an alcohol using acid catalysis (or an alkoxide). Therefore, finish the synthesis by converting the starting materials to an epoxide (1-35 to get to the alkene then RCO_3H) and primary alcohol (hydroboration/oxidation to give the non-Markovnikov product alcohol).

Signature _____

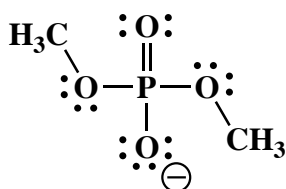
Pg 17 _____(10)

18. (12 pts) As we emphasized at the end of the semester, a key paradigm in organic chemistry is that reactions of functional groups work the same in complex molecules as they do in the simpler molecules we usually examine in first semester courses. The following complex molecules and reactions were used in actual syntheses. In the space provided, write the reagents that will produce the transformation shown.

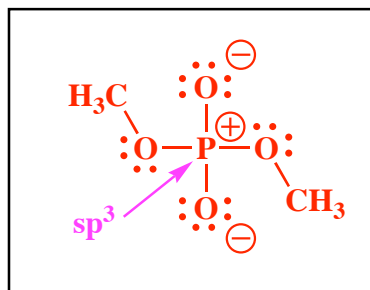
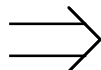


19. (8 pts) At the beginning of the semester I pointed out that two types of functional groups common to biological systems are written in an inappropriate way the vast majority of the time. Below is drawn the common but inappropriate structures. In the spaces provided, draw the more accurate structures that are a much better representation of the true hybridization state of the central atom.

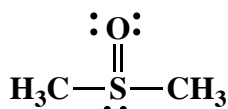
A.



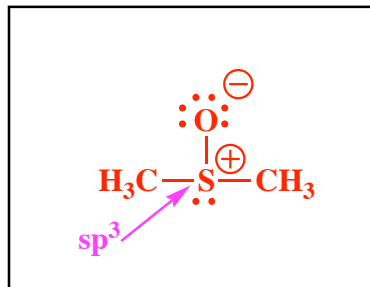
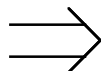
A more
accurate
representation
would be:



B.



A more
accurate
representation
would be:



C. What is the hybridization state implied for the P and S atoms in the structures you drew?

sp³

20. (3 pts.) The chirality of amino acids is still commonly referred to with an old terminology in which "D" and "L" are used, not "R" and "S". The "D" and "L" refer to comparison of the amino acid with another molecule. In the space provided, state the molecule that is the basis of the "D" and "L" assignment and briefly explain the basis for this designation.

The "D" and "L" designations refer to comparison of the chiral center of the amino acid with Dextrorotary (+) and Levorotary (-) glyceraldehyde.