Easily Legible Printed Name:_____

CHEM 3351 (100), Fall 2016
Professor Walba
Second Hour Exam
October 18, 2016

scores:

1) 20

2) 25

3) 25

4) 20

5) 10

_____

CU Honor Code Pledge: On my honor, as a University of Colorado at Boulder Student, I have neither given nor received unauthorized assistance.

Signature: Key

Recitation TA Name: _____

Recitation day and time: _____

This is a closed-book exam. The use of notes, calculators, scratch paper, or cell phones will not be allowed during the exam. You may use models brought in a clear Ziploc bag. Please put all your answers on the test in the appropriate place. Use the backs of the pages for scratch (there are two additional blank scratch sheets after the last page of the exam). DO NOT PUT ANSWERS ON THE SCRATCH SHEETS.

PLEASE read the questions very carefully!

PLEASE legibly print your name on each page of the exam.

Partial Periodic Table

1A	2A	3A	4A	5A	6A	7A	8A
1 H							2 He
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
						35 Br	
						53 I	

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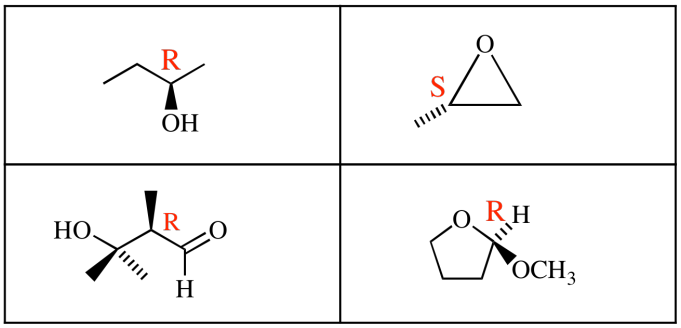
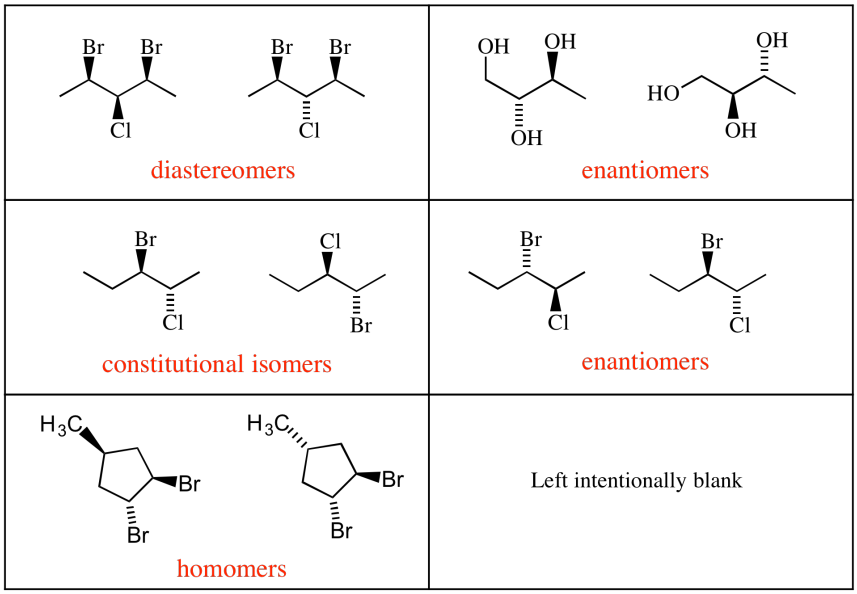
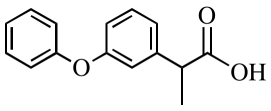
1 (20 pts) a) For each molecule below, carefully give the configuration of each tetrahedral stereocenter using the R/S stereochemical descriptor system.



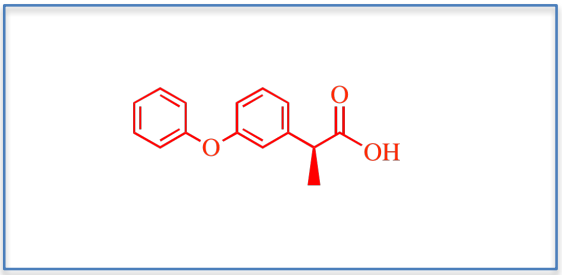
b) All of the following **pairs** of molecules (in each box) are isomers. For each of these pairs of molecules, describe their relationship using the standard organic pairwise descriptors for isomers (homomers, enantiomers, diastereomers, constitutional isomers). Put your answers just below the structures in the same box.



c) Nalfon, a non-steroidal anti-inflammatory drug, has the structure given at right - not showing stereochemistry.



The active drug has the (S) configuration.
Carefully draw the structure of (S)-Nalfon in the box, showing stereochemistry. Use the "Wedges and Dashes" method for showing the stereochemistry, as I did in the structures in parts a) and b) above.



Total points for this page:

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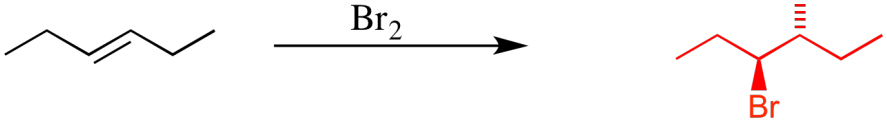
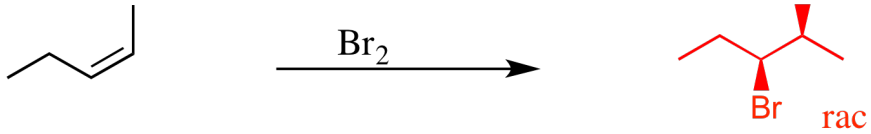
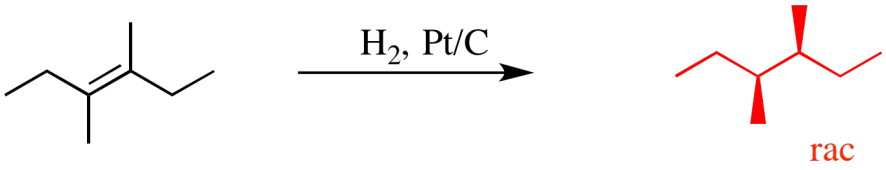
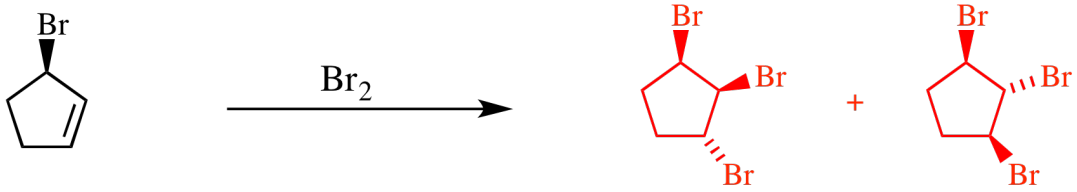
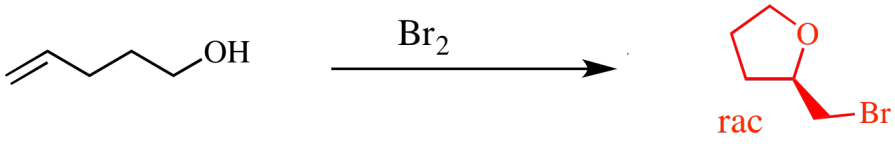
2) (25 pts) Give the single major product (or two major products if two are formed) for each of the following reactions, carefully showing stereochemistry using wedges and dashes if appropriate. If a racemate is formed, show only one enantiomer and label it "rac." Assume chiral starting materials are single pure enantiomers unless they are labeled "rac."

a) 

b) 

c) 

d) 

e) 

Hint: The molecular formula of this product is C_5H_9OBr

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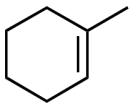
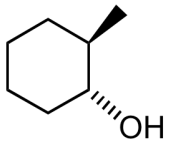
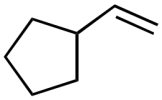
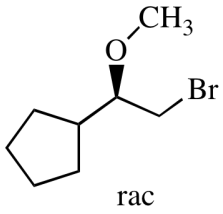
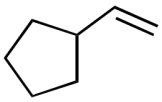
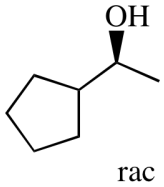
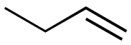
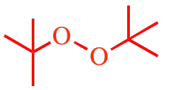
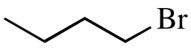
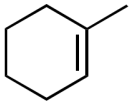
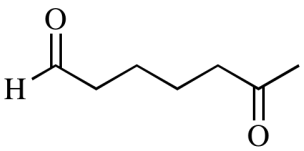
3) (25 pts) Propose reagents for accomplishing each of the following transformations. For reactions involving sequential addition of reagents, label the two steps using letters. Make your synthesis efficient (i.e. the target product should be the major product). Assume chiral starting materials and products are single pure enantiomers unless they are labeled "rac."

a)  a) $BH_3 \bullet THF$ b) H_2O_2, NaOH  rac

b)  Br_2, CH_3OH  rac

c)  a) $Hg(OAc)_2$, H_2O b) NaBH4, NaOH  rac

d)  HBr  or "peroxides" 

e)  a) O_3 b) $(CH_3)_2S$ 

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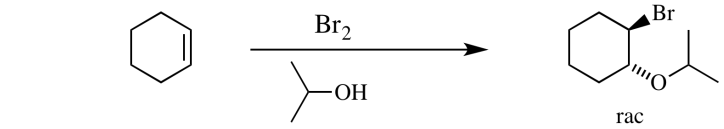
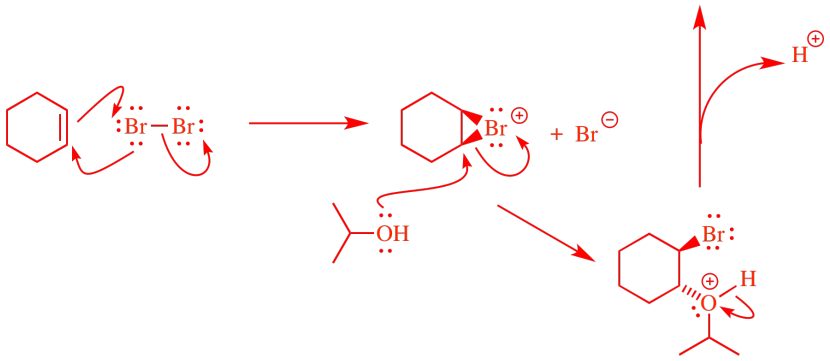
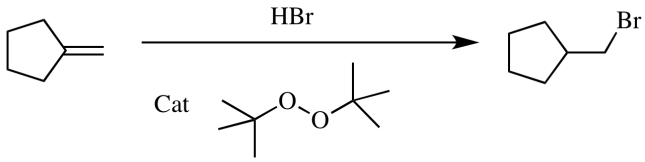
4) (20 pts) a) Propose an **arrow-pushing mechanism** for the following reaction. Be sure to carefully draw the structure of reactive intermediates in your mechanism (this is a hint – this reaction involves one or more reactive intermediates), but **do not show transition states**.

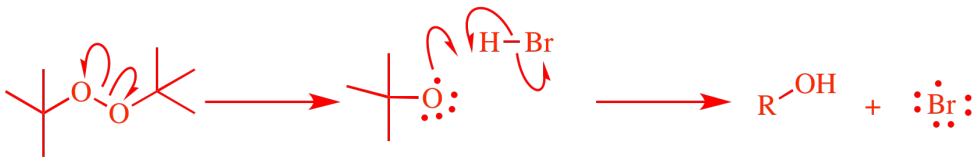




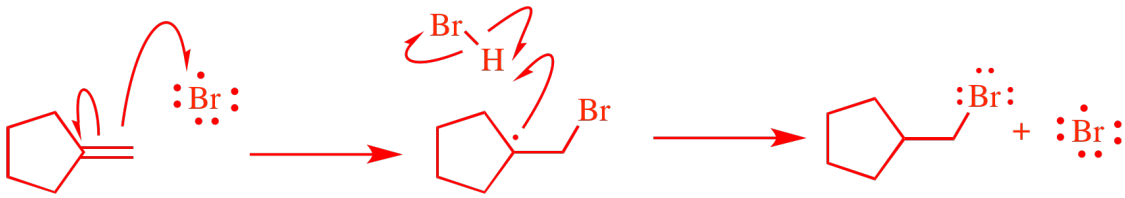
b) The following transformation proceeds in two distinct parts (Initiation and Propagation), as indicated below. Give an arrow-pushing mechanism for both parts of the reaction. Each part may require multiple steps. Be sure to carefully draw the structure of reactive intermediates, but **do not show transition states**.



Initiation



Propagation



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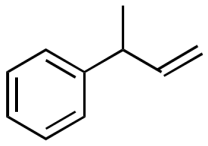
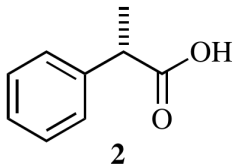
5) (10 pts) Suppose you isolate an alkene from a plant, and determine the basic structure to be compound **1** as shown below. This product is chiral, and being a natural product you figure it's probably a single enantiomer, but you don't know which enantiomer you have.



1

Luckily, you can buy compound **2** of known absolute configuration, with the optical rotation indicated (this compound is actually commercially available from 117 sources!).



2

$[\alpha]_{20}^{D} = +121.6°$

a) What is the configuration of compound **2**, using the R/S descriptors (put your answer in the box)? S

b) Explain **briefly** in the space below how you could use the information you have, coupled with one or more chemical reactions and the ability to measure the sign and magnitude of optical rotation (i.e. you have a polarimeter) to determine the stereochemical structure of your compound **1**. Be sure to give the reagents for accomplishing the chemical reaction(s) you are using.

Run an ozonolysis on compound **1**, using H_2O_2 workup – this gives compound **2** of unknown chirality
Purify the product, and measure the optical rotation under the standard conditions
If the rotation is +121.6°, compound **1** has the (R) configuration. If the rotation is -121.6, compound **1** has the (S) configuration.

 Total points for this page: