

CHEM 3351 (100), Fall 2015  
 Professor Walba  
 Second Hour Exam  
 October 20, 2015

scores:

1) 20

2) 20

3) 20

4) 20

5) 20

---

 100

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.

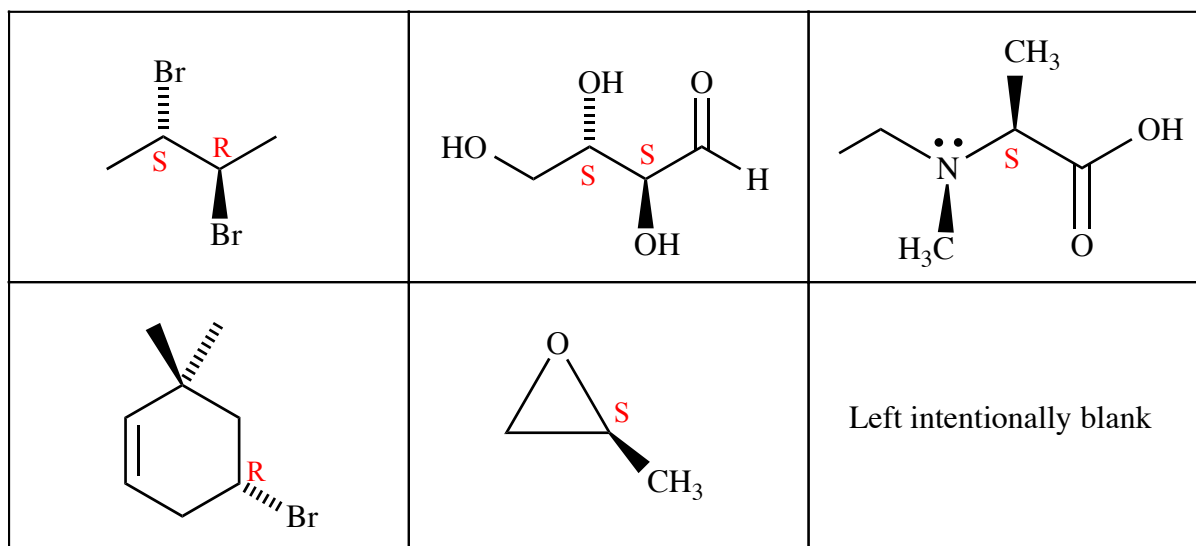
*PLEASE read the questions very carefully!*

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

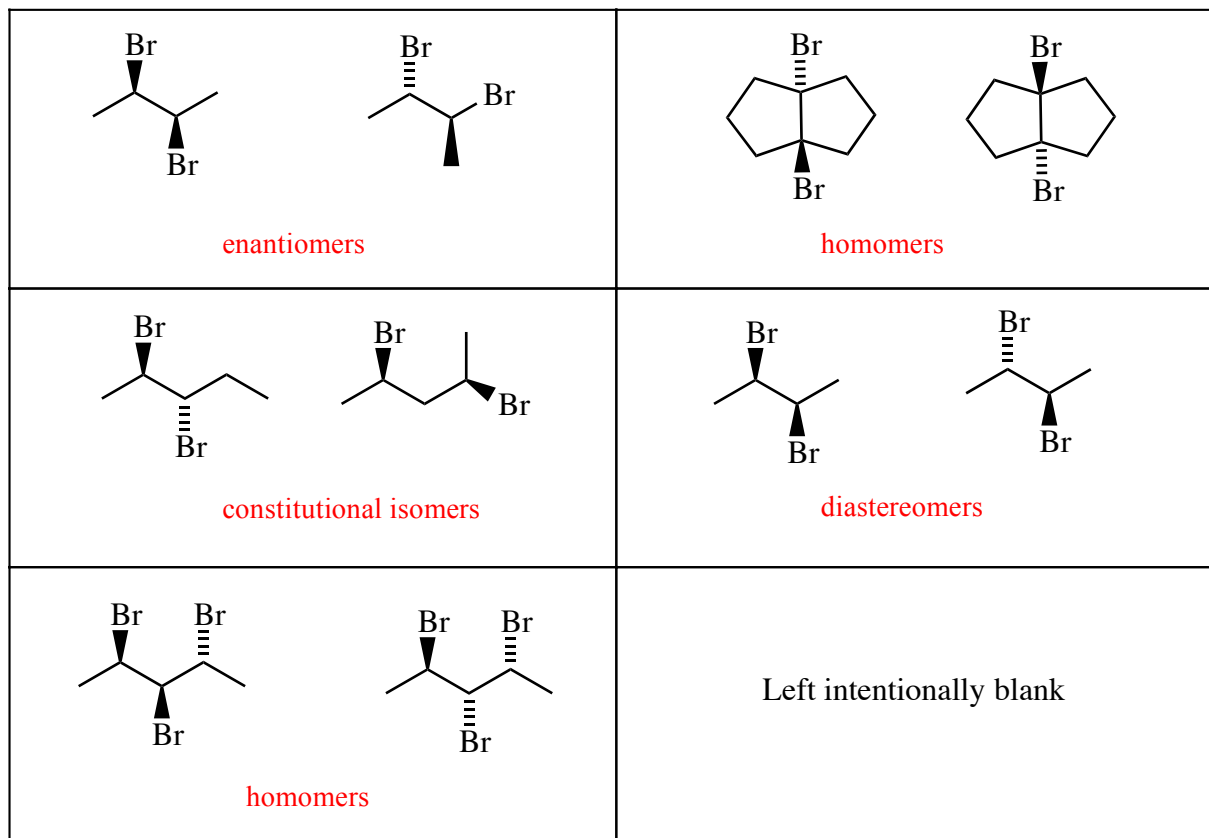
Partial Periodic Table									
1A							8A		
1 H							2 He		
	2A	3A	4A	5A	6A	7A			
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne		
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar		
						35 Br			
						53 I			

Printed Name: \_\_\_\_\_

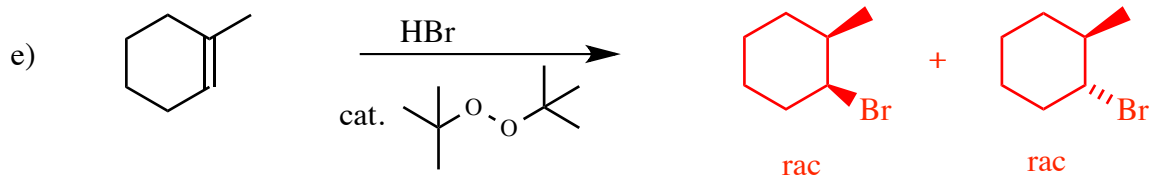
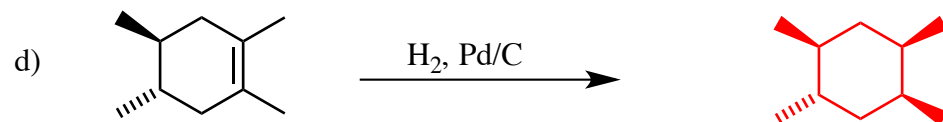
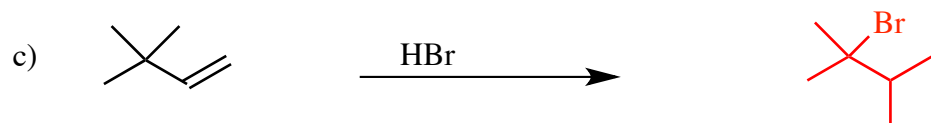
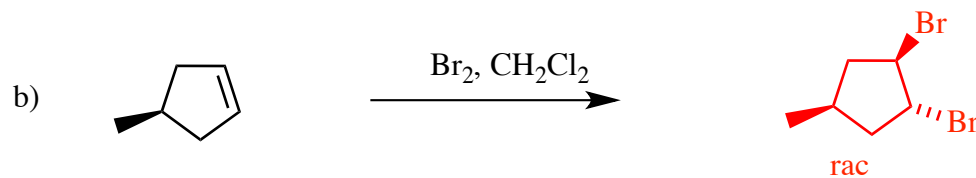
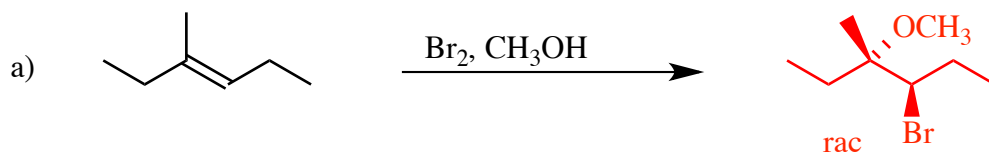
1 (20 pts) a) For each of the molecules below, carefully give the configuration of each tetrahedral stereocenter using the R/S stereochemical descriptors.



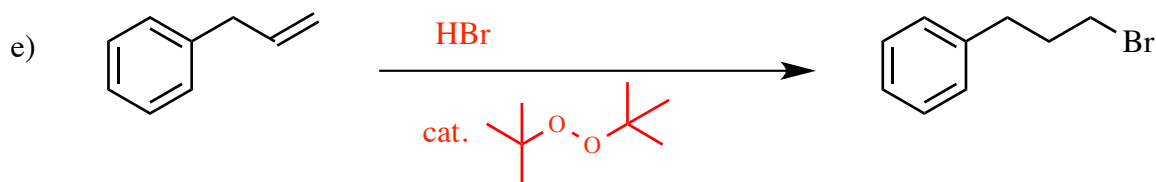
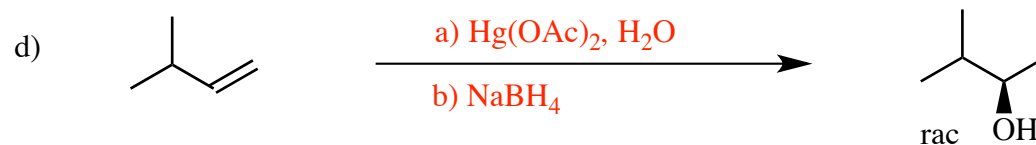
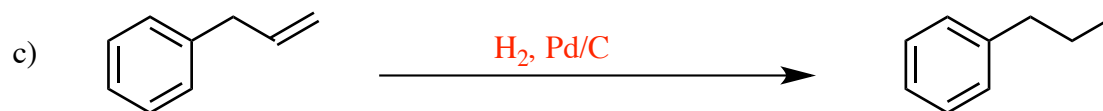
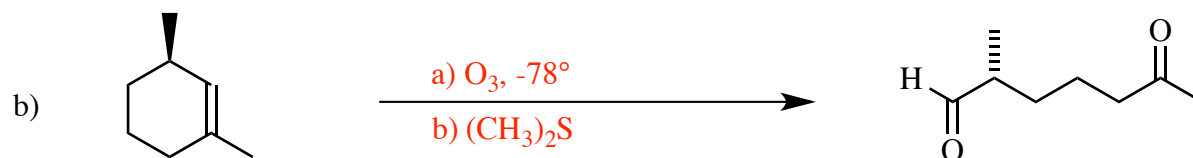
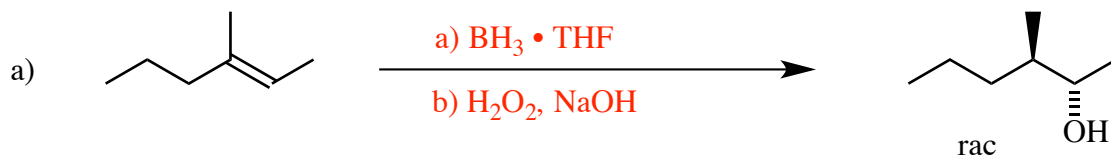
b) Write the relationship between each of the following pairs of structures (homomers, enantiomers, diastereomers, or constitutional isomers). Put your answers just below the structures in the same box.



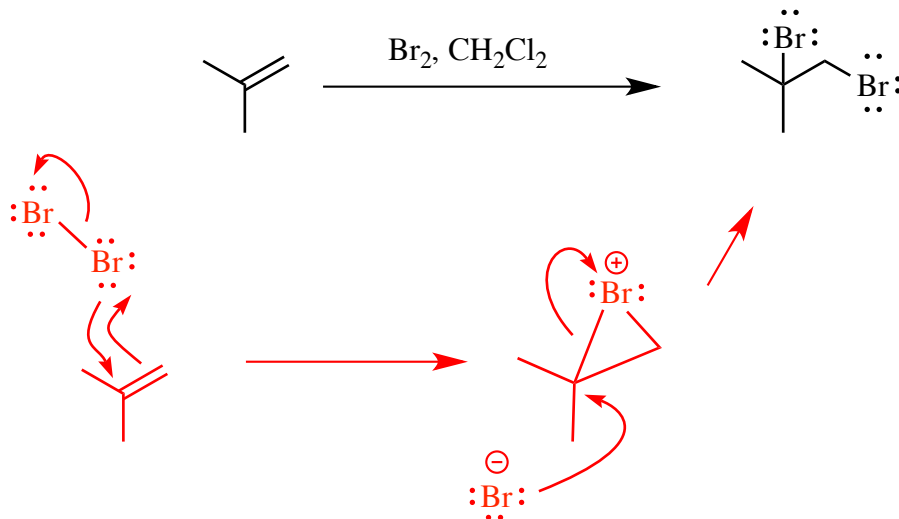
2) (20 pts) Give the single major product (or two major products if two are formed) for each of the following reactions, carefully showing stereochemistry using wedges and dashes if appropriate. If a racemate is formed, show only one enantiomer and label it "rac." Assume chiral starting materials are single pure enantiomers unless they are labeled "rac."



3) (20 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."



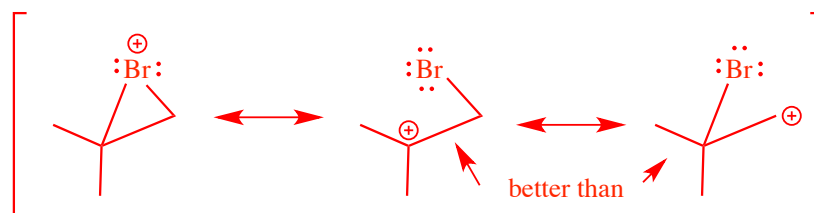
4) (20 pts) a) The mechanism of the following reaction involves formation of a high energy cationic intermediate. Propose an arrow-pushing mechanism, carefully showing the structure of the cationic intermediate, **including the correct relative bond lengths** for bonds in the intermediate. Be sure all your structures are complete, including all lone pairs.



b) Briefly explain in the box below your reasoning for the structural features of the cationic intermediate in 4a)

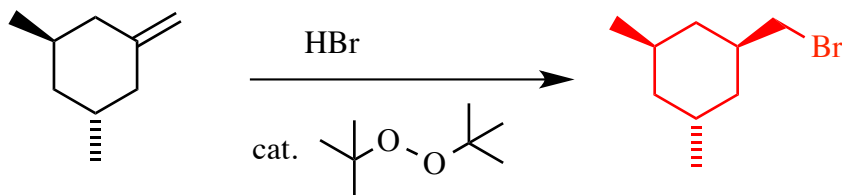
In the bromonium ion intermediate, the Br-C bond to the tertiary carbon is longer than the Br-C bond to the primary carbon because the charge is delocalized such that the two carbons connected to the Br<sup>+</sup> atom have partial positive charge, and the tertiary carbon has more positive charge than the primary carbon. The tertiary carbon can better accommodate positive charge due to the polarization of the electrons on the methyl groups. The H atoms on the primary carbon are less able to accommodate positive charge since there are no “extra” electrons (beyond the electrons in the C-H bonds) to polarize.

This makes the tertiary carbon-Br bond weaker, and makes the tertiary carbon more positive and electrophilic. The Br<sup>⊖</sup> nucleophile reacts at the more electrophilic tertiary carbon, breaking the weaker bond.

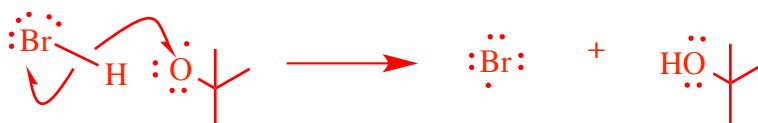
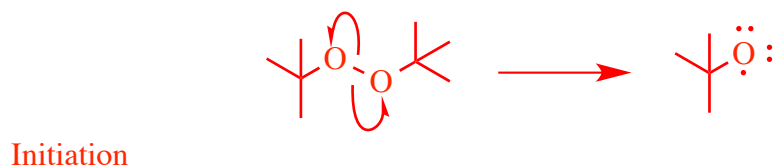


4 – Continued

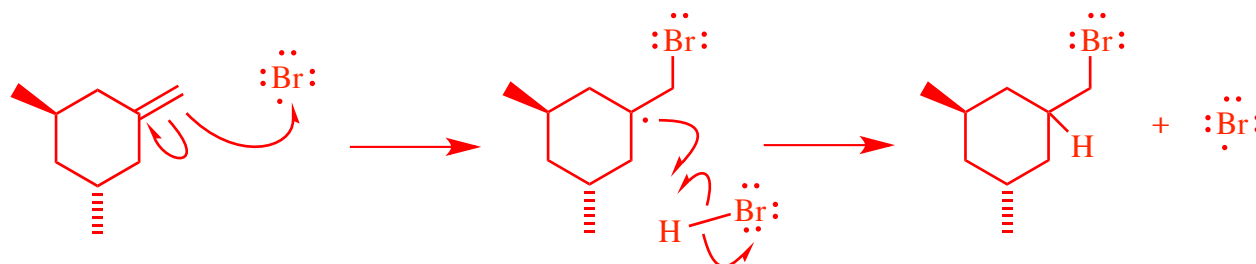
b) Give the single major product (or two major products if two are formed) for the following reaction, carefully showing stereochemistry using wedges and dashes if appropriate. If a racemate is formed, show only one enantiomer and label it “rac.” Assume chiral starting materials are single pure enantiomers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



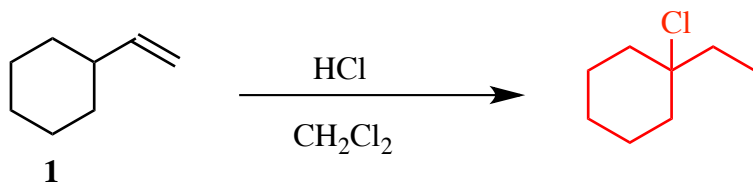
c) Propose an arrow-pushing mechanism for the initiation and propagation steps for the reaction in 4b).



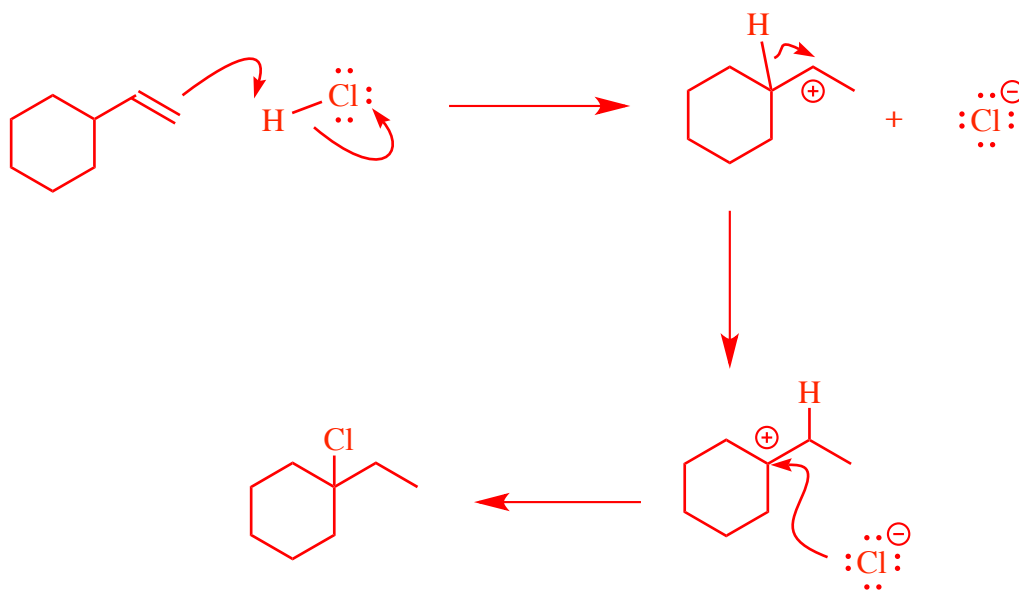
propagation



5) (20 pts) a) Hydrochloric acid (HCl) reacts with cyclohexylethylene (**1**) in dichloromethane solvent. Give the **single major product** of this reaction.



b) Propose an arrow-pushing mechanism for the transformation in part 5a) leading to the single major product.



5 – Continued

c) Carefully complete the energy diagram for the reaction in part 5a) leading to the single major product. Label the horizontal axis with structures of all molecules existing in a well on the hypersurface on the path from starting material and product (including, of course, the product).

