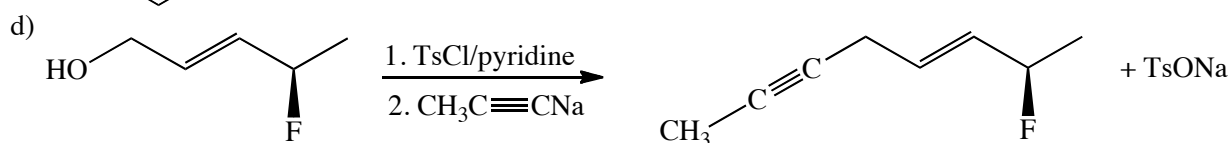
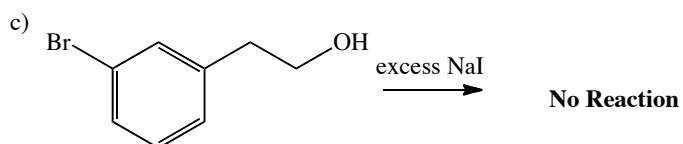
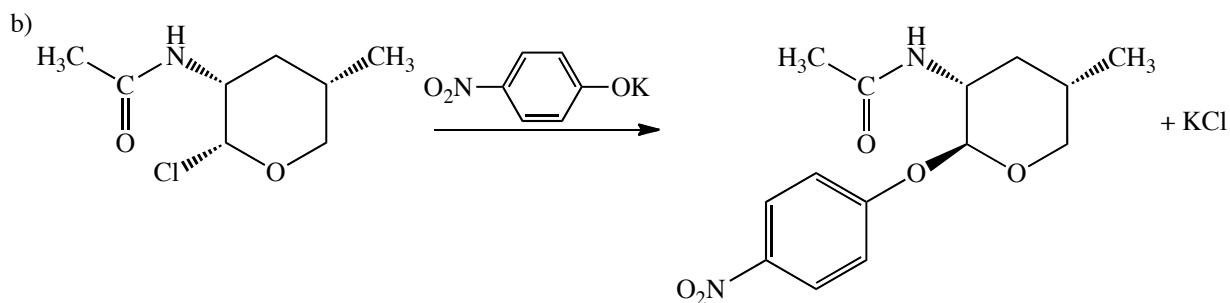
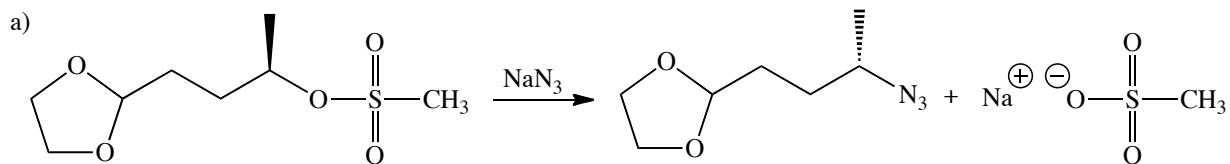


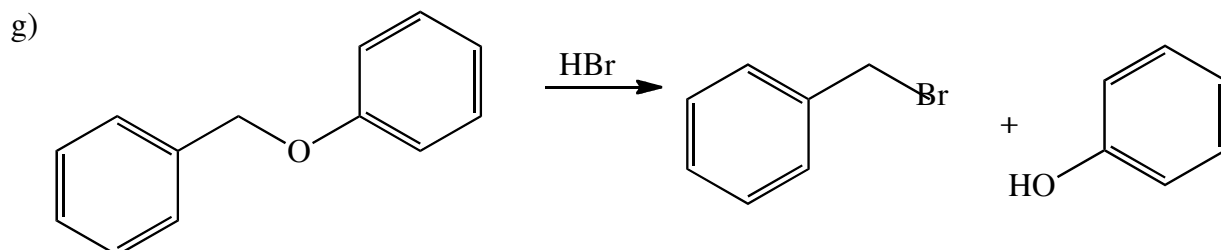
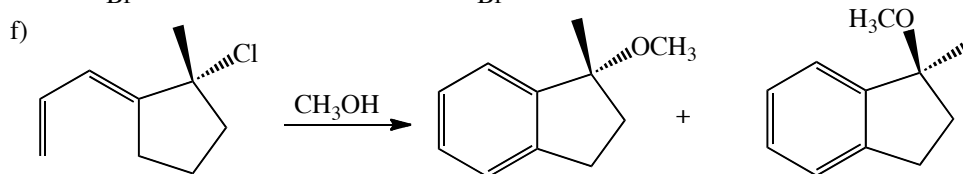
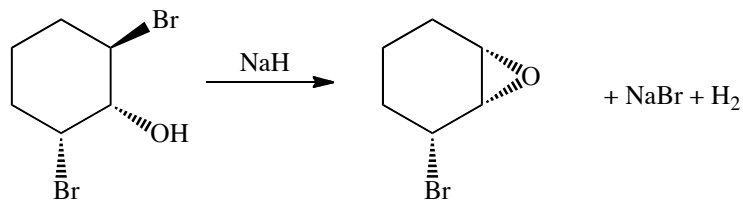
Chemistry 250 -- Exam #2 Answer Key -- October 16, 2009

There are 5 pages.

1. (21 pts) Complete the following reactions. If the stereochemistry of the reactants is shown, show the stereochemistry of the products. If there is no reaction, then say "No Reaction".

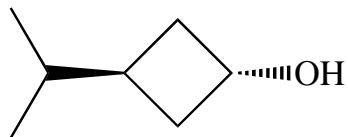


e) Hint: Product has only one bromine.

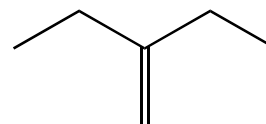


2. (11 pts) Name the following compounds. If the stereochemistry is shown, include appropriate stereochemical descriptors.

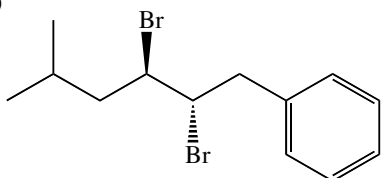
a)

**trans-3-isopropylcyclobutanol**

b)

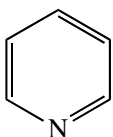
**2-ethyl-1-butene**

c)

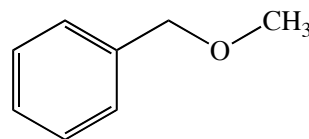
**(2*S*,3*R*)-2,3-dibromo-5-methyl-1-phenylhexane**

3. (10 pts) Draw structures for the following compounds. If a stereochemical descriptor is used, be sure to show the stereochemistry.

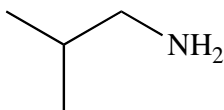
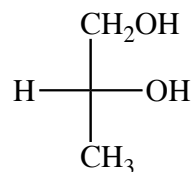
a) pyridine



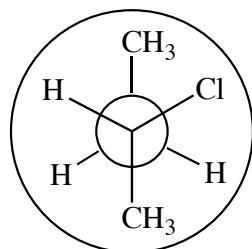
b) benzyl methyl ether



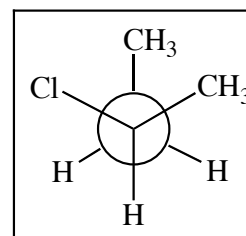
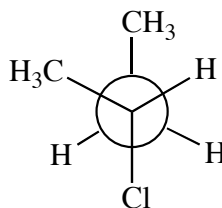
c) isobutylamine

d) Fischer projection of (*R*)-1,2-propanediol

4. (8 pts) Draw Newman projections down the C2-C3 bond for the staggered conformers of (*R*)-2-chlorobutane. Circle the lowest energy conformer and put a square around the highest energy conformer.

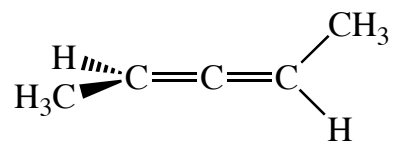


lowest energy



highest energy

5. (3 pts) Draw a 3D structure of a molecule that does NOT have a chiral center, but is chiral.



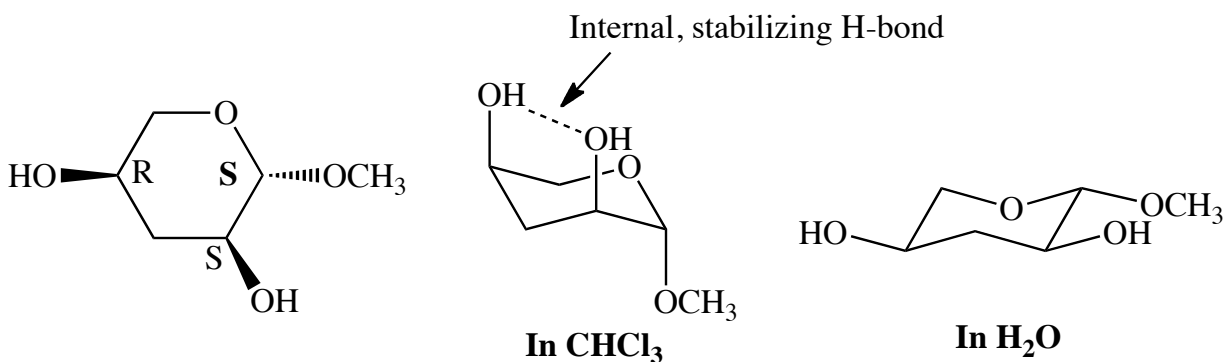
6. (13 pts) Answer the following questions for the compound shown below.

a) Indicate the configuration (R or S) at each of the stereocenters.

b) When the molecule shown above is dissolved in chloroform the major conformation has the methoxy (CH_3O -) group axial. **Draw this conformation below and label it “In CHCl_3 ”.**

c) In contrast, when this molecule is dissolved in water the alternative chair conformation (with the methoxy group equatorial) is preferred. **Draw this conformation and label it “In H_2O ”.**

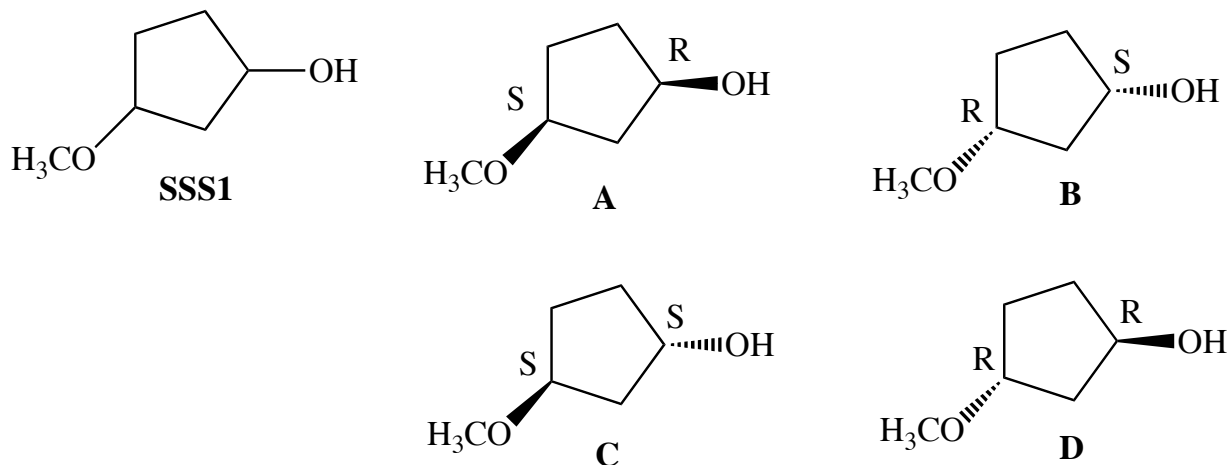
d) Propose a plausible explanation for this difference. Start by explaining which of the two conformers you would normally expect to be more stable and why. Then explain why the other conformer might be more stable when you change solvents.



Normally we expect equatorial oriented groups to be more stable than axial ones due to reduction in gauche interactions with the ring. However, with the 1,3-hydroxyl groups we have the potential for making a stabilizing internal H-bond when they are both axial. In H_2O this internal hydrogen bond is not as important since the OH groups are able to hydrogen bond with the solvent. In addition, this hydrogen bonding of the OH groups with the solvent increases their effective size thus making the equatorial conformer more favorable relative to the axial.

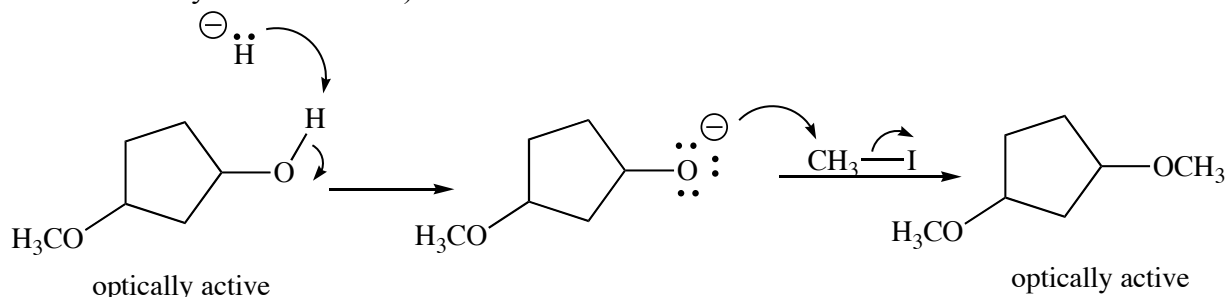
7. (17 pts) Sally science student isolated compound SSS1 (see below) from a natural source. She put it in a polarimeter and found that it was optically active.

a) Draw the structure of all the possible stereoisomers of SSS1. Identify which are enantiomers and which are diastereomers of each other. Indicate the absolute configuration (R or S) for the stereocenters in these stereoisomers.



A and B are enantiomers
C and D are enantiomers
A or B is a diastereomer of C or D

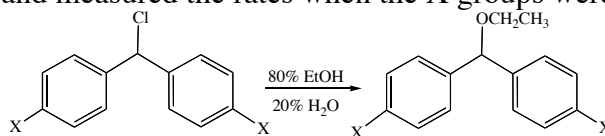
b) To help determine which isomer she had, Sally treated SSS1 with sodium hydride (NaH), followed by methyl iodide to give compound SSS2. Write out the **mechanisms** (using curved arrows) for these reactions, clearly showing the products formed. (You may use any one of the stereoisomers you drew above.)



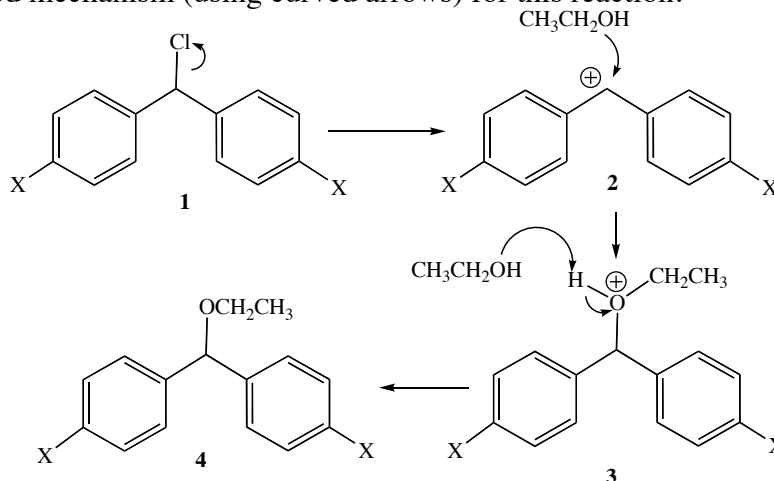
c) The resulting product from part b, SSS2, was purified, placed in the polarimeter, and found to be optically active. From the results of this information what can Sally deduce about the stereochemistry of the 3-methoxycyclopentanol that she originally isolated? Explain.

Since the 1,3-dimethoxycyclopentane produced in part b is optically active, Sally can deduce that the original 3-methoxycyclopentanol she isolated must be one of the trans-isomers, since either of the cis-isomers would have produced an achiral (meso) 1,3-dimethoxycyclopentane.

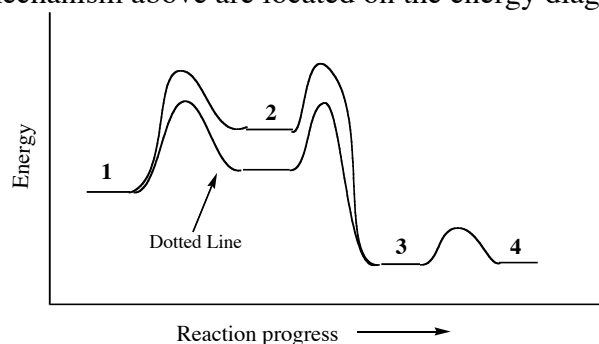
8. (17 pts) An article in the *Journal of the American Chemical Society* (2005, 127, 2641-2649) described a method for constructing reaction energy profiles for S_N1 reactions. They studied the following reactions and measured the rates when the X groups were varied.



a) Draw a detailed mechanism (using curved arrows) for this reaction.



b) Draw an approximate energy diagram for this reaction when X=H. Clearly indicate where the structures in your mechanism above are located on the energy diagram.



c) Will the reaction go faster or slower if it is run in 100% ethanol? Briefly explain.

The reaction will go slower since the ethanol is less polar than the water and therefore replacing water with ethanol will result in a less polar solution that will provide less stabilization to the polar carbocation intermediate (and the TS leading to it).

d) Will the reaction with X=OCH₃ go faster or slower than the one with X=H? Clearly explain your reasoning. Illustrate your answer by using a dotted line to draw the reaction energy diagram when X=OCH₃ on the energy diagram above.

The reaction with X=OCH₃ will go faster since the intermediate carbocation will be stabilized by resonance (see below) with the lone pair on the oxygen. Since the intermediate carbocation is stabilized, the transition state for its formation, which has some carbocation character, will also be stabilized (Hammond postulate).

