

Reduction of Camphor Computational Analysis Chem 223L

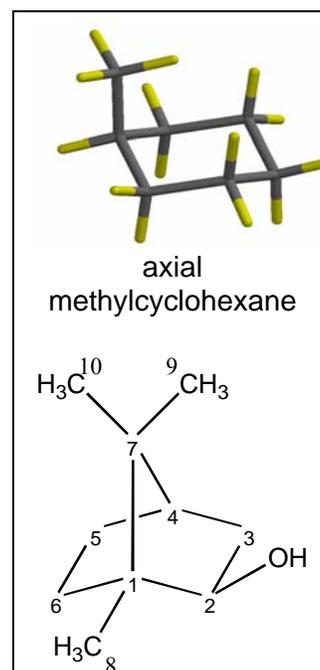
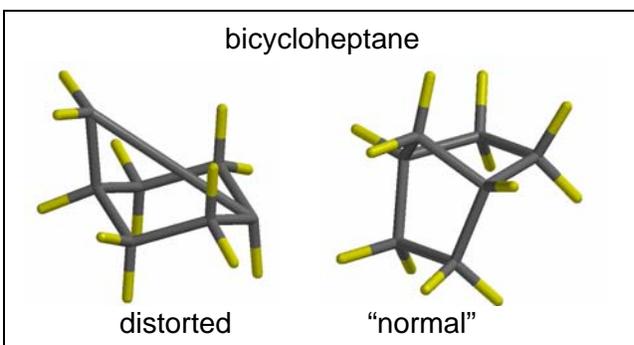
MEST-RE-C: MNR Analysis

- View, integrate, and print the ^1H NMRs of authentic samples of camphor, borneol and isoborneol. Examine the spectra to find places where they differ. Probably the best place to distinguish between borneol and isoborneol is $\delta 3.4-4.2$, but you may find another that you like better.
- View the spectrum of the actual reaction product. Determine the composition of the product (camphor, borneol, and isoborneol) by analysis of the integrated spectrum. Report the composition of the product (%). Is there any unreacted camphor present?

SPARTAN Analysis:

Building Camphor, Borneol and Isoborneol with Spartan: bring Thinkpad and power supply to lab. Have Spartan downloaded before coming to lab. Results used to answer post-lab questions.

1. Open a new file in Spartan Essentials using the dropdown menu File→New.
2. On the bottom right-hand side of the screen beside the word “Rings” select cyclohexane from the dropdown menu. Click in the middle of the screen. A chair conformation of cyclohexane should appear.
3. Now click on the sp^3 hybridized carbon in the table and add an sp^3 C to one of the **axial** positions on cyclohexane. The methyl group is bonded to C-1 and will itself become C-7 in the bicyclic ring system.
4. Make a bond between an open valence on the methyl group and the **equatorial** valence directly across the ring (on C-4) using the ‘make bond’ icon (). (Click on the icon and then on the two open valences.) This should produce a distorted bicycloheptane system. Upon clicking the minimize button () , you should be given a more normal bicycloheptane.



5. Finish the molecule by adding three sp^3 C's and the O that will become the OH. (Add OH exo for isoborneol or endo for borneol.) Recall the Spartan will assume that any remaining open valences are bonds to H.
6. Click .
7. Click  and carefully check the structure you have built. If you need to alter the structure, click  to get back into the builder.

- Save the file under the name of the molecule you built. Repeat the process, or edit an existing file, for the remaining molecules. To edit a molecule, go to the builder (+). Make required changes, minimize the energy (E) and view the new structure (V).

Finding the Lowest Energy Conformations of Camphor, Borneol and Isoborneol:

- Open a file containing one of the three molecules we are interested in.
- Use the dropdown menu Setup → Calculations. Choose "Conformer Distribution" with "Semi-Empirical" "AM1." Click submit.
- Once the calculation is complete, use the dropdown menu Display→Output to view the results. Scroll down the display window until you see "Lowest energy conformation." Write down the energy value in kcal/mole. Repeat for the other two molecules.

To View and Capture the Lowest Energy Conformation Images:

- Close all Spartan files and Open filename.Conformers1.spartan for either borneol or isoborneol.
- Use the dropdown menu Model → Tube to display the molecule in a less bulky format.
- Use the dropdown menu Display → Spreadsheet. Three molecules should be listed in the table. They differ from each other only in the conformation about the O-H bond.
- In the window that opens, click "Add." (If you are asked if you want to add a new molecule, answer no and click add again.) Choose "rel E" for relative energy.
- Select the lowest energy molecule (by clicking on any cell in the lowest energy row in the spreadsheet.) Close the spreadsheet window. The conformer on the screen represents the lowest energy conformation of the molecule. Copy and paste the image into Word for your report. (Position the molecule in the Spartan window EXACTLY as you wish it to appear in Word.)
- Repeat for the other two molecules.

Postlab Questions

- Use your results from Spartan calculations to answer these questions. Include a labeled printout in your report that shows each lowest energy conformation and its energy in kcal/mole.
 - Sketch by hand a reaction coordinate for this reaction showing camphor, borneol and isoborneol. Which compound is more stable, borneol or isoborneol and is the reaction endothermic or exothermic?
 - Can you suggest the likely source of the strain that is present in the less stable isomer? Hint: Use Spartan to look for crowding as evidenced by distorted bond angles. To measure bond angles, open a structure, click  and then 3 atoms. Spartan will display the angle in the bottom right corner of the screen. The angle displayed is the angle about the 2nd atom you choose, so choose them in order!
- Is the lower energy product the major product of the reaction? Is the reaction proceeding under thermodynamic or kinetic control?
- If the borohydride reduction is performed on the compound shown to the right, the exo vs. endo percents are almost exactly reversed as compared to camphor. Suggest an explanation for this reversal in product stereochemistry.
- Give another method (other than ¹H NMR) that could be used to look for unreacted camphor in this experiment.

