Include the Prelab Exercise on p. 205 of the lab text in your prelab outline. Answer the same for 2-butanol. Review Chapter 15 on Molecular Mechanics, paying particular attention to the section on local vs global minima (p. 302, 303) and also p. 304, 305. Review Wade, Section 7-7 (A-C) and your previous Molecular Modeling handout and report. **Although the lab experiment is short and straightforward, you will need to put additional effort into the report. It is expected that such additional effort will be expended. Note also that unlike previous experiments, in which the procedure was spelled out quite exactly in the handout, this experiment and others to follow will rely more on the procedures given in the lab text.** Be sure to carefully read the section below on calculations before you carry them out.

Experiment Notes: **Be extremely careful in using conc sulfuric acid**. Instead of the 10 cm column/collection tube described in the book, use the longer chromatography column to collect the product. Much of the first slow bubbling that occurs is simply air being displaced from the heated reaction tube. Once product formation begins, the bubbling becomes rapid. To ensure that the butenes and not just air is being collected, allow the reaction to proceed until the tube is at least about 3/4 full.

Calculations: From the GC analysis, determine the relative amounts of the three isomers produced in the reaction. These will be used to compute energies which will be compared with calculated and other experimental values. Note that the assumption that peak area is directly proportional to molar amount is not necessarily correct. The detector responds differently to different compounds. Usually however, for structurally similar compounds, as in this case, the assumption is valid. Air will elute first, followed by the butenes in order of boiling point.

For the equilibrium as drawn above, calculate $\Delta G°$, using the relationship, $\Delta G° = -RT\ln K_{eq}$, where R = 1.99 cal/mol deg Kelvin, T = 373° Kelvin, and $K_{eq} = N_{(cis)} / N_{(1\text{-butene})}$, where $N_{(1\text{-butene})}$ = mol fraction of 1-butene and $N_{(cis)}$ = mol fraction of *cis* -2-butene. (Why is T = 373° K used?) Be careful to use the correct sign for $\Delta G°$ for the equilibrium and to not mix units (cal vs kcal).

In the same way, calculate $\Delta G°$ for the following equilibrium:
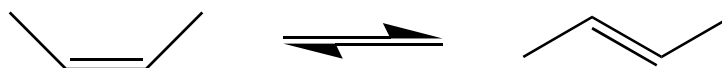
<u>Other experimental data - heats of hydrogenation</u>: use the heat of hydrogenation data given in Wade, Table 7-1 (for example, $\Delta H° = -1.0$ kcal/mol for the equilibrium cis to trans 2-butene). (Heats of combustion, if available could also be compared and would provide the same qualitative results, within experimental error.) As stated in the other handout for this experiment, "An Experimental and Computational Investigation of the Dehydration of 2-Butene", you will find additional experimental heat of formation data from the web.

<u>Computational Chemistry</u>: Instructions for using the SPARTAN molecular modeling program is provided in the handout, "An Experimental and Computational Investigation of the Dehydration of 2-Butanol". Using the SPARTAN computer program, calculate the strain energy (steric energy) for the three butene isomers using molecular mechanics (MMFF) calculations, and also calculate the heats of formation using semi-empirical MO calculations (AM1).

<u>A word about local minima</u>. Recall the molecular mechanics calculations that you did previously for butane. If you had minimized the energy when the molecule was in or near the gauche conformation, you would have concluded that the minimum energy conformation of butane was the gauche conformation. This is because the gauche conformation is in an energy well (surrounded by energy barriers). In other words, the energy goes up as you rotate the C-C bond slightly one way or the other from the gauche conformation. The program therefore thinks that the gauche is the minimum energy conformation. The gauche conformation actually represents a <u>local minimum</u>. If you rotate the C-C bond from the gauche conformation to or near the anti conformation, then minimize, the program would tell you that the minimum energy conformation of butane is the anti conformation. Indeed, the anti conformation would be lower in energy than the gauche. If you rotate around the central C-C bond by 360°, as you did in the modeling experiment, checking energy along the way, you would see that the anti conformation has the lowest energy of all conformations. The energy of the anti conformation represents the <u>global minimum</u>. This is the conformation of lowest energy. <u>In doing molecular modeling calculations, you must always be aware that even though you have minimized the energy of a structure, it may be at a local, not a global, minimum.</u> The way to get around this problem is to rotate C-C single bonds in small increments, as you did with butane, and minimize the energy at each point along the way. This will normally allow you to find the global minimum. If there are several C-C bonds in the molecule, there may be many local minima, making the job of finding the global minimum very time-consuming. In the present case, with the butenes, the SPARTAN program allows this conformer search to be done automatically. If set to do a conformer search, the program rotates specified bonds in a systematic way and minimizes the energy for each conformation. If the correct bonds were specified by the user and the magnitude of rotation chosen to be sufficiently small, the global minimum would be found. One can imagine the complexity of doing this for a molecule having a large number of single bonds. Even for a molecule having only 5 single bonds and stepping through a rotation using 120°
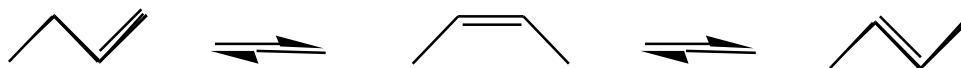
(large) increments results in 243 conformations to be calculated. If each calculation took 10 sec, 40 minutes of computer time would be needed to find the global minimum. For larger molecules, and for more sophisticated calculations, calculations for each conformation might take an hour or more. Fortunately for the butenes, which have only two C-C single bonds, using a rotation step of 120° results in only 9 conformations. Because AM1 calculations are fairly simple and because these molecules are fairly small, this is an easily-doable task. Note that you could do a conformer search manually for simple molecules such as these. One would draw a model, minimize and record the energy, select a C-C bond and rotate it by some amount, minimize and record the energy, rotate, minimize, and record, until it was fairly certain that the global minimum had been found. In any case, searching for the global minimum must be done carefully. If the rotation increment is too large, the global minimum may be missed.

As part of the report, construct a table (see sample data table at end) which allows for a clear comparison of all experimental and calculated energy differences. Comment on the agreement and/or the disagreement of the resulting energies. Do not expect to see perfect agreement. Concentrate more on the predicted direction of equilibrium and order of magnitude of the energies. Remember that the sign for $\Delta G°$ and $\Delta H°$ is absolutely crucial and depends upon the way in which the equilibrium is drawn.

Summary: for the three isomeric butenes produced in the dehydration of 2-butanol do the following:

1)   determine product distributions using GC, and from those, free energies.

2)   compare your exp'l values with hydrogenation energies from Wade.

3)   calculate energies by MMFF and AM1.

4)   compare your experimental data with the experimental values from the NIST website (see other handout) and with your calculated values and comment on the correlations or lack thereof.

5)   draw the mechanism and energy diagram for the reaction and discuss results found in terms of transition state energies and structures, how structures of transition states correspond to structures of products and therefore energies of products.

6.)   comment on the product distribution predicted from statistical considerations only vs. what you found.

Sample Data Table

$\Delta G°$ (your exp)	_____		_____	
$\Delta H°$ (hydrog)	_____		_____	
$\Delta H°$ (NIST)	_____		_____	
ΔE (MM)	_____		_____	
ΔE (AM1)	_____		_____	