

Problem Set 1

Out: October 2, 1998

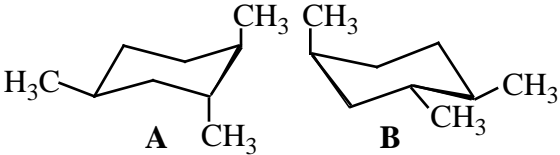
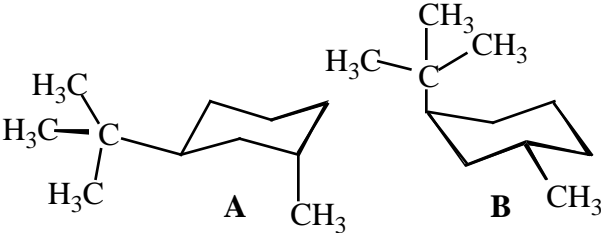
Due Back: October 9, 1998

Chemistry 221, 1998

Answers to the following problems should be written, in order and labeled, on 8 1/2 x 11 inch paper. Answers written on the problem set itself will not be graded.

Section A

- For each of the two pairs of conformers below:
 - Recopy the two chair forms shown below.
 - Identify the more stable of the two.
 - Give the energy difference between the two. Show calculations.

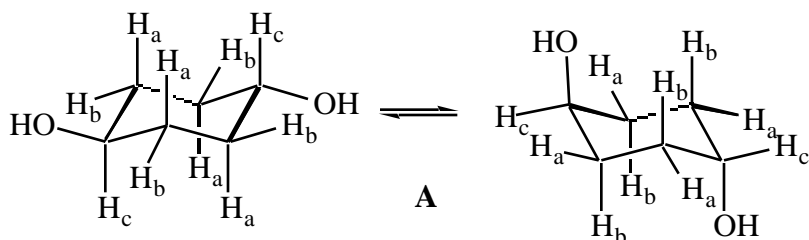
	B is more stable. A has 2 sets of 1,3-diaxial interactions (1.8 kcal each, total of 3.6 kcal) while B has one set (1.8 kcal) and one <u>gauche</u> (0.9 kcal) for a total of 2.7 kcal. Energy difference: 0.9 kcal in favor of B .
	A is more stable. A has smaller destabilizing effects (2 CH ₃ to H for 1.8), in contrast to B , which has two C(CH ₃) ₃ to H diaxial interactions (5.4 kcal). Total: 3.6 kcal/mole.

- Molecules **A** and **B** below respond differently to a technique which probes the types of hydrogens in a compound.¹ Molecule **A** shows signs of three types of hydrogens, while molecule **B** shows signs of only two. You will need to know that this technique looks at molecules much like a camera with a slow shutter speed: the result of conformational change is the display of only one signal from any hydrogens which exchange types due to these changes.

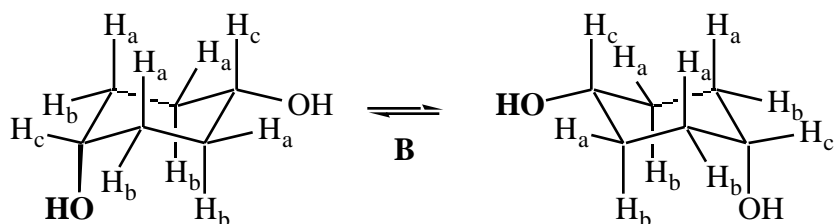
- Explain why these compounds show the number of signals that they do.
- Show clearly which hydrogens are in each of the groups (3 for **A** and 2 for **B**).

You all get to learn a new phrase: *mea culpa*. It means "I am guilty", and I use it when I screw up. There are indeed, on close examination, four hydrogen environments in each molecule (including the OH hydrogens, which I omitted for reasons we'll see later on this year). Each molecule has three cyclohexane environments, one with 2 H's in it, and two with 4 H's in each. I had originally thought that all but two of the H's in **B** (H's a and b, above) interchanged completely. On careful examination, they do interchange between axial and equatorial, but the two axial types are not the same (axial H_a on the left is not the same as axial H_b on the right, as H_a axial is trans to the OH's, while the H_b axial is cis to the OH's. The equatorials can likewise be related to the OH's in two different ways: cis and trans. Note how the axial H_a's are converted on ring-flipping to the equatorial H_a's; likewise with the H_b's and H_c's.

¹NMR spectroscopy uses a powerful magnet and radio waves to probe the hydrogen nuclei, determining the exact chemical environment of each hydrogen. Hydrogens which are in exactly the same environment will overlap, giving one signal, while hydrogens in other environments give separate signals. We will study NMR in chapter 13.



For compound A, the cyclohexane H's are divided into three normal groups. Looking at the more stable conformation drawn to the left, there are groups H_c , the H's on the carbon attached to the OH (which is called the *carbinol* carbon), the axial (H_a) and equatorial (H_b) H's on the other carbons. The axial H_a 's are *cis* to the OH on each end, while the equatorial H_b 's are *trans*. Even after the chair-chair interconversion, the H_a group is *cis* to the OH's (although H_a hydrogens are now equatorial), and the H_b group is still *trans* to the OH's (H_b 's are now axial). Even counting the conformational changes, these are distinct groups.

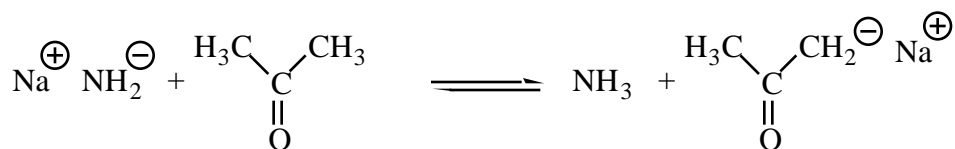


For compound B, the situation is quite different in terms of groups. Now there are three cyclohexane groups, with the carbinol H's distinct as before (H_c). However, the a and b groups are not pure axial and equatorial as before, but *cis* and *trans* to the OH's. Group H_a , which is *trans* to the OH's, has two axial, and two equatorial hydrogens. These hydrogens switch roles on the conformational change. If you look at one specific H_a atom before and after the ring flip, you'll notice that if it is axial before, it is equatorial after. This interchange makes the axial and equatorial H's (if they are *trans* to the OH's) look identical to this technique.

The goal of this question was to get you to look carefully at cyclohexanes undergoing chair-chair interconversions. I hope it did at least that.

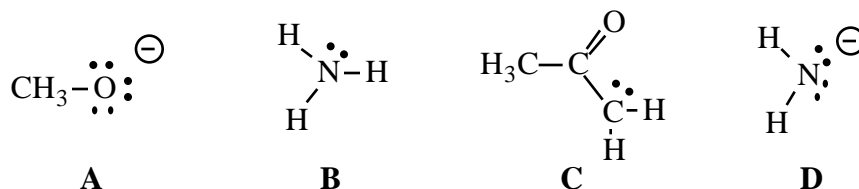
Section B

- Complete the following Brønsted acid/base equation, and use pK_a values to determine whether or not the reaction is favorable. Show calculations.



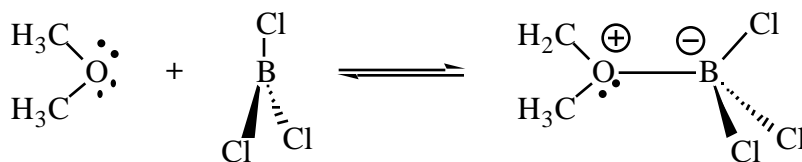
The reaction is favorable. The acid formed (ammonia) has a pK_a of 33; the acid destroyed (acetone) has a pK_a of 22. The stronger acid is destroyed in favor of the weaker. The reaction is favorable with a $pK_{\text{eq}} = -11 = 22-33 \Rightarrow K_{\text{eq}} \sim 10^{11}$.

2. Arrange the following molecules in order of *base strength*. Draw the conjugate acid for each base. Support your ranking with data (how did you know?) and explain the molecular basis for the ranking, as best you can.



Strongest base (pK_a of conjugate acid given): **D** (33), **C** (22), **A** (17), **B** (10)....weakest base.

3. Write the products of the following Lewis acid/base reaction. Label each of the reactants as either Lewis acid or Lewis base.

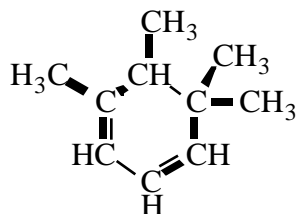


Section C

Provide IUPAC names for the following compounds:

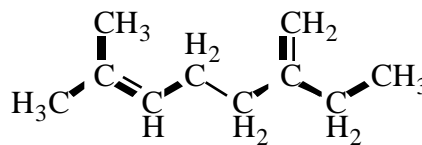
1. Also, redraw these, and show the **isoprene units** in them (they could be terpenes).

a.



1,5,5,6-tetramethyl-1,3-cyclohexadiene

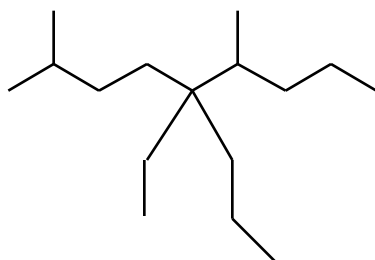
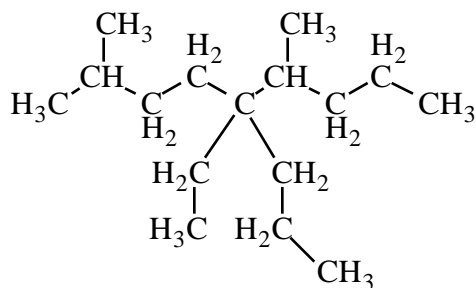
b.



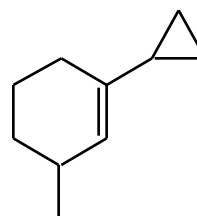
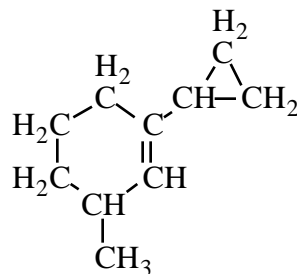
2-ethyl-6-methyl-1,5-heptatriene

2. Draw a clear representation of the following compounds:

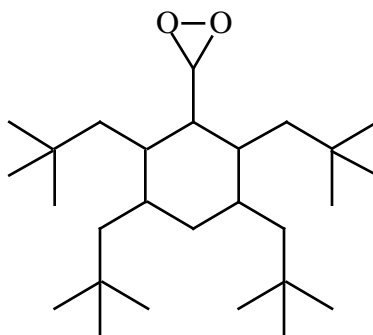
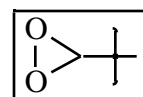
a. 2,6-dimethyl-5-ethyl-5-propylnonane



b. 1-cyclopropyl-3-methylcyclohexene



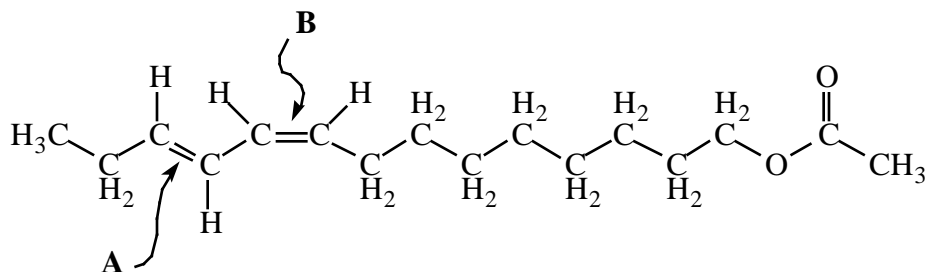
Bonus: Draw a skeleton representation of 1-(2,3-dioxiranyl)-2,3,5,6-tetra(2,2-dimethylpropyl)cyclohexane. The oxiranyl group is drawn in the box to the right; try drawing it at the top of the structure.



OK. It's pretty goofy-looking. Lighten up.

Section D

Determine the configuration of the identified double bonds in this molecule.¹ Use the letters E, Z or NA (Not Applicable).



A: E

B: Z

¹This is Prodlure, a major component of sex pheromone of female *Spodoptera litura* (F.) and Egyptian cotton leafworm, *S. littoralis* (Boisd.).

