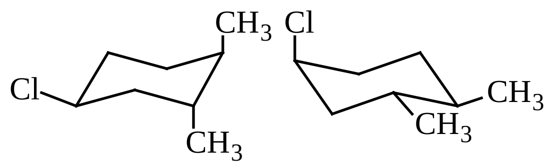
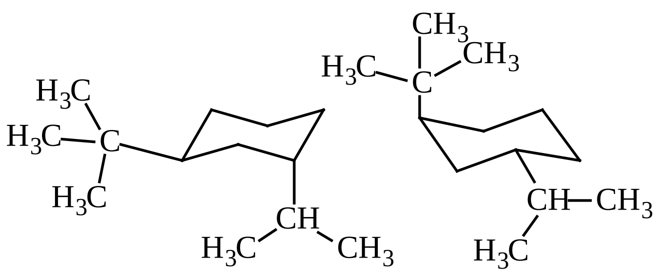
Problem Set 1   Out: October 8, 1999   Due Back: **October 18**, 1999

Chemistry 221, 1999

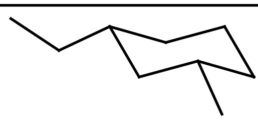
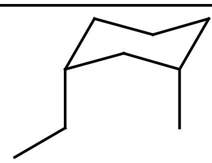
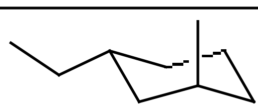
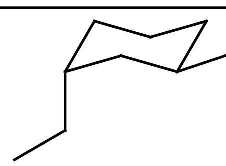
Answers to the following problems should be written, in order and labeled, on 8 1/2 x 11 inch paper. Answers written on the problem set itself will not be graded.

Section A

1. 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 (0.5 kcal) and one gauche (0.9 kcal) for a total of 1.4 kcal. Energy difference: 2.2 kcal in favor of **B.**
	**A** is more stable. **A** has smaller destabilizing effects (2 C_3H_7 to H for 2.2), in contrast to **B**, which has two $C(CH_3)_3$ to H diaxial interactions (5.4 kcal). Total: 3.2 kcal/mole.

2. Draw both chair forms of both isomers of 1-ethyl-3-methylcyclohexane. [You should end up with 4 structures]
- •Calculate the energy difference between the different chair forms for each isomer.
- •Does it appear that one isomer is more stable than the other (taking into account either or both of the chair forms for each isomer)? If so, which, and why?

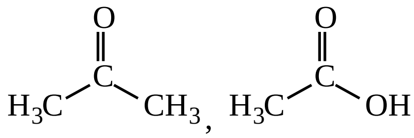
		Energy difference is a little over 5.5 kcal per mole. The chair form on the lefthas no strain energy, while that on the right has one CH_3 to H, one CH_2CH_3 to H and one CH_3 to CH_2CH_3 (0.9 + 0.95 + 3.7 = 5.55). The last value is an estimate--the best value you have is the methyl to methyl value; this interaction would be slightly worse.
		The molecule on the left is slightly more stable (by 0.1 kcal/mole). Each has strain energy: the left molecule has 1.8, while the right has 1.9 (0.95 x 2).

Section B

1. From the list of 10 compounds below: •Show reactions for all combinations which will give a favorable ($K_{eq} > 1$) Brønsted acid/base reaction. •Calculate the approximate

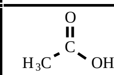
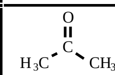
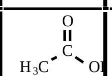
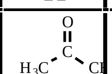
K_{eq} for each reaction you write. •Label the acid, base, conjugate acid and conjugate base in each reaction you write (you may wish to set this up as a table, with the columns labeled).

H_2O, NH_3, NaOH, $NaNH_2$, CH_4, Na^+ $^-CH_3$, H_3O^+ Cl^-, CH_3OH,



Perhaps you can see some structure if we order these in a matrix. On the left are the acids, listed in decreasing order of strength (pK_a). On the top are the same compounds, but we are asking if they could be a base, and therefore looking for the pK_a of their conjugate acids (and strange ones, sometimes. Conjugate acid for H_3O^+? No doubt H_4O^{+2}!). Then, you can see that only the pairs for which the base's pK_q^* is bigger than the acid's pK_a will show favorable reaction.

Only for favorable reactions are the values placed on the table. The log K_{eq} is listed for each of these. For example, for H_2O and $NaNH_2$, the value of log K_{eq} is 19, leading to an equilibrium constant of 10^{19}.

	pK_a*:	50	35	16	10	-2	-2	-6	-7	-20?	-20?
Acids' pK_a's		$^-CH_3$	$NaNH_2$	NaOH	NH_3	CH_3OH	H_2O			H_3O^+ Cl^-	CH_4
-2	H_3O^+ Cl^-	52	37	18	12						
5		45	30	11	5						
16	H_2O	34	19								
17	CH_3OH	33	18								
22		28	13								
35	NH_3	15									
40?	NaOH	10									
50?	$NaNH_2$										
50	CH_4										
70?	Na^+ $^-CH_3$										

Sample reaction:

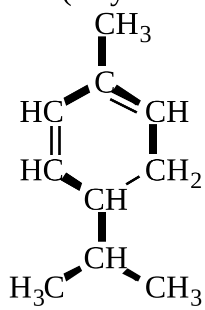
$H_2O + {}^{\ominus}CH_3 \rightleftharpoons HO^{\ominus} + CH_4$

H_2O	$^{\ominus}CH_3$		$HO^{\ominus}$	CH_4
acid	base		conj. base	conj. acid

Section C

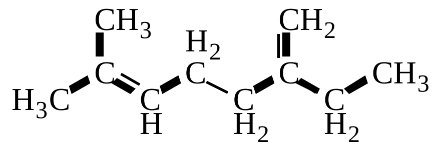
1. Provide IUPAC names for the following compounds. Also, redraw these, and show the isoprene units in them (they could be terpenes).

a.[1]



2-methyl-5-(1-methylethyl)-1,3-cyclohexadiene
or
5-isopropyl-2-methyl-1,3-cyclohexadiene

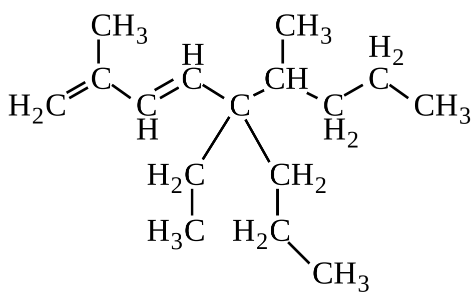
b.

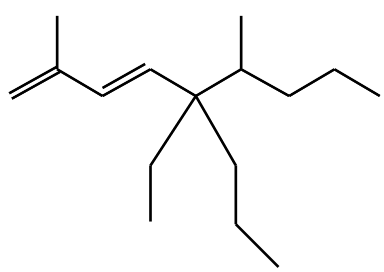


2-ethyl-6-methyl-1,5-heptatriene

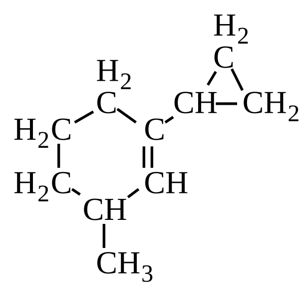
2. Draw a clear representation of the following compounds:

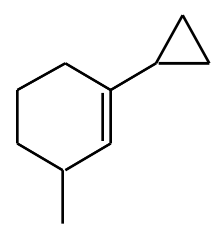
a. 2,6-dimethyl-5-ethyl-5-propyl-1,3-nonadiene





b. 1-cyclopropyl-3-methylcyclohexene

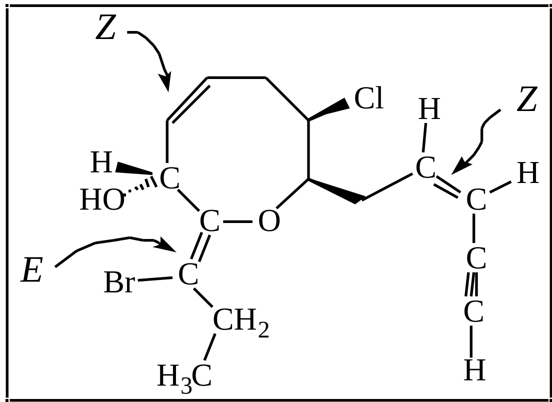




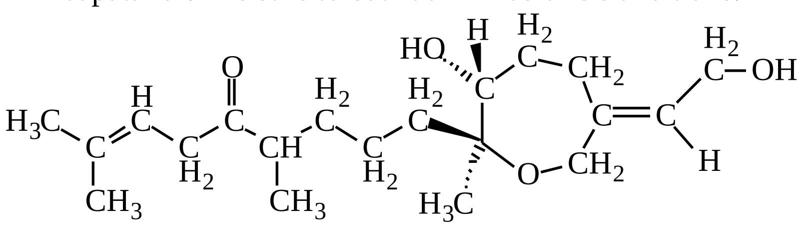
[1]-Phellandrene. From essential oils of Eucalyptus and from oil of bitter fennel.

Section D

1. Redraw this molecule (Chondrial, anti-viral compound from red algae) and show the configuration of each of the double bonds in this molecule. Use E, Z or NA (Not Applicable).



2. How many *cis-trans* isomers are possible in the fertility-regulating compound zoapatanol? Be sure to count all kinds of cis and trans.



There are 4 *cis-trans* isomers possible for this molecule. There are two places where one can make cis and trans forms. The double bond to the right can show them (it is in the *E* form as shown, could also be *Z*). The ring can also have isomers--look at the OH and the CH_3. They are cis as shown, but could be trans (on opposite sides of the ring.

Section E

1. Choose a group of 2-4 members, and choose a molecule from the examples provided, or by mutual agreement with the instructor. Schedule an appointment for a 15-20 minute time with the instructor. Study the molecule carefully, and come to the appointment ready to answer questions about the bonding, conformational analysis, possible isomers, or other structural questions that may come up.