Dr. Steven Pedersen September 29, 2003

Chemistry 3A

Midterm #1

Student name: _____

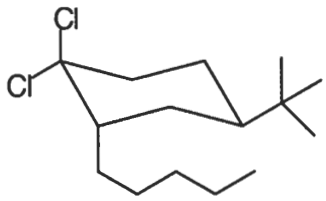
Student signature: _____

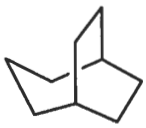
TA's name or section number:_____

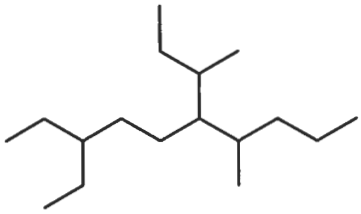
Problem 1	_____	(12 pts)
Problem 2	_____	(12 pts)
Problem 3	_____	(15pts)
Problem 4	_____	(12 pts)
Problem 5	_____	(10 pts)
Problem 6	_____	(15 pts)
Problem 7	_____	(14 pts)
Problem 8	_____	(10 pts)
Total Points	_____	(100 pts)

No Calculators Allowed
Be Sure Your Exam has 11 Pages
Be Sure To Try All Parts of Each Problem!

1A. Provide a systematic name for the following compounds. Use common nomenclature for any branched substituents. (12 pts)







B. Draw a structure for the following names. For cycloalkanes use flat rings. For all others use bond-line notation.

- 6-iso-butyl-3-cyclopropyl-3,5,7-trimethyldecane

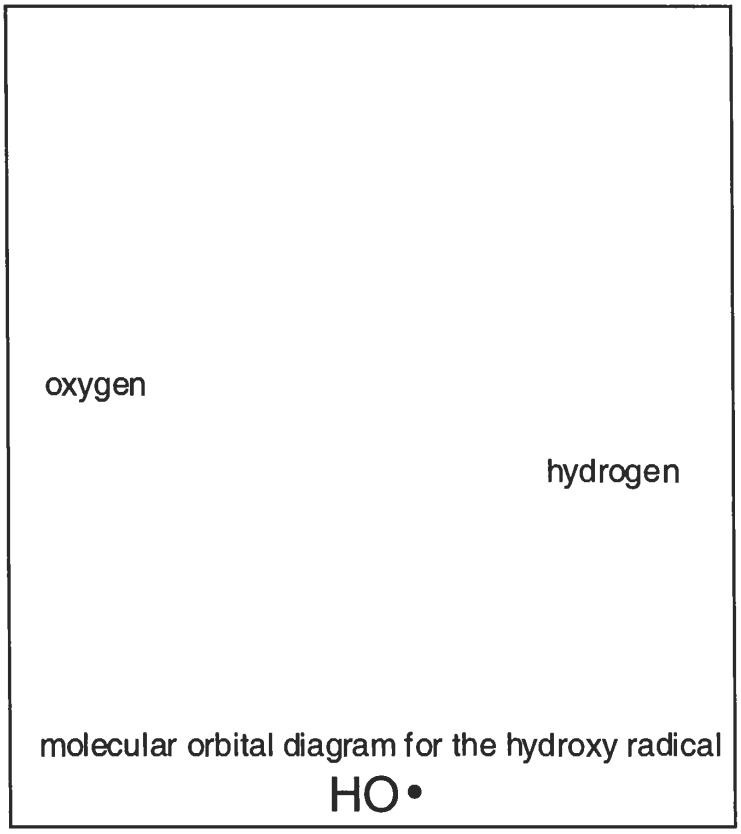
- trans-3-iodo-1-ethylcylcopentane

- spiro[4.3]octane

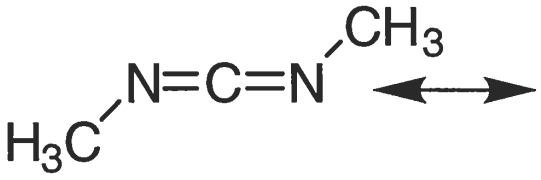
2. (12 pts)

A. Construct a molecular orbital diagram for the hydroxy radical, $HO^{\bullet}$, using the following guidelines and labeling schemes. BE SURE TO INCLUDE EVERYTHING ASKED FOR BELOW.

- Assume that the oxygen is SP^2 hybridized.
- The relative energies for oxygen and hydrogen are provided below.
- Indicate the relative energy levels of any atomic and hybrid orbitals on both sides of the diagram.
- Clearly indicate which orbitals are being combined to make molecular bonding orbitals.
- Fill in all of the electrons.
- Label all the levels as σ, π, nb (non-bonding) etc.
- Label the HOMO and LUMO



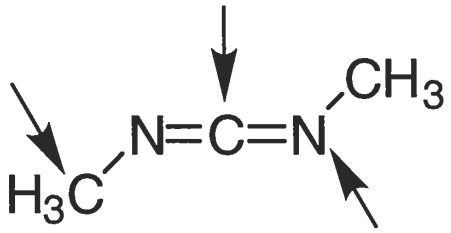
3. (15 pts)
The structure of N,N'-dimethylcarbodiimide is shown below.
a. Draw two additional resonance structures of this molecule in which ALL non-hydrogen atoms have filled octets.



N,N'-dimethylcarbodiimide

two more resonance structures, with all non-hydrogen atoms having filled octets

b. Identify the hybridization at each atom that has an arrow pointed at it.



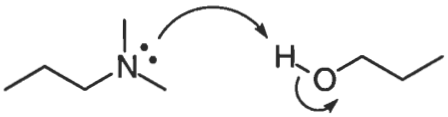
N,N'-dimethylcarbodiimide

c. Sketch the orbitals involved with π-bonding in this molecule (this means only the π -bonds!).

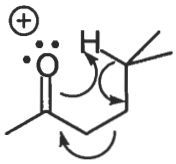
d. Draw the molecular orbital diagram for N,N'-dimethylcarbodiimide. YOU DO NOT HAVE TO CONSTRUCT IT. Note that C-H bonds are stronger than C-N bonds. For any different C-N bonds, use your best guess as to which is stronger. Label all the levels as σ, π, nb (non-bonding) etc. Fill in the electrons. Label the HOMO and LUMO.

4. (12 pts)

A. Show the product you would expect to get from each of the following arrow-pushing mechanisms. Be sure to include all formal charges on your product(s).

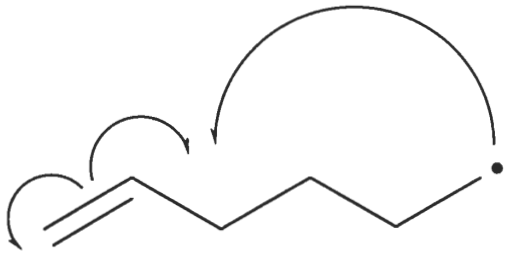


show all products

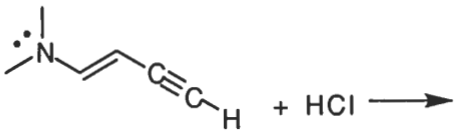


the McLafferty rearrangement

show all products

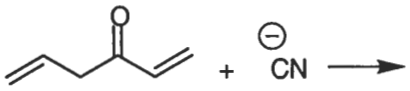


B. Show the expected products from the following reactions. Also write a rational arrow pushing mechanism leading to one of the products in each reaction. Be sure to use the hints in the product boxes to guide you.



3 products, each the result of a proton transfer from HCl to the other reactant

a rational arrow pushing mechanism leading to one of the above products



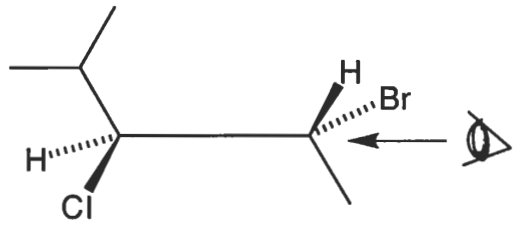
cyanide ion

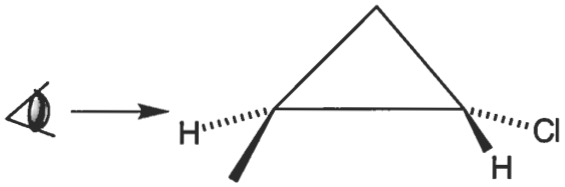
2 products, each resulting from carbon-carbon bond formation between the cyanide ion and the other reactant.

a rational arrow pushing mechanism leading to one of the above products

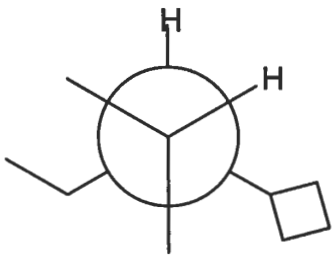
5. (10 pts)

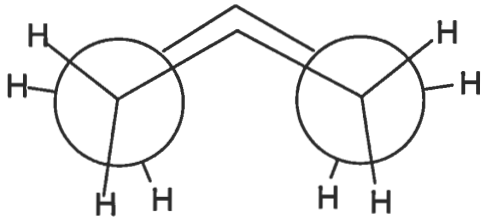
A. Draw Newman projections for the bond line structures shown below. Make sure your projection is representative of the conformation shown and the direction of the "eyeball".





B. Draw bond-line structures, including wedges and dashes where appropriate, that exactly represent the conformations depicted by the following Newman projections.

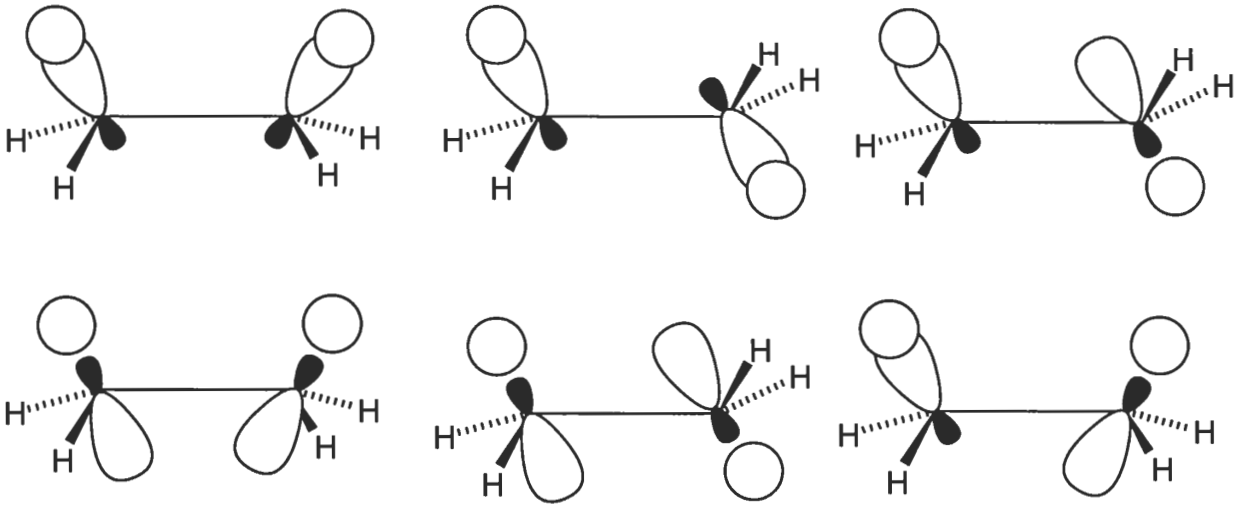




eclipsed

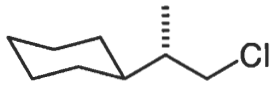
Continued on next page

C. Which diagram below best represents the stabilizing effect of hyperconjugation in ethane (circle your answer).

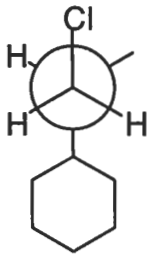


D. Define hyperconjugation (one or two sentences will suffice!).

6. The following questions have to do with the molecule shown below. (15 pts)



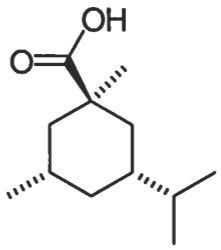
A. Starting with the Newman projection shown below, draw 5 other Newman projections representing 60 ° rotations of THE FRONT CARBON IN A CLOCKWISE DIRECTION.



B. On your diagrams in part A, write GA next to each gauche interaction involved with looking down the bond in question. Every incorrect label will cancel a correct label.

C. Assign relative energies to all six projections in part A using the numbers 1 through 6 where 1 is the lowest energy conformation and 6 is the highest energy conformation. If two or more conformations have the same energy, give them the same number (in which case you do not need to use all six numbers). HINT: NOT ALL GAUCHE INTERACTIONS HAVE THE SAME ENERGY.

7. (14 pts)



A. In the boxes at the bottom of the page, draw the two ring-flipped conformations of the molecule shown above.
B. Calculate ΔG for this equilibrium (use the values from Table 4-3 on your handout). Show your work in the appropriately labeled box. Place your answer in the box labeled $\Delta G =$.
C. Based on your answer, use arrows to indicate which side the equilibrium would favor .
D. Would you expect the experimental ΔG to be the same or significantly different from the calculated value? Explain your answer using specific terms discussed in lecture.

chair structure

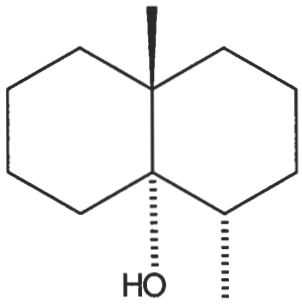
$\Delta G =$

express the direction of K here

ring flipped chair

show your work for calculating ΔG here

8. (10 pts)
Geosmin is a volatile, naturally occurring compound with an "earthy" odor.



geosmin

A. Provide a name for the bicyclic core of geosmin. That is, leave out the substituents in your name.

B. Draw two stereoisomers of geosmin using flat cyclohexanes.

two stereoisomers

C. On the structure of geosmin at the top of the page, clearly identify one of each of the following types of carbon atoms.

- a primary carbon; label as 1°
- a secondary carbon; label as 2°
- a tertiary carbon; label as 3°
- a quaternary carbon; label as 4°
- a bridgehead carbon; label as BH

D. Redraw the structure of geosmin using chair conformations to represent the cyclochexane rings. Clearly show the relative orientations of all the substituents on geosmin.