Hour Examination #1, Chemistry 301/301A, October 11, 2004

> Chemiftry is the art of decompounding bodies, that is, of refolving compound bodies into their more fimple parts, and by combining thefe together, to reproduce the original compound with all its properties, and even to compound new bodies, from the different mixtures of other bodies, and that by the help of fire.
>
> Thomas Southwell, 1764

1 (20 points). Hydrazine has the structure: H_2NNH_2. But, of course, this formula hides much possible structural diversity.

a) Draw a perfect Lewis "dot" picture of hydrazine.

b) Make drawings of hydrazine with:

(i) both nitrogens hybridized sp^2 and all six atoms in the same plane. Show any lone pairs!

(ii) a staggered arrangement with both nitrogens hybridized approximately sp^3

(iii) There is more than one structure that fits the criterion of (ii). Use Newman projections to draw two staggered conformations in which both nitrogens are approximately sp^3.

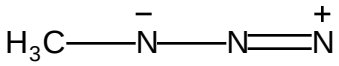
c) The structure you drew in (ii), with approximately sp^3 nitrogen atoms, is the better one (more stable than i). Please explain this observation. To preempt an incomplete answer, we'll tell you that N—H/N—H bond eclipsing in (i) has only a little to do with it. There is another, much larger factor favoring (ii) over (i).

2 (24 points)

a) Draw full Lewis "dot" structures for $^{-}BF_4$ and BF_3. Indicate the hybridization of the boron atom next to each Lewis structure.

b) The B—F bond length in $^{-}BF_4$ is approximately 1.5 Angstroms. In BF_3, the bond length is much shorter, about 1.3 Angstroms. Provide two reasons for this difference. Hint: electrostatics does not play a significant role. Hint: Think "sigma" for one reason, and "pi" for the other.

c) Methyl azide, a linear molecule that has no net charge, is drawn below with all electron dots left out.

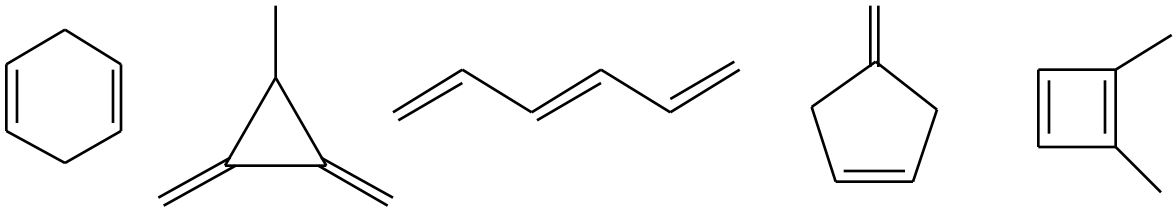


(i) Put in the electron dots. What is the hybridization of the central nitrogen?

(ii) Use an arrow formalism to write another resonance form in which each atom maintains a proper octet. What is the hybridization of the central nitrogen in this form?

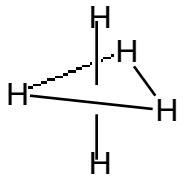
3 (15 points). Draw all the *cyclic* isomers of the formula C_6H_8 *that contain* ***one, repeat one****, four-membered ring but are* ***not*** *cyclobutadienes or cyclopropanes.* For reasons you do not yet know, 1,3-cyclobutadienes are very, very unstable, so don't write any. The structures below, though C_6H_8, are all *wrong* answers. Draw out all isomers capable of *Z/E* isomerism in both forms. Draw out all chiral isomers in both *R* and *S* forms.

wrong answers:



Now write us two (only) isomers that contain more than one four-membered ring.

4 (21 points). The compound H_5 could have the trigonal bipryamidal structure **X**. Regardless of whether or not it does have this structure (or even if H_5 exists), we can calculate the molecular orbitals for such a species. Do so. We insist that you do it in the following way.

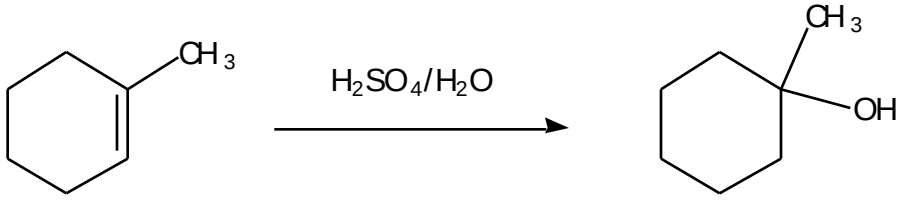


X

a. Start with the MOs of two easily-constructed pieces, H_2 and cyclic H_3. You may use the MOs directly if you remember them.
b. Determine how many molecular orbitals **X** will have.
c. Combine the molecular orbitals for H_2 and cyclic H_3 in an appropriate way to make **X**. Be very careful to show the molecular orbitals you are using and show how you are combining them to make the molecular orbitals of **X. *Be neat and hyper-organized!*** Remember: you need only interact the orbitals closest in energy.
d. Order the molecular orbitals of **X** in energy.
e. Place the appropriate number of electrons in the orbitals. Don't forget to take account of electron spin.

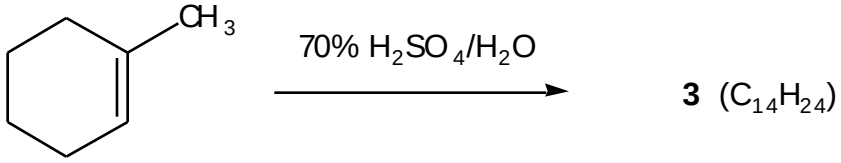
5 (20 points). The acid-catalyzed hydration of 1-methyl-1-cyclohexene (**1**) affords 1-methylcyclohexanol (**2**).

a. Write a very detailed arrow formalism mechanism for this reaction that is consistent with the observed regiochemistry.



1 **2**

b. When the acid-catalyzed hydration is run in more concentrated H_2SO_4 - less water, more acid - very little **2** is formed. Instead the major product is a compound **3** of the formula $C_{14}H_{24}$. Use an analysis of the mechanism of this reaction to assign a structure to **3**.



1 (C_7H_{12})

"I pledge that I have not violated the honour code on this examination."