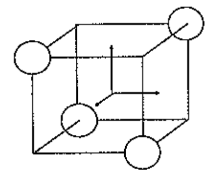
No Analytical Crib Available for November 11 exam

Written by Dr. Simpson

No Biochemistry Crib Available for November 11 exam

Written by Dr. Davidson

Answers 11-06 Inorganic Cume



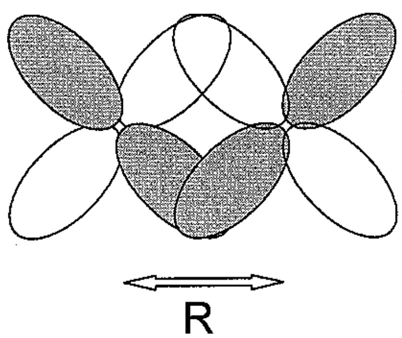
1A. MnO_4^{2-} is d^1 and tetrahedral. The SOMO is x^2-y^2 or z^2.

B. $Co(NH_3)_6^{3+}$ is octahedral, low-spin, and d^6. The LUMO's are x^2-y^2 and z^2.

C. $CuCl_2^-$ is linear and d^{10}. The HOMO is the filled σ* MO which is mainly z^2.

D. The HOMO of $Mo_2Cl_8^{4-}$ is the δ-bonding orbital which is the in-phase combination of d(xy) orbitals overlapping in a face-on fashion. Each molybdenum is formally d^4.

2. See the article for details but consider the dπ MO. At large R the overlap tends toward 0. As R decreases the positive overlap increases until the nuclei get so close that positive lobes on one metal center begin to overlap negative lobes on the other. As R continues to shrink, the net overlap goes through 0. Finally, in the united atom limit, the overlap is net negative, and the magnitude is 1 because of normalization.



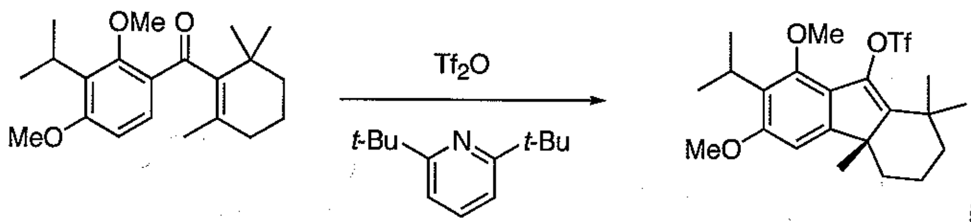
3. A2 is the LUMO because it has more nodes and no net bonding.
B1 is the LUMO because it is σ*. The other is a filled non-bonding orbital.
C1 is the SOMO because NO has 11 valence electrons. C2 is the weakly bonding pσ.
D2 is a π* LUMO while D1 is a filled pσ MO.
E1 is a π* LUMO, and E2 is a filled, non-bonding orbital with π symmetry.

Organic Cumulative Exam – November 2006

Beth, Would you please make me copies of these JACS papers? Thanks! Jean

Please provide a mechanism for the following five reactions.

1. JACS, (2006) 128, 11022.



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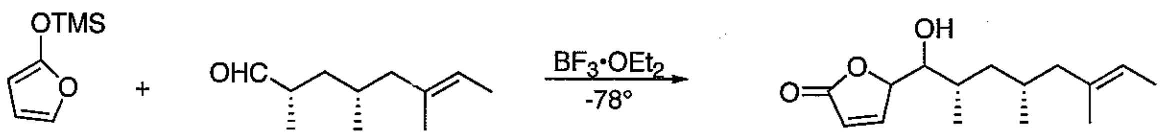
2. JACS, (2006) 128, 11032.



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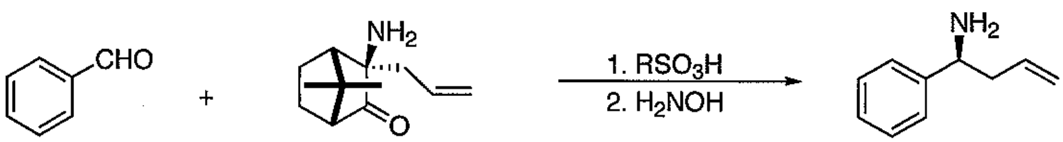
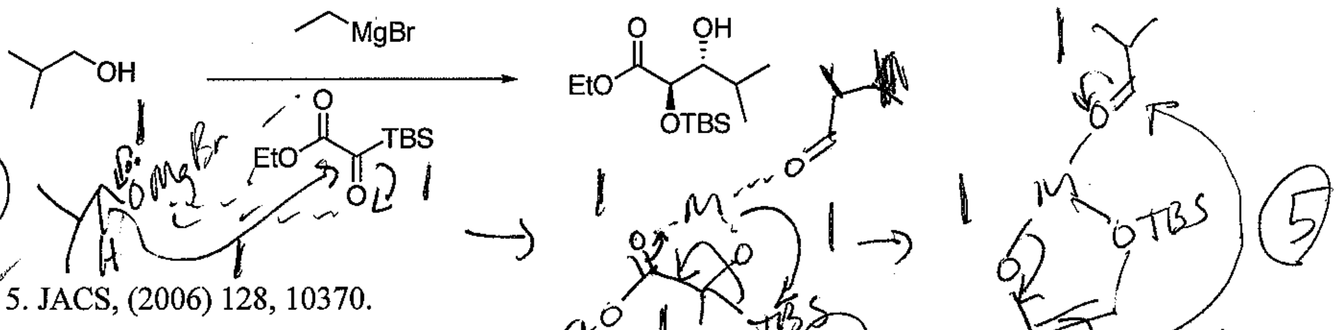
3. JACS, (2006) 128, 11038.



~~26~~ ~~31~~ 29

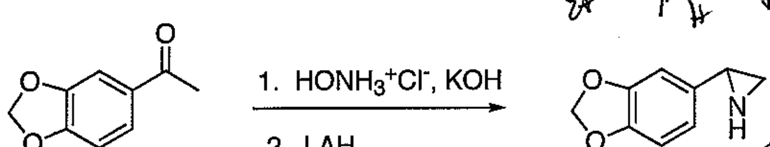
9+15=24

4. JACS, (2006) 128, 9302.



5 5 5

5. JACS, (2006) 128, 10370.



20

15
12
31
24
20

100

1.

Solution to
P. Chem. Cumulative Exam
Nov. 11, 2006

a. From information on exam

$$\bar{\nu}_D = \left(\frac{1}{1^2} - \frac{1}{2^2}\right) R_D = \frac{3}{4} R_D = 82{,}281.476 \text{ cm}^{-1}.$$

Similarily

$$\bar{\nu}_H = \frac{3}{4} R_H = 82{,}259.098 \text{ cm}^{-1}.$$

$$\therefore \quad \frac{R_D}{R_H} = \frac{\mu_D}{\mu_H} = \frac{82{,}281.476}{82{,}259.098}$$

or

$$\frac{\mu_D}{\mu_H} = 1.000272043.$$

But

$$\frac{\mu_D}{\mu_H} = \frac{m_D m_e (m_p + m_e)}{m_p m_e (m_D + m_e)} = \frac{m_p m_D m_e (1 + m_e/m_p)}{m_p m_D m_e (1 + m_e/m_D)}$$

or

$$\frac{\mu_D}{\mu_H} = \frac{(1 + m_e/m_p)}{(1 + m_e/m_D)} = 1.000272043.$$

$$\therefore \quad \left(1 + \frac{m_e}{m_D}\right) = \frac{(1 + m_e/m_p)}{1.000272043} = (1 + m_e/m_p)\, 0.999728031$$

or

$$m_D = \left[\left(1 + \frac{m_e}{m_p}\right) 0.999728031 - 1\right]^{-1} m_e.$$

Using $m_e = 9.10938 \times 10^{-31}$ kg and $m_p = 1.67262 \times 10^{-27}$ kg in above equation gives

$$\boxed{m_D = 3.3429 \times 10^{-27} \text{ kg.}}$$

The result for m_D must be close to twice the value for m_p and it is

b. Here we use $\mu_{pos} = \frac{m_e}{2}$. Also it is sufficient to use

$$\mu_H = \frac{m_p m_e}{m_p + m_e} \cong \frac{m_p m_e}{m_p} = m_e .$$

The binding energy is the same as the energy needed to remove an electron from the atom in its $n=1$ state to infinity. Thus from the first equation in cm^{-1} it is

$$\bar{\nu}_{be} = R_N \left[\frac{1}{1^2} - \frac{1}{\infty^2} \right] = R_N$$

But

$$\frac{R_{N=\text{positronium}}}{R_H} = \frac{\mu_N}{\mu_H} = \frac{m_e}{2} \frac{1}{m_e} = \frac{1}{2}$$

$\therefore$

$$\boxed{\bar{\nu}_{be}\,(\text{Positronium}) = \frac{1}{2} R_H = 54{,}833.5 \text{ cm}^{-1}}$$