No Analytical crib available

April 28, 2007

Written by Professor Cooks

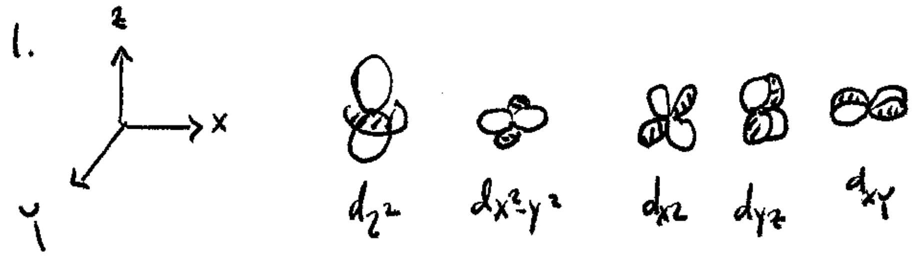
No Biochemistry crib available

April 28, 2007

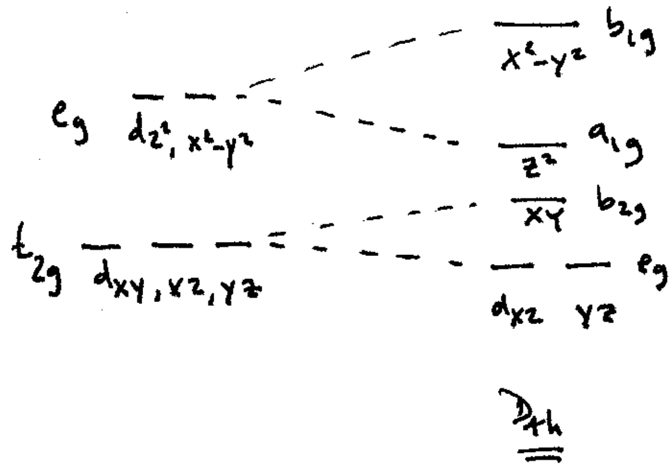
Written by Professor VanEtten

INORG. CHEM.
April 07.

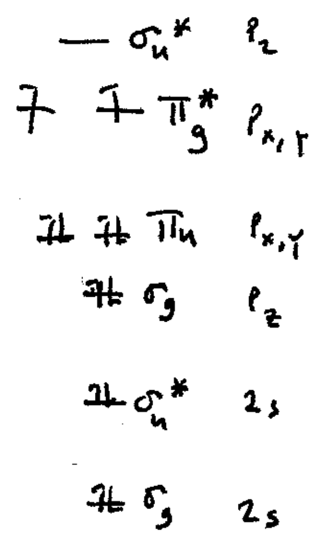
1.



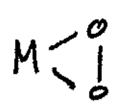
2.



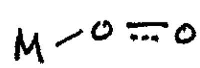
3. O_2



Ground state $^3\Sigma$ (triplet)

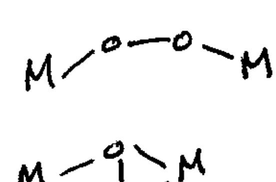


peroxo



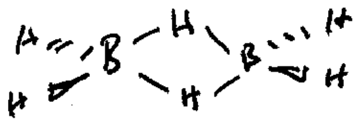
superoxo

also



} bridging

4. B_2H_6 D_{2h}



bridging H
3-center-2-electron bonds.

5. See on exam.

6. See on exam.

Inorganic Cumulative Exam
April 28, 2007

1. (10 points) Draw the five d-orbitals and label them.

2. (15 points) Start with the splitting of d-orbitals in an octahedron field and show how the d-orbitals splitting would change as the O_h molecule distorts (Jahn-Teller) to lower symmetry (D_{4h}).

3. (20 points) Construct a molecular orbital (MO) diagram for molecular oxygen. According to the Pauli exclusion-principle, show the electron occupancy in your MO diagram. What is the spin for ground state oxygen? Show the different binding modes O_2 could adopt as a ligand on a transition metal.

4. (15 points) What is the point group for B_2H_6? Discuss briefly the bonding in this molecule.

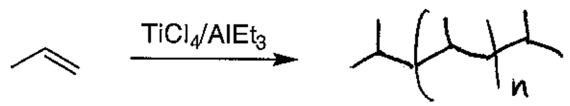
5. (20 points) Give the products for the following reactions:

(a) $Xe + PtF_6 \rightarrow$ $XeF^+ PtF_6^- / XeF^+ Pt_2F_{11}^- / XeF_2$

(b) $Pt(py)Cl_3^- + py \rightarrow$ cis-$Pt(py)_2Cl_2$

(c) $(C_5H_5)MgBr + FeCl_3 \rightarrow$ Cp_2Fe

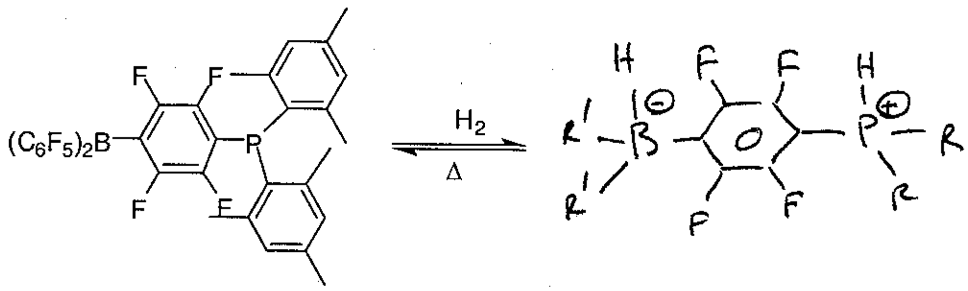
(d) Re_2O_7 + xs $CO \rightarrow$ $Re_2(CO)_{10}$

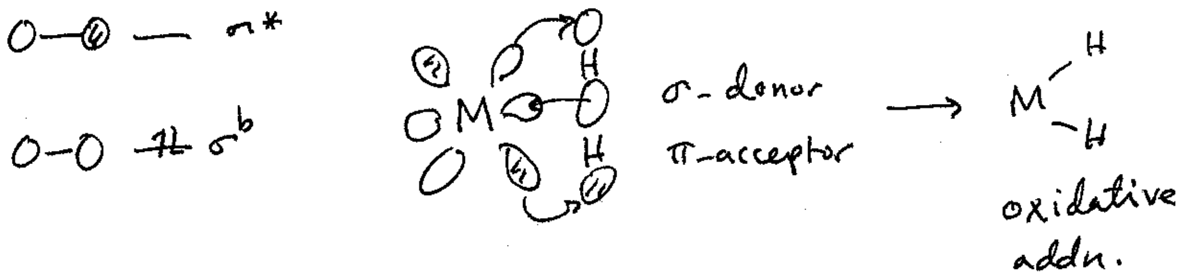
(e) 

polypropylene

(f) C + steam (H_2O) $\xrightarrow{\text{Cat./ high temp.}}$ $CO + H_2 \longrightarrow CO_2 + H_2$

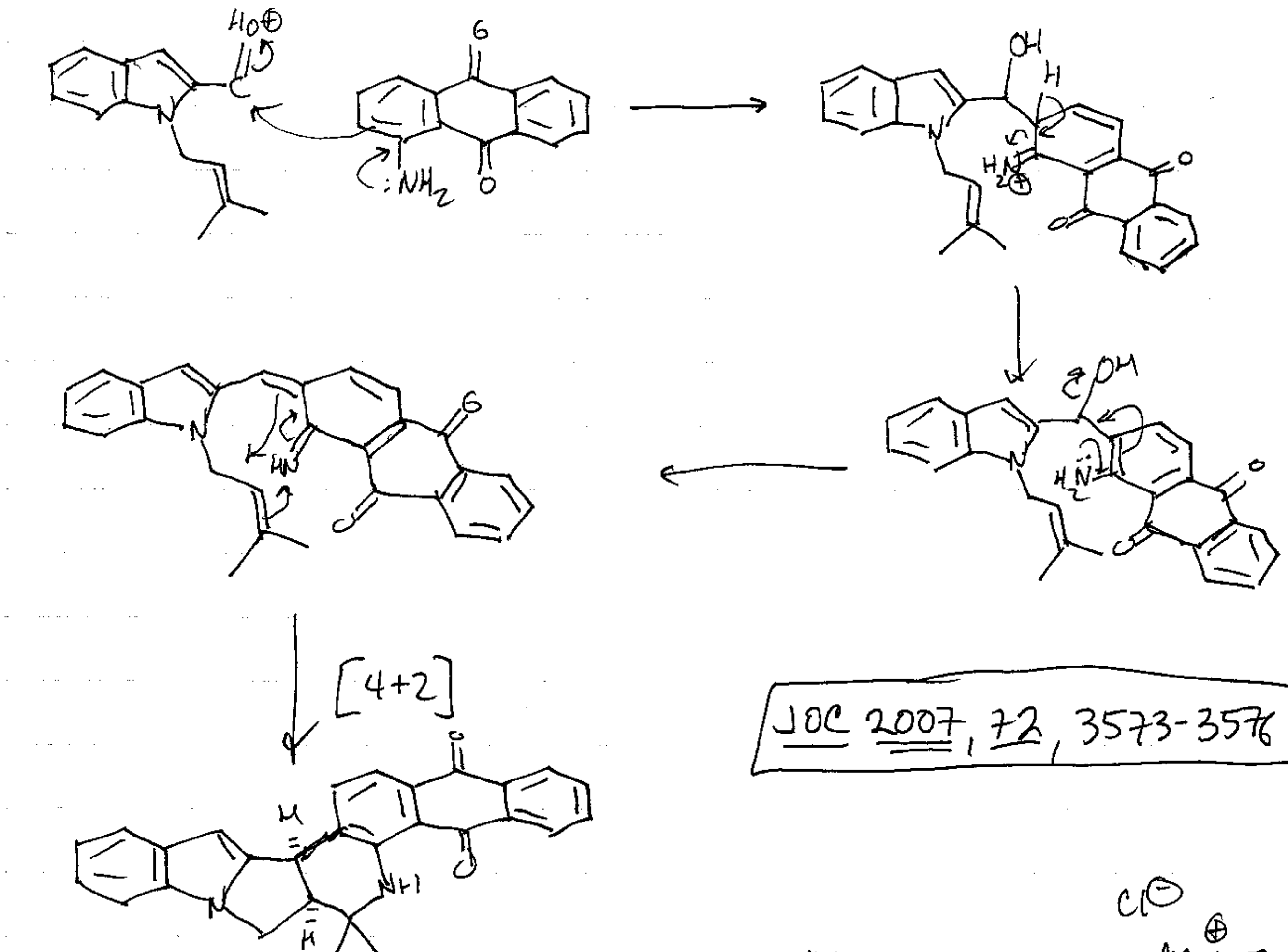
6. (20 points) Construct an MO diagram for dihydrogen and discuss how transition metals affect dihydrogen splitting more successfully than main group compounds. A recent paper in *Science* reported (*Science* **2006**, *314*, 1124) reversible binding of H_2 to the main group compound shown below. Suggest what the product is.


(C6F5)2B
F
P
H2
Δ
H
R'
B
P
R


σ*
σb
M
H
σ-donor
π-acceptor
oxidative
addn.

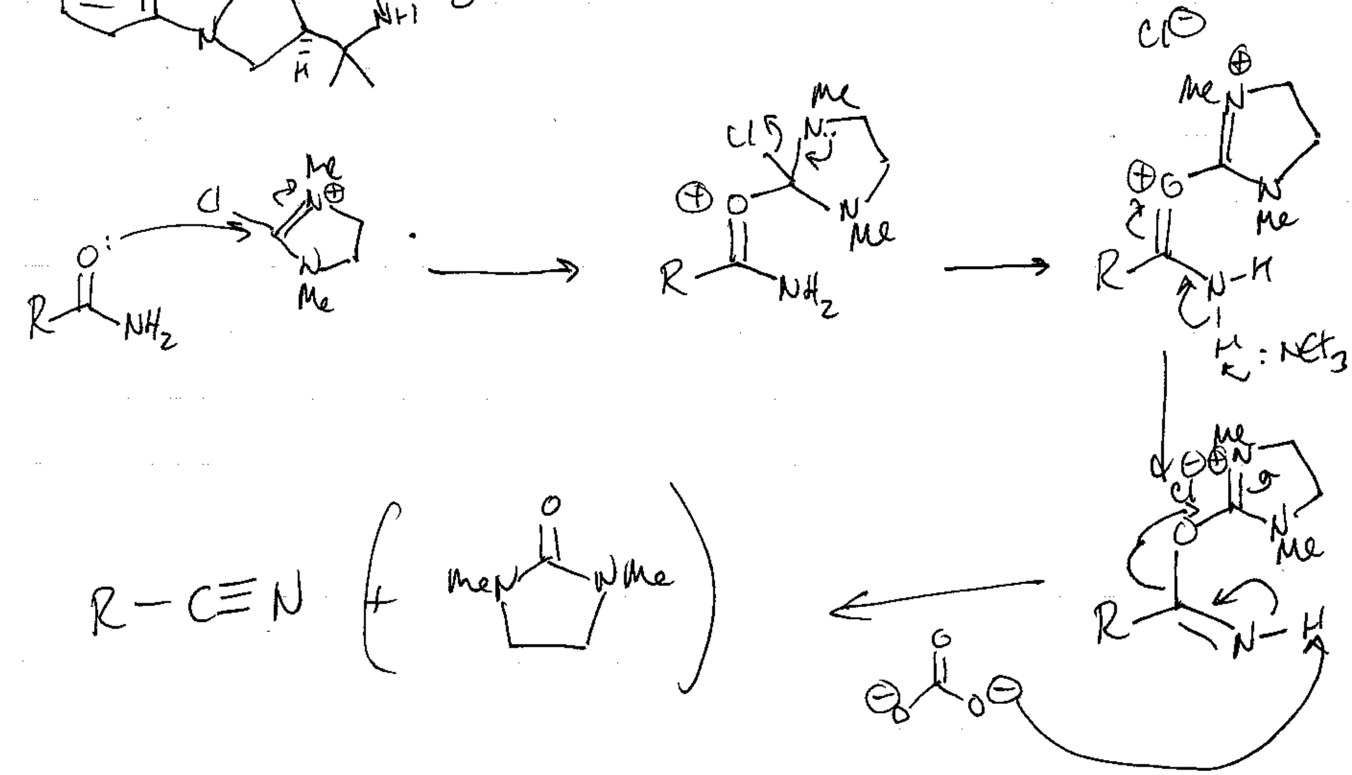
ORGANIC CRIB APRIL 28, 2007

(1)



JOC 2007, 72, 3573-3576

(2)

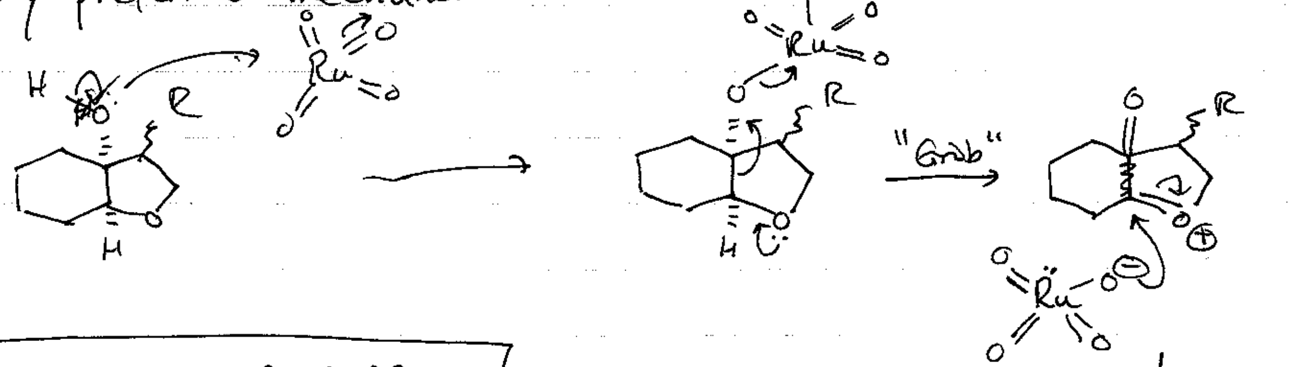


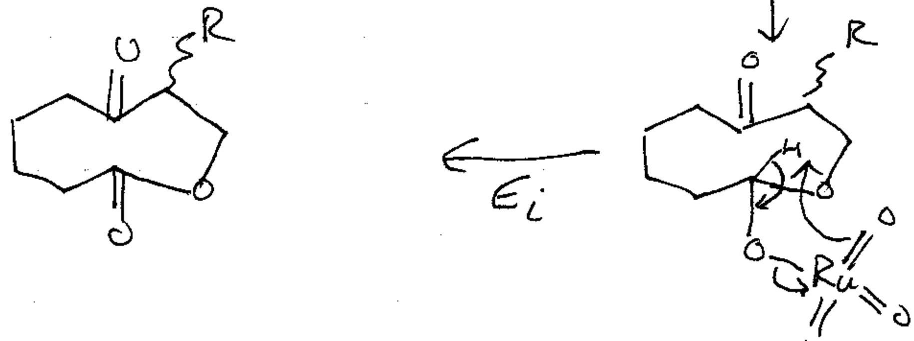
JOC 2007, 72, 2744-2756

(3) Many possible answers, but all involve RuO_4:

$$RuCl_3 + NaIO_4 \longrightarrow RuO_4$$

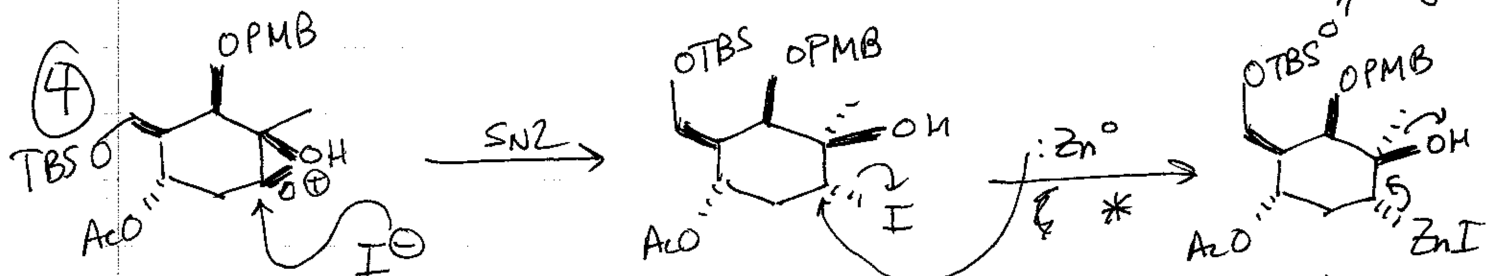
my preferred mechanism:

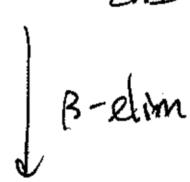


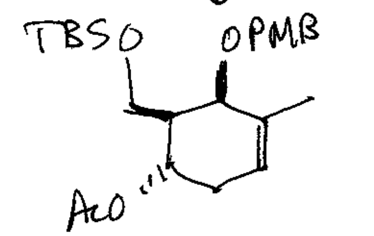


JOC 2007, 72, 2945–2950

(4)



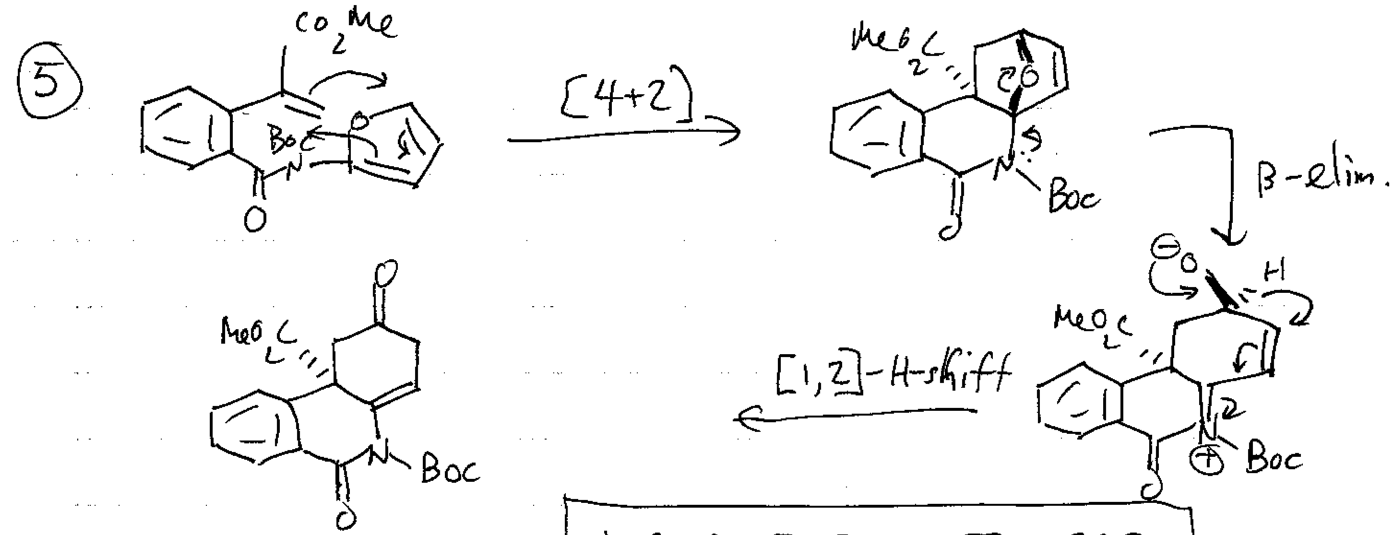




* I show it as a displacement for convenience only; it's almost certainly a sequence of 2 SET events

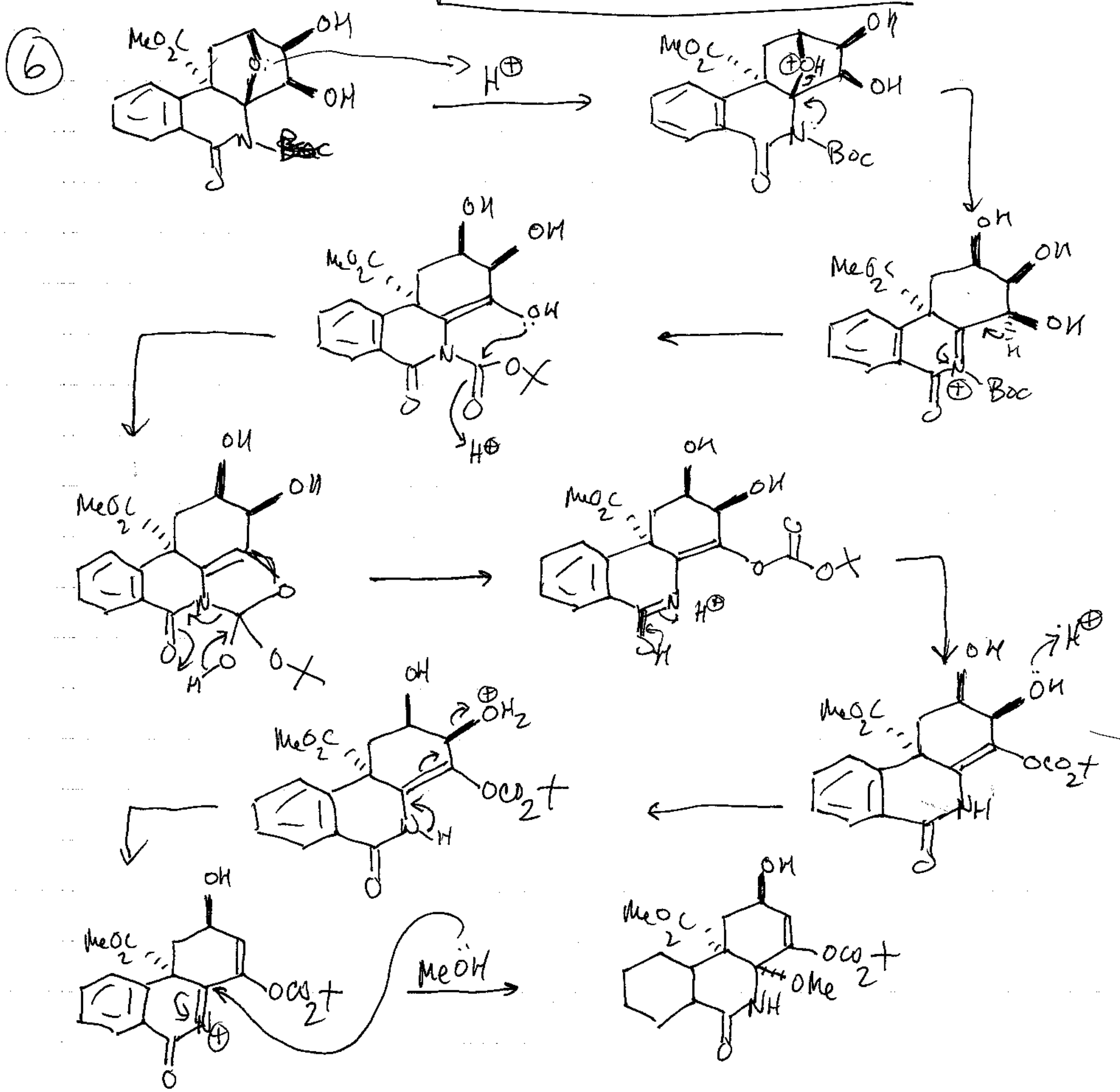
JOC 2007, 72, 2344–2350

(5)

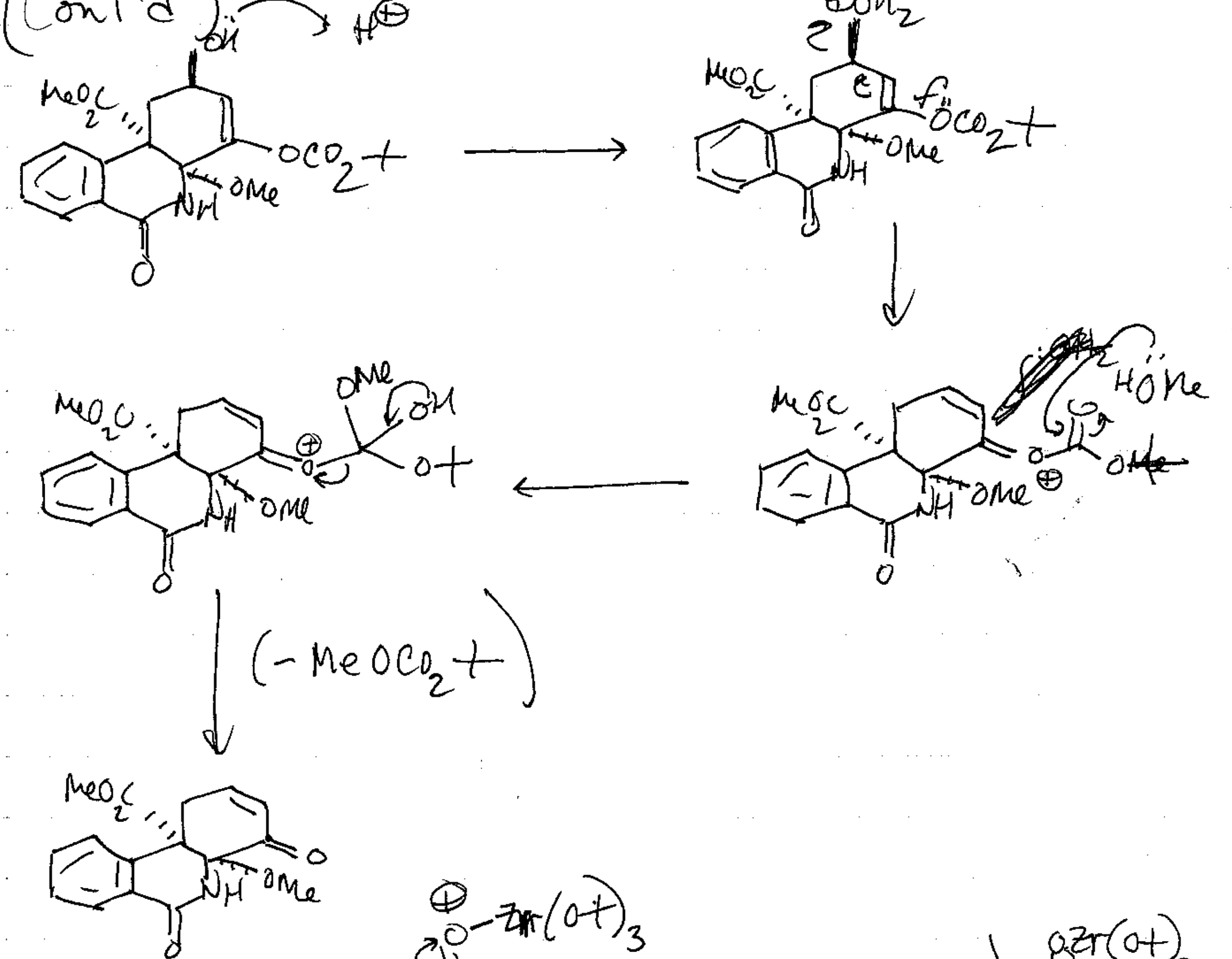


JOC 2007, 72, 2570-2582

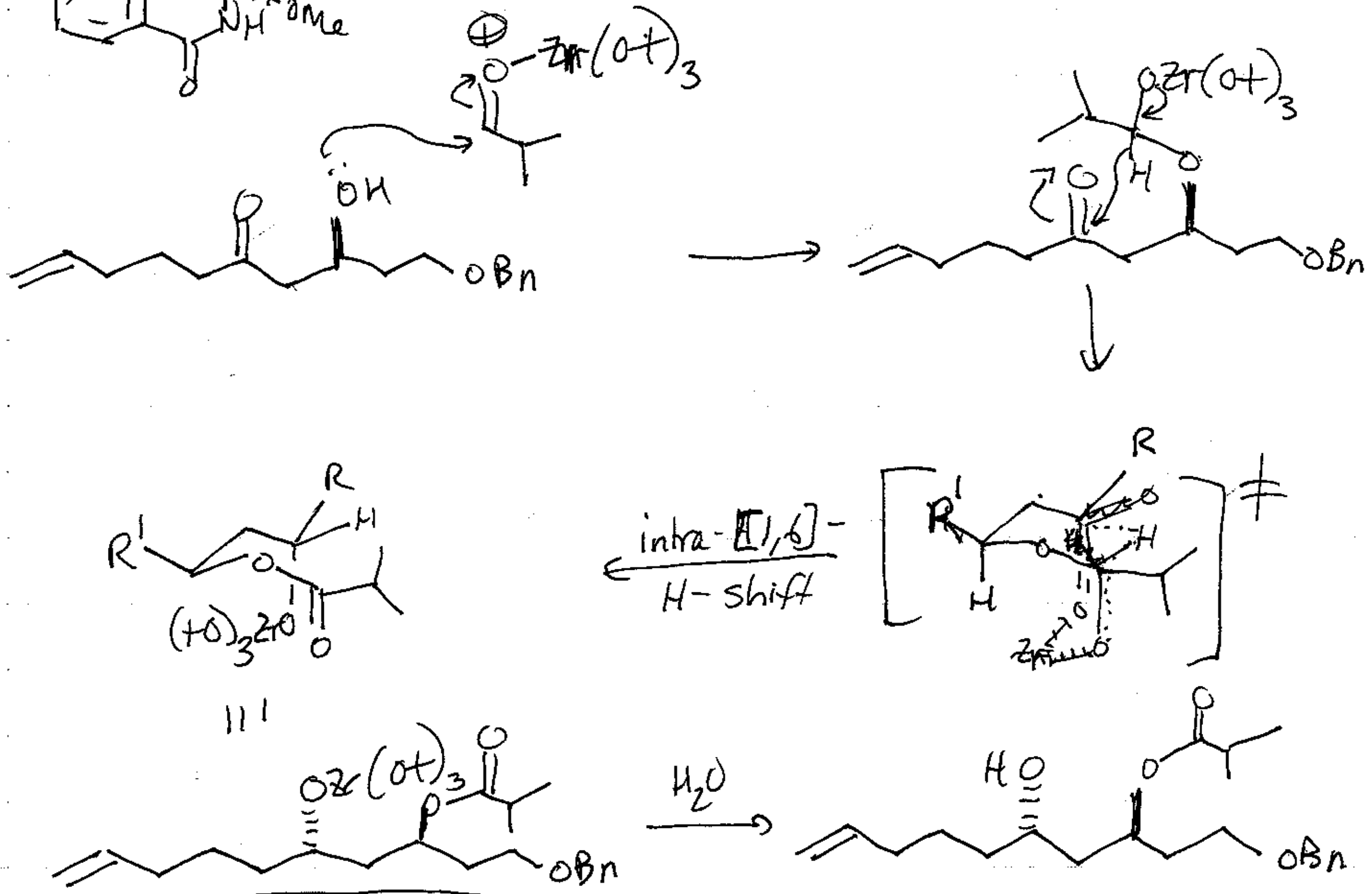
(6)



(6) (Cont'd)



(7)



JOC 2007, 72, 2602–2611

Solutions to P. Chem Cume for April 2007

25 points

1. Assume a surface of area A, perpendicular to the direction of motion, x. A molecule with $V_x > 0$ will strike the surface in a time interval Δt if it is within a distance $d \le V_x \Delta t$. Therefore, we need to know the number of molecules in the volume $A V_x \Delta t$ with $V_x > 0$. This number is the volume multiplied by the number density of molecules, or $A V_x \Delta t N$, where $N = \frac{n N_A}{V} = P/kT$. We need to sum over all possible velocities and the probability distribution of velocities:

$$\text{number striking surface} = N A \Delta t \int_0^\infty V_x f(V_x)\, dx$$

collision frequency is number per unit time, per area:

$$Z = N \int_0^\infty V_x f(V_x)\, dx$$

$$= \frac{P}{kT} \int_0^\infty \left(\frac{m}{2\pi kT}\right)^{1/2} V_x e^{-mV_x^2/2kT} dV_x$$

Using the integral given this becomes:

$$Z = \frac{P}{kT}\left(\frac{m}{2\pi kT}\right)^{1/2} \frac{kT}{m} = \boxed{\frac{P}{(2\pi m k T)^{1/2}}}$$

Solutions (continued)

25 points

2. On a typical metal surface you can assume about 10^{15} atoms/cm². From problem 1,

$$Z = \frac{p}{(2\pi m k T)^{1/2}}$$

$$p = Z\,(2\pi m k T)^{1/2}$$

$T = 298$ K

assume* $M = 32$ g/mol

$m = M/N_A = 5.314 \times 10^{-26}$ kg

*this is for ~~air~~ oxygen. The component of air that will react with the surface is oxygen. However, since the problem asks for the air pressure, this problem could be done using the average mass for air, approximately 29 g/mol.

We need Z to be about 10^{14} cm^{-2} over a period of 30 min (1800 sec). This gives a value of $Z = 5.6 \times 10^{10}$ cm^{-2} s^{-1} $= 5.6 \times 10^{14}$ m^{-2} s^{-1}

$$p = (5.6 \times 10^{14}\ \text{m}^{-2}\text{s}^{-1})\left[2\pi(5.3 \times 10^{-26}\ \text{kg})(1.381 \times 10^{-23}\ \tfrac{\text{kg m}^2}{\text{s}^2\text{K}})(298\ \text{K})\right]^{1/2}$$

$$= (5.6 \times 10^{14}\ \text{m}^{-2}\text{s}^{-1})\left(1.37 \times 10^{-45}\ \tfrac{\text{kg}^2\text{m}^2}{\text{s}^2}\right)^{1/2}$$

$$= (5.6 \times 10^{14}\ \text{m}^{-2}\text{s}^{-1})\left(3.71 \times 10^{-23}\ \text{kg}\ \tfrac{\text{m}}{\text{s}}\right)$$

$$\boxed{p = 2.08 \times 10^{-8}\ \text{Pa} = 1.56 \times 10^{-10}\ \text{Torr}}$$

Solutions (continued)

35 points

3. We will need to get expressions for the rates first. In the exaple given on the exam paper, we see that the rate of adsoption is a fraction of the ~~number~~ fraction of available surface sites. With this bimoleculer reaction, the ~~number~~ fraction of available surface sites is given by $1-\Theta_A-\Theta_B$. Since each step is similar to the simple one, we can derive the rates, by analogy. From the first step of this process, we can say that the rates of adsorption and desorption will be:

$$Rate_{dA} = k_d^A N \Theta_A \equiv V_d^A$$

$$Rate_{aA} = k_a^A [A](1-\Theta_A-\Theta_B)N \equiv V_a^A$$

similarly for the second step:

$$V_d^B = k_d^B N \Theta_B$$

$$V_a^B = k_a^B [B](1-\Theta_A-\Theta_B)N$$

At equilibrium:

$$k_d^A \Theta_A = k_a^A [A](1-\Theta_A-\Theta_B)$$

$$\frac{k_a^A}{k_d^A} = \frac{\Theta_A}{[A](1-\Theta_A-\Theta_B)}$$

$$K_A[A] = \frac{\Theta_A}{(1-\Theta_A-\Theta_B)}$$

similarly

$$K_B[B] = \frac{\Theta_B}{(1-\Theta_A-\Theta_B)}$$

Rearranging gives:

$$\boxed{\Theta_A = \frac{K_A[A]}{1+K_A[A]+K_B[B]}}$$

$$\boxed{\Theta_B = \frac{K_B[B]}{1+K_A[A]+K_B[B]}}$$

Solutions (continued)

15 points

4. a. increase in pressure will **decrease** the diffusion constant because the mean free path is inversely proportional to pressure:

$$\lambda = \frac{kT}{\sqrt{2}\,\sigma P}$$

b. increase in temperature will **increase** the diffusion constant because the mean speed is directly proportional to temperature:

$$\bar{c} = \left(\frac{8kT}{\pi m}\right)^{1/2}$$

c. increasing the size will increase the collision cross section, σ, which will decrease the mean free path. This will **decrease** the diffusion coefficient