No Analytical crib available
February 9, 2013
Written by Professor Mao
Ph# 40498

Biochemistry Cumulative Exam February 3, 2013

1. Briefly describe the best method to perform each of the following experiments. (7 points each)

   a) Determine the distance from the lipid bilayer to the adrenaline binding site on the beta adrenergic receptor in a cell membrane.
   Label the hormone adrenaline with a fluorescent dye (fluorescent donor) at a site on the hormone that does not interfere with beta adrenergic receptor binding. Then, add a lipophilic fluorescent dye to the membrane bilayer that has an excitation spectrum that overlaps with the emission spectrum of the above fluorescence donor. Fluorescence resonance energy transfer (FRET) will occur from the adrenaline-linked donor to the membrane bilayer embedded fluorescent acceptor, and the efficiency of this energy transfer will be proportion to $1/r^6$, where r is the distance between the donor and acceptor. From the efficiency of energy transfer, the distance between the adrenaline binding site and the membrane bilayer can be calculated.

   b) Reconstitute your favorite membrane-spanning protein (dissolved in a detergent solution) into an egg phosphatidylcholine bilayer.
   Add a chloroform: methanol (3:1) solution of egg PC to a round bottom flask and rotoevaporate until all the organic solvent is gone and the phospholipid has formed a thin film on the flask. Add the detergent solubilized protein and swirl until the lipid is dissolved in the protein/detergent micelles. Then, slowly remove the detergent to reconstitute the protein into the lipid bilayers. Slow removal of the detergent can be achieved by dialysis if the detergent is dialyzable or by incubation with hydrophobic beads (e.g. SM2 Biobeads) if the detergent is not dialyzable. Other methods for detergent removal also exist.

   c) Encapsulate large quantities of the drug doxorubicin with high efficiently into liposomes.
   Prepare liposomes in a high concentration of ammonium sulfate or some other sulfate solution using the thin film method described in the answer to the above question. Then add doxorubicin to the preformed liposomes. The doxorubicin will diffuse into the liposomes and form an insoluble salt with the sulfate and precipitate out of solution. This will eventually result in very high concentrations of doxorubicin entrapped inside the liposomes. This is how the $700MM/year drug Doxil is prepared.

   d) Determine the change in fluidity of a liver cell plasma membrane upon stimulation with hepatocyte growth factor.
   This is best analyzed by addition of a lipophilic fluorescent dye to the membrane and measuring its fluorescence polarization. Then use the Perrin equation to convert the

polarization value to membrane viscosity. Alternatively, the change in membrane fluidity can be quantitated using fluorescence recovery after photobleaching (FRAP).

e) Predict the number and sequence positions of membrane-spanning alpha helices in your newly sequenced membrane protein.
Construct a hydropathy plot from the amino acid sequence information on the protein and locate the stretches of positive hydropathy that are greater or equal to 20 amino acids in length.

f) Measure the bilayer to hexagonal phase transition temperature of an egg phosphatidylethanolamine suspension.
This can only be done using ^{31}P NMR by analyzing the change in line shape with temperature as temperature is raised. The line shapes of the two phospholipid dispersions are opposite in shape.

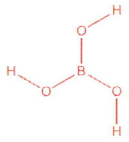
g) Determine the rate of calcium influx into a cell following stimulation with thrombin.
This can be done by using a calcium sensitive fluorescent dye that can be loaded into cells (e.g. FLUO-3AM or FURA-2AM) and monitoring the change in fluorescence upon addition of thrombin. Alternatively, a calcium influx can be quantitated using radioactive calcium (i.e. $^{45}Ca^{++}$).

2. Draw the structure of stearoylsphingomyelin and explain why it might tend to segregate into sphingolipid-rich domains in a cell membrane (15 points).
See any textbook for the structure of stearoylsphingomyelin. Sphingolipids tend to segregate into separate domains in membranes because they are commonly comprised of long chain saturated fatty acids and because the free hydroxyl in their backbones tends to H-bond with the free hydroxyls of other sphingolipids, thereby promoting their collection into patches of sphingolipids.

3. Explain how a transmembrane electrical potential is most commonly maintained across a mammalian cell plasma membrane. Then describe with one or more examples how this transmembrane potential is used to mediate cellular functions (15 points).
Transmembrane electrical potentials in living cells are primarily created by the Na/K-ATPase, also known as the sodium/potassium pump. This enzyme pumps 3 Na+ out of the cell for every 2 K+ it pumps into the cell, thereby establishing a charge separation across the membrane required for a transmembrane potential.
This transmembrane potential is used for ion and solute pumping, as well as for signaling in neurotransmission and other signaling events.

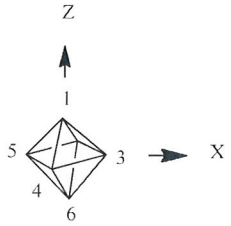
Inorganic Chemistry Cumulative Exam
Purdue University
Saturday, February, 2013

1. **(32 points)** An improper S_3 axis (rotary-reflection) generates a point symmetry group of order 6, even though the traditional name for the group comes from other, co-existing symmetry elements.
   A. In particular, what simple symmetry operation is equivalent to S_3^3, i. e., three successive S^3 operations? σ_h
   B. Same question for S_3^4. C_3
   C. What is the usual name of the point group in question? Draw the structure of a molecule that has that symmetry. C_{3h}



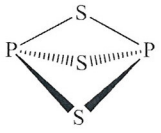
   D. What three subgroups does it have of orders 3, 2, and 1, respectively?
   C_3, C_s, E

2. **(20 points)** The octahedron shown below has four-fold axes running along the z, x, and y axes, the latter pointing more or less toward the reader. The numbers along the vertices are there merely for tracking purposes (index 2 not shown for clarity). Find the symmetry operation equivalent to the product $C_4(z) \times C_4(x)$, which means do $C_4(x)$ followed by $C_4(z)$. Assume all rotations are counter-clockwise. Note that the two symmetry elements combine to generate another. Describe the location of the generated symmetry element .

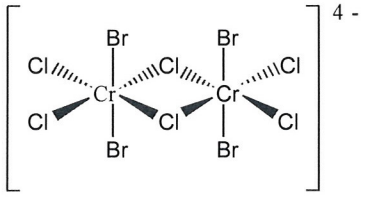


C_3 through 1,2,3 triangular face

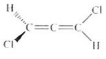
3. **(48 points)** Assign point groups to the following molecules or ions.

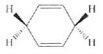
A 

D_{3h}

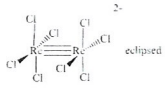
B. 

D_{2h}

C. C_2 

D.  D_{2h}

E. C_{2h}

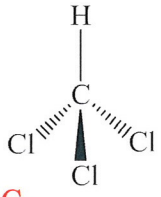
F. 

D_{4h}

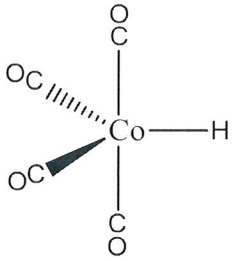
Inorganic Chemistry Cumulative Exam, Continued.

G.

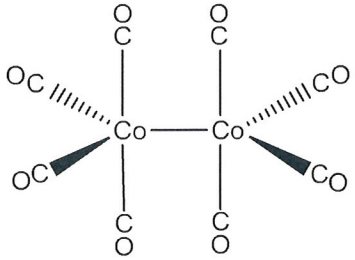
$D_{\infty h}$

H. 

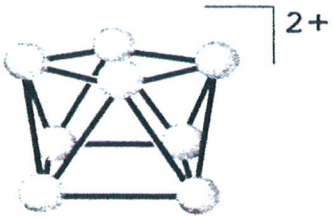
C_{3v}

I. 

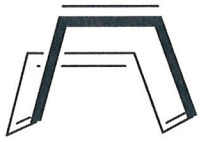
C_{3v}

J. 

D_{2h}

K. 

D_{4d}

L. 

D_{2d}

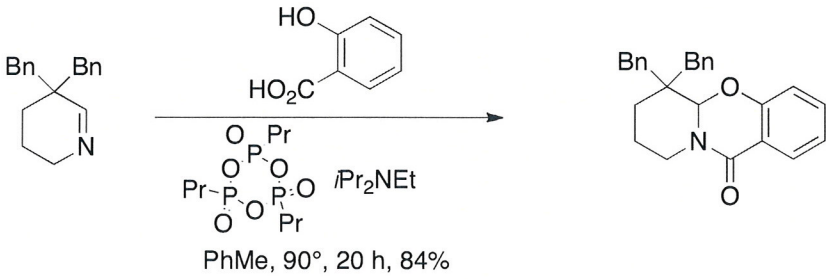
Point groups for <u>selected</u> groups included for convenience. Not all groups.

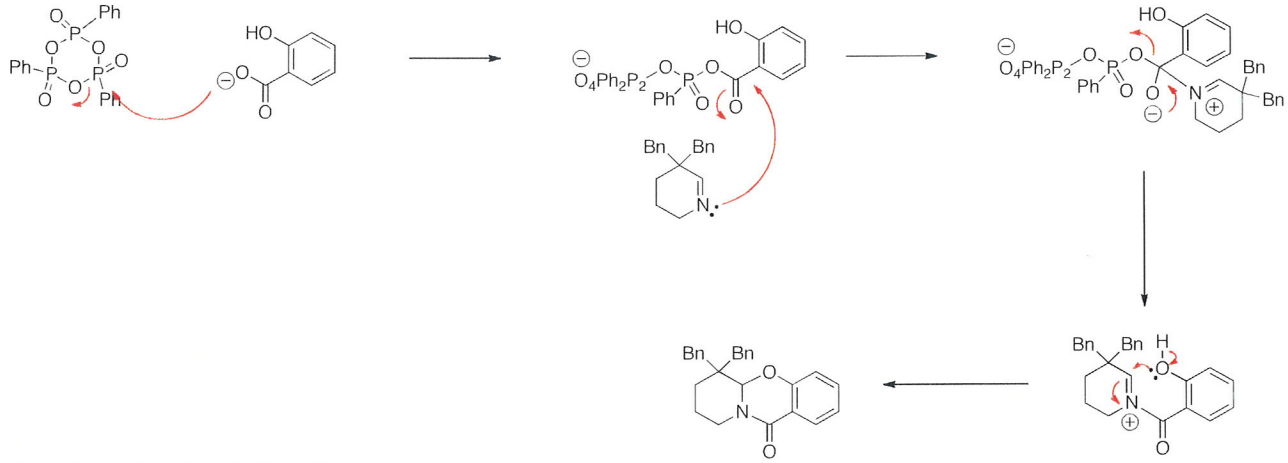
Organic Cumulative Examination – Heterocyclic Synthesis from Org. Lett. 2013

Feb. 9, 2013

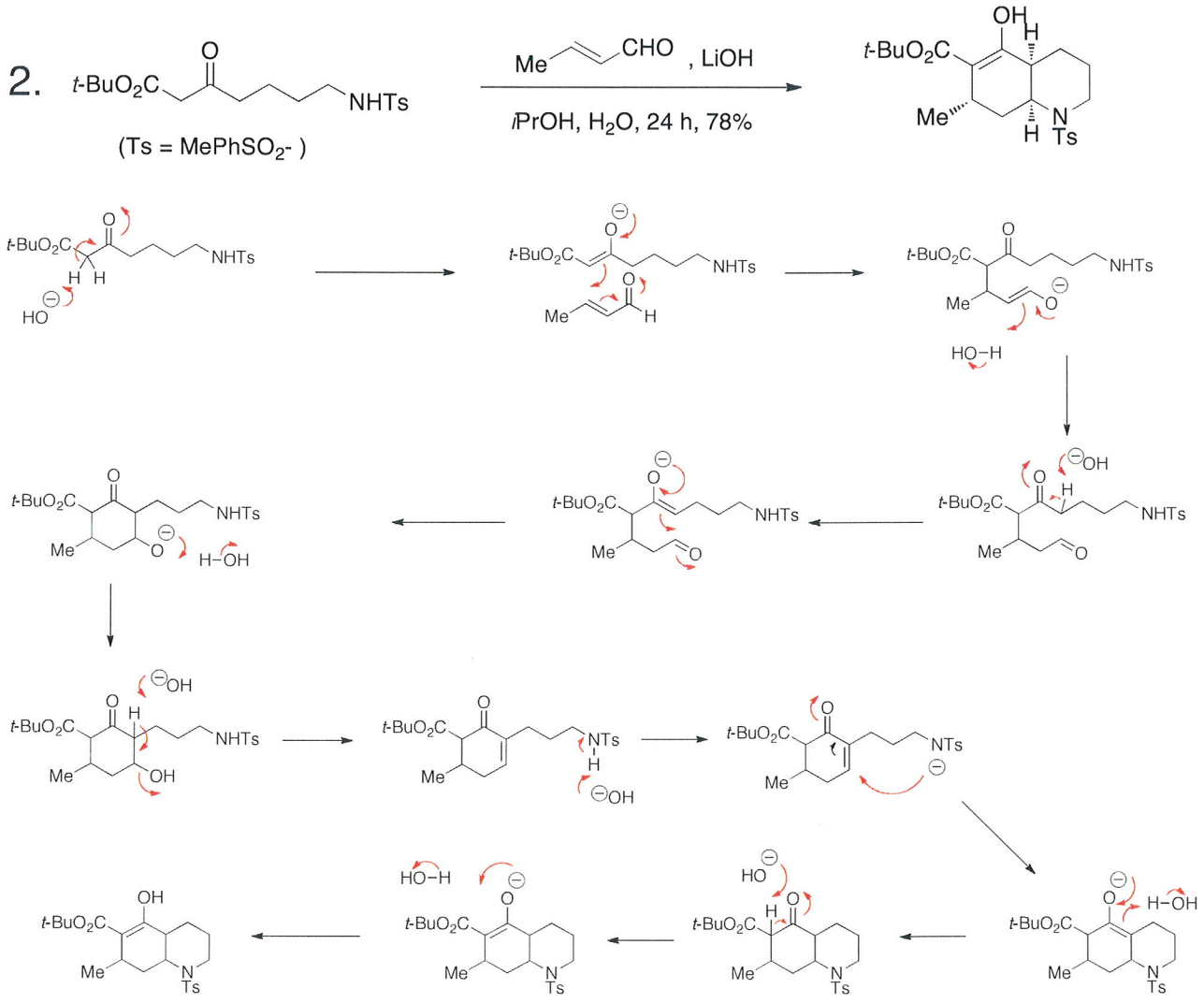
Propose stepwise mechanisms to explain **4** of the **7** following transformations. Use curved arrow formalism to show electron movement and show <u>all</u> likely intermediates.

1.



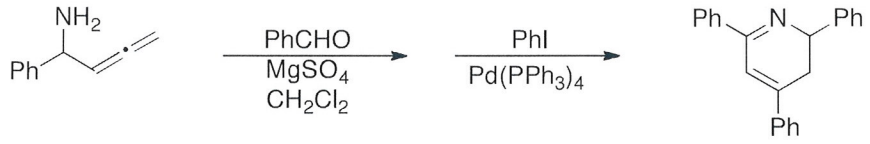


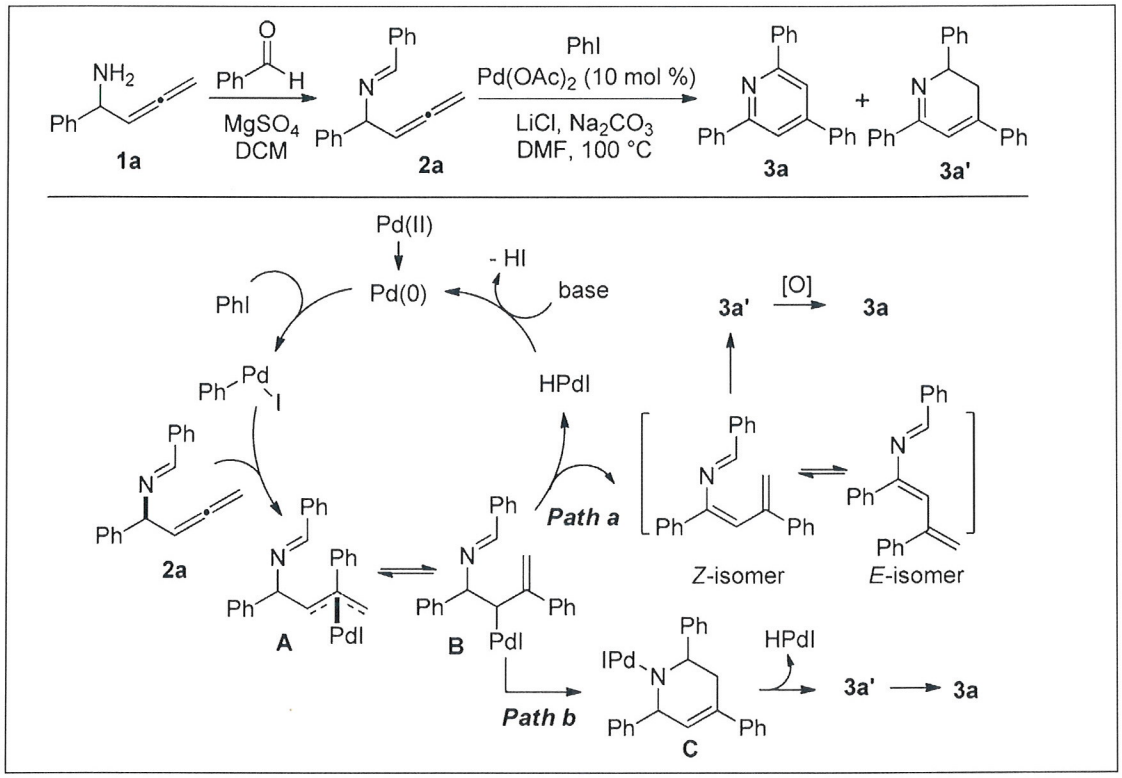
Org. Lett. **2013**, *15*, 258-261



Org. Lett. **2013**, *15*, 326-329.

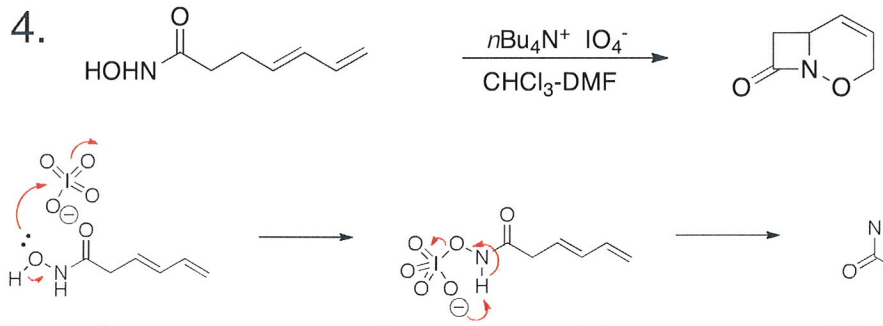
3.





Org. Lett. **2013**, *15*, 334-347.

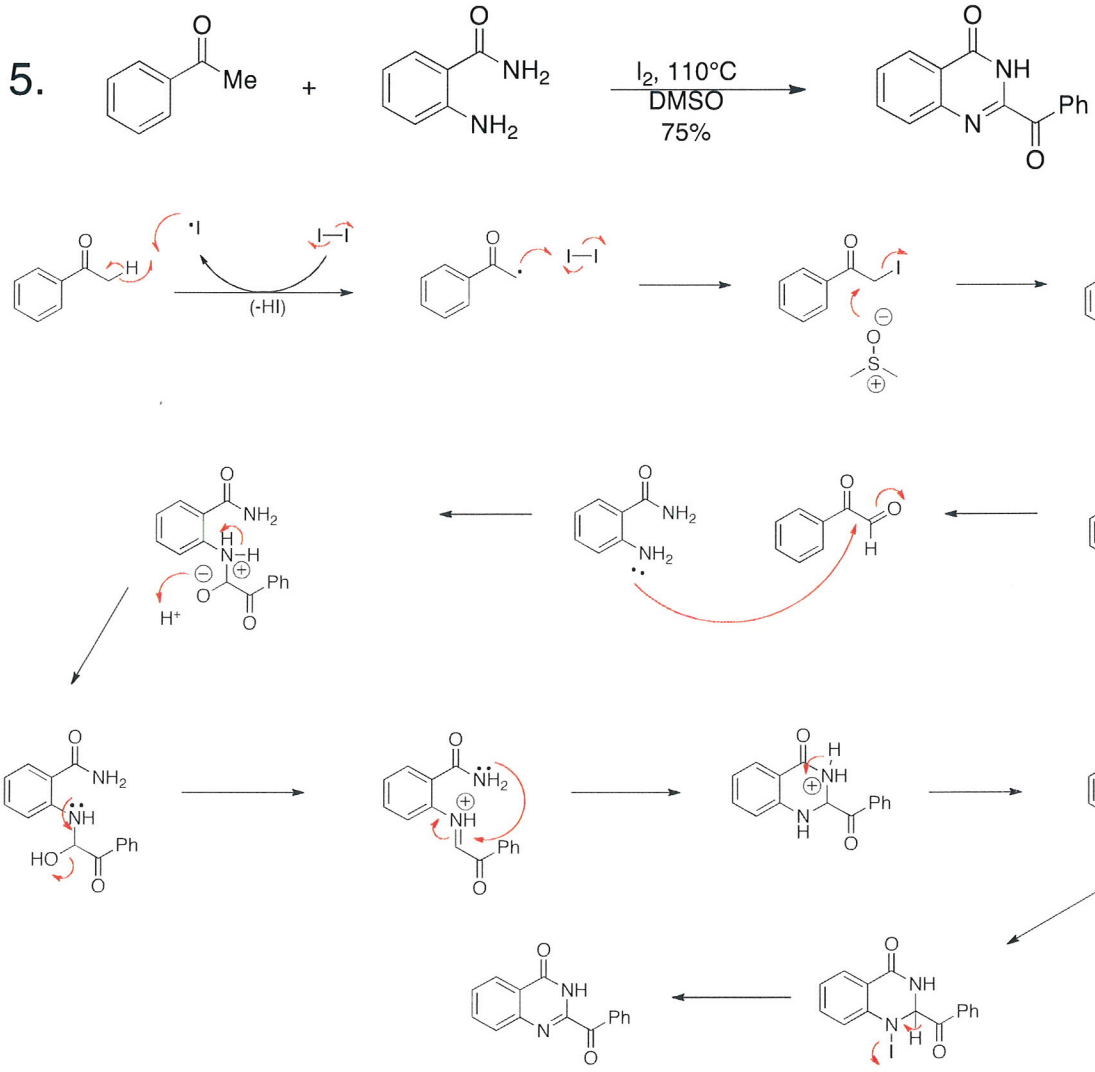
4.



(note: there was an error in the structure of the starting material, which had an extra carbon)

Org. Lett. **2013**, *15*, 358-361

5.



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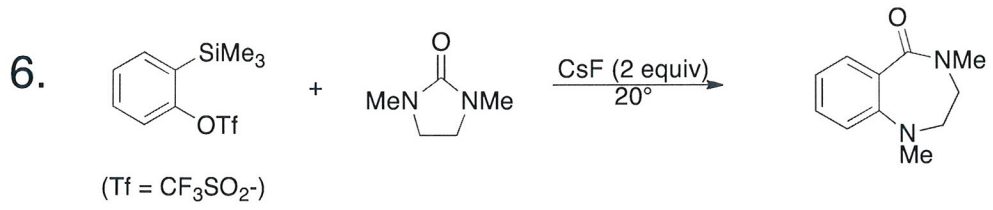
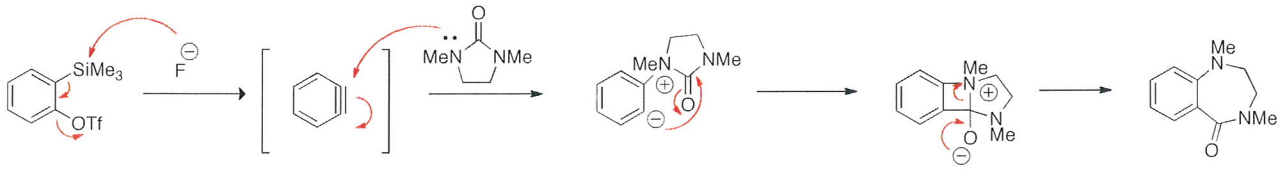
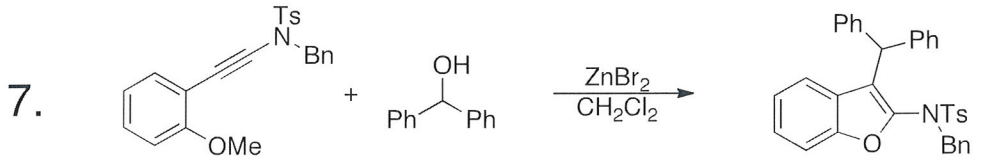
6.

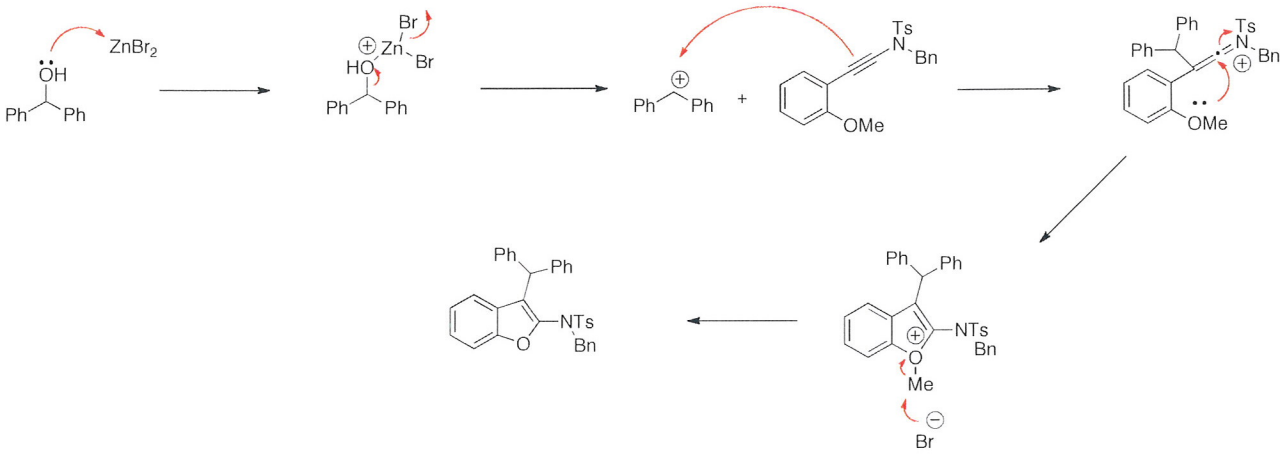




Org. Lett. **2013**, *15*, 386-389.

7.





Org. Lett. **2013**, *15*, 422-425.

Physical Chemistry Cumulative Exam

1. The time-dependent Schrodinger equation (TDSE) in one dimension has the form:

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = \hat{H}\Psi(x,t)$$

where H is the Hamiltonian operator. If H is independent of time, we can use separation of variables to simplify this partial differential equation into two ordinary differential equations in x and t, respectively.

Assume that $\Psi(x,t) = \psi(x)\cdot f(t)$, and plug this form into the TDSE to show that for time-independent Hamiltonians:

$$\Psi_n(x,t) = \psi_n(x)\cdot e^{-iE_nt/\hbar} \quad \text{and} \quad H\psi_n(x) = E_n\psi_n(x).$$

Solution: (15 pts)

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi}{\partial t}$$

Assume $\Psi(x,t) = \psi(x)\cdot f(t)$

Plug into TDSE:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}\cdot f(t) + V(x)\psi(x)f(t) = i\hbar\frac{\partial f}{\partial t}\cdot\psi(x)$$

Divide both sides by $\Psi(x,t) = \psi(x)\cdot f(t)$:

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} + V(x) = i\hbar\frac{1}{f(t)}\frac{\partial f}{\partial t}$$

Only variables=position Only variable = time

Since x, t are independent variables, the only way the two sides of the eqn can be equal for all x,t is for each side to be equal to the same constant = E.

- ⇨ Turns a partial differential eqn into two ordinary DE's.
- ⇨ RHS: **f(t) = exp(-iEt/ħ)**
- ⇨ LHS: This is just the time-independent Schrodinger Eqn. in 1D:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) = E\cdot\psi(x)$$

It has solutions: $\psi_n(x)$ where $\hat{H}\psi_n(x) = E_n\psi_n(x)$ where E_n = allowed energies.

Thus, $\Psi_n(x,t) = \psi_n(x)\cdot e^{-iE_nt/\hbar}$.

2. Any physically realizable wave function $\Psi(x,t)$ for our system can always be written as a linear combination of the basis functions $\Psi_n(x,t)$; that is,

$$\Psi(x,t) = \sum_n c_n \cdot \Psi_n(x,t) .$$

a) **(10 pts)** Derive an expression for the expectation value of the Hamiltonian for a system with wave function $\Psi(x,t)$. If you are familiar with it, you are encouraged to use Dirac bracket notation in your derivation.

$$< \hat{H} >= \left\langle \Psi(x,t) \middle| \hat{H} \middle| \Psi(x,t) \right\rangle = \sum_n \sum_m c_n{}^* c_m \left\langle \psi_n(x) e^{-iE_n t/\hbar} \middle| \hat{H} \middle| \psi_m(x) e^{-iE_m t/\hbar} \right\rangle$$

$$< \hat{H} >= \sum_n \sum_m c_n{}^* c_m E_m \left\langle \psi_n(x) e^{-iE_n t/\hbar} \middle| \psi_m(x) e^{-iE_m t/\hbar} \right\rangle = \sum_n \sum_m c_n{}^* c_m E_m e^{i(E_n - E_m)t/\hbar} \left\langle \psi_n(x) \middle| \psi_m(x) \right\rangle$$

Since the eigenfunctions of the Hamiltonian form a complete orthonormal basis set,

$$\left\langle \psi_n(x) \middle| \psi_m(x) \right\rangle = \delta_{nm}$$

$$< \hat{H} >= \sum_n \sum_m c_n{}^* c_m E_m e^{i(E_n - E_m)t/\hbar} \delta_{nm} = \sum_n |c_n|^2 E_n$$

In the above expression $\delta_{nm} = 1$ for n=m, = 0 for n≠m. This turns the double sum into a single sum with terms for which n=m.

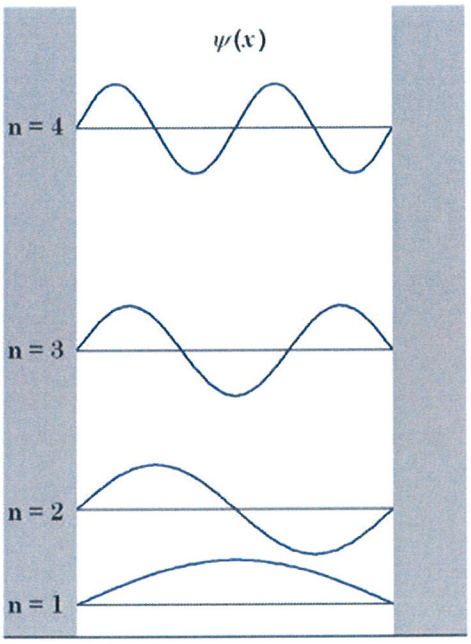
b) **(10 pts)** If you made repeated measurements of the total energy E for this system, what is the probability of obtaining the answer E_n?

The above expression tells us that if we make repeated measurements of the energy, we will get the answer E_n with probability $|c_n|^2$. That is, the coefficient of ψ_n in the expression for $\Psi(x,t)$ determines the probability for getting the answer E_n associated with the energy eigenfucntion $\psi_n(x)$.

3. Now consider a particle in a one-dimensional box of length L positioned between x=0 and L. Suppose that at t=0,

$$\Psi(x,t=0)=\frac{1}{\sqrt{2}}\cdot\psi_{n=1}(x)+\frac{1}{\sqrt{2}}\cdot\psi_{n=2}(x)\,.$$

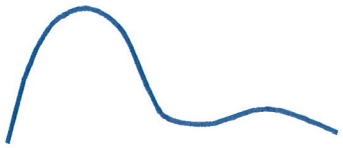
(10 pts) a) Write out an expression for the probability density at t=0, $|\Psi(x,t=0)|^2$, and sketch it.



Since $\psi_n(x) = \psi_n^*(x)$ for these wave functions,

$$|\Psi(x,t=0)|^2=\frac{1}{2}|\psi_{n=1}(x)|^2+\frac{1}{2}|\psi_{n=2}(x)|^2+\psi_{n=1}(x)\cdot\psi_{n=2}(x)$$

It will look something like this,



b) **(5 pts)** What do you notice about the probability for finding the particle in the box relative to either the n=1 or n=2 wave functions by themselves?

The probability is partially localized on the left-hand side of the box.

c) **(10 pts)** Determine an expression for the probability density, $|\Psi(x,t)|^2$ as a function of time.

Since in general,

$$\Psi(x,t)=\sum_n c_n\cdot\Psi_n(x,t) \qquad \Psi_n(x,t)=\psi_n(x)\cdot e^{-iE_nt/\hbar}$$

where

Then

$$\Psi(x,t)=\frac{1}{\sqrt{2}}\psi_{n=1}(x)\cdot e^{-iE_1t/\hbar}+\frac{1}{\sqrt{2}}\psi_{n=2}(x)\cdot e^{-iE_2t/\hbar}\backslash$$

$$|\Psi(x,t)|^2=\Psi^*(x,t)\cdot\Psi(x,t)=\left(\frac{1}{\sqrt{2}}\psi_{n=1}{}^*(x)\cdot e^{+iE_1t/\hbar}+\frac{1}{\sqrt{2}}\psi_{n=2}{}^*(x)\cdot e^{+iE_2t/\hbar}\right)\cdot\left(\frac{1}{\sqrt{2}}\psi_{n=1}(x)\cdot e^{-iE_1t/\hbar}+\frac{1}{\sqrt{2}}\psi_{n=2}(x)\cdot e^{-iE_2t/\hbar}\right)$$

$$|\Psi(x,t)|^2=\frac{1}{2}|\psi_{n=1}(x)|^2+\frac{1}{2}|\psi_{n=2}(x)|^2+\frac{1}{2}\psi^*_{n=1}(x)\cdot\psi_{n=2}(x)e^{i(E_1-E_2)t/\hbar}+\frac{1}{2}\psi^*_{n=2}(x)\cdot\psi_{n=1}(x)e^{i(E_2-E_1)t/\hbar}$$

But since $\cos\theta = {}^1/_2(e^{i\theta}$

$$\left|\Psi(x,t)\right|^2 = \frac{1}{2}\left|\psi_{n=1}(x)\right|^2 + \frac{1}{2}\left|\psi_{n=2}(x)\right|^2 + \psi_{n=1}(x)\cdot\psi_{n=2}(x)\cos(\omega_{21}t)$$

$$\left|\Psi(x,t)\right|^2 = \frac{1}{2}\left|\psi_{n=1}(x)\right|^2 + \frac{1}{2}\left|\psi_{n=2}(x)\right|^2 + \psi_{n=1}(x)\cdot\psi_{n=2}(x)\cos(\omega_{21}t)$$

d) **(10 pts)** Show that it oscillates with period $T = \frac{8mL^2}{3h}$. In what way does this recover some of our classical intuition regarding a classical particle moving in a one-dimensional box?

Since $\nu_{21} = (E_2\text{-}E_1)/h$, and $E_n = \frac{n^2h^2}{8mL^2}$

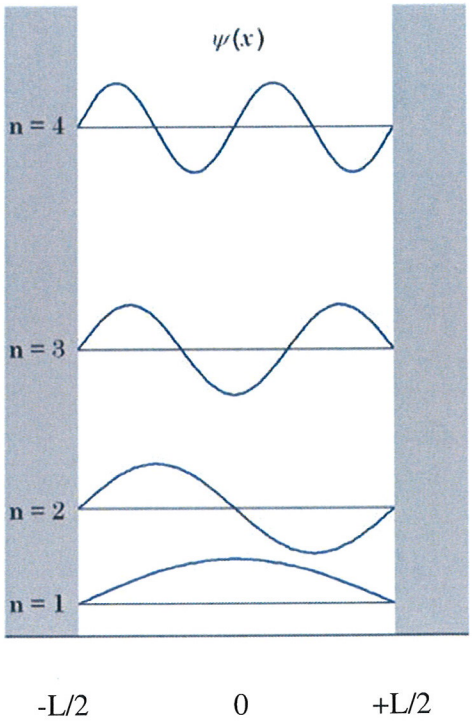
$$\nu = \frac{(E_2 - E_1)}{h} = \frac{(4-1)}{h}\left(\frac{h^2}{8mL^2}\right) = \frac{3h}{8mL^2}\text{; and } T = \frac{1}{\nu} = \frac{8mL^2}{3h}$$

Our picture of a classical particle in a box is that, starting from a given starting position and having a certain momentum, the particle will bounce back and forth in the box at a particular oscillation frequency.

e) **(5 pts)** What is the expectation value of the energy for this wave function?

$$<\hat{H}> = \left|c_1\right|^2 E_1 + \left|c_2\right|^2 E_2 = \frac{1}{2}E_1 + \frac{1}{2}E_2 = \frac{5}{2}\left(\frac{h^2}{8mL^2}\right) = \frac{5h^2}{16mL^2}$$

4. The diagram to the right shows the first four energy levels and wave functions for the one-dimensional particle-in-a-box, but this time with the box shifted so that its left edge is at –L/2 and its right edge at +L/2.



(a) Do the wave functions have well-defined symmetry with respect to reflection through x=0?
If so, identify which functions are even, and which are odd. **(10 pts)**

Yes, they have symmetry, with the n=1,3,5,... wave functions having even symmetry (that is, $\psi_n(-x) = +\psi_n(+x)$), and n=2,4,6,... wave functions being 'odd' (that is, . $\psi_n(-x) = -\psi_n(+x)$).

(b) Use symmetry to determine the following expectation values for a system in the n=1 state with energy $E_{n=1} = \frac{h^2}{8mL^2}$: **(5 pts each)**

(i) <p>, the momentum.

$$\hat{p} = -i\hbar\frac{\partial}{\partial x} = \text{odd function}$$

$\psi_{n=1}(x)$ = even function

$$\langle p \rangle = \int_{-L/2}^{+L/2} even \cdot odd \cdot even = \int_{-L/2}^{+L/2} odd = 0$$

(ii) <KE>, the kinetic energy.

Since $\langle H \rangle = E_{n=1}$, and with a potential V=0 inside the box, $\langle KE \rangle = E_{n=1} = h^2/8mL^2$.

(iii) <x>, the position.

Since x is an odd function with respect to reflection through x=0,

$$\langle x \rangle = \int_{-L/2}^{+L/2} even \cdot odd \cdot even = \int_{-L/2}^{+L/2} odd = 0$$

In each case, briefly defend your answer.

Formula sheet for the P-Chem cume

Quantum mechanical particle of mass 'm' confined to a one-dimensional box of length L:

Assume that V(x)=0 for $0 \le x \le L$ and $V(x) = +\infty$ for x<0 and x>L.

$$H\psi_n(x) = -\frac{\hbar^2}{2m}\frac{\partial^2\psi_n(x)}{\partial x^2} = E_n\psi_n(x)$$ inside the box.

Energy eigenfunctions: $\psi_n(x) = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n\pi x}{L}\right)$.

Energy eigenvalues: $E_n = \frac{n^2h^2}{8mL^2}$

Even function: $\psi(-x) = \psi(+x)$
Odd function: $\psi(-x) = -\psi(+x)$