Name: Answer Key

Chem 633: Advanced Organic Chemistry 2013 ··· Final Exam

Please answer the following questions *clearly and concisely*. In general, use pictures and less than 10 words in your answers.

Write your answers in the space provided.

Write your initials on each page you want graded.

There are 12 total pages to this exam. The last 2 pages were intentionally left blank and may be used for scratch paper. Please be sure your copy has 12 pages before you begin.

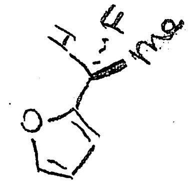
Molecular models are allowed.

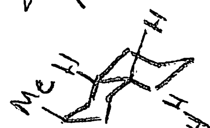
Calculators are unnecessary and prohibited.

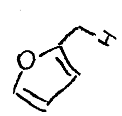
Potentially Useful Information
$k_B/h = 2.083 \times 10^{10}\ s^{-1}K^{-1}$
$\kappa = 1$ (kappa)
R = 1.98 cal/mol·K
$\log (X^n) = n \log X$
$\log (X \cdot Y) = \log X + \log Y$

Problem	Points
1	8 /20
2	25 /40
3	14 /20
4	13 /20
TOTAL	57 **/100**

Averages.

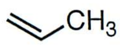




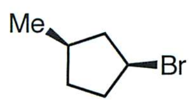


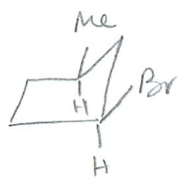
5 points each (all or nothing)

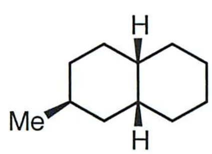
1. (20 points) Please draw the lowest energy conformation of the following molecules.

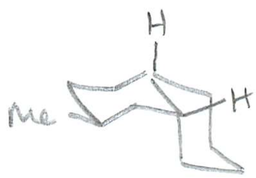
(a) 

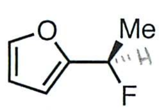
(eclipsed)

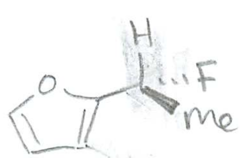
(b) 



(c) 

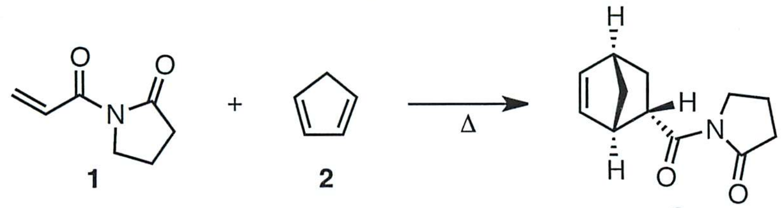


(d) 



5 point each

2. (40 points) Please consider the following reaction:



1 2 3

(a) What type of reaction is this? Please classify this reaction as is appropriate for its reaction type.

+2

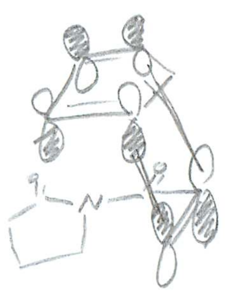
[Cycloaddition (Diels-Alder)

[4πs + 2πs] (or [4 + 2])

+3

(b) Please show why this reaction is allowed under thermal conditions.

FMO Theory:



} HOMO of diene

} LUMO of dienophile

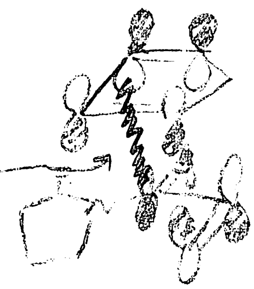
NET BONDING.

(2 – continued)

(c) Please explain the observed diastereoselectivity. ENDO PRODUCT

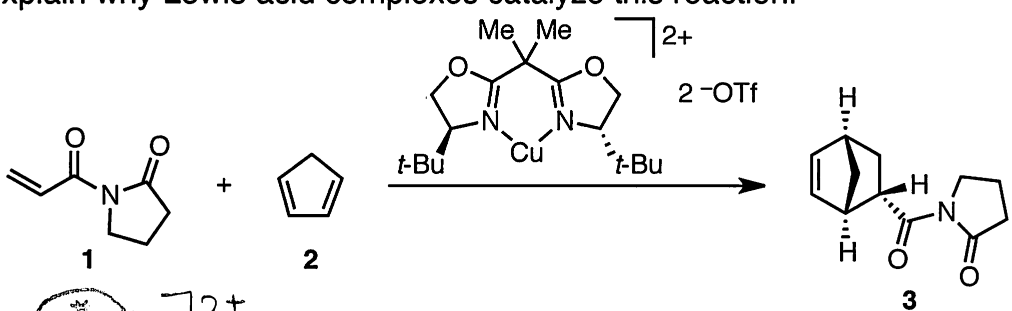
↓

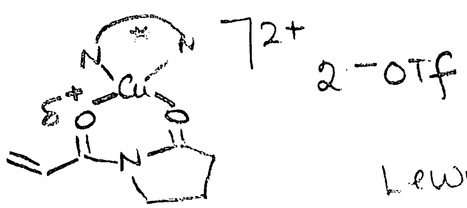
2° orbital overlap



2nd orbital overlap stabilizes endo TS.

(d) This reaction is accelerated by Lewis acid catalysts, such as the Cu(II) salt below. Please explain why Lewis acid complexes catalyze this reaction.





Lewis acid binds oxygen of carbonyl

↓

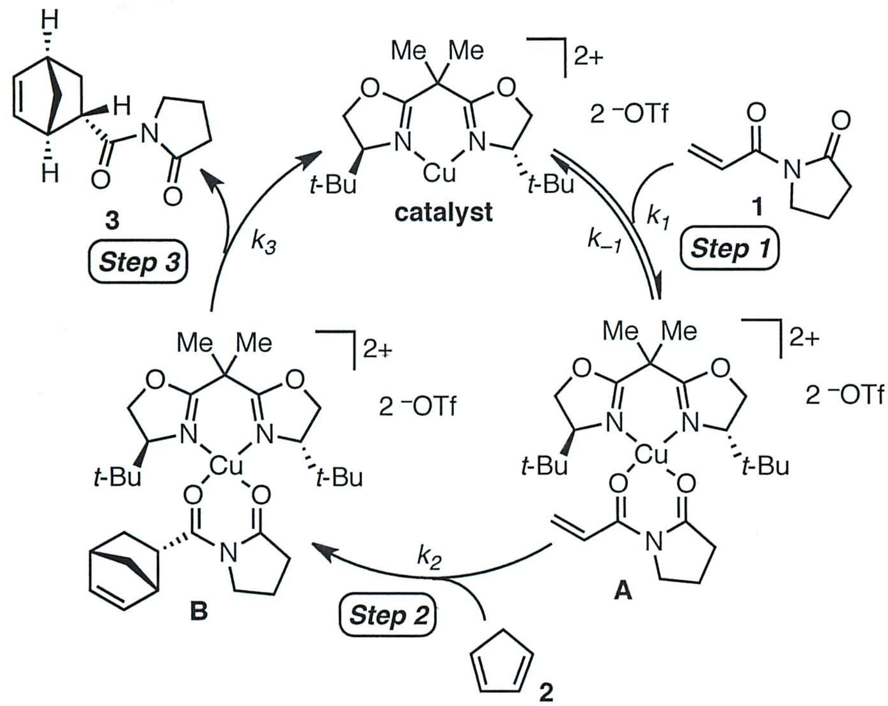
Lowers LUMO

↓

Faster Normal-Electron-Demand D-A.

(2 – continued)

(e) Consider the following catalytic cycle. If Step 2 is rate-determining and subsequent steps to regenerate **catalyst** are fast and irreversible, write a rate law for this catalytic cycle.



$$\text{rate} = \frac{\dfrac{k_1 k_2 [Cu]_{Total}[1][2]}{k_{-1} + k_2[2]}}{1 + \dfrac{k_1[1]}{k_{-1} + k_2[2]}}$$

+1 if "1+ format"

+1 if use [cat] instead of $[cat]_T$

-1/mistake

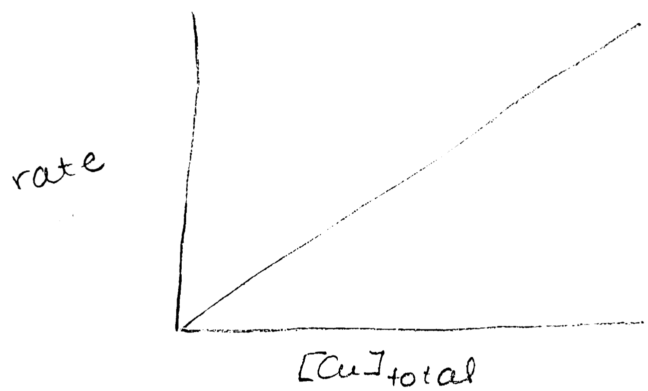
$$\text{rate} = \frac{k_1 k_2 [Cu]_T [1][2]}{k_{-1} + k_2[2] + k_1[1]}$$

(2 – continued)

(f) Describe the experiments you would do to support this rate law and the assignment of the rate-determining step. Draw the plots you expect, clearly labeling the axes.

(1) Determine rate dependence on $[Cu]_{total}$: Change $[Cu]_{total}$, Observe $\frac{d[1]}{dt}$ & $\frac{d[3]}{dt}$ for multiple $[Cu]_{total}$

If 1^{st} order (as expected):



(2) Determine rate dependence on [1]

Expect saturation behavior

(3) Determine rate dependence on [2]

When $k_2[2] >> k_{-1}$

rate = $\frac{k_1 k_2 [Cu]_T [1][2]}{k_2[2]}$ [illegible]

$$\frac{\dfrac{k_1 k_2 [Cu]_T [1][2]}{k_{-1} + k_2[2]}}{1 + \dfrac{k_1[1]}{k_{-1} + k_2[2]}} = \frac{\dfrac{k_1 k_2 [Cu]_T [1][2]}{\cancel{k_{-1} + k_2[2]}}}{\dfrac{k_{-1} + k_2[2] + k_1[1]}{\cancel{k_{-1} + k_2[2]}}}$$

$$= \frac{k_1 k_2 [Cu]_T [1][2]}{k_{-1} + k_2[2] + k_1[1]}$$

(2 – continued)

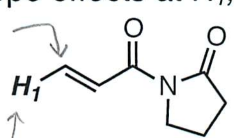
(g) Simplify your rate law, assuming that **A** is the only catalyst resting state.

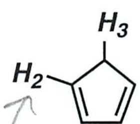
$$rate = \frac{\dfrac{k_1 k_2 [Cu]_{total}[1][2]}{k_{-1} + k_2[2]}}{\dfrac{k_1[1]}{k_{-1} + k_2[2]}}$$

$$rate = k_2 [Cu]_{total} [2]$$

(h) Given the proposed mechanism, please predict the expected value (or range of values) of the kinetic isotope effects at H_1, H_2, and H_3.

inverse $sp^2 \rightarrow sp^3$ 2° KIE



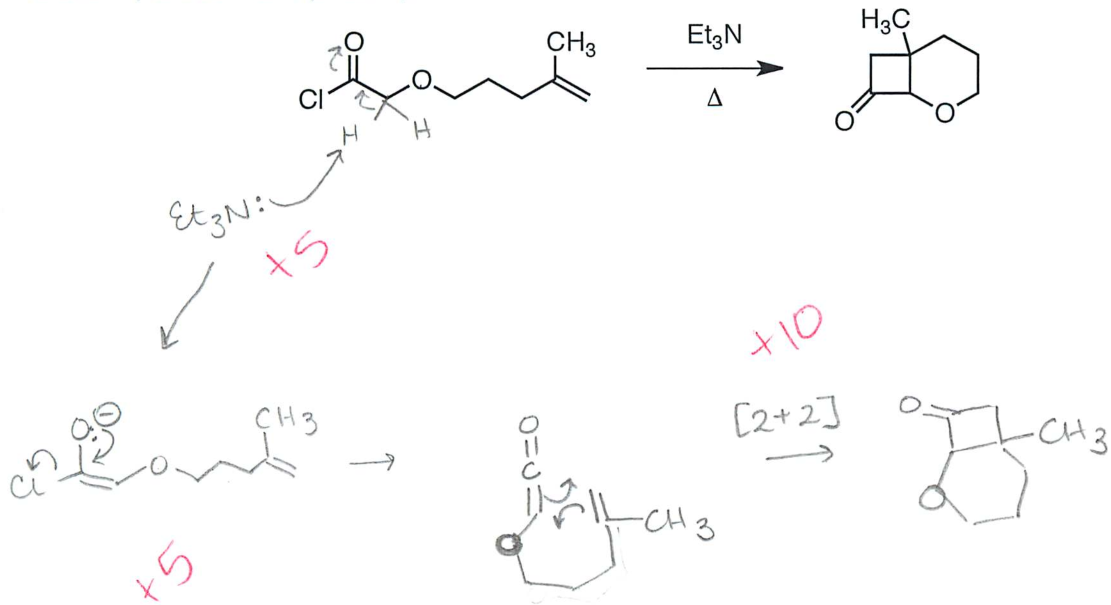


$k_H/k_D = 1$ +1

$k_H/k_D = 0.7 - 1.0$ +2

$k_H/k_D = 0.7 - 1.0$ +2

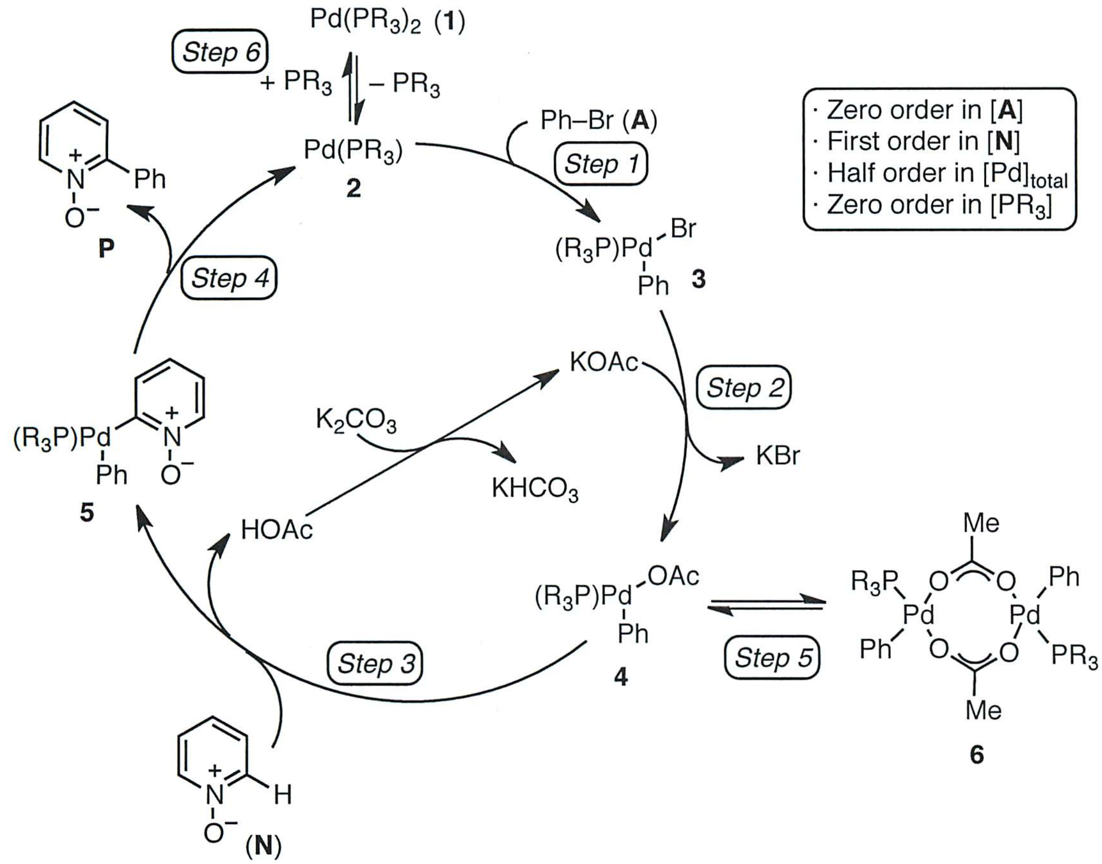
3. (20 points) Please draw a reasonable arrow-pushing mechanism for the following reaction (Grossman, p. 221).



Initials: ___________

5 points each

4. (20 points) Please consider the following catalytic cycle and kinetic data.



(a) Given the kinetic data above, what is the catalyst resting state?

6

(b) What are the possible rate-determining steps?

Step 3 or Step 4.

↓ C-H Activation

↓ Reductive Elimination

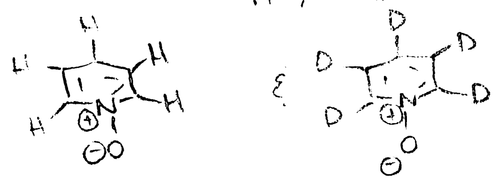
-2 for every extra step or any missing step

(4 – continued)

(c) Please propose an experiment to differentiate between the possible rate-determining steps. Be specific about your experimental design.

Kinetic Isotope Effect Experiment (intermolecular):

Determine k_H / k_D using



as substrates

If Step 3 is rds → expect 1° KIE (k_H/k_D = 2 – 7)

If Step 4 is rds → expect no KIE.

(d) Propose **two** possible mechanisms for the C–H activation step (Step 3).

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