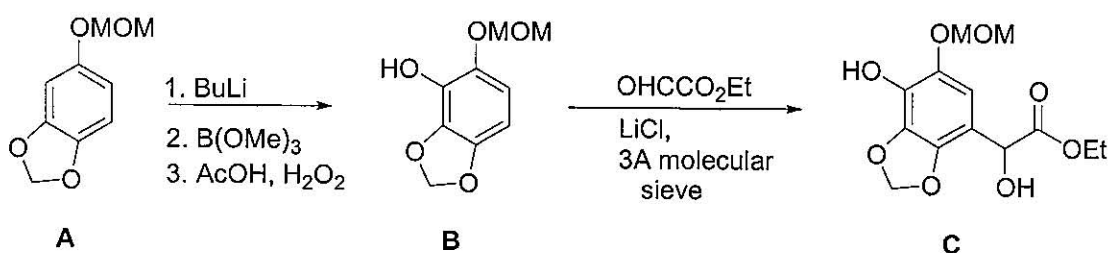


Cumulative Examination-Organic Chemistry

Question 1 (18 points)

Recently, Zhu has developed a total synthesis of ecteinascidin 743, a potential anticancer drug in phase II/III clinical trials. During the course of synthesis they synthesized several key starting materials. For example, **C** was synthesized from **A** according to the following scheme.

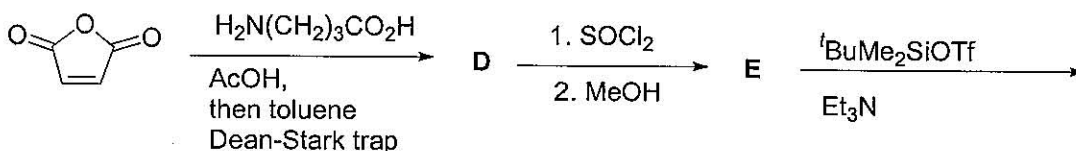


- (a) Show all intermediates in the transformation from **A** to **B**. [6 points]
 (b) Write the possible mechanism to show how phenol **B** is formed in the last step. [6 points]
 (c) Conversion of **B** into **C** is essentially a Friedel-Crafts reaction. Explain why no strong Lewis acid is used in this reaction? [6 points]

[JACS 2006, 128, 87.]

Question 2 (12 points)

Complete the following transformations.

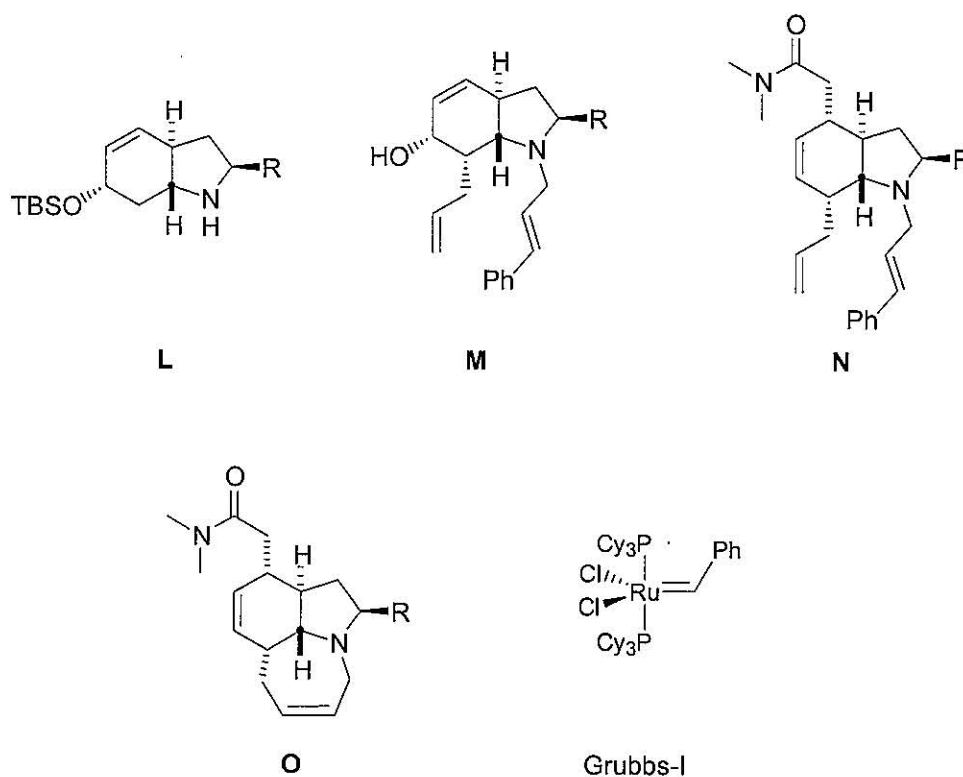


[JACS 2006, 128, 426]

Question 3 (35 points)

Ring closing metathesis (RCM) is one of the most useful reactions for the construction of a range of cyclic compounds. Thus, compound **L** is used to convert into **M**.

Treatment of the allylic alcohol **M** with *N,N*-dimethylacetamide dimethylacetal followed by refluxing in xylene gives **N**. RCM of **N** with Grubbs-I catalyst give the desired product **O**.



(a) Propose a synthesis of **M** from **L**. [18 points]

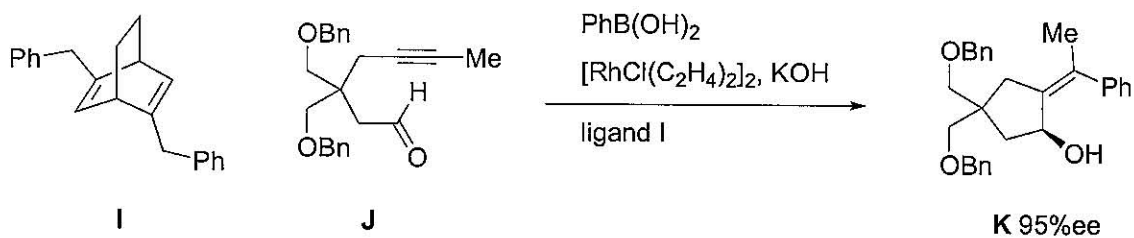
(b) What is the mechanism for the conversion of **M** to **N**? [10 points]

(c) Write the mechanism of the RCM reaction of **N**. [7 points]

[*JACS* 2005, 127, 225.]

Question 4 (35 points)

Recently, Tamio Hayashi gave a seminar at our Department on chiral diene ligands in catalysis. He found that **I** can be used in rhodium-catalyzed asymmetric arylation cyclization of alkynals **J**.



- (a) What is(are) the absolute configuration(s) in **I**? [3 points]
- (b) Write the mechanism for rhodium-catalyzed asymmetric arylation of alkynes **J** to yield **K**. [10 points]
- (c) When the two BnOCH_2 groups in the starting material **J** are replaced by two hydrogen atoms, would you expect the rate of cyclization to be faster or slower? Give your reasoning. [7 points]
- (d) Propose a synthesis of **J** from diethyl malonate. [15 points]
 [*JACS* 2005, 127, 54.]

Inorganic Chemistry – Qum Exam

March 24, 2007

(Show all your processes which lead to the answers)

1. Explain the differences and similarities between IR and Raman spectrometers in terms of
 - (a) the light source and detector
 - (b) the informations obtained concerning the bondings
 - (c) the selection rule (10%)

2.
 - (a) Construct the M.O. energy level diagram of the “carbonyl” group in H_2CO , and indicate the bonding, antibonding and non-bonding orbitals. (6%)
 - (b) What are the symmetry representations of the states which arise from $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively? Are they allowed transitions? If so, what is its polarization orientation? (6%)
 - (c) Determine the symmetry representations of all the vibrational modes of H_2CO . (10%)
 - (d) Explain whether or not the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions will gain intensity from vibronic coupling. (4%)

3.
 - (a) Derive the term symbols with spin multiplicity for the metal center of $3d^2$ configuration. (10%)
 - (b) Determine the irreducible representations of the ground state term split in an O_h ligand field. (5%)

4.
 - (a) For the “trigonal bipyramidal” $M(CO)_5$, how many CO stretching bands do you expect to see in IR and Raman spectra, respectively? (6%)
 - (b) Show the combination of C-O stretching vibrations corresponding to each of the above bands. (8%)
 - (c) If one of the CO ligands on $M(CO)_5$ is replaced by NH_3 , what do you expect to see the changes in the IR bands in the CO stretching region? (10%)

5. Using the descending of symmetry if necessary, find the term symbols for the following electron configuration in tetrahedral crystal field. (10%)
 - (a) $t_2^1 e^1$
 - (b) t_2^2

6. The spectrum of $[Cr(NCS)_6]^{3-}$ has a very weak band near $16,000\text{ cm}^{-1}$, a band at $17,700\text{ cm}^{-1}$ with $\epsilon_{\max} = 160\text{ M}^{-1}\text{ cm}^{-1}$, a band at $23,800\text{ cm}^{-1}$ with $\epsilon_{\max} = 130\text{ M}^{-1}\text{ cm}^{-1}$, and a very strong band at $32,400\text{ cm}^{-1}$.

Correlation table

Td	C _{4v}	C _{2v}
A ₁	A ₁	A ₁
A ₂	B ₁	A ₂
E	A ₁ + B ₁	A ₁ + A ₂
T ₁	A ₂ + E	A ₂ + B ₁ + B ₂
T ₂	B ₂ + E	A ₁ + B ₁ + B ₂

C _{2v}	E	C ₂	σ _v (xz)	σ _v '(yz)		
A ₁	1	1	1	1	z	x ² , y ² , z ²
A ₂	1	1	-1	-1	R _z	xy
B ₁	1	-1	1	-1	x, R _y	xz
B ₂	1	-1	-1	1	y, R _x	yz

C _{3v}	E	2C ₃	3σ _v		
A ₁	1	1	1	z	x ² + y ² , z ²
A ₂	1	1	-1	R _z	
E	2	-1	0	(x, y)(R _x , R _y)	(x ² - y ² , xy)(xz, yz)

T _d	E	8C ₃	3C ₂	6S ₄	6σ _d		
A ₁	1	1	1	1	1		x ² + y ² + z ²
A ₂	1	1	1	-1	-1		
E	2	-1	2	0	0		(2z ² - x ² - y ² , x ² - y ²)
T ₁	3	0	-1	1	-1	(R _x , R _y , R _z)	
T ₂	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1	R_z	x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1		xy
B_{2g}	1	-1	1	-1	1	-1	1	-1		xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1	z	
B_{1u}	1	1	-1	-1	-1	-1	1	1		y
B_{2u}	1	-1	1	-1	-1	1	-1	1		x
B_{3u}	1	-1	-1	1	-1	1	1	-1		

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$			
A_1'	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$	
A_2'	1	1	-1	1	1	-1		(x, y)	$(x^2 - y^2, xy)$
E'	2	-1	0	2	-1	0	z		
A_1''	1	1	1	-1	-1	-1		(R_x, R_y)	(xz, yz)
A_2''	1	1	-1	-1	-1	1			
E''	2	-1	0	-2	1	0			

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

O	E	$6C_4$	$3C_2(=C_4^2)$	$8C_3$	$6C_2$		
A_1	1	1	1	1	1	$(R_x, R_y, R_z); (x, y, z)$	$x^2 + y^2 + z^2$
A_2	1	-1	1	1	-1		$(2z^2 - x^2 - y^2, x^2 - y^2)$
E	2	0	2	-1	0		(xy, xz, yz)
T_1	3	1	-1	0	-1		
T_2	3	-1	-1	0	1		

PROBLEM 1. A model for a spin in a magnetic field can be obtained from statistical mechanics. The energy of a spin- I nucleus in a magnetic field is:

$$H_{\text{mag}} = -\gamma\hbar HI_z$$

where \hbar is Planck's constant, γ is a constant called the "gyromagnetic ratio", H is the external field, and I_z is the projection of the total spin along the direction of the external field (i.e., it is the magnetic quantum number and can take on values $-I, -I+1, \dots, I-1, I$).

- a) Work out an expression for the canonical partition function. HINT: Recall that for geometric series:

$$\sum_{j=M}^N x^j = \frac{x^{N+1} - x^M}{x - 1}$$

and that

$$\sinh x = \frac{e^x - e^{-x}}{2}$$

- b) By using a canonical ensemble, derive expressions for the average magnetization, energy, and entropy per spin in the presence of the external field. Ignore all interactions between different spins.
 c) What is the expression for the constant external field heat capacity? How does it behave at high and low temperatures? HINT: note that

$$\text{csch}^2(x) \equiv \frac{1}{\sinh^2 x} \approx \begin{cases} \frac{1}{x^2} - \frac{1}{3} + \mathcal{O}(x^2), & \text{as } x \rightarrow 0 \\ 4e^{-2x} + \mathcal{O}(e^{-4x}), & \text{as } x \rightarrow \infty \end{cases}$$

- d) Sketch C_H as a function of temperature.

PROBLEM 2.

- a) Write out the expression for the Helmholtz free energy per molecule for an ideal gas of homonuclear diatomic molecules. Assume that the temperature is high when compared to the characteristic rotational energies. Make sure that you state the definitions of any characteristic temperatures in terms of the molecular properties of the molecules (e.g., masses, bond lengths, etc.).
 b) Use your result in 1 to derive molecular expressions for the pressure, chemical potential, and energy of the gas. How do your results change if the molecules are heteronuclear?
 c) Derive the low temperature form of the rotational-nuclear partition function for a gas homonuclear diatomic molecules. Assume that the nuclei have spin I and indicate how your expressions change for Bosons and for Fermions.

Analytical Cumulative Examination

March 24, 2007

I Fluorescence (20%)

- (a) Give a definition of quantum yield. (5%)
- (b) Compare **fluorescence** and **Raman** spectroscopy in terms of principles, instrumentation, and applications? (15%)

II ELISA (25%)

- (a) How can ELISA work on detecting analytes? Why is it so sensitive? What are the advantages? (15%)
- (b) Give at least two detection methods commonly used in ELISA. Compare their advantages and disadvantages. (10%)

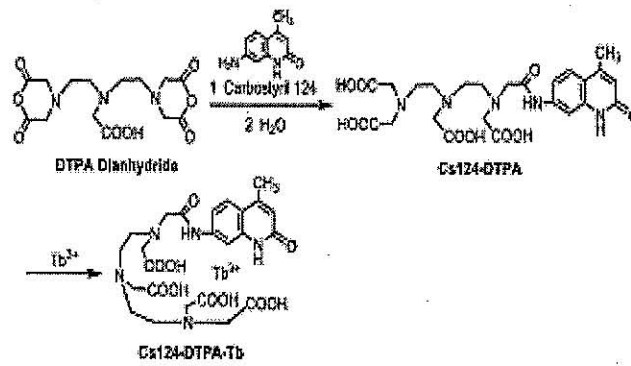
(III) Cell images (20%)

- (a) A brief scheme of a fluorescence microscopic system. (10%)
- (b) Describe a technique allowing detection of local pH inside single cells. (10%)

(IV) Time-resolved fluorescence (TRF) (35%)

- (a) What are the advantages of TRF? (5%)
- (b) Can TRF and resonance energy transfer be combined to become a useful analytical tool? If your answer is yes, how does it work and what are the advantages of the techniques when compared to TRF? (10%)
- (c) Write an **abstract in English** for a paper entitled "Sensitized Luminescent Terbium Nanoparticles: Preparation and Time-Resolved Fluorescence Assay for DNA". The attached schemes and figure (Page 2) are provided for your references. (20%)

Scheme 1. Structure and Synthesis of Cs124-DTPA-Tb



Scheme 2. Cs124-DTPA-Tb Nanoparticles Conjugated with Oligonucleotide

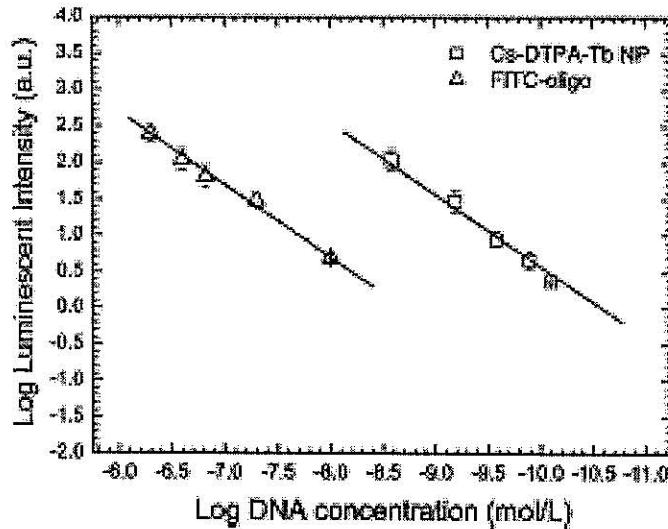
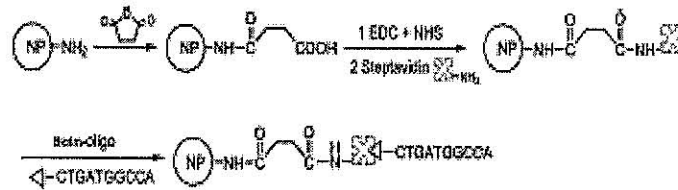


Figure 5. Different concentrations of target DNA versus response of Cs124-DTPA-Tb NPs and FITC in 0.1 mol/L NaOH uncoupling solution. FITC: general fluorescence assay, Cs124-DTPA-Tb NP: time-resolved fluorescence assay. Other determining conditions are the same.