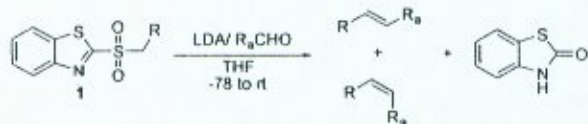


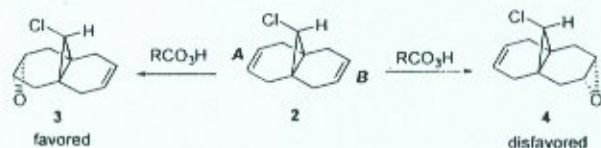
Part A. (5 pts) Please answer ONLY ONE of the following two questions (1 and 2). If you answer both two, the lower score will be counted.

- The stereoselective construction of *trans* olefins through carbanion-mediated condensation process has still not been rendered general. One transformation that may be used in certain circumstances is the *Julia* transformation illustrates below:



Please draw out each of the intermediates that might be anticipated in the transformation of **1** into olefin products. (*Synthesis*, 1996, 285)

- In 1991, an article reported the surprising selective olefin epoxidation illustrated below. In this reaction, olefin **B** in compound **2** was found to be much less reactive than olefin **A**.



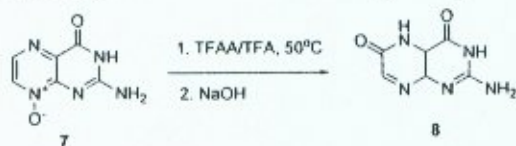
Using your knowledge of STEREOELECTRONIC effects provides an explanation for the reduced reactivity of olefin **B** in compound **2**.

Part B. (20 pts, 10pts for each) Please pick up TWO of the following four questions (3 to 6) to answer. If more than two questions are answered, the two lower score will be counted.

- Nowadays, Dess-Martin Periodinane (DMP) becomes more and more popular oxidizing agent because of its stability, mild reactivity, and safety. The following transformation is a key step in Boeckman's synthesis of laurenynes, which was started from oxidation by DMP (*Org. Lett.* 2002, 4, 3891). Please give the structure of DMP and provide a mechanism for this reaction.



heterocycles. Please provide a mechanism for the specific example of the Katada rearrangement shown below (*J. Org. Chem.* **1975**, 2431). When heterocycle **7** was treated with trifluoroacetic anhydride and trifluoroacetic acid. The unexpected compound **8** was isolated. Please provide a mechanism for this unusual rearrangement. *hint: a sigmatropic rearrangement was proposed*

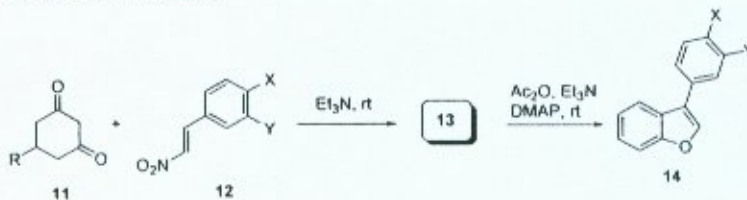


5. The following transformation was recently reported by Rodriguez (*Org. Lett.* **2001**, 3, 1181).

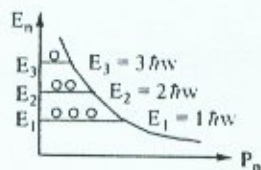


Provide a mechanism for the illustrated rearrangement(s) of **9** to **10**. Where stereochemical issues are presented, provide clear three dimensional drawings to support your answer.

6. An interesting multistep conversion of nitrostyrenes into benzofurans has been published recently. After treating the indicated compounds with a catalytic amount of  $\text{Et}_3\text{N}$  (rt, 12 h), intermediate **13** is formed that has a molecular weight(MW) that is the sum of the MWs of the two starting materials minus the MW of water. (*Org. Lett.* **2005**, 7, 1211)



Please show the correct structure of **13** and present a mechanism for the overall transformation. *Hint: the reaction was proposed to start from Michael addition.*



(1) 如上圖所示，當 \$T > 0\$ 時原子在不同能階振動的平均能量

$$\langle E \rangle = (3E_1 + 2E_2 + E_3) = \sum_n E_n P_n \quad \text{請利用左式及 } P_n = A \exp\left[-\frac{E_n}{kT}\right] \text{ 推導}$$

$$\langle E \rangle = \frac{\sum_n n \hbar \omega e^{-n \hbar \omega / k_B T}}{\sum_n e^{-n \hbar \omega / k_B T}}$$

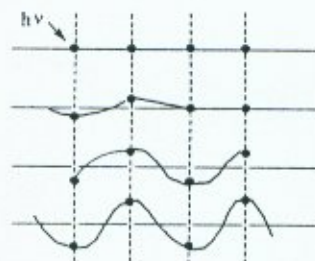
(2) 根據 Einstein 的量子假設 1 mole 單原子振動產生的內能為

$$U = 3N_A \langle E \rangle = 3N_A \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1}$$

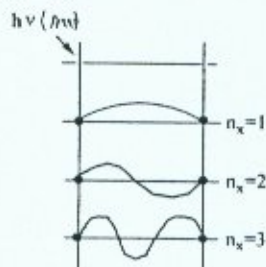
(a) 當 \$k\_B T \gg \hbar \omega\$ 時，證明熱含量 \$C = \frac{dU}{dT} = 3N\_A k\_B\$

(b) 當 \$k\_B T \ll \hbar \omega\$ 時，請證明 \$C \propto e^{-\frac{\hbar \omega}{k\_B T}}\$

(3) Debye 認為，當晶格中一原子受到入射光作用時，會迅速的將振動的能量傳遞給鄰近的原子，如同聲波在固體中快速傳遞的現象一般。



圖(一)



圖(二)

請利用公式  $\frac{d^2 \psi}{dx^2} + k^2 \psi = 0, k^2 = \frac{2mE}{\hbar^2}$  算出代表上列圖(二)中一維空間振動地波函數及能量

(a)  $\psi_1 = ? \psi_2 = ? \psi_3 = ?$

(b)  $E_1 = ? E_2 = ? E_3 = ?$

1. What is mean by the term "chelate effect"? Give an example. (4%)
2. Discuss the important factors affecting the magnitude of  $10 Dq$ . (4%)
3. Give the ground state term symbol of  $Cr^{3+}$  and Mg, with consideration of the spin-orbit coupling effect. (4%)
4. What is metal carbene? Please give at least two different type metal carbene examples. (4%)
5. Prove a plausible reason for the difference in IR absorptions between the pairs:  $C_5H_5Mn(CO)_3$ : 2023, 1939  $cm^{-1}$ , vs  $C_5Me_5Mn(CO)_3$ : 2017, 1928  $cm^{-1}$ . (5%)
6. How do you distinguish a coordinated NO group as either a one-electron or three-electron donor in metal complexes structurally? (4%)



**Analytical Chemistry (25%)**

1. Except for the different optical activity, enantiomers have almost identical physical and chemical properties. Therefore, it is impossible to separate enantiomers well by using a regular reverse phase HPLC column. Now, you are requested to separate a pair of enantiomers; however, the only one column you can find in your lab is an ordinary reverse phase column. How can you do?

If you are allowed to purchase a new column for this work, which kind of stationary phases should you choose? (15%)

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2. The Scanning Tunneling Microscope (STM) is one member of the scanning-probe-microscope family. Please define STM.

Please describe the characteristics of STM and its advantages, comparing to the well-know SEM (scanning electron microscope) used for surface morphology observation. (10%)