

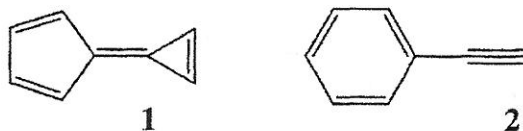
科目：有機化學

系所組：化學系碩士班甲組

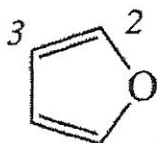
PART I (50 points)

1. Please explain

(a) Compound 1 has much dipole moment than its isomer 2. (3 points)



(b) Furan attacks electrophiles exclusively at C2 not at C3. (3 points)

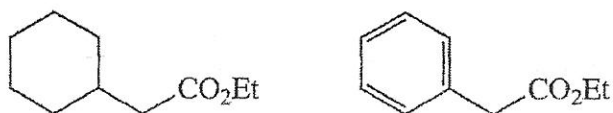


2. Indicate which each pair of compound is likely to be more acidic and why? (3 points each, 9)

(a)



(b)



(c)



※ 注意：1. 考生須在「彌封答案卷」上作答。

2. 本試題紙空白部分可當稿紙使用。

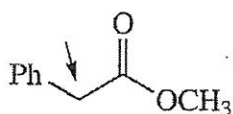
3. 考生於作答時可否使用計算機、法典、字典或其他資料或工具，以簡章之規定為準。

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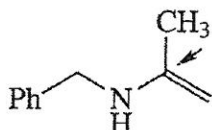
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3. In the following compounds, please determine the indicated atom is *nucleophilic*, *electrophilic*, *acidic* or *none*? (2 points each, 10)

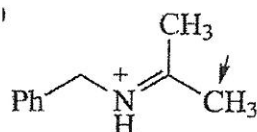
(a)



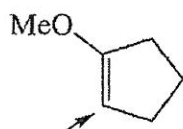
(b)



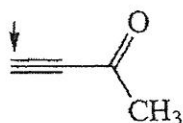
(c)



(d)

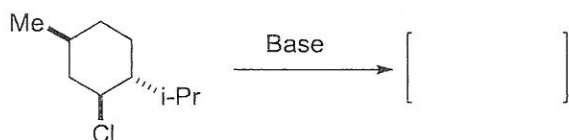


(e)



4. Draw two mechanisms for the following two reactions and provide the correct products (4 points each, 8)

(a)



(b)



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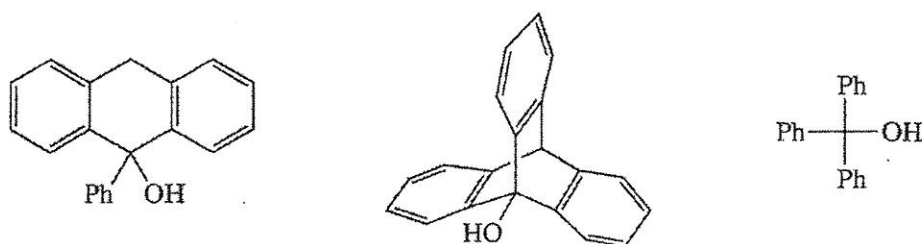
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5. Rank each set of compounds by the ease with which they ionize under acidic conditions, please explain! (3 points each, 6)

(a)

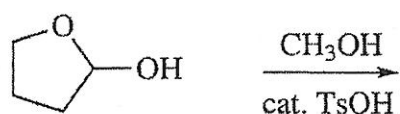


(b)

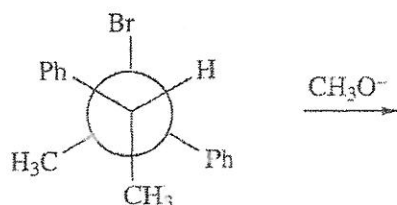


6. Indicate the major product of the following reactions and draw the mechanism. Be sure to indicate the stereochemistry of the product where applicable. ? (3 points each, 6)

(a)



(b)



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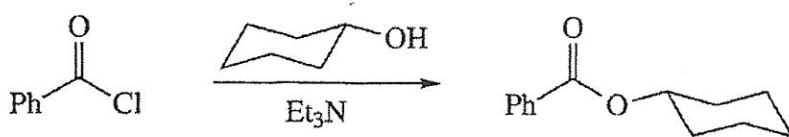
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7. Draw the mechanisms for the following reactions (5 points)



## PART II (50 points)

1. Which of the following compound will undergo an  $\text{S}_{\text{N}}1$  reaction most readily? (3 points)

- (a)  $\text{CH}_3\text{CH}_2\text{CHBrCH}_2\text{CH}_3$  (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$  (c)  $(\text{CH}_3)_3\text{CBr}$   
 (d)  $(\text{CH}_3)_3\text{CF}$  (e)  $(\text{CH}_3)_2\text{CHBr}$

2. Which of the following substitution reactions is  $\text{S}_{\text{N}}2$  reaction? (3 points)

- (a) (b)   
 (c) (d)

3. Which of the molecule shown below can be properly described as a meso compound? (3 points)

- (a) (b) (c) (d)

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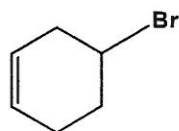
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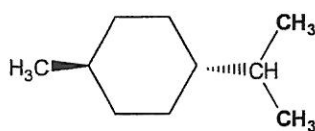
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4. Which of the following compound is chiral? (3 points)

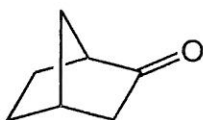
(a)



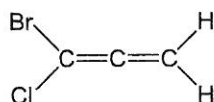
(b)



(c)



(d)

5. Which of the following alcohols will oxidize with chromic acids ( $\text{H}_2\text{CrO}_4$ )? (3 points)

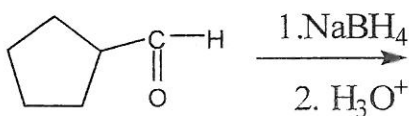
- (a) *tert*-butanol  
 (b) cyclohexanol  
 (c) pentan-1-ol  
 (d) both A and B  
 (e) both B and C  
 (f) both A and C

6. Predict the major products of the following reaction. Include stereochemistry where appropriate. (21 points)

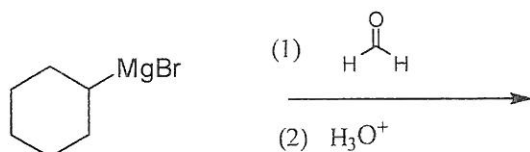
(a)



(b)



(c)



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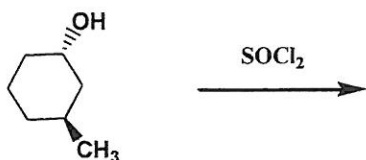
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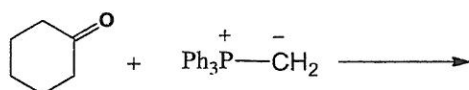
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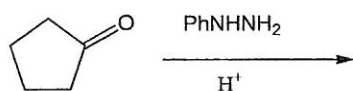
(d)



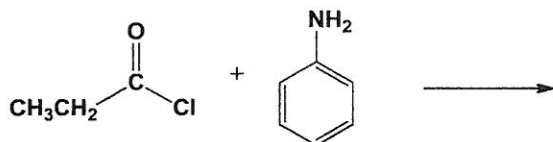
(e)



(f)



(g)

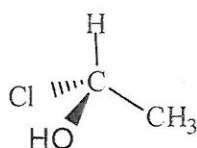


7. Predict which compound in each pair has higher boiler point. (4 points)

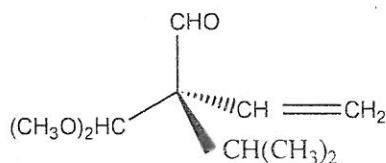
(a)  $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$  or  $(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{CH}_2-\text{CH}(\text{CH}_3)_2$ (b)  $\text{CH}_3\text{CH}_2\text{OCH}_3$  or  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ 

8. Determine the R or S configuration to each of the following compounds. (4 points)

(a)



(b)



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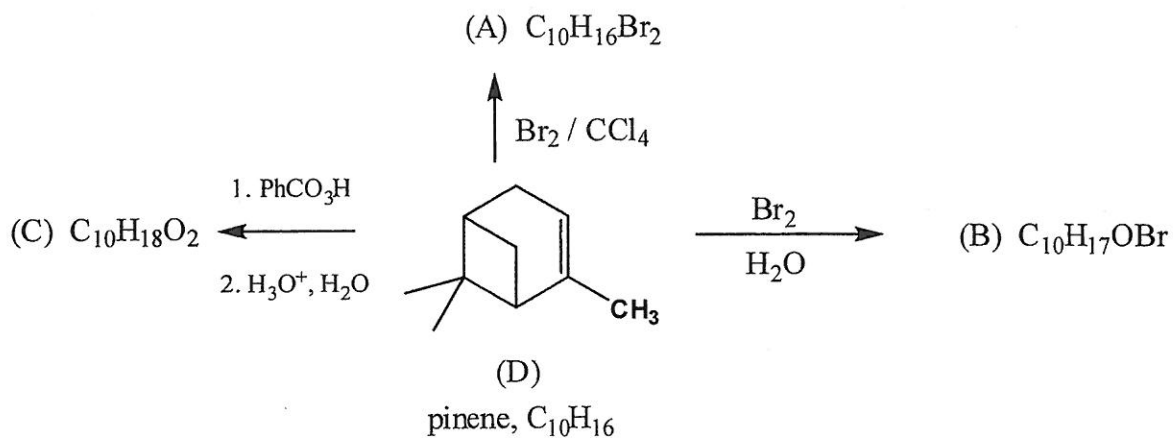
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9. The following scheme give the structure and reactions of pinene (D). Determine the reaction products of (A), (B), (C). Include **stereochemistry** where appropriate. (6 points)



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1. (20 pts) Identify the molecular symmetry point group of the following molecules:  
(a) H<sub>2</sub>O; (b) benzene; (c) methane; (d) NH<sub>3</sub>.
2. (10 pts) Classify the following as *closo*, *nido*, or *arachno*:  
(a) B<sub>7</sub>H<sub>7</sub><sup>2-</sup>; (b) PCB<sub>9</sub>H<sub>11</sub><sup>-</sup>.
3. (10 pts) Determine the metal-metal bond order consistent with the 18-electron rule for the following complex:
- $$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2]_2^{2-}$$
4. (10 pts) Sketch the metal-ligand  $\sigma$ -donation and  $\pi$ -acceptance molecular orbitals for the C<sub>2</sub>H<sub>4</sub> molecule.
5. (a) How many microstates for the electron configuration of  $p^3$ . (10 pts)  
(b) Construct the microstate table and reduce the table to its constituent free-ion terms for electron configuration of  $p^3$ . (15 pts)  
(c) Identify the  $J$  values for each free-ion term. (5%)
6. (20 pts) For the hypothetical molecule  $(\eta^4\text{-C}_4\text{H}_4)\text{Mo}(\text{CO})_4$ :  
Assuming C<sub>4v</sub> geometry, predict the number of IR-active CO bands.

C <sub>4v</sub>	E	2C <sub>4</sub>	C <sub>2</sub>	2σ <sub>v</sub>	2σ <sub>d</sub>	
Γ	4	0	0	2	0	
A <sub>1</sub>	1	1	1	1	1	z
B <sub>1</sub>	1	-1	1	1	-1	
E	2	0	-2	0	0	(x, y)

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科目：物理化學

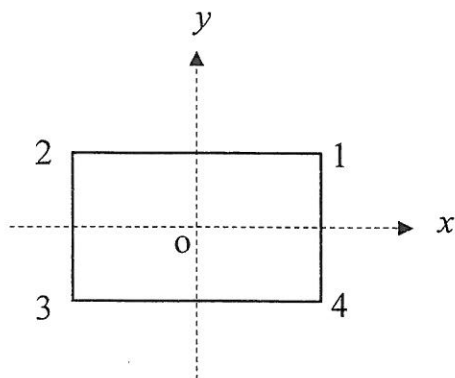
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**PART I**

- 1) Consider a consecutive reaction  $A + B \xrightleftharpoons[k_{-1}]{k_1} C \xrightarrow{k_2} P$ , where  $C$  is the intermediate.
- Write down for the rate of  $[C]$  and  $[P]$ . (9%)
  - If  $C$  is in a pre-equilibrium with the reactants, find the reaction order of the product  $P$  in terms of the reactants and its resulting rate constant. (9%)
- 2) The equilibrium constant of a reaction at 1 atm is fitted to the expression  $\ln K = -1.04 - \frac{1090}{T} + \frac{15.1 \times 10^5}{T^2}$  between 300K to 600K.
- Calculate the standard reaction Gibbs energy at 500K.. (8%)
  - Calculate the standard reaction enthalpy at 500K. (8%)

**PART II**

1. The symmetry properties of the plane figure formed by the four points at the corners of a rectangle (not a square), the following figure can be described in terms of four symmetry operations, the identify operation and three rotations. (i) Describe these symmetry operations. (8 pts) (ii) Construct the matrix representation of the above group. (8 pts)



2. In quantum mechanics, electron spin is sometimes represented by the three Pauli spin matrices:

$$S_x = \frac{1}{2}\hbar \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad S_y = \frac{1}{2}\hbar \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad S_z = \frac{1}{2}\hbar \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

- (i) Find the commutators  $[S_x, S_y]$ . (5 pts)

- (ii) Find  $S_x^2 + S_y^2 + S_z^2$ . (5 pts)

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3. Solve the Hückel molecular-orbital problem for the allyl radical  $\text{CH}_2\text{CHCH}_2$  in terms of the Hückel

$$(\alpha - E)c_1 + \beta c_2 = 0$$

parameters  $\alpha$  and  $\beta$ :  $\beta c_1 + (\alpha - E)c_2 + \beta c_3 = 0$  (7 pts)

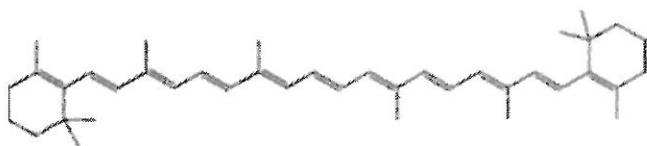
$$\beta c_2 + (\alpha - E)c_3 = 0$$

## PART III

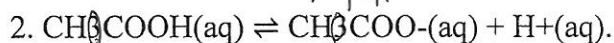
Show all works in detail and note the unite representation. Indicate units for all numerical answers.

Constants and units:  $h: 6.628\text{E-}34$  (Js);  $e: 1.602\text{E-}19$  (Coul);  $c: 2.998\text{E+}08$  ( $\text{ms}^{-1}$ ); $m_e: 9.109\text{E-}31$  (kg);  $\epsilon_0: 8.854 \times 10^{-12}$  ( $\text{C}^2/\text{N} \cdot \text{m}^2$ );  $1\text{eV}: 1.602\text{E-}19$  (J)Gas constant  $R = 8.31447 \text{ J K}^{-1}\text{mol}^{-1} = 0.08206 \text{ dm}^3\text{atmK}^{-1}\text{mol}^{-1}$ 

1.  $\beta$ -Carotene is treated as a linear polyene in which 10 single and 11 double bonds alternate along a chain of 22 carbon atoms. If we take each CC bond length to be about 140 pm. Please **calculate** the absorption energy in which one electron is promoted from  $n = 11$  to  $n = 12$ . And **derive** the corresponding energy in each of the following units of frequency ( $\text{s}^{-1}$ ), wavenumber ( $\text{cm}^{-1}$ ), wavelength (m), and energy in J, and eV. [13pts]

1  $\beta$ -Carotene

下標 3

a) Calculate  $\Delta G^\circ$  for the following acid dissociation reaction at 298 K.b) Calculate pKa and pH value when  $[\text{CH}_3\text{COOH}] = 0.1 \text{ M}$  at 298 K. [10pts]

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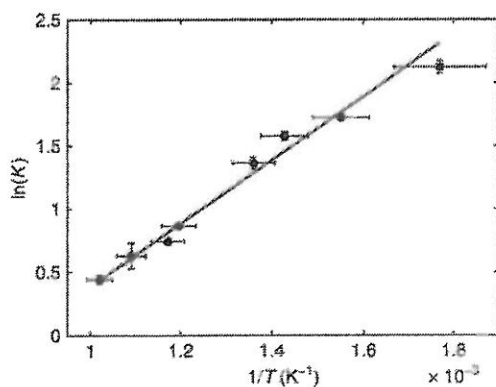
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3. Measured values of the equilibrium constant for the charge-localized to charge-delocalized states of the N,N'-dimethylpiperazine (DMP), both states can be observed molecule are shown as a function of reciprocal temperature estimated from the photon energy. The red line shows a linear best fit providing an estimate of the energy and entropy difference between the two states. Show your work for the estimate of enthalpy, entropy and Gibbs free energy at 298K [10pts]



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科目：分析化學

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1. What kind of gradient is used in SFC, GC and LC in chromatography? (15 pts)
2. What's a mass spectrometer and what does it do? What are the basic components of MS? Explain what is the ion source? Give three kinds of ion source. (20 pts)
3. State the advantages and disadvantages of the inductively coupled plasma compared with Conventional flames in atomic spectroscopy. (10 pts)
4. (a) Explain the difference between systematic and random error. (5 pts) (b) Explain the difference between precision and accuracy. (5 pts)
5. What's the electrical double layer, salt bridge and junction potential? (15 pts)
6. The dibasic compound B ( $pK_{b1} = 5.00$ ,  $pK_{b2} = 9.00$ ) was titrated with 1.00 M HCl. The initial solution of B was 0.100 M and had a volume of 100.0 mL. Find the pH at the following volumes of acid added and make a graph of pH versus  $V_a$ :  $V_a = 0, 1, 5, 12, \text{ and } 23$  mL. (20 pts)
7. What's the solid phase extraction (SPE), liquid-liquid extraction and dispersive solid phase extraction (d-SPE) and QuEChERS? (10 pts)