國立清華大學 100 學年度碩士班入學考試試題

系所班組別:生醫工程與環境科學系乙組(環境分子科學組)(0526) 考試科目(代碼):有機化學與物理化學(2604)

一、有機化學 (50%; 務必作答於答案卷內)

1. Please provide the structure of the major product for each of the following reactions, and include stereochemistry where appropriate (21%, 3 % of each).

$$\begin{array}{c} O & O \\ \hline \end{array} \\ -CCH_2CH_2CCH_3 + P_4S_{10} \end{array}$$

(D)

$$H_3O^+$$

(E)

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(F)

O

1. LDA, THF

2. HC
$$\equiv$$
 CC=OCCH₃

2. Please propose a step-by-step reaction mechanism for the following reactions (6%)

- 3. Explain the differences in appearance of two ¹H NMR spectra of 1-chloropentane shown at 60 MHz and 500 MHz. Please assign the signals to specific hydrogens in the molecules. (5%)
- 4. S_N2 reactions of halocyclopropane and halocyclobutane substrates are very much slower than those of analogous acyclic secondary haloalkanes. Suggest an explanation for this phenomenon. (5%)

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5. Propose two possible mechanisms for the following reaction. Please derive an isotope-labeling experiment or a procedure that might distinguish your two mechanisms. (7%)

- 6. What is the longest wavelength electronic transition in each of the following species? Please use molecular –orbital designation such as $n \to \pi^*$, $\pi_1 \to \pi_2$ in your answer. (6%)
 - (A) 2-propenyl cation; (B) 2-propenyl radical; (C) formaldehyde; (D) H₂C=O; (E) pentadienyl anion; and (F) 1,3,5-hexatriene.

二、物理化學 (50%; 務必作答於答案卷內)

- 7. Describe the major topics of physical chemistry and what you learned in the course. Name the author of physical chemistry textbook you used. Write down at least three important scientists and describe their contributions in physical chemistry field. (15%)
- 8. Consider the reaction $C_{(s, graphite)} \hookrightarrow C_{(s, diamond)}$. The densities of graphite and diamond are 2.25 and 3.51 g/cm³, respectively. Using the information given in Table 1, (a) calculate the equilibrium constant for the reaction at 25 °C; (b) estimate the pressure necessary for the chemical equilibrium of the reaction at 25 °C; (c) estimate the pressure necessary to make diamond from graphite at a temperature of 3298 K. (15%)

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Table 1. Thermodynamic data

Substance	$\Delta H_f^{\circ} (kJ/mol)$	S _m ° (J/Kmol)	C _{p,m} (J/Kmol)	ΔG _f ° (kJ/mol)
C(s, graphite)	0	5.74	8.527	0
C(s, diamond)	1.897	2.377	6.113	2.90

^{*}Standard molar enthalpies of formation, standard absolute entropies, and molar heat capacities are for 298.15K.

- 9. A liquid mixture consists of 33 g of component A and 99 g of component B. Answer the following questions, using the accompanying figure.
 - (a) At what temperature would the mixture begin to boil?
 - (b) What is the composition of the vapor when boiling first occurs?
 - (c) If the distillation is continued until the boiling point is raised by 2 °C, what would be the composition of the liquid left in the still?
 - (d) If fractional distillation is used in the experiment and the efficiency of the fractionating column is 100%, under the conditions in (c), what are the composition and mass of the two components collected over the initial 2 °C interval? (20%)

