國　立　清　華　大　學　命　題　紙

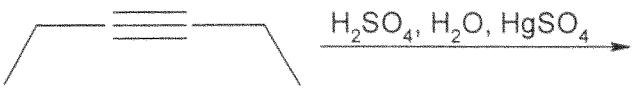
98 學年度 生醫工程與環境科學系 系（所） 乙(環境分子科學) 組碩士班入學考試

科目 有機化學與物理化學 科目代碼 2404 共 3 頁第 1 頁 *請在【答案卷卡】內作答

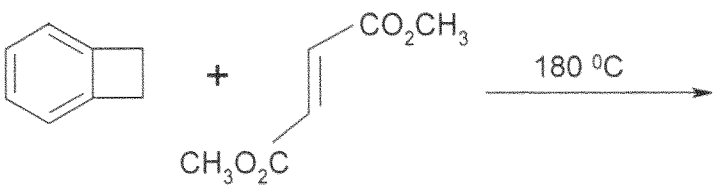
一、有機化學 (50%；務必作答於答案卷內)

I. Please provide the structure of the major product for each of the following reactions, and include stereochemistry where appropriate (24%, 3 % of each).

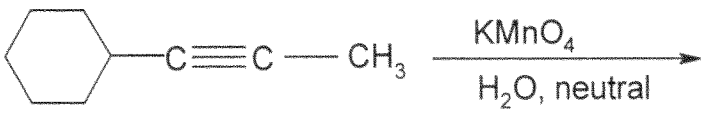
(a)



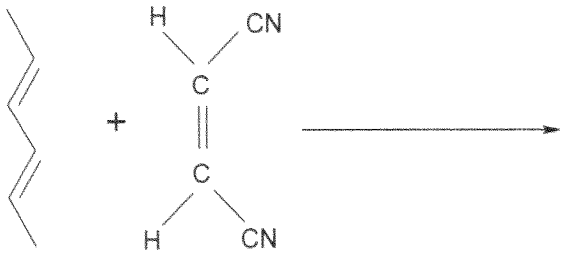
(b)



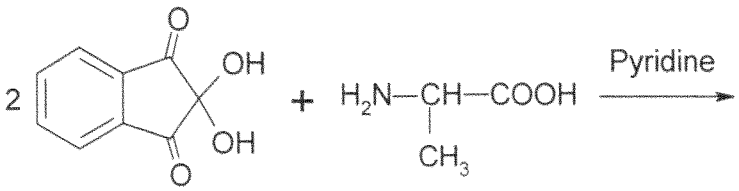
(c)



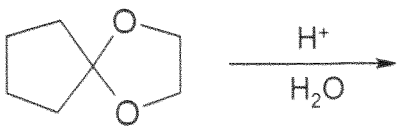
(d)



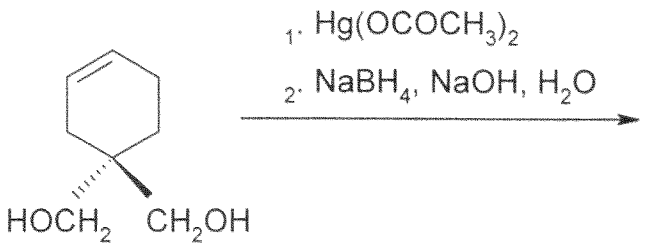
(e)



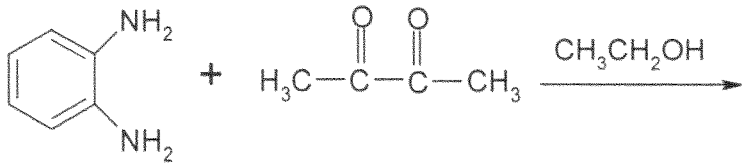
(f)



(g)

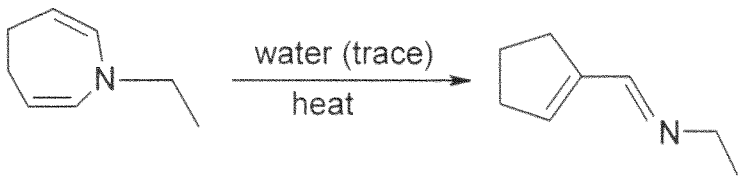


(h)

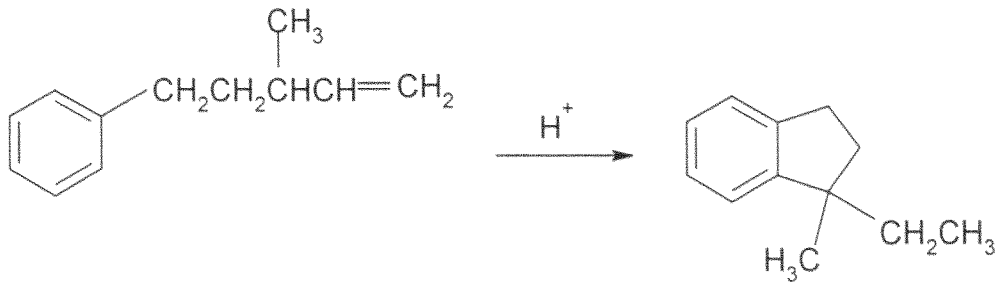


II. Please propose a step-by-step reaction mechanism for the following reactions (12%, 6% of each)

(a)



(b)



III. Two unknowns, X and Y, both having the molecular formula C_4H_8O, give the following results with four chemical tests. Propose structures for X and Y consistent with this information. (6%)

	Bromine	Na metal	Chromic acid	Lucas reagent
Compound X	decolorizes	Bubbles	Orange to green	No reaction
Compound Y	No reaction	No reaction	No reaction	No reaction

IV. (a) Optically active 2-bromobutane undergoes racemization on treatment with a solution of KBr. Please show your reaction. (2%)

(b) In contrast, optically active 2-butanol does not racemize on treatment with a solution of KOH. Explain why a reaction like that in part (a) does not occur. (2%)

(c) Optically active 2-butanol can racemize in dilute acid. Please propose a mechanism for this reaction. (4%)

二、物理化學 (50%；務必作答於答案卷內)

Water is the most commonplace of substances, and yet its properties are unique among chemical compounds. The following questions are related to the Mickey Mouse molecule.

1. Calculate the boiling temperature of water at an altitude of 8900 m, the top of the world (Mount Everest). Assume that the atmosphere is at equilibrium at a temperature of 20 °C and the use of the Boltzmann distribution to estimate the barometric pressure. Air is a single gas with molar mass 0.028 kg/mol and the molar enthalpy change of vaporization of water is equal to 40.66 kJ/mol. State any other assumptions. (10%)

2. When 1 mole of supercooled water ($H_2O(l)$ at -10 °C) freezes isothermally at 1.00 atm, what are the entropy changes of the system and surroundings? Is this process spontaneous? Given the molar enthalpy of melting of ice at 0 °C is 6025 J/mol, the molar heat capacities of ice and water are 38 and 75 J/Kmol, respectively. (15%)

3. Calculate the effect on the chemical potentials of ice and water of increasing the pressure from 1.00 atm to 2.00 atm at 0°C. The density of ice is 0.917 g/cm^3 and that of liquid water is 0.999 g/cm^3 under these conditions. Sketch a graph representing the chemical potentials of ice and water as a function of the temperature in the vicinity of the solid-liquid phase transition at 1.00 atm and 2.00 atm. Is the freezing temperature increasing or decreasing when the pressure increases? Justify your answer. (10%)

4. (a) Derive an expression for the relaxation time for the reaction $H_2O(l) \leftrightarrows H^+(aq) + OH^-(aq)$ when the system is subjected to a small perturbation from equilibrium. Assume the forward reaction to be first-order and the reverse reaction to be second-order overall, first order with respect to each reactant.

(b) After a temperature-jump, the above reaction returns to equilibrium with a relaxation time of 37μs at 298K and pH at 7.0. Given the equilibrium constant for the autoprotolysis of water $K_w = 1.008\times10^{-14}$ at 298K, calculate the rate constants for the forward and reverse reactions, k_f and k_r, respectively. (15%)