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## Organic Chemistry (7題,50分)

1. Please name (in English) each of the following compounds and groups. (15 points)

(a) Bz-, (b) NBS, (c) MCPBA, (d) DMSO, (e) TsO-, (f) CH<sub>2</sub>=CHCH<sub>2</sub>MgI,

$$(g) \longrightarrow (h) \longrightarrow (i) \longrightarrow (j) \longrightarrow (k) \longrightarrow (h) \longrightarrow (h)$$

2. Please identify each of the following compounds from their <sup>1</sup>H NMR data and molecular formula. The number of hydrogens responsible for each signal is shown in parentheses. (6 points)

(a)  $C_4H_8Br_2$ 

(b) C<sub>8</sub>H<sub>9</sub>Br

1.97 ppm (6) singlet

2.01 ppm (3) doublet

3.89 ppm (2) singlet

5.14 ppm (1) quartet

7.35 ppm (5) broad singlet

3. Please identify structures A through D in the following reactions. (8 points)

$$\begin{array}{c} \overset{O}{\underset{\text{H}_{3}\text{C-C-N-CH(CO}_{2}\text{Et})_{2}}{\text{C}}} & \overset{\text{(i) NaOEt}}{\underset{\text{(ii) CH}_{2}=\text{CHCN}}{\text{C}}} & \text{A } (C_{12}\text{H}_{18}\text{N}_{2}\text{O}_{5}) & \xrightarrow{\text{H}_{2}} & \text{B } (C_{12}\text{H}_{22}\text{N}_{2}\text{O}_{5}) \\ \hline \\ & \overset{\text{gentle}}{\underset{\text{warming}}{\text{marming}}} & \text{C } (C_{10}\text{H}_{16}\text{N}_{2}\text{O}_{4}) & \xrightarrow{\text{HCl(aq)}} & \text{D } (C_{5}\text{H}_{14}\text{N}_{2}\text{O}_{2}\text{Cl}_{2}) \\ \hline \\ & \text{Ornithine dihydrochloride} \end{array}$$

4. Please outline a synthesis of Orange II starting with  $\beta$ -naththol and p-aminobenzenesulfonic acid. (5 points)

OH 
$$H_2N$$
—SO<sub>3</sub>H  $OH$  Orange II

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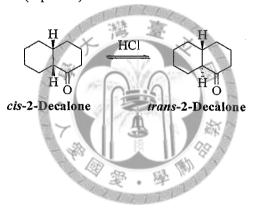
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5. The specific rotation of (R)-mandelic acid is  $-158^{\circ}$ . A solution of mandelic acid (0.10g/mL) has an observed rotation of  $+6.32^{\circ}$  when placed in a polarimeter tube 20 cm long. What is the percent of each enantiomer in the solution? (6 points)

- 6. The hydrolysis of triphenylmethyl benzoate in water does not require the presence of added acid or base and, in fact, is not influenced significantly by small amounts of added acid or base. Account for these results by suggesting a mechanism for the reaction. (5 points)
- 7. When *cis-2-*decalone is dissolved in ether containing a trace of HCl, an equilibrium is established with *trans-2-*decalone. The latter ketone predominates in the equilibrium. Please propose a mechanism for this isomerization and account for the fact that the *trans* isomer predominates at equilibrium. (5 points)



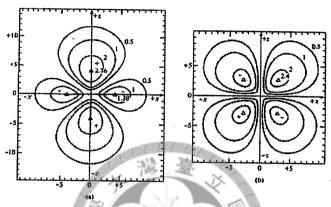
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8. Write the electronic configurations for the atom of Z = 7 is of ground state? Excited state? Or forbidden? Explain. (6 points)

9. Draw MO's and their corresponding energy diagram for the  $\pi$  orbitals in C<sub>3</sub>H<sub>5</sub> radical (6 points)

10. With the given electron density contour below, describe the two atomic orbitals in the figures below and determine the corresponding n and l values. Explain. (6 points)



11. Al(OH)<sub>3</sub> is not very soluble in water, unless the solution is acidic or basic, explain "hydrolysis" and elaborate how it affects the chemical behavior of Al(OH)<sub>3</sub> in aqueous solutions? (6 points)

12. With the kinetic data for the ligand exchange of the complex shown below, evaluate the rate constant and propose a mechanism that is in agreement with the rate law. (8 points)

13. Urea ligands usually bond through the oxygen atom. 2-Pyridylmethylurea (below) is found to form the N,N'-bonded square planar complex with Cu in (N-N')CuMeCl, but N,O-bonded tetrahedral complex with Zn in (N-O)ZnMeCl. Draw the possible stereoisomers for these two complexs. (8 points)

14. Rationalize the following data of bond lengths (pm) in Cr(CO)<sub>5</sub>L. (10 points)

4L	Cr-P	Cr-C	Cr-C	C-O	C-0
		(trans to P)	(trans to CO)	(trans to P)	(trans to CO)
CO	-	_	191.5(2) av	-	114.0(2) av
P(OPh) <sub>3</sub>	230.9(1)	186.1(4)	189.6(4) av	113.6(6)	113.1(6) av
(PCH <sub>2</sub> CH <sub>2</sub> CN) <sub>3</sub>	236.4(1)	187.6(4)	189.1(4) av	113.6(4)	113.8(4) av
PPh <sub>3</sub>	242.2(1)	184.4(4)	188.0(4) av	115.4(5)	114.7(6) av