

**Figure 2.** Linear sweep polarograms. A: Mordant Red 19, B: Mordant Blue 9, C: Purpurin Soutlion;  $1.0 \times 10^{-3}$  M Ligand +  $\text{La}^{3+}$  in 0.1 M NaCl, pH=9.2, Scan Rate=100 mV/sec. a and b represent ligand and complex, respectively.

**Table 1.** Electrochemical Parameters of  $\text{La}^{3+}$ -Ligand System

Ligands	$-E_p$ , ligand (mV)	$-E_p$ , complex (mV)	$\Delta E_p$ (mV)	$\lambda_{\text{max}}^a$ (nm)
Mordant Red 19	670	745	75	472
Mordant Blue 9	710	840	130	516
Purpurin	810	945	135	485
	1040			

<sup>a</sup> $\lambda_{\text{max}}$  of ligand. <sup>b</sup>Molar absorptivity,  $\text{cm}^{-1}\text{M}^{-1}$ . Scan Rate=100 mV/sec.

them for the selective determination of lanthanide in a certain mixture. Detailed electrochemical behaviors, composition of the complex, and analytical applications are under investigation and will be reported later.

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## An Effective Diastereofacial Control by Built-in Oxazolidinone Ring System: An Application to the Total Synthesis of $\alpha$ -Allokainic Acid

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$\alpha$ -Allokainic acid **1**, isolated from the algae, *Digenea Simplex*<sup>1</sup> and *Centrocerus clavulatum*<sup>2</sup> has attracted considerable attention due to its neuroexcitatory activity, although its activity is much less than that of kainic acid<sup>3</sup>. Structurally  $\alpha$ -allo-

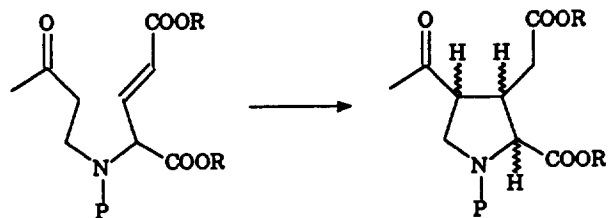
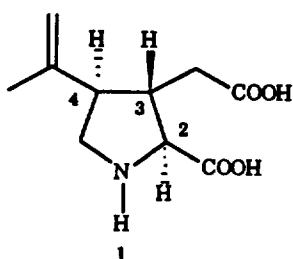


Figure 1.



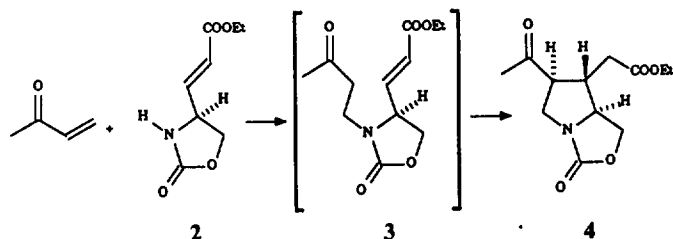
kainic acid is a derivative of proline with two side chains at C3, C4 positions having all trans stereochemical arrangements to the adjacent side chains.

Previously<sup>4</sup> we have reported our result on an effective construction of a necessary skeleton for  $\alpha$ -allokainic acid and  $\alpha$ -kainic acid by using intramolecular Michael reaction as shown in Figure 1. However, the major drawback of the system was in rather poor diastereochemical control in intramolecular Michael reaction to give rise to a mixture of stereoisomers, in contrast to good stereochemical controls claimed by Barco<sup>5</sup> in a similar system.

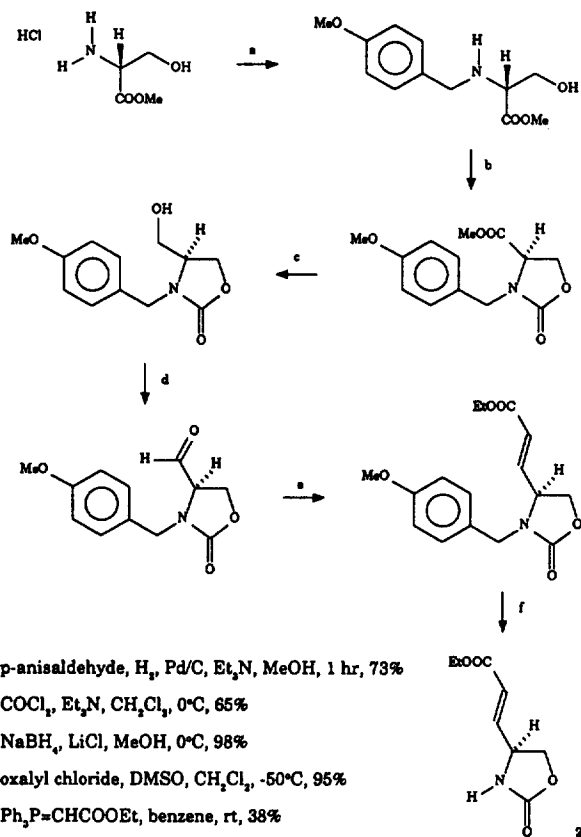
Since then we have been interested in a notion that the stereochemistry of two chiral centers could be effectively controlled by a rigid built-in template. Among others, an oxazolidinone ring system was chosen on the basis of the following reasons. First, the oxazolidinone ring is conformationally rigid enough to expect a good diastereofacial control. Second, it is not only a protected form for the basic nitrogen but also will provide a necessary carboxylic acid moiety at C2 by subsequent hydrolysis and oxidation. The oxazolidinone system has been previously used by Baldwin<sup>6</sup> in their cobalt-mediated cyclization reaction but reported to have rather poor stereochemical control, and by Shirahama<sup>7</sup> in their intramolecular Diels-Alder reaction successfully.

Thus the key intermediate **2** was prepared by a sequence of the reactions as shown in Scheme 1 starting with a HCl salt of serine methyl ester.

Then the intermediate **2** was treated with methyl vinyl

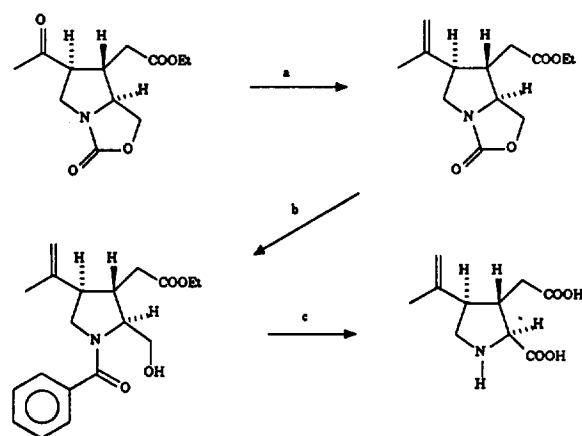


ketone in the presence of a catalytic amount of sodium ethoxide in benzene at room temperature and the reaction proceeded smoothly to give a single product in high yield. The product was found to be a cyclized product **4** which was



- a) *p*-anisaldehyde, H<sub>2</sub>, Pd/C, Et<sub>3</sub>N, MeOH, 1 hr, 73%
- b) COCl<sub>2</sub>, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, 0°C, 65%
- c) NaBH<sub>4</sub>, LiCl, MeOH, 0°C, 98%
- d) oxalyl chloride, DMSO, CH<sub>2</sub>Cl<sub>2</sub>, -50°C, 95%
- e) Ph<sub>3</sub>P=CHCOOEt, benzene, rt, 38%
- f) Ceric ammonium nitrate, CH<sub>3</sub>CN, H<sub>2</sub>O, 45%

Scheme 1.



- a) Ph<sub>3</sub>P=CH<sub>2</sub>, toluene, 0°C, 69%
- b) i) NaOEt, EtOH, reflux ii) PhCOCl, K<sub>2</sub>CO<sub>3</sub>, 2 steps 42%
- c) i) Jones reagent, acetone, 0°C ii) 4N HCl, reflux, 2 steps 70%

Scheme 2.

presumably formed by the intramolecular cyclization of **3**, an 1,4-addition product. Furthermore, it was found to be a single stereoisomer and none of other stereoisomers were detected. The structure along with its stereochemistry was easily determined by <sup>1</sup>H-NMR spectroscopy<sup>8</sup>. However, its definite structure and stereochemistry were confirmed by the transformation of **4** to the final product by the sequence of the reactions shown in Scheme 2 and by comparing the product with  $\alpha$ -allokainic acid.

In conclusion we have shown that the built-in oxazolidinone ring turned out to be an effective way of controlling the diastereofacial approach of two side chains and the overall strategy has been successfully applied to the total synthesis of  $\alpha$ -allokainic acid.

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8. NMR data for 4:  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.29 (t, 3H), 2.23 (s, 3H), 2.39 (m, 1H), 2.60 (dd, 2H), 3.08 (m, 1H), 3.57 (dd, 1H), 3.78 (q, 1H), 3.82 (m, 1H), 4.15 (q, 2H), 4.45 (dd, 1H), 4.57 (dd, 1H).  $^{13}\text{C-NMR}$  (75.469 MHz,  $\text{CDCl}_3$ )  $\delta$  14.21, 29.03, 35.92, 41.86, 47.25, 57.95, 61.04, 64.27, 67.94, 160.57, 171.31, 205.48

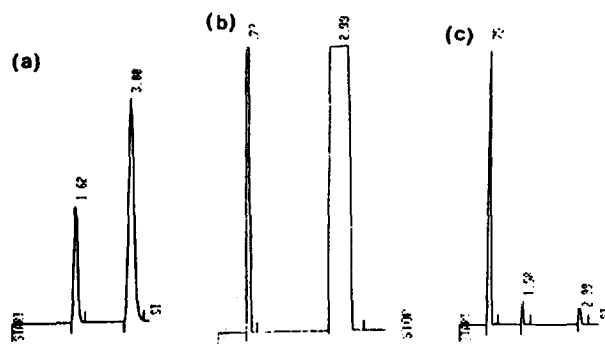
### Light-Induced Hydrogen and Oxygen Generation from Water with Vesicle-Stabilized Colloidal Mercury Sulfide and Sodium Metaborate

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Photochemical solar energy storage is a popular candidate as a possible source of alternative energy. We are interested in a quantum conversion, particularly hydrogen and oxygen generation from water with the vesicle-stabilized colloidal mercury sulfide and sodium metaborate. The availability of photochemical solar energy conversion using  $\text{TiO}_2^{1-5,12}$  and  $\text{CdS}^{6-13}$  are studied extensively and intensively. In general, the leading scientists have obtained hydrogen and oxidized product from water and the sacrificial electron donor, respectively. A photochemical system which can be returned to the original state after producing hydrogen and oxygen from water has to be established. Here, we, for the first time, report photochemical hydrogen and oxygen generation from



**Figure 1.** Gas chromatographs of air (a),  $\text{H}_2$  diluted with nitrogen (b) and gases in vesicle-stabilized  $\text{HgS}$  system (c). Retention time (min):  $\text{H}_2$ ; 0.73-0.75,  $\text{O}_2$ ; 1.58-1.62,  $\text{N}_2$ ; 2.99-3.00.

water using vesicle-stabilized colloidal mercury sulfide particle with Rh particles and metaborate.

We select  $\text{HgS}$  colloidal particles instead of  $\text{CdS}$ , because the band gap of  $\text{HgS}$  is high enough to reduce and oxidize water. We also think metaborate can generate oxygen cyclically by reacting with hydrogen peroxide produced in the photochemical reaction of the vesicle-stabilized colloidal mercury sulfide with Rh particles. DODAB vesicle (dioctadecyl dimethyl ammonium bromide) containing  $\text{HgS}$  colloid was prepared as described previously by Fendler *et al.*<sup>10</sup> The vesicle was prepared by sonication of the mixture of surfactant (DODAB, 0.12 g,  $2 \times 10^{-4}$  moles) and water (200 ml, triply distilled).  $\text{HgCl}_2$  stock solution (0.1 M, 1 ml) was added to the vesicle and then shaken thoroughly. If hydrogen sulfide gas was bubbled through the vesicle for 1 minute, the color of the vesicle turned to black. The superfluous  $\text{H}_2\text{S}$  was eliminated by argon bubbling through vesicle for 2 hrs. Transmission electron microscope of absorbed  $\text{HgS}$  particles on DODAB vesicle surface confirmed that colloid particles were mainly attached on the focussed vesicle surface. The colloidal  $\text{HgS}$  formed in vesicle had a band gap of 350 nm compared to 498 nm of  $\text{CdS}$ <sup>10</sup>.

The colloidal  $\text{HgS}$  vesicles<sup>14</sup> (20 ml) were added to 30 ml-pyrex cell with a rubber stopper. Rh colloids (50  $\mu\text{l}$ ) which were obtained by reduction of  $\text{RhCl}_3$  with  $\text{NaBH}_4$ , and  $\text{NaBO}_2$  (1 M, 50  $\mu\text{l}$ ) were added to the 30 ml-pyrex cell and then degassed with argon for 30 min. When the colloidal  $\text{HgS}$  vesicles (20 ml) with Rh colloids were irradiated under anaerobic condition by 500 W-Xenon lamp using 0.4 M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution filter, hydrogen and oxygen were obtained. The gases were identified with authentic samples by G.C. The retention times of hydrogen, oxygen and nitrogen in molecular sieve column (5 A molecular sieve, 1/8 inch, 6 ft column, oven temp.  $50^\circ\text{C}$ ) were 0.75, 1.58 and 3.00, respectively. Gas chromatographs of air, hydrogen diluted with nitrogen, and gases on  $\text{HgS}$ -metaborate system are shown in Figure 1. Some portion of the peak of retention time 1.58 ( $\text{O}_2$ ) and all portion of the peak of retention time 3.0 ( $\text{N}_2$ ) came from air leaking during reaction and/or injection times. The amount of hydrogen and oxygen were determined with standard lines of authentic samples and by comparing the ratio of oxygen and nitrogen of air. The amount of hydrogen and oxygen produced *vs.* irradiation time is shown in Table 1. Hydrogen and oxygen were produced continuously. Hydro-