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A Convenient Preparation of Optically Active 1,1'-Binaphthyl-2,2'-diol via Enzymatic Hydrolysis of the Racemic Diester

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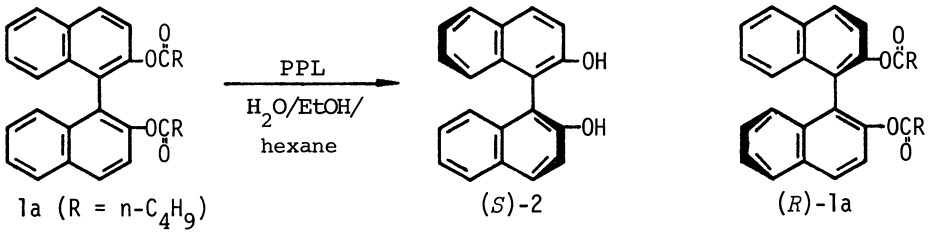
Commercially available porcine pancreatic lipase can conveniently be utilized for a highly enantioselective hydrolysis of valeric acid diester of racemic 1,1'-binaphthyl-2,2'-diol to give the (*S*)-diol (95% ee at 46% conversion).

In the past few years, much attention has been centered on the asymmetric reaction by the use of axially dissymmetric biaryl skeleton as the chirality-recognizing unit.[1] Although 1,1'-binaphthyl-2,2'-diol (2) has been one of the most successfully utilized biaryls,[2] conventional preparation of optically active 2, at least when needed in substantial quantities, still relies on tedious optical resolution via cyclic phosphoric acid ester of 2.[3,4] Recently, two groups have reported kinetic resolution of racemic diester of 2 via microbial hydrolysis.[5] Although the reaction proceeds with high enantioselectivity, it requires incubation of the substrate diester in nutrient medium under rather dilute conditions (1 mg substrate/ml medium) for a long period (10 d). Moreover, the handling of living microorganisms may not always be welcome to synthetic organic chemists.

Herein, we wish to report that a commercial porcine pancreatic lipase (PPL) preparation[6] can advantageously be utilized as an inexpensive, easy to handle, but highly enantioselective hydrolysis reagent for valeric acid diester 1a.[7] The reaction can simply be carried out by vigorously stirring an emulsion of 1a in EtOH/hexane/0.1 M phosphate buffer with PPL. In a typical run,[8] the reaction was terminated at 46% conversion (R.T., 20 h) to give (*S*)-2 of 95% ee as evidenced by HPLC[9] as well as optical rotation. It seems crucial that substrate diester 1 should be finely dispersed in the heterogeneous reaction system; diacetate (1b, R = CH_3), which precipitated out during the attempted preparation of the emulsion, was hardly hydrolyzed, but with high enantioselectivity to give (*S*)-2 (<95% ee).



1a (R = n-C_4H_9) (*S*)-2 (*R*)-1a

Although the procedure requires the lipase in rather large quantities at present,[10] it may replace the conventional method for the preparation of optically active 2; scaling up of the process and efforts to develop a method for reuse of the lipase are in progress.

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References

1) Review: S. Miyano and H. Hashimoto, Yuki Gosei Kagaku Kyokai Shi, 44, 713(1986).
2) For example, R. Noyori, I. Tomino, Y. Tanimoto, and M. Nishizawa, J. Am. Chem. Soc., 106, 6709 (1984).
3) a) S. Miyano, M. Tobita, and H. Hashimoto, Bull. Chem. Soc. Jpn., 54, 3522 (1981); b) E. P. Kyba, G. W. Gokel, F. de Jong, K. Koga, L. R. Sousa, M. G. Siegel, L. Kaplan, G. D. Y. Sogah, and D. J. Cram, J. Org. Chem., 42, 4173 (1977).
4) Cf. J. Brussee, J. L. G. Groenendijk, J. M. te Koppele, and A. C. A. Jansen, Tetrahedron, 41, 3313 (1985).
5) Y. Fujimoto, H. Iwadate, and N. Ikekawa, J. Chem. Soc., Chem. Commun., 1985, 1333; S.-H. Wu, L.-Q. Zhang, C.-S. Chen, G. Girdaukas, and C. J. Sih, Tetrahedron Lett., 26, 4323 (1985).
6) Purchased from Tokyo Kasei Kogyo Co., Ltd., and stored at 4 °C; specific activity, 10^4 olive oil unit per g of solid.
7) Other lipase preparations, such as Rhizopus delemars from Tanabe Pharmaceutical Co., Ltd. (Talipase) and from Seikagaku Kogyo Co., Ltd., and Candida cylindracea from Meito Sangyo Co., Ltd. (lipase My), were far less active.
8) A solution of 1a (1.60 g, 3.52 mmol) in EtOH (4.7 ml) and hexane (1.5 ml) was ultrasonically agitated, to which was added 2.7 ml of 2 wt% aq polyvinyl alcohol solution[11] followed by 26 ml of 0.1 M phosphate buffer (pH 7.4) to form an emulsion. To the vigorously stirred emulsion was added portionwise 3.2 g of PPL,[6] with taking care not to cause agglomeration. Stirring was continued at ambient temperature (25 – 27 °C) till the conversion reached 46% as monitored by HPLC[9]; accumuration of the monoester was negligible (>2%).[5] The reaction was terminated by adding 200 ml of EtOH-acetone (1/1) to precipitate the enzyme. After bulk of the solvent was removed in vacuo, reaction products were taken into CH_2Cl_2 and treated as usual; chromatography on silica-gel column with CH_2Cl_2 as the eluent gave 380 mg of (*S*)-2 (95% ee, $[\alpha]_D^{25}$ -33.6° (c 3.01, THF), mp 206.5 °C)[12] and 830 mg of (*R*)-1a (84% ee[13]).
9) The HPLC was carried with a Pirkle Type 1-A column eluted with i-PrOH-hexane.
10) See footnote (10) of the following: G. Kirchner, M. P. Scollar, A. M. Klibanov, J. Am. Chem. Soc., 107, 7072 (1985).
11) Prepared by dissolving 1.85 g of Kurare PVA 117 and 150 mg of PVA 205 to make 100 ml solution.
12) Enantiomerically pure (*S*)-2; $[\alpha]_D^{22}$ -35.0° (c 1.18, THF), mp 209 – 210 °C.[3a]
13) Determined by HPLC after conversion to 2 by hydrolysis with KOH in aq EtOH.[3a]

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