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Preparation of Enantiomerically Pure 1,1'-Bi-2-naphthol Via Cyclic Borate Ester

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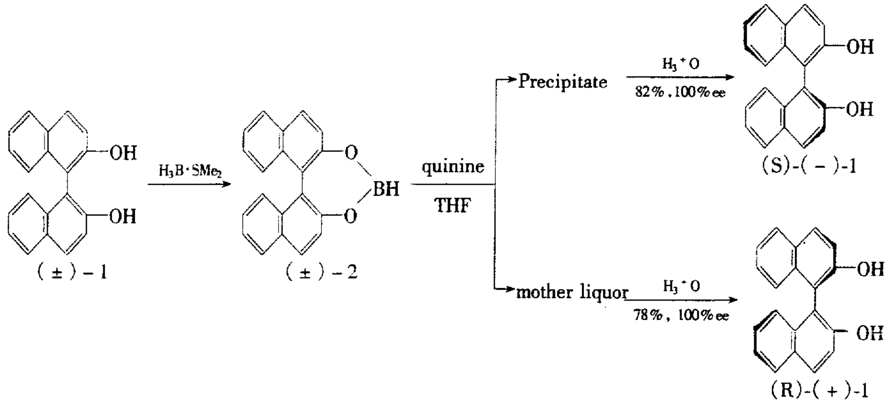
Abstract: The first example of the preparation of enantiomerically pure 1,1'-bi-2-naphthol via cyclic borate ester was described. Both enantiomers were obtained with about 80% yield and 100% ee. Copyright © 1996 Published by Elsevier Science Ltd

Both enantiomers of 1,1'-bi-2-naphthol are very useful chiral auxiliaries in a wide range of asymmetric reactions, such as asymmetric reductions[1], asymmetric alkylations[2] and asymmetric catalysis[3]. There are numerous methods for the preparation of optically active 1,1'-bi-2-naphthol in literature, chief among them are, fractional crystallization of the diastereomeric cyclic phosphate ester derivatives[4] and chiral complexes[5] of 1,1'-bi-2-naphthol, enantiospecific hydrolysis using microorganisms or enzymes[6] and enantioselective synthesis[7]. Although chromatagraphy using a chiral stationary phase is developing rapidly, it is difficult to apply to the preparation in large amounts for the time being. The cyclic phosphate ester method is still the best current method so far, because it can not only yield both enantiomers of high enantiomeric purity, but can also be carried out on a synthetic scale. However, there are also some disadvantages for the method, it is laborious due to a diastereoisomeric intermediate, such as cinchoninium 1,1'-bi-2-naphtholphosphate, must be purified repeatly and lithium aluminium hydride must be used for obtaining both enantiomers of 1,1'-bi-2-naphthol owing to the great stability of cyclic phosphate esters to hydrolysis. Considering that formation or cleavage of boron-oxygen bonds is easy, we undertook an exploratory study for resolving racemic 1,1'-bi-2-naphthol by formation of a borate ester. We examined the reactions of 1,1'-bi-2-naphthol-borane with a few alkaloids including ephedrine, cinchonine and quinine in several solvents, respectively. We finally found tetrahydrofuran is an excellent solvent for the resolution of both diastereomers of 1,1'-bi-2-naphtholborane quinine derivative. Here we wish to report the first example of the preparation of enantiomerically pure 1,1'-bi-2-naphthol via a cyclic borate ester. Racemic 1,1'-bi-2-naphthol (1) reacted with borane-dimethyl sulfide in diethyl ether, tetrahydrofuran, dichloromethane or benzene at room temperature to offer a homogeneous solution of 1,1'-bi-2-naphtholborane(2) with the evolution of hydrogen. After the solvent and the volatile substances were removed under reduced pressure, followed by treatment with quinine in tetrahydrofuran, a white solid precipitated. The precipitate and the mother liquor were separated, acidified and purified to obtain (R)-(+)-and (S)-(−)-1,1'-bi-2-naphthol of about 80% yield and 100%ee, respectively (Scheme 1).



Scheme 1

It should be pointed out that when $H_3B\cdot SMe_2$ was replaced by trimethoxyborane or boric acid, both enantiomers with 100% ee could be also ohtained[8].

The preparation of enantiomerically pure 1,1'-bi-2-naphthol via a cyclic borate ester possesses a number of advantages. This procedure is easy to carry out, it has a short period for preparation, it can offer both enantiomers in high optical purity, and it does not require to use lithium aluminium hydride. It goes without saying that the cyclic borate ester approach is one of the most attractive methods for preparing enantiomerically pure 1,1'-bi-2-naphthol.

Experimental

A dry 100ml round-bottom two-neck flask charged with 1.88g (6.57mmol) of racemic 1,1'-bi--2-naphthol was fitted with a magnetic stirring bar, a 25ml pressure-equalized addition fannel with a rubber septum and an oil bubbler with a stopcock. Under a positive pressure of argon, 45ml of anhydrous Et_2O was introduced, then a solution of 1mL 8.86 M of $H_3B\cdot SMe_2$ in 10ml Et_2O was added dropwise with stirring and maintained the reaction temperature below 20℃. After the evolution of hydrogen stopped, the solvent and the volatile substances were removed under reduced pressure. 2.13g(6.57mmol) of quinine and 30mL THF were added, stirred, the solids dissolved rapidly, after a while, a new white precipitate began to appear. Following stirring for 2h and filtration, the solid was washed with THF, dried, and transferred into a 100mL flask, treated with 10mL chloroform and 10mL 2N HCl for 2h, 20ml Et_2O was added, after additional stirring for ten minuts, the organic layer was separated, the water phase was extracted with Et_2O (2 × 10ml), the organic phase was combined and dried over anhydrous Na_2SO_4, filtered, the filtrate was concentrated to dryness under reduced pressure, the residue was reextracted with 25mL Et_2O, 0.87g of (S)-(−)-1,1'-bi-2-naphthol was obtained from the extract. It was recrystallized carefully from Et_2O to give 0.77g of transparent crystal, the yield is 82%, m.p. 206 − 207℃, $[\alpha]_D^{20} = -35.2$ (THF, C1), 100% ee.

The THF mother liquor removed the white precipitate was concentrated to dryness, the residue was washed with a small quantity of dry Et_2O, then treated as above procedure to offer 0.90g of (R)-(+)-1,1'-bi-2-naphthol, after careful recrystallization from Et_2O, 0.73g of crystalline product was obtained, the yield is 78%, m.p. 206 − 207℃. $[\alpha]_D^{20} = +35.3$ (THF, C1), 100%ee.

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Reference and Notes

1. (a) Suzuki, M.; Morite, Y.; Koyano. H.; Koga, M. and Noyori, R. *Tetrahedron*, **1990**, 46, 4809; (b) Noyori, R.; Tomino, I.; Yamada, M.; Nishizawa, M. *J. Am. Chem. Soc.* **1984**, 106, 6717; (c) Noyori, R, *Chem. Soc. Rev.* **1989**.18.187.
2. (a) Maglioli, P.; De Lucchi, O.; Delogu, G. and Valle, G. *Tetrohedron, Asymmetry*, **1992**, 3(3), 365; (b) Fuji, K.; Node, M. and Tanaka, F. *Tetrahedron Lett.* **1990**, 31 (45), 6553.
3. (a) Chapuis, Ch.; Jurczak, J. *Helv. Chim. Acta* **1987**, 70, 436; (b) Bao, J.; Wulff, W.D.; Rheingold, A.L. *J. Am. Chem. Soc.* **1993**, 115, 3814; (c) Maruoka, K.; Itoh, T.; Shirasaka, T. and Yamamoto, H. *J. Am. Chem. Soc.* **1988**, 110, 310; (d) Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H,; Miyashita, A.; Noyori, R. and *Otsuka*, S. *J. Am. Chem. Soc.* **1984**, 106, 5208; (e) Terada, M.; Motoyama, Y. and Mikami, K. *Tetrahedron Lett.* **1994**, 35, 6693; (f) Mikami, K.; Matsukawa, S. *Tetrahedron Lett.* **1994**, 35, 3133; (g) Sakane, S.; Maruoka, K.; Yamamoto, H. *Tetrahedron Lett.* **1985**, 20, 5535.
4. (a) Jacques, J.; Fouquay. *Org. Synth.* **1988**, 67, 1; (b) Truesdale, L. K. *Ibid.* **1988**, 67, 13; (c) Brunel, J − M. and Buono, G. *J. Org. Chem.* **1993**, 58, 7313; (d) Fabbri, D; Delogu, G.; De Lucehi, O. *J. Org. Chem.* **1993**, 58, 1748; (e) Gong, B − q; Chen, W. − y. and Hu, B. − f. *J. Org. Chem.* **1991**, 56, 423; (f) Tamai, Y.; Heung − cho, P.; Iizuka, k.; Okamura, A. and Miyano, S. *Synth.* **1990**, (3), 222.
5. (a) Toda, F.; Tanaka, K.; Nakamatsu, S. *Tetrahedron lett.* **1984**, 25, 4929; (b)

Kawashima, M.; Hirata, R. *Bull. Chem. Soc. Jpn.* **1993**, 66, 2002; (c)Tode, F.; Tanaka, K.; Stein, Z.; Goldberg, I. *J. Org. Chem.* **1994**, 59, 5748; (d)Cai, D.-w.; Hughes, D. L.; Verhoeven, T. R. and Reider, P. J. *Tetrahedron Lett.* **1995**, 36 (44), 7991.

6. (a)Kazlauskas, R.J. *J. Am. Chem. Soc.* **1989**, 111, 4953; (b)Kazlauskas, R.J. *Org. Synth.* **1991**, 70, 60; (c)Miyano, S.; Kawahara, K.; Inone, Y.; Hashimoto, H. *Chem. Lett.* **1987**, (2), 355; (d)Fujimoto, Y.; Iwadate, H.; Ikekawa, N. *J. Chem. Soc. Chem. Commun.* **1985**, 1333; (e)Wu, S.-h.; Zhang, L.-q.; Chen, C.-s.; Girdaukas, G.; Sih, C.J. *Tetrahedron Lett.* **1985**, 26, 4323;
7. (a)Brussee, J.; Groemendijk, J.L.G.; te Kopple, J.M.; Janse, A.C.A. *Tetrahedron* **1985**, 41, 3313; (b)Miyano, S.; Handa, S.; Shimizu, K.; Tagami, K.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1984**, 57, 1943; (c)Miyano, S.; Tobita, M.; Nawa, M.; Sato, S.; Hashimoto, J. *J. Chem. Soc. Chem. Commun.* **1980**, 1223; (d)Smricina, M.; Lorenc, M.; Hanus, V.; Sedmera, P. and Kocovsky, P. *J. Org. Chem.* **1992**, 57, 1917.
8. For example, the solid obtained from reacting of 1.1′-bi-2-naphthol with an excess of boric acid or trimethoxyborane in boiling toluene or benzene(using 4A molecular sieve or anhydrous zinc chloride etc. as methanol-absorbing meterial), reacted with quinine under refluxing condition in the same solvents as above for 3-5h to produce a white precipitate of 1.1′-bi-2-naphtholborane quinine derivative and a mother liquor. The mother liquor and the precipitate were treated in accordance with the procedure in the Experimental of the paper, (R)-(+)- and (S)-(-)-1.1′-bi-2-naphthol were obtained with 54-78% yield and 92-100%ee. Study on the optimum conditions for the resolution of 1.1′-bi-2-naphthol using trimethoxyborane or boric acid as borate source is proceeding.

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