J. Org. Chem. 1993, 58, 7313-7314

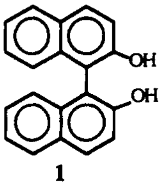
A New and Efficient Method for the Resolution of 1,1'-Binaphthalene-2,2'-diol

Jean-Michel Brunel and Gérard Buono*

Ecole Nationale Supérieure de Synthèses, de Procédés et d'Ingénierie Chimiques d'Aix-Marseille (ENSSPICAM), U.R.A. 1410, Réactivité Catalyse, Faculté des Sciences et Techniques de St Jérôme, Université Aix-Marseille III, Avenue Escadrille Normandie Niemen, 13397 Marseille Cedex 20, France

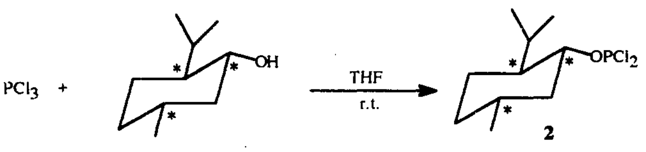
Received August 4, 1993

Chiral bidentate ligands based on the 1,1'-binaphthalyl system have achieved remarkable success in asymmetric synthesis giving high enantioselectivity in many cases (>90%).[1] This success has focused interest on a more convenient synthesis of homochiral 1,1'-binaphthalene-2,2'-diol (1), ligand and chiral building block for the preparation of atropisomeric chiral molecule possessing a C_2 axis of symmetry. Numerous efficient methods of optical resolution of 1 by enantioselective complex formation using specially prepared tartaric amide[2] or binaphthyl phosphoric acid derivatives[3,4] have been reported. However, these multistep procedures are time consuming and proceed in low overall yields. Recently, Hu[5] and De Lucchi[6] described a good method of resolution with chiral phosphoramidates as resolving agents prepared from (*S*)-(−)-α-methylbenzylamine.



1

We wish to report a new, inexpensive, practical, and efficient method for the resolution of racemic 1,1'-binaphthalene-2,2'-diol (1). Contrary to the previously mentioned methods involving tetracoordinated chiral organophosphorus compounds, we have choosen a tricoordinated compound easily prepared from phosphorus trichloride and (L)-menthol as chiral resolving agent. Equimolar amounts of PCl_3 and (1*R*,2*S*,5*R*)-(−)-menthol react in THF at room temperature to afford the corresponding menthyl phosphorodichloridite (2) in quantitative chemical yield. As shown by ^{31}P NMR, this reagent is stable for weeks under inert atmosphere, but is very sensitive to moisture: it cannot be purified and is to be used crude. Compound 2 reacts with racemic binaphthol 1, in presence of 2 equiv of NEt_3, to give a 1:1 mixture of diastereoisomers **3a** and **3b** in quantitative yield (Scheme I). Complete separation of the two diastereoisomers was achieved in a single recrystallization from diethyl ether. The diastereoisomer **3a** crystallized first and was shown to be derived from (*S*)-(−)-1,1'-binaphthalene-2,2'-diol. The diastereoisomer **3b** crystallized by concentration of the mother solution followed by cooling to 0 °C for 48 h. Compounds **3a** and **3b** react rapidly with a 30% hydrogen peroxide solution to afford the corresponding phosphates **4a** and **4b** in 95% chemical yield. Compounds **4a** and **4b** were reduced by lithium aluminum hydride to afford enantiomerically pure **1a** and **1b** in 81 and 85% yield, respectively (Scheme II).



The present work offers a simpler resolution method of 1,1'-binaphthalene-2,2'-diol (1). This four-step method allows the large-scale synthesis of both enantiomers of 1 with high enantiomeric purity with overall chemical yields of 74%. Reagent 2 offers several advantages: 2 is cheap and easily prepared from two industrial products PCl_3 and (L)-menthol; due to the inherent reactivity of tricoordinated dihalogeno phosphorus compounds, reaction with 1 is fast. The intermediate phosphites **3a** and **3b** may find applications in organophosphorus chemistry in the synthesis of homochiral P(IV) and P(V) compounds, and their use as ligands in enantioselective catalysis is presently investigated.

Experimental Section

Tetrahydrofuran (THF) was distilled immediately before use from sodium benzophenone ketyl. Specific rotations were measured on a Perkin Elmer 241MC polarimeter. The melting points were determined on a Mel-Temp capillary melting point apparatus and are uncorrected. ^{1}H NMR (100.00 MHz) data were recorded with a AC 100 Bruker spectrometer using TMS as internal standard, ^{31}P NMR (40.54 MHz) data were recorded using 85% H_3PO_4 as external standard.

Preparation of Menthyl Phosphorodichloridite (2). A solution of phosphorus trichloride (5.0 g, 38 mmol) in dry THF (10 mL) was added dropwise under N_2 atmosphere to a solution of (1*R*,2*S*,5*R*)-(−)-menthol (6.0 g, 38 mmol) in THF (10 mL). The mixture was stirred at room temperature for 1 h. Compound 2 cannot be isolated in pure form and was used in solution without further purification, ^{31}P NMR 175.1 ppm ($CDCl_3$) (single signal).

Preparation of Diasteromerically Pure Phosphites 3a and 3b. In a two-necked round-bottom flask, triethylamine (11 mL, 78 mmol) was slowly added to a stirred THF solution of 2 (20 mL, 38 mmol), cooled in an ice bath. After the addition was complete, the mixture was stirred at room temperature for 15 min and racemic 1,1'-binaphthalene-2,2'-diol (1) (11.0 g, 38 mmol) was added as solid. The solution was stirred for a few minutes and the solvent was removed in vacuo to afford 18.0 g of a pale yellow oil. Pure **3a** was obtained by crystallization from diethyl ether (15 mL) as crystalline plates (8.5 g, 96% yield): mp 178–180 °C; $[\alpha]^{20}_D$ +288.3° (c = 1, CH_2Cl_2); ^{31}P NMR 149.88 ppm ($CDCl_3$) (single signal); ^{1}H NMR ($CDCl_3$) δ 0.76 (d, 6H), 0.92 (d, 3H), 0.93-1.70 (m, 10H), 7.25–7.55 (m, 8H), 7.87–8.01 (m, 4H). Anal. Calcd for

---

(1) For pertinent references on C_2 symmetry and asymmetric induction see: (a) Whitesell, J. K. *Chem. Rev.* 1989, *89*, 1581–1590. (b) Narasaka, K. *Synthesis* 1991, 1. (c) Cram, D. J.; Sogah, G. D. Y. *J. Chem. Soc, Chem. Commun.* 1981, 605. (d) Apsimon, J. W.; Collier, T. L. *Tetrahedron* 1986, *42*, 5157. (e) Noyori, R.; Kitamura, M. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer Verlag; Berlin, 1989, 115. (f) Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* 1991, *91*, 1179. (g) Kagan, H. B.; Riant O. *Chem. Rev.* 1992, *92*, 1007–1019.

(2) Toda, F.; Tanaka, K. *J. Org. Chem.* 1988, *53*, 3607.

(3) Jacques, J.; Fouguey, C. *Org. Synth.* 1988, *67*, 1–12.

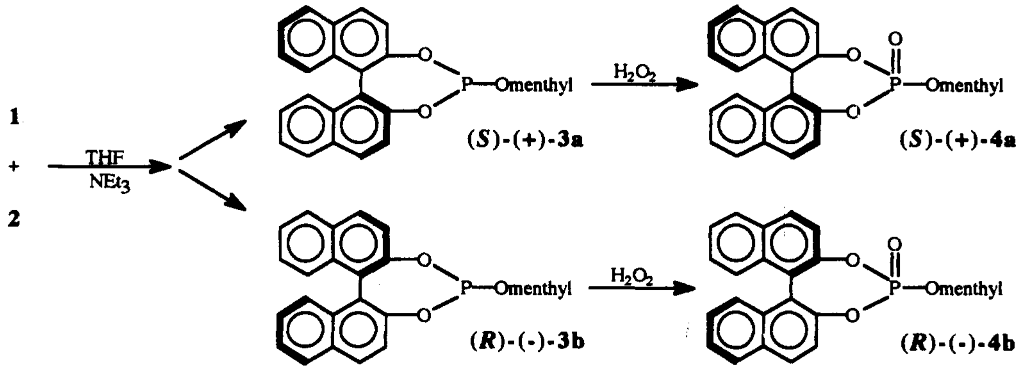
(4) Truesdale, L. K. *Org. Synth.* 1988, *67*, 13–19.

(5) Gong, B. Q.; Chen, W. Y.; Hu, B. F. *J. Org. Chem.* 1991, *56*, 423–425.

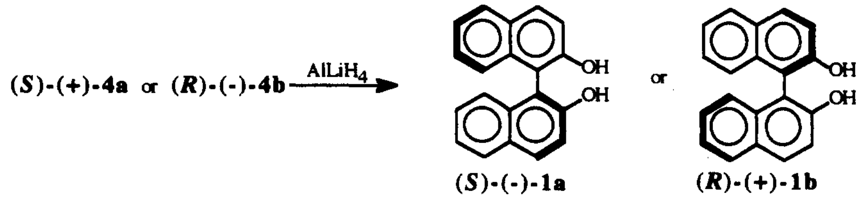
(6) Fabbri, D.; Delogu, G.; De Lucchi, O. *J. Org. Chem.* 1993, *58*, 1748–1750.

0022-3263/93/1958-7313$04.00/0

Scheme I



Scheme II



$C_{30}H_{31}O_3P$: C, 76.59; H, 6.59; O, 10.21; P, 6.59. Found: C, 76.30; H, 6.45; O, 10.80; P, 6.45.

The filtrate was concentrated under reduced pressure to half its volume and then refluxed to dissolve the solid. After 48 h at 0 °C, the enantiomerically pure diastereoisomer **3b** crystallized to afford 8.1 g of white crystals (91% yield): mp 185–187 °C; $[\alpha]^{20}_D$ −288.3° (c = 1, CH_2Cl_2); ^{31}P NMR 153.91 ppm ($CDCl_3$) (single signal); ^1H NMR ($CDCl_3$) δ 0.76 (d, 6H), 0.92 (d, 3H), 0.93-1.70 (m, 10H), 7.25–7.55 (m, 8H), 7.87–8.01 (m, 4H). Anal. Calcd for $C_{30}H_{31}O_3P$: C, 76.59; H, 6.59; O, 10.21; P, 6.59. Found: C, 76.23; H, 6.47; O, 10.92; P, 6.42.

Preparation of Diasteromerically Pure Phosphates 4a and 4b. In a two-neck round-bottomed flask, diasteromerically pure **3a** (8.5 g, 18 mmol) was stirred with a 30% hydrogen peroxide solution (20 mL) for 1 h at room temperature. Extraction with diethyl ether (3 × 10 mL), drying over sodium sulfate, and removal of the solvent gave **4a** as a white crystalline solid (8.3 g, 95 % yield): mp 175–176 °C; $[\alpha]^{20}_D$ +181.2° (c = 1, CH_2Cl_2); ^{31}P NMR −1.03 ppm ($CDCl_3$) (single signal); ^1H NMR ($CDCl_3$) δ 0.69–1.09 (m, 9H), 1.12 (m, 8H), 2.22–2.36 (m, 2H), 7.18–7.65 (m, 8H), 7.89–8.06 (m, 4H). Anal. Calcd for $C_{30}H_{31}O_4P$: C, 74.07; H, 6.37; O, 13.16; P, 6.37. Found: C, 74.23; H, 6.35; O, 13.12; P, 6.32.

Diastereomerically pure **4b** was obtained similarly. Colorless crystals 8.1 g (94%): mp 176–177 °C; $[\alpha]^{20}_D$ −181.2° (c = 1, CH_2Cl_2); ^{31}P NMR 3.86 ppm ($CDCl_3$) (single signal); ^1H NMR ($CDCl_3$) δ 0.69–1.09 (m, 9H), 1.12 (m, 8H), 2.22–2.36 (m, 2H), 7.18–7.65 (m, 8H), 7.89–8.06 (m, 4H). Anal. Calcd for $C_{30}H_{31}O_4P$: C, 74.07; H, 6.37; O, 13.16; P, 6.37. Found: C, 74.12; H, 6.39; O, 13.21; P, 6.30.

Reduction of 4a and 4b. As described in the literature,[7] diasteromerically pure **4a** (8.3 g, 17 mmol) in dry THF (20 mL) was cooled at 0 °C under nitrogen. Lithium aluminum hydride (3.2 g, 85 mmol) was added in portions under vigorous magnetic stirring. After 2 h, water (5 mL) and dilute NaOH solution were cautiously added until the solution was slightly basic. The solution was then extracted with CH_2Cl_2 (2 × 15 mL) and dried over Na_2SO_4. Removal of the solvent gave the enantiomerically pure (*S*)-(−)-1,1′-binaphthalene-2,2′-diol as a colorless crystalline solid (3.9 g) in 81% chemical yield: mp 208–209 °C; $[\alpha]^{20}_D$ −34.3° (c = 1, THF). Analogously, enantiomerically pure (*R*)-(+)-1,1′-binaphthalene-2,2′-diol was obtained from **4b** as a colorless crystalline solid (4.1 g) in a 85% chemical yield: mp 208–209 °C; $[\alpha]^{20}_D$ +34.3° (c = 1, THF).

Determination of Enantiomeric Purity. The enantiomeric purity of the resolved 1,1′-binaphthalene-2,2′-diol (1) was assessed by ^{31}P NMR nonequivalence of diastereomeric salts.[8]

---

[7] Kyba, E. P.; Gokel, G. W.; de Jong, F.; Koga, K.; Sousa, L. R.; Siegel, M. G.; Kaplan, L. G.; Dotsevi, G.; Sogah, Y.; Cram, D. J. *J. Org. Chem.* **1977**, *42*, 4173.

[8] Mikolajezk, M.; Omelaneznk, J.; Leitloff, M.; Drabowicz, J.; Fjchart, A.; Jurczak, J. *J. Am. Chem. Soc.* **1978**, *100*, 7003.