Diastereoselective Synthesis of 1,1′-Binaphthyl-2,2′-diol

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In the past few years, much attention has been focused on the chirality recognition properties of chiral crown ether hosts containing the binaphthyl unit,[1] and the application of chiral 1,1′-binaphthyl-2,2′-diol (**1**) in asymmetric synthesis has proven fruitful.[2] Consequently, the preparation of optically active binaphthol is of current interest. Previous synthetic approaches have been reviewed in our earlier paper.[3] Therein an efficient method entailing resolution of cyclic phosphoramidate was reported. During the synthesis of (*S*,*R*)-1,1′-binaphthyl-2,2′-diyl *N*-(*S*)-(α-methylbenzyl)phosphoramidate, we noted that the rate of formation of one enantiomer is greater than that of the other. In light of this observation, we have designed a new method for obtaining chiral 1,1′-binaphthyl-2,2′-diol by the diastereoselective reactions of 1,1′-binaphthyl-2,2′-diylphosphoryl chloride (**2**) with chiral amines (**3**) (Scheme 1). The diastereomeric excesses obtained in the formation of **4a–c** by the reaction of racemic **2** and (*S*)-α-phenylethylamine (**3a**), (*S*)-1-(4-chlorophenyl)-2-methylpropylamine (**3b**), or (*S*)-1-(2-methoxymethylphenyl)-2-methylpropylamine (**3c**) at different temperatures are presented in Table 1.

Results and Discussion

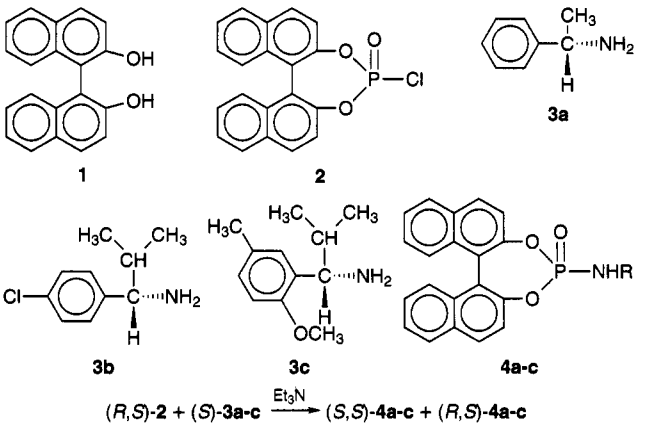
The tabulated results reveal that the diastereoselectivity of the reaction decreases with increasing reaction temperature and with increasing steric hindrance by the substituents on the carbon atom α to the nitrogen atom and on the orthoposition of the benzene ring of the chiral amine. This method of synthesis of chiral 1,1′-binaphthyl-2,2′-diol is efficient and convenient. The overall yield of optically pure **1** from racemic **1** was 73%. The chiral amine used in the reaction is only half the amount of the phosphoryl chloride and is easily recovered in 90% yield with retention of its original enantiomeric purity.

Table 1. Results of Diastereoselective Reaction of 2 with 3a–c

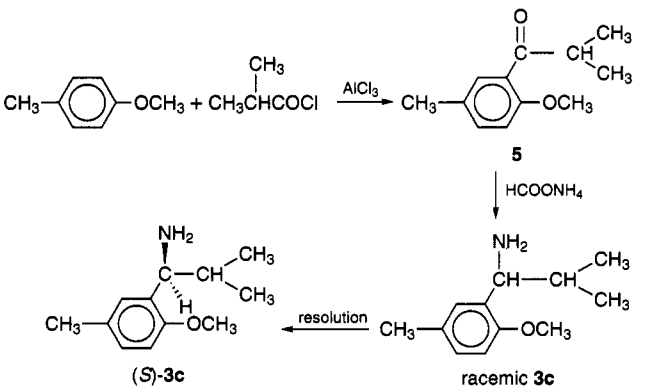
amine	temp (°C)	deg[b] (%)
3a	0	27
	10	24
	20	20
3b	0	38
	10	31
	20	24
3c	0	82
	10	68
	20	33

[a] The reactions were carried out for 12 h at 20 °C, 24 h at 10 °C and 48 h at 0 °C. [b] The values of % deg were determined by ^{31}P NMR.

Scheme 1



Scheme 2



Experimental Section

1. Preparation of Optically Active Amines. The (*S*)-α-phenylethylamine (**3a**) is a commercial product, (*S*)-1-(4-chlorophenyl-)-2-methylpropylamine (**3b**) was prepared according to a known procedure,[4] and (*S*)-1-(2-methoxy-5-methylphenyl)-propylamine (**3c**) was prepared by the following procedure (Scheme 2).

1.1. Preparation of 1-(2-Methoxy-5-methylphenyl)-2-methyl-1-propanone (5). A solution of 39 g (0.32 mol) of 4-methylanisole in 50 mL of dichloroethane was added to 45.5 g (0.34 mol) of aluminum trichloride suspended in 200 mL of dichloroethane, and then 36.5 g (0.34 mol) of isobutyroyl chloride in 50 mL of dichloromethane was added with stirring (the reaction temperature was kept under 10 °C during the addition). After the addition, the mixture was stirred for 3 h at 30–35 °C. The reaction mixture was hydrolyzed with concentrated hydrochloric acid and then extracted twice with ether (100 mL/time). The combined extracts was dried over anhydrous sodium sulfate and distilled under reduced pressure, giving a colorless liquid (49.5 g, yield 85.9%): bp 142–145 °C/1.3 × 10^3 Pa; ^1H NMR ($CDCl_3$, TMS) 6.78–7.03 (m, 3H, Ar–H), 3.48 (s, 3H, OCH_3), 3.32–3.64 (m, 1H, CH), 2.24 (s, 3H, $ArCH_3$), 1.10–1.18 (d, 6H, CH_3).

1.2. Preparation of 1-(2-Methoxy-5-methylphenyl)-2-methylpropylamine (racemic 3c). A solution of 19.2 g of **5** and 25.8 g of ammonium formate was heated to 150 °C, the resulting water was distilled off at the same temperature for 3 h, and then the mixture was heated to 180 °C and maintained for 5 h. After the mixture was cooled to room temperature, 80 mL of concentrated hydrochloric acid was added, and the mixture was refluxed for 3 h and then cooled. The reaction mixture was washed with benzene, and the aqueous layer was made alkaline with 40% sodium hydroxide and extracted three times with benzene. The combined extracts were dried over anhydrous potassium carbonate and distilled under reduced pressure, giving a colorless liquid (10 g, yield 51.8%): bp 153–156 °C/1.3 × 10^3 Pa; ^1H NMR ($CDCl_3$, TMS) 6.60–6.96 (m, 3H,

(1) 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.
(2) Miyashita, A.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932.
(3) Gong, B.-q.; Chen, W.-y.; Hu, B.-f. *J. Org. Chem.* **1991**, *56*, 423.
(4) Wang, M., Hu, B.-f. *Chem. Abstr.* **1990**, *112*, 198336m.

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ArH), 3.66–3.80 (d, 1H, NCH), 3.60 (s, 3H, OCH_3), 2.20 (s, 3H, $ArCH_3$), 1.80–2.04 (m, 3H, CH and NH_2), 0.62–0.95 (dd, 6H, CH_3).

1.3. Resolution of Racemic 3c. A racemic mixture of **3c** (19.3 g, 0.1 mol) and D-(−)-tartaric acid (15 g, 0.1 mol) in 60% ethanol (1200 mL) was refluxed until all the solid was dissolved and then cooled to room temperature and allowed to stand for 1 day at room temperature (about 13 °C). The resulting precipitate was filtered off and recrystallized from 60% ethanol twice, and the optically pure amine was liberated by treating the crystal with 10% sodium hydroxide, extracting with ether, and distilling, giving a colorless liquid (6.86 g 71% yield): $[\alpha]^{20}_D$ = −5.62 (neat).

1.4. Determination of Enantiomeric Purity of 3c. The enantiomeric purity of **3c** was assessed by ^{31}P NMR nonequivalence of the two diastereomers, (*S*)-1,1′-binaphthyl-2,2′-diyl *N*-(*S*)-phosphoramidate ((*S*,*S*)-**4c**) and (*S*)-1,1′-binaphthyl-2,2′-diyl *N*-(*R*)-phosphoramidate ((*S*,*R*)-**4c**). The enantiomerically pure **2** was prepared according to the known procedure[3] via (*S*)-1,1′-binaphthyl-2,2′-diol ($[\alpha]^{20}_D$ = 35.2, *c* = 1, THF, 100% enantiomeric purity) and phosphorus oxychloride and then reacted with **3c** to give quantitatively the phosphoramidate with a single ^{31}P NMR signal only (13.05 ppm), indicating the 100% enantiopurity of **3c**.

2. Reactions of 1,1′-Binaphthyl-2,2′-diylphosphoryl Chloride (2) with Chiral Amines 3a–c. A mixture of chiral amine (5 mmol) and triethylamine (5.2 mmol) in 10 mL of dried dichloromethane was added dropwise to a solution of 1,1′-binaphthyl-2,2′-diylphosphoryl chloride [from **1** (10 mmol)] in 20 mL of dried dichloromethane at temperature *T* and then stirred for several hours. The ^{31}P NMR data showed the the presence of two diastereomeric phosphoramidates and unreacted **2** [12.7 ppm ((*S*,*S*)-**4a**), 12.68 ppm ((*R*,*S*)-**4a**), and 10.43 ppm (**2**) for **3a**; 12.58 ppm ((*S*,*S*)-**4b**), 13.39 ppm ((*R*,*S*)-**4b**) and 10.43 ppm (**2**) for **3b**; 13.05 ppm ((*S*,*S*)-**4c**), 14.60 ppm ((*R*,*S*)-**4c**), and 10.43 ppm (**2**) for **3c**]. The % de value of the products were determined by ^{31}P NMR spectra as shown in Table 1.

3. Separation of (*S*,*S*)-4c, (*R*,*S*)-4c, and 2. The reaction mixture of **2** and **3c** was washed with cold water and dried over anhydrous magnesium sulfate. The solution was chromatographed by the vacuum liquid chromatographic method[5] (silica gel, 300 mesh, 1:10) with anhydrous ether as eluent. A mixture of (*S*,*S*)-**4c** and (*R*,*S*)-**4c** was obtained (2.1 g, 93% yield). Another fraction contained **2** (1.7 g). The (*S*,*S*)-**4c** was obtained by recrystallization from anhydrous ethanol, giving 1.8 g of crystalline product (^{31}P NMR, 13.05 ppm), mp 264–265 °C, 86% yield.

4. Preparation of (*S*)-1 and (*R*)-1. (*S*)-**1** was obtained by reduction of (*S*,*S*)-**C** according to the known procedure,[1] yielding a colorless crystalline solid (1.05 g, mp 206–207 °C, $[\alpha]^{20}_D$ = −35.2, *c* = 1.0, THF, 92% yield). (*R*)-**1** was obtained by reduction of the recovered **2** with LAH, and the crude crystalline product was recrystallized from benzene to give a colorless crystalline solid (1.04 g, mp 206–207 °C, $[\alpha]^{20}_D$ = +35.2, *c* = 1.0, THF, 73% yield). The chiral amine **3c** was recovered in 90% yield, $[\alpha]^{20}_D$ = −5.62 (neat).

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(5) Targett, N. M.; Kijcoyne, J. P.; Green, B. *J. Org. Chem.* **1979**, *44*, 4962.