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A convenient resolution method for 1,1′-bi-2-naphthol and 4,4′-dibromo-1,1′-spirobiindane-7,7′-diol with menthyl chloroformate in the presence of TBAB

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Abstract—A convenient resolution method for 1,1′-bi-2-naphthol and 4,4′-dibromo-1,1′-spirobiindane-7,7′-diol has been developed with crude (−)-menthyl chloroformate as the resolution reagent in the presence of tetrabutylammonium bromide acting as a phase transfer catalyst in an aqueous $NaOH/CH_2Cl_2$ two phase solution. The deprotection of the hydroxy group was carried out via an aqueous KOH/EtOH solution. Both enantiomers of 1,1′-bi-2-naphthol and 4,4′-dibromo-1,1′-spirobiindane-7,7′-diol were obtained in high yields. Both ee's of (*S*)-(+) and (*R*)-(−)-4,4′-dibromo-1,1′-spirobiindane-7,7′-diol were above 99%. Most of the (−)-menthol could be easily recovered in a deprotection procedure and thus be reused for the formation of (−)-menthyl chloroformate without further purification.

1. Introduction

Enantiopure 1,1′-bi-2-naphthol (BINOL) is one of the most important C_2 symmetric chiral compounds,[1] and occupies a prominent position in catalytic asymmetric synthesis.[2] It is widely used for the resolution of racemic compounds[3] and as a chiral source.[4] Recently, a new C_2 symmetrical diol, 1,1′-spirobiindane-7,7′-diol (SPINOL), has proven to be an excellent framework for chiral ligands.[5] Several methods have successfully been developed for the resolution of BINOL and other diols, such as the classical crystallization of diastereomeric derivatives,[6] enantioselective formation of inclusion crystals with chiral host molecules,[7] and enzymatic hydrolysis of esters.[8] In 1995, Lucchi and co-workers reported a resolution method for BINOL, based on the separation of a pair of diastereomers, which were derived from BINOL and (−)-menthyl chloroformate under anhydrous conditions, then deprotection of the diastereomers with $LiAlH_4$ to afford enantiopure BINOL.[9] This method has also been used for the resolution of other racemic compounds, such as binaphthyl, biphenyl diol systems.[9,10] In our efforts toward optimizing the electronic and steric properties of the chiral ligands, we were particularly interested in this method for the resolution of 4,4′-dibromo-1,1′-spirobiindane-7,7′-diol (DBSPINOL) and BINOL because of the abundance of nonracemic menthol. We found that the reaction of BINOL or DBSPINOL with crude (−)-menthyl chloroformate in aqueous $NaOH/CH_2Cl_2$ solution in the presence of tetrabutylammonium bromide (TBAB) was very fast (the two diastereomers could be easily separated by recrystallization) and that the deprotection of the hydroxy group of the diastereomers could be performed via an aqueous KOH/EtOH solution instead of with $LiAlH_4$. Herein, we report a convenient procedure for the resolution of BINOL and DBSPINOL.

2. Results and discussion

Although (−)-menthyl chloroformate is commercially available, it can be conveniently prepared with commercially available (−)-menthol and triphosgene. In our experiment, we found that the purity of (−)-menthyl chloroformate had no effect on the formation of diastereomers with BINOL. After workup, crude (−)-menthyl chloroformate could be directly used for the next step. It was found that the formation of diastereomers could be greatly accelerated in the presence of TBAB in aqueous $NaOH/CH_2Cl_2$ (reaction 1 in Scheme 1). Compared to Lucchi's procedure,[9] the formation of

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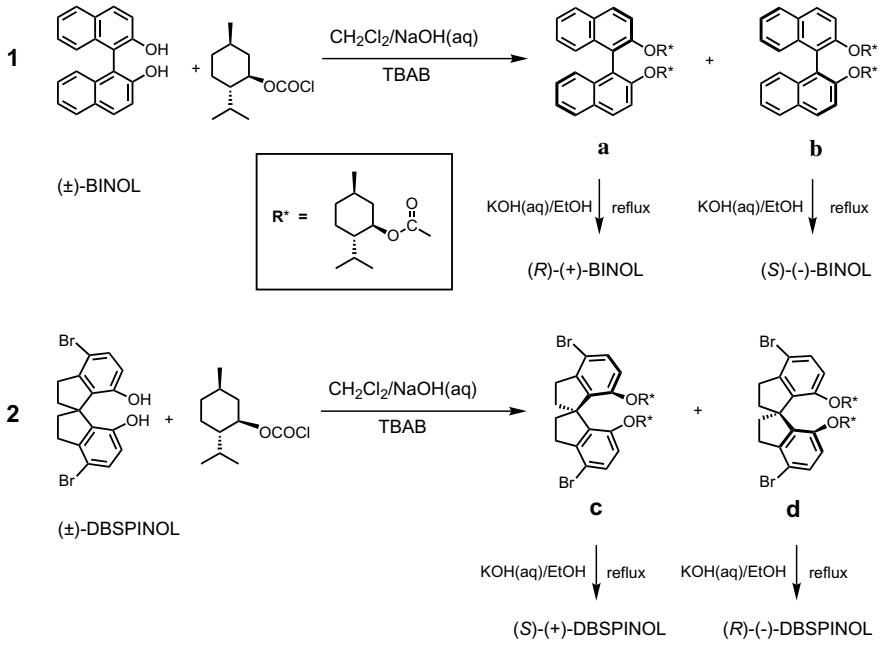

Scheme 1.

diastereomers in our experiment was quicker. We tried to optimize the reaction in other solvents, such as toluene, benzene, and *n*-hexane; however, the reaction did not go to completion under similar conditions as evidenced by TLC. We then increased the reaction temperature: the reaction proved to be faster at high temperatures but at the same time produced more impurities as detected by TLC. The optimal reaction conditions for the formation of the diastereomers was in aqueous $NaOH/CH_2Cl_2$ with 0.2 mol equiv of TBAB and 3 mol equiv of (−)-menthyl chloroformate at 0 °C. After phase separation and removal of solvent, the crude mixture of the diastereomers was obtained in high yield. We then tried to purify the crude diastereomers via recrystallization in *n*-hexane. Successfully, one of the diastereomers **a** precipitated from this recrystallization procedure in high yield. This allowed us to avoid column separation of diastereomers. The other zdiastereomers **b** in the mother liquid was then separated through a short silica-gel column with *n*-hexane/EtOAc as the eluent, to give the diastereomer **b**. After carefully optimizing the separation procedure, diastereomer **a** was obtained in 90% yield and diastereomer **b** in 86% yield.

Deprotection to form homochiral BINOL was usually accomplished with $LiAlH_4$ as reported in the literature.[9,10a–e] Very recently, our colleagues, Hu and co-workers reported a method using KOH/EtOH to perform deacetylation with no racemization being observed in the biphenyl backbone.[11] We also found that deprotection of the hydroxy group of diastereomer **a** can be performed at reflux in aqueous KOH/EtOH solution instead of $LiAlH_4$. Parallel experiments showed that the quantity of water in the system was very important for a successful hydrolysis of the diastereomer and excess KOH was necessary to complete the reaction. The deprotection of the diastereomers was carried out smoothly at reflux in 1:4 (v/v) aqueous EtOH with more than 4 equiv of KOH for 1 h. After the hydrolysis was completed, most of the EtOH was removed by distillation under reduced pressure. The residue was extracted with *n*-hexane to remove (−)-menthol. The aqueous layer was then acidified with HCl. The resulting precipitate was extracted with diethyl ether. The diethyl ether layer was dried over anhydrous Na_2SO_4, filtered, and the solvent evaporated to afford (*R*)-BINOL in 92% yield with >99% ee. Using a similar procedure of treatment of diastereomer **b**, (*S*)-BINOL was obtained in 96% yield with 91% ee. These results were close to the procedure with $LiAlH_4$.[9] Moreover, (−)-menthol in *n*-hexane extraction, which had been dried over Na_2SO_4, can be recovered in high yield after evaporation of solvent. The recovered (−)-menthol can be used directly to prepare (−)-menthyl chloroformate. Therefore, this method provides the possibility of a large-scale resolution of BINOL. To the best of our knowledge, no such liquid/liquid phase-transfer catalytic reaction has been shown in the resolution of the BINOL using related ammonium salts as catalysts.

In fact, our studies on the resolution method were applied to the recently developed chiral backbone DBSPINOL, which was derived from chiral SPINOL.[5e] Because chiral SPINOL was proven to provide an excellent framework for chiral ligands,[5] we were interested in developing new chiral ligands by optimizing the electronic and steric property of SPINOL derivatives for asymmetric catalysis with DBSPINOL as the chiral backbone. When enough racemic DBSPINOL was prepared according to the literature procedure,[12] we tried to resolve DBSPINOL (reaction 2 in Scheme 1) with the above improved resolution method for BINOL. Using this similar procedure, (*S*)-(+)-DBSPINOL in 98% yield with >99% ee and (*R*)-(−)-DBSPINOL in 98% yield with >92% ee were successfully obtained.[13] A simple recrystallization of the latter isomer from

n-hexane afforded enantiopure (*R*)-(−)-DBSPINOL in 74% yield with >99% ee. Moreover, (−)-menthol in *n*-hexane extraction was recovered in high yield after evaporation of solvent. The recovered (−)-menthol can then be directly reused. This resolution procedure is the only method so far reported for DBSPINOL.

3. Conclusion

In conclusion, we have developed a convenient resolution method for BINOL with crude (−)-menthyl chloroformate in the presence of TBAB in aqueous NaOH/CH_2Cl_2 solution. The deprotection of the hydroxy group of the diastereomers can be smoothly performed at reflux in aqueous KOH/EtOH solution. Racemic DBSPINOL was successfully resolved with the above method for resolution BINOL to afford enantiopure (*S*)-(+)-DBSPINOL and (*R*)-(−)-DBSPINOL in high yield. Moreover, (−)-menthol in the deprotection procedure can easily be recovered and reused. This improved method provides the possibility of a large-scale resolution of racemic diols. Further studies concerning other phase-transfer catalyst and using chiral DBSPINOL as the backbone for asymmetric chiral ligand are currently underway.

4. Experimental

4.1. General procedures

Melting points were measured on a Yazawa micro-melting point apparatus and are uncorrected. Optical rotations were measured on a HORIBA SEPA-200 highly sensitive polarimeter. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz). Elemental analyses were performed using an Elementar vario EL instrument. High resolution mass spectra (HRMS) were recorded on a Mariner-TOF 5303 (Applied Biosystems, USA). Enantiomeric excess values were analyzed by HPLC on a Chiralcel AD column (4.6 mm × 250 mm) at room temperature with *n*-hexane/*i*-propanol (4:1) as eluent. All reagents were of commercial quality and used as purchased. Flash chromatography was carried out with silica gel 230–400 mesh eluting with appropriate solution in the stated v/v proportions. Analytical thin-layer chromatography (TLC) was performed with 0.25 mm thick silica-gel plates. (−)-Menthol, boron tribromide, and triphosgene were purchased from Aldrich Chem. Co. Dichloromethane was distilled from CaH_2 and toluene was distilled from sodium and benzophenone for the preparation of menthyl chloroformate and DBSPINOL.

4.2. Preparation of menthyl chloroformate

Triphosgene (3.16 g, 11 mmol) and toluene (60 mL) were added into a 100 mL three-necked round-bottom flask fitted with addition funnel and argon inlet. The solution was cooled to −10 °C. (−)-Menthol (5.00 g, 32 mmol) was then added into the flask. After it completely dissolved, pyridine (4.13 g, 32 mmol) was added dropwise over a period of 30 min. After stirring for 18 h at room temperature, the mixture was filtered off, and the filtrate washed with water (2 × 60 mL). The organic layer was dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded the crude (−)-menthyl chloroformate, which could be used for the next step without further purification. The content of menthyl chloroformate was determined by titration.[14]

4.3. Resolution of BINOL

An aqueous solution of racemic BINOL[15] (1.0 g, 3.49 mmol) and NaOH (0.6 g, 15.0 mmol) in water was made up to 10 mL. To it 0.2 g (0.62 mmol) of tetrabutylammonium bromide dissolved in 10 mL of chloroform was added. With rapid stirring, (−)-menthyl chloroformate 2.84 g (10.5 mmol, 80.9% w/w) was added. After stirring at room temperature for 5 min, the two phases were separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic phases were dried over Na_2SO_4 and evaporation of the solvent under reduced pressure afforded a crude product, which was recrystallized from *n*-hexane to give the diastereomer of (*R*)-BINOL **a** 1.03 g, 90% yield. Mp 195–198 °C; $[\alpha]_D^{25} = -134.9$ (*c* 1.1, $CHCl_3$). ^1H NMR δ 0.17 (d, $J = 6.8$ Hz, 6H), 0.53 (d, $J = 6.8$ Hz, 6H), 0.68–1.21 (series of m, 20H), 1.53 (d, 4H), 1.75 (t, 2H), 4.21 (td, 4.0 Hz, 2H), 7.25 (m, 4H), 7.43 (t, $J = 7.2$ Hz, 2H), 7.49 (d, $J = 8.8$ Hz, 2H), 7.90 (d, $J = 8.8$ Hz, 2H), 7.99 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR ($CDCl_3$) 16.08, 20.50, 22.14, 23.54, 26.01, 31.47, 34.14, 40.54, 46.86, 78.98, 121.51, 123.47, 125.80, 126.44, 126.84, 127.99, 129.89, 131.79, 133.21, 146.96, 152.91. IR (KBr pellet, cm^{-1}): 2958, 2935, 1756, 1223, 1251, 962.

The solution was evaporated to dryness, and the residue chromatographed through a short column of silica gel with *n*-hexane/EtOAc as eluent, to afford the diastereomer of (*S*)-BINOL **b**, 0.98 g, 86% yield. Mp 60–65 °C; $[\alpha]_D^{25} = -19.1$ (*c* 0.95, $CHCl_3$). ^1H NMR δ 0.64 (d, $J = 6.8$ Hz, 6H), 0.77 (d, $J = 6.8$ Hz, 12H), 0.45–1.21 (series of m, 14H), 1.53 (d, 4H), 4.20 (td, 4.0 Hz, 2H), 7.29 (d, $J = 4$ Hz, 4H), 7.43 (m, $J = 4$ Hz, 2H), 7.49 (d, 2H), 7.89 (d, 2H), 7.98 (d, 2H). ^{13}C NMR ($CDCl_3$) 16.44, 20.79, 22.00, 23.40, 26.05, 31.23, 34.12, 39.74, 46.56, 79.07, 121.54, 123.49, 125.80, 126.46, 126.82, 127.98, 129.91, 131.77, 133.22, 147.08, 152.71. IR (KBr pellet, cm^{-1}): 2958, 2935, 1756, 1223, 1251, 962.

To a solution of KOH (8.7 g, 155 mmol) in 4:1 ethanol/degassed water (180 mL), 1.03 g (1.58 mmol) of **a** was added and the mixture refluxed for 1 h after which none of **a** remained (TLC). The mixture was then cooled and rotoevaporated. To it was added 20 mL of water and extracted with *n*-hexane (2 × 30 mL). Simple workup gave enantiomerically pure (−)-menthol (0.48 g, 97% recovery yield). The aqueous layer was separated and acidified with concentrated HCl resulting in a white precipitate that was extracted with diethyl ether

(2×30 mL). The ether layer was dried over Na_2SO_4, filtered off, and the solvent evaporated in vacuo to give (*R*)-(+)-BINOL 0.42 g, 92% yield. Mp 210–211 °C; $[\alpha]_D^{25} = +34.6$ (*c* 1.0, THF) with >99% ee. Similar treatment of **b** (0.858 g, 1.32 mmol) gave (*S*)-(−)-BINOL 0.36 g, 96% yield. Mp 209–210 °C; $[\alpha]_D^{25} = -30.9$ (*c* 1.0, THF) of 91% ee and enantiomerically pure (−)-menthol (0.40 g, 97% recovery yield).

4.4. Preparation of DBSPINOL[12]

A solution of 4,4′-dibromo-7,7′-dimethoxy-1,1′-spirobiindane[16] (1.35 g, 2.71 mmol) in 15 mL of CH_2Cl_2 in a flame-dried flask, under nitrogen, was cooled to −78 °C, treated with 1 M BBr_3 in CH_2Cl_2 (9.0 mL, 2.9 equiv), and allowed to warm to rt overnight. The reaction mixture was diluted with CH_2Cl_2 and washed with water until the washings had a neutral reaction. The solution was dried over Na_2SO_4, evaporated, and the residue recrystallized from *n*-hexane to give 1.20 g of the racemic DBSPINOL (95% yield). Mp 148–149 °C. ^{1}H NMR δ 2.24 (m, 2H), 3.00 (m, 4H), 4.63 (S, 2H), 6.55 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR ($CDCl_3$) 33.0, 37.0, 60.6, 111.1, 116.7, 132.4, 132.6, 145.5, 152.0. HRMS calcd for $C_{17}H_{14}Br_2O_2$ $(M-1)^-$: 406.92768; found: 406.92779.

4.5. Resolution of DBSPINOL

A solution of racemic DBSPINOL (1.388 g, 3.38 mmol) and NaOH (0.6 g, 15 mmol) in water was made up to 10 mL. To it, 0.50 g (1.56 mmol) of tetrabutylammonium bromide dissolved in 10 mL of chloroform were added. With rapid stirring, (−)-menthyl chloroformate 3.16 g (10.1 mmol, 70.1% w/w) was added. After the solution was stirred at room temperature for 7 min, the two phases were separated. The aqueous phase was extracted two times with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and evaporation of the solvent under reduced pressure afforded a crude product, which was recrystallized from *n*-hexane to give the diastereomer of (*S*)-(+)-DBSPINOL **c**,[13] 1.175 g, 89% yield. Mp 220–222 °C; $[\alpha]_D^{25} = -91.0$ (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 0.71 (d, 6H), 0.81–0.98 (m, 18H), 1.30–1.40 (m, 4H), 1.63 (d, 6H), 1.85 (d, 2H), 2.24–2.28 (m, 4H), 2.97–3.07 (m, 4H), 4.36 (d, 2H), 6.87 (d, $J = 8.8$, 2H), 7.35 (d, $J = 8.8$, 2H). ^{13}C NMR ($CDCl_3$) 16.0, 20.6, 21.9, 23.2, 26.0, 31.2, 32.8, 34.0, 38.4, 40.1, 46.6, 61.6, 61.8, 116.4, 122.5, 131.2, 140.4, 145.4, 146.7, 152.6. Anal. Calcd for $C_{39}H_{50}Br_2O_6$: C, 60.47; H, 6.51. Found: C, 60.35; H, 6.53.

The solution was rotoevaporated to dryness, and the residue chromatographed through a short column of silica gel with *n*-hexane/EtOAc to afford the diastereomer of (*R*)-(−)-DBSPINOL **d**, 1.171 g, 89% yield. Mp 49–53 °C. ^{1}H NMR ($CDCl_3$) δ 0.68 (d, 6H), 0.81–0.98 (m, 18H), 1.24 (t, 2H), 1.41 (s, 2H), 1.64 (d, 6H), 1.88 (d, 2H), 2.25–2.34 (m, 4H), 2.99–3.06 (m, 4H), 4.32 (d, 2H), 6.92 (d, $J = 8.4$, 2H), 7.35 (d, $J = 8.4$, 2H). ^{13}C NMR ($CDCl_3$) 16.4, 21.0, 22.3, 23.3, 25.9, 31.5, 33.0, 34.2, 37.9, 40.5, 46.7, 61.8, 79.2, 116.3, 122.1, 131.2, 140.2, 145.4, 146.8, 152.3. Anal. Calcd for $C_{39}H_{50}Br_2O_6$: C, 60.47; H, 6.51. Found: C, 60.48; H, 6.66.

To solution of KOH (8.7 g, 155 mmol) in 10% degassed water/ethanol (180 mL) 1.0 g of **c** (1.3 mmol) was added and the mixture refluxed for 1 h after which none of **c** remained (TLC). The mixture then cooled and rotoevaporated. To it was added 20 mL of water and extracted with *n*-hexane (2×30 mL). Simple workup gave enantiomerically pure (−)-menthol (0.40 g, 99% recovery yield). The aqueous layer was separated and acidified with 6 M HCl, producing a white precipitate that was extracted with diethyl ether (2×30 mL). The ether layer was dried over Na_2SO_4, filtered off and the solvent evaporated in vacuo to give (*S*)-(+)-DBSPINOL 0.52 g, 98% yield. Mp 161–162 °C; $[\alpha]_D^{18} = +93.9$ (*c* 0.5, THF) with >99% ee. HRMS calcd for $C_{17}H_{14}Br_2O_2$ $(M-1)^-$: 406.92768; found: 406.92588. The rest of the physical data was identical in all respects to the racemate.

Similar hydrolysis treatment of **d** (1.0 g, 1.3 mmol) gave (*R*)-(−)-DBSPINOL 0.52 g, 98% yield with >92% ee, followed by recrystallization from *n*-hexane to give (*R*)-(−)-DBSPINOL 0.40 g, 74% yield. Mp 160–161 °C; $[\alpha]_D^{18} = -93.5$ (*c* 0.5, THF) with above 99% ee and enantiomerically pure (−)-menthol (0.40 g, 99% recovery yield). HRMS calcd for $C_{17}H_{14}Br_2O_2$ $(M-1)^-$: 406.92768; found: 406.92866. The rest of the physical data was identical in all respects to the racemate.

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13. The absolute configuration of (*S*)-(+)-DBSPINOL was assigned as follows. Method A: We double-checked the specific rotation data of our (+)-DBSPINOL and compared the rotation sign of the literature.[5e] Method B: Debromination of diastereomer **c** with *n*-BuLi followed by hydrolysis afforded (*S*)-(−)-SPINOL.[16] Thus we can confirm the absolute configuration of (+)-DBSPINOL to be *S*.
14. Weigh accurately the crude (−)-menthyl chloroformate samples (0.3563 g) dissolved in a solution of 2.0 mL of water and 0.3 mL of pyridine. The mixture was stirred at room temperature for 10 min. Then, nitric acid (20 mL, 6.0 mol L^{-1}), 3.0 mL of $NH_4Fe(SO_4)_2$ indicator (saturated, 3.0 mL), and $AgNO_3$ (20.00 mL, 0.1 mol L^{-1}) were added. The contents were then titrated by adding NH_4SCN (0.1022 mol L^{-1}) to a pink end point, 5.15 mL of NH_4SCN be added. The blank value was 18.05 mL of NH_4SCN through the whole procedure without pyridine. The (−)-menthyl chloroformate was calculated from

$$\%\text{menthyl chloroformate} = \frac{M_{NH_4SCN}(V_{blank} - V_{pyridine})}{0.3563} \times 0.2187 \times 100\% = 80.9\%$$

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