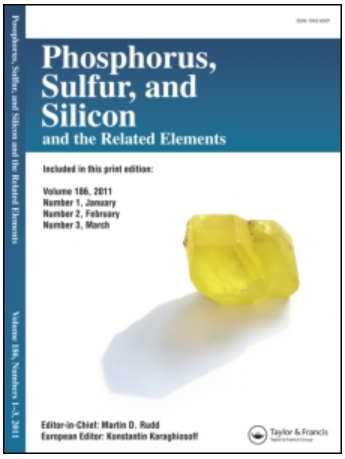

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An Improved Method for the Resolution of 1,1'-Binaphthalene-2,2'-Diol via a Phosphite Using (-)-Menthol as a Resolving Agent

Jue Xiao Cai[a]; Zheng Hong Zhou[a]; Kang Ying Li[a]; Chi Hung Yeung[b]; Chu Chi Tang[a]
[a] State Key Laboratory of Elemento-Organic Chemistry, Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, P. R. China [b] Open Laboratory of Chirotechnology and Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Kong, P. R. China

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AN IMPROVED METHOD FOR THE RESOLUTION OF 1,1′-BINAPHTHALENE-2,2′-DIOL VIA A PHOSPHITE USING (−)-MENTHOL AS A RESOLVING AGENT

Jue Xiao Cai,[a] *Zheng Hong Zhou, Kang Ying Li,*[a] *Chi Hung Yeung,*[b] *and Chu Chi Tang*[a]
State Key Laboratory of Elemento-Organic Chemistry, Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, P. R. China, 300071[a] *and Open Laboratory of Chirotechnology and Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Kong, P. R. China*[b]

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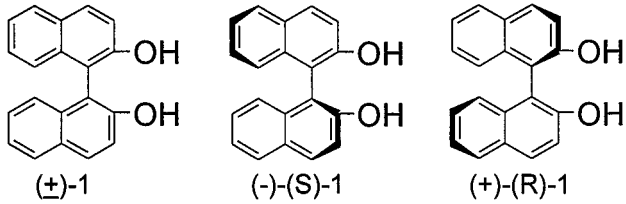
(−)-Menthol reacts with phosphorus trichloride to afford menthyl phosphorodichloridite ***2****, which further reacts with racemic 1,1′-binaphthalene-2,2′-diol to give phosphite (±)-****3*** *in the presence of triethylamine. (±)-****3*** *can be easily separated by fractional crystallization to form the crystal (+)-(****S****)-****3*** *and the mother liquor (−)-(****R****)-****3****. Then both the crystal and the mother liquor are treated with the AcOH-H_2O to obtain enantiomeric pure (−)-(****S****)-****1*** *and (+)-(****R****)-****1*** *respectively, with enantiomeric excess up to 99.7%.*

Keywords: Fractional crystallization; optically activity; phosphite; resolution

INTRODUCTION

Optically active 1,1′-binaphthalene-2,2′-diol has become quite an important chiral source in different fields of chirotechnology, especially in asymmetric synthesis.[1–13] Its synthesis and resolution have been extensively studied and various resolution methods have been reported.[14] Among the reported resolution methods, the formation of phosphoric acid derivatives,[15–22] boric acid derivatives,[23–25] and inclusion complexes[26–34] are the most important.

Address correspondence to Chu Chi Tang, State Key Laboratory of Elemento-Organic Chemistry, Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, P. R. China, 300071.

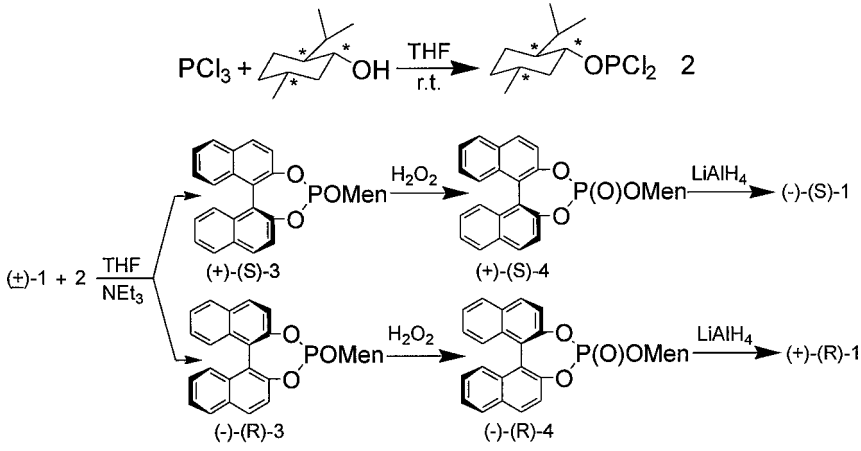


The resolution based on cyclic phosphoric acid and its derivatives is the earliest and most widely used method so far because many types of resolving agents can be utilized and yield both enantiomers with high enantiomeric purity. However, the main shortcoming of this method is that cyclic phosphoric acid derivatives have to be cleaved by $LiAlH_4$ to obtain optically active **1**, leading to added expense, strict experiment conditions, and difficulty to for large scale preparations.

Recently a new convenient method via cyclic borate ester has been reported. Compared with the phosphoric acid method, $LiAlH_4$ is not required. But the utility of borane as the starting material restricts its application in large-scale preparation.

Compound **1** can also react with many chiral amines, such as alkaloids, to form an inclusion complex containing two diasteromers. Both enantiomers of **1** can be obtained easily by separation of the diasteromeric inclusion complexes. This method has proved to be convenient and can be applied to large scale preparation due to mild reaction conditions. However, the alkaloid resolving agents are too expensive.

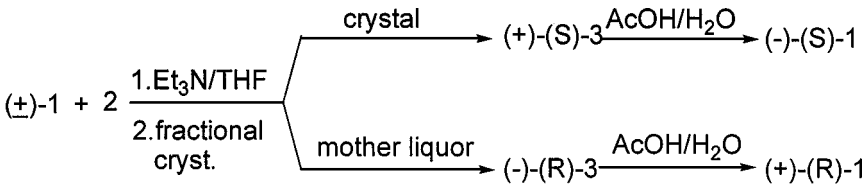
Herein we report a novel convenient method via phosphite that proved to be very simple and effective for resolution of racemic 1,1′-binaphthalene-2,2′-diol.



RESULTS AND DISCUSSION

Buono has reported a method via cyclic phosphite using (−)-menthol as the resolving agent.[22] In Buono's procedure, (−)-menthol reacts with PCl_3 to afford menthyl phosphorodichloridite **2**. Then crude **2** is treated with racemic **1** to give corresponding cyclic phosphites **3**. Both diasteromerically pure phosphites (+)-(**S**)-**3** and (−)-(**R**)-**3** can be easily separated by fractional crystallization and are further oxidized to the corresponding (+)-(**S**)-**4** and (−)-(**R**)-**4**, which are then treated with $LiAlH_4$ to afford (−)-(**S**)-**1** and (+)-(**R**)-**1**. This resolution method employs readily available (−)-menthol as the resolving agent, providing both enantiomers high optical purity and overall yield. However, the method suffers from a high price and inconvenience of $LiAlH_4$, especially for large scale preparations.

Recently we found that AcOH—H_2O hydrolysis of phosphites (+)-(**S**)-**3** and (−)-(**R**)-**3** proceeds smoothly in satisfactory yield to give optically active (−)-(**S**)-**1** and (+)-(**R**)-**1**. The experimental results show that phosphites can be directly hydrolyzed to obtain the target compounds without further oxidation nor $LiAlH_4$ reduction. These improvements make the method more practical and easier to perform for large-scale preparations. The resolution process is shown in Scheme 1.



SCHEME 1

EXPERIMENTAL SECTION

Specific rotations were measured by a Perkin Elmer 241MC polarmeter. The e.e. values were determined by HPLC with a chiral column (Kromasil KR100-100CHI-TBB, Hexane/i-PrOH = 95:5). ^{1}H NMR (200MHz) data were recorded with a Bruker AC-200 spectrometer using TMS as an internal standard, ^{31}P NMR (80.1MHz) data were recorded using 85% H_3PO_4 as an external standard.

Preparation and Resolution of Phosphites 3

Phosphites **3** were prepared and resolved using Buono's method.[22] From the crystal fraction, diasteromerically pure (+)-(**S**)-**3** was obtained with

83.2% yield: m.p. 176 ~ 180°C; $[\alpha]_D^{20} = +364.8°$(c1, CH_2Cl_2); ^{31}P NMR δ 151.9 ppm ($CDCl_3$) (single signal); ^{1}H NMR ($CDCl_3$) δ 0.67 ~ 0.97 (m, 5H), 1.41 ~ 1.60(m, 5H), 1.65(d, 2H), 2.10(d, H), 2.24 ~ 2.44(m, H), 7.24 ~ 7.53(m, 8H), 7.67 ~ 7.98(m, 4H). The mother liquor containing (−)-(**R**)-**3** was used for the next step.

Preparation of Optically Active 1

To the diasteromerically pure (+)-(**S**)-**3** AcOH (15 mL) and H_2O (5 mL) were added under stirring and heated to reflux to give a clear solution. After refluxing for an additional 30 min, the solvent was removed under reduced pressure to yield a semisolid residue. After 24 h at room temperature, large white crystals formed and were collected by filtration. The white solid separated was washed with toluene (10 mL × 2) and recrystallized from toluene (70 mL) to give 9.3 g of (−)-(**S**)-**1**: m.p. 208 ~ 210°C; $[\alpha]_D^{20} = -37.3°$(c1, THF); 99.7% e.e.; overall yield is 97.1% (based on starting racemic **1**).

The mother liquor containing (−)-(**R**)-**3** was evaporated to dryness under reduced pressure to give 25 g of viscous oil. To the residue, AcOH (15 mL) and H_2O (5 mL) were added and heated under reflux until a clear solution was obtained. After refluxing for additional 30 min, the reaction mixture was cooled to room temperature. After 2 h, powdery crystals were observed. Racemic **1** (3.8 g; m.p. 216 ~ 219°C; $[\alpha]_D^{20} = 0°$, c1, THF) was collected by filtration. The filtrate was distilled in vacuum to yield a viscous oil. White crystals formed after 24 h at room temperature. The white crystals (8.6 g; $[\alpha]_D^{20} = +35.0°$, c1, THF) were collected by filtration and washed with toluene (7 mL × 2), then recrystallized from toluene (50 mL) to give 7.0 g of white crystals (+)-(**R**)-**1**: m.p. 208 ~ 210°C; $[\alpha]_D^{20} = +37.2°$(c1, THF); 99.9% e.e.; overall yield is 73.3% (based on starting racemic **1**).

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