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A New Convenient Method for the Resolution of 1, 1′-Binaphthalene-2, 2′-diol *Via* a Phosphite Using (-)-Menthol as Resolving Agent

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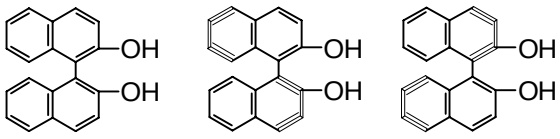
Abstract: (-)-Menthol reacts with phosphorus trichloride to afford menthyl phosphorodichloridite **2**, which further reacts with racemic 1, 1′-binaphthalene-2, 2′-diol to give phosphite **(±)-3** in the presence of triethylamine. **(±)-3** can be easily separated by fractional crystallization to form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

Keywords: optically active 1,1′-binaphthalene-2, 2′-diol, L-menthol, phosphite, fractional crystallization, resolution.

Optically active 1,1′-binaphthalene-2, 2′-diol has become a quite important chiral source in different fields of chirotechnology, especially in asymmetric synthesis[1]. Its synthesis and resolution has been extensively studied and various resolution methods have been reported[2]. Among the reported resolution methods, the following three, namely, *via* the formation of phosphoric acid derivatives[3], boric acid derivatives[4] and inclusion complexes[5], are the most important.



(±)-1 **(-)-(S)-1** **(+)-(R)-1**

Buono has reported a method *via* cyclic phosphite using (-)-menthol as resolving agent[3h] (shown in **Scheme 1**). In Buono's procedure, (-)-menthol reacts with PCl_3 to afford menthyl phosphorodichloridite **2**, then crude **2** reacts 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

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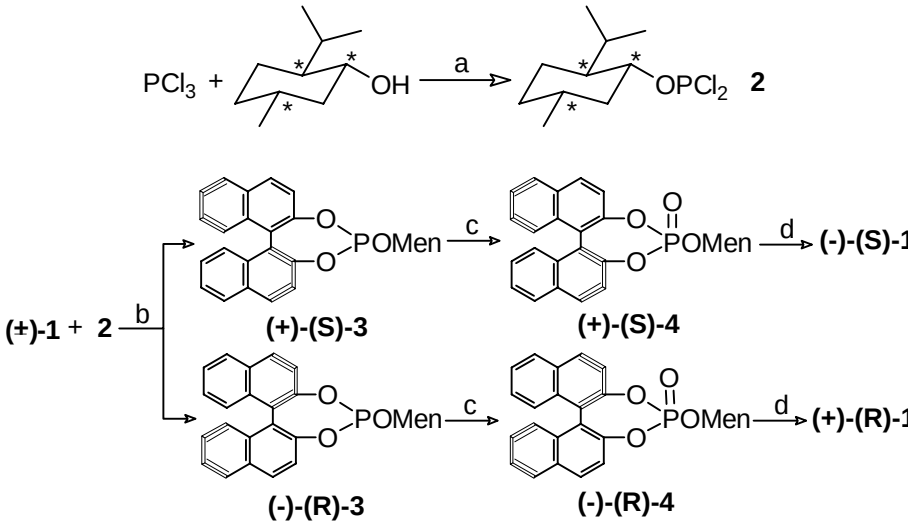
(+)-(R)-1. This resolution method employs readily available (-)-menthol as the resolving agent, providing both enantiomers with high optical purity and overall yield. However, the method suffers from the high price and inconvenience of $LiAlH_4$, especially in large-scale preparation.

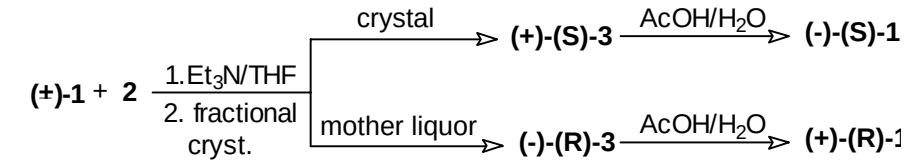
Scheme 1



a. THF, r.t.; b. Et_3N.THF; c. H_2O_2; d. $LiAlH_4$

Recently we found that acid hydrolysis of phosphites **(+)-(S)-3** and **(-)-(R)-3** can proceed smoothly with satisfactory yield and give optically active **(-)-(S)-1** and **(+)-(R)-1** in an AcOH-H_2O medium. Experimental results show that phosphites can be directly hydrolyzed to obtain the target compounds without further oxidation nor reduction. These improvements make the method more practical and easier to be performed on large-scale preparation. In addition, this is the first resolution method *via* a cyclic phosphite and is also the first that do not use $LiAlH_4$ in the phosphorus derivative method. The resolution process is shown in **Scheme 2**.

Scheme 2



Preparation of compound 2

O-menthyl phosphorodichloridite **2** was prepared from excess phosphorous trichloride and (-)-menthol at room temperature. Pure compound **2** was obtained after distillation of excess phosphorous trichloride. The yield of the compound **2** is almost 100%: B.p. 110~112°C/266Pa, n_D^{25} = 1.4946, $[\alpha]_D^{16}$ = +52.0 (neat), ^{31}P NMR: 176.45ppm, ^1H NMR($CDCl_3$, δ): 0.783(d,3H) 0.90(d,3H) 1.24(m,5H) 1.67(d,2H) 2.00(m,H) 2.34(d,Hz) 4.47(dq,H).

Procedure for preparation of optically active compound 1

Phosphites **3** were prepared and resolved using Buono's method[3h]. Through fractional crystallization diasteromerically from ether pure **(+)-(S)-3** was obtained with 83.2% yield and **(-)-(R)-3** remained in the mother liquor. Then diasteromerically pure **(+)-(S)-3** was treated with AcOH-H_2O to obtain enantiomeric pure **(-)-(S)-1**in 97.1% yield: m.p. 208~210°C, $[\alpha]_D^{20}$ =-37.3 (c 1,THF)(lit.[3h] $[\alpha]_D^{20}$ -34.3). Analogously, **(-)-(R)-3** contained in the mother liquor was also treated with AcOH-H_2O to obtain enantiomeric pure **(+)-(R)-1** in 73.3% yield: m.p.208~210°C; $[\alpha]_D^{20}$ =+37.2 (c 1, THF) (lit.[3h] $[\alpha]_D^{20}$ +34.3). The enantiomeric excess are up to 99.7%(determined by HPLC with a chiral column (Kromasil KR100-100CHI-TBB, Hexane/i-PrOH=95:5)).

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