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Direct Optical Resolution of 2,2'-Dihydroxy-1,1'-binaphthyl

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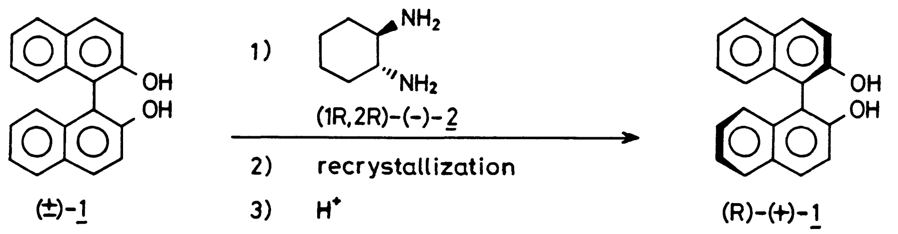
2,2'-Dihydroxy-1,1'-binaphthyl (1) was directly resolved with (1R,2R)-1,2-diaminocyclohexane to afford (R)-(+)-1 in a high yield with a high optical purity.

Optically active 2,2'-dihydroxy-1,1'-binaphthyl (1) has been used as an effective atropisomeric compound in various asymmetric syntheses,[1] and the practical applications have been progressively carried out. Also synthetic methods of optically active 1 have been intensively investigated. For example, optical resolution of racemic 1 with a chiral amine *via* its phosphoric ester,[2] enzymatic optical resolution of racemic 1 *via* its carboxylic ester,[3] optical resolution of racemic 1 by host-guest complexation method,[4] and oxidative coupling of 2-naphthol using chiral amine-Cu(II) complex[5] were developed. However, these methods have disadvantages such as use of the expensive chiral amine, multi-step resolution including transformation of 1 to the ester, difficulty in acquisition of chiral host, and troubles in handling the chiral amine, respectively.

Here, we wish to report a convenient and practical method for the direct optical resolution of 1 with economical optically active amine, 1,2-diaminocyclohexane (2), which dissolves all of the disadvantages in previous methods.

Racemic 1 25.1 g (87.7 mmol) and (1R,2R)-(-)-2 ($[\alpha]_D^{24}$ -36.7° (c 4.14, H_2O)) 10.0 g (87.6 mmol) were added to benzene (750 cm^3). The mixture was heated to a homogeneous solution and cooled to room temperature. Precipitates were filtered and twice recrystallized from benzene (each 750 cm^3) to afford 21.0 g of crystalline compound 3, which consisted of (R)-(+)-1,



(1R, 2R)-(-)-2, and benzene (1:1:2).[6] Treatment of 3 with 1 mol dm^{-3} hydrochloric acid and methanol at room temperature gave (R)-(+)-1 (10.8 g, 37.7 mmol) in a yield of 86% based on the enantiomer presents in the racemate. Optical purity of the obtained (R)-(+)-1 ($[\alpha]_D^{23}$ +34.4° (c 0.502, THF)) was 94%.[7] Evaporation of the mother liquor from the above crystallization gave oily residue; treatment with dilute hydrochloric acid as mentioned above gave (S)-(-)-1 in a yield of 57% with an optical purity of 62%. Complexation of the (S)-(-)-1 with (1S, 2S)-(+)-2, recrystallization of the obtained crystalline precipitate from benzene, and treatment with dilute hydrochloric acid afforded (S)-(-)-1 with an optical purity of 96% in a yield of 84% based on the enantiomer presents in the racemate.

Also optically active threo-1,2-diamino-1,2-diphenylethane (4)[8] was effective for the resolution of 1. Resolution using 4 was carried out in a similar manner as that using 2. Thus, (R)-(+)-1 was obtained by the resolution with (R, R)-(+)-4 (O.P. 95%) in a yield of 78% based on the enantiomer presents in the racemate and in an optical purity of 92%.

As described above, direct resolution of 1 with optically active 2 provides a convenient and practical method for the synthesis of optically active 1.

References

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6) 3: mp 148-151 °C (released benzene molecule to whiten at above 80 °C); ^1H-NMR ($CDCl_3$) δ=1.00-2.00 (m, 8H, $-(CH_2)_4-$), 3.60 (br, 10H, $-NH_2$, -OH and CH-N), 7.13-8.33 (m, 12H, Naph-H), 7.35 (s, 12H, PhH); IR (KBr) 3450, 3380, 3300, 3060, 2950, 2860, 1620, 1600, 1515, 1460, 1380, 1360, 1230, 1210, 960, 820, 745, 695 cm^{-1}; $[\alpha]_D^{23}$ -16.1° (c 1.01, $CHCl_3$).
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