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Direct Optical Resolution of Vicinal Diols and an α-Hydroxy Oxime with a Vicinal Diamine

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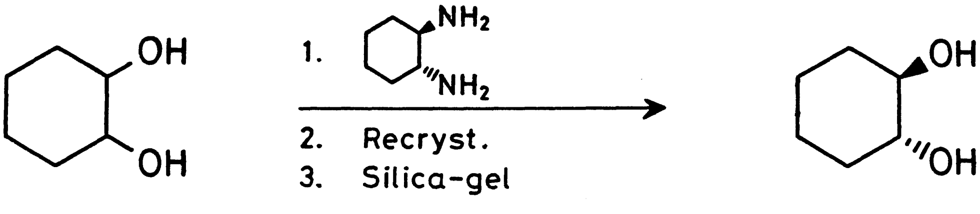
Vicinal diols, such as 1,2-cyclohexanediol, 1,2-cyclooctanediol, 2,3-butanediol, and 1,2-diphenyl-1,2-ethanediol, were directly resolved with (1<u>R</u>,2<u>R</u>)-(-)-1,2-cyclohexanediamine (<u>1</u>). (<u>E</u>)-1,2-Diphenyl-2-(hydroxyimino)ethanol was also resolved efficiently with <u>1</u>.

Although asymmetric syntheses of vicinal diols have been reported,[1)] direct optical resolution of vicinal diols has never been reported to our knowledge. In general, optical resolutions of vicinal diols have been carried out by multi-step procedures <u>via</u> the acylated derivatives.[2)]

Previously we reported[3)] the direct optical resolution of 2,2'-dihydroxy-1,1'-binaphthyl with optically active 1,2-cyclohexanediamine (<u>1</u>), where the efficient resolution seemed to be due to the situation that the binaphthyl and <u>1</u> have the same structural symmetry of C_2 and further a pair of hydrogen-bonds are probably formed between them to favor the resolution. So we planned the resolution of compounds with vicinal alcoholic, instead of phenolic, dihydroxy groups.



When the mixture of (1R,2R)-(-)-1 ($[\alpha]_D^{24}$ -36.7° (c 4.14, H_2O)) 2.00 g (17.5 mmol) and racemic trans-1,2-cyclohexanediol (2a) 1.97 g (17.0 mmol) in benzene (4 cm^3) was heated to give a homogeneous solution and allowed to cool to room temperature, crystalline precipitates were obtained. They were recrystallized twice from benzene (each 4 cm^3). The ^1H-NMR and IR spectra of the crystalline compound showed that the compound consisted of (1R,2R)-(-)-1 and 2a (1:1).4) Treatment of the solution of the crystalline compound in ethanol with silica-gel short column afforded (1R,2R)-(-)-2a ($[\alpha]_D^{23}$ -31.3° (c 0.02, H_2O)) 0.718 g (6.18 mmol) in a yield of 73% based on the enantiomer existing in the racemate. Optical purity of the resolved 2a was 67%.5)

The results of optical resolution of other vicinal diols, such as 1,2-cyclooctanediol (2b), 2,3-butanediol (2c), and 1,2-diphenyl-1,2-ethanediol (2d), with (1R,2R)-(-)-1 are summarized in Table 1.

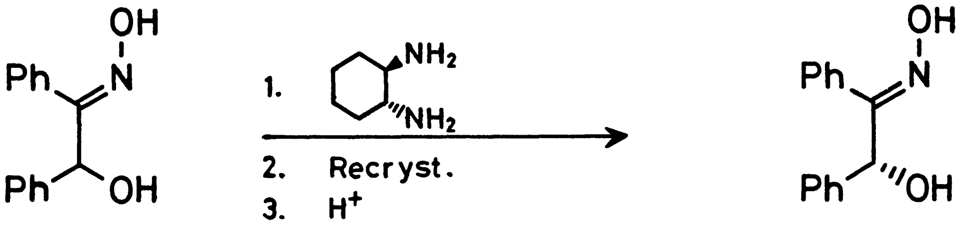
Table 1. Optical Resolution of Vicinal Diols with (1R,2R)-(-)-1a)

Diol	Resolved enantiomer	Chemicalb) yield/%	$[\alpha]_D^{20}$/°	Opticalc) purity/%
2b	(1R,2R)	36	-14.8 (c 1.33, EtOH)	88
2c	(2R,3R)	16	-9.16 (c 1.09, CH_3COCH_3)	74
2d	(1S,2S)	62	-90.4 (c 2.50, EtOH)	91

a) All optical resolutions were carried out in the same manner as described in the text except for the isolation of optically active 2d: The crystalline compound, which consisted of (1R,2R)-(-)-1 and (1S,2S)-(-)-2d, was treated with dilute hydrochloric acid, and (1S,2S)-(-)-2d was extracted with CH_2Cl_2. b) Chemical yields were based on the enantiomer in the racemate. c) Optical purities were calculated from the optical rotations based on the reported values of $[\alpha]_D$ in the literature.6)

Moreover, optical resolution of an α-hydroxy oxime, which also has two hydroxy groups, with optically active diamine is of interest. Though α-hydroxy oximes are useful compounds in organic syntheses,7) their optical resolution has not yet been reported.

Optical resolution of α-hydroxy oxime (3) was performed in the same manner as in the cases of diols described above. When the mixture of (1R,2R)-(-)-1 2.00 g (17.5 mmol) and racemic (E)-1,2-diphenyl-2-(hydroxyimino)ethanol (3) 4.00 g (17.6 mmol) in benzene (10 cm^3) was heated to homogeneous solution and allowed to cool to room temperature, crystalline precipitates were obtained, which were twice recrystallized from benzene (each 50 cm^3). The ^1H-NMR and IR spectra of the purified crystalline compound showed that the compound was composed of (1R,2R)-(-)-1 and 3 (1:1).8) Then the crystalline compound was treated with 1 mol dm^{-3} hydrochloric acid and ethanol to afford (R)-(-)-(E)-3 ($[\alpha]_D^{23}$ -5.12°(c 0.508, $CHCl_3$)) 1.11 g (4.90 mmol) in a yield of 56% based on the enantiomer in the racemate. Optical rotation of the resolved 3 was larger than the reported value.9)



As described above, C_2-symmetrical vicinal diols (2) and α-hydroxy oxime (3) were directly and conveniently resolved with C_2-symmetrical vicinal diamine (1). The novel optical resolutions offer important methods for the acquisitions of optically active vicinal diols and α-hydroxy oximes.

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6) (1S,2S)-(+)-2b, $[\alpha]_D^{22}$ +16.9° (c 1.33, EtOH), E. J. Corey and J. I. Shulman, Tetrahedron Lett., 1968, 3655; (2S,3S)-(+)-2c, $[\alpha]_D^{31}$ +12.3° (c 3.5, CH$_3$COCH$_3$), K. A. Thaker and N. S. Dave, J. Sci. Ind. Res., Sec. B, 20, 329 (1961); (1S,2S)-(-)-2d, $[\alpha]_D^{22}$ -99.1° (c 1.1, EtOH), J. Brugidou, H. Christol and R. Sales, Bull. Soc. Chim. Fr., 1974, 2033.

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8) (1R,2R)-(-)-1•3 (1:1): mp 85-100 °C; ^{1}H-NMR(CDCl$_3$-CD$_3$SOCD$_3$) δ 0.7-2.7 (m, 10H), 2.7-4.6 (brs, 6H), 5.6 (s, 1H), 7.2 (s, 10H); IR(KBr) 3500, 3450, 3360, 3330, 3300, 3250, 3600-2400, 960, 710 cm^{-1}; $[\alpha]_D^{20}$ -13.7° (c 1.03, CHCl$_3$).

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