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MUTUAL OPTICAL RESOLUTION OF 2,2'-DIHYDROXY-1,1'-BINAPHTHYL AND ALKYL ARYL OR DIALKYL SULFOXIDES BY COMPLEX FORMATION

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Summary: By complexation with optically active 2,2'-dihydroxy-1,1'-binaphthyl, alkyl aryl and dialkyl sulfoxides were resolved very efficiently. Reversely, by complexation with optically active alkyl aryl or dialkyl sulfoxides, 2,2'-dihydoxy-1,1'-binaphthyl was resolved very efficiently. In all cases, 100% optically pure (+)- and (-)-enantiomers were obtained in good yields.

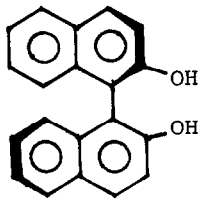
Previously, we have reported a simple optical resolution method of 3-methylcycloalkanones,[1a] 5-methyl-γ-butyrolactone,[1a] and 2,3-epoxycyclohexanones[1b] by complexation with optically active 1,6-bis(*o*-halophenyl)-1,6-diphenylhexa-2,4-diyne-1,6-diol. Recently, we found that 2,2'-dihydroxy-1,1'-binaphthyl (1) and alkyl aryl (2) or dialkyl sulfoxides (3) form a crystalline complex in which each component recognizes the chirality of the other very efficiently; mutual optical resolution can be done very easily by using the complex formation.

Optically active 1 is an useful compound for the preparation of chiral crown ethers[2] and enantioselective reducing reagents for ketones,[3] and for the stereoselective polymerization of heterocycles[4] and stereoselective Ullmann coupling reaction.[5] Optical activation of 1 by resolution have been reported.[2,6] The simplest and most successful preparative method for optically active 1 is a stereoselective coupling reaction[7] of 2-hydroxynaphthalene by cupric nitrate in the presence of (*S*)-(+)-1-phenyl-2-propanamine.[7c] Nonetheless, this method does not give 100% optically pure 1. Furthermore, (*S*)-(+)-1-phenyl-2-propanamine is a central stimulant. Preparation of optically pure sulfoxides is not easy, even though some preparative methods by optical resolution[8] and stereoselective reaction[9] have been reported. Our mutual resolution method is very

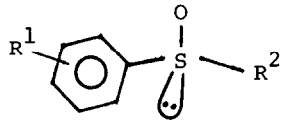
simple and can be used to obtain optically pure 1, 2, and 3 in both enantiomeric forms.

When a solution of 100% ee (*R*)-(+)-1 (3.0 g, 10.5 mmol, $[\alpha]_D$ +37.7°[10]) and (±)-methyl *m*-methylphenyl sulfoxide (2) (3.23 g, 21.0 mmol) in benzene-n-hexane (1:1, 20 ml) was kept at room temperature for 12 h, a 1:1 complex of (*R*)-(+)-1 and (+)-2 (4.10 g, 89%, $[\alpha]_D$ +52.7°) was obtained as colorless prisms. Recrystallization from benzene (30 ml) gave a complex (3.57 g, 77%, mp 152-154 °C, $[\alpha]_D$ +69.7°), which upon chromatography[11] gave 100% ee[12] (+)-2 (1.24 g, 77%, $[\alpha]_D$ +140°) and 100% ee (*R*)-(+)-1 (2.32 g, 77%, $[\alpha]_D$ +37.7°). The mother liquor left from the initial complexation reaction was evaporated to dryness and the residue was chromatographed to give 62% ee (-)-2 (1.30 g, 80%, $[\alpha]_D$ -86.2°). When a solution of the 62% ee (-)-2 (1.30 g, 8.44 mmol) and 100% ee (*S*)-(-)-1 (2.41 g, 8.44 mmol, $[\alpha]_D$ -37.7°) in benzene (10 ml) was kept at room temperature for 12 h, a 1:1 complex (2.39 g, 52%, $[\alpha]_D$ -62.9°) was obtained. Recrystallization from benzene (15 ml) gave a complex (1.79 g, 39%, mp 152-154 °C, $[\alpha]_D$ -69.8°), which upon chromatography gave 100% ee (-)-2 (0.62 g, 38%, $[\alpha]_D$ -140°) and 100% ee (*S*)-(-)-1 (1.16 g, 48%, $[\alpha]_D$ -37.7°).

Conversely, optically active 2 can be used for an optical resolution of 1. When a solution of 100% ee (-)-2 (1.40 g, 9.10 mmol, $[\alpha]_D$ -140°) and (±)-1 (2.60 g, 9.10 mmol) in benzene-n-hexane (1:2, 15 ml) was kept at room temperature for 12 h, a 1:1 mixture of (-)-2 and (*S*)-(-)-1 (2.0 g, 100%, $[\alpha]_D$ -61.3°) was obtained as colorless prisms. Recrystallization from benzene (5 ml) gave a complex (1.66 g, 83%, mp 152-154 °C, $[\alpha]_D$ -69.7°) which upon chromatography gave 100% ee (*S*)-(-)-1 (1.08 g, 83%, $[\alpha]_D$ -37.7°) and 100% ee (-)-2 (0.52 g, 74%, $[\alpha]_D$ -140°). The mother liquor left from the initial complexation reaction was evaporated to dryness and the residue was chromatographed to give 85% ee (*R*)-(+)-1 (1.12 g, 86%, $[\alpha]_D$ +32.1°). When a solution of the 85% ee (*R*)-(+)-1 (1.12 g, 3.92 mmol) and 100% ee (+)-2 (0.60 g, 3.92 mmol, $[\alpha]_D$ +140°) in benzene (10 ml) was kept at room temperature for 12 h, a 1:1 complex of (*R*)-(+)-1 and (+)-2 (1.52 g, 76%, mp 152-154 °C, $[\alpha]_D$ +69.7°) was obtained. Chromatography of the complex gave 100% ee (*R*)-(+)-1 (0.99 g, 76%, $[\alpha]_D$ +37.7°) and 100% ee (+)-2 (0.50 g, 83%, $[\alpha]_D$ +140°).

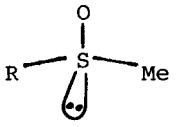


1



2

a: R^1=H; R^2=Me
b: R^1=*o*-Me; R^2=Me
c: R^1=*m*-Me; R^2=Me
d: R^1=*m*-Me; R^2=Et
e: R^1=*p*-Me; R^2=Me



3

a: R=n-Bu
b: R=i-Bu
c: R=s-Bu
d: R=n-Pr
e: R=i-Pr
f: Et

By the same procedure as that described above, ethyl *m*-methylphenyl sulfoxide (2d) can also be resolved easily to give 100% ee (+)- and (-)-enantiomers ($[\alpha]_D$ 199°) in almost the same yields as those of (+)- and (-)-2c. Optical resolution of 1 by complexation with optically active 2d was also successful. However, methyl phenyl sulfoxide (2a) was poorly resolved by one complexation with optically active 1, and gave approximately 5% ee enantiomer.[8b] Interestingly, methyl *o*-methylphenyl (2b) and methyl *p*-methylphenyl sulfoxide (2e) did not form complex with 1. These results show that molecular shape of sulfoxide is important for the formation of complex with 1 and for efficient chiral recognition in the complex. These are interesting subjects in molecular science.

Some dialkyl sulfoxides (3) are also available to the mutual optical resolution with 1. n-Butyl methyl (3a) and methyl n-propyl sulfoxide (3d) are easily resolved by the complexation with optically active 1 to give 100% ee (+)- and (-)-enantiomers of 3a ($[\alpha]_D$ 111°) and of 3d ($[\alpha]_D$ 123°), respectively in good yields. Of course, optical resolution of 1 by complexation with optically active 3a or 3d was also successful. However, optical resolution of i-butyl methyl (3b) and ethyl methyl sulfoxide (3f) was not effective and approximately 25% ee enantiomer of 3b and 3f were obtained by one complexation with optically active 1. s-Butyl methyl (3c) and methyl i-propyl sulfoxide (3e) did not form complex with 1.

We also found that 1 forms crystalline complex with various ketones, ethers, amines, and amides. Application to their resolutions is interesting.

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10. All the $[\alpha]_D$ values of 1, sulfoxides (2, 3), and complex of 1 and sulfoxide were measured in THF, EtOH, and EtOH, respectively, at a concentration *c* 1.0 with a 1-dm cell at 25 °C.

11. All the chromatographies were carried out on silica gel by using benzene-ethyl acetate (1:1) as solvent. Complex of 1 and 2 or 3 can also be decomposed into the component by dissolving in aqueous sodium hydroxide.

12. The enantiomeric excess (% ee) of 2 and 3 was determined by NMR analysis in $CDCl_3$ using the chiral shift reagent, tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III).

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