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Enantiomeric 2,2'-Dihydroxy-1,1'-Binaphthyl and O,O'-(1,1'-Binaphthyl-2,2'-Diyl)-Dithiophosphoric Acid as Chiral Auxiliaries in the Preparation of Optically Active Sulfinyl Derivatives

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Chiral sulfinates and sulfoxides constitute the two most important groups of optically active sulfinic acid derivatives. They can be prepared by a variety of approaches with the use of different chiral auxiliaries.¹ Until now, the enantiomers of binaphthol 5, which are important chiral compounds commonly used in asymmetric synthesis,² have rarely been used for the preparation of optically active sulfinic acid derivatives. In continuation of our interest in the application of atropisomeric reagents for the separation of racemates,³ as chiral shift reagents⁴ and for the formation of chiral metal complexes⁵ we would like to present in this paper our recent results on the use of these reagents as chiral auxiliaries in the preparation of optically active sulfoxides and sulfinic esters.

The preparation of optically active sulfoxides is based on the kinetic resolution of racemic sulfoxides 1 by their partial reduction with optically active dithiophosphoric acid 2 (Table 1).

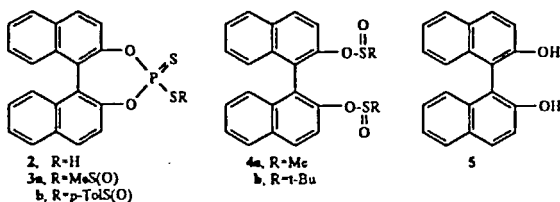


Table 1. Kinetic Resolution of Racemic Sulfoxide **1** by the Reaction with Optically Active BNDTPA-2.

R	R'	Time [h]	$[\alpha]_{D}^{25}$ (solvent)	ee [%]	Abs. conf.
Me	Ph	312	- 6.0 (CHCl ₃)	3.2	S
t-Bu	Ph	312	+1.0 (CCl ₄)	0.5	R
Me	p-Tol	23	- 2.3 (acetone)	1.5	S
Et	p-Tol	264	- 4.1 (acetone)	2.0	S
t-Bu	p-Tol	336	+5.0 (acetone)	2.1	R
t-Bu	Me	168	+0.3 (methanol)	3.0	S
t-Bu	Et	168	+5.5 (acetone)	4.0	R

We have also found that diastereomeric thioanhydrides **3a,b** formed in the reaction between (-)-**2** and methane or p-toluene sulfinyl chlorides were not stable enough to be isolated as pure chemical species.

Diastereomeric alkanesulfonates **4a,b** were prepared by two asymmetric reactions. The first one was based on the asymmetric condensation of methane or t-butanedisulfinyl chlorides with racemic binaphthol **5** in the presence of optically active N,N-dimethyl- α -phenylethylamine or N,N-dimethylamphetamine as a chiral inducing agent. In the second condensation we used the dextrorotatory enantiomer of binaphthyl **5** as a chiral substrate. Its reaction with t-butanedisulfinyl chloride in the presence of (-)-N,N-dimethyl- α -phenylethylamine gave a mixture of diastereomeric sulfonates **4b** in a ratio 13:3.6:1.5:0.7. The typical column chromatography of this mixture on silica gel allowed the isolation of a sample in which only two diastereomers of **4b** with a ratio 4:35 were present. It is interesting to note that the ratio of the diastereomeric t-butane sulfonates **4b** was substantially changed when 4-N,N-dimethyl-pyridine was used as a base in the reaction of t-butanedisulfinyl chloride with (+)-**5**.

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