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Optically Active Spirosulfuranes via Nonclassical Resolution with 2,2'-Dihydroxy 1,1'-Binaphthol*

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Abstract: The first optically active spirosulfuranes containing a tridentate ligand have been obtained via nonclassical resolution procedure with optically active 2,2-dihydroxy-1,1'-binaphthol as a chiral host. The spirosulfurane **4a** was found to be optically stable under conditions in which symmetrical spirosulfuranes **2** with bidentate ligands lose their optical activity rapidly.

Synthesis of optically active sulfuranes especially structures having bidentate or tridentate ligands is interesting not only as an synthetic goal but also from the theoretical point of view. It is connected with the fact, that an access to optically active sulfuranes would make possible determination of their optical stability, thus allowing to have a new insight to the problem of pseudorotation in hypervalent organosulfur derivatives having a trigonal bipyramidal geometry with the lone electron pair occupying an equatorial site. Up to now only a few sulfuranes have been prepared as optically active species, among them monochlorosulfurane 1[1] and symmetrical spirosulfuranes 2[2] and 3[3].

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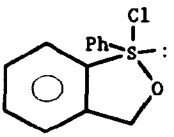
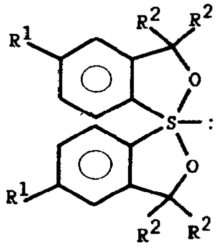
* This paper is dedicated to the memory of Professor Gunther Snatzke who died on January 14, 1992.

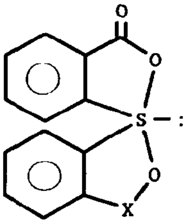


1



2

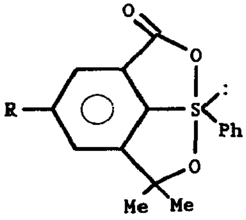
a R^1=H; R^2=CH_3
b R^1=t-Bu; R^2=CF_3



3

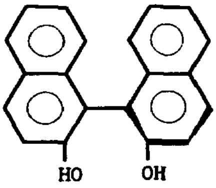
a X= CH_2
b X= C=O

Here we would like to report on the first optically active spirosulfuranes **4** which contain a tridentate ligand derived from o,o'-unsymmetrically substituted thiophenol. They were obtained as optically active species via nonclasical resolution with 2,2'-dihydroxy-1,1'-binaphthol **5** as a chiral host, which recently was found to be effective agent for the optical resolution of various chiral structures.[4]



4

a R=H
b R=t-Bu



5

We have found that racemic **5** forms also crystalline complexes with spirosulfuranes **2** and **4**[5]. Moreover, we observed a very effective optical resolution of racemic sulfurane **4a** through the formation of crystalline adduct with (+)-(R)-**5**. For example, when the racemic sulfurane **4a** (114 mg-0.4 mmol) and optically active **5** (27.2 mg-0.2 mmol) were dissolved in CH_2Cl_2 (1.4 ml) a 1:1 complex of (+)-(R)-**5** and (+)-**4** was formed instantaneously. It had $[\alpha]_D$=+8.0 ($CHCl_3$).[6a] Partial decomposition of this complex by washing with 10% KOH gave the optically active spirosulfurane **4a** having $[\alpha]_D$=+18.1±0.3 (0.4 $CHCl_3$)[6a] and the water soluble complex of (+)-(R)-**5** and (+)-**4** and KOH of unknown composition. Upon acidification of the water solution of this complex with concentrated HCl a new 2:1 complex of (+)-(R)-**5** and (+)-**4** was formed. This complex is not soluble in water and could be easily isolated by extraction with chloroform. Its decomposition by chromatography on a silica gel column with $CHCl_3$ as an eluent afforded again the optically active spirosulfurane **4a** having $[\alpha]_{589}=+17.8$ ($CHCl_3$).[6b] We were also able to isolate the optically active spirosulfurane **4a** nonbonded by (+)-(R)-**5**. It had obviously the opposite optical rotation equal to $[\alpha]_D=-17.8$ ($CHCl_3$).[6b] The optical purity of this sample of optically active spirosulfurane was determined by the ^{1}H-NMR technique. In the ^{1}H-NMR spectrum of the mixture of this optically active sulfurane (3.5 mg) and (-)-(R)-2,2,2-trifluoro-1-(9-anthranyl)ethanol (7 mg) dissolved in 0.4 ml of $CDCl_3$ only two singlets of equal intensity at 1.346 and 1.678 ppm were observed for the magnetically nonequivalent geminal methyl groups (see spectrum A Figure 1). When one drop of the chloroform-d solution containg the opposite enantiomer of the spirosulfurane **4a** was added to this mixture and the ^{1}H-NMR spectrum recorded again two sets of singlets of unequal intensity were observed (spectrum B in Figure 1).[7] This observation evidently indicates that the enantiomeric excess in the sample of the optically active spirosulfurane having $[\alpha]_{589}=-17.8$ ($CHCl_3$) is equal to 100%.

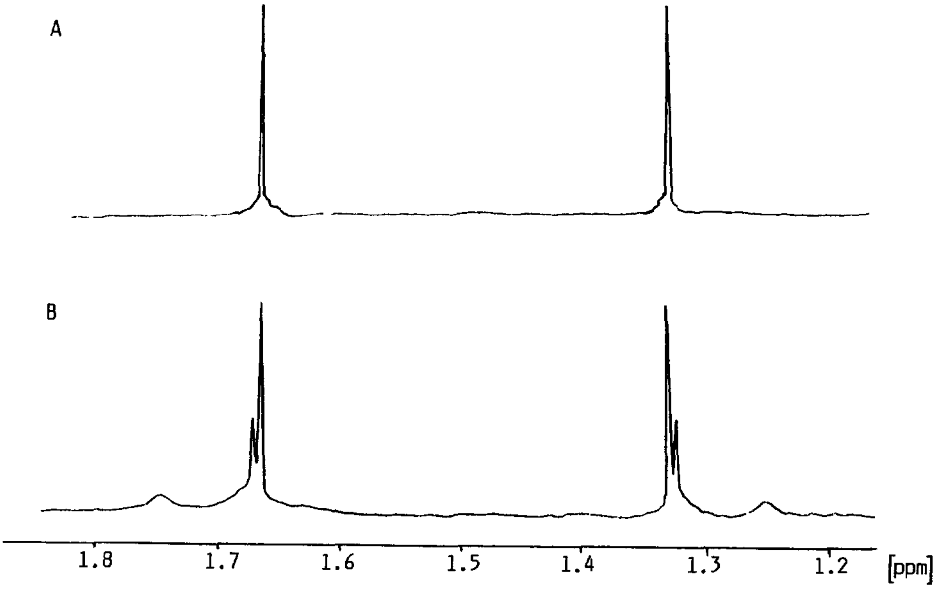


Figure 1. ^{1}H-NMR spectra of optically active spirosulfurane **4a**, $[\alpha]_{589}=-17.8$ ($CHCl_3$) in the presence of (-)-(R)-2,2,2-trifluoro-1-(9-anthranyl)ethanol. A - the pure enantiomer, B - after addition of a solution containing the opposite enantiomer.

It should be noted that the described resolution of the racemic spirosulfurane **4a** constitutes the first example of a kinetic resolution procedure affording both pure enantiomers of the resolved compounds in a single operation. In this context, it should also be noted that the efficiency of this kinetic resolution of the racemic spirosaulfuranes **4** through the formation of complexes with the optically active binapthol **5** is very strongly influenced by minor changes in their structure. Thus, the application of this procedure for the optical resolution of the racemic spirosulfurane **4b**, which differs from the spirocompound **4a** only by the presence of the t-butyl group in the para position of the aromatic ring, gave compounds showing only germinal optical rotation.

Having in hands the sample of optically active spirosulfurane **4a**, we were able to look for its optical stability. We have found that in sharp constrast to symmetrical spirosulfuranes **2** which rapidly racemize in the presence of moisture and organic acid at room temperature, the spirosulfurane **4a** keeps its optical activity under such conditions even at temperature above 130 °C. The origin of these striking differences in optical stability of closely related spirosulfurane structures is under current investigations and the results will be reported in due course.

References and Notes

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5. These complexes contain usually one molecule of a solvent in which spirosulfurane and racemic binapthol were dissolved. Full details will be disscused elsewhere.
6. The optical activity measurements were performed on: a) an Antopol III automatic polarimeter and a 1-dm sample tube; b)a Perkin-Elmer 241 photopolarimeter.
7. ^{1}H-NMR spectra were taken on a Bruker 300 MHz spectromater with TMS as an internal standard.