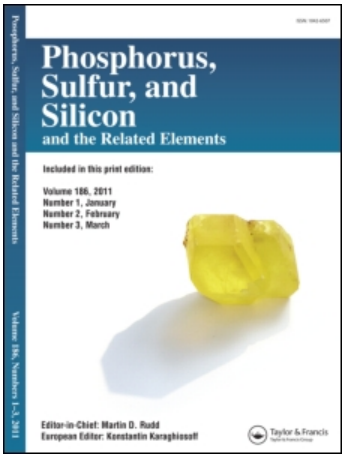

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The First Optically Active Spirosulfurane Oxides: Stereoselective Syntheses and Racemization Processes

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THE FIRST OPTICALLY ACTIVE SPIROSULFURANE OXIDES: STEREOSELECTIVE SYNTHESES AND RACEMIZATION PROCESSES

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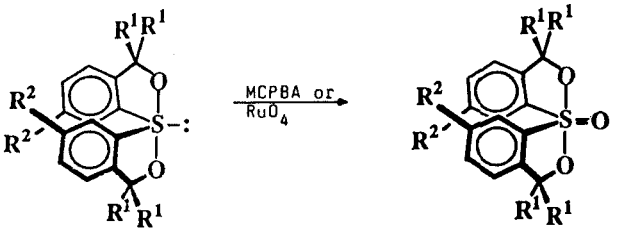
Syntheses of optically active organosulfur derivatives having a trigonal bipyramidal structure are of a great interest either from the theoretical or from the stereochemical points of view. Although the first optically active sulfurane, (+)-1-chloro-3,3-dimethyl-1-phenyl[3H-2,1--benzoxathiole] was reported as early as 1975[1], the first optically active spirosulfuranes have only recently been prepared either by an asymmetric dehydration approach[2] or by the stereoselective dehydration of the suitably constructed, optically active, orto-substituted diaryl sulfoxides[3]. Although the first attempt to synthetize optically active sulfurane oxide was reported as early as 1978[4], such structures have not been isolated in enantiomeric forms until now. Having in hands optically active spirosulfuranes 1a,b[2,5], and knowing details of their thermal and acid-catalyzed racemization it was reasonable to expect that the corresponding sulfurane oxides 2a,b should be isolated in optically active form at ambient temperature.



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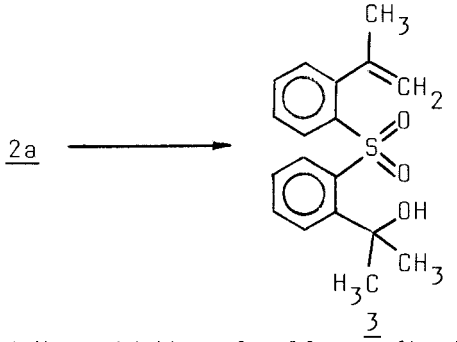
1a R^1 = Me, R^2 = H
1b R^1 = CF_3, R^2 = t-Bu

1a; $[\alpha]_{589}$ = 4.2° $\xrightarrow{MCPBA}$ 2a; $[\alpha]_{365}$ = --30°
1b; $[\alpha]_{589}$ = +216.5° $\xrightarrow{RuO_4}$ 2b; $[\alpha]_{589}$ = 111.8°

To check these predictions we have decided to investigate the stereochemical aspects of the oxidation of the parent, optically active spirosulfuranes 1a,b. The instantaneous oxidation of the dextrorotatory spirosulfurane 1a with m-chloroperbenzoic acid (MCPBA) was found to give the levorotatory spirosulfurane oxide 2a almost quantitatively (NMR assay). The isolated, crude oxide 2a was found to lose rapidly optical activity upon dissolving in chloroform d-1 containing an excess of pyridine d-5. Simultaneous recording of the ^{1}H-NMR spectra and the measurement of optical rotation of this solution, as a function of the time, indicates that racemization of 2a is accompanied by its conversion into the corresponding sulfone-olefin 3 and that the latter reaction is much slower than racemization.



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On the other hand the oxidation of sulfurane 1b with MCPBA is very slow. However, this sulfurane can be very easily converted into the dextrorotatory oxide 2b upon treatment with ruthenium tetraoxide. In contrast to the oxide 2a the spirosulfurane 2b is chemically and optically stable infinitely at room temperature. Its racemization, without traces of the chemical decomposition, occurs with the rate conveniently followed by polarimetry only at temperatures above 80^{o}C. These results clearly indicate that the different mechanisms are responsible for the racemization processes of the spirosulfurane oxides 2a and 2b.

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