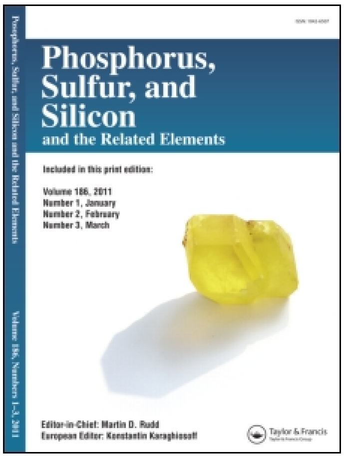

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Józef Drabowicz; Marian Mikolajczyk

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Hypervalent Structures Derived from the Perfluorocumyl and Cumyl Ligands: New Synthetic Procedures, Optical Activity and the Selected Interconversions*

JÓZEF DRABOWICZ and MARIAN MIKOŁAJCZYK

*Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences,
90-363 Łódź, Sienkiewicza 112, Poland*

The aim of this presentation is to report new procedures for the preparation of the selected hypervalent sulfur, selenium and silicon structures derived from the perfluorocumyl or cumyl ligands, including attempts to obtain some of them as optically active species. Stability, reactivity and stereochemical aspects of the selected interconversions of the isolated structures are also briefly described.

Keywords: sulfuranes; selenuranes; selenurane oxide; silane; siliconate; optical activity; hypervalency

INTRUDUCTION

In spite of the fact that the concept of hypervalent molecules was established by Musher [1] in 1969, hypervalency even today is considered as an intriguing phenomenon. Moreover, the unique reactivity of hypervalent compounds makes them useful reagents in organic synthesis.

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* Dedicated to Professor Richard Neidlein on the occasion of his 70th birthday.

Therefore, the preparation of achiral and chiral structures still constitutes the synthetic challenge [2].

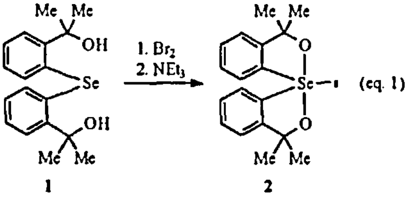
It is well known that the presence of the bidentate ligands derived from perfluorocumyl or cumyl alcohol stabilizes enormously heteroatom hypervalent strucutres having trigonal bipyramidal (TBP) geometry due to: a) five-membered ring annelation, b) gem dialkyl effect on ring closure, c) apical alkoxy-group of highly effective electronegativity. These bidentate ligands have been used to stabilize 10-S-4, [3,4,5,6] 10-S-5 [5], 12-S-6 [7], 10-Si-5 [8] and 10-P-5 [8] species.

As a continuation of our interest in the chemistry of hypervalent organosulfur compounds [9] we would like to present in this communication new procedures for the preparation of hypervalent sulfur, selenium and silicon derivatives derived from these ligands, including attempts to obtain some of them as optically active species.
Stability, reactivity and stereochemical aspects of the selected interconversions of the isolated structures are also briefly discussed.

RESULTS AND DISCUSSION

Synthesis of hypervalent spiroselenuranes and their oxides.

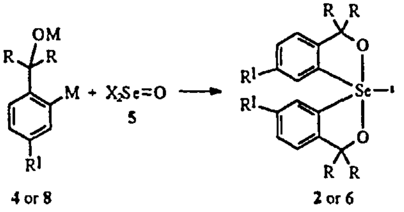
The first acyclic diacyloxyselenuranes or dialkoxyselenuranes have been known since 1914 [10] or 1967 [11], respectively. In spite of this fact the number of synthetic procedures which allow easy preparation of these structures, especially of chiral spirosystems having C_2 symmetry, is rather limited. The only known compound of this type was prepared by Reich [12] by sequential treatment of the tertiary diol 1 with elemental bromine and triethyl amine [eq. 1].



(eq. 1)

Here we would like to report new procedures for the preparation of spiroselenuranes having C_2 symmetry which are based on the reaction of the bidentate nucleophiles derived from 2-bromocumyl or perfluorocumyl alcohols by *ortho*-metallation with selenenous acid derivatives such as seleninyl chloride or dialkyl selenites[16].

The reaction of *ortho*-bromocumyl alcohol **3** with magnesium (after protection of the OH group by treatment with methylmagnesium bromide) gave the bidentate reagent **4** which under went cyclization to the spiroselenurane **2** by treatement with seleninyl chloride or dialkyl selenites. Symmetrical spirosulfurane **6** derived from *p*-*t*-butylperfluorocymyl alcohol **7** was prepared by the reaction of the bidentate nucleophile **8**, generated in situ from the alcohol 7, by the *ortho*-lithiation, with diethyl selenite.

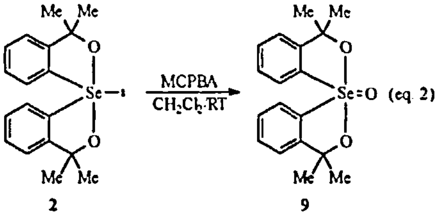


5	Yield [%]	
X	2	6
Cl	trace	
OMe	15	
OEt	73	73

R=Me, R^1=H; M=MgBr for **4** and **2**
R=CF_3, R^1=t-Bu; M=Li for **8** and **6**

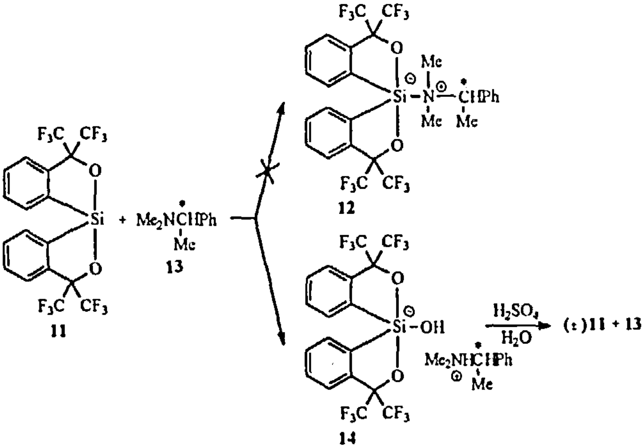
Scheme 1

Treatment of the selenurane **2** with 3 equivalents of meta-chloroperbenzoic acid (MCPBA) in a methylene chloride solution at room temperature for 24 h gave the corresponding selenurane oxide **9** quantitatively (eq. 2). In a sharp contrast to the analogous sulfurane oxide, which is converted very rapidly under such reaction conditions into the corresponding unsaturated sulfone [13], the selenurane oxide **9** formed could be easily isolated and kept without decomposition at room temperature for months. Similar treatment of the perfluoro analogue **6** gave unchanged starting material even after 12 days[16]



An attempt to isolate optically active 3,3,3',3'-tetrakis(trifluoromethyl)-1,1'(3H,3'H)-spirobi[2,1-benzoxasilole].

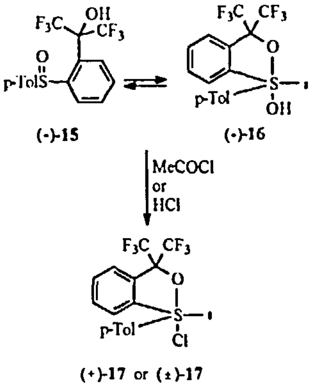
Due to topological properties the silane **11** [14] represents a very interesting example of a chiral structure. Therefore, its isolation in optically active form constitutes the synthetic challenge. Our approach to achieve this goal was based on the formation of the diastereomeric complexes **12** between the silane **11** and (-)-N,N-dimethyl-α-methylbenzyl amine **13** and their decomposition under acidic conditions. However, in contrast to the literature report [15], the reaction of the silane **11** with the amine **13** gave the hydroxysiliconate **14** instead of the expected complex **12**. Decomposition of **14** gave the starting silane **11** having a germinal optical rotation in the 365-589 nm region (Scheme 2)[16].



Scheme 2

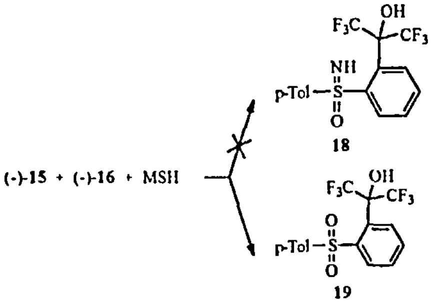
The first optically active hydroxysulfurane detected by ¹⁹F-NMR spectroscopy.

In our recent experiments [16] on the preparation of optically active *p*-tolyl *ortho*-(2-hydroxy-1,2-ditrifluoromethylpropyl)phenyl sulfoxide **15** we have noticed, based on the analysis of the ^{19}F-NMR spectra, that this sulfoxide exists in an equilibrium with the corresponding hydroxysulfurane **16**. This structure constitutes the first example of a hydroxysulfurane ever detected by spectroscopic technique. We have observed that the isolated mixture of the sulfoxide **15** and sulfurane **16** can be easily converted into the corresponding optically active chlorosulfurane **17** upon treatment with acetyl chloride. However, the chlorosulfurane **17** formed in the reaction with gaseous HCl was racemic (Scheme 3).



Scheme 3

It is of interest to note that the reaction of the mixture of **15** and **16** with O-mesitylsulfonylhydroxylamine (MSH) [17] gave instead of the expected optically active sulfoximine **18** the corresponding achiral sulfone **19** (Scheme 4).



Scheme 4

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