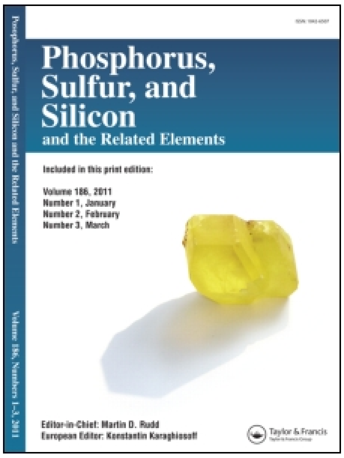

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Reaction of Orthometallated Perfluorocumyl Alkoxides with Sulfinyl Derivatives: Synthetic and Mechanistic Aspects

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Reaction of Orthometallated Perfluorocumyl Alkoxides with Sulfinyl Derivatives: Synthetic and Mechanistic Aspects

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The reaction of 1,1,1,3,3,3-hexafluoro-2-(p-tert-butyl)phenyl-2-propanol with n-butyl-lithium / N,N,N′,N′-tetramethylethylenediamine (TMEDA) provides dilithio-derivative ***1b****, which, upon reaction with thionyl chloride, gave cyclic and acyclic sulfites* ***3*** *and* ***4*** *as precursors of the sulfurane* ***2b*** *with simultaneous formation of cyclic sulfinate* ***5****. This ester was utilized for the preparation of asymmetrical spiro-sulfuranes* ***7*** *or ortho-perfluorocumylaryl(alkyl) sulfoxides* ***8****. Attempts to obtain it as an optically active species are also mentioned.*

Keywords Cyclic sulfinates; cyclic sulfites; ortho-lithiation; ortho-perfluorocumyl aryl(alkyl) sulfoxides

INTRODUCTION

The bidentate ligands derived by ortho-lithiation of perfluorocumyl alcohols are extraordinarily well suited for the preparation of stable hypervalent species.[1] The main advantage is the enhancement of the difference in electronegativity between the central atom and apical ligand, which occurs in structures constructed using these ligands. The enhanced electronegativity differences then strengthen the hypervalent bonds.[2,3] These ligands are also thought to provide extra stabilization by the five-membered-ring effect[4] and the gem-dialkyl (Thorpe–Ingold) effect,[5] favoring the ring-closed hypervalent species.

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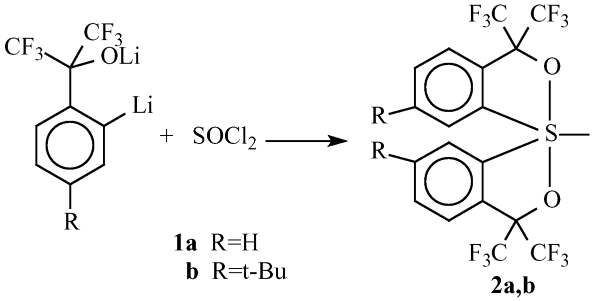
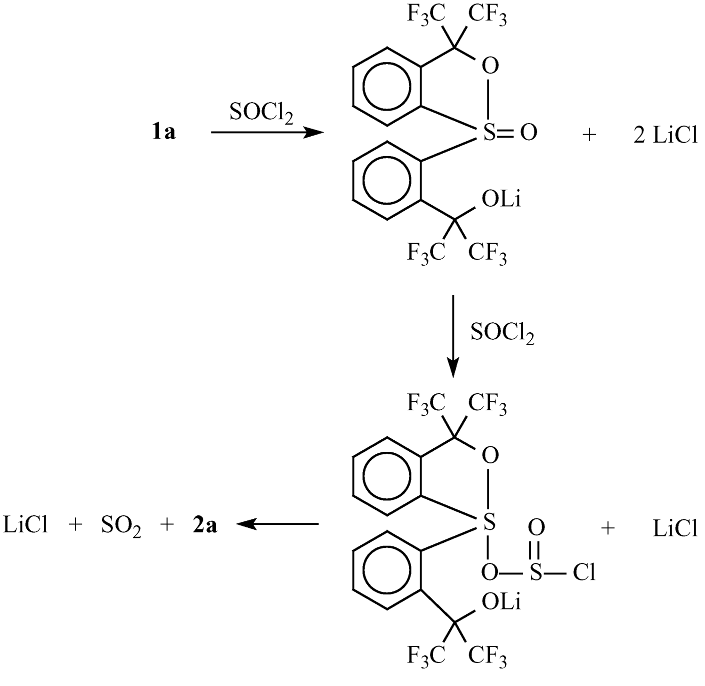
Earlier, the reaction of orthometallated perfluorocumyl alkoxide **1a** with thionyl chloride has been reported[1] to give cleanly spirosulfurane **2a** (Equation 1) in highest yield (62% based on unrecovered perfluorocumyl alcohol) when an excess of thionyl chloride was used at 0°C.



(1)

The requirement of an excess of thionyl chloride suggests the involvement of a mechanism pictured below (Scheme 1).

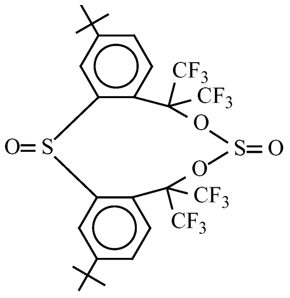


SCHEME 1

In our attempts to extend this procedure for the preparation of the tert-butyl-substituted spirosulfurane **2b**, starting from the dilithioderivative **1b** and thionyl chloride, we have observed a different reaction course with intermediary generation of cyclic and acyclic sulfites as direct precursors of the spirosulfurane **2b** and simultaneous formation of cyclic sulfinate (sultine) that have perfluoroalkoxy residue.

RESULTS AND DISCUSSION

Dilithioderivative **1b** was prepared by the reaction of 1,1,1,3,3,3-hexafluoro-2-(p-tert-butyl)phenyl-2-propanol **2b** in diethyl ether with 2.2 equiv of a hexane solution of n-butyllithium and N,N,N′N′-tetramethylethylenediamine (TMEDA).[1] Using the TMEDA/n-BuLi ratio equal to 0.1, the degree of ortholithiation was found to be above 95% after 24 h (as determined by the level of incorporation of the ortho ring deuterium upon quenching with D_2O). To the prepared solution of lithioderivative **1b** cooled to −70°C a solution of thionyl chloride (1.35 equiv) in hexane was added with stirring. The reaction mixture was allowed to warm up slowly to room temperature and then was kept for 12 h. Then the reaction mixture was hydrolyzed with water, giving a suspension of a solid, which, after removal by filtration, was identified as cyclic sulfite **3**. A semisolid isolated from organic phase was found to be a mixture of sulfurane **2b** and acyclic sulfite **4**, accompanied by nonreacted starting alcohol and a few other fluorine-containing unidentified by-products. The sulfite **4** was converted into the sulfurane



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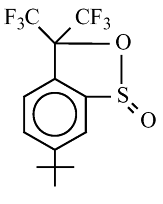

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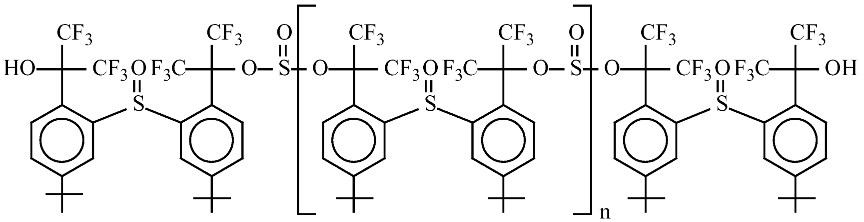

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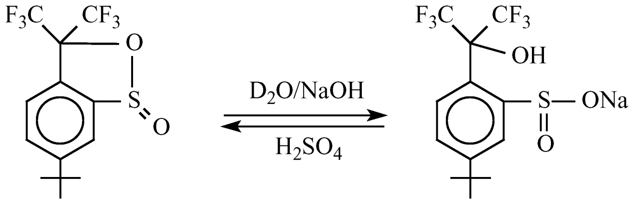
2b upon dissolving in chloroform and refluxing the chloroform solution containing sulfuric acid. The water phase formed during hydrolysis of the reaction mixture was extracted with diethyl ether and made acidic (aq 5% H_2SO_4). This treatment gave an oil, which was found to be cyclic sulfinic ester (sultine) **5**.

It is interesting to note that the sulfine **5** is very easily hydrolyzed under strongly basic conditions to form sodium salt of the perfluorosubstituted 5-tert-betylbenzenesulfinic acid **6**. This salt is immediately reconverted to the starting sulfinate **5** upon acidification. Both reactions (Equation 2) could be very easily followed by ^{19}F NMR spectroscopy.

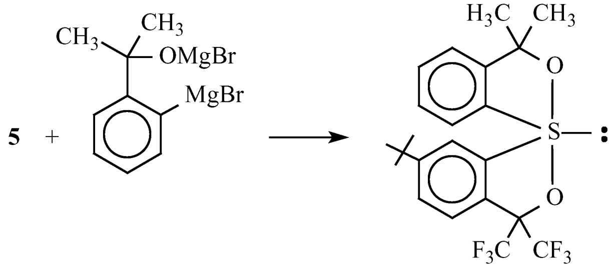
It should also be noted here that acidification of water solution of the salt **6** with optically active acids (d-camphorosulfonic acid and mandelic acid) afforded the sulfinic ester **5**, which has, however, germinal optical rotation.



(2)

5 **6**

Having in hand sultine **5**, we used it as a substrate for the preparation of asymmetrical spriosulfurane **7** (Equation 3) and a few pefluorocumyl alkyl(aryl) sulfoxides **8**.



(3)

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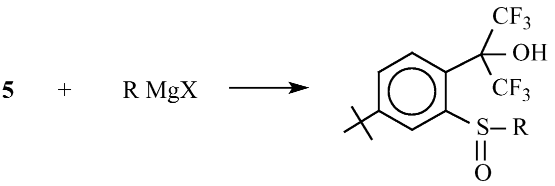

(4)

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