Communication

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$Q^+ = [K(18\text{-crown-}6)]^+,$
$Me_4N^+, (Me_2N)_3S^+$

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Noncyclic [10-*S*-5] Sulfuranide Dioxide Salts with Three S–C Bonds: A New Class of Stable Hypervalent Compounds

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Fluorinated compounds are indispensable in many fields of modern agrochemistry and material sciences, and in the pharmaceutical industry.[1] The importance for practical applications is only one of the reasons for the growing interest in such substances. The unique properties of fluorine, the highest electronegativity and relatively small atomic radius, result in significant changes in the features of substituted compounds when compared to their non-fluorinated analogues, making the fluorinated derivatives extremely attractive for theoretical chemistry. In particular, polyfluoroalkyl substituents increase the stability of electron-rich compounds remarkably due to their powerful electron-withdrawing ability and special conformational features. This fact is often decisive for the modeling and synthesis of unknown molecular types.

During the past several decades, besides syntheses using traditional "building block" strategies, numerous methods have been developed for the direct indroduction of fluorinated substituents into substrate molecules.[2] One of the most useful classes of reagents for nucleophilic polyfluoroalkylation is the silanes R^FSiR_3.[3,4] Introduction of the R^F moiety via these reagents requires catalytic or equimolar amounts of an ionic activator Q^+X^- to derive initially the hypervalent species $[R^FSiR_3X]^-Q^+$, that is, the intermediate responsible for the transfer of the R^F anion. This approach seems to be especially attractive for the introduction of a CF_3 group,[4] because CF_3MgX and CF_3Li are difficult to prepare and unstable (e.g., CF_3Li decomposes even at -100 °C), in contrast to the long-chain analogues.[2] Utilization of trifluoromethyl derivatives of Zn and Cd[2] as well as hemiaminals $CF_3CH(OR')NR_2$[5] is restricted due to their limited reactivity.

Hence, a wide variety of organic and organometallic electrophiles has been trifluoromethylated using CF_3SiMe_3 reagent during the last 13 years.[4] In such a manner, quite a few hypervalent[6] derivatives of P,[7] Bi,[8] Si,[9] S,[10] Te, and I[11] were synthesized. Herein, we report the synthesis, characterization, and selected chemical properties of new unusual hypervalent sulfur derivatives as a logical development of previous investigations dealing with high-coordinated trifluoromethyl-element compounds, carried out in our group.[7,9a]

The treatment of phenyl triflate **1** with a 3-fold excess of CF_3-$SiMe_3$ and 1.1 equiv of anhydrous KF in the presence of a stoichiometric amount of 18-crown-6 at -40 °C in DMF followed by stirring for 20 h at 0 °C gave a brown turbid solution of the hypervalent [10-*S*-5] compound **2a** as an only trifluoromethylated product (Scheme 1). After recrystallization, **2a** was obtained in 50% isolated yield. Similar reactions using anhydrous Me_4NF or $(Me_2N)_3S^+Me_3SiF_2^-$ carried out in THF furnished the corresponding hypervalent derivatives **2b** and **2c** in 79% and 65% isolated yields, respectively (Scheme 1).

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Scheme 1. Synthesis of Compounds **2**

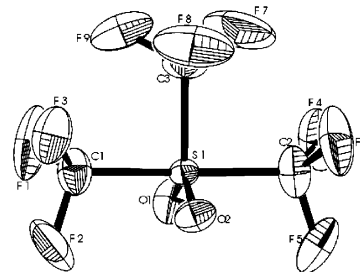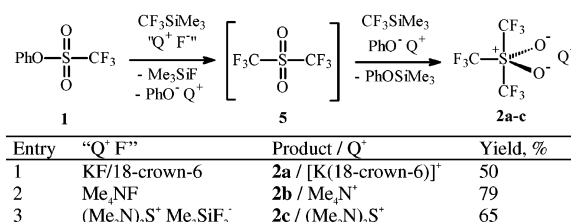| Entry	"Q⁺ F⁻"	Product / Q⁺	Yield, %
1	KF/18-crown-6	**2a** / [K(18-crown-6)]⁺	50
2	Me₄NF	**2b** / Me₄N⁺	79
3	(Me₂N)₃S⁺ Me₃SiF₂⁻	**2c** / (Me₂N)₃S⁺	65

Figure 1. General view of anion of **2a**.

These results are in contrast to alkyl triflate reactions with R^F-$SiMe_3/Me_4NF$, where a nucleophilic attack not on the sulfur, but on the sp³-carbon atom occurred.[12] The salts **2** are analogues to the intermediate postulated for an associative nucleophilic attack at sulfonyl sulfur[13] (C-nucleophilic attack in our case). To the best of our knowledge, such species are very rare. In addition to $[F_3SO_2]^-Cs^+$ (**3**), which was isolated in a matrix and investigated by IR spectroscopy,[13a] only **4** with two alkoxy substituents in axial positions of tricyclic anion has been isolated and characterized unambiguously.[13b,c] Thus, the hypervalent derivative **2a** obtained by us is the first isolated noncyclic [10-*S*-5] sulfuranide dioxide (terminology proposed by Martin[13c]), and generally the first compound of this type possessing three S–C bonds, proven by X-ray analysis (Figure 1).
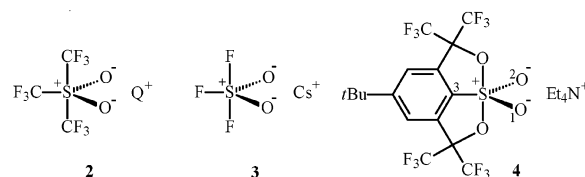
During the course of the formation of compound **2** monitored by ¹⁹F NMR spectroscopy, Me_3SiF, traces of sulfone **5**,[14] and CF_3H as a side product were always present. Probably, the reaction mechanism involves the intermediary formation of $CF_3SO_2CF_3$ (cf., ref 10a) followed by the PhO⁻-mediated trifluoromethylation step, leading to **2** (Scheme 1). As indirect support for this assumption and, generally, for the reaction mechanism, PhOSiMe₃ could be

Table 1. Selected Structural Parameters of Anions of **2a** and **4**

bond	bond length, pm		
	$[(CF_3)_3SO_2]^{-\ a}$	$[(CF_3)_3SO_2]^{-\ b}$	anion of **4**^{c}
S(1)−C(1)	191.3(5)	196.1	
S(1)−C(2)	192.4(6)	196.1	
S(1)−C(3)	190.8(6)	194.1	177.2(3)
S(1)−O(1)	145.7(4)	146.5	141.7(2)
S(1)−O(2)	144.6(3)	146.5	142.6(2)

^{a} X-ray investigation data, this work. ^{b} Calculated data [B3PW91/6-311+G(3d)], this work. ^{c} X-ray investigation data.[13c]

determined by mass spectrometry in the reaction mixture. No evidence was obtained for the formation of any other products, that is, silylated derivative $(CF_3)_3S(O)OSiMe_3$. In the case of $(Me_2N)_3$-$C^+Me_3SiF_2^-$ as the fluoride source, the formation of $(Me_2N)_3C−CF_3$ only ($\delta_F = -63$), along with Me_3SiF and an impurity of CF_3H, was observed in accordance with previous results.[9a,15]

The new compounds **2a,c** are colorless crystals, whereas **2b** was obtained as a grayish powder. **2a,b** are stable in a dry nitrogen atmosphere at ambient temperature for days and can be stored without decomposition at −30 °C for months. **2c** is stable up to 0 °C but decomposes above 10 °C to furnish a brownish oil.

The salts obtained were characterized by elemental analysis, multinuclear NMR spectroscopy, vibrational spectroscopy, and X-ray analysis. Dissolved in common solvents, especially in protic ones, the CF_3-containing sulfuranide dioxides decompose upon proton or deuterium abstraction to afford $CF_3H(D)$ and sulfone **5**; for example, for the 0.03 M solutions of **2a** in Py-d_5 and CD_3CN at 20 °C, the decomposition half times were found to be ca. 13 h and 10 min, respectively, monitored by ^{19}F NMR spectroscopy.

The X-ray investigation of **2a** revealed a slightly distorted trigonal-bipyramidal structure of anion [C(1)−S(1)−C(2) 178.9-(3)°, C(3)−S(1)−C(1) 89.1(3)°, O(2)−S(1)−O(1) 129.2(2)°, O(2)−S(1)−C(3) 114.4(3)°] (Figure 1). The equatorial and axial S−C bonds are almost equal (see Table 1) and considerably longer as compared to the equatorial S(1)−C(3) bond of **4** determined by X-ray analysis.[13c] The C−F bonds of the axial trifluoromethyl groups are somewhat longer than the corresponding ones in equatorial CF_3 − ca. 133 versus 129 pm. The S−O bonds are longer as compared to the respective bond lengths of **4** (Table 1) and are similar to the S−O bonds of dimethyl sulfone.[16] For the related $(CF_3)_2SiMe_3^{-\ 9a}$ and $(CF_3)_2PMe_3^{\ 7a}$ species with the same TBP structure type, longer axial E−CF_3 distances [Si−CF_3 205.6(4), P−CF_3 197.4(4) vs S−C(1)F$_3$ 191.3(5) pm in **2a**] were found.

The calculated [B3PW91/6-311+G(3d)] structural parameters and vibrational frequencies of the $[(CF_3)_3SO_2]^-$ ion are in good agreement with the X-ray analysis data (see Table 1), as well as with the experimental IR and Raman frequencies (cf., Supporting Information).

The structures of compounds **2** in Py-d_5, CD_3CN, and THF-d_8 solutions were investigated by ^{19}F NMR spectroscopy for the temperature interval between −30 and 20 °C. Noteworthy, signals of two different types of CF_3 groups with an integral intensities ratio of 2:1, split by a ^4J (F,F) coupling constant of 16 Hz, were detected even at ambient temperature. This fact indicates the absence of an exchange of axial and equatorial trifluoromethyl substituents at the NMR time scale in the temperature interval investigated. The ^{13}C NMR spectrum of **2a** measured at −30 °C for a THF-d_8 solution also showed resonances of two different types of CF_3 groups, the signal of the equatorial CF_3 group is a first-order quartet of septets, while the resonance of the axial CF_3 groups exhibits a complex $A_3B_3M_3X$ spin system with A = $F_3^{12}C_{ax}$, B = $F_3^{13}C_{ax}$, M = $F_3^{12}C_{eq}$, X = $^{13}C_{ax}$. The experimental spectrum is in excellent agreement with the simulated spectrum (Figure 2).
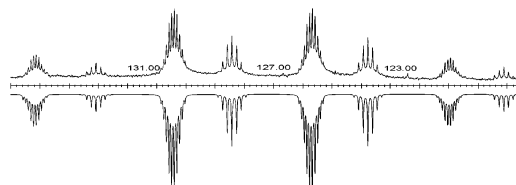
Figure 2. Experimental ^{13}C NMR spectrum of the anion of **2a** recorded at 243 K as compared to the simulated one (lower trace).

The reactivity of salts **2** as a trifluoromethyl anion source was demonstrated by reactions of **2b** with SO_2Cl_2 and Me_3SnCl, and **2a** with benzaldehyde to give CF_3SO_2Cl (^{19}F NMR yield 91%, based on the transfer of one CF_3 group), Me_3SnCF_3 (58%), and 2,2,2-trifluoro-1-phenylethanol (48%), respectively.

In conclusion, the first noncyclic [10-*S*-5] sulfuranide dioxides with three S−C bonds were synthesized and fully characterized. The syntheses of these compounds starting from different sulfur electrophiles, the preparation of similar [10-*S*-5] species bearing other substituents, and the study of chemical properties of newly obtained compounds are underway in our group.

Supporting Information Available: Preparation, analytical data, and spectral parameters of compounds **2**, experimental details of their reactions with electrophiles, and X-ray investigation data of **2a** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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