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Polyfluoroalkyl *N*-(Trifluoromethylsulfonyl)amidosulfites, Number One Stable NH-Containing Amidosulfites

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Abstract—We prepared for the first time NH-containing amidosulfites, polyfluoroalkyl *N*-(trifluoro-methylsulfonyl)amidosulfites $CF_3SO_2NHS(O)OR_F$, by reaction of N-sulfinyl-trifluoromethanesulfonamide $CF_3SO_2N{=}S{=}O$ with alcohols R_FOH. Amidosulfites were formed also in reaction of chlorosulfites $R_FOS(O)Cl$ with trifluoromethanesulfonamide, with its sodium salt, and N-trimethylsilyl derivative.

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Organic derivatives of sulfurous acid, like dialkyl sulfites $(RO)_2S{=}O$, chlorosulfites ROS(O)Cl (intermediates in alcohols chlorination with thionyl chloride), and N-sulfinylamines RN=S=O, are well known and extensively used as very reactive synthons [1–11]. In contrast, amidosulfites ROS(O)NHR' are unstable intermediates whose formation has been only presumed, for instance, in addition reactions of alcohols ROH to substituted N-sulfinylamines R'N=S=O [12, 13]. Only cyclic amidosulfites ROS(O)NR' were stable, first obtained by Etlis et al [14] (and not in [15] as claimed Deyrup and Moyer). Under acid conditions the amidosulfites readily hydrolyzed with SO_2 liberation [14, 16, 17]. As to acyclic amidosulfites, only *N*,*N*-dialkyl amidosulfites $ROS(O)NMe_2$ prepared either by aminolysis of chloro-sulfites ROS(O)Cl [18], or from tetraalkyl diamidosulfites and phenyl isocyanate [19, 20].

$$ROS(O)Cl + R'_2NH \longrightarrow ROS(O)NR'_2$$
$$\xleftarrow{ROH} [(R'_2N)_2S{=}O + PhN{=}C{=}O] \qquad (1)$$

Many among the compounds decomposed on heating with SO_2 elimination and formation of tertiary amines [20]. Amidosulfites containing an NH group were not described.

Among N-functionally substituted *N*-sulfinylamines the best understood are *N*-sulfinylsulfonamides $RSO_2N{=}S{=}O$ formed at treating with thionyl chloride of aromatic [10, 11] or perfluoroalkyl-substituted sulfonamides [12, 13]. *N*-Sulfinylperfluoroalkanesulfonamides $R_FSO_2N{=}S{=}O$ are very reactive. At treating the substances with aromatic aldehydes [21, 22], dimethylformamide [22], and carboxylic acids [23] SO_2 liberated and formed products of general formula $R_FSO_2N{=}Y$ [Y = Ar, $CHNMe_2$, and C(OH)R' respectively]. In the latter case the prototropic tautomerization led to the formation of mixed amides of carboxylic and sulfonic acids $R_FSO_2NHC(O)R'$. With anilines $ArNH_2$ transamination occurred giving amides $R_FSO_2NH_2$ and *N*-sulfinylanilines ArN=S=O [12], and the treatment with alkene oxides gave rise to N-perfluoroalkanesulfonyl-substituted cyclic amidosulfites[24]. Adducts like $R_FSO_2NHS(O)X$ were successfully prepared only with PH- and CH-acids [X = $P(O)(OMe)_2$, $CH(CHCOOEt)_2$] [12]. The attempts to stop the reaction with proton-donor reagents ROH (water, alcohols, acids, amines) at the stage of adducts $R_FSO_2NHS(O)OR$ formation were doomed to failure. The reaction with alcohols gave rise to dialkyl sulfites and perfluoroalkanesulfonamides, and it was stated in [12] that all attempts to isolate the intermediate amidosulfites $R_FSO_2NHS(O)OR$ were unsuccessful.

$$R_FSO_2N{=}S{=}O + R'OH \longrightarrow [R_FSO_2NHS(O)OR']$$
$$\xrightarrow{R'OH} R_FSO_2NH_2 + (R'O)_2S{=}O \qquad (2)$$

R_F = $I(CF_2)_2O(CF_2)_2$, $Cl(CF_2)_2O(CF_2)_2$, $H(CF_2)_2O(CF_2)_2$; R' = CH_3, Me_3C, $H(CF_2)_2CH_2$.

We found that the reaction of equimolar amounts of N-sulfinyltrifluoromethanesulfonamide $CF_3SO_2N{=}S{=}O$ (**I**) and fluorinated alcohols R_FOH **II** led to the formation of *N*-[(polyfluoro-alkoxy)sulfinyl]trifluoromethanesulfonamides **IIIa–IIIc**.

$$\underset{\mathbf{I}}{CF_3SO_2N{=}S{=}O} + \underset{\mathbf{II}}{R_FOH} \longrightarrow \underset{\mathbf{IIIa–IIIc}}{CF_3SO_2NHS(O)OR_F} \quad (3)$$

R_F = $CH_2(CF_2)_2H$ (**a**), $CH_2(CF_2)_4H$ (**b**), CH_2CF_3 (**c**).

The structure of compounds **IIIa–IIIc** was unambiguously proved by the presence in their ^1H NMR spectra of signals belonging to diastereotopic protons of the CH_2 group in the radical R_F that appear as two *AB* quartets (due to coincidence of coupling constants $^2J_{HH}$ and $^3J_{HF}$ for compounds **IIIa** and **IIIb**) or as two doublets of quartets (for compound **IIIc**) in the region 4.3–4.7 ppm with a constant $^2J(H^AH^B)$ ~13 Hz. The observed spectral pattern is caused by the presence in these molecules of a chiral center (sulfur atom). This picture coincides with that described for their structural analogs $CH_3CH_2OS(O)CF_3$ and $CF_3CH_2OS(O)CF_3$ [3, 4, 25].

The relative stability of amidosulfites **III** cannot be directly ascribed to the higher acidity of the polyfluorinated alcohols compared to their nonfluorinated analogs, for the reaction of even more acidic substances, for instance, carboxylic acids, with *N*-sulfinylperfluoroalkanesulfonamides $R_FSO_2N{=}S{=}O$ proceeds with sulfur dioxide elimination and results in *N*-perfluoroalkanesulfonamides R_FSO_2NHCOR [23].

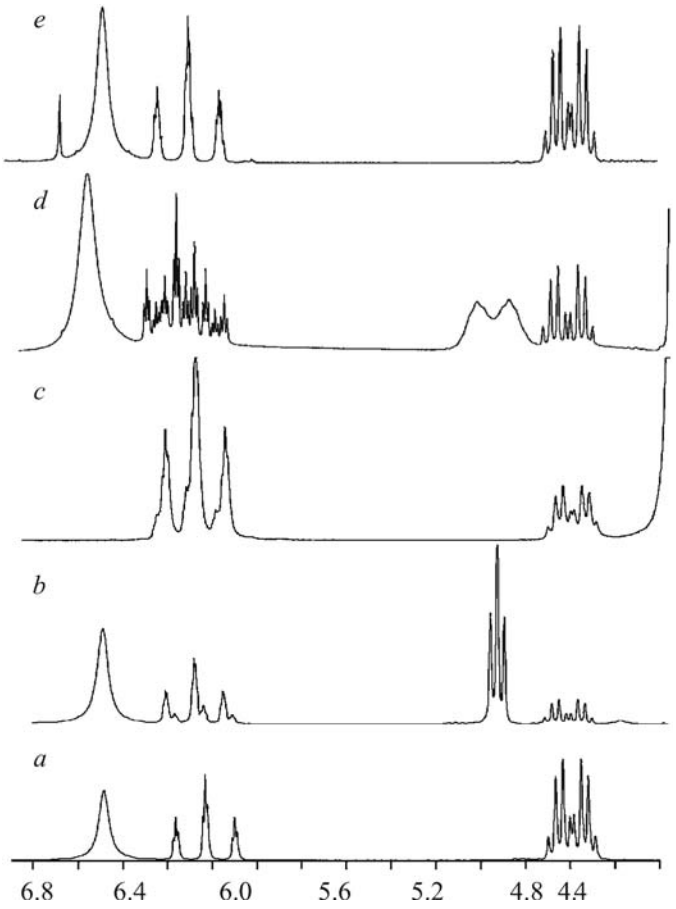
We also investigated the alternative procedures for preparation of amidosulfites **III** by reaction (4) of N-substituted trifluoromethanesulfonamide CF_3SO_2NHR' (**IV**) with chlorosulfites of polyfluorinated alcohols $R_FOS(O)Cl$ (**V**) or by a three-component reaction involving trifluoromethanesulfonamide **IVa**, thionyl chloride, and polyfluorinated alcohols **II**.

In all cases on mixing the components at room temperature or at slight heating, as in reaction (3), amidosulfites **III** were obtained. Their formation was

$$\underset{\mathbf{IVa–IVc}}{CF_3SO_2NHR'} + \underset{\mathbf{Va–Vc}}{R_FOS(O)Cl} \longrightarrow \underset{\mathbf{IIIa–IIIc}}{R_FOS(O)NHSO_2CF_3}$$

$$\longleftarrow \underset{\mathbf{IVa}}{CF_3SO_2NH_2} + SOCl_2 + \underset{\mathbf{IIa–IIc}}{R_FOH} \quad (4)$$

R' = H (**a**), $SiMe_3$ (**b**), Na (**c**); R_F = $CH_2(CF_2)_2H$ (**a**), $CH_2(CF_2)_4H$ (**b**), CH_2CF_3 (**c**).



^1H NMR spectra of reaction mixtures in CD_3CN: (*a*) (**I**) + (**IIa**); (*b*) (**IVa**) + (**Va**); (*c*) CF_3SO_2NHNa + (**Va**); (*d*) $CF_3SO_2NHSiMe_3$ + (**Va**); (*e*) (**IIa**) + (**IVa**) + $SOCl_2$.

confirmed by the presence in the ^1H NMR spectra of the same multiplet of the diastereotopic protons of the CH_2 group (see the figure), and also by comparison with the published data on the chemical shifts and coupling constants in the ^1H, ^{13}C, and ^{19}F NMR spectra of the initial compounds and probable reaction products, like $R_FOS(O)Cl$ [5, 9] and $(R_FO)_2S{=}O$ [12].

Compounds **III** are readily hydrolyzed giving trifluoromethanesulfonamide **IVa**, alcohol R_FOH, and SO_2.

EXPERIMENTAL

NMR spectra were registered on a spectrometer Bruker DPX-400 [operating frequencies 400 (^1H), 100 (^{13}C), and 376 MHz (^{19}F)], internal reference HMDS, chemical shifts are reported with respect to TMS (^1H, ^{13}C) and CCl_3F (^{19}F).

Chlorosulfites of polyfluorinated alcohols **V** were obtained by procedure [9]. All reactions were carried out under an argon atmosphere.

3-[(Chlorosulfinyl)oxy]-1,1,2,2-tetrafluoropropane (Va). Yield 75%, bp 22–23°C (2 mm Hg), n_D^{19} 1.3860 {bp 61°C (40 mm Hg), n_D^{20} 1.3704 [5]}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.56 d.t (1H, H^A, $^2J_{HH}$ 11.8, $^3J_{HF}$ 11.8 Hz), 4.81 d.t (1H, H^B, $^2J_{HH}$ 11.8, $^3J_{HF}$ 11.8 Hz), 5.92 t (1H, CHF_2, $^2J_{HF}$ 52.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 59.20 t (CH_2, $^2J_{CF}$ 30.0 Hz), 109.15 t.t (CHF_2, $^1J_{CF}$ 250.7, $^2J_{CF}$ 36.6 Hz), 113.48 t.t (CF_2, $^1J_{CF}$ 250.6, $^2J_{CF}$ 28.8 Hz). ^{19}F NMR spectrum (CD_3CN), δ, ppm: –122.41 s (2F, CF_2), –136.83 d.d (2F, CHF_2, *J* 53.4, 12.05 Hz).

5-[(Chlorosulfinyl)oxy]-1,1,2,2,3,3,4,4-octafluoropentane (Vb). Yield 87%, bp 40–42°C (2 mm Hg), n_D^{18} 1.3680 {bp 64°C (5 mm Hg), n_D^{20} 1.3630 [9], bp 98.5–99°C (50 mm Hg), n_D^{20} 1.3580 [5]}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.86–4.89 m (2H, CH_2), 6.06 t (1H, CHF_2, $^3J_{HF}$ 51.96 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 59.14 t (CH_2, $^2J_{CF}$ 27.5 Hz), 107.59 t.t (CHF_2, $^1J_{CF}$ 254.4, $^2J_{CF}$ 31.3 Hz), 110.08 t.t (CF_2, $^1J_{CF}$ 264.14, $^2J_{CF}$ 30.1 Hz), 110.71 t.t (CF_2, $^1J_{CF}$ 264.45, $^2J_{CF}$ 33.3 Hz), 113.87 t.t (CF_2, $^1J_{CF}$ 258.9, $^2J_{CF}$ 31.3 Hz). ^{19}F NMR spectrum (CD_3CN), δ, ppm: –137.31 d (2F, CHF_2, $^2J_{HF}$ 52.2 Hz), –129.83 s (2F, $CHF_2C\underline{F}_2$), –125.10 s (2F, CH_2CF_2), –119.67 quintet (2F, $CF_2C\underline{F}_2CF_2$, $^3J_{FF}$ 11.8 Hz).

2-[(Chlorosulfinyl)oxy]-1,1,1-trifluoroethane (Vc). Yield 40%, bp 92–96°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.65 d (2H, CH_2, $^2J_{HF}$ 67.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 59.84 q (CH_2, $^2J_{CF}$ 38.8 Hz), 122.12 q (CF_3, $^1J_{CF}$ 277.3 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –73.88 t (3F, CF_3CH_2, $^3J_{HF}$ 8.0 Hz).

***N*-[(2,2,3,3-Tetrafluoropropoxy)sulfinyl]trifluoromethanesulfonamide (IIIa)**. *a*. To 0.195 g (1 mmol) of compound **I** was added at vigorous stirring while cooling with ice (5°C) 0.132 g (1 mmol) of 2,2,3,3-tetrafluoropropanol (**IIa**), the mixture was stirred at room temperature for 6 h, left standing at this temperature for 16 h, and then it was evaporated to dryness. Yield 0.46 g (70%), colorless crystals that sublime with decomposition at 70°C. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 4.41 d.t (1H, H^A, $^2J_{HH}$ 13.1, $^3J_{HF}$ 13.1 Hz), 4.53 d.t (1H, H^B, $^2J_{HH}$ 13.2, $^3J_{HF}$ 13.2 Hz), 6.17 t.t (CHF_2, $^2J_{HF}$ 52.3, $^3J_{HF}$ 4.6 Hz), 6.62 br.s (1H, NH). ^{13}C NMR spectrum (CD_3CN + $CDCl_3$), δ, ppm: 58.38 t (CH_2, $^2J_{CF}$ 29.1 Hz), 109.74 t.t (CHF_2, $^1J_{CF}$ 250.3, $^2J_{CF}$ 35.3 Hz), 114.56 t.t (CF_2, $^1J_{CF}$ 250.5, $^2J_{CF}$ 27.6 Hz), 120.17 q (CF_3SO_2, $^1J_{CF}$ 319.4 Hz). ^{19}F NMR spectrum (CD_3CN + $CDCl_3$), δ, ppm: –80.41 s (3F, CF_3SO_2), –125.38 m (2F, CF_2), –139.36 d (2F, CHF_2, $^2J_{HF}$ 52.2 Hz). Found, %: C 13.94; H 1.09; N 4.01. $C_4H_4F_7N_1O_4S_2$. Calculated, %: C 14.68; H 1.23; N 4.28.

b. To a solution of 0.745 g (5 mmol) of compound **IVa** in 2 ml of CD_3CN was added at stirring and cooling to 5°C 1.07 g (5 mmol) of sulfinylchloride **Va**. Signals in the ^{1}H NMR spectrum of the reaction mixture after stirring for 1.5 h at room temperature coincided with the signals of amidosulfite **IIIa** prepared by procedure *a* (see the figure, *b*).

c. To 1.11 g (5 mmol) of *N*-trimethylsilyltrifluoromethanesulfonamidea (**IVb**) was added at stirring 1.07 g (5 mmol) of sulfinylchloride **Va**. Signals in the ^{1}H NMR spectrum of the reaction mixture after stirring for 1 h at room temperature coincided with the signals of amidosulfite **IIIa** prepared by procedure *a* (see the figure, *c*).

d. A mixture of 0.40 g (2.3 mmol) of trifluoromethanesulfonamide sodium salt (**IVc**), 0.56 g (2.6 mmol) of sulfinylchloride **Va**, and 2 ml of CD_3CN was stirred at room temperature for 1 h, then heated at 80°C for 10 min. Signals in the ^{1}H NMR spectrum of the reaction mixture registered after cooling coincided with the signals of amidosulfite **IIIa** prepared by procedure *a* (see the figure, *d*).

e. A mixture of 0.149 g (1 mmol) of trifluoromethanesulfonamide (**IVa**), 0.132 g (1 mmol) of 2,2,3,3-tetrafluoropropanol (**IIa**), and 0.118 g (1 mmol) of thionyl chloride in 2 ml of benzene was stirred at room temperature for 4 h. On evaporating benzene in a vacuum in the ^{1}H NMR spectrum of the residue signals were observed coinciding with the signals of amidosulfite **IIIa** prepared by procedure *a* (see the figure, *e*).

***N*-[(2,2,3,3,4,4,5,5-Octafluoropentyloxy)sulfinyl]-trifluoromethanesulfonamide (IIIb)** was prepared similarly to compound **IIIa** by procedure *a*. ^{1}H NMR spectrum (CD_3CN + $CDCl_3$), δ, ppm: 4.63 d.t (1H, H^A, $^2J_{HH}$ 13.6, $^3J_{HF}$ 13.6 Hz), 4.50 d.t (1H, H^B, $^2J_{HH}$ 13.3, $^3J_{HF}$ 13.3 Hz), 6.34 t.t (CHF_2, $^2J_{HF}$ 51.5, $^3J_{HF}$ 6.7 Hz), 6.53 br.s (1H, NH). ^{13}C NMR spectrum (CD_3CN + $CDCl_3$), δ, ppm: 58.88 t (CH_2, $^2J_{CF}$ 26.8 Hz), 109.03 t.t (C^5F_2, $^1J_{CF}$ 253.2, $^2J_{CF}$ 31.1 Hz), 115.59 t.t (C^2F_2, $^1J_{CF}$ 256.7, $^2J_{CF}$ 31.3 Hz), 120.78 q (CF_3SO_2, $^1J_{CF}$ 319.4 Hz). We failed to identify the signals of atoms C^3 and C^4 because of their low intensity. ^{19}F NMR spectrum (CD_3CN), δ, ppm: –80.52 sC (3F, CF_3SO_2), –120.20 quintet (2F, C^3F_2, $^3J_{FF}$ 12.3 Hz), –125.47 s (2F, C^2F_2), –130.48 s (2F, C^4F_2), –138.74 d (2F, CHF_2, $^2J_{HF}$ 51.6 Hz).

***N*-[(2,2,2-Trifluoroethoxy)sulfinyl]trifluoromethanesulfonamide (IIIc)** was prepared similarly to compound **IIIa** by procedure *a*. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 4.48 d.q (1H, H^A, $^2J_{HH}$ 12.8, $^3J_{HF}$ 8.4 Hz), 4.56 d.q (1H, H^B, $^2J_{HH}$ 12.8, $^3J_{HF}$ 8.4 Hz), 6.63 br.s (1H, NH). ^{13}C NMR spectrum (CD_3CN), δ, ppm: 59.61 q (CH_2, $^2J_{CF}$ 37.3 Hz), 120.91 q (CF_3SO_2, $^1J_{CF}$ 318.5 Hz), 124.23 q ($\underline{C}F_3CH_2$, $^1J_{CF}$ 276.7 Hz). ^{19}F NMR spectrum (CD_3CN), δ, ppm: –80.65 s (1F, CF_3SO_2), –74.78 t (1F, CF_3CH_2, $^3J_{HF}$ 8.6 Hz).

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