Syntheses of Cyclic and Acyclic Bis(perfluoroalkylthio)nitronium Salts

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$(F_3CS)_3N$ (**1**) is oxidized quantitatively by AsF_5 to the first bis(perfluoroalkylthio)nitronium salt $(F_3CS)_2N^+AsF_6^-$ (**2**). Addition of halide ions (F^-, Cl^-, Br^-, I^-) to the cation of **2** destroys the S−N−S chain. $(F_2CSCl)_2$ undergoes with ammonia a cyclization reaction to $\overline{S-CF_2-CF_2-S-N}-H$ (**3**), which can be derivatized with F_3CSCl or $(F_2CSCl)_2$ to $\overline{S-CF_2-CF_2-S-N}-SCF_3$ (**3a**) and $(\overline{S-CF_2-CF_2-S-N}-SCF_2-)_2$ (**3b**), respectively. Oxidation of **3a** with AsF_5 yields $(\overline{S-CF_2-CF_2-S-N}^+AsF_6^-$ (**4**) and byproducts, which suggest formation of a $(\mathbf{3a})^{+\bullet}$ radical cation as an intermediate in this reaction. Pure **4** is accessible by reaction of **3** with AsF_5 in 54% yield. The chemical and spectroscopic properties of the new species are discussed.

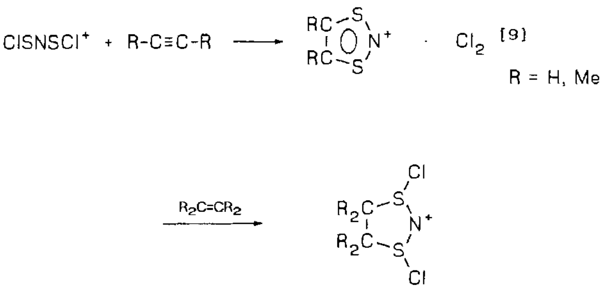
The first bis(halogenthio)nitronium ion was prepared and identified by Glemser and coworkers in 1969 by the reaction of NSF_3 with BCl_3[1] (eq. 1). More efficient procedures for the preparation of this cation were later found with a variety of anions like $AlCl_4^-$[2,4,5], $SbCl_6^-$[2,4], AsF_6^-, SbF_6^-[3,5,6], $FeCl_4^-$[4,5], $F_3CSO_3^-$, and $SeCl_6^{2-}$[6]. The only bis(bromothio)nitronium ion was generated by the addition of Br_2 to the $S{=}N{=}S^+$ cation[7] (eq. 2). Similar ions with one perfluoroalkyl group instead of a halogen atom are accessible by addition of R_fS-Cl [$R_f = F_3C$, $(F_3C)_2C{=}N$] to the triple bond of the $N{\equiv}S^+$ cation but no further data are given[3].

The chemistry of the $ClSNSCl^+$ ion comprehends dehalogenation with $SnCl_2$[8] and [2 + 3] cycloadditions of alkynes and alkenes[9] (eqs. 2−4).

$$4\ NSF_3 + 6\ BCl_3 \longrightarrow 2\ (ClS)_2N^+\ BCl_4^- + N_2 + 3\ Cl_2 + 4\ BF_3\ ^{[1]} \qquad (1)$$

$$S{=}N{=}S^+\ AsF_6^- \underset{SnCl_2/-SnCl_2X_2}{\overset{X_2}{\rightleftarrows}} XSNSX^+\ AsF_6^-\ ^{[7,8]} \qquad (2)$$

$X = Cl, Br$



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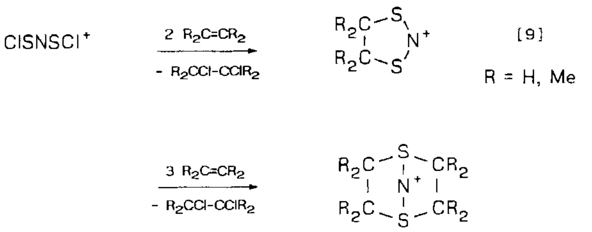

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Results and Discussion

We have recently shown that F_3CS-substituted methanes are oxidized by AsF_5 to yield stable carbenium ions[10]. This type of reaction is not restricted to (trifluoromethylthio)carbons but applies also to nitrogen analogs. Thus, $(F_3CS)_3N$ (**1**)[11], which must be purified from all contaminations having donor abilities by treatment with BCl_3 before use, is oxidized by AsF_5 quantitatively to the bis(perfluoroalkylthio)nitronium salt $(F_3CS)_2N^+AsF_6^-$ (**2**) (eq. 5). Salt **2** shows very good solubility in SO_2, a bright yellow color, and melts without decomposition at 170°C. Its structure is assumed to be *cis/cis* as it is found in its halide analogs $XSNSX^+$[1,5]. A *cis/trans* orientation of the F_3C groups is not likely, due to a single singlet in the ^{19}F-NMR spectrum recorded at ambient temperature. Halide ions (F^-, Cl^-, Br^-, I^-) react fast with the cation of **2** without generation of $(F_3CS)_2N-X$ or $F_3CS-N{=}S(X)CF_3$ but with formation of decomposition products (N_2, F_3CSSCF_3, F_3CSCl, Br_2, I_2). The stability of the molecules therefore is questionable, just as that of their halogenated analogs $ClS-N{=}SCl(X)$ ($X = F, Cl$)[5].

In order to synthesize the smallest possible cyclic perfluoroalkyl-SNS cation $S{=}CF_2$[12] was treated with $SN^+AsF_6^-$[13] (eq. 6). Under the conditions chosen, no [2 + 2] cycloaddition took place. This is probably due to an excessively high activation barrier, not to the instability of the strained ring itself as a comparison with similar carbenium ions indicates[10].

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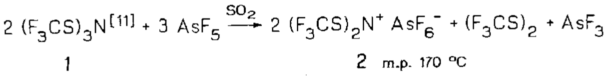
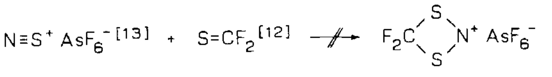
The synthesis of an analogous five-membered cation by a symmetry-allowed [2 + 3] cycloaddition of $F_2C=CF_2$ to the $S=N=S^+$ cation was tried unsuccessfully by Shriver[9,14]. This is in contrast to the facile addition of $H_2C=CH_2$ to the same cation[15] (eq. 7) and is attributed to the poor donor abilities of tetrafluoroethene[9].



$$\underset{1}{2\ (F_3CS)_3N^{[11]}} + 3\ AsF_5 \xrightarrow{SO_2} \underset{2\ \text{m.p. } 170\ °C}{2\ (F_3CS)_2N^+AsF_6^-} + (F_3CS)_2 + AsF_3 \quad (5)$$



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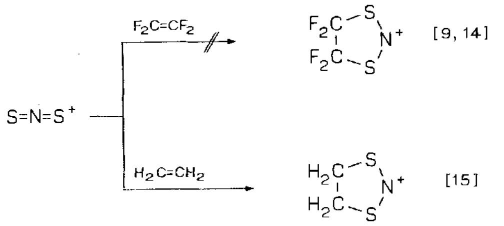

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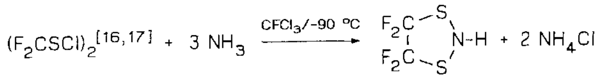

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(8)

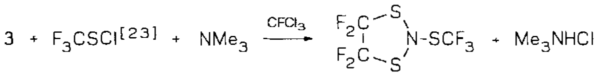
In a different approach to that cation we have synthesized $S-CF_2-CF_2-S-N-H$ (**3**) from $(-CF_2-S-Cl)_2$[16,17] and NH_3 (eq. 8). *N*-Substituted derivatives of **3** have been prepared earlier from the same precursor and silylated amines[18].

Compound **3** shows two spectroscopic properties, which differ substantially from those of its acyclic analog $(F_3CS)_2NH$[11,19]. The N−H stretching frequency is reduced by 104 wavenumbers to 3320 cm^{-1} in **3**. Secondly, the $^1J(H^{15}N)$ value is reduced in the latter from 99.1[20,21] to 73.5 Hz. Both features indicate a change in nitrogen hybridization from sp^2 in $(F_3CS)_2NH$ to sp^3 in **3**. This interpretation has been confirmed by a combination of gas diffraction, X-ray diffraction, and ab initio study[22], which reveals that the most stable conformation of **3** is the "envelope" type with one sulfur bent out of an essentially planar C_2SN fragment. The nitrogen atom in **3** has a pyramidal environment with the N−H bond in axial position.

Unlike $S-CF_2-CF_2-S-N-Si(CH_3)_3$ which failed to react with S_2Cl_2[18], the proton in **3** can be replaced by F_3CSCl[23] or $(F_2CSCl)_2$ to form **3a**, **b** (eqs. 9, 10). The result is a rare exception to the general rule that silylated amines react under milder conditions giving higher yields than amines themselves. Compounds **3a** and **3b** are stable at ambient temperatures, decompose near 100°C, and like **1** do not form adducts with BCl_3[11]. When **3a** is treated with AsF_5, $S-CF_2-CF_2-S-N^+AsF_6^-$ (**4**) is formed in ca. 50% yield (determined by ^{19}F-NMR spectroscopy) (eq. 11). The second major product **5** is likely to have the displayed structure, based on NMR spectroscopy and its chemistry.

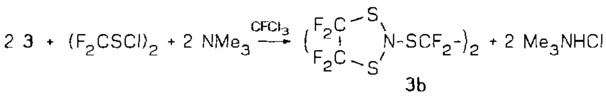
The branching of this reaction can be understood by assuming a single-electron oxidation as the initial step. The formed radical cation {**3a**$^{+\bullet}$} can then split an exocyclic N−S bond homolytically to produce an $F_3CS^\bullet$ radical and the cation of **4**. The dication of **5** results from radical combination of two {**3a**$^{+\bullet}$} ions via two ring-membered sulfur atoms (eq. 12). An acyclic structure of **5** like $(F_3C-SNS^+-CF_2-CF_2-S-)_2$ is ruled out, since it needs a $^1J(CF_3)$ coupling constant in the range of 322−330 Hz as it is found with **2** and other comparable cations[10,24,25]. The additional production of **2** in this reaction shows that other and more complicated steps may follow the initial formation of a radical cation.

The yield of **4** can be improved to some extent by prolonged warming of the dry crude product to 80°C, whereby **5** is slowly converted to **4** and $(F_3CS)_2$ which is identified by its gas IR spectrum (eq. 13). This procedure does not afford a pure material but confirms the assumed structure of **5**.



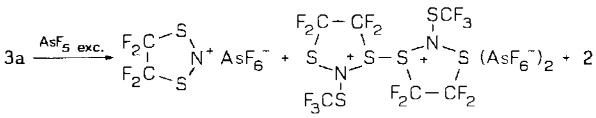
3a

(9)



3b

(10)



4 5

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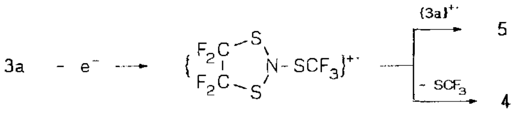

(12)

$$5 \xrightarrow{100\ °C} 2\ 4 + (F_3CS)_2 \quad (13)$$

$$3 + 3\ AsF_5 \xrightarrow{SO_2} 4 + HAsF_6 + AsF_3 \quad (14)$$

Pure **4** is finally accessible by the reaction of **3** with AsF_5 (eq. 14). The crystalline crude product of this reaction appears clean in color, had the exact calculated weight, and gives a good elemental analysis. The ^{19}F-NMR analysis however shows only a 70% conversion to **4** together with two impurities, the smaller of them containing a C_2F_5

group, the other appearing as a polymer due to the broadness of its signals. Recrystallization from $SO_2/SOCl_2$ gives pure **4** in 54% recovered yield. Compound **4** has a pale yellow color, dissolves less well than **2** in SO_2 and melts at 210°C (dec.).

The ^{19}F- and ^{13}C-NMR data are compiled in Table 1. The chemical shifts of the ^{19}F and ^{13}C nuclei are found in their typical ranges and show no effect on ionization. The $^{1}J(C,F)$ coupling in **2** however is increased drastically by 12.9 Hz compared to its neutral precursor **1**, considered the total range of coupling constants in F_3CS derivatives is 307–330 Hz. In the case of **4** a similar trend is found, but exact numbers cannot be given due to the complexity of the AA'BB'X-type spectrum. The missing of a $^{3}J(F,F)$ coupling between the adjacent CF_2 groups in **5** is not in contradiction to the proposed structure since ^{3}J couplings occasionally are very small like in **3b**, where only the ^{13}C satellites of the CF_2' groups are split into triplets.

The new title species are readily accessible as shown above. In contrast to their halogenated analogs, where only ^{14}N- and ^{15}N-NMR spectroscopy are of some use for their investigation in solution[27], they contain spin 1/2 nuclei of higher abundance and sensitivity. This allows an easier and more detailed study of the chemistry of this very electrophilic cationic species. The ongoing interest in sulfur-nitrogen chemistry[28] is likely to make use of the redox behavior as well as cycloaddition and electrophilic substitution potential of the new materials.

Experimental

All experiments were carried out in oven-dried glassware with strict exclusion of moisture. Volatile materials and solvents were transferred in vacuo, solids in an argon glove box. – Raman: Bruker FRA 106 connected to IFS 66, Nd YAG laser, λ = 1064 nm. – IR: Bruker IFS 66 or 85. – NMR: Bruker WP 80 or AM 400. Covalent compounds were recorded as 20–40% solutions in $CDCl_3$ with $CFCl_3$ as internal ^{19}F standard, salts as 15–30% solutions in SO_2 with the inner-tube method and external lock and standard (^{19}F) or without lock (^{13}C). Chemical shifts were referenced to TMS. The ^{15}N-NMR spectrum was acquired at natural abundance by a DEPT experiment using NH_4NO_3 in D_2O as external standard. – MS: Varian MAT CH7A, 70 eV. – Elemental analyses: Carlo Erba 1106 elemental analyzer, Mikroanalytisches

Tab. 1. ^{19}F- and ^{13}C-NMR data of cyclic and acyclic perfluoroalkylthio molecules and cations

Compound	^{19}F-NMR data [ppm, Hz]			^{13}C-NMR data [ppm, Hz]		
No.	CF_3	CF_2	CF_2'	CF_3	CF_2	CF_2'
$(F_3CS)_3N$	-52.1 (s)[a]	–	–	130.0 (q)	–	–
1	$^{6}J(F,F) = 3.6$[b]	–	–	$^{6}J(C,F) = 315.7$	–	–
$(F_3CS)_2N^+$	-54.6 (s)	–	–	125.2 (q)	–	–
2	$^{6}J(F,F) = 0.4$[b]	–	–	$^{1}J(C,F) = 328.6$	–	–
$(-F_2CSCl)_2$	–	-89.5 (s)	–	–	122.8 (m)	–
$\overline{SCF_2CF_2SN}H$	–	-97.7 (d)	–	–	132.4 (t, t)	–
3	–	$^{4}J(F,H) = 1.8$	–	–	$^{1}J(C,F)$ □ 299.0	–
	–	$^{3}J(F,F) = 3.9$[b]	–	–	$^{2}J(C,F)$ □ 26.0	–
$\overline{SCF_2CF_2SN}SCF_3$	-53.3 (quint)	-97.3 (s)	–	126.64 (q)	132.4 (t, t)	–
3a	$^{6}J(F,F) = 0.6$	($\Delta\nu 1/2$[c] = 2)	–	$^{1}J(C,F) = 310.7$	$^{1}J(C,F)$ □ 302.1	–
	–	$^{3}J(F,F) = 3$[b]	–	–	$^{2}J(C,F) = 26.1$	–
$(\overline{SCF_2CF_2SN}SCF_2'{-})_2$	–	-96.95 (s)	-97.4 (s)	–	132.2 (t, t)	123.1 (t, t)
3b	–	($\Delta\nu 1/2 = 3.5$)	($\Delta\nu 1/2 = 1.8$)	–	$^{1}J(C,F) = 302.2$	$^{1}J(C,F) = 294.4$
	–	–	$^{3}J(F,F)$ □ 10[b]	–	$^{2}J(C,F) = 26.2$	$^{2}J(C,F) = 34.3$
$(\overline{SCF_2CF_2SN})^+$	–	-97.8 (s)	–	–	125.6 (m)	–
4						
$(\overline{CF_2CF_2SNS}^+{-})_2$	-45.85 (t, t)	-87.7 (q)[d]	-91.4 (s)[d]	128.45 (q)	123.9 (t, t)[d]	121.7 (t, t)[d]
F_3CS	$^{6}J(F,F) = 5.3$	$^{6}J(F,F) = 5.3$	($\Delta\nu 1/2 = 15$)	$^{1}J(C,F) = 314.8$	$^{1}J(C,F) = 313.3$	$^{1}J(C,F) = 297.5$
5	$^{6}J(F,F) = 2.0$	–	–	–	$^{2}J(C,F) = 39.6$	$^{2}J(C,F)$ □ 32.7

[a] Data are in agreement with literature values[11,26]. – [b] Derived from ^{13}C satellites. – [c] $\Delta\nu_{1/2}$: peak widths at half height. – [d] Not assigned.

Laboratorium Beller, Göttingen (**2**). – The compounds NH_3 (Messer Griesheim), ND_3 (Merck & Co., Can.), and BCl_3 (J. T. Baker, Ned.) were used as received. $CFCl_3$ (Hoechst AG) and SO_2 (Messer Griesheim) were dried over P_4O_{10}, Me_3N was dried over KOH before use. AsF_5 was prepared from As (Preussag) and F_2 (Solvay, Ger.); **1**[11], $S{=}CF_2$[12], $N{\equiv}S^+AsF_6^-$[13], $(F_2CSCl)_2$[16,17], and F_3CSCl[23] were prepared according to literature procedures.

Bis(trifluoromethylthio)nitronium Hexafluoroarsenate (**2**): Into a 200-ml Carius tube equipped with a teflon-stemmed Young valve 8.5 g (26.8 mmol) of **1**, 7.1 g (42 mmol) of AsF_5, and ca. 30 g of SO_2 were condensed at −196°C. After 20 h at room temp. a clear solution with an intense yellow color developed. After the volatile products had been pumped off [AsF_5, AsF_3, $(F_3CS)_2$, and SO_2], 10.9 g of **2** remained in quantitative yield as a bright yellow microcrystalline solid, m.p. 170°C. – IR: $\tilde{\nu}$ = 1264 cm^{-1} s, 1244 vs, 1214 s, 1112 vs, 1036 vs, 757 s, 713 s, 699 vs, 675 vs, 561 w, 473 m. – Raman: $\tilde{\nu}$ = 1127 cm^{-1} vw, 1029 w, 769 s, 723 s, 681 s, 578 w, 557 w, 475 m, 369 w, 341 w, 254 vs, 178 m, 114 vs, 83 m. – MS, *m/z* (%): 216 (14), 163 (10), 151 (71), 132 (14), 113 (12), 94 (11), 78 (34), 69 (100), 63 (13), 46 (62). – $C_2AsF_{12}NS_2$ (405.1): calcd. As 18.50, N 3.46, S 15.8; found As 18.6, N 3.46, S 16.3.

Attempted Preparation of $F_2\overline{C-S-N-S}^+AsF_6^-$: Into a Carius tube, loaded with 3.6 g (15 mmol) of $N{\equiv}S^+AsF_6^-$, 1.3 g (16 mmol) of $S{=}CF_2$ and ca. 15 g of SO_2 were condensed at −196°C, and the mixture was allowed to warm up. The clear solution was kept for 5 h at ambient temp. after which time no change of color was observed. After the volatile products had been pumped off 3.6 g of unchanged $N{\equiv}S^+AsF_6^-$ was recovered.

4,4,5,5-Tetrafluoro-1,3,2-dithiazolidine (**3**): 6.8 g (29 mmol) of $(F_2CSCl)_2$ and 126 g of $CFCl_3$ were condensed into a 300-ml Carius tube at −196°C, then warmed up to −90°C by means of an ethanol cooling bath giving a clear greenish solution. The Carius tube was connected to a vacuum line of ca. 250 ml volume by means of a flexible Teflon hose. From a lecture bottle ca. 500 mbar of NH_3 were filled into the line, then the valve of the Carius tube was opened. This procedure was repeated interruptedly by vigorous shaking of the tube. When a total of 1.6 g (94 mmol) had been added, the produced slurry was allowed to warm to room temp. Vacuum fractionation into −78, −196, and −196°C traps yielded 4.4 g (85%) of **3** as colorless crystals in the −78°C trap, m.p. −35°C, vapor pressure at 0°C: 6 mbar. In the Carius tube remained 3.7 g of a colored residue. The $CFCl_3$ was resuable for similar experiments. – IR (gas): $\tilde{\nu}$ = 3320 cm^{-1} m, 1229 vs, 1138 vs, 1112 s, 975 s, 923 m, 901 m, 793 s, 648 m. – ^1H NMR: δ = 4.8 (s, $\Delta\nu_{1/2}$ = 23 Hz), $^1J(H,^{15}N)$ = 73.5 Hz. – ^{15}N NMR (CD_2Cl_2): δ = 12.7 (s). – MS, *m/z* (%): 179 (100) [M^+], 100 (35), 97 (33), 96 (33), 82 (34), 69 (20), 64 (22), 63 (46), 47 (70), 46 (52), 31 (25). – $C_2HF_4NS_2$ (179.1): calcd. C 13.41, H 0.56, N 7.82, S 35.77; found C 13.3, H 0.6, N 8.0, S 35.1.

[D]-3: From $(F_2CSCl)_2$ and ND_3 the *N*-deuterated **3** was obtained in a similar procedure and yield. – IR (gas): Same as **3**, except: $\tilde{\nu}$ = 3320→2464 cm^{-1} m, 901→778 m, 648→603 m.

4,4,5,5-Tetrafluoro-2-(trifluoromethylthio)-1,3,2-dithiazolidine (**3a**): To a solution of 6.2 g (34.6 mmol) of **3** and 4.7 g (34.4 mmol) of F_3CSCl in ca. 100 g of $CFCl_3$ in a Carius tube kept at −80°C, Me_3N was added in small portions (ca. 0.1 g). After each addition the mixture was shaken. After a total of 2.1 g (36 mmol) of Me_3N had been added the tube was allowed to warm to ambient temp. Vacuum fractionation into −78, −196, and −196°C traps yielded 9.1 g of crude **3a** in the −78°C trap and 3.8 g of nonvolatile material. For further purification the crude **3a** was treated with 1.5 g (13 mmol) of BCl_3 at room temp. and then objected again to vacuum fractionation (−78, −196°C). 1.0 g of nonvolatile products was left behind, and 8.1 g (84%) of solid **3a** was obtained in the dry-ice trap. Compound **3a** contained a trace of **1** (ca. 1%, determined by ^{19}F-NMR analysis) as a result of scrambling, but was not further purified, m.p. −54°C (ca. 99% pure), vapor pressure at 24°C: 18 mbar. – IR (gas): $\tilde{\nu}$ = 1230 cm^{-1} s, 1190 s, 1176 s, 1144 s, 1129 vs, 970 s, 923 m, 763 w, 638 w, 481 w. – MS, *m/z* (%): 279 [M^+] (54), 178 (84), 147 (11), 110 (14), 100 (13), 82 (36), 78 (85), 69 (100), 64 (20), 63 (28), 46 (49). – $C_3F_7NS_2$ (279.2): calcd. C 12.91, N 5.02; found C 12.7, N 5.5.

2,2'-[(1,1,2,2-Tetrafluoro-1,2-ethanediyl)bis(thio)]bis[4,4,5,5-tetrafluoro-1,3,2-dithiazolidine] (**3b**): 4.4 g (24.6 mmol) of **3**, 2.9 g (12.3 mmol) of $(F_2CSCl)_2$, and 1.5 g (25 mmol) of Me_3N were allowed to react as described for **3a**. After the volatile products had been pumped off 8.8 g of a solid was left behind, which was treated for 16 h with 3.4 g (29 mmol) of BCl_3 at room temp. without solvent. BCl_3 was absorbed almost quantitatively yielding 12.1 g of nonvolatile material from which 5.7 g was transferred to a 100-ml flask for sublimation at 10^{-2} mbar/60°C giving 1.1 g of crude **3b**. Recrystallization from 5 g of CH_2Cl_2 by cooling a filtered solution of **3b** slowly to −50°C produced 0.8 g (26%) of colorless, crystalline **3b**, m.p. 56°C. – IR (KBr pellet): $\tilde{\nu}$ = 1400 cm^{-1} vw, 1216 s, 1207 s, 1158 s, 1147 s, 1127 s, 1099 vs, 1021 vw, 960 s, 918 s, 860 vw, 833 m, 816 m, 635 w, 606 w, 576 w, 466 w, 421 w. – Raman: $\tilde{\nu}$ = 1232 cm^{-1} vw, 1080 vw, 813 w, 784 w, 675 w, 638 m, 565 w, 508 vs, 463 w, 430 m, 392 w, 360 w, 324 w, 290 w, 243 w, 226 m, 198 m, 88 m. – MS, *m/z* (%): 506 [M^+] (12), 210 (9), 178 (100), 164 (25), 82 (16), 78 (64), 64 (35), 63 (18), 46 (31). – $C_6F_{12}N_2S_6$ (520.5): calcd. C 13.85, N 5.38, S 36.97; found C 13.7, N 5.0, S 36.2.

4,4,5,5-Tetrafluoro-1,3,2-dithiazolidinium Hexafluoroarsenate (**4**) *and 4,4,4',4',5,5,5',5'-Octafluoro-2,2'-bis(trifluoromethylthio)-1,1'-bi-1,3,2-dithiazolidin-1-ium Bis(hexafluoroarsenate)* (**5**) *from* **3a**: The reaction of 3.14 g (11.3 mmol) of **3a** with 3.1 g (18 mmol) of AsF_5 according to the procedure used for the preparation of **2** (with the exception of a shorter reaction time = 3 h) yielded 4.76 g of an orange nonvolatile solid. Heating of the dry crude product to 85°C for 6 d caused slow release of $(F_3CS)_2$, which was identified by its gas IR spectrum. The ^{19}F-NMR spectrum of the heated material showed besides the broad AsF_6^- quartet at δ = −58 and traces of impurities only two singlets at δ = −53.0 (**2**) and −97.3 (**4**). – A similar NMR-tube experiment starting with 0.12 g of **3a** showed besides a broad signal centered at δ = −58 (AsF_6^-) and singlets for **2** and **4** three major signals attributed to **5**, corresponding to 25 mol-% relative to **4** (see Table 1).

4,4,5,5-Tetrafluoro-1,3,2-dithiazolidinium Hexafluoroarsenate (**4**) *from* **3**: Into a Carius tube 1.74 g (9.7 mmol) of **3**, 5.1 g (30 mmol) of AsF_5, and ca. 20 g of SO_2 were condensed at −196°C. When warming up the mixture, an intense red color occurred, which faded to yellow after 2 h at 0°C. Removal of the volatile products (SO_2, AsF_3, $HAsF_6$) left 3.57 g of a yellow microcrystalline solid. Its ^{19}F-NMR spectrum showed besides a broad signal at δ = −59 (AsF_6^-) signals at −82.4 (t, *J* = 2.6 Hz, 7%), −87.3 to −89.3 (m, broad, 18%), −95.6 (q, *J* = 2.6 Hz, 5%) and 97.7 (s, 70%). For recrystallization 2.50 g of the crude product was placed in one limb of a two-limbed glass vessel and dissolved in ca. 17 g of SO_2. The solution was cooled to dry-ice temp. without the formation of a precipitate. Then 6 g of $SOCl_2$ was condensed onto the solution kept at −78°C for 4 h. After warming of the solution to ambient temp. – avoiding any shaking of the vessel – a red solution over a yellow precipitate was obtained. The solution was carefully transferred to the empty limb of the vessel, then concentrated to dryness by evaporation of the solvent. The yellow crystalline precipitate amounted to 1.35 g and proved to be pure **4**, yield 54%, m.p. 210°C (dec.) – IR (nujol): $\tilde{\nu}$ = 1233 cm^{-1} s, 1225 s, 1205 s, 1158 s, 1025 s, 922 m, 868 m, 753 m, 721 vs, 698 vs, 622 w, 614 w, 585 w, 515 w. – Raman: $\tilde{\nu}$ = 1226 cm^{-1} vw, 1029 vw, 924 vw, 868 vw, 752 vs, 684 s, 623 w, 581 vw, 572 vw, 512 m, 400 vw, 379 vs, 323 vw, 269 w, 235 vw, 82 m. – MS, *m/z* (%): 178 (59), 164 (28), 151 (100), 148 (36), 132 (44), 129 (14), 113 (62), 100 (30), 95 (17), 94 (20), 82 (45), 78 (72), 69 (21), 64 (51), 63 (44), 50 (12), 48 (48), 47 (43), 46 (46). – $C_2AsF_{10}NS_2$ (367.1): calcd. C 6.54, N 3.83, S 17.47; found C 6.4, N 4.0, S 17.6.

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