experiment by reacting 15.98 g (100 mmol) of pyrazabole with 21.65 g (200 mmol) of 1,3-propanedithiol (bath temperature 180 °C; reaction time 8 days). The material is recrystallized from toluene to yield 19.2 g (52%) of the desired product, mp 202-207 °C.

NMR data (solution in $CDCl_3$): $\delta(^1H)$ = 8.45 (d, 2 H), 6.55 (t, 1 H), 2.77 (unresolved t, 4 H), 1.97 (p, 2 H); $\delta(^{11}B)$ = 4.5; $\delta(^{13}C)$(proton decoupled) = 138.2, 107.0, 24.7.

Registry No. I (R = CH_3; *n* = 2), 77172-65-7; I (R = CH_3; *n* = 3), 76356-55-3; II (R = R′ = C_3H_7; X = Y = H), 77189-78-7; II (R = R′ = C_4H_9; X = Y = H), 14695-77-3; II (R = R′ = X = Y = H), 16998-91-7; II (R = R′ = C_6H_5; X = Y = H), 6431-90-9; II (R = R′ = OC_6H_5; X = Y = H), 16243-64-4; II (R = C_6H_5; R′ = SC_2H_5; X = Y = H), 77210-78-7; II (R = C_6H_5; R′ = $C_3H_3N_2$; X = Y = H), 77255-14-2; II (R = R′ = SC_2H_5; X = Y = H), 77189-77-6; II (R = R′ = $C_3H_3N_2$; X = Y = H), 16243-58-6; II (R = R′ = NC_4H_4; X = Y = H), 77210-77-6; II (R = R′ = X = H; Y = Cl), 18601-55-3; II (R = R′ = H; X = Y = Br), 18601-63-3; III, 77189-81-2; IV (*n* = 2), 77189-80-1; IV (*n* = 3), 77189-79-8; 1,3-dimethyl-2-(4-chloropyrazol-1-yl)-1,3,2-diazaboracyclohexane, 77172-66-8; 1,3-dimethyl-2-(3,4,5-tribromopyrazol-1-yl)-1,3,2-diazaboracyclohexane, 77172-67-9; pyrazole, 288-13-1; $B(SCH_3)_3$, 997-49-9; $B(SC_2H_5)_3$, 998-26-5; $C_6H_5B(SC_2H_5)_2$, 1870-68-4; *N*,*N*′-dimethyl-1,2-diaminoethane, 110-70-3; *N*,*N*′-dimethyl-1,3-diaminopropane, 111-33-1; pyrrole, 109-97-7; 1,2-ethanedithiol, 540-63-6; 1,3-propanedithiol, 109-80-8.

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N-Substituted (*F*-Tetramethylene)sulfimides from Reactions of Lithium (*F*-Tetramethylene)sulfimide

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Lithium (*F*-tetramethylene)sulfimide, $CF_2CF_2CF_2CF_2S{=}NLi$, is a moderately stable precursor to several new (*F*-tetramethylene)sulfimides. With $ClSi(CH_3)_3$, $ClC(O)CF_3$, ClCN, FSO_2CF_3, and FSO_2Cl, $CF_2CF_2CF_2CF_2S{=}NSi(CH_3)_3$, $CF_2CF_2CF_2CF_2S{=}NC({=}O)CF_3$, $CF_2CF_2CF_2CF_2S{=}NCN$, $CF_2CF_2CF_2CF_2S{=}NSO_2CF_3$, and $CF_2CF_2CF_2CF_2S{=}NSO_2Cl$ form. The bis[(*F*-tetramethylene)sulfimide], $CF_2CF_2CF_2CF_2S{=}NC({=}O)N{=}SCF_2CF_2CF_2CF_2$, is formed with $COCl_2$. The reaction of $FC({=}O)C({=}O)F$ with $CF_2CF_2CF_2CF_2S{=}NLi$ and $(CF_3)_2S{=}NLi$ results in the formation of $CF_2CF_2CF_2CF_2S{=}NC({=}O)C({=}O)N{=}SCF_2CF_2CF_2CF_2$ and $(CF_3)_2S{=}NC({=}O)C({=}O)N{=}S(CF_3)_2$, respectively. While $CF_2CF_2CF_2CF_2S{=}NSi(CH_3)_3$, $CF_2CF_2CF_2CF_2S{=}NC({=}O)CF_3$, and $CF_2CF_2CF_2CF_2S{=}NSO_2Cl$ are nonvolatile liquids at 25 °C, the remainder of the N-substituted (*F*-tetramethylene)sulfimides are solids. With $(CF_3)_2C{=}NF$, $CF_2CF_2CF_2CF_2S{=}NLi$ gives the diazirine $(CF_3)_2C{-}N{=}N$.

Introduction

SF_4 reacts with NH_3 even at low temperature (−95 °C), giving rise to the formation of tetrasulfur tetrafluoride as the principal product.[2] By raising the reaction temperature to 25 °C, the formation of tetrasulfur tetranitride decreases with the concomitant increase in the formation of thiazyl fluoride. However, the isolation of the sulfimide, $SF_2{=}NH$, has been unsuccessful because of its instability with respect to NSF and HF at room temperature. However, its *N*-halogeno derivatives like $SF_2{=}NCl$[3] and $SF_2{=}NBr$[4] are well characterized.

Recently, it has been reported that bis(trifluoromethyl)sulfimide, $(CF_3)_2S{=}NH$, forms when $(CF_3)_2SF_2$ is treated with NH_3 in the presence of benzylamine.[5] Furthermore, the lithium salt $(CF_3)_2S{=}NLi$, which is formed by the reaction of $(CF_3)_2S{=}NH$ and *n*-BuLi, has been shown to be a valuable precursor to a large number of new compounds and interesting reactions.[6]

In an earlier paper, we demonstrated that $CF_2CF_2CF_2CF_2SF_2$ forms (*F*-tetramethylene)sulfimide, $CF_2CF_2CF_2CF_2S{=}NH$, in good yields when treated with $LiNH_2$ in the presence of NH_3.[7]

Now we will describe a modified method for the preparation of $(CF_3)_2S{=}NLi$, the first preparation of $CF_2CF_2CF_2CF_2S{=}NLi$, and the reactions of $CF_2CF_2CF_2CF_2S{=}NLi$ to produce several new derivatives which contain the $CF_2CF_2CF_2CF_2S{=}N$ moiety.

Results and Discussion

It is known that the preparation of $LiN{=}S(CF_3)_2$ from the metalation of $HN{=}S(CF_3)_2$ is very difficult compared with that of $LiN{=}C(CF_3)_2$ because of the occurrence of side reactions.[6] A reddish black solid forms invariably unless $(CF_3)_2S{=}NH$ is added in very small aliquots to the *n*-BuLi–hexane solution. (*F*-Tetramethylene)sulfimide, $CF_2CF_2CF_2CF_2S{=}NH$, is converted to its lithium salt by reaction with *n*-BuLi–hexane solution in a similar manner. However, we have found that, if anhydrous ether is used as the solvent, when the sulfimide is added to *n*-BuLi–hexane solution, the metalation reaction proceeds very smoothly and the lithium salt is stabilized.

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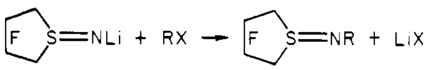
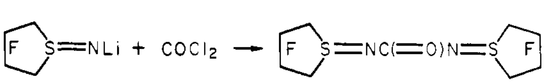
The lithium salts of $CF_2CF_2CF_2CF_2S{=}NH$ and $(CF_3)_2S{=}NH$, which are prepared by adding the corresponding sulfimides to the solution of *n*-BuLi–hexane–ether mixture, followed by removing the solvents under dynamic vacuum, are orange and yellow gelatinous compounds, respectively. These lithium salts can be stored for few days at room temperature without decomposition. These salts are likely solvated with ether because ether is always found as one component among the products when the salts are reacted with substrates susceptible to nucleophilic attack.

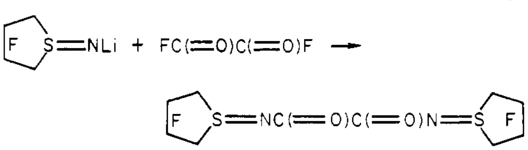
Thus, $CF_2CF_2CF_2CF_2S{=}NLi$ gives new compounds with $ClSi(CH_3)_3$, $ClC({=}O)CF_3$, $ClCN$, FSO_2CF_3, and FSO_2Cl as shown in eq 1.


(1)

R = $Si(CH_3)_3$ (66%), $C({=}O)CF_3$ (65%), CN (13%), SO_2CF_3 (22%), SO_2Cl (45%)

With $COCl_2$ and $FC({=}O)C({=}O)F$, bis[(*F*-tetramethylene)sulfimides], $CF_2CF_2CF_2CF_2S{=}NC({=}O)N{=}SCF_2CF_2CF_2CF_2$ and $CF_2CF_2CF_2CF_2S{=}NC({=}O)C({=}O)N{=}SCF_2CF_2CF_2CF_2$ are formed, respectively (eq 2 and 3).


(34%) (2)


(45%) (3)

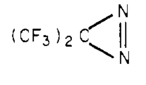
Because the disubstituted product of $(CF_3)_2N{=}S$ with oxalyl $(CF_3)_2S{=}NC({=}O)C({=}O)N{=}S(CF_3)_2$ had not been synthesized previously, the reaction of $(CF_3)_2S{=}NLi$ with $FC({=}O)C({=}O)F$ was conducted (eq 4). In the infrared spectra

$$(CF_3)_2S{=}NLi + FC({=}O)C({=}O)F \rightarrow (CF_3)_2S{=}NC({=}O)C({=}O)N{=}S(CF_3)_2 \quad (39\%) \qquad (4)$$

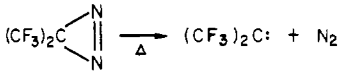
of these disubstituted compounds, very intense bands are observed due to $\nu_{C=O}$ at 1621 cm^{-1} for $CF_2CF_2CF_2CF_2S{=}NC({=}O)N{=}SCF_2CF_2CF_2CF_2$, at 1610–1625 cm^{-1} for $CF_2CF_2CF_2CF_2S{=}NC({=}O)C({=}O)N{=}SCF_2CF_2CF_2CF_2$, and at 1617 cm^{-1} for $(CF_3)_2S{=}NC({=}O)C({=}O)N{=}S(CF_3)_2$. Characteristically, in the mass spectrum of $(CF_3)_2S{=}NC({=}O)C({=}O)N{=}S(CF_3)_2$, the base peak was *m/e* 212 $[(CF_3)_2S{=}NC({=}O)]^+$ which may be ascribed to the easy scission of the C—C bond of $C({=}O)C({=}O)$. Other ions observed were *m/e* 454 $[M]^+$, 355 $[M - CF_3]^+$, 255 $[M - CF_3SCF_3]^+$, 170 $[CF_3SCF_3]^+$, 124 $[CF_2SNC({=}O)]^+$ and 69 $[CF_3]^+$. In the case of $CF_2CF_2CF_2CF_2S{=}NC({=}O)C({=}O){=}SCF_2CF_2CF_2CF_2$, the molecular ion was not observed, and the base peak was *m/e* 232 $[C_4F_8S]^+$. Other major ions were *m/e* 316 $[CF_2CF_2CF_2CF_2S{=}NC({=}O)C({=}O)]^+$, 274 $[CF_2CF_2CF_2CF_2S{=}NC({=}O)]^+$, 150 $[C_3F_6]^+$, and 100 $[C_2F_4]^+$.

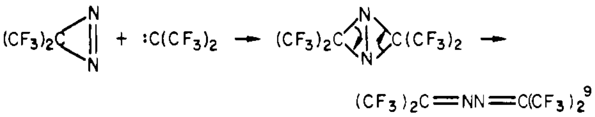
With the exception of $CF_2CF_2CF_2CF_2S{=}NSi(CH_3)_3$, $CF_2CF_2CF_2CF_2S{=}NC({=}O)CF_3$, and $CF_2CF_2CF_2CF_2S{=}NSO_2Cl$, the new derivatives of (*F*-tetramethylene)sulfimide synthesized in the present investigation are solids at 25 °C. Purification of $CF_2CF_2CF_2CF_2S{=}NSi(CH_3)_3$ was very difficult due to its highly hygroscopic character. The use of gas chromatography to remove small quantities of the impurity $CF_2CF_2CF_2CF_2S{=}NH$ always resulted in decomposition of the silane. Therefore, $CF_2CF_2CF_2CF_2S{=}NSi(CH_3)_3$ was only characterized by means of ^{19}F and ^1H NMR and mass spectroscopy.

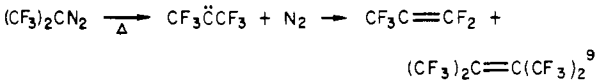
The reaction of $CF_2CF_2CF_2CF_2S{=}NLi$ with $FN{=}C(CF_3)_2$ was conducted in an effort to obtain $CF_2CF_2CF_2CF_2S{=}NN{=}C(CF_3)_2$. However, instead, a gaseous compound was produced as well as almost an equal quantity of $CF_2CF_2CF_2CF_2S$. The new gas showed a singlet at ϕ −68.3 in the ^{19}F NMR spectrum. Its mass spectrum showed *m/e* 231 $[C_5F_9]^+$ as the highest *m/e*, in addition to such ions assigned as *m/e* 212 $[C_5F_8]^+$, 188 $[C_3F_8]^+$, 178 $[C_3F_6N_2]^+$, 169 $[C_3F_7]^+$, 150 $[C_3F_6]^+$, and 100 $[C_2F_4]^+$. The pyrolysis of this compound in a sealed vessel was found to give $(CF_3)_2C{=}N{-}N{=}C(CF_3)_2$[8] in an almost quantitative yield. The formation of this dimer substantiates the suggestion that this gaseous compound is bis(trifluoromethyl)diazirine



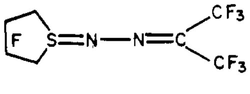
Krespan et. al have reported the formation of bis(trifluoromethyl)diazirine (colorless gas, bp −12 °C) and its isomer bis(trifluoromethyl)diazomethane, $(CF_3)_2CN_2$ (pale yellow liquid, bp 13 °C), from the oxidation of bis(trifluoromethyl)diaziridine and bis(trifluoromethyl)hydrazone with lead tetraacetate, respectively.[9] On pyrolysis, the diazirine decomposes to hexafluoroacetone azine, $(CF_3)_2C{=}NN{=}C(CF_3)_2$, while the diazomethane gives largely hexafluoropropene, viz., eq 5–7. On the basis of these observations, the gaseous compound was assumed to be bis(trifluoromethyl)diazirine.


(5)


(6)


(7)

A plausible explanation of the reaction of $CF_2CF_2CF_2CF_2S{=}NLi$ with $FN{=}C(CF_3)_2$ would appear to involve the intermediacy of



followed by the scission of the S=N bond, viz., eq 8.

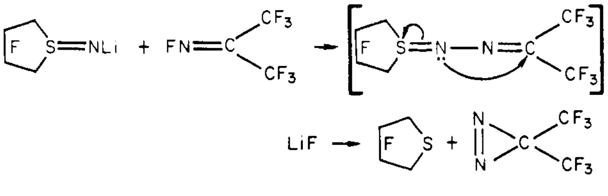

(8)

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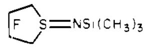
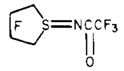
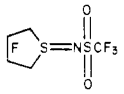
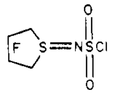
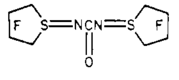
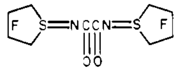
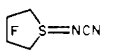
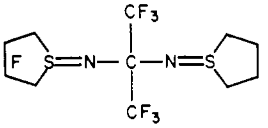
Table I. ^{19}F and ^{1}H NMR Spectra of $\overline{CF_2CF_2CF_2CF_2S}$=N-Containing Compounds

compd	α-CF$_2$	β-CF$_2$	others
	−117.8 (complex) (1)	$\left\{\begin{matrix}-129.5\\-132.4\end{matrix}\right.$ (1) J_{AB} = 258.9 Hz	δ(CH$_3$) 0.17
	$\left\{\begin{matrix}-102.7\\-105.4\end{matrix}\right.$ (4) J_{AB} = 207.3 Hz	$\left\{\begin{matrix}-128.0\\-130.5\end{matrix}\right.$ (4) J_{AB} = 262.7 Hz	φ(CF$_3$) −74.1 (s) (3)
	−105.6 (complex) (4)	$\left\{\begin{matrix}-128.3\\-131.4\end{matrix}\right.$ (4) J_{AB} = 262.3 Hz	φ(CF$_3$) −78.2 (complex) (3)
	−104.0 (complex) (1)	$\left\{\begin{matrix}-127.9\\-131.1\end{matrix}\right.$ (1) J_{AB} = 266.1 Hz	
	$\left\{\begin{matrix}-106.3\\-108.5\end{matrix}\right.$ (1) J_{AB} = 209.5 Hz	$\left\{\begin{matrix}-128.4\\-131.2\end{matrix}\right.$ (1) J_{AB} = 260.3 Hz	
	$\left\{\begin{matrix}-107.2\\-110.3\end{matrix}\right.$ (1) J_{AB} = 214.9 Hz	$\left\{\begin{matrix}-129.6\\-133.0\end{matrix}\right.$ (1) J_{AB} = 257.3 Hz	
	$\left\{\begin{matrix}-106.1\\-107.4\end{matrix}\right.$ (1) J_{AB} = 213.8 Hz	$\left\{\begin{matrix}-129.8\\-132.9\end{matrix}\right.$ (1) J_{AB} = 264.9 Hz	

The reaction of $\overline{CF_2CF_2CF_2CF_2S}$=NLi with $\overline{CF_2CF_2CF_2CF_2S}$=NCF((CF$_3$)$_2$) failed to give



No reaction took place in this case. The reaction of $\overline{CF_2CF_2CF_2CF_2S}$=NCF((CF$_3$)$_2$) with LiNS((CF$_3$)$_2$) also fails.[7]

The ^{19}F NMR spectra of these $\overline{CF_2CF_2CF_2CF_2S}$=N-substituted compounds such as $\overline{CF_2CF_2CF_2CF_2S}$=NC(=O)CF$_3$, $\overline{CF_2CF_2CF_2CF_2S}$=NCN, $\overline{CF_2CF_2CF_2CF_2S}$=NC(=O)N=$\overline{SCF_2CF_2CF_2CF_2}$, and $\overline{CF_2CF_2CF_2CF_2S}$=NC(=O)C(=O)N=$\overline{SCF_2CF_2CF_2CF_2}$ showed typically two sets of AB patterns due to the coupling of geminal fluorines both at α- and β-carbon of the ring. However, for $\overline{CF_2CF_2CF_2CF_2S}$=NSi(CH$_3$)$_3$, $\overline{CF_2CF_2CF_2CF_2S}$=NSO$_2CF_3$, and $\overline{CF_2CF_2CF_2CF_2S}$=NSO$_2$Cl, resonance bands assigned to geminal fluorines at the α-carbons are observed as a complex peak. Their coupling constants are 207–215 Hz for α-CF$_2$, and 258–266 Hz for β-CF$_2$, respectively.

Experimental Section

Materials. Literature methods were used to prepare $\overline{CF_2CF_2CF_2CF_2S}$=NH,[7] (CF$_3$)$_2$S=NH,[5] FSO$_2CF_3$, FSO$_2$Cl, FN=(CCF$_3$)$_2$[10] and $\overline{CF_2CF_2CF_2CF_2S}$=NCF(CF$_3$)$_2$.[7] ClSi(CH$_3$)$_3$ (PCR), ClC(=O)CF$_3$(PCR), ClCN (K and K Lab), COCl$_2$ (Matheson), and FC(=O)C(=O)F (Pflatz and Bauer) were used as received without further purification.

General Procedures. Most gases and volatile liquids were handled in a conventional Pyrex glass vacuum apparatus equipped with a Heise Bourdon tube gauge. All starting materials and products were purified by trap-to-trap distillation and gas chromatography. Infrared spectra were recorded with a Perkin-Elmer 599B spectrometer with use of a 10-cm cell equipped with KBr windows. ^{19}F NMR spectra were obtained on a Varian HA-100 spectrometer and JEOL FX-90Q spectrometer by using CCl$_3$F as an internal standard. ^{1}H NMR spectra were obtained on a Varian EM-360 spectrometer with tetramethylsilane as an internal standard. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E spectrometer operating at an ionization potential of 17 eV. Elemental analyses were performed by Beller Laboratories, Göttingen, Germany, or at the University of Idaho.

Preparation of $\overline{CF_2CF_2CF_2CF_2S}$=NLi. Typically, into a 100-mL flask fitted with a Kontes Teflon stopcock were charged 0.91 mL of 2.2 M *n*-BuLi-hexane solution (equivalent to 2.0 mmol of *n*-BuLi) and 2 mL of dry ether. Onto this mixture was condensed 2.05 mmol of $\overline{CF_2CF_2CF_2CF_2S}$=NH at −196 °C, and the flask was gradually warmed to −78 °C while being agitated on a mechanical shaker until all of the solid had disappeared. After 1 h, the reaction mixture was warmed to 25 °C, and solvents and unreacted imide were removed under dynamic vacuum to give the orange gelatinous compound $\overline{CF_2CF_2CF_2CF_2S}$=NLi.

Preparation of (CF$_3$)$_2$S=NLi. Into a 100-mL reaction vessel which contained 0.55 mL of 2.2 M *n*-BuLi-hexane solution (equivalent to 1.2 mmol of *n*-BuLi) and 2 mL dry ether was condensed 1.4 mmol of (CF$_3$)$_2$S=NH at −196 °C. While being shaken, the reaction mixture was gradually warmed to 25 °C during a 15-min period. The solvents and unreacted imide were removed to leave the yellow gelatinous compound (CF$_3$)$_2$S=NLi.

Preparation of $\overline{CF_2CF_2CF_2CF_2S}$=NSi(CH$_3$)$_3$. In a reaction vessel which contained 2.05 mmol of $\overline{CF_2CF_2CF_2CF_2S}$=NLi, 2.5 mmol of (CH$_3$)$_3$SiCl, and 10 mmol of *i*-C$_5$H$_{12}$ were condensed at −196 °C. The use of *i*-C$_5$H$_{12}$ as a heat sink was found to improve the product yield slightly. The reaction mixture was warmed gradually to −78 °C over 5 h and then kept at 0 °C. After 14 h, the products were separated by trap-to-trap distillation. The compound (0.43 g) collected at −40 °C was found to be $\overline{CF_2CF_2CF_2CF_2S}$=NSi(CH$_3$)$_3$ which was contaminated with small quantities of $\overline{CF_2CF_2CF_2CF_2S}$=NH. Its yield was about 66%. This compound is a colorless liquid which has a vapor pressure of 20 torr to 25 °C. However, gas chromatographic purification to obtain the pure $\overline{CF_2CF_2CF_2CF_2S}$=NSi(CH$_3$)$_3$ resulted in its decomposition.

The ^{19}F and ^{1}H NMR spectral data are in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The

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infrared spectrum (low resolution) is as follows: 2965 (s), 2910 (w), 1315 (m), 1258 (m), 1073 (m), 855 (vs), 762 (w), 700 (w) cm^{-1}.

Preparation of $CF_2CF_2CF_2CF_2S{=}NC(O)CF_3$. Into a reaction vessel which contained 2.0 mmol of $CF_2CF_2CF_2CF_2S{=}NLi$ were condensed 3.0 mmol of $CF_3C(O)Cl$ and 10 mmol of i-C_5H_{12} at −196 °C. The reaction mixture was warmed to −78 °C during 3 h and kept at 0 °C. After 13.5 h, the product was separated by trap-to-trap distillation using traps cooled to −64 and −23 °C. The compounds which were retained at −64 °C were traces of ether and unreacted $CF_3C(O)Cl$, while that retained at 25 °C trap was found to be pure $CF_2CF_2CF_2CF_2S{=}NC(O)CF_3$ (4.31 mmol, yield 65.2%). This compound is a colorless liquid which has a vapor pressure of 0.5 torr at 25 °C.

The ^{19}F NMR spectral data are in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum (capillary film) is as follows: 1650–1680 (s) ($\nu_{C=O}$), 1347 (s), 1300 (s), 1150–1255 (vs), 1060 (m), 990 (vs), 955 (vs), 892 (w), 846 (m, sh), 830 (m), 772 (m), 739 (m), 676 (w), 642 (w), 612 (m), 536 (w), 502 (w) cm^{-1}.

Anal. Calcd for $C_6F_{11}SNO_2$: C, 20.06; N, 3.90. Found: C, 19.58; N, 4.13.

Preparation of $CF_2CF_2CF_2CF_2S{=}NCN$. In a reaction vessel which contained 2.5 mmol of $CF_2CF_2CF_2CF_2S{=}NLi$ were condensed 10 mmol of i-C_5H_{12} and 3 mmol of ClCN at −196 °C. The reaction mixture was warmed gradually to −78 °C during 3 h and kept at 0 °C. After 13.5 h, the volatile compounds were removed by dynamic vacuum, yielding a brown solid. When this solid was rinsed with small aliquots of CH_2Cl_2 and the solvent was evaporated to dryness, a transparent yellow viscous liquid remained. By sublimation from this compound, $CF_2CF_2CF_2CF_2S{=}NCN$ was obtained in a yield of 13.3%. This compound is a colorless solid and smells badly. It melts at 38.5–40.5 °C.

The ^{19}F NMR spectral data are found in Table I. The mass spectrum of this compound shows no molecular ion but shows *m/e* 232 [M − CN]$^+$ ion as the highest *m/e*, and there are appropriate fragment ions. The infrared spectrum (KBr disk) is as follows: 2198 (s) ($\nu_{C\equiv N}$), 1348 (s), 1298 (s), 1233 (vs), 1193 (s, sh), 1171 (vs), 1060 (m), 985 (s), 961 (s), 798 (w), 775 (w), 613 (w) cm^{-1}.

Anal. Calcd for $C_5F_8SN_2$: C, 22.06; N, 10.29. Found: C, 21.99; N, 10.25.

Preparation of $CF_2CF_2CF_2CF_2S{=}NSO_2CF_3$. In a reaction vessel which contained 2.8 mmol of $CF_2CF_2CF_2CF_2S{=}NLi$ was condensed 5 mmol of CF_3SO_2F at −196 °C. The reaction mixture was warmed gradually to 25 °C. After 18 h, the volatile compounds (unreacted CF_3SO_2F, ether, and $CF_2CF_2CF_2CF_2S{=}NH$ which was formed as a result of a hydrolytic reaction of the Li salt) were removed under dynamic vacuum to leave a brown solid. The workup of this solid is the same as we described for the preparation of $CF_2CF_2CF_2CF_2S{=}NCN$. A colorless solid, $CF_2CF_2CF_2CF_2S{=}NSO_2CF_3$, was obtained in a yield of 21.9%. It melts at 42.5–44.5 °C.

The ^{19}F NMR spectral data are given in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum (KBr disk) is as follows: 1371 (m) (ν_{asym,SO_2}), 1348 (m), 1303 (m), 1198–1248 (vs), 1175 (s), 1141 (s), 1062 (m), 988 (vs), 948 (vs), 792 (w), 750 (w), 678 (w), 624 (s), 612 (s, sh), 583 (w), 533 (w) cm^{-1}.

Anal. Calcd for $C_5F_{11}S_2NO_2$: C, 15.83; N, 3.69. Found: C, 15.53; N, 3.92.

Preparation of $CF_2CF_2CF_2CF_2S{=}NSO_2Cl$. In a reaction vessel which contained 2.6 mmol of $CF_2CF_2CF_2CF_2S{=}NLi$ was condensed 5 mmol of $ClSO_2F$ at −196 °C. The reaction mixture was gradually warmed to 25 °C. After 18 h, the volatile compounds were removed under dynamic vacuum, yielding a brown solid. The brown solid was worked up as above. A transparent liquid which solidifies at 25 °C was obtained. This was found to be $CF_2CF_2CF_2CF_2S{=}NSO_2Cl$ (yield 45.1%).

The ^{19}F NMR spectral data are found in Table I. The mass spectrum shows molecular ions with appropriate isotope ratios and appropriate fragment ions. The infrared spectrum (capillary film) is as follows: 1382 (ms) (ν_{asym,SO_2}), 1348 (m), 1301 (ms), 1246 (vs), 1175 (vs), 1059 (m), 987 (vs), 947 (vs), 846 (w), 768 (m), 676 (w), 590–610 (m–ms), 466 (m) cm^{-1}.

Anal. Calcd for $C_4F_8S_2NO_2Cl$: C, 13.89; N, 4.05. Found: C, 14.00; N, 4.15.

Preparation of $CF_2CF_2CF_2CF_2S{=}NC(O)N{=}SCF_2CF_2CF_2CF_2$. Into a reaction vessel which contained 3.4 mmol of $CF_2CF_2CF_2CF_2S{=}NLi$ were condensed 1.7 mmol of $COCl_2$ and 10 mmol of i-C_5H_{12} at −196 °C. The reaction mixture was gradually warmed to 25 °C. After 17 h, the volatile compounds were removed under dynamic vacuum, leaving a brown solid. This brown solid was worked up as above. A creamy colored solid which was found to be $CF_2CF_2CF_2CF_2S{=}NC(O)N{=}SCF_2CF_2CF_2CF_2$ was obtained in a yield of 34.1% on the basis of $COCl_2$ consumed. It melts at 77.0–81.5 °C.

The ^{19}F NMR spectral data are given in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum (KBr disk) is as follows: 1621 (s) ($\nu_{C=O}$), 1345 (m), 1296 (s), 1165–1240 (vs), 1140 (m, sh), 1150 (m), 984 (vs), 950 (s), 913 (m), 850 (w), 835 (w), 755 (w), 680 (w), 650 (w), 573 (w), 542 (w) cm^{-1}.

Anal. Calcd for $C_9F_{16}S_2N_2O$: C, 20.77; N, 5.39. Found: C, 21.00; N, 5.32.

Preparation of $CF_2CF_2CF_2CF_2S{=}NC(O)C(O)N{=}SCF_2CF_2CF_2CF_2$. Into a reaction vessel which contained 2.4 mmol of $CF_2CF_2CF_2CF_2S{=}NLi$ was condensed 1.1 mmol of $FC(O)C(O)F$ at −196 °C. The reaction mixture was gradually warmed to 25 °C. After 9 h, the volatile compounds were removed under dynamic vacuum, leaving a brown solid. This solid was worked up as above. A light yellow creamy solid, $CF_2CF_2CF_2CF_2S{=}NC(O)C(O)N{=}SCF_2CF_2CF_2CF_2$, was obtained in a yield of 44.6% on the basis of the $FC(O)C(O)F$ consumed. It melts at 103–105.0 °C.

The ^{19}F NMR spectral data are in Table I. The mass spectrum has no molecular ion, but a peak at *m/e* 316 [$C_6F_8SN_2O_2$]$^+$ is the highest *m/e*, and appropriate fragment ions are observed. The IR spectrum (KBr disk) is as follows: 1610–1625 (vs) ($\nu_{C=O}$), 1345 (m), 1317 (m, sh), 1298 (s), 1280 (m, sh), 1235 (vs), 1200 (m, sh), 1188 (s), 1170 (s), 1068 (m), 990 (vs), 956 (s), 872 (w), 851 (w), 618 (m), 598 (m), 502 (m), 442–483 (w) cm^{-1}.

Anal. Calcd for $C_{10}F_{16}S_2N_2O_2$: C, 21.90; N, 5.11. Found: C, 22.12; N, 5.22.

Preparation of $(CF_3)_2S{=}NC(O)C(O)N{=}S(CF_3)_2$. Into a reaction vessel which contained 3.0 mmol of $(CF_3)_2S{=}NLi$ was condensed 1.5 mmol of $FC(O)C(O)F$ at −196 °C. The reaction mixture was gradually warmed to 25 °C. After 8 h, the volatile compounds were removed under dynamic vacuum, leaving a brown solid. This solid material was worked up as above. A creamy solid, $(CF_3)_2S{=}NC(O)C(O)N{=}S(CF_3)_2$, was obtained in a yield of 39.3% on the basis of $FC(O)C(O)F$ consumed. It melts at 64.5–65.6 °C.

The ^{19}F NMR spectrum shows a resonance at ϕ −60.1 due to the CF_3 group. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum (KBr disk) is as follows: 1617 (vs) ($\nu_{C=O}$), 1310 (m), 1230–1250 (vs–s), 1202 (vs), 1126 (vs), 1066 (vs), 880 (m), 762 (m), 613 (ms), 582 (w), 550 (w) cm^{-1}.

Anal. Calcd for $C_6F_{12}S_2N_2O_2$: C, 16.98. Found: C, 17.00.

Reaction of $CF_2CF_2CF_2CF_2S{=}NLi$ with $FN{=}C(CF_3)_2$. Into a reaction vessel which contained 2.2 mmol of $CF_2CF_2CF_2CF_2S{=}NLi$ was condensed 2.5 mmol of $FN{=}C(CF_3)_2$ at −196 °C. Then, the reaction mixture was gradually warmed to 25 °C. After 5 h, the product was separated by trap-to-trap distillation through a trap at −196 °C which retained the compound found to be bis(trifluoromethyl)diazirine (1.8 mmol), a trap at −98 °C which retained $CF_2CF_2CF_2CF_2S$ (2.2 mmol), and a trap at −40 °C which retained traces of a yellow material.

The ^{19}F NMR of bis(trifluoromethyl)diazirine contained a singlet at ϕ −68.3. Its infrared spectrum is as follows: 1350 (vs), 1290 (vs), 1261 (ms), 1240 (ms, sh), 1215 (vs), 1025 (w), 985 (s), 949 (w), 740 (w), 714 (w) cm^{-1}.

Pyrolysis of Bis(trifluoromethyl)diazirine. In a 30-mL Hoke cylinder, 0.97 mmol of bis(trifluoromethyl)diazirine was condensed at −196 °C and heated at 165 °C for 2.2 h. The product was checked by infrared spectroscopy, but it was found that no reaction took place. The reaction mixture was again heated at 250–260 °C for 5 h. The products were separated by trap-to-trap distillation through a trap at −196 °C which retained the compound found to be $(CF_3)_2C{=}N{-}N{=}C(CF_3)_2$ (0.46 mmol).

Reaction of $CF_2CF_2CF_2CF_2S{=}NLi$ with $CF_2CF_2CF_2CF_2S{=}NCF((CF_3)_2)$. Into a 100-mL reaction vessel which retained 2.0 mmol of $CF_2CF_2CF_2CF_2S{=}NLi$ was condensed 2.15 mmol of $CF_2CF_2CF_2CF_2S{=}NCF(CF_3)_2$ at −196 °C. The reaction mixture was gradually warmed to 25 °C.[3] After 6 h, the product was separated by trap-to-trap distillation. However, only starting material ($CF_2CF_2CF_2CF_2S{=}NCF(CF_3)_2$, 1.76 mmol) and small amounts of $CF_2CF_2CF_2CF_2S$ were found.

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Registry No. $CF_2CF_2CF_2CF_2S{=}NSi(CH_3)_3$, 77110-78-2; $CF_2CF_2CF_2CF_2S{=}NC(O)CF_3$, 77110-79-3; $CF_2CF_2CF_2CF_2S{=}NSO_2CF_3$, 77110-80-6; $CF_2CF_2CF_2CF_2S{=}NSO_2Cl$, 77110-81-7; $CF_2CF_2CF_2CF_2S{=}NC(O)N{=}SCF_2CF_2CF_2CF_2$, 77110-82-8; $CF_2CF_2CF_2CF_2S{=}NC(O)C(O)N{=}SCF_2CF_2CF_2CF_2$, 77110-83-9; $CF_2CF_2CF_2CF_2S{=}NCN$, 77110-84-0; $(CF_3)_2N{=}SC(O)C(O)S{=}N(CF_3)_2$, 77110-85-1; bis(trifluoromethyl)diazirine, 3024-50-8; $CF_2CF_2CF_2CF_2S$, 706-76-3; $(CF_3)_2C{=}NN{=}C(CF_3)_2$, 1619-84-7; $CF_2CF_2CF_2CF_2S{=}NLi$, 77110-86-2; $(CF_3)_2S{=}NLi$, 61097-18-5; $CF_2CF_2CF_2CF_2S{=}NH$, 77110-87-3; $(CF_3)_2S{=}NH$, 60646-40-4; $(CH_3)_3SiCl$, 75-77-4; $CF_3C(O)Cl$, 354-32-5; ClCN, 506-77-4; CF_3SO_2F, 335-05-7; $ClSO_2F$, 13637-84-8; $COCl_2$, 75-44-5; $FC(O)C(O)F$, 359-40-0; $FN{=}C(CF_3)_2$, 2802-70-2.

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Syntheses and Properties of $FOIF_4O$, $ClOIF_4O$, $HOIF_4O$, and Tetrafluoroperiodates

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Mixtures of *cis*- and *trans*-$CsIF_4O_2$ were prepared by the interaction of $CsIO_4$ with either anhydrous HF, BrF_5, ClF_3, ClF_5, or F_2. The vibrational spectra of these mixtures were recorded, and partial assignments are given for *cis*- and *trans*-$IF_4O_2^-$. The assignments for *trans*-$IF_4O_2^-$ were supported by a normal-coordinate analysis. The $CsIF_4O_2$ salt dissolves in CH_3CN with the formation of $IF_4O_2^-$ anions but undergoes solvolysis in anhydrous HF with formation of $HOIF_4O$. An improved synthesis of $HOIF_4O$ from $CsIF_4O_2$ and BiF_5 in anhydrous HF is reported, and its Raman and ^{19}F NMR spectra were recorded. The interaction of $CsIF_4O_2$ with NF_4SbF_6 in anhydrous HF results in solutions containing NF_4^+, HF_2^-, and $HOIF_4O$. When standing or when pumped to dryness, these mixtures decompose to yield NF_3 and the new compound $FOIF_4O$ in high yield. The latter compound, the first known example of an iodine hypofluorite, was thoroughly characterized and shown by vibrational and NMR spectroscopy to be a mixture of the cis and trans isomers. For comparison, the vibrational spectra of IF_5O have also been recorded. The reaction of $CsIF_4O_2$ with $ClOSO_2F$ was shown to yield the novel compound $ClOIF_4O$. The fluorination reactions of $CsIO_4$, $CsIF_4O_2$, IF_5O, and $HOIF_4O$ with elementary fluorine were also studied.

Introduction

The number of elements known to form stable hypofluorites is very limited.[1] Thus stable hypofluorites are known only for carbon-, nitrogen-, sulfur-, selenium-; fluorine-, and chlorine-containing compounds. In addition, the unstable hypofluorous acid, HOF, has been prepared.[2] Since recent work in our laboratory had shown that the thermal decomposition of certain NF_4^+ salts of oxyanions such as NF_4ClO_4[3] and NF_4SO_3F[4] produces the corresponding hypofluorites in high yield, it was interesting to apply this method to the synthesis of novel hypofluorites. Preliminary results[5] showed that $FOIF_4O$, the first known example of an iodine hypofluorite, can be prepared in this manner. In this paper, detailed information is given on the synthesis, properties, and reaction chemistry of this interesting compound and of related iodine oxyfluoride derivatives such as $ClOIF_4O$, $HOIF_4O$, and the $IF_4O_2^-$ anion.

The literature on the synthesis and properties of salts containing the $IF_4O_2^-$ anion is scant. The first report on the existence of $IF_4O_2^-$ salts was published in 1971 by Engelbrecht and co-workers[6] but was limited to a one-sentence statement that $HOIF_4O$ interacts with either alkali-metal fluorides or trifluoroacetates to yield the corresponding salts. In a subsequent paper,[7] this statement was repeated, but again no data were given. In 1975, Aubke and co-workers reported[8] that CsF combines with an excess of IF_3O_2 to give $Cs^+IF_4O_2^-$. A melting point, elemental analysis, and incomplete vibrational spectra were given, which were incorrectly interpreted in terms of a cis isomer. In 1976, Selig and Elgad reported[9] that partial hydrolysis of IF_7 produces IF_5O, $HOIF_4O$, and, with increased water addition, the $IF_4O_2^-$ anion, which was identified by ^{19}F NMR and vibrational spectroscopy as the cis isomer. Although Selig and Elgad reported only solution data, their vibrational spectra strongly disagreed with those reported by Aubke for solid $Cs^+IF_4O_2^-$. In 1977, Gillespie and Krasznai reported[10] that solutions of KIO_4 in IF_5 contain a mixture of IO_2F, IOF_3, and *cis*- and *trans*-$IF_4O_2^-$. On cooling solutions of KIO_4 dissolved in boiling IF_5, they isolated a $KIF_4O_2{\cdot}2IF_5$ adduct, which could be converted into KIF_4O_2. Both compounds were shown by ^{19}F NMR and Raman spectroscopy to

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