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Bis(perfluoroalkyl)sulfur Oxyimines and Silver Bis(trifluoromethyl)sulfur Oxyimine

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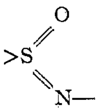
Received June 4, 1971

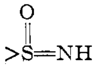
The first bis(perfluoroalkyl)sulfur oxyimines, $(CF_3)_2S(O)NH$, $CF_3(C_2F_5)S(O)NH$, and $(C_2F_5)_2S(O)NH$, have been synthesized by the reaction of ammonia with bis(perfluoroalkyl)sulfur oxydifluorides. As typical of the compounds in the above series, the reactions of bis(trifluoromethyl)sulfur oxyimine have been investigated to produce the new compounds $(CF_3)_2S(O)NSCF_3$, $(CF_3)_2S(O)NCN$, $(CF_3)_2S(O)NS(O)CF_3$, $(CF_3)_2S(O)NC(O)CF_3$, $(CF_3)_2S(O)NSi(CH_3)_3$, and $AgNS(O)(CF_3)_2$. The last compound reacts with CH_3I and Cl_2 to give $(CF_3)_2S(O)NCH_3$ and $(CF_3)_2S(O)NCl$. With the exception of the silver salt which is a solid, these compounds are colorless liquids which have been characterized by infrared, nmr, and mass spectra as well as elemental analyses and vapor pressure data.

Recently there has been considerable interest in the chemistry of compounds containing the sulfur oxyimine moiety



Polymers are formed when sulfur oxytetrafluoride reacts with ammonia in the absence of solvent.[1,2] A white sublimable solid was also isolated which was shown to have the formula $NH_4NS(O)F_2$. In analogous reactions, we find that bis(perfluoroalkyl)sulfur oxydifluorides react with ammonia to provide a facile synthesis of bis(perfluoroalkyl)sulfur oxyimines.

No reactions of



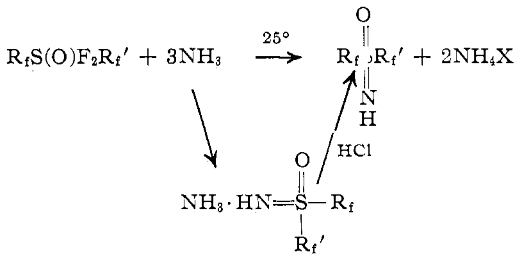
$$>\overset{\overset{\displaystyle O}{\|}}{S}{=}NH$$

with labile halides and no bis(perfluoroalkyl)sulfur oxyimine derivatives have been reported. The derivatives of difluorosulfur oxyimine in the literature have been formed by the reaction of primary amines with sulfur oxytetrafluoride,[3] reactions of $Hg(NS(O)F_2)_2$,[4-6] halogenation of *N*-fluoroformyl derivatives,[7] and elemental fluorination of *N*-sulfinyl compounds in the presence of ultraviolet radiation.[8-11] In our present study, we have found that bis(trifluoromethyl)sulfur oxyimine reacts with labile halides only if a base is present.

The silver salt $AgN{=}S(O)(CF_3)_2$ results when bis(trifluoromethyl)sulfur oxyimine reacts with silver(I) oxide in benzene solution. Reaction of this silver salt with either methyl iodide or elemental chlorine produces the appropriate imine derivative and silver halide in essentially quantitative yield.

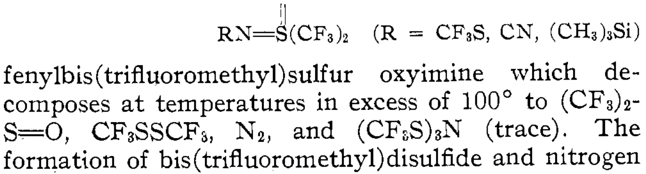
Results and Discussion

The reactions of bis(perfluoroalkyl)sulfur oxydifluorides with ammonia provide a direct route to the synthesis of bis(perfluoroalkyl)sulfur oxyimines



where $R_f = R_f' = CF_3$ or C_2F_5 or where $R_f = CF_3$ and $R_f' = C_2F_5$. Under similar conditions without solvent, sulfur oxytetrafluoride reacts with ammonia to give polymers.[1,2] Since dehydrofluorination cannot occur in the bis(perfluoroalkyl)sulfur oxyimines, such polymerization does not occur. However, in all cases, a white sublimable solid is formed. This solid is believed to have the formula $(R_f)_2S(O)NH \cdot NH_3$, analogous to the solid isolated in the reaction of ammonia with sulfur oxytetrafluoride.[1] In our case, the free bis(perfluoroalkyl)sulfur oxyimines are produced quantitatively when the sublimable solid is treated with anhydrous hydrogen chloride.

The reaction of bis(trifluoromethyl)sulfur oxyimine with labile chlorides does not occur neat. However, in the presence of a base, reaction proceeds smoothly at −20°. Generally tertiary amines were used to utilize the driving force of the formation of quatenary ammonium chlorides. Reactions with cyanogen chloride, trimethylchlorosilane, and trifluoromethylsulfenyl chloride proceed in this manner to yield the appropriate N-substituted bis(trifluoromethyl)sulfur oxyimine. In general, they are thermally stable to their boiling points, with the exception of *N*-trifluoromethylsulfenylbis(trifluoromethyl)sulfur oxyimine which decomposes at temperatures in excess of 100° to $(CF_3)_2S{=}O$, CF_3SSCF_3, N_2, and $(CF_3S)_3N$ (trace). The formation of bis(trifluoromethyl)disulfide and nitrogen arises either through the intermediate $CF_3SN{=}NSCF_3$ or from $(CF_3S)_3N$ directly.[12] Bis(trifluoromethyl)disulfide and tris(trifluoromethylsulfenyl)amine are also formed as side products in the initial reaction.



$$RCl + (CF_3)_2S(O)NH \xrightarrow{R_3N} RN{=}\overset{\overset{\displaystyle O}{\|}}{S}(CF_3)_2 \quad (R = CF_3S,\ CN,\ (CH_3)_3Si)$$

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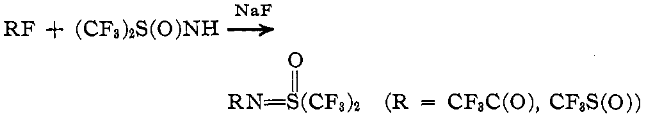
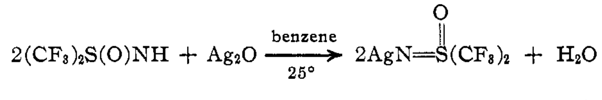
[1] F. Seel and G. Simon, *Angew. Chem.*, **72**, 709 (1960).
[2] G. W. Parshall, R. Cramer, and R. E. Foster, *Inorg. Chem.*, **1**, 677 (1962).
[3] R. Cramer and D. D. Coffman, *J. Org. Chem.*, **26**, 4010 (1961).
[4] K. Seppelt and W. Sundermeyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 905 (1970).
[5] K. Seppelt and W. Sundermeyer, *Z. Naturforsch. B*, **26**, 65 (1971).
[6] O. Glemser, H. Saran, and R. Mews, *Chem. Ber.*, **104**, 696 (1971).
[7] J. K. Ruff, *Inorg. Chem.*, **5**, 1787 (1966).
[8] H. W. Roesky and D. P. Babb, *ibid.*, **8**, 1733 (1969).
[9] H. W. Roesky, *Inorg. Nucl. Chem. Lett.*, **6**, 795 (1970).
[10] H. W. Roesky and D. P. Babb, *Angew. Chem., Int. Ed. Engl.*, **8**, 510 (1969).
[11] H. W. Roesky, *Z. Anorg. Allg. Chem.*, **378**, 168 (1970).
[12] A. Haas and P. Schott, *Chem. Ber.*, **101**, 3407 (1968).

With acid fluorides, NaF was used to remove HF. Although trace amounts of products were observed in the reaction without NaF, the presence of a base greatly enhances the yield. In the absence of NaF, no HF addition across S═N occurs. Reaction of bis(trifluoromethyl)sulfur oxyimine with trifluoromethylsulfinyl fluoride or acetyl fluoride in the presence of dry NaF proceeded smoothly at room temperature to give the products in high yield.



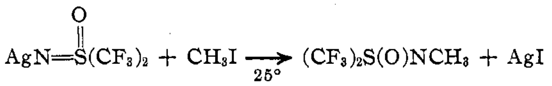
$$RF + (CF_3)_2S(O)NH \xrightarrow{NaF} RN{=}\overset{O}{\overset{\|}{S}}(CF_3)_2 \quad (R = CF_3C(O),\ CF_3S(O))$$

Bis(trifluoromethyl)sulfur oxyimine reacts with silver(I) oxide in benzene solution to form the silver salt AgN═S(O)(CF$_3$)$_2$.[13,14] Reaction of the silver

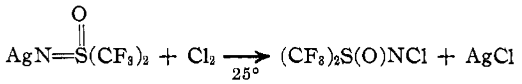


$$2(CF_3)_2S(O)NH + Ag_2O \xrightarrow[25^\circ]{benzene} 2AgN{=}\overset{O}{\overset{\|}{S}}(CF_3)_2 + H_2O$$

salt with methyl iodide produces N-methylbis(trifluoromethyl)sulfur oxyimine which is identical with a sample produced when bis(trifluoromethyl)sulfur oxydifluoride reacts with methylamine. With elemental chlorine at 25° N-chlorobis(trifluoromethyl)sulfur oxyimine is formed. Trace amounts of HCl in the chlorine source produce a small amount of the free imine which cannot be separated from the N-chloro compound by fractional condensation or gas chromatography.



$$AgN{=}\overset{O}{\overset{\|}{S}}(CF_3)_2 + CH_3I \xrightarrow[25^\circ]{} (CF_3)_2S(O)NCH_3 + AgI$$



$$AgN{=}\overset{O}{\overset{\|}{S}}(CF_3)_2 + Cl_2 \xrightarrow[25^\circ]{} (CF_3)_2S(O)NCl + AgCl$$

The bis(perfluoroalkyl)sulfur oxyimines ((CF$_3$)$_2$S(O)NH, CF$_3$(C$_2$F$_5$)S(O)NH, and (C$_2$F$_5$)$_2$S(O)NH) are easily identified by their characteristic spectra. The (M − CF$_3$)$^+$ ions and expected fragmentation ions are observed. Either molecular or (M − CF$_3$)$^+$ ions are formed in the mass spectra of the derivatives of bis(trifluoromethyl)sulfur oxyimine. In all cases, the expected fragmentation ions are observed. However the mass spectrum of N-trimethylsilylbis(trifluoromethyl)sulfur oxyimine contains many recombination ions. The S═N$^+$ ion is the base peak with the recombination ion (CH$_3$)$_2$SiF$^+$ being 70.2% base. For the structurally similar N-trimethylsilylsulfur oxydifluoride, the recombination ion (CH$_3$)$_2$SiF$^+$ is the base peak.[5,6] In N-trifluoromethylsulfenylbis(trifluoromethyl)sulfur oxyimine, a large peak at m/e 230 occurs in the mass spectrum and is assigned to CF$_3$SN═NSCF$_3$$^+$. Since a heated inlet chamber (150°) was used, this species may appear as a result of pyrolysis of the parent molecule.

The ^{19}F nmr spectra show resonances which occur in the regions (Table I) expected and integrate to give the proper ratios. As is the case for HNS(O)F$_2$,[2] no spin–spin coupling interactions are observed in bis(trifluoromethyl)sulfur oxyimine or its derivatives with the exception of N-methylbis(trifluoromethyl)sulfur oxyimine. The ^{1}H resonance of the methyl group is a septet (J = 1.2 Hz) centered at δ 3.04 while the ^{19}F resonance is a quartet at 71.1 ppm. In the spectrum (Figure 1) of trifluoromethylpentafluoroethylsulfur oxyimine, the proton couples with the methylene fluorine atoms (J_{H-F} = 32 Hz). The fluorine atoms attached to the methylene carbon are nonequivalent due to the presence of an asymmetric center in the molecule and coupling occurs ($J_{F_a-F_b}$ = 26.3 Hz). Such nonequivalence is also observed for the bis(perfluoroalkyl) sulfoxides.[15,16] The spectrum is further complicated since the coupling $J_{F_A-CF_3S} \neq J_{F_B-CF_3S}$ and interactions with the adjacent trifluoromethyl group ($J_{F_A-CF_3C}$ = 0.6, $J_{F_B-CF_3C}$ = 0.8) also occur (Table I).

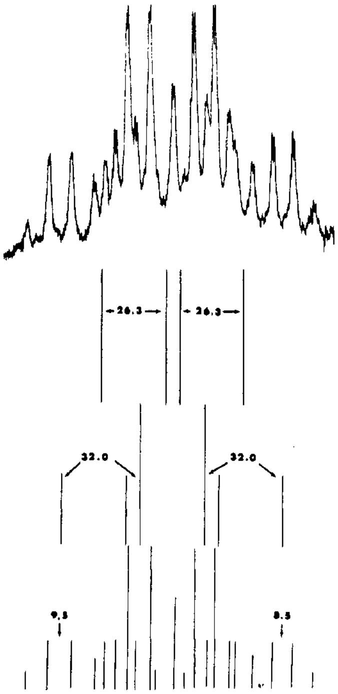


Figure 1.—The methylene ^{19}F nmr spectrum of CF$_3$S(O)(NH)CF$_2$CF$_3$.

The infrared spectra of the bis(perfluoroalkyl)sulfur oxyimines are given in Table I. Bands at 3416, 3410, and 3405 cm^{-1} for (CF$_3$)$_2$S(O)NH, CF$_3$(C$_2$F$_5$)S(O)NH, and (C$_2$F$_5$)$_2$S(O)NH are assigned to the NH stretching frequency. Absorption bands at 1353, 1351, and 1350 cm^{-1} may be assigned to the S═O stretching frequency shown in Table II. In the analogous HN═S(O)F$_2$ system, the band at 1448 cm^{-1} is assigned to the S═O stretching frequency. Assignments of the S═O bands in the infrared spectra of the bis(trifluoromethyl)sulfur oxyimine derivatives are also listed in Table II, although such assignments become increasingly difficult as the number and complexity of the perfluoroalkyl groups are introduced into the molecule. The assigned bands follow the trends established for the S═O stretching frequencies of the iminosulfur oxydifluoride derivatives. The S═N stretching frequency of HN═S(O)F$_2$ occurs at 1210 cm^{-1}. In an analogous fashion we assign bands at

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[13] H. W. Roesky and H. H. Giere, *Inorg. Nucl. Chem. Lett.*, **7**, 171 (1971).

[14] J. K. Ruff, *Inorg. Chem.*, **4**, 1446 (1965).

[15] D. T. Sauer and J. M. Shreeve, *Chem. Commun.*, 1679 (1970).

[16] D. T. Sauer and J. M. Shreeve, *J. Fluorine Chem.*, **1**, 1 (1971).

TABLE I

NMR AND INFRARED SPECTRA

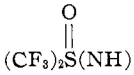
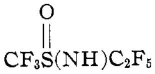
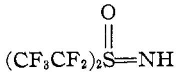
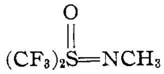
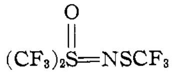
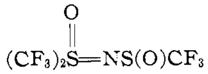
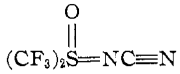
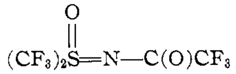
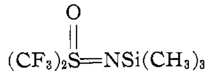
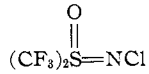
Compound	φ or δ, ppm	Assignment	*J*, Hz	Ir, cm⁻¹
 $(CF_3)_2\overset{O}{\overset{\|}{S}}(NH)$	74.7 4.18	$(CF_3)_2S(O)$ NH (broad)		3416 m, 1353 s–vs, 1250 vs, 1199 s, 1143 s, 1088 s, 857 m, br, 755 w, br, 600 m, 509 m
 $CF_3\overset{O}{\overset{\|}{S}}(NH)C_2F_5$	72.9 78.6 113.0 4.16	$CF_3S(O)$ CF_3C CF_2 NH (broad)	$J_{F_B-CF_3C} = 0.8$ $J_{CF_3C-CF_3S} = 3.0$ $J_{H-CF_2} = 32.0$ $J_{CF_3S(O)-F_A} = 9.5$ $J_{CF_3S(O)-F_B} = 8.5$ $J_{F_A-CF_3C} = 0.6$	3410 m, 1351 vs, 1278 sh, m–s, 1239 vs, br, 1188 m–s, 1135 m, 1095 m–s, 975 m, 857 m, br, 755 w–m, 594 m, 540 w, 520 w, 500 w
 $(CF_3CF_2)_2\overset{O}{\overset{\|}{S}}=NH$	78.3 111.6 4.18	CF_3C CF_2 NH (broad)	Multiplet Multiplet	3405 m, 1350 s, 1315 m–s, 1300 m–s, 1254 vs, 1236 s–vs, 1228 s–vs, 1165 m, 1138 m, br, 1030 w, 988 m, 945 w, sh, 908 w–m, br, 758 w–m, 600 w, 566 w–m, 510 w–m
 $(CF_3)_2\overset{O}{\overset{\|}{S}}=NCH_3$	71.1 3.04	$(CF_3)_2S(O)$ CH_3	$J_{CF_3S-CH_3} = 1.2$	2960 w, 2876 w, 1451 w–m, 1370 s, 1243 vs, 1194 s, 1142 vs, 1120 s, 857 w–m, 750 w, 622 m, 580 w–m, 518 w–m
 $(CF_3)_2\overset{O}{\overset{\|}{S}}=NSCF_3$	69.0 51.8	$(CF_3)_2S(O)$ CF_3S		1331 s, 1257 vs, 1213 s, 1178 s, 1130 vs, 1049 s, 763 w–m, 700 w, 613 m, 580 w–m, sh, 513 w–m
 $(CF_3)_2\overset{O}{\overset{\|}{S}}=NS(O)CF_3$	69.9 79.4	$(CF_3)_2S(O)$ $CF_3S(O)$		1339 vs, 1263 vs, 1225 vs, 1132 s–vs, 1062 vs, 764 w–m, 685 m, 615 m, 519 w, 455 w
 $(CF_3)_2\overset{O}{\overset{\|}{S}}=NC\equiv N$	66.9	$(CF_3)_2S(O)$		2256 m–s, 1369 s, 1268 vs, 1222 s, 1126 vs, 837 w–m, 753 w–m, 630 m, 580 w, 515 w, 443 w
 $(CF_3)_2\overset{O}{\overset{\|}{S}}=N-C(O)CF_3$	63.6 74.4	$(CF_3)_2S(O)$ $CF_3C(O)$		1751 m–s, 1362 m–s, 1334 s, 1263 s, 1248 s, 1224 m–s, 1192 m–s, 1113 vs, 995 w, 817 w, 760 w, 731 w–m, 601 m, 528 w, 511 w–m
 $(CF_3)_2\overset{O}{\overset{\|}{S}}=NSi(CH_3)_3$	74.6 0.28	$(CF_3)_2S(O)$ CH_3		2976 w–m, 2912 w, 1500 m, 1440 s, 1266 m–s, 1240 vs, 1195 s, 1148 s, 1119 s–vs, 860 s, 764 w, 611 m, 520 w
 $(CF_3)_2\overset{O}{\overset{\|}{S}}=NCl$	64.0	$(CF_3)_2S(O)$		1328 s–vs, 1257 vs, 1215 s, 1175 m, 1120 s, 1037 s, 742 w–m, 668 w–m, 612 m, 512 w–m, 482 w

TABLE II

S=O STRETCHING FREQUENCIES (CM⁻¹)

Compd	$\nu_{S=O}$	Compd	$\nu_{S=O}$	Ref
$(CF_3)_2S(O)NH$	1353	$F_2S(O)NH$	1448	*a*
$CF_3(C_2F_5)S(O)NH$	1351	$F_2S(O)NSi(CH_3)_3$	1495	*b, c*
$(C_2F_5)_2S(O)NH$	1350	$F_2S(O)NF$	1409	*d, e*
$(CF_3)_2S(O)NCH_3$	1243	$F_2S(O)NCl$	1409	*e*
$(CF_3)_2S(O)NSCF_3$	1331	$F_2S(O)NBr$	1404	*d*
$(CF_3)_2S(O)NCN$	1369	$F_2S(O)NI$	1370	*d*
$(CF_3)_2S(O)NS(O)CF_3$	1339	$F_2S(O)NC(O)F$	1433	*e*
$(CF_3)_2S(O)NC(O)CF_3$	1362	$F_2S(O)NCH_3$	1290	*f*
$(CF_3)_2S(O)NCl$	1328	$[F_2S(O)N]_2C=O$	1421	*g*
$(CF_3)_2S(O)F_2$	1325	$F_2S(O)F_2$	1383	*h*
$(CF_3)_2S(O)NSi(CH_3)_3$	1266			

[a] Reference 2. [b] Reference 4. [c] Reference 6. [d] Reference 5. [e] Reference 7. [f] Reference 3. [g] O. Glemser, R. Mews, and S. P. von Halasz, *Inorg. Nucl. Chem. Lett.*, **5**, 321 (1969). [h] F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *J. Amer. Chem. Soc.*, **78**, 1553 (1956).

1199, 1188, and 1165 cm⁻¹ to represent the S=N absorptions in $(CF_3)_2S(O)NH$, $CF_3(C_2F_5)S(O)NH$, and $(C_2F_5)_2S(O)NH$, respectively. It is noted that assignment of these bands is difficult due to the close proximity to the CF region. Because of the increased complexity in this region of the bis(trifluoromethyl)sulfur oxyimine derivatives, no assignment of the S=N stretching frequency was attempted.

Experimental Section

The bis(perfluoroalkyl)sulfur oxydifluorides were prepared as described previously.[17] Trifluoroacetyl fluoride and trimethylchlorosilane were purchased from PCR, Inc., cyanogen chloride from K & K Laboratories, and elemental chlorine from J. T. Baker and Co. Silver oxide was obtained from Fisher Scientific Supply and methyl iodide from Eastman Organic Chemicals. Trifluoromethylsulfinyl fluoride was prepared by the reaction of CF_3SSCF_3 (PCR, Inc.) and AgF_2 (Ozark-Mahoning).[18] Trifluoromethylsulfenyl chloride was prepared by the reaction of CCl_3SCl (Eastman) and NaF (J. T. Baker and Co.).[19]

General Procedures.—The gases and volatile liquids were handled in a conventional glass vacuum apparatus. Gaseous starting materials and purified products were measured quantitatively by standard *PVT* techniques. Purification of products was carried out by fractional condensation and gas chromatog-

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[17] D. T. Sauer and J. M. Shreeve, *Z. Anorg. Allg. Chem.*, in press.

[18] E. W. Lawless and L. D. Harman, *Inorg. Chem.*, **7**, 391 (1968).

[19] C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2061 (1960).

TABLE III

ELEMENTAL ANALYSES AND VAPOR PRESSURE DATA

												$\log P_{\text{mm}} = A - B/T$			
	% C		% H		% S		% N		% F						
Compd	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Bp, °C	ΔS_{vap}, eu	A	B	ΔH_{vap}, kcal mol^{-1}
$(CF_3)_2S(O)NH$	11.94	11.80	0.50	0.43	15.92	16.09	6.96	6.96	56.7	56.9	72.7	24.2	8.18	1830.4	8.38
$CF_3S(O)(NH)C_2F_5$	14.32	14.10	0.40	0.34	12.75	12.99	5.58	5.96	60.6	60.6	84.9	24.2	8.16	1891.2	8.67
$(C_2F_5)_2S(O)NH$	15.94	15.64	0.33	0.38	10.70	11.17	4.65	5.00	63.2	63.7	93.0	23.3	7.90	1838.6	8.51
$(CF_3)_2S(O)NCH_3$	16.74	16.44	1.39	1.36	14.88	14.81	6.51	6.86	53.0	52.9	65.1	21.7	7.62	1602.5	7.33
$(CF_3)_2S(O)NSCF_3$	11.96	11.55			21.26	21.19	4.65	4.97	56.8	56.2	87.2	20.7	7.40	1627.7	7.45
$(CF_3)_2S(O)NS(O)CF_3$	11.36	11.29	...	...	20.19	20.43	4.42	4.42	53.9	53.8	115.1	22.9	7.89	1944.3	8.90
$(CF_3)_2S(O)NCN$	15.82	15.93	...	...	14.34	14.16	12.36	12.39	50.4	50.4	108.7	19.3	7.09	1605.7	7.35
$(CF_3)_2S(O)NC(O)CF_3$	16.16	16.36			11.77	11.27	4.71	4.68	57.6	58.1	89.9	23.2	7.94	1835.9	8.40
$(CF_3)_2S(O)NSi(CH_3)_3$	21.98	22.00	3.30	3.29	11.72	11.77	5.13	5.30	41.8	41.9	104.8	21.2	7.51	1748.8	8.00

raphy. The chromatograph columns were constructed of 0.25-in. copper tubing packed with 20% Kel-F polymer oil (3M Co) on Chromasorb P.

Apparatus.—Infrared spectra were recorded with a Perkin-Elmer Model 457 infrared spectrometer using a 10-cm gas cell fitted with KBr windows and were calibrated against known absorption bands in polystyrene film. Fluorine nmr were determined with a Varian HA-100 nmr spectrometer using $CFCl_3$ as an internal standard. Mass spectra were obtained using a Hitachi Perkin-Elmer Model RMU-6E mass spectrometer. Beller Mikroanalytisches Laboratorium performed the elemental analyses.

General Preparation of Imines.—All of the bis(perfluoroalkyl)sulfur oxyimines were prepared in essentially the same manner. In a typical reaction, 4 mmol of bis(trifluoromethyl)sulfur oxydifluoride is condensed into a Pyrex vessel and 8 mmol of ammonia added. The vessel is maintained at −78° for 15 min and then slowly warmed to room temperature. Initially, the mixture is trap-to-trap distilled through a trap at −78° which retains the imine, some unreacted bis(trifluoromethyl)sulfur oxydifluoride, and a white sublimable solid. The imine is separated from the sulfur oxydifluoride by gas chromatography. The sublimable solid, believed to have the formula $(CF_3)_2S(O)NH \cdot NH_3$ is treated with anhydrous HCl to release $(CF_3)_2S(O)NH$ and form NH_4Cl. Overall yields of the bis(perfluoroalkyl)sulfur oxyimines follow: $(CF_3)_2S(O)NH$, 80%; $CF_3S(O)(NH)C_2F_5$, 70%; $(C_2F_5)_2S(O)NH$, 68%.

Properties of the Bis(perfluoroalkyl)sulfur Oxyimines.—All the bis(perfluoroalkyl)sulfur oxyimines ($(CF_3)_2S(O)NH$, $CF_3S(O)NHC_2F_5$, and $(C_2F_5)_2S(O)NH$) are colorless liquids at 25°. They do not react with mercury and are stable when stored in Pyrex at 25°. Infrared and nmr spectral data are presented in Table I; elemental analyses and vapor pressure data are included in Table III.

Preparation of $CF_3SNS(O)(CF_3)_2$.—$(CF_3)_2S(O)NH$ (1.3 mmol) and 5 mmol of CF_3SCl were condensed into a Pyrex bulb. Two millimoles of triethylamine was added and the mixture was allowed to react at −20° for 15 min. After the mixture was allowed to warm to room temperature, the products were distilled through a trap at −78°. The trap at −183° contained unreacted CF_3SCl and CF_3SSCF_3. The contents of the −78° trap were separated by gas chromatography to give $(CF_3)_2S(O)NH$, $(CF_3S)_3N$, and the CF_3S product in 70% yield. A small sample was pyrolyzed in a Pyrex tube at 120° for 0.5 hr. Decomposition products included CF_3SSCF_3, $CF_3S(O)CF_3$, $(CF_3S)_3N$, and N_2.

Preparation of $(CF_3)_2S(O)NS(O)CF_3$.—The trifluoromethylsulfinyl product was produced in 90% yield when 1.5 mmol of $(CF_3)_2S(O)NH$ and 4.5 mmol of $CF_3S(O)F$ were allowed to react in a Pyrex vessel containing excess dry NaF. $(CF_3)_2S(O)NS(O)CF_3$ was separated from excess $CF_3S(O)F$ by passage through a trap at −78° which retained the former compound. Gas chromatography was then utilized to remove traces of $(CF_3)_2S(O)NH$.

Preparation of $(CF_3)_2S(O)NC(O)CF_3$.—Bis(trifluoromethyl)sulfur oxyimine (1.3 mmol) and 5 mmol of $CF_3C(O)F$ were condensed into a Pyrex vessel containing excess dry NaF. The mixture was allowed to react at room temperature for 4 hr and then separated by passage through a trap at −78°. Final separation to free the *N*-trifluoroacetylbis(trifluoromethyl)sulfur oxyimine from unreacted starting materials was performed by gas chromatography (yield 82%).

Preparation of $(CF_3)_2S(O)NCN$.—Cyanogen chloride (5 mmol) was condensed into a Pyrex vessel containing 1 mmol of $(CF_3)_2S(O)NH$. Two millimoles of triethylamine was added and the mixture was allowed to react at −20° for 1 hr. After passage through a trap at −78° which retained the *N*-cyanobis(trifluoromethyl)sulfur oxyimine, final purification to remove traces of $(CF_3)_2S(O)NH$ was performed by gas chromatography, isolating the product in 70% yield.

Preparation of $(CF_3)_2S(O)NSi(CH_3)_3$.—*N*-Trimethylsilylbis(trifluoromethyl)sulfur oxyimine was produced in 74% yield when 1.3 mmol of $(CF_3)_2S(O)NH$ and 5 mmol of $(CH_3)_3SiCl$ were allowed to react in the presence of 2 mmol of $(CH_3)_3N$ at 25° for 30 min. The $(CH_3)_3SiNS(O)(CF_3)_2$ was then trapped at −78° while unreacted $(CH_3)_3SiCl$ and $(CH_3)_3N$ passed into a −183° trap. The contents of the trap at −78° were then further purified by gas chromatography to isolate the pure product.

Properties of Bis(trifluoromethyl)sulfur Oxyimine Derivatives.—All of the above derivatives are colorless liquids at room temperature which condense to colorless solids. They do not react with mercury and are thermally stable with the exception of *N*-trifluoromethylsulfenylbis(trifluoromethyl)sulfur oxyimine which decomposes as previously described. Infrared and nmr spectral data appear in Table I while Table III contains the elemental analyses and vapor pressure data. Sample purity was ensured by final gas chromatographic separations in all cases.

Preparation of $AgNS(O)(CF_3)_2$.—The reaction of silver oxide with bis(trifluoromethyl)sulfur oxyimine in benzene solution was utilized in preparing the desired silver salt. In a typical reaction, 0.64 mmol of Ag_2O was placed in a Pyrex vessel. $(CF_3)_2S(O)NH$ (1.3 mmol) and ~30 ml of benzene were condensed in and the mixture was warmed to room temperature. After 3 hr, the volatiles were removed and the salt was dried by pumping on the sample at 60° for 6 hr.

Reactions of $AgNS(O)(CF_3)_2$. (a) **With CH_3I.**—One millimole of methyl iodide was condensed into a Pyrex vessel containing 1.2 mmol of silver salt. The mixture was allowed to react at room temperature for 6 hr. The volatiles were purified by gas chromatography, and $CH_3NS(O)(CF_3)_2$ was isolated in nearly quantitative yield.

This compound also is readily prepared when methylamine reacts with bis(trifluoromethyl)sulfur oxydifluoride. Reaction of 1.5 mmol of bis(trifluoromethyl)sulfur oxydifluoride with 5 mmol of methylamine at room temperature produced the *N*-methylbis(trifluoromethyl)sulfur oxyimine in >92% yield. Initial separation was performed by fractional condensation using traps at −78 and 183°. The trap at −183° contained unreacted methylamine while the *N*-methyl compound was retained in the −78° trap. The product was purified by using a 3-ft Kel-F on Chromasorb P column.

(b) **With Cl_2.**—Cl_2 (0.8 mmol) was condensed into a Pyrex vessel containing 1.0 mmol of $(CF_3)_2S(O)NAg$ which was dried by pumping on the sample at 60° for 6 hr. The mixture was allowed to react at 25° for 3 hr and the volatiles were removed. In addition to the *N*-chlorobis(trifluoromethyl)sulfur oxyimine, bis(trifluoromethyl)sulfur oxyimine was also present. The mixture could not be separated by conventional fractional condensation or gas chromatography. A mass spectrum of the mixture shows the presence of a molecular ion for the *N*-chlorobis(trifluoromethyl)sulfur oxyimine. Also present were peaks assigned to $(M - CF_3)^+$ and $(M - 2CF_3)^+$ ions. Infrared and nmr spectral data are provided in Table I.

Acknowledgments.—Fluorine research at the University of Idaho is supported by the Office of Naval Research and the National Science Foundation. We are grateful to Mr. R. A. De Marco for mass spectra. J. M. S. thanks the Alfred P. Sloan Foundation for a fellowship.

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Hexafluoropropylideniminolithium Reactions with Halides

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Received June 10, 1971

Substitution of the hexafluoroisopropylidenimino group for chlorine or fluorine occurs readily when the lithium salt of $(CF_3)_2C{=}NH$ is reacted with inorganic compounds of groups IIIa–VIa. The formation of lithium halide prevents nucleophilic attack on the double bond and allows the new ketimides to be obtained in yields from 38 to 100%. Compounds obtained from reactions with SOX_2 and COX_2 result from extensive rearrangement.

Following the synthesis of the imine of hexafluoroacetone ($(CF_3)_2C{=}NH$) by Knunyants, *et al.*,[2] and the discovery of the facile one-step synthesis from hexafluoroacetone,[3] a number of papers have appeared describing the electrophilic character of this imine.[2–11] The strongly electron-withdrawing CF_3 groups cause the double bond to be electron deficient thus making it susceptible to attack by nucleophiles which give rise to products of unusually high stability. Although isolated compounds are cited[3,6,11] in which the imine functional group is preserved or regenerated during the course of a reaction, it is the stability of the adduct resulting from nucleophilic attack which generally renders direct reaction of the imine with substrate unacceptable for introducing the intact imine group as a ligand.

We have found that the hexafluoroisopropylidenimino group can be readily introduced by a simple metathetical reaction between the lithium salt of the imine and chlorine- or fluorine-containing inorganic compounds of groups IIIa–VIa, as in

$$RX_n + nLiN{=}C(CF_3)_2 \longrightarrow R(N{=}C(CF_3)_2)_n + nLiX$$

where RX_n = BCl_3, $(CH_3)_3SiCl$, PCl_3, PF_2Cl, PF_3, $AsCl_3$, SCl_2, CF_3SCl, or $CF_3S(O)F$. In these cases, the totally substituted compound is obtained as the major reaction product in yields ranging from 38 to 100%. However, reactions with sulfur(IV) compounds which contain more than one labile halogen and with $COCl_2$ and COF_2 produce compounds in which extensive rearrangement has taken place. This rearrangement is rationalized on the basis of stepwise substitution followed by halide migration to a more electropositive center.

While our preliminary report was in press,[12] the synthetic versatility of this general method was further demonstrated[13] by the reaction of hexafluoroisopropylideniminolithium with transition metal chlorides to obtain the expected ketimides.

Experimental Section

Materials.—Hexafluoroisopropylidenimine, $(CF_3)_2C{=}NH$,[3] and $CF_3S(O)F$[14] were prepared according to the literature. *n*-Butyllithium in hexane (Alfa Inorganics) was transferred into small-volume glass bottles in an inert-atmosphere box for ease in handling but otherwise was used as purchased. Sulfur dichloride was redistilled prior to use. All other chemicals were used as received.

General Procedures.—Gases and volatile liquids were handled in a conventional Pyrex vacuum apparatus equipped with a Heise Bourdon-tube gauge. Volatile starting materials and purified products were measured quantitatively by *PVT* techniques. Reactants and products of lower volatility were weighed. For gas chromatographic separations the columns were constructed of 0.25-in. aluminum or copper tubing packed with 20% Kel-F polymer oil (3M Co.) or 8% SE-30 (Loenco) on Chromosorb W. In most cases, fractional condensation was used to effect crude separation prior to gas chromatography. Vapor pressure studies were run by using the method of Kellogg and Cady[15] or by an isoteniscopic method.

Infrared spectra were recorded with a Perkin-Elmer 457 or Perkin-Elmer 621 spectrometer by using a 5-cm gas cell equipped with KBr windows. Fluorine-19 nmr spectra were obtained with a Varian HA-100 spectrometer using trichlorofluoromethane as an internal standard. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E mass spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Preparation of Hexafluoroisopropylideniminolithium (I).—In an inert-atmosphere box, 8 ml of 2.3 *M* *n*-BuLi in hexane was transferred *via* a syringe into a rigorously dried glass vessel which had been purged with dry nitrogen. The vessel was cooled to −196° and 20 mmol of $(CF_3)_2C{=}NH$ was introduced. The vessel was allowed to warm slowly from −196 to +25°. An exothermic reaction occurred at about 0° which resulted in a detonation in some cases when 2.67 *M* *n*-BuLi in hexane was used. Explosions did not occur when an additional 10 ml of dry pentane was added to the more concentrated *n*-BuLi in the reaction

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