CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM AND HAAS COMPANY,
REDSTONE RESEARCH LABORATORIES, HUNTSVILLE, ALABAMA

Some Perfluoroalkyliminosulfur Derivatives

BY MAX LUSTIG

Received March 28, 1966

Trifluoromethyliminosulfur dichloride and pentafluoroethyliminosulfur dichloride are prepared by reaction of aluminum trichloride with trifluoromethyliminosulfur difluoride and pentafluoroethyliminosulfur difluoride, respectively. These imino dichlorides react with silver oxide to give N-sulfinyltrifluoromethylamine and N-sulfinylpentafluoroethylamine. Some physical and chemical properties of these new perfluoroalkyliminosulfur dichlorides and N-sulfinylperfluoroalkylamines are reported.

Introduction

Trifluoromethyliminosulfur dichloride, $CF_3N{=}SCl_2$, and pentafluoroethyliminosulfur dichloride, $C_2F_5N{=}SCl_2$, are the first examples of compounds containing the iminosulfur dichloride linkage which are stable in the isolated state. The only other member of this class of compounds, $C_6H_5N{=}SCl_2$, has been reported to be stable only in solution.[1] These compounds are structurally similar to thionyl chloride with the oxygen atom in the latter replaced with the $=N-R_f$ group in the former.

They are prepared by treating the corresponding difluoride derivatives[2] with $AlCl_3$ in reactions similar to those reported by Solomon and Dee.[3] In this case, however, the reactions with the acyclic compounds, $CF_3N{=}SF_2$ and $C_2F_5N{=}SF_2$, in nitrobenzene take place under more moderate conditions, *i.e.*, at much lower temperature and with shorter times than those employed for the neat reactions involving the acyclic unsaturated C—F compounds.[3] When more severe conditions are employed in this work, allylic chlorine substitution is also observed, but the products were not studied.

When the iminosulfur dichlorides noted above are treated with silver oxide, conversion to N-sulfinyltrifluoromethylamine, $CF_3N{=}S{=}O$, and N-sulfinylpentafluoroethylamine, $C_2F_5N{=}S{=}O$, is achieved. Aromatic and aliphatic N-sulfinylamines have been described earlier,[4,5] but the compounds reported herein are the first examples of fluorocarbon derivatives.

Experimental Section

Reagents.—Reagent grade aluminum trichloride (anhydrous) and silver oxide were obtained from Baker and Adamson Products, Allied Chemical Corp. The nitrobenzene, which was stored over 5A molecular sieves, was procured from Eastman Kodak Co., and $CF_3N{=}SF_2$ and $C_2F_5N{=}SF_2$ were prepared by the literature method.[2]

General Procedure.—The silver oxide, aluminum trichloride, and nitrobenzene were handled within a nitrogen drybox. The reactions took place within 100-ml Pyrex round-bottom bulbs with stopcock and joint attachments. A standard Pyrex vacuum apparatus was used for transfer, purification, and measurement of volatile materials. Gaseous mixtures were analyzed by using a mass spectrometer, calibrated with the pure components, along with *PVT* measurements.

Preparation of $CF_3N{=}SCl_2$.—The $AlCl_3$, 2.0 g (15.2 mmoles), was dissolved in 15 ml of nitrobenzene by allowing the mixture to be stirred for 15 min. The bulb was then pumped upon for several minutes to remove the nitrogen and any HCl which may have been formed by $AlCl_3$ hydrolysis. The solution was cooled to −196°, and 1.69 g (10.6 mmoles) of $CF_3N{=}SF_2$ was added. The bulb was warmed to 7°, at which temperature it was allowed to stand for 45 min while stirring the solution. The solution turned orange-red. The volatile products were then passed through traps held at −33, −95, and −196°. The former retained some solvent and trace amounts of an unidentified material while the −95° trap contained pure $CF_3N{=}SCl_2$ and the latter held Cl_2, CO_2, CF_4, and small amounts of unidentified species. The liquid phase was not examined. It slowly turned brown and became viscous. The weight of the $CF_3N{=}SCl_2$, 0.909 g (4.89 mmoles), corresponded to 40.7% yield based on the iminosulfur difluoride reactant.

Preparation of Pentafluoroethyliminosulfur Dichloride.—The reaction method and conditions employed were similar to those given above using 2.0 g (15.2 mmoles) of $AlCl_3$, 10 ml of nitrobenzene, and 1.54 g (7.58 mmoles) of $C_2F_5N{=}SF_2$. The reaction temperature was 5° and the solution was stirred for 0.5 hr. The products were crudely fractionated by passage through −33, −80, and −196° traps. The −33° trap held nitrobenzene while the −80° trap contained $C_2F_5N{=}SCl_2$ and the −195° traps held 95% Cl_2; the remainder contained an unidentified substance. The yield of the dichloride derivative was 1.76 g (7.46 mmoles) corresponding to 98.4%. The content of the −80 trap was passed through a 4-ft Kel-F No. 10 oil on acid treated Anachrome ABS column at 60°, and only one substance was observed.

Preparation of N-Sulfinylperfluoromethylamine.—In a typical experiment 90.4 mg (0.380 mmole) of $CF_3N{=}SCl_2$ was distilled into the reactor at −196° which contained 20 ml of nitrobenzene and 1.0 g (4.32 mmoles) of Ag_2O. The bulb was warmed rapidly to 7° where it stood for 20 min while the reaction mixture was being stirred. The products were then passed through traps set at −95, −126, and −196° while pumping for 1 hr. The first contained nitrobenzene and unreacted $CF_3N{=}SCl_2$, the −126° trap retained pure $CF_3N{=}S{=}O$, and the −196° trap held SO_2 and small quantities of CO_2, SiF_4, and COF_2. Analysis of the product mixture indicated $CF_3N{=}S{=}O$ (0.302 mmole), 79.5% yield, $CF_3N{=}SCl_2$ (trace), SO_2 (0.068 mmole), CO_2 (0.026 mmole), COF_2 (trace), and SiF_4 (0.023 mmole).

Preparation of N-Sulfinylperfluoroethylamine.—The method of preparation of this compound is similar to that given for the $CF_3N{=}S{=}O$ case using 143 mg (0.607 mmole) of $C_2F_5N{=}SCl_2$ and 1.0 g (4.32 mmoles) of Ag_2O in 10 ml of nitrobenzene. In this case the reaction time was only 16 min for total consumption

---

[1] A. Michaelis, *Ann.*, **274**, 173 (1893).

[2] W. C. Smith, C. W. Tullock, R. D. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 551 (1960).

[3] W. C. Solomon and L. A. Dee, paper presented at the 3rd International Fluorine Symposium, Munich, Germany, 1965.

[4] A. Michaelis and R. Herz, *Ber.*, **23**, 3480 (1890).

[5] G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Platzschke, H. Smalla, and A. Trede, *Angew. Chem. Intern. Ed. Engl.*, **1**, 89 (1962).

of the iminosulfur dichloride reactant. The mixture of products contained $C_2F_5N=S=O$ (0.399 mmole) corresponding to 65.7% yield, $C_2F_5N=SF_2$ (0.02 mmole), CF_3CN (0.154 mmole), SO_2 (0.172 mmole), and SiF_4 (0.02 mmole). All of the products excepting the sulfinylamine passed through a trap set at −95°. Longer reaction times and/or elevated temperatures increased the yield of CF_3CN, SO_2, and $C_2F_5N=SF_2$.

Analysis.—Carbon analyses were performed by conventional combustion with the exception that MgO was also used in the combustion tube. Nitrogen was determined by the Kjeldahl method. The sulfur was determined as sulfate by boiling the substrates in fuming HNO_3 solution followed by titration with $BaCl_2$ using a tetrahydroxyquinone indicator. The chlorine composition was determined as gravimetric AgCl after hydrolysis of the dichloride derivatives. The fluorine content was obtained by reduction of the compounds with lithium in *n*-propylamine with subsequent distillation and titration using the thorium nitrate method. In the case of $CF_3N=S=O$, fluoride was determined after alkaline hydrolysis.

Anal. Calcd for CCl_2F_3NS: C, 6.45; Cl, 38.2; F, 30.6; N, 7.52. Found: C, 6.42; Cl, 38.5; F, 29.3; N, 7.45. Calcd for $C_2Cl_2F_5NS$: C, 10.17; Cl, 30.1; F, 40.3; N, 5.93. Found: C, 10.32; Cl, 30.1; F, 40.6; N, 5.76. Calcd for CF_3NSO: F, 43.5; S, 24.6. Found: F, 42.8; S, 24.4. Calcd for C_2F_5NSO: F, 52.4; S, 17.7. Found: F, 51.5; S, 16.4.

Properties.—Physical and spectral properties were determined by known methods described below. A summary of some physical properties is presented in Table I.

TABLE I

PHYSICAL PROPERTIES

	$CF_3N=SCl_2$	$C_2F_5N=SCl_2$	$CF_3N=S=O$	$C_2F_5N=S=O$
Melting point range, °C	. . .	−110 ± 1.0	. . .	− 84.5 ± 1.5
Boiling point (extrap), °C	88.9	106.6	18.0	45.1
$\Delta\tilde{H}°_{vap}$, kcal/mole	8.27	8.95	6.47	6.94
$\Delta\tilde{S}°_{vap}$, eu	22.83	23.57	22.20	21.80
Molecular density				
Vapor density	189.8	239.5	130.5	183.2
Effusiometry	. . .	. . .	129.0	. . .
Calcd	186.0	236.0	131.1	181.1

(A) **Melting Point.**—The melting points were observed visually by placing samples in 5-mm Pyrex tubes which were then submerged in a cold pentane bath which warmed at a rate of 0.25°/min. Both $CF_3N=SCl_2$ and $CF_3N=S=O$ could not be made to crystallize.

(B) **Vapor Pressures.**—These were measured at various temperatures and at constant volume by use of a gauge similar to that described by Foord[6] with a reference pointer as an aid in null detection. Some vapor pressure data for $CF_3N=SCl_2$ are given as T (°C), P (mm): 10.8, 31.0; 27.2, 69.8; 40.0, 124.7; 53.8, 215.6; 64.2, 308.2; 70.8, 380.5; for $C_2F_5N=SCl_2$: 24.4, 43.2; 61.2, 178.6; 75.9, 304.0; 85.8, 426.8; 101.7, 706.4; for $CF_3N=S=O$: −33.9, 67.0; −29.2, 85.2; −23.7, 111.0; −12.7, 203.0; −1.0, 334.8; 15.2, 682.0; and for $C_2F_5N=S=O$: −28.4, 27.8; −3.4, 103.0; 18.4, 272.6; 24.0, 348.4; 29.4, 409.9 The temperature dependence of the vapor pressure is expressed by the equations $\log P_{mm} = 7.870 - 1806/T$ for $CF_3N=SCl_2$; $\log P_{mm} = 8.031 - 1956/T$ for $C_2F_5N=SCl_2$; $\log P_{mm} = 7.733 - 1413/T$ for $CF_3N=S=O$; and $\log P_{mm} = 7.643 - 1516/T$ for $C_2F_5N=S=O$.

(C) **Molecular Weights.**—The molecular weights of the compounds were obtained by vapor density measurements assuming ideal gas behavior. The molecular weight of $CF_3N=S=O$ was also determined by the effusion rate of its molecules through the leak in the mass spectrometer inlet system[7,8] by measuring the peak height decrease with time due to the fragment ion corresponding to mass number 131.

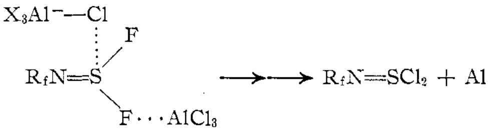
(D) **Infrared Spectra.**—The spectra in the 4000-250-cm^{-1} region were taken using a Perkin-Elmer 521 grating infrared spectrometer. A 10-cm path length cell with CsBr windows was used with sample pressures varying between 5 and 15 mm. The frequencies (cm^{-1}) are as follows. $CF_3N=SCl_2$: 1425 (w), 1309 (vs), 1215 (s), 1190 (s), 1140 (s), 800 (m), 658 (m), 620 (m), 540 (m), 460 (sh), 439 (s), 410 (s). $C_2F_5N=SCl_2$: 1372 (w), 1290 (vs), 1151 (m), 1130 (s), 1028 (s), 950 (vs), 760 (vw), 706 (m), 619 (vw), 580 (vw), 530 (vw), 498 (vw), 422 (m), 388 (wm), 350 (vw). $CF_3N=S=O$: 1430 (vw), 1360 (sh), 1310 (vs), 1210 (vs, b), 1088 (ms, PQR), 695 (vw), 622 (vw), 565 (vw), 480 (m). $C_2F_5N=S=O$: 1330 (vw), 1350 (sh), 1290 (vs), 1225 (vs), 1170 (s), 1112 (s), 1000 (s), 761 (w, complex), 705 (w, m, complex), 655 (w), 580 (vw), 535 (vw), 440 (w, m, complex).

(E) **Mass Spectra.**—A Consolidated Engineering Corp. Model 21-620 spectrometer with a heated-inlet system and operating with an ionization potential of 100 ev was used. The following are the mass numbers (species) and relative abundances for some of the more prominent peaks. $CF_3N=SCl_2$: 31 (CF^+), 4.2; 32 (S^+), 10.9; 46 (SN^+), 100.0; 67 (SCl^+), 7.0; 69 (CF_3^+, $^{34}SCl^+$, $S^{37}Cl^+$), 45.6; 115 (CF_3NS^+), 14.5; 150 (CF_3NSCl^+), 52.8; 152 ($CF_3N^{34}SCl^+$, $CF_3NS^{37}Cl^+$), 18.4. $C_2F_5N=SCl_2$: 31 (CF^+), 11.1; 32 (S^+), 14.8; 46 (SN^+), 100.0; 67 (SCl^+), 34.0; 69 (CF_3^+, $^{34}SCl^+$, $S^{37}Cl^+$), 58.1; 200 ($C_2F_5NSCl^+$), 15.6. $CF_3N=S=O$: 31 (CF^+), 6.4; 32 (S^+), 8.2; 46 (SN^+), 100.0; 48 (SO^+, $^{34}SN^+$), 46.1; 50 (CF_2^+), 5.0; 67 (SCl^+), 10.9; 69 (CF_3^+, $^{34}SCl^+$, $S^{37}Cl^+$), 87.3; 112 (CF_2NSO^+) 6.5; 181 (CF_3NSO^+), 37.3. $C_2F_5N=S=O$: 31 (CF^+), 18.0; 32 (S^+), 12.0; 46 (SN^+), 52.8; 48 (SO^+, $^{34}SN^+$), 63.7; 50 (CF_2^+), 13.0; 67 (SCl^+), 25.0; 69 (CF_3^+, $^{34}SCl^+$, $S^{37}Cl^+$), 85.4; 112 (CF_2NSO^+), 100.0.

(F) **Nmr Spectra.**—Spectra were taken using a Varian Model V4310A spectrometer operating at 40 Mc. Samples were measured at 25° using trichlorofluoromethane as an internal reference. Area ratios were obtained by current integration. The results are recorded below.

Results and Discussion

Substitution of chlorine atoms for the fluorine bonded to the sulfur(IV) atom in the perfluoroalkyliminosulfur dichlorides takes place with rapidity in nitrobenzene solvent at 7° or below. Although it is not known how this reaction is facilitated, one route may involve the removal of fluoride by $AlCl_3$ acting as a Lewis acid with subsequent or simultaneous attack by the tetrahaloaluminate ion or free chloride ion.



$X = F$ and/or Cl

Further, substitution of KCl, which is insoluble in nitrobenzene, for $AlCl_3$ results in no reaction even

---

(6) Foord, *J. Sci. Instr.*, **11**, 126 (1934).

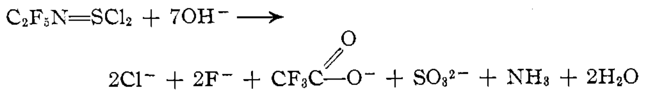
(7) M. Eden, B. E. Burr, and A. W. Pratt, *Anal. Chem.*, **23**, 1735 (1951).

(8) P. D. Zemany, *J. Appl. Phys.*, **23**, 924 (1952).

after heating at 100° for 1 hr. Either the insolubility of KCl or the failure of chloride ion alone to coordinate may be the reason for no reaction. When the oxidation state of the sulfur atom is increased to VI, *e.g.*, in the case of bis(trifluormethylimino)sulfur difluoride, $(CF_3N{=})_2SF_2$, no substitution is observed in the presence of $AlCl_3$ even after reflux at 80° for 1 hr. At higher temperatures degradation takes place and none of the desired iminosulfur dichloride is formed.

Like thionyl chloride, trifluoromethyliminosulfur dichloride hydrolyzes rapidly in the presence of excess water with the latter yielding CO_2, SO_2, HCl (in a 1:1:2 ratio), and ammonium fluorides. If equimolar quantities of gaseous dichloride and water are allowed to react, unreacted dichloride as well as small amounts of SiF_4 are also present in the product mixture indicating that once initial attack on the dichloride takes place, further degradation of the molecule occurs in preference to attack of water on the remaining unaltered substrate. In the presence of dilute alkali, analysis reveals that both $CF_3N{=}SCl_2$ and $C_2F_5N{=}SCl_2$ hydrolyze substantially as

$$CF_3N{=}SCl_2 + 9OH^- \longrightarrow 2Cl^- + 3F^- + CO_3^{2-} + SO_3^{2-} + NH_3 + 3H_2O$$



$$C_2F_5N{=}SCl_2 + 7OH^- \longrightarrow 2Cl^- + 2F^- + CF_3C({=}O){-}O^- + SO_3^{2-} + NH_3 + 2H_2O$$

On the other hand, the corresponding perfluoroalkyliminosulfur difluorides, analogous to thionyl fluoride, hydrolyze much more slowly in a manner similar to that shown above.

There is fleeting indication that N-sulfinylperfluoroalkylamines may be produced in trace quantities according to mass spectral analysis by allowing the iminosulfur difluorides to stand over water, although it has been reported the pentafluorosulfuriminosulfur difluoride yields N-sulfinylpentafluorosulfuramine by similar treatment.[9] However, the N-sulfinylperfluoroalkylamines are produced in high yield by reaction of the iminosulfur dichlorides with silver oxide under very similar conditions used in the preparation of the dichloride derivatives. The iminosulfur difluorides are unreactive toward Ag_2O below 110°.

The spectral data are consistent with the assigned structures. The infrared spectra are complicated and, consequently, only a few tentative assignments are made. Both $CF_3N{=}SCl_2$ and $C_2F_5N{=}SCl_2$ have bands of weak intensity at 1425 and 1372 cm^{-1}, respectively, which are assigned to the S=N stretching frequency. In contrast the same bands in the spectra of the corresponding difluorides are of high intensity. The perfluoroalkylsulfinylamines, $CF_3N{=}S{=}O$ and $C_2F_5N{=}S{=}O$, also have an absorption in the same region, *viz.*, 1430 cm^{-1}, which is presumably associated with the N=S=O group. Another band expected for this group at lower frequency[5] may be obscured by the multiple bands due to C—F stretching modes which are found in the spectra of all the compounds prepared above within the 1310–1000-cm^{-1} region. The bands at 439 and 410 cm^{-1} are assigned to the SCl_2 group symmetric and asymmetric stretching vibrations in the spectrum of $CF_3N{=}SCl_2$ and, similarly, are those at 422 and 385 cm^{-1} in that of $C_2F_5N{=}SCl_2$. The same motions are located at lower frequencies, *viz.*, 490 and 443 cm^{-1} in $SOCl_2$.[10] Similarly the SF_2 group stretching vibrations of SOF_2 and SO_2F_2 are located at higher frequencies than those of analogous imino derivatives.[10, 11]

The mass spectra of these compounds are characteristic. The species corresponding to mass number 46, SN^+, has a relative intensity of 100 in both dichloride derivatives. The same mass number is of high intensity in the spectra of corresponding difluoride compounds and also in those of the N-sulfinylperfluoroalkylamines, although the intensity of the peak is significantly larger in the N-sulfinylperfluoromethyl derivative than it is in the ethyl. Instead, the 112 peak is the largest in the latter which presumably corresponds to the cumulene-type structure, $CF_2{=}\overset{+}{N}{=}S{=}O$. The stability of this ion may be attributed to positive charge stabilization by distribution between heteroatoms represented by the resonance forms

$$\overset{-}{C}F_2{-}N{=}S{=}O \longleftrightarrow CF_2{=}\overset{+}{N}{=}S{=}O \longleftrightarrow CF_2{=}N{-}\overset{+}{S}{=}O$$

To obtain the cumulene structure the C—F bond must be split in the methyl derivative and the generally weaker C—C in the ethyl.[12] The same phenomenon is observed in the structurally similar isocyanates and isothiocyanates;[13] *e.g.*, the peak corresponding to mass number 56 in the spectrum of $CH_3{-}N{=}C{=}O$ presumably is due to the ion, $CH_2{=}\overset{+}{N}{=}C{=}O$, having a relative intensity of 36.8, while the same peak in the spectra of the ethyl and propyl derivatives has a relative intensity equal to 100.[14] This effect is presumably due to the enhanced strength of the C—H bond over the C—C.

The ^{19}F nmr spectra of $CF_3N{=}SCl_2$ and $CF_3N{=}S{=}O$ each show one resonance absorption at ϕ 56.4 and 53.6, respectively, while $C_2F_5N{=}SCl_2$ has absorptions at ϕ 86.5 and 96.6, having an area ratio of 3.1:2.0 assigned to the CF_3 and CF_2 group fluorine atoms, respectively. The spectrum of $C_2F_5N{=}S{=}O$ also has two bands due to the C_2F_5 group, one at ϕ 86.7 and the other at ϕ 90.8 also having an area ratio of nearly 3:2. Within the resolution of the spectrometer, each perfluoroethyl group resonance in both $C_2F_5N{=}SCl_2$ and $C_2F_5N{=}S{=}O$ is unsplit.

Acknowledgment.—This work was performed under Army Ordnance Contract DA-01-021 AMC-11536 (Z).

---

[9] B. Cohen, T. R. Hooper, and R. D. Peacock, *Chem. Commun.*, 32 (1966).

[10] R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **39**, 2171 (1961).

[11] M. Lustig and J. K. Ruff, *Inorg. Chem.*, **4**, 144 (1965).

[12] T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworth and Co. Ltd., London, 1958, p 274.

[13] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., New York, N. Y., 1964, p 119.

[14] J. A. Lovinger and M. Lustig, unpublished results.