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Addition to the Carbon–Nitrogen Double Bond of Fluorosulfuryl Isocyanate, FSO_2NCO

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Fluorine fluorosulfate, trifluoromethyl hypofluorite, and fluorine have been found to react with fluorosulfuryl isocyanate under the influence of ultraviolet radiation to produce a new class of compounds containing the $FSO_2NC(O)F$ group. Some of the chemical and physical properties of these materials and additional characterization of FSO_2NCO are presented.

The chemistry of isocyanates has received much attention in recent years, especially that of organic isocyanates and their derivatives.[1-4] 1,2-Dipolar addition has been found to occur readily across the C–N double bond in isocyanates. The polarizing effect of the sulfuryl group in sulfuryl isocyanates enhances this tendency.[1] However, studies of gas-phase free-radical addition to the carbon–nitrogen double bond in sulfuryl isocyanates have not appeared in the literature. This paper reports the reaction of fluorosulfuryl isocyanate with various fluorine-containing free radicals to produce a new class of compounds incorporating the fluorocarbonylfluorosulfurylamino group ($FSO_2NC(O)F$).

Experimental Section

Infrared spectra were recorded on a Beckman IR-5A infrared spectrophotometer by using 10- and 13-cm gas cells equipped with either AgCl or NaCl windows.

Fluorine-19 nmr spectra were obtained using Varian Models HR-60, HA-100, and 4311B high-resolution nmr spectrometers.

Chemical analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium in Max Planck Institut, Mülheim (Ruhr), West Germany, and by R. Anderson of Allied Chemical Co.

Vapor pressures were determined by the method of Kellogg and Cady[5] or by direct measurement in a static system employing a Wallace and Tiernan pressure gauge.

Ultraviolet light sources used in this work included a 450-w lamp (Hanovia L-679A36, Hanovia Lamp Division, Engelhard Hanovia, Inc., Engelhard, N. J.) and a Hanau 70-w lamp (Q-81, Brinkman Instruments, Westbury, N. Y.). Corex and Pyrex filters were obtained from Hanovia.

For separation of complex product mixtures, gas chromatography employing a 9.5 ft × 0.25 in. Al column packed with 20% Kel-F No. 3 polymer oil on acid-washed Chromosorb P was used. He flow rates were 70 cc/min. When circumstances permitted, fractional condensation was used to separate mixtures.

Materials.—Fluorosulfuryl isocyanate was prepared by the method of Appel and Rittersbacher[6] with some important modifications.

Preparation of $SO_2(NCO)_2$.—The method of Graf[7] which involves the reaction of solid BrCN with liquid SO_3 was used. The product mixture was first distilled at atmospheric pressure to remove most of the Br_2 and SO_2 formed in the reaction, and then at reduced pressure (1 mm) to distil a mixture of $SO_2(NCO)_2$ and $S_2O_5(NCO)_2$. The product was not fractionated further.

Preparation of FSO_2NCO.—The mixture prepared above was placed in a distillation flask and heated under reflux to 170° ($S_2O_5(NCO)_2$ decomposes to $SO_2(NCO)_2$ and SO_3 at 130°) while small aliquots of $HOSO_2F$ (*ca.* 0.25 ml) were added in the course of a few hours. As soon as FSO_2NCO was formed, it distilled into a collection vessel held at 0°. The crude product was contaminated with SO_3, Br_2, and small amounts of SO_2 and CO_2. SO_3 was removed by passing the crude material under vacuum through a column packed with glass wool saturated with concentrated H_2SO_4. (Care must be taken that the column does not heat appreciably because FSO_2NCO reacts with H_2SO_4 at elevated temperature.) Several passes using fresh H_2SO_4 were necessary to free the product from SO_3 completely. Traces of CO_2 and SO_2 were removed by pumping at −78°. Finally, Br_2 was removed by shaking the product with dry Hg. (In a separate experiment, it was determined that FSO_2NCO did not react with Hg at 25°.) The final product was clear, colorless FSO_2NCO. Vapor density: calcd, 125.0; found, 126.0; yield, 29% based on BrCN.

$FOSO_2F$ was collected as a by-product in the preparation of $S_2O_6F_2$[8] and purified by fractional condensation.

Trifluoromethyl hypofluorite was prepared by reaction of CO with F_2 at 350°.[9]

Fluorine was obtained from the General Chemical Division of Allied Chemical Co. and was passed through a trap held at −183° prior to use.

The sulfur trioxide used was stabilized Sulfan B (Allied Chemical Co., Morristown, N. J.).

Cyanogen bromide was obtained from Matheson Coleman and Bell.

Preparation of $FSO_2N(OSO_2F)C(O)F$.—FSO_2NCO (0.1086 g, 0.87 mmol) and $FOSO_2F$ (0.1301 g, 1.10 mmol) were condensed in a 1-l. Pyrex vessel equipped with a water-cooled quartz probe. The mixture was allowed to warm to 25° and then photolyzed in the gas phase through a Pyrex filter with light from a 450-w uv lamp. After 2 hr, the product mixture was examined. No noncondensable gases (−183°) were produced; the mixture contained only unreacted starting materials and the product $FSO_2N(OSO_2F)C(O)F$ as determined by examination of ^{19}F nmr and infrared spectra. The amount of unconsumed $FOSO_2F$ (0.0794 g, 0.67 mmol) indicated that 49.5% conversion was achieved. Other experiments employing larger amounts of reactants and longer irradiation times resulted in different conversion percentages. For example, when a mixture of FSO_2NCO (0.5280 g, 4.22 mmol) and $FOSO_2F$ (0.5957 g, 5.02 mmol) was photolyzed for 6 hr under the above conditions, the amount of unconsumed $FOSO_2F$ (0.2344 g, 1.99 mmol) indicated that 72.5% conversion had taken place.

If the photolysis was allowed to proceed through quartz in the absence of the Pyrex filter, O_2, SO_2F_2, SiF_4, and a polymeric-

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(1) H. Ulrich, *Chem. Rev.*, **65**, 369 (1965).

(2) R. G. Arnold and J. A. Nelson, *ibid.*, **57**, 47 (1957).

(3) C. V. Wilson, *Org. Chem. Bull.*, **35** (2), 1 (1963).

(4) C. V. Wilson, *ibid.*, **35** (3), 1 (1963).

(5) K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).

(6) R. Appel and H. Rittersbacher, *Chem. Ber.*, **97**, 849 (1964).

(7) R. Graf, German Patent 940,351 (1956).

(8) J. M. Shreeve and G. H. Cady, *Inorg. Syn.*, **7**, 124 (1963).

(9) G. H. Cady, *ibid.*, **8**, 165 (1966).

appearing material were observed to form in addition to $FSO_2N(OSO_2F)C(O)F$.

Separation of the product mixture was accomplished by fractional condensation at −23, −78, and −183°. The unreacted $FOSO_2F$ was easily isolated in the trap held at −183° but repeated passes were necessary to isolate pure $FSO_2N(OSO_2F)C(O)F$ in the trap held at −23°. FSO_2NCO was retained in the trap held at −78°.

Identification and Properties of $FSO_2N(OSO_2F)C(O)F$.—The infrared spectrum of $FSO_2N(OSO_2F)C(O)F$ taken in the gas phase at 5 mm in a 10-cm cell with NaCl windows showed absorptions at 1890 (s), 1495 (s), 1250 (s), 1205 (s), 1053 (m), 1021 (m), 854 (s), 827 (s), 788 (ms), and 738 (w) cm^{-1}.

The ^{19}F nmr spectrum consisted of three resonances at +6.58 (–C(O)F), −43.6 ($-OSO_2F$), and −54.6 ($-SO_2F$) ppm relative to an external reference of CCl_3F. The relative areas under the three peaks were in the ratio of 1.02:0.96:1.00. Under high resolution these peaks were split into three pairs of doublets of equal intensity ($J_{SO_2F-OSO_2F}$, 4.4 cps; $J_{SO_2F-C(O)F}$, 8.5 cps; $J_{OSO_2F-C(O)F}$, 11.4 cps).

The vapor density was determined by the method of Regnault (calcd, 243; found, 242).

Anal. Calcd for $FSO_2N(OSO_2F)C(O)F$: F, 23.44; S, 26.38; N, 5.76; C, 4.94; O, 39.48. Found: F, 24.40; S, 25.84; N, 5.76; C, 5.31; O (difference), 38.69.

Vapor pressures were measured over the range 325–392°K using the method of Kellogg and Cady.[5] The approximate molar heat of vaporization at the boiling point was calculated to be 8.77 kcal/mole from the slope of the vapor pressure curve with the aid of the Clausius–Clapeyron equation. The boiling point was estimated to be 121.8 ± 0.4° by extrapolation of the vapor pressure curve. These values yield a Trouton constant of 22.2 eu. Vapor pressure data fit the expression: $\log P_{mm} = 7.6695 - (1895/T)$.

All attempts to crystallize the compound resulted in the formation of a glass.

The hydrolysis of $FSO_2N(OSO_2F)C(O)F$ can be easily followed by infrared spectroscopy. When moist air was admitted into an ir cell containing a pure sample of $FSO_2N(OSO_2F)C(O)F$ and the spectrum was rescanned, bands were observed for CO_2 and SiF_4. In addition, bands attributed to C=O and C—F stretching modes in the C(O)F group were observed to decrease in intensity with time.

Preparation of $FSO_2N(OCF_3)C(O)F$.—In a typical series of preparations, FSO_2NCO (3.5 mmol) and CF_3OF (3.8 mmol) were photolyzed for 7 hr in the gas phase through a Corex filter with radiation from a 450-w uv lamp. The Corex filter was found to be important in reducing degradation of the reactants. The product mixture was fractionated at −110 and −183°. A small amount of a noncondensable gas was present. The fraction which condensed at −183° was examined by infrared spectroscopy and shown to consist of CF_3OF, COF_2, SiF_4, CO_2, and traces of SO_2F_2. The fraction which condensed at −110° was separated by gas chromatography and consisted of three major components which were found to be $S_2O_5F_2$ (R_t = 8 min), unreacted FSO_2NCO R_t = 11 min), and $FSO_2N(OCF_3)C(O)F$ (0.2277 g, 0.99 mmol, 28%, R_t = 14 min) by infrared spectroscopy. In addition to traces of volatile materials (R_t = 4 min), one other component was observed on the gas chromatogram but was present in amounts too small for identification.

Identification and Properties of $FSO_2N(OCF_3)C(O)F$.—The infrared spectrum of the material in the gas phase at 5 mm in a 13-cm cell with AgCl windows showed bands at 1888 (s), 1494 (s), 1308 (s), 1250 (vs), 1206 (vs), 1177 (vs), 1088 (m), 1027 (m), 888 (w), 823 (vs), 776 (w), 747 (w), and 654 (m) cm^{-1}.

Three intense resonances were observed on the ^{19}F nmr spectrogram for $FSO_2N(OCF_3)C(O)F$ at +68.4 ($-OCF_3$), +6.6 (–C(O)F), and −50.4 ($-SO_2F$) ppm relative to an external reference of CCl_3F with areas in a ratio of 3:1:1. Under high resolution fine structure was observed. The first resonance was split into two similar doublets, the second resonance into a broad quintet, and the third resonance into two partially superimposed quartets ($J_{C(O)F-OCF_3}$, 4.3 cps; $J_{OCF_3-SO_2F}$, 1.8 cps; $J_{C(O)F-SO_2F}$, 5.4 cps; J_{calcd} for two overlapping quartets to form a quintet, 4.6 cps; J_{obsd}, 4.6 cps). The vapor density was calculated to be 229; found, 228 ± 2.

Anal. Calcd for $FSO_2N(OCF_3)C(O)F$: F, 41.48; S, 13.97; N, 6.11; C, 10.48; O, 27.96. Found: F, 37.59; S, 15.80; N, 6.87; C, 9.78; O (difference), 29.96.

Vapor pressures were determined in a static system by using cold baths. Data (P_{mm}, T°K) obtained for $FSO_2N(OCF_3)C(O)F$ are: 33.0, 277.0; 39.5, 280.7; 46.0, 284.2; 57.0, 289.0; 60.0, 290.0.

Preparation of $(FSO_2NC(O)F)_2$.—FSO_2NCO (2.99 mmol) and F_2 (3.4 mmol) were photolyzed in a 1-l. Pyrex vessel for 20 min. The 70-w uv lamp was located in a water-cooled quartz probe which fit into the center of the vessel. No filter was used. The product mixture was fractionated at −78 and −183°. A noncondensable gas (F_2) was present and was pumped away through a column packed with soda lime. The fraction which condensed in the trap held at −183° contained COF_2, SiF_4, and SO_2F_2 identified by infrared analysis. The material which condensed at −78° was refractionated at −23 and −183°. The fraction held in the trap at −23° was $(FSO_2NC(O)F)_2$ (1.02 mmol, 69%). The material volatile at this temperature was $S_2O_5F_2$ (0.28 mmol) contaminated with a trace of FSO_2NCO. A white solid remained in the reaction vessel. When treated with moist air, it evolved a brown gas (NO_2). This result indicated that the white solid was probably $(NO)_2SiF_6$.

Identification and Properties of $(FSO_2NC(O)F)_2$.—The infrared spectrum of $(FSO_2NC(O)F)_2$ at 3 mm in a 10-cm cell showed absorptions at 1888 (s), 1494 (s), 1295 (w), 1284 (s), 1225 (s), 1178 (m), 1060 (m), 894 (w), 870 (w), 842 (sh), 829 (s), 727 (vw), and 662 (w) cm^{-1}.

The ^{19}F nmr spectrum exhibited resonances at 9.08 (s) and −57.4 (s) ppm relative to an external standard of CCl_3F. Relative areas of these peaks were in the ratio of 1:1. No fine structure was observed under high resolution.

The calculated vapor density for $(FSO_2NC(O)F)_2$ is 288; found, 294 ± 10.

Anal. Calcd for $(FSO_2NC(O)F)_2$: F, 26.38; S, 22.25; C, 8.34; N, 9.72; O, 33.33. Found: F, 27.0; S, 23.01; C, 8.54; N, 10.85; O (difference), 30.60.

Vapor pressures were determined in a static system. Data (P_{mm}, T°K) obtained for $(FSO_2NC(O)F)_2$ are: 1.5, 273.2; 2.8, 282.2; 3.2, 284.7; 4.0, 287.7; 7.5, 296.2

$(FSO_2NC(O)F)_2$ hydrolyzed in moist air to give CO_2. Bands due to C=O and C—F stretching modes in the C(O)F group were observed to decrease with time.

Reaction of FSO_2NCO with $S_2O_6F_2$.—FSO_2NCO and $S_2O_6F_2$ did not react when allowed to stand together in a glass tube for 2 hr. The mixture was heated to 100°, and, after 12 hr, the characteristic yellow-brown color of $\cdot OSO_2F$ radicals[10] was still observed in the reaction vessel.

FSO_2NCO (0.6112 g, 4.89 mmol) and $S_2O_6F_2$ (1.0229 g, 5.17 mmol) were condensed in a 1-l. Pyrex bulb and irradiated through quartz with uv light from a 450-w lamp for 5.5 hr. No noncondensable gases (−183°) were observed to form. The product mixture was separated crudely by fractional condensation. The most volatile fraction was SiF_4, the next most volatile fraction consisted of $S_2O_6F_2$ and FSO_2NCO, and the least volatile fraction was mostly $FSO_2N(OSO_2F)C(O)F$ contaminated with FSO_2NCO and $S_2O_6F_2$. In addition, a white, flaky material was isolated and shown to be SO_3 by chemical tests. No evidence was found for the presence of $FSO_2N(OSO_2F)C(O)OSO_2F$, the expected product. Apparently, the reaction was

$$FSO_2NCO + S_2O_6F_2 \xrightarrow{h\nu} FSO_2N(OSO_2F)C(O)F + SO_3$$

Further Characterization of FSO_2NCO.—The properties reported for FSO_2NCO in the literature include the boiling point

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(10) F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.*, **85**, 3375 (1963).

(62°,[11] 61.5°[6]) and chemical analysis. Additional data were obtained in the present work.

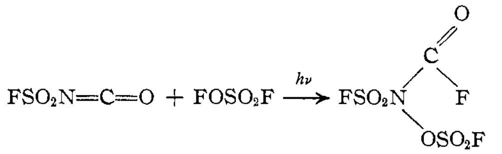
Infrared spectrum (5 mm, 10-cm cell): 2265 (vs), 1467 (s), 1380 (s), 1235 (s), 833 (s), 763 (s), 649 (s) cm^{-1}.

The ^{19}F nmr spectrum consisted of a singlet at -61.1 ppm from an external reference of CCl_3F.

The experimental vapor density was 126.0; calcd, 125.0 The equilibrium vapor pressure at 25° was 155 mm.

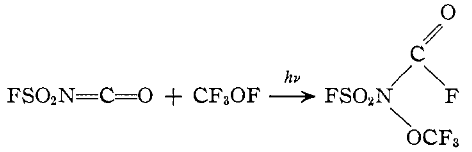
Results and Discussion

Fluorine fluorosulfate was found to react with FSO_2NCO in the gas phase under the influence of Pyrex-filtered ultraviolet radiation according to



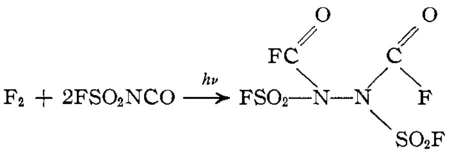
The ^{19}F nmr spectrum of the product showed resonances due to $FSO_2N(OSO_2F)C(O)F$ only and suggested that no isomers were formed. Total conversion of the reactants to the product was never achieved but in 7 hr conversions approached 80% when 4 mmol of each of the starting materials was used. When the irradiation was run in the absence of the Pyrex filter, the product was formed in lower yield and some degradation of the starting materials took place. $FOSO_2F$ is known to produce free radicals under thermal excitation.[10] Heating a mixture of $FOSO_2F$ and $FSO_2N{=}C{=}O$ at 100° for 12 hr resulted in the formation of the addition product in lower yields with some degradation of the starting materials.

Trifluoromethyl hypofluorite reacted with FSO_2NCO under the influence of ultraviolet radiation to form $FSO_2N(OCF_3)C(O)F$ in 28% yield

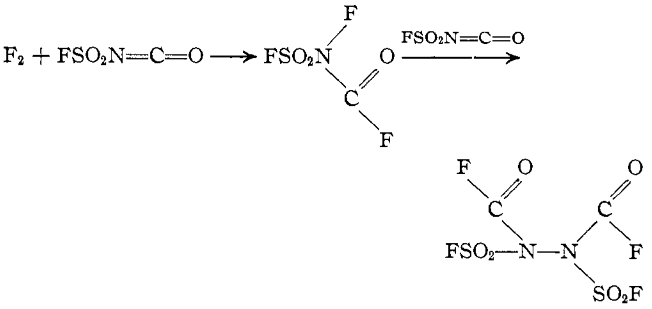


The product mixture was less complex when a Corex glass filter was used than when the uv radiation was allowed to pass directly through quartz. The presence of the other possible isomer, $FSO_2N(F)C(O)OCF_3$, was not detected.

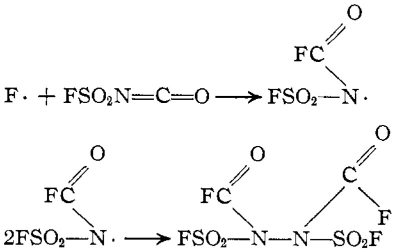
When an equimolar mixture of FSO_2NCO and F_2 was exposed to uv radiation through quartz for 15 min, $(FSO_2NC(O)F)_2$ was isolated in 69% yield. Some degradation products were also observed. The mechanism



by which this substituted hydrazine is formed may involve the preliminary formation of the F_2 addition product which then adds to FSO_2NCO



or $FSO_2NC(O)F$ radicals may form and recombine



The infrared spectra of the three derivatives show similarities, and comparison with other spectra allows some general assignments to be made. Strong bands in the region of 1888 cm^{-1} are assigned to carbonyl stretching of the $-C(O)F$ group.[12] The C–F stretching modes of the $-C(O)F$ group have been found to occur at 1190 cm^{-1} in $FSO_2OC(O)F$[13] and 1221 and 1178 cm^{-1} in $(FC(O)O)_2$[14] which correspond with bands in the region 1177–1205 cm^{-1} in the fluorosulfuryl isocyanate derivatives; these assignments should be regarded as tentative. Absorptions in the region 1494 and 1250 cm^{-1} may be ascribed to asymmetric and symmetric S=O stretching vibrations of the $-SO_2F$ group. These values are in line with those found for similar compounds containing the $-SO_2F$ group, *i.e.*, $-N(SO_2F)_2$[15] and $=NSO_2F$.[16] A doublet might be expected to appear for the S=O asymmetric stretching mode in $FSO_2N(OS_2OF)C(O)F$ but none was observed probably owing to overlap of the two bands. $CF_3OSO_2OSO_2F$ shows only one band for the S=O asymmetric stretching mode.[17] The strong absorptions at 854 and 827 cm^{-1} are assigned to S—F asymmetric and symmetric stretching modes in $FSO_2N(OSO_2F)C(O)F$.[16,18] Bands at 842–823 cm^{-1} are assigned to S—F stretching modes in $FSO_2N(OCF_3)C(O)F$ and $(FSO_2NC(O)F)_2$.

The ^{19}F nmr spectra of the isocyanate addition products support their proposed structures. $FSO_2N(OSO_2F)C(O)F$ shows three resonances of equal area appearing at $+6.6$, -43.6, and -54.6 ppm from an external reference of CCl_3F. The first resonance is assigned to the F atom attached to the carbonyl group since other molecules containing a fluorocarbonyl group bonded to nitrogen have been found to absorb near

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[11] H. Jonas and D. Voigt, *Angew. Chem.*, **70**, 572 (1958).

[12] J. H. Simons, "Fluorine Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1954, p 485.

[13] W. B. Fox and G. Franz, *Inorg. Chem.*, **5**, 946 (1966).

[14] A. J. Arvia and P. J. Aymonino, *Spectrochim. Acta*, **18**, 1299 (1962).

[15] J. K. Ruff, *Inorg. Chem.*, **5**, 732 (1966).

[16] M. Lustig, C. L. Bumgardner, F. A. Johnson, and J. K. Ruff, *ibid.*, **3**, 1165 (1964).

[17] W. P. Van Meter and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 6005 (1960).

[18] H. C. Clark and H. J. Emeléus, *J. Chem. Soc.*, 190 (1958).

this region.[19-21] The resonances at -43.8 and -54.6 ppm are in the regions associated with OSO_2F and SO_2F groups, respectively.[15,22,23] Under high resolution each of these singlets was split into a pair of doublets arising from coupling of the two nonequivalent F atoms with the third one. Although no nitrogen coupling was observed, the resonance attributed to the $-C(O)F$ group was broadened indicating that quadrupole interactions may be important. Broadening of nmr signals for F on $-C(O)F$ have been observed in compounds containing $-C(O)F$ groups bonded to nitrogen.[24] The larger J value observed for coupling of F on $-OSO_2F$ with F on $-C(O)F$ suggests that through-space interactions may be important since F on OSO_2F is four atoms removed from F on $-C(O)F$. Such through-space interactions have been found to be important in the perfluoroalkyl derivatives of sulfur hexafluoride.[25] In the case of $FSO_2N(OCF_3)C(O)F$, three resonances were also observed at $+68.3$, $+6.6$, and -50.4 ppm relative to CCl_3F. The areas were in the ratio of 3:1:1 and are in the regions associated with the $-OCF_3$, $-C(O)F$, and $-SO_2F$ groups, respectively. The high-resolution spectrum showed a high-field pair of doublets arising from coupling of two nonequivalent F atoms with those of the $-OCF_3$ group. The resonance at 6.6 ppm was observed as a broadened quintet in the ratio 1:4:6:4:1 arising from two overlapping quartets due to coupling of the $-C(O)F$ fluorine atom with those of the $-OCF_3$ and $-SO_2F$ groups. The low-field resonance appeared as two partially superimposed quartets due to coupling of the F atom on the $-SO_2F$ group with those on the $-C(O)F$ and $-OCF_3$ groups. $(FSO_2NC(O)F)_2$ exhibited two resonances of equal intensity located at $+9.08$ and -57.4 ppm attributed to F atoms in the $-C(O)F$ and $-SO_2F$ groups, respectively. No fine structure was observed. Although the results of infrared, nmr, and chemical analyses indicate that the empirical formula is $(FSO_2NC(O)F)_n$, they do not show that n equals 2. The conclusion that n equals 2 follows after a consideration of rules of chemical valence, comparison of observed with expected volatility, and the fact that the material is uncolored indicating that it is probably not a free radical.[26]

It is interesting to note that apparently **only** one isomeric form of each new compound reported here is formed in isolable quantities. The fact that the carbonyl stretching frequency is invariant at 1888 cm^{-1} lends support to the argument that this must arise from a $-C(O)F$ group since in perfluoracyl fluorosulfates[27] the $C{=}O$ stretch is found at 1845–1850 cm^{-1}. However, in fluoroformyl fluorosulfate this stretch is shifted to 1910 cm^{-1}.[13] The nmr spectra leave essentially no doubt as to the absence of $>NF$ in these compounds since $>NF$ resonances in general occur at higher fields than the resonances assigned here to $-C(O)F$, *e.g.*, for $C_2F_5N(F)C(O)F$, $CF_3N(F)SF_5$,[28] and $FN(SO_2F)_2$,[16] $>NF$ resonances occur at ϕ 49.4, 48.2, and 28.5, respectively.

The compounds are hydrolyzed by traces of moisture. Hydrolytic attack probably occurs first at the fluorocarbonyl group followed by very slow hydrolysis of the fluorosulfuryl group.[23]

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(24) J. K. Ruff, *ibid.*, **5**, 1787 (1966).

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Fragmentation and Rearrangement Processes in the Mass Spectra of Fluoroalkylphosphorus Compounds.
II. Compounds Containing Two or More Phosphorus Atoms

By R. G. CAVELL and R. C. DOBBIE

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The mass spectra of five fluoroalkylphosphorus compounds containing two or more phosphorus atoms have been obtained and partial fragmentation patterns deduced. Rearrangement to give ions with P–F bonds was detected in all of the spectra.

Introduction

It has been demonstrated that trifluoromethylarsenic[1] and -phosphorus[2] compounds rearrange under electron impact in the mass spectrometer, with the migration of fluorine from carbon to arsenic or phosphorus. The mass spectra of some fluoroalkyl com-

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(1) R. C. Dobbie and R. G. Cavell, *Inorg. Chem.*, **6**, 1450 (1967).

(2) R. G. Cavell and R. C. Dobbie, *ibid.*, **7**, 101 (1968).