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Fluorination of Some Perfluoroalkyliminosulfur Difluorides

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The fluorination of trifluoromethyliminosulfur difluoride and perfluoroethyliminosulfur difluoride leads to the formation of four new compounds: bis(trifluoromethylimino)sulfur difluoride, $(CF_3N{=})_2SF_2$, trifluoromethylpentafluorosulfurfluoramine, CF_3NFSF_5, bis(perfluoroethylimino)sulfur difluoride, $(C_2F_5N{=})_2SF_2$, and perfluoroethylpentafluorosulfurfluoramine, $C_2F_5NFSF_5$.

The successful catalytic addition of fluorine across the sulfur–oxygen bond in thionyl tetrafluoride[1] and the catalyzed conversion of thionyl fluoride to pentafluorosulfur hypofluorite[1,2] suggested that similar techniques might be applicable to the fluorination of perfluoroalkyliminosulfur difluorides.[3] The sulfur atom in this class of compounds is formally isoelectronic with the sulfur atom in thionyl fluoride and might be expected to behave in an analogous manner.

A catalyzed static fluorination of $CF_3N{=}SF_2$ produced the expected product, CF_3NFSF_5, in low yield together with large amounts of sulfur hexafluoride and trifluoromethyldifluoramine. When the fluorination was carried out in the absence of a catalyst a second reaction simultaneously occurred and bis(trifluoromethylimino)sulfur difluoride, $(CF_3N{=})_2SF_2$, was formed in addition to the products found in the catalyzed reaction. The behavior of perfluoroethyliminosulfur difluoride toward fluorination was found to be analogous to that of the trifluoromethyl derivative.

Experimental

Materials.—Fluorine was obtained from the General Chemical Co. and was used after passage through a sodium fluoride scrubber. The perfluoroalkyliminosulfur difluorides were prepared by the literature methods.[3]

Reaction between $CF_3N{=}SF_2$ and Fluorine.—It was found that the best yields of both $(CF_3N{=})_2SF_2$ and CF_3NFSF_5 were obtained using a 1.5 to 2 molar ratio of F_2 to $CF_3N{=}SF_2$ and the reactions took >20 hr. for completion. In a typical experiment 1.30 g. (8.5 mmoles) of $CF_3N{=}SF_2$ containing trace amounts of SOF_2 was condensed into a 150-ml. stainless steel Hoke cylinder equipped with a needle valve. Fluorine (0.483 g., 12.7 mmoles) was allowed to expand into the cylinder while it was maintained at −196°. The cylinder stood for 3 days at ambient temperature and all of the fluorine was consumed. Mass spectral, infrared, and *PVT* analyses indicated the products obtained from the reactions consisted of CF_3NF_2 (1.0 mmole), SF_6 (3.8 mmoles), $(CF_3N{=})_2SF_2$ (2.6 mmoles), and CF_3NFSF_5 (1.5 mmoles). Trace quantities of $CF_3N{=}SF_2$, CO_2, SOF_2, and SOF_4 were present. The product mixture was fractionated through traps maintained at −119, −145, and −196°. The first trap contained primarily $(CF_3N{=})_2SF_2$ while the −145° trap contained CF_3NFSF_5 and trace amounts of $CF_3N{=}SF_2$. The −196° trap contained SF_6, CF_3NF_2, and traces of SOF_2 and SOF_4. Further purification of $(CF_3N{=})_2SF_2$ was achieved by gas phase chromatography at −35° using a 15-ft. perfluorotri-*t*-butylamine on Chromosorb P column. Purification of CF_3NFSF_5 was also accomplished by chromatography at −10° using the above column. *Anal.* Calcd. for $C_2F_8N_2S$: C, 10.17; N, 11.86. Found: C, 10.60; N, 11.48. Calcd. for CF_9NS: F, 74.7. Found: F, 75.4. The vapor density molecular weights of $(CF_3N{=})_2SF_2$ (found 236, calcd. 236) and of CF_3NFSF_5 (found 230, calcd. 229) are in accord with the above formulations.

In a catalytic reaction, 0.16 g. (1.04 mmoles) of $CF_3N{=}SF_2$ and 0.091 g. (2.39 mmoles) of fluorine were combined at −196° in a second stainless steel cylinder which contained 5.0 g. of CsF. The reactor was allowed to warm to ambient temperature and stand for 2 days. All the fluorine was again consumed and the products consisted of CF_3NFSF_5 (0.17 mmole), SF_6 (0.67 mmole), and CF_3NF_2 (0.68 mmole). A small amount of $CF_3N{=}SF_2$ (0.14 mmole) was also recovered.

Reaction between $C_2F_5N{=}SF_2$ and Fluorine.—The uncatalyzed reaction between $C_2F_5N{=}SF_2$ and fluorine was performed in a manner similar to that described above using 0.13 g. (3.4 mmoles) of fluorine and 0.41 g. (2.0 mmoles) of $C_2F_5N{=}SF_2$. It was somewhat faster than when $CF_3N{=}SF_2$ was employed and it was only necessary to let the reactor stand for 16 hr. at ambient temperature before the reaction was complete. The total product mixture consisted of $(C_2F_5N{=})_2SF_2$ (0.23 mmole), $C_2F_5NFSF_5$ (0.33 mmole), $C_2F_5N{=}SF_2$ (0.38 mmole), SF_6 (0.92 mmole), $C_2F_5NF_2$ (0.91 mmole), and SOF_2 (0.13 mmole), the presence of which is unexplained. The product mixture was fractionated through −95, −126, and −196° traps on the vacuum line. The first trap contained a mixture of $(C_2F_5N{=})_2SF_2$ and starting material. Further rectification by gas phase chromatography was successful when a 15-ft. diisodecyl phthalate on Chromosorb P column was operated at −10°. The −126° trap contained a mixture of starting material and $C_2F_5NFSF_5$. The latter product was obtained pure by gas chromatography using the same column as above at room temperature. *Anal.* Calcd. for $C_4H_{12}N_2S$: C, 14.29; F, 67.9. Found: C, 14.82; F, 64.3. Calcd. for $C_2F_{11}NS$: C, 8.60. Found: C, 9.16. The vapor density molecular weights of $(C_2F_5N{=})_2SF_2$ (found 336, calcd. 336) and of $C_2F_5NFSF_5$ (found 271, calcd. 279) are in agreement with the assigned formulas.

Spectral Properties of the New Compounds; Infrared Spectra.—The infrared spectra were taken with a Perkin-Elmer Model 21 spectrophotometer using gaseous samples. The bands observed are listed in Table I.

^{19}F N.m.r. Spectra.—The ^{19}F n.m.r. spectra of the new compounds were obtained in CCl_3F solutions using a Varian Model V4310A spectrometer operating at 40 Mc. See the Results and Discussion section for the data.

Mass Spectra.—The mass spectra of the new compounds were obtained using gaseous samples with a Consolidated Engineering Corp. Model 21-620 spectrometer. The ionizing voltage was 100 volts. The mass number, ion species, and relative abundance for some of the more prominent peaks for $(CF_3N{=})SF_2$ are as follows: 69, CF_3^+, 100; 46, SN^+, 18.6; 236, $(CF_3N{=})_2SF_2^+$, 6.7; 70, SF_2^+, 5.0; 51, SF^+, 5.0; 115, $CNSF_3^+$, 4.8; 217, $(CF_3N{=})_2SF^+$, 4.1; for CF_3NFSF_5: 127, SF_5^+, 100; 69, CF_3^+, 56.2; 89, SF_3^+, 53.6; 31, CF^-, 4.6; 70, SF_2^+, 4.5; 108, SF_4^+,

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(1) J. K. Ruff and M. Lustig, *Inorg. Chem.*, **3**, 1422 (1964).

(2) F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *J. Am. Chem. Soc.*, **78**, 1553 (1956).

(3) W. C. Smith, C. W. Tullock, R. D. Smith, and V. A. Engelhardt, *ibid.*, **82**, 551 (1960).

TABLE I

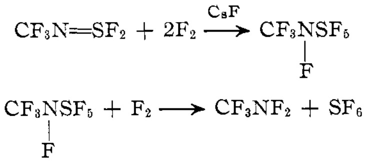
INFRARED SPECTRA (CM.$^{-1}$) OF SOME IMINOSULFUR DIFLUORIDES AND PENTAFLUOROSULFUR FLUORAMINES

$CF_3N=SF_2$	$(CF_3N=)_2SF_2$	CF_3NFSF_5	$C_2F_5N=SF_2$	$(C_2F_5N=)_2SF_2$	$C_2F_5NFSF_5$
1511 w	1404 s	1280 s	1411 s	1429 s	1351 m
1387 vs	1235 s	1241 s	1342 s	1342 vs	1250 vs
1205 s	1198 s	1212 ms	1238 vs	1242 vs	1220 s
1176 s	1183 vs	1040 mw	1153 s	1143 vs	1193 s
820 m	883 m	957 mw	814 m	1024 s	1101 s
760 m	847 m	920 vs	758 s	861 s	1032 m
714 m	766 w	852 vs	714 s	833 s	930 vs
	676 w	733 w	635 w	797 m	893 vs
	618 w	707 mw	504 m	758 ms	870 w
	593 w	608 m		727 s	823 s
	551 w	580 w			741 ms
	478 w				705 ms
					680 w

3.8; for $(C_2F_5N=)_2SF_2$: 69, CF_3^+, 100; 46, SN^+, 53.3; 119, $C_2F_5^+$, 44.8; 267, $C_3N_2SF_9^+$, 22.7; 134, $CNSF_4^+$, 17; 31, CF^+, 14.3; 153, $CNSF_5^+$, 13.5; 70, SF_2^+, 12.2; 51, SF^+, 10.2; 50, CF_2^+, 10.0; 217, $C_2N_2SF_7^+$, 9.2; and for $C_2F_5NFSF_5$: 127, SF_5^+, 100; 84, NSF_2^+, 47.3; 69, CF_3^+, 36.7; 119, $C_2F_5^+$, 26.0; 31, CF^+, 6.5; 129, $^{34}SF_5^+$, 4.4; 50, CF_2^+, 4.0; 70, SF_2^+, 4.0; 108, SF_4^+, 3.4; 46, SN^+, 2.3.

Results and Discussion

The fluorination of the $S=N$ bond was not as straightforward as that found for the fluorination of the $S=O$ bond in thionyl fluoride. Instead of obtaining a high yield of the fully saturated compounds, SF_5NFR_f, in the cesium fluoride catalyzed fluorination, considerable cleavage of the product resulted and sulfur hexafluoride and trifluoromethyldifluoramine were produced in good yield.



$$CF_3N=SF_2 + 2F_2 \xrightarrow{CsF} CF_3\underset{\displaystyle F}{\underset{|}{N}}SF_5$$

$$CF_3\underset{\displaystyle F}{\underset{|}{N}}SF_5 + F_2 \longrightarrow CF_3NF_2 + SF_6$$

This occurred to a large extent even when a deficiency of fluorine was employed. The uncatalyzed fluorination of a pure sample of $C_2F_5NFSF_5$ also resulted in the formation of $C_2F_5NF_2$ and SF_6 in a 1:1 ratio. In the catalytic fluorination of thionyl fluoride little or no cleavage of the $S—O$ bond in the product, pentafluorosulfur hypofluorite, was observed. That is, perhaps, not unexpected since mass spectrometric studies suggest that the $S—N$ bond in SF_5NF_2 is quite weak and, thus, should be susceptible to further fluorination.[4] A second mode of reaction was observed when the fluorination was performed in the absence of cesium fluoride. In addition to the saturated product and its cleavage fragments a bis(perfluoroalkylimino)sulfur difluoride and sulfur hexafluoride were formed.

$$2R_fN=SF_2 + 2F_2 \longrightarrow SF_6 + R_fN=SF_2=NR_f$$

Formation of the saturated product R_fNFSF_5 in the "uncatalyzed" fluorination is, perhaps, attributable to catalysis by the metal fluorides present in the stainless steel reactors. None of the bis(perfluoroalkylimino)-sulfur difluorides were formed in the catalyzed fluorination. An attempt to fluorinate $CF_3N=SF_2$ in the absence of metal fluorides using a Pyrex bulb was not successful since the large amount of silicon tetrafluoride formed made the results unreliable.

The infrared spectra of both imino derivatives, $(CF_3N=)_2SF_2$ and $(C_2F_5N=)_2SF_2$, show bands at 1404 and 1428 cm.$^{-1}$, respectively, which are believed to arise from the $S=N$ bond.[3] No bands are observed in the spectra of the saturated compounds in this wave number region (see Table I). The assignment of bands to the $S—F$ stretching modes in $(CF_3N=)_2SF_2$ is more difficult. However, a tentative assignment of the bands at 883 and 847 cm.$^{-1}$ to $S—F$ stretching frequencies can be made by comparison of the spectra of SOF_2 and SO_2F_2 with those of $CF_3N=SF_2$ and $(CF_3N=)_2SF_2$. The $S—F$ stretching vibrations for SOF_2 at 801 and 721 cm.$^{-1}$ are displaced to higher frequencies than those for SO_2F_2,[5] *viz.*, 848 and 885 cm.$^{-1}$. The same shift to higher frequencies is observed in the spectrum of $CF_3N=SF_2$, with bands at 760 and 714 cm.$^{-1}$ assigned to $S—F$ frequencies, and $(CF_3N=)_2SF_2$, with absorptions stated above. Correspondingly, the bands at 861 and 833 cm.$^{-1}$ are assigned to the $S—F$ vibrations in $(C_2F_5N=)_2SF_2$. Both of the bis(perfluoroalkyl) derivatives also have bands in the $C—F$ region. More definite assignments must await a careful study of the infrared and Raman spectra of these imino compounds. Both of the saturated compounds, CF_3NFSF_5 and $C_2F_5NFSF_5$, show bands in the $C—F$, $N—F$, and $S—F$ stretching regions but exact assignment is difficult.

The mass spectra of the new compounds show some distinct differences between the unsaturated and saturated derivatives. The largest peak in the mass spectra of CF_3NFSF_5 and $C_2F_5NFSF_5$ is that due to the SF_5^+ ion while that in the spectra of the imino derivatives is due to the CF_3^+ ion. Furthermore, the compounds containing the $S=N$ bonds, including the starting materials, have a large contribution to the cracking pattern from the peak due to the SN^+ ion, while those containing an $S—N$ bond, such as is found in the SF_5 derivatives and in several other fluorosulfur–nitrogen derivatives, do not.[6]

The ^{19}F n.m.r. spectrum of $(CF_3N=)_2SF_2$ further sup-

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[4] G. Paulett and M. Lustig, *J. Am. Chem. Soc.*, **87**, 1020 (1965).

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

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

ports the assigned structure. The spectrum consists of a septuplet (J_{FF} = 8 c.p.s.) at ϕ −57.2, which is assigned to the fluorines bound to sulfur, and a triplet (J_{FF} = 8 c.p.s.) at ϕ 48.2, which is assigned to the fluorine atoms on carbon. The respective relative area ratio is 1.0:3.1. Thus the two perfluoromethyl groups must be equivalent. The spectrum of $(C_2F_5N{=})_2SF_2$ is similar and consists of a quintuplet (J_{FF} = 8 c.p.s.) centered at ϕ −63.1, which is assigned to the SF_2 group. The quintuplet arises from coupling with two equivalent CF_2 groups. The bands in the C—F region consist of a triplet (J_{FF} = 8 c.p.s.) centered at ϕ 86.5 which overlaps with a singlet at slightly lower field. The triplet is assigned to the CF_2 group and the singlet to the CF_3 group. Apparently the CF_2 group and the CF_3 group do not couple. The area ratio due to the SF_2, CF_3, and CF_2 group fluorine atom resonances is 2.0:5.9:4.1, respectively. The ^{19}F n.m.r. spectra of the saturated products, CF_3NFSF_5 and $C_2F_5NFSF_5$, are more complex. No attempt was made to analyze the bands attributable to the SF_5 groups which have AB_4 patterns. The major bands of these groups are centered at ϕ −58.2 and −60.5 for CF_3NFSF_5 and $C_2F_5NFSF_5$, respectively. The two other bands in the spectrum of CF_3NFSF_5 are found at ϕ 48.2 and 70.3 and are assigned to the NF and CF_3 groups. The area ratio for SF_5:NF:CF_3, 5.1:1.0:3.1, respectively, is consistent with the assignments. In the spectrum of $C_2F_5NFSF_5$ the broad band at ϕ 49.4 is assigned to the NF fluorine while the doublet (J_{FF} = 10 c.p.s.) at ϕ 81.7 and the band at ϕ 110.1 are assigned to the CF_3 and CF_2 groups, respectively. The band at ϕ 81.7 coalesced into a singlet when the band at ϕ 49.4 was saturated. Therefore the fluorines on the CF_3 and NF groups are coupled while the fluorines on the CF_2 group do not couple with those on the CF_3 group. The ratio of the areas of the SF_5, NF, CF_3, and CF_2 group fluorine resonances is 4.63:1.0:3.17:1.90, respectively, and is, again, consistent with the above assignment.

The observation that the CF_3 groups and the C_2F_5 groups in $(CF_3N{=})_2SF_2$ and $(C_2F_5N{=})_2SF_2$, respectively, are equivalent and the evidence from the infrared and mass spectra for the presence of an S=N bond in these compounds support the above proposed formulation. An alternate possibility which must be considered is $R_{f2}NN{=}SF_2$. Some evidence against this formulation is found in the mass spectrum of $(C_2F_5N{=})_2SF_2$. Peaks corresponding to ions which contain one carbon, one nitrogen, and one sulfur are found (*e.g.*, 115, $CNSF_3^+$, 2.7%; 134, $CNSF_4^+$, 17.0%; and 153, $CNSF_5^+$, 13.5%). These fragments cannot arise from the above structure unless a rearrangement involving the formation of a C—N bond occurred. This is felt to be unlikely. Similar peaks are observed in the mass spectrum of $(CF_3N{=})_2SF_2$. Furthermore, $(CF_3N{=})_2SF_2$ is resistant to hydrolysis, being unaffected by aqueous 20% solutions of sodium hydroxide or hydrochloric acid at reflux for 4 hr. This is analogous to the behavior of SO_2F_2. The N—N structure presumably would not resist hydrolysis to this extent.

Attaway and co-workers[7] reported an unstable compound having the tentatively assigned structure $SF_5CF_2NF_2$, but Roberts speculates that an alternate structure, SF_5NFCF_3,[8] is more likely. Nevertheless, no structural characterization has been given prior to that reported in this paper which is consistent with the monofluoramine structure.

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[8] H. L. Roberts, *Quart Rev.* (London), **15**, 30 (1961).

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The Imidodisulfuryl Fluoride Ion

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Imidodisulfuryl fluoride is an acid in aqueous media, and several salts containing the $N(SO_2)F_2$ anion have been prepared. The silver salt forms a stable complex with benzene. Cesium imidodisulfuryl fluoride behaves as a 1:1 electrolyte in nitromethane.

Although the chemistry of imidodisulfuryl fluoride has not been extensively investigated,[1,2] the reported observations indicate that the nitrogen possesses little basicity.[1] In fact, imidodisulfuryl fluoride exhibits acidic behavior toward ammonia. It was suggested that ammonium imidodisulfuryl fluoride was formed, but no conclusive evidence was presented.[1] This investigation was undertaken in order to characterize further the imidodisulfuryl fluoride ion.

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[1] R. Appel and G. Eisenhauer, *Ber.*, **95**, 246 (1962).

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