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Regiospecific Addition of Trifluoramine Oxide to Trifluorovinyl Olefins

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New compounds containing the *N,N*-difluorohydroxylamino group have been prepared by the addition of NF_3O to olefins in the presence of catalytic amounts of a Lewis acid. The new compounds R_fONF_2 (R_f = $CF(CF_3)$-*n*-C_5F_{11}, $-CF(CF_3)C(O)F$, $CF(CF_3)SF_5$, $-CF(CF_3)CF_2OCF_2CF(SO_2F)CF_3$, $-CF(CF_3)CF_2OCFOCF(CF_3)CF_2OCF(CF_3)$, $-CF_2CF_2OC_2F_5$, $-CF_2CF_2OCF_2CF(CF_3)O$-*n*-C_3F_7) were obtained and characterized. The orientation of addition can be explained by electrophilic attack of NF_2O^+ on the double bonds: perfluoroalkenes gave Markovnikov products while pefluorovinyl ethers yielded products with the opposite orientation due to the reversed polarity of the double bond.

Introduction

Since the discovery of NF_3O by several workers in the 1960's,[1-3] a number of attempts have been made to prepare organic or fluoroorganic derivatives of this novel compound. Although NF_3O is by itself kinetically inert, several compounds of the class of *N,N*-difluoro-*O*-hydroxylamines were prepared, either by reaction of fluoroalkyl hypofluorites with N_2F_4,[4-6] with $KF\cdot HNF_2$[7] by the homolytic cleavage of fluorinated peroxides in the presence of N_2F_4,[8] or by the reaction of a hydroxylamine with NF_2Cl and CsF.[9] Only recently has the synthesis of $\cdot ONF_2$ derivatives from BF_3-catalyzed addition of NF_3O to simple fluoroethylenes been reported.[10] With arsenic pentafluoride as a catalyst, it is now possible to add NF_3O directly to many trifluoroethylene derivatives.

Results and Discussion

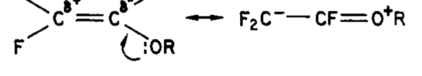
When trifluoramine oxide is reacted with strong Lewis acids such as AsF_5 or SbF_5, either at ambient temperature or by condensing the two compounds together in a 1:1 ratio at −196 °C and allowing the mixture to warm to 25 °C, white solids of the composition $NF_2O^+MF_6^-$ (M = As, Sb) are formed. At 25 °C, the AsF_5 adduct is observed to be partially dissociated to the parent materials:[2]

$$NF_3O + AsF_5 \overset{25\ °C}{\rightleftharpoons} NF_2O^+AsF_6^- \qquad (1)$$

The salt, which is very hygroscopic, is readily hydrolyzed to give hydrogen fluoride and $NO_2^+AsF_6^-$. When a trifluorovinyl olefin is added to the salt, in the presence of excess NF_3O, the formation of the corresponding *N,N*-difluorohydroxylamine in yields approaching 33% is observed. In the case of totally fluorinated alkyl 1-olefins such as C_3F_6 and C_7F_{14} or with other trifluorovinyl olefins such as trifluorovinyl sulfur pentafluoride and trifluoroacryloyl fluoride, only Markovnikov-type addition is observed to give the compounds $(CF_3)_2CFONF_2$, $CF_3CF(ONF_2)C_5F_{11}$, $CF_3CF(ONF_2)SF_5$, and $CF_3CF(ONF_2)C(O)F$, respectively. In the latter three cases, conversion of the olefin to the *N,N*-difluorohydroxylamine was low unless the reaction mixture was heated at 50–55 °C for 24 h. This can be accounted for by the more sterically hindered double bond relative to *F*-propene. Of these compounds, only heptafluoro-2-(*N,N*-difluorohydroxylamino)propane, *i*-$C_3F_7ONF_2$, had been reported previously. It was prepared by the high-pressure reaction of $(CF_3)_2CO$ with N_2F_4 and N_2F_2 at 100 °C and 1000 atm pressure in a platinum tube[11] and, more recently,[7] via the low-temperature reaction of $(CF_3)_2CFOF$ with HNF_2 over KF. The infrared and ^{19}F NMR spectra are identical with those already reported.[7,11] All the *N,N*-difluorohydroxylamines prepared gave distinctive IR bands in the range 1020–1060, 898–930, and 846–865 cm^{-1} due to the symmetric and asymmetric NF stretching frequencies and the N–O stretching frequency, respectively.[4] The latter band proved to be an especially useful clue to the presence of the ONF_2 moiety. Similarly, a somewhat broad resonance (or resonances) at +124 to +136 ppm (relative to CCl_3F) in the ^{19}F NMR spectra was a distinctive feature of the ONF_2-containing compounds. In some cases, e.g. where $R_f = SF_5$, C(O)F, or C_5F_{11}, the chiral center at carbon gives rise to nonequivalent fluorine atoms on nitrogen in the ^{19}F NMR spectra where pairs of doublets with differences in chemical shift of 7–12 ppm and $2J_{FF}$ = 350–366 Hz are observed.

In olefins, $F_2C{=}CFr$, where R = OC_2F_5, $OCF_2CF(CF_3)OC_3F_7$, Cl, or Br, only anti-Markovnikov-type addition occurred to give the corresponding difluorohydroxylamines: $F_2NOCF_2CF_2OC_2F_5$, $F_2NOCF_2CF_2OCF_2CF(CF_3)OC_3F_7$, $F_2NOCF_2CF_2Cl$, and $F_2NOCF_2CF_2Br$. The latter two compounds have been prepared previously via the addition of $NF_2O^+BF_4^-$ to the corresponding olefins at low temperature.[10] Published infrared and ^{19}F NMR spectra confirm the identity of these products.

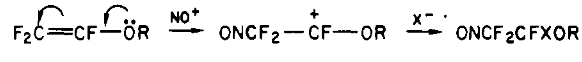
The reversal of orientation of addition that was observed is similar in principle to the electrophilic addition of FNO to alkyltrifluorovinyl ethers observed by Dyatkin et al.[12] to give alkyl 1,1,2,2-tetrafluoronitrosoethyl ethers in lieu of the expected Markovnikov product. This was explained by the ability of the oxygen lone pair to be transferred to the carbon–oxygen bond, thus reversing the normal polarity of the double bond:



(2)

R = CH_3, C_2H_5

During the addition of the NO^+ species, the more stable carbonium ion formed is secondary, not primary, as is normally expected:



(3)

To test the relationship between orientation of addition and the presence of an atom in the vinylic position above to donate electrons as in eq 2, NF_3O was added to the pentafluoroallylic ethers $CF_2{=}CFCF_2OCF_2CF(SO_2F)CF_3$ and $CF_2{=}CFCF_2OCFOCF(CF_3)CF_2OCF(CF_3)$. Under conditions

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[1] Bartlett, N.; Passmore, J; Wells, E. J. *Chem. Commun.* **1966**, 213.
[2] Fox, W. B.; MacKenzie, J. S.; Vanderkooi, N.; Sukornik, B.; Wamser, C. A.; Holmes, J. R.; Eibeck, R. E.; Stewart, B. B. *J. Am. Chem. Soc.* **1966**, *88*, 2604.
[3] Maya, W. U.S. Patent 3 320 147, 1967.
[4] Hale, W. M.; Williamson, S. M. *Inorg. Chem.* **1965**, *4*, 1342.
[5] Shreeve, J. M.; Duncan, L. C.; Cady, G. H. *Inorg. Chem.* **1965**, *4*, 1516.
[6] Ruff, J. K. *Inorg. Chem.* **1965**, *4*, 1788.
[7] Maya, W.; Pilipovich, D.; Warner, M. G.; Wilson, R. D.; Christe, K. O. *Inorg. Chem.* **1983**, *22*, 810.
[8] Fox, W. B.; Franz, G.; Anderson, L. R. *Inorg. Chem.* **1968**, *7*, 382.
[9] Lott, J. A.; Babb, D. P.; Pullen, K. E.; Shreeve, J. M. *Inorg. Chem.* **1968**, *7*, 2593.
[10] Wilson, R. D.; Maya, W.; Pilipovich, D.; Christe, K. O. *Inorg. Chem.* **1983**, *22*, 1355.
[11] Christe, K. O., private communication.
[12] Dyatkin, B. L.; Bekker, R. A.; Konstantinov, Yu. S.; Knunyants, I. L. *Dokl. Acad. Nauk SSSR*, **1965**, 1200; *Chem. Abstr.* **1966**, *64*, 9581*b*.

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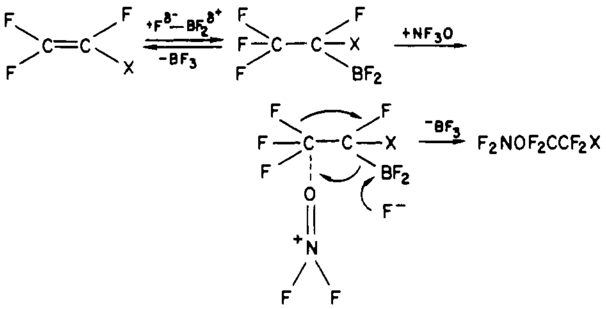
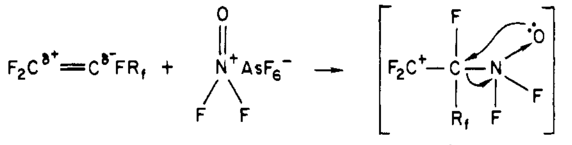
identical with those of the earlier reactions, NF_3O adds to olefins to give exclusively the Markovnikov-type products $CF_3CF(ONF_2)CF_2OCF_2CF(SO_2F)CF_3$ and $CF_3CF(ONF_2)CF_2OCFOCF(CF_3)CF_2OCF(CF_3)$ (in 28 and 15% yields, respectively), as determined by ^{19}F NMR.

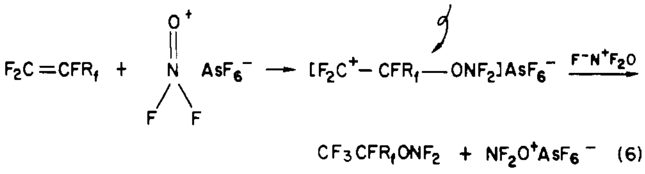
The order of reactivity of fluoro olefins was investigated to determine the possible mechanism of addition of NF_3O. With olefins containing an internal double bond such as *cis*- or *trans*-*F*-2-butene, -*F*-cyclobutene, or -1,2-dichloro-1,2-difluoroethylene or a geminally disubstituted olefin such as 1,1-dichloro-2,2-difluoroethylene, only fully fluorinated products were obtained, presumably through the well-known nucleophilic fluorination mechanism. This fact, plus the necessity for a Lewis acid catalyst for addition to proceed, is evidence for an electrophilic addition mechanism.[13] In this case, the electrophile is NF_2O^+. Other workers[10] have proposed a mechanism with Lewis acid addition to the olefin as the first step followed by a concerted NF_3O addition with fluorine migration and displacement of the Lewis acid, e.g., BF_3:



(4)

We have conducted variable-temperature ^{19}F NMR studies in an attempt to observe an addition product, $(CF_3)_2CFAsF_4$, formed with $CF_3CF{=}CF_2$ and AsF_5. Between −83 and +30 °C, no evidence for interaction was detected. Additionally, we and others[14] have found addition of NF_3O to proceed most reliably in the presence of free NF_3O, which should preclude the existence of free BF_3 or AsF_5 at the temperature described, according to eq 1. Therefore, we believe that addition must occur via electrophilic attack on the olefin by the ONF_2^+ species, followed by (1) rearrangement and fluoride ion attack if a C–N bond is formed initially (eq 5) or (2) fluorination


(5)

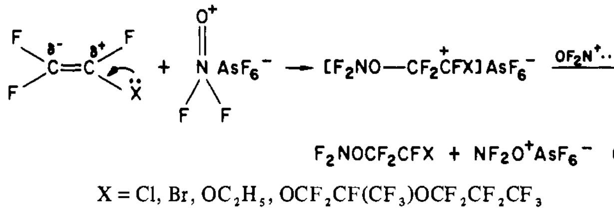


(6)

$R_f = CF_3, C_5H_{11}, C(O)F, SF_5, CF_2OCF_2CF(SO_2F)CF_3, CF_2OCFOCF(CF_3)CF_2OCF(CF_3)$

if a C–O bond is formed (eq 6). In the event of an atom with an available lone pair of electrons in the vinylic position, attack of the NF_2O^+ occurs at the more negative terminal carbon (eq 7).

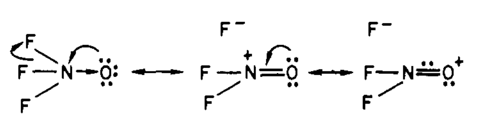
An interesting feature of the equations (6) and (7) is the effective delocalization of the N=O bond to provide an



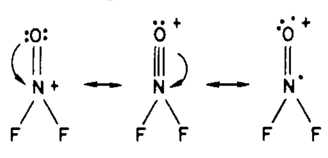
(7)

$X = Cl, Br, OC_2H_5, OCF_2CF(CF_3)OCF_2CF_2CF_3$

electron-deficient oxygen atom. Ab initio,[15] electron diffraction,[16] and photoelectron spectroscopy[17] studies on NF_3O indicate substantial delocalization of the oxygen lone pair to form a multiple N–O bond (eq 8). In NF_2O^+ salts, the



frequency of the NO stretch (1857 cm^{-1})[2] is shifted 172 cm^{-1} to higher energy from the parent NF_3O, indicating an N–O bond strength similar to NO (ν_{NO} = 1840 cm^{-1}). Presumably, canonical forms of the type in eq 8 may also be written for NF_2O^+ as is shown in eq 9, where electrons may be donated


(9)

to the vacant nitrogen 3p or 3d orbitals. These orbitals should be significantly contracted and lowered in energy by the presence of the strongly electronegative fluorine atoms.[15,16]

In light of this argument, one might expect the as yet hypothetical molecule NF_5 to exist, resulting from a combination of nitrogen 2p and 3p or 3d orbitals with the 2p orbitals of fluorine. However, as Wallmeier[18] has pointed out, steric and not quantum-mechanical considerations are responsible for the absence of pentavalent nitrogen compounds. The coordination of five fluorine atoms around nitrogen in a trigonal-bipyramidal arrangement would require the axial flourine atoms to be closer than the sum of the van der Waals radii to at least one of the equatorial fluorine atoms. This crowding would probably preclude formation of NF_5 and, if formed at all, would result in the dissociation to the more stable NF_3 and F_2. Because of the presence of fewer atoms around the central nitrogen, both NF_3O and NF_2O^+ may employ the 3p or 3d orbitals on nitrogen without such serious steric effects.

The concept of an NO multiple bond in NF_3O may also be supported by analogies with phosphoryl compounds, R_3PO. Wagner[19] has studied P–O bond character with ligands of varying electronegativity and has found that increasingly electronegative ligands stabilize P–O multiple bonds over the alternate $R_3P^+O^-$ form, by inductively lowering the energy of the 3d orbitals on phosphorus and hence allowing back-bonding to take place. Additionally, the presence of electronegative fluorine atoms on phosphorus serves to lessen the electronegativity difference between P and O, lowering the ionic contribution to the P–O bond. In NF_3O and NF_2O^+, the same sort of effects may be occurring to give an enhanced multiple-bond character to the NO bond, as well as creating a situation in which the oxygen atom is electron deficient, relative to the nitrogen atom.

The compounds formed in the reaction are colorless, thermally stable liquids. In the presence of strong Lewis acids such

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(13) Banks, R. E. "Fluorocarbons and Their Derivatives"; McDonald and Co.: London, 1970; p 35 and references therein.

(14) Wamser, C. A.; Sukornik, B.; Holmes, J. R.; Fox, W. B. Eibeck, R. E.; Steward, B. B.; Juurik, R.; Vanderkooi, N., private communication.

(15) Olsen, J. F.; Howell, J. M. *J. Fluorine Chem.* **1977**, *10*, 197.

(16) Plato, V.; Hartford, W. D.; Hedberg, K. *J. Chem. Phys.* **1970**, *53*, 3488.

(17) Jolly, W. L.; Evermann, C. J.; Kinkead, S. A.; Shreeve, J. M.; Xiang, S. F. *J. Fluorine Chem.* **1983**, 24, 389.

(18) Wallmeier, H.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1979**, *101*, 2804.

(19) Wagner, E. L. *J. Am. Chem. Soc.* **1963**, *85*, 161.

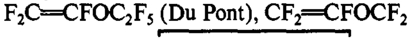
as AsF_5, $(CF_3)_2CFONF_2$ is rapidly converted to the parent fluoroalkane.

$$(CF_3)_2CFONF_2 + AsF_5 \xrightarrow[6\ h]{25\ ^\circ C} C_3F_8 + NO^+AsF_6^- \qquad (10)$$

The colorless nitrosonium hexafluoroarsenate solid was identified by its Raman spectrum.[20]

This new route to *N,N*-difluorohydroxylamines provides ready access to a wide variety of previously unknown compounds in usual yields and with excellent regiospecificity. In addition, this method avoids the problem of manipulating unstable hypofluorites and hypochlorites and the hazards of handling the dangerous compound difluoramine.

Experimental Section

Materials. Trifluoramine oxide (Allied Chemical Corp.) was passed through two traps cooled to −78 °C to remove NO_2 formed from the decomposition of FNO. Arsenic pentafluoride (Ozark Mahoning), C_3F_6 (PCR, Inc.), C_7F_{14} (PCR, Inc.), $F_2C{=}CFC(O)F$ (Du Pont), $F_2C{=}CFOC_2F_5$ (Du Pont), $CF_2{=}CFOCF_2CF(CF_3)OC_3F_7$ (Daikin),  $CF_2{=}CFCF_2OCFOCF(CF_3)CF_2OCF(CF_3)$ (Du Pont), and $CF_2{=}CFCF_2OCF_2CF(SO_2F)CF_3$ (Du Pont) were used as received. The literature method was used to prepare $CF_2{=}CFSF_5$.[21]

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system equipped with a Heise Bourdon tube gauge. Most of the starting materials and products were measured quantitatively by using *PVT* techniques. Products were purified by fractional condensation (trap-to-trap distillation) and, when necessary, on a Varian Aerograph Model A-700 or Hewlett-Packard 5710A gas chromatograph equipped with Valco gas sample injection valves. The products were separated on 2-, 4-, 8-, or 24-ft columns, containing 25% w/w Kel-F oil No. 3 on Chromosorb P. Infared spectra were recorded with a Perkin-Elmer 599 spectrometer by using a 10-cm cell equipped with KBr windows. ^{19}F NMR spectra were obtained on either a JEOL FX-90Q Fourier transform spectrometer or a Varian EM-360 L spectrometer, using $CFCl_3$ as an internal reference. Chemical shifts upfield of the reference are assigned negative values. Molecular weights were determined by the vapor density method. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6E spectrometerr operating at 17 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Reaction of Trifluorovinyl Olefins with NF_3O. To an evacuated 75-mL stainless-steel Hoke cylinder fitted with a stainless-steel Hoke valve are added NF_3O (7.0 mmol) and AsF_5 (2.0 mmol) at −196 °C. The cylinder is then warmed to room temperature over a period of 1 h. After the cylinder was recooled to −196 °C, the trifluorovinyl olefin (5.0 mmol) is added and the cylinder is rewarmed to room temperature and then heated at 55 °C for 24 h.

$CF_3{}^aCF^b(ONF^cF^d)CF_2{}^eCF_2{}^fCF_2{}^gCF_2{}^hCF_3{}^i$. After trap-to-trap distillation, the trap at −78 °C contained $CF_3CF(ONF_2)C_5F_{11}$, in addition to unreacted olefin and C_7F_{16}. Gas chromatographic separation on a 4-ft Kel-F oil column gave a 24% yield of pure $CF_3CF(ONF_2)C_5F_{11}$. The infrared spectrum (gas phase) is as follows: 1324 sh, 1252 vs, 1233 vs, 1157 m, 1060 w, 1026 w, 913 m, 846 s, 816 w, 740 pqr, m, 677 m, and 538 w cm^{-1}. A molecular ion is not observed in the mass spectrum. The highest peak is at *m/e* 369 ($C_7F_{15}^+$, 17.6%). Other principal peaks are observed at *m/e* 269 ($C_5F_{11}^+$, 44.1%), 181 ($C_4F_7^+$, 23.5%), 169 ($C_3F_7^+$, 57.3%), 168 ($CF_3CFONF_2^+$, 47%), 119 ($C_2F_5^+$, 23.5%), 69 (CF_3^+, 100%), and 52 (NF_2^+, 100%). The ^{19}F NMR spectrum shows a pair of broad doublets centered at ϕ +132.5 and ϕ +125.8 ($^2J_{FF}$ = 366 Hz) due to the nonequivalent fluorine atoms on nitrogen. The remainder of the NMR spectrum consists of ϕ −77.1 ($CF_3{}^a$), ϕ −83.0 ($CF_3{}^i$ tr, $^3J_{FF}$ = 10 Hz), ϕ −121.0 ($CF_2{}^g$, m), ϕ −121.7 ($CF_2{}^f$, m), ϕ −123.7 ($CF_2{}^e$, tr, $^3J_{FF}$ = 7 Hz), ϕ −127.6 ($CF_2{}^f$, m), ϕ −135.4 (CF^b, m). Anal. Calcd for $C_7F_{17}NO$: F, 73.91; N, 3.20. Found: F, 73.8; N, 3.14. The pure material boils at 104 °C.

$(CF_3{}^a)_2CF^bONF_2{}^c$. Following the reaction, the material is distilled through traps held at −78, −98, and −196 °C. The trap at −98 °C contains 1.64 mmol (32.8%) of a colorless liquid. The infrared spectrum of the material, which shows bands at 1322 s, 1260 vs, 1218 w, 1192 m, 1170 vs, 1118 s, 1058 s, 978 s, 908 s, 842 vs, 802 w, 739 m, and 725 m cm^{-1}, was identical with that previously reported.[7,10] The ^{19}F NMR spectrum consists of a broad singlet at ϕ +130.1 (F^c), a multiplet at ϕ −78.4 (F^a), and a septet at ϕ −138.6 (F^b), which was also consistent with the previously reported data.[7]

$CF_3{}^aCF^b(ONF^cF^d)SF_4{}^eF^f$. The reaction products are distilled through traps held at −78, −116, and −196 °C. The trap at −78 °C contains 0.39 mmol (7.8%) of a colorless to pale yellow liquid, while the trap at −116 °C contains 3.4 mmol of the unreacted $CF_2{=}CFSF_5$. The compound $CF_3CF(ONF_2)SF_5$ has the following bands in the infrared spectrum: 1315 w, 1258 s, 1238 s, 1197 m, 1056 w, 982 w, 907 vs, 882 s, 865 m, 831 s, 765 m, 701 w, 617 m, 592 w cm^{-1}. The ^{19}F NMR shows broad doublets at ϕ +136.2 and ϕ +124.1 ($^2J_{FF}$ = 351 Hz) due to the nonequivalent fluorine atoms on nitrogen. An AM_4 pattern ($^2J_{F_{ax}F_e}$ = 141.6 Hz) exists for the axial fluorine atoms on sulfur at ϕ +61.4, while the equatorial fluorine atoms consist of a doublet of doublets at ϕ 47.9. A signal at ϕ −78.4 (q of d, $^4J_{FF}$ = 8 Hz, $^3J_{FF}$ = 3 Hz) is assigned to the $CF_3{}^a$ group, and a multiplet at ϕ −126.9 is assigned to F^b. The extrapolated boiling point is 96.7 °C. Anal. Calcd for $CF_3CF(ONF_2)SF_5$: F, 70.83; N, 4.74. Found: F, 72.6; N, 4.53.

$CF_3{}^aCF^b(ONF^cF^d)C(O)F^e$. The reaction products are distilled through traps at −78, −116, and −196 °C. The trap at −196 °C contains NF_3O and $C_2F_5C(O)F$. In the trap at −116 °C is found 1.1 mmol of a colorless liquid, which after gas chromatography separation yielded 0.7 mmol (14%) of $CF_3CF(ONF_2)C(O)F$. The infrared spectrum is as follows: 1878 m, 1315 sh, 1258 s, 1228 vs, 1171 s, 1113 m, 1071s, 1031 m, 991 s, 914 s, 858 vs, 813 m, 764 w, 707 s, 659 m, 628 w cm^{-1}. The ^{19}F NMR spectrum measured at ambient temperature showed a pair of doublets at ϕ +134.1 and ϕ +126.0 ($^2J_{FF}$ = 353 Hz) due to the nonequivalent fluorine atoms bonded to nitrogen. The carbonyl fluorine F^e gives a singlet at ϕ +27.6, $CF_3{}^a$ resonance occurs at ϕ −79.9 (m), and the CF^b signal occurs at ϕ −122.0 (m). The extrapolated boiling point is 19.4 °C. Molecular weight: calcd 215.0; found 204.

$F_2{}^aNOCF_2{}^bCF_2{}^cOCF_2{}^dCF_3{}^e$. After reaction, the products are distilled through traps cooled to −78, −116, and −196 °C. In the trap at −78 °C, 1.76 mmol of a colorless liquid is found, which after purification via gas chromatography gives about 1.6 mmol (32%) of $F_2NOCF_2CF_2OC_2F_5$. The infrared spectrum is as follows: 1341 w, 1294 m, 1241 vs, 1212 vs, 1179 vs, 1156 vs, 1110 m, 1093 m, 1028 m, 946 w, 898 br−m, 849 m, 744 m, 725 m cm^{-1}. A molecular ion (*m/e* 303) is not observed. The principal peaks are as follows: *m/e* 216 ($C_4F_8O^+$, 15.8%), 200 ($C_4F_8^+$, 3.5%), 168 ($F_2NOCF_2CF_2^+$, 3.5%), 131 ($C_3F_5^+$, 5.3%), 119 ($C_2F_5^+$, 100%), 97 ($C_2F_3O^+$, 8.85%), 78 ($C_2F_2O^+$, 43.9%), 69 (CF_3^+, 26.3%), 52 (NF_2^+, 12.3%), 30 (NO^+, 12.3%). The ^{19}F NMR shows a broad singlet at ϕ +127.4 integrating to two fluorine atoms due to F^a. The other peaks in the NMR are ϕ −85.9 (2, F^c, m), ϕ −87.4 (3, F^e, m), ϕ −89.1 (2, F^d, m), ϕ −92.8 (2, F^b, t, $^3J_{FF}$ = 3.3 Hz). The extrapolated boiling point is 42.6 °C. Molecular weight: calcd 303; found 299. Anal. Calcd for $F_2NOCF_2CF_2OC_2F_5$: F, 68.98; N, 4.62. Found: F, 72.6; N, 4.85. (The fluorine analysis is marginal because of the high volatility of the compound).

$F_2{}^aNOCF_2{}^bCF_2{}^cOCF_2{}^dCF^e(CF_3{}^f)OCF_2{}^gCF_2{}^hCF_3{}^i$. Removal of volatile products at −78 °C gives about 1.5 mL of a colorless liquid. Purification via gas chromatography results in 30% of $F_2NOCF_2CF_2OCF_2CF(CF_3)OCF_2CF_2CF_3$. The vapor-phase infrared spectrum shows 1306 w, 1259 vs, 1214 s, 1158 m, 1098 sh, 1030 w, 998 m, 919 w, 855 m, 762 m, and 728 pqr, m cm^{-1}. The ^{19}F NMR, recorded at ambient temperature, shows a broad singlet at ϕ 127.4 (2, F^a), a multiplet at ϕ −80.0 (3, $CF_3{}^f$), a multiplet at ϕ −81.2 (2, $CF_2{}^d$), a triplet at ϕ −81.5 (3, $CF_3{}^i$, ^3J = 6.5 Hz), a multiplet at ϕ −82.6 (2, $CF_2{}^g$), a multiplet at ϕ −86.6 (2, $CF_2{}^c$), a triplet at ϕ −92.2 (2, $CF_2{}^b$, ^3J = 25 Hz), a multiplet at ϕ −129.6 ppm (2, $CF_2{}^h$), and a triplet at ϕ −144.8 (1, CF^e, ^4J = 22.5 Hz). The boiling point is 117 °C. Anal. Calcd for $F_2NOC_2F_4OC_3F_6OC_3F_7$: F, 69.56; N, 2.70. Found: F, 70.9; N, 2.95.

$CF_3{}^aCF^b(ONF_2{}^c)CF_2{}^dOCF_2{}^eCF^f(SO_2F^g)CF_3{}^h$. Removal of volatile products at −78 °C gives about 1 mL of a colorless liquid. Purification by gas chromatography (2 ft; column temperature 50 °C) results in 28.0% yield of $CF_3CF(ONF_2)CF_2OCF_2CF(SO_2F)CF_3$. The vapor-phase infrared spectrum is as follows: 1447 m, 1259 vs, 1241 sh, 1167 m, 1125 m, 1059 s, 1034 m, 996 m, 913 w, 849 m, 827 m, 800 m, 741 s, 623 w cm^{-1}. The room-temperature ^{19}F NMR spectrum shows a broad singlet at ϕ 128.1 (2, F^c), a doublet of pentets at ϕ 53.3 (1, F^g, $^4F_{FF}$ = 10.1 Hz, $^3J_{FF}$ = 4.1 Hz), a pentet at ϕ −73.8 (3,

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[20] Qureshi, A. M.; Aubke, F. *Can. J. Chem.* **1970**, *48*, 3117.

[21] Stewart, J.; Kegley, L.; White, H. F.; Gard, G. L. *J. Org. Chem.* **1969**, *34*, 760.

$CF_3{}^h$), a multiplet at ϕ −76.5 (2, $CF_2{}^e$), a triplet of doublets at ϕ −79.3 (3, $CF_3{}^a$, ${}^4J_{FF} = 8.8$ Hz, ${}^3J_{FF} = 1.5$ Hz), a broad multiplet at ϕ −82.0 (2, $CF_2{}^d$), a multiplet at ϕ −140.0 (1, CF^b), and a multiplet at ϕ −168.0 (1, CF^f).

$CF_3{}^aCF^b(ONF_2{}^c)CF_2{}^dO\overline{CF^eOCF^f(CF_3{}^g)CF^hF^iOC}F^j(CF_3{}^k)$. Removal of volatile products at −78 °C gives about 0.5 mL of a colorless liquid. The yield by gas chromatography (4 ft; inlet and detector temperature 150 °C; column temperature 55 °C) is 15.4%. The vapor-phase infrared spectrum (2 torr) is as follows: 1423 m, 1296 sh, 1260 vs, 1176 s, 1142 m, 1051 s, 986 m, 918 w, 852 m, 833 w, 767 w, 750 vw, 746 vw, 686 vw, 626 w cm^{-1}. The room-temperature ^{19}F NMR gave the following signals: a broad singlet at ϕ +128.2 (2, F^c), a multiplet at ϕ −73.4 (2, F^d), a multiplet at ϕ −76.4 (1, F^i), a multiplet at ϕ 79.1 (3, F^a), a multiplet at ϕ −81.9 (1, F^b), a multiplet at ϕ −82.8 (1, F^j), a multiplet at ϕ −83.3 (3, F^g), a doublet of doublets at ϕ −84.1 (3, F^k, ${}^4J_{FF} = 4J_FF\,{}^4J_{FF}$ 21.2 Hz, ${}^3J_{FF} = 8.1$ Hz), a multiplet at ϕ −84.3 (1, F^h), a multiplet at ϕ −134.4 (1F, F^e), a multiplet at ϕ −139.9 (1, F^b).

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Registry No. $CF_3CF(ONF_2)(CF_2)_4CF_3$, 91391-15-0; $(CF_3)_2CFONF_2$, 84194-25-2; $CF_3CF(ONF_2)SF_5$, 91391-16-1; $CF_3CF(ONF_2)C(O)F$, 91391-17-2; $F_2NOCF_2CF_2OCF_2CF_3$, 91391-18-3; $F_2NOCF_2CF_2OCF_2CF(CF_3)OCF_2CF_2CF_3$, 91391-19-4; $CF_3CF(ONF_2)CF_2OCF_2CF(SO_2F)CF_3$, 91391-20-7; $F_2NOCF_2CF_2Cl$, 24684-27-3; $F_2NOCF_2CF_2Br$, 24684-28-4; C_3F_6, 116-15-4; C_7F_{14}-1-ene, 355-63-5; $F_2C{=}CFOC_2F_5$, 10493-43-3; $F_2C{=}CFOCF_2CF(CF_3)OC_3F_7$, 1644-11-7; $F_2C{=}CFCl$, 79-38-9; $F_2C{=}CFBr$, 598-73-2; $CF_2{=}CFCF_2OCF_2CF(SO_2F)CF_3$, 67635-65-8; $CF_2{=}CFCF_2OCFOCF(CF_3)CF_2OCF(CF_3)$, 67641-34-3; $CF_3CF(ONF_2)CF_2OCFOCF(CF_3)CF_2OCF(CF_3)$, 91391-21-8; (trifluorovinyl)sulfur pentafluoride, 1186-51-2; *cis*-perfluoro-2-butene, 1516-65-0; *trans*-perfluoro-2-butene, 1516-64-9; perfluorocyclobutene, 697-11-0; 1,2-dichloro-1,2-difluoroethylene, 598-88-9; 1,1-dichloro-2,2-difluoroethylene, 79-35-6; trifluoroacryloyl fluoride, 667-49-2.

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Reactions of Bis(2,2,2-trifluoroethyl) Sulfite, Bis(hexafluoroisopropyl) Sulfite, and Diethyl Sulfite with Chlorine Fluoride: Evidence of an Arbuzov Rearrangement

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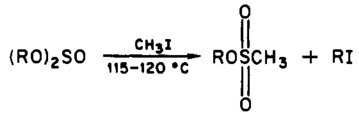
Polyfluoroalkyl or alkyl sulfites, $(R_fO)_2SO$ [$R_f = CF_3CH_2$, $(CF_3)_2CH$, CH_3CH_2], gave fluorosulfates, R_fOSO_2F, when reacted with chlorine fluoride. With $(CF_3CH_2O)_2SO$, XeF_2 also gave the fluorosulfate. An Arbuzov rearrangement is suggested as a plausible reaction mechanism. The fluorosulfates were also obtained in lower yields from the reactions of $R_fOH{\cdot}Et_3N$ with SO_2ClF.

Polyfluoroalkyl sulfites, $(R_fO)_2SO$, were first reported in 1974.[2,3] However, in spite of the ease of their syntheses, the reaction chemistry of these stable compounds is entirely unexplored. The bis(perfluoroalkyl) sulfides, R_fSR_f' ($R_f = CF_3$; $R_f' = CF_3$, C_2F_5, C_3F_7) can be oxidatively fluorinated with ClF to bis(perfluoroalkyl)sulfur difluorides, $R_fSF_2R_f'$,[4] or to bis(perfluoroalkyl)sulfur tetrafluorides, $R_fSF_4R_f'$,[5] depending upon the stoichiometry and reaction conditions employed. Although an earlier attempt to oxidize bis(nonafluoro-*tert*-butyl) sulfite to $[(CF_3)_3CO]_2S(O)F_2$ with ClF had been unsuccessful,[2] we investigated the analogous reactions of ClF with several other sulfites, including bis(2,2,2-trifluoroethyl) sulfite, $(CF_3CH_2O)_2SO$, bis(hexafluoroisopropyl) sulfite, $[(CF_3)_2CHO]_2SO$, and diethyl sulfite, $(C_2H_5O)_2SO$. We, also, were unable to isolate $(R_fO)_2S(O)F_2$, but instead we are now able to report a new route to fluorosulfates and the previously unknown fluorosulfate $(CF_3)_2CHOSO_2F$. Formation of fluorosulfates from sulfites and ClF can be rationalized by invoking an Arbuzov rearrangement. Although a common occurrence in reactions of phosphorus compounds, Arbuzov rearrangements have been reported only infrequently in the case of sulfur compounds.[6]

Results and Discussion

One of the examples of an Arbuzov rearrangement in sulfur compounds[6] is



$$(RO)_2SO \xrightarrow[115-120\ ^\circ C]{CH_3I} RO\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}CH_3 + RI$$

R = CH$_3$

Later workers[7] demonstrated that this rearrangement was catalyzed by tertiary amines and the yields of the sulfonate products depend on the size of the R group, no reaction occurring when R is *n*-butyl. Chlorine behaves as a suitable electrophile with organosulfites to form chlorosulfates.[8]

In our unsuccessful attempts to synthesize $(R_fO)_2S(O)F_2$ from the reactions of ClF with $(R_fO)_2SO$, polyfluoroalkyl fluorosulfates were formed.

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[2] De Marco, R. A.; Kovacina, T. A.; Fox, W. B. *J. Fluorine Chem.* **1975**, *5*, 221.

[3] Kovacina, T. A.; De Marco, R. A.; Fox, W. B.; Young, D. E. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 763.

[4] Sauer, D. T.; Shreeve, J. M. *J. Fluorine Chem.* **1971/72**, *1*, 1.

[5] Abe, T.; Shreeve, J. M. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 465.

[6] Arbuzov, B. A. *Zh. Russ. Fiz.-Khim. Ova., Chast Khim.* **1909**, *41*, 429; *Method. Chim.* **1978**, *7B*, 704.

[7] Bissinger, W. E.; Kung, F. E.; Hamilton, C. W. *J. Am. Chem. Soc.* **1948**, *70*, 3940.

[8] Buncel, E. *Chem. Rev.* **1970**, *70*, 323 and references therein.

[9] Mohrig, J. R.; Keegstra, K. *J. Am. Chem. Soc.* **1967**, *89*, 5492.

[10] Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1973**, *12*, 2886.