4122 *Inorg. Chem.* **1991**, *30*, 4122–4125

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Two Fluorinated Fluoroxy Compounds Containing a Fluorosulfonyl Group

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Received March 1, 1991

The fluoride-catalyzed fluorination of the respective acid fluorides leads to the fluoroxy compounds $FOCF_2CF_2SO_2F$ and $FOCF_2CF(CF_3)SO_2F$. Their thermal and photolytic stability was investigated as well as their reactions with CO, SO_2, SO_3, and PF_3. Perfluorinated ethers are formed from the reactions with C_2F_4 and C_3F_6 by insertion into the F–O bond.

Introduction

In the last 30 years considerable research has been done in the field of fluoroxy compounds (hypofluorites). A variety of organic and inorganic hypofluorites, mostly perfluorinated, have been prepared;[1,2] some of them are unusually stable compared to their chlorine analogues, if they exist. The number of functionalized fluorocarbon fluoroxy compounds is very limited at present. Due to their promise as a commercial source of fluorinated ethers, it is important to explore the range of functional groups and substituents that can exist in fluorocarbon hypofluorites. The latter is not easily predicted.

Our work on fluorinated chloroxy compounds containing a fluorosulfonyl group[3,4] led to a number of addition products by insertion of suitable reagents such as olefins and carbon monoxide into the Cl–O bond. Since these hypochlorites were found to be relatively stable, we predicted that the fluorine analogues would be of comparable or higher stability. If so, there would be the possibility of synthesizing perfluorinated fluorosulfonyl compounds in an analogous way. The well-known synthetic pathway[1,2] is the fluoride-catalyzed fluorination of corresponding acyl fluorides, $FC(O)CFXSO_2F$ ($X = F, CF_3$), or in some cases fluorination of metal salts $MOCF_2CFXSO_2F$ is an appropriate method. Herein we report the successful isolation of the first fluorosulfonyl hypofluorites from the acid fluorides.

Experimental Section

General Methods. Gases and volatile materials were handled in either stainless-steel or glass vacuum systems, fitted with Teflon-packed stainless-steel valves or with glass–Teflon stopcocks, respectively. Amounts of gases were determined by *PVT* measurements using a Wallace and Tiernan Series 1500 differential pressure gauge or by direct weighing. Reactions were carried out in passivated (1 atm of F_2, 25 °C) stainless-steel cylinders (75 mL) or in Pyrex glass reactors (100 mL) fitted with glass–Teflon stopcocks and containing a Teflon-coated magnetic stirbar.

IR spectra were recorded on a Perkin-Elmer Model 1430 spectrometer with a 3600 Data Station using 10-cm gas cells with KCl or AgCl windows. In general, NMR spectra were measured on a JEOL FX-90Q or on an IBM NR 200AF spectrometer using $CDCl_3$ solutions of 1–2 mmol/L concentrations. The chemical shift values are negative to high field of $CFCl_3$ used as the internal standard. Mass spectra were obtained on a Hewlett-Packard 5985-B spectrometer at 70 eV and 200 °C source temperature for CI (CH_4) and EI; samples were introduced by gas injection.

Reagents. Starting compounds F_2, CO, SO_2, SO_3, PF_3, C_2F_4, C_3F_6, and KF were obtained commercially whereas $FC(O)CF_2SO_2F$ (**1**), $FC(O)CF(CF_3)SO_2F$ (**3**), and $KOCF_2CF_2SO_2F$ (**12**) were prepared according to literature methods.[3,5] Dry KF (not activated) was stored and handled inside a drybox. *Caution!* Fluorine should only be handled by experienced personnel or after careful consultation of available literature on the safe handling of fluorine. Hypofluorites **2** and **4** under certain conditions are capable of an energetic explosive decomposition and must be handled with extreme caution.

Preparation of the Hypofluorites. 1,1,2,2-Tetrafluoro-1-(fluoroxy)-2-(fluorosulfonyl)ethane (2). A stainless-steel cylinder (75 mL), containing nonactivated potassium fluoride (5.0 g; 86.2 mmol) was charged with $FC(O)CF_2SO_2F$ **1** (0.7 g; 3.9 mmol), followed by fluorine (22 mmol) at −196 °C. The reactor was allowed to warm to room temperature during the course of 3 h in a cold empty dewar. The reactor was then cooled to −196 °C, and the excess fluorine was removed by pumping it through a soda lime column. Pure hypofluorite **2** (3.5 mmol; 90.5%) was then obtained as a colorless liquid by pumping through a trap at −110 °C as the reactor warmed to 22 °C in the air.

$F^{A}OCF_2{}^{B}CF_2{}^{C}SO_2F^{D}$: IR (10 Torr, AgCl) 1475 (vs), 1301 (s), 1249 (vs), 1211 (vs), 1186 (s), 1144 (s), 1127 (s), 994 (s), 896 (OF, m), 829 (s), 804 (s) 656 (m), 610 (s), 537 (m) cm^{-1}; ^{19}F NMR (−33 °C) A 152.4 (t-t), B −90.8 (sep), C −109.8 (pent.), D 44.8 (t-t) ppm, $^{3}J(AB) = 6.4$, $^{4}J(AC) = 4.6$, $^{3}J(BC) = 3.9$, $^{4}J(BD) = 6.5$, $^{3}J(CD) = 4.4$ Hz.

1,1,2,3,3,3-Hexafluoro-1-(fluoroxy)-2-(fluorosulfonyl)propane (4). The same procedure was followed as reported for the preparation of hypofluorite **2**, **3** (1.64 g; 7.1 mmol) and fluorine (61 mmol) over KF (5 g; 86.2 mmol) gave pure hypofluorite **4** (1.91 g; 7.1 mmol; 100%) as a pale yellow liquid in a trap cooled to −110 °C.

$F^{A}OCF_2{}^{B}CF^{C}(CF_3{}^{D})SO_2F^{E}$: vapor pressure 140 Torr (26 °C); IR (7 Torr, AgCl) 1475 (vs), 1255 (vs), 1192 (s), 1126 (s), 975 (s), 894/879 (OF, w), 826 (s), 800 (s), 737 (m), 617 (s), 544 (w) cm^{-1}; ^{19}F NMR (−45 °C) A 157.7 (s, b), B −84.6 (sep), C −165.7 (sep), D −71.3 (pent.), E 55.9 (d-sex.) ppm, $^{4}J(BE) \simeq {}^{4}J(DE) \simeq 10.5$, $^{4}J(BD) \simeq {}^{3}J(CD) \simeq 8.8$, $^{3}J(BC) = 8.3$, $^{3}J(CE) = 5.1$ Hz; MS, major *m/z* (assignment, %), CI 249 ($(M - F)^+$, 6.5), 231 ($(MH - 2F)^+$, 15.7), 211 ($(M - 3F)^+$, 75.5), 145 ($C_2F_3O_2S^+$, 29.7), 135 ($C_2F_5O^+$, 71.5), 131 ($C_3F_5^+$, 31.4), 119 ($C_2F_5^+$, 100), 103 ($HSO_2F_2^+$, 39.4), 101 ($C_2HF_4^+$, 75.5); MS, major *m/z* (assignment, %), EI 119 ($C_2F_5^+$, 35.4), 69 (CF_3^+, 100), 67 (SOF^+, 63.4).

Reaction of $KOCF_2CF_2SO_2F$ (12) with Fluorine. Method A. A stainless-steel cylinder (75 mL) was loaded with **12** (0.54 g; 2.3 mmol) and evacuated, and at −196 °C, fluorine (2.3 mmol) was condensed in. The reactor was then transferred into a Freon-11 bath (−110 °C) and warmed to −40 °C during a period of 4 h. The cylinder was shaken and a small explosion occurred inside, indicated by a ping. After the cylinder was warmed to room temperature (5 min), volatile products were separated by trap to trap distillation. No noncondensable materials were observed. Sulfonyl fluoride and carbonyl fluoride (3.5 mmol) were trapped at −158 °C, and tetrafluoromethane (0.56 mmol) was trapped at −196 °C. The solid remaining in the cylinder (0.3 g) was KF and unreacted **12**.

Method B. A stainless-steel cylinder (75 mL) was charged with **12** (0.41 g; 1.71 mmol) and fluorine (2.0) at −196 °C in vacuo; the bomb was warmed to −70 °C from −196 °C during a period of 2 h in a cold empty dewar. The fractionation gave a mixture of COF_2 and CF_3SO_2F[6] (2.0 mmol) at −110 °C and a mixture of CF_4 and SO_2F_2 (0.23 mmol) at −196 °C. The products were identified by their infrared as well as by their ^{19}F NMR spectra. The remaining solid (0.1 g; 1.7 mmol) was found to be KF.

General Procedure for Reactions Involving Hypofluorites 2 and 4. A glass reactor (100 mL), fitted with a Teflon stopcock was loaded successively with the corresponding hypofluorite, $CFCl_3$ solvent, if used, and the suitable reactant at −196 °C in vacuo. The vessel was transferred into a Freon-11 bath (−110 °C) and warmed to room temperature during the time as indicated, or the bulb was warmed in a cold empty dewar within 3 h. Purification was done under dynamic vacuum by trap to trap fractionation. In one case, reaction of **2** with C_2F_4, products were separated by gas chromatography. The compounds were characterized as follows, and the reactions are summarized in Table I.

$CF_3{}^{A}CF_2{}^{B}OCF_2{}^{C}CF_2{}^{D}SO_2F^{E}$ (**5**): IR (10 Torr) 1472 (vs), 1328 (s), 1235 (vs), 1156 (vs), 1105 (vs), 994 (m), 825 (s), 802 (s), 728 (m), 647

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0020-1669/91/1330-4122$02.50/0

Table I. Summary of Reactions of Fluoroxy Compounds

reactants (mmol)	conditions time, h; g of $CFCl_3$	products (mmol; %; trap temp, °C)
2 (5.0); C_2F_4 (5.5)	6; 3	**5** (0.2, 4.0; −112 (GC)); **6**[7] (0.2; 4.0; −112 (GC)); $COF_2 + C_2F_6 + C_2F_4 + CF_3SO_2F$ (2.3; −196)
2 (2.0); C_3F_6 (2.5)	10; 1.4	**7** + **8** (0.1; 5.4; −60); $COF_2 + C_3F_6 + CF_3SO_2F$ (5.0; −196)
4 (3.0); C_2F_4 (3.4)	30; 3.2	**9** (1.0; 33.3; −60); $CFCl_3 + C_2F_5SO_2F$[8] (3.5 g; −110); COF_2 (0.7; −196)
4 (2.0); C_3F_6 (2.5)	10; 1.4	**10** + **11** (0.9; 47; −60); $COF_2 + C_3F_6 + C_2F_5SO_2F$ (2.2; −196)
4 (2.0); CO (3.0)	15; 3.2	**3** + $C_2F_5SO_2F + CFCl_3$ (−110); COF_2 (0.3; 15; −196)
4 (2.9); SO_2 (3.1)	15; 4.1	$C_2F_5SO_2F + SO_2 + CFCl_3$ (−110); $COF_2 + CFCl_3 + SO_2$ (3.8; −196)
4 (1.0); SO_3 (1.0)	24; none	$C_2F_5SO_2F$ (1.0; 100; −110); SO_3 (1.0, −60); COF_2 (1.0; 100; −196)
4 (1.0); PF_3 (1.0)	3; none	**3** (1.0; 100; −110); $PF_5 + POF_3$ (1.0; 100; −196)

(m), 609 (m) cm^{-1}; MS, major *m/z* (assignment, %), CI 319 ($(M + H)^+$, 2.0), 299 ($(M - F)^+$, 6.4), 183 ($C_2F_4SO_2F^+$, 100), 133 ($CF_2SO_2F^+$, 11.7), 119 ($C_2F_5^+$, 29.1), 100 ($C_2F_4^+$, 7.0); ^{19}F NMR A −87.1 (pent.), B −88.5 (d-d-m), C −82.5 (br m), D −112.7 (d-t), E 45.3 (pent.) ppm, $^3J_{AB} \simeq {}^5J_{AC} \simeq 1.0$, $^4J_{BC} = 12.7$, $^3J_{CD} = 2.9$, $^4J_{CE} \simeq {}^3J_{DE} \simeq 6.2$ Hz.

$FSO_2CF_2CF_2SO_2F$ (**6**):[7] IR (12 Torr) 1474 (vs), 1243 (vs), 1212 (vs), 1149 (vs), 876 (s), 827 (vs), 805 (s), 779 (s), 617 (vs), 561 (s), 483 (m), 453 (m) cm^{-1}; ^{19}F NMR SO_2F 47.9 (pent.), CF_2 −107.5 ("t") ppm, $^3J_{FF} \simeq {}^4J_{FF} = 7.3$ Hz.

$CF_3{}^ACF_2{}^BCF_2{}^COCF_2{}^DCF_2{}^ESO_2F^F$ (**7**) (70%) and $(CF_3{}^A)_2CF^BOCF_2{}^CCF_2{}^DSO_2F^E$ (**8**) (30%): IR (10 Torr) 1472 (vs), 1349 (m), 1318 (s), 1256 (vs), 1212 (vs), 1159 (vs), 1132 (s), 997 (s), 822 (s), 731 (m), 647 (m), 612 (m) cm^{-1}; MS, major *m/z* (assignment, %), CI 437 ($(M + CF_3)^+$, 3.1), 387 ($(M + F)^+$, 1.4), 369 ($(M + H)^+$, 0.7), 349 ($(M - F)^+$, 4.6), 285 ($(M - SO_2F)^+$, 100), 233 ($C_3F_7SO_2{}^+$, 16.7), 183 ($C_2F_4SO_2F^+$, 73.8), 169 ($C_3F_7{}^+$, 13.2), 147 ($C_3F_5O^+$, 35.7), 119 ($C_2F_5{}^+$, 37.7), 100 ($C_2F_4{}^+$, 13.1); MS, major *m/z* (assignment, %), EI 169 ($C_3F_7{}^+$, 38.1), 133 ($CF_2SO_2F^+$, 7.1), 119 ($C_2F_5{}^+$, 75.5), 100 ($C_2F_4{}^+$, 21.7), 69 ($CF_3{}^+$, 100), 67 (SOF^+, 70.7); ^{19}F NMR (**7**) A −81.6 (t), B −130.2 (s), C −84.4 (t-q), D −82.4 (m), E −112.7 (d-t), F 45.51 (pent.) ppm, $^3J_{AB} < 1$, $^4J_{AC} = 7.3$, $^3J_{BC} < 1$, $^4J_{CD} = 20.6$, $^3J_{DE} = 2.7$, $^4J_{DF} = 6.1$, $^3J_{EF} = 6.1$ Hz; ^{19}F NMR (**8**) A −81.0 (d-t), B −145.5 (m-t), C −80.0 (m), D −112.4 (d-t), E 45.2 (pent.) ppm, $^3J_{AB} = 2.1$, $^5J_{AC} = 5.1$, $^4J_{BC} = 20.9$, $^3J_{CD} = 3.3$, $^4J_{CE} = 6.0$, $^3J_{DE} = 5.5$ Hz.

$CF_3{}^ACF_2{}^BOCF_2{}^CCF^D(CF_3{}^E)SO_2F^F$ (**9**): IR (5 Torr) 1473 (vs), 1254 (vs), 1207 (s), 1164 (vs), 1132 (vs), 1103 (s), 1058 (m), 976 (m), 822 (s), 800 (m), 744 (m), 712 (m), 615 (s), 533 (w) cm^{-1}; MS, major *m/z* (assignment, %), CI 487 ($(M + C_2F_5)^+$, 9.0), 349 ($(M - F)^+$, 82.3), 285 ($(M - SO_2F)^+$, 20.1), 233 ($(M - C_2F_5O)^+$, 100), 211 ($C_3F_5O_3S^+$, 23.9), 169 ($C_3F_7{}^+$, 23.4), 119 ($C_2F_5{}^+$, 15.0), 101 ($C_2HF_4{}^+$, 5.9); MS, major *m/z* (assignment, %), EI 169 ($C_3F_7{}^+$, 8.5), 131 ($C_3F_5{}^+$, 12.2), 119 ($C_2F_5{}^+$, 39.0), 100 ($C_2F_4{}^+$, 9.5), 83 (SO_2F^+, 10.3), 69 ($CF_3{}^+$, 86.9), 67 (SOF^+, 100); ^{19}F NMR A −87.3 (m), B −88.8 (d-d-q), C −75.2 (d-d-t-q), D −166.2 (d-sex.), E −71.9 (d-q), F 55.1 (d-sex.) ppm, $^3J_{AB} = 2.2$, $^4J_{BC} = 12.9$, $^3J_{CD} = 7.7$, $^4J_{CE} = 9.7$, $^3J_{DE} = 7.3$, $^4J_{CF} \sim {}^4J_{EF} = 10.2$, $^3J_{DF} = 3.9$ Hz.

$CF_3{}^ACF_2{}^BCF_2{}^COCF_2{}^DCF^E(CF_3{}^F)SO_2F^G$ (**10**) (67%) and $(CF_3{}^A)_2CF^BOCF_2{}^CCF^D(CF_3{}^E)SO_2F^F$ (**11**) (33%): IR (7 Torr) 1474 (vs), 1345 (s), 1262 (vs), 1165 (vs), 1122 (vs), 1003 (s), 974 (s), 848 (w), 821 (s), 780 (w), 746 (m), 723 (m), 710 (m), 617 (s), 537 (w) cm^{-1}; MS, major *m/z* (assignment, %), CI 433 ($(M + CH_3)^+$, 6.0), 399 ($(M - F)^+$, 100), 335 ($(M - SO_2F)^+$, 11.2), 233 ($C_3F_6SO_2F^+$, 69.2), 211 ($C_3F_5O_3S^+$, 9.5), 169 ($C_3F_7{}^+$, 52.2); MS, major *m/z* (assignment, %), EI 169 ($C_3F_7{}^+$, 83.2), 119 ($C_2F_5{}^+$, 14.1), 100 ($C_2F_4{}^+$, 10.7), 69 ($CF_3{}^+$, 100), 67 (SOF^+, 56.9); ^{19}F NMR (**10**) A −81.7 (t), B −30.2 (s), C −84.6 (t-q), D −75.0 (m), E −166.2 (d-sex.), F −71.9 (pent.), G 55.2 (d-sex.) ppm, $^3J_{AB} < 1$, $^4J_{AC} = 7.3$, $^3J_{BC} < 1$, $^4J_{CD} = 13.1$, $^3J_{DE} = 8.0$, $^3J_{EF} = 8.0$, $^4J_{DG} = 10.2$, $^3J_{EG} = 4.0$, $^4J_{FG} = 10.2$ Hz; ^{19}F NMR (**11**) A −81.05 (br s), B −145.9 (t-m), C −72.54 (m), D −165.9 (d-sex.), E −71.9 (pent.), F 54.9 (d-sex.) ppm, $^3J_{AB} = 2.2$, $^4J_{BC} = 21.8$, $^3J_{CD} = 7.2$, $^4J_{CE} = 8.5$, $^4J_{CF} = 10.2$, $^3J_{DE} = 7.2$, $^3J_{DF} = 4.0$, $^4J_{EF} = 10.2$ Hz.

Results and Discussion

Preparation of Hypofluorites. The fluoroxy compounds **2** and **4** were obtained in excellent yields when the acid fluorides **1** and **3** were treated with an excess of fluorine over nonactivated (dried under vacuum at 100 °C, but not fused and ground to a fine powder) potassium fluoride catalyst (eq 1). When activated KF or CsF was used under the same conditions, no fluoroxy compounds were observed; instead a mixture of CF_4, COF_2, SO_2F_2, and SF_6 was obtained.

$$\underset{\substack{\mathbf{1},\ X = F\\ \mathbf{3},\ X = CF_3}}{FC(O)CFXSO_2F} + F_2 \xrightarrow{KF} \underset{\substack{\mathbf{2}\ (90.5\%)\\ \mathbf{4}\ (100\%)}}{FOCF_2CFXSO_2F} \qquad (1)$$

Scheme I

$$\underset{\mathbf{2},\ \mathbf{4}}{FOCF_2CFXSO_2F} \longrightarrow F\cdot + \cdot OCF_2CFXSO_2F$$

$$\cdot OCF_2CFXSO_2F \longrightarrow OCF_2 + \cdot CFXSO_2F$$

$$\cdot CFXSO_2F + \mathbf{2}\ \text{or}\ \mathbf{4} \longrightarrow FCFXSO_2F + \cdot OCF_2CFXSO_2F$$

The reaction of the potassium alkoxide **12** with fluorine, in two cases, led to different results but did not yield the fluoroxy compound **2** (eqs 2 and 3); only fragments of **12** or **2** were formed in the explosive reaction (eq 2). The reactivity of **12** is apparently too high under these conditions, and the reaction was uncontrolled.

$$\underset{\mathbf{12}}{KOCF_2CF_2SO_2F} + 2F_2 \xrightarrow[-40\ °C]{\text{explodes}} KF,\ COF_2,\ CF_4,\ SO_2F_2 \qquad (2)$$

$$\mathbf{12} + F_2 \xrightarrow{-110\ °C\ \text{to room temp}} KF,\ COF_2,\ CF_4,\ SO_2F_2,\ CF_3SO_2F \qquad (3)$$

Both hypofluorites are identified by their infrared and ^{19}F NMR spectra; **4** is also identified by its mass spectrum, which of course shows a fragmentation similar to that of its precursor **3**. Significant vibrations observed in the IR spectra are $\nu(SO_2) = 1475$ cm^{-1} and $\nu(OF) = 896$ (**2**) and 894 (**4**) cm^{-1} in addition to strong bands in the region for $\nu(CF)$ and $\nu(SO_2)$ between 1300 and 1100 cm^{-1} and $\nu(SF) = 829$ (**2**) and 826 (**4**) cm^{-1}.

The ^{19}F NMR chemical shift values and coupling constants of the CF and SF fluorines are similar to the ones observed for the respective chloroxy compounds.[3] The resonance of the FO fluorine is observed in the typical low-field region[9] at +152.4 (**2**) and +157.7 (**4**) ppm. No J_{FF} coupling across the oxygen atom is observed in **4** whereas for **2** the OF signal is a triplet of triplets with coupling constants similar to those found for $ClCF_2CF_2OF$.[9]

Stability. The thermal and photolytic behavior of the hypofluorites was tested in the same way as was done for the respective chlorine derivatives,[3] by observing the change of the IR spectra at 10 Torr of samples of **2** and **4** in a 10-cm cell. The decomposition in $CDCl_3$ solution was also checked by ^{19}F NMR spectroscopy at 25 °C. The thermolysis proceeds according to eqs 4 and 5 in the gas phase as well as in solution.

$$\underset{\mathbf{2}}{FOCF_2CF_2SO_2F} \xrightarrow{40°C,\ \text{dark}} \underset{(100\%,\ 10\ \text{min.})}{CF_3SO_2F + COF_2} \qquad (4)$$

$$\underset{\mathbf{4}}{FOCF_2CF(CF_3)SO_2F} \xrightarrow{40°C,\ \text{dark}} \underset{\substack{+\ \mathbf{3}\ +\ \text{"}F_2\text{"}\\ (100\%,\ 10\ \text{h})}}{C_2F_5SO_2F + COF_2} \qquad (5)$$

The major products are carbonyl fluoride and the corresponding perfluoroalkylsulfonyl fluorides. The respective products were found in the photolysis of the hypochlorites,[3] whereas the thermolysis of the latter led to **1** and **3** by the loss of ClF. The analogous reaction (eq 5) is true for **4**, forming **3** (definitely not

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[7] Koshar, R. J. Eur. Pat. Appl. EP57,327; U.S. Appl. 229,870, Jan 30, 1981. NMR data are identical with that of an authentic sample.

[8] DeMarco, R. A.; Shreeve, J. M. *Inorg. Chem.* **1973**, *12*, 1896.

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present in **4**) and fluorine (assumed) as minor products. Irradiation of the gaseous hypofluorites with UV light from a medium-pressure Hg lamp gives the same products (eqs 6 and 7); no acyl fluorides **1** or **3** were observed.

$$2 \xrightarrow{h\nu,\ 25^{\circ}C} \underset{(100\%,\ 5\ \text{min.})}{CF_3SO_2F + COF_2} \tag{6}$$

$$4 \xrightarrow{h\nu,\ 25^{\circ}C} \underset{(100\%,\ 1\ \text{h})}{C_2F_5SO_2F + COF_2} \tag{7}$$

From this work an interesting comparison can be made with the analogous hypochlorites[3] regarding thermal and photolytic stability:

thermal: $ClOCF_2CF(CF_3)SO_2F \simeq FOCF_2CF(CF_3)SO_2F > ClOCF_2CF_2SO_2F > FOCF_2CF_2SO_2F$

photolytic: $FOCF_2CF(CF_3)SO_2F \gg ClOCF_2CF(CF_3)SO_2F \simeq FOCF_2CF_2SO_2F > ClOCF_2CF_2SO_2F$

In all cases, the branched CF_3 compound is much more stable than the primary derivatives. A reasonable process for the decomposition is shown in Scheme I. When X = CF_3 (**4**), the greater stability can then be rationalized on the basis of the higher stability of $^{\bullet}OCF_2CF(CF_3)SO_2F$ and/or $^{\bullet}CF(CF_3)SO_2F$ and a slower chain transfer step.

Reactions with Olefins. With respect to our work on the hypochlorites $ClOCF_2CFXSO_2F$ (X = F, CF_3),[4] we provide some comparative results of the reaction chemistry of the corresponding fluoroxy compounds with simple olefins.

Since $XOCF_2CF_2SO_2F$ (X = F, Cl) and $XOCF_2CF(CF_3)SO_2F$ (X = F, Cl) each show similar thermal and photochemical stabilities, they are expected to have comparable reactivities in the reactions with olefins. In order to obtain perfluorinated ethers with a fluorosulfonyl functional group, **2** and **4** were reacted with tetrafluoroethene and hexafluoropropene (eqs 8–11).

$$2 + C_2F_4 \longrightarrow \underset{5\ (4\%)}{C_2F_5OCF_2CF_2SO_2F} + \underset{6\ (4\%)}{FSO_2CF_2CF_2SO_2F} \tag{8}$$

$$4 + C_2F_4 \longrightarrow \underset{9\ (33.3\%)}{C_2F_5OCF_2CF(CF_3)SO_2F} \tag{9}$$

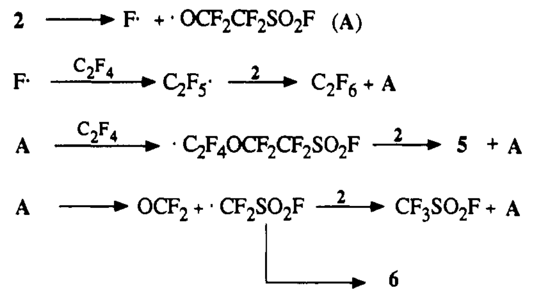
$$\underset{(5\%)}{2 + C_3F_6} \longrightarrow \underset{7\ (70\%)}{CF_3CF_2CF_2OCF_2CF_2SO_2F} + \underset{8\ (30\%)}{(CF_3)_2CFOCF_2CF_2SO_2F} \tag{10}$$

$$\underset{(47\%)}{4 + C_3F_6} \longrightarrow \underset{10\ (67\%)}{CF_3CF_2CF_2OCF_2CF(CF_3)SO_2F} + \underset{11\ (33\%)}{(CF_3)_2CFOCF_2CF(CF_3)SO_2F} \tag{11}$$

All reactions lead mainly to COF_2 and CF_3SO_2F (from **2**) and $C_2F_5SO_2F$ (from **4**), as decomposition products. The yield of all ethers, in general, is lower than that obtained from the analogous hypochlorites.[4] In the reaction of **2** with C_2F_4, small amounts of C_2F_6 and **6** were isolated in addition to the low yield of **5**. These products, along with the major decomposition products of **2** (Scheme I) can be rationalized as shown in Scheme II. One might reasonably expect to observe **6** and C_3F_8 in the reaction of **2** with C_3F_6, but none were detected.

The reaction of **2** or **4** with hexafluoropropene, in both cases, yields a mixture of the possible regioisomers **7**/**8** and **10**/**11**, respectively. The pairs are distinguishable by their ^{19}F NMR spectra recorded at 188.131 MHz; the integration of certain multiplets (fluorines labeled B in **7**/**8** and **10**/**11** in the Experimental Section) indicates the ratio of the two isomers *n*:iso = 70%:30%. The FO– compounds exhibit a much lower regioselectivity than the ClO– analogues.[4] Similar regiospecificity has been observed for reactions of C_3F_6 with $FOClO_3$,[10] CF_3OF,[11] and TeF_5OF.[12]

Scheme II



All compounds **5**–**11** are well identified by their mass, IR, and ^{19}F NMR spectra. The ^{19}F NMR spectrum of **6** was identical with that of an authentic sample. The mass spectra of **5** and **7** + **8** contain only weak peaks of $(MH)^+$ and $(M - F)^+$; the base peak for **7** + **8** is $(M - SO_2F)^+$. Intense fragments in the spectra of **9** and **10** + **11** are $(M - F)^+$ or $(M - C_2F_5O)^+$ (**9**). In the CI mass spectra of the mixture of **7**–**8** and of **9**, ions corresponding to the addition of CF_3 and C_2F_5, respectively, to the parent M^+ are observed. These are assumed to be a result of recombination reactions and could not be assigned to any reasonable impurity. The IR spectra of all addition compounds, including **6**, show a very strong band for $\nu(SO_2)$ = 1472–1474 cm^{-1} and several very strong and broad bands for $\nu(CF)$ and $\nu(SO_2)$ in the region 1300–1100 cm^{-1}, as well as a characteristic strong band at 827–821 cm^{-1} for $\nu(SF)$. The ^{19}F NMR signals are found in the expected regions and show comparable coupling constants for the analogous addition compounds with the respective hypochlorites.[4]

Reactions of 4 with CO, SO_2, SO_3, and PF_3. Since **4** is more stable than **2**, it was used for the reactions with the titled compounds. In the case of the chloro analogues of **2** and **4**, both readily insert CO into the Cl–O bond, forming stable chloroformates.[3] When reacted with SO_2, however, they decompose to $ClCFXSO_2F$ (X = F, CF_3) and COF_2 by SO_2 catalysis. The attempted synthesis of a fluoroformate,[13] $FC(O)OCF_2CF(CF_3)SO_2F$, a fluorosulfonyl ester, $FSO_2OCF_2CF(CF_3)SO_2F$, and a peroxyfluorosulfonyl ester sulfate,[14] $FSO_2OOCF_2CF(CF_3)SO_2F$, from **4** was unsuccessful (eq 12).

$$4 \xrightarrow{(CO,\ SO_2,\ SO_3)} C_2F_5SO_2F + COF_2 \tag{12}$$

No sulfur–fluorine-containing products other than $C_2F_5SO_2F$ were observed with SO_2 or SO_3. This result is quite different from that reported for the reactions of the most stable hypofluorite CF_3OF with SO_2 and SO_3.[2]

Fluoroxytrifluoromethane is known to oxidatively fluorinate phosphorus(III) compounds to difluorophosphorus(V) compounds,[15] and $CF_2(OF)_2$ converts PF_3 to PF_5 and POF_3.[16] Similarly, the oxidation of phosphorus trifluoride to phosphorus pentafluoride by **4** succeeded in quantitative yield (eq 13) as expected. A trace of phosphoryl fluoride was also observed.

$$PF_3 + 4 \rightarrow PF_5 + 3 \tag{13}$$

Conclusion

The successful isolation of the first functionalized fluoroxy compounds containing the fluorosulfonyl group was achieved. The stabilizing effect of a β-CF_3 group in these new compounds was

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clearly demonstrated. Compared to analogous hypochlorites, these fluoroxy compounds give only low yields of addition products with fluorinated olefins due to the rapid decomposition of the intermediate $\cdot OCF_2CFXSO_2F$ radicals formed in these reactions.

Acknowledgment. The partial financial support of this research by the National Science Foundation and the Gas Research Institute (Grant 5084-260-1086) is gratefully acknowledged.

Registry No. **1**, 677-67-8; **2**, 115784-53-7; **3**, 754-41-6; **4**, 115784-54-8; **5**, 67990-78-7; **6**, 84246-33-3; **7**, 14856-94-1; **8**, 132145-34-7; **9**, 135773-61-4; **10**, 135773-62-5; **11**, 135773-63-6; **12**, 81439-24-9; C_2F_4, 116-14-3; C_3F_6, 116-15-4; $FC(O)OCF_2CF(CF_3)SO_2F$, 135773-64-7; $FSO_2OCF_2CF(CF_3)SO_2F$, 135773-65-8; $FSO_2OOCF_2CF(CF_3)SO_2F$, 135773-66-9; $C_2F_5SO_2F$, 354-87-0.

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Reactions of *N*,*N*,*N'*-Tris(trimethylsilyl)benzamidine with Organochalcogen Halides: Formation of Diazenes via the Resonance-Stabilized Radicals $PhCN_2(EPh)_2^{\cdot}$ and the X-ray Structure of $PhCN_2(SCCl_3)_3$

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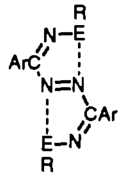
Received July 13, 1991

The reactions of *N*,*N*,*N'*-tris(trimethylsilyl)benzamidine (**1**) with organosulfur chlorides in a 1:1 or 1:3 molar ratio in methylene dichloride produce the metathetical products $PhC[N(SiMe_3)_2](NSR)$ [R = Ph, CCl_3, $2,4\text{-}C_6H_3(NO_2)_2$] or $PhCN_2(SR)_3$ [R = CCl_3, $2,4\text{-}C_6H_3(NO_2)_2$], respectively. The structure of $PhCN_2(SCCl_3)_3$ (**4b**) was determined by X-ray crystallography. The crystals of **4b** are triclinic, space group $P\bar{1}$, with $a = 9.972$ (2) Å, $b = 10.517$ (3) Å, $c = 10.968$ (3) Å, $\alpha = 109.75$ (2)°, $\beta = 93.31$ (2)°, $\gamma = 102.76$ (2)°, $V = 1044.8$ Å^3, and $Z = 2$. By contrast, the compound $PhCN_2(SPh)_3$ is thermally unstable and the reactions of **1** with PhECl (E = S, Se) in a 1:3 molar ratio in methylene dichloride produce the intensely colored diazenes *trans*-PhEN(Ph)CN=NC(Ph)NEPh. The ESR spectra of these reaction mixtures consist of a five-line (1:2:3:2:1) signal consistent with a radical mechanism involving the intermediate formation of the resonance-stabilized radicals $PhC(NEPh)_2^{\cdot}$ (E = S, $g = 2.0071$, $a_N = 0.575$ mT; E = Se, $g = 2.0201$, $a_N = 0.59$ mT). The reactions of **1** with $RSeCl_3$ (R = Me, Ph) also yield the diazenes *trans*-RSeN(Ph)CN=NC(Ph)SeR (**2a**, R = Me; **2b**, R = Ph). The reaction of $4\text{-}CF_3C_6H_4CN_2(SiMe_3)_3$ with PhSCl in a 1:3 molar ratio produces the eight-membered ring $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2Ph_2$, as a minor product, in addition to the isomeric diazene. The eight-membered rings $Ph_2C_2N_4S_2R_2$ [R = CCl_3, $2,4\text{-}(NO_2)_2C_6H_3$] are obtained from the reaction of $PhC(NSR)[N(SiMe_3)_2]$ with 2 molar equiv of PhSeCl.

Introduction

Organic sulfur–nitrogen (S–N) compounds have attracted widespread attention in recent years.[1,2] This activity is due to an intrinsic curiosity in the unusual molecular and electronic structures of these π-electron-rich compounds and to their possible role as low-dimensional conducting materials.[3,4] This interest has been extended to organic selenium–nitrogen (Se–N) compounds, e.g. the cyclic 7-π-electron radicals 1,2,4,6-selenatriazinyl, $Ph_2C_2N_3Se^{\cdot}$,[5] and 1,2,3,5-diselenadiazolyl, $PhCN_2Se_2^{\cdot}$.[6] In a seminal paper Woodward et al. reported the first dithiatetrazocines $1,5\text{-}R_2C_2N_4S_2$ (R = Me_2N, Ph) and showed that the structures of these ring systems are remarkably dependent on the nature of the exocyclic substituent.[7] In an attempt to prepare the unknown $C_2N_4Se_2$ ring, we found that the reaction of $PhCN_2(SiMe_3)_3$ (**1**) with $RSeCl_3$ (R = Me, Ph) produces intensely colored materials identified by an X-ray structure determination of **2a** as diazenes.[8] We also mentioned briefly that the diazene **2b** and its sulfur analogue, **2c**, can be prepared in good yields by the reaction of **1** with PhECl (E = S, Se) in a 1:3 molar ratio.



2a (E = Se, R = Me, Ar = Ph)
2b (E = Se, R = Ph, Ar = Ph)
2c (E = S, R = Ph, Ar = Ph)
2d (E = S, R = Ph, Ar = $4\text{-}CH_3C_6H_4$)
2e (E = S, R = Ph, Ar = $4\text{-}CF_3C_6H_4$)

We describe here the full details of an investigation of the reactions of **1** with organochalcogen chlorides, which includes (a) the preparation and characterization of the monosubstituted products $PhCN_2(SiMe_3)_2(SR)$ [**3a**, R = Ph; **3b**, R = CCl_3; **3c**, R = $2,4\text{-}C_6H_3(NO_2)_2$(DNP)], (b) the preparation of the trisubstituted derivatives $PhCN_2(SR)_3$ [**4b**, R = CCl_3; **4c**, R = 2,4-DNP] and the X-ray structure of **4b**, (c) the identification by ESR spectroscopy of the resonance-stabilized radicals $PhC(NEPh)_2^{\cdot}$ [**5a**, E = S; **5b**, E = Se] as intermediates in the formation of the diazenes **2b** and **2c**, and (d) the characterization of the eight-membered rings $Ar_2C_2N_4S_2R_2$ [**6a**, Ar = $4\text{-}CF_3C_6H_4$, R = Ph; **6b**, Ar = Ph, R = CCl_3; **6c**, Ar = Ph, R = $2,4\text{-}(NO_2)_2C_6H_3$].

Experimental Section

Reagents and General Procedures. All reactions and the manipulation of moisture-sensitive compounds were carried out under an atmosphere

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