Synthesis of Pentafluorophenoxy Derivatives of Sulfur(IV) and -(VI) Fluorides

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The reactions of potassium pentafluorophenoxide with SOF_2, SO_2F_2, and CF_3SO_2Cl have been investigated and found to result in $FS(O)OC_6F_5$, $FS(O)_2OC_6F_5$, and $CF_3S(O)_2OC_6F_5$. Physical and spectral data (mass, ir, NMR) on the three new compounds are reported.

Esters of the type $R_fOS(O)_2F$ (*2, 4, 6, 9–13, 15, 16*) and $R_fOS(O)F$ (*3*) are known but no examples have been reported where R_f is a pentafluorophenyl group. The successful utilization of potassium pentafluorophenoxide in the preparation of pentafluorophenoxy derivatives of carbon and phosphorus has recently been demonstrated in the reaction of KOC_6F_5 with acid fluorides and phosphorus halides (*8*). Therefore, the potential for the extension of the use of KOC_6F_5 as a reagent to introduce the pentafluorophenoxy group into sulfur compounds was investigated.

Experimental Section

General. Standard high vacuum techniques were used throughout. Quantities of reactants and products were measured either by direct weighing or by the relationship $n = PV/RT$ measuring pressures on a Wallace and Tiernan Model FA 145 differential pressure gauge. Vapor pressure curves were obtained by a static method and the data analyzed by a computer assisted least-squares fit to both linear and quadratic equations with the best results reported. The ^{19}F NMR spectra were obtained at ambient temperature on a Varian XL-100-15 NMR spectrometer on solutions containing 80 mol % $CFCl_3$ as an internal standard. Ir spectra were obtained on a Perkin-Elmer Model 180 spectrometer using a 10-cm gas cell fitted with AgCl windows. Mass spectral data were obtained on a AEI MS9 mass spectrometer operating at 70 eV with a source temperature of 150°.

Reagents. Thionyl fluoride and trifluoromethanesulfonyl chloride were obtained from P.C.R., Inc., and used without further purification. Sulfuryl fluoride was prepared by the fluorination of SO_2Cl_2 with SbF_3. Potassium pentafluorophenoxide was prepared by a modification of the literature method, and volatiles were removed under high vacuum with gentle heating (*1*).

Reactions. Stoichiometric data, yields, and reaction times are summarized in Table I. The reactions were performed in a 100-ml glass reaction bulb equipped with a Teflon-glass valve. The usual procedure was to condense at −196° the appropriate amount of sulfur halide onto a known amount of potassium pentafluorophenoxide. The reaction vessel was allowed to warm to 23° and stand for the times indicated in Table I. The reaction system was then cooled to −196° and opened to a pressure gauge. No noncondensables were observed in any of the reactions. The volatile reaction products were distilled into a trap held at −196° (as some of the products are of low volatility, a considerable time was allowed for removal of volatile products from solid products) and separated by trap to trap distillation.

***$CF_3S(O)_2OC_6F_5$*.** Clear liquid at 23°; forms a clear glass at low temperature; bp 94° (63.2 mm), 81.5° (37.6 mm); ir (cm^{-1}) 1525 (s), 1455 (m), 1310 (w), 1247 (m), 1232 (s), 1142 (m), 1020 (m), 1005 (s), 980 (m), 798 (m), 759 (w), 609 (m); mass spectrum (relative intensities and assignments in parentheses) 316 (93, $C_7F_8O_3S^+$), 252 (69, $C_7F_8O^+$), 233 (1.3, $C_7F_7O^+$), 231 (3.4, $C_6F_5O_2S^+$), 205 (3.1, $C_6F_7^+$), 200.9 (0.3, metastable), 183 (93, $C_6F_5O^+$), 167 (11.9, $C_6F_5^+$), 155 (88, $C_5F_5^+$), 136 (1, $C_5F_4^+$), 131.3 (0.4, metastable), 124 (4, $C_4F_4^+$), 117 (18, $C_5F_3^+$), 105 (12.5, $C_4F_3^+$), 98 (3, $C_5F_2^+$), 93 (11, $C_3F_3^+$), 86 (6, $C_4F_2^+$), 77.5 (0.5, $C_5F_5^{++}$), 69 (100, CF_3^+), 64 (6, SO_2^+), 50 (1.3, CF_2^+), 48 (5, SO^+), 31 (6, CF^+).

***$FS(O)_2OC_6F_5$*.** Clear liquid at 23°; forms clear glass at low temperatures; bp 157.9°; $\log P(\text{mm}) = 9.0048 - 2954.0/T + 13\,548/T^2$ (57–96°); ΔH_{vap} 10.64 kcal/mol; ΔS_{vap} 24.69 eu; ir (cm^{-1}) 1528 (s), 1521 (s), 1484 (m), 1454 (w), 1289 (w), 1240 (m), 1230 (sh), 1142 (w), 1020 (m), 1004 (s), 844 (m), 799 (w), 759 (w), 706 (w), 612 (w); mass spectrum (relative intensities and assignments in parentheses) 266 (30, $C_6F_6SO_3^+$), 247 (2, $C_6F_5SO_3^+$), 183 (100, $C_6F_5O^+$), 167 (3, $C_6F_5^+$), 164 (2, $C_6F_4O^+$), 155 (90, $C_5F_5^+$), 136 (7, $C_5F_4^+$), 131.3 (0.5, metastable), 124 (4, $C_4F_4^+$), 117 (15, $C_5F_3^+$), 105 (10, $C_4F_3^+$), 98 (3, $C_5F_2^+$), 93 (8, $C_3F_3^+$), 86 (5, $C_4F_2^+$), 77.5 (1, $C_5F_5^{2+}$), 74 (4, $C_3F_2^+$), 69 (12, CF_3^+), 67 (5, SOF^+ or C_4F^+), 64 (3, SO_2^+), 48 (3, SO^+), 31 (6, CF^+).

***$FS(O)OC_6F_5$*.** Clear liquid at 23°; mp −34.3°; bp 154.6°; $\log P(\text{mm}) = 8.1458 - 2304.6/T + 22\,380/T^2$ (71–95°); ΔH_{vap} 10.07 kcal/mol; $\Delta S_{\text{vap}} = 23.53$ eu; ir (cm^{-1}) 1522 (vs), 1460 (w), 1310 (w), 1290 (m), 1231 (m), 1142 (m), 1018 (m), 1000 (vs), 795 (w), 762 (m), 709 (m), 610 (m); mass spectrum (relative intensities and assignments in parentheses) 250 (22, $C_6F_6SO_2^+$), 183 (96, $C_6F_5O^+$), 167 (5, $C_6F_5^+$), 164 (2, $C_6F_4O^+$), 155 (100, $C_5F_5^+$), 136 (17, $C_5F_4^+$), 131.3 (0.5, metastable), 124 (5, $C_4F_4^+$), 117 (28, $C_5F_3^+$), 105 (17, $C_4F_3^+$), 98 (5, $C_5F_2^+$), 93 (12, $C_3F_3^+$), 86 (10, $C_4F_2^+$), 78 (30, $C_2F_2O^+$), 77.5 (1, $C_5F_5^{2+}$), 69 (17, CF_3^+), 67 (17, SOF^+ or C_4F^+), 64 (7, SO_2^+), 50 (2, CF_2^+), 48 (12, SO^+), 31 (7, CF^+).

Results and Discussion

The nucleophilic displacement of halide on sulfur by pentafluorophenoxide ion has resulted in the formation of $FS(O)OC_6F_5$, $FS(O)_2OC_6F_5$, and $CF_3S(O)_2OC_6F_5$ (eq 1–3).

$$SOF_2 + KOC_6F_5 \rightarrow FS(O)OC_6F_5 + KF \tag{1}$$

$$SO_2F_2 + KOC_6F_5 \rightarrow FS(O)_2OC_6F_5 + KF \tag{2}$$

$$CF_3S(O)_2Cl + KOC_6F_5 \rightarrow CF_3S(O)_2OC_6F_5 + KCl \tag{3}$$

Observation of involatile oils as concurrent products with $FS(O)OC_6F_5$ suggests some of the disubstituted compound, $(C_6F_5O)_2SO$, is formed in eq 1. This premise is supported by the observation of higher yields of the monosubstituted product with increased excess of thionyl fluoride. Likewise, higher excesses of both sulfuryl fluoride and trifluoromethanesulfonyl chloride enhance the recoverable yields of their respective reactions. However, this appears to be a kinetic effect in these cases. A comparison of the reaction times required to produce comparable yields shows the attack of $OC_6F_5^-$ on SOF_2 to be faster than that on $CF_3S(O)_2Cl$ which in turn is considerably faster than that on SO_2F_2. This suggests the nucleophilic displacement of chlorine from sulfur(VI) to be a more favorable process than replacement of fluorine. However, a fluorine attached to sul-

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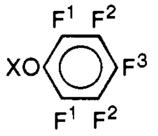
Table I. Summary of KOC_6F_5 Reactions

Reactant[a]	KOC_6F_5[a]	Time	Products[a]	Yield,[b] %
9.81 $CF_3S(O)_2Cl$	3.25	3.5 hr	1.83 $CF_3S(O)_2OC_6F_5$[c]	56
7.79 SO_2F_2	1.48	6 days	1.00 $FS(O)_2OC_6F_5$[d]	68
15.38 SOF_2	3.41	14 min	2.10 $FS(O)OC_6F_5$[e]	59

[a] Amounts in millimoles. [b] Yields based on KOC_6F_5. [c] Collected at −31°. [d] Collected at −78°. [e] Collected at −40°.

Table II. ^{19}F NMR Data



X[a, b]	ϕ_X*	ϕ_1*	ϕ_2*	ϕ_3*	$J_{F^XF^1}$	$J_{F^1F^2}$	$J_{F^2F^3}$
$FS(O)_2$	−42.0	+151.8	+160.6	+153.3	11.2	16.2	20.5
$CF_3S(O)_2$	+73.4	+151.2	+161.0	+154.1	6.6	16.5	20.5
$FS(O)$	−69.6	+151.0	+162.0	+155.7	9.0	16.8	20.8

[a] Chemical shifts relative to $CFCl_3$ in parts per million. [b] Coupling constants expressed in hertz.

fur(IV) is more susceptible to nucleophilic displacement than both the chlorine and fluorine derivatives of sulfur(VI).

An alternate method of preparation of $FS(O)OC_6F_5$ and $FS(O)_2OC_6F_5$ by reaction of $SOCl_2$ or SO_2Cl_2 with KOC_6F_5 to produce $ClS(O)OC_6F_5$ and $ClS(O)_2OC_6F_5$, which could then be fluorinated, may be envisioned. However, control of the reaction to produce the monosubstituted derivatives, $ClS(O)OC_6F_5$ and $ClS(O)_2OC_6F_5$, and subsequent fluorination might be difficult (*3*). In the preparation of $CF_3S(O)_2OC_6F_5$, $CF_3S(O)_2Cl$ was used as a starting material. Since only one reaction site is available, advantage was taken of the more reactive chloro compound to shorten the required reaction times. Although a large number of reactions have not been investigated, the reaction of KOC_6F_5 with $RS(O)_2X$ (X = F, Cl) and $RS(O)X$ (X = F, Cl) is probably quite general and thus, should provide a convenient one-step synthesis to $RS(O)_2OC_6F_5$ and $RS(O)OC_6F_5$. However, purification problems may arise if inadequately dried KOC_6F_5 is used. In this case large amounts of C_6F_5OH can be formed in the reaction system. This material is difficult to separate from the new compounds.

Unequivocal characterization of $FS(O)OC_6F_5$, $FS(O)_2OC_6F_5$, and $CF_3S(O)_2OC_6F_5$ has been obtained by the use of NMR, ir, and mass spectroscopy. The mass spectrum of each compound contained a strong peak corresponding to the molecular ion. All other peaks have been easily assigned to fragments of the molecule. Each spectrum contains a metastable at *m/e* 131.3 which confirms the transition of 183 → 155 via loss of a neutral particle which in this case is CO. This particular transition has been found in all of the pentafluorophenoxy derivatives we have investigated (12 examples) (*8*). Thus, we consider it to be characteristic of the presence of OC_6F_5 in the molecule. In addition, isotope peaks (not reported in the experimental section for brevity) are consistent with the assignments made.

Ir data for each new compound are consistent with the assigned structures. Each compound shows a strong absorption band in the 1525-cm^{-1} region which is characteristic of C_6F_5 compounds (*1*, *8*). Absorption bands due to $\nu(S{=}O)$ are observed for each compound: 1455 and ~1230 cm^{-1} (obscured by $\nu(CF_3)$) $CF_3S(O)_2OC_6F_5$, 1484 and 1240 cm^{-1} $FS(O)_2OC_6F_5$, and 1290 cm^{-1} $FS(O)OC_6F_5$. In $FS(O)OC_6F_5$ and $FS(O)_2OC_6F_5$ strong absorptions which can be assigned to $\nu(SF)$ are observed at 844 and 762 cm^{-1}, respectively.

NMR data of the new compounds are summarized in Table II. In each compound the chemical shifts, multiplicity, and relative areas of the observed signals are consistent with the assigned structures. Assignments for the pentafluorophenyl portion of the NMR spectra were made by analogy with previous assignments for the C_6F_5 group (*7*). The NMR signals of the fluorines in each molecule which were not on the ring system all appear as triplets of appropriate relative areas due to the coupling with the ring fluorines ortho to the substituted groups. Chemical shifts of *F*$S(O)_2OC_6F_5$, C*F*$S(O)_2OC_6F_5$, and *F*$S(O)OC_6F_5$ are consistent in magnitude with those observed in similar compounds (*3*, *5*).

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