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SHORT COMMUNICATION

Introduction of Functional Groups into Some Chlorofluorocarbon Ethers .

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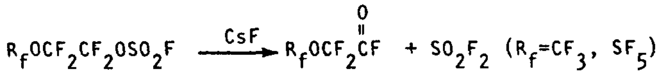
The addition of hypochlorites, such as CF_3OCl and SF_5OCl, to perfluoroolefins is a straightforward route to chlorofluorocarbon ethers [1,2]. These materials are very stable entities. Both the hypochlorite addition and the derived ethers would be more useful if functional groups could be introduced into these compounds. This paper describes a method to achieve this goal. It involves the conversion of the $-CF_2Cl$ end group into a $-CF_2OSO_2F$ group:

$$R_fOCF_2CF_2Cl + ClOSO_2F \xrightarrow{Br_2} R_fOCF_2CF_2OSO_2F + Cl_2$$

$$R_f{=}CF_3,\ SF_5$$

This reaction was found to occur in high yield (70-90%) but at a slow rate. Two to three weeks were required for complete conversion of the starting material at 110-140°. The addition of 10-20 mole % of bromine which results in <u>in situ</u> $BrOSO_2F$ formation was necessary to obtain these reaction rates. Pure $ClOSO_2F$ or FO_2SOOSO_2F did not produce appreciable reaction under the same conditions. Higher temperatures were not investigated since attack on the stainless steel reactors by the halogen fluorosulfates becomes significant. In view of the general inertness of the $-CF_2Cl$ group, it is encouraging that high conversions are obtainable and that the ether function is unaffected.

The resulting fluorocarbon fluorosulfates can be converted into the corresponding acyl fluorides in essentially quantitative yield via the CsF catalyzed elimination of sulfuryl fluoride [3].



$$R_fOCF_2CF_2OSO_2F \xrightarrow{CsF} R_fOCF_2\overset{\overset{O}{\|}}{C}F + SO_2F_2 \quad (R_f{=}CF_3,\ SF_5)$$

Both of these acyl fluorides have been reported as products from other reactions. Thus, CF_3OCF_2CFO was obtained in 3% yield from the thermal, flow tube reaction of perfluoropropene and oxygen [4] and also from $CF_3OCF_2CO_2K$ (unspecified origin) [5] in 52% yield. Additional characterizing data for these compounds has been obtained (see Experimental Section). The sulfur analogue was reported to result, unexpectedly and inexplicably, from the reaction of ozone and $SF_5CF{=}CF_2$ with an estimated yield of 67%. Our observed properties are in good agreement with those previously reported [6].

It has previously been shown for SF_5OCF_2CFO that these acid fluorides can readily be converted to typical derivatives, such as acid and amide [6]. We have found that another derivative, the hypofluorite, can readily be made in high yield.

$$CF_3OCF_2CFO + F_2 \xrightarrow{CsF} CF_3OCF_2CF_2OF$$

This reactive compound is easily identified by its ^{19}F NMR chemical shift, characteristic for the hypofluorite fluorine [7] as are the SF_5-, $-SO_3F$, and -CFO groups which are summarized in Table 1.

Table 1: ^{19}F NMR Data Chemical Shifts (ppm)^a and Coupling Constants (Hz)

Compound	RF_nO-	$-CF_2-$	$-CF_2-$	-F
$CF_3OCF_2CF_2OSO_2F$	57.6(t) (J=8.6)	92.1(q) (J=8.6)	90.0(d) (J=8.2)	-49.6(t) (J=8.3)
CF_3OCF_2CFO	56.3(t) (J=8.5)	79.6(q,d)		-13.4(t) (J=2.8)
$CF_3OCF_2CF_2OF$	56.0(t) (J≅8.5)	85.8(q)^b (J≅8.5)	98.1(d) (J≅8.5)	-138.8(q) (J≅8.5)
$SF_5OCF_2CF_2OSO_2F$	-60.2(ax.) -72.5(eq.)	89.1(q) (J=11.6)	88.4(d) (J=7.9)	-49.7(t) (J=7.9)
SF_5OCF_2CFO	-61.4(ax.) -72.0(eq.)	77.9(q,d) (J=10.7, 3.4)		-13.2(t) (J=3.4)

a) Upfield from internal $CFCl_3$. b) Apparent quintet due to approximately equal coupling to CF_3O- and OF Fluorines

In summary, the above results demonstrate that the successful conversion of the $-CF_2Cl$ group to a fluorosulfate offers a simple and efficient route to a variety of conventional functional groups.

EXPERIMENTAL

The apparatus and instruments used in this work have previously been described [8]. Literature procedures were employed to prepare $CF_3OCF_2CF_2Cl$ [1,2], $SF_5OCF_2CF_2Cl$ [1,2], $ClOSO_2F$ [9], and $S_2O_6F_2$ [10].

$CF_3OCF_2CF_2OSO_2F$. A 30 ml stainless steel cylinder was loaded with $CF_3OCF_2CF_2Cl$ (1.38 mmol), $ClOSO_2F$ (2.10 mmol), and Br_2 (0.2 mmol) at

-196°: After warming to ambient temperature the reactor was heated for two weeks at 110°. Fractional condensation through U-traps cooled to -45, -78, -112, and -196° was used to separate the $CF_3OCF_2CF_2OSO_2F$ product from the by-products $BrOSO_2F$, $S_2O_5F_2$, BrCl and small amounts of unreacted $CF_3OCF_2CF_2Cl$ and $ClOSO_2F$. The desired $CF_3OCF_2CF_2OSO_2F$ was retained in both the -78 and -112° traps and was treated with Hg to remove traces of colored impurities furnishing the purified material in 90% yield. The product was identified by infrared, cm^{-1}; 1498(s), 1295(S), 1252(S), 1173(S), 1157(S), 1143(S), 1091(S), 928(W), 915(W), 840(M),769(W), 682(V-W), 551(W): mass spectrum, 40 ev, M/e (assign. rel. intens.) 265 (M-F, 0.02), 252 ($M-O_2$, 0.02), 249 (M-O,F, 0.02), 199 ($M-CF_3O$, 0.9), 185 ($M-SO_3F$, 0.8), 182 ($C_3F_6O_2$, 0.35), 163 ($C_3F_5O_2$, 0.06), 149 (CF_2SO_3F, 3.7), 135 (C_2F_5O, 4), 119 (C_2F_5, 45), 102 (SO_2F_2, 0.35), 100 (C_2F_4, 0.7), 97 (C_2F_3O, 4.5), 83 (SO_2F, 53) 80 (SO_3, 6), 69 (CF_3, 100), 67 (SOF 8), 64 (SO_2, 5), 50 (CF_2, 3.5), 48 (SO , 4), and 47 (COF, 16): ^{19}F NMR.

$SF_5OCF_2CF_2OSO_2F$. By analogy with $CF_3OCF_2CF_2Cl$, a sample of $SF_5OCF_2CF_2Cl$ (1.20 mmol) was reacted with $ClOSO_2F$ (2.26 mmol) and Br_2 (0.5 mmol) for three weeks at 130°. The desired product was retained in the -78° trap and was obtained in 71% yield after purification. Identification was based on infrared, cm^{-1}; 1496(S), 1265(S), 1230(S), 1203(S), 1160(S), 1087(S), 947(S), 930(S), 870(S), 845(S), 822(S), 766(M), 600(S), 557(M): mass spectrum, 40 ev, M/e (assign. rel. intens.) 323 (M-F, vw), 310 ($M-O_2$, vw), 243 ($SF_5OC_2F_4$, 0.03), 199 ($C_2F_4SO_3F$, 2.4), 193 (SF_5OCF_2, 0.2), 149 (CF_2SO_3F, 2.7), 127 (SF_5, 100), 119 (C_2F_5, 46), 108 (SF_4, 0.9), 105 (SF_3O, 55), 100 (C_2F_4, 1.3), 97 (C_2F_3O, 3), 89 (SF_3, 11.5), 83 (SO_2F, 60), 70 (SF_2, 2.8), 69 (CF_3, 16), 67 (SFO, 11), 66 (CF_2O, 2), 64 (SO_2, 6.5), 51 (SF, 1), 50 (CF_2, 8), 48 (SO, 8), and 47 (CFO, 25): ^{19}F NMR.

CF_3OCF_2CFO and SF_5OCF_2CFO. Both compounds were prepared in 95 + % yield by heating a sample (0.5 mmol) of the respective fluorosulfate in the presence of 10 mmol CsF, for 14 hrs to 110°. The only volatile product was SO_2F_2. The acyl fluorides were obtained by vacuum pyrolysis of the formed salt, $R_fOCF_2CF_2OCs$. For CF_3OCF_2CFO, the vapor density was 179 g/mol (theory=182). The infrared spectrum observed was, cm^{-1}; 1893(S), 1340(M), 1280(S), 1247(VS), 1198(M), 1145(VS), 1092(M), 925(W), 910(W), 831(VW), 760(VW), 732(VW), 700(VW) and the mass spectrum, 40 ev, M/e (assign. rel. intens.), 135(M-CFO, 5), 97($M-CF_3O$, 10), 85(CF_3O, 8), 78(C_2F_2O, 0.5), 69(CF_3, 100), 66(CF_2O, 1.5), 50(CF_2, 12), and 47(CFO, 28). The ^{19}F NMR spectrum agreed with the literature [4]. For SF_5OCF_2CFO the observed vapor density was 342 g/mol (theory=344). The observed infrared spectrum was as reported [6] and in addition showed a strong 603 cm^{-1} band which was beyond the range of the previous study. The mass spectrum noted was; 193(M-CFO, 1.6), 127(SF_5, 100), 108(SF_4, 2), 105(SF_3O, 26), 97(M-SF_5O, 12), 89(SF_{31}, 15), 86(SF_2O, 1), 83(SO_2F, 0.5), 69(CF_3, 28), 67(SFO, 2.6), 66(CF_2O, 1.2), 50(CF_2, 4.5), and 47(CFO, 23). The ^{19}F NMR was as reported [6].

$CF_3OCF_2CF_2OF$. A sample of CF_3OCF_2CFO (0.27 mmol) was allowed to react with with F_2 (2.2 mmol) in the presence of CsF (~8 mmol) by slowly warming the the condensed reactants to ambient temperature overnight. After removal of the excess F_2 by pumping at -196°, the only volatile product found was $CF_3OCF_2CF_2OF$ in 88% yield. In addition to the ^{19}F NMR spectrum further identification of this hypofluorite was obtained from its infrared spectrum, cm^{-1}; 1347(M), 1291(S), 1249(VS), 1214(S), 1194(S), 1156(VS), 1086(M), 895(MW), 804(W), 697(W). Below M/e 100 the mass spectrum was qualitatively much like CF_3OCF_2CFO but showed weak peaks at 201(M-F), 185(M-OF) and intense 135(C_2F_5O), 119(C_2F_5), and 116(C_2F_4O) peaks.

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