Short Communication

Synthesis of pentafluorosulfuroxydifluoroacetyl fluoride

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Although pentafluorosulfur fluoroformate [1], $SF_5OC(O)F$, and pentafluorosulfuroxytetrafluoropropionyl fluoride [2], $SF_5OC_2F_4C(O)F$, have been reported in the literature, no reference has been made to pentafluorosulfuroxydifluoroacetyl fluoride, $SF_5OCF_2C(O)F$. This compound was unexpectedly prepared by the action of both ozone and oxygen on the olefin $SF_5CF=CF_2$ [3]. Based on previous work on the ozonolysis of perfluoroolefins [4], it was anticipated that $SF_5CF=CF_2$ would be readily cleaved by ozone to form $SF_5C(O)F$ [1]. Under the conditions employed, it had been expected that oxygen would react with $SF_5CF=CF_2$ to form $SF_5CF_2C(O)F$ [5] in a similar manner to the reaction of oxygen and $ClCF=CF_2$ to form $ClCF_2C(O)F$ [6]. In both cases none of the expected reaction products were formed, but instead $SF_5OCF_2C(O)F$ was the major product from both reactions. It was separated from the by-products SOF_2, SO_2F_2, SF_5OSF_5 and any unidentified SF_5-containing species by gas chromatographic techniques and was identified by infrared spectroscopy, ^{19}F NMR analysis, molecular weight and the formation of various derivatives. It is readily converted to the amide and methyl ester by treatment with appropriate reagents. It hydrolyzes readily to give the carboxylic acid.

Experimental section
    Reagents
    The $SF_5CF=CF_2$ used in these experiments was obtained from the Chemical Research Laboratories of Allied Chemical Corporation. The olefin, of approximately 87 mol % purity by GLPC analysis, was used without further purification. The major impurity was SF_5CHFCF_2Cl. The O_3 used was purchased from the Matheson Company, Inc. as a solution in CF_3Cl. Its initial purity in the vapor phase was approximately 15 mol %. The mixture contained trace amounts of O_2 which accumulated slowly with O_3 decomposition. Oxygen was extra dry U.S.P. grade, purchased from the Linde Division of Union Carbide. The solvent used was FC-43, trademark of the 3-M Company for their product perfluorotributylamine, b.p. 174 °C.

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General method

Reactions were carried out in Fisher–Porter Aerosol Compatibility tubes fitted with a stainless-steel inlet tube, pressure gauge, Hoke needle valve and Teflon-coated magnetic stir bar. Reactions with O_3 were conducted in the solvent FC-43; oxygen reactions were run without a solvent. The reaction tubes were evacuated and the required amount of olefin, calculated from the ideal gas law, was transferred from a glass vacuum line into the tube at liquid nitrogen temperature. At -80 °C, the tube was charged with an excess of O_3 or O_2. Because of the low concentration of O_3 in the O_3/CF_3Cl mixture and to avoid pressures exceeding *ca.* 14 atm, it was necessary to add the O_3 in portions. Thus, a portion of O_3 was added, allowed to react (as noted by the reduction in pressure) and then the pressure (mostly CF_3Cl) was released while the reaction tube was held at -111 °C. This process was repeated several times until the desired amount of O_3 was added. The progress of the reaction could also be followed by periodically sampling the reaction mixture and noting the appearance in the IR spectrum of the absorption at 1898 cm^{-1} (C=O) and the disappearance of the band at 1780 cm^{-1} (C=C). Upon completion of the reaction, a crude separation of the products was made by trap-to-trap condensation and the fraction containing acid fluoride transferred to a stainless-steel Hoke cylinder and separated by GLPC. The fractions were collected in a flow-through IR cell as they were eluted from the column and identified when possible by comparison with known spectra. The $SF_5OCF_2C(O)F$ was further identified by ^{19}F NMR spectroscopy, molecular weight and the formation of various derivatives.

Gas chromatographic separations were carried out with a preparative-scale, 6 m × 9 mm column containing 30% QF-1 (Fluorosilicone) absorbed on 70% Chromosorb P. An Aerograph Autoprep Model A-700 was used. Samples for GLPC were taken from the liquid phase by inverting the Hoke cylinder and allowing the liquid to vaporize into the column.

Infrared spectra were recorded on a Perkin–Elmer 137 Infrared spectrophotometer. The IR cell was a flow-through micro-gas cell fabricated of nickel with a path length of 10.0 cm, a volume of 36 cm^3 and fitted with NaCl optics.

The ^{19}F and ^1H NMR spectra were obtained with a Varian Model A-56/60 instrument. Samples for ^{19}F NMR analysis were sealed in 5 mm Pyrex tubes with approximately 50 mol % $CFCl_3$ as an internal standard. Samples for ^1H NMR analysis were sealed with 50 mol % tetramethylsilane as internal standard.

Reaction of $SF_5CF=CF_2$ and O_3

The reaction tube was charged with 10.0 cm^3 of FC-43, degassed and 6.0 g (28.9 mmol) of 87% $SF_5CF=CF_2$ condensed in at -196 °C. The contents were warmed to -80 °C and approximately 34 mmol of ozone was added incrementally over a period of 6 h. The mixture was stirred overnight at 25 °C. An IR spectrum on a sample of the material indicated that reaction

TABLE 1

Results of gas chromatographic separation

Retention time	Area (%)	Component
5.9	3.5	CF_3Cl
6.6	1.6	SOF_2
8.5	1.1	Unknown
10.1	2.8	SO_2F_2
14.3	4.3	SF_5OSF_5
16.3	7.5	Unknown
20.0	6.8	$SF_5FC=CF_2$
23.0	72.0	$SF_5OCF_2-C(O)F$
30.0	0.4	$SF_5CHF-CClF_2$

was complete after this time. The products were separated from the solvent and other volatiles at $-111\,^\circ$C and 5.5 g of crude acid fluoride was transferred to a 100 cm^3 stainless-steel cylinder for GLPC separation. The results of chromatography are shown in Table 1. Based on this analysis the yield of $SF_5OCF_2C(O)F$ was estimated to be 67% based on $SF_5CF=CF_2$ charged.

Tentative recognition of $SF_5OCF_2C(O)F$ came from its IR spectrum.

Infrared spectrum of $SF_5OCF_2C(O)F$
The peaks together with their intensities are as follows: 1898(s), 1310(m), 1210(s), 1160(s), 1100(s), 935(vvs), 910(s), 865(w), 840(s), 722(w) cm^{-1} (s = strong; m = medium; w = weak; v = very). By analogy with numerous spectra of acid fluorides, the absorption at 1898 cm^{-1} was assigned to C=O. The presence of the OSF_5 group is indicated by absorptions in the 923 - 935 cm^{-1} range by analogy with $SF_5OC_2F_5$, SF_5OF and other SF_5O adducts [7]. Further confirmation of this structure came from the ^{19}F NMR spectra. The NMR data, summarized in Figure 1, showed that the spectrum of SF_5 was similar to that of other SF_5 compounds and fell in the same portion of the spectrum. The peaks due to fluorines attached to carbon atoms fell in two distinct regions of the spectrum, one typical of fluorocarbonyl groups and the other typical of alkyl C—F groups.
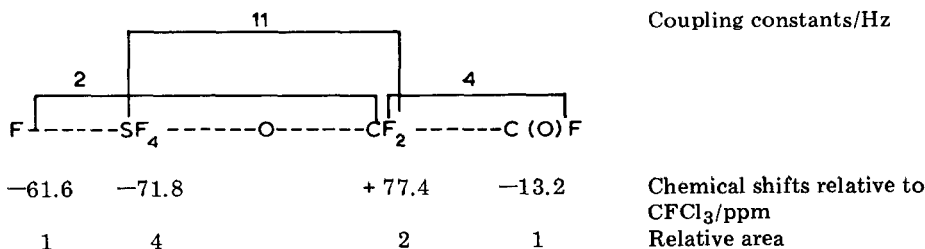

Fig. 1. ^{19}F nuclear magnetic resonance data observed for $SF_5OCF_2C(O)F$. The signs of the coupling constants are relative to one another and not necessarily absolute.

The gas density expressed in molecular weight units gave an average value of 233. The calculated molecular weight of $SF_5OCF_2C(O)F$ is 240.

Reactions of $SF_5OCF_2C(O)F$

When the acid fluoride was heated with water, a high boiling liquid (vapour pressure 6 mmHg at 24 °C) was isolated and identified as SF_5OCF_2 COOH by IR, ^{19}F and ^{1}H NMR analysis as well as by its neutralization equivalent. The IR spectrum showed the disappearance of the C=O absorption at 1898 cm^{-1} and the appearance of the new absorption at 1775 cm^{-1} in the region for CO(OH). An absorption at 3600 cm^{-1} may be assigned to OH stretch. The ^{19}F NMR spectrum is also consistent with the acid structure. This data is summarized in Figure 2.
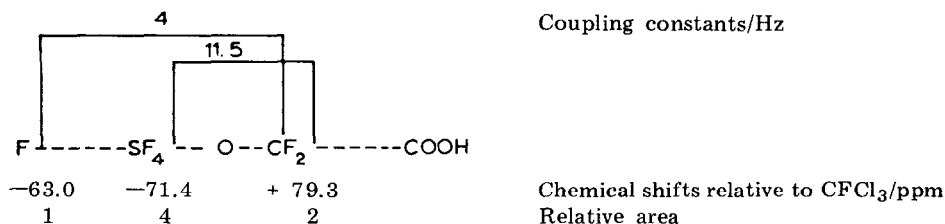

Coupling constants/Hz

F-------SF$_4$---O--CF$_2$------COOH

−63.0	−71.4	+ 79.3	Chemical shifts relative to CFCl$_3$/ppm
1	4	2	Relative area

Fig. 2. [19]F nuclear magnetic resonance data observed for SF_5OCF_2COOH. The signs of the coupling constants are relative to one another and not necessarily absolute.

The ^{1}H NMR spectrum shows a singlet at 8.07 ppm which may be assigned to the COOH group. The high integration as well as the higher than normal field position of this peak suggest water as an impurity.

Titration of an aqueous solution of the acid with dilute sodium hydroxide using phenolphthalein as an indicator gave a neutral equivalent value of 239.0. The calculated value is 238.1.

Treatment of the acid fluoride with gaseous anhydrous ammonia yielded a white solid. After washing with water to remove NH_4F, filtering and drying, a solid m.p. 94 - 95 °C (uncorrected) was isolated. Disappearance of the C(O)F absorption at 1898 cm^{-1} and the appearance of a new absorption at 1720 cm^{-1} [C(O)NH$_2$] and two new absorptions at 3275 and 3500 cm^{-1} [N—H stretch in C(O)NH$_2$] as well as retention of SF$_5$ absorptions indicated that the amide was formed.

A small-scale reaction of impure acid fluoride and absolute methanol indicated that the acid fluoride is converted to the methyl ester. Infrared analysis on the volatile reaction products showed the disappearance of the C(O)F group and the appearance of absorptions in regions where those corresponding to C(O), (OCH$_3$) and C—H are normally found.

Reaction of $SF_5CF=CF_2$ and O_2

In a manner similar to that described above, 5.09 g (24 mmol) of 87% $SF_5CF=CF_2$ was charged to a 100 cm^3 tube. Oxygen at a pressure of 11 atm

was then introduced at 0 °C and the reactants were stirred at ambient temperature for 0.5 h. There was no visible sign of reaction. More oxygen was added to a pressure of 13 atm and the reactants heated to about 45 °C using a warm-water bath. Within *ca.* 15 min at this temperature the pressure dropped to 11 atm and a brownish ring of solid material deposited on the sides of the tube.

The reactants were stirred overnight at ambient temperature. The tube was attached to a vacuum line and all volatiles at 25 °C collected in a −196 °C trap. A brown solid and a high boiling liquid remained in the reaction tube. The volatiles were separated by a gas chromatographic technique. The major component representing 52% of the peak area was shown by IR spectroscopic analysis to be identical to $SF_5OCF_2C(O)F$ prepared as described above in the reaction with O_3. Other materials identified by IR spectroscopy together with percentage peak area were: SO_2F_2 (6%), SOF_2 (4.0%), unknown SF_5 material (21.0%) and $SF_5CF=CF_2$ (3.2%). Four other components representing 13.8% area were not identified.

The small amount of liquid left in the reaction tube was separated from the solid. The IR spectrum of a film of the material indicated the presence of an acid functionality. The neutralization equivalent on the acid from the two determinations gave an average value of 218. The identity of this liquid and solid was not determined.

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