to interpret. As a first approximation for every peak observed with MCD spectra, *two* will be observed in the corresponding MORD curve. Second, in solutions, a rather sizable solvent rotation (commonly larger than the rotation of the solute being studied) must be subtracted from the measured solution rotation when measuring magnetic optical rotations. With MCD spectra one uses a transparent solvent just as for ordinary spectral measurements in solution. (This advantage of MCD is particularly striking when studying glasses, as the authors realized when measuring MCD spectra and MORD curves of a Corning CS-138 rare earth filter.) On the other hand, one drawback to the MCD measurements may be a somewhat less favorable signal to noise ratio. One can show theoretically that a circular dichrometer capable of measuring differences of 10^{-4} between the absorption of right- and left-handed light should be able to do as well as a polarimeter sensitive to $10^{-3\circ}$. But judging from our experience thus far, it is not possible to measure a useful MCD spectrum for some compounds for which MORD curves are now published; e.g., acetone.[1]

The most useful application of MCD spectra (and MORD curves) will probably be to a classification of spectral transitions. For example, the transitions of Figure 1 look superficially similar in an ordinary ab-sorption spectrum but qualitatively different in the MCD spectrum. At present, there do not seem to be any simple relationships between the symmetry of a molecule and the presence or absence of MCD in a particular band such as exists for naturally active molecules. (Actually the usual statement about nonsuperimposable mirror image molecules exhibiting optical activity does not say that any *particular* band will exhibit circular dichroism. It simply states that there *is* at least one absorption band exhibiting dichroism.) To the best of the authors' knowledge, all known substances exhibit a Faraday effect, and therefore all substances must have at least one band exhibiting magnetic circular dichroism. Thus it would appear that there either are no symmetry requirements or they are very weak ones. A relationship might also be expected between the paramagnetism of a sample and its magnetic circular dichroism. It is true that all of the compounds studied thus far which give appreciable MCD spectra are paramagnetic, but most paramagnetic compounds did not give any measurable dichroism. Furthermore, Shashoua reports[1] MORD anomalies for a number of diamagnetic compounds.

Preparation and Characterization of New Fluoroxy Compounds[1,2]

Julianne H. Prager and Phillip G. Thompson

Contribution No. 304 from the Central Research Laboratories, Minnesota Mining and Manufacturing Company, St. Paul 19, Minnesota. Received September 2, 1964

The preparation and characterization of the following fluoroxy-containing compounds are presented: CF_3CF_2OF, $CF_3CF_2CF_2OF$, $(CF_3)_2CFOF$, $(CF_3)_3COF$, $O_2N-CF_2CF_2OF$, $ClCF_2CF_2OF$, Cl_2CFCF_2OF, and Cl_3CCF_2OF. These materials are obtained by direct fluorination of appropriate carbon–oxygen compounds under mild conditions. Fluorine nuclear magnetic resonance was found to be particularly useful in establishing their identity. Other data presented include infrared spectra, elemental analyses, molecular weights, and oxidizing power. Certain reactions are described, including those with reducing agents. These compounds are thermally stable at room temperature for extended periods of time. Mechanisms of reactions involving reduction, as well as chain decomposition, are discussed.

Introduction

The only substances known which contain carbon and the OF group are CF_3OF and the unstable acyl-OF compounds, $CF_3C(O)OF$ and $C_2F_5C(O)OF$.[3] The compound CF_3OF was first prepared by Cady and Kellogg[4] by the AgF_2-catalyzed fluorination of methanol, carbon monoxide, or carbonyl fluoride at 160–180°. In the 16 years following the disclosure of CF_3OF, several attempts to prepare higher fluoroxyperfluoroalkanes were reported. Toward this goal, the fluorination[3,5–8] of a variety of substances, including ethanol, *t*-butyl alcohol, acetic acid, acetone, and cyclohexanone, was investigated, as well as the reaction[7] of O_2F_2 with certain olefins. No higher fluoroxyperfluoroalkanes were thus obtained.

(1) In accordance with the recommendations of the ACS Committee on Nomenclature of Highly Fluorinated Molecules, we have named these materials as fluoroxy derivatives.

(2) (a) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 30–Sept. 4, 1964. (b) This research was supported by the Advanced Research Projects Agency under Contract NOrd 18688 and was monitored by the Bureau of Naval Weapons.

(3) G. H. Cady and K. B. Kellogg, *J. Am. Chem. Soc.*, **75**, 2501 (1953); A. Menefee and G. H. Cady, *ibid.*, **76**, 2020 (1954).

(4) K. B. Kellogg and G. H. Cady, *ibid.*, **70**, 3986 (1948).

(5) G. H. Cady and K. B. Kellogg, U. S. Patent 2,689,254 (1954).

(6) J. W. Dale, Abstracts of the First International Fluorine Symposium, Birmingham, England, July 14–17, 1959, p. 29.

(7) R. T. Holzmann and M. S. Cohen, *Inorg. Chem.*, **1**, 972 (1962).

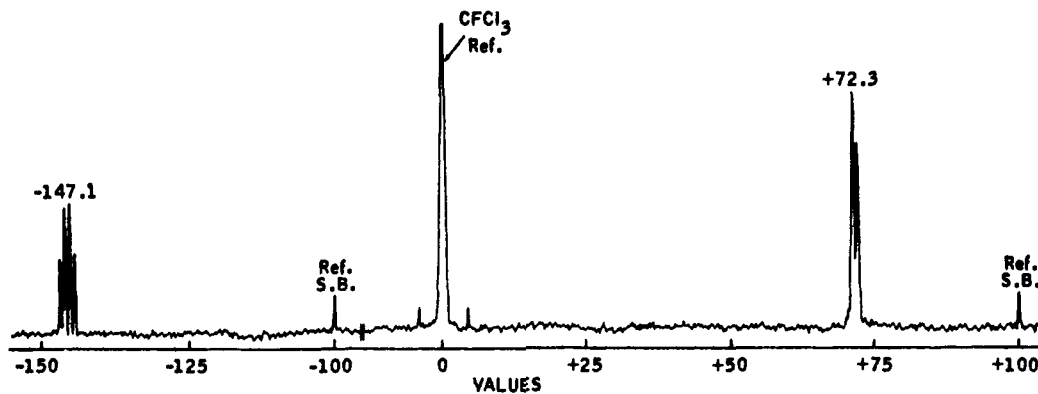(8) G. H. Cady, *Proc. Chem. Soc.*, 133 (1960).

Figure 1. N.m.r. spectrum of CF_3OF

In this paper we wish to report the preparation of several carbon-containing OF compounds. These include CF_3CF_2OF, $CF_3CF_2CF_2OF$, $(CF_3)_2CFOF$, $(CF_3)_3COF$, $O_2NCF_2CF_2OF$, $ClCF_2CF_2OF$, Cl_2CFCF_2OF, Cl_3CCF_2OF. The characterization and certain reactions of these compounds are also given.

Discussion

The fluoroxy compounds described in this paper are obtained by direct fluorination, under mild conditions, of various oxygen-containing starting materials, including alcohols and ketones. In general, the OF-containing products are accompanied by other compounds formed in the course of the fluorination reaction, including cleavage products. When highly fluorinated starting materials are used, the yields of fluoroxy compounds are often excellent. The formation of 2-fluoroxyperfluoro-2-methylpropane from perfluoro-t-butyl alcohol is a case in point. Yields tend to be lower, however, when starting materials containing large amounts of hydrogen are used. 1-Fluoroxy-2-nitroperfluoroethane, for example, was formed in approximately 5% yield by the direct fluorination of 1,1,1-trichloro-3-nitro-2-propanol.

These OF-containing compounds have not proved extremely difficult to handle. They are not especially sensitive to glass or moisture, and standard vacuum-line techniques have been found satisfactory for their isolation. Their reactivity toward mercury and toward some CH-containing compounds, however, requires that provision be made to avoid these substances. Thus, pressure transducers were substituted for mercury manometers, and Kel-F stopcock grease was employed. Purification of the fluoroxy compounds was accomplished by gas chromatography. Diatomaceous silica coated with perfluorotributylamine has proved to be a satisfactory stationary phase. Several techniques were used to establish the identity of the new compounds, including nuclear magnetic resonance and infrared spectroscopy, molecular weight determination, elemental analysis, and certain simple chemical reactions.

Nuclear magnetic resonance spectroscopy has been found to be a particularly useful technique for the characterization of fluoroxy compounds. A brief discussion of the spectrum of CF_3OF will serve to illustrate this point. The n.m.r. spectrum of CF_3OF has been reported by Cady and Merrill[9] using SF_6 as solvent and

(9) G. H. Cady and C. I. Merrill, *J. Am. Chem. Soc.*, **84**, 2261 (1962).

internal reference. The spectrum with $CFCl_3$ as reference is given in Figure 1, so that ϕ^* values[10] for the new fluoroxy compounds may be compared with those of CF_3OF. The absorption attributed to the OF group is at -147.1 ϕ^*. This absorption is split into a quadruplet owing to spin–spin coupling with the three fluorines of the CF_3 group. The absorption at 72.3 ϕ^* is assigned to the CF_3 group and is a doublet as predicted by simple first-order spin–spin analysis. The coupling constant between the CF_3 and OF groups is 33.8 c.p.s. The peak areas were found to be in the ratio of 1.0:3.0.

There are two features of this spectrum which are worthy of note and which are also exemplified in the spectra of the compounds described in this paper. The shielding value for fluorine on oxygen is distinctly different from the shielding values of fluorines in CF groups. Thus, the absorption of the fluoroxy group is well outside the range of most other fluorine absorptions. Furthermore, fluorine atoms attached to oxygen give clear, sharp spectra. This is a consequence of the fact that the predominant isotope of oxygen has no magnetic or quadrupole moment. Thus, not only can n.m.r. spectroscopy be used to demonstrate the presence of the OF group, but in many instances the details of the fine structure (caused by spin–spin coupling), as well as the relative area ratios, permit an unequivocal assignment of structure to the OF compound.

Results

Fluoroxyperfluoroethane, CF_3CF_2OF. Fluoroxyperfluoroethane was obtained by the direct fluorination of 1,1-dihydroperfluoroethanol.[11] Many other products

$$CF_3CH_2OH \xrightarrow{F_2} CF_3CF_2OF$$
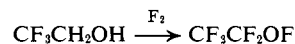
were also formed in this reaction, e.g., carbon tetrafluoride, carbonyl fluoride, carbon dioxide, and perfluoroacetyl fluoride, as well as higher boiling materials, including $CF_3C(O)CH_2CF_3$. Fluoroxyperfluoroethane was separated by standard vacuum-line techniques and was purified by gas chromatography. The infrared spectrum of CF_3CF_2OF is shown in Figure 2; the absorption at 11.10 μ is assigned to the OF group.

Structure confirmation of fluoroxyperfluoroethane by the assignment and analysis of the fluorine nuclear magnetic resonance is illustrated in Figure 3. The

(10) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

(11) Fluoro chemicals have been named in accordance with the recommendations of the ACS Committee on Nomenclature of Highly Fluorinated Molecules.
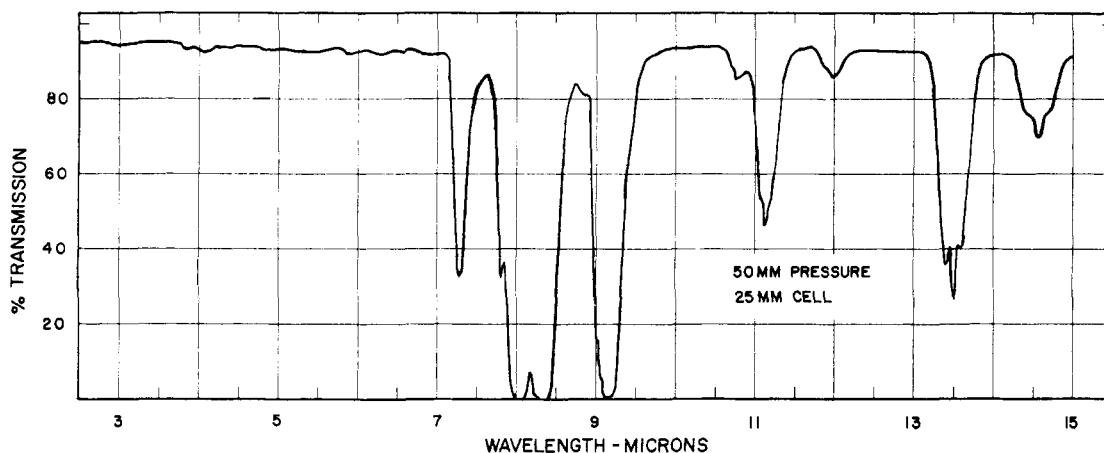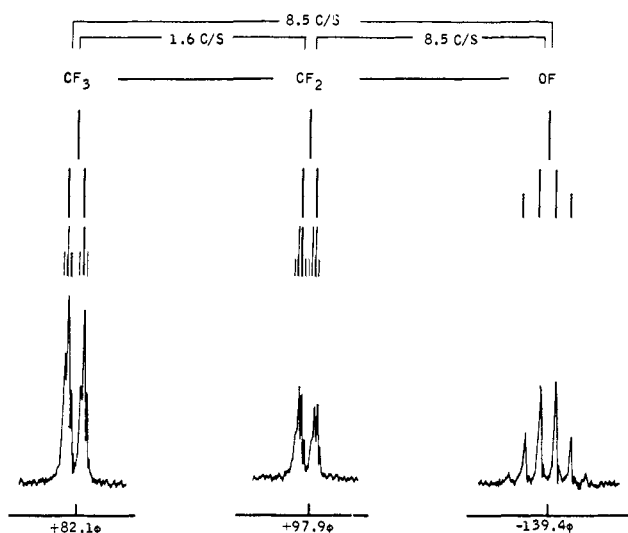
Figure 2. Infrared spectrum of CF_3CF_2OF.

Figure 3. N.m.r. spectrum of CF_3CF_2OF.

absorption at -139.4 ϕ^* is assigned to the OF group upon consideration of the shielding value and spin-spin analysis (see above discussion for n.m.r. spectrum of CF_3OF). The CF_2 group signal is at 97.9 ϕ^* and that of CF_3 at 82.1 ϕ^*. The peak areas were found to be the ratio of 1.0:2.0:3.0. The coupling constant between CF_3 and CF_2 is 1.6 c.p.s.; the coupling value between OF and either CF_3 or CF_2 is 8.5 c.p.s. Since the coupling constants between the OF–CF_3 and OF–CF_2 groups are coincidentally identical, all five fluorine nuclei of the C_2F_5 group are seen to be magnetically equivalent. Thus, according to the "$n + 1$ rule," the OF absorption is split sixfold with relative intensities of 1, 5, 10, 10, 5, 1. The absorption of the fluorine nuclei in the CF_2 group is split into a doublet owing to spin–spin coupling with the OF group; each mode of this is further split into a quadruplet by the CF_3 moiety. The absorption of the CF_3 group is likewise split into a double triplet owing to coupling with the OF and CF_2 groups, respectively. As is often observed with compounds containing the perfluoroethyl structure, the CF_3 coupling with fluorine in the adjacent CF_2 group is less than that with fluorine, two atoms removed.

Samples of pure fluoroxyperfluoroethane have been stored for over 2 years at room temperature with only

minor decomposition. One sample was stored for a 3-year period at room temperature; the greater portion of this sample was recovered unchanged. On heating, CF_3CF_2OF undergoes decomposition as shown in eq. 1.

$$CF_3CF_2OF \xrightarrow{\Delta} CF_4 + COF_2 \qquad (1$$
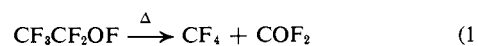
Differential thermal analysis indicates that a gradual exothermic decomposition begins at about 110°. The products were shown to be CF_4 and COF_2.

This decomposition can also be brought about by certain chemical initiators or fragmentizing agents, as well as by heat. Many CH-containing compounds, including methane, heptane, benzene, ethanol, acetone, triethylamine, acetic acid, and methyl trifluoroacetate (also hydrocarbon-type stopcock greases), serve to initiate this reaction. Thus, the apparent stability of samples of C_2F_5OF depends to a large extent upon the purity of the sample and the condition of the container. Fluoroxyperfluoroethane, in the presence of an equimolar amount of methane, is decomposed almost completely in 24 hr. No mixed CFH-containing compounds were detected among the products; the methane was recovered substantially completely. Even a small amount of methane (0.04 mole fraction) was found to decompose a sample of CF_3CF_2OF completely in a 13-day period.[12] These results appear to indicate that the chemically-initiated fragmentation of CF_3CF_2OF is a chain reaction. The propagation sequence shown in eq. 2 is believed to be involved. The initiation and

$$CF_3CF_2O\cdot \longrightarrow COF_2 + CF_3\cdot \qquad (2)$$
$$CF_3\cdot + CF_3CF_2OF \longrightarrow CF_4 + CF_3CF_2O\cdot$$
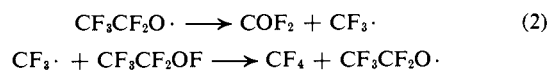
termination steps in this reaction are not known. However, it is possible that initiation takes place as

$$CH_4 + CF_3CF_2OF \longrightarrow HF + CH_3\cdot + CF_3CF_2O\cdot$$
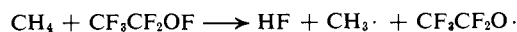
Fluoroxyperfluoroethane has been found to be oxidizing toward mercury, ferrocene,[13] potassium iodide, potassium bromide, and aqueous alkali. It does not

(12) There is an interesting contrast in behavior here between CF_3-CF_2OF and CF_3OF. Allison and Cady report that the latter undergoes no reaction with methane in the absence of ultraviolet irradiation or a spark: see J. A. C. Allison and G. H. Cady, J. Am. Chem. Soc., 81, 1089 (1959).

(13) The use of ferrocene to bring about the reductive defluorination of NF-containing compounds has been reported: R. A. Mitsch, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 30–Sept. 4, 1964.
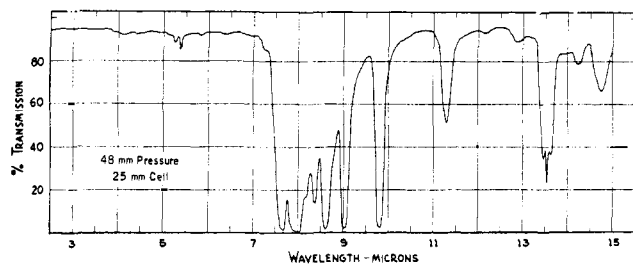
react, at least not rapidly, with aqueous acidic solutions of chromic or manganous ions. With mercury CF_3CF_2OF forms perfluoroacetyl fluoride, carbonyl fluoride, and carbon tetrafluoride. Apparently, the first step in this reaction again involves the abstraction of the fluorine atom of the fluoroxy group. The perfluoro-

$$CF_3CF_2OF \xrightarrow{Hg} CF_3CF_2O \cdot$$

ethoxy radical so formed may react with a second atom of mercury, undergoing reduction to perfluoroacetyl fluoride, or it may decompose to carbonyl fluoride and the perfluoromethyl radical (eq. 3). The latter can then participate in the chain decomposition reaction described above. So reduction of the OF group can

$$CF_3CF_2O \cdot \xrightarrow[\;\;\;\;Hg\;\;\;\;]{\text{redn.}} CF_3CFO \qquad (3)$$
$$\Big\downarrow \begin{array}{l}\text{chain}\\ \text{decompn.}\end{array}$$
$$COF_2 + CF_3 \cdot$$

occur by two distinct reactions: (1) reductive defluorination, a straightforward two-electron reduction by various added reducing agents; and (2) chain decomposition with cleavage of the C–C bond adjacent to the OF group. It appears that the relative amount of reductive defluorination vs. chain decomposition (in this as well as the following reactions) depends upon the contact of the fluoroxy compound with the reducing agent. Unless the reaction vessel is agitated, mercury quickly becomes covered with a film of fluoride, hindering the reductive defluorination mode. With potassium iodide (in water or in acetonitrile–water mixtures), the two-electron reductive defluorination takes place almost exclusively. The perfluoroacetyl fluoride so formed is hydrolyzed to the perfluoroacetate ion. The overall reaction can be expressed by eq. 4. Since this oxida-

$$CF_3CF_2OF + 2KI + H_2O \longrightarrow$$
$$I_2 + CF_3CO_2K + KHF_2 + HF \quad (4)$$

tion of iodide to iodine occurs rapidly and without appreciable side reactions, the process can be used for a quantitative measure of the oxidizing power of the fluoroxy compound. Determination of the oxidizing power of a sample of chromatographed C_2F_5OF by this reaction gave a value of 12.3 mequiv. of iodine/g. of sample (calculated for two-electron change, 13.0).[14]

Fluoroxyperfluoroethane reacts with ferrocene to form perfluoroacetyl fluoride as the principal product (eq. 5).[15] Both ferrocene and potassium iodide are

$$CF_3CF_2OF + 2(C_5H_5)_2Fe \longrightarrow CF_3CFO + 2(C_5H_5)_2Fe^+F^- \quad (5)$$
orange   dark blue

useful reagents for the detection of OF-containing compounds because of the characteristic color changes which they undergo upon oxidation. (Of course, they are not specific OF reagents, inasmuch as they react with other oxidizing species, as well.) For many purposes, ferrocene is found to be more convenient than is potassium iodide, because the former can be used in a nonaqueous system (e.g., as a suspension in a fluorocarbon oil) and also because its oxidized form is nonvolatile.

Fluoroxyperfluoroethane rapidly[16] oxidizes aqueous alkali, liberating oxygen according to eq. 6. The chain

$$CF_3CF_2OF + 4NaOH \longrightarrow$$
$$0.5O_2 + CF_3CO_2Na + 3NaF + 2H_2O \quad (6)$$

decomposition reaction occurs only to a minor extent, yielding (in the presence of sodium hydroxide) carbon tetrafluoride, sodium carbonate, and possibly trifluoromethane. In contrast, with its behavior with base, fluoroxyperfluoroethane reacts only very slowly with water or acidic media; in fact, this compound can be washed with water to free it of acyl fluorides.

The polarographic half-wave potential of C_2F_5OF, measured by means of an indicating platinum electrode vs. a saturated aqueous calomel electrode as reference, was found to be approximately 0.5 v. The half-wave potential of CF_3OF is 0.55 v. The measurements were carried out in acetonitrile containing 0.1 M sodium perchlorate and 0.01 % water.

1-Fluoroxyperfluoropropane, $CF_3CF_2CF_2OF$. 1-Fluoroxyperfluoropropane was prepared by the direct fluorination of 1,1-dihydroperfluoropropanol. Other

$$CF_3CF_2CH_2OH \xrightarrow{F_2} CF_3CF_2CF_2OF$$

products were also obtained, including carbonyl fluoride, perfluoroethane, and perfluoropropionyl fluoride.

Isolation of 1-fluoroxyperfluoropropane was accomplished by fractional distillation–condensation, followed by gas chromatography. The infrared spectrum[17] of n-C_3F_7OF contains an absorption at 11.25 μ, which is assigned to the OF group. The remainder of the spectrum is similar to that of other compounds containing the n-C_3F_7 moiety.

The F^{19} nuclear magnetic resonance spectrum[18] of $CF_3CF_2CF_2OF$ contains an absorption at -144.3 ϕ^*, which is assigned to the OF group. Other absorptions are observed at 93.9 ϕ^* for the CF_2 group attached to the fluoroxy group, at 127.0 ϕ^* for the next adjacent CF_2 group, and at 82.5 ϕ^* for the CF_3 group. The peak areas were found to be in the ratio of 1.0:2.1:2.0:3.0.

The chemical properties of n-C_3F_7OF appear to be similar to those of C_2F_5OF. No appreciable hydrolysis occurs upon contact with neutral or acidic water at room temperature; however, rapid reaction takes place in alkaline media. 1-Fluoroxyperfluoropropane is strongly oxidizing toward mercury, ferrocene, and potassium iodide. It decomposes readily in the presence of initiating agents, such as hydrocarbons, to yield

(14) A sample of chromatographed CF_3OF gave an oxidizing power of 18.9 mequiv. of iodine/g. (calculated for two-electron change, 19.5).
(15) Ferrocene reacts with CF_3OF, yielding carbonyl fluoride.

(16) Complete reaction occurs within a few minutes; the reaction of CF_3OF with aqueous sodium hydroxide is even more rapid than that of C_2F_5OF.
(17) Absorptions are found at 7.42 (w), 7.62 (w), 8.05 (s), 8.90 (m), 10.05 (m), 10.75 (vw), 11.25 (w), 12.25 (w), 13.40 (m), and 14.20 μ (w). Symbols are as follows: s, strong; m, medium; w, weak; vw, very weak.
(18) Coupling constants in c.p.s. are

Since there are so many coupling constants of rather small and essentially equal values, complete separation of the various splittings could not be achieved with the resolution of the n.m.r. spectrometer used in this work.

Figure 4. Infrared spectrum of (CF₃)₂CFOF.

Figure 5. N.m.r. spectrum of (CF₃)₂CFOF.
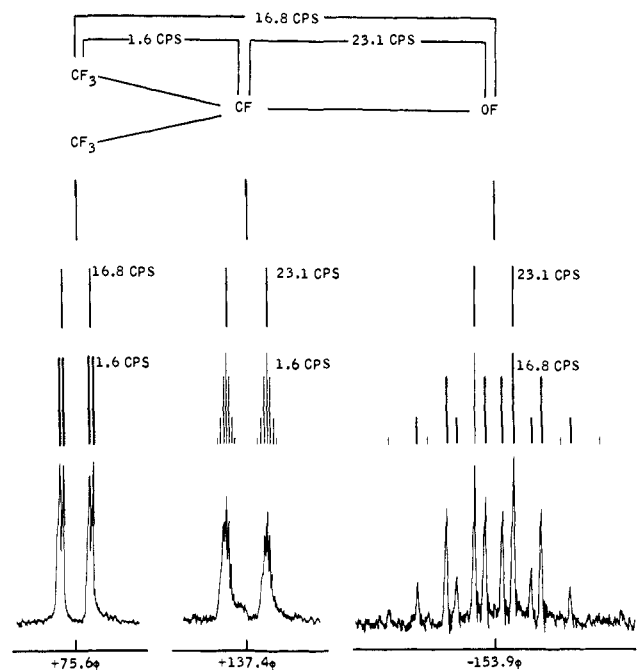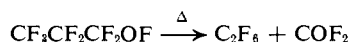

Figure 6. Infrared spectrum of (CF₃)₃COF.

perfluoroethane and carbonyl fluoride. Thermal decomposition takes place in a similar manner, resulting in cleavage of the C–C bond adjacent to the OF group as discussed above for fluoroxyperfluoroethane.

$$CF_3CF_2CF_2OF \xrightarrow{\Delta} C_2F_6 + COF_2$$

2-Fluoroxyperfluoropropane, *(CF₃)₂CFOF*. 2-Fluoroxyperfluoropropane was synthesized by the direct fluorination of the hydrate of perfluoroacetone. Other

$$CF_3CCF_3 \cdot H_2O \xrightarrow{F_2} CF_3CFCF_3$$
$$\overset{\|}{O} \qquad\qquad \overset{|}{OF}$$
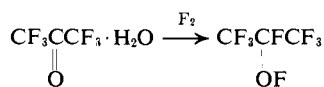
products included carbon dioxide, carbonyl fluoride, perfluoroacetyl fluoride, perfluoroacetone, carbon tetrafluoride, and perfluoroethane. Isolation of (CF₃)₂CFOF was accomplished by trap-to-trap fractionation followed by gas chromatography. The infrared spectrum of 2-fluoroxyperfluoropropane is shown in Figure 4. The absorption at 11.3 μ is assigned to the OF group.

The F^{19} n.m.r. spectrum of (CF₃)₂CFOF (Figure 5) shows an absorption at −153.9 φ*, which is assigned to the OF group. This absorption is split into two sevenfold peaks corresponding to coupling with the single fluorine nucleus and the six equivalent fluorine nuclei, respectively. Other absorptions occur at 137.4 φ* (two

sevenfold peaks) for the CF group and 75.6 φ* (double doublet) for the perfluoromethyl groups. The peak areas were found to be in the ratio of 1.0 : 1.0 : 5.8.

The decomposition of (CF₃)₂CFOF can be brought about by heat and by chemical initiators, such as hydrocarbons. Carbon tetrafluoride and perfluoroacetyl fluoride are formed. Early preparations of (CF₃)₂-

$$(CF_3)_2CFOF \xrightarrow{\Delta} CF_4 + CF_3C\overset{O}{\underset{F}{\diagup\!\!\!\backslash}}$$
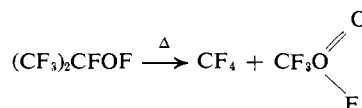
CFOF proved relatively unstable. It is believed that decomposition in these cases was brought about by hydrocarbon contaminants derived from diethyl ether present in the hexafluoroacetone hydrate used as starting material.

2-Fluoroxyperfluoropropane is a strong oxidizing agent. For example, it reacts with ferrocene, presumably to form the 2-perfluoropropoxy radical. This

$$CF_3CFCF_3 \xrightarrow{(C_5H_5)_2Fe} CF_3CFCF_3 \Big\langle \begin{array}{l} \rightarrow CF_2C\overset{O}{\underset{F}{\diagup\!\!\!\backslash}} + CF_3\cdot \\ \xrightarrow[(C_5H_5)_2Fe]{} CF_3CCF_3 \end{array}$$
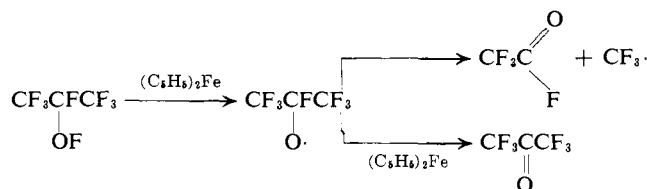
radical can participate in chain decomposition with formation of perfluoroacetyl fluoride and carbon tetrafluoride. Or, in the presence of a reducing agent, it apparently can eliminate a second fluorine atom to form perfluoroacetone. All three of these compounds have been obtained upon treatment with ferrocene.

2-Fluoroxyperfluoro-2-methylpropane. The fluorination of perfluoro-*t*-butyl alcohol to 2-fluoroxyperfluoro-2-methylpropane proceeds very cleanly. The unfractionated reaction product consists of greater than 95% of this tertiary OF compound. The absence of

$$(CF_3)_3COH \xrightarrow{F_2} (CF_3)_3COF$$
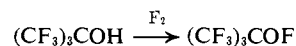
cleavage products in this reaction is of interest and shows that direct fluorination does not inevitably lead to a profusion of products.

2-Fluoroxyperfluoro-2-methylpropane can be further purified by gas chromatography. The infrared spectrum of (CF₃)₃COF (Figure 6) shows an absorption at 11.3 μ, which is assigned to the OF group. The F^{19} n.m.r. spectrum of (CF₃)₃COF (Figure 7) displays an absorption owing to the OF group at −149.6 φ*, which is split into a tenfold peak by the nine magnetically equivalent fluorines on carbon. A doublet observed at 69.5 φ* is assigned to the CF₃ groups; the coupling con-
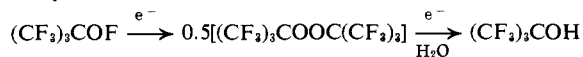
stant is 15.5 c.p.s. The peak areas were found to be in the ratio of 1.0:8.5.

2-Fluoroxyperfluoro-2-methylpropane is relatively stable. A sample stored at room temperature for 7 weeks underwent only about 5% decomposition forming perfluoroacetone and carbon tetrafluoride. These same products are also obtained upon thermal decomposition.
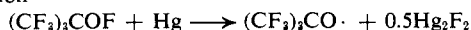
$$(CF_3)_3COF \xrightarrow{\Delta} (CF_3)_2C{=}O + CF_4$$
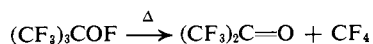
The oxidizing power of 2-fluoroxyperfluoro-2-methyl-propane was found to be of considerable interest. A value of 4.03 mequiv. of iodine/g. was initially obtained (calculated for one-electron change per OF, 3.93); however, the value steadily increased with time toward that expected for a two-electron change per OF group (7.87). When an acidic solution of ammonium molybdate[19] was added, the resulting solution gave an immediate value of 7.34 mequiv. of iodine/g. This suggests that perhaps a one-electron reduction occurs first to yield the peroxide, $(CF_3)_3CO{-}OC(CF_3)_3$ (formed by coupling of two perfluoro-t-butoxy radicals), and that this species then undergoes further reduction by iodide ion, giving the over-all result of a two-electron reduction. With mercury, chain decomposition occurs as well as reduction; $(CF_3)_3COF$ is thus seen to react with reducing agents by two alternative courses.

(1) Stepwise two-electron reduction

$$(CF_3)_3COF \xrightarrow{e^-} 0.5[(CF_3)_3COOC(CF_3)_3] \xrightarrow[H_2O]{e^-} (CF_3)_3COH$$

(2) Reductive chain decomposition
Initiation
$$(CF_3)_3COF + Hg \longrightarrow (CF_3)_3CO\cdot + 0.5Hg_2F_2$$

Propagation[20]
$$(CF_3)_3CO\cdot \longrightarrow (CF_3)_2C{=}O + CF_3\cdot$$

$$CF_3\cdot + (CF_3)_3COF \longrightarrow CF_4 + (CF_3)_3CO\cdot$$
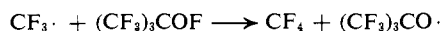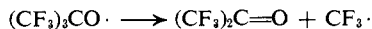
2-Fluoroxyperfluoro-2-methylpropane does not hydrolyze readily in acid solution; 98% sulfuric acid, for example, brought about less than 5% hydrolysis in 2 hr. at room temperature. Perfluoro-t-butyl alcohol is formed. However, $(CF_3)_3COF$ reacts rapidly in basic solution; apparently reductive chain decomposition to carbon tetrafluoride and the sodium hydroxide adduct of perfluoroacetone[21] is the predominant mode of reaction. In this reaction small amounts of sodium trifluoroacetate and trifluoromethane are obtained, perhaps as a result of perfluoroacetone undergoing the haloform reaction. It is possible that some oxidation of base to oxygen also occurs.

Substituted Fluoroxyperfluoroethanes, XCF_2CF_2OF. 1-Fluoroxy-2-nitroperfluoroethane, 1,1-dichloro-2-fluoroxyperfluoroethane, and 1,1,1-trichloro-2-fluoroxyperfluoroethane were obtained by the direct fluorination of 1,1,1-trichloro-3-nitro-2-propanol. Other products

$$O_2NCH_2CHCClₐ \xrightarrow{F_2} O_2NCF_2CF_2OF + Cl_2CFCF_2OF +$$
$$\underset{OH}{|}$$

$$Cl_3CCF_2OF$$
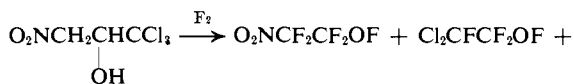
included carbonyl fluoride, carbon dioxide, chloro-

(19) Standard procedure for many organic peroxides.
(20) The perfluoroacetone obtained in the mercury-initiated decomposition forms a complex or salt with residual mercury.
(21) This adduct has previously been prepared and characterized: see J. H. Prager, to be published.
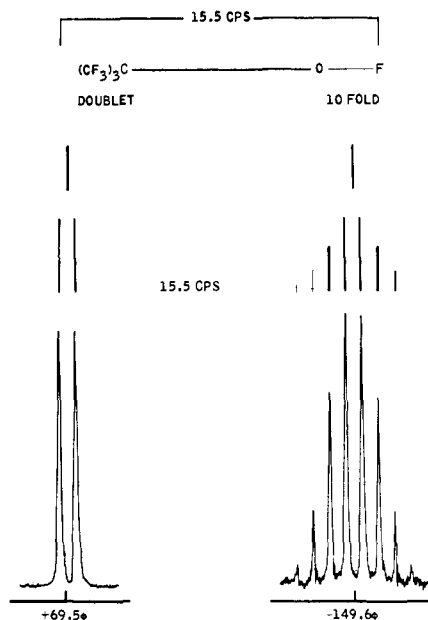

Figure 7. N.m.r. spectrum of $(CF_3)_3COF$.

trifluoromethane, dichlorodifluoromethane, trichlorofluoromethane, fluorine nitrate, nitrogen oxides (N_2O and NO_2), and many higher-boiling substances which were not identified.

1-Fluoroxy-2-nitroperfluoroethane was isolated by fractional distillation–condensation. The infrared spectrum of $O_2NCF_2CF_2OF$ shows a strong absorption at approximately 6.1 μ, which is due to the NO_2 group, and one at approximately 11.15 μ, assigned to the OF group. The F^{19} n.m.r. spectrum of this compound shows a triple triplet at -150.6 ϕ^* for the OF group, a double triplet at 93.4 ϕ^* for the CF_2 attached to OF, and a complex absorption at 98.9 ϕ^* for the CF_2 attached to the NO_2 group. The coupling constant between the OF and contiguous CF_2 is 11.3 c.p.s.; that between OF and the CF_2 attached to NO_2 is 5.8 c.p.s. The coupling constant between the two CF_2 groups is 1.5 c.p.s. The peak areas were found to be in the ratio of 1.0:2.0:2.0.

Extended stability studies were not carried out on this compound, but no decomposition was observed (by n.m.r. examination of its solution in $CFCl_3$) of a sample which stood at room temperature for 5 days. 1-Fluoroxy-2-nitroperfluoroethane undergoes thermal decomposition in a manner comparable with that of the simple fluoroxyperfluoroalkanes.

$$O_2NCF_2CF_2OF \xrightarrow{\Delta} CF_3NO_2 + COF_2$$
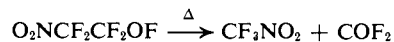
1-Chloro-2-fluoroxyperfluoroethane and also 1,1-dichloro-2-fluoroxyperfluoroethane were obtained by the direct fluorination of 2,2,2-trichloroethanol. Other

$$Cl_3CCH_2OH \xrightarrow{F_2} ClCF_2CF_2OF + Cl_2CFCF_2OF$$

products included CF_3OF, carbonyl fluoride, carbon dioxide, dichlorodifluoromethane, and trichlorofluoromethane. 1,1,1-Trichloro-2-fluoroxyperfluoroethane was not observed, but it is probable that this material would be obtained under milder reaction conditions.

1-Chloro-2-fluoroxyperfluoroethane was isolated by fractional distillation–condensation at $-111°$ on a vacuum line. It was purified by gas chromatography.

The infrared spectrum[22] of $ClCF_2CF_2OF$ contains absorption in the usual OF region. The n.m.r. spectrum of $ClCF_2CF_2OF$ (Table I) shows an absorption at $-140.2 \phi^*$, which is assigned to the OF group. Other absorptions are observed at $95.9 \phi^*$ for the CF_2 attached to OF and at $69.4 \phi^*$ for the CF_2 attached to chlorine. The fluoroxy absorption is fivefold,[23] indicating that OF is coupled with four approximately equivalent fluorine nuclei. Both the absorption of the CF_2 adjacent to OF and that of the CF_2 adjacent to Cl are split into double triplets as is consistent with the assigned structure. The peak areas were found to be in the ratio of 1.0:2.0:2.0.

The chemical properties of 1-chloro-2-fluoroxyperfluoroethane appear to be similar to those described above for fluoroxyperfluoroethane. The chloro derivative is relatively stable. Thus, a slightly impure sample of this compound, sealed in a glass n.m.r. tube with $CFCl_3$ as internal reference, was found still to contain about one-third of the fluoroxy compound after 6 months at room temperature. After 9 months the sample had undergone essentially complete decomposition to chlorotrifluoromethane and carbonyl fluoride (which in turn reacted with the glass producing carbon dioxide and silicon tetrafluoride). 1-Chloro-2-fluoroxyperfluoroethane is found to form these same products upon thermal decomposition.

$$ClCF_2CF_2OF \xrightarrow{\Delta} ClCF_3 + COF_2$$
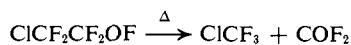
It is interesting to compare the fluorine n.m.r. spectra of the full series of β-chlorinated derivatives of CF_3CF_2OF (Table I). It can be seen that there is a small but definite progressive shift downfield to lower shielding values in the absorptions of both the OF group and the CF_2 group as fluorine atoms in the CF_3 group are replaced by the less electronegative chlorine substituent. The coupling constants between the fluorine of the OF group and the other fluorines also decrease as fluorine atoms are replaced by chlorine.

Table I. N.m.r. Spectra of Chlorinated Derivatives of CF_3CF_2OF

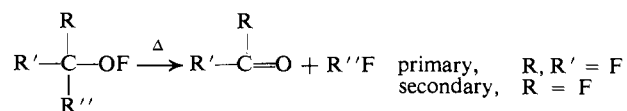| | Peaks, ϕ^* | | | J, c.p.s. | |
Compound	Cl_{3-x}-CF_x	CF_2	OF	CX_3-OF^d	CF_2-OF
CF_3CF_2OF	82.1	97.9	-139.4	8.5	8.5
$ClCF_2CF_2OF$	69.3	96.0	-140.2	6.2	5.6
$Cl_2CFCF_2OF^a$	71.8	93.7	-141.6	3.8	3.8
$Cl_3CCF_2OF^b$		91.6	-141.8^c		2.2

^{a} The peak areas were found to be in the ratio of 1.0:2.0:1.0. ^{b} The peak areas were found to be in the ratio of 1.0:2.0. ^{c} It appears that this peak may shift, as the concentration is varied, to a higher degree than is seen with most n.m.r. absorptions. ^{d} Splitting between F of fluoroxy group and F's on β-carbon atom.

The di- and trichloro derivatives of fluoroxyperfluoroethane undergo thermal decomposition in a manner analogous to that of the other primary fluoroxy compounds, yielding carbonyl fluoride and dichlorodifluoromethane or trichlorofluoromethane, respectively.

(22) Absorptions are found at 7.63 (m), 8.01 (m), 8.24 (s), 8.46 (s), 8.98 (s), 10.24 (s), 10.85 (w), 11.20 (w), 11.50 (w), and 12.38 μ (m).
(23) The coupling constant between OF and the fluorines on the α-carbon (5.6 c.p.s.) is slightly different from that between OF and the fluorines on the β-carbon (6.2 c.p.s.); however, they are so nearly equal that the difference is not perceptible in the OF absorption at this resolution.

Assignments of Structure. We have made these assignments of structure, first of all, on the basis of n.m.r. spectra. The chemical shifts, the spin–spin interactions, and the area ratios thus obtained specify the types of fluorine atoms present in the molecule and the relative numbers of each type. Note that the fluorine absorptions assigned to the OF group in these nine carbon-containing fluoroxy compounds occur within a very small range (-139 to -154 ϕ^*). The thermal decomposition reaction of these compounds has also proved to be indicative of their structure. The products show whether a primary, secondary, or tertiary OF group is present (carbonyl fluoride from a primary, an acyl fluoride from a secondary, and a ketone from a tertiary). The identities of R, R', and R'' are easily

$$R'-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R''}{|}}{C}}-OF \xrightarrow{\Delta} R'-\overset{\overset{\displaystyle R}{|}}{C}=O + R''F \quad \begin{matrix} \text{primary,} & R, R' = F \\ \text{secondary,} & R = F \end{matrix}$$

ascertained by comparison of the infrared and n.m.r. spectra of the fluorocarbon and carbonyl compound with those of authentic samples.

In our opinion, these two types of evidence combine to permit an unequivocal determination of structure for the simple compounds described in this paper. In most cases, however, we have also obtained additional supporting evidence, such as oxidizing power, elemental composition, molecular weight, mass spectra, and infrared spectra. Volatility characteristics, gas chromatographic retention times, and structure of the product relative to that of the reactant also support these characterizations. All evidence has been found to be consistent with the assigned structures.

Experimental

General Procedures. In general, these direct fluorination reactions were carried out by a static-bed procedure. The apparatus consisted of a copper, brass, or monel reactor, equipped with a brass blow-out cap, a gas-inlet tube for the introduction of fluorine and/or nitrogen, and a gas-outlet tube leading through a sodium fluoride scrubber (for the removal of hydrogen fluoride) to a collection trap. The piping was of copper; a glass rotameter was used for nitrogen, Kel-F rotameters (Brooks Rotameter Co., Lansdale, Pa.) for fluorine. The liquid or finely-divided solid reactant was placed in the reaction vessel, which could be immersed in a cooling bath. Fluorine (General Chemical Division, Allied Chemical Corp.) diluted with nitrogen to the desired concentration was introduced into the reactor; the volatile reaction products were trapped at liquid oxygen temperature ($-183°$).[24]

The fluorination products were worked up by means of standard vacuum-line techniques. Glass equipment, lubricated with Kel-F No. 90 grease (Minnesota Mining and Manufacturing Co.), was used. Pressure was measured by means of transducers.[25] Gas chromatographic analyses were carried out with a Perkin-Elmer vapor fractometer (model 154-D) equipped with gas sampling and backflush valves. Perfluorotributyl-

(24) A liquid nitrogen bath ($-196°$) should be avoided, since fluorine (b.p. $-188°$) may condense.
(25) Pace Engineering Co.

amine[26] (67% on 30/60 mesh acid-washed Celite[27]) gave the best results of all the stationary phases examined. For preparative scale separations a column 8 ft. 7 in. in length and 0.5 in. in diameter was employed. Dry helium at flow rates of 150 to 320 ml./min. was used as the carrier gas. Low boiling fluoroxy compounds were chromatographed at $-30°$, higher-boiling products at $0°$. Relative retention times were not found to be completely reliable for the identification of the various fluoroxy compounds, inasmuch as times have varied somewhat, depending upon the temperature gradient of the column (cooled in a large dewar flask) and the relative amounts of the other components in the mixture. The variation is greatest for those compounds which are liquids at the temperature of the column.

Infrared spectra were obtained on a Perkin-Elmer Model 21 double beam instrument with a 2.5-cm. gas cell with sodium chloride windows. Fluorine nuclear magnetic resonance spectra were measured with a Varian V-4300-2 instrument operating at 40.0 Mc. Trichlorofluoromethane was used as an internal standard for the determination of shielding values. The shielding values are reported in ϕ^* units[10] at dilutions of about 15–30%, negative values for low field. All precision measurements (chemical shifts and spin–spin splittings) were made according to techniques described by Tiers.[28] Side bands were produced by amplitude modulation of the radiofrequency[29] instead of field modulation[28] or frequency modulation[10] because of these very significant advantages[29]: (1) no frequency shifts upon modulation; (2) side-band intensity virtually constant from approximately 200 to 20,000 c.p.s.; and (3) negligible loss of intensity from the sample signal at all modulation frequencies.

Elemental analyses for carbon and fluorine were carried out by the procedure developed in these laboratories for highly fluorinated compounds.[30] Thus, the sample is burned in moist oxygen at $1100°$, yielding carbon dioxide (which is absorbed on Ascarite and weighed) and inorganic fluorides, including hydrogen fluoride and silicon tetrafluoride (which are absorbed in water and titrated with base). Scrupulous care must be taken to protect purified fluoroxy compounds from contact with fragmentizing agents during the analytical sampling procedure.

Safety Precautions. It should be noted that the OF-containing compounds described in this paper are somewhat hazardous, although they have been handled, for the most part, without great difficulty. However, explosions have occurred in the course of this work, and it is recommended that suitable protective equipment[31] be used when preparing, treating, or storing these compounds. No detailed toxicity studies have been carried out on these substances, but it would appear advisable to avoid exposure to any OF-containing compound in view of the known toxicity of OF_2.

(26) FC-43 (Minnesota Mining and Manufacturing Co.)
(27) Chromosorb P (Johns-Manville)
(28) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).
(29) G. V. D. Tiers, *ibid.*, **67**, 928 (1963).
(30) H. E. Freier, B. W. Nippoldt, P. B. Olson, and D. G. Weiblen, *Anal. Chem.*, **27**, 146 (1955).
(31) We have operated without injury within a quantity limit of 1 g. using 0.25-in. poly(methyl methacrylate) shielding and wearing heavy-duty face shields, leather coats, and leather gloves. Nonflammable slush baths are, of course, preferred.

Preparation of Fluoroxyperfluoroethane. A 3.0-g. (30 mmoles) sample of 1,1-dihydroperfluoroethanol (Columbia Organic Chemicals Co., Inc.) was treated with 0.14 mole of fluorine at $0°$ at a concentration of 15% over a 5-hr. period. The trapped gases (13 mmoles) were fractionated at <0.1-mm. pressure through traps at -111 and $-196°$. The lower boiling fraction was found to contain CF_3CF_2OF. Fluoroxyperfluoroethane was purified by gas chromatography at $-30°$; its retention time was found to be 28 relative to trichlorofluoromethane. It is a colorless gas with an estimated boiling point of $-50°$. Elemental analyses were obtained on a sample of chromatographed CF_3CF_2OF. A molecular weight determination (vapor density) on this material gave a value of 148 (calcd., 154).

Anal. Calcd. for C_2F_6O: C, 15.6; F, 74.0. Found: C, 15.6; F, 74.9.

Identification of C_2F_5OF was on the basis of n.m.r., infrared, and mass spectra, molecular weight, elemental analysis, oxidizing power, thermal decomposition products, and the reductive defluorination reaction.

The product distribution in a typical run was as follows: CF_3CF_2OF (10%), perfluoroacetyl fluoride (40%), carbon dioxide (20%), carbon tetrafluoride (15%), carbonyl fluoride (5%), and higher boiling products (10%), including 3,3-dihydroperfluorobutanone-2.

Preparation of 1-Fluoroxyperfluoropropane. A 1-g. (7 mmoles) sample of 1,1-dihydroperfluoropropanol (Columbia Organic Chemicals Co., Inc.) was treated with 0.2 mole of fluorine at room temperature; the fluorine concentration was gradually increased from 0 to 40% over a 6-hr. period. The effluent gases were fractionated at reduced pressure through traps at -78, -111, and $-196°$. The middle fraction was found to contain $CF_3CF_2CF_2OF$ (over-all yield, approximately 3%). 1-Fluoroxyperfluoropropane was purified by gas chromatography at $0°$. Its retention time is approximately 65 relative to trichlorofluoromethane.

Identification of $n\text{-}C_3F_7OF$ was on the basis of n.m.r., infrared, and mass spectra, thermal decomposition products, and the reductive defluorination reaction.

Preparation of 2-Fluoroxyperfluoropropane. Perfluoroacetone hydrate was prepared by the aqueous permanganate oxidation of perfluoroisobutylene according to the Morse, Ayscough, and Leitch modification[32] of the procedure of Brice, *et al.*[33] A 3-g. (16 mmoles) sample of this material was treated with 0.3 mole of fluorine under the following conditions: $-20°$, 3%, 1 hr.; $-20°$, 15%, 1 hr.; $25°$, 15%, 2 hr. The effluent gases were fractionated under reduced pressure through traps at -78, -119, and $-196°$. The middle fraction was found to contain 14 mmoles, from which pure 2-fluoroxyperfluoropropane was isolated (45% over-all yield) by water hydrolysis of acyl fluorides, followed by gas chromatography at $-30°$. The retention time of $(CF_3)_2CFOF$ is approximately 140 relative to trichlorofluoromethane.

Elemental analyses were determined on a sample of chromatographed $(CF_3)_2CFOF$ diluted with 55% nitrogen.

(32) A. T. Morse, P. B. Ayscough, and L. C. Leitch, *Can. J. Chem.*, **33**, 453 (1955).
(33) T. J. Brice, J. D. LaZerte, L. J. Hals, and W. H. Pearlson, *J. Am. Chem. Soc.*, **75**, 2698 (1953); U. S. Patent 2,617,836 (1952).

Anal. Calcd. for C_3F_8O (diluted with 55.0% N_2): C, 7.9; F, 33.5. Found: C, 8.2; F, 33.0.

Identification of $(CF_3)_2CFOF$ was on the basis of n.m.r. and infrared spectra, elemental analysis, thermal decomposition products, and the reductive defluorination reaction.

Preparation of 2-Fluoroxyperfluoro-2-methylpropane. Perfluoro-*t*-butyl alcohol was kindly supplied by Dr. F. J. Pavlik of our Chemical Division Laboratories. Fluorination of 0.87 g. (3.7 mmoles) of this compound was carried out over a 5-hr. period at $-20°$ with 0.12 mole of fluorine (5% in nitrogen). The collection trap was found to contain 1.7 mmoles, consisting principally (>95%) of $(CF_3)_3COF$. 2-Fluoroxyperfluoro-2-methylpropane was purified by gas chromatography at 0°. Elemental analyses of chromatographed $(CF_3)_3COF$ are shown below. The molecular weight of this material was found to be 252 (calcd., 254).

Anal. Calcd. for $C_4F_{10}O$: C, 18.9; F, 74.8. Found: C, 18.9; F, 74.4.

Identification of $(CF_3)_3COF$ was on the basis of n.m.r. and infrared spectra, elemental analysis, molecular weight, oxidizing power, thermal decomposition products, and other chemical reactions.

Preparation of 1-Nitro-2-fluoroxyperfluoroethane. A 3-g. (14 mmoles) sample of 1,1,1-trichloro-3-nitro-2-propanol (K & K Laboratories, Inc.) was treated with 1.3 moles of fluorine at 20° under the following conditions: 4%, 2.5 hr.; 11%, 1.5 hr.; 25%, 1.5 hr.; 41%, 2.5 hr. The contents of the collection trap were fractionated at reduced pressure through traps at -78, -111, and $-196°$. 1-Nitro-2-fluoroxyperfluoroethane was found in both the -78 and $-111°$ fractions. The yield of this material was approximately 5%. The $-78°$ fraction was also found to contain 1,1-dichloro-2-fluoroxyperfluoroethane and 1,1,1-trichloro-2-fluoroxyperfluoroethane.

Identification of $O_2NCF_2CF_2OF$ was on the basis of n.m.r. and infrared spectra and thermal decomposition products. Identifications of Cl_2CFCF_2OF and Cl_3CCF_2OF were on the basis of n.m.r. spectra and thermal decomposition products.

Preparation of 1-Chloro-2-fluoroxyperfluoroethane. A 2-g. (13 mmoles) sample of 2,2,2-trichloroethanol (Columbia Organic Chemicals Co., Inc.) was treated with 0.3 mole of fluorine at a concentration of 40% at $-20°$ for 3.0 hr. and then at 20° for 2.0 hr. The contents of the collection trap were fractionated at reduced pressure through traps at -78, -111, and $-196°$. The medium boiling fraction was found to contain $ClCF_2CF_2OF$ in less than 2% yield. The high boiling fraction was found to contain Cl_2CFCF_2OF in approximately 5% yield. 1-Chloro-2-fluoroxyperfluoroethane was purified by gas chromatography at 0°. Its retention time was 70 relative to trichlorofluoromethane. Elemental analysis was carried out on a sample of chromatographed $ClCF_2CF_2OF$.

Anal. Calcd. for C_2F_5OCl: C, 14.1; F, 55.7. Found: C, 14.0; F, 56.0.

Identification of $ClCF_2CF_2OF$ was on the basis of n.m.r. and infrared spectra, elemental analysis, and thermal decomposition products.

The Quantitative Synthesis and Dimethylamine Reaction of Tris(trifluoromethyl)phosphine Oxide[1]

Anton B. Burg and Adib J. Sarkis

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007. Received September 16, 1964

The phosphine $(CF_3)_3P$ with NO_2 quantitatively forms NO and the oxide $(CF_3)_3PO$ (m.p. $-89°$; b.p. 32°), which with $(CH_3)_2NH$ quantitatively forms HCF_3 and the new phosphinic amide $(CF_3)_2P(O)N(CH_3)_2$ (m.p. $-21°$; b.p. 154.6° estd.). This reversibly forms a solid 1:1 BF_3 adduct, the dissociation pressures of which give $\Delta F = 27.42 - 0.07257T$ kcal. The amide can be converted by excess pressure of HCl to $(CF_3)_2P(O)Cl$ (over 98%), thus offering a convenient route to other fluorocarbonphosphinyl chemistry. Accurate infrared spectra are reported for $(CF_3)_3PO$, $(CF_3)_2P(O)N(CH_3)_2$, and $(CF_3)_2-P(O)Cl$.

The phosphine oxide $(CF_3)_3PO$ was first made, in yields approaching 70%, by the reaction of $(CF_3)_3PCl_2$ with oxalic acid.[2] We have found that it can be made quantitatively by a reaction occurring well below room temperature, namely

$$(CF_3)_3P + NO_2 \longrightarrow (CF_3)_3PO + NO$$
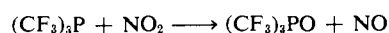
The value of this phosphine oxide for further syntheses

(2) R. C. Paul, *J. Chem. Soc.*, 574 (1955).