1,3-Bis(fluoroxy)perfluoropropane and Other Oxygen-Containing Compounds by Direct Fluorination[1]

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The direct fluorination of 1-hydroxy-3-trichloroacetoxypropane yields a variety of species. The major products are CO_2 and COF_2. Several OF-containing substances are produced in this reaction, including the well-known CF_3OF and the recently reported CF_3CF_2OF, $ClCF_2CF_2OF$, Cl_2CFCF_2OF, and Cl_3CCF_2OF. Two new fluoroxy compounds were isolated, $FOCF_2CF_2CF_2OF$ and $FOCF_2CF_2CF(=O)$. A cyclic peroxide, $\overline{CF_2CF_2CF_2OO}$, was obtained and also the epoxide, $\overline{CF_2CF_2O}$. In addition, many other cleavage products containing chlorine, acid fluoride groups, or both were observed.

Discussion

Direct fluorination is a well-known technique for the preparation of fluorine-containing compounds. This paper describes the fluorination of 1-hydroxy-3-trichloroacetoxypropane,[2] a reaction which affords a variety of products (Chart I), including several species not previously reported.

All of the products could logically be derived by straightforward cleavage and fluorination. No rearrangements were observed, except in the case of V, wherein a chlorine atom has been introduced. Intramolecular ring closures are noted in the case of I and IV.

Several OF-containing compounds were formed in this reaction. These include CF_3OF, first obtained by Kellogg and Cady,[3] and fluoroxyperfluoroethane and three of its chlorine-substituted analogs, recently reported by Prager and Thompson.[4] Two new OF-containing compounds are described: 1,3-bis(fluoroxy)-perfluoropropane (II), a difunctional species, and 3-fluoroxyperfluoropropionyl fluoride (III), a fluoroxy acid fluoride. These materials behave like the simpler fluoroxy compounds. They are stable at room temperature for prolonged periods in pure state but are decomposed by heat or by chemical initiators, including hydrocarbons. The decomposition of 1,3-bis(fluoroxy)perfluoropropane produces tetrafluoromethane and 2 moles of carbonyl fluoride. Thus, this di-

$$FOCF_2CF_2CF_2OF \xrightarrow[RH]{\Delta \text{ or}} CF_4 + 2COF_2$$

functional primary fluoroxy compound appears to decompose in a manner analogous to that observed for the monofunctional primary compounds having more than one carbon atom. The latter reaction is

$$R_FCF_2OF \xrightarrow[RH]{\Delta \text{ or}} R_FF + COF_2$$

believed to be a chain process involving formation of a perfluoroalkoxy radical by abstraction of the fluorine of the OF group, followed by cleavage to carbonyl fluoride and the chain carrier $R_F\cdot$.

The fluorinated cyclic peroxide IV has not been reported previously. It is similar to a compound prepared earlier by Talbott,[5] but appears to be more stable. The fluorinated epoxide, $\overline{CF_2CF_2O}$, was first disclosed in a patent issued to Kauck and Simons[6] in 1952. Some spectral data have been reported recently for this compound.[7] These data are not completely consistent with those obtained in our laboratory.

Experimental Section

General Procedures.—The fluorinations were carried out by a static-bed procedure similar to that described previously.[4] In the present work, a reactor equipped with a horizontally mounted Monel sintered plate was used. Fluorine was introduced below and passed through the reactant–sodium fluoride mixture spread thinly on the plate, and gaseous products were removed above.

Separations were accomplished by trap-to-trap fractionation, followed by gas chromatography, carried out with a Perkin-Elmer vapor fractometer (Model 154-D) equipped with gas sampling and backflush valves. Perfluorotributylamine[8] (67% on 30–60 mesh acid-washed Celite[9]) was used as the stationary phase, except in the case of perfluoroethylene oxide (see below).

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 nmr 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^*[10] units at dilutions of about 15–30%, negative values for low field. A Consolidated Electrodynamics Corp. mass spectrometer, Model 21-103-C, was used to obtain the mass spectra and for the determination of molecular weights by effusion rate studies. An ionization potential of 70 v and an ionization chamber temperature of 250° were employed.

Precautions for Handling Fluoroxy Compounds.—The OF-containing compounds described in this paper are somewhat hazardous, and it is recommended that suitable protective equipment be used when preparing, treating, or storing them.[11] 1,3-Bis(fluoroxy)perfluoropropane is sensitive to friction; the use of beaded traps was discontinued with this material because of the high incidence of explosions. In addition, many fluoroxy

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[1] This research was supported by the Advanced Research Projects Agency under Contract NOrd 18688 and was monitored by the Bureau of Naval Weapons.

[2] The nmr spectrum of this material indicates that it exists principally as the straight-chain half-ester. No evidence was found for the presence of the tautomeric cyclic ortho ester, postulated by H. Hibbert and M. E. Greig [*Can. J. Res.*, **4**, 254 (1931)] and by H. Meerwein and H. Sönke [*Ber.*, **B64**, 2375 (1931); *J. Prakt. Chem.*, **137**, 295 (1933)].

[3] K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).

[4] J. H. Prager and P. G. Thompson, *ibid.*, **87**, 230 (1965).

[5] R. L. Talbott, *J. Org. Chem.*, **30**, 1429 (1965).

[6] E. A. Kauck and J. H. Simons (to Minnesota Mining and Manufacturing Co.), British Patent 672,720 (May 28, 1952).

[7] V. Caglioti, M. Lenzi, and A. Mele, *Nature*, **201**, 610 (1964).

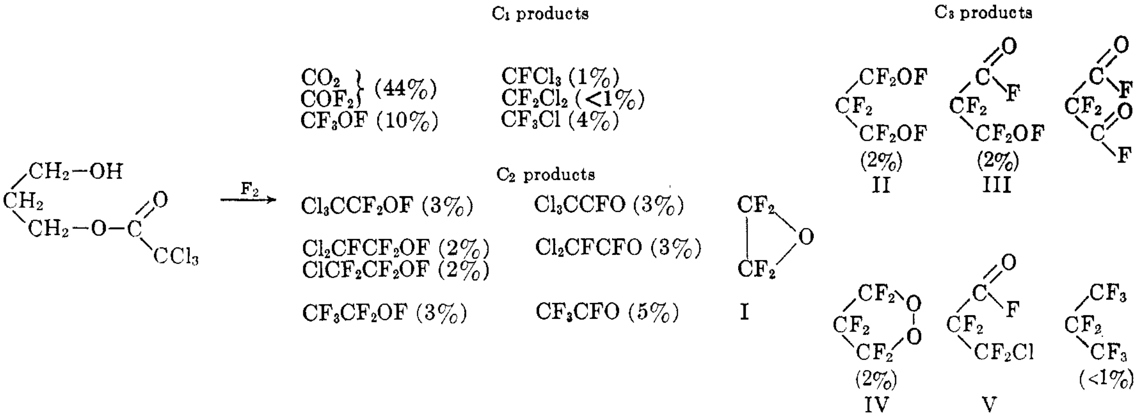
[8] FC-43 (Minnesota Mining and Manufacturing Co.).

[9] Chromosorb P (Johns-Manville).

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

[11] 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 heavy leather gloves. Nonflammable slush baths are, of course, preferred.

CHART I



compounds, including those reported here, have been found to be decomposed by CH-containing substances.[4] Stable samples of these fluoroxy compounds are obtained only when they have been freed of such decomposition initiators.

Preparation of 1-Hydroxy-3-trichloroacetoxypropane.—1-Hydroxy-3-trichloroacetoxypropane was prepared according to the procedure of Hibbert and Grieg[2] from trichloroacetyl chloride and 1,3-propanediol. Nmr spectroscopy was found helpful in the identification of the products, which also included 1,3-bis(trichloroacetoxy)propane.

Fluorination Procedure.—A total of 63 runs was carried out. The following is a description of a typical one. A 2.0-g (9 mmoles) sample of 1-hydroxy-3-trichloroacetoxypropane was combined with 8 g of sodium fluoride and treated with 2.1 moles of fluorine under the following conditions: 20°, 2%, 2.5 hr; 20°, 6%, 1.5 hr; 20°, 15%, 1.5 hr; 20°, 23%, 1.5 hr; and 30–35°, 36%, 7 hr. The effluent gases were fractionated under reduced pressure (<0.1 mm) and collected as follows: low-boiling fraction (−196° trap), 3.2 mmoles; medium-boiling fraction (−111° trap), 0.7 mmole; and high-boiling fraction (−78° trap), 1.0 mmoles.

The low-boiling fractions from several[11] runs were combined and chromatographed at −30°. The following compounds were isolated and identified by infrared and/or nmr spectroscopy: CO_2, COF_2, CF_3OF, CF_3Cl, CF_3CFO, SO_2F_2, SF_6, CF_3CF_2OF, $CF_3CF_2CF_3$, CF_2Cl_2, and $FClO_3$. A compound which proved to be $\overline{CF_2CF_2O}$ was characterized as described below.

The medium-boiling fractions from several runs were combined and chromatographed at a temperature between 0 and −10°. The following components were identified by means of infrared and/or nmr spectroscopy: $ClCF_2CF_2OF$, $CFCl_3$, and $ClCF_2CF_2CFO$. In addition, $FOCF_2CF_2CF_2OF$, $FOCF_2CF_2CFO$, and $\overline{CF_2CF_2CF_2OO}$ were isolated from the medium-boiling fraction; their characterization is given below.

The high-boiling fractions from several runs were combined and chromatographed at 0°. The products included additional amounts of $FOCF_2CF_2CF_2OF$ and $CFCl_3$, as well as Cl_2CFCFO, Cl_2CFCF_2OF, Cl_3CCFO, and Cl_3CCF_2OF, plus several compounds which were not identified.

1,3-Bis(fluoroxy)perfluoropropane.—1,3-Bis(fluoroxy)perfluoropropane (II) was purified by gas chromatography at a temperature between 0 and −10°. Its retention time at 0° is 630 relative to dichlorodifluoromethane. 1,3-Bis(fluoroxy)perfluoropropane is a colorless gas, which is oxidizing toward ferrocene and aqueous potassium iodide. It has shown a pronounced tendency to explode, especially when subjected to friction (as in a beaded chromatography trap). All attempts to date to obtain elemental analyses and molecular weight data have resulted in explosions. The compound otherwise appears to be relatively stable at room temperature when obtained free from hydrocarbon impurities. The greater part of a sample stored for 9 weeks was recovered unchanged.

The infrared spectrum of $FOCF_2CF_2CF_2OF$ contains absorptions at 7.67 (s), 8.23 (vs), 8.58 (m), 8.98 (s), 10.13 (s), 10.83 (w), 11.29 (m), 12.29 (w), 12.68 (m), and 12.99 (w) μ.[12] The peak at 11.29 μ is attributed to the OF group. The F^{19} nmr spectrum shows a broad absorption at ϕ^* −146.0 which is assigned to the OF group. Other absorptions occur at ϕ^* 93.4 for the CF_2 groups attached to fluoroxy groups and at ϕ^* 122.8 for the center CF_2 group. Both of these absorptions are also broad. The peak areas were found to be in the ratio of 1.1:2.0:1.1.

Perfluoro-1,2-dioxolane and 3-Fluoroxyperfluoropropionyl Fluoride.—Perfluoro-1,2-dioxolane (IV) was isolated by trap-to-trap fractionation at reduced pressure, followed by gas chromatography at a temperature between 0 and −10°. Perfluoro-1,2-dioxolane was found to elute with a compound believed to be 3-fluoroxyperfluoropropionyl fluoride (III) (retention time at −10°, 85 relative to chlorotrifluoromethane). The latter compound could be removed by water washing to provide pure $\overline{CF_2CF_2CF_2OO}$. Perfluoro-1,2-dioxolane is a colorless gas. It is more stable than either of the isomers of perfluoro-3,5-dimethyl-1,2-dioxolane[5] and, in fact, appears to be storable at room temperature indefinitely.

The infrared spectrum of perfluoro-1,2-dioxolane shows absorptions at 7.18 (w), 7.46 (s), 8.07 (s), 8.77 (s), 9.22 (s), 9.73 (w), 10.20 (m), and 14.06 (m) μ. The F^{19} nmr spectrum of this compound contains absorptions at ϕ^* 96.6 (triplet) for the CF_2 groups adjacent to oxygen and at ϕ^* 125.0 (fivefold) for the other CF_2 group. The coupling constant is 3.3 cps. The peak areas were found to be in the ratio of 2:1. The mass spectrum fragmentation pattern exhibits the peaks shown in Table I.

TABLE I

MASS SPECTRUM OF PERFLUORO-1,2-DIOXOLANE

m/e	Ion	Relative intensity
16	O^+	3.3
19	F^+	3.4
20	HF^+	1.3
24	C_2^+	1.4
28	CO^+	21.4
31	CF^+	47.3
32	O_2^+	2.3
43	C_2F^+	1.2
44	CO_2^+	1.6
47	CFO^+	92.4
50	CF_2^+	100.0
66	CF_2O^+	19.8
69	CF_3^+	60.6
78	$C_2F_2O^+$	4.2
82	$CF_2O_2^+$	1.2
85	CF_3O^+	5.2
100	$C_2F_4^+$	16.2
119	$C_2F_5^+$	0.3
131	$C_3F_5^+$	0.5
150	$C_3F_6^+$	0.4
182	$C_3F_6O_2^+$	0.3

The pattern is consistent with the assigned structure, although the relative intensity of m/e 69 appears to be high for a recombination peak. The molecular weight, determined by effusion

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[12] Symbols are as follows: s, strong; m, medium; and w, weak.

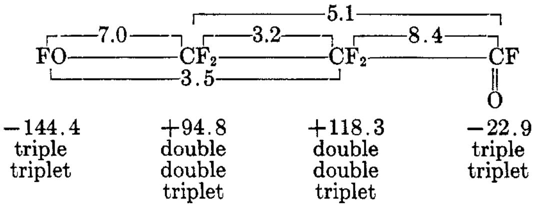

Figure 1.—Schematic representation of the nmr spectrum of 3-fluoroxyperfluoropropionyl fluoride.

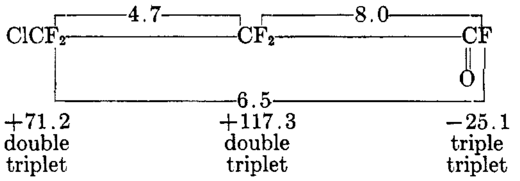

Figure 2.—Schematic representation of the nmr spectrum of 3-chloroperfluoropropionyl fluoride.

rate from the mass spectrometer, was 184 (calcd 182). Elemental analyses were in good agreement with theory.

Anal. Calcd for $C_3F_6O_2$: C, 19.8; F, 62.6. Found: C, 19.9; F, 62.5.

The compound which eluted with perfluoro-1,2-dioxolane is believed to be 3-fluoroxyperfluoropropionyl fluoride (III). This structural assignment was made on the basis of its F^{19} nmr spectrum. Figure 1 shows the absorptions (ϕ^*) and coupling constants (cycles per second) attributed to this compound. The peak areas were found to be in the ratio of 1:2:2:1. 3-Fluoroxyperfluoropropionyl fluoride is found to be oxidizing toward ferrocene and aqueous potassium iodide. Prolonged stability studies were not carried out on this compound. However, in a 22-day period no decomposition was observed in a sample containing only this compound and its coeluent, perfluoro-1,2-dioxolane.

Perfluoroethylene Oxide.—Preliminary isolation of perfluoroethylene oxide (I) was accomplished by trap-to-trap fractionation, followed by gas chromatography at −30° on a column of acid-washed Celite coated with perfluorotributylamine. The fraction having a retention time of 35 relative to dichlorodifluoromethane was subjected again to gas chromatography at −27° on a column of acid-washed Celite coated with Dow Corning SE-30 (a silicone polymer). In the second chromatographic procedure, perfluoroethylene oxide was separated from CF_3CFO, SO_2F_2, and SF_6 (the latter two are present in small amounts in fluorine). Perfluoroethylene oxide was identified by spectral means. Its F^{19} nmr spectrum shows a single sharp peak at ϕ^* 111.0. This value is consistent with the average found for the CF_2 group in higher members of this series. It differs substantially (after appropriate corrections) from that reported by Caglioti and co-workers.[7] However, a comparison of their infrared spectrum with ours leaves no doubt that both materials are the same. The mass spectrum fragmentation pattern of perfluoroethylene oxide exhibits the peaks shown in Table II. The molecular weight, determined by effusion rate from the mass spectrometer, was 118 (calcd 116).

TABLE II

MASS SPECTRUM OF PERFLUOROETHYLENE OXIDE

m/e	Ion	Relative intensity
19	F^+	2.6
31	CF^+	43.1
47	CFO^+	73.3
50	CF_2^+	100.0
51	$C^{13}F_2^+$	1.4
66	CF_2O^+	2.8
69	CF_3^+	57.1
97	$C_2F_3O^+$	2.0
100	$C_2F_4^+$	4.7

Nmr Spectra.—Some further F^{19} nmr data are given below. Perfluoromalonyl fluoride exhibits an absorption (a triplet) at ϕ^* −20.2 for the fluorines attached to carbonyls and one (also a triplet) at ϕ^* 111.6 for the CF_2 group. The coupling constant is 10.9 cps. Figure 2 shows the absorptions (ϕ^*) and coupling constants (cycles per second) for $ClCF_2CF_2CFO$.

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Alkali Sensitivity of a Dinitro Compound in the Cyclopropane Series[1]

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The synthesis of *trans*-1,2-dinitro-3,3-dimethylcyclopropane was accomplished by monobromination of 1,3-dinitro-2,2-dimethylpropane and subsequent elimination with potassium acetate. It displays the expected high level of cyclopropyl hydrogen lability as revealed by hydrogen exchange under acetate catalysis at room temperature. With sodium hydroxide it is converted irreversibly to the salt of 1,2-dinitro-3-methyl-2-butene, which is liberated upon acidification in the presence of urea; otherwise, a reaction with nitrite ion leads to the formation of 3,4-dinitro-5,5-dimethyl-2-isoxazoline.

Despite the very great immunity of nitrocyclopropane[2] to basic reagents, there are good reasons to suppose that a vicinal dinitrocyclopropane might be exceedingly sensitive and possibly not accessible synthetically by ring closures with alkaline reagents. The known propensity of nitrocyclopropyl ketones to undergo ring-opening reactions with bases under mild conditions is conditional, as Smith and Engelhardt[3] established, upon having a cyclopropyl hydrogen α to a nitro group and a carbonyl function on the adjoining carbon. A second nitro group would be expected to serve even more effectively than carbonyl to provide the necessary activation for ionization and to facilitate rearrangement of the anion to a more stable open-chain species. Secondly, there is an instability associated with *vic*-dinitroalkanes, illustrated, for example, by the elimination of the elements of nitrous acid from 1,2-dinitrocyclohexane on treatment with sodium hydroxide.[4] Nevertheless, it seemed that an entry might be made into the series by cyclization under the mildest possible conditions starting from the readily available 1,3-dinitroneopentane where,

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[1] Work performed under Air Force Office of Scientific Research, Grant No. AFOSR-80-63.

[2] H. B. Hass and H. Schechter, *J. Am. Chem. Soc.*, **75**, 1382 (1953).

[3] L. I. Smith and V. A. Engelhardt, *ibid.*, **71**, 2676 (1949).

[4] A. T. Nielsen, *J. Org. Chem.*, **27**, 2001 (1962).