**Preparation of Fluoroxybis(perfluoromethylperoxy)fluoromethane (VIII).**—The procedure was the same as the procedure for the preparation of peroxide VII. The same reaction vessel was charged with 0.51 mmol of pure peroxide V and 1.02 mmol of fluorine, and the cylinder was then kept overnight in the −78° bath. Recovery of the product gave 0.52 mmol of pure fluoroxybis(perfluoromethylperoxy)fluoromethane (VIII, quantitative yield within experimental error). Peroxide VIII exhibits very strong, complex absorption in the infrared spectrum between 7.70 and 8.10 μ with peaks at 7.71, 7.87, and 8.00 μ, as well as other peaks at 8.60 (s), 8.85 (vs), and 10.62 μ (w, broad). The fluorine nmr spectrum shows three complex peaks, as shown in Table I. The mass spectrum of peroxide VIII shows prominent peaks at mass numbers 44 ($CO_2^+$), 47 ($COF^+$, largest peak), and 69 ($CF_3^+$); medium intensity peaks at mass numbers 28 ($CO^+$), 63 ($CFO_2^+$), and 66 ($CF_2O^+$); and lower intensity peaks at mass numbers 16 ($O^+$), 19 ($F^+$), 31 ($CF^+$), 32 ($O_2^+$), 50 ($CF_2^+$), 85 ($CF_3O^+$), 113 ($C_2F_3O_2^+$), and 129 ($C_2F_3O_3^+$). No parent ion or ions near the molecular weight of the parent molecule were observed. The absence of peaks in the pattern attributable to fragments containing carbon–carbon bonds or elements other than carbon, fluorine, and oxygen is further support for the structure. Compound VIII liberates iodine from aqueous potassium iodide solution but is thermally stable at room temperature. The nmr sample in trichlorofluoromethane showed no decomposition after storage at room temperature in the nmr tube for several months.

*Anal.* Calcd for $C_3F_8O_6$: C, 13.43; F, 56.72. Found: C, 13.1; F, 55.5.

**Registry No.**—I, 692-74-0; II, 16118-40-4; V, 16156-35-7; VI, 16156-36-8; VII, 16156-37-9; VIII, 16156-38-0.

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# *Notes*

## Fluorocarbonyl Trifluoromethyl Peroxide

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A recent article[1] reporting the synthesis of FC(O)OF by the photochemical reaction of $(FCO)_2O_2$ with fluorine stated that the new compound $FC(O)OOCF_3$ was formed as a by-product. The yield was about 5%, based upon the quantity of $(FCO)_2O_2$ consumed. This new compound is the same as one now described by Talbott, who has used the name fluoroformyl perfluoromethyl peroxide and clearly established the formula.[2] In our work, samples of the pure compound were obtained through separation either by gas chromatography using the column described in ref 1 or by fractional codistillation. The observed properties are given below.

**Molecular Weight.**—The average molecular weight obtained from four vapor density measurements was 148 g/mol (theory for $FC(O)OOCF_3$, 148).

**Volatility.**—Fractional codistillation indicated a boiling point within 10° of −16°.

**Infrared Spectrum.**—The infrared spectrum of the gas as observed with a Beckman Model IR10 spectrometer is shown in Figure 1. The substance was in a cell 10 cm long with silver chloride windows. Absorption bands (cm$^{-1}$) were found at 1918, vs, C═O stretch; 1300, vs, CF stretch; 1247, vs, CF stretch; 1172, vs, CF stretch; 1007, m, CO stretch; 932, m, CO stretch; 753, m; 691, w, $CF_3$ symmetrical deformation; and 615, m. All assignments should be considered tentative.

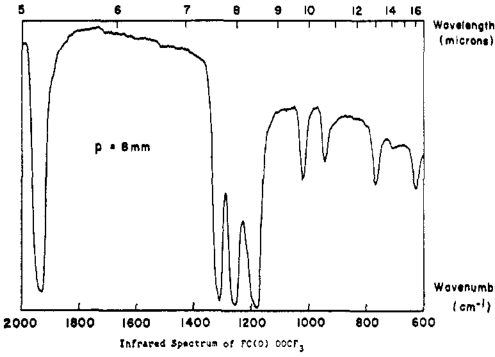

Figure 1.—Infrared spectrum of $FC(O)OOCF_3$.

**Nuclear Magnetic Resonance Spectrum.**—The $^{19}F$ nmr spectrum was taken at 40 Mc with a Varian Model No. V4311 spectrometer using 76 mol % $CCl_3F$ as an internal standard. The resultant spectrum consisted of a sharply defined doublet with a chemical shift of 68.8 ppm for the $CF_3$ group and a quadruplet with a chemical shift of 32.3 ppm for the FC═O group. The coupling constant, $J$, was 1.7 cps.

For comparison, the chemical shift of the FC═O group, with respect to external $CCl_3F$, of $(FCO)_2O_2$,[3] and of internal $CCl_3F$ of $FC(O)OOSF_5$,[4] was +34.4 ppm. The chemical shift of the $OCF_3$ group with respect to internal $CCl_3F$ of $CF_3OOCF_3$ was +69.0 ppm.[5]

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(1) R. L. Cauble and G. H. Cady, *J. Amer. Chem. Soc.*, **89**, 5161 (1967).

(2) Richard L. Talbott, *J. Org. Chem.*, **33**, 000 (1968).

(3) W. Fox and G. Franz, *Inorg. Chem.*, **5**, 946 (1966).

(4) R. Czerepinski and G. Cady, submitted for publication.

(5) P. Thompson, *J. Amer. Chem. Soc.*, **89**, 1811 (1967).

**Reactions.**—Iodine was liberated when the peroxide was brought into contact with KI solution.

**Registry No.**—Fluorocarbonyl trifluoromethyl peroxide, 16118-40-4.

**Acknowledgment.**—This work was performed in part under contract with the Office of Naval Research. The nmr spectrum was acquired by B. J. Nist.

## Metal Derivatives of Fluorinated *gem*-Diols

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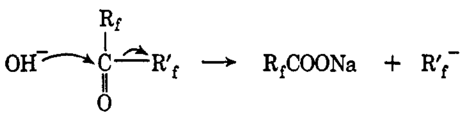
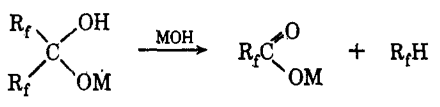
Although the strongly acidic properties of fluorinated *gem*-diols are well known and $pK_a$ values for the first ionization of these compounds have been recorded,[1] their salts have not previously been described. Hexafluoroacetone and chloropentafluoroacetone have been reported to react with excess metal hydroxide to produce the metal trifluoroacetate without haloform formation.[2] Other ketones such as perfluoro-4-heptanone and nitropentafluoroacetone, however, have been shown to form the corresponding haloform with excess base,[3] presumably by a displacement reaction, *i.e.*



$$OH^- + R_fC(=O)R'_f \longrightarrow R_fCOONa + R'^-_f$$

We have examined the reaction of aqueous solutions of several fluorinated ketones with metal hydroxides and find that addition of 1 equiv of base produces salts which are stable and detectable in solution.

Some of these can be isolated, but in most cases such attempts bring about decomposition. In the presence of *excess* base all of these salts decompose, more or less easily, to the related carboxylate and in most cases a haloform. Thus, hexafluoroacetone produces



duces fluoroform in 60% yield upon treatment with excess base, and perfluoro-4-heptanone is converted almost quantitatively into 1-hydroperfluoropropane. Chlorodifluoromethane was obtained only in about 5–10% yield, however, from chloropentafluoroacetone.

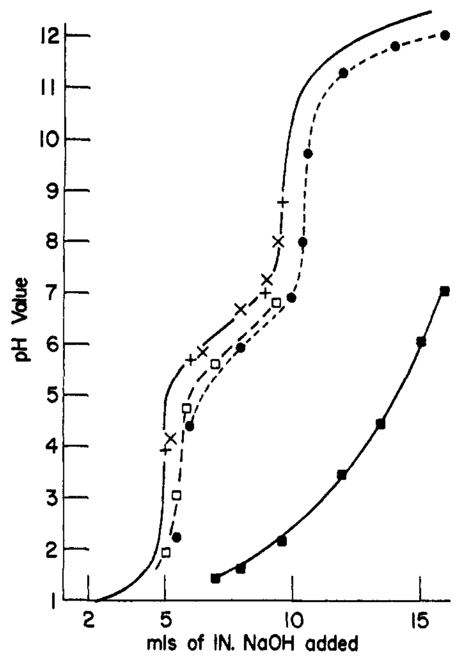


Figure 1.—+, titration of $(CF_3)_2C{=}O$ with sodium hydroxide; ×, titration of $(CF_2Cl)_2C{=}O$ with sodium hydroxide; ●, back-titration of solution + with perchloric acid; ■, back-titration of solution × with perchloric acid; □, back-titration of × from pH 7.0.

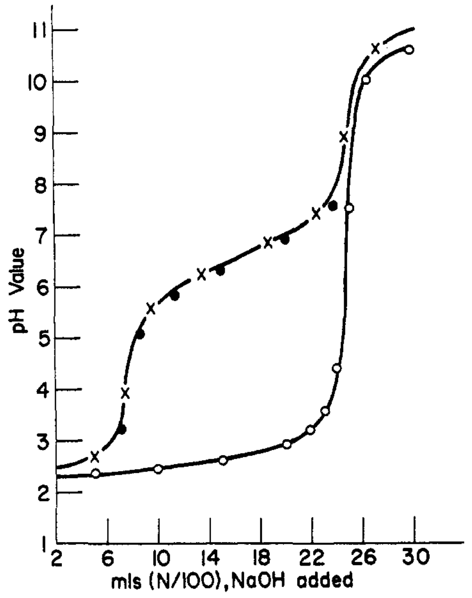


Figure 2.—×, titration of $(C_3F_7)_2C{=}O$ with sodium hydroxide; ○, back-titration of × with perchloric acid; ●, back-titration of × from pH 8.0.

The basic hydrolysis of the metal salts of fluorinated *gem*-diols presumably occurs as in Scheme I. The low yield of chlorodifluoromethane from the hydrolysis of chloropentafluoroacetone is believed to result from the reduced stability of the chlorodifluoromethyl anion, which rapidly eliminates chloride ion. The resulting difluorocarbene yields carbon dioxide, and not a haloform, upon hydrolysis. The reactivity of the chlorodifluoromethyl anion was noted by Hine[4] during the hydrolysis of chlorodifluoromethane. The rapid rate at which $CHF_2Cl$ reacted indicated that the half-life of $CF_2Cl^-$ is very short (or possibly that difluorocarbene is eliminated by a concerted reaction).

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[1] W. J. Middleton and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **86**, 4948 (1964).

[2] Allied Chemical Co., Product Data Sheet PD 56FK-663, 1962.

[3] (a) I. L. Knunyants, *et al.*, *Zh. Vses. Khim. Obshchest.*, **7**, 709 (1962); (b) R. N. Haszeldine, *J. Chem. Soc.*, 1748 (1953).

[4] J. Hine and P. B. Langford, *J. Amer. Chem. Soc.*, **79**, 5497 (1957).