fluoroacetone, hexafluoro-2,2-propanediol, and the metal trifluoroacetate. Such decomposition products give some support for the previously described mechanism of reaction of fluorinated ketone hydrates with alkali. Thermal decomposition probably involves initial elimination of 1 mol of base from the salt, with subsequent attack of this base on residual salt to form the observed products.

Since the metal salts are unstable in the presence of base, not surprisingly we were unable to prepare dimetal salts.[5a] Evaporation of a solution containing 1 equiv of *gem*-diol and 2 equiv of metal hydroxide yielded metal trifluoroacetate.

Experimental Section

Measurements of pH were made with a Beckman Model G pH meter using a Coleman Instrument 0-11 glass electrode. Infrared spectra were measured on a Perkin-Elmer Model 21 double beam instrument using a 2.5-cm gas cell fitted with NaCl windows or as Nujol mulls. Nuclear magnetic resonance spectra were measured on a Varian V-4502 instrument operating at 40.0 Mc, utilizing acetone as the solvent and an internal reference of trichlorofluoromethane for the determination of chemical shifts. The values reported are phi (ϕ^*) values[6] at a dilution of 10–25%.

Preparation of Metal Salts of Hexafluoro-2,2-propanediol.—A stirred aqueous solution of hexafluoro-2,2-propanediol was carefully titrated with aqueous normal metal hydroxide solution until the pH value reached 8.0. The solution was then evaporated to dryness at room temperature in a stream of air over a period of several days, and finally dried in a vacuum desiccator. The white solid residue was identified as the metal salt of hexafluoro-2,2-propanediol by its infrared and F^{19} nmr spectra together with elemental analyses. These data are summarized in Table I. The ^{19}F nmr spectrum shows a single peak at about ϕ^* 83 corresponding to the CF_3 group, and the infrared spectrum shows broad absorptions at 2.7–4.5 μ, corresponding to OH stretching, and a strong absorption at about 9.5 μ, corresponding to OH bending. In all cases, characteristic absorptions were also present at approximately 8.3, 9.3, 10.4, and 13.9 μ. Strong evidence for the presence of water of crystallization was also observed in the spectra of the lithium, sodium, and potassium salts.

Basic Hydrolysis of Fluorinated *gem*-Diols.—The *gem*-diols, (a) hexafluoro-2,2-propanediol, (b) chloropentafluoro-2,2-propanediol, and (c) perfluoro-4,4-heptanediol, were hydrolyzed by heating with excess 1 *N* sodium hydroxide solution in a conventional hydrolysis bulb. The volatile components were transferred into a vacuum system and distilled through a −78° slush bath. The low-boiling materials were identified by their infrared spectra as (a) fluoroform (60% conversion of $(CF_3)_2C{=}O$), (b) chlorodifluoromethane (5–10% conversion of $CF_3(CF_2Cl)C{=}O$) and carbon dioxide, and (c) 1-hydroperfluoropropane (90% conversion of $(C_3F_7)_2C{=}O$).

Thermal Decomposition of the Sodium Salt of Hexafluoro-2,2-propanediol.—The sodium salt of hexafluoro-2,2-propanediol (2.0 g) was heated under vacuum at 100° for 8 hr and the volatile products (1.2 g) were trapped at −196°. The volatile products were subsequently identified as a mixture of fluoroform, hexafluoroacetone, and hexafluoro-2,2-propanediol by their infrared spectra.

The solid residue (0.7 g) was shown by its infrared spectrum and X-ray powder photograph to contain sodium trifluoroacetate and some sodium fluoride. Although no evidence of sodium hydroxide was detected by this method, this material was probably present in an amorphous state. Pyrolysis of the residue at 270° under vacuum for 1 hr produced further volatile material which was identified by its infrared spectrum as a mixture of carbon dioxide and perfluoroacetyl fluoride. These are typical pyrolysis products from sodium trifluoroacetate.[7] The solid residue was shown by its X-ray powder photograph to be predominantly sodium fluoride.

Attempted Preparation of the Salt of Perfluoro-4,4-heptanediol.—An aqueous solution of perfluoro-4,4-heptanediol was carefully titrated with 0.1 *N* sodium hydroxide solution until a pH value of 8.0 was obtained. Subsequent evaporation to dryness in a stream of dry air at room temperature produced a white solid which was shown, by examination of its infrared spectrum, to be mainly sodium heptafluorobutyrate.

Acknowledgment.—The authors are indebted to Dr. J. J. McBrady for interpreting the F^{19} nmr and infrared spectra and to Mr. P. B. Olson for elemental analyses.

[5a] NOTE ADDED IN PROOF.—It has now been found that careful pyrolysis of $(CF_3)_2C(OH)OLi$ does produce $(CF_3)_2C(OLi)_2$.

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

[7] F. Swarts, *Bull. Sci. Acad. Roy. Belg.*, **8**, 343 (1922).

Synthesis of Esters of ω-Nitroso Perfluorinated Carboxylic Acids[1]

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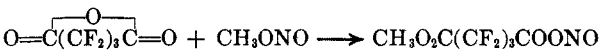
As part of a program to investigate the synthesis and polymerization of functionally substituted, fluorine-containing nitroso compounds, we have found that methyl nitrite will react with both perfluorosuccinic anhydride and perfluoroglutaric anhydride to give the corresponding nitrite esters.

$$\overbrace{O{=}C(CF_2)_2C{=}O}^{O} + CH_3ONO \longrightarrow CH_3O_2C(CF_2)_2COONO$$

I



$$\overbrace{O{=}C(CF_2)_3C{=}O}^{O} + CH_3ONO \longrightarrow CH_3O_2C(CF_2)_3COONO$$

II

The reaction was generally carried out by condensing equimolar amounts of the reactants into a sealed glass tube and allowing the tube to warm to room temperature. Larger scale reactions, however, could be run in a three-neck flask at atmospheric pressure by bubbling methyl nitrite into the stirred anhydride and returning unreacted methyl nitrite to the flask by a condenser. The reaction is spontaneous and exothermic, and results in high conversions into the amber, liquid nitrite ester.

The nitrite esters were decarboxylated either by pyrolysis or ultraviolet irradiation to give the corresponding blue, liquid nitroso esters, which could be purified by distillation. Conversions were low

$$CH_3O_2C(CF_2)_2COONO \xrightarrow[\Delta]{\text{uv or}} \underset{\text{III}}{CH_3O_2C(CF_2)_2NO}$$

$$CH_3O_2C(CF_2)_3COONO \xrightarrow[\Delta]{\text{uv or}} \underset{\text{IV}}{CH_3O_2C(CF_2)_3NO}$$

(20–25%) by either method, which may be partially attributed to the formation of nearly equal amounts of a high boiling, colorless by-product. This material was identified as the triester, $[CH_3O_2C(CF_2)_{2,3}]_2NO(CF_2)_{2,3}CO_2CH_3$, (V and VI), which presumably was formed by radical attack on the nitroso ester to give a trisubstituted hydroxylamine.

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[1] (a) Presented at the 154th meeting of the American Chemical Society, Chicago, Ill., Sept 1967. (b) This work was sponsored by the U. S. Army Natick Laboratories, Natick, Mass., under Contract DA 19-129(AMC)-152 (N) with C. B. Griffis as Project Engineer for the Army.

$$\mathrm{CH_3O_2C(CF_2)_{\mathit{n}}COONO \xrightarrow[\Delta]{\text{uv or}} CO_2 + CH_3O_2C(CF_2)_{\mathit{n}}\cdot + NO}$$

$$\mathrm{CH_3O_2C(CF_2)_{\mathit{n}}\cdot + NO \longrightarrow CH_3O_2C(CF_2)_{\mathit{n}}NO}$$

$$\mathrm{CH_3O_2C(CF_2)_{\mathit{n}}\cdot + CH_3O_2C(CF_2)_{\mathit{n}}NO \longrightarrow [CH_3O_2C(CF_2)_{\mathit{n}}]_2NO\cdot}$$

$$\mathrm{CH_3O_2C(CF_2)_{\mathit{n}}\cdot + [CH_3O_2C(CF_2)_{\mathit{n}}]_2NO\cdot \longrightarrow [CH_3O_2C(CF_2)_{\mathit{n}}]_2NO(CF_2)_{\mathit{n}}CO_2CH_3}$$

(where $n = 2$ or 3)

A similar compound, $(C_3F_7)_2NOC_3F_7$, has been obtained by the pyrolysis of C_3F_7NO.[2] Dimethyl perfluorosuberate was also isolated as an intermediate fraction in the distillation of the perfluoroglutaric anhydride derivative. Formation of this compound would be explained by coupling of $CH_3O_2C(CF_2)_3\cdot$ radicals.

The triester derivative (VI) was converted into the triacid (VII) by basic hydrolysis and into the triamide (VIII) and trinitrile (IX) by reaction with excess ammonia and subsequent dehydration.

$$\mathrm{[CH_3O_2C(CF_2)_3]_2NO(CF_2)_3CO_2CH_3 \xrightarrow{OH^-} \underset{\text{VII}}{[HO_2C(CF_2)_3]_2NO(CF_2)_3CO_2H}}$$

$$\mathrm{[CH_3O_2C(CF_2)_3]_2NO(CF_2)_3CO_2CH_3 + NH_3 \longrightarrow \underset{\text{VIII}}{[H_2NOC(CF_2)_3]_2NO(CF_2)_3CONH_2}}$$

$$\mathrm{[H_2NOC(CF_2)_3]_2NO(CF_2)_3CONH_2 \xrightarrow{P_2O_5} \underset{\text{IX}}{[NC(CF_2)_3]_2NO(CF_2)_3CN}}$$

The nitroso esters may also be converted into nitroso acids by hydrolysis. Methyl 4-nitrosoperfluorobutyrate, for example, could be hydrolyzed to 4-nitrosoperfluorobutyric acid[3] using neutral, acidic, or slightly basic (0.1 *N*) conditions. When stronger (5%) base

$$\mathrm{CH_3O_2C(CF_2)_3NO + H_2O \longrightarrow HO_2C(CF_2)_3NO}$$

was used, the blue color of the nitroso compound faded after 10 min at room temperature. Consequently, neutral or acidic hydrolysis is preferred. Although hydrolysis occurs more rapidly in acidic media (<1 day) than in neutral media (4–5 days), conversions as high as 75% were obtained with the latter method. The blue nitroso acid was isolated either by extraction or by salting out with sodium chloride.

Infrared, nmr (Tables I and II, respectively), and elemental analyses of all new compounds reported here were consistent with the assigned structures.

TABLE I
INFRARED SPECTRA OF NEW COMPOUNDS PREPARED

Compd	Major absorption peaks, μ
I (l)	3.37, 5.01, 5.40, 5.61, 5.95, 8.5 (broad)
II (l)	3.38, 5.05, 5.40, 5.62, 5.9–6.0, 8.5 (broad)
III (g)	3.32, 3.38, 5.55, 6.25, 6.90, 7.51, 8.06, 8.31, 8.62, 9.25
IV (l)	3.37, 5.60, 6.20, 6.90, 7.5–9.0 (unresolved)
V (l)	3.37, 5.60, 6.91, 7.50, 8.32, 8.75, 9.62, 9.80
VI (l)	3.38, 5.60, 6.91, 7.50, 8.38, 8.72, 9.00, 9.20, 10.20
VII	2.97, 5.65, 5.99, 7.20, 7.99, 8.2–8.7 (unresolved)
VIII (KBr)	2.92, 3.12, 5.84, 6.18, 7.01, 7.51, 7.61, 8.20, 8.50, 8.92, 9.05
IX (l)	4.43, 6.88, 8.0–9.0 (broad)

Experimental Section

Methyl nitrite was prepared by the addition of concentrated sulfuric acid to a solution of sodium nitrite in methanol and water (50:50 by volume).

Perfluorosuccinic anhydride and perfluoroglutaric anhydride were obtained from Peninsular ChemResearch stock.

3-Carbomethoxyperfluoropropionyl Nitrite (I).—Methyl nitrite (12.2 g, 0.2 mol) and perfluorosuccinic anhydride (34.2 g, 0.2 mol) were condensed into a Fischer-Porter aerosol compatibility tube and allowed to warm to room temperature. The tube was shaken to ensure thorough mixing and soon became warm. After about 1–2 hr the tube had cooled and contained an amber liquid. Unreacted starting material was removed at reduced pressure. The yield was nearly quantitative.

Anal. Calcd for $C_5H_3F_4NO_5$: C, 25.76; H, 1.29; F, 32.60. Found: C, 25.84; H, 1.33; F, 45.25, 36.91.

4-Carbomethoxyperfluorobutyryl Nitrite (II).—Methyl nitrite (12.2 g, 0.2 mol) and perfluoroglutaric anhydride (44.4 g, 0.2 mol) were allowed to react as described above with similar results.

Anal. Calcd for $C_6H_3F_6NO_5$: C, 25.44; H, 1.06; F, 40.28. Found: C, 25.70; H, 1.28; F, 40.53.

Methyl 3-Nitrosoperfluoropropionate (III).—A 250-ml, two-necked flask was fitted with an addition funnel containing $CH_3O_2C(CF_2)_2COONO$ (52 g, 0.223 mol) and a 15-in. Vigreaux column which was fitted with an air-cooled condenser constructed on the order of a Dean–Stark apparatus. The condenser was vented to a vacuum system through a −183° trap, and a total vacuum was maintained throughout the system as the nitrite was dropped into the flask, which was heated to 200°. The Vigreaux column was heated to 250°. After the pyrolysis had been going for several minutes, a blue product collected in the −183° trap and a colorless liquid began to condense in the air-cooled condenser. This liquid was periodically removed. The −183° trap was allowed to warm to room temperature and the remaining liquid product was washed with water. The blue product was separated and distilled twice by distilling from one trap to another under vacuum, discarding the last several milliliters of liquid each time. Glpc analysis of the final product (8.3 g, 20% conversion) showed it to be 100% pure.

Anal. Calcd for $C_4H_3F_4NO_3$: C, 25.40; H, 1.60; F, 40.21. Found: C, 25.66; H, 1.72; F, 40.42.

Methyl 4-Nitrosoperfluorobutyrate (IV). **A. By Pyrolytic Decarboxylation.**—4-Carbomethoxyperfluorobutyryl nitrite (33.0 g, 0.116 mol) was decarboxylated by the method described in the preceding example. Glpc analysis of the final product showed it to be 100% pure. A total of 13 g of pure $CH_3O_2C(CF_2)_3NO$ was obtained; conversion was 47%.

Anal. Calcd for $C_5H_3F_6NO_3$: C, 25.11; H, 1.25; F, 47.70. Found: C, 25.30; H, 1.17; F, 47.40.

B. By Photolytic Decarboxylation.—4-Carbomethoxyperfluorobutyryl nitrite (40 g, 0.14 mol) was placed in a 1-l. flask equipped with a Vycor immersion well and an outlet connected to a vacuum system through a trap cooled in liquid air. The nitrite was irradiated by a No. 8A36 Hanovia lamp suspended in the immersion well. Irradiation was continued for 48 hr at 0.1-mm pressure. The blue liquid product was removed from the trap and combined with the product from a similar experiment using 33 g of nitrite. The combined products were fractionated to give 12 g (20% conversion) of pure methyl 4-nitrosoperfluorobutyrate, bp 24–26° (26 mm).

Isolation of Tris(3-carbomethoxyperfluoropropyl)hydroxylamine (VI).—High boiling liquid by-products from the preparation of $CH_3O_2C(CF_2)_3NO$ were combined and fractionated using a 24-in. glass helix-packed column. The major portion of this material was removed at 137–140° (0.1 mm). Infrared and nmr analyses were consistent with the structure $[CH_3O_2C(CF_2)_3]_2NO(CF_2)_3CO_2CH_3$.

Anal. Calcd for $C_{15}H_9F_{18}NO_7$: C, 27.45; H, 1.37; F, 52.00; N, 2.13. Found: C, 27.80; H, 1.60; F, 52.98; N, 2.40.

Tris(3-carboxyperfluoropropyl)hydroxylamine (VII).—Compound VI (30 g, 0.046 mol) was placed in a flask containing 250 ml of 5% KOH in H_2O and heated at 50–60° for 20 hr. The solution was then made slightly acidic with dilute HCl. The volume of the resulting solution was reduced until crystals began depositing on the walls of the flask. These crystals were collected, analyzed, and found to be KCl, indicating that the tricarboxylic acid derivative is more water soluble than KCl.

The solution was evaporated to dryness leaving 20 g of a white solid mixture of compound VII and KCl. Analysis for

(2) R. E. Banks, M. A. Bartow, R. N. Haszeldine, and M. K. McCreath, *J. Chem. Soc.*, 7203 (1965).

(3) G. H. Crawford, D. E. Rice, and D. R. Yarian, U. S. Patent 3,192,260 (June 29, 1965).

TABLE II

NMR SPECTRA OF NEW COMPOUNDS PREPARED

Compd	Chemical shift (F)[a]	Chemical shift (H), τ
$CH_3O_2CCF_2CF_2CO_2NO$	41.5, 47.2	6.44[b]
$CH_3O_2CCF_2CF_2CF_2CO_2NO$ A B A	41.7(A), 47.5(B)	6.45[b]
$CH_3O_2CCF_2CF_2NO$	40.2, 43.3	6.83[b]
$CH_3O_2CCF_2CF_2CF_2NO$ A C A B B	38.9(A,B), 42.9(A,B), 48.9(C)	6.88[b]
$(CH_3O_2CCF_2CF_2)_2NOCF_2CF_2CO_2CH_3$ C B A C D D	12.7(A), 19.8(B), 39.5(C,D), 43.1(C,D)	6.24[b]
$(CH_3O_2CCF_2CF_2CF_2)_2NOCF_2CF_2CF_2CO_2CH_3$ D E B A F D C	10.2(A), 14.9(B,C), 17.3(B,C), 40.0(D), 42.1(E), 45.8(F)	6.22[b]
$(HO_2CCF_2CF_2CF_2)_2NOCF_2CF_2CF_2COOH$ D E B A F D C	9.5(A), 15.9(B,C), 17.7(B,C), 39.8(D), 43.2(E), 46.9(F)	...
$(H_2NOCCF_2CF_2CF_2)_2NOCF_2CF_2CF_2CONH_2$ D E B A F D C	8.7(A), 14.9(B,C), 17.3(B,C), 40.0 (D), 42.1 (E), 45.8 (F)	2.36[b]
$(NCCF_2CF_2CF_2)_2NOCF_2CF_2CF_2CN$ D E B A F D C	9.7(A), 14.5(B,C), 19.4(B,C), 28.2(D), 43.1(E), 47.3(F)	3.40[c]

[a] Parts per million upfield from trifluoroacetic acid. [b] Acetaldehyde reference. [c] Tetramethylsilane reference.

chloride showed that the mixture contained 10.5% KCl. All attempts to obtain compound VII free from KCl by extraction, recrystallization, or sublimation were unsuccessful.

The melting point of the tricarboxylic acid was found by differential scanning calorimetry to be 220°.

Tris(3-carbamylperfluoropropyl)hydroxylamine (VIII).—Ethyl ether (150 ml) and $[CH_3O_2C(CF_2)_3]_2NO(CF_2)_3CO_2CH_3$ (VI) (113.5 g, 0.173 mol) were placed in a 250-ml flask and cooled in ice water. Ammonia was bubbled into the solution with rapid stirring until uptake of ammonia ceased. Ether was removed under vacuum and the residue was ground to a powder and dried in a vacuum oven at 50° to give 65 g (72% conversion) of a white solid, mp 157–160°. Infrared and nmr analysis were consistent with the structure $[H_2NOC(CF_2)_3]_2NO(CF_2)_3CONH_2$.

Anal. Calcd for $C_{12}H_6F_{18}N_4O_4$: C, 23.50; H, 0.98; F, 55.90; N, 9.15. Found: C, 23.59; H, 1.03; F, 55.54; N, 9.19.

Tris(3-cyanoperfluoropropyl)hydroxylamine (IX).—A 250-ml flask containing thoroughly mixed P_2O_5 (150 g) and the triamide (VIII) (72.6 g, 0.119 mol) from the preceding reaction was heated to 200° under vacuum. A liquid product distilled from the flask and was caught in a cold trap. Distillation gave 21.7 g (33% conversion) of $[NC(CF_2)_3]_2NO(CF_2)_3CN$ boiling at 110–115° (60 mm). Infrared and nmr analysis were consistent with the assigned structure.

Anal. Calcd for $C_{12}F_{18}N_4O$: C, 25.82; F, 61.28; N, 10.04. Found: C, 25.68; F, 61.12; N, 10.16.

Hydrolysis of Methyl 4-Nitrosoperfluorobutyrate.—Methyl 4-nitrosoperfluorobutyrate (10 g, 0.042 mol) was placed in an erlenmeyer flask containing distilled water (60 ml) and a magnetic stirring bar. The aqueous layer gradually acquired a blue color as the ester hydrolyzed. After 5 days the lower, organic layer was not longer present. The product, 4-nitrosoperfluorobutyric acid (7.0 g, 75% conversion), was isolated by salting out with sodium chloride.

Registry No.—I, 16005-34-8; II, 16005-35-9; III, 7660-01-7; IV, 16031-01-9; V, 16031-02-0; VI, 16005-37-1; VII, 16005-24-6; VIII, 16005-25-7; IX, 16005-26-8.

Acknowledgment.—We wish to express our appreciation to Dr. Wallace S. Brey of the University of Florida, Department of Chemistry, for carrying out and interpreting the nmr analyses reported here.

A Superior Method for Preparing Sulfinyl Chlorides[1a]

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Previous papers from this laboratory have reported that sulfinyl chlorides can be prepared by the solvolysis of organosulfur trichlorides[2] or by the action of chlorine on a mixture of disulfide and glacial acetic acid.[3] Both of these methods have the disadvantage that a large volume of hydrogen chloride is produced in the reaction.

We have recently observed that if an anhydrous mixture of an alkyl or aryl disulfide and acetic anhydride is chlorinated at 0° to −10° the disulfide is smoothly converted into the corresponding sulfinyl chloride and the anhydride is converted into acetyl chloride. The over-all reaction is shown in eq 1. The

$$RSSR + 2(CH_3CO)_2O + 3Cl_2 \longrightarrow 2R\overset{O}{S}Cl + 4CH_3COCl \quad (1)$$

end point of the chlorination is indicated by the disappearance of the colored sulfenyl chloride formed by the reaction shown in eq 2. The other sequential steps are

$$RSSR + Cl_2 \longrightarrow 2RSCl \quad (2)$$

shown in eq 3 and 4. Reaction 4 is noteworthy in that

$$RSCl + Cl_2 \longrightarrow RSCl_3 \quad (3)$$

$$RSCl_3 + (CH_3CO)_2O \longrightarrow RSOCl + 2CH_3COCl \quad (4)$$

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(1) (a) Taken in part from the Ph.D. Thesis of R. V. Norton, University of Maine, Orono, Maine, 1967; (b) to whom inquiries should be sent.

(2) I. B. Douglass and D. R. Poole, *J. Org. Chem.*, **22**, 536 (1957).

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