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RESEARCH IN NF COMPOUNDS

By

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ABSTRACT

2, 2-Diperchloratopropane was further characterized by equivalent weight determination. It failed to react with potassium fluoride. Reactions of perfluoroacetone and of cyclopentanone with perchloric acid were investigated.

Iodine and bis(carboalkoxyfluoramino)mercury gave isopropyl fluoroiodocarbamate, which reacted with cyclopentene and cyclohexene to give the corresponding 2-(carboisopropoxyfluoramino)iodocycloalkanes. The mercury compound reacted with thionyl chloride to give N, N'-difluoro-N, N'-bis(carboisopropoxy)sulfurous acid amide, with benzyl bromide to give isopropyl N-fluoro-N-benzylcarbamate and with trimethylchlorosilane to give carboisopropoxyfluoraminotrimethylsilane. The latter reacted with 2-fluoro-2, 2-dinitroethanol to give (2-fluoro-2, 2-dinitroethoxy)-trimethylsilane. The mercury compound reacted with diphenyldichlorosilane to give bid(carboalkoxyfluoramino)diphenylsilane.

The silver salt of isopropyl fluorocarbamate was prepared from silver oxide and isopropyl fluorocarbamate. It reacted with bromoethane to give isopropyl N-ethylfluorocarbamate. The silver salt and N-bromosuccinimide gave isopropyl bromofluorocarbamate and isopropyl fluoroformate. The silver salt and chlorotriphenylmethane gave isopropyl triphenylmethylfluorocarbamate.

A manuscript covering earlier work on reactions of 2-fluoro-2, 2-dinitroethanol is included as an appendix.

CONTRACT FULFILLMENT STATEMENT

This annual technical report is submitted in partial fulfillment of the contract and covers the period from 1 December 1969 through 1 June 1970.

AEROJET-GENERAL CORPORATION

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CONTENTS

INTRODUCTION

The objectives of this program are to develop synthesis methods for new types of high-energy compounds and to increase our understanding of the processes involved. Work was continued in perchloric acid chemistry, an area of investigation which we entered in the preceding report period. The mercury derivative of a fluorocarbamate was first prepared in the preceding report period. Reactions of this compound and the subsequently prepared silver derivative, leading to novel types of heteroatom NF compounds were explored.

Some earlier work in fluoronitro chemistry was assembled as a journal manuscript and is included as an appendix. Some of this work was supported by the Naval Ordnance Laboratory and the Air Force Armament Laboratory under Contracts N60921-67-C-0290 and F08635-69-C-0125.

PERCHLORIC ACID CHEMISTRY

In the preceding report*, the preparation and characterization of gem-diperchlorates from the reaction of acetone and of 2-butanone with perchloric acid in halogenated solvents was described. The acetone product was characterized further by equivalent weight determination. Quenching the material with ice followed by alkali titration gave an equivalent weight of 126 compared to 120.5 theoretical for the diperchlorate.

To determine the effects of electronegative substiuents on this reaction, perfluoroacetone was examined as a substrate. Condensing perfluoroacetone into a slight excess of a solution of anhydrous perchloric acid in chloroform appeared to proceed in the same manner as the acetone reaction. A heavy liquid separated. Stripping the organic solutions gave a pale yellow liquid which detonated immediately on exposure to the atmosphere.

Cyclopentanone also reacted with perchloric acid under the same conditions used for acetone. The mmr spectrum showed an A_2B_2 pattern, with members of equal area centered at δ 2.2 and 2.8. Analytical data, however, was erratic (calc'd: C 22.5; H 3.00;
found: C, 14.55 to 17.65; H, 1.93 to 3.25)

A solution of 2,2-diperchloratopropane in methylene chloride was treated with solid potassium fluoride at room temperature. No reaction took place.

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*Aerojet-General Report 5015-2, January 1970, p. 2

REACTIONS OF BIS(CARBOISOPROPOXYFLUORAMINO)MERCURY

In the preceding report* the synthesis of bis(carboisopropoxyfluoramino) mercury from mercuric oxide and isopropyl N-fluorocarbamate in ether was described. The compound gave insertion products with olefins.

Subsequently, the rate of formation of bis(carboisopropoxyfluoramino) mercury was improved considerably by using as the solvent, methylene chloride, in which the product was found to be soluble. In ether the product was insoluble and coated the unreacted mercuric oxide. Bis(carboisopropoxyfluoramino)-mercury was also prepared in aqueous solutions, but the reaction was slow because of product insolubility.

The fluorine nmr spectrum of bis(carboisopropoxyfluoramino)mercury ($CDCl_3$) consists of a very broad signal of ϕ 88.9. The spectrum in dimethyl sulfoxide consisted of two broad signals of ϕ 91.2 and 95.6. The two signals sharpened on heating.

The observed insertion reactions of cyclohexene and hexene-1 with bis(carboisopropoxyfluoramino)mercury suggested that other reactions of this mercury compound might parallel those of simple dialkylmercury derivatives. Consequently, a number of such reactions were investigated.

The halogenation of bis(carboisopropoxyfluoramino)mercury was expected to give the corresponding isopropyl halofluorocarbamates and mercuric halides:

$$Hg(NFCO_2C_3H_7)_2 + 2X_2 \longrightarrow 2\,XNFCO_2C_3H_7 + HgX_2$$

$$X = Cl,\ Br,\ \text{or}\ I.$$

This reaction offered a route to N-fluoro-N-iodo derivatives, an unreported class of compounds. When iodine was added to a methylene chloride or carbon tetrachloride solution of bis(carboisopropoxyfluoramino)mercury, the violet

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[*] Aerojet-General Corporation Report No. 5015-2, January 1970, p. 12.

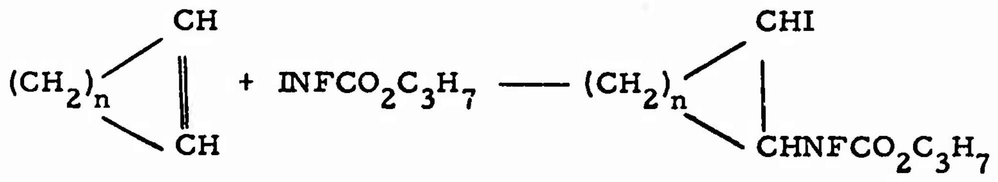
color was bleached instantaneously, and mercuric iodide precipitated. Isopropyl fluoroiodocarbamate was identified in carbon tetrachloride solution by nmr spectrum. The proton spectrum showed the expected isopropyl group, and the fluorine spectrum exhibited a somewhat broadened singlet at ϕ 19.9*. This chemical shift continues the trend shown by those of previously reported** halofluorocarbamates.

Fluorine Chemical Shifts of $XNFCO_2R$

X	=	F	Cl	Br	I
ϕ^*	=	-32.7	-2.6	5.5	19.9

An attempt to strip a methylene chloride solution at ambient temperature resulted in an explosion before the solvent was completely removed. No further attempts were made to isolate the material.

Additional evidence for the fluoroiodocarbamate structure was obtained from its reaction with olefins. Isopropyl fluoroiodocarbamate solutions reacted instantaneously with cyclopentene and cyclohexene and the products were characterized as the 2-(carboisopropoxyfluoramino)iodocycloalkanes:



n = 3 or 4

The fluorine nmr spectra of these adducts were similar to those of the chlorofluorocarbamate and bromofluorocarbamate adducts except that only one (<u>cis</u> or <u>trans</u>) isomer of the N-alkyl fluorocarbamate was formed, and larger amounts of fluoriminocarbonates were produced.

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*V. Grakauskas and K. Baum, J. Am. Chem. Soc., 91, 1679 (1969).

**Aerojet-General Corporation, Report No. 5015-2 (Annual), January 1970, p. 14.

Bis(carboisopropoxyfluoramino)mercury reacted with thionyl chloride to give N, N-difluoro-N, N'-bis(carboisopropoxy)sulfurous acid amide:

$$Hg(NFCO_2C_3H_7)_2 + SOCl_2 \longrightarrow SO\ (NFCO_2C_3H_7)_2 + HgCl_2$$

The mercurial reacted slowly (3 days) with benzyl bromide to give isopropyl N-fluoro-N-benzylcarbamate:

$$Hg(NFCO_2C_3H_7)_2 + 2C_6H_5CH_2Br \longrightarrow 2C_6H_5CH_2NFCO_2C_3H_7 + HgBr_2$$

Reaction with bromocyclohexane, on the other hand, did not yield the expected alkylation product, isopropyl N-cyclohexyl-N-fluorocarbamate. The products of this reaction were cyclohexene, fluorocarbamate and mercuric bromide:

$$2\ C_6H_{11}Br + Hg(NFCO_2C_3H_7)_2 \longrightarrow 2\ C_6H_{10} + 2\ NHFCO_2C_3H_7 + HgBr_2$$

Bis(carboisopropoxyfluoramino)mercury was examined in silylation reactions. The compound reacted readily with trimethylchlorosilane and the product was identified as carboisopropoxyfluoraminotrimethylsilane:

$$Hg(NFCO_2C_3H_7)_2 + 2(CH_3)_3SiCl \longrightarrow 2(CH_3)_3SiNFCO_2C_3H_7 + HgCl_2$$

Subsequently, the same compound was obtained in direct silylation of isopropyl N-fluorocarbamate with N, O-bis(trimethylsilyl)acetamide:

$$2NHFCO_2C_3H_7 + CH_3C\left[= NSi(CH_3)_3\right] OSi(CH_3)_3 \longrightarrow 2(CH_3)_3SiNFCO_2C_3H_7 + CH_3CONH_2$$

Carboisopropoxyfluoraminotrimethylsilane, characterized by elemental analysis and nmr spectra, represents a novel type of bonding where the NF moiety is attached to a silicon atom. The fluorine nmr spectrum of the silane exhibited three signals: two sharp doublets at ϕ^* 79.8 and 80.6 and a broad signal at ϕ^* 108. The latter signal, assigned to the silane, resolved into two sharp singlets separated by 325 Hz when the nmr sample was cooled to <u>ca</u> -50°.

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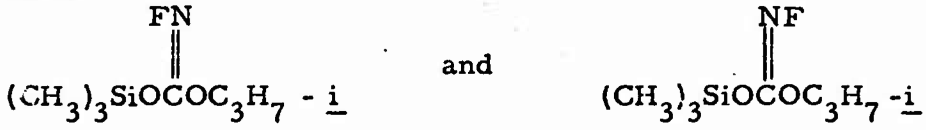
* Aerojet-General Corporation Report No. 5015-2 (Annual), January 1970, p. 9.

The 108 signal sharpened when the sample was warmed to 40-50°. This temperature dependance of the ϕ^* 108 signal was attributed to restricted rotation of the silane molecule around N-C bond, analogous to that observed for simple amides. The two relatively weak singlets of unequal area, were assigned to the syn- and anti-isomers of isopropyl trimethylsilyl fluorimino-carbonates:



$$(CH_3)_3SiO\overset{\overset{FN}{\|}}{C}OC_3H_7\text{-}\underline{i} \quad \text{and} \quad (CH_3)_3SiO\overset{\overset{NF}{\|}}{C}OC_3H_7\text{-}\underline{i}$$

These products are analogous to the fluoriminocarbonates obtained in reactions of fluorohalocarbamate with olefins.

Carboisopropoxyfluoraminotrimethylsilane is hydrolyzed only very slowly by water, probably because of its insolubility. The compound reacts readily with alcohols. Its reaction product with 2-fluoro-2, 2-dinitroethanol was characterized as 2-fluoro-2, 2-dinitroethoxytrimethylsilane:

$$(CH_3)_3SiNFCO_2C_3H_7 + FC(NO_2)_2CH_2OH \longrightarrow (CH_3)_3SiOCH_2CF(NO_2)_2 + NHFCO_2C_3H_7$$

Carboisopropoxyfluoraminotriethylsilane was obtained in the reaction of bis(carboisopropoxyfluoramino)mercury with triethylchlorosilane. Its fluorine nmr spectrum was analogous to that of the trimethyl homologue.

The silylation of fluorocarbamates was extended to difunctional compounds. Bis(carboisopropoxyfluoramino)mercury reacted with diphenyldichlorosilane to give bis(carboisopropoxyfluoramino)diphenylsilane:

$$Hg(NFCO_2C_3H_7)_2 + (C_6H_5)_2SiCl_2 \longrightarrow (C_6H_5)_2Si(NFCO_2C_3H_7)_2 + HgCl_2$$

The compound was characterized by elemental analysis. Its proton nmr spectrum was consistent with the above structure. The fluorine spectrum consisted of a singlet at ϕ^* 75.2. The compound is much more susceptible

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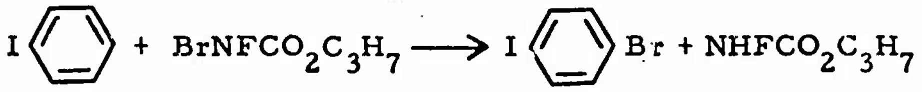
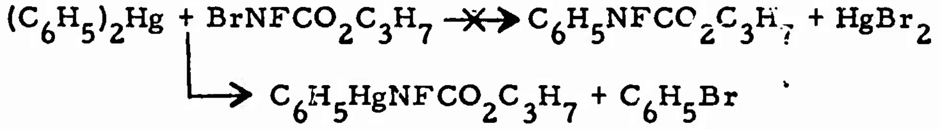
[*] Aerojet-General Corporation Report No. 5015-2 (Annual), January 1970, p. 9.

to hydrolysis than carboisopropoxyfluoraminotrimethylsilane; it hydrolyzed slowly in the air, and instantaneously when added to water. A dry box, however, was not needed for its preparation, purification, and analysis.

Isopropyl bromofluorocarbamate reacted with iodobenzene to give p-bromoiodobenzene:



The reaction of bromofluorocarbamate with diphenylmercury gave carboisopropoxyfluoramineophenylmercury instead of the desired isopropyl N-fluoro-N-phenylcarbamate:



$$(C_6H_5)_2Hg + BrNFCO_2C_3H_7 \not\rightarrow C_6H_5NFCO_2C_3H_7 + HgBr_2$$

$$\rightarrow C_6H_5HgNFCO_2C_3H_7 + C_6H_5Br$$

Experimental

Bis(carboisopropoxyfluoramino)mercury

1. Improved Method - To a stirred solution of 24.5 g (0.2 mol) of isopropyl fluorocarbamate in 170 ml of methylene chloride was added portionwise (5 min) 21.6 g (0.1 mol) of yellow mercuric oxide. In 10 min a cloudy, colorless solution resulted. The solution was decanted from a small amount of sticky solid and diluted with an equal volume of chloroform. On standing at 0° overnight the mercury compound crystallized as a fluffy white solid. The compound was collected in a funnel, washed with cold chloroform and air-dried (25 g). An additional 16 g was obtained when the mother liquor was concentrated to concentrated to 70 ml (93% yield).

2. Aqueous Method - To a solution of 2.42 g (0.02 mol) of isopropyl fluorocarbamate in 100 ml of water was added 2.16 g (0.01 mol) of yellow mercuric oxide and the mixture was stirred vigorously at 25° for 8 hours. The mixture of bis(carboisopropoxyfluoramino)mercury and mercuric oxide was filtered, washed with water, and air-dried. The crude material was crystallized from chloroform to give 1.7 g (40% conversion, 90% yield) of bis(carboisopropoxyfluoramino)mercury mp 132° (d); 1.1 g of mercuric oxide was recovered.

Isopropyl N-Fluoro-N-iodocarbamate - To a stirred suspension of 1.1 g (0.0025 mol) of bis(carboisopropoxyfluoramino)mercury in 35 ml of methylene chloride was added portionwise, over a period of 10 min, 1.27 g (0.005 mol) of iodine (I_2). Initially, the violet color of iodine was discharged rapidly, but when half of iodine was consumed, the mixture gradually darkened. Yellow mercuric iodide precipitated. The dark red reaction mixture was filtered and the filtrate containing isopropyl N-fluoro-N-iodocarbamate was used in the reaction with cyclohexene (see below).

In another experiment an attempt was made to distill the product, but the mixture exploded when most of the methylene chloride was removed at 25° at reduced pressure.

In another experiment, isopropyl N-fluoro-N-iodocarbamate was prepared as above but in carbon tetrachloride (20 ml) rather than methylene chloride solution. Proton nmr spectrum (CCl_4): δ4.99 (septet, J = 6.3 Hz, CH) and 1.36 (d, J = 6.3 Hz, $2CH_3$). Fluorine nmr: ϕ^* 19.9 (s).

2-(Carboisopropoxyfluoramino)iodocyclohexane - To the methylene chloride solution of isopropyl fluoroiodocarbamate prepared above was added 4 g of cyclohexene. In 10 min, the originally dark red solution was bleached. The solution was concentrated and the pale-yellow liquid was dried at 85°/0.1 mm to give 0.9 g of 2-(carboisopropoxyfluoramino)iodocyclohexane. The material was not further purified.

Anal. Calcd for $C_{10}H_{17}NFIO_2$: C, 36.5; H, 5.2; N, 4.3; F, 5.8. Found: C, 37.0: H, 5.4; N, 3.7; F, 5.2

Proton nmr spectrum ($CDCl_3$): δ 5.91 (m, ring -CHO), 5.15 (septet, J = 6.3 Hz, isopropyl CH), 4.42 (m, ring CHI and CHNF-), 2.8 - 1.3 (complex multiplets of ring CH_2), and 1.38 (d, J = 6.2 Hz, 2 CH_3). Fluorine nmr: ϕ^* 87.6 (s), 88.1 (s), and 92.7 (d, J = 37 Hz).

2-(Carboisopropoxyfluoramino)iodocyclopentane - The title compound was obtained quantitatively by the above procedure. The compound, a pale-yellow liquid, was dried at 65°/0.1 mm and was not further purified.

Anal. Calcd for $C_9H_{15}NFIO_2$: C, 34.3; H, 4.8; N, 4.4; F, 6.0.

Found: C, 34.4; H, 4.8; N, 4.4; F, 6.3.

Proton nmr spectrum (neat): δ4.96 (septet, J = 6.1 Hz, CH of isopropyl group), 4.71 (multiplet, CHNF), δ4.32 (multiplet, CHI), 1.8 (m, ring CH_2), and 1.32 (d, J = 6.1 Ha, 2 CH_3). Fluorine nmr: ϕ85.1 (s), 87.1 (s), and 89.9 (d, J_{HF} = 42.6 Hz).

N, N'-Difluoro-N, N'-di(carboisopropoxy)sulfurous Acid Amide - To a stirred solution of 2.2 g (0.005 mol) of bis(carboisopropoxyfluoramino)mercury in 85 ml of methylene chloride was added a solution of 0.6 g (0.005 mol) of thionyl chloride in 5 ml of methylene chloride. The reaction mixture turned turbid. After 45 min, the mixture was filtered to remove mercuric chloride. The filtrate was concentrated and the residual viscous pale-yellow oil was dried at 75°/0.01 mm. The material amounting to 1.1 g was not further purified.

Anal. Calcd for $C_8H_{14}N_2F_2SO_5$: C, 33.3; H, 4.9; N, 9.8; F, 13.2. Found: C, 33.7; H, 5.0; N, 9.9; F, 12.6.

Proton nmr spectrum (CCl_4): δ5.29 (septet, J = 6.4 Hz, 2 CH) and 1.45 (d, J = 6.4 Hz, 2 CH_3). Fluorine nmr: ϕ^* 74.4 (s). Infrared spectrum, peaks at μ: 3.35 (m), 3.41 (sh), 3.47 (sh), 5.62 (s), 5.78 (s), 6.85 (m), 6.90 (sh), 7.22 (sh), 7.29 (m), 7.41 (m), 7.48 (sh), 7.78-8.40 (broad, s), 8.49 (s), 8.75 (m), 9.15 (s), 9.40 (m), 11.12 (m), 11.25 (m), 12.07 (m), 13.20 (m), and 14.40 (m).

Isopropyl N-Benzyl-N-fluorocarbamate - A suspension of 2.2 g (0.005 mol) of bis(carboisopropoxyfluoramino)mercury and 0.85 g (0.005 mol) of benzyl bromide in 40 ml of methylene chloride was allowed to stand at ambient temperature for 5 days. The mixture was treated with 20 ml of carbon tetrachloride, cooled to -20° to precipitate a small amount of dissolved mercuric bromide, and filtered. The filtrate was distilled to give 1.1 g (95% yield) of isopropyl N-benzyl-N-fluorocarbamate, bp 77-78°/0.1 mm.

Anal. Calcd for $C_{11}H_{14}NFO_2$: C, 62.6; H, 6.6; N, 6.6; F, 9.0. Found: C, 62.2; H, 6.4; N, 6.2; F, 9.0.

Proton nmr spectrum (CCl_4): δ 7.26 (s, ring protons), 4.73 (d, J_{HF} = 35.2 Hz, CH_2NF), 4.94 (septet, J = 6.3 Hz, isopropyl CH), and 1.9 (d, J = 6.3 Hz, 2 CH_3). Fluorine nmr: ϕ^* 66.7 (t, J_{HF} = 33 Hz).

Reaction of Bis(carboisopropoxyfluoramino)mercury with Bromocyclohexane -

A suspension of 2.2 g (0.005 mol) of bis(carboisopropoxyfluoramino)mercury in *ca* 25 g of bromocyclohexane was allowed to stand at 25°. No noticeable reaction was observed during the first week, but during the subsequent 7 days the mercury compound gradually disappeared. The mixture was filtered to remove mercuric bromide and the filtrate was examined by nmr. The proton and fluorine nmr spectra showed that the products of this reaction were isopropyl fluorocarbamate and cyclohexene.

Carboisopropoxyfluoraminotrimethylsilane

1. From Trimethylchlorosilane - To a stirred suspension of 4.4 g (0.01 mol) of bis(carboisopropoxyfluoramino)mercury in 35 ml of methylene chloride was added dropwise over a period of 5 min a solution of 2.2 g (0.02 mol) of trimethylchlorosilane in 10 ml of methylene chloride. The mercurial was consumed rapidly and mercuric chloride deposited. After 10 minutes, the mixture was filtered and the filtrate was distilled to give 3.35 g (8% yield) of carboisopropoxyfluoraminotrimethylsilane, bp 75°/25 mm, n_D^{23} 1.4095.

Anal. Calcd for $C_7H_{16}NFSiO_2$: C, 43.5; H, 8.3; N, 7.2; F, 9.8. Found: C, 43.2; H, 8.4; N, 7.4; F, 9.5.

Proton nmr spectrum (CCl_4): δ 4.98 (septet, J = 6.1 Hz, CH), 1.28 (d, J = 6.1 Hz, 2 CH_3) and 0.38 (superposition of sharp singlets, CH_3Si). Fluorine nmr: ϕ^* 79.4 (s), 80.4 (s), and 108 (very broad signal). The latter signal resolved into two sharp singlets, separated by 325 Hz, when the sample was cooled to -40 to -50°, and sharpened into a singlet when the sample was warmed to 40-50°.

2. From Isopropyl Fluorocarbamate - To a stirred solution of 4.85 g (0.04 mol) of isopropyl N-fluorocarbamate in 60 ml of methylene chloride was added 4.05 g (0.02 mol) of N,O-bis(trimethylsilyl)acetamide. After 5 hrs, the mixture was distilled to give 5.4 g of carboisopropoxyfluoraminotrimethylsilane, bp 30-31°/0.2 mm (57% yield).

Carboisopropoxyfluoraminotriethylsilane - bp 55-56°/0.1 mm was obtained in 85% yield by reacting bis(carboisopropoxyfluoramino)mercury with equimolar amount of triethylchlorosilane.

Anal. Calcd for $C_{10}H_{22}NFO_2$: C, 51.1; H, 9.4; N, 6.0; F, 8.1. Found: C, 50.9; H, 9.8; N, 6.0; F, 8.1.

The differential thermal analysis showed an exotherm of 170°. Proton nmr spectrum: δ 4.99 (septet, CH), 1.32 and 1.30 (doublets for two different CH_3 of isopropyl groups), ~ 1.0, multiplets of CH_2 and CH_3 of the three ethyl groups. Fluorine nmr: ϕ^* 78.9 (s), 79.8 (s) and two very broad signals at 106 and 111.

2-Fluoro-2,2-dinitroethoxytrimethylsilane - To a solution of 0.92 g (0.005 mol) of carboisopropoxyfluoraminotrimethylsilane in 15 ml of methylene chloride was added 0.77 g (o.005 mol) of 2-fluoro-2,2-dinitroethanol. After 4 days the solution was distilled to give 1.65 g of colorless liquid, bp 29-33°/ 0.05 mm which was found (nmr) to be a mixture of the desired silane and isopropyl N-fluorocarbamate. The mixture was washed with 25 ml of saturated aqueous sodium bicarbonate and an insoluble heavy liquid was separated, dried, and redistilled to give 0.5 g of 2-fluoro-2,2-dinitroethoxytrimethylsilane, bp 29°/0.1 mm, n_D^{23} 1.4095.

Anal. Calcd for $C_5H_{11}N_2FCl_5Si$: C, 26.6; H, 5.0; N, 12.4; F, 8.4. Found: C, 26.3; H, 4.9; N, 12.1; F, 8.7. Proton nmr spectrum (CCl_4): δ 4.62 (d, J_{HF} - 17.9 Hz, CH_2) and 0.21 (s, $3CH_3$). Fluorine nmr: ϕ^* 112.8 (t).

Bis(carboisopropoxyfluoramino)diphenysilane - to a stirred suspension of 2.2 g (0.005 mol) of bis(carboisopropoxyfluoramino)mercury in 45 ml of chloride was added 1.25 g (0.005 mol) of diphenyldichlorosilane. After 5 min, the mixture was filtered and the solvent was removed. The pale-yellow liquid, bis(carboisopropoxyfluoramino)diphenylsilane, was dried at 50°/0,1 mm (2.1 g). The material was not further purified.

Anal. Calcd for $C_{20}H_{24}N_2F_2O_4Si$: C, 56.9; H, 5.7; N, 6.6; F, 9.0. Found: C, 56.8; H, 5.6; N, 6.1; F, 8.8.

Proton nmr spectrum (CCl_4): δ 7.9-7.1, complex multiplets of aryl protons, 4.61 (septet, J = 6.1 Ha, isopropyl CH), and 1.13 (superposition of doublets, $J \cong 6$ Hz, $2CH_3$). Fluorine nmr: ϕ^*75.2 (s).

Carboisopropoxyfluoraminophenylmercury - To a stirred solution of 1.77 g (0.005 mol) of diphenylmercury in 25 ml of methylene chloride was added dropwise over a period of 5 min 1.0 g (0.005 mol) of isopropyl bromofluorocarbamate resulting in a mildly exothermic reaction. After 10 minutes, the mixture was distilled to give 0.7 g of bromobenzene, bp 53°/25 mm (identified by ir). A solid remaining in the distillation flash was crystallized from chloroform - hexane to give 1.9 g (95% yield) of carboisopropoxyfluoraminophenylmercury, mp 133° (d), a white crystalline solid.

Anal. Calcd for $C_{10}H_{12}NFO_2Hg$: C, 30.2; H, 3.0; N, 3.5; F, 4.8. Found: C, 29.9; H, 2.8; N, 3.6; F, 5.1.

Proton nmr spectrum ($CDCl_3$): δ 7.33 (s, aromatic protons), 5.03 (septet, J = 6.2 Hz, isopropyl CH), and 1.31 (d, J = 6.3 Hz, $2CH_3$). Fluorine nmr: ϕ^* 93.9 (s) and 102.9 (s).

1-(Carboisopropoxyfluoramino)-2-bromohexane - A solution of 0.45 g (0.0054 mol) of hexene-1 and 1.0 g (0.005 mol) of isopropyl bromofluorocarbamate in 20 ml of methylene chloride was allowed to stand at 25° for 18 hrs. The mixture was distilled to give 1.3 g (92% yield) of the title compound, bp 72-73°/0.025 mm, identical with that reported previously.

Reaction of Isopropyl Bromofluorocarbamate with Iodobenzene - A solution of 1.02 g (0.005 mol) of iodobenzene and 1.0 g (o.005 mol) of isopropyl bromofluorocarbamate in 10 ml of methylene chloride was allowed to stand at 25° for 8 days. The mixture was distilled to give 0.5 g of isopropyl N-fluorocarbamate (identified by its ^{19}F nmr spectrum). A solid remaining in the distillation flask was crystallized from 3 ml of methylene chloride to give 1.3 g of p-bromoiodobenzene, mp 91-93° (rep[**] mp 91°). The compound (Anal: Calcd for C_6H_4BrI: C, 25.4; H, 1.4. Found: C 25.6; H, 1.3) was also characterized by proton nmr.

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[*] Aerojet-General Corporation Report No. 5015-2 (Annual), January 1970, p. 16.

[**] P. S. Varma and S. Shankararayanan, J. Indian Chem. Soc., 13, 31 (1936).

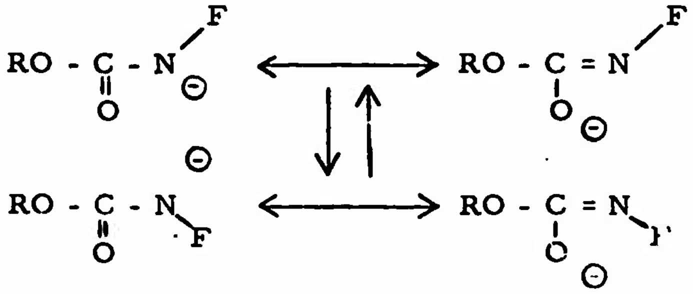
SILVER FLUOROCARBAMATES

The reaction of silver nitrate with an aqueous solution of the sodium salt of isopropyl fluorocarbamate was found previously to give a silver mirror in a complex reaction.* Recent success in preparing the corresponding mercury salt under anhydrous conditions prompted a reinvestigation of this reaction.

Silver oxide was found to react with a solution of isopropyl fluorocarbamate in methylene chloride to give a white solid which was identified by elemental analysis and nmr as the silver salt of isopropyl fluorocarbamate. When a slight excess of fluorocarbamate was used, the conversion of silver oxide was quantitative.

$$2(CH_3)_2CHOCONHF + Ag_2O \longrightarrow 2(CH_3)_2CHOCONF\ Ag$$

The silver salt was insoluble in methylene chloride, ether, hydrocarbons, and water, but was soluble in dimethyl sulfoxide and in acetonitrile. The fluorine nmr spectrum in dimethyl sulfoxide consisted of two signals, slightly broadened singlets at ϕ^* 94.2 and 99.7 with relative areas of 2:3. This spectrum is most readily rationalized in terms of a resonance stabilized ionic or ion pair structure, with negative charge distributed between the nitrogen and oxygen atoms. Partial double bond character of the carbon-nitrogen bond would give spectroscopically distinguishable <u>cis</u> and <u>trans</u> forms, which would be in equilibrium.



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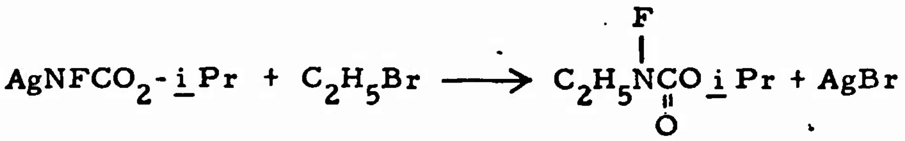
*Aerojet-General Report No. 3551, July, 1968, p. A-3 (Confidential).

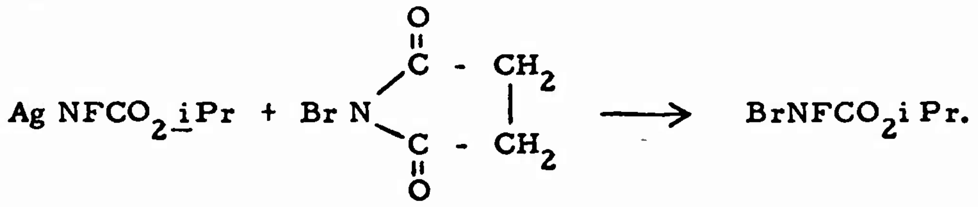
The silver salt of isopropyl fluorocarbamate decomposed at 120-130° on a melting point block, but a 1 g sample heated under vacuum exploded at 100°. No volatile pyrolysis products were isolated at lower temperatures. The dry salt is sensitive to friction, and care must be used in removing the material from sintered glass filters.

The reaction of the silver salt of isopropyl fluorocarbamate with alkylating agents was studied. Bromoethane was found to react heterogeneously with the salt at room temperature to give isopropyl N-ethylfluorocarbamate. By contrast, aqueous alkali salts of fluorocarbamates require strong alkylating agents such as dimethyl sulfate.



$$\mathrm{AgNFCO_2\text{-}\underline{i}\,Pr} + \mathrm{C_2H_5Br} \longrightarrow \mathrm{C_2H_5}\overset{\displaystyle F}{\overset{|}{N}}\underset{\displaystyle O}{\underset{\|}{C}}\mathrm{O\,\underline{i}\,Pr} + \mathrm{AgBr}$$

The reaction of the silver salt of isopropyl fluorocarbamate with isopropyl bromofluorocarbamate was examined with the objective of preparing the difluorohydrazine derivative. The only product isolated after a 2-day reaction period with methylene chloride as solvent was isopropyl fluorocarbamate. The reaction of the silver salt with N-bromosuccinimide, also examined with the objective of preparing a fluorohydrazine, resulted in a bromination reaction. Isopropyl bromofluorocarbamate was obtained. In addition isopropyl fluoroformate was formed in a mechanistically obscure reaction.



The reaction of the silver salt with 2,4-dinitrobenzenesulfenyl chloride resulted only in the isolation of isopropyl fluorocarbamate. Since the free radical $\mathrm{RO}\underset{O}{\underset{\|}{C}}\mathrm{NF}$ has been shown to abstract hydrogens even from simple hydrocarbons,* the result is not surprising inasmuch as the dinitrobenzenesulfenyl moiety is a good free radical source.

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*Aerojet-General Report No. 5015-2, January 1970

The silver salt of isopropyl fluorocarbamate reacted with triphenylmethyl chloride to give isopropyl triphenylmethylfluorocarbamate, a viscous oil which could not be crystallized or distilled. The compound was identified by nmr spectra. The driving force of the formation of the highly stable triphenylmethyl cation was not sufficient to give ionic character to this NF compound. The fluorine spectrum was a singlet at ϕ^* 64.4, which is in the normal region for N-substituted fluorocarbamates.

$$(C_6H_5)_3C\ Cl + Ag\ NFCO_2\underline{i}\ Pr \longrightarrow (C_6H_5)_3C\text{-}NFCO_2\underline{i}Pr$$

The silver salt was not sufficiently reactive to be alkylated by iodobenzene. The starting materials were recovered. Likewise, no reaction took place with toluenesulfonyl chloride. The silver salt reacted with cyclohexene to give a complex nonvolatile product which gave analyses indicating several cyclohexyl units were condensed with each fluorocarbamate unit.

Experimental

Silver Salt of Isopropyl Fluorocarbamate - Silver oxide (0.58 g, 0.010 mol Ag_2O) was added to a solution of 0.80 g (0.66 mol) of isopropyl fluorocarbamate in 10 ml of methylene chloride. The suspension was stirred for 2 hrs, until the precipitate became white. The solid was filtered, washed with methylene chloride and dried under a stream of nitrogen to give 1.1 g of white solid (96.5% yield).

Anal. Calcd for Ag $C_4H_7NO_2F$: C, 21.05; H, 3.07; N, 6.15; F, 8.34. Found: C, 20.84; H, 2.69; N, 5.84; F, 8.12.

The fluorine nmr spectrum consisted of two slightly broadened singlets at ϕ^* 94.2 and 99.7 (area ratio 2:3) in dimethyl sulfoxide.

On a melting point block, the material darkened gradually at 120-130° but did not melt. A 1.0 g sample was heated under vacuum to 100° over a 1-hr period, at which point it exploded. No volatile decomposition products were formed prior to the explosion.

The silver salt was stored for prolonged periods in a freezer with no observable decomposition. At ambient conditions without protection from light, darkening was noted after 24 hrs. The material is sensitive to friction, and care must be used in removing the dry salt from a sintered glass filter. In one case, a fume-off occurred as a result of scraping a metal spatula against a sintered glass funnel.

The salt has low solubility in pentane, methylene chloride, chloroform, ether and water. It is soluble in acetonitrile and dimethyl sulfoxide.

Isopropyl N-Ethylfluorocarbamate - Silver sluorocarbamate (1.0 g, 0.00438 mol) was added to 10 ml of bromoethane. Silver bromide formation appeared to be complete after 1 hr but the mixture was allowed to stand overnight. The mixture was filtered and the precipitate was washed with additional bromoethane. Distillation of the bromoethane solution gave 0.33 g (51% yield) of isopropyl N-ethylfluorocarbamate, bp 45° (5 mm); proton nmr δ 4.29 (septet, J = 6.2 Hz) and 1.32 (d, J = 6.2 Hz) isopropyl group, 1.24 (t, J = 7.0 Hz, $\underline{CH_3}CH_2$) and 3.64 (d of q, J_{HF} = 33.5 Hz, J_{HH} = 7.0 Hz, $CH_3\underline{CH_2}NF$); fluorine nmr ϕ^* 74.0 (t, J = 33.6 Hz); ir 5.72, 5.83 c=o.

Anal. Calcd for $C_6H_{12}NO_2F$: C, 48.32; H, 8.05; N, 9.40; F, 12.75.
Found: C, 47.96; H, 8.33; N, 9.27; F, 12.93.

Reaction of Silver Salt of Isopropyl Fluorocarbamate with Isopropyl Bromofluorocarbamate - A mixture of 0.80 g (0.0035 mol) of the silver salt of isopropyl fluorocarbamate and 0.67 g (0.0034 mol) of isopropyl fluorobromocarbamate in 4 ml of methylene chloride was allowed to stand 2 days at ambient temperature. The mixture was filtered and the solids were washed with methylene chloride. Removal of the solvent left 0.15 g of isopropyl fluorocarbamate, identified by its ir spectrum.

Reaction of the Silver Salt of Isopropyl Flurocarbamate with 2,4-Dinitrobenzenesulfenyl chloride - A mixture of 0.5 g of the silver salt, 0.6 g of 2,4-dinitrobenzenesulfenyl chloride and 4 ml of methylene chloride was allowed to stand 2 days at ambient temperature. The mixture was filtered and the solids were washed with methylene chloride. Distillation gave 0.15 g of isopropyl fluorocarbamate.

Reaction of the Silver Salt of Isopropyl Fluorocarbamate with N-Bromosuccinimide - A mixture of 6.7 g (0.0294 mol) of the silver salt of isopropyl fluorocarbamate, 5.24 g (0.0294 mol) of N-bromosuccinimide and 60 ml of methylene chloride was allowed to stand 24 hrs at ambient temperature. The mixture was centrifuged and the precipitate was washed with methylene chloride. The fluorine nmr spectrum of the solution showed only a broadened signlet at ϕ^* 6.09 (isopropyl bromofluorocarbamate)* and a symmetrical multiplet at ϕ^* 15.7 (isopropyl fluoroformate)**, in a ratio of 3:1. Distillation of the combined methylene chloride solutions gave 1.7 g (29% conversion) of isopropyl bromofluorocarbamate, bp 44° (1.5 mm). From the distillation residue 1.2 g of N-bromosuccinimide was recovered.

Reaction of the Silver Salt of Isopropyl Fluorocarbamate with Triphenylmethyl Chloride - Silver salt of isopropyl fluorocarbamate (4.56 g, 0.020 mol) was added to a solution of 5.0 g (0.018 mol) of triphenylmethyl chloride in 100 ml of methylene chloride. Silver chloride was precipitated immediately, and was removed by centrifuging. Removal of the solvent left a very viscous oil. Addition of pentane gave 1.08 g of white solid, mp 162-3°, identified as triphenylcarbinol. Removal of the solvent gave a viscous oil which was shown to be a mixture containing 86% isopropyl triphenylmethylfluorocarbamate and 14% isopropyl fluorocarbamate by nmr analysis. Proton nmr signals of isopropyl triphenylmethylfluorocarbamate were δ 7.0-7.6 (m, 18H, Ar-H), 4.71 (septet, 1 H, J = 6.1 Hz, $Me_2\underline{CH}$) and 0.93 (d, 6 H, J = 6.1 Hz, CH_3), and the fluorine spectrum (CCl_4) consisted of a singlet, ϕ^* 64.4.

Attempts to crystallize the compound from a variety of solvents were unsuccessful.

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*V. Graukauskas and K. Baum, J. Amer. Chem. Soc., 91, 1679 (1969).

**K. Baum, J. Org. Chem., 33, 4333 (1968).

Report No. 5015-3

APPENDIX

Alkylation Reactions of 2-Fluoro-2, 2-dinitroethanol[1]

Vytautas Grakauskas

Contribution from the Environmental Systems Division,
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ABSTRACT

2-Fluoro-2, 2-dinitroethanol in aqueous alkali reacted with dimethyl sulfate, allyl bromide, acetic, anhydride, ethyl chloroformate, and oxalyl chloride yielding 2-fluoro-2, 2-dinitroethyl methyl ether, allyl 2-fluoro-2, 2-dinitroethyl ether, 2-fluoro-2, 2-dinitroethyl acetate, ethyl 2-fluoro-2, 2-dinitroethyl carbonate, and 2-fluoro-2, 2-dinitroethyl oxalyl chloride, respectively. Ethylene oxide, propylene oxide, epihalohydrins, and butadiene dioxide yielded 2-fluoro-2, 2-dinitroethyl 2-hydroxyethyl ether, 2-fluoro-2, 2-dinitroethyl 2-hydroxylpropyl ether, 2-fluoro-2, 2-dinitroethyl glycidyl ether, and 4-(2-fluoro-2, 2-dinitroethoxy)-3-hydroxybutene-1, 2 oxide, respectively. Pyridine-catalyzed reactions of 2-fluoro-2, 2-dinitroethanol with thionyl chloride and sulfuryl chloride gave bis(2-fluoro-2, 2-dinitroethyl) sulfite and 2-fluoro-2, 2-dinitroethyl chloride, respectively. Tris-(2-fluoro-2, 2-dinitroethyl) borate was obtained in the ester-exchange reaction. Reactions of 2-fluoro-2, 2-dinitroethyl 2-hydroxyethyl ether, 2-fluoro-2, 2-dinitroethyl 2-hydroxypropyl ether, and 2-fluoro-2, 2-dinitroethyl oxalyl chloride were investigated.

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Although the synthesis of 2-fluoro-2,2-dinitroethanol was only recently reported,[2,3] the reactions of this unusual polynitroalcohol have been already explored by several groups of investigators.[2-6] 2-Fluoro-2,2-dinitroethanol undergoes deformylation in aqueous alkaline solutions in a manner similar to other 2,2-dinitroalcohols,[7] but unlike the other polynitroalcohols 2-fluoro-2,2-dinitroethanol in basic medium may also exist in equilibrium with its alkoxide ions:

$$FC(NO_2)_2CH_2OH \overset{OH^-}{\rightleftharpoons} FC(NO_2)_2CH_2O^- \rightleftharpoons FC(NO_2)_2^- + CH_2O$$

The dissociation to alkoxide ions, attributed to the reported destabilization of nitronate anion by α-fluorines,[8] was recently demonstrated in the Michael reaction of 2-fluoro-2,2-dinitroethanol with ethyl propiolate[6] where, in addition to 3-fluoro-3,3-dinitrocrotonate, the "normal" Michael adduct, β(2-fluoro-2,2-dinitroethoxy)acrylate was also obtained. This finding suggested that the observed alkoxide reaction may not be limited to the α,β-unsaturated carbonyl compounds, but may represent an example of much broader class of nucleophilic reactions of 2-fluoro-2,2-dinitroethoxide anions. With this anticipation in mind, alkali-catalyzed reactions of 2-fluoro-2,2-dinitroethanol with a number of electrophilic reagents were examined and the results are presented in this paper.

Aqueous alkaline 2-fluoro-2,2-dinitroethanol was reacted with dimethyl sulfate and allyl bromide at ambient temperature to give 2-fluoro-2,2-dinitroethyl methyl ether[9] (75% yield) and allyl 2-fluoro-2,2-dinitroethyl ether (30% yield), respectively.

$$\begin{aligned} \mathrm{FC(NO_2)_2CH_2OH + NaOH/H_2O} &\xrightarrow{\mathrm{(CH_3)_2SO_4}} \mathrm{FC(NO_2)_2CH_2OCH_3} \\ &\xrightarrow{\mathrm{CH_2{=}CHCH_2Br}} \mathrm{FC(NO_2)_2CH_2OCH_2CH{=}CH_2} \end{aligned}$$

The Williamson reactions of simple alcohols with dialkyl sulfates or alkyl halides are usually carried out in nonaqueous media under more rigorous reaction conditions.[10] The Williamson reactions of 2,2-dinitroalcohols were not investigated because in alkaline solution these polynitroalcohols undergo deformylation to nitronate salts.[7] Several known polynitroethers were synthesized indirectly. Thus, 2,2-dinitropropyl ethyl ether was obtained by addition of ethanol to 2-nitropropene, followed by the oxidative nitration of the adduct.[11]

In connection with characterization of polynitroethers, we synthesized 2,2-dinitropropyl methyl ether by heating 2,2-dinitropropanol with dimethyl sulfate. 2,2-Dinitropropyl methyl sulfate was also obtained in this reaction:

$$\begin{aligned} \mathrm{CH_3C(NO_2)_2CH_2OH + (CH_3)_2SO_4} \xrightarrow{95^\circ} &\ \mathrm{CH_3C(NO_2)_2CH_2OCH_3} + \\ &\ \mathrm{CH_3OSO_2OCH_2C(NO_2)_2CH_3} \end{aligned}$$

This reaction seems to be of general utility in the synthesis of "mixed" nitroalkyl ethers. Thus, 2,2-dinitropropanediol reacted with dimethyl sulfate to give 1,3-dimethoxy-2,2-dinitropropane and 3-methoxy-2,2-dinitropropyl methyl sulfate:

$$\begin{aligned} \mathrm{(NO_2)_2C(CH_2OH)_2 + (CH_3)_2SO_4} \longrightarrow &\ \mathrm{(NO_2)_2C(CH_2OCH_3)_2} + \\ &\ \mathrm{CH_3OCH_2C(NO_2)_2CH_2OSO_2OCH_3} \end{aligned}$$

On the other hand, attempts to synthesize 2-fluoro-2,2-dinitroethyl ethers from 2-fluoro-2,2-dinitroethanol were unsuccessful under these reaction conditions.

Acetic anhydride and ethyl chloroformate reacted with aqueous alkaline 2-fluoro-2,2-dinitroethanol to give 2-fluoro-2,2-dinitroethyl acetate[5] and ethyl 2-fluoro-2,2-dinitroethyl carbonate, respectively in 70-80% yields:

$$FC(NO_2)_2CH_2OH + NaOH/H_2O \begin{array}{l} \xrightarrow{Ac_2O} FC(NO_2)_2CH_2OCOCH_3 \\ \xrightarrow{ClCO_2Et} FC(NO_2)_2CH_2OCO_2C_2H_5 \end{array}$$

Pyridine-catalyzed reaction of 2-fluoro-2,2-dinitroethanol with oxalyl chloride yielded, depending on the stoichiometry of reagents, bis(2-fluoro-2,2-dinitroethyl) oxalate[12] and 2-fluoro-2,2-dinitroethyl oxalyl chloride. The bis ester was still the major product at a 1:1 ratio of the reagents but 2-fluoro-2,2-dinitroethyl oxalyl chloride was obtained in 20%. The Curtius reaction of this ester-chloride gave carbo(2-fluoro-2,2-dinitroethoxy) isocyanate:

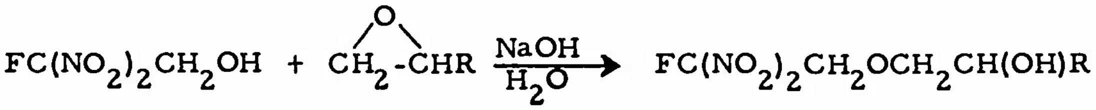
$$\begin{array}{rl} FC(NO_2)_2CH_2O_2CCOCl + NaN_3 \xrightarrow[C_2H_4Cl_2]{H_2O} & \left[FC(NO_2)_2CH_2O_2CCON_3\right] \\ & \quad\quad \downarrow \Delta \\ & FC(NO_2)_2CH_2O_2CNCO \end{array}$$

The isocyanate polymerized readily at room temperature and its elemental analysis was not obtained.[13] The freshly prepared compound exhibited the characteristic NCO infrared absorption peak and reacted with 2-fluoro-2,2-dinitroethanol to give bis(2-fluoro-2,2-dinitroethyl) iminodicarboxylate, characterized by elemental analysis and proton nmr spectrum:

$$FC(NO_2)_2CH_2O_2CNCO + HOCH_2CF(NO_2)_2 \longrightarrow NH\left[CO_2CH_2CF(NO_2)_2\right]_2$$

Simple carboalkoxy isocyanates could not be synthesized via the Curtius reaction[14] and this example seems to represent the first case of this rearrangement.

The above alkylation reactions suggested that in a manner similar to that of simple alkoxides[15] 2-fluoro-2,2-dinitroethoxide may react with 1,2-epoxides to give the corresponding 2-fluoro-2,2-dinitroethyl 2-hydroxyalkyl ethers. This was found to be the case. Ethylene oxide and propylene oxide reacted with 2-fluoro-2,2-dinitroethanol in aqueous sodium hydroxide to give 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl and 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ethers, respectively, in 40 to 60% yields:

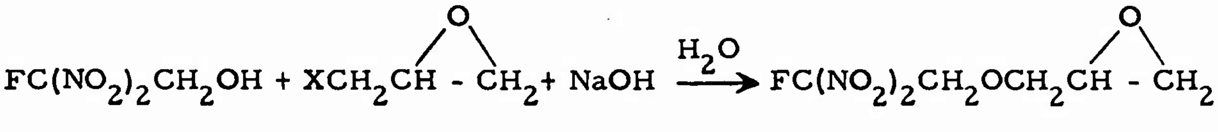


$$FC(NO_2)_2CH_2OH + \overset{O}{CH_2\text{-}CHR} \xrightarrow[H_2O]{NaOH} FC(NO_2)_2CH_2OCH_2CH(OH)R$$

R = H or CH_3

The yields of products were not optimized but a significant increase in yields resulted when excess of an epoxide was used, the concentration of reagents was increased, and the reaction temperature was kept low (0-5°). 2-Fluoro-2,2-dinitroethyl 2-hydroxypropyl ether was also obtained in 12% yield in stannic chloride-catalyzed reaction of 2-fluoro-2,2-dinitroethanol with propylene oxide.

2-Fluoro-2,2-dinitroethanol reacted with epichlorohydrin or epibromohydrin in aqueous sodium hydroxide to give 2-fluoro-2,2-dinitroethyl glycidyl ether in 15 to 30% yields:

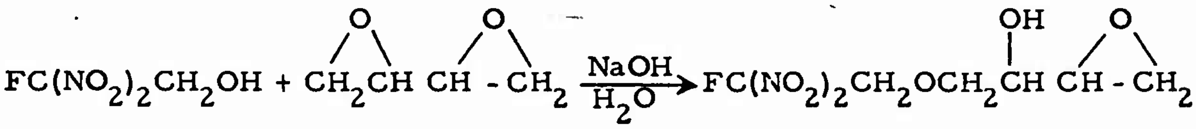


$$FC(NO_2)_2CH_2OH + XCH_2\overset{O}{\overbrace{CH - CH_2}} + NaOH \xrightarrow{H_2O} FC(NO_2)_2CH_2OCH_2\overset{O}{\overbrace{CH - CH_2}}$$

X = Cl, Br

At least stoichiometric amounts of sodium hydroxide were required in these reactions to effect the cyclization of halohydrin intermediates.

The reaction of butadiene dioxide with 2-fluoro-2,2-dinitroethane in aqueous sodium hydroxide yielded 4-(2-fluoro-2,2-dinitroethoxy)-3-hydroxybutene-1,2 oxide, identified by elemental analysis and nmr spectra:

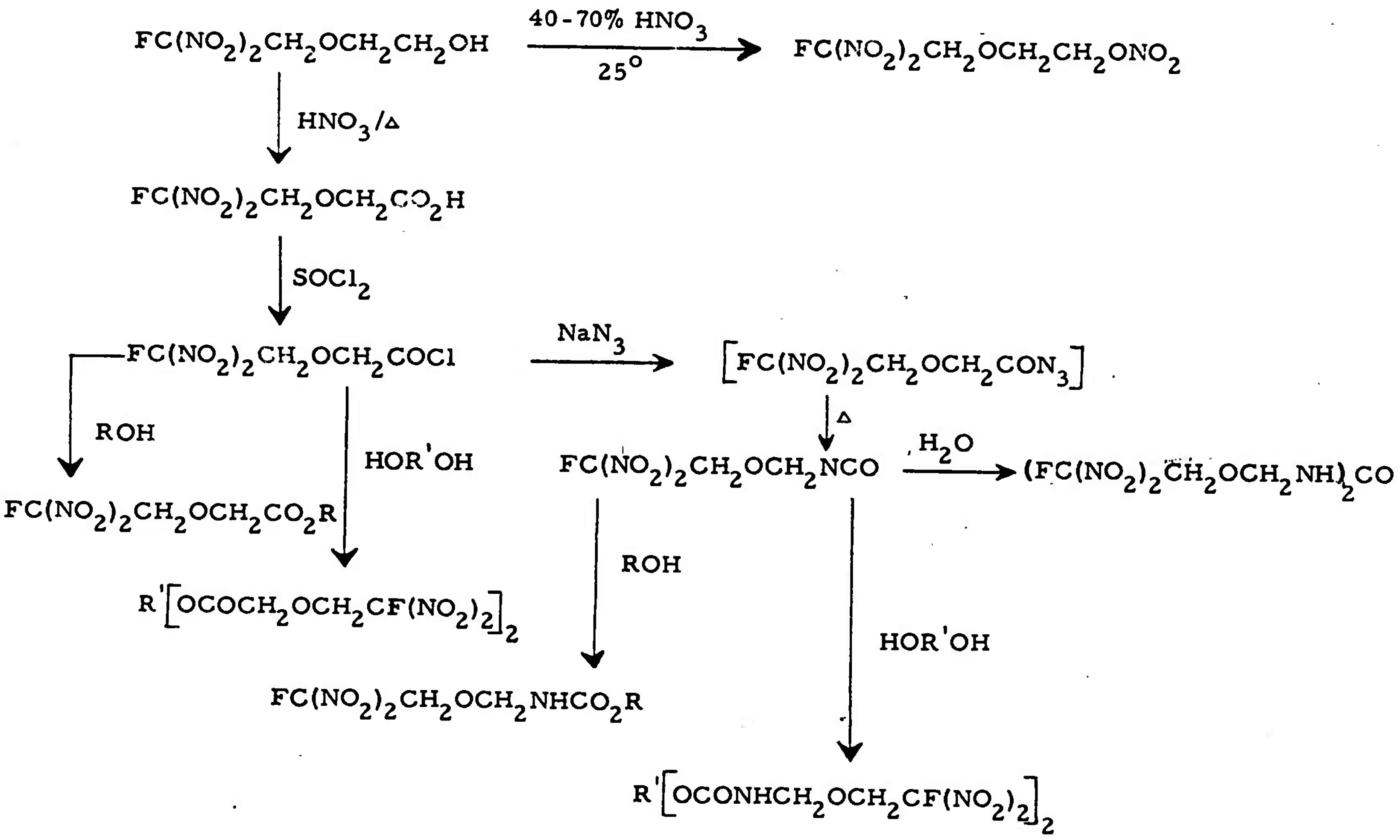


$$FC(NO_2)_2CH_2OH + \overset{O}{\overbrace{CH_2CH}}\ \overset{O}{\overbrace{CH - CH_2}} \xrightarrow[H_2O]{NaOH} FC(NO_2)_2CH_2OCH_2\overset{OH}{CH}\ \overset{O}{\overbrace{CH - CH_2}}$$

The proton nmr spectrum of the distillation residue remaining in the purification of the 1:1 alkylation product suggested that the 1:2 adduct, 1,4-bis(2-fluoro-2,2-dinitroethoxy)-2,3-butanediol, was also produced in the above reaction but the elemental analysis of the material was only in a fair agreement with this structure.

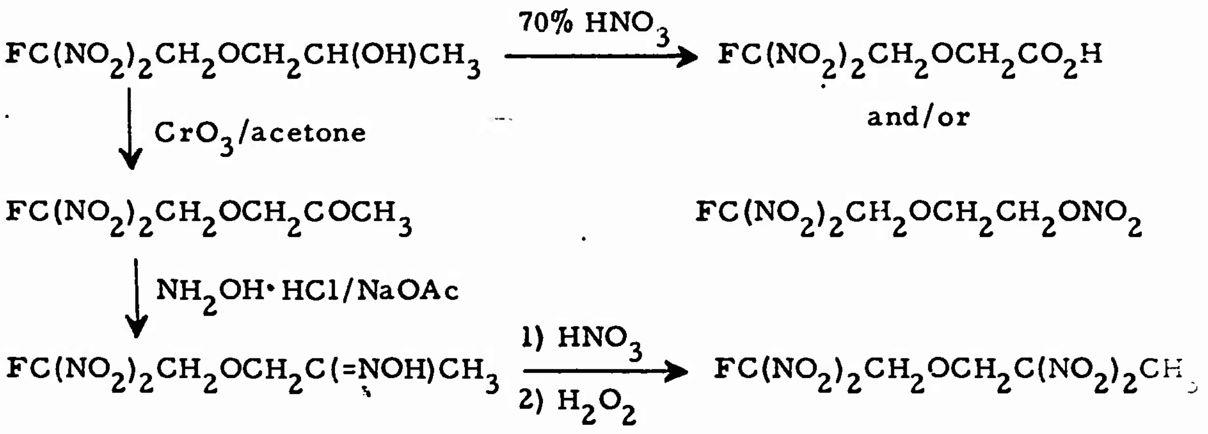
2-Fluoro-2,2-dinitroethyl 2-hydroxyethyl ether and 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether were found to be useful starting materials in the synthesis of other 2-fluoro-2,2-dinitroethoxy derivatives and their reactions were investigated.

2-Fluoro-2, 2-dinitroethyl 2-hydroxyethyl ether was oxidized with 70% nitric acid to give 2-fluoro-2, 2-dinitroethoxyacetic acid in 91% yield. The acid was converted to 2-fluoro-2, 2-dinitroethoxyacetyl chloride with thionyl chloride. The Curtius reaction of the acid chloride gave 2-fluoro-2, 2-dinitroethoxymethyl isocyanate. 2-Fluoro-2, 2-dinitroethoxyacetyl chloride was reacted with 2-fluoro-2, 2-dinitroethanol, 2, 2-dinitropropanol, and 2, 2-dinitropropanediol to give the corresponding esters quantitatively. 2-Fluoro-2, 2-dinitroethoxymethyl isocyanate also reacted with the above nitroalcohols to give the corresponding N-(2-fluoro-2, 2-dinitroethoxymethyl)carbamic acid esters. N, N'-Bis[(2-fluoro-2, 2-dinitroethoxy)methyl]urea was obtained by reacting the isocyanate with water. Several attempts to oxidize 2-fluoro-2, 2-dinitroethyl 2-hydroxyethyl to the corresponding aldehyde with dilute nitric acid under mild conditions failed, but small amounts of 2-fluoro-2, 2-dinitroethoxyethyl nitrate were obtained. The reactions of 2-fluoro-2, 2-dinitroethyl 2-hydroxyethyl ether are summarized below. All the compounds are new and were characterized by their elemental analyses and their infrared and nmr spectra.



R = $FC(NO_2)_2CH_2$-, $CH_3C(NO_2)_2CH_2$-; R' = -$CH_2C(NO_2)_2CH_2$-

The reactions of 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether were explored to a lesser degree than those of 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether. The compound was oxidized with 70% nitric acid to give 2-fluoro-2,2-dinitroethoxyacetic acid in 40% yield. Oxidation with chromic acid in acetone yielded 2-fluoro-2,2-dinitroethoxyacetone in 95% yield. The ketone was reacted with hydroxylamine to give the corresponding oxime, which was nitrated and the resulting nitronitroso intermediate oxidized to 2-fluoro-2,2-dinitroethyl 2,2-dinitropropyl ether, following the procedure of Bull et al.[16] The ether was contaminated with 2-fluoro-2,2-dinitroethoxyacetone and some difficulties were encountered with its purification. The reactions of 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether are summarized below.



$$\begin{tikzcd} FC(NO_2)_2CH_2OCH_2CH(OH)CH_3 \arrow[r, "70\%\ HNO_3"] \arrow[d, "CrO_3/acetone"] & FC(NO_2)_2CH_2OCH_2CO_2H \\ & \text{and/or} \\ FC(NO_2)_2CH_2OCH_2COCH_3 \arrow[d, "NH_2OH\cdot HCl/NaOAc"] & FC(NO_2)_2CH_2OCH_2CH_2ONO_2 \\ FC(NO_2)_2CH_2OCH_2C(=NOH)CH_3 \arrow[r, "1)\ HNO_3", "2)\ H_2O_2"'] & FC(NO_2)_2CH_2OCH_2C(NO_2)_2CH \end{tikzcd}$$

In addition to the reactions of 2-fluoro-2,2-dinitroethanol in aqueous alkali, several related reactions of the alcohol were carried out in the presence of pyridine.[17] Under these conditions, the alcohol reacted with thionyl chloride to give bis(2-fluoro-2,2-dinitroethyl) sulfite[18] (80-85% yield) and a small amount (5-7% yield) of 2-fluoro-2,2-dinitroethyl chloride.

$$2FC(NO_2)_2CH_2OH + SOCl_2 + 2C_5H_5N \xrightarrow{CH_2Cl_2} \left[FC(NO_2)_2CH_2O\right]_2SO + FC(NO_2)_2CH_2Cl$$

2-Fluoro-2,2-dinitroethyl chloride was obtained in 75% yield in the pyridine-catalyzed reaction of the alcohol with sulfuryl chloride.

Tris(2-fluoro-2,2-dinitroethyl) borate was obtained quantitatively in the ester exchange reaction between triethyl borate and 2-fluoro-2,2-dinitroethanol:

$$B(OC_2H_5)_3 + 3FC(NO_2)_2CH_2OH \xrightarrow{90^\circ} B\left[OCH_2CF(NO_2)_2\right]_3 + 3C_2H_5OH$$

2-Fluoro-2,2-dinitroethyl nitrate was obtained in 75% yield in the reaction of 2-fluoro-2,2-dinitroethanol with sulfuric-nitric acid mixture.

$$FC(NO_2)_2CH_2OH + HNO_3/H_2SO_4 \longrightarrow FC(NO_2)_2CH_2ONO_2$$

The compound has been recently synthesizes by Eremenko and Natsibullin[5] in 30% yield.

Experimental Section

Caution.— 2-Fluoro-2,2-dinitroethanol is a severe skin irritant. Safety shielding should be used in work with fluorodinitro compounds.

2-Fluoro-2,2-dinitroethyl Methyl Ether.[2,3]— To a stirred solution of 2.0 g (0.05 mol) of sodium hydroxide and 6.24 g (0.04 mol) of 2-fluoro-2,2-dinitroethanol in 55 ml of water was added dropwise at 25° over a period of 10 min. 5.1 g (0.04 mol) of dimethyl sulfate. After 45 min. the reaction mixture was extracted with 35 ml of methylene chloride and distilled to give 5.1 g of 2-fluoro-2,2-dinitroethyl methyl ether (75% yield) bp 27°/0.1 mm, (rep[2] bp 47-48°/4 mm), n_D^{25} 1.4045.

Anal. Calcd for $C_3H_5N_2FO_5$: C, 21.4; H, 3.0; N, 16.7; F, 11.3. Found: C, 41.2; H, 2.7; N, 16.2; F, 10.6.

Proton nmr ($CDCl_3$): δ 4.60 (d, J_{HF} = 18 Hz, CH_2O) and 3.61 (s, CH_3). Fluorine nmr: ϕ110.9 (s).

Allyl 2-Fluoro-2,2-dinitroethyl Ether. - A mixture of 1.6 g (0.04 mol) of sodium hydroxide in 30 ml of water, 4.62 g (0.04 mol) of 2-fluoro-2,2-dinitroethanol and 4.85 g (0.04 mol) of allyl bromide was stirred at 25° for 3 hrs. The product was extracted with 30 ml of methylene chloride and distilled to give 2.5 g of alkyl 2-fluoro-2,2-dinitroethyl ether (34% yield), bp 31-32°/0.2 mm.

Anal. Calcd for $C_5H_7N_2FO_5$: C, 30.9; H, 3.6; N, 14.4; F, 9.8. Found: C, 30.6; H, 3.4; N, 13.9; F, 9.9.

Proton nmr ($CDCl_3$): δ5.56-6.20 (d, d, t, $J_{\underline{cis}}$ = 9 Hz, $J_{\underline{trans}}$ = 17.5 Hz, J_{allyl} = 5.5 Hz, CH), 5.06-5.51 (m, CH_2=), 4.15 (d, J_{HH} = 5.5 Hz, CH_2), and 4.58 (d, J_{HF} = 18 Hz, OCH_2CF). Fluorine nmr: ϕ111.0 (t, J_{HF} = 17.3 Hz).

2,2-Dinitropropyl Methyl Ether.— A mixture of 20 g (0.16 mol) of dimethyl sulfate and 10.0 g (0.067 mol) of 2,2-dinitropropanol was heated at 95-100° for 10 hrs and distilled to give 18 g of colorless liquid, bp 30-90°/0.1 mm, and a residue amounting to ca 10 g. The distillate, containing mainly dimethyl sulfate, was stirred with 100 cc of 15 % aqueous sodium hydroxide at 25° for 16 hrs. An insoluble liquid was extracted with 25 ml of methylene chloride, and distilled to give 2.5 g of 2,2-dinitropropyl methyl ether, bp 35°/0.1 mm, n_D^{25} 1.4295.

Anal. — Calcd for $C_4H_8N_2O_5$: C, 29.3; H, 4.9; N, 17.1. Found: C, 29.0; H, 4.8; N, 17.5.

Proton nmr (CCl_4): δ4.13 [s, $OCH_2C(NO_2)_2$], 3.39 (s, OCH_3), and 2.13 (s, CH_3).

2,2-Dinitropropyl Methyl Sulfate. — The distillation residue above was washed with 100 ml of water and an insoluble liquid was distilled in a molecular still at 100°/25μ to give 1.5 g of colorless oil, n_D^{25} 1.4470.

Anal. — Calcd for $C_4H_8N_2SO_8$: C, 19.7; H, 3.3; N, 11.5. Found: C, 20.0; H, 3.3; N, 11.8.

Proton nmr (CCl_4): δ4.85 (s, 2), 3.92 (s, 3), and 2.25 (s, 3).

1,3-Dimethoxy-2,2-dinitropropane. — A solution of 5.0 g (0.03 mol) of 2,2-dinitropropanediol in 24 g (0.19 mol) if dimethyl sulfate was heated at 90-95° for 7 hrs and distilled at 50-90°/0.1 mm to give 19 g of a colorless liquid (mainly dimethyl sulfate) and a residue amounting to 9.0 g.

The distillate was stirred with 200 ml of 10% aqueous sodium hydroxide at 25° for 16 hrs. An insoluble liquid was extracted with 15 ml of methylene chloride and distilled to give 0.7 g of 1,3-dimethoxy-2,2-dinitropropane, bp 38°/0.05 mm, n_D^{25} 1.4302.

Anal. — Calcd for $C_5H_{10}N_2O_6$: C, 30.9; H, 5.2; N, 14.4. Found: C, 30.7; H, 5.1; N, 14.6.

Proton nmr (CCl_4): δ3.47 (s, 3) and 4.28 (s, 2).

Methyl 3-Methoxy-2,2-dinitropropyl Sulfate.— The distillation residue above was stirred with 100 ml of water. The product was extracted with 30 ml of methylene chloride and distilled in a molecular still at 100-102°/25 μ to give 0.9 g of colorless liquid, n_D^{25} 1.4460.

Anal. Calcd for $C_5H_{10}N_2SO_9$: C, 21.9; H, 3.7; N, 10.2. Found: C: 22.2; H, 3.7; N, 11.0.

2-Fluoro-2,2-dinitroethyl Acetate.— To a stirred solution of 4.4 g (0.11 mol) of sodium hydroxide and 15.4 g (0.1 mol) of 2-fluoro-2,2-dinitroethanol in 150 ml of water was added dropwise (10 min) with cooling at 0-2° 10.2 g (0.1 mol) of acetic anhydride. The reaction mixture was stirred for 1.5 hrs, the product extracted with 50 ml of methylene chloride and distilled to give 16.4 g (83 % yield) of 2-fluoro-2,2-dinitroethyl acetate, bp 91°/50 mm, n_D^{21} 1.4198 (reported[4] bp 90-90.5°/50 mm, n_D^{20} 1.4200).

2-Fluoro-2,2-dinitroethyl Ethyl Carbonate.— To a stirred solution of 4.4 g (0.11 mol) of sodium hydroxide and 15.4 g (0.1 mol) of 2-fluoro-2,2-dinitroethanol in 75 ml of water was added at 0-2° with cooling over a period of 15 min. 10.8 g (0.1 mol) of ethyl chloroformate. After 45 min. the product was extracted with 50 ml of methylene chloride and distilled to give 18.2 g (80 % yield) of 2-fluoro-2,2-dinitroethyl ethyl carbonate, bp 53-54°/0.1 mm, n_D^{23}1.4215.

Anal. Calcd for $C_5H_7N_2FO_7$: C, 26.6; H, 3.1; N, 12.4; F, 8.4. Found: C, 26.3; H, 3.2; N, 13.1; F, 8.5.

Proton nmr (CCl_4): δ1.33 (t, CH_2), 4.23 (q, J = 7.1 Hz, CH_2), and 5.17 (d, J_{HF} = 15.7 Hz, CH_2). Fluorine nmr: φ111.3 (s).

2-Fluoro-2,2-dinitroethyl Oxalyl Chloride.— To a stirred solution of 12.7 g (0.1 mol) of oxalyl chloride in 75 ml of diethyl ether was added at 5-10° with cooling over a period of 15 min. a solution of 15.4 g (0.1 mol) of 2-fluoro-2,2-dinitroethanol and 7.9 g (0.1 mol) of pyridine in 75 ml of diethyl ether. The reaction mixture was filtered and the filter cake was washed with three 25 ml portions of diethyl ether. The combined filtrate and washings were distilled to give 4.5 g of 2-fluoro-2,2-dinitroethyl oxalyl chloride, bp 66-67°/0.1 mm.

Anal. Calcd for $C_4H_2N_2FClO_7$: C, 19.6; H, 0.8; N, 11.5; F, 7.8; Found: C, 20.0; H, 0.8; N, 11.3; F, 7.4.

Carbo(2-fluoro-2,2-dinitroethoxy) Isocyanate.— A solution of 2.45 g (0.01 mol) of 2-fluoro-2,2-dinitroethyl oxalyl chloride in 25 ml of ethylene chloride was added dropwise over a period of 8 min. at 12-15° to a stirred solution of 0.8 g (0.012 mol) of sodium azide in 15 ml of water and the mixture was stirred for 15 min. The ethylene chloride solution was washed with 30 ml of ice-water, dried over anhydrous sodium sulfate, and filtered. The filtrate was warmed at 50° for 45 min. in a distillation apparatus protected from the atmospheric moisture and concentrated at 25 mm. The pale-yellow liquid was dried at 35°/0.1 mm; weight 2.0 g. The infrared spectrum of the freshly prepared material showed intense absorption peaks at 4.5 and 6.25 μ, attributed to -NCO and $-NO_2$ groups, respectively.

Soon after its preparation (20-30 min), the clear liquid started to turn turbid and on standing in a closed vial at room temperature for several days it solidified into a white solid.

2-Fluoro-2, 2-dinitroethyl Iminodicarboxylate.— To a solution of 1.0 g of freshly prepared carbo(2-fluoro-2, 2-dinitroethoxy) isocyanate and 0.75 g of 2-fluoro-2, 2-dinitroethanol in 15 ml of ethylene chloride was added a catalytic amount of ferric acetylacetonate. After 18 hrs a white crystalline solid was filtered, washed with two 1 ml portions of ethylene chloride and dried; weight 1.0 g, mp 182-183°.

Anal. Calcd for $C_6H_5N_5F_2O_{12}$: C, 19.1; H, 1.3; N, 18.6; F, 10.1. Found: C, 18.8; H, 1.3; N, 17.8; F, 10.4.

Proton nmr (d_6-acetone): δ10.11 (s, 1, NH) and 5.58 (d, 4, J_{HF} = 16 Hz, CH_2).

2-Fluoro-2, 2-dinitroethyl 2-Hydroxyethyl Ether.— To a stirred solution of 4.0 g (0.1 mol) of sodium hydroxide in 90 ml of water at 0-5° was added 15.5 g (0.1 mol) of 2-fluoro-2, 2-dinitroethanol and 5.5 g (0.125 mol) of ethylene oxide. After standing for 16 hrs at 0° the reaction mixture was extracted with three 25 ml portions of methylene chloride and the combined extracts were distilled to give 5.4 g (27 % yield) of 2-fluoro-2, 2-dinitroethyl 2-hydroxyethyl ether, bp 74-75°/50 μ, n_D^{23}1.4370.

Anal. Calcd for $C_4H_7N_2FO_6$: C, 24.5; H, 3.6; N, 14.1; F, 9.6. Found: C, 24.3; H, 3.6; N, 13.8; F, 9.5.

The infrared spectrum showed absorption peaks at (μ): 3.0 (s); 3.44 (m); 3.50 (sh); 6.27 (s); 6.86 (m); 7.43 (m); 7.62 (s); 8.15 (w); 8.83 (s); 9.40 (s); 11.83 (s); and 12.20 (s).

Proton nmr ($CDCl_3$): δ4.77 $\left[d, J_{HF} = 18\ Hz, OCH_2CF(NO_2)_2\right]$, 3.82 (s, CH_2), and 3.25 (s, OH). Fluorine nmr: ϕ111.0 (t, J_{HF} = 18 Hz).

Higher yields (68 %) and conversion (57 %) were observed in a large-scale run using 185 g (1.2 mol) of 2-fluoro-2,2-dinitroethanol, 30 g (0.75 mol) of sodium hydroxide and 125 g (2.86 mols) of ethylene oxide in 750 ml of water. p-Toluenesulfonate, bp 160-163°/25 μ (molecular still), n_D^{23} 1.5035, was obtained quantitatively by reacting the hydroxyether with p-toluenesulfonyl chloride in methylene chloride-pyridine solution.

Anal. Calcd for $C_{11}H_{13}N_2FSO_8$: C, 37.5; H, 3.7; N, 8.0; F, 5.4. Found: C, 37.7; H, 3.6; N, 7.6; F, 5.5.

2-Fluoro-2,2-dinitroethyl 2-Hydroxypropyl Ether.— To a solution of 2.2 g (0.055 mol) of sodium hydroxide in 70 ml of water at 0° was added 9.24 g (0.06 mol) of 2-fluoro-2,2-dinitroethanol and 3.5 g (0.06 mol) of propylene oxide. The reaction mixture was allowed to stand at 0° for 18 hrs, extracted with three 30 ml portions of diethyl ether, and the combined etheral extracts were distilled to give 3.1 g of colorless liquid(25 % yield), bp 62°/0.05 mm, n_D^{23} 1.4325.

<u>Anal.</u> Calcd for $C_5H_9N_2FO_6$: C, 28.3; H, 4.3; N, 13.2; F, 9.0. Found: C, 28.0; H, 4.1; N, 13.0; F, 9.3.

Proton nmr ($CDCl_3$): δ4.75 $\left[d, J_{HF} = 18\ Hz, OCH_2CF(NO_2)_2\right]$, 4.00 (d, q, CH), and 3.6 (s, OCH_2 and OH; AB pattern after D_2O exchange). Fluorine nmr: ϕ110.8 (t, J_{HF} = 17.5 Hz).

The yield of the product increased to 45 and 63 %, respectively, when a 2:1 and a 4:1 molar ratio of propylene oxide to 2-fluoro-2,2-dinitroethanol were employed in the above reaction.

An acid-catalyzed reaction was carried out as follows: To a solution 9.24 g (0.06 mol) of 2-fluoro-2,2-dinitroethanol and 4.0 g (0.068 mol) of propylene oxide in 50 ml of methylene chloride was added 3 drops of stannic chloride and the reaction mixture was allowed to stand at 25° for 18 hrs. The solution was washed with 50 ml of water, dried, and distilled to give 1.5 g (12 % yield) of 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether, identified by its infrared spectrum.

<u>p</u>-Toluenesulfonate, bp 150-153°/25 μ (molecular still) n_D^{23}1.4975, was obtained quantitatively in the same manner as that of 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether (see above).

<u>Anal.</u> Calcd for $C_{12}H_{15}N_2FSO_8$: C, 39.4; H, 4.1; N, 7.6; F, 5.2. Found: C, 39.5; H, 4.1; N, 7.2; F, 5.3.

2-Fluoro-2,2-dinitroethyl Glycidyl Ether.— Epichlorohydrin, 3.7 g (0.04 mol) and 6.24 g (0.04 mol) of 2-fluoro-2,2-dinitroethanol was added at 0° to a stirred solution of 2.5 g of sodium hydroxide in 75 ml of water. After standing at 0-3° for 48 hrs the reaction mixture was extracted with 30 ml of methylene chloride and the extract was distilled to give 2.6 g (31 % yield) of 2-fluoro-2.2-dinitroethyl glycidyl ether, bp 70-71°/0.1 mm, n_D^{23} 1.4362.

Anal. Calcd for $C_5H_7N_2FO_6$: C, 28.6; H, 3.3; N, 13.3; F, 9.0. Found: C, 28.4; H, 3.2; N, 12.8; F, 8.8.

Proton nmr (CCl_4): δ4.71 $[d, J_{HF} = 18\text{ Hz}, OCH_2CF(NO_2)_2]$, 4.1 and 3.5 (d, d, OCH_2), 3.11 (m, CH), and 3.7 and 3.5 (d, d, ring CH_2). Fluorine nmr: φ111.9 (t, J_{HF} = 18 Hz).

2-Fluoro-2,2-dinitroethyl glycidyl ether was obtained in 15 % yield when epibromohydrin instead of epichlorohydrin was used in the above reaction.

4-(2-Fluoro-2,2-dinitroethoxy)-3-hydroxybutene-1,2 Oxide.— To a solution of 30.8 g (0.2 mol) of 2-fluoro-2,2-dinitroethanol and 8.6 g (0.1 mol) of butadiene dioxide in 150 ml of water at 0° was added a solution of 8.0 g (0.2 mol) of sodium hydroxide in 75 ml of water. After standing at 0° for 5 days, the product was extracted with 75 ml of methylene chloride and dried to give 19 g of viscous oil. A 1.5 g aliquot of the material was distilled at 120-125°/10 μ (molecular still) to give 0.9 g of colorless oil.

Anal. Calcd for $C_6H_9FN_2O_7$: C, 30.0; H, 3.8; N, 11.7; F, 7.0. Found: C, 29.7; H, 3.8; N, 11.9; F, 7.4.

Proton nmr ($CDCl_3$): δ4.70 [d, J_{HF} = 18 Hz, $OCH_2CF(NO_2)_2$], 3.75 (m, CH_2 and CH), 2.71 (ABM pattern, ring protons), and 3.12 (s, OH; confirmed by D_2O exchange).

2-Fluoro-2,2-dinitroethoxyacetic Acid.— 2-Fluoro-2,2-dinitroethyl 2-hydroxyethyl ether, 3.1 g (0.02 mol), was added dropwise with stirring at 25° to 6.5 ml of 70 % nitric acid and the solution was allowed to stand at 25° for 18 hrs. The mixture was heated at 65-70° for 3 hrs, evaporated to dryness at reduced pressure (3-5 mm), and a yellow solid was crystallized from methylene chloride to give 3.1 g (91 % yield) of 2-fluoro-2,2-dinitroethoxyacetic acid, white crystalline solid, mp 69-70°.

Anal. Calcd for $C_4H_5N_2FO_7$: C, 22.6; H, 2.3; N, 13.2; F, 9.0. Found: C, 22.5; H, 2.1; N, 12.9; F, 8.9.

Proton nmr (d_6-acetone): δ10.29 (s, CO_2H), 5.00 [d, J_{HF} = 17.2 Hz, $OCH_2CF(NO_2)_2$], and 4.37 (s, CH_3).

2-Fluoro-2,2-dinitroethoxyacetic acid was also obtained in the oxidation of 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether as follows. A solution of the ether, 4.3 g, in 20 ml of 70 % nitric acid was allowed to stand at 25° for 18 hrs and then was heated at 55-60° for two hours. The mixture was evaporated to dryness at reduced pressure, and the product was recrystallized from methylene chloride to give 1.5 g of the acid, 40 % yield, mp 68-69°.

2-Fluoro-2,2-dinitroethoxyacetyl Chloride.— To a solution of 10.6 g (0.05 mol) of 2-fluoro-2,2-dinitroethoxyacetic acid and 8.0 g (0.067 mol) of thionyl chloride in 30 ml of ethylene chloride was added 2 drops of pyridine and the reaction mixture was warmed at 65-70° until the evolution of hydrogen chloride and sulfur dioxide ceased (30 min). The solution was distilled to give 11.6 g (quantitative yield) 2-fluoro-2,2-dinitroethoxyacetyl chloride, bp 67-68°/0.1 mm, n_D^{23} 1.4505.

Anal. Calcd for $C_4H_4N_2ClFO_6$: C, 20.8; H, 1.7; N, 12.2; F, 8.3. Found: C, 20.6; H, 2.1; N, 11.6; F, 8.5.

2-Fluoro-2,2-dinitroethoxymethyl Isocyanate.— To a stirred solution of 7.8 g (0.12 mol) of sodium azide in 50 ml of water and 150 ml of ethylene chloride at 15-16° was added dropwise over a period of 10 min. 23 g (0.1 mol) of 2-fluoro-2,2-dinitroethoxyacetyl chloride. The reaction mixture was stirred at 10-12° for 35 min, phases separated, and the ethylene chloride solution was dried over anhydrous sodium sulfate and filtered. The filtrate was placed in a 250 ml round-bottomed flash equipped with a reflux condenser protected from the atmospheric moisture by a drying tube, and heated at 60-65° until the evolution of nitrogen ceased (45 min). The solution was distilled to give 20.7 g (100 % yield) of 2-fluoro-2,2-dinitroethoxymethyl isocyanate, bp 55-56°/50 µ, n_D^{23} 1.4420.

Anal. Calcd for $C_4H_4N_3FO_6$: 23.0; H, 1.9; N, 20.1; F, 9.0. Found: C, 22.7; H, 1.9; N, 19.9; F, 8.7.

Proton nmr ($CDCl_3$): δ4.93 (s, CH_2NCO) and 4.71 (d, J_{HF} = 17.3 Hz, CH_2). Fluorine nmr: ϕ110.3 (t, J_{HF} = 16.5 Hz).

2-Fluoro-2,2-dinitroethyl 2-Fluoro-2,2-dinitroethoxyacetate.— To a stirred solution of 3.45 g (0.015 mol) of 2-fluoro-2,2-dinitroethoxymethyl chloride and 2.31 g (0.015 mol) of 2-fluoro-2,2-dinitroethanol in 15 ml of methylene chloride was added dropwise over a period of 5 min at 25-28° a solution of 1.2 g (0.015 mol) of pyridine in 15 ml of methylene chloride. After 20 min, the solution was washed with 70 ml of 3 % sulfuric acid and distilled in a molecular still at 110-115°/25 μ to give 5.2 g (100 % yield) of a colorless liquid, n_D^{23} 1.4485.

Anal. Calcd for $C_6H_6N_4F_2O_{11}$: C, 20.7; H, 1.7; N, 16.1; F, 10.9. Found: C, 20.5; H, 1.7; N, 15.9; F, 10.8.

Proton nmr ($CDCl_3$): δ5.31 (d, 1, J_{HF} = 16 = 16 Hz), 4.73 (d, 1, J_{HF} = 17 Hz), and 4.40 (s, 1). Fluorine nmr: ϕ110.1 (t, J_{HF} = 15 Hz) and ϕ111.1 (t, J_{HF} = 17 Hz).

2,2-Dinitropropyl 2-Fluoro-2,2-dinitroethoxyacetate.— 2,2-Dinitropropyl 2-fluoro-2,2-dinitroethoxyacetate, bp 138-143°/25 μ (molecular still), n_D^{24} 1.4645, was obtained quantitatively in the reaction of 2,2-dinitropropanol and 2-fluoro-2,2-dinitroethoxyacetyl chloride following the above described procedure.

Anal. Calcd for $C_7H_9N_4FO_{11}$: C, 24.4; H, 2.6; N, 16.3; F, 5.5. Found: C, 24.4; H, 2.6; N, 15.8; F, 5.6.

Proton nmr ($CDCl_3$): δ5.00 (s, OCH_2CO), 4.73 [d, J_{HF} = 17.5 Hz, $OCH_2CF(NO_2)_2$], 4.33 [s, $OCH_2C(NO_2)_2$-], and 2.23 (s, CH_3). Fluorine nmr: ϕ111.2 (t, J_{HF} = 17.4 Hz).

Bis(2-Fluoro-2,2-dinitroethoxyacetate) of 2,2-Dinitropropanediol.—

Bis(2-fluoro-2,2-dinitroethoxyacetate)of 2,2-dinitropropanediol was obtained quantitatively in the reaction of 2,2-dinitropropanediol with two moles of 2-fluoro-2,2-dinitroethoxyacetyl chloride following the above procedure. The viscous oil,degassed at 100°/0.1 mm, was not further purified.

Anal. Calcd for $C_{11}H_{12}N_6F_2O_{18}$: C, 23.8; H, 2.2; N, 15.2; F, 6.9.
Found: C, 23.6; H, 2.1; N, 14.7; F, 6.9.

Proton nmr ($CDCl_3$-d_6-acetone): 5.12 (s, 1, $COCH_2O$), 4.78 [d, 1, J_{HF} = 17 Hz, $OCH_2CF(NO_2)_2$], and 4.38 (s, 1, CH_2). Fluorine nmr: ϕ111.2 (t, J_{HF} = 16.2 Hz).

2-Fluoro-2,2-dinitroethyl 2-Fluoro-2,2-dinitroethoxymethylcarbamate.—

To a solution of 2.1 g (0.01 mol) of 2-fluoro-2,2-dinitroethoxymethyl isocyanate and 1.65 g (0.011 mol) of 2-fluoro-2,2-dinitroethanol in 20 ml of methylene chloride at 25° was added a catalytic amount of ferric acetylacetonate (FeAA). The reaction mixture was kept at 35° for 20 min. and distilled in a molecular still at 155-160°/25 µ to give 3.5 g of viscous colorless oil, n_D^{25} 1.4585.

Anal. Calcd for $C_6H_7N_5F_2O_{11}$: C, 19.8; H, 1.9; N, 19.3; F, 10.5. Found:
Found: C, 19.6; H, 1.8; N, 19.3; F, 10.2.

The infrared spectrum showed major abosprtion peaks at (µ):2.90; 5.72; 6.25; 7.62; 8.10; 8.95; 11.79; 12.52; and 13.02.

Proton nmr ($CDCl_3$): δ 6.25 (t, J = 7.5 Hz, NH), 5.30 (d, J_{HF} = 16 Hz), 4.72 $\left[d,\ J_{HF} = 17.8\ Hz,\ OCH_2CF(NO_2)_2\right]$, and 4.83, (d, J = 7.5 Hz, NCH_2). Fluorine nmr: ϕ110.5 (t, J_{HF} = 15.6 Hz) and ϕ111.0 (t, J_{HF} = 17.4 Hz).

Bis(2-fluoro-2,2-dinitroethoxymethylcarbamate) of 2,2-Dinitropropanediol.– Bis(2-fluoro-2,2-dinitroethoxymethylcarbamate) of 2,2-dinitropropanediol was obtained quantitatively in the reaction of 2,2-dinitropropanediol with two moles of 2-fluoro-2,2-dinitroethoxymethyl isocyanate following the above procedure. The material, a viscous oil, was purified only by drying at 100°/0.1 mm.

Anal. Calcd for $C_{11}H_{14}N_8F_2O_{18}$: C, 22.6; H, 2.4; N, 19.2; F, 6.5. Found: C, 22.4; H, 2.3; N, 19.0; F, 6.4.

The infrared spectrum showed the following major absorption peaks (μ): 2.93; 5.76; 6.30; 7.68; 8.20; 9.35; 11.82; and 12.56.

Proton nmr (d_6-acetone): δ 7.90 (t, J = 7.3 Hz, NH), 5.22 $\left[s,\ C\underline{H}_2C(NO_2)_2C\underline{H}_2\right]$, 4.97 $\left[d,\ J_{HF} = 18\ Hz,\ OCH_2CF(N)_2)_2\right]$, and 4.92 (d, $J_{NH\text{-}CH_2}$ = 7 Hz, NCH_2). Fluorine nmr: ϕ110.8 (t, J_{HF} = 17.7 Hz).

N,N'-Bis(2-fluoro-2,2-dinitroethoxymethyl)urea.– A suspension of 0.7 g of 2-fluoro-2,2-dinitroethoxymethyl isocyanate in 5 ml of water was stirred at 25-30° for 45 min. The product. a viscous oil, extracted with 10 ml of methylene chloride, was purified only by drying at 100°(0.1 mm). Weight 0.6 g, n_D^{23} 1.4703.

Anal. Calcd for $C_7H_{10}N_6F_2O_{11}$: C, 21.4; H, 2.6; N, 21.4; F, 9.8. Found: C, 21.1; H, 2.4; N, 20.6; F, 9.9.

2-(2-Fluoro-2,2-dinitroethoxy)ethyl Nitrate.— A solution of 4.0 g of 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether in 10 ml of 70% nitric acid was allowed to stand at 25° for 16 hrs. The product was added to 50 ml of ice-water and extracted with 30 ml of methylene chloride to give 2.5 g of semisolid. The material was treated with 50 ml of 10% aqueous sodium bicarbonate and extracted with 10 ml of methylene chloride to give 0.5 g of a colorless liquid. (The amount of the material was too small to determine the boiling point; estimated bp 85-90°/0.1 mm).

Anal. Calcd for $C_4H_6N_3FO_8$: C, 19.8; H, 2.5; N, 17.3; F, 7.8. Found: C, 19.8; H, 2.6; N, 16.8; F, 7.8.

Proton nmr ($CDCl_3$): δ4.67 $\left[d,\ J_{HF} = 18\ Hz,\ OCH_2CF(NO_2)_2\right]$ and 3.9-4.6 (AA'BB' pattern, CH_2).

2-Fluoro-2,2-dinitroethoxyacetone. - Sulfuric-chromic acid solution was prepared by adding 8.7 ml of concentrated sulfuric acid to a solution of 10.0 g of chromium trioxide in 19 ml of water following the procedure of Eisenbraum.[18] The chromic acid solution was added dropwise, over a period of 1 hr, at 25-28° to a stirred solution of 15.9 g (0.075 mol) of 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether in 190 ml of acetone until the color of Cr^{+6} persisted (only ca 2/3 of the chromic acid solution was required). The reaction mixture was stirred at 25° for 1.5 hrs and the excess Cr^{+6} was destroyed with few drops of isopropanol. The mixture was filtered and the filter cake was washed with two 35 ml portions of acetone. The combined filtrate and washings were stirred with 10 g of sodium bicarbonate for 25 min, filtered, and concentrated to ca 40 ml. Extraction with 45 ml of methylene chloride and distillation gave 14.5 g (92 % yield) of 2-fluoro-2,2-dinitroethoxyacetone, bp 70°/0.05 mm, n_D^{23} 1.4335.

Anal. Calcd for $C_5H_7N_2FO_6$: C, 28.6; H, 3.3; N, 13.3; F, 9.0. Found: C, 28.4; H, 3.4; N, 13.2; F, 9.1.

Proton nmr (CCl_4): δ2.12 (s, CH_3), 4.35 (s, CH_2CO), and 4.74 [d, J_{HF} = 17.4 Hz, $OCH_2CF(NO_2)_2$]. Fluorine nmr: ϕ109.3 (t, J_{HF} = 17.3 Hz).

2-Fluoro-2,2-dinitroethoxyacetone Oxime.— A mixture of 2.3 g (0.033 mol) of hydroxylamine hydrochloride, 2.1 g (0.01 mol) of 2-fluoro-2,2-dinitroethoxyacetone, and 4.53 g (0.033 mol) of sodium acetate trihydrate in 85 ml of absolute ethanol was refluxed for 45 min, and then ca 70 ml of ethanol was removed at 25°/25 mm. The residue was added to 100 ml of ice-water and the product was extracted with 40 ml of methylene chloride and dried at 100°/0.1 mm to give 2.15 g (95.5% yield) of colorless liquid which was not further purified.

Anal. Calcd for $C_5H_8N_3FO_6$: C, 26.7; H, 3.6; N, 18.7; F, 8.4. Found: C, 26.5; H, 3.4; N, 18.5; F, 8.3.

Proton nmr (CCl_4): δ4.52 [d, J_{HF} = 17.0 Hz, $OCH_2CF(NO_2)_2$], 4.20 (s, CH_2), 1.91 (s, CH_3), and δ9.75 (s, NOH). Fluorine nmr: ϕ108.7 (t, J_{HF} = 17.0 Hz).

2,2-Dinitropropyl 2-Fluoro-2,2-dinitroethyl Ether.— To a stirred solution of 0.9 g of 2-fluoro-2,2-dinitroethoxyacetone oxime in 25 ml of methylene chloride was added dropwise over a period of 10 min at 0-3° with cooling 5 ml of 100% nitric acid. The deep-blue solution was stirred for 45 min and then to it was added dropwise (5 min) 4 ml of 32% hydrogen peroxide. After 15 min, the pale-yellow solution was washed with two 25 ml portions of ice-water. The methylene chloride solution was distilled in a molecular still at 75°/10 μ to give 0.45 of colorless liquid. The proton nmr spectrum showed that the distillate was contaminated with 2-fluoro-2,2-dinitroethoxyacetone (13%), which could not be removed by fractionation. An analytical sample of the ether was obtained by washing the mixture with carbon tetrachloride, where the ketone is much more soluble than the ether.

Anal. Calcd for $C_5H_7N_4FO_9$: C, 21.0; H, 2.4; N, 19.6; F, 6.6. Found: C, 21.0; H, 2.4; N, 18.6; F, 6.6.

Proton nmr (d_6-acetone-$CDCl_3$): $\delta 4.95$ [d, J_{HF} = 16.8 Hz, $OCH_2CF(NO_2)_2$], 4.65 (s, CH_2) and 2.20 (s, CH_3). Fluorine nmr: $\phi 109.2$ (t, J_{HF} = 17.1 Hz).

Bis(2-fluoro-2,2-dinitroethyl) Sulfite.[17]— A solution of 3.6 g (0.03 mol) of thionyl chloride in 20 ml of methylene chloride was added at 25-28° to a stirred solution of 9.26 g (0.06 mol) of 2-fluoro-2,2-dinitroethanol and 5.0 g (0.063 mol) of pyridine in 50 ml of methylene chloride. After standing at 25° for 16 hrs, the product was washed with 100 ml of cold 2% sulfuric acid and distilled to give 6.8 g (70 % yield) of bis(2-fluoro-2,2-dinitroethyl) sulfite, bp 100-105°/25 μ (molecular still), n_D^{23} 1.4607.

Anal. Calcd for $C_4H_4N_4F_2SO_{11}$: C, 13.6; H, 1.1; N, 15.8', F, 10.7.

Found: C, 13.4; H, 1.0; N, 15.2; F, 10.6.

Proton nmr ($CDCl_3$): a pair of very closely spaced doublets centered at 307 Hz. Fluorine nmr: ϕ110.0 (t, J_{HF} = 16.2 Hz).

Fractionation of methylene chloride removed in the purification of the sulfite gave 0.5 g of 2-fluoro-2,2-dinitroethyl chloride, identified by comparing its infrared spectrum with that of an authentic sample (see below).

2-Fluoro-2,2-dinitroethyl Chloride. - To a stirred solution of 6.24 g (0.04 mol) of 2-fluoro-2,2-dinitroethanol and 3.95 g (0.04 mol) of pyridine in 50 ml of methylene chloride was added dropwise at 0-5° with cooling 2.7 g (0.02 mol) of sulfuryl chloride. No visible reaction. After 45 min, the reaction mixture was warmed to 25° and was allowed to stand for 7 days. The solution was washed with 200 ml of ice-cold 1% sulfuric acid and distilled to give 3.4 g of 2-fluoro-2,2-dinitroethyl chloride, bp 22-23°/0.2 mm, n_D^{23} 1.4270.

Anal. Calcd for $C_2H_2N_2ClFO_4$: C, 13.9; H, 1.2; N, 16.2; F, 11.0.

Found: C, 13.8 g; H, 1.0; N, 15.4; F, 11.1.

Differential thermal analysis showed an endotherm at 156°, - the boiling point of the compound.

Proton nmr (CCl_4): δ4.60 (d, J_{HF} = 16.1 Hz). Fluorine nmr: ϕ108.2 (s, broad).

Tris(2-fluoro-2,2-dinitroethyl) Borate.— A mixture of 10.8 g (0.07 mol) of 2-fluoro-2,2-dinitroethanol and 2.92 g (0.02 mol) of triethyl borate was heated in a distillation apparatus protected from the atmospheric moisture at 95° for 3 hrs, and then ethanol was distilled at reduced pressure. The remaining solid was recrystallized from methylene chloride to give 8.9 g of white crystalline solid which hydrolyzed slowly when exposed to the moist air.

Anal. Calcd for $C_6H_6N_6BF_3O_{15}$: C, 15.3; H, 1.3; N, 17.9; F, 12.1. Found: C, 15.0; H, 1.3; N, 16.9; F, 11.7.

Proton nmr (CH_3CN): δ4.96 (d, J_{HF} = 16.5 Hz). Fluorine nmr: ϕ111.9 (t, J_{HF} = 16.2 Hz).

2-Fluoro-2,2-dinitroethyl Nitrate.— To a stirred mixture of 12 ml of 100% nitric acid and 12 ml of concentrated sulfuric acid was added dropwise (5 min) at 0-5° 7.7 g of 2-fluoro-2,2-dinitroethanol. The reaction mixture was stirred for 15 minutes, added to 100 g of crushed ice, a water-insoluble liquid separated, and washed with 50 ml of water; weight 7.5 g (75% yield), bp 62-63°/5 mm, n_D^{23} 1.4377 (reported[4] bp 62-62.5°/5-6 mm, n_D^{20} 1.4372).

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2,2-Diperchloratopropane was further characterized by equivalent weight determination. It failed to react with potassium fluoride. Reactions of perfluoroacetone and of cyclopentanone with perchloric acid were investigated.

Iodine and bis(carboalkoxyfluoramino)mercury gave isopropyl fluoroiodocarbamate, which reacted with cyclopentene and cyclohexene to give the corresponding 2-(carboisopropoxyfluoramino)iodocycloalkanes. The mercury compound reacted with thionyl chloride to give N,N'-difluoro-N,N'-bis-(carboiospropoxy)sulfurous acid amide, with benzyl bromide to give isopropyl N-fluoro-N-benzylcarbamate and with trimethylchlorosilane to give carboisopropoxyfluoraminotrimethylsilane. The latter reacted with 2-fluoro-2,2-dinitroethanol to give (2-fluoro-2,2-dinitroethoxy)trimethylsilane. The mercury compound reacted with diphenyldichlorosilane to give bis(carboalkoxyfluoramino)diphenylsilane.

The silver salt of isopropyl fluorocarbamate was prepared from silver oxide and isopropyl fluorocarbamate. It reacted with bromoethane to give isopropyl N-ethylfluorocarbamate. The silver salt and N-bromosuccinimide gave isopropyl bromofluorocarbamate and isopropyl fluoroformate. The silver salt and chlorotriphenylmethane gave isopropyl triphenylmethylfluorocarbamate.

A manuscript covering earlier work on reactions of 2-fluoro-2,2-dinitroethanol is included as an appendix.

14 KEY WORDS	LINK A		LINK B		LINK C	
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