1.3 g (6.4 mmol). The mixture was stirred for 30 min; 7 ml of MeOH was added, followed after 45 min with 17 ml of H_2O. The aqueous phase was separated, washed with $MeCl_2$, and adjusted to pH 3.6 with saturated $(NH_4)HCO_3$ solution. The precipitated 7-ADCA (**2**) weighed 900 mg (75% overall yield).

***p*-Nitrobenzyl 7-Amino-3-methyl-3-cephem-4-carboxylate (3) Hydrochloride Salt.**—*p*-Nitrobenzyl 7-amino-3-methylenecepham-4-carboxylate (**16b**) hydrochloride salt, 386 mg (1 mmol), was dissolved in 5 ml of DMAc containing triethylamine, 198 mg (2 mmol). The mixture was stored at room temperature for 3 hr. The reaction mixture was poured into H_2O–EtOAc. The EtOAc layer was separated, washed with H_2O, dried ($MgSO_4$), and concentrated *in vacuo* to a volume of about 10 ml; 10 ml of 0.1 *N* HCl in EtOAc was added. A crystalline precipitate formed immediately. The product was filtered, washed with EtOAc, and vacuum dried, yield 320 mg (83%).

See Table II for analytical data.

Acknowledgment.—We are grateful to Drs. M. Gorman, G. V. Kaiser, and C. F. Murphy for counsel and encouragement; Mr. G. M. Maciak and associates for microanalyses; Mr. L. A. Spangle and associates for nmr spectra; and Mr. J. B. Campbell for hydrogenation.

Registry No.—**4a**, 3595-30-0; **4b**, 40704-26-5; **4e**, 7027-88-5; **4g**, 40704-27-6; **4h**, 40704-28-7; **4i**, 40704-29-8; **6a**, 37794-96-0; **6b**, 37794-95-9; **6c**, 37794-97-1; **6c** Na salt, 37049-56-2; **6d**, 40704-34-5; **6e**, 36996-01-7; **7**, 23958-11-4; **8**, 40704-38-9; **10**, 37795-02-1; **13a**, 40704-40-3; **13b**, 40704-41-4; **15a**, 40704-37-8; **15b**, 40704-42-5; **15c**, 37795-04-3; **15d**, 37795-05-4; **16a** tosylate, 40704-45-8; **16a** HCl, 40704-46-9; **16b** tosylate, 40704-47-0; **16b** HCl, 40704-48-1; **17a**, 40704-49-2; **17b**, 37795-06-5.

Polynitroalkyl Ethers[1]

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Polynitroethyl ethers were prepared by nitration of the corresponding oximes. Thus, nitration of (2-fluoro-2,2-dinitroethoxy)acetaldoxime followed by oxidation of the nitroso intermediate yielded 2-fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether (**1**). Fluorination and chlorination of **1** yielded bis(2-fluoro-2,2-dinitroethyl) and 2-chloro-2,2-dinitroethyl 2-fluoro-2,2-dinitroethyl ether, respectively. Formaldehyde and **1** yielded 3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropyl formal. 2-Fluoro-2,2-dinitroethyl glycidyl ether reacted with 2-fluoro-2,2-dinitroethanol to give 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2-propanol, which was oxidized with chromic acid to 1,3-bis(2-fluoro-2,2-dinitroethoxy)acetone. Nitration of the oxime of this ketone and oxidation of the nitroso intermediate yielded 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropane. Decomposition of 2-fluoro-2,2-dinitroethanol in alkaline solutions is suppressed by formaldehyde. Under these conditions propargyl bromide gave 2-fluoro-2,2-dinitroethyl propargyl ether. Five 1-(2-fluoro-2,2-dinitroethoxy)-2-propanol derivatives, $FC(NO_2)_2CH_2OCH_2CH(OH)CH_2X$ [X = Cl, Br, I, ONO_2, $OCOC(CH_3)_3$], were synthesized by treating 2-fluoro-2,2-dinitroethyl glycidyl ether with HX. Three of these were oxidized to the corresponding acetone derivatives, $FC(NO_2)_2CH_2OCH_2COCH_2X$ [X = Cl, ONO_2, $OCOC(CH_3)_3$].

Although 2-fluoro-2,2-dinitroethanol can be alkylated in aqueous alkaline solution by reagents such as allyl bromide, methyl sulfate, and simple epoxides to give the corresponding 2-fluoro-2,2-dinitroethyl ethers,[2] alkylating agents with nitro substituents do not yield polynitroalkyl ethers.[3] 2-2-Dinitro alcohols cannot be dehydrated to the corresponding ethers,[4] and bis(2,2-dinitroalkyl) ethers, therefore, must be synthesized indirectly. A recent patent[5] describes the synthesis of bis(2-fluoro-2,2-dinitroethyl) ether in low yield starting with bis(2-iodoethyl) ether. The ether was treated with silver nitrite to give bis(2-nitroethyl) ether. The oxidative nitration of bis(2-nitroethyl) ether with formaldehyde present gave a mixture of methylol derivatives of trinitro- and tetranitrodiethyl ether which was fluorinated to give bis(2-fluoro-2,2-dinitroethyl) ether.

2-Fluoro-2,2-dinitroethyl 2,2-dinitropropyl ether[2] was prepared by nitration of (2-fluoro-2,2-dinitroethoxy)acetone oxime followed by oxidation of the resulting nitroso intermediate with hydrogen peroxide. The precursor ketone was obtained by oxidation of 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether. In the present paper the generality of this route to 2,2-dinitroalkyl ethers is explored.

Although aryldinitromethanes can be readily obtained from aromatic aldoximes[6] by nitration and oxidation, this reaction is not applicable to simple aliphatic aldoximes. It was of interest to determine whether electronegative substituents would facilitate this reaction.

(2,2-Dinitroalkoxy)acetaldehydes have not been described in the literature. A convenient starting material for their synthesis was 3-(2-fluoro-2,2-dinitroethoxy)-1,2-propanediol.[7] (2-Fluoro-2,2-dinitroethoxy)acetaldehyde was obtained by cleaving this diol with either periodic acid or lead tetraacetate. This aldehyde

$$FC(NO_2)_2CH_2OCH_2CH(OH)CH_2OH \xrightarrow[\text{or } Pb(OAc)_4/C_6H_6]{H_5IO_6/H_2O} FC(NO_2)_2CH_2OCH_2CHO + HCHO$$

reacted with hydroxylamine to give (2-fluoro-2,2-dinitroethoxy)acetaldoxime in 90–95% yields. The oxime was nitrated with 90% nitric acid in methylene chloride to give the deep blue nitro–nitroso derivative, which was not isolated. Oxidation of this intermediate

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[1] The sponsor of this work was Air Force Armament Laboratory, ADTC (DLRW) Eglin AFB, Fla. 32542.

[2] V. Grakauskas, *J. Org. Chem.*, **35**, 3030 (1970).

[3] H. G. Adolph, *J. Org. Chem.*, **36**, 806 (1971).

[4] H. G. Adolph and M. J. Kamlet, *J. Org. Chem.*, **34**, 45 (1969).

[5] H. G. Adolph, U. S. Patent 3,531,534 (Sept 28, 1970).

[6] W. Charlton, J. C. Earl, J. Kenner, and A. A. Luciano, *J. Chem. Soc.*, 30 (1932).

[7] The diol was prepared by hydrolysis of 2-fluoro-2,2-dinitroethyl glycidyl ether by a procedure of M. B. Frankel (private communication) as modified by H. J. Marcus, Aerojet-General Corp., Technical Report AFATL-TR-69-140, Oct 1969. Available through the Defense Documentation Center, Cameron Station, Alexandria, Va.

with hydrogen peroxide yielded 2-fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether (**1**). The nitration of (2-fluoro-2,2-dinitroethoxy)acetaldoxime was found to be very sensitive to reaction conditions, such as the order of addition of reagents, temperature, and reaction time. In experiments where yields of **1** were low, large amounts of (2-fluoro-2,2-dinitroethoxy)acetic acid[2] were obtained. The ether **1** is only moderately stable and decomposes to (2-fluoro-2,2-dinitroethoxy)acetic acid and nitrogen oxides in 2–3 days at ambient temperature.

$$\mathrm{FC(NO_2)_2CH_2OCH_2CHO} \xrightarrow{\mathrm{NH_2OH}} \mathrm{FC(NO_2)_2CH_2OCH_2CH{=}NOH} \xrightarrow{\mathrm{HNO_3}} \mathrm{FC(NO_2)_2CH_2OCH_2CH(NO)NO_2} \xrightarrow{\mathrm{H_2O_2}} \underset{\mathbf{1}}{\mathrm{FC(NO_2)_2CH_2OCH_2CH(NO_2)_2}}$$

$$\mathrm{FC(NO_2)_2CH_2OCH_2CH(NO_2)} \longrightarrow \mathrm{FC(NO_2)_2CH_2OCH_2CO_2H}$$

The sparingly water soluble **1** dissolved in aqueous alkali to give orange-red solutions of the corresponding nitronate salts from which **1** can be recovered on acidification.

$$\mathrm{FC(NO_2)_2CH_2OCH_2CH(NO_2)_2} \underset{\mathrm{H_3O^+}}{\overset{\mathrm{OH^-}}{\rightleftharpoons}} \mathrm{FC(NO_2)_2CH_2OCH_2C(NO_2)_2^-}$$

The anion was found to undergo normal halogenation, formylation, and Michael reactions. Direct fluorination of the aqueous sodium salt of **1**, a reaction general for nitronate salts,[8] gave bis(2-fluoro-2,2-dinitroethyl) ether in 50–60% yields, and reaction of **1** with sodium hypochlorite gave 2-chloro-2,2-dinitroethyl 2-fluoro-2,2-dinitroethyl ether.

$$\mathrm{FC(NO_2)_2CH_2OCH_2C(NO_2)_2^-Na^+ + F_2} \xrightarrow{\mathrm{H_2O}} \mathrm{[FC(NO_2)_2CH_2]_2O + NaF}$$

$$\mathrm{FC(NO_2)_2CH_2OCH_2C(NO_2)_2H + NaOCl} \xrightarrow{\mathrm{H_2O}} \mathrm{FC(NO_2)_2CH_2OCH_2C(NO_2)_2Cl}$$

The reaction of **1** with methyl vinyl ketone was briefly examined and the proton nmr spectrum of the product was consistent with the expected 6-(2-fluoro-2,2-dinitroethoxy)-5,5-dinitro-2-hexanone structure.

$$\mathrm{FC(NO_2)_2CH_2OCH_2C(NO_2)_2H + CH_2{=}CHCOCH_3} \xrightarrow[\mathrm{H_2O}]{\mathrm{NaOH}} \mathrm{FC(NO_2)_2CH_2OCH_2C(NO_2)_2CH_2CH_2COCH_3}$$

Difficulties were encountered with the purification of this ketone and a satisfactory elemental analysis was not obtained.

3-(2-Fluoro-2,2-dinitroethoxy)-2,2-dinitropropanol was obtained in 85–95% yields when **1** was treated with aqueous formaldehyde. This alcohol could be deformylated on treatment with aqueous alkali. The formylation of **1** provides a practical way to stabilize this compound for storage.

$$\mathrm{FC(NO_2)_2CH_2OCH_2C(NO_2)_2H + HCHO} \underset{\mathrm{OH^-}}{\rightleftharpoons} \mathrm{FC(NO_2)_2CH_2OCH_2C(NO_2)_2CH_2OH}$$

3-(2-Fluoro-2,2-dinitroethoxy)-2,2-dinitropropanol reacted with *s*-trioxane in concentrated sulfuric acid to give bis[3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropyl] formal.

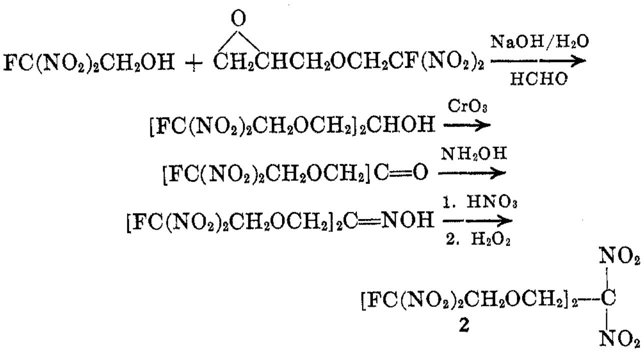
$$\mathrm{FC(NO_2)_2CH_2OCH_2C(NO_2)_2CH_2OH + (CH_2O)_3} \xrightarrow{\mathrm{H_2SO_4}} \mathrm{[FC(NO_2)_2CH_2OCH_2C(NO_2)_2CH_2O]_2CH_2}$$

The nitration method used to synthesize **1** was also applied to the preparation of 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropane (**2**). The starting material in this reaction scheme, 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2-propanol, was unknown. The rate of reaction of 2-fluoro-2,2-dinitroethanol with 2-fluoro-2,2-dinitroethyl glycidyl ether in aqueous base was so slow that decomposition of the alcohol occurred before a significant amount of addition product could be formed. The decomposition of 2-fluoro-2,2-dinitroethanol, however, was found to be retarded by formaldehyde. In the presence of a base, 2-fluoro-2,2-dinitroethanol is known to be in equilibrium with formaldehyde and fluorodinitromethane anion.[2,9] Excess of formaldehyde shifts this equilibrium to the left and reduces the concentration of this unstable anion.

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

In the presence of a large excess of formaldehyde, 2-fluoro-2,2-dinitroethanol reacted with 2-fluoro-2,2-dinitroethyl glycidyl ether to give 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2-propanol in 40% yield. The alcohol was also obtained in 30–40% yield by treating epichlorohydrin with 2 mol of 2-fluoro-2,2-dinitroethanol for 5 days under similar reaction conditions.

1,3-Bis(2-fluoro-2,2-dinitroethoxy)-2-propanol was oxidized to 1,3-bis(2-fluoro-2,2-dinitroethoxy)acetone in 95–100% yields with Jones reagent.[10] This ketone was treated with hydroxylamine to give 1,3-bis(2-fluoro-2,2-dinitroethoxy)acetone oxime, an oil which was not analyzed. Its proton nmr spectrum was consistent with the structure. The oxime was nitrated with 90% nitric acid and the blue nitro–nitroso intermediate was ozidized *in situ* with hydrogen peroxide to give compound **2**.



$$\mathrm{FC(NO_2)_2CH_2OH} + \mathrm{\overset{O}{CH_2CH}CH_2OCH_2CF(NO_2)_2} \xrightarrow[\mathrm{HCHO}]{\mathrm{NaOH/H_2O}} \mathrm{[FC(NO_2)_2CH_2OCH_2]_2CHOH} \xrightarrow{\mathrm{CrO_3}} \mathrm{[FC(NO_2)_2CH_2OCH_2]C{=}O} \xrightarrow{\mathrm{NH_2OH}} \mathrm{[FC(NO_2)_2CH_2OCH_2]_2C{=}NOH} \xrightarrow[\text{2. } \mathrm{H_2O_2}]{\text{1. } \mathrm{HNO_3}} \underset{\mathbf{2}}{\mathrm{[FC(NO_2)_2CH_2OCH_2]_2C(NO_2)_2}}$$

The above observed formaldehyde effect was exploited in a number of other alkylation reactions of 2-fluoro-2,2-dinitroethanol. Formaldehyde-stabilized solutions allowed higher reaction temperatures and longer reaction times. Higher yields of 2-fluoro-2,2-dinitroethyl ethers by a factor of two or more than previously reported[2] were obtained with allyl bromide (see Experi-

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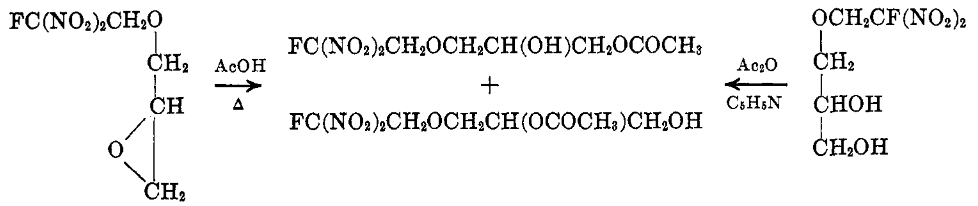
[8] V. Grakauskas and K. Baum, *J. Org. Chem.*, **33**, 3080 (1968).

[9] H. G. Adolph and M. J. Kamlet, *J. Amer. Chem. Soc.*, **88**, 4761 (1966).

[10] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).



(1)

mental Section), propylene oxide, and epichlorohydrin as alkylating agents.[11] In this way 2-fluoro-2,2-dinitroethanol reacted with propargyl bromide to give 2-fluoro-2,2-dinitroethyl propargyl ether[12] in 55% yield. This ether could not be synthesized without added formaldehyde.

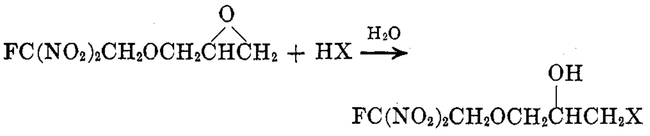
$$\mathrm{FC(NO_2)_2CH_2OH + BrCH_2C{\equiv}CH \xrightarrow[\text{HCHO}]{\text{NaOH/H}_2\text{O}} FC(NO_2)_2CH_2OCH_2C{\equiv}CH}$$

Suppression of deformylation of 2-fluoro-2,2-dinitroethanol by formaldehyde was further confirmed by its reactions with α,β-unsaturated carbonyl compounds. While 2-fluoro-2,2-dinitroethanol normally reacts with unsaturated carbonyl compounds in alkaline aqueous solution to give the corresponding Michael reaction adducts of fluorodinitromethane,[13] no reaction takes place when a large excess of formaldehyde is added.

$$\begin{tikzcd}
\mathrm{FC(NO_2)_2CH_2OH + CH{=}CH_2X} \arrow[r, "\mathrm{NaOH}", "\mathrm{H_2O}"'] \arrow[d, "\mathrm{NaOH/H_2O}", "\mathrm{HCHO}"'] & \mathrm{FC(NO_2)_2CH_2CH_2X + HCHO} \\
\text{no reaction} &
\end{tikzcd}$$

$$\mathrm{X = COCH_3,\ CO_2C_2H_5,\ CN}$$

Other 2-fluoro-2,2-dinitroethyl 2-hydroxyalkyl ethers useful in the above reaction schemes were synthesized by the reaction of 2-fluoro-2,2-dinitroethyl glycidyl ether with acids. Thus, dilute hydrochloric, hydrobromic, hydriodic, and nitric acid gave 1-chloro-2-hydroxypropyl, 1-bromo-2-hydroxypropyl, 1-iodo-2-hydroxypropyl, and 1-nitrato-2-hydroxypropyl 2-fluoro-2,2-dinitroethyl ether, respectively, in 80–100% yields.[14]



$$\mathrm{FC(NO_2)_2CH_2OCH_2\overset{O}{CHCH_2} + HX \xrightarrow{H_2O} FC(NO_2)_2CH_2OCH_2\overset{OH}{C}HCH_2X}$$

$$\mathrm{X = Cl,\ Br,\ I,\ NO_3}$$

While in the above reaction there was no evidence of the isomeric primary alcohols, a mixture of the two isomeric monoacetates of 3-(2-fluoro-2,2-dinitroethoxy)-1,2-propanediol was obtained when 2-fluoro-2,2-dinitroethyl glycidyl ether was treated with acetic acid or 3-(2-fluoro-2,2-dinitroethoxy)-1,3-propanediol was acylated with 1 mol of acetic anhydride (eq 1). On the other hand, 3-(2-fluoro-2,2-dinitroethoxy)-1,2-propanediol reacted with the more sterically hindered pivaloyl chloride to give only one isomer, 3-(2-fluoro-2,2-dinitroethoxy)-2-hydroxy-1-propyl pivalate.

$$\mathrm{FC(NO_2)_2CH_2OCH_2CH(OH)CH_2OH + (CH_3)_3CCOCl \xrightarrow[C_5H_5N]{CH_2Cl_2} FC(NO_2)_2CH_2OCH_2CH(OH)CH_2OCOC(CH_3)_3}$$

Three of these isopropyl alcohol derivatives, 1-(2-fluoro-2,2-dinitroethoxy)-3-chloro-2-propanol, 1-(2-fluoro-2,2-dinitroethoxy)-3-nitrato-2-propanol, and 3-(2-fluoro-2,2-dinitroethoxy)-2-hydroxy-1-propyl pivalate, were oxidized to the corresponding ketones in 85–95% yields with Jones reagent. The preparation of oximes of these ketones was not investigated.

$$\mathrm{FC(NO_2)_2CH_2OCH_2CH(OH)CH_2X \xrightarrow[CH_3COCH_3]{CrO_3/H_2SO_4} FC(NO_2)_2CH_2OCH_2COCH_2X}$$

$$\mathrm{X = Cl,\ ONO_2,\ OCOC(CH_3)_3}$$

Experimental Section

General.—Explosive properties of the polynitro ethers described below have not been investigated. Adequate safety shielding should be used in all operations. 2-Fluoro-2,2-di-dinitroethanol is a severe skin irritant and contact should be avoided.

Proton and fluorine nmr spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane and trichlorofluoromethane as the respective internal standards.

(2-Fluoro-2,2-dinitroethoxy)acetaldehyde.—To a stirred solution of 2.0 g (0.0132 mol) of 1-(2-fluoro-2,2-dinitroethoxy)-2,3-propanediol[7] in 10 ml of water was added dropwise over a period of 5 min at 25–28° a solution of 3.0 g (0.0132 mol) of periodic acid (H_5IO_6) in 5 ml of water. The reaction was mildly exothermic and in a few minutes a water-insoluble liquid began to separate. The mixture was stirred for 30 min, saturated with sodium chloride, and extracted with 20 ml of methylene chloride. The methylene chloride extract was distilled to give 2.15 g (83% yield) of (2-fluoro-2,2-dinitroethoxy)acetaldehyde, bp 83–84° (0.1 mm), $n^{25}\mathrm{D}$ 1.4365.

Anal. Calcd for $C_4H_5N_2FO_6$: C, 24.5; H, 2.5; N, 14.3; F, 9.7. Found: C, 24.71; H, 2.34; N, 13.74; F, 9.5.

Proton nmr (CCl_4) δ 4.80 (d, J_{HF} = 18.0 Hz, 2 H, $FCCH_2O$–), 4.41 (s, 2 H, –CH_2CHO), and 9.78 (s, 1 H, –CHO); ir 5.77 (C=O), 6.29 μ (NO_2).

(2-Fluoro-2,2-dinitroethoxy)acetaldehyde was also obtained in comparable yields by oxidizing the diol with lead tetraacetate in benzene solution at ambient temperatures.

(2-Fluoro-2,2-dinitroethoxy)acetaldoxime.—A mixture of 4.9 g (0.025 mol) of (2-fluoro-2,2-dinitroethoxy)acetaldehyde, 5.75 g (0.0825 mol) of hydroxylamine hydrochloride, and 11.3 g (0.0825 mol) of sodium acetate trihydrate in 70 ml of absolute ethanol was refluxed for 45 min, and then *ca.* 60 ml of ethanol was removed at 25° (25 min). The residue was added to 100 ml of ice water and the product was extracted with 35 ml of methylene chloride. The extract was dried and concentrated to leave 5.2 g of liquid which was distilled in a molecular still

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[11] The crude reaction products obtained in alkylation reaction employing excesses of formaldehyde were contaminated with polymethylene oxides introduced by formaldehyde solutions. These impurities presented some problems in the purification of alkylation products.

[12] 2-Fluoro-2,2-dinitroethyl propargyl ether represents a new class of polynitro ethers and some of its reactions were briefly examined. The ether readily added 1 mol of bromine to give 2-fluoro-2,2-dinitroethyl 2,3-dibromoallyl ether.

$$\mathrm{FC(NO_2)_2CH_2OCH_2C{\equiv}CH + Br_2 \longrightarrow FC(NO_2)_2CH_2OCH_2CBr{=}CHBr}$$

Concentrated sulfuric acid hydrated the propargyl ether to give (2-fluoro-2,2-dinitroethoxy)acetone.[2]

$$\mathrm{FC(NO_2)_2CH_2OCH_2C{\equiv}CH \xrightarrow{H_2SO_4} FC(NO_2)_2CH_2OCH_2COCH_3}$$

See Experimental Section for details.

[13] V. Grakauskas and K. Baum, *J. Org. Chem.*, **34**, 3927 (1969).

[14] 1-Chloro-2-hydroxypropyl and 1-bromo-2-hydroxypropyl 2-fluoro-2,2-dinitroethyl ethers were isolated as by-products in the preparation of 2-fluoro-2,2-dinitroethyl glycidyl ether from aqueous alkaline 2-fluoro-2,2-dinitroethanol and epichlorohydrin and epibromohydrin, respectively. Methanolic potassium hydroxide cyclized these halohydrins to 2-fluoro-2,2-dinitroethyl glycidyl ether (see Experimental Section).

at 100–105° (0.1 mm) to give 4.8 g, 91% yield, of (2-fluoro-2,2-dinitroethoxy)acetaldoxime.

Anal. Calcd for $C_4H_6N_3FO_6$: C, 22.75; H, 2.84; N, 19.90; F, 9.01. Found: C, 22.46; H, 2.58; N, 19.60; F, 9.1.

Proton nmr ($CDCl_3$) δ 8.44 (s, broad, 1 H, =NOH), 7.42 (t, J = 5.8 Hz, *ca.* 60% anti CH=), 6.84 (t, J = 4.0 Hz, *ca.* 40% syn CH=), 4.62 (d, J = 19.1 Hz, $FCCH_2$–, syn isomer), 4.53 (d, J = 19.0 Hz, $FCCH_2$–, anti isomer), 4.50 (d, J = 4.0 Hz, –OCH_2C=, syn isomer), and 4.25 (d, J = 5.8 Hz, OCH_2C anti isomer); fluorine nmr ϕ 110.9 (t, J_{HF} = 18.7 Hz).

2-Fluoro-2,2-dinitroethyl 2,2-Dinitroethyl Ether (1).—To a stirred and cooled solution of 4.2 g (0.02 mol) of (2-fluoro-2,2-dinitroethoxy)acetaldoxime in 60 ml of methylene chloride was added dropwise at 3–5° over a period of 7–8 min 10 g of 90% nitric acid. The mixture became turbid and then turned blue in a moderately exothermic reaction. The deep blue solution was stirred for 20 min and then to it was added dropwise, over a period of 20 min, 6.5 ml of 30% hydrogen peroxide until the blue color was discharged. The mixture was stirred with 90 ml of ice water for a few minutes. The methylene chloride solution was dried over anhydrous sodium sulfate, filtered, and concentrated to leave 3.5 g (65% yield) of crude 1, a colorless liquid. An analytical sample was distilled at 105–110° (50 μ) in a molecular still.

Anal. Calcd for $C_4H_5N_4FO_9$: C, 17.64; H, 1.84; N, 20.59. Found: C, 18.2; H, 1.64; N, 19.2.

Proton nmr ($CDCl_3$) δ 6.51 (t, J = 6.0 Hz, 1 H, CH), 4.94 (d, J_{HF} = 15.8 Hz, 2 H, $FCCH_2$–), and 4.80 (d, J = 6.0 Hz, 2 H, CH_2).

Bis(2-fluoro-2,2-dinitroethyl) Ether.—2-Fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether, 3.5 g (above), was added at 0° to a solution of 1.0 g of sodium hydroxide in 65 ml of water and the resulting orange-red solution was fluorinated with elementary fluorine (diluted fourfold with nitrogen) until the solution became colorless (10 min). The mixture was extracted with 35 ml of methylene chloride to give 2.3 g of bis(2-fluoro-2,2-dinitroethyl) ether, 62% yield, bp 100° (0.4 mm), *d* 1.629.

Anal. Calcd for $C_4H_4N_4F_2O_9$: C, 16.6; H, 1.4; F, 13.1. Found: C, 16.7; H, 1.3; F, 12.9.

Proton nmr ($CDCl_3$) δ 4.84 (d, J_{HF} = 16.0 Hz); fluorine nmr ϕ 109.2 (poorly resolved triplet).

2-Chloro-2,2-dinitroethyl 2-Fluoro-2,2-dinitroethyl Ether.—To 20 ml of 5.3% aqueous sodium hypochlorite was added 0.5 g of 1. The mixture was stirred for 10 min and extracted with 20 ml of carbon tetrachloride to give 0.55 g of 2-chloro-2,2-dinitroethyl 2-fluoro-2,2-dinitroethyl ether, a colorless liquid, which was not further purified.

Anal. Calcd for $C_4H_4N_4ClFO_9$: C, 15.66; H, 1.30; F, 6.20. Found: C, 16.1; H, 1.09; F, 6.3.

Proton nmr (CCl_4) δ 5.03 (d, J = 16 Hz, 2 H, $FCCH_2$–) and 4.97 (s, 2 H, CH_2CCl).

Reaction of Methyl Vinyl Ketone with 1.—To a stirred suspension of 0.6 g (2.0 mmol) of 1 and 0.14 g (2.0 mmol) of methyl vinyl ketone in 10 ml of water at 25° was added a few drops of 10% aqueous potassium hydroxide. After 15 min the mixture was extracted with 10 ml of methylene chloride and the extract was evaporated to give 0.5 g of crude product, a viscous oil: proton nmr ($CDCl_3$) δ 4.71 (d, J_{HF} = 18.6 Hz, 2 H, $FCCH_2$), 4.52 (s, 2 H, –OCH_2C–), 2.55–2.85 (m, 4 H, –CH_2CH_2CO), and 2.20 (s, 3 H, CH_3).

3-(2-Fluoro-2,2-dinitroethoxy)-2,2-dinitropropanol.—To a suspension of 1.0 g of 1 in 10 ml of water was added 1.0 g of 37% aqueous formaldehyde and a few drops of 5% aqueous sodium hydroxide. The mixture was stirred for 20 min at 18–25° and then acidified with a few drops of 10% hydrochloric acid. The mixture was extracted with two 7-ml portions of methylene chloride. The combined methylene chloride extracts were concentrated to leave 0.95 g (86% yield) of 3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropanol. An analytical sample was distilled at 120–125° (0.1 mm) in a molecular still.

Anal. Calcd for $C_5H_7N_4FO_{10}$: C, 19.87; H, 2.33; F, 6.28. Found: C, 20.12; H, 2.01; F, 6.1.

Proton nmr ($CDCl_3$) δ 4.70 (d, J_{HF} = 16 Hz, 2 H, $FCCH_2$–), 4.63 (s, 2 H, –OCH_2CC–), 4.43 (s, 2 H, CH_2CCH_2OH), and 2.72 (broad s, 1 H, OH).

Bis[3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropyl] Formal.—To a stirred solution of 0.6 g (0.002 mol) of 3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropanol and 0.03 g (0.001 equiv) of *s*-trioxane in 10 ml of methylene chloride at 5–10° was added 1.0 ml of concentrated sulfuric acid. The mixture was stirred at 22–25° for 2 hr and phases were separated. The sulfuric acid phase was extracted with two 10-ml portions of methylene chloride. The methylene chloride solution was combined with extracts. The solution was washed with 20 ml of water and evaporated to give 0.4 g of a colorless, viscous oil, *d* 1.641, which was not further purified.

Anal. Calcd for $C_{11}H_{14}N_8F_2O_{20}$: C, 21.47; H, 2.12; F, 6.17. Found: C, 21.28; H, 1.97; F, 6.41.

Proton nmr ($CDCl_3$) δ 4.77 (s, 2 H, formal CH_2), 4.75 (d, J_{HF} = 16 Hz, 4 H, 2 $FCCH_2$–), 4.65 (s, 4 H, 2 $FCCH_2OCH_2$–), and 4.37 (s, 4 H, –$C\mathbf{H_2}OCH_2OC\mathbf{H_2}C$–).

1,3-Bis(2-fluoro-2,2-dinitroethoxy)-2-propanol.—To a solution of 4.0 g (0.026 mol) of 2-fluoro-2,2-dinitroethanol in 35 g of 37% aqueous formaldehyde was added 1.32 g (0.02 mol) of 85% potassium hydroxide in 4 ml of water, 4.2 g (0.02 mol) of 2-fluoro-2,2-dinitroethyl glycidyl ether, and 5.0 ml of methanol. The reaction mixture was stirred at 22–25° for 20 hr, diluted with water to 120 ml, and extracted with 50 ml of methylene chloride to give 3.0 g of 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2-propanol. An analytical sample was distilled in a molecular still at 155–160° (0.1 mm).

Anal. Calcd for $C_7H_{10}N_4F_2O_{11}$: C, 23.08; H, 2.76; F, 10.43. Found: C, 23.30; H, 2.61; F, 9.8.

Proton nmr ($CDCl_3$) δ 4.65 (d, J_{HF} = 17.6Hz, 4 H, $FCCH_2$–), 2.52 (broad s, 1 H, OH), and 3.52–4.02 (superimposed multiplets, 5 H, –CH_2CHCH_2–); fluorine nmr ϕ 111.2 (poorly resolved triplet).

1,3-Bis(2-fluoro-2,2-dinitroethoxy)acetone.—To a stirred solution of 13.1 g (0.036 mol) of crude 1,2-bis(2-fluoro-2,2-dinitroethoxy)-2-propanol (above), in 120 ml of acetone at 20–22° was added dropwise, over a period of 45 min, a solution of 10.0 g (0.1 mol) of chromium trioxide and 8.0 g of concentrated sulfuric acid in 10 ml of water (Jones reagent[10]) until chromate color persisted. The unreacted chromate was destroyed with a few drops of isopropyl alcohol. The mixture was filtered and the filtrate was stirred with 10 g of sodium bicarbonate for 10 min. The mixture was filtered again and the filtrate was concentrated to *ca.* 15 ml. The concentrate was added to 200 ml of water and a water-insoluble liquid was extracted with 60 ml of methylene chloride to give 12.8 g (quantitative yield) of 1,3-bis(2-fluoro-2,2-dinitroethoxy)acetone, a colorless liquid. An analytical sample was distilled in a molecular still at 140° (0.1 mm).

Anal. Calcd for $C_7H_8N_4F_2O_{11}$: C, 23.21; H, 2.22; F, 10.49. Found: C, 23.43; H, 2.06; F, 10.3.

Proton nmr ($CDCl_3$) δ 4.72 (d, J_{HF} = 16.4 Hz, 4 H, 2 $FCCH_2$–) and 4.43 (s, 4 H, –CH_2COCH_2–); fluorine nmr ϕ 111.2 (poorly resolved triplet).

1,3-Bis(2-fluoro-2,2-dinitroethoxy)acetone Oxime.—To a solution of 10.0 g (*ca.* 0.03 mol) of crude 1,3-bis(2-fluoro-2,2-dinitroethoxy)acetone (above) in 70 ml of methanol was added 5.1 g of hydroxylamine hydrochloride and 10 g of sodium acetate trihydrate and the mixture was refluxed for 2 hr. The hot mixture was filtered and the filtrate was concentrated to 20 ml. The concentrated mixture was added to 100 ml of water and water-insoluble oil was extracted with 50 ml of methylene chloride. The methylene chloride solution was concentrated to give 10 g of crude 1,3-bis(2-fluoro-2,2-dinitroethoxy)acetone oxime: proton nmr ($CDCl_3$) δ 7.40 (s, broad, 1 H, =NOH), 4.72 (d, J_{HF} = 16.8 Hz, 4 H, 2 $FCCH_2$–), and 4.67 and 4.28 [s, 4 H, –CH_2C(=NOH)CH_2–].

1,3-Bis(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropane (2).—To a stirred solution of 2.0 g of crude 1,3-bis(2-fluoro-2,2-dinitroethoxy)acetone oxime (above) in 30 ml of methylene chloride at 0.5° was added dropwise, over a period of 10 min, 3.5 g of 90% nitric acid. The reaction mixture first turned turbid and then deep blue. After 20 min, 30% hydrogen peroxide was added dropwise (20 min) until the blue color of the solution was discharged. The mixture was added to 60 ml of ice water and the phases were separated. The methylene chloride solution was stripped to give 1.4 g of crude 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropane. The crude material was purified by passing its $CDCl_3$ solution through a 0.5 × 25 mm column of basic alumina (Biorad, AGIO, 100–200 mesh).

Anal. Calcd for $C_7H_8N_6F_2O_{14}$: C, 19.18; H, 1.84; F, 8.67. Found: C, 20.30; H, 2.01; F, 8.4.

Proton nmr ($CDCl_3$) δ 4.70, (d, J_{HF} = 16 Hz, 4 H, 2 $FCCH_2$–) and 4.55 [s, 4 H, –$CH_2C(NO_2)_2CH_2$–]; fluorine nmr ϕ 110.8 (poorly resolved triplet).

Allyl 2-Fluoro-2,2-dinitroethyl Ether.—To 35 ml of 37–40% aqueous formaldehyde in 150 ml of water was added 30.8 g (0.2

mol) of 2-fluoro-2,2-dinitroethanol and a solution of 10.8 g (0.26 mol) of sodium hydroxide in 10 ml of water. To the solution was added 36.3 g (0.3 mol) of allyl bromide and the mixture was stirred for 45 hr at 23–25°. The mixture was extracted with 50 ml of methylene chloride to give 25.5 g (66% yield) of allyl 2-fluoro-2,2-dinitroethyl ether, bp 31° (0.2 mm) [lit.[2] bp 31–32° (0.2 mm)].

2-Fluoro-2,2-dinitroethyl Propargyl Ether.—To a mixture of 3.1 g (0.02 mol) of 2-fluoro-2,2-dinitroethanol, 20 ml of 18% aqueous formaldehyde, and 1.0 g (0.025 mol) of sodium hydroxide was added 2.4 g *(0.02 mol) of propargyl bromide. The reaction* mixture was stirred vigorously at 22–25° for 30 hr and then was extracted with 25 ml of methylene chloride. The methylene chloride extract was distilled to give 2.1 g of 2-fluoro-2,2-dinitroethyl propargyl ether (55% yield), a colorless liquid, bp 35° (0.3 mm).

Anal. Calcd for $C_5H_5N_2FO_5$: C, 31.25; H, 2.62; N, 14.58; F, 9.89. Found: C, 31.56; H, 2.52; N, 14.0; F, 9.4.

Proton nmr (CCl_4) δ 4.59 (d, J_{HF} = 17.8 Hz, 2 H, $FCCH_2$), 4.28 (d, J_{HH} = 3 Hz, 2 H, $OCH_2C{=}$), and 2.56 (t, J_{HH} = 3 Hz, 1 H, $-C{\equiv}CH$); fluorine nmr ϕ 110.7 (poorly resolved triplet).

2-Fluoro-2,2-dinitroethyl 2,3-Dibromoallyl Ether.—To a stirred suspension of 1.92 g (0.01 mol) of 2-fluoro-2,2-dinitroethyl propargyl ether in 25 ml of water was added 1.6 g (0.01 mol) of bromine. The reaction mixture was stirred at 25° for 30 min and then was extracted with 20 ml of methylene chloride. The methylene chloride extract was fractionated to give 2.28 g of 2-fluoro-2,2-dinitroethyl 2,3-dibromoallyl ether, a colorless liquid, bp 80° (0.1 mm).

Anal. Calcd for $C_5H_5N_2FBr_2O_5$: C, 17.05; H, 1.43; F, 5.39. Found: C, 17.41; H, 1.33; F, 5.54.

Proton nmr ($CDCl_3$) δ 6.82 (s, 1 H, $=CHBr$), 4.55 (d, J_{HF} = 17.0 Hz, 2 H, $FCCH_2-$), and 4.57 (s, 2 H, $-CH_2CBr{=}$); fluorine nmr ϕ 112.0 (poorly resolved triplet).

(2-Fluoro-2,2-dinitroethoxy)acetone.—2-Fluoro-2,2-dinitroethyl propargyl ether, 0.5 g, was added dropwise at 25° to 10 ml of concentrated sulfuric acid. The reaction temperature increased to 30–32° and the mixture darkened. After 5 min, the reaction mixture was added to 50 ml of ice water and extracted *with 5 ml of carbon tetrachloride. The proton nmr spectrum of* the extract showed that it contained 80% of the starting material and 20% of (2-fluoro-2,2-dinitroethoxy)acetone.[2]

1-Chloro-3-(2-fluoro-2,2-dinitroethoxy)-2-propanol.—A suspension of 2.1 g (0.01 mol) of 2-fluoro-2,2-dinitroethyl glycidyl ether in 30 ml of 8% hydrochloric acid was stirred at 25° for 16 hr. The mixture was extracted with 20 ml of methylene chloride to give 2.45 g (100% yield) of 1-chloro-2-(2-fluoro-2,2-dinitroethoxy)-2-propanol. An analytical sample was distilled at 100° (0.1 mm) in a molecular still.

Anal. Calcd for $C_5H_8N_2ClFO_6$: *C, 24.53; H, 3.25; N, 11.36;* F, 7.7. Found: C, 24.57; H, 2.91; N, 10.86; F, 7.6.

Proton nmr ($CDCl_3$) δ 4.65 (d, J_{HF} = 17.4 Hz, 2 H, $FCCH_2-$), 2.70 (broad s, 1 H, OH), and superimposed multiplets at 3.47–2.17 (5 H, CH_2CHCH_2); fluorine nmr ϕ 111.0 (poorly resolved triplet).

The compound was also isolated as the side reaction product (incomplete cyclization) in the synthesis of 2-fluoro-2,2-dinitroethyl glycidyl ether from 2-fluoro-2,2-dinitroethanol and epichlorohydrin.

2-Fluoro-2,2-dinitroethyl Glycidyl Ether.—To a stirred solution of 1.23 g (0.05 mol) of 1-chloro-3-(2-fluoro-2,2-dinitroethoxy)-2-propanol in 5 ml of methanol at 22–25° was added, dropwise, a solution of 0.34 g (0.05 mol) of 85% potassium hydroxide in 5 ml of methanol. The mixture was stirred for 15 min, diluted with 50 ml of ice water, and extracted with 25 ml of methylene chloride. The extract was distilled to give 2.0 g (95% yield) of 2-fluoro-2,2-dinitroethyl glycidyl ether, bp 71° (0.1 mm) [lit.[2] bp 70–71° (0.1 mm)].

1-Bromo-3-(2-fluoro-2,2-dinitroethoxy)-2-propanol.—The title compound, a colorless liquid, distilled in a molecular still at 110° (0.1 mm), was obtained in 90% yield by treating 2-fluoro-2,2-dinitroethyl glycidyl ether with 10% hydrobromic acid.

Anal. Calcd for $C_5H_8N_2BrFO_6$: C, 20.62; H, 2.76; N, 9.62; F, 6.52. Found: C, 20.80; H, 2.31; N, 9.50; F, 6.4.

Proton nmr δ 4.65 (d, J_{HF} = 17.2 Hz, 2 H, $FCCH_2-$), 2.58 (d, J_{H-OH} = 3.8 Hz, 1 H, OH), and 3.33–4.13 (superimposed multiplets, 5 H, CH_2CHCH_2); fluorine nmr ϕ 109.5 (poorly resolved triplet, J_{HF} = 17 Hz).

1-Iodo-3-(2-fluoro-2,2-dinitroethoxy)-2-propanol.—The title compound, a colorless liquid, distilled in a molecular still at 115–120° (0.1 mm), was obtained in 92% yield by treating 2-fluoro-2,2-dinitroethyl glycidyl ether with 15% hydroiodic acid following the procedure used for the synthesis of the chloro analog.

Anal. Calcd for $C_5H_8N_2FIO_6$: C, 17.76; H, 2.38; N, 8.28; F, 5.62. Found: C, 18.08; H, 2.31; N, 7.8; F, 5.7.

Proton nmr ($CDCl_3$) δ 4.63 (d, J_{HF} = 17.1 Hz, 2 H, $FCCH_2-$), 2.67 (broad s, 1 H, OH), 3.13–4.05 (superimposed multiplets, 5 H, CH_2CHCH_2); fluorine nmr ϕ 109.6 (t, J_{HF} = 17.0 Hz).

1-(2-Fluoro-2,2-dinitroethoxy)-3-nitrato-2-propanol.—To a stirred solution of 7.0 ml of 70% nitric acid in 14 ml of water at *25° was added 2.1 g (0.01 mol) of 2-fluoro-2,2-dinitroethyl* glycidyl ether. After 20 min the solution was extracted with 15 ml of methylene chloride. The extract was concentrated to leave 2.2 g of 1-(2-fluoro-2,2-dinitroethoxy)-3-nitrato-2-propanol (80% yield), a colorless liquid. An analytical sample was distilled in a molecular still at 125° (0.1 mm).

Anal. Calcd for $C_5H_8N_3FO_9$: C, 21.98; H, 2.95; F, 6.95. Found: C, 21.92; H, 2.68; F, 7.1.

Proton nmr ($CDCl_3$) δ 4.67 (d, J_{HF} = 16.0 Hz, 2 H, $FCCH_2-$), 2.80 (broad s, 1 H, OH), and 3.50–4.50 (superimposed multiplets, 5 H, $-CH_2CHCH_2-$); fluorine nmr ϕ *110.7* (poorly resolved triplet).

3-(2-Fluoro-2,2-dinitroethoxy)-2-hydroxy-1-propyl Pivalate.—To a stirred solution of 2.28 g (0.01 mol) of 3-(2-fluoro-2,2-dinitroethoxy)-1,2-propanediol and 0.84 g (0.01 mol) of pyridine in 20 ml of methylene chloride was added at 20–25° dropwise (3 min) a solution of 1.20 g (0.01 mol) of pivaloyl chloride in 5 ml of methylene chloride. The mixture was stirred for 10 min, washed with 50 ml of 3% hydrochloric acid, dried, and concentrated to give 3.05 g (98% yield) of 3-(2-fluoro-2,2-dinitroethoxy)-2-hydroxyl-1-propyl pivalate. An analytical sample was distilled in a molecular still at 135° (0.1 mm).

Anal. Calcd for $C_{10}H_{17}N_2FO_8$: C, 38.46; H, 5.48; N, 8.97; F, 6.08. Found: C, 38.80; H, 5.48; N, 8.69; F, 5.92.

Proton nmr ($CDCl_3$) δ 4.72 (d, J_{JF} = 18.0 Hz, 2 H, $FCCH_2-$), 3.25 (broad s, 1 H, OH), 1.22 [s, 9 H, $-(CCH_3)_3$], and 3.25–363 (superimposed multiplets, $-CH_2CHCH_2-$); fluorine nmr ϕ 110.0 (t, J_{HF} = 17.8 Hz).

1-Chloro-3-(2-fluoro-2,2-dinitroethoxy)acetone.—To a stirred *solution of 4.94 g (0.02 mol) of 1-chloro-3-(2-fluoro-2,2-dinitro*ethoxy)-2-propanol in 75 ml of acetone was added at 20–23° dropwise over a period of 45 min chromic–sulfuric acid solution (Jones reagent prepared by adding 1.75 ml of concentrated sulfuric acid to a solution of 2.0 g of chromium trioxide in 1 ml of water). The mixture was stirred for 45 min and the excess of chromium trioxide was destroyed with a few drops of isopropyl alcohol. The mixture was filtered and the filter cake was washed with two 5-ml portions of acetone. The combined filtrate and washings were stirred with 5 g of sodium bicarbonate for 10 min, filtered, and concentrated to *ca.* 10 ml. The concentrated solution was diluted with 80 ml of water and extracted with 45 ml of methylene chloride to give 4.6 g (94% yield) of 1-chloro-3-(2-fluoro-2,2-dinitroethoxy) acetone, a colorless liquid. An analytical sample was distilled in a molecular still at 125° (0.1 mm).

Anal. Calcd for $C_5H_6N_2ClFO_6$: C, 24.55; H, 2.45; N, 11.45; F, 7.76. Found: C, 24.69; H, 2.61; N, 11.31; F, 7.98.

Proton nmr (50:50 $CDCl_3-CCl_4$) δ 4.66 (d, J_{HF} = 17.0 Hz, 2 H, $FCCH_2-$), 4.52 (s, 2 H, OCH_2CO), and 4.8 (s, 2 H, $-CH_2Cl$); fluorine nmr ϕ 109.7 (poorly resolved triplet, J_{HF} = 17 Hz).

3-(2-Fluoro-2,2-dinitroethoxy)-2-oxo-1-propyl Pivalate.—The title compound, a colorless oil, was prepared in 85% yield by oxidation of 3-(2-fluoro-2,2-dinitroethoxy)-2-hydroxy-1-propyl pivalate with Jones reagent following the above procedure. An analytical sample was distilled in a molecular still at 145° (0.1 mm).

Anal. Calcd for $C_{10}H_{15}N_2FO_8$: C, 38.71; H, 4.87; N, 9.03; F, 6.12. Found: C, 38.73; H, 5.30; N, 9.18; F, 5.96.

Proton nmr ($CDCl_3$) δ 4.75 (d, J_{HF} = 16.4 Hz, 2 H, $FCCH_2-$), 4.63 (s, 2 H, OCH_2CO), 4.37 (s, 2 H, CH_2), and 1.25 [s, 9 H, $C(CH_3)$]; fluorine nmr ϕ 110.6 (poorly resolved triplet, J_{HF} = 16.5 Hz).

1-(2-Fluoro-2,2-dinitroethoxy)-3-nitratoacetone.—The title compound, a colorless liquid, was prepared in 90% yield by the oxidation of 1-(2-fluoro-2,2-dinitroethoxy)-3-nitrato-2-propanol with Jones reagent following the procedure described above for the 3-chloro analog. An analytical sample was distilled in a molecular still at 125° (0.1 mm).

Anal. Calcd for $C_5H_6N_3FO_9$: C, 22.14; H, 2.23; F, 7.0. Found: C, 21.93; H, 2.03; F, 7.1.

Proton nmr ($CDCl_3$) δ 5.13 (s, 2 H, CH_2ONO_2), 4.75 (d, $J_{HF} = 17.0$ Hz, 2 H, $FCCH_2-$), and 4.48 (s, 2 H, CH_2); fluorine nmr ϕ 109.4 (poorly resolved triplet).

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Registry No.—**1**, 40695-29-5; **2**, 40695-30-8; (2-fluoro-2,2-dinitroethoxy)acetaldehyde, 40696-31-9; 1-(2-fluoro-2,2-dinitroethoxy)-2,3-propanediol, 40696-32-0; periodic acid, 10450-60-9; (2-fluoro-2,2-dinitroethoxy)acetaldoxime, 40696-33-1; hydroxylamine hydrochloride, 5470-11-1; sodium acetate, 127-09-3; bis(2-fluoro-2,2-dinitroethyl) ether, 30290-64-3; 2-chloro-2,2-dinitroethyl 2-fluoro-2,2-dinitroethyl ether, 40696-35-3; methyl vinyl ketone, 78-94-4; 3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropanol, 40696-36-4; bis[3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropyl] formal, 40696-37-5; *s*-trioxane, 110-88-3; 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2-propanol, 35323-16-1; 2-fluoro-2,2-dinitroethanol, 17003-75-7; 2-fluoro-2,2-dinitroethyl glycidyl ether, 40696-32-0; 1,3-bis(2-fluoro-2,2-dinitroethoxy)acetone, 40696-41-1; 1,3-bis(2-fluoro-2,2-dinitroethoxy)acetone oxime, 40696-42-2; 2-fluoro-2,2-dinitroethyl propargyl ether, 40696-43-3; 2-fluoro-2,2-dinitroethyl-2,3-dibromoallyl ether, 40696-44-4; bromine, 7726-95-6; (2-fluoro-2,2-dinitroethoxy)acetone, 25172-32-1; 1-chloro-3-(2-fluoro-2,2-dinitroethoxy)-2-propanol, 40696-46-6; 1-bromo-3-(2-fluoro-2,2-dinitroethoxy)-2-propanol, 40696-47-7; hydrobromic acid, 10035-10-6; 1-iodo-3-(2-fluoro-2,2-dinitroethoxy)-2-propanol, 40696-48-8; hydriodic acid, 10034-85-2; 1-(2-fluoro-2,2-dinitroethoxy)-3-nitrato-2-propanol, 40696-49-9; nitric acid, 7697-37-2; 3-(2-fluoro-2,2-dinitroethoxy)-2-hydroxy-1-propyl pivalate, 40696-50-2; 3-(2-fluoro-2,2-dinitroethoxy)-1,2-propanediol, 40696-32-0; pyridine, 110-86-1; 1-chloro-3-(2-fluoro-2,2-dinitroethoxy)acetone, 40696-52-4; 3-(2-fluoro-2,2-dinitroethoxy)-2-oxo-1-propyl pivalate, 40696-53-5; 1-(2-fluoro-2,2-dinitroethoxy)-3-nitratoacetone, 40696-54-6.

Synthesis of α-Monosubstituted Indoles

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The preparation of α-monosubstituted indoles by (a) the Madelung reaction, (b) *o*-nitrobenzyl ketone reduction, and (c) *o*,β-dinitrostyrene reduction was explored. The Madelung reaction is limited to use on those toluidides which do not have double bonds or active hydrogens present. Toluidides having tertiary benzylamine groups can be used. *o*-Nitrobenzyl ketone preparations were attempted by the arylation of β-keto esters with *o*-fluoronitrobenzene. This reaction is limited to α-unsubstituted acetoacetic esters. The dinitrostyrene route appears to be useful when the appropriate primary nitro compound is available for condensation with *o*-nitrobenzaldehyde.

Of the many reported syntheses of indole alkaloids, most have used reaction sequences involving either the formation of the disubstituted indole by means of a Fisher indole synthesis or the preparation of an appropriate β-substituted indole followed by a ring closure into the α position of the indole ring.[2] It was thought, however, that it would be advantageous in some cases to first prepare an α-monosubstituted indole and then utilize the higher reactivity of the β position[3] to facilitate the subsequent ring closure.[4] This approach would also avoid the formation of intermediate 3,3-disubstituted 3*H*-indoles, which could rearrange to give a mixture of products.[5]

While a number of methods have been reported for the exclusive preparation of α-substituted indoles,[6] with the exception of the triethylphosphite reduction of *o*-nitrostyrenes[7] and the pyrolysis of *o*-azidostyrenes,[8] little is known about their generality and scope. Thus, the following methods for the preparation of α-monosubstituted indoles were investigated: (1) the Madelung reaction;[9a] (2) *o*-nitrobenzyl ketone reductions;[9b] (3) *o*,β-dinitrostyrene reductions.[9c]

The Madelung reaction,[9a] which involves the heating of an *o*-toluidide with a strong base, has been used successfully for the preparation of a number of α-alkyl-substituted indoles,[10] as well as indoles having alkyl groups on the 5 or 7 positions.[9a] It appears that nitro-[11] or halogen- substituted[12] indoles cannot be prepared by this method. This procedure has been used for the synthesis of 2-(*N*,*N*-dimethylaminomethyl)indole (**1**).[13] In a study of this reaction[13b] it was found that reasonably good yields of **1** were obtained if sodium amide was used as the base but that the use of other bases gave much poorer results. However, in this[13b] and subsequent work[14] utilizing

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[1] (a) NSF Graduate Traineeship recipient, summer, 1971; (b) NSF Graduate Traineeship recipient, summer, 1970.

[2] For some examples see (a) R. J. Sundberg, "The Chemistry of Indoles," Academic Press, New York, N. Y., 1970, pp 251–269; (b) J. E. Saxton in "The Alkaloids," Vol. VII, R. H. F. Manske, Ed., Academic Press, New York, N. Y., 1960, Chapter 10.

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