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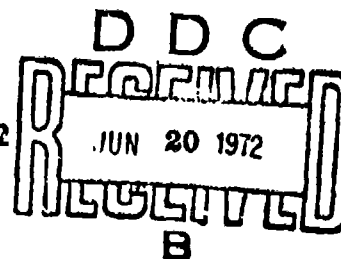
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SYNTHESIS OF ALIPHATIC EXPLOSIVE COMPOUNDS

FLUOROCHEM, INC.

TECHNICAL REPORT AFATL-TR-72-47

MARCH 1972



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AIR FORCE ARMAMENT LABORATORY

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EGLIN AIR FORCE BASE, FLORIDA

Synthesis Of Aliphatic Explosive Compounds

V. Grakauskas

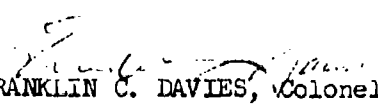
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FOREWORD

This final report documents work performed during the period 15 March 1971 to 15 February 1972 under Contract F08635-71-C-0112 administered under the direction of the Air Force Armament Laboratory, Air Force Systems Command, Eglin Air Force Base, Florida. This effort was conducted under Project 2511, Task 01, Work Unit 013. The program monitor for the Armament Laboratory was Major Duncan E. Dodds (DLIW).

The synthesis program was conducted by Fluorochem, Inc., Azusa, California and was managed by V. Grakauskas. The experimental work was performed by Dr. V. Grakauskas with consultation by Dr. K. Baum.

This report has been reviewed and is approved.


FRANKLIN C. DAVIES, Colonel, USAF
Chief, Flame, Incendiary, and Explosives Division

ABSTRACT

A number of new energetic polynitroethers and intermediates were synthesized utilizing reactions of 2-fluoro-2,2-dinitroethanol and its derivatives.

The oxidation and nitration of (2-fluoro-2,2-dinitroethoxy)acetaldoxime yielded 2-fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether which was fluorinated to give 2-fluoro-2,2-dinitroethyl ether. 2-Fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether and formaldehyde gave 3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropanol which was used to synthesize bis [3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitro-propyl] formal.

Five 1-(2-fluoro-2,2-dinitroethoxy)-2-propanol derivatives of the general structure $FC(NO_2)_2CH_2OCH_2CH(OH)CH_2X$ [$X=Cl, Br, I, ONO_2, COC(CH_3)_3$] were synthesized by reacting 2-fluoro-2,2-dinitroethyl glycidyl ether with HX and the alcohol derivatives were oxidized to the corresponding acetone derivatives, $FC(NO_2)_2CH_2OCH_2COCH_2X$ [$X=Cl, ONO_2, COC(CH_3)_3$].

1,3-Bis-(2-fluoro-2,2-dinitroethoxy)-2-propanol was synthesized by reacting 2-fluoro-2,2-dinitroethyl glycidyl ether with 2-fluoro-2,2-dinitroethanol. The alcohol was oxidized to 1,3-bis(2-fluoro-2,2-dinitroethoxy)-acetone. Nitration and oxidation of the oxime of this ketone yielded 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropane.

Other new compounds synthesized were: 2-fluoro-2,2-dinitroethyl propargyl ether, 4-(2-fluoro-2,2-dinitroethyl)semicarbazide and (2-fluoro-2,2-dinitroethoxy)vinylene diisocyanate.

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SECTION I

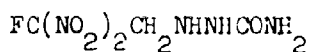
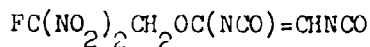
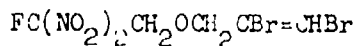
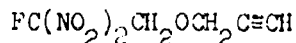
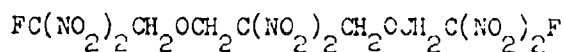
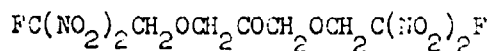
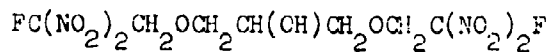
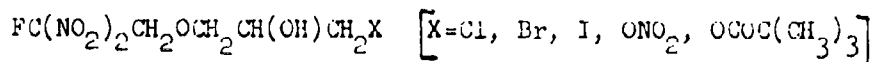
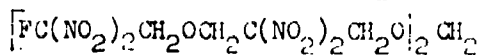
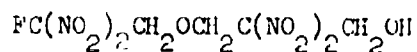
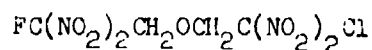
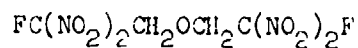
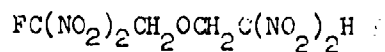
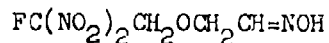
INTRODUCTION

The objective of this program was to synthesize and characterize new energetic nitroaliphatic compounds for potential use in explosive formulations. The major emphasis of this work was on the reactions of 2-fluoro-2,2-dinitroethanol.

SECTION 11

SUMMARY

The following new fluorodinitro compounds were synthesized and characterized under this contract using 2-fluoro-2,2-dinitroethanol and its readily available derivatives as the starting materials.



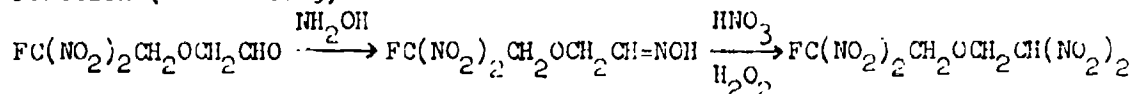
SECTION III

TECHNICAL DISCUSSION

A. PREPARATION AND REACTIONS OF 2-FLUORO-2,2-DINITROETHYL 2,2-DINITROETHYL ETHER

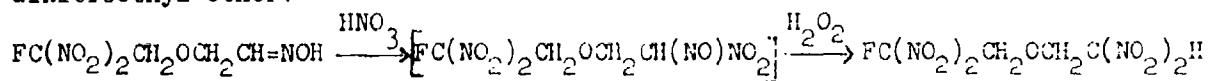
Polynitroalkyl ethers are promising plasticizers but are difficult to synthesize. Direct synthesis of these ethers briefly explored by ourselves and other investigators (Reference 1) failed. In the present work an indirect reaction scheme leading to 2-fluoro-2,2-dinitroethyl ether was explored.

2-Fluoro-2,2-dinitroethoxyacetaldehyde, synthesized several years ago (Reference 2), appeared to be a potentially useful starting material in the synthesis of 2-fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether by the Ponzio reaction (Reference 3):

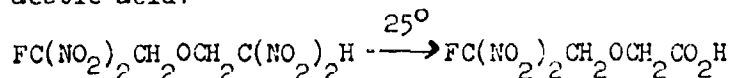


Although gem-dinitroalkane derivatives can be readily synthesized from the corresponding ketones by this procedure (Reference 4), analogous reactions of aliphatic aldoximes were not reported prior to the present work. Aryldinitromethanes, on the other hand, were obtained in nitration and oxidation of aromatic aldoximes (Reference 5).

2-Fluoro-2,2-dinitroethoxyacetaldoxime was obtained in 80-95% yield by reacting 2-fluoro-2,2-dinitroacetaldehyde with hydroxylamine under conventional reaction conditions. The compound, a liquid, contained a mixture of syn and anti isomers. The oxime was nitrated with fuming nitric acid in methylene chloride to give a deep blue solution of the nitro-nitroso intermediate which upon treatment with hydrogen peroxide yielded 2-fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether:



The ether, a colorless liquid obtained in 50-65% yields, was characterized by its nmr spectra and elemental analysis. The compound was only moderately stable at room temperature and decomposed in a few days to 2-fluoro-2,2-dinitroethoxyacetic acid:

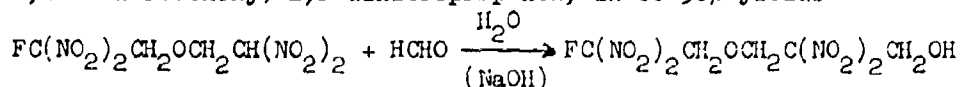


This decomposition appears to be autocatalytic.

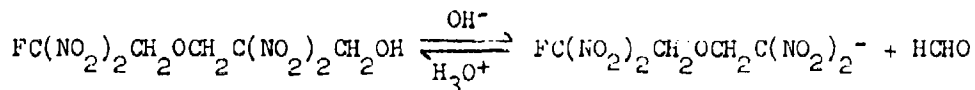
A more detailed investigation of the nitration of 2-fluoro-2,2-dinitroethoxyacetaldoxime showed that this reaction is very sensitive to reaction conditions. Reaction variables, such as the order of addition of reagents, temperature, and reaction time, can be varied only over a narrow range.

Attempts to employ nitrogen tetroxide as the nitrating agent were unsuccessful. Further work is needed to explore this reaction. It also would be important to determine the scope and limitations of these reactions with respect to other aliphatic aldoximes.

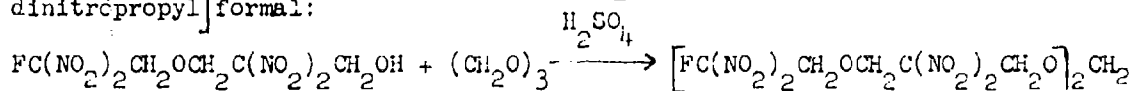
2-Fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether reacted with aqueous formaldehyde to give the corresponding methylol derivative, 3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropanol, in 80-90% yields:



This sparingly water-soluble polynitroalcohol could be distilled in a molecular still and is storable at ambient temperatures. The formylation of 2-fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether is a practical way to stabilize the compound for storage. As with other 1,1-dinitroalkanes, the formylation of 2-fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether is a reversible reaction:

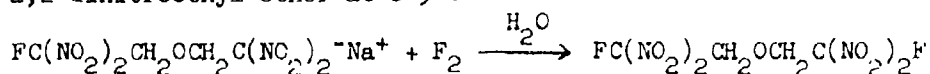


3-(2-Fluoro-2,2-dinitroethoxy)-2,2-dinitropropanol reacted with s-trioxane in concentrated sulfuric acid to give bis[3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropyl] formal:



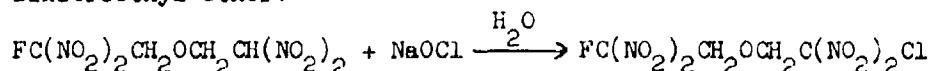
The formal, a viscous colorless liquid, $d = 1.641$, was characterized by elemental analysis and nmr spectra.

Bis(2-Fluoro-2,2-dinitroethyl) ether was obtained in 50-70% yield by direct fluorination of the aqueous sodium salt of 2-fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether at 0-5°:



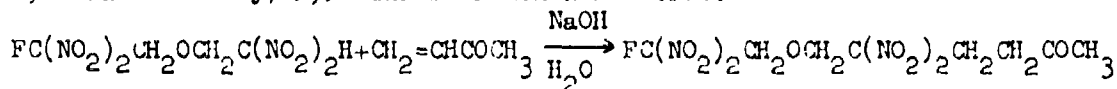
The compound, a colorless liquid, $d = 1.629$, bp 100° (0.3 mm), was characterized by its proton and fluorine nmr spectra and by elemental analysis. A 5 g sample of the ether was submitted to Lawrence Radiation Laboratory, Livermore, California who have specialized equipment for stability evaluation. These test results are not yet available.

Similarly, chlorination of 2-fluoro-2,2-dinitroethyl 2,2-dinitropropyl ether with sodium hypochlorite yielded 2-chloro-2,2-dinitroethyl 2-fluoro-2,2-dinitroethyl ether:



The above reactions of 2-fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether suggested that the compound should undergo other reactions common to 1,1-dinitroalkanes, such as, for example, Michael and Mannich reactions. Its

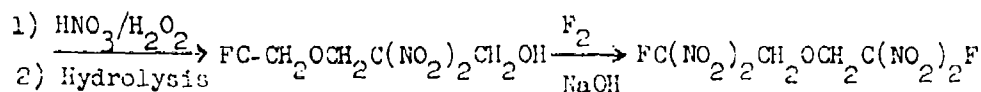
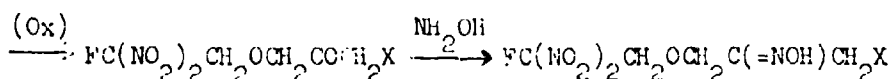
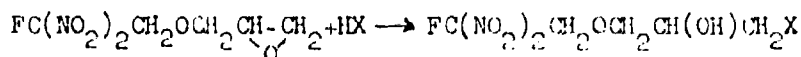
reaction with methyl vinyl ketone was briefly explored, and the proton nmr spectrum of the reaction product was consistent with the expected 6-(2-fluoro-2,2-dinitroethoxy)-5,5-dinitro-2-hexanone structure:



Some difficulties were encountered with the purification of the ketone and elemental analysis was not obtained.

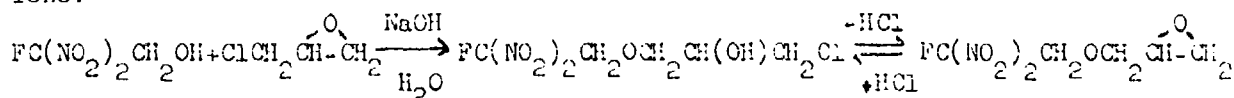
B. SYNTHESIS AND REACTIONS OF 1-(2-FLUORO-2,2-DINITROETHOXY)-2-PROPANOL DERIVATIVES

In conjunction with the synthesis of 2-fluoro-2,2-dinitroethyl ether alternative routes were explored, and a number of interesting intermediates were synthesized. One such alternate approach is based on the following reaction of 2-fluoro-2,2-dinitroethyl glycidyl ether:



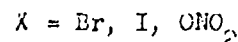
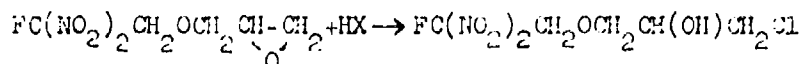
Due to time limitations only the first three steps of the above reaction scheme could be explored. A number of useful 1-(2-fluoro-2,2-dinitroethoxy)-isopropanol derivatives and their reaction products are described below.

A side-reaction product, 1-(2-fluoro-2,2-dinitroethoxy)-3-chloro-2-propanol, was isolated and identified in the purification of crude 2-fluoro-2,2-dinitroethyl glycidyl ether synthesized by reacting aqueous alkaline 2-fluoro-2,2-dinitroethanol with epichlorohydrin. This chlorohydrin, subsequently obtained quantitatively by reacting the glycidyl ether with dilute hydrochloric acid, might be either the incompletely cyclized intermediate or the product of reversible equilibrium between the glycidyl ether and chloride ions:



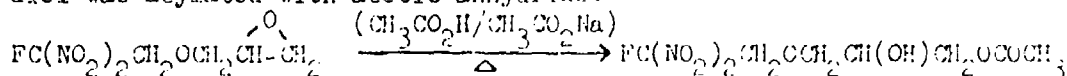
It was found that the epoxide ring of 2-fluoro-2,2-dinitroethyl glycidyl ether can also readily be opened with other dilute aqueous mineral acids. Thus, dilute hydrobromic, hydroiodic and nitric acid gave the correspondingly substituted 1-(2-fluoro-2,2-dinitroethoxy)-2-propanol derivatives in 75-95%

yields:

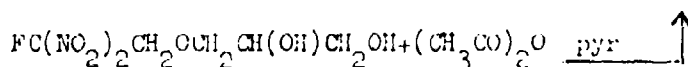
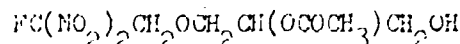


All these compounds were characterized by their elemental analyses and nmr spectra.

A mixture of the two isomers resulted when the glycidyl ether was reacted with acetic acid or when 1-(2-fluoro-2,2-dinitroethoxy)-2,3-propanediol was acylated with acetic anhydride:

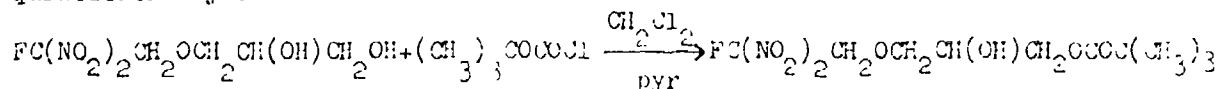


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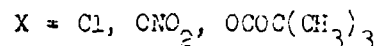
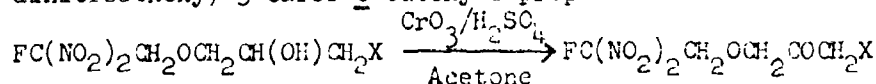


The compounds in the mixture were identified by their proton nmr spectra, but no attempts were made to isolate and to characterize the individual components.

On the other hand, when 1-(2-fluoro-2,2-dinitroethoxy)-2,3-propanediol was reacted with the more sterically hindered pivaloyl chloride, the corresponding isopropanol derivative was obtained almost exclusively in quantitative yield:



The next step in the alternative reaction scheme to 2-fluoro-2,2-dinitroethyl ether required the oxidation of the above 1-(2-fluoro-2,2-dinitroethoxy)-2-propanol derivatives to the corresponding ketones. This oxidation was accomplished in excellent yields with Jones reagent (Reference 6) using three isopropanol derivatives: 1-(2-fluoro-2,2-dinitroethoxy)-3-chloro-2-propanol, 1-(2-fluoro-2,2-dinitroethoxy)-3-nitrate-2-propanol, and 1-(2-fluoro-2,2-dinitroethoxy)-3-carbo-t-butoxy-2-propanol:



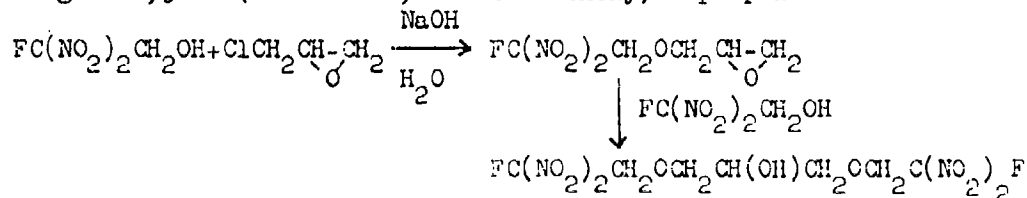
All three 1-(2-fluoro-2,2-dinitroethoxy)acetone derivatives were distilled in a molecular still and characterized by elemental analyses and nmr spectra.

Time limitations did not permit completion of the work on the alternative reaction scheme leading to 3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropanol and 2-fluoro-2,2-dinitroethyl ether. In a series of small-scale preliminary experiments using 1-(2-fluoro-2,2-dinitroethoxy)-3-(carbo-t-butoxy)acetone as the substrate, it was shown that the ketone reacted with hydroxylamine to give the corresponding oxime which then was nitrated and oxidized to the corresponding gem-dinitro derivative, 1-(2-fluoro-2,2-dinitroethoxy)-3-(carbo-t-butoxy)-2,2-dinitropropane. These compounds were tentatively characterized by their proton n.m.r. spectra.

The above results showed that the alternate route to 3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropanol as outlined at the beginning of this section is feasible, but further work is needed. Some of the intermediates synthesized above might be useful in other reactions.

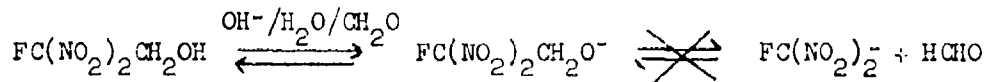
C. SYNTHESIS OF 1,3-BIS(2-FLUORO-2,2-DINITROETHOXY)-2,2-DINITROPROPANE

The successful alkylation of 2-fluoro-2,2-dinitroethanol with epichlorohydrin in aqueous alkaline solution to give 2-fluoro-2,2-dinitroethyl glycidyl ether (Reference 6) suggested that under suitable reaction conditions the glycidyl ether might react with another mole of 2-fluoro-2,2-dinitroethanol to give 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2-propanol:

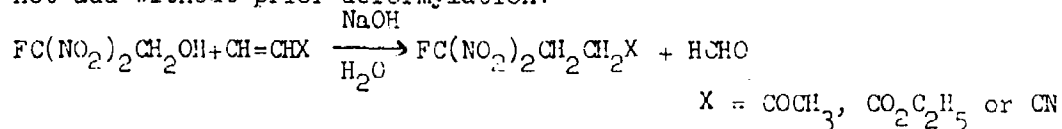


Several attempts to affect the above condensation were unsuccessful.

Towards the end of the present research program it was observed that alkylation reactions of 2-fluoro-2,2-dinitroethanol are facilitated by formaldehyde. In the presence of base 2-fluoro-2,2-dinitroethanol is known to be in equilibrium with formaldehyde and fluorodinitromethane anions (References 1 and 7). It was reasoned that an excess of formaldehyde would shift this equilibrium to the left:



Suppression of deformylation of 2-fluoro-2,2-dinitroethanol in alkaline aqueous solutions was shown by the following experiment. 2-Fluoro-2,2-dinitroethanol in aqueous alkaline solution reacts readily with α,β -unsaturated carbonyl compounds to give the corresponding Michael reaction adducts of fluorodinitromethane (Reference 8). The fluorodinitroethoxy moiety did not add without prior deformylation:



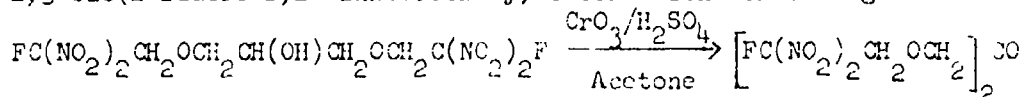
It was now found that these reactions do not take place when a large excess of formaldehyde is added indicating that under these conditions the concentration of fluorodinitromethane anions is negligible.

The above observed formaldehyde effect was exploited in a number of alkylation reactions of 2-fluoro-2,2-dinitromethanol. Decomposition of 2-fluoro-2,2-dinitroethanol in aqueous alkaline solutions is attributed to the instability of fluorodinitromethyl anions. Formaldehyde stabilized alkaline 2-fluoro-2,2-dinitroethanol solutions allowing higher reaction temperatures and longer reaction times. Higher yields of 2-fluoro-2,2-dinitroethyl ethers by a factor of two or more were obtained under these conditions using allyl bromide, propargyl bromide, propylene oxide and epichlorohydrin as alkylating agents.

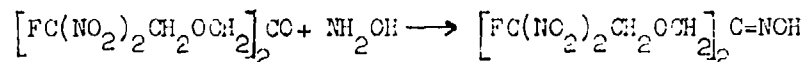
The crude reaction products obtained in alkylation reaction employing excess of formaldehyde were usually contaminated with small amounts of polymeric products (polymethyleneoxides ?) introduced by formaldehyde solutions. These impurities presented some problems in the purification of alkylation products.

The above described alkylation conditions using formaldehyde to suppress deformylation of 2-fluoro-2,2-dinitroethanol were applied in the synthesis of 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2-propanol. 2-Fluoro-2,2-dinitroethyl glycidyl ether reacted with alkaline 2-fluoro-2,2-dinitroethanol in formaldehyde solution to give the desired alcohol in 40-50% yields. The compound could be distilled in a molecular still and was characterized by its elemental analysis and proton nmr spectrum.

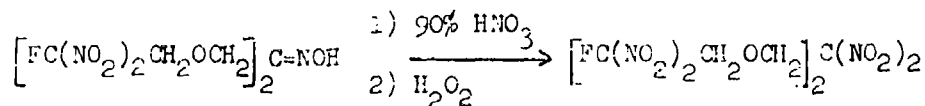
1,3-Bis(2-fluoro-2,2-dinitroethoxy)-2-propanol was used as the starting material in the synthesis of 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropane. This synthesis was accomplished via the corresponding ketone and oxime. 1,3-Bis(2-fluoro-2,2-dinitroethoxy)-2-propanol was oxidized to 1,3-bis(2-fluoro-2,2-dinitroethoxy)acetone with Jones reagent:



The ketone, obtained in 95-100% yield, was distilled and was characterized by elemental analysis and nmr spectra. It reacted with hydroxylamine to give 1,3-bis(2-fluoro-2,2-dinitroethoxy)acetone oxime:



The oxime was not purified but its proton nmr spectrum was consistent with the structure. The crude material was nitrated and oxidized to give 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropane:

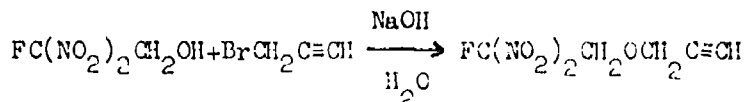


1,3-Bis(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropane, the bis(2-fluoro-2,2-dinitroethyl) ether of 2,2-dinitropropanol, was purified by chromatography using basic alumina and characterized by elemental analysis and its proton nmr spectrum.

D. MISCELLANEOUS REACTIONS OF 2-FLUORO-2,2-DINITROETHANOL

During the course of this work a number of other reactions of 2-fluoro-2,2-dinitroethanol were explored. These unrelated reactions are summarized below.

Aqueous alkaline 2-fluoro-2,2-dinitroethanol reacted slowly with propargyl bromide to give trace amounts of 2-fluoro-2,2-dinitroethyl propargyl ether:

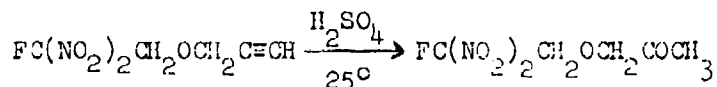


The ether was subsequently obtained in 40-65% yields by adding formaldehyde to the reaction mixture, as discussed in the previous section. The compound was characterized by elemental analysis and nmr spectra.

2-Fluoro-2,2-dinitroethyl propargyl ether reacted with one mole of bromine to give 2-fluoro-2,2-dinitroethyl 2,3-dibromoallyl ether:

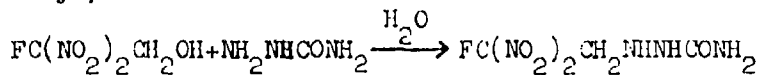


In concentrated sulfuric acid 2-fluoro-2,2-dinitroethyl propargyl ether was slowly hydrated to give (2-fluoro-2,2-dinitroethoxy)acetone:



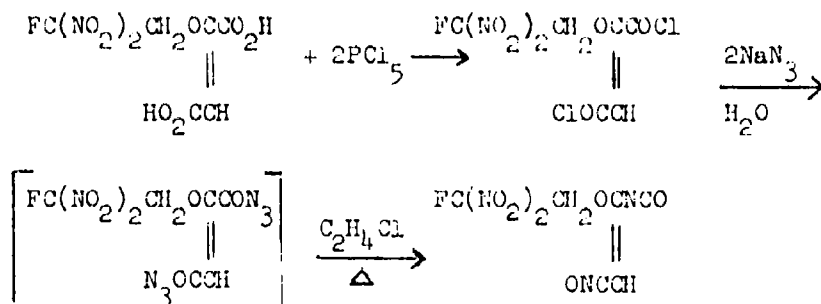
This ketone was previously synthesized in the oxidation of 1-(2-fluoro-2,2-dinitroethoxy)-2-propanol which in turn was obtained in the alkylation of 2-fluoro-2,2-dinitroethanol with propylene oxide (Reference 6).

2-Fluoro-2,2-dinitroethanol reacted slowly with aqueous semicarbazide to give the corresponding Mannich condensation product, 4-(2-fluoro-2,2-dinitroethyl)semicarbazide:



The halogenation of 2-fluoro-2,2-dinitroethylamine and bis(2-fluoro-2,2-dinitroethyl)amine with sodium hypochlorite and sodium hypobromite was briefly explored but the results are inconclusive. It appears that the corresponding N-halo derivatives might have been produced in this manner, but more work is needed. N-Halo(2-fluoro-2,2-dinitroethylamines) were intended to be used in Rasching reactions leading to polynitroalkylhydrazine derivatives.

Another reaction briefly explored was the synthesis of (2-fluoro-2,2-dinitroethoxy)vinylene diisocyanate from (2-fluoro-2,2-dinitroethoxy)fumaric acid via the Curtius reaction:



The preparation of (2-fluoro-2,2-dinitroethoxy)fumaryl chloride was previously reported (Reference 2). The reaction of the acid chloride with aqueous sodium azide and the Curtius rearrangement of the latter to (2-fluoro-2,2-dinitroethoxy)vinylene diisocyanate proceeded in a normal manner. The diisocyanate was characterized by elemental analysis and its proton nmr spectrum. The compound polymerized readily at ambient temperature in a matter of hours. Samples of the diisocyanate containing acyl chloride polymerization inhibitors could be stored in a refrigerator for several months.

The successful nitration and oxidation of (2-fluoro-2,2-dinitroethoxy)-acetaldoxime with fuming nitric acid-hydrogen peroxide suggested that other aliphatic aldoximes might also undergo analogous reactions to give the corresponding 1,1-dinitro derivatives. With this objective in mind, a number of exploratory nitration reactions were carried out using acetaldoxime and methoxyacetaldoxime as model compounds. Only trace-amounts of the corresponding 1,1-dinitro derivatives were obtained with both substrates and the yield could not be improved under a number of different reaction conditions. The nitration with nitrogen tetroxide was also briefly examined but again yields were very low. More work is needed in this area.

SECTION IV

EXPERIMENTAL

GENERAL

Some of compounds synthesized on this program might be sensitive to impact and friction and should be handled with care. 2-Fluoro-2,2-dinitroethanol and its derivatives show varying degree of toxicity.

Nmr spectra were measured on a Varian T-60 spectrometer. Proton and fluorine chemical shifts are reported in ppm relative to TMS and fluoro-trichloromethane as internal standards, respectively.

(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 mm). 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 the solvent was removed to leave 5.2 g of liquid which was distilled in a molecular still at 100-105° (0.1 mm) to give 4.8 g of a colorless liquid, 91% yield.

Anal. Calcd for $C_4H_6N_2FO_6$: 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, 1H, =NCH), 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, $FCCH_2^-$ -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: δ 110.9 (t, J_{HF} =18.7 Hz).

2-FLUORO-2,2-DINITROETHYL 2,2-DINITROETHYL ETHER

To a stirred and cooled (ice-water bath) solution of 4.2 g (0.02 mol) of (2-fluoro-2,2-dinitroethoxy)acetaldoxime in 60 ml of methylene chloride at 3-5° was added dropwise over a period of 7-8 min 10 g of 90% nitric acid. The mixture became turbid and then 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 reaction 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 2-fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether, 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, 1H, CH), 4.94 (d, $J_{HF}=15.8$, 2H, $F\dot{C}CH_2^-$), and 4.80 (d, $J=6.0$ Hz, 2H, CH_2).

2-FLUORO-2,2-DINITROETHYL ETHER

2-Fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether, 3.5 g (above), was dissolved at 0° in 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 2-fluoro-2,2-dinitroethyl ether, 62% yield, bp 100° (0.4 mm).

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 4.57 (d, $J_{HF}=16.0$ Hz). Fluorine nmr: δ 109.2, a 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 2-fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether. The mixture was stirred for 10 min and extracted with 20 ml of carbon tetrachloride to leave 0.55 g of 2-chloro-2,2-dinitroethyl 2-fluoro-2,2-dinitroethyl ether, a colorless liquid.

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, 2H, $F\dot{C}CH_2^-$) and 4.97 (s, 2H, $CH_2\dot{O}Cl$).

3-(2-FLUORO-2,2-DINITROETHOXY)-2,2-DINITROPROPANOL

To a suspension of 1.0 g of crude 2-fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether in 10 cc 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 $18-25^\circ$ 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 $120-125^\circ$ (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, 2H, $F\dot{C}CH_2^-$), 4.63 (s, 2H, CH_2 ,

-OCH₂CH₂-), 4.43 (s, 2H, CH₂, -C(CH₂OH)), and 2.72 (broad s, 1H, OH).

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 hrs 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 C₁₁H₁₃N₈F₂O₂₀: C, 21.47; H, 2.12; F, 6.17. Found: C, 21.28; H, 1.97; F, 6.41.

Proton nmr (CDCl₃): δ 4.77 (s, 2H, formal CH₂), 4.75 (d, *J*_{HF}=16 Hz, 4H, 2FCH₂-), 4.65 (s, 4H, 2FCH₂-CH₂OCH₂-), and 4.37 (s, 4H, -CCH₂OCH₂OCH₂-).

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 hrs. The mixture was extracted with 20 ml of methylene chloride to give 2.45 g (100% yield) of 1-chloro-3-(2-fluoro-2,2-dinitroethoxy)-2-propanol. An analytical sample was distilled at 100° (0.1 mm) in a molecular still.

Anal. Calcd for C₅H₉N₂ClFO₆: 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 (CDCl₃): δ 4.65 (d, *J*_{HF}=17.4 Hz, 2H, FCH₂-), 2.70 (broad s, 1H, OH), and superimposed multiplets at 3.47-4.17, 5H, CH₂CHCH₂). Fluorine nmr: δ 111.0 (poorly resolved triplet).

The compound was also obtained 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)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. (Reference 7) 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 reacting 2-fluoro-2,2-dinitroethyl glycidyl ether with 10% hydrobromic acid following the above procedure.

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, 2H, $F\dot{C}CH_2-$), 2.58 (d, $J_{H-OH}=3.8$ Hz, 1H, OH), and 3.33-4.13 (superimposed multiplets, 5H, $CH_2\dot{C}HCH_2$). Fluorine nmr: ϕ 109.5 (poorly resolved triplet, $J_{HF}=17$ Hz).

The compound was also identified as the side reaction product in the synthesis of 2-fluoro-2,2-dinitroethyl glycidyl ether from 2-fluoro-2,2-dinitroethanol and epibromohydrin in aqueous sodium hydroxide solution.

1-iodo-3-(2-FLUORO-2,2-DINITROETHOXY)PROPANOL

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

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, 2H, $F\dot{C}CH_2-$), 2.67 (broad s, 1H, OH), 3.13-4.05 (superimposed multiplets, 5H, $CH_2\dot{C}HCH_2$). Fluorine nmr: ϕ 109.6 (t, $J_{HF}=17.0$ Hz).

1-CARBO-t-BUTOXY-3-(2-FLUORO-2,2-DINITROETHOXY)-2-PROPANOL

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 1-carbo-t-butoxy-3-(2-fluoro-2,2-dinitroethoxy)-2-propanol. 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, $J_{HF}=18.0$, 2H, $F\dot{C}CH_2-$), 3.25 (broad s, 1H, OH), 1.22 (s, 9H, $-CCCH_3$), and 3.25-3.63 (superimposed multiplets, $-CH_2\dot{C}HCH_2-$). Fluorine nmr: ϕ 110.0 (t, $J_{HF}=17.8$ 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 was added 2.1 g (0.01 mole) of 2-fluoro-2,2-dinitroethyl glycidyl ether and the mixture was kept at 22-25° for 20 min. The solution was extracted with 15 ml of methylene chloride and 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, 2H, FCH_2-), 2.80 (broad s, 1H, OH), and 3.50-4.50 (superimposed multiplets, 5H, $-CH_2CH_2-$). Fluorine nmr: δ 110.7 (poorly resolved triplet).

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-dinitroethoxy)-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 4 ml of water). The mixture was stirred for an additional 45 min and the excess of chromium trioxide was destroyed with a few drops of isopropanol. 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 added to 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, 2H, FCH_2-), 4.52 (s, 2H, OCH_2CO), and 4.08 (s, 2H, $-CH_2Cl$). Fluorine nmr: δ 109.7 (poorly resolved triplet, J_{HF} =17 Hz).

1-(2-FLUORO-2,2-DINITROETHOXY)-3-(CARBO-t-BUTOXY)ACETONE

The title compound, a colorless oil, was prepared in 85% yield by oxidation of 1-(2-fluoro-2,2-dinitroethoxy)-3-(carbo-t-butoxy)-2-propanol 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): 4.75 (d, $J_{\text{HF}}=16.4$ Hz, 2H, FC-CH_2-), 4.63 (s, 2H, OCH_2CO), 4.37 (s, 2H, CH_2), and 1.25 (s, 9H, $\text{C}(\text{CH}_3)_3$). Fluorine nmr: δ 110.6 (poorly resolved triplet, $J_{\text{HF}}=16.5$ 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 analogue. An analytical sample was distilled in a molecular still at 125° (0.1 mm).

Anal. Calcd for $\text{C}_5\text{H}_6\text{N}_3\text{FO}_9$: 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, 2H, CH_2ONO_2), 4.75 (d, $J_{\text{HF}}=17.0$ Hz, 2H, FCCH_2-), and 4.48 (s, 2H, CH_2). Fluorine nmr: δ 109.4 (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 resulting solution was added 36.3 g (0.3 mol) of allyl bromide and the mixture was stirred for 45 hrs 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. (Reference 7) bp 31-32° (0.2 mm).

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 of 85% potassium hydroxide (0.02 mol) 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 hrs, diluted with water to 120 ml, and extracted with 50 ml of carbon tetrachloride. An insoluble oil separated, which was extracted with 40 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 $\text{C}_7\text{H}_{10}\text{N}_4\text{F}_2\text{O}_{11}$: C, 23.06; H, 2.76; F, 10.43. Found: C, 23.30; H, 2.61; F, 9.8.

Proton nmr (CDCl_3): δ 4.65 (d, $J_{\text{HF}}=17.6$, 4H, FCCH_2-), 2.52 (broad s, 1H, OH), and 3.52-4.02 (superimposed multiplets, 5H, $-\text{CH}_2\text{CHCH}_2-$). Fluorine nmr: δ 111.2 (poorly resolved triplet).

2-Fluoro-2,2-dinitroethyl glycidyl ether, 1.6 g (0.0076 mol), was

recovered on evaporation of carbon tetrachloride phase above. The yield of 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2-propanol amounted to 66.5%.

1,3-BIS(2-FLUORO-2,2-DINITROETHOXY)ACETONE

To a stirred solution of 13.1 g (0.036 mol) of crude 1,3-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 10.0 g (0.1 mol) of chromium trioxide and 8.0 g of concentrated sulfuric acid in 10 ml of water (Jones reagent) until chromate color persisted. The unrelated chromate was destroyed with a few drops of isopropanol. 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 $C_8H_8N_4F_2O_{11}$: 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, 4H, $2FCH_2-$), and 4.43 (3, 4H, $-CH_2COCH_2-$). 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 (see 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 3 hrs. The hot mixture was filtered and the filtrate 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, 1H, =NOH), 4.72 (d, $J_{HF}=16.8$, 4H, $2FCH_2-$), and 4.67 and 4.28 (s, 4H, $-CH_2C(=NOH)CH_2-$, for syn and anti isomers). These preliminary assignments are subject to changes.

1,3-BIS(2-FLUORO-2,2-DINITROETHOXY)-2,2-DINITROPROPANE

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 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 x 25 mm column of basic alumina (Biorad, AG10, 100-200 mesh).

Anal. Calcd for $\text{C}_7\text{H}_8\text{N}_2\text{F}_2\text{O}_4$: 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, $J_{\text{HF}} \approx 16\text{ Hz}$, 4H, 2FCCH_2-) and 4.55 (s, 4H, $-\text{CH}_2\text{C}(\text{NO}_2)_2\text{CH}_2-$). Fluorine nmr: ϕ 110.8 (poorly resolved triplet).

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 hrs 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 $\text{C}_5\text{H}_5\text{N}_2\text{FO}_5$: 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, $J_{\text{HF}} = 17.8\text{ Hz}$, 2H, FCCH_2), 4.28 (d, $J_{\text{HH}} = 3\text{ Hz}$, 2H, $\text{OCH}_2\text{C}\equiv$), and 2.56 (t, $J_{\text{HH}} = 3\text{ Hz}$, 1H, $-\text{C}\equiv\text{CH}$). 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 $\text{C}_5\text{H}_5\text{N}_2\text{FBr}_2\text{O}_5$: 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, 1H, $=\text{CHBr}$), 4.55 (d, $J_{\text{HF}} = 17.0\text{ Hz}$, 2H, FCCH_2-), and 4.57 (s, 2H, $-\text{CH}_2\text{CBr}=\text{}$). Fluorine nmr: ϕ 112.0 (poorly resolved triplet).

HYDRATION OF 2-FLUORO-2,2-DINITROETHYL PROPARGYL ETHER TO (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 (Reference 7).

4-(2-FLUORO-2,2-DINITROETHYL)SEMICARBAZIDE

To a stirred solution of 3.35 g (0.03 mol) of semicarbazide hydrochloride and 4.62 g (0.03 mol) of 2-fluoro-2,2-dinitroethanol in 25 ml of water was added dropwise, at 0-5°, a solution of 1.2 g (0.03 mol) of sodium hydroxide in 10 ml of water. No visible change occurred. A white crystalline solid, 3.5 g (55% yield), mp 104-105°, gradually deposited at 0°, and was collected by filtration after six weeks. An analytical sample was crystallized from water.

Anal. Calcd for $C_3H_6N_4FO_5$: C, 17.06; H, 2.84; N, 33.18; F, 9.00. Found: C, 16.78; H, 2.49; N, 33.09; F, 9.0.

Proton nmr (D_2O): δ 4.68 (s, 4H, NH and NH₂), and 4.28 (d, J_{HF} =17.6 Hz, 2H, CH₂).

(2-FLUORO-2,2-DINITROETHOXY)VINYLENE DIISOCYANATE

To a stirred and cooled solution of 1.95 g (0.03 mol) of sodium azide in 20 ml of water at 15-18° was added dropwise over a period of 5 min a solution of 3.05 g (0.01 mol or 0.02 equiv.) of (2-fluoro-2,2-dinitroethoxy)fumaryl chloride (Reference 2) in 35 ml of ethylene chloride. After 30 min, the mixture was cooled to 5° and the phases were separated. The ethylene chloride solution was dried over anhydrous sodium sulfate and filtered. The filtrate was warmed to 65-70° in a distillation apparatus protected from moisture by a CaCl₂ drying tube. When gas evolution ceased (ca 20 min), the solution was refluxed for 5 min. The solvent was removed to give 2.6 g (100% yield) of crude (2-fluoro-2,2-dinitroethoxy)vinylene diisocyanate, a dark liquid. An analytical sample was distilled at 90-95° (50 μ) in a molecular still to give pale-yellow liquid.

Anal. Calcd for $C_6H_3N_4FO_7$: C, 27.44; H, 1.14; N, 21.40; F, 7.3. Found: C, 27.4; H, 1.05; N, 20.8; F, 7.0.

Proton nmr ($CDCl_3$): δ 5.41 (s, 1H, CH) and 5.10 (d, J_{HF} =16.0 Hz, 2H, CH₂).

The diisocyanate polymerized in a matter of hours at room temperature to give very viscous oil.

The proton nmr spectrum of (2-fluoro-2,2-dinitroethoxy)fumaryl azide, the intermediate to the diisocyanate above, was recorded in carbon tetrachloride. The spectrum consisted of a singlet at δ 6.23 (s, 1H, CH) and 5.20 (d, J_{HF} =16.0 Hz, 2H, CH₂).

REFERENCES

1. H.G. Adolph and M.J. Kamlet, J. Org. Chem., 34, 45 (1969).
2. V. Grakauskas, "Synthesis of New Aliphatic Explosive Compounds(U)", Technical Report AFATL-TR-69-127, September 1969, pp 19-20 (Conf).
3. G. Ponzio, J. Prakt. Chem., 73, 494 (1906).
4. For improved Ponzio reaction see L.F. Fieser and W. von E. Doering, J. Am. Chem. Soc., 68, 2292 (1946). For more recent work, see J.R. Bull, E.R.H. Jones and G.F. Meakins, J. Chem. Soc., 1965, 2801; G.I. Kolesetskaya, I.V. Tsolinskii, and I.I. Bagal, Zh. Org. Khim., 6, 334 (1970).
5. W. Charlton, J.C. Earl, J. Kenner, and A.A. Luciano, J. Chem. Soc., 1932, 30.
6. K. Bowden, I.M. Keilbron, E.R.H. Jones, and B.C.L. Weedon, J. Chem. Soc., 39 (1946).
7. V. Grakauskas, J. Org. Chem., 35, 3030 (1970).
8. V. Grakauskas and K. Baum, J. Org. Chem., 34, 3927 (1969).

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13. ABSTRACT A number of new energetic polynitroethers and intermediates were synthesized utilizing reactions of 2-fluoro-2,2-dinitroethanol and its derivatives. The oxidation and nitration of (2-fluoro-2,2-dinitroethoxy)acetaldoxime yielded 2-fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether which was fluorinated to give 2-fluoro-2,2-dinitroethyl ether. 2-Fluoro-2,2-dinitroethyl 2,2-dinitroethyl ether and formaldehyde gave 3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropanol which was used to synthesize bis [3-(2-fluoro-2,2-dinitroethoxy)-2,2-dinitro-propyl] formal. Five 1-(2-fluoro-2,2-dinitroethoxy)-2-propanol derivatives of the general structure $FC(NO_2)_2CH_2OCH_2CH(OH)CH_2X$ [$X=Cl, Br, I, ONO_2, COC(CH_3)_3$] were synthesized by reacting 2-fluoro-2,2-dinitroethyl glycidyl ether with HX and the alcohol derivatives were oxidized to the corresponding acetone derivatives, $FC(NO_2)_2CH_2OCH_2COCH_2X$ [$X=Cl, ONO_2, COC(CH_3)_3$]. 1,3-Bis-(2-fluoro-2,2-dinitroethoxy)-2-propanol was synthesized by reacting 2-fluoro-2,2-dinitroethyl glycidyl ether with 2-fluoro-2,2-dinitroethanol. The alcohol was oxidized to 1,3-bis(2-fluoro-2,2-dinitroethoxy)acetone. Nitration and oxidation of the oxime of this ketone yielded 1,3-bis(2-fluoro-2,2-dinitroethoxy)-2,2-dinitropropane. Other new compounds synthesized were: 2-fluoro-2,2-dinitroethyl propargyl ether, 4-(2-fluoro-2,2-dinitroethyl)semicarbazide and (2-fluoro-2,2-dinitroethoxy)-vinylene diisocyanate.		

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2-Fluoro-2,2-dinitroethanol						
Polynitroalkyl ethers						
Explosive compounds						
2-Fluoro-2,2-dinitroethyl ether						
Nitration of aldoximes						
2-Fluoro-2,2-dinitroethoxy derivatives						
(2-Fluoro-2,2-dinitroethoxy)vinylene diisocyanate						
Nuclear magnetic resonance spectra						

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