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Synthesis of Energetic Monomers and Polymers
Annual Progress Report for the Office of Naval Research
Work Request N0001480WR00114 Project RR024-02-01

H. G. Adolph

Research and Technology Department

March 1981

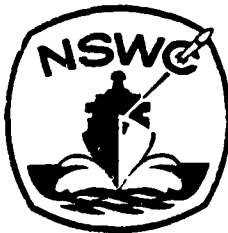
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The synthesis of the following energetic monomers was investigated: 2,2,2-Fluorodinitroethoxyoxirane, 3-fluorodinitromethylcaprolactone; glycidyl bis(fluorodinitroethyl)amine. The reaction of fluorodinitromethyl and nitro-substituted diols with formaldehyde and sulfuric acid was studied, and substituent effects on cyclic vs. polyformal formation were elucidated. Efforts to polymerize bis(fluorodinitromethyl)dioxepane and bis(fluorodinitromethyl)dioxocane were mostly unsuccessful.			

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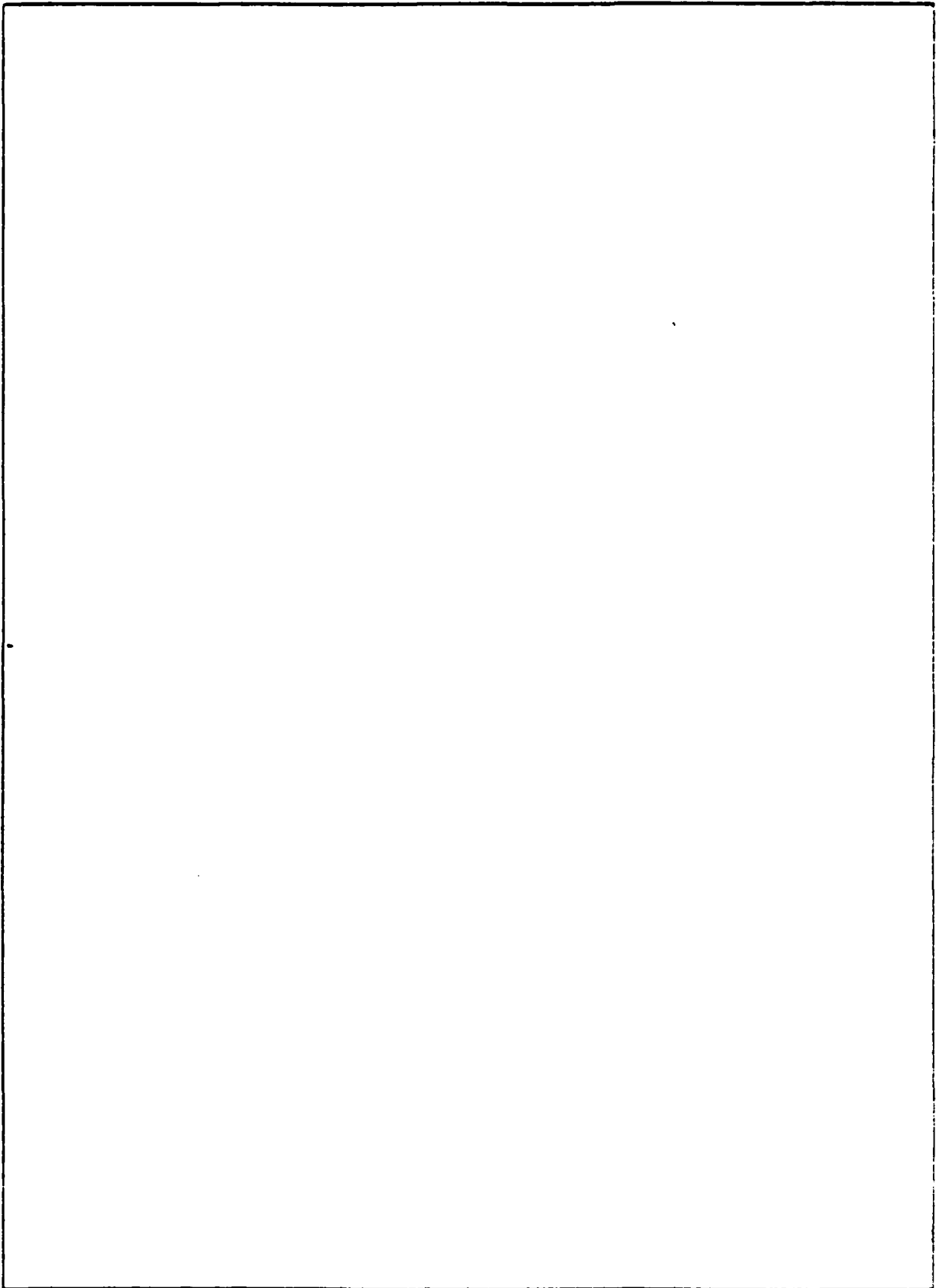
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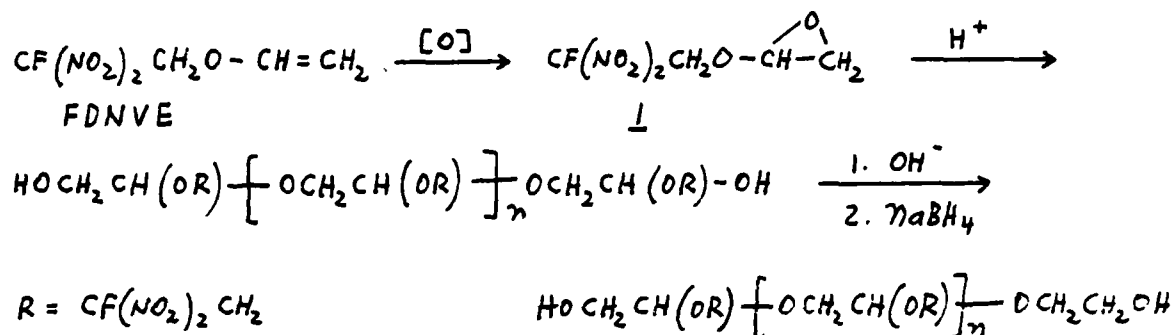
Synthesis of Energetic Monomers and Polymers

Introduction

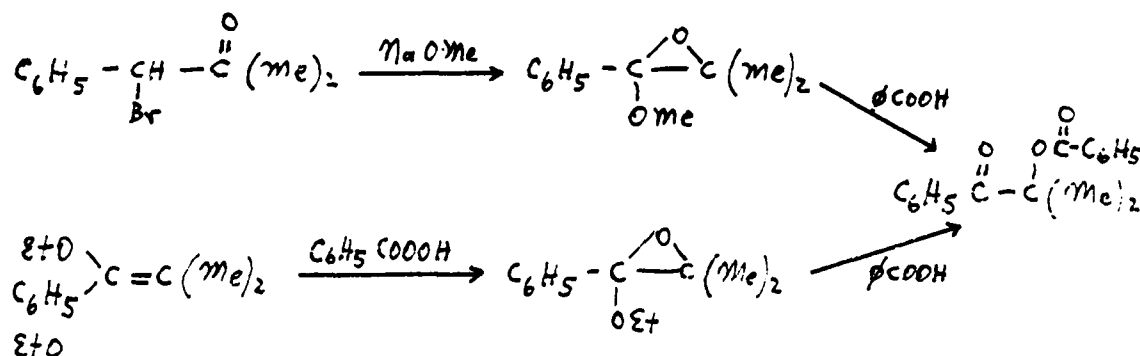
The objective of this work is the synthesis of new energetic monomers and their conversion to prepolymers with functionality suitable for cross-linking. The preferred functional groups are hydroxy groups which can be reacted with di- and/or triisocyanate, to provide the desired cross-linked polymer matrix for use in plastic-bonded explosives and as propellant binders. During this first year effort several approaches to new monomer structures were evaluated with initial emphasis on the synthesis of fluorodinitro ethoxyoxirane, 1.

Synthesis of fluorodinitroethoxyoxirane, 1.

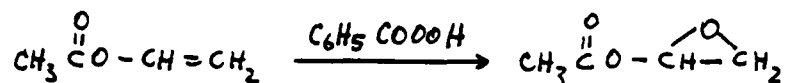
Fluorodinitroethyl vinyl ether (FDNVE) was prepared several years ago as a potential energetic monomer.¹ However, attempts to polymerize this compound with either cationic or radical catalysts were not successful. In addition the polymer, if it could be prepared, would not have a sufficient number of functional groups for cross-linking. It appeared that oxidation of this vinyl ether to the epoxide would provide an alternative monomer which should be easier to polymerize and give a polymer with the desired functionality after chemical modification of the initially formed end groups.



α -Alkoxyoxiranes are not a widely studied class of compounds, but several examples are known.^{2,3} Their reported synthesis provide examples for the oxidation of vinyl ethers to α -alkoxyoxiranes.



Similarly, α -acetoxyoxirane was prepared by peracid oxidation of vinyl acetate.⁴



The α -alkoxy- and acetoxyoxiranes are readily attacked by acids to give acyloxycarbonyl compounds as indicated above. This reactivity presents a problem in their preparation by peracid oxidation, because the corresponding carboxylic acid is formed as a by-product. Precautions must be taken to prevent the interaction of the oxirane and the acid in the reaction mixture.

FDNVE reacted only slowly with *m*-chloroperbenzoic acid (MCPBA). In order to minimize contact of *m*-chlorobenzoic acid with the other reaction product(s) the reaction was run in CCl_4 and hexane in which the acid has low solubility. Despite this a mixture of products was obtained from which a single pure compound could not be isolated by distillation or column chromatography. However, the mixture was readily separated by GC as shown in Figure 1.

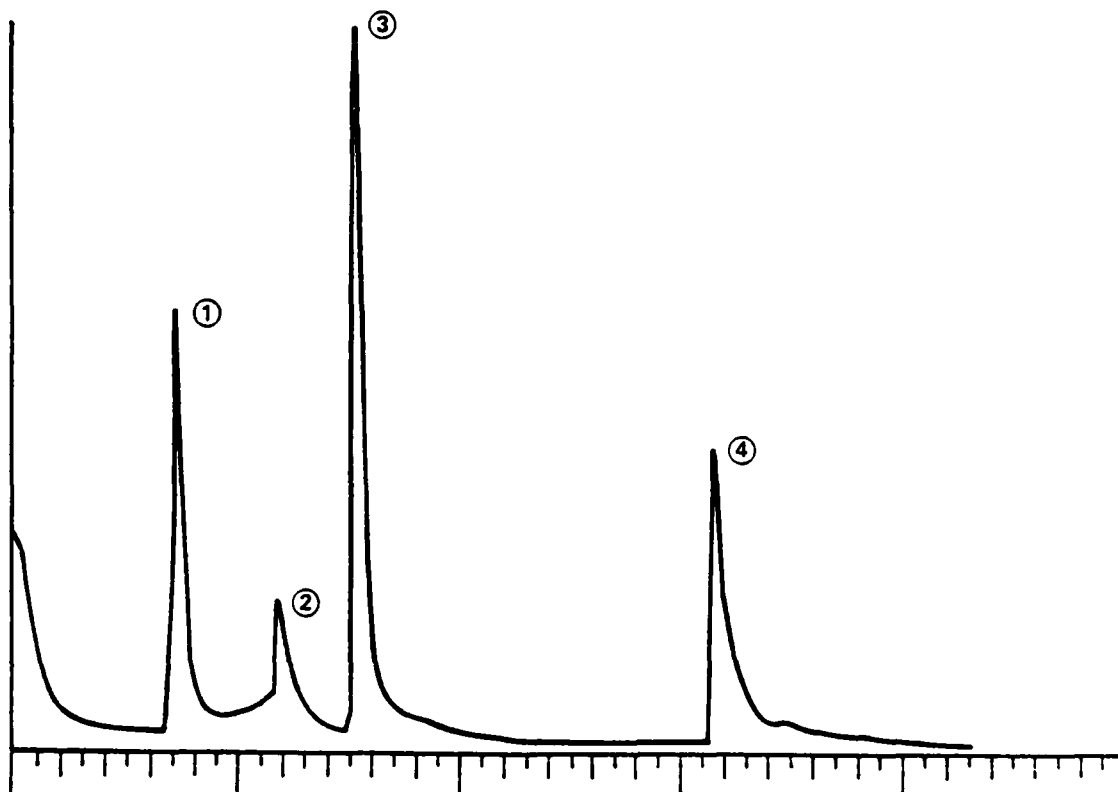


FIGURE 1. GAS-CHROMATOGRAM OF FDNVE OXIDATION PRODUCT

It was independently verified that FDNVE does not react with m-chlorobenzoic acid under the reaction conditions used here. Therefore all products must arise from the transformation of an initial product formed from FDNVE and MCPBA. The reaction mixture was successfully analyzed by GC/MS and reasonable structures could be assigned to all products from the mass spectral data obtained with $\text{CI}(\text{CH}_4)$. The structure assignments are as follows:

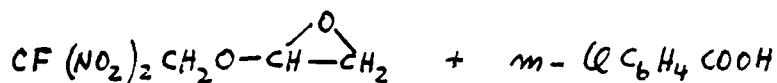
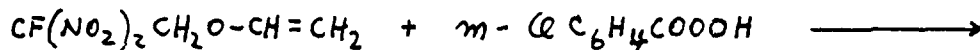
peak 1: FDNVE. Basepeak 181 (M+1); also present 209 (M+29; 4.5%) and 221 (M+41; 0.3%). Major fragments: 155 (M+1 - NO_2); 125 (M+1 - NO - NO_2)

peak 2: Fluorodinitroethanol. Basepeak 125 (M+1 - CH_2O); highest mass 153 (M+1; 10.1%)

peak 3: Fluorodinitroethoxyoxirane, 1. Basepeak 197 (M+1); also present 225 (M+29; 0.5%); 237 (M+41; 0.6%). Major fragments: 167 (M+1 - NO); 155 ($\text{CF}(\text{NO}_2)_2\text{CH}_2\text{OH}+1$?); 125 ($\text{CF}(\text{NO}_2)_2\text{H}+1$?)

peak 4: m-Chlorobenzoyloxy acetaldehyde. Basepeak 139 (141) ($\text{m-ClC}_6\text{H}_4\text{CO}$); highest mass 199 (201) (M+1; 7.9 and 2.4%); also present 228 (M+29); 239 (241) (M+41)

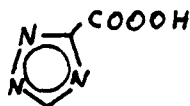
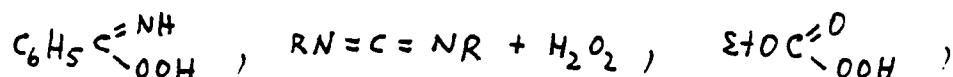
This mixture of products is what is expected if the initial reaction products, m-chlorobenzoic acid and 1, undergo further partial reaction according to the scheme observed for other α -alkoxyoxiranes.^{2,3}



Since no m-chlorobenzoic acid was found in the CCl_4 -soluble part of the reaction mixture, any of it still present after work-up must have reacted completely with 1. From the reaction in CCl_4 , 70% of the theoretical amount of m-chlorobenzoic acid was filtered off as insoluble product. When the crude reaction mixture from the peracid oxidation in CCl_4 was exhaustively extracted with 0.02, then 0.1N NaOH and, after drying, the solvent was removed, a viscous oil remained whose ir spectrum indicated the presence of $\text{CF}(\text{NO}_2)_2$ as well as a small quantity of m- $\text{ClC}_6\text{H}_4\text{COO}$. It is assumed that this material is a polymer derived from 1.

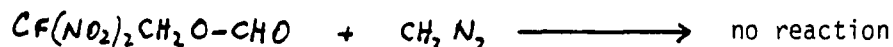
The existence of 1 seems established beyond reasonable doubt, even though it was not isolated in pure form. It is possible that reaction between 1 and carboxylic acid can be minimized further and that pure 1 could be obtained from the reaction used here. This will not be easy because of the long reaction time required and the sensitivity of 1 to bases which prevents easy scavenging of the acid. However, this reaction has not been studied exhaustively and scavenging techniques using diazomethane or immobilized peracid are unexplored.

A number of other oxidizing agents were explored briefly for the epoxidation of FDNVE. Thus, 2-hydroperoxyhexafluoro-2-propanol has been shown to be a useful epoxidizing agent for acid-sensitive substrates since its reduction product, hexafluoroacetone hydrate, is a weak acid.⁵ This hydroperoxide did undergo a reaction when contacted with FDNVE in CH₂Cl₂ solution with consumption of the FDNVE, but no 1 was formed. Instead, the reaction product contained much fluorodinitroethanol, and two new, unidentified products (GC analysis). Ryang and Foote⁶ recently reported a new epoxidation reaction by an intermediate formed in the Pd(OAc)₂ catalyzed oxygenation of azibenzil. This process occurs under mild conditions and does not involve acidic or basic reactants and products. However, the intermediate generated from azibenzil did not react with FDNVE in CH₂Cl₂ under the conditions reported in the literature. Additional oxidizing agents such as molybdenyl peroxide complexes and other acyl-OOH reagents giving non-acidic reduction products:



have not been tried.⁷

Another approach to the synthesis of 1 tried was the reaction of fluorodinitroethyl formate with diazomethane. This reaction was in analogy to the reported⁸ conversion of an α -nitroester into an oxirane with diazoethane. However, in the case investigated here, no reaction took place. When BF₃ etherate was added, the diazomethane decomposed.

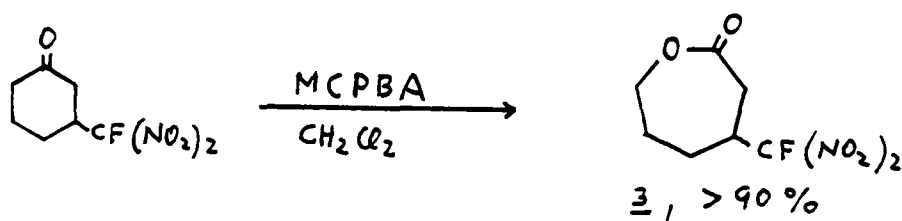
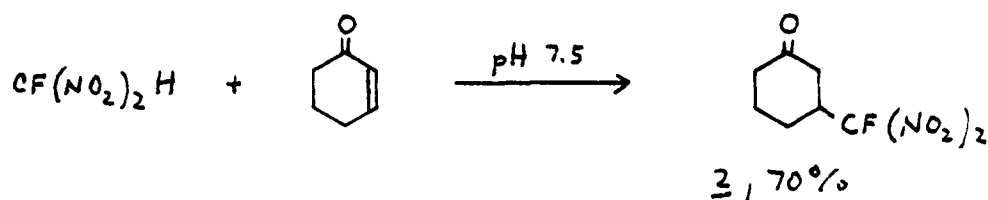


Even the still more negatively substituted fluorodinitroethyl trifluoroacetate did not react significantly with diazomethane.

Nitro-Substituted Caprolactones

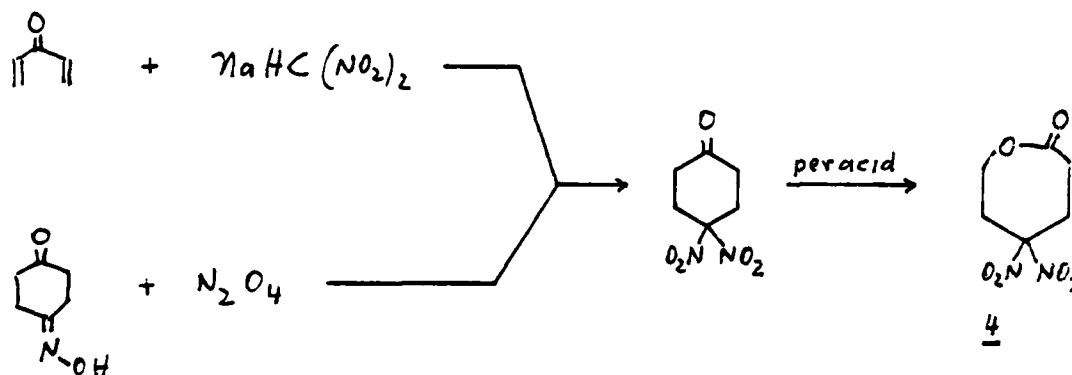
Since caprolactone is polymerized anionically, it was expected that the introduction of nitrosubstituents would facilitate polymerization. This is in contrast to cationically polymerizing monomers which are generally retarded by electron-withdrawing substituents. Therefore, the synthesis of nitrocaprolactones was attempted.

Fluorodinitromethane was added to cyclohexenone in aqueous solution in 70% yield, and the resulting 3-fluorodinitromethylcyclohexanone (2) reacted with MCPBA in refluxing CH_2Cl_2 to give 3-fluorodinitromethyl caprolactone (3) in >90% yield.



Polymerization studies with this monomer have not been carried out as yet.

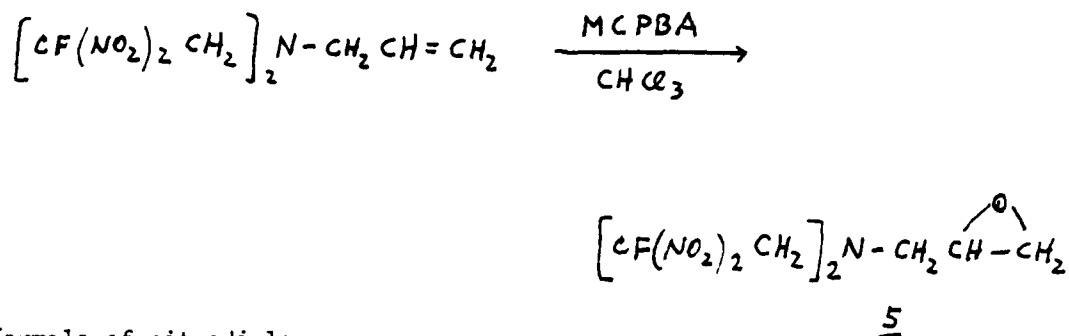
Work was also begun on the synthesis of 4,4-dinitrocaprolactone (4) by the reactions of divinylketone with sodium dinitromethane and of cyclohexanedione mono-oxime with N_2O_4 to give 4,4-dinitro cyclohexanone, followed by peracid oxidation to 4.



Preliminary evidence was obtained for the formation of 4,4-dinitrocyclohexanone via the divinyl ketone route. This effort was not completed due to shift of emphasis towards polyformals (see below).

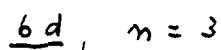
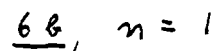
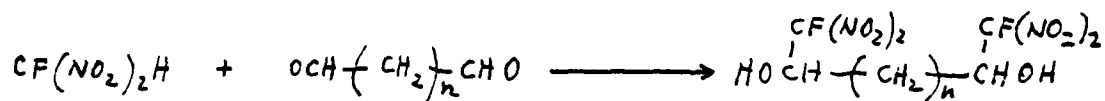
Glycidyl bis(fluorodinitroethyl)amine

Allyl bis(fluorodinitroethyl)amine⁹ reacted readily with MCPBA at elevated temperature in CHCl_3 solution to give on work-up a viscous oil which has tentatively been identified as the glycidyl amine 5. However, purification and characterization of this compound is at present incomplete.

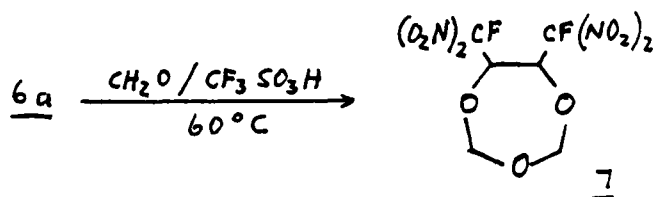
Formals of nitrodiols

The formal moiety is a well known linkage group for alcohols and has been used with great success for the preparation of valuable plasticizers and other energetic binder ingredients from polynitroalcohols.¹⁰ Attempts have also been made to prepare polyformals derived from 2,2-dinitropropane-1,3-diol (A-diol) and from 2,2,8,8-tetranitro-4,6-dioxanone-1,9-diol (DINOL) but have apparently not been successful because of preferred formation of the cyclic formal, 5,5-dinitro-1,3-dioxane from both precursors under the strongly acidic reaction conditions required. However, the preparation of formals from other nitrodiols, especially ones that could not form 5- or 6-membered rings, has not been reported. It was thought that such diols might form polyformals more readily than A-diol or DINOL.

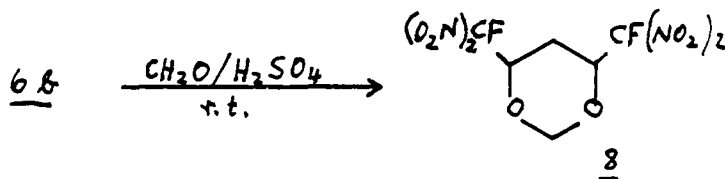
The diols 6a-6d were prepared by us several years ago by addition of fluorodinitromethane (FDM) to the corresponding dialdehydes.¹¹ Except for 6a, mixtures of both diastereomers are obtained in all cases.



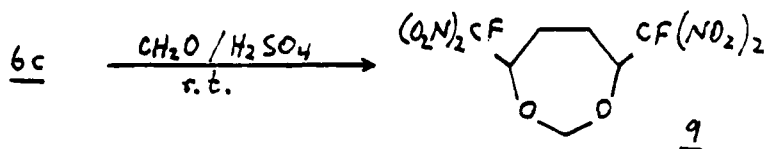
We have now investigated the reaction of 6a - 6d with formaldehyde and strong acids. Alcohol 6a is unreactive under the usual conditions of formal formation from polynitroalcohols¹⁰, i.e., paraformaldehyde/conc. H_2SO_4 . This could be due in part to the poor solubility of 6a in this medium. Since the 6a obtained from the FDM addition to glyoxal is the meso isomer¹², the fluorodinitromethyl groups would be cis in the 5-membered ring formal and its formation should be sterically impeded or impossible. Thus, the formation of a polyformal could be expected. However, when the reaction was forced - $\text{CF}_3\text{SO}_3\text{H}$ solvent, 60°C - the trioxaheptane 7 was obtained instead. This compound is a liquid and may be of interest as a plasticizer. The stability of the trioxepine structure under the highly acidic conditions is noteworthy.



Not suprisingly, 6b reacted readily with $\text{CH}_2\text{O}/\text{H}_2\text{SO}_4$ to the cyclic formal 8 in excellent yield. A mixture of stereoisomers corresponding to the composition of the starting material is obtained.



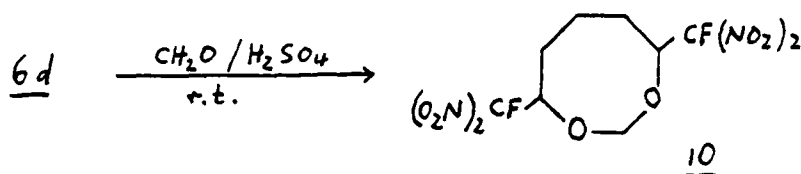
When 6c was reacted in a similar fashion, the cyclic formal 9 was obtained in almost quantitative yield.



A minor by-product detected by TLC is thought to be the 14-membered ring dimer, but this has not been fully established. When the reaction with paraformaldehyde was run in 15% oleum, no product was obtained. In $\text{CF}_3\text{SO}_3\text{H}$, 9 was formed as the major product, but in low yield (ca. 30%). 9 is very stable and several attempts to polymerize it by treatment with acid catalysts were fruitless. Thus, heating

with a catalytic amount of H_2SO_4 in $\text{ClCH}_2\text{CH}_2\text{Cl}$ solution gave a small quantity of the by-product mentioned above (TLC analysis), but no polymer. Treatment of 9 with PF_5 in CH_2Cl_2 at room temperature, elevated temperature, and at low temperature¹³ had no effect.

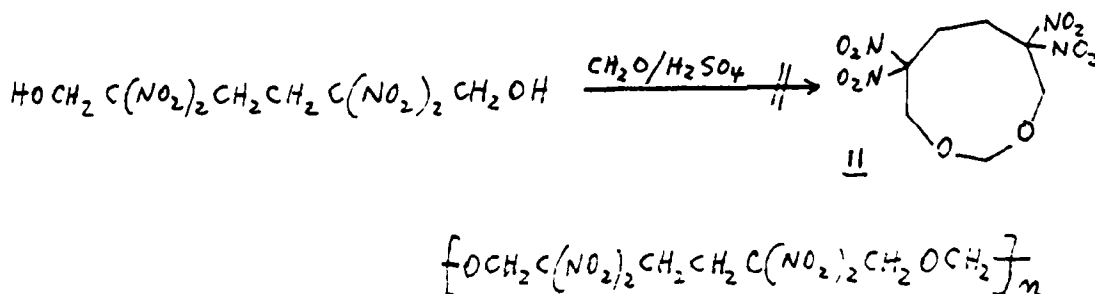
Finally, when 6d was reacted with $\text{CH}_2\text{O}/\text{H}_2\text{SO}_4$ under the usual conditions, the major product (ca. 70% yield) was the cyclic formal 10. Several minor by-products as well as origin material were observed by TLC analysis. As with 6c no product was obtained in 15% oleum. A run in which a solution of para-formaldehyde in conc. H_2SO_4 was added slowly to



the conc. acid solution of 6d gave 10 as the sole product in 67% yield. When the diol was dissolved in CH_2Cl_2 and treated with paraformaldehyde and only a small quantity of sulfuric acid, the result was the same (see below for a different result with $\text{BrCH}_2\text{CH}(\text{OH})\text{CF}(\text{NO}_2)_2$).

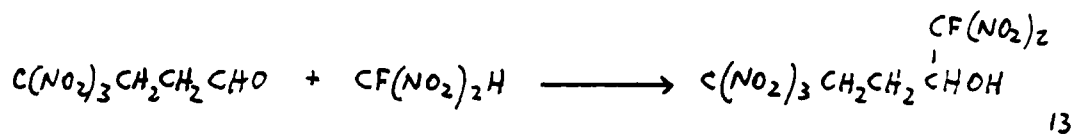
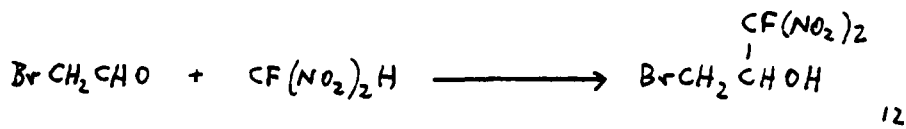
The ring of 10 is more easily cleaved than that of 9. Thus when 10 was heated in $\text{ClCH}_2\text{CH}_2\text{Cl}$ with a catalytic amount of $\text{CF}_3\text{SO}_3\text{H}$ at 90°C , an insoluble polymeric material was formed, albeit in low conversion. The extent of this polymerization varied in several repeating trials. PF_5 in CH_2Cl_2 under the same conditions as above (6c) had no effect. With $\text{H}_2\text{SO}_4/\text{HOAc}$, 10 was cleaved to a mixture of unidentified acetates and 6d. Treatment with $\text{CF}_3\text{SO}_3\text{H}$ in sulfolane gave partial cleavage to 6d.

The above results suggest that the stability of the ring decreases from 9 to 10. This is in accordance with literature reports¹⁴ which indicate a further reduction of thermodynamic stability for the 9-membered ring. Also, literature reports on substituent effects on ring-opening polymerization indicate that bulky substituents often favor ring over open chain structures. In order to test these effects in the case of nitrodiols, 2,2,5,5-tetranitro-hexanediol¹⁵ was reacted with $\text{CH}_2\text{O}/\text{H}_2\text{SO}_4$. The product was essentially completely insoluble in CH_2Cl_2 which rules out the presence of the 9-membered ring formal 11. The material is completely soluble in THF and GPC analysis of this solution indicated that a mixture of oligomers of 11 was at hand. The molecular weights estimated from the GPC are in the range 1,500-2,500.

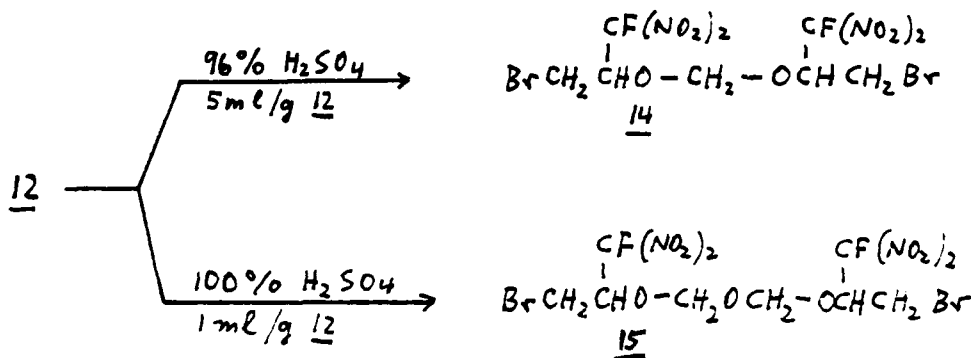


No efforts to optimize this reaction or further characterize the product have been made. However, in view of this result future efforts will be directed at the preparation of formals from nitrohexane- or heptanediols in which one or both of the fluorodinitromethyl groups present in 6a-6d have been replaced by a dinitromethylene function such as present in the tetranitrohexanediol. The polyformal from the tetranitrohexanediol itself should be of interest as well.

In order to learn more about the formation of linear formals of 1-substituted fluorodinitroethanols, which had not been previously reported, the preparation of some monomeric model compounds was tried. The alcohols 12 and 13 were obtained in good yields by addition of FDM to the corresponding aldehydes.



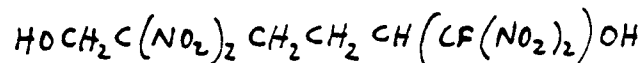
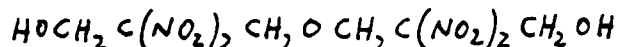
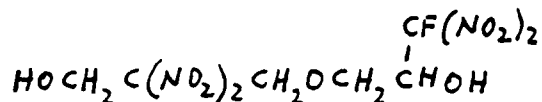
So far, only the reaction of 12 with paraformaldehyde and acid has been studied in some detail. It was found that the formal 14 is formed under the usual conditions, but only in low yield (ca. 25%). Some 12 is recovered but 50% of the starting material is not accounted for. At lower temperature the result was the same but at 50°C no 14 was obtained. Similarly, with 100% H₂SO₄ and with CF₃SO₃H little or no formal was formed. Reducing the amount or the strength of the H₂SO₄ did not improve the yield of 14; instead a second product appeared which becomes the only product with still lesser amounts of H₂SO₄. This material is the oxymethylene homolog 15.



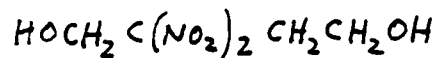
These results may indicate that the formation of linear formals of 1-substituted fluorodinitroethanols occurs much less readily than that of the cyclic formals from 6b-6d. The reasons for this are not yet clear, but the implication is clearly that future efforts should be directed to formals derived from diols with at least one primary hydroxy group.

Plans

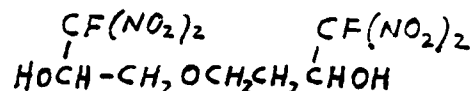
1. As already indicated, a number of diols will be synthesized which can give formal of ringsize 9 ± 1 , containing no more than one fluorodinitromethyl substituent. Representative structures are as follows:



Also prepared will be a butanediol having no fluorodinitromethyl groups,



and a hexanediol with 2 fluorodinitromethyl groups:



or the all-C analog

2. Formal formation will be studied for these diols and also for 2,2,5,5-tetra-nitrohexanediol. This should permit a conclusive elucidation of ringsize and substituent effects on this reaction for polynitrodiols.

3. Polymers formed will be characterized by GPC.

4. Optimization of polymer formation and preliminary evaluation will be conducted to the extent that project funds permit.

5. The work on the synthesis of nitrocaprolactones and glycidyl bis(fluoro-dinitroethyl)amine will be completed.

ExperimentalGeneral

See reference 11 for precautions in working with fluorodinitromethane and other fluorodinitro compounds. Melting points are uncorrected. Microanalyses are by Galbraith Labs., Knoxville, Tenn. Nmr spectra were obtained in part by Biomeasure, Inc. Hopkinton, MA, and in part on the NSWC/WO Varian XL-200 spectrometer; chemical shifts are in ppm rel. to TMS as internal standard.

Oxidation of FDNVE

To a solution of 3.6 g FDNVE¹ in 50 ml carbon tetrachloride was added in portions 4.1 g MCPBA (purity ca. 85%). The mixture was stirred for 22 h, then a few drops of Na₂SO₃ solution were added to reduce unreacted MCPBA (KI test), and the mixture was filtered. 2.85 g MCBA was recovered. The filtrate was washed twice with a pH 7 buffer solution, was dried (MgSO₄), and freed from solvent in vacuo to give 4.0 g of an oil which was analyzed by GC/MS as described on p. 3. In another run employing the same quantities of FDNVE and MCPBA, 30 ml hexane was used as reaction medium. After stirring the mixture overnight, the solution was decanted, the gummi solid was triturated with CH₂Cl₂, and the mixture stirred with water to which NaHCO₃ and NaHSO₃ solution was added until the KI test was negative and the pH remained >7. After separation of the phases, the organic phase was dried (MgSO₄) and freed from solvent in vacuo. The residual oil gave an ir spectrum very similar to that from the above CCl₄ product. The combined oils from both runs were dissolved in CH₂Cl₂ and exhaustively extracted with 0.02N, and once with 0.1 N NaOH. After drying and removing volatiles, 2.5 g of a highly viscous oil remained. The ir spectrum showed strong peaks near 1600 and 1300 cm⁻¹ and a medium to weak absorption near 1740 cm⁻¹. This indicates that the material is probably a polymer of 1 containing some m-Cl-C₆H₄COO groups.

Reaction of FDNVE with (CF₃)₂CH(OH)OOH

8.3 g of hexafluoroacetone was condensed onto 1.7 g 90% H₂O₂, and the excess allowed to evaporate. The residue was dissolved in 100 ml CH₂Cl₂. 25 ml of this solution was added to 1.8 g FDNVE and the mixture stirred 72 h at ambient temperature. The solution was dried and freed from solvent and the residue analyzed by GC; the products found were fluorodinitroethanol (major) and 2 unidentified components of higher retention times.

Reaction of FDNVE with Azibenzil/O₂

Oxygen gas was bubbled into a solution of 1.8 g FDNVE, 2.2 g azibenzil, and 0.025 g Pd(OAc)₂ in 25 ml CH₂Cl₂ for 24 h. GC analysis indicated no change in the FDNVE concentration while the azibenzil was completely decomposed.

3-Fluorodinitromethyl cyclohexanone, 2

A mixture of 10 ml CH₂Cl₂, 75 ml pH 7.5 buffer, 5 g cyclohexenone, and 6.25 g fluorodinitromethane was stirred 16 h at room temperature. The solid product was dissolved in additional CH₂Cl₂, the solution dried, concentrated and chilled to give 7.9 g, 70.2%, mp. 94-95°C. Nmr (CDCl₃): δ 3.53 (m, CFCH, 1), ca. 2.4 (m, 5), ca. 1.8 (m, 3). Anal. Calc'd for C₇H₈FN₂O₅: C, 38.36; H, 3.65; N, 12.79; F, 8.68. Found: C, 38.24; H, 4.17; N, 12.62; F, 8.54.

4-Fluorodinitromethyloxepanone-2, 3

A mixture of 1.1 g 2, 1.08 g m-chloroperbenzoic (ca. 35% active), and 15 ml CH₂Cl₂ was refluxed for 48 h. The mixture was then stirred with NaHCO₃ solution to which NaHSO₃ was added slowly until a negative KI test was obtained. The organic phase was washed with water, dried, and freed from solvent to give 1.05 g (90%) crude 3. After recrystallization from CH₂Cl₂/hexane, 3 had mp. 122-123°C. Nmr (CDCl₃): δ 4.3 (m) 3.5 (m, CFCH), 2.7 (m), 1.9 (m). Anal. Calc'd for C₇H₈FN₂O₆: C, 35.74; H, 3.40; N, 11.91; F, 8.09. Found: C, 35.76; H, 3.86; N, 11.88; F, 8.05.

Glycidyl bis(fluorodinitroethyl)amine, 5

3.3 g crude allyl bis(fluorodinitroethyl)amine⁹, 2.0 g m-chloroperbenzoic acid (ca. 85% active), and 15 ml CHCl_3 were refluxed for 48 h. The cooled solution was filtered, washed with dil. NaHCO_3 solution, dried and freed from solvent to give a viscous oil. TLC analysis showed a major product in addition to origin material, and the absence of starting material. Similarly, the methine protons (δ 5.84, 5.15) of the starting material were absent from the otherwise complex Nmr spectrum. The ir spectrum had a band at 1250 cm^{-1} which is attributable to the epoxide group.

6,7-Bis(fluorodinitromethyl)trioxepane, 7

0.75 g of 6a¹¹ was added to a solution of 0.075 g paraformaldehyde in 5 ml $\text{CF}_3\text{SO}_3\text{H}$ and the mixture heated at 60°C for 20 h. After drowning on crushed ice and extracting with CH_2Cl_2 , the CH_2Cl_2 solution was washed with NaHCO_3 solution, dried (MgSO_4), and freed from solvent in vacuo to give 0.4 g (45%) of a mobile oil which was >95% pure by GC analysis. Nmr (CD_2Cl_2): δ 5.90 (m, 2, $\text{CF}(\text{NO}_2)_2\text{CH}$), δ 5.45, 5.30, 5.19 (4+ CHDCl_2 , OCH_2O). Anal. Calc'd for $\text{C}_6\text{H}_6\text{F}_2\text{N}_4\text{O}_{11}$: C, 25.81; H, 1.62; F, 10.21; N, 15.06. Found: C, 25.50; H, 1.91; F, 10.48; N, 14.75.

General procedure for preparation of 8, 9, 10

0.5 mmol diol was added to a cooled and stirred solution of 0.28 mmol trioxane or p-formaldehyde in 15 ml conc. sulfuric acid. Stirring was continued for 16 h, the mixture was poured over crushed ice and the product extracted into CH_2Cl_2 . This solution was analyzed by TLC. Pure product was isolated by washing the CH_2Cl_2 solution with NaHCO_3 solution, drying, adding hexane, and chilling.

8: not yet characterized.

9: mp $100\text{--}125^\circ\text{C}$; Nmr (CDCl_3): δ 5.2 (m, CFCH), 4.8 (s, OCH_2O), 2.17 (m), 1.94 (m). Anal. Calc'd for $\text{C}_7\text{H}_8\text{F}_2\text{N}_4\text{O}_{10}$: C, 24.29; H, 2.33; F, 10.98; N, 16.19. Found: C, 24.35; H, 2.40; F, 11.05; N, 15.97.

Also prepared was a single diastereomer of 9 from one of the diastereomers of 6c. This material was submitted to NRL for determination of the crystal structure. The crystal structure confirms the chemical structure assigned to 9.¹⁶

10: TLC analysis showed the presence of one major component near the solvent front in addition to several minor spots and origin material. A pure sample of 10 was obtained by filtration of a CH_2Cl_2 solution through a column of silica and collection of the initial material zone. Nmr (CDCl_3): δ 1.9 (m); 4.7 (d); 4.8 (s); 5.1 (d); 5.2 (t). Anal. Calc'd for $\text{C}_8\text{H}_{10}\text{F}_2\text{N}_4\text{O}_{10}$: C, 26.67; H, 2.80; F, 10.55; N, 15.56. Found: C, 27.00; H, 2.95; F, 10.80; N, 15.36.

Attempted Polymerization of 10 with $\text{CF}_3\text{SO}_3\text{H}$

To a solution of 1g 10 in 5 ml $\text{ClCH}_2\text{CH}_2\text{Cl}$ was added 1 drop $\text{CF}_3\text{SO}_3\text{H}$, and the mixture was stirred and heated at 90°C for 2 days. After cooling, the mixture was washed with water and dried. TLC analysis indicated the presence of a significant amount of origin material. Addition of hexane to the cloud point and refrigeration gave 0.2 g solid. This was dissolved in THF and analyzed by GPC with 10 and polystyrene used as m. w. calibration standard. The m. w. range found was considerably above that of 10 with the maximum estimated at ca. 3,000.

2,2,5,5-Tetranitrohexane-1,6-diol and CH₂O/H₂SO₄

A 0.5 g sample of tetranitrohexanediol was added to a stirred solution of 0.05 g paraformaldehyde in 3 ml 90% H₂SO₄, the mixture stirred at room temperature for 4 h, and poured over crushed ice. The precipitate was filtered off (0.25 g, air-dried) and digested with CH₂Cl₂. Only 0.03 g was soluble. This indicates the absence of any significant amount of cyclic formal which is expected to be soluble in CH₂Cl₂. The CH₂Cl₂ insoluble solid was dissolved in THF and analyzed by GPC. The m. w. range present was fairly low (ca. 1,500-2,500).

1-Fluoro-1,1-dinitro-3-bromo-propanol-2, 12

A mixture of 9 g bromoacetaldehyde diethylacetal, 40 ml water, 10 ml MeOH, and 5 ml 2N H₂SO₄ was stirred at 70°C until it became homogeneous. The solution was cooled to <10°C and 5.7 g fluorodinitromethane was added, and the pH adjusted to ca. 7 with NaHCO₃ solution. After several h stirring with ice cooling, the mixture was acidified, saturated with NaCl and extracted 3x with CH₂Cl₂. The dried extracts were freed from solvent to give 11.0 g (96%) crude 12. TLC analysis showed the presence of only one component. A fraction was purified by chromatography on Silica and had the same ir spectrum as the crude product.

1-Fluoro-1,1,5,5,5-pentanitropentanol-2, 13

A mixture of 2.07 g 4,4,4-trinitrobutyraldehyde and 15 ml pH 7 buffer was cooled in an ice bath, 1.25 g fluorodinitromethane was added and the mixture stirred for 4 h with continued cooling. After acidification the mixture was extracted with CH₂Cl₂, the extracts dried and freed from solvent to give 3.0 g crude 13. The ir spectrum showed strong OH absorption, but also some residual C=O. The compound has not yet been completely characterized.

1-Fluoro-1,1-dinitro-3-bromopropyl-(2)-formal, 14

2.5 g 12 was added to a solution of 0.15 g paraformaldehyde in 7.5 ml conc. H₂SO₄, the mixture stirred 3 h at room temperature, then poured on crushed ice and the product extracted into CH₂Cl₂. The extract was washed with NaHCO₃ solution and worked up as usual to give 1.3 g of an oil which by TLC analysis was a mixture of 12 and 14. The 2 components were readily separated by chromatography on Silica and pure 14 was obtained as a pale yellow oil. Nmr (CDCl₃) δ 3.54 (m, BrCH₂CH); 5.11 (d, OCH₂O); 5.2 (m, CF-CH). Anal. Calc'd for C₇H₈F₂Br₂N₄O₁₀: C, 16.61; H, 1.59; F, 7.51; Br, 31.58; N, 11.07. Found: C, 16.40; H, 1.71; Br, 31.85; N, 10.80.

1-Fluoro-1,1-dinitro-3-bromopropoxy-(2)-methyl ether, 15

When the above reaction was conducted with 2 ml 100% H₂SO₄ for 1 h and worked up in a similar manner, 1.5 g of an oil was obtained which by LC analysis contained little 12 or 14. The main product was obtained fairly pure by chromatography on Silica. The Nmr spectrum is compatible with structure 15. Nmr (CDCl₃): δ 3.48 (m, BrCH₂CH, 4); 4.86 (m, OCH₂OCH₂O, 4); 5.21 (m, CFCH, 2).

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