

Synthesis of *N,N*-Bis(2-fluoro-2,2-dinitroethyl)-*N*-alkylamines

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A new reaction for preparing *N,N*-bis(2-fluoro-2,2-dinitroethyl)-*N*-alkylamines, which involves the reaction of fluorodinitromethane with *N,N*-bis(alkoxymethyl)-*N*-alkylamines, is described. A number of compounds containing different functional groups suitable for further reaction have been prepared. Some initial observations on the scope, limitations, and mechanism are presented.

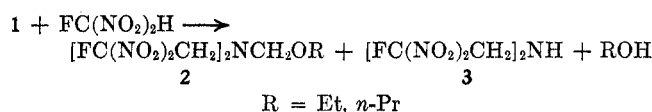
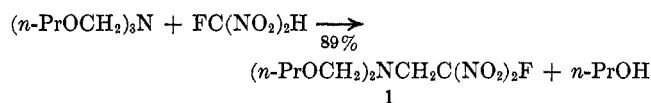
The Mannich reaction with gem dinitroparaffins¹ was first investigated by Feuer, Bachman, and May² and has proved to be a versatile method for the preparation of polynitroalkylamines. However, the literature reports only two examples of the direct synthesis of an *N,N*-bis(2,2-dinitroalkyl)-*N*-alkylamine. Bis(2,2-dinitropropyl)glycine³ was isolated from the reaction of sodium glycinate with 2,2-dinitropropanol in aqueous solution at pH 9.0. Recently, Eremenko and coworkers have reported the preparation of dipotassium tris(2,2-dinitroethyl)amine.⁴ While these are the only examples of acyclic tertiary amines of this type, a number of *N*-alkyl-3,3,5,5-tetranitropiperidines have been prepared.^{2,5}

Fluorodinitromethane⁶ will react with certain carbonium ion precursors containing potential stabilizing groups.⁷ During this investigation, it was desired to assess the properties of the amino group in this regard. The compounds which were chosen for reaction were the *N*-substituted *N,N*-bis(alkoxymethyl)amines.⁸ It was considered that a major advantage, as opposed to the Mannich reaction, would be that the concentration of carbonium ion precursor would be maximum throughout the reaction. A second consideration was that the reaction would be subject to mild acid catalysis.⁹ It was thereby hoped that a number of *N*-substituted *N,N*-bis(2-fluoro-2,2-dinitroethyl)amines¹⁰ could be prepared which otherwise would be inaccessible.

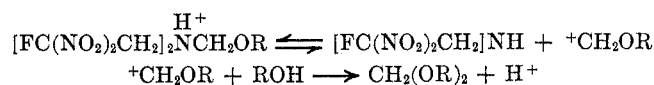
Results

A first equivalent of fluorodinitromethane reacted readily at ambient temperature with tris(propoxymethyl)amine to form *N,N*-bis(propoxymethyl)-2-

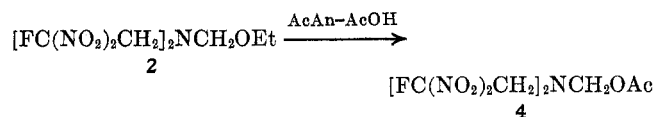
fluoro-2,2-dinitroethylamine (1). A second equivalent of fluorodinitromethane reacted much more slowly to give the bis derivative 2 in 81% yield; a heating



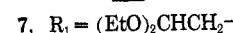
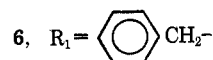
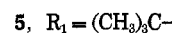
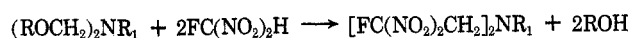
period of 72 hr at 80° was required to complete the reaction. A by-product obtained in 15% yield was bis-(fluorodinitroethyl)amine (3). The latter could arise by *N*-protonation of 2 followed by expulsion of an alkoxymethyl carbonium ion.



A third equivalent of fluorodinitromethane did not react to yield the tris amine even under forcing conditions. Apparently fluorodinitromethane is too weakly acidic for catalysis of the last step.¹¹ Reaction did occur, however, with acetic anhydride-acetic acid to form the acetate 4.



The expected products were obtained in good to excellent yields from the reactions of fluorodinitromethane with *N,N*-bis(ethoxymethyl)-*tert*-butylamine, *N,N*-bis(*n*-propoxymethyl)benzylamine, and *N,N*-bis(ethoxymethyl)-2-aminoacetaldehyde diethyl acetal.



The *tert*-butyl^{12a,b} 5, benzyl^{12c} 6, and alkoxymethyl derivatives 2 were easily dealkylated with strong acid

(11) Addition of a strong acid to catalyze trisamine formation is ineffective since the ionization of fluorodinitromethane is thereby depressed.

(12) (a) H. G. Adolph of this laboratory has used the *tert*-butyl group as a protective group during the synthesis of fluorodinitroethylamides. (b) R. N. Lacey, *J. Chem. Soc.*, 1633 (1960). (c) B. Loev, M. A. Haas, and F. Dowals, *Chem. Ind. (London)*, 973 (1968).

(1) A summary of the Mannich reaction through 1962 is included in a review by P. Nobel, Jr., F. G. Borgardt, and W. L. Reese, *Chem. Rev.*, **61**, 19 (1964).

(2) H. Feuer, G. Bryant Bachman, and W. May, *J. Amer. Chem. Soc.*, **76**, 5124 (1954).

(3) M. B. Frankel and K. Klager, *ibid.*, **79**, 2953 (1957).

(4) L. T. Eremenko, R. G. Gafurov, and S. I. Sviridov, *Zh. Org. Khim.*, **5**, 31 (1969).

(5) (a) S. S. Novikov, A. A. Fainzil'berg, S. N. Shvedova, and V. I. Guhevskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2056 (1960); (b) M. B. Frankel, *J. Org. Chem.*, **20**, 4709 (1961); (c) E. E. Hamel, *Tetrahedron*, **19**, 85 (1963). (d) The relatively facile synthesis of the piperidine compounds is undoubtedly related to the relief of NO₂-NO₂ nonbonded interactions in the *N*-alkyl-*N*-(2,2,4,4-tetranitrobutyl)hydroxymethylamine intermediates by ring formation.

(6) M. J. Kamlet and H. G. Adolph, *J. Org. Chem.*, **33**, 3073 (1968).

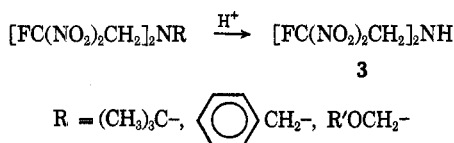
(7) Unpublished data from this laboratory by W. H. Gilligan.

(8) (a) L. H. Book, U. S. Patent 2,295,709 (Sept 15, 1942). (b) A simple modification of Bock's method was the replacement of hexamethylenetetramine by an appropriate substituted amine.

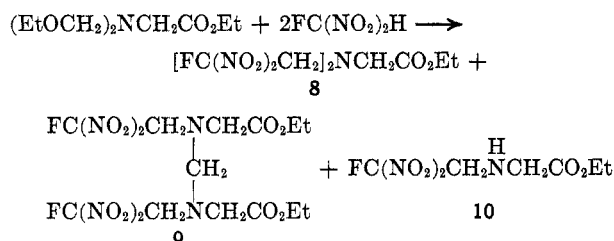
(9) The p*K*_a of fluorodinitromethane is 7.70 as determined by T. N. Hall of this laboratory. The same value was reported by V. I. Slovetskii, L. V. Okhobystina, A. A. Fainzil'berg, A. I. Ivanov, L. B. Biryukova, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2063 (1965).

(10) The synthesis of the parent compound bis(fluorodinitroethyl)amine has been reported by H. G. Adolph and M. J. Kamlet, *J. Org. Chem.*, **34**, 45 (1969).

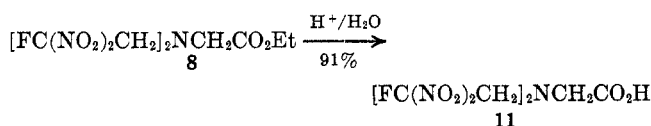
to give bis(fluorodinitroethyl)amine (3). Overall yields of 85–88% of 3 based on fluorodinitromethane were obtained from the *tert*-butyl derivative.



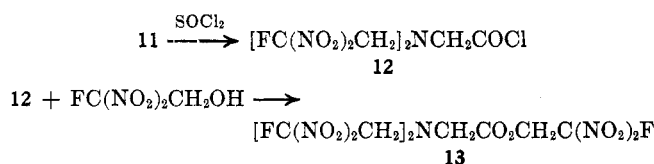
The formation of ethyl *N,N*-bis(fluorodinitroethyl)aminoacetate (8) required a heating period of 11 days at 80°. A 63% yield of the desired bis amine 8 together



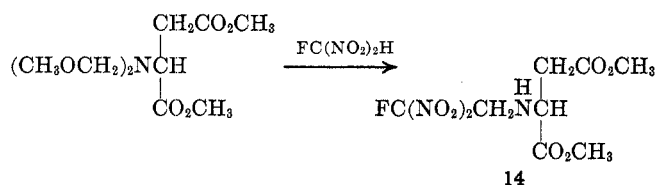
with 5% of *N,N'*-methylenebis(ethyl *N*-fluorodinitroethylaminoacetate) (9) were obtained. The crude reaction mixture also contained an undetermined amount of ethyl *N*-fluorodinitroethylaminoacetate (10).¹³ 8 hydrolyzed normally to the carboxylic acid 11 under



acidic conditions. The acid 11 was converted into the acyl chloride 12 by treatment with thionyl chloride and, without isolation, was reacted with fluorodinitroethanol⁶ to give fluorodinitroethyl *N,N*-bis(fluorodinitroethyl)aminoacetate (13).



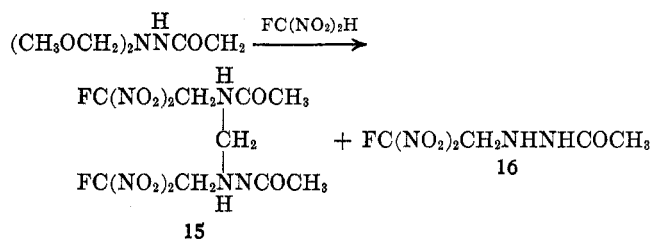
In contrast to the results obtained with ethyl *N,N*-bis(ethoxymethyl)aminoacetate, the only product which could be isolated from the reaction of fluorodinitromethane with dimethyl *N,N*-bis(methoxymethyl)-*dl*-aspartate was dimethyl *N*-fluorodinitroethyl-*dl*-aspartate (14).¹⁴ The formation of a methylenebis com-



pound similar to 9 which might be expected from this reaction is probably precluded because of steric crowding.

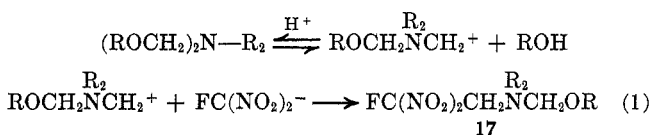
The products from *N,N'*-bis(methoxymethyl)-*N*-acetylhydrazide were the methylenebis compound 15 and

N'-fluorodinitroethyl-*N*-acetylhydrazide (16) isolated in 52 and 20% yields, respectively.



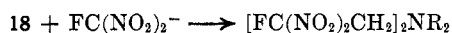
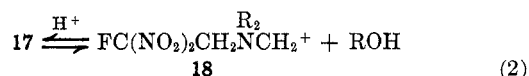
Discussion

The first equivalent of fluorodinitromethane reacts rapidly and, within experimental error, quantitatively to give stable isolable compounds with all of the bis-(alkoxymethyl)amines which have been tested.



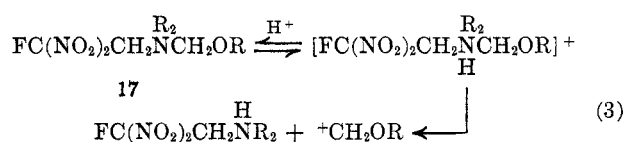
R = Et or *n*-Pr
R₂ = alkyl substituent

A summary of the results collected in Table I strongly indicates that the reaction of a second equivalent of fluorodinitromethane depends on the electronegativity of the attached groups. As the electron-withdrawing

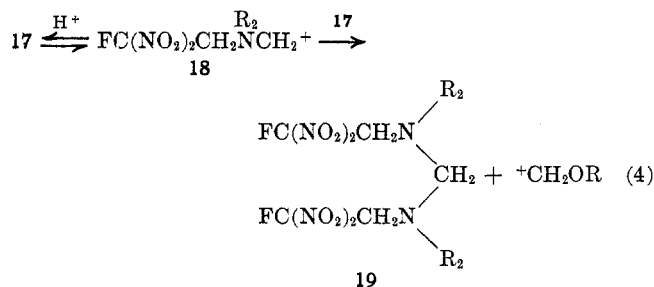


R = Et or *n*-Pr
R₂ = substituent

effect increases, side reactions increase to the eventual exclusion of the bis(fluorodinitroethyl)amino compound. These side reactions appear to fall into two main categories: (1) protonation on the amine nitrogen with expulsion of an alkoxymethyl carbonium ion



and (2) the formation of a destabilized (energetic) carbonium ion which attacks the mono compound 17, present in much greater concentration than the fluorodinitromethide ion again followed by the expulsion of an alkoxy carbonium ion.



Reaction 3 will predominate when the carbonium ion 18 is strongly destabilized and steric factors decrease the possibility of the formation of a methylenebis compound. Reaction 4 will tend to predominate when

(13) Identified by tlc and glc comparison of 10 with an authentic sample.

(14) The aspartate 14 was purified by chromatography on silica gel and identified by comparison with an authentic sample.

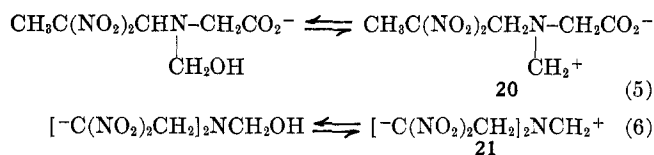
TABLE I
 PRODUCT DISTRIBUTIONS FOR THE REACTIONS OF 17 *vs.* $\sigma_{R_2}^*$ VALUES

R_2	$\sigma_{R_2}^*{}^a$	% yield of products ($R_1 = \text{FC}(\text{NO}_2)_2\text{CH}_2$)				Reaction conditions	
		$(R_1)_2\text{NR}_2$	$\text{CH}_2(\text{NR}_1\text{R}_2)_2$	R_1NR_2	$(R_1)_2\text{NH}$	Temp, °C	Time, hr
$\text{C}(\text{CH}_3)_3$	-0.30	90				85	2
$\text{CH}_2\text{C}_6\text{H}_5$	0.22	83				100	2
$\text{CH}_2\text{CH}(\text{OEt})_2$	0.37 ^b	100				80	7
CH_2OEt	0.52 ^b	81			15	80	72
$\text{CH}_2\text{CO}_2\text{Et}$	0.76	63	5	<i>e</i>		80	264
$\text{CH}_2\text{CO}_2\text{CH}_3$							
CH	0.98	0	0	<i>f</i>		80	144
CO_2CH_3							
$\text{FC}(\text{NO}_2)_2\text{CH}_2$	1.57 ^c				68 ^g	100	54
$\text{CH}_3\text{CONH}-$	1.74 ^d	0	52	20		80	24 ^h

^a R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13. ^b Value used is that for CH_3OCH_2 . ^c L. A. Kaplan and H. B. Pickard, *J. Org. Chem.*, **35**, 2044 (1970), report a σ^* value of 4.41 for the $\text{FC}(\text{NO}_2)_2$ - groups. A factor of 2.8 was used to determine the value for $\text{FC}(\text{NO}_2)_2\text{CH}_2$. ^d Calculated from σ_I value reported in ref 15b. ^e No attempt was made to isolate the mono compound 10. ^f After hydrolytic work-up the only products that could be detected by tlc and glc were the monoaspartate 14 and fluorodinitroethanol. ^g The reaction mixture contained 12% of starting material and 4.6% of bis(fluorodinitroethyl)methylamine. ^h Heating the reaction mixture at higher temperatures and sustained periods of time led to decomposition and complex product mixtures.

steric factors are suitable for methylene coupling and when the intermediate carbonium ion 18 is less stable than the alkoxyethyl carbonium ion.

The relationship between the Mannich reaction and those of alkoxyethylamines is obvious and the same influences should be operative in both, though certainly not to the same degree. For the synthesis of bis(2,2-dinitropropyl)glycine⁴ and tris(2,2-dinitroethyl)amine,⁵ the influence of pH has been emphasized, but it would be perhaps more precise to point to the importance of ionized intermediates for these reactions in stabilizing the respective ions 20 and 21 by decreasing the electro-negativity of the attached groups.¹⁵



No doubt other 2,2-dinitroalkyl derivatives can be used in place of fluorodinitromethane. The possibility also exists that, by a judicious choice of the 2,2-dinitroalkyl reactants to minimize inductive effects a number of mixed tris(2,2-dinitroalkyl)amines can be prepared. These aspects are now being investigated.

Experimental Section

General (Caution).—The polynitro compounds described in this paper are explosives with undetermined properties and should be handled with due care.

Microanalyses were by Galbraith Laboratories, Knoxville, Tenn. Melting points and boiling points are uncorrected.

Thin Layer Chromatography of Fluorodinitro Compounds.—Extensive use was made of thin layer chromatography to monitor

(15) (a) Using σ_I values based on ¹⁹F shielding effects reported by Taft,^{15b} σ^* values of +0.47 and -0.78 can be calculated for the $\text{CH}_2\text{CO}_2\text{Et}$ and the CH_2CO_2^- groups, respectively. A value of +0.7 can be estimated for the $\text{CH}_2\text{CO}_2\text{H}$ group. Using $\text{p}K_a$ values for malonic and ethyl malonic acids, σ^* values are calculated to be 0.76 ($\text{CH}_2\text{CO}_2\text{Et}$), -0.65 (CH_2CO_2^-), and +1.05 ($\text{CH}_2\text{CO}_2\text{H}$). A similar decrease in electronegativity would be expected upon ionization of the dinitroethyl group. (b) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709 (1963); R. W. Taft and I. C. Lewis, *ibid.*, **80**, 2436 (1958).

the formation of fluorodinitro compounds. The plates were coated with silica gel G ("Merck"; Brinkmann Instruments, Inc., Westbury, N. Y.) and developed with methylene chloride, benzene, or chloroform.

After drying, the plates were sprayed with a 25% solution of KOH in methanol and dried at 40° for 15 min. The potassium nitrite produced in this step was detected by spraying the plates with an 0.03% solution of diphenylamine in 60% aqueous sulfuric acid. Intense blue spots are formed.

***N,N*-Bis(*n*-propoxymethyl)-2-fluoro-2,2-dinitroethylamine (1).**—To 9.8 g (0.042 mol) of tris(*n*-propoxymethyl)amine, at ice-bath temperature, was added 5.22 g (0.042 mol) of fluorodinitromethane with stirring. The mixture was allowed to come to ambient temperature and let stand for 2 hr. The reaction mixture was then distilled through a short Vigreux column and the fraction boiling at 80–81° (0.02 mm) was collected. The yield was 11.05 g (89%).

Anal. Calcd for $\text{C}_{10}\text{H}_{20}\text{FN}_3\text{O}_6$: C, 40.40; H, 6.78; F, 6.39; N, 14.14. Found: C, 40.56; H, 6.81; F, 6.52; N, 14.30.

The nmr spectrum in CCl_4 showed two triplets at δ 0.92 (CH_3) and 3.27 (CH_2O), a multiplet at 1.55 (CH_2), a doublet at 4.07 (FCCH_2), and a singlet at 4.19 (NCH_2O).

***N,N*-Bis(2-fluoro-2,2-dinitroethyl)ethoxymethylamine (2).**—A mixture of 3.14 g (0.025 mol) of fluorodinitromethane and 2.39 g (0.0125 mol) of tris(ethoxymethyl)amine was heated at a bath temperature of 80–82° for 72 hr. After cooling and removal of the volatiles *in vacuo*, the residual oil weighing 4.12 g was chromatographed on silica gel (G. Frederick Smith, Columbus, Ohio). The bisethoxymethylamine 2, 3.48 g (81%), was first eluted with CCl_4 - CHCl_3 1:1.

The nmr spectrum in CCl_4 consisted of a quartet at δ 3.34 (OCH_2 , $J_{\text{HH}} = 7$ Hz), a triplet at 1.18 (CH_3 , $J_{\text{HH}} = 7$ Hz), a doublet at 4.26 (FCCH_2 , $J_{\text{HF}} = 17$ Hz), and a singlet at 4.10 (NCH_2O). Later eluates contained 0.54 g (15%) of bis(fluorodinitroethyl)amine which was identified by comparison with an authentic sample.

Anal. Calcd for $\text{C}_7\text{H}_{11}\text{F}_2\text{N}_3\text{O}_5$: C, 24.21; H, 3.19; F, 10.94; N, 20.18. Found: C, 24.28; H, 3.08; F, 11.06; N, 20.30.

***N,N*-Bis(2-fluoro-2,2-dinitroethyl)-*tert*-butylamine (5).**—A mixture of 6.28 g (0.05 mol) of fluorodinitromethane and 4.73 g (0.025 mol) of *N,N*-bis(ethoxymethyl)-*tert*-butylamine was heated at a bath temperature of 85° for 2 hr. After cooling, 7.79 g (90%) of product was obtained by crystallization from ethanol: mp 53–54°; nmr (CDCl_3) δ 1.09 s (CH_3 , 9 H), 4.15 d (CH_2 , $J_{\text{HF}} = 14$ Hz, 4 H).

Anal. Calcd for $\text{C}_8\text{H}_{15}\text{F}_2\text{N}_3\text{O}_5$: C, 27.83; H, 3.80; F, 11.01; N, 20.29. Found: C, 27.74; H, 3.67; F, 11.24; N, 20.31.

***N,N*-Bis(2-fluoro-2,2-dinitroethyl)benzylamine (6).**—A mixture of 6.28 g (0.050 mol) of fluorodinitromethane and 6.28 g (0.025 mol) of *N,N*-bis(propoxymethyl)benzylamine was heated at 100° for 2 hr. Upon cooling, the product crystallized and was recrystallized from absolute ethanol to give 7.83 g (83%):

mp 77–79°; nmr (CDCl₃) δ 7.08–7.41 m (phenyl hydrogens), 4.10 d (NCH₂CF, J_{HF} = 17 Hz), 3.93 s (NCH₂).

Anal. Calcd for C₁₁H₁₁F₂N₅O₈: C, 34.83; H, 2.92; F, 10.02; N, 18.47. Found: C, 35.05; H, 3.06; F, 9.90; N, 18.24.

N,N-Bis(2-fluoro-2,2-dinitroethyl)aminoacetaldehyde Diethyl Acetal (7).—A mixture of 6.28 g (0.050 mol) of fluorodinitromethane and 6.23 g (0.025 mol) of N,N-bis(ethoxymethyl)aminoacetaldehyde diethyl acetal was heated at a bath temperature of 80° for 7 hr. After cooling, the reaction mixture was taken up in methylene chloride and washed consecutively with 0.33 N NaOH and water. After drying with anhydrous magnesium sulfate the solvent was removed *in vacuo* to leave an oil weighing 10.11 g (100%).

The nmr spectrum in CCl₄ showed a multiplet at δ 3.30–3.70 (COCH₂, J_{HH} = 7 Hz), two triplets at 4.40 (HCO₂, J_{HH} = 4 Hz) and 1.20 (OCCH₃, J_{HH} = 7 Hz), and two doublets at 4.26 (FCCH₂, J_{HF} = 17 Hz) and 2.85 (NCH₂C, J_{HH} = 4 Hz). When the multiplet at 3.30–3.70 was irradiated, the triplet at 1.20 collapsed to a singlet. Irradiation of the broadened triplet at 4.40 caused the doublet at 2.85 to collapse to a singlet.

Anal. Calcd for C₁₀H₁₇F₂N₅O₁₀: C, 29.64; H, 4.23; F, 9.38; N, 17.27. Found: C, 29.88; H, 4.43; F, 9.57; N, 17.46.

Bis(2-fluoro-2,2-dinitroethyl)amine (3) by Dealkylation of 5.—A solution of 39.45 g (0.114 mol) of 5 in 60 ml of trifluoroacetic acid–methylene chloride 5:1 was allowed to stand at ambient temperature for 18 hr. At this time the solution was clear red and tlc analysis showed only the presence of the bis amine 3. The solvents were removed *in vacuo* and the residue was recrystallized from CH₂Cl₂–CCl₄ 1:1 to yield 30.89 g (95%) of product, mp 44–45°. The identity was confirmed by comparison with an authentic sample.

Ethyl N,N-Bis(2-fluoro-2,2-dinitroethyl)aminoacetate (8) and N,N-Methylenebis(ethyl N-fluorodinitroethylaminoacetate) (9).—A solution of 4.71 g (0.038 mol) of fluorodinitromethane and 4.16 g (0.019 mol) of ethyl N,N-bis(ethoxymethyl)aminoacetate in 4 ml of absolute ethanol was heated at a bath temperature of 80° for 11 days, allowed to cool, and stripped of volatiles *in vacuo*.

The residue was dissolved in benzene and chromatographed on silica gel. The fractions were analyzed by tlc. The first material eluted was 8. After removal of the benzene this was recrystallized from carbon tetrachloride to give 4.33 g (63%): mp 69–70°; nmr (CDCl₃) δ 1.30 t (CH₃, J_{HH} = 7 Hz), 3.55 s (NCH₂CO₂), 4.19 d (FCCH₂, J_{HF} = 19 Hz), 4.21 q (OCH₂, J_{HH} = 7 Hz).

The methylenebis compound 9 was present in the later eluates and, after removal of the solvent, was recrystallized from carbon tetrachloride to give 0.33 g (5%): mp 85–86°; nmr (CDCl₃) δ 1.31 t (CH₃, J_{HH} = 7 Hz), 3.42 s (NCH₂CO₂), 3.89 s (CH₂), 4.09 d (FCCH₂, J_{HF} = 19 Hz), 4.33 q (OCH₂, J_{HH} = 7 Hz).

Anal. Calcd for C₁₃H₂₀F₂N₆O₁₂: C, 31.84; H, 4.11; F, 7.75; N, 17.14; mol wt, 490.33. Found: C, 32.02; H, 4.35; F, 7.94; N, 16.90; mol wt, 488.

N,N-Bis(2-fluoro-2,2-dinitroethyl)aminoacetic Acid (11).—A solution of 2.55 g (0.007 mol) of 8 in 10 ml of trifluoroacetic acid and 4 ml of 6 N hydrochloric acid was refluxed for 8 hr and allowed to cool, and the volatiles were removed *in vacuo*. The solid residue was recrystallized from methylene chloride to yield 2.14 g (91%), mp 140–142°.

The nmr spectrum in CD₃CN showed a singlet at δ 3.56 (NCH₂CO₂) and a doublet at 4.44 (FCCH₂, J_{HF} = 18.5 Hz). The H

ratio was 2:4. The position of the proton could not be ascertained.

Anal. Calcd for C₆H₇F₂N₅O₁₀: C, 20.76; H, 2.03; F, 10.95; N, 20.18. Found: C, 20.65; H, 2.07; F, 11.21; N, 20.14.

2-Fluoro-2,2-dinitroethyl N,N-Bis(2-fluoro-2,2-dinitroethyl)aminoacetate (13).—To a solution of 1.0 g (0.003 mol) of N,N-bis(fluorodinitroethyl)aminoacetic acid 11 in 5 ml of ethylene chloride was added 0.5 ml of thionyl chloride and a few drops of pyridine. The mixture was gradually heated to 90° and allowed to cool, and the solvent was then removed *in vacuo*. The residue was dissolved in 5 ml of methylene chloride and, after cooling the solution in an ice bath, 0.4 ml of fluorodinitroethanol and 0.3 ml of pyridine were added. The mixture was allowed to warm to ambient temperature and was refluxed for 1 hr. Additional methylene chloride was added, and the solution was washed consecutively with dilute hydrochloric acid, water, and 0.1 N sodium hydroxide. After drying with anhydrous magnesium sulfate, the solvents were removed *in vacuo* to give 1.2 g (88%) of a viscous oil: nmr (CDCl₃) δ 3.75 s (NCH₂CO₂), 4.22 d (FCCH₂N, J_{HF} = 17.5 Hz), 5.28 d (FCCH₂O, J_{HF} = 15 Hz). No impurities could be detected by tlc.

Anal. Calcd for C₈H₈F₈N₇O₁₄: C, 19.88; H, 1.67; F, 11.80; N, 20.30. Found: C, 20.09; H, 1.63; N, 20.08.

Methylenebis Derivative of N'-Fluorodinitroethyl-N-acetylhydrazide (15) and N'-Fluorodinitroethyl-N-acetylhydrazide (16).—A solution of 6.28 g (0.05 mol) of fluorodinitromethane in 5 ml of dry ethanol was heated to reflux temperature. Over a period of 2.5 hr, 4.05 g (0.025 mol) of N',N'-bis(methoxymethyl)-N-acetylhydrazide in 5 ml of absolute ethanol was added. After refluxing overnight the solution was cooled and the crystalline material which deposited was removed by filtration. After recrystallizing from methanol 2.7 g of 15 (52% based on acetylhydrazide) was obtained: mp 164–166° dec; nmr (CD₃OD) δ 1.91 s (COCH₃), 4.09 s (NCH₂N), 4.42 d (FCCH₂, J_{HF} = 17 Hz); nmr (CD₃CN) δ 8.08 s (NHNH).

Anal. Calcd for C₉H₁₄F₂N₈O₁₀: C, 25.01; H, 3.26; F, 8.79; N, 25.93; mol wt, 432.28. Found: C, 25.37; H, 3.21; F, 8.91; N, 26.01; mol wt, 430, 433.

The solvent was removed from the above filtrate and the residue was chromatographed on silica gel. By elution with CH₂Cl₂–MeOH 1:1, followed by removal of the solvent and recrystallization of the residue from chloroform, 1.02 g (20%) of 16 was obtained: mp 115–118°; nmr (CD₃OD) δ 1.88 s (COCH₃), 4.22 d (FCCH₂, J_{HF} = 19 Hz), 4.80 s (CD₃OH).

Anal. Calcd for C₄H₇FN₄O₅: C, 22.86; H, 3.36; F, 9.04; N, 26.67. Found: C, 23.03; H, 3.56; F, 8.84; N, 26.61.

Registry No.—1, 29925-38-0; 2, 29925-39-1; 5, 29925-40-4; 6, 29925-41-5; 7, 29853-44-9; 8, 29925-42-6; 9, 29925-43-7; 11, 29925-44-8; 13, 29925-45-9; 15, 29925-46-0; 16, 29925-47-1.

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