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NEW COMPOUNDS

Synthesis of Novel Energetic Aliphatic Compounds. 2

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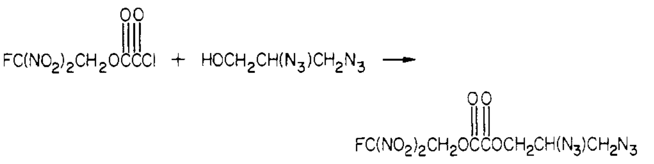
Reported here are the syntheses and physical properties of 10 novel energetic aliphatic compounds. These include eight azides which contain other energetic groups, such as fluorodinitroethyl, *gem*-dinitro, trinitro, and nitramino. In addition, two new energetic difluoramino compounds containing fluorodinitroethyl and trinitro groups are reported.

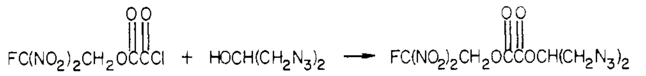
This is our second paper reporting the syntheses of novel energetic aliphatic compounds. The first appeared in this journal in July 1979 (*1*). Contained herein is the syntheses of eight new azides and two new difluoramino compounds each of which contains other energetic groups such as fluorodinitroethyl, *gem*-dinitro, trinitro, and/or nitramine. The types of azides prepared were esters, ethers, formals, amines, and carbamates. The difluoramino compounds were both esters.

The azido esters which were synthesized were 1,2-diazidopropyl fluorodinitroethyl oxalate (I), 1,3-diazido-2-propyl fluorodinitroethyl oxalate (II), and 1,2-diazidopropyl 4-fluoro-4,4-dinitrobutyrate (III).



$$FC(NO_2)_2CH_2O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}Cl + HOCH_2CH(N_3)CH_2N_3 \rightarrow FC(NO_2)_2CH_2O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OCH_2CH(N_3)CH_2N_3$$

I



$$FC(NO_2)_2CH_2O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}Cl + HOCH(CH_2N_3)_2 \rightarrow FC(NO_2)_2CH_2O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OCH(CH_2N_3)_2$$

II

$$FC(NO_2)_2CH_2CH_2COCl + HOCH_2CH{=}CH_2 \rightarrow FC(NO_2)_2CH_2CH_2CO_2CH_2CH{=}CH_2 \xrightarrow{\substack{1.\ Br_2 \\ 2.\ NaN_3}} \underset{\text{III}}{FC(NO_2)_2CH_2CH_2CO_2CH_2CH(N_3)CH_2N_3}$$

The azido ether which was synthesized was 3-azido-2,2-dinitropropyl 2,3-diazidopropyl ether (IV).

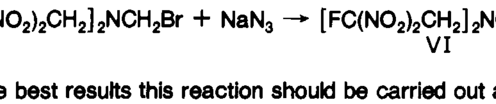
$$KC(NO_2)_2CH_2OCH_2CH{=}CH_2 + CH_2O \rightarrow HOCH_2C(NO_2)_2CH_2OCH_2CH{=}CH_2 \xrightarrow{CH_3C_6H_4SO_2Cl} CH_3C_6H_4SO_2OCH_2C(NO_2)_2CH_2OCH_2CH{=}CH_2 \xrightarrow{\substack{1.\ Br_2 \\ 2.\ NaN_3}} \underset{\text{IV}}{N_3CH_2C(NO_2)_2CH_2OCH_2CH(N_3)CH_2N_3}$$

All of the reactions proved to be quite straightforward. It was noted however that in the last step the replacement of Br_2 with N_3 was quite rapid (overnight) whereas the replacement of tosylate with N_3 required 4.5 days.

The azido formal which was synthesized was bis(1,2-diazido-4-oxa-6,6-dinitroheptyl) formal (V).

$$HOCH_2C(NO_2)_2CH_2OCH_2CH{=}CH_2 + Br_2 \rightarrow HOCH_2C(NO_2)_2CH_2OCH_2CH(Br)CH_2Br \xrightarrow{CH_2O/H_2SO_4} CH_2[OCH_2C(NO_2)_2CH_2OCH_2CH(Br)CH_2Br]_2 \xrightarrow{NaN_3} \underset{\text{V}}{CH_2[OCH_2C(NO_2)_2CH_2OCH_2CH(N_3)CH_2N_3]_2}$$

The first and last steps in the synthesis presented no problems; however, the second or formylation step yielded a byproduct in ~15% yield which created some workup problems. This byproduct was a low-melting (52.5–54 °C) white solid which was eventually removed from the desired tetrabromo compound by sublimation. Elemental analysis showed the byproduct to be cyclic 5,5-dinitro-1,3-dioxane (*2*). It probably was formed by rupture of the ether linkage in the starting dibromo material forming a diol which then reacted with CH_2O.



The azido amines which were synthesized were (azidomethyl)bis(fluorodinitroethyl)amine (VI) and *O*-(1,2-diazidopropyl)-*N*,*N*-bis(fluorodinitroethyl)aminomethanol (VII).

$$[FC(NO_2)_2CH_2]_2NH \xrightarrow[NaBr]{CH_2O/H_2SO_4} [FC(NO_2)_2CH_2]_2NCH_2Br$$

$$[FC(NO_2)_2CH_2]_2NCH_2Br + NaN_3 \rightarrow \underset{\text{VI}}{[FC(NO_2)_2CH_2]_2NCH_2N_3}$$

For the best results this reaction should be carried out at 0 °C under an inert atmosphere. The presence of moisture converts the starting bromo compound to the corresponding hydroxy material which is then easily unzipped back to bis amine.

$$[FC(NO_2)_2CH_2]_2CH_2]_2NCH_2Br \xrightarrow{H_2O} [FC(NO_2)_2CH_2]_2NCH_2OH \xrightarrow{-CH_2O} [FC(NO_2)_2CH_2]_2NH$$

$$[FC(NO_2)_2CH_2]_2NCH_2Br + HOCH_2CH(N_3)CH_2N_3 \rightarrow \underset{\text{VII}}{[FC(NO_2)_2CH_2]_2NCH_2OCH_2CH(N_3)CH_2N_3}$$

The azido carbamate that was synthesized was 1,3-diazido-2-propyl *N*-nitro-*N*-(trinitropropyl)carbamate (VIII).

$$(NO_2)_3CCH_2CH_2NCO + HOCH(CH_2N_3)_2 \rightarrow (NO_2)_3CCH_2CH_2N(H)CO_2CH(CH_2N_3)_2 \xrightarrow{HNO_3/Ac_2O} \underset{\text{VIII}}{(NO_2)_3CCH_2CH_2N(NO_2)CO_2CH(CH_2N_3)_2}$$

Two new energetic difluoramino esters were also synthesized.

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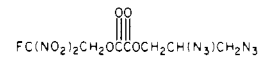
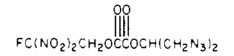
Table I. Novel Energetic Azides[a]

compd	yield, %	n_D^{23}	d^{23}, g/cm^3
 $FC(NO_2)_2CH_2O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OCH_2CH(N_3)CH_2N_3$	50	1.4896	1.502
 $FC(NO_2)_2CH_2O\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}OCH(CH_2N_3)_2$	52	1.4891	1.501
$FC(NO_2)_2CH_2CH_2CO_2CH_2CH(N_3)CH_2N_3$	58	1.4882	1.442
$N_3CH_2C(NO_2)_2CH_2OCH_2CH(N_3)CH_2N_3$	41	1.5128	1.406
$CH_2[OCH_2C(NO_2)_2CH_2OCH_2CH(N_3)CH_2N_3]_2$	33	1.5082	1.418
$[FC(NO_2)_2CH_2]_2NCH_2N_3$	86	1.4873	1.638
$[FC(NO_2)_2CH_2]_2NCH_2OCH_2CH(N_3)CH_2N_3$	49	1.4932	1.521
$(NO_2)_3CCH_2CH_2N(NO_2)CO_2CH(CH_2N_3)_2$	75	1.5203	1.563

[a] Elemental analyses were carried out on all compounds. They were, in every case, consistent with the proposed structure.

Table II. Energetic Difluoramino Esters[a]

compd	yields, %	n_D^{23}	d^{23}, g/cm^3
$CH_3C(NF_2)_2CH_2CO_2CH_2C(NO_2)_2F$[b]	44	1.4198	
$CH_3C(NF_2)_2CH_2CO_2CH_2C(NO_2)_3$	32	1.4496	1.582

[a] Elemental analyses were carried out on all compounds. They were, in every case, consistent with the proposed structure.
[b] Boiling point, 76 °C/0.1 mmHg.

They were fluorodinitroethyl 3,3-bis(difluoramino)butyrate (IX) and trinitroethyl 3,3-bis(difluoramino)butyrate (X).

$$CH_3C(NF_2)_2CH_2COCl \xrightarrow{FC(NO_2)_2CH_2OH} \underset{\text{IX}}{CH_3C(NF_2)_2CH_2CO_2CH_2C(NO_2)_2F}$$

$$\xrightarrow{(NO_2)_3CCH_2OH} \underset{\text{X}}{CH_3C(NF_2)_2CH_2CO_2CH_2C(NO_2)_3}$$

A summary of these new energetic compounds and their properties are given in Tables I and II.

Experimental Section

General Procedures. **Caution!** Most of the products and starting materials described are explosives of moderate to considerable sensitivity to initiation by impact, shock, friction, and other means and should be handled with care.

Melting and boiling points are uncorrected. In cases where the boiling points were high, isolation and purification were accomplished by liquid chromatography for safety reasons. Infrared analyses were carried out with a Perkin-Elmer 137 infrared spectrophotometer. Gas-chromatographic analyses were carried out on an F&M 700 instrument using a 10 ft × $^3/_{16}$ in. stainless-steel column packed with 3% QF-1 on 40/80 mesh Chromosorb T. Final structure proof was obtained in every case with complete elemental analyses.

1,2-Diazidopropyl Fluorodinitroethyl Oxalate (I). To a solution of 1.5 g (6 mmol) of 2-fluoro-2,2-dinitroethyl oxalyl chloride (*3*) in 10 mL of ethylene dichloride was added dropwise 0.87 g (6 mmol) of 2,3-diazido-1-propanol. The resulting reaction mixture was stirred at reflux temperature overnight. It was cooled and the solvent removed, yielding 2.1 g of yellow oil. The oil was dissolved in methylene chloride, and this solution was then washed 3 times with water. After the solution was dried, the solvent was removed, yielding 1.2 g of crude I. Pure I was obtained as a colorless oil in 50% yield via liquid chromatography using silica gel as the absorbent.

1,3-Diazido-2-propyl Fluorodinitroethyl Oxalate (II). To a solution of 12.2 g (0.05 mol) of 2-fluoro-2,2-dinitroethyl oxalyl chloride in 50 mL of ethylene dichloride was added 7.1 g (0.05 mol) of 1,3-diazido-2-propanol (*4*). The resulting reaction mixture was stirred at reflux temperature for 1.5 days. It was cooled and the solvent removed, yielding 26 g of yellow oil. The oil was dissolved in methylene chloride, and this solution was washed 3 times with water. After the solution was dried, the solvent was removed, yielding 13.4 g of crude II. Pure II was obtained as a nearly colorless oil in 50% yield by means of liquid chromatography using silica gel as the adsorbent.

Allyl 4-Fluoro-4,4-dinitrobutyrate. To a solution of 10 g (0.047 mol) of 4-fluoro-4,4-dinitrobutyryl chloride in 20 mL of ethylene dichloride was added 2.7 g (0.047 mol) of allyl alcohol. This reaction mixture was then stirred at ambient temperature overnight. The solvent was removed, and the remaining yellow oil was identified as allyl 4-fluoro-4,4-dinitrobutyrate from its infrared spectrum. Gas-chromatographic analysis indicated it to be 99% pure; its refractive index was $n^{25}{}_D$ 1.4457. The yield was quantitative.

1,2-Dibromopropyl 4-Fluoro-4,4-dinitrobutyrate. A solution of 10.9 g (0.046 mol) of allyl 4-fluoro-4,4-dinitrobutyrate in 30 mL of carbon tetrachloride was cooled to 0 °C. Bromine (8.8 g, 0.055 mol) was added dropwise, the temperature being maintained at 0 °C, and the reaction mixture was stirred an additional 30 min at that temperature. It was then warmed to and stirred at ambient temperature overnight. It was finally heated to 70 °C for 4 h. After the mixture was cooled, the solvent was removed, yielding 17.2 g (94%) of yellow oil. This material was identified as 1,2-dibromopropyl 4-fluoro-4,4-dinitrobutyrate from its infrared spectrum. Gas-chromatographic analysis indicated its purity to be 100%; its refractive index was $n^{25}D$ 1.5036.

1,2-Diazidopropyl 4-Fluoro-4,4-dinitrobutyrate (III). To a solution of 6.4 g (16.16 mmol) of 1,2-dibromopropyl 4-fluoro-4,4-dinitrobutyrate in 30 mL of dimethylformamide (DMF) was added 3.5 g (48.5 mmol) of sodium azide. The resulting reaction mixture was then stirred at 40–45 °C for 60 h. After the mixture was cooled, an equal quantity of methylene chloride was added, and the resulting solution was washed 8 times with water. Pure III was obtained as a nearly colorless oil by means of liquid chromatography using silica gel as the adsorbent.

3-Hydroxy-2,2-dinitropropyl Allyl Ether. To a mixture of 37.4 g (0.175 mol) of potassium 2,2-dinitroethyl allyl ether (*5*), 7.17 g (0.239 mol) of formaldehyde, and 200 mL of water was added dropwise 13.6 mL of glacial acetic acid. The slightly exothermic reaction was controlled at ambient temperature with a cooling bath. After addition was complete, the reaction mixture was stirred an additional hour at the same temperature. The reaction mixture was extracted with methylene chloride which was then back-washed with water. The organic portion was dried over $MgSO_4$ and concentrated to yield 33 g (92% yield) of crude product. Pure product was obtained by means of liquid chromatography using silica gel as the adsorbent. Gas-chromatographic analysis indicated a purity of 99+%; its refractive index was n^{23}_D 1.4658.

3-Tosyl-2,2-dinitropropyl Allyl Ether. A mixture of 15 g (0.073 mol) of 3-hydroxy-2,2-dinitropropyl allyl ether, 15.37 g (0.08 mol) of *p*-toluenesulfonyl chloride, 7.6 g (0.08 mol) of pyridine *N*-oxide, and 75 mL of carbon tetrachloride was heated at 60 °C for 4 days. After being cooled, the reaction mixture was washed with water, sodium bicarbonate, and finally water to a neutral pH. After the solution was dried and the solvent removed, there remained 19.5 g (74% yield) of crude product. Pure product was obtained by means of liquid chromatography using silica gel as the adsorbent. Gas-chromatographic analysis indicated its purity to be 100%; its refractive index was n^{25}_D 1.5097.

3-Tosyl-2,2-dinitropropyl 2,3-Dibromopropyl Ether. A solution of 8.6 g (23.9 mmol) of 3-tosyl-2,2-dinitropropyl allyl ether in 30 mL of carbon tetrachloride was cooled to 0 °C under a nitrogen blanket. At this temperature, 4.59 g (28.7 mmol) of bromine was added dropwise and the reaction mixture was stirred an additional 30 min at 0 °C. It was then warmed to and stirred at ambient temperature for 16 h. The solvent was removed, yielding a yellow solid. This solid was recrystallized from hexane–carbon tetrachloride to give 12.0 g (97% yield) of a white solid, mp 66–67 °C. Its structure was confirmed by IR, GC, and elemental analyses.

3-Azido-2,2-dinitropropyl 2,3-Diazidopropyl Ether (IV). A mixture of 11.4 g (0.022 mol) of 3-tosyl-2,2-dinitropropyl 2,3-dibromopropyl ether, 6.4 g (0.099 mol of NaN_3, and 75 mL of DMF was heated at 55 °C for 4.5 days. After the mixture was cooled, most of the DMF was removed in vacuo. Methylene chloride was added, and the insoluble solid was removed by centrifugation. The methylene chloride solution was then washed 6 times with water to remove the remaining DMF. Removal of methylene chloride yielded 4.8 g (70% yield) of crude IV. Pure IV was obtained by means of liquid chromatography using silica gel as the adsorbent.

3-Hydroxy-2,2-Dinitropropyl 2,3-Dibromopropyl Ether. A solution of 5 g (24.3 mmol) of 3-hydroxy-2,2-dinitropropyl allyl ether in 20 mL of carbon tetrachloride was cooled to 0 °C under a nitrogen blanket. At this temperature 4.7 g (29 mmol) of bromine was added dropwise, and the reaction mixture was stirred an additional 30 min at 0 °C. It was then warmed to 25 °C and stirred at ambient temperature for 16 h. The solvent was removed, yielding 8.6 g (96% yield) of crude product. This material was pure enough to be used as an analytical sample.

Bis(1,2-dibromo-4-oxa-6,6-dinitroheptyl) Formal. To a solution of 5.2 g (14 mmol) of 3-hydroxy-2,2-dinitropropyl 2,3-dibromopropyl ether and 0.213 g (2.33 mmol) of trioxane in 35 mL of methylene chloride at ambient temperature was added dropwise 20 mL of sulfuric acid. The reaction mixture was then stirred an additional hour at ambient temperature. The layers were separated, and the acid layer was extracted with methylene chloride. The methylene chloride extract together with the organic layer was then washed twice with 2% sodium hydroxide and finally with water to a neutral pH. Removal of the solvent yielded 4.6 g of crude product. Pure product (3.6 g, 68% yield) was obtained by means of liquid chromatography using silica gel as the adsorbent.

Bis(1,2-Diazido-4-oxa-6,6-Dinitroheptyl) Formal (V). A mixture of 1.97 g (2.65 mmol) of bis(1,2-dibromo-4-oxa-6,6-dinitroheptyl) formal, 1.03 g (15.9 mmol) of NaN_3, and 20 mL of DMF was heated at 60 °C for 1.5 days. After the mixture was cooled, most of the DMF was removed in vacuo. Methylene chloride was added, and the insoluble solid was removed by centrifugation. The methylene chloride solution was then washed 6 times with water to remove the remaining DMF. Removal of methylene chloride yielded 1 g of crude V. Pure V (0.8 g, 50% yield) was obtained by means of liquid chromatography using silica gel as the adsorbent.

(Azidomethyl)bis(fluorodinitroethyl)amine (VI). A solution of 30 g (0.079 mol) of (bromomethyl)bis(fluorodinitroethyl)amine (*6, 7*) in 80 mL of DMF, under a nitrogen blanket, was cooled to 0 °C. Sodium azide (10.2 g, 0.157 mol) was added at 0 °C, and the reaction mixture was then stirred at this temperature overnight. Gas-chromatographic analysis at this point showed the disappearance of starting material and the appearance of one new material. The reaction solids were removed by centrifugation, an equal quantity of methylene chloride was added, and the organic mixture was washed 10 times with water to remove DMF. Removal of methylene chloride yielded 24.2 g (90% yield) of crude VI. Pure VI was isolated as a colorless liquid by means of liquid chromatography using silica gel as the adsorbent.

O-(1,2-Diazidopropyl)-N,N-bis(fluorodinitroethyl)aminomethanol (VII). A solution of 11.8 g (0.031 mol) of (bromomethyl)bis(fluorodinitroethyl)amine in 75 mL of acetonitrile, under a nitrogen blanket, was cooled to 0 °C. To this cold solution was added 4.38 g (0.031 mol) of 2,3-diazido-1-propanol followed by the dropwise addition of 3.12 g (0.031 mol) of triethylamine. The reaction mixture was stirred at 0 °C for 1 h, then at ambient temperature overnight, and finally at 50 °C for 4 days. Periodic IR and GC analyses dictated the time of reaction and also its temperature. At reaction's end, there remained a heavy slurry of white solid. Acetonitrile was removed, and to the resulting solids–oil mixture was added 100 mL of ether. In this way, the oil was completely solubilized and the solid remained insoluble. The solid was filtered and identified as triethylamine hydrobromide. The filtrate was concentrated, yielding 13 g of yellow oil. Pure VII was isolated from this yellow oil in ~50% yield via liquid chromatography using silica gel as the adsorbent.

1,3-Diazido-2-Propyl N-(Trinitropropyl)Carbamate. A mixture of 11 g (0.05 mol) of 3,3,3-trinitropropyl isocyanate, 7.1 g (0.05 mol) of 1,3-diazido-2-propanol, and 50 mL of ethylene dichloride was heated at reflux for 4 days. The reaction mixture was cooled and concentrated to yield 19 g of crude 1,3-diazido-2-propyl *N*-(trinitropropyl)carbamate. The pure material was obtained via liquid chromatograph using neutral alumina as the adsorbent.

1,3-Diazido-2-propyl N-Nitro-N-(trinitropropyl)carbamate (VIII). To a mixture of 25 mL of 98% nitric acid and 35 mL of methylene chloride was added dropwise 25 mL of acetic anhydride while the temperature was kept at 0–10 °C. At this temperature there was then added dropwise 9.4 g (0.026 mol) of 1,3-diazido-2-propyl *N*-(trinitropropyl)carbamate. The reaction mixture was stirred at 0–10 °C for an additional 1.5 h, after which time it was poured onto ice. The layers were separated and the aqueous portion was extracted with 50 mL of methylene chloride. The combined organic portion was then washed 3 times with ice water, dried over $MgSO_4$, and concentrated to yield 10.7 g of crude VIII. Pure product was obtained via liquid chromatography using silica gel as the adsorbent.

Fluorodinitroethyl 3,3-Bis(difluoramino)butyrate (IX). To a mixture of 0.82 g (5.3 mmol) of fluorodinitroethanol and 1.1 g (5.27 mmol) of 3,3-bis(difluoramino)butyryl chloride in 10 mL of chloroform, at ambient temperature, was added 0.05 g of freshly sublimed aluminum chloride. The reaction mixture was then stirred at ambient temperature for an additional 4 h. At this point, GC analysis indicated that the starting materials had disappeared. The reaction mixture was washed with dilute HCl and then with water to a neutral pH. It was dried over $MgSO_4$ and filtered, and the solvent removed to yield 1.4 g of crude IX. Pure IX was obtained as a colorless oil via liquid chromatography using neutral alumina as the absorbent.

Trinitroethyl 3,3-Bis(difluoramino)butyrate (X). A mixture of 4.7 g (0.023 mol) 3,3-bis(difluoramino)butyryl chloride (*8*), 4.2 g (0.023 mol) of trinitroethanol, 3.1 g (0.023 mol) of anhydrous

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aluminum chloride, and 100 mL of alcohol-free chloroform was refluxed for 16 h. The mixture was cooled and filtered, and the filtrate concentrated to give 5.0 g of yellow oil, $n^{22.5}{}_D$ 1.4680. The crude product was purified on a silica chromatographic column to give a colorless liquid: $n^{24.5}$ 1.4555; GC purity of 99.6%.

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Derivatives of a Weakly Basic Amine. *N*,*N*-Bis(2-fluoro-2,2-dinitroethyl)amine

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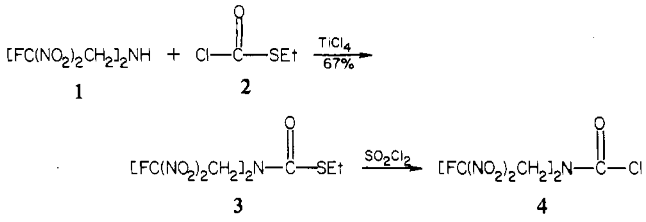
The use of *S*-ethyl carbonochloridothioate (2) as a chlorocarbonylation reagent for the preparation of *N*,*N*-bis(2-fluoro-2,2-dinitroethyl)carbamyl chloride (4) is described. 4 is a reactive intermediate which can be used to introduce the *N*,*N*-bis(2-fluoro-2,2-dinitroethyl)amino group into a variety of compounds. The preparation and some reactions of a number of these derivatives are presented.

N,*N*-Bis(2-fluoro-2,2-dinitroethyl)amine (1), first prepared by Adolph and Kamlet, is a weakly basic amine, as evidenced by the fact that it can be recrystallized unchanged from trifluoroacetic acid, is insoluble in 50% sulfuric acid, and does not form isolable salts with mineral acids (*1*). The weak nucleophilic properties of the amine 1 toward protons appear to parallel equally weak nucleophilic properties toward carbon. Under usual conditions, 1 is unreactive toward acetylating agents such as anhydrides or acyl chlorides, though a limited number of amides have been prepared by the use of mixed anhydrides (2). Since heretofore the number of successful reactions of 1 has been quite limited, it appeared that a general method which would allow the preparation of derivatives of 1 (or for that matter other similarly weak nucleophilic amines) would be of value.

A possible intermediate for the synthesis of derivatives of 1 is *N*,*N*-bis(2-fluoro-2,2-dinitroethyl)carbamyl chloride (4). Because of the unreactivity of 1, 4 cannot be prepared by the usual method, i.e., reacting 1 with excess phosgene. However, a method recently reported from this laboratory by Gilligan and Stafford (3) for the chlorocarbonylation of β-nitroethanols suggested the following route to the carbamyl chloride 4:

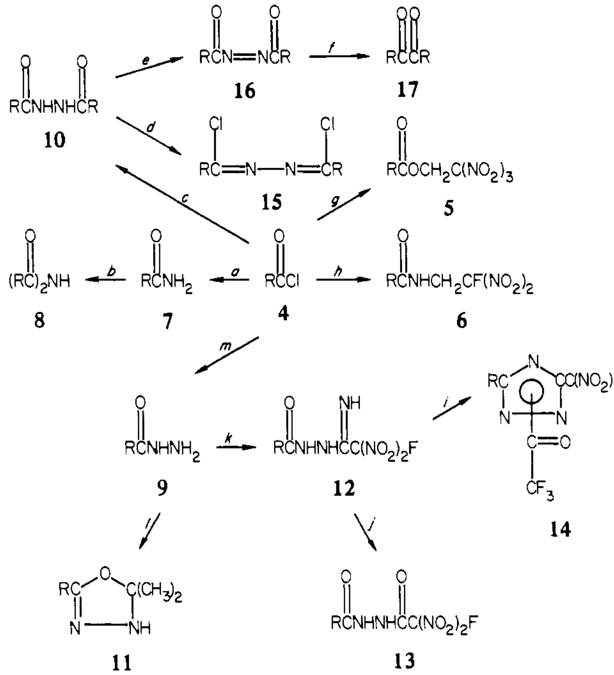


$$\underset{1}{[FC(NO_2)_2CH_2]_2NH} + \underset{2}{Cl-\overset{O}{\overset{\|}{C}}-SEt} \xrightarrow[67\%]{TiCl_4}$$

$$\underset{3}{[FC(NO_2)_2CH_2]_2N-\overset{O}{\overset{\|}{C}}-SEt} \xrightarrow{SO_2Cl_2} \underset{4}{[FC(NO_2)_2CH_2]_2N-\overset{O}{\overset{\|}{C}}-Cl}$$

This report describes the synthesis of 4 and derivatives prepared therefrom.

Scheme I. Derivatives of *N*,*N*-Bis(2-fluoro-2,2-dinitroethyl)carbamyl Chloride



^{a} NH_3. ^{b} 4. ^{c} NH_2NH_2. ^{d} $POCl_3/PCl_5$. ^{e} 70% HNO_3. ^{f} 150-160 °C. ^{g} $(NO_2)_3CCH_2OH$. ^{h} $F(NO_2)_2CCH_2NH_2$. ^{i} $(CF_3CO)_2O$. ^{j} Aqueous HCl. ^{k} $F(NO_2)_2CCN$. ^{l} $(CH_3)_2C{=}O$. ^{m} Excess NH_2NH_2.

Results and Discussion

The preparation of derivatives of 4 is outlined in Scheme I. The proton NMR spectrum of 14 indicated that it was a mixture of isomers, which differed in the position of the trifluoroacetyl group. An attempt to remove the trifluoroacetyl group from 14 by hydrolysis was complicated by the fact that the fluorodinitromethyl group on the ring also proved to be susceptible to hydrolysis.

Attempts to cyclize the biscarbamylhydrazide 10 to a 1,3,4-oxadiazole were unsuccessful. Use of phosphorus pentachloride/phosphorus oxychloride as the cyclization agent gave