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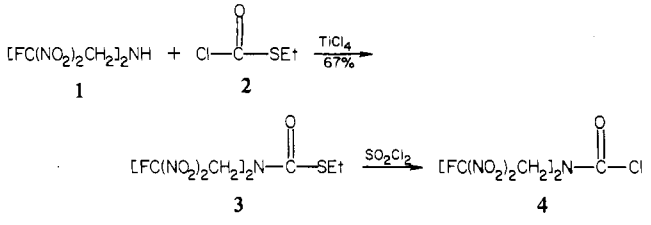
The use of *S*-ethyl carbonochloridothioate (2) as a chlorocarbonylation reagent for the preparation of *N,N*-bis(2-fluoro-2,2-dinitroethyl)carbamyl chloride (4) is described. 4 is a reactive intermediate which can be used to introduce the *N,N*-bis(2-fluoro-2,2-dinitroethyl)amino group into a variety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

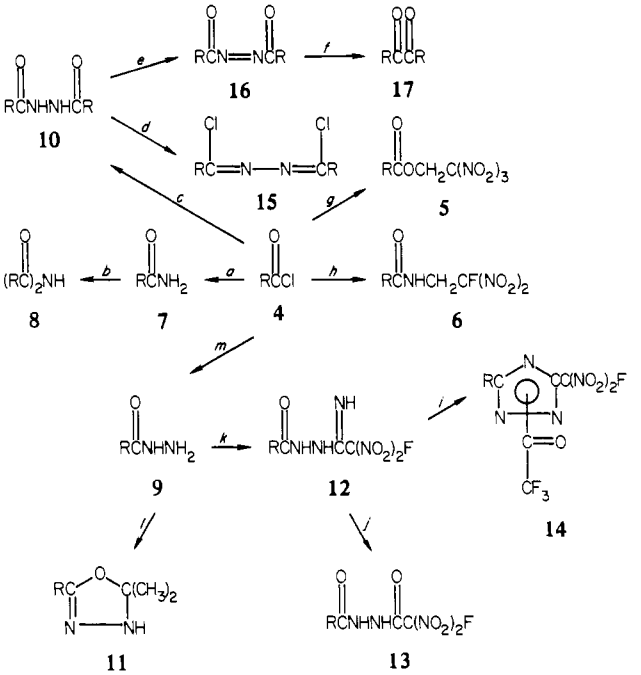
N,N-Bis(2-fluoro-2,2-dinitroethyl)amine (1), first prepared by Adolph and Kamlet, is a weakly basic amine, as evidenced by the fact that it can be recrystallized unchanged from trifluoroacetic acid, is insoluble in 50% sulfuric acid, and does not form isolable salts with mineral acids (*1*). The weak 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:



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

Table I. Spectral Data for *N,N*-Bis(2-fluoro-2,2-dinitroethyl)amine Derivatives

compd	^{1}H NMR[a] ppm	solvent[b]	IR (KBr), cm^{-1}	mass spectrum (CI)
3	4.83 d, 2.96 q, 1.26 t	I	1670 (C=O), 1610 (NO_2)	
4	4.97 d	I	1745 (C=O), 1605 (NO_2)	
5	5.95 s, 5.24 d	II	1740 (C=O)	
6	7.50 broad t, 5.17 d, 4.76 pair of ds	II	3450 (NH), 1690 (C=O)	
7	6.36 s, 5.08 d	II	3490, 3390 (NH_2); 1665 (C=O)	
8	5.27 broad m, 2.70 s	II	3450 (NH); 1795, 1735 (C=O)	
9	4.93 d, 4.75 s	III	1650 (C=O)	
10	8.70 s, 5.18 d	II	3330 (NH), 1650 (C=O)	
11	5.00 d, 2.68 s, 2.58 s	IV	3200 (NH), 1710 (C=N) (weak)	
12	8.95 broad s, 6.89 broad s, 5.25 d, 2.96 broad s	II	3450, 3340, 3210 (NH); 1675 (C=O)	
13	10.95 broad s, 9.36 s, 5.22 d	II	3350, 3200 (NH); 1745, 1670 (C=O)	
14	5.16 d (large), 4.80 d (small), 4.08 d (small), mixture of isomers	I	1760 (C=O),[c] 1600 (NO_2), 1200 (CF_3)	575 (M + 1)
15	5.42 d	II	1605 (NO_2)	
16	5.54 m	II	1745 (C=O)	
17	5.37 d, 5.27 d	II	1690, shoulder at 1700 (C=O)	633 (M + 1)

[a] Tetramethylsilane was used as an internal standard. [b] I = chloroform, II = acetone, III = methanol, IV = trifluoroacetic acid. [c] Liquid film on NaCl plates.

the dichloro compound **15**. Reactions of **15** with ammonia, hydrazine, or water did not lead to cyclic compounds, nor could the chlorine atoms be replaced by fluorine either with HF/pyridine or KF and crown ethers. The main products from an attempted cyclization with thionyl chloride were the biuret **8** and the azo compound **16**.

Thus, although we have employed only a few of the multitude of nucleophiles available to the organic chemist, it is evident that the carbamyl chloride **4** is a valuable intermediate for the introduction of the bis(fluorodinitroethyl)amino group into organic molecules. In addition, while the results in this paper have been restricted to bis(fluorodinitroethyl)amine, *N*-chlorocarbonylation via the *S*-ethyl thiocarbamates should prove to be a useful method for other amines where phosgene is not a suitable reagent.

Experimental Section

***General Information*. Caution.** The polynitro compounds described in this paper are explosives and should be handled with due care. In particular, reactions should be run on a small scale behind adequate shielding. Personnel should be equipped with safety glasses and fire-retardant laboratory coats.

The elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Satisfactory analyses were obtained for all compounds and were submitted for review. Analyses were performed for all elements except oxygen. The melting points are uncorrected. Spectral data are in Table I.

***S*-Ethyl *N,N*-Bis(2-fluoro-2,2-dinitroethyl)thiocarbamate (3).** A mixture of 55.0 g (0.19 mol) of **1**, 38 mL of chloroform, 40 mL of **2**, and 20 mL of $TiCl_4$ was heated in an oil bath at 65–67 °C for 17 h. Chloroform (100 mL) was added to the warm mixture, which was then filtered through Celite, and the filter cake was washed with chloroform. The solvent was removed from the dark-colored filtrate on a rotary evaporator under vacuum. The oily residue was dissolved in methanol, treated with charcoal (Darco G-60), and filtered. After the solvent was removed from the filtrate, the residue was recrystallized from chloroform to give 48.0 g (67%) of product, mp 74–75 °C.

***N,N*-Bis(2-fluoro-2,2-dinitroethyl)carbamyl Chloride (4).** A mixture of 30.4 g of **3**, 60 mL of sulfuryl chloride, and 120 mL of 1,2-dichloroethane was cautiously heated to the reflux point (SO_2 evolution) and held at reflux for 8 h. The volatiles were removed in vacuo to give a residual oil. The oil was washed twice with 340 mL of dry hexane by decantation and the oil crystallized by dissolving in $CHCl_3$ (25 mL) and cooling to −20 °C to yield 24.2 g (85%) of **4**, mp 45–47 °C.

***O*-(2,2,2-Trinitroethyl) *N,N*-Bis(2-fluoro-2,2-dinitroethyl)carbamate (5).** A solution of 3.5 g (0.01 mol) of **4** and 2.0 g (0.011 mol) of trinitroethanol in 6 mL of CH_2Cl_2 was stirred in an ice bath while 4 mL of pyridine *N*-oxide (2.6 M in CH_2Cl_2) was added dropwise over a 10-min period. Additional CH_2Cl_2 (30 mL) was added, and the mixture was stirred for 30 min at 3–5 °C and then overnight at ambient temperature. The mixture was filtered, and volatiles were removed from the filtrate on a rotary evaporator. The residue was chromatographed on silica gel and the carbamate **5** recovered by elution with CH_2Cl_2/hexane: 1.21 g (25%), mp 85–86 °C.

***N,N,N'*-Tris(2-fluoro-2,2-dinitroethyl)urea (6).** A solution of 1.97 g (5.6 mmol) of **4** in CH_2Cl_2 (5 mL) was added dropwise over a period of 10 min to a CH_2Cl_2 solution (9 mL) of 2-fluoro-2,2-dinitroethylamine (1.9 g, 12 mmol) and 0.5 mL of pyridine at 3–5 °C. The mixture was stirred in the ice bath for 1.5 h and an additional 3 h at room temperature. The mixture was taken up in CH_2Cl_2 and washed consecutively with dilute aqueous HCl and water. The CH_2Cl_2 solution was dried ($MgSO_4$) and filtered, and the solvent was removed from the filtrate in vacuo. The residue was recrystallized from $CHCl_3$ to give 1.6 g (62%) of **6**, mp 109–111 °C.

***N,N*-Bis(2-fluoro-2,2-dinitroethyl)urea (7).** A solution of 4.0 g (0.011 mol) of **4** in 30 mL of ether was stirred in an ice bath while gaseous NH_3 was passed into the solution until it remained slightly basic to moist pH paper. The ether layer was then washed with water (30 mL), dried ($MgSO_4$), and filtered. The filtrate was concentrated by distillation while $CHCl_3$ was slowly added until the distillate temperature reached 60 °C and crystals formed in the hot solution. Cooling gave 3.14 g (83.5%) of **7**, mp 119–121 °C. Recrystallization from ether/$CHCl_3$ raised the melting point to 120–122 °C.

***N,N,N'',N''*-Tetrakis(2-fluoro-2,2-dinitroethyl)biuret (8).** A solution of 1.40 g (4.0 mmol) of **4**, 0.66 g (2.0 mmol) of **7**, and 0.4 mL of pyridine in 15 mL of CH_2Cl_2 was allowed to stand for 18 h. The solution was then decanted from a small amount of dark insoluble material and was extracted with 10% aqueous HCl (20 mL) after which crystals began to precipitate from solution. The solution was cooled and filtered to remove the dark-colored crystals (0.68 g) which were recrystallized from methanol–water (charcoal) to give 0.42 g (33%) of colorless crystals, mp 140–143 °C. A second recrystallization from CH_2Cl_2 raised the melting point to 142–144 °C.

[*N,N*-Bis(2-fluoro-2,2-dinitroethyl)carbamyl]hydrazide (9). A mixture of 3.2 g of hydrazine hydrate (85% solution) and 20 mL of ethyl ether was stirred rapidly at −15 °C while a solution of 4.0 g (11.4 mmol) of **4** in 20 mL of ethyl ether was added in two portions. After 5 min cold water (50 mL) was

added and the ether layer was separated, dried ($MgSO_4$), and filtered. The filtrate was allowed to evaporate to give 3.63 g (90%) of white crystals, mp 100–101 °C (decomp). An analytical sample from CH_2Cl_2 had mp 102–104 °C (decomp).

***1,2-Bis[N,N-bis(2-fluoro-2,2-dinitroethyl)carbamyl]-hydrazide* (10).** A solution of 8.0 g (22.8 mmol) of **4** in 40 mL of ether was rapidly stirred in a water bath at 25 °C while 2.7 g of hydrazine hydrate (85% solution) was added dropwise over a 35-min period. After an additional 10 min cold water (50 mL) was added and the ether layer was separated, dried ($MgSO_4$), and filtered. The filtrate was concentrated to 25 mL by distillation, and then $CHCl_3$ was slowly added until the distillate temperature reached 60 °C. After cooling, the crystals were filtered off and then digested with hot CH_2Cl_2 to give 4.23 g (56%) of colorless crystals, mp 195–197 °C (decomp). An analytical sample from ether/$CHCl_3$ melted at 200–201 °C (decomp). The hydrazide **10** was also prepared in 83% yield by treating **9** and **4** in ether solution with pyridine.

***2-[N,N-Bis(2-fluoro-2,2-dinitroethyl)amino]-5,5-dimethyl-1,3,4-Δ²-oxadiazoline* (11).** Acetone (0.5 mL) was added to a solution of 0.34 g of **9** in 5 mL of ether. Within 5 min, crystals began to precipitate, and after standing overnight the yellow crystals were filtered to give 0.35 g (90%), mp 148–150 °C (decomp). Recrystallization from 1,2-dichloroethane raised the melting point to 151–152 °C (decomp).

***1-[N,N-Bis(2-fluoro-2,2-dinitroethyl)carbamyl]-2-(2-fluoro-2,2-dinitroethanimidoyl)hydrazide* (12).** The hydrazide **9** (1.0 g) was added in 10 portions to a stirred solution of 3.0 g of fluorodinitroacetonitrile[4] in 5 mL of CH_2Cl_2. Crystals began to precipitate within 15 min, and after standing overnight the crystals were removed by filtration and washed with cold CH_2Cl_2. The cream-colored crystals (1.23 g, 86%) melted at 109–110 °C (decomp). Recrystallization did not raise the melting point.

***1-[N,N-Bis(2-fluoro-2,2-dinitroethyl)carbamyl]-2-(2-fluoro-2,2-dinitroacetyl)hydrazide* (13).** The hdyrazide **12** (0.79 g) was stirred with 10 mL of concentrated HCl until dissolved (10 min) after which the solution was allowed to stand overnight. The solution was then diluted with 30 mL of water and extracted with ether. Evaporation of the ether gave 0.68 g of an oily residue which was crystallized from CH_2Cl_2/$CHCl_3$ to give 0.37 g of **13**. Recrystallization from CH_2Cl_2 gave mp 140–141 °C.

***3-[Bis(2-fluoro-2,2-dinitroethyl)amino]-5-(fluorodinitromethyl)-trifluoroacetyl-1,2,4-triazole* (14).** A mixture of 1.12 g of **12** and 10 mL of trifluoroacetic anhydride was stirred at ambient temperature for 48 h. The volatiles were removed with a stream of N_2 and gentle heating (30–35 °C) to give an oil which was dried in a vacuum desiccator over KOH to a constant weight (1.31 g, 100%). The ^1H NMR spectrum ($CDCl_3$) showed a large doublet at 5.16 ppm and much smaller doublets at 4.80 and 4.08 indicating a mixture of isomers differing in the position of the trifluoroacetyl group.

***2,5-Dichloro-1,1,6,6-tetrakis(2-fluoro-2,2-dinitroethyl)-1,3,4,6-tetraazahexa-2,4-diene* (15).** A mixture of 2.66 g of **10**, 2.7 g of PCl_5, and 15 mL of $POCl_3$ was refluxed for 6.5 h. After cooling the mixture was poured into ice water with stirring. When the insoluble material solidified, it was removed by filtration and washed with cold water to give 2.69 g (96%) of a yellow solid, mp 138–142 °C. Recrystallization raised the melting point to 143–145 °C.

***1,2′-Azobis[N,N-bis(2-fluoro-2,2-dinitroethyl)carbamyl]* (16).** A mixture of 4.66 g of **10** and 60 mL of 70% nitric acid was stirred for 5 h at ambient temperature, at which time 80 mL of cold water was added. The product was removed by filtration, washed with water, and dried to yield 4.46 g (96%) of light-orange crystals, mp 158–160 °C (decomp). Recrystallization did not raise the melting point.

***N,N,N′,N′-Tetrakis(2-fluoro-2,2-dinitroethyl)oxamide* (17). Caution!** This experiment should only be done on a small scale since it involves heating a neat explosive to a high temperature. Five samples (0.3 g each) of the azo compound **16** were heated *separately* in an oil bath at 150–160 °C until the color of the melts changed from red to light orange (ca. 20 min). The melts were cooled and were dissolved in ethyl ether. Some unreacted azo compound **16** was removed by filtration, and the filtrate was chromatographed on silica gel. The column was eluted first with benzene and then with 50% CH_2Cl_2/hexane with a gradual increase to 100% CH_2Cl_2. A total of 0.51 g (36%) of white crystals was obtained, mp 90–93 °C. Recrystallization from $CHCl_3$ raised the melting point to 92–94 °C.

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Carbon-13 Nuclear Magnetic Resonance Spectra of 2*H*-Cyclopenta[*d*]pyridazines and Cyclopenta[*c*]thiapyran

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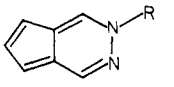
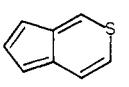
The proton-decoupled ^{13}C NMR spectra of cyclopenta[*d*]pyridazine, its 2-methyl and 2-phenyl derivatives, and cyclopenta[*c*]thiapyran are reported.

Studies on ^{13}C NMR spectra of heterocyclic aromatic compounds (*1–4*) do not seem to have included heteroanalogues of nonbenzenoid hydrocarbons. Compounds I–IV were selected as examples of the latter and their proton-decoupled spectra recorded.



I, R = H
II, R = CH_3
III, R = C_6H_5



IV

The spectrum of I was quite simple. The assignments are given in Table I. The finding of single peaks for the 1 and 4, 5 and 7, and 8 and 9 pairs of carbons had been anticipated

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