groups are far apart may have the counterproductive result of relatively stabilizing the cyclic hydrogen-bonded form of the monoprotonated diamine as well as the desired result of relatively stabilizing the transition state for iminium ion formation. However, studies with molecular models indicate that when the two amino groups have rigidly been given the optimum relative geometry for internally acid-catalyzed iminium ion formation, their relative geometry is unfavorable for internal hydrogen bonding.

The reactions were not thoroughly tested for general acid and base catalysis. However, several tests, such as the four runs on 1 near pH 9.09, give no indication of general catalysis. Furthermore, none was found previously in similar reactions, where the case of 2-dimethylaminoethylamine was tested several times. Hence, general catalysis is not likely to be very important.

Experimental Section

The synthesis and properties of **1**, **2**, and **3** have been described previously,[15] as have the methods used in following the kinetics of oximation[3] and the pK values used for the amines.

Registry No.—1, 53369-68-9; 2, 53369-73-6; 3, 53403-34-2; acetone, 67-64-1; acetone-d_6, 666-52-4; hydroxylamine, 7803-49-8; neopentylamine, 5813-64-9; 2-*endo*-norbornanamine, 31002-73-0.

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Oxidation Reactions of 2,2,2-Fluorodinitroethylamine and Some *N*-Alkyl-2,2,2-fluorodinitroethylamines

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2,2,2-Fluorodinitroethylamine is readily oxidized to the hydroxylamine, oxime, and nitrile oxide; further oxidation under forcing conditions leads to cleavage of the carbon–carbon bond. *N*-*tert*-Butyl-2,2,2-fluorodinitroethylamine behaves similarly, but *N*-alkyl derivatives possessing an α-methylene group are converted to *N*-fluorodinitroethylamides.

Oxidation reactions of β-polynitroalkylamines have apparently not been studied, although many such amines have been prepared by the Mannich reaction of β-polynitroalkanols and aliphatic amines (eq 1).[1,2]

$$XC(NO_2)_2CH_2OH + HNRR' \longrightarrow XC(NO_2)_2CH_2NRR' \quad (1)$$

X = halogen, alkyl, NO_2

R, R′ = alkyl, H

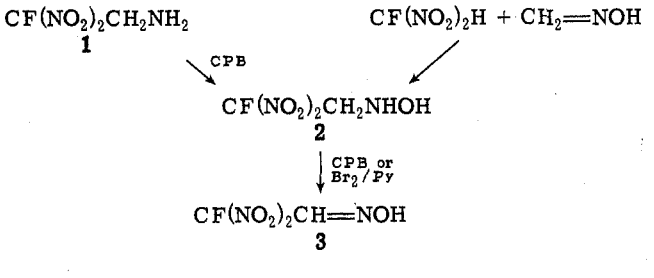
Most of the known β-polynitroalkylamines are secondary and tertiary; primary ones have limited stability and only one has been described.[3]

We report here on a number of oxidation reactions of 2,2,2-fluorodinitroethylamine and some of its derivatives. Since the electronic effects of the dinitroalkyl group appear to determine the reactivity behavior of these materials, many of our observations are probably applicable to oxidations of other β-polynitroalkylamines such as 2,2-dinitropropyl- and 2,2,2-trinitroethylamines as well.

Peracid Oxidations of 2,2,2-Fluorodinitroethylamine (1). The presence of strongly electron-withdrawing substituents in **1** (the fluorodinitromethyl group is reported to have a σ^* of 4.4)[4] decreases its basicity and has a general deactivating effect on its reactivity toward oxidizing agents. Thus, **1** is not affected by hydrogen peroxide in aqueous or methanolic solution, even in the presence of catalysts such as sodium tungstate and molybdate which bring about the rapid oxidation of primary alkyl- and aralkylamines.[5]

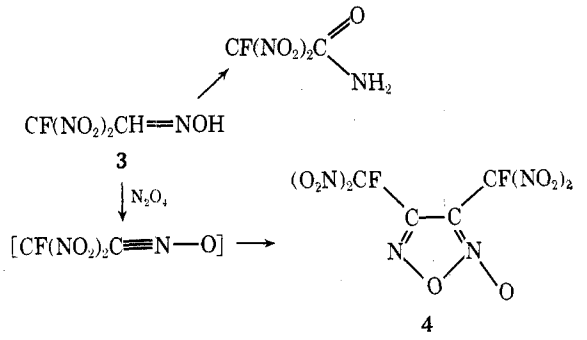
Oxidation occurred readily with various peracids, however. One equivalent of *m*-chloroperbenzoic acid (CPB) converted **1** to fluorodinitroethylhydroxylamine (**2**), which was isolated in 69% yield. It is noteworthy that here the oxidation can be halted at the hydroxylamine stage while simple alkylhydroxylamines can usually not be made in good yield by partial oxidation of primary amines.[6] The structure of **2** is supported by its independant preparation by the addition of fluorodinitromethane to formaldoxime (Scheme I).

Scheme I



Oxidation of 2 with a second equivalent of CPB or with bromine in the presence of pyridine gave fluorodinitroacetaldoxime (3), in moderate yield. 3 is not stable to extended storage and in the course of several weeks at ambient temperature was observed to rearrange quantitatively to fluorodinitroacetamide (Scheme II).

Scheme II



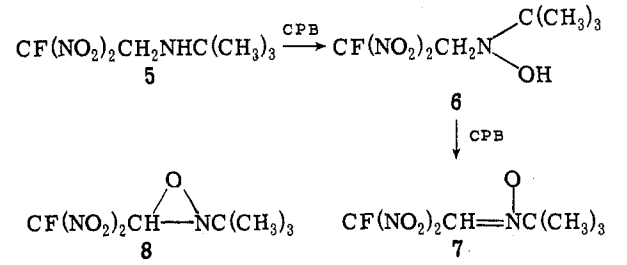
Further oxidation of the oxime 3 or of the hydroxylamine 2 beyond the oxime stage, with nitric acid or aqueous chromic acid, did not yield any useful products; a low yield of fluorodinitromethane was obtained in some cases, indicating C–C bond breaking during the oxidation process. 3 was also oxidized slowly by trifluoroperacetic acid, giving a product mixture which contained bis(fluorodinitromethyl)furoxane (4, isolated in ca. 10% yield), *N*-(2,2,2-fluorodinitroethyl)formamide (2–3% yield), and, as main component, an unidentified carbonyl compound which decomposed on standing.

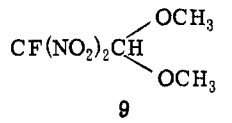
Formal further oxidation of 3 also occurs with N_2O_4, which converted the oxime to bis(fluorodinitromethyl)furoxane (4) in moderate yield (Scheme II). Fluorodinitroacetonitrile oxide appears to be an intermediate, since strong ir absorption at ca. 2300 cm^{-1} is exhibited during the reaction by the methylene chloride solution of the reactants. The reaction thus probably follows the established addition–elimination–dimerization path of other oxime–N_2O_4 reactions.[7]

The structure assignment of 4 is based on analytical data including molecular weight determinations, the absence of proton signals in the NMR spectrum, and the similarity of its uv spectrum to those of other furoxans, particularly bis(1,1-dinitroethyl)furoxane.[8] The latter had λ_{max} (EtOH) 264 nm (ϵ 4400). 4 was unstable in ethanol. Therefore its uv spectrum was obtained in 1,2-dichloroethane: λ_{max} 268 nm (ϵ 3,700). The possibility of 4 having the isomeric 1,2,4-oxadiazole 4-oxide structure is not completely ruled out, however.

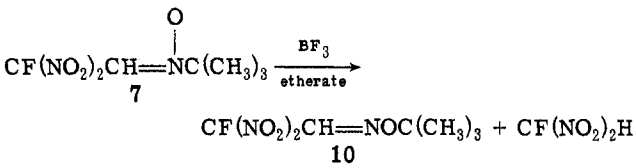
Peracid Oxidations of *N*-*tert*-Butyl-2,2,2-fluorodinitroethylamine (5). The oxidation of 5 with peracids parallels to some extent that of 1; however, the hydroxylamine 6 (a surprisingly unstable material, see Experimental Section) is readily oxidized further and could only be isolated in low yield. Oxidation of 5 with 2 equiv of CPB gave a substance whose ir and NMR spectra were in agreement with the nitrone structure 7 (Scheme III). The structure of 7 is also supported by analytical results (see Experimental Section). Further corroboration was sought by attempting 1,3-dipolar additions of 7 to phenyl isocyanate, propiolic acid, and methyl acrylate, but only intractable tars were obtained in all of these reactions. The alternate oxirane structure 8 can be ruled out with good certainty on the basis of the NMR data as follows: the methine proton signal is shifted only slightly from that of –CH= in the oxime 3 (δ 7.66 in 7 vs. 7.98 in 3); the methine proton of 9, on the other hand, is observed at δ 5.65. Additionally, the F–H coupling constants in such compounds are typically 15 ± 3 Hz when H is attached to sp^3 carbon, but are much lower (7 ± 2 Hz) when H is attached to sp^2 carbon.[9] Compound 7 has a H–F coupling constant of 6 Hz.

Scheme III





The nitrone 7 is somewhat more stable than the hydroxylamine 6, but also decomposes slowly on storage. Reaction with trifluoroacetic anhydride gave a complex mixture of products. Treatment with boron trifluoride etherate effected partial transformation to the oxime ether 10. The



structure assignment of 10 was again based on the characteristic shift and coupling constant to F of the methine proton which indicated the presence of the –CH= moiety; further, the migration of the *tert*-butyl group from positive nitrogen to neutral oxygen is indicated by the methyl signal shift from δ 1.57 to 1.30. A second, minor product of the reaction of 9 with boron trifluoride etherate was fluorodinitromethane.

Further oxidation of 7 with trifluoroperacetic acid in refluxing chloroform gave fluorodinitromethane as essentially the only fluoronitro species. The same product was formed in better yield by oxidation with 40–50% nitric acid.

Exploratory attempts were made to replace CPB in the oxidations of 1 and 5 by the more readily available commercial 40% peracetic acid. Somewhat less pure products were obtained than with CPB, but with proper attention to reaction conditions 40% peracetic acid should be suitable for these oxidations.

Reaction of *N*-*tert*-Butyl-2,2,2-fluorodinitroethylamine with Other Oxidizing Agents. The action of a number of other oxidizing agents on 5 was investigated briefly. No reaction was observed at ambient temperature with sodium dichromate and with the $K_2S_2O_8$–Ag^+ system in aqueous sulfuric acid. Manganese (IV) oxide in methylene chloride suspension was similarly without effect. Alkaline sodium hypochlorite also reacted very sluggishly; to the extent that reaction occurred, fluorochlorodinitromethane was formed.

Chromic Acid Oxidation of *N*-Alkylfluorodinitroethylamines. The course these oxidations take depends strongly on reaction conditions as well as on the structure of the substrate. The few examples studied indicate a considerable variation of behavior of *N*-alkylfluorodinitroethylamines toward chromic acid.

As has been mentioned above, *N*-*tert*-butylfluorodini-

troethylamine is fairly resistant to chromic acid oxidation. If an α proton is present in the alkyl group, oxidation occurs more readily but may be accompanied by extensive degradation. For example, the dichromate oxidation of *N,N'*-bis(fluorodinitroethyl)ethylenediamine (**11**) was studied in some detail as a potential method for the preparation of *N,N'*-bis(dinitroalkyl)oxamides. In dilute sulfuric acid oxidative degradation of **11** predominated; nitrous acid, apparently generated in the process, nitrosated part of the diamine to **13** which was stable under the reaction

$CF(NO_2)_2CH_2NHCH_2CH_2NHCH_2CF(NO_2)_2$

11

$CF(NO_2)_2CH_2NH-C(=O)-C(=O)-NHCH_2CF(NO_2)_2$

12

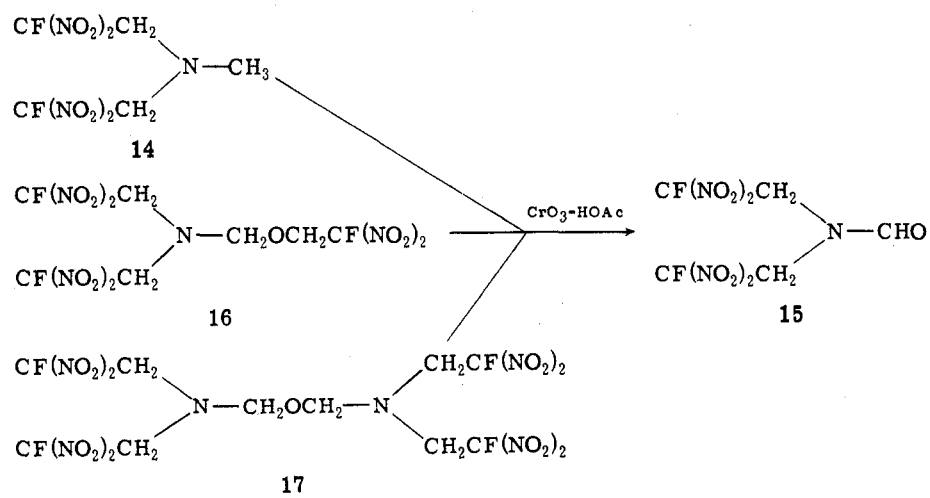
$CF(NO_2)_2CH_2N(NO)-CH_2CH_2-N(NO)CH_2CF(NO_2)_2$

13

conditions and could be isolated in low yield. At acid concentrations near 50% the desired oxidation occurred to some extent and the oxamide **12** was formed in ca. 20% yield. With further increasing acid concentrations the yield of **12** decreased and only degradation was again observed at acid strengths of 70–80%.

The oxidation of some *N*-alkylbis(2,2,2-fluorodinitroethyl)amines with chromium trioxide in acetic acid proceeded much smoother. The methyl group in **14** was oxidized to the formyl function in near quantitative yield. This reaction may be useful for the preparation of other bis(fluorodinitroethyl)amides, but its scope has not been explored. Further oxidation of **15** with potassium permanganate in acetone gave only degradation products. Oxidation of the amino ethers **16** and **17** with chromium trioxide–acetic acid also gave **15** in excellent yields (Scheme IV); the expected urethanes could not be found in either case. It may be assumed that intermediate chromic esters are formed in these oxidations which are readily fragmented or solvolyzed to **15**.

Scheme IV



Experimental Section

Caution. Most materials described here are explosives and appropriate care should be taken in their handling. Precautions recommended in working with fluorodinitromethyl compounds, especially 2,2,2-fluorodinitroethanol, have been described elsewhere.[10] Neat 2,2,2-fluorodinitroethylamine (**1**) must be handled with extreme care.[3]

Melting and boiling points are uncorrected; elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. NMR spectra were obtained on a Varian HA-100 spectrometer; chemical shifts are relative to Me_4Si as internal standards.

***N*-(2,2,2-Fluorodinitroethyl)hydroxylamine (2). A. By Oxidation of 1.** To a stirred solution of 4.45 g of crude **1**[3] in 30 ml of methylene chloride was added at 0° 5.85 g of 86% *m*-chloroperbenzoic acid and the mixture was stirred for 2 hr with continued cooling. After washing with a solution of 6 g of sodium bicarbonate in 50 ml of water in several portions, the methylene chloride solution was dried ($MgSO_4$), concentrated, and chilled to give 3.4 g (68.6%) of **2**, mp 87.5–88.5° (from methylene chloride).

B. From Fluorodinitromethane and Formaldoxime. A mixture of 15 g of a 15% solution of formaldoxime in ether, 6.25 g of fluorodinitromethane, and 40 ml of water was cooled to 0°, 0.15 g of sodium bicarbonate was added, and the mixture was stirred for 20 hr at 0°. The phases were separated, the aqueous phase was extracted with ether, and the combined ethereal solutions were dried and freed from solvent in vacuo. The remaining oil was taken up in methylene chloride and the solution was chilled to give 1.95 g of **2** in two crops: NMR (CD_3CN) δ 6.20 s (NHOH), 5.88 broad s (NHOH), 4.19 d ($CFCH_2$, J_{HF} = 16.5 Hz).

Anal. Calcd for $C_2H_4N_3O_5F$ (169.07): C, 14.21; H, 2.38; N, 24.85; F, 11.24. Found: C, 14.3; H, 2.3; N, 24.4; F, 11.2.

Fluorodinitroacetaldoxime (3). A. By Oxidation of 1 with Peracid. To an ice-cooled and stirred solution of 7.65 g of crude **1** in 70 ml of methylene chloride was added 20 g of 86% *m*-chloroperbenzoic acid in small portions; the mixture was stirred for 3 hr with continued cooling and chilled in a Dry Ice–acetone bath, and the solids were filtered off. The filter cake was washed with precooled methylene chloride, and the filtrate was concentrated and again chilled with Dry Ice–acetone. In this manner 15 g of *m*-chlorobenzoic acid was obtained in three crops. When the methylene chloride solution was freed from solvent an oil admixed with some solid material remained. An ir spectrum of the oil showed all the bands present in the spectrum of **3** prepared from **2** and Br_2–pyridine as described below. No attempts at further purification were made.

B. From 2 with Br_2–Pyridine. To a solution of 1.7 g of **2** in 40 ml of methylene chloride was added 1.6 g of bromine in 10 ml of methylene chloride. Then 1.6 g of pyridine was added dropwise with stirring. After stirring for 1 hr the yellow solution was washed with dilute sulfuric acid and dried ($MgSO_4$), and the solvent was removed in vacuo. Infrared, NMR, and GLC analysis of the remaining oil indicated that it was essentially pure **3**. The compound could not be distilled or induced to crystallize and was not purified further: ir (film) 3560 (OH), 1605 (asymmetrical NO_2), 1415, 1310 (symmetrical NO_2), 995, 950, 815, 790 cm^{-1}; NMR ($CDCl_3$) δ 9.47 s (C=NOH), 7.98 d (CFCH=N, J_{HF} = 8 Hz).

After several weeks of storage at ambient temperature the ir spectrum of this material had changed drastically; it was now essentially superimposable on a spectrum of an authentical sample

of fluorodinitroacetamide, prepared by the procedure of Wiesboeck and Ruff.[11]

Bis(fluorodinitromethyl)furoxane (4). 3 was prepared from 7.65 g of 1 as described above, and after separation of the bulk of the *m*-chlorobenzoic acid the methylene chloride solution of 3 was diluted to ca. 75 ml and cooled in an ice bath. Dry N_2O_4 (7.5 g) was bubbled in and the solution was stored at ca. 0° overnight. The mixture was then heated to reflux for 24 hr until the evolution of nitric oxides had ceased, allowed to cool, washed twice with a dilute solution of sodium bicarbonate, dried, and freed from solvent in vacuo. The residual semisolid material was triturated with 50 ml and then with 30 ml of pentane–methylene chloride (9:1), the combined filtrates were freed from solvents in vacuo, and the remaining oil was taken up in a small amount of the same solvent mixture and chromatographed on silica (G. F. Smith, Columbus, Ohio) with 9:1 pentane–methylene chloride as eluent. All fractions collected had superimposable ir spectra and were devoid of proton signals in the NMR; only one product peak was found when dilute methylene chloride solutions were analyzed by GLC (flame ionization detector). Obtained was a total of 4 g of essentially pure 4. The material was rechromatographed as described above and a center fraction was used for analytical purposes: ir (film) 1660 (furoxane ring), 1615 (asymmetrical NO_2), 1300 (symmetrical NO_2), 1260 (C–F stretch), 990, 840, 800 cm^{-1}.

Anal. Calcd for $C_4F_2N_6O_{10}$ (330.08): C, 14.55; F, 11.51; N, 25.46. Found: C, 14.5; F, 11.2; N, 25.2; mol wt (MEK), 325, 330.

***N*-*tert*-Butyl-2,2,2-fluorodinitroethylhydroxylamine (6).** A solution of 5 g of 86% *m*-chloroperbenzoic acid in 50 ml of methylene chloride was added with cooling to 5 g of 5[12] in 50 ml of methylene chloride, the mixture was stirred for 2 hr at 0–5° and filtered, and the filtrate was washed twice with dilute sodium hydrogen sulfite solution, twice with dilute sodium bicarbonate solution, and twice with dilute sulfuric acid, dried ($MgSO_4$), and freed from solvent in vacuo at a temperature not exceeding 30–35°. The resulting mixture of 6 and 7 can be separated into its components by fractional crystallization from 2:1 hexane–methylene chloride, in which 7 is less soluble. Fairly pure 6 was obtained in this manner as an unstable oil which decomposed on standing (*Caution:* some samples fumed off after a few hours at room temperature): ir (film) 3650, 3500 (OH, broad), 1605, 1310 (NO_2 stretch), 1370, 1080, 850, 808 cm^{-1}; NMR ($CDCl_3$) δ 5.14 s (OH), 3.935 d (J_{HF} = 17 Hz), 1.09 s (CH_3).

***N*-*tert*-Butyl-α-fluorodinitromethylnitrone (7).** To a solution of 10 g of 5[12] in 100 ml of methylene chloride was added at 0–5° and with efficient stirring 19.4 g of 86% *m*-chloroperbenzoic acid portionwise over a 0.5-hr period. After stirring for 2 hr at ice-bath and 1 hr at room temperature, the mixture was poured into a solution of 10 g of sodium bicarbonate and 0.5 g of sodium sulfite in 200 ml of water and triturated until the gas evolution ceased. The organic phase was dried ($MgSO_4$) and freed from solvent to give 10.4 g of crude 7, mp 65–67° dec (from methylene chloride–hexane). The material decomposed slowly when stored at room temperature: ir (ATR spectrum) 1625 (asymmetrical NO_2), 1560 (C=N?), unidentified bands at 1370, 1305, 1275, 1165, 1085, 855, 785, 760 cm^{-1}; NMR ($CDCl_3$) δ 7.66 d (CFCH=N, J_{HF} = 6 Hz), 1.58 s [$NC(CH_3)_3$].

Anal. Calcd for $C_6H_{10}FN_3O_5$ (223.16): C, 32.29; H, 4.52; F, 8.51; N, 18.83. Found: C, 32.0; H, 4.4; F, 8.8; N, 18.7.

Fluorodinitroacetaldoxime *tert*-Butyl Ether (10). Boron trifluoride etherate (3 ml) was added to an ice-cold solution of 5 g of 7 in 15 ml of methylene chloride and the mixture was stirred for 24 hr at room temperature. The product was washed thoroughly with water and dried ($MgSO_4$) and the solvent was distilled off. The remaining oil was vacuum transferred at 0.1 mm into a Dry Ice cooled trap and then fractionated. At 15 mm there was obtained ca. 0.8 g of fluorodinitromethane; 10, 2.3 g, boiled at 42–43° (0.5 mm). Refractionation gave the analytical sample: NMR ($CDCl_3$) δ 7.78 d (J_{HF} = 7 Hz), 1.30 s; area ratio, 1:9.

Anal. Calcd for $C_6H_{10}FN_3O_5$: C, 32.29; H, 4.52; F, 8.51; N, 18.83. Found: C, 32.1; H, 4.4; F, 8.6; N, 18.9.

Oxidation of 7 with Nitric Acid. To 40 ml of ice-cold 40% nitric acid was added in small portions 4.5 g of 7 and the mixture was stirred for 1 hr with continued cooling. The reaction mixture was diluted with an equal volume of water and extracted with methylene chloride. After drying ($MgSO_4$) and distilling off the solvent there remained 2.25 g of an oil whose main component was identified by GLC retention time and NMR and ir spectra as fluorodinitromethane.

***N*,*N*′-Bis(2,2,2-fluorodinitroethyl)oxamide (12) from 11.** A sample of 11 was prepared in situ by stirring a mixture of 25 ml of water, 5.4 g of 2,2,2-fluorodinitroethanol, and 1.05 g of ethylenediamine for 2 hr at room temperature.[13] The mixture was then cooled and 35 ml of concentrated sulfuric acid was added slowly, followed by 15 g of sodium dichromate dihydrate. After stirring overnight the mixture was poured on crushed ice and 1.3 g of crude 12 was isolated by filtration. The product was identified by comparison with an authentic sample.[12]

Preparation of *N*,*N*-Bis(2,2,2-fluorodinitroethyl)methylamine (14) and Oxidation to *N*,*N*-Bis(2,2,2-fluorodinitroethyl)formamide (15). A mixture of 13.75 g of crude *N*-(2,2,2-fluorodinitroethyl)methylamine,[14] 12.9 g of 2,2,2-fluorodinitroethanol, and 40 ml of methanol was heated to 65–70° for 72 hr, the mixture was poured into cold dilute sulfuric acid, and the product was taken up with methylene chloride. After filtration through a short column of silica (G. F. Smith, Columbus, Ohio) to remove unreacted fluorodinitroethanol, the solvent was removed in vacuo to give 16.1 g (64.5%) of crude 14: mp 43–43.5° (from methylene chloride–pentane); NMR ($CDCl_3$) δ 4.04 d (J_{HF} = 18 Hz), 2.63 s; areas, 4:3.

Anal. Calcd for $C_5H_7F_2N_5O_8$ (303.14): C, 19.81; H, 2.33; F, 12.54; N, 23.10; O, 42.22. Found: C, 19.8; H, 2.4; F, 12.1; N, 23.0.

To a mixture of 2 g of chromium trioxide and 15 ml of glacial acetic acid was added a solution of 3 g of 14 in 10 ml of glacial acetic acid. The mixture was stirred for 3 days at room temperature and poured into water to give 3.05 g (97%) of 15: mp 123.5–124.5° (from chloroform); NMR (CD_3CN) δ 8.18 s (CHO), 4.85, unsymmetrical multiplet ($CFCH_2$); area ratio, 1:4.

Anal. Calcd for $C_5H_5F_2N_5O_9$ (317.14): C, 18.92; H, 1.59; F, 11.98; N, 22.09. Found: C, 18.9; H, 1.8; F, 11.7; N, 21.4.

Preparation of *N*,*N*-Bis(2,2,2-fluorodinitroethyl)-*N*-2,2,2-fluorodinitroethoxymethylamine (16) and Oxidation to 15. A solution was made of 5.8 g of bis(2,2,2-fluorodinitroethyl)amine[3] and 0.6 g of paraformaldehyde in 25 ml of 90% sulfuric acid. After the solution was stirred at room temperature for 15 min, 4 g of sodium bromide was added. Stirring was continued for an additional 15 min, during which time some methylene chloride was added to prevent the mixture from becoming too thick. The phases were separated and the acid phase was extracted once with methylene chloride. The combined methylene chloride solutions were dried ($MgSO_4$) and freed from solvent in vacuo. The remaining oil crystallized on standing. It was assumed to be *N*-bromomethyl-*N*,*N*-bis(2,2,2-fluorodinitroethyl)amine, but was not characterized further.

The crude bromomethylamine (1.9 g) was added to a solution of 0.8 g of 2,2,2-fluorodinitroethanol and 0.5 g of triethylamine in 10 ml of acetonitrile, the mixture was stirred at room temperature for 2 hr and drowned, and the product was extracted into methylene chloride. After the solution was washed thoroughly with 0.01 *N* sodium hydroxide it was dried ($MgSO_4$) and freed from solvent. The remaining oil was taken up in 1:1 methylene chloride–hexane, and the solution was filtered to remove some insoluble solid and chromatographed on silica (G. F. Smith, Columbus, Ohio). The fractions containing pure 16 were combined and recrystallized from methylene chloride–hexane: mp 56–57.5°; yield ca. 0.7 g; NMR ($CDCl_3$) δ 4.48 d (J_{HF} = 17 Hz, $CFCH_2O$), 4.42 s (OCH_2N), 4.255 d (J_{HF} = 17 Hz, $CFCH_2N$).

Anal. Calcd for $C_7H_8F_3N_7O_{13}$ (455.18): C, 18.47; H, 1.77; F, 12.52; N, 21.54. Found: C, 18.4; H, 1.8; F, 12.3; N, 21.1.

A mixture of 0.9 g of 16, 0.35 g of chromium trioxide, and 10 ml of glacial acetic acid was stirred for 20 hr at ambient temperature and drowned, and the solid material was filtered off to give 0.6 g (95%) of 15.

Preparation of Bis(2,2,2-fluorodinitroethyl)aminomethyl Ether (17) and Oxidation to 15. A mixture of 9.6 g of bis(2,2,2-fluorodinitroethyl)amine,[3] 1 g of trioxane, and 50 ml of concentrated sulfuric acid was stirred at ambient temperature for 48 hr and poured over crushed ice and the semisolid product was taken up with methylene chloride. The solution was dried ($MgSO_4$), hexane was added to the cloud point, and the solution was chilled to give 5.4 g of 17, which upon recrystallization from methylene chloride–hexane had mp 116.5–117.5°: NMR (CD_3CN) δ 4.34 d (J_{HF} = 17 Hz, $CFCH_2$), 4.07 s (NCH_2O).

Anal. Calcd for $C_{10}H_{12}F_4N_{10}O_{17}$ (620.28): C, 19.38; H, 1.95; F, 12.26; N, 22.59. Found: C, 19.5; H, 2.0; F, 11.8; N, 22.2.

To a solution of 2.45 g of 17 in 20 ml of acetic acid was added 1.2 g of chromium trioxide, the mixture was stirred at ambient temperature for 3 days and poured into water, and the product was isolated by filtration. Obtained was 2 g of crude 15.

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Registry No.—**1**, 18139-02-1; **2**, 55702-16-4; **3**, 55702-17-5; **4**, 55702-18-6; **5**, 33046-34-3; **6**, 55702-19-7; **7**, 55702-20-0; **10**, 55702-21-1; **11**, 32765-49-4; **12**, 33191-90-1; **14**, 55702-22-2; **15**, 55702-23-3; **16**, 55702-24-4; **17**, 55702-25-5; fluorodinitromethane, 7182-87-8; formaldoxime, 75-17-2; 2,2,2-fluorodinitroethanol, 17003-75-7; ethylenediamine, 107-15-3; *N*-(2,2,2-fluorodinitroethyl)methylamine, 30409-33-7; *N*-bromomethyl-*N*,*N*-bis(2,2,2-fluorodinitroethyl)amine, 55702-26-6.

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Oxidation of Carbohydrates with Chromic Acid. Synthesis of 6-Acetamido-6-deoxy-D-*xylo*-hexos-5-ulose[1]

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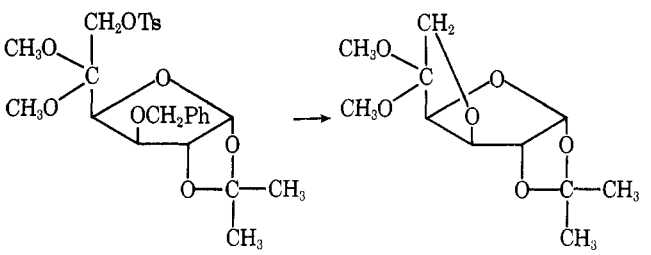
Preparation of the title compound (**8**) was routed through 6-azido-6-deoxy-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**4**). Oxidation of **4** with the Jones reagent[3] gave the ketone **6**, which yielded crystalline 6-acetamido-6-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranos-5-ulose (**7**) upon catalytic hydrogenolysis of the azido and benzyl groups, followed by N-acetylation of the intermediate amine. Alternatively, the hydrogenolyzable groups of **4** were first cleaved to give 6-acetamido-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**5**), which, in turn, was selectively oxidized at the C-5 hydroxyl group with the chromic acid reagent to give **7**. Hydrolysis of the isopropylidene group of **7** afforded the δ-dicarbonyl amino sugar **8** as a mixture of pyranose and furanose ring forms.

Chromic acid in acetone (the Jones reagent[3,4]) is a very convenient and well-known reagent for the oxidation of secondary alcohols to ketones. As far as we are aware, recently published results from this laboratory described the first application of this oxidizing agent in the synthesis of dicarbonyl monosaccharide derivatives.[5] In this paper we describe the synthesis of a new δ-dicarbonyl amino sugar derivative, 6-acetamido-6-deoxy-D-*xylo*-hexos-5-ulose (**8**). As yet, no biological role for **8** or its parent amino sugar has been described, nor have these compounds been isolated from a natural source. However, they are structurally related to the unknown δ-dicarbonyl diamino sugar, 2,6-diamino-2,6-dideoxy-D-*xylo*-hexos-5-ulose, a predicated biogenetic precursor for neosamines B and C.[6] These amino sugars are components of the neomycins and a number of related aminoglycoside antibiotics. In the described synthesis of **8** the key oxidation of a secondary alcohol function was efficiently achieved with chromic acid reagent.

Results and Discussion

The first approach to the synthesis of the title compound began with the conversion of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranos-5-ulose dimethyl acetal[7] to the corresponding 6-*O*-tosyl derivative **1**. However, compound **1** remained completely unchanged when treated with sodium azide in refluxing aqueous acetone. When **1** was treated with sodium azide under more vigorous conditions (in refluxing dimethylformamide) a single syrupy product, identified as the 3,6-anhydro derivative **2**, was isolated. Formation of **2** from **1** can be accounted for on the basis of a simple, direct nucleophilic displacement of the C-6 tosyloxy group by the oxygen of the C-3 benzyloxy group. Alternatively, it may be that a methoxy oxygen provides anchimeric assistance for removal of the proximate tosyloxy group, a step which is then followed by formation of the five-membered ether ring through the C-3 oxygen. Winstein and coworkers[8] concluded from a solvolysis study of 2-methyl-2-methoxy-1-propyl *p*-bromobenzenesulfonate that methoxyl group participation in the rate-determining ionization step is significant and takes place via a three-membered cyclic methyloxonium ion. The same mode of methoxy anchimeric assistance may be operative in the transformation of **1** to **2**.



1 **2**

Ph = C_6H_5
Ts = *p*-$CH_3C_6H_4SO_2$

Alternate routes to **8** were then initiated originating from the azide **4**, a compound previously prepared by Saeki and Ohki.[9] Catalytic hydrogenolysis of the azido and benzyl groups of **4**, in acetic acid solution, was then followed by N-acetylation of the resulting amino sugar to give 6-acetamido-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose[10] (**5**). The C-5 hydroxyl group of **5** was then selectively oxidized with the chromic acid reagent, affording **7** in 38%