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SYNTHESIS AND CRYSTAL STRUCTURE OF 2,3-BIS(DINITROFLUOROMETHYL)-1,4-DIOXANE

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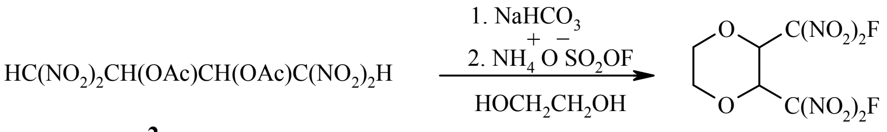
For the first time the dinitromethyl group was modified to dinitrofluoromethyl group in the series of aliphatic polynitro compounds in the case of the reaction of 1,1,4,4-tetranitro-2,3-butanediol diacetate with ammonium fluoroxysulfate in the presence of sodium bicarbonate and ethylene glycol. Previously unknown 2,3-bis(dinitrofluoromethyl)-1,4-dioxane was synthesized. Its structure was determined by X-ray diffraction analysis.

Keywords: ammonium fluoroxysulfate, 2,3-bis(dinitrofluoromethyl)-1,4-dioxane, X-ray diffraction analysis, fluorination.

Inorganic fluoroxysulfate salts [1] have recently found increasing use in synthetic organic chemistry as mild fluorinating agents for heteroorganic, aromatic, and nitroaromatic compounds [2-4]. Meanwhile, there are no data on their use for introducing fluorine atoms into compounds containing dinitromethyl groups. In order to fill this gap we undertook the synthesis of 1,4-difluoro-1,1,4,4-tetranitro-2,3-butanediol diacetate (**1**) from 1,1,4,4-tetranitro-2,3-butanediol diacetate (**2**) and ammonium fluoroxysulfate. We supposed that if successful this new method of the synthesis of dinitrofluoromethyl compounds could be preferred to direct fluorination with elemental fluorine. It should be noted that diacetate **2** is extremely labile in alkaline media. For this reason, clearly, attempts to fluorinate it directly with elemental fluorine to produce the dinitrofluoromethyl compound **1** have been unsuccessful so far. It was found that the reaction takes place in a more complicated way, and in the reaction of diacetate **2** with ammonium fluoroxysulfate in the presence of sodium bicarbonate in ethylene glycol we isolated the previously unknown heterocyclic compound, 2,3-bis(dinitrofluoromethyl)-1,4-dioxane (**3**) instead of the expected compound **1**. Dioxane **3** is formed with 60% yield by successive treatment of a solution of diacetate **2** in ethylene glycol first with an aqueous solution of sodium bicarbonate and then with aqueous solution of ammonium fluoroxysulfate.



2 **3**

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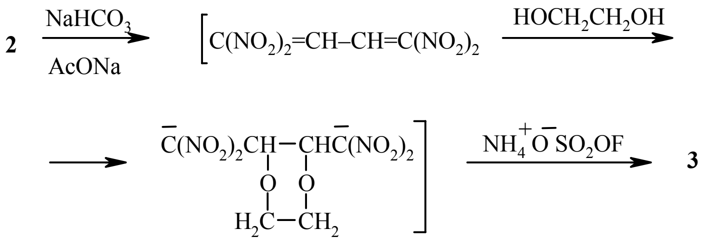
In the reaction both the vicinal ester groups taking part in the formation of the dioxane ring and the dinitromethyl groups involved in the fluorination reaction are affected. We note also that ethylene glycol, which we used as reaction medium, itself takes part as reagent in ring formation. Compound **3** is easily purified by crystallization from 70% nitric acid.

The obtained result can be explained by the following consecutive reactions: deacylation of diacetate **2** to the intermediate 1,1,4,4-tetranitro-1,3-butadiene, its cyclization with ethylene glycol to form the dianion of 2,3-bis(dinitromethyl)-1,4-dioxane, and finally fluorination.



$$\mathbf{2}\xrightarrow[\text{AcONa}]{\text{NaHCO}_3}\left[C(NO_2)_2{=}CH{-}CH{=}C(NO_2)_2\right.\xrightarrow{HOCH_2CH_2OH}$$

$$\longrightarrow\left.\begin{array}{c}\bar{C}(NO_2)_2CH-CH\bar{C}(NO_2)_2\\ |\quad\;\;|\\ O\quad O\\ |\quad\;\;|\\ H_2C-CH_2\end{array}\right]\xrightarrow{NH_4^+\,\bar{O}SO_2OF}\mathbf{3}$$

Here, the ease of the deacylation of compound **2** in the presence of nucleophilic substances and the formation of 1,1,4,4-tetranitro-1,3-butadiene *in situ* agree well with data in [5, 6].

According to X-ray diffraction analysis, the molecule of compound **3** in the crystal is located in a general position, but the local twofold symmetry axis, passing along the orthogonal C(2)–C(3) bond is easily traced (Fig. 1).

Earlier [7], we showed that attractive interaction is observed between the halogen atoms and the oxygen atoms of the nitro groups in the halodinitromethyl fragment in the molecules of 1,1,4,4-tetranitro-2,3-butanediol. Here the two unshared electron pairs of the halogen atom interact simultaneously with the highest levels of the π-type unshared electron pair of the both nitro groups in two mutually perpendicular planes. In turn, the antibonding combination of the unshared electron pairs can interact with the vacant antibonding MO of the polar C–N bond. In the final analysis the p–π interaction leads to approach of the O···Hal atoms and also to shortening of the N–O and C–Hal bonds and elongation of the C–N bonds, which agrees fully with the calculations and with experiment.

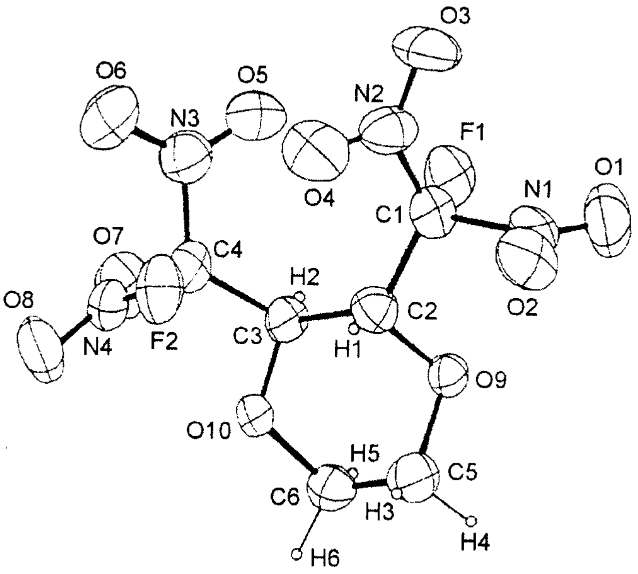


Fig. 1. The molecule of compound **3**.

In the molecule of dioxane **3** the dinitrofluoromethyl fragment has the analogous structure typical of this group of compounds: the fluorine atom is located fairly precisely in the plane of one of the nitro groups, at the same time remaining approximately in the plane of the second nitro group. The intramolecular nonbonding contacts between the fluorine atoms and the oxygen atoms of the nitro group in this molecule are substantially

TABLE 1. The Bond Lengths in the Molecule of Compound **3** ($\times10^4$)

Bond	*l*, Å	Bond	*l*, Å
F(1)–C(1)	1.325(6)	F(2)–C(4)	1.332(6)
O(10)–O(3)	1.421(6)	O(10)–C(6)	1.445(7)
O(9)–C(2)	1.408(6)	O(9)–C(5)	1.454(9)
N(1)–C(1)	1.551(8)	N(1)–O(1)	1.211(6)
N(1)–O(2)	1.209(7)	N(4)–O(7)	1.212(6)
N(4)–O(8)	1.207(6)	N(4)–C(4)	1.549(7)
C(2)–C(1)	1.526(7)	C(2)–C(3)	1.551(8)
C(2)–H(1)	0.990(5)	C(1)–N(2)	1.535(6)
N(3)–C(4)	1.515(7)	N(3)–O(5)	1.205(6)
N(3)–O(6)	1.211(6)	C(4)–C(3)	1.528(7)
O(3)–N(2)	1.199(6)	C(3)–H(2)	0.950(5)
O(4)–N(2)	1.213(6)	C(6)–C(5)	1.470(1)
C(6)–H(6)	0.980(5)	C(6)–H(5)	0.980(5)
C(5)–H(3)	1.040(6)	C(5)–H(4)	0.990(8)

TABLE 2. The Bond Angles in the Molecule of Compound **3** ($\times10^4$)

Angle	ω, deg.	Angle	ω, deg.
C(3)–O(10)–C(6)	113.2(4)	C(2)–O(9)–C(5)	112.3(5)
C(1)–N(1)–O(1)	116.8(5)	C(1)–N(1)–O(2)	114.8(5)
O(1)–N(1)–O(2)	128.4(5)	O(7)–N(4)–O(8)	128.2(5)
O(7)–N(4)–C(4)	114.6(4)	O(8)–N(4)–C(4)	117.2(4)
O(9)–C(2)–C(1)	101.3(4)	O(9)–C(2)–C(3)	107.2(4)
O(9)–C(2)–H(1)	114.0(3)	C(1)–C(2)–C(3)	117.9(5)
C(1)–C(2)–H(1)	107.0(3)	C(3)–C(2)–H(1)	110.0(3)
F(1)–C(1)–N(1)	107.5(4)	F(1)–C(1)–C(2)	114.2(4)
F(1)–C(1)–N(2)	107.7(4)	N(1)–C(1)–C(2)	108.0(4)
N(1)–C(1)–N(2)	102.9(4)	C(2)–C(1)–N(2)	115.6(4)
C(4)–N(3)–O(5)	117.4(4)	C(4)–N(3)–O(6)	115.7(5)
O(5)–N(3)–O(6)	126.9(5)	F(2)–C(4)–N(4)	107.5(4)
F(2)–C(4)–N(3)	107.7(4)	F(2)–C(4)–C(3)	113.2(4)
N(4)–C(4)–N(3)	102.4(4)	N(4)–C(4)–C(3)	108.5(4)
N(3)–C(4)–C(3)	116.7(4)	O(10)–C(3)–C(2)	108.0(4)
O(10)–C(3)–C(4)	99.3(4)	O(10)–C(3)–H(2)	112.0(3)
C(2)–C(3)–C(4)	118.4(5)	C(2)–C(3)–H(2)	111.0(3)
C(4)–C(3)–H(2)	108.0(3)	C(1)–N(2)–O(3)	115.8(4)
C(1)–N(2)–O(4)	116.4(4)	O(3)–N(2)–O(4)	127.8(5)
O(10)–C(6)–C(5)	108.8(6)	O(10)–C(6)–H(6)	103.0(3)
O(10)–C(6)–H(5)	110.0(3)	C(5)–C(6)–H(6)	112.0(3)
C(5)–C(6)–H(5)	112.0(3)	H(6)–C(6)–H(5)	110.0(4)
O(9)–C(5)–C(6)	108.1(7)	O(9)–C(5)–H(3)	105.0(4)
O(9)–C(5)–H(4)	105.0(4)	C(6)–C(5)–H(3)	109.0(4)
C(6)–C(5)–H(4)	115.0(4)	H(3)–C(5)–H(4)	114.0(6)

TABLE 3. The Atomic Coordinates in the Structure of Compound **3** ($\times 10^4$)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
F(1)	365(4)	1119(2)	-52(3)	C(3)	1509(8)	726(3)	2767(5)
F(2)	3170(4)	1685(2)	4401(3)	C(4)	1345(7)	1420(3)	3577(5)
O(1)	2809(6)	681(2)	-1069(4)	C(5)	4010(1)	-519(5)	2671(9)
O(2)	5489(6)	1129(2)	567(4)	C(6)	2580(1)	-577(3)	3345(7)
O(3)	1987(6)	2475(2)	-90(4)	N(1)	3675(8)	989(2)	-3(5)
O(4)	3610(6)	2337(2)	2031(4)	N(2)	2669(6)	2105(2)	912(5)
O(5)	-777(6)	2026(2)	1623(4)	N(3)	102(7)	2099(2)	2806(5)
O(6)	126(8)	2666(2)	3454(4)	N(4)	134(7)	1175(2)	4428(5)
O(7)	-1612(5)	959(2)	3795(1)	H(1)	4340(6)	990(3)	2640(4)
O(8)	1027(6)	1210(2)	5617(4)	H(2)	150(6)	600(2)	2170(5)
O(9)	3165(5)	28(2)	1588(3)	H(3)	4000(1)	-1040(4)	2210(6)
O(10)	2313(5)	178(2)	3806(3)	H(4)	5400(1)	-320(3)	3220(7)
C(1)	2310(7)	1233(3)	752(5)	H(5)	1250(7)	-790(3)	2760(5)
C(2)	3003(8)	774(3)	2040(5)	H(6)	3170(7)	-880(3)	4160(5)

shortened compared with the sum of the van der Waals radii. These distances are as follows: F(1)···O(1) = 2.511 and F(2)···O(8) = 2.508 Å. Molecular mechanics calculations (MMX) lead to a new unstressed conformation of the molecule with F···O > 2.6 Å, i.e., to new conformational angles differing from those in the real molecule.

Consequently, it can be supposed that the strained conformation of the molecule of compound **3** in the crystal is stabilized as a result of orbital interactions between the nitro groups and the fluorine atoms.

The bond lengths in compound **3** (Table 1) alternate: increased multiplicity for the C(1)–C(2) and C(3)–C(4) bonds with weakening of the C(2)–C(3) bond. In the six-membered ring C(2)O(9)C(5)C(6)O(10)C(3), which has the "chair" conformation, the bonds also alternate. Here the bonds C(2)–O(9) = 1.408 and C(3)–O(10) = 1.421 Å are shorter than the bonds O(9)–C(5) = 1.454 and O(10)–C(6) = 1.445 Å, while the bond C(5)–C(6) = 1.47 Å is substantially shorter than a simple single C–C bond.

EXPERIMENTAL

The IR spectrum was recorded on a Specord M-80 spectrophotometer in tablets with potassium bromide. The ^{1}H NMR spectrum was obtained on a Bruker 200 spectrometer at 200 MHz. The melting point was determined on a Boetius RNMK-0.5 instrument.

2,3-Bis(dinitrofluoromethyl)-1,4-dioxane (3). To solution of sodium bicarbonate (2.69 g, 32 mmol) in water (45 ml) at -5 to -7°C we added with vigorous stirring successively solution of compound **2** (5.66 g, 16 mmol) in ethylene glycol (150 ml), solution of ammonium fluoroxysulfate (5.32 g, 40 mmol) obtained by bubbling fluorine–nitrogen mixture (20-30%) through solution of ammonium sulfate (6 g, 45.5 mmol) in water (12 ml), and sulfuric acid (*d* 1.84) (0.2 ml) over 20-30 min. The reaction mixture was stirred for a further 1 h 30 min at -5 to -7°C. The white crystalline precipitate was filtered off and recrystallized from 70% nitric acid. We obtained 3.24 g (61%) of dioxane **3**; mp 75-76°C, d_4^{20} 1.78 g/cm^3 (pycnometry). IR spectrum, ν, cm^{-1}: 1362, 1600 (NO_2). ^{1}H NMR spectrum (CD_3CN), δ, ppm, *J*, (Hz): 5.6 (2H, d, *J* = 24.0, CH); 3.9 (4H, m, *J* = 9.0, CH_2). Found, %: C 21.8; H 1.7; F 11.4; N 17.0. $C_6H_6F_2N_4O_{10}$. Calculated, %: C 21.68; H 1.81; F 11.45, N 16.87.

X-Ray Investigation. The investigation was carried out on a crystal in the form of a plate (0.1 × 0.2 × 0.3 mm).

The crystals of $C_6H_6F_2N_4O_{10}$ (**3**) are monoclinic, M = 332.13, a = 7.048(2), b = 17.379(6); c = 10.954(4) Å; γ = 112.97(3)°, V = 1235.41 Å^3, d_c = 1.785 g/cm^3, λ = 0.710 Å, space group $P2_1/n$, Z = 4.

In the diffraction experiment 1519 nonequivalent nonzero reflections were measured on a four-circle KM-4 diffractometer (KUMA-Diffraction) with χ geometry and an $\omega/2\theta$ scan were. The structure was solved by the direct method on a personal computer using the SHELX-86 software. The coordinates of the atoms in the structure of compound **3** (Table 3) were refined in full-matrix approximation to $R = 0.022$. The temperature parameters were refined in anisotropic approximation for the nonhydrogen atoms and in isotropic approximation for the hydrogen atoms. The conformation of the molecule and its geometric parameters are given in Fig. 1.

REFERENCES

1. E. H. Appelman, L. J. Basile, and R. C. Thompson, *J. Am. Chem. Soc.*, **101**, 3384 (1979).
2. S. Stavber and M. Zupan, *J. Org. Chem.*, **50**, 3609 (1988).
3. N. S. Zefirov, V. V. Zhdankin, and A. S. Koz'min, *Tetrahedron*, **44**, 6505 (1988).
4. A. A. Gakh, S. V. Romanenko, B. I. Ugrak, and A. A. Fainzil'berg, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1615 (1991).
5. A. T. Baryshnikov, V. I. Erashko, N. I. Zubanova, B. I. Ugrak, S. A. Shevelev, A. A. Fainzil'berg, and V. V. Semenov, *Izv. Akad. Nauk. Ser. Khim.*, 2123 (1992).
6. G. V. Nekrasova, E. S Lipina, V. P. Pozdnyakov, and V. V. Perekalin, *Zh. Org. Khim.*, **17**, 2502 (1984).
7. B. S. Fedorov, N. I. Golovina, L. S. Barinova, V. V. Arakcheeva, R. F. Trofimova, and L. O. Atovmyan, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 2372 (1991).