

# Organic Chemistry

## A new reaction of fluorodinitromethyl group

### 1. Denitration of fluorodinitromethane and some of its derivatives

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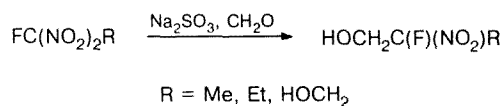
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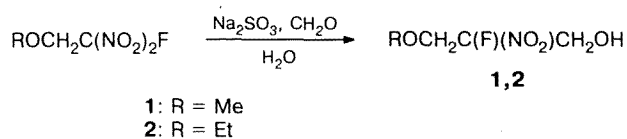
A general reaction of the transformation of the fluorodinitromethyl group into the fluoronitromethyl group by denitration upon treatment with  $\text{Na}_2\text{SO}_3$  or KI in aqueous formaldehyde was found. A preparative method for synthesizing fluoronitroalcohols was developed on the basis of this reaction.

**Key words:** denitration, fluorodinitromethane, fluorodinitroalkanes, fluorodinitroalcohols, sodium sulfite, potassium iodide.

We have shown for the first time<sup>1</sup> the possibility of transforming the fluorodinitromethyl group into the fluoronitromethyl group by its denitration on treatment with  $\text{Na}_2\text{SO}_3$  under the conditions of phase transfer catalysis, using aqueous  $\text{CH}_2\text{O}$  for binding the fluoronitromethyl anion.



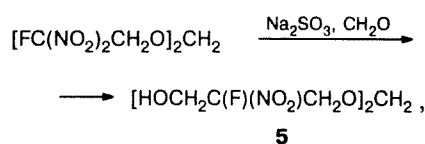
We applied this method to fluorodinitromethane derivatives with various functional substituents in order to develop a general method for synthesizing fluoronitroalcohols. It was found that hydroxymethyl-substituted ethers (**1**) and (**2**) are formed in 87–88 % yields according to the following scheme:



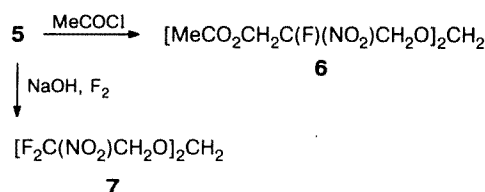
To isolate compounds **1** and **2**, the reaction mixture was treated with  $\text{NaNO}_2$  and dilute  $\text{HNO}_3$  in order to remove an admixture of formaldehyde, then with urea and sodium carbonate.

Compounds **1** and **2** undergo esterification on treatment with mineral acids and carboxyl chlorides. The structures of **1** and **2** were confirmed by transforming them into nitrates (**3**) and (**4**) on treatment with a mixture of concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ .

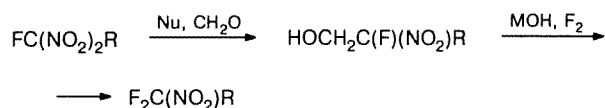
This method also proved to be effective in the synthesis of dione **5**:



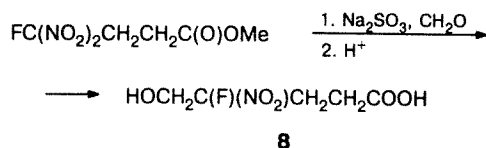
which was either acetylated to give diacetate **6** or fluorinated in an alkaline aqueous medium to give fluorodeoxymethylation product (**7**).



The synthesis of compound **7** makes it possible to use the general method for obtaining compounds with the difluoronitromethyl group.

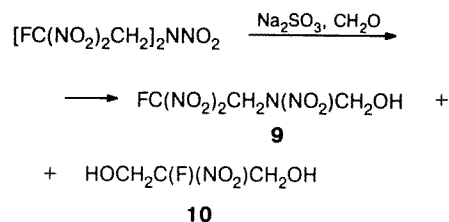


The denitration of methyl 4-fluoro-4,4-dinitrobutanoate results in the saponification of the ester group



The acidification of the reaction mixture gives product **8** in 81 % yield.

The reaction with 1,5-difluoro-1,1,3,5,5-pentanitro-3-azapentane is more complex.



This reaction occurs by the cleavage of the C—N bond to give 4-fluoro-2,4,4-trinitro-2-azabutan-1-ol (**9**) (yield 54 %) and 2-fluoro-2-nitropropane-1,3-diol (**10**) (yield 42 %). The structure of compound **9** was confirmed by NMR spectroscopy and by transformation into acetate (**11**). The latter has m.p. 44–45 °C after recrystallization from a CCl<sub>4</sub>—CHCl<sub>3</sub> mixture and does not give m.p. depression with an authentic sample of **11** obtained by the known procedure.<sup>2</sup> Using the same

**Table 1.** Characteristics of the compounds obtained

Starting compounds	Reaction products	Reaction time /days	B.p./°C (p/Torr) [M.p./°C]	$n_D^{20}$	Yield (%)
MeC(NO <sub>2</sub> ) <sub>2</sub> F	MeC(F)(NO <sub>2</sub> )CH <sub>2</sub> OH	16	49–50(1)	1.4203	84.6
EtC(NO <sub>2</sub> ) <sub>2</sub> F	EtC(F)(NO <sub>2</sub> )CH <sub>2</sub> OH	21	64–65(1)	1.4226	86.1
<i>n</i> -PrC(NO <sub>2</sub> ) <sub>2</sub> F	<i>n</i> -PrC(F)(NO <sub>2</sub> )CH <sub>2</sub> OH	28	67–68(0.5)	1.4242	83.7
HOCH <sub>2</sub> C(NO <sub>2</sub> ) <sub>2</sub> F	HOCH <sub>2</sub> C(F)(NO <sub>2</sub> )CH <sub>2</sub> OH	16	[85–86]	—	68.6
MeOCH <sub>2</sub> C(NO <sub>2</sub> ) <sub>2</sub> F	MeOCH <sub>2</sub> C(F)(NO <sub>2</sub> )CH <sub>2</sub> OH	14	118–119(1)	1.4290	96.5
EtOCH <sub>2</sub> C(NO <sub>2</sub> ) <sub>2</sub> F	EtOCH <sub>2</sub> C(F)(NO <sub>2</sub> )CH <sub>2</sub> OH	14.5	125–126(1)	1.4282	98.6
[FC(NO <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> O] <sub>2</sub> CH <sub>2</sub>	[HOCH <sub>2</sub> C(F)(NO <sub>2</sub> )CH <sub>2</sub> O] <sub>2</sub> CH <sub>2</sub>	14.5	[43–44]	—	92.3

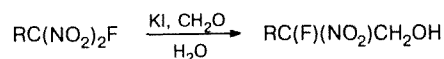
**Table 2.** Yields and some properties of fluoronitroalcohol nitrates

Starting compounds	Fluoronitroalcohol nitrates	B.p./°C (p/Torr) [M.p./°C]	$n_D^{20}$	Yield (%)
MeC(NO <sub>2</sub> ) <sub>2</sub> F	MeC(NO <sub>2</sub> )(F)CH <sub>2</sub> ONO <sub>2</sub> ( <b>12</b> )	51–52(1)	1.4260	68.5
EtC(NO <sub>2</sub> ) <sub>2</sub> F	EtC(NO <sub>2</sub> )(F)CH <sub>2</sub> ONO <sub>2</sub> ( <b>13</b> )	62–63(1)	1.4282	66.7
<i>n</i> -PrC(NO <sub>2</sub> ) <sub>2</sub> F	<i>n</i> -PrC(NO <sub>2</sub> )(F)CH <sub>2</sub> ONO <sub>2</sub> ( <b>14</b> )	79–80(1)	1.4311	58.1
MeOCH <sub>2</sub> C(NO <sub>2</sub> ) <sub>2</sub> F	MeOCH <sub>2</sub> C(NO <sub>2</sub> )(F)CH <sub>2</sub> ONO <sub>2</sub> ( <b>15</b> )	81–82(0.5)	1.4320	92.0
EtOCH <sub>2</sub> C(NO <sub>2</sub> ) <sub>2</sub> F	EtOCH <sub>2</sub> C(NO <sub>2</sub> )(F)CH <sub>2</sub> ONO <sub>2</sub> ( <b>16</b> )	82–84(0.3)	1.4300	90.1
HOCH <sub>2</sub> C(NO <sub>2</sub> ) <sub>2</sub> F	O <sub>2</sub> NOCH <sub>2</sub> C(NO <sub>2</sub> )(F)CH <sub>2</sub> ONO <sub>2</sub> ( <b>17</b> )	[37–38]	—	54.4

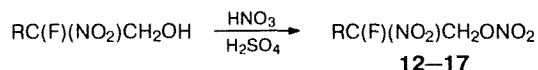
procedure, diol **10** was obtained in 50 and 86 % yields from 2-fluoro-2,2-dinitroethanol acetate and 1,2-difluoro-1,1,2,2-tetranitroethane, respectively.

Thus, the denitration of compounds, labile in basic media, with  $\text{Na}_2\text{SO}_3$  can be accompanied by side reactions.

Therefore, we denitrated the fluorodinitromethyl group by treatment with a highly nucleophilic reagent, KI.



The reaction conditions and the characteristics of the compounds obtained are presented in Table 1. According to TLC data, the purity of the products is 96–97 % in all cases. Therefore, denitration products were subjected to oxidative purification without distillation *in vacuo* and then nitrated with a sulfuric-nitric mixture to give nitrates **12–17** in high yields (Table 2).



For comparison, Table 3 presents the yields of fluoronitroalcohols obtained by denitration of the fluorodimethyl group on treatment with  $\text{Na}_2\text{SO}_3$  and KI in the presence of formaldehyde. It follows from the data in Table 3 that the denitration of the fluorodinitromethyl group with KI occurs with high selectivity and in high yields, as in the case of the trinitromethyl group.<sup>3</sup> However, the denitration of the fluorodinitromethyl group occurs considerably more slowly. The rate of denitration with KI is also much lower than that with  $\text{Na}_2\text{SO}_3$  and requires enhanced temperatures.

### Experimental

$^1\text{H}$  NMR spectra were recorded on an NMR spectrometer (294 MHz) at the Institute of Chemical Physics in

Chernogolovka of the Russian Academy of Sciences. IR spectra were recorded on a Specord M-82 spectrometer.

The purity of the products was monitored by GLC on a Chrom-4 chromatograph using a flame ionization detector and a  $4 \times 100$  cm column packed with Inerton-Super with 5 % OV-225 and by TLC on Silufol UV-254.

**2-Fluoro-2-nitropentanol.** A mixture of 1-fluoro-1,1-dinitrobutane (8.3 g, 50 mmol), Formalin (100 mL),  $\text{Na}_2\text{SO}_3$  (60 g, 476 mmol), and NaOH (2 g, 50 mmol) was stirred for 6.5 h at 70–80 °C. The mixture was cooled to ~20 °C, diluted with  $\text{H}_2\text{O}$  (50 mL), saturated with NaCl, and extracted with ether (4 × 40 mL). The extracts were combined, washed with  $\text{H}_2\text{O}$ , and dried with  $\text{MgSO}_4$ . The ether was distilled off, and 5 %  $\text{HNO}_3$  (18 mL),  $\text{NaNO}_2$  (1.66 g), urea (until saturation), and sodium carbonate (to pH 7.0) were added to the residue (oil). The mixture was extracted with ether (5 × 10 mL); the extracts were combined, washed with  $\text{H}_2\text{O}$ , and dried with  $\text{MgSO}_4$ . The ether was distilled off, and the residue was distilled to give 6.83 g (90.4 %) of 2-fluoro-2-nitropentanol, b.p. 67–68 °C (0.5 Torr),  $n_D^{20}$  1.4243 (cf. Ref. 4).

**2-Fluoro-2-nitropropyl methyl ether (1).**  $\text{Na}_2\text{SO}_3$  (6 g, 48 mmol) was added over a period of 30 min to a mixture of 2-fluoro-2,2-dinitroethyl methyl ether (1.7 g, 10 mmol), Formalin (15 mL), and  $\text{H}_2\text{O}$  (5 mL), and the mixture was stirred for 6 h at ~20 °C. The mixture was cooled to ~20 °C, diluted with  $\text{H}_2\text{O}$  (25 mL), saturated with NaCl, and extracted with ether (3 × 40 mL). The combined extracts were dried with  $\text{MgSO}_4$ , and the ether was distilled off. 5 %  $\text{HNO}_3$  (3.2 mL),  $\text{NaNO}_2$  (0.33 g), urea and sodium carbonate (to pH 7.0) were added to the residue. The mixture was extracted with ether (5 × 8 mL), and the extract was dried with  $\text{MgSO}_4$ . The ether was distilled off, and the residue was distilled to give 1.36 g (87.7 %) of product **1** with b.p. 119–120 °C (1 Torr),  $n_D^{20}$  1.4290.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ),  $\delta$ : 3.34 (s, 3 H, Me); 3.70–4.30 (m, 2 H,  $\text{CH}_2$ ); 4.00 (br.s, H, OH); ~3.90 (2 H,  $\text{OCH}_2\text{CF}$ , AB — part of an ABX spectrum,  $\Delta\nu_{\text{AB}} = 52.07$ ;  $^2J_{\text{AB}} = -11.89$  Hz;  $^3J_{\text{AX}} = 28.04$  Hz,  $^3J_{\text{BX}} = 10.66$  Hz).

**Ethyl 2-fluoro-2-nitropropyl ether (2).**  $\text{Na}_2\text{SO}_3$  (6 g, 48 mmol) was added over a period of 30 min to a mixture of ethyl 2-fluoro-2,2-dinitroethyl ether (1.82 g, 10 mmol), Formalin (15 mL), and  $\text{H}_2\text{O}$  (5 mL). The mixture was kept for 6 h at ~20 °C and then was worked-up similarly to the procedure described above to give 1.47 g of product **2** (88 %) with b.p. 126–127 °C (1 Torr),  $n_D^{20}$  1.4288. Found (%): C, 35.74; H, 6.01; N, 8.27; F, 11.40.  $\text{C}_5\text{H}_{10}\text{FNO}_4$ . Calculated (%): C, 35.93; H, 5.99; N, 8.38; F, 11.37.

**Ethyl 2-fluoro-2-nitropropyl ether nitrate (4).** Compound **2** (1.5 g, 9 mmol) was added at 0 °C over a period of 2 min to a

**Table 3.** Yields of fluoronitroalcohols in the denitration on treatment with  $\text{Na}_2\text{SO}_3$  and KI

Starting compounds	Reaction products	Yield (%)	
		$\text{Na}_2\text{SO}_3$	KI
$\text{HC}(\text{NO}_2)_2\text{F}$	$\text{HOCH}_2\text{C}(\text{NO}_2)(\text{F})\text{CH}_2\text{OH}$	81.2	—
$\text{MeC}(\text{NO}_2)_2\text{F}$	$\text{MeC}(\text{NO}_2)(\text{F})\text{CH}_2\text{OH}$	88.1	84.6
$\text{EtC}(\text{NO}_2)_2\text{F}$	$\text{EtC}(\text{NO}_2)(\text{F})\text{CH}_2\text{OH}$	88.0	86.1
$n\text{-PrC}(\text{NO}_2)_2\text{F}$	$n\text{-PrC}(\text{NO}_2)(\text{F})\text{CH}_2\text{OH}$	90.4	83.7
$\text{HOCH}_2\text{C}(\text{NO}_2)_2\text{F}$	$\text{HOCH}_2\text{C}(\text{NO}_2)(\text{F})\text{CH}_2\text{OH}$	83.5	68.6
$\text{MeOCH}_2\text{C}(\text{NO}_2)_2\text{F}$	$\text{MeOCH}_2\text{C}(\text{NO}_2)(\text{F})\text{CH}_2\text{OH}$	87.7	96.5
$\text{EtOCH}_2\text{C}(\text{NO}_2)_2\text{F}$	$\text{EtOCH}_2\text{C}(\text{NO}_2)(\text{F})\text{CH}_2\text{OH}$	88.0	98.6
$[\text{FC}(\text{NO}_2)_2\text{CH}_2\text{O}]_2\text{CH}_2$	$[\text{HOCH}_2\text{C}(\text{NO}_2)(\text{F})\text{CH}_2\text{O}]_2\text{CH}_2$	86.0	92.3

mixture of  $\text{HNO}_3$  (2.4 mL,  $d$  1.5 g  $\text{cm}^{-3}$ ) and  $\text{H}_2\text{SO}_4$  (2.4 mL,  $d$  1.84 g  $\text{cm}^{-3}$ ). The mixture was stirred at 0 °C for an additional 2 h and poured into ice water. The product was extracted with  $\text{CH}_2\text{Cl}_2$  (3×7 mL); the extract was washed with 5 % aqueous sodium carbonate and water and dried with  $\text{MgSO}_4$ . Removal of the  $\text{CH}_2\text{Cl}_2$  and distillation of the residue gave 1.83 g of product **4** (96.1 %), b.p. 82–84 °C (0.2 Torr),  $n_D^{20}$  1.4300. Found (%): C, 28.16; H, 4.12; N, 13.04; F, 9.00.  $\text{C}_5\text{H}_9\text{FN}_2\text{O}_6$ . Calculated (%): C, 28.30; H, 4.25; N, 13.21; F, 8.96.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ),  $\delta$ : 1.15 (t, 3 H, Me,  $^3J = 6.87$  Hz); 3.60 (m, 2 H,  $\text{CH}_2$ ); 4.08 (2 H,  $\text{OCH}_2\text{CF}$ , AB — part of an ABX spectrum,  $\Delta\nu_{\text{AB}} = 21.62$ ,  $^2J_{\text{AB}} = -11.79$  Hz,  $^3J_{\text{AX}} = 23.06$  Hz,  $^3J_{\text{BX}} = 12.20$  Hz); 5.16 (2 H,  $\text{CFCH}_2\text{ONO}_2$ , AB — part of an ABX spectrum,  $\Delta\nu_{\text{AB}} = 19.04$ ;  $^2J_{\text{AB}} = -13.74$  Hz,  $^3J_{\text{AX}} = 10.80$  Hz,  $^3J_{\text{BX}} = 24.46$  Hz).

**2-Fluoro-2-nitropropyl methyl ether nitrate (3).** Compound **1** (13.77 g, 90 mmol) was added at 0 °C over a period of 5 min to a mixture of  $\text{HNO}_3$  (30 mL,  $d$  1.5 g  $\text{cm}^{-3}$ ) and  $\text{H}_2\text{SO}_4$  (30 mL,  $d$  1.84 g  $\text{cm}^{-3}$ ). The mixture was stirred at 0 °C for an additional 2 h and poured into ice water. The product was extracted with  $\text{CH}_2\text{Cl}_2$  (3×50 mL); the extract was washed with 5 % aqueous sodium carbonate and water and dried with  $\text{MgSO}_4$ . Removal of the  $\text{CH}_2\text{Cl}_2$  and distillation of the residue gave 16.78 g (94.2 %) of product **3**, b.p. 81 °C (0.5 Torr),  $n_D^{20}$  1.4320. Found (%): C, 24.08; H, 3.46; N, 14.10; F, 9.64.  $\text{C}_4\text{H}_7\text{FN}_2\text{O}_6$ . Calculated (%): C, 24.24; H, 3.54; N, 14.14; F, 9.59.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ),  $\delta$ : 3.41 (s, 3 H, Me); 4.09 (2 H,  $\text{OCH}_2\text{CF}$ , AB — part of an ABX spectrum,  $\Delta\nu_{\text{AB}} = 19.39$ ;  $^2J_{\text{AB}} = -11.99$  Hz;  $^3J_{\text{AX}} = 22.34$  Hz;  $^3J_{\text{BX}} = 12.92$  Hz); 5.22 (2 H,  $\text{CFCH}_2\text{ONO}_2$ , AB — part of an ABX spectrum,  $\Delta\nu_{\text{AB}} = 18.67$ ;  $^2J_{\text{AB}} = -13.86$  Hz;  $^3J_{\text{AX}} = 7.88$  Hz;  $^3J_{\text{BX}} = 21.52$  Hz).

**2,8-Difluoro-2,8-dinitro-4,6-dioxanonane-1,9-diol (5).** 1,7-Difluoro-1,1,7,7-tetranitro-3,5-dioxasheptane (9.7 g, 30 mmol) was mixed with Formalin (100 mL) and  $\text{H}_2\text{O}$  (5 mL), and  $\text{Na}_2\text{SO}_3$  (19 g, 150 mmol) was then added over 45 min. The mixture was stirred for 2 h at 25–30 °C, cooled to ~20 °C, diluted with  $\text{H}_2\text{O}$  (50 mL), saturated with NaCl, and extracted with ether. The ether was distilled off; the residue was mixed with 10 %  $\text{HNO}_3$  (30 mL), and  $\text{NaNO}_2$  was added until nitrogen oxides appeared. Urea was added, and the mixture was extracted with ether (3×25 mL). The extract was washed with 1 % sodium carbonate (10 mL) and dried with  $\text{MgSO}_4$ . The ether was distilled off to give 7.5 g (85.9 %) of product **5**,  $n_D^{20}$  1.4505. Compound **5** crystallizes on standing for three weeks, m.p. 43–44 °C. Found (%): C, 28.82; H, 4.02; N, 9.54; F, 13.01.  $\text{C}_7\text{H}_{12}\text{F}_2\text{N}_2\text{O}_8$ . Calculated (%): C, 28.96; H, 4.14; N, 9.66; F, 13.10.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ),  $\delta$ : 3.70–4.30 (m, 10 H,  $\text{CH}_2\text{CF}(\text{NO}_2)\text{CH}_2\text{OH}$ ); 4.68 (m, 2 H,  $\text{OCH}_2\text{O}$ ).

**2,8-Difluoro-2,8-dinitro-4,6-dioxanonane-1,9-diol diacetate (6).** A mixture of compound **5** (2.9 g, 10 mmol) and  $\text{MeCOCl}$  (1.18 g, 15 mmol) was kept for 35 min at 20–30 °C and extracted with  $\text{CH}_2\text{Cl}_2$  (30 mL); the extract was washed with 2 % aqueous sodium carbonate and  $\text{H}_2\text{O}$  and dried with  $\text{MgSO}_4$ . The  $\text{CH}_2\text{Cl}_2$  was distilled off to give 3.7 g of product **6**, yield 90 %,  $n_D^{20}$  1.4440. Found (%): C, 35.16; H, 4.20; N, 7.52; F, 10.02.  $\text{C}_{11}\text{H}_{16}\text{F}_2\text{N}_2\text{O}_{10}$ . Calculated (%): C, 35.29; H, 4.28; N, 7.48; F, 10.16. IR,  $\nu/\text{cm}^{-1}$ : 1757 (C=O); 1578 (C–NO<sub>2</sub>); 1318 (C–NO<sub>2</sub>); 1225 (C–O); 1046 (C–O–C); 850 (C–N).

**1,1,7,7-Tetrafluoro-1,7-dinitro-3,5-dioxasheptane (7).** Compound **5** (7 g, 24 mmol) was mixed with  $\text{H}_2\text{O}$  (200 mL). 20 % NaOH (20 mL) was added at 0 °C, and a  $\text{F}_2\text{—N}_2$  mixture (1 : 10) was passed through the mixture to pH 6.0. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3×20 mL). The extract was washed with 2 % NaOH and  $\text{H}_2\text{O}$  and dried with  $\text{MgSO}_4$ . The  $\text{CH}_2\text{Cl}_2$  was distilled off; the residue was dissolved in  $\text{CHCl}_3$ , and the solution was passed through a column with silica gel, collecting

the first fractions. The solvent was evaporated, and the residue was distilled to give 2 g (32.1 %) of product **7**, b.p. 70–71 °C (0.5 Torr), purity 96 % (TLC data, cf. Ref. 5). Found (%): C, 22.50; H, 2.14; N, 10.44; F, 28.40.  $\text{C}_5\text{H}_6\text{F}_4\text{N}_2\text{O}_6$ . Calculated (%): C, 22.56; H, 2.26; N, 10.53; F, 28.57.

**4-Fluoro-2,4,4-trinitro-2-azabutan-1-ol (9).** A solution of  $\text{Na}_2\text{SO}_3$  (12 g, 95 mmol) in  $\text{MeCO}_2\text{H}$  (6 mL) and Formalin (50 mL) was added with stirring at 3–5 °C to a mixture of 1,5-difluoro-1,1,3,5,5-pentanitro-3-azapentane (5 g, 15 mmol), DMSO (25 mL), and 30 % Formalin (20 mL). The mixture was stirred for 20 h at 5–10 °C, diluted with  $\text{H}_2\text{O}$  (100 mL), saturated with NaCl, and extracted with  $\text{CHCl}_3$  (10×15 mL). The extract was dried with  $\text{MgSO}_4$  and concentrated *in vacuo*. The residue was passed through a column with silica gel using a  $\text{CHCl}_3\text{—CCl}_4$  mixture as the eluent. The solvent was distilled off under a reduced pressure, and the residue was crystallized from a  $\text{CCl}_4\text{—CHCl}_3$  mixture to give 1.84 g (54 %) of product **9**, m.p. 56–57 °C.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ),  $\delta$ : 4.09 (d, 2 H,  $\text{CH}_2$ ,  $J_{\text{HF}} = 5$  Hz); 4.04 (d, 2 H,  $\text{CH}_2$ ,  $J_{\text{HF}} = 13.5$  Hz); 2.2 (H,  $\text{CH}_2$ ,  $J_{\text{HF}} = 13.5$  Hz); 2.2 (H, OH).

The reaction mixture left after the separation of  $\text{CHCl}_3$  was extracted with ether (6×15 mL). The extract was washed with  $\text{H}_2\text{O}$  (1×2 mL) and dried with  $\text{MgSO}_4$ . The ether was distilled off to give a thick oil, which crystallized after a few days to give 0.87 g of 2-fluoro-2-nitropropane-1,3-diol, yield 42 %, m.p. 84–86 °C.

**2-Fluoro-2-nitropropane-1,3-diol dinitrate (17).**  $\text{Na}_2\text{SO}_3$  (50 g, 395 mmol) was added at 20–25 °C over a period of 30 min to a mixture of 1,2-difluoro-1,1,2,2-tetranitroethane (11.8 g, 48 mmol) and 30 % Formalin (180 mL). The mixture was stirred for 6 h at 20–25 °C and then saturated with NaCl and extracted with ether (3×40 mL). The ether was distilled off, and the remaining liquid was treated with  $\text{NaNO}_2$  in 10 %  $\text{HNO}_3$ . The product was extracted with ether (4×30 mL) and dried with  $\text{MgSO}_4$ . The ether was distilled off, and the residue was nitrated with a  $\text{HNO}_3\text{ : H}_2\text{SO}_4$  (1 : 1) mixture and poured into ice water. Extraction with ether followed by the ordinary treatment gave 9.26 g (84.3 %) of 2-fluoro-2-nitropropane-1,3-diol dinitrate, m.p. 37–38 °C (cf. Ref. 6). Found (%): C, 15.61; H, 1.70; N, 18.42; F, 8.24.  $\text{C}_3\text{H}_4\text{FN}_3\text{O}_8$ . Calculated (%): C, 15.72; H, 1.75; N, 18.34; F, 8.29.

**2-Fluoro-2-nitropropane-1,3-diol (10).** A mixture of 2-fluoro-2,2-dinitroethyl acetate (1.96 g, 10 mmol), 30 % Formalin (15 mL), and  $\text{Na}_2\text{SO}_3$  (8 g, 63 mmol) was stirred for 3 h at ~20 °C, saturated with NaCl, and extracted with ether (5×10 mL). The extract was dried with  $\text{MgSO}_4$ . The ether was distilled off; the ordinary work-up gave 0.7 g (50.4 %) of product **10**, m.p. 85–86 °C (cf. Ref. 6).

**2-Fluoro-2-nitropropanol nitrate.** A mixture of 1-fluoro-1,1-dinitroethane (2.8 g, 20 mmol), KI (15 g, 90 mmol), and Formalin (15 mL) in MeOH (15 mL) was kept for 80 h at 60–70 °C and for 300 h at ~20 °C. The mixture was diluted with water (50 mL), saturated with NaCl, and extracted with ether (3×20 mL). The extract was washed with aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  until discoloring occurred and was dried with  $\text{MgSO}_4$ . The ether was distilled off; the residue was treated with a solution of  $\text{NaNO}_2$  in 10 %  $\text{HNO}_3$ , then urea was added until saturation, and the pH was adjusted to 7.0 with sodium carbonate. The resulting mixture was extracted with ether (5×10 mL), and the extract was washed with water and dried with  $\text{MgSO}_4$ . The ether was distilled off. The residue was nitrated with a  $\text{HNO}_3\text{—H}_2\text{SO}_4$  mixture (1 : 1); the reaction mixture was then kept for 2 h at 0 °C and poured into 80 mL of ice water. The product was extracted with  $\text{CH}_2\text{Cl}_2$  (3×10 mL); the extract was washed with 5 % sodium carbonate and  $\text{H}_2\text{O}$  and then was dried with  $\text{MgSO}_4$ . The  $\text{CH}_2\text{Cl}_2$  was distilled off, and the residue was

distilled to give 2.3 g (68.5 %) of 2-fluoro-2-nitropropanol nitrate, 51–52 °C (1 Torr),  $n_D^{20}$  1.4261.

Nitrates **12–17** were synthesized in a similar way. Their yields and characteristics are listed in Table 2.

**2,8-Difluoro-2,8-dinitro-4,6-dioxanonane-1,9-diol (5).** A mixture of 1,7-difluoro-1,1,7,7-tetranitro-3,5-dioxaheptane (3.3 g, 10 mmol), Formalin (35 mL), MeOH (52 mL), and KI (35 g, 0.21 mol) was kept for 66 h at 50–60 °C and for 270 h at –20 °C. The mixture was diluted with H<sub>2</sub>O, saturated with NaCl, and extracted with ether (3×40 mL). The extract was washed with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> until discoloring occurred and was dried with MgSO<sub>4</sub>. The ether was distilled off, and the residue was dissolved in 10 % HNO<sub>3</sub> (10 mL). NaNO<sub>2</sub> was gradually added until nitrogen oxides appeared, and then urea was added until saturation, and the pH was adjusted to 7.0 with sodium carbonate. The mixture was extracted with ether, and the extract was dried with MgSO<sub>4</sub>. The ether was distilled off to give 2.76 g (92.3 %) of product **5**,  $n_D^{20}$  1.4505. Compound **5** crystallizes on standing in the cold, m.p. 43–44 °C.

Fluoronitroalcohols listed in Table 1 were synthesized in a similar way.

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