4. V. I. Bregadze, T. K. Dzhashiashvili, D. N. Sadzhaya, M. V. Petriashvili, O. B. Ponomareva, T. M. Shcherbina, V. Ts. Kampel', L. B. Kukushkina, and V. Ya. Rochev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 907 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 824 (Engl. Transl.)].
5. M. G. Voronkov, E. A. Maletina, and V. K. Roman, *Geterosiloksany* [*Heterosiloxanes*], Nauka, Novosibirsk, 1984, 143 (in Russian).
6. M. Gielen, F. Kauser, O. B. Zhidkova, V. Ts. Kampel, V. I. Bregadze, Dic de Vos, M. Biesemans, B. Mahieu, and R. Willem, *Metal Based Drugs*, 1955, **2**, 37.
7. L. A. Leites, L. E. Vinogradova, V. T. Aleksanyan, and S. S. Bukalov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 2480 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1976, **25** (Engl. Transl.)].
8. L. A. Leites, L. E. Vinogradova, S. S. Bukalov, V. Ts. Kampel', and V. I. Bregadze, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2035 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 1670 (Engl. Transl.)].
9. L. A. Leites, L. E. Vinogradova, S. S. Bukalov, I. A. Garbuzova, M. V. Petriashvili, V. Ts. Kampel', and V. I. Bregadze, *Metalloorg. Khim.*, 1989, **2**, 654 [*Organomet. Chem. USSR*, 1989, **2** (Engl. Transl.)].

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Effect of the nucleophile on the direction of denitration of compounds with two fluorodinitromethyl groups

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Previously,[1] it was demonstrated that both fluorodinitromethyl groups are involved in the reaction of 1,7-difluoro-1,1,7,7-tetranitro-3,5-dioxaheptane (**1**) with Na_2SO_3 in an aqueous-methanolic solution of formaldehyde:

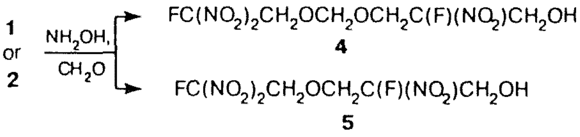
$$\underset{\mathbf{1}}{[FC(NO_2)_2CH_2O]_2CH_2} \xrightarrow{Na_2SO_3, CH_2O} [HOCH_2C(F)(NO_2)CH_2O]_2CH_2$$

The reaction with 1,5-difluoro-1,1,5,5-tetranitro-3-oxapentane (**2**) proceeds in a similar fashion:[2]

$$\underset{\mathbf{2}}{[FC(NO_2)_2CH_2]_2O} \xrightarrow{Na_2SO_3, CH_2O} \underset{\mathbf{3}}{[HOCH_2C(F)(NO_2)CH_2]_2O}$$

We isolated and identified the previously unknown 2,6-difluoro-2,6-dinitro-4-oxa-1,7-heptanediol (in the form of diacetate); the yield was 80 %.

In this work we found that, unlike Na_2SO_3, NH_2OH denitrates compounds **1** and **2** at only one of the fluorodinitromethyl groups:



$$\mathbf{1} \text{ or } \mathbf{2} \xrightarrow{NH_2OH, CH_2O} \underset{\mathbf{4}}{FC(NO_2)_2CH_2OCH_2OCH_2C(F)(NO_2)CH_2OH} + \underset{\mathbf{5}}{FC(NO_2)_2CH_2OCH_2C(F)(NO_2)CH_2OH}$$

Examples of this direction of denitration of compounds with two fluorodinitro- or trinitromethyl groups have not been described until now.

2,6-Difluoro-2,6-dinitro-4-oxa-1,7-heptanediol. M.p. 62—64 °C, the purity grade was 99.1 % (GLC). ^{1}H NMR (CD_3CN), δ: a mixture of optical isomers: 2.04 (s, 6 H, CH_3); 4.00—4.43 (m, 4 H, $CF(NO_2)CH_2O$, AB is the portion of the ABX spectrum); 4.50—4.70 (m, 4 H, $CH_2OC(O)CH_3$, AB is the portion of the ABX spectrum). IR, ν/cm^{-1}: 803, 847 (NO_2); 1059, 1221 (C—O); 1146 (C—F); 1312, 1589 ($C-NO_2$); 1756(C=O); 2920, 2943 (CH_2).

2,8-Difluoro-2,8,8-trinitro-4,6-dioxa-1-octanol (**4**) was formed in a yield of 37—38 % under the action of NH_2OH (9-fold excess, 0—5 °C, 1 h) on **1**. The reaction mixture was poured into water, and unreacted **1** was isolated and extracted with Et_2O. Then the solvent was removed, and compound **4** was identified in the form of acetate (colorless oil, n_D^{20} 1.4463). Found (%): C, 27.44; H, 3.01; F, 10.64; N, 11.97. $C_8H_{11}F_2N_3O_{10}$. Calculated (%): C, 27.66; H, 3.17; F, 10.95; N, 12.10. ^{1}H NMR (CD_3CN), δ: 1.99 (s 3 H, CH_3); 4.18 (2 H, $OCH_2CF(NO_2)$, AB is the portion of the ABX spec-

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trum); 4.72 (2 H, $CF(NO_2)CH_2$, AB is the portion of the ABX spectrum); 4.75 (s, 2 H, OCH_2O). IR, ν/cm^{-1}: 653 (NO_2); 800, 851 (C—N); 1052 (C—F and C—O); 1130 (C—O); 1223 (C—O) from —C(O)—O); 1316, 1580 ($C-NO_2$ from $FC(NO_2)$); 1607 ($C-NO_2$) from $FC(NO_2)_2$—); 1760 (C=O); 1415, 1454, 2915, 2960 (CH_2).

Under identical conditions, ether **5** (colorless oil, n_D^{20} 1.4508) forms from **2** and NH_2OH in a yield of ~48 %. Found (%): C, 21.64; H, 2.50; F, 13.76; N, 15.09. $C_5H_7F_2N_3O_8$. Calculated (%): C, 21.82; H, 2.55; F, 13.82; N, 15.27. ^1H NMR (CD_3CN), δ: 4.05 (2 H, $CF(NO_2)CH_2OH$, AB is the portion of the ABX spectrum); 4.30 (2 H, $OCH_2CF(NO_2)$, AB is the portion of the ABX spectrum); 4.65 (br.s, H, OH); 4.85 (CH_2, $CF(NO_2)CH_2O$, AB is the portion of the ABX spectrum). IR, ν/cm^{-1}: 764 (NO_2); 800, 851 (C—N); 1067 (C—OH overlaps with C—F); 1148 (C—O); 1313, 1547 (NO_2 from $CF(NO_2)$); 1604 (NO_2) from $FC(NO_2)_2$); 2925, 2946 (CH_2), 3416, 3579 (OH).

The corresponding acetate (colorless oil, n_D^{20} 1.4420, purity 99.5 % (GLC)) was obtained upon treatment of ether **5** with acetyl chloride in a yield of 93 %. ^1H NMR (CD_3CN), δ: 2.03 (s, 3 H, CH_3); 4.4 (2 H, $OCH_2CF(NO_2)$, AB is the portion of the ABX spectrum); 4.65 (2 H, $CF(NO_2)CH_2OCO$, AB is the portion of the ABX spectrum); 4.85 (2 H, $CF(NO_2)_2CH_2$, AB is the ABX spectrum). All spectra of the ABX type exhibit strong interactions, Δν, and *J* were not determined.

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References

1. B. S. Fedorov, M. A. Fadeev, V. V. Arakcheeva, L. S. Barinova, and L. T. Eremenko, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 392 [*Russ. Chem. Bull.*, 1996, **45**, 376 (Engl. Transl.)].
2. H. G. Adolph, U.S. Pat. 3 531 534, 1970.

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Preparative synthesis of dimethylaluminum hydride

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Methylaluminoxanes (MAO) are widely used for polymerization of olefins.[1,2] The synthesis of MAO by the incomplete hydrolysis of Me_3Al is complicated by the formation of $Al(OH)_3$, instability of the composition and the structure of MAO, *etc.*[3] It is conceivable that the substitution of Me_2AlH for Me_3Al could result in controlled hydrolysis because of the insignificant difference in bond activity of Al—C and Al—H.

Since the known procedures for the synthesis of Me_2AlH make it difficult to isolate the target product in preparative amounts, we elaborated a simple method for the synthesis of Me_2AlH from Me_3Al and crystalline AlH_3, following the reaction:

$$2Me_3Al + AlH_3 \longrightarrow 3Me_2AlH\,.$$

The synthesis of nonsolvated AlH_3 free from organic admixtures was carried out through the crystallization of AlH_3 from an ether—toluene solution followed by the elimination of ether according the known procedure.[5]

The synthesis of Me_2AlH from crystalline AlH_3. A suspension of AlH_3 (6.5 g, 0.217 mol) in $AlMe_3$ (28.6 g, 0.397 mol) was stirred at 120—126 °C (Ar) for 0.5 h. Distillation from the same flask (air condenser, distillation "pig", receiving vessels) yielded Me_2AlH (26.5 g, 74 %), b.p. ~90 °C (70—90 Torr). (Me_2AlH becomes glass-like at ~20 °C, taking on sufficient mobility at ~90 °C, which determined the distillation conditions). During the distillation, Me_2AlH decomposed partially to metallic Al. A condensate solidified on the walls of the condenser and distillation "pig" and did not get to the receiving vessels. The distillation at atmospheric pressure is accompanied by considerable decomposition. Me_2AlH was obtained in a <60 % yield, b.p. 152—154 °C (*cf.* Ref. 4).

References

1. Kh. G. Al't, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 7 [*Russ. Chem. Bull.*, 1995, **44**, 1 (Engl. Transl.)].
2. E. A. Fushman, A. D. Margolin, S. S. Lalayan, and V. E. L'vovskii, *Vysokomol. Soedin.*, 1995, **37B**, 1589 [*Polym. Sci. USSR*, 1995, **37B** (Engl. Transl.)].
3. N. N. Korneev and I. M. Khrapova, *Khimiya organoaliumoksanov* [*Chemistry of Organoalumoxanes*], NIITEKhIM/ГNIIKhTEOS, Moscow, 1984, 52 pp. (in Russian).

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