Organic Chemistry

Polymethylenepolynitramines and their derivatives
1. Synthesis of *N*-fluoro-substituted polymethylenepolynitramines

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Hitherto unknown *N*-fluoro-substituted polymethylenepolynitramines were synthesized by fluorinating the respective polymethylenepolynitramines with elemental fluorine in anhydrous acetonitrile.

Key words: polymethylenepolynitramines; 1,3,5-trinitro-1,3,5-triazapentane; 1,3,5,7-tetranitro-1,3,5,7-tetraazaheptane; *N*-fluoro-*N*-nitramines; fluorination.

In the last 10 years, the synthesis and X-ray diffraction studies of the two first homologs of symmetric polymethylenepolynitramines (PMPNA), namely, 1,3,5-trinitro-1,3,5-triazapentane (**1**) and 1,3,5,7-tetranitro-1,3,5,7-tetraazaheptane (**2**), have been reported.[1—4] However, at this time there are no data on the reactivity of these compounds or asymmetric PMPNA's, such as $RCH_2N(NO_2)CH_2NXNO_2$ with X = H or Hal.

In the present work we studied the fluorination of PMPNA's with elemental fluorine. Previously,[5—7] fluorination of alkaline-metal salts of primary *N*-nitramines with elemental fluorine in an aqueous medium made it possible to obtain *N,N'*-difluoro-*N,N'*-dinitroethylenediamine, *N*-fluoro-*N*-nitroaniline, *N*-fluoro-*N*-nitrocyclohexylamine, *N*-fluoro-*N*-nitrobutylamine, 1,7-difluoro-1,4,7-trinitro-1,4,7-triazaheptane, and *N*-fluoro-*N*-nitrourea in 61—86 % yields. In the case of sterically hindered isobutyl- and isopropylnitramines, fluorination products are formed in yields of 40 and 50 %, respectively.[8]

However, we found that this simple method is not suitable for the *N*-fluorination of PMPNA's due to their decomposition in aqueous alkali according to the following scheme:

$$RCH_2N(NO_2)CH_2NHNO_2 + OH^- \longrightarrow$$

$$\longrightarrow RCH_2N{=}NO_2^- + NH(NO_2)CH_2OH\ .$$

Therefore, we chose acetonitrile, which has been successfully used in the nitration of various organic compounds with nitryl fluoride (FNO_2),[9,10] as the medium for the fluorination of PMPNA's. PMPNA's were fluorinated in the H-form. When solutions of PMPNA's in MeCN (concentration 10—15 %) were fluorinated at −5 to 5 °C, the corresponding *N*-fluoro-derivatives could be isolated after pouring the reaction mixture into water and the usual workup. The yields of the fluorination products were 22—56 %.

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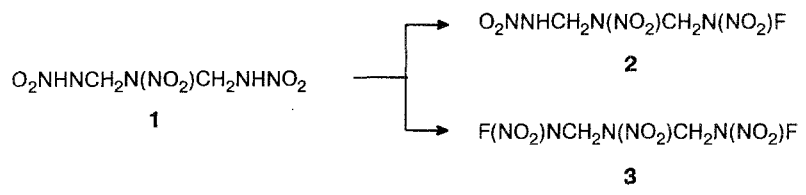
Scheme 1



In the case of PMPNA **1**, the conditions for the synthesis of both the mono-substituted asymmetrical monofluorination product **2** and symmetric product **3** (Scheme 1) were found.

Using this procedure, we obtained the symmetrical difluorination product **5** from PMPNA **4**.

$O_2NNHCH_2N(NO_2)CH_2N(NO_2)CH_2NHNO_2$ ⟶

4

⟶ $F(NO_2)NCH_2N(NO_2)CH_2N(NO_2)CH_2N(NO_2)F$

5

Similarly, *N*-monofluorination product **7** was synthesized from PMPNA **6**.

$F(NO_2)_2CCH_2N(NO_2)CH_2NH(NO_2)$ ⟶

6

⟶ $F(NO_2)_2CCH_2N(NO_2)CH_2N(NO_2)F$

7

The method of fluorination of the H-form of PMPNA's in MeCN is also suitable for the simplest *N*-nitroalkylamines. For example, fluorination of *N*-nitrobutylamine (**8**) under similar conditions afforded *N*-fluoro-*N*-nitrobutylamine (**9**) in 53.4 % yield.

The structures of *N*-fluoro-substituted PMPNA's were confirmed by elemental analysis and ^1H NMR spectral data (see Experimental). These compounds have low thermal stability and are unstable both toward nucleophilic (alkali-metal hydroxides) and electrophilic reagents (mineral acids).

Experimental

NMR spectra were recorded on a spectrometer (300 MHz) manufactured at an experimental instrument-building plant of the RAS in Chernogolovka.

1-Fluoro-1,3,5-trinitro-1,3,5-triazapentane (2). A fluorine—nitrogen mixture (1 : 10, 13.44 L) was bubbled for 30 min at −5 to 0 °C with vigorous stirring through a solution of 1,3,5-trinitro-1,3,5-triazapentane **1** (6.3 g, 30 mmol) in dry MeCN (150 mL), and the reaction mixture was poured into ice water (800 mL). The oil that formed was extracted with Et_2O (3×60 mL), and the extract was dried with $MgSO_4$. The Et_2O was distilled off *in vacuo*, and the residue was recrystallized from a $ClCH_2CH_2Cl$—$CHCl_3$ mixture to give 3.66 g (53.6 %) of monofluoride **2**, m.p. 69—70 °C (dec.). Found (%): C, 10.6; H, 2.6; N, 36.9; F, 8.8. $C_2H_5FN_6O_6$. Calculated (%): C, 10.53; H, 2.21; N, 36.84; F, 8.33. ^1H NMR (MeCN, Me_4Si), δ: 5.42 (d, 2 H, CH_2, $^3J_{H,H}$ = 5.0 Hz); 6.00 (d, 2 H, CH_2, $^3J_{H,F}$ = 25.5 Hz); 10.5 (m, H, NH).

1,5-Difluoro-1,3,5-trinitro-1,3,5-triazapentane (3). A fluorine—nitrogen mixture (1 : 10, 30 L) was bubbled for 35 min at −2 to 0 °C with vigorous stirring through a solution of 1,3,5-trinitro-1,3,5-triazapentane **1** (6.3 g, 30 mmol) and freshly calcined KF (4.71 g, 81 mmol) in dry MeCN (210 mL), and the reaction mixture was poured into an ice—water mixture (850 mL). The oil that formed was extracted with Et_2O (3×70 mL) and the extract was dried with $MgSO_4$. The Et_2O was distilled off *in vacuo*, the residue (oil) was dissolved in $ClCH_2CH_2Cl$ (50 mL), and the solution was passed through a column with silica gel. The solution was concentrated to 1/4 of the original volume and placed in a freezer. After two days, difluoride **3** precipitated as white crystals. Evacuation (0.05 Torr) for 2 h at ~20 °C gave 1.62 g (22.0 %) of product **3**, m.p. 35—36 °C. Found (%): C, 9.6; H, 1.4; N, 34.4; F, 15.6. $C_2H_4F_2N_6O_6$. Calculated (%): C, 9.76; H, 1.63; N, 34.15; F, 15.45. ^1H NMR (MeCN, Me_4Si), δ: 6.00 (d, 4 H, CH_2, $^3J_{H,F}$ = 26 Hz).

1,7-Difluoro-1,3,5,7-tetranitro-1,3,5,7-tetraazaheptane (5). A fluorine—nitrogen mixture (1 : 10, 10 L) was bubbled for 30 min at −2 to 0 °C with vigorous stirring through a solution of 1,3,5,7-tetranitro-1,3,5,7-tetraazaheptane **4** (4.8 g, 17 mmol) in dry MeCN (150 mL), and the reaction mixture was poured into ice water (600 mL). The oil that formed was extracted with CH_2Cl_2 (3×50 mL), and the extract was dried with $MgSO_4$ and treated with basic Al_2O_3. The solution was concentrated *in vacuo*, and the residue was recrystallized from dry $CHCl_3$ to give 3 g (55.5 %) of difluoride **5**, m.p. 92—93 °C (dec.), d_4^{20} = 1.816 g cm^{-3}. Found (%): C, 11.5; H, 1.9; N, 34.9; F, 12.5. $C_3H_6F_2N_8O_8$. Calculated (%): C, 11.25; H, 1.89; N, 35.00; F, 11.87. ^1H NMR (MeCN, Me_4Si), δ: 6.05 (d, 4 H, CH_2, $^3J_{H,F}$ = 26 Hz); 5.85 (s, 2 H, CH_2).

1,5-Difluoro-1,1,3,5-tetranitro-3,5-diazapentane (7). A fluorine—nitrogen mixture (1 : 10, 7.5 L) was bubbled for 35 min at −2 to 0 °C with vigorous stirring through a solution of 1-fluoro-1,1,3,5-tetranitro-3,5-diazapentane **6** (6 g, 23 mmol) in dry MeCN (100 mL), and the reaction mixture was poured into ice water (500 mL). The oil that formed was extracted with CH_2Cl_2 (3×30 mL) and the extract was dried with $MgSO_4$. The solution was concentrated *in vacuo* to give an oil (2.8 g), which was crystallized from CCl_4 to give 2.6 g (40.6 %) of white product **7**, m.p. 27.5—29 °C. Found (%): C, 12.1; H, 1.3; N, 28.4; F, 12.9. $C_3H_4F_2N_6O_8$. Calculated (%):

C, 12.42; H, 1.38; N, 28.97; F, 13.10. ^{1}H NMR (MeCN, Me_4Si), δ: 5.39 (d, 2 H, CH_2, $^3J_{H,F}$ = 1.5 Hz); 5.92 (d, 2 H, CH_2, $^3J_{H,F}$ = 3.0 Hz).

***N*-Fluoro-*N*-nitrobutylamine (9).** A fluorine—nitrogen mixture (1 : 10, 29 L) was bubbled for 45 min at −5 to 0 °C with vigorous stirring through a solution of *N*-nitrobutylamine **8** (11.8 g, 0.10 mol). The reaction mixture was poured into ice water (700 mL), the mixture was saturated with NaCl, and the oil that formed was extracted with CH_2Cl_2 (2×50 mL). The extract was washed with aqueous $NaHCO_3$ (1×80 mL) and water (2×50 mL) and dried with $MgSO_4$. The solution was concentrated *in vacuo* and the residue (oil) was distilled *in vacuo* to give 7.26 g (53.4 %) of product **9**, b.p. 46 °C (30 Torr), n_D^{20} 1.4042 (*cf.* Ref. 6: b.p. 40 °C (25 Torr), n_D^{20} 1.404).

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