NEW COMPOUNDS

Synthesis of Novel Polynitrodiols

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The synthesis of a number of polynitroalkanediols of widely varying structure is reported. Several of the synthesis methods described constitute novel variations or improvements of known reactions: some polynitroaliphatic carboxylic acids were found to undergo the Schmidt reaction only in triflic acid as reaction medium; 3-nitropropyl acetate was advantageously prepared by a variation of the Kornblum reaction with aqueous Me_2SO as solvent; 3,3-dinitropropanol was obtained by an intramolecular variant of the alkaline nitration method.

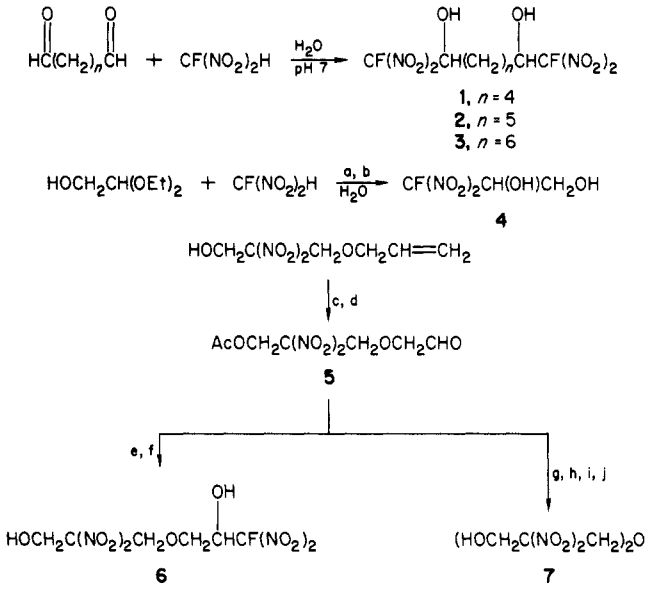
Polynitrodiols are of interest as components of nitropolymers. We present here the results of efforts to synthesize new nitrodiols of sufficiently varied structures to permit structure–property relationship studies of polyformals, polyesters, and polyethers derived from them.

Fluorodinitromethane adds to aldehydes to give stable secondary fluorodinitromethylcarbinols (*1*, *2*). Adaptations of this reaction were used for the synthesis of the diols **1**–**4** and **6** (Scheme I). (In Scheme I, the letters a–j represent the following: (a) 2 N H_2SO_4; (b) $NaHCO_3$ to pH 6; (c) AcCl; (d) OsO_4, $NaIO_4$; (e) $CF(NO_2)_2H$, 65% MeOH; (f) concentrated H_2SO_4; (g) $HONH_2$·HCl, 75% dioxane; (h) 90% HNO_3, 30% H_2O_2, CH_2Cl_2; (i) 36% CH_2O, 75% dioxane; (j) concentrated H_2SO_4.)

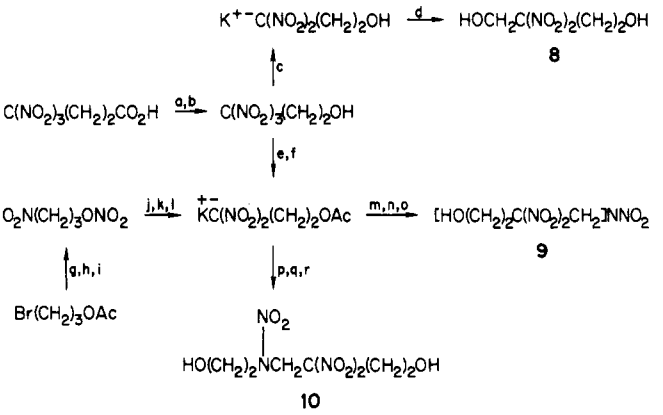
3-Hydroxy-2,2-dinitropropyl ether (**7**) has been reported earlier (*3*) but had not been obtained pure. Attempts to isolate pure **7** by chromatography from the literature mixture proved to be extremely tedious and gave only trace quantities of the material. The alternative method of synthesis reported here (HNO_3/H_2O_2 oxidation of the oxime (*4*) of **5** followed by Henry reaction of the product with formaldehyde and hydrolysis) provides a more tractable albeit still low yield route to **7**.

Diols **8**–**10** are derived from 3,3,3-trinitropropanol which has been claimed in a patent as resulting from the reduction of 3,3,3-trinitropropionyl chloride (*5*). However, no detailed description of the synthesis of either the alcohol or the acid chloride is given. In this work, the trinitropropanol was prepared via a trinitropropylamine salt (*6*) by an adaptation of Eremenko's procedure for 3,3,3-fluorodinitropropanol (*7*) or directly from 4,4,4-trinitrobutyric acid by a modified Schmidt reaction using triflic acid as the reaction medium. The conversion to 3,3-dinitropropanol and its acetate is straightforward. An alternative synthesis for the latter is based on the intramolecular alkaline nitration of 3-nitropropyl nitrate, a reaction type which was earlier observed by Salazar (*8*) and Stevens (*9*). The conversion of 3,3-dinitropropanol or its acetate to **8**, **9**, and **10** is summarized in Scheme II. (In Scheme II, the letters a–r represent the following: (a) CF_3SO_3H, NaN_3; (b) $NaNO_2$; (c) KI, MeOH; (d) 36% CH_2O, HCl; (e) AcCl, CH_2Cl_2; (f) KI, MeOH; (g) $NaNO_2$, Me_2SO; (h) concentrated HCl, MeOH; (i) 90% HNO_3, concentrated H_2SO_4; (j) KOH, CH_3OH; (k) HOAc, AcCl; (l) KOH, MeOH; (m) 36% CH_2O, NH_4OH; (n) 90% HNO_3, Ac_2O; (o) concentrated HCl, CH_3OH; (p) 36% CH_2O, $H_2NCH_2CH_2OAc$·HCl; (q) 90% HNO_3, Ac_2O; (r) concentrated HCl, 70% MeOH.)

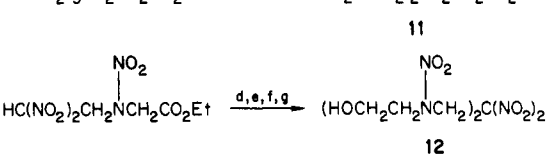
Scheme I



Scheme II



Scheme III



Alcohols **11** and **12** were prepared by known methods as indicated in Scheme III. (In Scheme III, the letters a–g represent the following: (a) KI, MeOH; (b) 36% CH_2O, HCl; (c) THF·BH_3; (d) 36% CH_2O, H_2NCH_2COOEt·HCl, $NaHCO_3$; (e) 90%

HNO_3, concentrated H_2SO_4; (f) AcOH, concentrated HCl; (g) BH_3·THF.)

Experimental Section

General Information. Caution. The polynitro compounds described in this paper are explosives and should be handled with due care. Fluorodinitromethane is a severe skin irritant.

Satisfactory elemental analyses were obtained for all new compounds (Galbraith Laboratories, Knoxville, TN) and were submitted for review. Chromatography was performed with Silica Gel 60 (EM Reagents). NMR spectra are reported in ppm downfield from Me_4Si used as an internal or external (sealed capillary for aqueous solutions) standard. Mass spectral data were obtained by chemical ionization (CH_4).

1,8-Difluoro-1,1,8,8-tetranitrooctane-2,7-diol (1). A well-stirred mixture of 1.71 g (0.015 mol) of hexanedial and 3.85 g (0.031 mol) of fluorodinitromethane in 25 mL of water was maintained at −3 to +3 °C during the dropwise addition of 5 N sodium hydroxide to establish pH 7. After 0.5 h the solution was acidified and extracted with dichloromethane (4 × 30 mL). Removal of volatiles from the dried (Na_2SO_4) extract gave a liquid residue from which 3.91 g of crude solid was obtained by recrystallization from chloroform. Recrystallization from dichloromethane–hexane gave 3.00 g (78%) of **1**: mp 60–63 °C; ^{1}H NMR (acetone-d_6) δ 6.07 (d, 2, J = 6 Hz), 5.17 (d, 2, J = 21 Hz), 1.71 (s, 8).

1,9-Difluoro-1,1,9,9-tetranitrononane-2,8-diol (2). The above procedure was followed with 2.56 g (0.020 mol) of heptanedial, 5.00 g (0.040 mol) of fluorodinitromethane, and 25 mL of water to give a crude liquid product of 7.0 g. Dissolution in chloroform (8 mL) followed by cooling gave 3.63 g (48%) of **2**: mp 75–77 °C; ^{1}H NMR ($CDCl_3$) δ 4.99 (m, 2), 2.64 (d, 2, J = 8 Hz), 1.61 (s, 10).

1,10-Difluoro-1,1,10,10-tetranitrodecane-2,9-diol (3). The above procedure provided 7.4 g of crude product from 2.84 g (0.020 mol) of octanedial, 5.20 g (0.042 mol) of fluorodinitromethane, and 70 mL of methanol–water (30/70). Two recrystallizations from chloroform gave 1.42 g (18%) of **3**: mp 80–82 °C; ^{1}H NMR ($CDCl_3$) δ 4.98 (m, 2), 2.65 (d, 2, J = 8 Hz), 1.51 (m, 12).

3,3,3-Fluorodinitro-1,2-propanediol (4). In a modification of the original procedure (*2*) a solution of 13.4 g (0.01 mol) of 2,2-diethoxyethanol and 1 mL of 2 N H_2SO_4 in 50 mL water was stirred approximately 1 h at 50 °C. After cooling in an ice bath, 12.4 g (0.01 mol) of fluorodinitromethane was added with stirring followed by saturated $NaHCO_3$ solution sufficient to give pH 6. The fluorodinitromethane slowly dissolved. After 1 h the mixture was acidified (H_2SO_4), saturated with NaCl, and extracted with ether. The extract was dried ($MgSO_4$) and freed from solvent to give 15.0 g (82%) of crude diol as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.29 (t), 6.60 (t), 3.15 (m), 2.55 (broad m).

3-Acetoxy-2,2-dinitropropyl Allyl Ether. 3-Hydroxy-2,2-dinitropropyl allyl ether (*10*) (2.06 g, 0.010 mol) and acetyl chloride (1.57 g, 0.020 mol) were heated in a 60 °C bath overnight to give, after removal of volatiles in vacuo, 2.48 g (100%) of the liquid title compound: ^{1}H NMR ($CDCl_3$) δ 5.80 (m, 1), 5.30 (m, 2), 5.01 (s, 2), 4.32 (s, 2), 4.09 (d, 2, J = 5.5 Hz), 2.09 (s, 3); mass spectrum, *m/e* (rel intensity) 249 (M + 1, 100), 162 (11), 115 (22), 81 (55).

6-Acetoxy-5,5-dinitro-3-oxahexanal (5). The addition of $NaIO_4$ (9.00 g, 0.042 mol) to a solution of 3-acetoxy-2,2-dinitropropyl allyl ether (5.00 g, 0.020 mol) and OsO_4 (0.05 g) in 100 mL of 75% dioxane was done in portions, to maintain 26–28 °C solution temperature (*11*). After 1.5 h the thick suspension of solids was extracted with ether (3 × 50 mL). Removal of volatiles in vacuo left 5.80 g of crude liquid product composed of a nearly quantitative yield of the title compound plus a small amount of dioxane: ^{1}H NMR ($CDCl_3$) δ 9.61 (s, 1), 5.04 (s, 2), 4.49 (s, 2), 4.26 (s, 2), 2.31 (s, 3); mass spectrum, *m/e* (rel intensity) 251 (M + 1, 100), 232 (8), 206 (57), 204 (18), 191 (48), 159 (15), 146 (30).

6-Acetoxy-5,5-dinitro-3-oxahexanal Oxime. A solution of 10.8 g (0.040 mol) of 6-acetoxy-5,5-dinitro-3-oxahexanal and 3.0 g (0.042 mol) of $HONH_2$·HCl in 60 mL of 75% dioxane was treated with a solution of 3.5 g (0.042 mol) of sodium acetate in 10 mL of water and stirred vigorously overnight. Dichloromethane extraction (2 × 100 mL) and removal of volatiles at 50 °C on a rotary evaporator gave 9.50 g (89%) of oxime (*E*/*Z* isomer composition of 60/40 by NMR) contaminated with 1 mol % dioxane by NMR analysis. An analytical sample was obtained as a light yellow liquid by column chromatography (dichloromethane): ^{1}H NMR ($CDCl_3$) *E* isomer δ 7.50 (t, 1, J = 6 Hz), 5.03 (s, 2), 4.42 (s, 2), 4.23 (d, 2, J = 6 Hz), 2.13 (s, 3); *Z* isomer 6.90 (t, 1, J = 3 Hz), 5.03 (s, 2), 4.51 (d, 2, J = 3 Hz), 4.46 (s, 2), 2.13 (s, 3); mass spectrum, *m/e* (rel intensity) 266 (M + 1, 100).

7-Acetoxy-1-fluoro-1,1,6,6-tetranitro-4-oxa-2-heptanol. To a mixture of 1.24 g (0.010 mol) of fluorodinitromethane and 2.68 g (0.084 mol) of 6-acetoxy-5,5-dinitro-3-oxahexanal in 60 mL of 65% methanol was added, in portions, sodium bicarbonate (total of 0.6 g) to maintain pH 5.5–6.0.

The solution was acidified after 3.5 h and extracted with dichloromethane (3 × 50 mL). A crude liquid product (2.8 g) that remained after removal of volatiles in vacuo provided 1.32 g (42%) of crystals (mp 76–80 °C) from dichloromethane/hexane. An analytical sample was obtained by further recrystallization, with mp 84–85 °C: ^{1}H NMR ($CDCl_3$) δ 5.18 (d of t, 1, J_{CH_2-CH} = 4 Hz, J_{CH-CF} = 18 Hz), 4.91 (s, 2), 4.34 (s, 2), 3.85 (d, 2, J = 4 Hz), 2.11 (s, 3).

1-Fluoro-1,1,6,6-tetranitro-4-oxa-2,7-heptanediol (6). A solution of 0.50 g of 7-acetoxy-1-fluoro-1,1,6,6-tetranitro-4-oxa-2-heptanol in 10 g of concentrated sulfuric acid was stirred for 2 h, drowned on ice, and extracted with ether to give 0.48 g of **6** contaminated with acetic acid. Storage over KOH pellets in vacuo gave 0.41 g (92%) of **6** as a light yellow liquid: ^{1}H NMR ($CDCl_3$) δ 5.22 (d of t, 1, J_{CH_2-CH} = 4 Hz, J_{CH-CF} = 9 Hz), 4.44 (s, 4), 3.91 (d, 2, J = 4 Hz), 2.7 (broad s, 2); mass spectrum, *m/e* (rel intensity) 333 (M + 1, 2), 191 (38), 167 (29), 149 (18), 147 (13), 125 (78), 119 (100), 115 (14), 101 (12).

7-Acetoxy-2,2,6,6-tetranitro-4-oxaheptanol. To a solution of 10.0 g (0.038 mol) of 6-acetoxy-5,5-dinitro-3-oxahexanal oxime in 100 mL of dichloromethane at 5 °C was added, dropwise, 18.8 mL of 90% nitric acid in 0.75 h (*4*). A −15 °C cooling bath of ice–methanol was used to maintain 5–8 °C solution temperature throughout the addition and especially to control an exotherm which occurs during the first part of the addition and which is accompanied by a transient blue color and evolution of brown fumes. The brown solution was further treated at 5–8 °C with 12.2 mL of 30% H_2O_2 and then poured on ice. The dried (Na_2SO_4) dichloromethane layer was concentrated to 9.4 g of light red liquid in vacuo. NMR analysis of an aliquot with an internal standard ($HCCl_2CCl_2H$) indicated the presence of 0.011 mol (28%) of $AcOCH_2C(NO_2)_2CH_2OCH_2C(NO_2)_2H$ as a triplet, $C(NO_2)_2H$, (J = 5.8 Hz) at δ 6.57 and 0.002 mol (5%) of 6-acetoxy-5,5-dinitro-3-oxahexanal as a singlet, CHO, at δ 9.68. To this mixture (9.0 g) was added 2.5 g (0.03 mol) of formalin solution (36%) in 50 mL of 75% dioxane (pH of solution at this point was 2). After 3 h the solution was extracted with dichloromethane (2 × 50 mL). After overnight stirring of the extract with sodium bisulfite solution (25%) and concentration in vacuo, a liquid residue was obtained which was chromatographed with dichloromethane–hexane (75/25) followed by dichloromethane and dichloromethane–ethyl acetate (95/5). This provided 2.23 g (17%) of pure title compound plus 0.90 g of slightly impure product: ^{1}H NMR ($CDCl_3$) δ 5.01 (s, 2), 4.59 (s, 2), 4.53 (s, 4), 2.16 (s, 3); mass spectrum, *m/e* (rel

intensity) 357 (M + 1, 80), 327 (18), 310 (7), 252 (33), 222 (14), 209 (12), 119 (100), 104 (48), 86 (34).

3-Hydroxy-2,2-dinitropropyl Ether (7). After 2 h stirring, a mixture of 2.42 g of the above acetate and 20 mL of concentrated sulfuric acid was poured on ice. Saturation with sodium chloride and extraction with ether (5 × 200 mL) gave 2.21 g of crude liquid product. The hygroscopic diol was obtained as a partially crystallized solid after storage over P_2O_5 in vacuo for several days, 1.65 g (77%). An analytical sample was obtained from dichloromethane: mp 77–79 °C; ^{1}H NMR (acetone-d_6) δ 4.74 (s, 4), 4.49 (s, 4); mass spectrum, *m/e* (rel intensity) 315 (M + 1, 52), 285 (24), 255 (8), 208 (3), 167 (65), 149 (20), 137 (24), 119 (100).

3,3,3-Trinitropropanol. A mechanically stirred solution of 210 g (0.94 mol) of 4,4,4-trinitrobutyric acid and 534 mL (908 g) of trifluoromethanesulfonic acid at 60 °C was treated with 100 g (1.54 mol) of sodium azide in approximately 2-g portions over a 6-h period, while a stream of nitrogen was swept through the system to remove the hydrazoic acid. (*Caution*. Inefficient HN_3 removal can result in an explosive decomposition.) Stirring was stopped and the thick mixture was heated overnight at 50 °C before it was poured onto ice to give an aqueous solution (2.5 L) which was extracted with dichloromethane (3 × 300 mL) to remove unreacted trinitrobutyric acid. The aqueous solution was maintained at 10–14 °C while a solution of 140 g of sodium hydroxide in 200 mL of water was added dropwise with good stirring. The solution was then heated to 35 °C and a solution of 121 g (1.75 mol) of sodium nitrite in 400 mL of water was added over a 0.5-h period. The solution was heated at 60 °C for 1.5 h before it was cooled to 25 °C and extracted with dichloromethane (2 × 500 mL). Further extraction (3 × 500 mL) after saturation with sodium chloride gave a combined yield of 161 g (88%) of crude trinitropropanol. An analytical sample was obtained by column chromatography with dichloromethane as solvent: mp 24–25 °C; ^{1}H NMR ($CDCl_3$) δ 4.10 (d of t, 2), 3.30 (t, 2), 1.87 (t, 1); mass spectrum, *m/e* (rel intensity) 196 (M + 1, 7), 178 (100).

Potassium 3,3-Dinitropropanol. To a stirred solution of 32.0 g (0.164 mol) of crude 3,3,3-trinitropropanol in 460 mL of methanol was added 68 g (0.41 mol) of potassium iodide. The mixture was stirred at ambient temperature for 5 days before the yellow precipitate was collected by filtration and washed with methanol. The salt was stirred with 150 mL of methanol, the solution cooled with ice, and the yellow solid collected (19.6 g, 64%). On further standing additional salt precipitated for a total yield of 25.2 g (82%): ^{1}H NMR (D_2O, Me_4Si capillary) δ 4.20 (t, 2), 3.33 (t, 2).

2,2-Dinitrobutane-1,4-diol (8). Crude potassium 3,3-dinitropropanol (19.6 g) in aqueous solution was treated with 20 mL of 36% formalin, followed by 11 mL of concentrated hydrochloric acid over a 3-min period. A small amount of precipitated iodine was removed by filtration and the filtrate (adjusted to pH 4) was allowed to stand 5 h before it was extracted with ether (3 × 90 mL). The solid isolated from this solution by evaporation was stirred with 80 mL of chloroform to give 13.4 g (72%) of white solid, mp 55–57 °C. Crystallization from dichloromethane gave 12.2 g of the diol: mp 56–58 °C; ^{1}H NMR ($CDCl_2$) δ 4.65 (d, 2), 3.95 (m, 2), 3.35 (t, 1), 2.92 (t, 2), 2.12 (t, 1).

Potassium 3,3-Dinitropropyl Acetate. A. From 3,3,3-Trinitropropanol. Overnight reflux of a dichloromethane solution of 150 g (0.77 mol) of crude trinitropropanol and 125 mL of acetyl chloride provided, after an ice water quench and removal of solvent, 183 g (100%) of crude acetate as a light green solid. Crystals from hexane/dichloromethane had mp 47–49 °C; ^{1}H NMR ($CDCl_3$) δ 4.55 (t, 2), 3.45 (t, 2), 2.06 (s, 3).

The 183 g (0.77 mol) of crude 3,3,3-trinitropropyl acetate in 2100 mL of methanol was heated at 40 °C for 24 h with 338 g (2.03 mol) of potassium iodide. The cooled solution (20 °C) was filtered and the collected salt stirred with 600 mL of methanol at 20 °C to give 88.5 g (50%) of yellow salt.

A similar reaction using 32.1 g of purified trinitropropyl acetate gave 20.4 g (66%) of potassium dinitropropyl acetate: ^{1}H NMR (D_2O with Me_4Si capillary) δ 4.93 (t, 2), 3.94 (t, 2), 2.54 (s, 3).

The free-acid form of the above product was also prepared by addition of potassium 3,3-dinitropropanol (4.15 g, 0.022 mol) to a vigorously stirred and ice-cooled mixture of 1.5 mL of concentrated H_2SO_4 and 10 mL of ether/10 mL of water. After 0.5 h the phases were separated and the aqueous layer was extracted with ether. The dried ($MgSO_4$) solution was concentrated on a rotary evaporator and the residue dissolved in 5 mL of acetyl chloride/5 mL of dichloromethane. After several hours reflux, followed by the usual workup, a 2.75-g (65%) quantity of 3,3-dinitropropyl acetate was isolated: ^{1}H NMR ($CDCl_3$) δ 6.40 (t, 1), 4.36 (t, 2), 2.58 (overlapping triplets, 2), 2.10 (s, 3).

B. Via 3-Nitropropyl Nitrate. To a well-stirred (mechanical stirrer) solution of 110.7 g of $NaNO_2$ in 52 mL of water and 640 mL of dimethyl sulfoxide was added 167.0 g of 3-bromopropyl acetate. After 4 h sufficient ice water was added to dissolve the precipitate (solution temperature should not exceed 25 °C) and the solution was poured into water (total of 1750 mL). Dichloromethane extraction (875, 700, and 525 mL) followed by water washes (4 × 875 mL, each containing 100 g of NaCl) and drying ($MgSO_4$) gave 97 g of crude 3-nitropropyl acetate after solvent removal: ^{1}H NMR ($CDCl_3$) δ 4.55 (t, 2), 4.27 (t, 2), 2.40 (t, 2), 2.13 (s, 3).

The crude product (95 g) was dissolved in 300 mL of methanol, 7 mL of concentrated HCl was added, and the mixture was heated to 60–65 °C for 24 h. Removal of solvent gave 62.5 g of crude 3-nitropropanol. This was added with ice cooling at <10 °C to 187 mL of 90% nitric acid and the mixture stirred 0.5 h at this temperature. Sulfuric acid (125 mL, concentrated) was added at <10 °C with stirring. After 1 h the mixture was poured on ice. Extraction with dichloromethane and usual workup gave 78.5 g of crude 3-nitropropyl nitrate: ^{1}H NMR ($CDCl_3$) δ 4.66 (2 overlapping triplets, 4), 2.53 (t, 2).

Crude 3-nitropropyl nitrate (8 g) was added with ice cooling to a stirred solution of 8 g of KOH in 40 mL of methanol. The mixture was stirred 1 h at ice bath and 1 h at ambient temperature, cooled again, and filtered. The product was washed with cold methanol and air-dried to give 5.88 g of potassium 3,3-dinitropropanol which was pure by NMR analysis: ^{1}H NMR (D_2O with external Me_4Si) δ 4.40 (t, 2), 3.83 (t, 2).

Potassium 3,3-dinitropropanol (0.60 g, 0.0032 mol) was stirred with 4 g of acetic acid at 20 °C for 1 h. Acetyl chloride (8 g) was added and the solution heated in a 50 °C bath for 5 h. Following the drowning of the solution, dichloromethane extraction, and removal of solvent, the isolated crude acetate was dissolved in methanol and precipitated from the solution at ice bath temperature by addition of 5 N KOH/methanol to give 0.50 g (68%) of potassium 3,3-dinitropropyl acetate.

3,3,7,7-Tetranitro-5-azanonane-1,9-diol 1,9-Diacetate. A solution of potassium 3,3-dinitropropyl acetate (43.5 g, 0.19 mol) in 525 mL of water and 42 mL of 36% formalin was stirred in an ice bath while 22.5 mL of concentrated HCl was added (pH approximately 3). The mixture was heated at 40 °C for 0.5 h, then cooled to 20 °C and 21.3 g of NH_4Cl was added. The mixture was stirred vigorously in an ice bath while concentrated NH_4OH solution was added over several hours until the aqueous phase remained yellow and the pH was 5.5–6. At this point an appreciable amount of semisolid had separated from solution and adhered to the walls of the flask. Continued *vigorous* stirring for a period of approximately 40 h and occasional NH_4OH addition to adjust the pH were required for the conversion of this material to a crystalline product. Filtration

gave 37 g (92%) of product with mp 75–76 °C. Chilling of the filtrate resulted in separation of an oil mixed with solid which was triturated with water overnight to give an additional 1.5 g of crude product. An analytical sample from dichloromethane–hexane had mp 75–76.5 °C; ^{1}H NMR ($CDCl_3$) δ 4.27 (t, 2), 3.85 (d, 2), 2.91 (t, 2), 2.06 (s, 3).

3,3,5,7,7-Pentanitro-5-azanonane-1,9-diol 1,9-Diacetate. Acetic anhydride (315 mL) was stirred in an ice bath to maintain 20–23 °C during the slow addition of 95 mL of 90% HNO_3. The solution was then cooled to 5 °C while 61.9 g (0.146 mol) of 3,3,7,7-tetranitro-5-azanonane-1,9-diol-1,9-diacetate was added in portions with good stirring. The solution was stirred at ambient temperature overnight before it was added slowly, with vigorous stirring, to room temperature water. After some additional stirring the solid was filtered off to give 66.5 g (97%) of the nitramine with mp 87–89 °C. A sample recrystallized from hexane–dichloromethane had mp 88–89 °C; ^{1}H NMR ($CDCl_3$) δ 5.20 (s, 2), 4.35 (t, 2), 3.00 (t, 2), 2.09 (s, 3).

3,3,5,7,7-Pentanitro-5-azanonane-1,9-diol (9). Crude diacetate (66.5 g) of the title compound was stirred in 615 mL of warm (50 °C) methanol while first water (265 mL) and then concentrated HCl (19 mL) was added. The mixture was heated at 67–69 °C (mild reflux) overnight before nearly all the solvent was removed at aspirator pressure on a rotary evaporator (35 °C bath). The white solid residue (mp 118–120 °C) was collected by filtration and washed with cold water. Crystallization from methanol–water gave 50.0 g, mp 121.5–123 °C. The second crop (2.9 g, mp 118–120 °C) resulted in a total yield of 97%: ^{1}H NMR (acetone-d_6 + 1 drop D_2O) δ 5.57 (s, 2), 2.90 (t, 2), 3.00 (t, 2).

3-(2-Acetoxyethyl)-5,5-dinitroperhydrooxazepine. A mixture of 11.65 g (0.140 mol) of 36% formalin, 87 mL of water, 11.85 g (0.0630 mol) of potassium 3,3-dinitropropanol, and 3.57 g (0.0256 mol) of 2-aminoethyl acetate hydrochloride was stirred initially with ice cooling, and then at ambient temperature for 1.5 h. Extraction with dichloromethane and usual workup gave 13.35 g (76%) of an oil which by NMR analysis was essentially pure title compound: ^{1}H NMR ($CDCl_3$) δ 4.34 (s, 2), 3.95–4.20 (2t, 1s, 6), 3.01 (t, 2), 2.80 (t, 2), 2.10 (s, 3).

3,5,5-Trinitro-3-azaheptanediol-1,7-diol (10). A solution of 17.9 g of crude acetoxyethyldinitroperhydrooxazepine, prepared as described above, in 10 mL of glacial acetic acid was added with stirring at 5–10 °C to a mixture of 211 mL of acetic anhydride and 63 mL of 90% HNO_3 (prepared at 20–25 °C). After 5 h at ca. 5 °C, the mixture was poured into 1000 mL of ice water and stirred vigorously for 1 h, and the product extracted into dichloromethane. The oil obtained on usual workup was mixed with 89 mL of 70% aqueous methanol and 25 drops of concentrated HCl and stirred at 65–70 °C overnight. After cooling, about two-thirds of the solvent was removed in vacuo, 100 mL of water was added, and the product was extracted with ether. Drying and stripping of the solvent gave 13.35 g of crude diol free of any major impurities, but containing a number of minor ones. Chromatography with dichloromethane–ethyl acetate (9:1 to 1:1) gave 7 g (51%) of solid diol plus 3–4 g of noncrystalline material (conditions for chromatography were not optimized). Dichloromethane recrystallization gave diol with mp 50–51.5 °C; ^{1}H NMR (CD_3OD) δ 5.23 (s, 2, 3.70–4.15 (3t, 6), 2.87 (t, 2).

The diol was further characterized by conversion to its dinitrate with 100% HNO_3: mp 64–66 °C; ^{1}H NMR (CD_2Cl_2) δ 5.07 (s, 2), 4.82 (d of t, 4), 4.19 (t, 2), 3.10 (t, 2).

2,2-Dinitropentane-1,5-diol (11). A mixture of 30.6 g of methyl trinitrobutyrate, 48 g of KI, and 290 mL of methanol was stirred at room temperature for 3 days and filtered to give a yellow salt which was washed with cold methanol and air-dried. A suspension of this crude salt in 120 mL of 70% aqueous tetrahydrofuran (THF) was cooled to 15 °C and 10.8 g of 36% formalin was added with stirring. Concentrated hydrochloric acid (10.2 g) was added until pH paper indicated pH 3.0 in the lower aqueous layer. The mixture was stirred at room temperature for 3 h, acidified, diluted with an equal volume of water, and extracted with dichloromethane (3 × 50 mL). This solution was concentrated to 20.9 g (73%) of liquid product which was identical by IR and NMR with an authentic sample of methyl 5-hydroxy-4,4-dinitropentanoate prepared by the method of Klager (*12*).

A solution of 14.7 g (0.0662 mol) of methyl 5-hydroxy-4,4-dinitropentanoate in an equal volume of THF was added in a steady stream to a THF·BH_3 solution (0.97 M, 109 mL, 0.106 mol). The solution was refluxed 1.5 h and quenched with dropwise addition of concentrated HCl (15 mL). Water (70 mL) and toluene (50 mL) were added and the organic layer was separated. The dried (Na_2SO_4) solution precipitated boric acid on standing overnight at 8 °C. An oily residue obtained from this filtered solution on removal of solvent was chromatographed with toluene, 6% ethyl acetate/toluene, and 10% ethyl acetate/toluene to give 7.4 g (54%) of the liquid diol [11]: ^{1}H NMR (D_2O, capillary Me_4Si) δ 5.03 (s, 2), 4.16 (t, 2), 3.20 (t, 2), 2.14 (m, 2).

2,4,4,6-Tetranitro-2,6-diaza-1,7-heptanedicarboxylic Acid. A solution of 22.8 g (0.086 mol) of ethyl 3,5,5-trinitro-3-azapentanoate (**13**), 185 mL of 50% aqueous methanol, 12.0 g (0.086 mol) of ethyl glycine hydrochloride, and 7.2 g of formalin (36%, 0.086 mol) was stirred at room temperature while 7.2 g (0.086 mol) of $NaHCO_3$ was added in small portions (15 mL additional methanol used to rinse walls of flask after this addition was complete). After 2 h the solution was extracted with dichloromethane and the extract concentrated on a rotary evaporator to an oil. Addition of this oil to a well-stirred and ice-cooled mixture of 51.5 mL of 90% HNO_3 and 51.5 mL of concentrated H_2SO_4 was followed by slow heating of the resultant solution to 55–60 °C. After 5 min at this temperature the solution was allowed to cool slowly to 20 °C and then poured on ice. Extraction with dichloromethane followed by removal of solvent gave the diethyl ester of the title compound as an oil. This was mixed with 85 mL of acetic acid and 17 mL of concentrated HCl and heated at 70 °C overnight. Volatiles were removed in vacuo, the residue diluted with water, and the diacid extracted with ether. The dried ether solution was concentrated in vacuo and the residue triturated with 100 mL of dichloromethane until it was converted to a powder. The isolated solid (14.3 g, 45%) had mp 173 °C (dec.); ^{1}H NMR (acetone-d_6) δ 5.43 (s, 4), 4.87 (s, 4).

3,5,5,7-Tetranitro-3,7-diaza-1,9-nonanediol (12). The above diacid (7.8 g, 0.021 mol) was added to an ice-cooled THF·BH_3 solution (1 M, 86 mL). After 24 h at 20 °C the solution was poured into water and this solution extracted with ether. The dried ether solution was concentrated in vacuo to 8.4 g of oil. A dichloromethane/methyl acetate (7:3) solution of the oil was filtered through silica gel and separate fractions were collected. The fractions which crystallized after evaporation of solvent were combined and recrystallized from dichloroethane/acetone to give 5.7 g (79%) of diol **12**. Material which was dried at 55 °C in vacuo overnight and in the presence of P_2O_5 had mp 95–97 °C; ^{1}H NMR (acetone-d_6) δ 5.42 (s, 4), 4.06 (m, 8).

Registry No. **1**, 99214-04-7; **2**, 99214-05-8; **3**, 99214-06-9; **4**, 26330-03-0; **5**, 99214-08-1; **6**, 99214-11-6; **7**, 84487-90-1; **8**, 99214-13-8; **9**, 99214-16-1; **10**, 94897-61-7; **11**, 99214-18-3; **12**, 99214-19-4; **13**, 32776-78-6; hexanedial, 1072-21-5; fluorodinitromethane, 7182-87-8; heptanedial, 53185-69-6; octanedial, 638-54-0; 2,2-diethoxyethanol, 621-63-6; 3-acetoxy-2,2-dinitropropyl allyl ether, 99214-07-0; 3-hydroxy-2,2-dinitropropyl allyl ether, 76828-30-3; acetyl chloride, 75-36-5; 6-acetoxy-5,5-dinitro-3-oxahexanal oxime, 99214-09-2; 7-acetoxy-1-fluoro-1,1,6,6-tetranitro-4-oxa-2-heptanol, 99214-10-5; 7-acetoxy-2,2,6,6-tetranitro-4-

oxaheptanol, 99214-12-7; 3,3,3-trinitropropanol, 87695-55-4; 4,4,4-trinitrobutyric acid, 5029-46-9; potassium 3,3-dinitropropanol, 12287-13-7; potassium 3,3-dinitropropyl acetate, 94921-20-7; 3,3-dinitropropyl acetate, 29610-00-2; 3-bromopropyl acetate, 592-33-6; 3-nitropropyl acetate, 21461-49-4; 3-nitropropanol, 25182-84-7; 3-nitropropyl nitrate, 99214-14-9; 3,3,7,7-tetranitro-5-azanonane-1,9-diol 1,9-diacetate, 99214-15-0; 3,3,5,7,7-pentanitro-5-azanonane-1,9-diol 1,9-diacetate, 99232-50-5; 3-(2-acetoxyethyl)-5,5-dinitroperhydroorazepine, 99214-17-2; 2-aminoethyl acetate hydrochloride, 20739-39-3; methyl trinitrobutyrate, 5857-63-6; methyl 5-hydroxy-4,4-dinitropentanoate, 29596-18-7; 2,4,4,6-tetranitro-2,6-diaza-1,7-heptanedicarboxylic acid, 99232-49-2.

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Syntheses of 2-(2-Hydroxyethylamino) Fatty Acids

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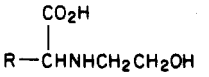
Eight 2-(2-hydroxyethylamino) fatty acids, 2-(2-hydroxyethylamino)decanoic, -undecanoic, -dodecanoic, -tetradecanoic, -hexadecanoic, -octadecanoic, -nonadecanoic, and -docosanoic acid, were synthesized by reacting 2-bromo fatty acids with more than 3 mol of 2-aminoethanol. The surface tension and the critical micelle concentration were determined for these compounds.

In an extension of my interest in the synthesis and study of the surface activity of nitrogenous surfactants derived from long chain fatty acids **1**, the 2-(2-hydroxyethylamino) fatty acids **3** were synthesized.

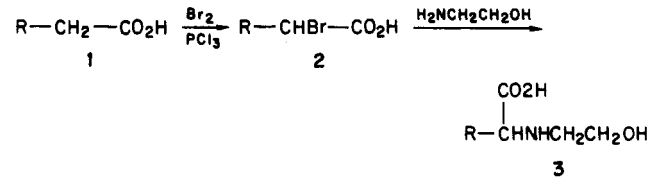


3A, R = *n*-C_8H_{17}; **3B**, R = *n*-C_9H_{19}
3C, R = *n*-$C_{10}H_{21}$; **3D**, R = *n*-$C_{12}H_{25}$
3E, R = *n*-$C_{14}H_{29}$; **3F**, R = *n*-$C_{16}H_{33}$
3G, R = *n*-$C_{17}H_{35}$; **3H**, R = *n*-$C_{20}H_{41}$

These compounds all have surface activity. The surface tensions and the critical micelle concentrations of compounds **3** were determined and are reported in Table II. The desired compounds were obtained according to the reaction pathway outlined in Scheme I. The synthesis of these compounds comprises the preparation of 2-bromo fatty acids by direct bromination of the appropriate fatty acids in the presence of phosphorous trichloride. More than 3 mol of 2-aminoethanol was allowed to react with the 2-bromo fatty acid to provide compound **3**.

The structural formulas of compounds **3** were confirmed by elemental analysis, infrared (IR) spectra, and nuclear magnetic resonance (^{1}H NMR) spectra. ^{1}H NMR spectra for **3D**, as a representative sample, exhibited the following signals (δ ppm): 0.91 (triplet, 3 H, CH_3, J = 5 Hz), 1.30 (singlet, 22 H, $C_{11}H_{22}$), 2.30 (triplet, 2 H, N–CH_2, J = 8 Hz), 3.25 (singlet, 1 H, NH), 3.60

Scheme I



(multiplet, 1 H, CH–CO_2H), 3.85 (triplet, 2 H, CH_2OH, J = 6 Hz), 4.75 (singlet, 1 H, OH). The IR spectra of **3D** showed the following bands: 3430, 3130, 1730, 720 cm^{-1}.

Experimental Section

Melting points were taken under a microscope on a Kofler hot plate and are uncorrected. ^{1}H NMR spectra were run in $CDCl_3$, on a Varian FT-80A spectrometer. The chemical shifts are in parts per million [δ values with $(CH_3)_4Si$ as internal reference]. The IR spectra, as KBr disks, were recorded on Perkin-Elmer 683 infrared spectrophotometer. The solvents were purified by standard procedures. The analytical samples of all new compounds were purified by column chromatography on silica gel (100–200 mesh) with absolute ethanol. The surface tensions were measured with a Model JZHY-180 tensiometer at room temperature with 10-min surface age (*1*). That exhibited sharp breaks in their surface tension curves which corresponded to critical micelle concentration of the compounds **3**.

***2-Bromoacids* (*2*).** These compounds were prepared by reacting dry bromine with a mixture of fatty acid and phosphorus trichloride respectively. An excess of bromine (0.2 mole), which had been previously dried with concentrated sulfuric acid, was slowly dropped into a mixture of 0.1 mole of fatty acid which was mixed with a drop of phosphorous trichloride. After most of the bromine had been added, the mixture was heated on a boiling water bath until the fumes of hydrobromic acid had practically ceased. The reddish, oily

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