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SYNTHESIS OF FLUORINE-CONTAINING NITRO COMPOUNDS

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SUMMARY

Fluoronitro alkanes (**5a** and **5b**), possessing the structure $-CF_2CH_2CH(NO_2)_2$, were synthesized from 1-iodo-1H,1H,2H,2H-perfluoroalkanes by displacing the iodide with sodium nitrite and then oxidatively nitrating the 1-nitro-1H,1H,2H,2H-perfluoroalkanes with tetranitromethane. Reaction with formaldehyde gave the dinitroalcohols, **6a** and **6b**. α,ω-Diiodoperfluoroalkanes (**1c** and **1d**) were similarly converted to tetranitrofluoroalkanes (**5c** and **5d**), characterized as tetranitrodiols, **6c** and **6d**, and Michael adducts with methyl acrylate, **7c** and **7d**.

INTRODUCTION

Synthesis of compounds containing the $-CF_2CH_2CH_2NO_2$ group has been limited to 1-nitro-1H,1H,2H,2H-perfluoropentane [1], prepared by the aldol condensation of nitromethane with perfluorobutyraldehyde, followed by acetylation, elimination, and reduction of the aldol adduct. Although displacement of an alkyl halide with silver nitrite (Victor-Meyer reaction) [2] or sodium nitrite [3] is a general method for preparing nitroalkanes, its application to fluorinated substrates has not been reported.

RESULTS AND DISCUSSION

Perfluoroalkyl iodides, 1-iodoperfluorohexane (**1a**) and 1-iodoperfluorodecane (**1b**), and diiodides, 1,4-diiodoperfluorobutane (**1c**) and 1,6-diiodoperfluorohexane (**1d**), were reacted with ethylene at 170 °C [4] to give the corresponding ethylene adducts **2a-d** in 85-95% yields.

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$$\underset{\textbf{1a,b}}{R_f\text{-}I} + CH_2{=}CH_2 \xrightarrow{170^\circ C} \underset{\textbf{2a,b}}{R_f\text{-}CH_2CH_2I}$$

a: $R_f = C_6F_{13}$; b: $R_f = C_{10}F_{21}$

$$\underset{\textbf{1c,d}}{I\text{-}(CF_2)_n\text{-}I} + CH_2{=}CH_2 \xrightarrow{170^\circ C} \underset{\textbf{2c,d}}{ICH_2CH_2\text{-}(CF_2)_n\text{-}CH_2CH_2I}$$

c: $n = 4$; d: $n = 6$

The displacement of **2b** with sodium nitrite in DMF, in the presence of urea and phloroglucinol, gave 1-nitro-1H,1H,2H,2H-perfluorododecane (**3b**) in 52% yield. The side product, 1H,1H,2H,2H-perfluorododecane-1-ol (**4b**), resulting from the hydrolysis of the corresponding nitrite ester, was isolated in 40% yield. Similarly, reactions of **2a**, **2c**, and **2d** with sodium nitrite in DMF gave 1-nitro-1H,1H,2H,2H-perfluorohexane (**3a**), 1,8-dinitro-1H,1H,2H,2H,-7H,7H,8H,8H-perfluorooctane (**3c**), and 1,10-dinitro-1H,1H,2H,2H,9H,9H,10H,10H-perfluorodecane (**3d**) in 24%, 27%, and 35% yields, respectively.

$$\underset{\textbf{2a,b}}{R_fCH_2CH_2\text{-}I} + NaNO_2 \xrightarrow[25^\circ C]{DMF} \underset{\textbf{3a,b}}{R_fCH_2CH_2\text{-}NO_2} + \underset{\textbf{4b}}{R_fCH_2CH_2\text{-}OH}$$

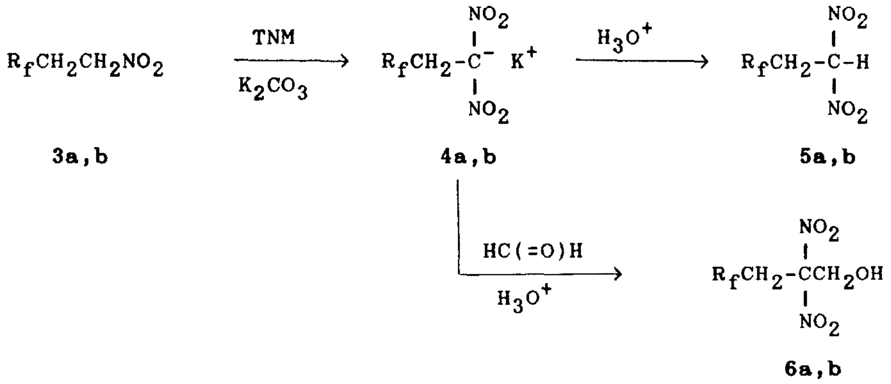
a: $R_f = C_6F_{13}$, b: $R_f = C_{10}F_{21}$

$$\underset{\textbf{2c,d}}{I\text{-}CH_2CH_2\text{-}(CF_2)_n\text{-}CH_2CH_2\text{-}I} \xrightarrow[DMF/25^\circ C]{NaNO_2} \underset{\textbf{3c,d}}{O_2NCH_2CH_2\text{-}(CF_2)_n\text{-}CH_2CH_2NO_2}$$

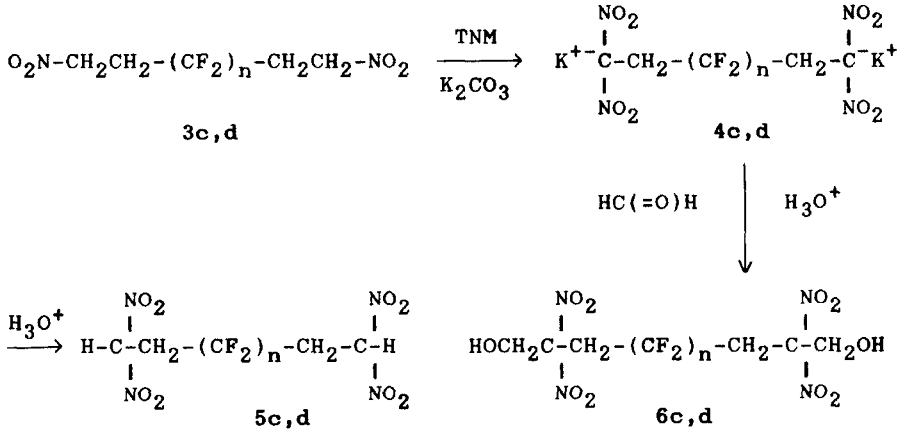
c: $n = 4$, d: $n = 6$

Attempts to convert the terminal nitroalkanes (**3a–d**) to terminal *gem*-dinitroalkanes by the Kaplan-Schecter oxidative nitration [5] or the potassium ferricyanide-sodium persulfate procedure [6] were unsuccessful. Alternatively, a modified oxidative nitration procedure, employing tetranitromethane (TNM) [7], was adopted. Nitro compounds **3a–d** were reacted with excess TNM in methanolic potassium carbonate solution to give the dinitro- and tetranitro potassium salts **4a–d**. Acidification of these salts with hydrochloric acid gave the *gem*-dinitro compounds **5a–d** in 36% to 68% yields.

Formylation of the potassium salts 4a-d with aqueous formaldehyde gave fluoronitro alcohols 6a-d in 51% to 75% yields.

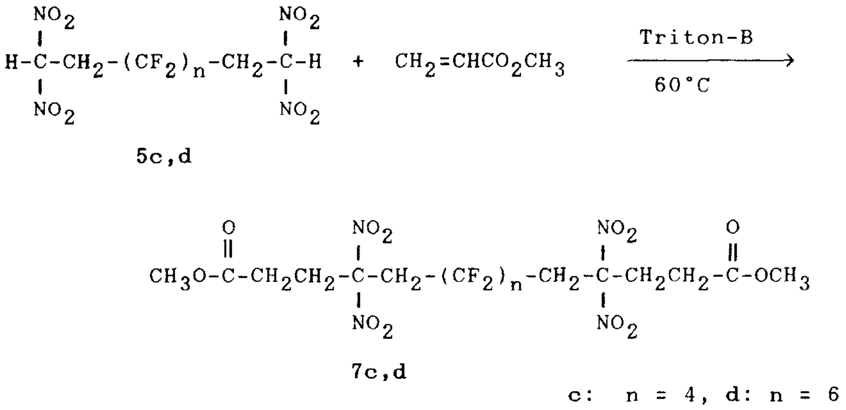


a: $R_f = C_6F_{13}$, b: $R_f = C_{10}F_{21}$



c: n = 4; d: n = 6

The reaction of 1,1,6,6-tetranitrohexane with methyl acrylate using sodium hydroxide in aqueous methanol was reported by Nielsen et al. [8] to give the corresponding diester in 83% yield. Extension of these reaction conditions to the fluorinated derivative 5c gave the bis-adduct, 6,6,7,7,8,8,-9,9-octafluoro-4,4,11,11-tetranitrotetradecanedioate (7c), in 17% yield. A 43% yield of 7c was obtained using aqueous dioxane as the solvent at 60 °C in the presence of Triton-B. Similarly, **5d** was reacted with methyl acrylate to give **7d** in 20% yield.



$$H\text{-}C(NO_2)_2\text{-}CH_2\text{-}(CF_2)_n\text{-}CH_2\text{-}C(NO_2)_2\text{-}H + CH_2{=}CHCO_2CH_3 \xrightarrow[60^\circ C]{\text{Triton-B}}$$

5c,d

$$CH_3O\text{-}C(=O)\text{-}CH_2CH_2\text{-}C(NO_2)_2\text{-}CH_2\text{-}(CF_2)_n\text{-}CH_2\text{-}C(NO_2)_2\text{-}CH_2CH_2\text{-}C(=O)\text{-}OCH_3$$

7c,d

c: n = 4, d: n = 6

EXPERIMENTAL

Perfluoroalkyl iodides **1a** and **1b** were purchased from Aldrich Chemical Co., whereas diiodides **1c** and **1d** were prepared by a literature procedure [9]. IR spectra were recorded on a Perkin-Elmer 700 spectrometer. ^1H and ^{19}F NMR spectra were recorded on a Varian T-60 spectrometer and are reported in ppm downfield relative to TMS and $FCCl_3$.

Caution: Polynitro compounds are potentially explosive and should be handled with appropriate precautions. Tetranitromethane (TNM) in hydrocarbon solvents forms an extremely hazardous mixture. Salts **4a-d** may be contaminated with potassium nitroform and should not be dried completely.

Preparation of Nitro Compounds by Sodium Nitrite Displacement

(a) 1-Nitro-1H,1H,2H,2H-perfluorooctane (**3a**)

A mixture of **2a** (16.5 *g*, 34.8 mmol), sodium nitrite (6.0 *g*, 87 mmol) and urea (5.5 *g*, 92 mmol) in DMF (350 mL) was stirred at *ca.* 0°C for 4 h. Phloroglucinol dihydrate (7.0 *g*, 43 mmol) was added and the mixture was stirred at room temperature for an additional 16 h. The reaction mixture was diluted with diethyl ether and poured over crushed ice and water. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3x). The combined ethereal layers were washed with water, aqueous sodium sulfite, water (2x), and brine (2x), dried, filtered and evaporated under reduced pressure to give 10.7 g of a brown oil. This oil was chromatographed over silica gel (90% dichloromethane/hexane) to give 3.7 g (27%) of **3a**: mp 27-29°C; IR (CH_2Cl_2) 2970, 1550 and 1100-1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.6-3.4 (m, 2 H) and 4.90 (t, J = 7 Hz, 2 H); ^{19}F NMR ($CDCl_3$) δ -80.4 (3 F), -111.6 (2 F), -120.0 (6 F), and -123.6 (2 F). **Anal** Calcd. for $C_8H_4F_{13}NO_2$: C, 24.4; H, 1.0; N, 3.6; F, 62.8. Found: C, 24.7; H, 1.0; N, 4.0; F, 62.9.

(b) 1-Nitro-1H,1H,2H,2H-perfluorododecane (**3b**)

A mixture of **2b** (1.3 g, 2.0 mmol), sodium nitrite (0.35 g, 5.1 mmol) and urea (0.35 g, 5.8 mmol) in 2:1 DMF/Freon 113 (30 mL) was stirred at ca. 0°C for 4 h, treated with phloroglucinol dihydrate (0.4 g, 2.5 mmol), and stirred at room temperature for 20 h. Work-up as described for **3a**, followed by chromatography of the crude product over silica gel (dichloromethane), gave 0.60 g (51%) of **3b**: mp 111-112°C (hexane/dichloromethane); IR (KBr) 1545 and 1100-1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.66 (t, J = 7 Hz, 2 H) and 2.92 (m, 2 H); ^{19}F NMR ($CDCl_3$) δ -80.2 (3 F), -111.6 (2 F), -118.2 (14 F) and -122.6 (2 F). **Anal.** Calcd for $C_{12}H_4F_{21}NO_2$: C, 24.3; H, 0.7; N, 2.4. Found: C, 23.9; H, 0.7; N, 2.5.

(c) 1,8-Dinitro-3,3,4,4,5,5,6,6-octafluorooctane (**3c**).

A mixture of **2c** (2 g, 4 mmol), sodium nitrite (1.5 g, 22 mmol) and urea (1.5 g, 25 mmol) in DMF (25 mL) was stirred at ca. 0°C for 4 h, treated with phloroglucinol dihydrate (1.1 g, 6.8 mmol), and stirred at room temperature for an additional 16 h. Work-up as described for **3a**, followed by chromatography of the crude product over silica gel (dichloromethane), gave 0.30 g (22%) of **3c**: mp 77-78°C (hexane/dichloromethane); IR (KBr) 3050, 1545 and 1100-1270 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.66 (t, J = 7 Hz, 4 H) and 2.89 (m, 4 H); ^{19}F NMR ($CDCl_3$) δ -112.0 (4 F) and -120.4 (4 F). **Anal.** Calcd for $C_8H_8N_2F_8O_4$: C, 27.6; H, 2.3; F, 43.6; N. 8.0. Found: C, 27.5; H, 2.4; F, 43.6; N, 8.0.

(d) 1,10-Dinitro-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodecane (**3d**)

A mixture of **2d** (1.8 g, 2.9 mmol), sodium nitrite (1.0 g, 14 mmol) and urea (1.0 g, 17 mmol) in DMF (25 mL) was stirred at ca. 0°C for 4 h, treated with phloroglucinol dihydrate (0.80 g, 4.9 mmol), and stirred at room temperature for an additional 18 h. Work-up as described for **3a**, followed by chromatography of the crude product over silica gel (dichloromethane), gave 0.45 g (34%) of **3d**: mp 100-101°C (hexane/dichloromethane); IR (KBr) 3050, 2975, 1540 and 1100-1280 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.69 (t, J = 6.5 Hz, 4 H) and 2.92 (m, 4 H); ^{19}F NMR ($CDCl_3$) δ -111.6 (4 F) and -118.4 to -120.0 (8 F). **Anal.**

Calcd for $C_{10}H_8F_{12}N_2O_4$: C, 26.8; H, 1.8; N, 6.2; F, 50.9. Found: C, 26.7; H, 1.9; N, 6.2; F, 50.6.

Oxidative Nitration

(a) 1,1,8,8-Tetranitro-1H,2H,2H,7H,7H,8H-perfluorooctane (**5c**)

A mixture of **3c** (0.73 g, 2.1 mmol) and potassium carbonate (1.3 g, 9.6 mmol) in methanol was stirred at room temperature for 30 min. Tetranitromethane (3.2 g, 16.3 mmol) was added over 10 min and the mixture was stirred at room temperature for an additional 18 h. The reaction mixture was diluted with dichloromethane (400 mL), filtered, and the solid was washed with dichloromethane. The yellow solid was dissolved in water (ca. 200 mL), cooled (ca. 5 °C), and acidified with cold 10% HCl. The aqueous layer was extracted with diethyl ether (3 x 100 mL) and the combined ethereal layers were washed with water (3 x 200 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a light brown solid (0.77 g). Recrystallization of the crude product from diethyl ether/hexane gave 0.63 g (68%) of **5c**: mp 104-105°C; IR (CH_2Cl_2) 1595 and 1100-1280 cm^{-1}; ^1H NMR ($CD_3CN/CDCl_3$) δ 7.5 (t, J = 8 Hz, 2 H) and 3.9 (m, 4 H); ^{19}F NMR (acetone-d_6) δ -107.7 (4 F) and -118.1 (4 F). **Anal.** Calcd for $C_8H_6F_8N_4O_8$: C, 21.9; H, 1.4; N, 12.8. Found: C, 22.1; H, 1.4; N, 12.5.

(b) 1,1-Dinitro-1H,2H,2H-perfluorooctane (**5a**)

A solution of **3a** (1.5 g, 3.8 mmol) in methanol (45 mL) was reacted with tetranitromethane (3.1 g, 15.8 mmol) in the presence of potassium carbonate (1.2 g, 8.7 mmol) to give, after acidification of the potassium salt with 10% aqueous HCl and recrystallization of the crude product from hexane/diethyl ether, 0.60 g (36%) of **5a**: mp 70-71.5°C; IR (CH_2Cl_2) 3000, 1590, and 1100-1250 cm^{-1}; ^1H NMR (acetone-d_6) δ 6.96 (t, J = 6 Hz, 1 H) and 3.53 (dt, J = 16 and 6 Hz, 2 H). **Anal.** Calcd for $C_8H_3F_{13}N_2O_4$: C, 21.9; H, 0.7; N, 6.4. Found: C, 22.6; H, 0.9; N, 6.6.

(c) 1,1-Dinitro-1H,2H,2H-perfluorododecane (**5b**)

A solution of **3b** (1.65 g, 2.8 mmol) in methanol (53 mL) was reacted with tetranitromethane (2.2 g, 11.2 mmol) in the presence of potassium carbonate (0.85 g, 6.2 mmol) to give, after acidification of the potassium salt with 10% aqueous HCl and recrystallization of the crude product from hexane/diethyl ether, 1.1 g (62%) of **5b**: mp 90-93°C ; IR (film) 3025, 1590, and 1100-1300

cm^{-1}; ^1H NMR (acetone-d_6) δ 7.0 (t, J = 7 Hz, 1 H) and 3.50 (m, 2 H). This material was converted directly to the alcohol **6b**.

(d) 1,1,10,10-Tetranitro-1H,2H,2H,9H,9H,10H-perfluorodecane (**5d**)

A solution of **3d** (1.0 g, 2.2 mmol) in methanol (80 mL) was reacted with tetranitromethane (3.5 g, 17.8 mmol) in the presence of potassium carbonate (1.42 g, 10.3 mmol) to give, after acidification of the potassium salt and recrystallization of the crude product from hexane/diethyl ether, 0.60 g (50%) of **5d**: mp 131-133°C; IR (neat) 3050, 1595, and 1150-1300 cm^{-1}; ^1H NMR (acetone-d_6) δ 6.95 (t, J = 7 Hz, 2 H) and 3.6 (dt, J = 7 Hz and 17 Hz, 4 H); ^{19}F NMR (acetone-d_6) δ -121.6 (4 F), -120.0 (4 F) and -110.4 (4 F). **Anal.** Calcd for $C_{10}H_6F_{12}N_4O_8$: C, 22.3; H, 1.1; F, 42.4. Found: C, 23.0; H, 1.2; F, 42.6.

Preparation of Fluoronitro Alcohols

(a) 2,2,9,9-Tetranitro-1H,1H,3H,3H,8H,8H,10H,10H-perfluorodecane-1,10-diol (**6c**)

A solution of **3c** (2.81 g, 8.08 mmol) and sodium carbonate (4.2 g, 39.6 mmol) in methanol (100 mL) was stirred at room temperature for 15 min. Tetranitromethane (12.0 g, 60.7 mmol) was added over 10 min and the mixture was stirred at room temperature for an additional 18 h. The mixture was diluted with CH_2Cl_2 (500 mL) and the precipitated salt (yellow solid) was filtered and washed with CH_2Cl_2 (2 x 100 mL). The solid was dissolved in methanol (40 mL) and 37% aqueous formaldehyde (25 mL), and the mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with water, acidified with glacial acetic acid, and extracted with diethyl ether. The combined ethereal extracts were washed with water (3x), dried, filtered and concentrated under reduced pressure to give a yellow solid. Recrystallization of this solid from diethyl ether/hexane gave 2.4 g (55%) of **6c**: mp 144-6°C; IR (neat) 1575, 1180, 1120 cm^{-1}; ^1H NMR (acetone-d_6) δ 4.53 (s, 4 H) and 3.75 (t, J = 18 Hz, 4 H); ^{19}F NMR (acetone-d_6) δ -121.2 (4 F) and -110.8 (4 F). **Anal.** Calcd. For $C_{10}H_{10}N_4F_8O_{10}$: C, 24.1; H, 2.0; F, 30.5. Found: C, 24.3; H, 2.1; F, 30.5.

(b) 2,2-Dinitro-1H,1H,3H,3H-perfluorononane-1-ol (**6a**)

A mixture of **3a** (1.0 g, 2.5 mmol), potassium carbonate (0.81 g, 5.9 mmol) and tetranitromethane (2 g, 10.2 mmol) in methanol (30 mL) was stirred at room temperature for 20 h. Dichloromethane was added and the precipitated salt was filtered, dissolved in methanol (15 mL), and reacted with 37% aqueous formaldehyde (22 mL) to give, after recrystallization from hexane/ dichloromethane, 0.67 g (55%) of **6a**: mp 91-92°C; IR (CH_2Cl_2) 3550, 3050, 1590 and 1150-1250 cm^{-1}; ^1H NMR (acetone-d_6) δ 5.30 (m, exchanges with D_2O), 4.33 (s, 2 H) and 3.60 (t, J = 17 Hz, 1 H). **Anal.** Calcd for $C_9H_5F_{13}N_2O5$: C, 23.1; H, 1.1; N, 5.9. Found: C, 22.8; H, 1.1; N, 5.9.

(c) 2,2-Dinitro-1H,1H,3H,3H-perfluorotridecane-1-ol (**6b**)

A mixture of **3b** (1.0 g, 1.7 mmol), potassium carbonate (0.52 g, 3.8 mmol) and tetranitromethane (1.3 g, 6.6 mmol) in a 3:1 mixture of methanol/THF (40 mL) was stirred at room temperature for 20 h. Dichloromethane was added and the precipitated salt was filtered, dissolved in methanol (7 mL) and reacted with 37% aqueous formaldehyde (15 mL) to give, after recrystallization from chloroform, 0.58 g (51%) of **6b**: mp 124.5-126°C; IR (thin film) 3550, 3050, 1590 and 1100-1300 cm^{-1}; ^1H NMR (acetone-d_6) δ 5.59 (m, exchanges with D_2O, 1 H), 4.63 (s, 2 H) and 3.82 (t, J = 17 Hz, 2 H). **Anal.** Calcd for $C_{13}F_{21}H_5O_5N_2$: C, 23.4; H, 0.7; N, 4.2. Found: C, 23.3; H, 0.7; N, 4.4.

(d) 2,2,11,11-Tetranitro-1H,1H,3H,3H,10H,10H,12H,12H-perfluorododecane-1,12-diol (**6d**)

A mixture of **3d** (3.62 g, 8.08 mmol), sodium carbonate (3.0 g, 28.3 mmol) and TNM (12.0 g, 60.7 mmol) in methanol (150 mL) was stirred at room temperature for 19 h. Dichloromethane was added and the precipitated salt was filtered, dissolved in methanol (40 mL), and reacted with 37% aqueous formaldehyde (25 mL) to give, after recrystallization from diethyl ether/ hexane, 3.65 g (75%) of **6d**: mp 152-4°C; IR (thin film) 3460, 1575 and 1125-1300 cm^{-1}; ^1H NMR (acetone-d_6) δ 4.60 (s, 4 H) and 3.55 (t, J = 17 Hz, 4 H); ^{19}F NMR (acetone-d_6) δ -121.3 (4 F), -119.6 (4 F) and -110.8 (4 F). **Anal.** Calcd for $C_{12}H_{10}F_{12}N_4O_{10}$: C, 24.1; H, 1.7; F, 38.1. Found: C, 24.5; H, 1.8; F, 37.8.

Preparation of Michael Adducts

(a) Dimethyl 6,6,7,7,8,8,9,9-octafluoro-4,4,11,11-tetranitrotetradecanedioate (7c)

A solution of methyl acrylate (1.1 g, 12.8 mmol) in 8:1 dioxane/water (17 mL) was added over 45 min to a preheated solution (ca. 60 °C) of **5c** (1.0 g, 2.3 mmol) and Triton-B (1.0 mL) in 5:1 dioxane/water (77 mL). After the mixture was stirred 21 h at 60°C, a second portion of methyl acrylate (0.8 g, 9.3 mmol), dissolved in dioxane (8 mL), was added and the mixture was stirred at 60°C for 6 h and at room temperature for 2 d. The mixture was diluted with dichloromethane and poured over crushed ice, water and concentrated HCl (3 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water (2x), 10% aqueous sodium carbonate (2x), and brine (2x), dried, filtered and evaporated under reduced pressure to give a brown semi-solid. The residue was triturated with diethyl ether, cooled and filtered to give 0.60 g (43%) of **7c**: mp 132-133°C (acetone/H_2O); IR (CH_2Cl_2) 2950, 1750, 1590 and 1100-1300 cm^{-1}; ^1H NMR (acetone-d_6) δ 4.01 (t, J = 17 Hz, 4 H), 3.71 (s, 6 H), 3.15 (t, J = 6 Hz, 4 H) and 2.78 (t, J = 6 Hz, 4 H); ^{19}F NMR ($CDCl_3$) δ -110.4 (4 F) and -121.2 (4 F). **Anal.** Calcd for $C_{16}H_{18}F_8N_4O_{12}$: C, 31.5; H, 3.0; N, 9.2; F, 24.9. Found: C, 31.3; H, 2.9; N, 9.1; F, 24.7.

(b) Dimethyl 6,6,7,7,8,8,9,9,10,10,11,11-dodecafluoro-4,4,13,13-tetranitrohexadecanedioate (**7d**)

A solution of **5d** (0.59 g, 1.07 mmol) in 5:1 dioxane/water (43 mL) was reacted with methyl acrylate (1.6 g, 18.6 mmol) in the presence of Triton-B (0.6 mL) at 60°C for 8 h. Work-up as described for **7c** followed by trituration of the residue with diethyl ether gave 0.16 g (20%) of **7d**: mp 139-140°C; IR (CH_2Cl_2) 3050, 2975, 1585, and 1100-1300 cm^{-1}; ^1H NMR (acetone-d_6) δ 4.04 (t, J = 18 Hz, 4 H), 3.75 (s, 6 H), 3.10 (t, J = 6 Hz, 4 H) and 2.83 (t, J = 6 Hz, 4 H). **Anal.** Calcd for $C_{18}H_{18}F_{12}N_4O_{12}$: C, 30.4; H, 2.5; F, 32.1. Found: C, 29.6; H, 2.6; F, 32.5.

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