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Ethyl butyrates bearing nitro and difluoroamino groups

Igor L. Dalinger, Tatyana K. Shkineva and Aleksei B. Sheremetev

All the reagents were of analytical grade, purchased from commercial sources, and used as received. Infrared spectra were determined in NaCl pellets on a Bruker Alpha spectrometer. The ^{1}H and ^{19}N NMR spectra were recorded on a Bruker AM-300 instrument at 300 and 282 MHz, respectively. The chemical shift values (δ) are expressed relative to the chemical shift of the [D]solvent or to external standard without correction CF_3CO_2H (^{19}F). Analytical TLC was performed using commercially pre-coated silica gel plates (Silufol UV254). Melting points were determined on Boetius melting point apparatus and they are uncorrected. Elemental analyses were obtained by using a CHNS/O Analyzer 2400 (Perkin-Elmer instruments Series II). Density was determined by helium gas pycnometer AccuPyc II 1340 at 298 K. Thermal stability of compounds was monitored using DSC 822e Mettler Toledo apparatus at a scan rate of 5 °C min^{-1}.

CAUTION: All difluoroamines are relatively sensitive high explosives and should be prepared and handled only by qualified personnel!

Methyl 4-difluoroamino-4,4-dinitrobutanoate **6**. Potassium salt **5** (4.57 g, 20 mmol) and $MgSO_4$ (50 g) were dissolved in water (100 mL) and cooled to 0 °C. Gaseous F_2NOSO_2F (10 g, 66 mmol) was then slowly bubbled through the solution for 1 h maintaining a temperature of 5°C. The resulting solution was then left to stir at 5°C for 2 h, purged with nitrogen and extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were washed sequentially with 2% Na_2CO_3 (3×25 mL) solution and water (3×15 mL), dried ($MgSO_4$) and evaporated under reduced pressure to leave a yellow oil. The residue was recrystallized from hexane affording product **6** as a colorless microcrystalline solid (1.83 g, 38%), mp 32-33 °C. ^{1}H NMR (CCl_4) δ: 2.62 (m, 2H, $CH_2C(O)$), 3.25 (t, 2H, $CH_2C(NO_2)_2NF_2$), 3.67 (s, 3H, OCH_3). ^{19}F NMR (CCl_4) δ: -111.2 (b.s, NF_2). IR (ν/cm^{-1}): 1740 (C=O), 1600, 1588, 1312 (NO_2), 1225, 1213 (C-O-C), 993, 915, 896, 840. Found (%): C, 24.75; H, 2.93; N, 17.22. Calc. for $C_5H_7F_2N_3O_6$ (243.12) (%): C, 24.70; H, 2.90; N, 17.28.

4-Difluoroamino-4,4-dinitrobutanoic acid **7**. A mixture of ester **6** (14.35 g, 59 mmol) and 38% HNO_3 (70 mL) was stirred for 4 h at ~70°C and then diluted with cold H_2O (300 mL) and extracted using CH_2Cl_2 (3×200 mL). The combined organic extracts were washed with H_2O (2×200 mL), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was recrystallized from CCl_4 to afford a colorless crystalline solid (11.3 g, 84%), mp 54.5-55.5 °C. ^1H NMR (CCl_4) δ: 2.63 (m, 2H, $CH_2C(O)$), 3.20 (m, 2H, $CH_2C(NO_2)_2NF_2$), 11.39 (b.s, 1H, OH). ^{19}F NMR (CCl_4) δ: -112 (b.s, NF_2). IR (ν/cm^{-1}): 2800-3300, 1740 (C=O), 1605, 1590, 1312 (NO_2), 1018, 988, 920. Found (%): C, 20.84; H, 2.25; N, 18.26. Calc. for $C_4H_5F_2N_3O_6$ (220.10) (%): C, 20.97; H, 2.20; N, 18.34.

4-Difluoroamino-4,4-dinitrobutanoyl chloride **8**. A mixture of acid **7** (6.66 g, 29 mmol) and $SOCl_2$ (12 mL, 167 mmol) was stirred at 77-80°C for 4 h. An excess of $SOCl_2$ was evaporated under reduced pressure. The residue was distilled *in vacuo* to give product **8** as colorless oil (6.47 g, 90%), bp 67-67.5 °C/ 0.5 Torr. ^1H NMR (CCl_4) δ: 3.22 (b.s, 4H, CH_2CH_2). ^{19}F NMR (CCl_4) δ: -111 (b.s, NF_2). IR (ν/cm^{-1}): 1793 (C=O), 1602, 1589, 1308 (NO_2), 1016, 985, 960, 923. Found (%): C, 19.40; H, 1.58; N, 16.91. Calc. for $C_4H_4ClF_2N_3O_5$ (247.54) (%): C, 19.41; H, 1.63; N, 16.97.

2,2,2-Trinitroethyl 4-difluoroamino-4,4-dinitrobutanoate **9**. Chloride **8** (11.78 g, 48 mmol) was dissolved in dry DCE (25 mL) and reacted with a solution of 2,2,2-trinitroethan-1-ol (11.22 g, 62 mmol) in dry DCE (25 mL) in the presence of $AlCl_3$ (7.24 g, 54 mmol) that was added at 5-10°C. The resulting mixture was heated to 75 °C for 0.5 h, heated under the temperature with stirring over additional 5 h and cooled to 10°C. Next portion of $AlCl_3$ (4.53 g, 34 mmol) was added slowly, and the mixture was then heated at 80 °C for 3 h. The mixture was cooled to 20°C, poured into a mixture of ice-hydrochloric acid (300 mL) and extracted with CH_2Cl_2 (5×150 mL). The combined organic extracts were washed sequentially with saturated $NaHCO_3$ (4×150 mL) solution and water (2×150 mL) and dried ($MgSO_4$). Removal of the solvent yielded a residue, which was purified by a short column chromatography (silica gel, EtOAc/hexane, 1:3) to give product **9** (8.91 g, 48%) as an off-white solid, mp 80-81°C. ^1H NMR (CCl_4) δ: 2.76 (m, 2H, $CH_2C(O)$), 3.20 (b.s., 2H, $CH_2C(NO_2)_2NF_2$), 5.41 (b.s, 2H, OCH_2). ^{19}F NMR (CCl_4) δ: -111.2 (b.s, NF_2). IR (ν/cm^{-1}): 1783 (C=O), 1610 (NO_2), 1165 (C-O-C), 1016, 922. Found (%): C, 18.45; H, 1.56; N, 21.40. Calc. for $C_6H_6F_2N_6O_{12}$ (392.14) (%): C, 18.38; H, 1.54; N, 21.43.

2-Difluoroamino-2,2-dinitroethyl 4-difluoroamino-4,4-dinitrobutanoate **10**. Chloride **8** (8.52 g, 34 mmol) was dissolved in dry DCE (15 mL) and reacted with a solution of 2-difluoroamino-2,2-dinitroethan-1-ol (9.88 g, 53 mmol) in dry DCE (20 mL) in the presence of

$AlCl_3$ (6.2 g, 46 mmol) that was added at 5-10°C. The resulting mixture was heated to 80 °C for 0.5 h, heated under the temperature with stirring over additional 3 h and cooled to 10°C. Next portion of $AlCl_3$ (2 g, 15 mmol) was added slowly, and the mixture was then heated at 80 °C for 3 h. The mixture was cooled to 20°C, poured into a mixture of ice-hydrochloric acid (300 mL) and extracted with CH_2Cl_2 (5×150 mL). The combined organic extracts were washed sequentially with saturated $NaHCO_3$ (4×150 mL) solution and water (2×150 mL) and dried ($MgSO_4$). Removal of the solvent yielded a residue, which was purified by a short column chromatography (silica gel, EtOAc/hexane, 1:3) to give product **10** (7.38 g, 54%) as an off-white solid, mp 74-75°C. ^1H NMR (CCl_4) δ: 2.70 (m, 2H, $CH_2C(O)$), 3.23 (m, 2H, $CH_2C(NO_2)_2NF_2$), 5.30 (t, 2H, OCH_2). ^{19}F NMR (CCl_4) δ: -111.5 (b.s, NF_2). IR (ν/cm^{-1}): 1780 (C=O), 1608, 1590, 1308 (NO_2), 1170 (C-O-C), 1010, 920. Found (%): C, 18.16; H, 1.55; N, 21.30. Calc. for $C_6H_6F_4N_6O_{10}$ (398.14) (%): C, 18.10; H, 1.52; N, 21.11.

2-Difluoroamino-2,2-dinitroethyl 4,4,4-trinitrobutanoate **12**. 4,4,4-Trinitrobutanoyl chloride (**11**, 3.74 g, 15 mmol) was dissolved in dry DCE (10 mL) and reacted with a solution of 2-difluoroamino-2,2-dinitroethan-1-ol (5.30 g, 28 mmol) in dry DCE (10 mL) in the presence of $AlCl_3$ (4.15 g, 31 mmol) that was added at 5-10°C. The resulting mixture was heated to 80 °C for 1 h, heated under the temperature with stirring over additional 6 h and cooled to 20°C, poured into a mixture of ice-hydrochloric acid (250 mL) and extracted with CH_2Cl_2 (4×150 mL). The combined organic extracts were washed sequentially with saturated $NaHCO_3$ (6×100 mL) solution and water (2×100 mL) and dried ($MgSO_4$). Removal of the solvent yielded a residue, which was twice freezed from CCl_4-hexane (-50°C) to give product **12** (4.90 g, 81%) as colorless solid, mp 80-81°C. ^1H NMR (acetone-d_6) δ: 3.10 (m, 2H, CH_2CO), 3.67 (m, 2H, $CH_2C(NO_2)_2NF_2$), 5.59 (t, 2H, OCH_2). ^{19}F NMR (acetone-d_6) δ: -114.4 (b.s, NF_2). IR (ν/cm^{-1}): 1770 (C=O), 1595, 1585, 1303 (NO_2), 1166 (C-O-C), 1007, 920. Found (%): C, 18.45; H, 1.57; N, 21.37. Calc. for $C_6H_6F_2N_6O_{12}$ (392.14) (%): C, 18.38; H, 1.54; N, 21.43.