

## **A simple and efficient synthesis of 3-(polyfluoroalkyl)propane-1,2,3-trione 2-oximes**

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Lithium enolates **1a-f** were obtained by condensation of polyfluorocarboxylic acid esters with methylketones by the procedure reported previously.<sup>1</sup> The characteristics of enolates **1a-f** are reported in ref. 2.

The purity of products was checked by TLC on Sorbfil plates (UV-254, CHCl<sub>3</sub> as the eluent). The plates were visualized using UV light and an aqueous solution of Cu(OAc)<sub>2</sub>.

Analytical studies were carried out using equipment of the Center for Joint Use “Spectroscopy and Analysis of Organic Compounds” at the Postovsky Institute of Organic Synthesis of the Russian Academy of Sciences (Ural Branch).

IR spectra were recorded with a Spectrum One B spectrometer (Perkin Elmer) using a diffuse reflectance unit.

Identification and quantitative estimation of the reaction products were carried out using a Trace GC Ultra DSQ II gas chromatography/mass spectrometer, USA, with a Thermo TR-5ms quartz capillary column, 30 m in length and 0.25 mm in diameter, film thickness 0.25 μm (polymethylsiloxane, 5% of phenyl groups), and a quadrupole mass spectrometric detector (GC-MS). The MS was used in total ion current scan mode with a mass range from 20-1000 Da electron ionization (70 eV). The initial column temperature was 40°C (held for 3 min), then heating was performed at a rate of 10°C/min. The final column temperature was 280°C. The inlet temperature was 250°C, the detector temperature was 200°C, and the transfer line temperature was 200°C. Helium was used as the carrier gas, flow division 1:50, flow through the column 1.0 ml/min.

<sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded using an Avance III AV-500 (500 (<sup>1</sup>H), 376 (<sup>19</sup>F)) spectrometer with Me<sub>4</sub>Si (<sup>1</sup>H) and C<sub>6</sub>F<sub>6</sub> (<sup>19</sup>F) as the internal standards. The melting points of compounds were determined using Boetius and Stuart SMP3 instruments. Elementary analyses were carried out on a CHN PE 2400 ser. II automatic analyzer (Perkin Elmer).

#### 4,4,4-Trifluoro-1-phenylbutane-1,2,3-trione 2-oxime 2b

The reaction of lithium diketonate **1b** (1.9 g, 7.5 mmol) and sodium nitrite (0.6 g, 8.6 mmol) gave 1.9 g (92%) of compound **2b**, mp 132–133°C. Found, %: C, 49.08; F 22.66, H, 2.45; N, 5.63. C<sub>10</sub>F<sub>3</sub>H<sub>6</sub>NO<sub>3</sub>. Calculated, %: C, 48.99; F 23.25, H, 2.47; N, 5.71. IR (ν, cm<sup>-1</sup>): 3266, 3202, 1729, 1647, 1615, 1594, 1422, 1277, 1208, 1182, 1167, 1055, 975, 882, 776, 737, 679, 656. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: [ (7.48 – 7.59 m, 2H), (7.63 - 7.73 m, 1H); (7.77 – 7.85 m, 2H) Ph], 9.35 (s, 1H, OH). <sup>19</sup>F NMR (470.5 MHz, CDCl<sub>3</sub>) δ: 89.04 (s, CF<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ: 96.14, 115.63 (q, C<sup>4</sup>, *J* 290.3 Hz), 129.17, 129.31, 133.79, 135.39, 152.05, 176.56 (q, C<sup>3</sup>, *J* 37.9 Hz), 188.167.

GC-MS (EI, in CHCl<sub>3</sub>, TIC): t<sub>R</sub> 18.44 min. MS), *m/z* (*I*, %): 245 [M]<sup>+</sup> (2.7), 201 [M-CH<sub>2</sub>NO]<sup>+</sup> (0.5), 148 [M-CF<sub>3</sub>CO]<sup>+</sup> (1.4), 131 [C<sub>6</sub>H<sub>5</sub>COCN]<sup>+</sup> (4.1), 105 [C<sub>6</sub>H<sub>5</sub>CO]<sup>+</sup> (100), 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup> (60.3), 69 [CF<sub>3</sub>]<sup>+</sup> (8.9), 51 [HCF<sub>2</sub>]<sup>+</sup> (22.8), 39 [HF<sub>2</sub>]<sup>+</sup> (1.8), 27 [HCN]<sup>+</sup> (1.2).

#### 4,4,4-Trifluoro-1-(4-methylphenyl)butane-1,2,3-trione 2-oxime 2c

The reaction of lithium diketonate **1c** (1.77 g, 7.5 mmol) and sodium nitrite (0.6 g, 8.6 mmol) gave 1.77 g (91%) of compound **2c**, mp 138.5–139°C. Found, %: C, 50.82; H, 3.19; N, 5.45, F 22.00. C<sub>11</sub>H<sub>8</sub>F<sub>3</sub>NO<sub>3</sub>. Calculated, %: C, 50.97; H, 3.11; N, 5.40, F 21.99. IR (ν, cm<sup>-1</sup>): 3251, 3210, 1720, 1650, 1616, 1595, 1426, 1278, 1233, 1200, 1148, 1136, 1043, 972, 802, 680, 600. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 2.45 (s, 3H, CH<sub>3</sub>), [(7.33 d, 2H, <sup>1</sup>J=8.2 Hz), (7.71 d, 2H, <sup>1</sup>J=8.2 Hz); Ph], 8.97 (s, 1H, OH). <sup>19</sup>F NMR (470.5 MHz, CDCl<sub>3</sub>) δ: 89.07 (s, CF<sub>3</sub>).

GC-MS (EI, in C<sub>2</sub>H<sub>5</sub>OH, TIC): t<sub>R</sub> 19.97 min. MS), *m/z* (*I*, %): 259 [M]<sup>+</sup> (4.2), 215 [M-CH<sub>2</sub>NO]<sup>+</sup> (0.5), 162 [M-CF<sub>3</sub>CO]<sup>+</sup> (0.9), 145 [CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>COCN]<sup>+</sup> (2.0), 119 [CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CO]<sup>+</sup> (100), 91 [CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>]<sup>+</sup> (56.1), 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup> (1.1), 69 [CF<sub>3</sub>]<sup>+</sup> (6.5), 65 [C<sub>3</sub>H<sub>5</sub>]<sup>+</sup> (19.2), 51 [HCF<sub>2</sub>]<sup>+</sup> (2.5), 39 [HF<sub>2</sub>]<sup>+</sup> (4.8), 27 [HCN]<sup>+</sup> (0.2).

#### 4,4,5,5,6,6,7,7,7-Nonafluoro-1-phenylheptane-1,2,3-trione 2-oxime 2d

The reaction of lithium diketonate **1d** (2.79 g, 7.5 mmol) and sodium nitrite (0.6 g, 8.6 mmol) gave 2.62 g (89%) of compound **2d** as a white powder, mp 130–131°C. Found, %: C, 39.52; H, 1.51; N, 3.55, F 42.86. C<sub>13</sub>H<sub>6</sub>F<sub>9</sub>NO<sub>3</sub>. Calculated, %: C, 39.51; H, 1.53; N, 3.54, F 43.27. IR (ν, cm<sup>-1</sup>): 3251, 3210, 1720, 1650, 1616, 1595, 1426, 1278, 1233, 1200, 1148, 1136, 1043, 972, 802, 680, 600. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: [7.52- 7.56 (m, 2H); 7.67 – 7.70 (m, 1H) 7.80 – 7.82 (m, 2 H) Ph], 9.03 (br. s, 1H, OH). <sup>19</sup>F NMR (470.5 MHz, CDCl<sub>3</sub>) δ: 36.13-36.29 (m, 2 F, CF<sub>2</sub>), 40.39-40.47 (m, 2 F, CF<sub>2</sub>), 47.31-47.38 (m, 2 F, CF<sub>2</sub>), 80.93 (tt, <sup>3</sup>J=9.8, <sup>4</sup>J=2.20 Hz, CF<sub>3</sub>).

GC-MS (EI, in CHCl<sub>3</sub>, TIC): t<sub>R</sub> 19.58 min. MS), *m/z* (*I* %): 395 [M]<sup>+</sup> (1.7), 351 [M-CH<sub>2</sub>NO]<sup>+</sup> (0.3), 219 [C<sub>4</sub>F<sub>9</sub>]<sup>+</sup> (0.5), 169 [C<sub>3</sub>F<sub>7</sub>]<sup>+</sup> (0.1), 148 [M-C<sub>4</sub>F<sub>9</sub>CO]<sup>+</sup> (1.0), 131 [C<sub>6</sub>H<sub>5</sub>COCN]<sup>+</sup> (2.9), 119 [C<sub>2</sub>F<sub>5</sub>]<sup>+</sup> (1.5), 105 [C<sub>6</sub>H<sub>5</sub>CO]<sup>+</sup> (100), 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup> (53.1), 69 [CF<sub>3</sub>]<sup>+</sup> (9.1), 51 [HCF<sub>2</sub>]<sup>+</sup> (11.2), 39 [HF<sub>2</sub>]<sup>+</sup> (0.5), 27 [HCN]<sup>+</sup> (0.3).

#### **4,4,5,5,6,6,7,7-Octafluoro-1-phenylheptane-1,2,3-trione 2-oxime 2e**

The reaction of lithium diketonate **1e** (1.33 g, 3.75 mmol) and sodium nitrite (0.3 g, 4.3 mmol) gave 1.82 g (65%) of compound **2e** as a white powder, mp 118–118.5°C. Found, %: C, 41.37; H, 1.64; N, 3.70, F 39.93. C<sub>13</sub>H<sub>7</sub>F<sub>8</sub>NO<sub>3</sub>. Calculated, %: C, 41.39; H, 1.87; N, 3.71, F 40.29. IR (ν, cm<sup>-1</sup>): 3250, 3210, 1718, 1651, 1616, 1596, 1426, 1226, 1172, 1127, 1045, 978, 787, 679, 585. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 6.1 (tt, <sup>1</sup>J=52, <sup>3</sup>J=5.3 Hz, H(CF<sub>2</sub>)<sub>4</sub>), [7.52- 7.56 (m, 2H); 7.67 – 7.70 (m, 1H) 7.80 – 7.82 (m, 2 H) Ph], 9.13 (br.s, 1H, OH).

GC-MS (EI, in C<sub>2</sub>H<sub>5</sub>OH, TIC): t<sub>R</sub> 21.16 min. MS), *m/z* (*I*, %): 377 [M]<sup>+</sup> (2.1), 201 [HC<sub>4</sub>F<sub>8</sub>]<sup>+</sup> (0.2), 176 [M-HC<sub>4</sub>F<sub>8</sub>]<sup>+</sup> (0.1), 148 [M-HC<sub>4</sub>F<sub>8</sub>CO]<sup>+</sup> (1.3), 131 [C<sub>6</sub>H<sub>5</sub>COCN]<sup>+</sup> (1.8), 113 [HC<sub>3</sub>F<sub>2</sub>]<sup>+</sup> (1.0), 105 [C<sub>6</sub>H<sub>5</sub>CO]<sup>+</sup> (100), 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup> (49.3), 69 [CF<sub>3</sub>]<sup>+</sup> (3.5), 51 [HCF<sub>2</sub>]<sup>+</sup> (13.9), 39 [HF<sub>2</sub>]<sup>+</sup> (0.5), 27 [HCN]<sup>+</sup> (0.3).

#### **4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-1-phenylnonane-1,2,3-trione 2-oxime 2f**

The reaction of lithium diketonate **1f** (1.77 g, 3.75 mmol) and sodium nitrite (0.3 g, 4.3 mmol) gave 1.66 g (90%) of compound **2f** as a white powder, mp 136.8–137°C. Found, %: C, 36.28; H, 1.01; N, 2.87, F 49.10. C<sub>15</sub>H<sub>6</sub>F<sub>13</sub>NO<sub>3</sub>. Calculated, %: C, 36.38; H, 1.22; N, 2.83, F 49.88. IR (ν, cm<sup>-1</sup>): 3262, 3210, 1717, 1653, 1617, 1424, 1235, 1206, 1142, 1089, 1044, 987, 924, 747, 698, 588. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: [7.52- 7.56 (m, 2H); 7.67 – 7.70 (m, 1H) 7.80 – 7.82 (m, 2 H) Ph], 9.03 (br.s, 1H, OH).

GC-MS (EI, in C<sub>2</sub>H<sub>5</sub>OH, TIC): t<sub>R</sub> 20.40 min. MS), *m/z* (*I*, %): 495 [M]<sup>+</sup> (0.7), 231 [C<sub>5</sub>F<sub>9</sub>]<sup>+</sup> (0.1), 181 [C<sub>4</sub>F<sub>7</sub>]<sup>+</sup> (0.2), 169 [C<sub>3</sub>F<sub>9</sub>] (0.8), 148 [M-C<sub>6</sub>F<sub>13</sub>CO]<sup>+</sup> (1.3), 131 [C<sub>6</sub>H<sub>5</sub>COCN]<sup>+</sup> (3.0), 119 [C<sub>2</sub>F<sub>5</sub>]<sup>+</sup> (3.3), 105 [C<sub>6</sub>H<sub>5</sub>CO]<sup>+</sup> (100), 77 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup> (44.6), 69 [CF<sub>3</sub>]<sup>+</sup> (7.5), 51 [HCF<sub>2</sub>]<sup>+</sup> (9.9), 39 [HF<sub>2</sub>]<sup>+</sup> (0.4), 27 [HCN]<sup>+</sup> (0.3).

## **References**

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