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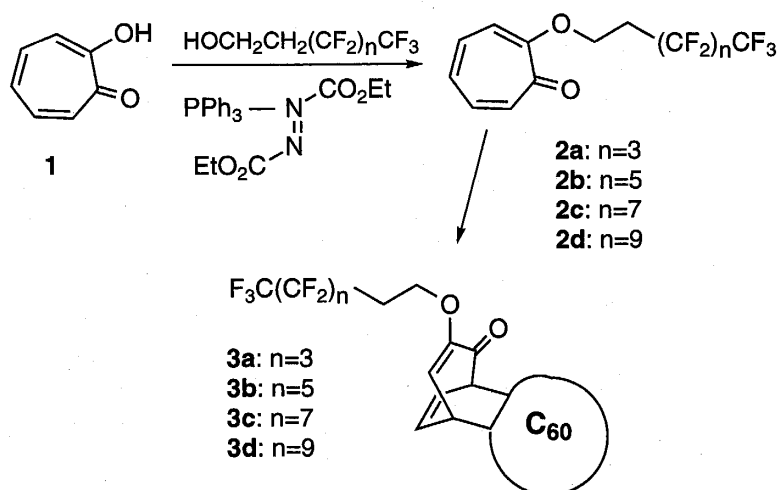
## Condensation of Polyfluoroalkanols to Tropolone to Form 2-(Polyfluoroalkoxy)tropones and Their High-Pressure Diels-Alder Reaction with [60] Fullerene

Ji-Feng LIU, Nobuo KATO, Akira MORI, Yukari IKEDA, and Hitoshi TAKESHITA

The Mitsunobu reaction of tropolone with 2-(perfluoroalkyl)ethanols, low-reactive nucleophiles, afforded 2-(polyfluoroalkoxy)tropones in good yields. The high-pressure (300 MPa) Diels-Alder reaction of several 2-(polyfluoroalkoxy)tropones with  $C_{60}$  gave the [4+2] cycloadducts. Modification of the fullerene with polyfluoroalkoxylated homobarrelenone framework resulted in the great enhancement of solubility in common organic solvents.

Now, it is known that the high-pressure Diels-Alder procedure is quite superior for introduction of organic segments in [60]fullerene, buckminsterfullerene ( $C_{60}$ ), nucleus;<sup>1-4</sup> the advantage is that even at 300 MPa, the cycloreversion is essentially inhibited to achieve good yields as high as over 80%. This generally applicable method should be employed to development of an advanced material synthesis. Herein described is an introduction of polyfluoroalkoxy group on the Diels-Alder adduct.

Modification of the 2-position of tropolone (1) with a long-chain polyfluoroalkoxy group is desirable in view of functionalization of this basic non-alternant system. The derivative should have an improved solubility to common organic solvents due to the decreased intermolecular interactions. However, the fluorinated alkoxy group has a low nucleophilicity due to the strongly electro-negative nature of the fluorine atom. Moreover, the once-formed alkoxy groups having a  $\beta$ -hydrogen atom have a tendency of



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Dedicated to Professor Hiroshi Kobayashi on the occasion of his retirement

sigmatropic *trans*-elimination via the  $[8\pi + 2\pi + 2\sigma]$  process,<sup>5)</sup> and the reaction temperature should be restricted to be low.

We now found that this could be achieved by diethyl azodicarboxylate (DEAD) treatment of **1** and polyfluoroalkanols in the presence of triphenylphosphine.<sup>6)</sup> Thus, 2-(3,3,4,4,5,5,6,6,6-nonafluorohexyloxy)troponone (**2a**), 2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)troponone (**2b**), and 2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorododecyloxy)troponone (**2c**), and 2-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heneicosafuorododecyloxy)troponone (**2d**) were obtained in good yields from **1** and the corresponding fluoroalkanols.<sup>7,8)</sup>

The high-pressure Diels-Alder reaction of C<sub>60</sub> with these **2** gave satisfactory results under 300 MPa at 100 °C in toluene. For all, single Diels-Alder adducts (**3a**, **3b**, **3c**, and **3d**) were obtained in good yields. As predicted, these **3** revealed very resembled <sup>1</sup>H NMR spectra and almost superimposable in each other; besides the signals due to the ethylene groups at  $\delta = 2.71$  to 2.91 (2H, m) and 4.20 to 4.35 (2H, m), the proton signals ascribable to those on *sp*<sup>3</sup>-carbons arising from troponone moiety appeared at  $\delta = 5.16$  (1H, ddd) and 5.41–5.42 (1H, dd), being characteristic of the bridgehead methine protons of C<sub>60</sub>-bound bicyclo[3.2.2]-nonadienone group. The low-field shifted vinyl proton signals at  $\delta = 6.86$  (1H, d), 7.14–7.15 (1H, ddd), and 7.52 (1H, ddd) were also consistent with the structures depicted; i.e., three vinylic proton signals of the cycloadduct (**A**) of C<sub>60</sub> and 2-methoxytroponone were at  $\delta = 6.73$ , 7.13 and 7.53, of which the latter two were almost the same as those of **3**, and for the remaining proton signals, vicinal to the alkoxy groups, the differences are as small as  $\Delta\delta = 0.1$ .

Direct formation of C-C bonds with C<sub>60</sub> by means of thermal cycloaddition reactions with **2** will be of value from the synthetic view point, and further study on the LB-film formation will be reported in due course.

## Experimental

### Preparation of 2-(Polyfluoroalkoxy)troponone (**2**) (General Method).

To a stirred THF solution (8 cm<sup>3</sup>) of tropolone (200 mg), polyfluoroalkanol (1.0 mmol) and Ph<sub>3</sub>P (645 mg) were added DEAD (390 mg) dropwise at 0 °C under an N<sub>2</sub> atmosphere. The resultant solution was stirred for 1 h at 15–25 °C. The mixture was then treated with 1 M-HCl to acidify the solution (ca. pH=4). The mixture was diluted with water and extracted with EtOAc. Flash chromatography of the organic layer afforded **2**.

**2a** [colorless crystals, mp 59–60.5 °C; 66%. Found: *m/z*, 368.0450 (M<sup>+</sup>). Calcd for C<sub>13</sub>H<sub>9</sub>O<sub>2</sub>F<sub>9</sub>: *m/z*, 368.0460 (M). <sup>1</sup>H NMR  $\delta = 2.04$ –2.91 (2H, m), 4.36 (2H, t, *J* = 7.3 Hz), 6.79 (1H, d, *J* = 9.9 Hz), 6.91 (1H, dddd, *J* = 11.0, 5.5, 3.3, 0.7 Hz), 7.06 (1H, ddd, *J* = 11.0, 9.9, 1.1 Hz), and 7.22–7.27 (2H, m); <sup>13</sup>C NMR  $\delta = 31.0$  (t, *J*<sub>C-C-F</sub> = 20.3 Hz), 61.3 (apparent d, *splitting* = 5.0 Hz), 105–125 (4C),<sup>9)</sup> 114.7, 129.0, 132.3, 136.5, 137.8, 164.0, and 180.3; MS *m/z*, 369 ([M+1]<sup>+</sup>, 16.4), 368 (M<sup>+</sup>, 79.2), 149 (33.0), 136 (4.0), 135 (40.0), 122 (7.8), 107 (17.2), 106 (74.2), 105 (100), 94 (36.4), 78 (27.7), and 77 (29.2); IR  $\nu$ : 1630, 1592, 1574, 1503, 1473, 1427, 1396, 1360, 1306, 1285, 1251, 1236, 1194, 1126, 1090, 1040, 1003, 912, 878, 826, 777, 750, 720, 699, 596, 528, and 474 cm<sup>-1</sup>].

**2b** [colorless crystals, mp 76–76.5 °C, 66%. Found: *m/z*, 468.0369 (M<sup>+</sup>). Calcd for C<sub>15</sub>H<sub>9</sub>O<sub>2</sub>F<sub>13</sub>: *m/z*, 468.0396 (M). <sup>1</sup>H NMR  $\delta = 2.81$  (2H, tt, *J* = 18.3, 7.3 Hz), 4.36 (2H, t, *J* = 7.3 Hz), 6.80 (1H, d, *J* = 9.5 Hz), 6.91 (1H, dddd, *J* = 10.6, 5.9, 3.3, 0.7 Hz), 7.06 (1H, ddd, *J* = 11.0, 9.5, 1.1 Hz), and 7.19–7.3 (2H, m); <sup>13</sup>C NMR  $\delta = 31.1$  (t, *J*<sub>C-C-F</sub> = 21.5 Hz), 61.4 (apparent d, *splitting* = 4.9 Hz), 105–125 (6C), 114.8, 129.0, 132.3, 136.5, 137.8, 164.0, and 180.3; MS *m/z*, 469 ([M+1]<sup>+</sup>, 16.2), 468 (M<sup>+</sup>, 85.4), 449 (18.4), 429 (11.9), 149 (38.9), 135 (38.8), 122 (9.3), 107 (19.9), 106 (89.7), 105 (100), 94 (25.1), and 78 (22.3)].

**2c** [colorless crystals, mp 97–98 °C; 66%. Found:  $m/z$ , 568.0361 ( $M^+$ ) Calcd for  $C_{17}H_9O_2F_{17}$ :  $m/z$ , 568.0331 ( $M$ ).  $^1H$  NMR  $\delta$ =2.82 (2H, ttm,  $J$ =18.3, 7.3 Hz), 4.36 (2H, t,  $J$ =7.3 Hz), 6.79 (1H, d,  $J$ =9.9 Hz), 6.91 (1H, dm,  $J$ =10.6 Hz), 7.06 (1H, ddm,  $J$ =10.6, 9.9 Hz), and 7.19–7.3 (2H, m);  $^{13}C$  NMR  $\delta$ =31.2 (t,  $J_{C-C-F}$ =21.5 Hz), 61.4 (apparent d,  $splitting$ =4.9 Hz), 105–125 (8C), 114.8, 129.0, 132.3, 136.5, 137.9, 164.1, and 180.4; MS  $m/z$ , 569 ( $[M+1]^+$ , 18.8), 568 ( $M^+$ , 79.1), 549 (36.2), 529 (11.1), 149 (42.9), 135 (43.2), 122 (10.5), 107 (22.4), 106 (100), 105 (96.9), 94 (23.2), 78 (22.7), and 77 (21.4)].

**2d** [colorless crystals, mp 119–120 °C; 66%. Found:  $m/z$ , 668.0248 ( $M^+$ ) Calcd for  $C_{19}H_9O_2F_{21}$ :  $m/z$ , 668.0269 ( $M$ ).  $^1H$  NMR  $\delta$ =2.81 (2H, tt,  $J$ =18.3, 7.3 Hz), 4.36 (2H, t,  $J$ =7.3 Hz), 6.79 (1H, d,  $J$ =9.9 Hz), 6.91 (1H, dm,  $J$ =10.6 Hz), 7.06 (1H, ddt,  $J$ =11.0, 9.9, 0.7 Hz), and 7.18–7.3 (2H, m);  $^{13}C$  NMR  $\delta$ =31.2 (t,  $J_{C-C-F}$ =21.5 Hz), 61.4 (apparent d,  $splitting$ =4.9 Hz), 105–125 (10C, m), 114.8, 129.0, 132.3, 136.5, 137.9, 164.1, and 180.4; MS  $m/z$ , 669 ( $[M+1]^+$ , 20.0), 668 ( $M^+$ , 82.9), 650 (10.2), 649 (46.2), 149 (42.0), 135 (41.5), 122 (10.0), 107 (22.5), 106 (100), and 105 (81.0)].

**Diels–Alder Reaction of  $C_{60}$  with 2 (General Method).** A toluene solution (5 cm<sup>3</sup>) of  $C_{60}$  (85%, 50 mg)<sup>10)</sup> and **2** (ca. 0.16 mmol) in a high-pressure furnace were heated at 100 °C for 36 h. After cooling off the apparatus, the dark-colored mixture was chromatographed on a silica-gel column. Then, the fractions obtained from hexane–benzene (1:1) were further purified with HPLC and recrystallized from benzene and CS<sub>2</sub> (1:1) to give **3**. Each **3** showed a single spot on a thin-layer chromatogram.

**3a** [black powders, mp ca. 160 °C (decomp), 66%.  $^1H$  NMR  $\delta$ =2.71–2.91 (2H, m), 4.21–4.35 (2H, m), 5.16 (1H, ddd,  $J$ =9.5, 7.3, 1.1 Hz), 5.41 (1H, dd,  $J$ =7.7, 1.1 Hz), 6.86 (1H, d,  $J$ =9.5 Hz), 7.14 (1H, ddd,  $J$ =8.4, 7.7, 1.1 Hz), and 7.52 (1H, ddd,  $J$ =8.4, 7.3, 1.1 Hz); IR  $\nu$ : 1678, 1544, 1477, 1460, 1428, 1234, 1181, 1133, 880, 682, 576, and 527 cm<sup>-1</sup>].

**3b** [black powders, mp ca. 160 °C (decomp), 83%.  $^1H$  NMR  $\delta$ =2.71–2.90 (2H, m), 4.21–4.34 (2H, m), 5.16 (1H, ddd,  $J$ =9.5, 7.3, 1.1 Hz), 5.42 (1H, dd,  $J$ =7.7, 1.1 Hz), 6.86 (1H, d,  $J$ =9.5 Hz), 7.14 (1H, ddd,  $J$ =8.4, 7.7, 1.1 Hz), and 7.52 (1H, ddd,  $J$ =8.4, 7.3, 1.1 Hz)].

**3c** [black powders, mp ca. 160 °C (decomp), 86%.  $^1H$  NMR  $\delta$ =2.71–2.90 (2H, m), 4.23–4.37 (2H, m), 5.16 (1H, ddd,  $J$ =9.5, 7.3, 1.1 Hz), 5.41 (1H, dd,  $J$ =7.7, 1.1 Hz), 6.86 (1H, d,  $J$ =9.5 Hz), 7.15 (1H, ddd,  $J$ =8.4, 7.7, 1.1 Hz), and 7.52 (1H, ddd,  $J$ =8.4, 7.3, 1.1 Hz)].

**3d** [black powders, mp ca. 160 °C (decomp), 84%.  $^1H$  NMR  $\delta$ =2.71–2.90 (2H, m), 4.20–4.34 (2H, m), 5.16 (1H, ddd,  $J$ =9.5, 7.3, 1.1 Hz), 5.42 (1H, dd,  $J$ =7.7, 1.1 Hz), 6.86 (1H, d,  $J$ =9.5 Hz), 7.14 (1H, ddd,  $J$ =8.4, 7.7, 1.1 Hz), and 7.52 (1H, ddd,  $J$ =8.4, 7.3, 1.1 Hz)].

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High-Pressure Diels-Alder Reactions of 2-(Polyfluoroalkoxy)tropones with (60)Fullerene

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- 8) We thank Mr. Tatsuya Ohtsuka, Daikin Kogyo Co., Ltd., Osaka, for generous donation of polyfluoroalkanols used in this study.
- 9) These figures do not represent the chemical shifts of fluorocarbon signals.
- 10) The sample was purchased from Kurita Co. Ltd., who provided the analytical figures, C<sub>60</sub>:C<sub>70</sub> = 80:16.