

SHORT  
COMMUNICATIONS

## Synthesis of Perfluorinated Dioxo Esters from Dimethyl Perfluoroadipate

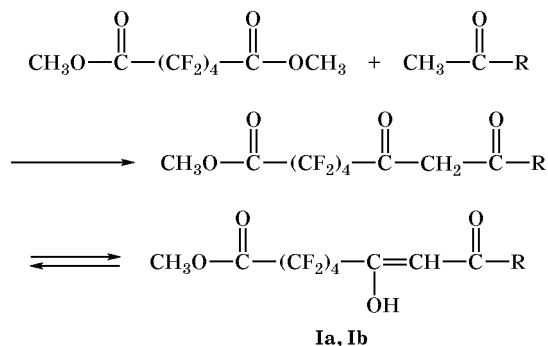
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Received December 26, 2001

Fluorinated keto esters can be prepared by ester condensation [1] or via organometallic syntheses [2]. We have found no published data on methods for preparation of fluorinated 6,8-diketo esters. However, these compounds attract interest as precursors of fluorinated polyketones [3] which are widely used in organic synthesis [4, 5].

We have studied the reaction of dimethyl perfluoroadipate with acetone, methyl ethyl ketone, and acetophenone and found that only one of the two ester groups is involved.



R = C<sub>2</sub>H<sub>5</sub> (a), Ph (b).

We failed to effect condensation at both ester groups through the use of excess ketone. Also, no condensation product with acetone was obtained under the given conditions. According to the <sup>1</sup>H NMR spectra, the fraction of the enol form for dioxo esters **Ia** and **Ib** is 90 and 84%, respectively.

**Methyl 6,8-dioxo-2,2,3,3,4,4,5,5-octafluorodecanoate (Ia)**. To a suspension of sodium methoxide (prepared from 0.552 g of metallic sodium and 15 ml of anhydrous methanol) in 15 ml of dry ether we added dropwise under stirring 6.36 g (0.02 mol) of

dimethyl perfluoroadipate and then 2.88 g (0.04 mol) of methyl ethyl ketone. The mixture was heated for 2 h under reflux and was left to stand for 12 h. The solvent and volatile components were distilled off on an oil bath (85–90°C) until a constant weight, the residue was treated in the cold with 8 ml of 10% sulfuric acid, and the product was extracted into ether. The extract was washed with water until neutral reaction and evaporated, and the residue was dried over CaCl<sub>2</sub> and distilled under reduced pressure. Yield 56%, bp 105–109°C (4 mm), *n*<sub>D</sub><sup>20</sup> = 1.3998. IR spectrum, *v*, cm<sup>-1</sup>: 1600 (C=C), 1732 (C=O), 1784 (C=O, ester), 3300–3400 (OH). <sup>1</sup>H NMR spectrum, *δ*, ppm: 1.2 t (3H, CH<sub>3</sub>), 2.63 q (2H, CH<sub>2</sub>CH<sub>3</sub>), 4.0 s (3H, OCH<sub>3</sub>), 6.17 s (1H, CH), 15.1 s (1H, OH). Mass spectrum, *m/z* (*I*<sub>rel</sub>, %): 358 (0.7) [*M*]<sup>+</sup>, 329 (3.1), 131 (3.6), 99 (100), 71 (1.9), 69 (21.6), 59 (26), 57 (38), 29 (35). Found, %: C 36.82; H 2.73; F 42.38. C<sub>11</sub>H<sub>10</sub>F<sub>8</sub>O<sub>4</sub>. Calculated, %: C 36.87; H 2.79; F 42.46.

**Methyl-6,8-dioxo-8-phenyl-2,2,3,3,4,4,5,5-octafluorooctanoate (Ib)** was synthesized in a similar way. Yield 31%, mp 40.5°C. IR spectrum, *v*, cm<sup>-1</sup>: 1592 (C=C), 1704 (C=O, ArCO), 1780 (C=O, ester), 3300–3400 (OH). <sup>1</sup>H NMR spectrum, *δ*, ppm: 2.55 s (2H, CH<sub>2</sub>), 4.0 s (3H, OCH<sub>3</sub>), 7.2 d (2H, *m*-H), 7.7 d (1H, *p*-H), 8.15 s (2H, *o*-H), 15.1 s (1H, OH). Mass spectrum, *m/z* (*I*<sub>rel</sub>, %): 406 (3.1) [*M*]<sup>+</sup>, 147 (100), 105 (29.9), 77 (3.2), 69 (92.6), 59 (21.2). Found, %: C 44.3; H 2.43; F 37.41. C<sub>15</sub>H<sub>10</sub>F<sub>8</sub>O<sub>4</sub>. Calculated, %: C 44.3; H 2.46; F 37.44.

The IR spectra were recorded on a Specord 75IR instrument from samples dispersed in mineral oil or prepared as thin films. The <sup>1</sup>H NMR spectra were obtained on a Bruker 500 spectrometer (500 MHz) using TMS as internal reference. The mass spectra (70 eV) were run on a Kratos MS-30 instrument.

## REFERENCES

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