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Efficient Synthesis of Fullerene Dimers Containing a Fluoroalkyl Group

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Abstract: Dimeric C_{60} derivatives containing a perfluoroalkyl group were synthesized by the photochemical reaction of C_{60} with perfluoroalkyl iodides in the presence of hexabutylditin or hexamethylditin. The dimers were produced by the addition of fluoroalkyl radicals to C_{60}, followed by the recombination of the fluoroalkylated fullerene radicals. © 1999 Elsevier Science Ltd. All rights reserved.

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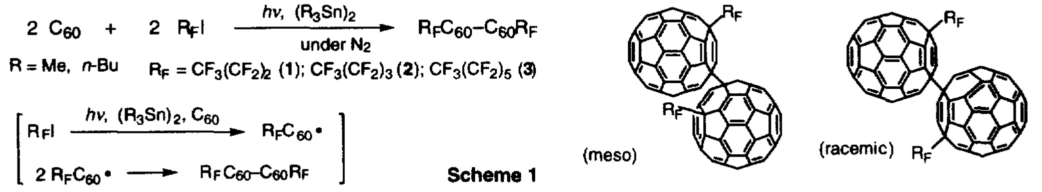
The singly-bonded fullerene dimer ($RC_{60}C_{60}R$), wherein two cages are directly linked, has attracted much attention for the interesting C_{60}–C_{60} bond with an unusually low dissociation energy, and as the model of C_{60} polymers [1,2]. The fullerene dimer is basically produced by the dimerization of the radical adducts of C_{60} [2, 3]. We have previously reported the reaction of C_{60} with a diacyl peroxide $[(C_3F_7CO_2)_2]$ to produce the C_{60} dimer ($C_3F_7C_{60}C_{60}C_3F_7$) as a byproduct [4]. However, the yield of the dimer was too low for the reaction to be used as a practical method for the synthesis of the C_{60} dimer. Now, we have found an efficient method for the synthesis of C_{60} dimers by the reaction of C_{60} with perfluoroalkyl iodides in the presence of $(R_3Sn)_2$ under photoirradiation (Scheme 1).



Scheme 1

The general experiment is as follows. A solution of C_{60} (0.05 mmol) and R_FI (0.25 mmol) in 1,2-dichlorobenzene (5 ml) in the presence of $(Bu_3Sn)_2$ (0.25 or 0.50 mmol) was illuminated with a 70 W metal-halide lamp for 5 - 8 h under N_2. From the reaction mixture, the dimers were isolated by column chromatography on silica gel, followed by gel permeation chromatography (GPC) using JAI model LC-908 liquid chromatography equipped with JAIGEL-1H-40 and 2H-40 columns. The yields of the dimers (**1** - **3**) under various conditions are summarized in Table 1. Though homolytic cleavage of $CF_3(CF_2)_2I$ under photoirradiation is known, the efficiency is not good enough to be applied for the synthesis of the C_{60} dimer under these conditions (Table 1, run 1). By the addition of 2.5 eq of hexamethylditin or hexabutylditin, the reaction proceeded smoothly, and in 8 h photoirradiation, the C_{60} was consumed in 42% and 61%, respectively; the dimer **1** was obtained in moderate yields (Table 1, run 2 and 3). The concentration of C_{60} and the amount of the ditin were further examined in order to optimize the conditions (Table 1, run 3 - 6). In the reactions with $CF_3(CF_2)_3I$ and $CF_3(CF_2)_5I$, the corresponding dimers **2** and **3** were also obtained in moderate yields (Table 1, run 7 and 8). From the NMR data,1) it was found that the dimers consisted of two inseparable isomers (**a** and **b**) (the ratios of the isomers; **1a** : **1b** = 1.31 : 1, **2a** : **2b** =1.44 : 1, **3a** : **3b** = 1.56 : 1). In the reaction of C_{60} with diacyl peroxide $[(C_3F_7CO_2)_2]$, three isomers (**1a** - **1c**) were formed [4]. However, the dimers obtained here (**1a** and **1b**) were identical with two of the three isomers. The spectral data of the two isomers shown here1) are consistent with the dimer structure. In the ^{13}C-NMR spectra of **1** - **3**, two kinds of sp^3 carbons were observed in each isomer. One was the carbon attached to the fluoroalkyl group, and it appeared as a triplet for CCF coupling. The other was assignable to the pivot carbon in the dimer, and the chemical shift was similar to that of the aminated fullerene dimer reported in the literature [5]. Among a large number of possible regio

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isomers for the C_{60} dimers, the most plausible isomer is 1,4-adduct, which has further meso and racemic forms (Scheme 1). Though spin densities of the R_FC_{60} radical are known to be highest at the 2-position and then at the 4-position [3,6], recombination at 2-position for the dimer formation should be unfavorable due to steric repulsion. The ^{19}F- and ^{13}C-NMR spectra of **1** - **3** show the unsymmetrical structure of the C_{60} skeleton in the dimer. The uv-vis spectra of **1** - **3** are quite similar to those observed in 1,4-adducts of C_{60} (**1**: λmax in benzene 327, 447nm).

Table 1. Synthesis of fullerene dimers **1** - **3**$^{a)}$

Run	C_{60} (conc. x 10^2 mol/L)	$R_FI^{b)}$	R of $(R_3Sn)_2$ (eq.)	Recovered C_{60} / %	Yield of the dimer / %$^{c)}$
1	1.0	$CF_3(CF_2)_2I$	none	~100	0
2	1.0	$CF_3(CF_2)_2I$	Me (2.5)	58	64
3	1.0	$CF_3(CF_2)_2I$	*n*-Bu (2.5)	39	56
4	0.75	$CF_3(CF_2)_2I$	*n*-Bu (5.0)	42	52
5	1.0	$CF_3(CF_2)_2I$	*n*-Bu (5.0)	31	55
6	1.5	$CF_3(CF_2)_2I$	*n*-Bu (5.0)	63	65
7	1.0	$CF_3(CF_2)_3I$	*n*-Bu (5.0)	40	56
8	1.0	$CF_3(CF_2)_5I$	*n*-Bu (5.0)	36	57

a) The synthesis of **1** - **3** was carried out using a 70 W metal-halide lamp (National Sky-beam MT-70, >360 nm).
b) 5.0 eq. of R_FI was used. c) The yields were determined by ^{19}F-NMR based on the consumed C_{60}.

The facile C_{60}-C_{60} bond cleavage of the dimers occurred by photoirradiation. ESR signals assignable to the $C_3F_7C_{60}$ radical were observed by the photoirradiation to a benzene solution of **1** in ESR cavity (JEOL JES-PE3X). Further, photoirradiation of a solution of a mixture of **1** and **3** in 1,2-dichlorobenzene gave the mixed dimer **4**. When the isolated **4** was irradiated under same conditions, both **1** and **3** appeared again; in the photostationary state, the ratio of **1** : **3** : **4** was about 1 : 1 : 2 (Scheme 2). These findings support the dimer structure of **1** - **3**.

$$C_3F_7C_{60}\text{–}C_{60}C_3F_7 \;\underset{\text{in benzene}}{\overset{h\nu}{\rightleftharpoons}}\; 2\,C_3F_7C_{60}\bullet \qquad \text{ESR; } g = 2.00289\ (A_1 = 2.36\ ,\ A_2 = 0.49\ \text{G})$$

$$\mathbf{1} + \mathbf{3} \;\overset{h\nu}{\rightleftharpoons}\; [\,2\,C_3F_7C_{60}\bullet + 2\,C_6F_{13}C_{60}\bullet\,] \;\underset{\text{in 1,2-dichlorobenzene}}{\overset{h\nu}{\rightleftharpoons}}\; 2\ \underset{\mathbf{4}}{C_3F_7C_{60}\text{–}C_{60}C_6F_{13}}$$

Scheme 2

1) The ^{13}C and ^{19}F-NMR were measured using CS_2-C_6D_6 (5 : 1) as a solvent with JEOL JNM LA-500 (125 MHz in ^{13}C and 470 MHz in ^{19}F); for ^{13}C-NMR measurement, $Cr(acac)_3$ was added as a relaxation reagent. **1a**; δ_C 67.55 (pivot carbon) and 61.00 (t, J_{CCF} = 23Hz, C-C_3F_7); δ_F (ppm from ex. CF_3COOH) -5.1, -29.3 (d, J = 274Hz), -31.9 (d, J = 274 Hz), -45.8; **1b**; δ_C 67.52 (pivot carbon) and 61.00 (t, J_{CCF} = 23Hz, C-C_3F_7); δ_F -5.1, -29.0 (d, J = 274Hz), -31.9 (d, J = 274 Hz), -45.9; **2a**; δ_C 67.58 (pivot carbon) and 60.83 (t, J_{CCF} = 22Hz, C-C_4F_9); δ_F -5.6, -28.9 (d, J = 273Hz), -31.6 (d, J = 273 Hz), -42.4, -50.4; **2b**; δ_C 67.56 (pivot carbon) and 60.83 (t, J_{CCF} = 22Hz, C-C_4F_9); δ_F -5.6, -28.5 (d, J = 273Hz), -31.5 (d, J = 273 Hz), -42.5, -50.4; **3a**; δ_C 67.61 (pivot carbon) and 61.01 (t, J_{CCF} = 23Hz, C-C_4F_9); δ_F -5.8, -28.8 (d, J = 273Hz), -31.5 (d, J = 273 Hz), -41.3, -46.4, -47.5, -51.0; **3b**; δ_C 67.58 (pivot carbon) and 61.01 (t, J_{CCF} = 23Hz, C-C_4F_9); δ_F -5.8, -28.6 (d, J = 273Hz), -31.3 (d, J = 273 Hz), -41.4, -46.4, -47.5, -51.0. The ^{13}C and ^{19}F-NMR data of **1c** obtained from the reaction of C_{60} with $[(C_3F_7CO_2)_2]$ were reported previously [4].

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