A General Method for the Synthesis of 2,2-[60]Fullerenoalkanals: The Reaction of [60]Fullerene with 2-Bromoenol Silyl Ethers

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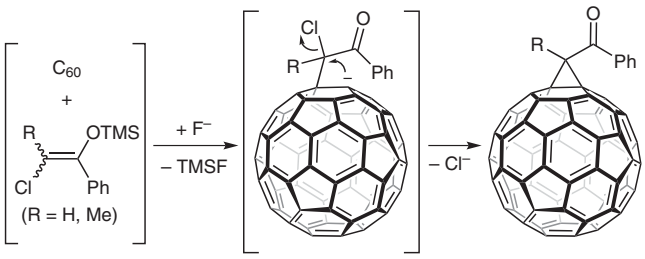
Abstract: Five kinds of 2,2-[60]fullerenoalkanals were synthesized by the fluoride ion-mediated reaction of [60]fullerene with 2-bromoenol silyl ethers, which were easily prepared by 2-bromination of the corresponding enol silyl ethers. The reactivity differed significantly depending on the stability of the 2-bromoenol silyl ethers. High yield and selectivity were achieved for the reaction of 2-bromoenol trimethylsilyl ethers under mild conditions (KF/18-crown-6-ether). The reaction of stable 2-bromoenol *tert*-butyldimethylsilyl ethers, on the other hand, required the use of more reactive tetrabutylammonium fluoride as a fluoride ion source.

Key words: fullerenes, cyclopropanation, silyl enol ethers, aldehydes, bromine

The introduction of a reactive functional group on a fullerene surface enables the construction of sophisticated fullerene-based functionalized molecules by functional group transformations.[2–4] Considering the high importance of a formyl group in organic synthesis, 2,2-[60]fullerenoalkanals (formylmethano[60]fullerenes), which have a formyl group at the bridgehead carbon of methano[60]fullerenes, would be a class of fundamental importance in fullerene chemistry. We have recently reported the synthesis[5] and application[6] of 2,2-[60]fullerenoalkanals; the cyclopropanation of [60]fullerene with α-formyl sulfonium ylides was found to be a fascinating method for the synthesis of 2,2-[60]fullerenoalkanals. However, this sulfonium ylide method has a fatal flaw: 2,2-[60]fullerenoalkanals even with simple groups, such as a benzyl group, at the bridgehead carbon could not be synthesized by this method,[5] although the reason is not clear at present. Moreover, Wang et al. have recently reported the synthesis of 2,2-[60]fullerenoalkanals through the rearrangement of [60]fullerene-fused tetrahydrofurans bearing an acetal moiety by BF_3 at 110 °C.[7] This rearrangement method enables the introduction of many kinds of substituents, including sterically large groups, at the bridgehead carbon. On the other hand, we have reported the synthesis of 2,2-[60]fullereno-1-phenylalkanones by the fluoride ion-mediated cyclopropanation of [60]fullerene with 2-halogenated 1-phenyl-1-alkenyl trimethylsilyl ethers (Scheme 1); [8] the 2-halogenated enol silyl ethers showed very high reactivity in the reaction. On the basis of these results, we considered that 2,2-[60]fullerenoalkanals could be directly synthesized by the reaction of [60]fullerene with alkanal-derived 2-halogenated enol silyl ethers. Herein, we report details of the synthesis of 2,2-[60]-fullerenoalkanals by the enol silyl ether (ESE) method.



Scheme 1 Synthesis of 2,2-[60]fullerenoalkanones by the ESE method

The preparation of 2-brominated enol silyl ethers (2-BrESEs) is summarized in Scheme 2. Among several methods available for the synthesis of 2-halogenated ESEs reported so far, the most convenient method was the one-pot reaction of enol silyl ethers with bromine followed by the elimination of hydrogen bromide by triethylamine to afford 2-BrESEs, because of the accessibility from commercially available starting materials.[9] According to this method, we synthesized several kinds of 2-BrESEs **1a–e** from enol trimethylsilyl ethers.[10] The 2-BrESEs **1a–e** were purified by distillation to afford *E*/*Z* mixtures in moderate yields; the *E*/*Z* ratios were 10:90 to 5:>95 (by ^{1}H NMR). The 2-bromoenol *tert*-butyldimethylsilyl ethers **1c′** and **1d′** were synthesized in a similar manner.[11,12] The compounds **1c′** and **2d′** were relatively stable compared to **1c** and **1d** and could be purified by silica-gel column chromatography, although the yields were rather low.

The 2-BrESEs were applied to the cyclopropanation of [60]fullerene (Scheme 3, Table 1).[13] At first, the reaction conditions were optimized by using **1a**. When tetrabutylammonium fluoride (TBAF; 1 M solution in THF) was used as a fluoride ion source, the reactions took place smoothly (entries 1 and 2); the reaction of [60]fullerene with three equivalents of **1a** and TBAF afforded the desired 2,2-[60]fullerenoalkanal **2a** in moderate yield with acceptable selectivity[14] that was comparable to those ob-

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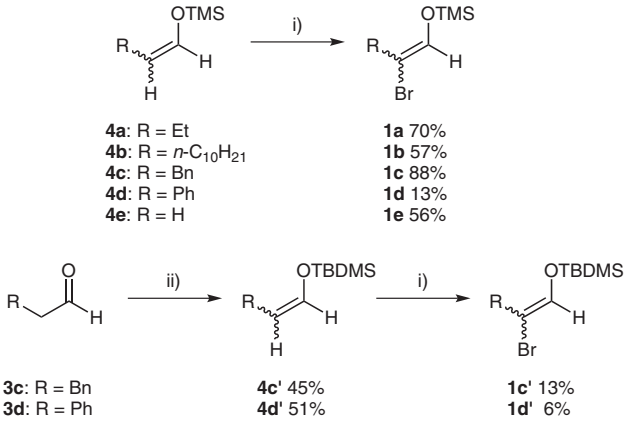
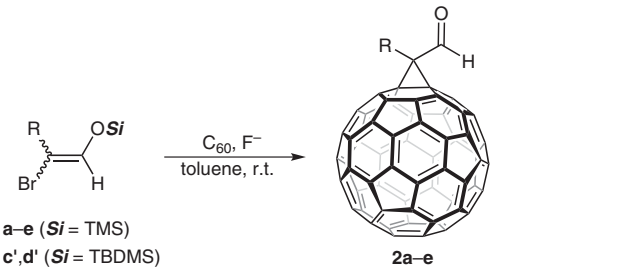


Scheme 2 Synthesis of the 2-bromoenol silyl ethers **1a–e**, **1c′** and **1d′**. *Reagents and conditions*: (i) Br_2 (1.0 equiv), Et_3N (1.5 equiv), CH_2Cl_2, –78 °C to r.t., 3 h; (ii) TBDMSOTf (1.25 equiv), Et_3N (2.5 equiv), THF, 0 °C to r.t.



Scheme 3 Synthesis of 2,2-[60]fullerenoalkanals **2a–e**. F^-: TBAF (1.0 M solution in THF) or KF/18-crown-6.

tained by the sulfonium ylide method. When an equimolar amount of KF/18-crown-6 was used as a fluoride ion source, on the other hand, higher yields and selectivities were achieved, although a considerably prolonged reaction time was required to complete the reaction (entry 3). Thus, KF/18-crown-6 was found to be more suitable than TBAF as the fluoride ion source in the present reaction. A further improvement in selectivity without lowering the yield was achieved by decreasing the amount of 18-crown-6-ether; the reaction of [60]fullerene with one equivalent of **1a** in the presence of one equivalent of KF and 0.2 equivalents of 18-crown-6-ether, resulted in good yield with high selectivity (entry 6).

We next carried out the synthesis of several kinds of 2,2-[60]fullerenoalkanals under the optimized reaction conditions (entries 7–14). All of the 2,2-[60]fullerenoalkanals **2b–e** were obtained in moderate yields by the reaction of [60]fullerene with the 2-BrESEs **1b–e**. It is noteworthy

Table 1 Synthesis of the 2,2-[60]Fullerenoalkanals **2a–e**

Entry	SEE (equiv)	F^- (equiv)	Time (h)	Yield (%)	Selectivity (%)[a]
1	**1a** (1.0)	TBAF (1.0)	3	20	39
2	**1a** (3.0)	TBAF (3.0)	3	37	45
3	**1a** (1.0)	KF (1.0), 18-crown-6 (1.0)	24	47	71
4	**1a** (3.0)	KF (3.0), 18-crown-6 (3.0)	24	26	30
5	**1a** (1.0)	KF (1.0), 18-crown-6 (0.2)	42	38	97
6	**1a** (1.0)	KF (1.0), 18-crown-6 (0.2)	72	47	85
7	**1b** (1.0)	KF (1.0), 18-crown-6 (0.2)	42	19	95
8	**1b** (3.0)	KF (3.0), 18-crown-6 (0.2)	42	45	69
9	**1c** (1.0)	KF (1.0), 18-crown-6 (0.2)	42	24	>99
10	**1c** (1.0)	KF (1.0), 18-crown-6 (0.2)	72	54	79
11	**1d** (1.0)	KF (1.0), 18-crown-6 (0.2)	24	51	94
12	**1d** (1.0)	KF (1.0), 18-crown-6 (0.2)	42	54	87
13	**1e** (1.0)	KF (1.0), 18-crown-6 (0.2)	42	2	>99
14	**1e** (1.0)	KF (1.0), 18-crown-6 (0.2)	48	17	>99
15	**1c′** (1.0)	KF (1.0), 18-crown-6 (0.2)	72	N.D.[b]	–
16	**1c′** (1.5)	TBAF (1.5)	3	37	49
17	**1d′** (1.0)	KF (1.0), 18-crown-6 (0.2)	72	N.D.[b]	–
18	**1d′** (1.0)	TBAF (1.0)	3	30	47
19	**1d′** (1.5)	TBAF (1.5)	3	33	48

[a] Yield based on consumed [60]fullerene.
[b] Not detected.

that it was possible to introduce a benzyl group at the bridgehead carbon of a 2,2-[60]fullerenoalkanal, which was impossible by using the sulfonium ylide method.

The 2-BrESEs **1c′** and **1d′**, on the other hand, required surprisingly long reaction times when KF/18-crown-6 was used as the fluoride ion source (entries 15 and 17). In contrast, when TBAF was applied as a fluoride ion source, the yields reached almost maximum values within a few hours after the addition of TBAF, to afford **2c** and **2d** in moderate yields with acceptable selectivities (entries 16, 18, and 19).

These results would indicate that the slow generation of enolates by the reaction of the 2-BrESEs with fluoride ions is essential because [60]fullerene and the enolates have highly electron-accepting and electron-donating properties, respectively. As a result, an electron transfer from the enolates to [60]fullerene takes place easily to cause the formation of unidentified by-products (low selectivity). In the case of the enol trimethylsilyl ethers **1a–e**, the fluoride ion would be able to easily attack the silicon atom to generate the corresponding enolates in a very short reaction time; the reaction using 0.2 equivalents of 18-crown-6 (entry 6) gave a better result than that using 1.0 equivalent of the crown ether (entry 3) and even that using TBAF (entry 2), although the reaction required a more prolonged reaction time. In contrast, in the case of the enol *tert*-butyldimethylsilyl ethers **1c′** and **1d′**, the attack of a fluoride ion on the silicon atom becomes very slow due to the steric congestion caused by the *tert*-butyl and dimethyl groups on the silicon atom. Therefore, the reaction of [60]fullerene would require fluoride ions in a concentration that is clearly higher than those generated from 1.0 equivalents of KF and 0.2 equivalents of the crown ether.

The 2-bromoenol silyl ethers **1a–e** were thermally unstable, which sometimes resulted in their decomposition during distillation. This means that the use of **1a–e** without purification by distillation is desirable. To this end, we conducted the reaction of [60]fullerene with **1a** prepared in situ. As a typical example, the use of five equivalents of **4a** for the one-pot reaction gave **2a** in 46% yield.[15] Thus, the reaction of [60]fullerene with **1** prepared in situ was also found to proceed smoothly.

In conclusion, various types of 2,2-[60]fullerenoalkanals were directly synthesized by the fluoride ion-mediated cyclopropanation of [60]fullerene with 2-brominated ESEs. This general and reliable reaction for the synthesis of 2,2-[60]fullerenoalkanals in a few steps should contribute to the development of new types of [60]fullerene-containing materials. The transformation of 2,2-[60]fullerenoalkanals thus obtained is now in progress.

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(10) General procedure for the synthesis 2-bromoenol trimethylsilyl ethers **1a–e**. Bromine (1.9 mL, 37 mmol) and triethylamine (7.7 mL, 55 mmol) were successively added dropwise to a solution of 1-trimethylsiloxy-1-alkene (37 mmol) in CH_2Cl_2 (28 mL) at –78 °C, and the mixture was stirred at r.t. for 3 h. Then, hexane (30 mL) was added to the mixture, and the resultant white precipitates were filtered off. The filtrate was washed with saturated $NaHCO_3$ (100 mL), H_2O (100 mL) and brine (100 mL), successively. The organic layer was dried over sodium sulfonate and filtered, and the solvent was removed under reduced pressure. The residue was purified by distillation under reduced pressure to afford the corresponding 2-BrESE (*E*/*Z* mixture) as a clear liquid.
2-Bromo-1-trimethylsiloxy-1-butene (1a): Ratio major/minor = 89:11 (determined by ^{1}H NMR). Bp 63–73 °C/15 mmHg. IR (neat): 2969, 2937, 2917, 2876, 2804, 1656, 1457, 1336, 1317, 1255, 1191, 1129, 1106, 1068, 1041, 942, 924, 867, 846, 754 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (major) = 6.47 (t, *J* = 0.6 Hz, 1 H), 2.5–2.4 (m, 2 H), 1.1–1.0 (m, 3 H), 0.3–0.2 (m, 9 H); δ (minor) = 6.15 (t, *J* = 0.6 Hz, 1 H), 2.5–2.4 (m, 2 H), 1.1–1.0 (m, 3 H), 0.3–0.2 (m, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.28, 111.51, 29.24, 14.38, –0.02. MS (EI): *m*/*z* (%) = 222 (100), 224 (100).
2-Bromo-1-trimethylsiloxy-1-dodecene (1b): Ratio major/minor = 92:8 (determined by ^{1}H NMR). Bp ~124 °C/1 mmHg. IR (neat): 2956, 2925, 2854, 1730, 1657, 1465, 1254, 1195, 870, 848, 756 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (major) = 6.44 (s, 1 H), 2.43 (t, *J* = 6.9 Hz, 2 H), 1.89 (br, 2 H), 1.26 (br, 16 H), 0.3–0.2 (m, 9 H); δ (minor) = 6.50 (s, 1 H), 2.43 (t, *J* = 6.9 Hz, 2 H), 1.89 (br, 2 H), 1.26 (br, 16 H), 0.3–0.2 (m, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.84, 35.49, 32.25, 29.94, 29.88, 29.81, 29.67, 29.63, 28.68, 28.56, 23.03, 14.47, –0.02. MS (EI): *m*/*z* (%) = 334 (100), 336 (100).

2-Bromo-3-phenyl-1-trimethylsiloxy-1-propene (1c): Ratio major/minor = 89:11 (determined by ^{1}H NMR). Bp ~112 °C/1.5 mmHg. IR (neat): 3029, 2958, 2900, 1731, 1659, 1603, 1495, 1454, 1419, 1333, 1254, 1210, 1172, 868, 849, 748, 698 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (major) = 7.3–7.2 (m, 5 H), 6.59 (t, *J* = 0.9 Hz, 1 H), 3.64 (s, 2 H), 0.3–0.2 (m, 9 H); δ (minor) = 7.3–7.2 (m, 5 H), 6.64 (t, *J* = 0.9 Hz, 1 H), 3.80 (s, 2 H), 0.3–0.2 (m, 9 H). ^{13}C NMR (75 Hz, $CDCl_3$): δ = 138.31, 137.19, 128.62, 128.36, 126.63, 107.44, 41.49, –0.34. MS (EI): *m*/*z* (%) = 284 (100), 226 (100).

2-Bromo-2-phenyl-1-(trimethylsiloxy)ethene (1d): Ratio major/minor = 90:10 (determined by ^{1}H NMR). Bp ~78 °C/1 mmHg. IR (neat): 3060, 3031, 2958, 1727, 1636, 1491, 1443, 1255, 1167, 935, 758, 694 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (major) = 7.5–7.2 (m, 4 H), 6.96 (s, 1 H), 0.30 (s, 9 H); δ (minor) = 6.50, 7.5–7.2 (m, 4 H), 6.90 (s, 1 H), 0.24 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.50, 129.25, 129.04, 128.32, 127.62, 127.37, –0.27. MS (EI): *m*/*z* (%) = 270 (100), 272 (100).

2-Bromo-1-trimethylsiloxyethene (1e): Bp ~74 °C/52 mmHg. IR (neat): 3106, 3010, 2960, 2901, 1636, 1329, 1255, 1241, 1166, 1094, 878, 849, 757, 708, 655, 605 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.73 (d, *J* = 3.9 Hz, 1 H), 5.24 (d, *J* = 3.9 Hz, 1 H), 0.24 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.41, 87.37, –0.43. MS (EI): *m*/*z* (%) = 194 (100), 196 (100)

(11) The enol *tert*-butyldimethylsilyl ethers **4c′** and **4d′** were synthesized according to a method in the literature,[16] and was purified by silica gel column chromatography.

1-*tert*-Butyldimethylsilyloxy-3-phenylpropene (4c′): IR(neat): 3029, 2955, 2929, 2858, 1655, 1255, 1115, 838 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4–7.1 (m, 5 H), 6.30 (dt, *J* = 5.7, 1.5 Hz, 1 H), 4.67 (dt, *J* = 5.7, 7.2 Hz, 1 H), 3.45 (dd, *J* = 1.5, 7.2 Hz, 2 H), 0.94 (s, 9 H), 0.15 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.97, 139.10, 128.32, 128.25, 125.58, 109.08, 29.92, 25.63, 18.26, –5.33. MS (EI): *m*/*z* = 248.

1-*tert*-Butyldimethylsilyloxy-2-phenylethene (4d′): Ratio major/minor = 52:48 (determined by ^{1}H NMR). IR (neat): 3030, 2955, 2930, 2885, 2858, 1645, 1471, 889, 838, 783, 692 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ (major) = 7.3–7.1 (m, 5 H), 7.00 (d, *J* = 12.3 Hz, 1 H), 6.03 (d, *J* = 12.3 Hz, 1 H), 0.96 (s, 9 H), 0.21 (s, 6 H); δ (minor) = 7.7–7.6 (m, 2 H), 7.3–7.1 (m, 3 H), 6.42 (d, *J* = 6.6 Hz, 1 H), 5.30 (d, *J* = 6.6 Hz, 1 H), 0.98 (s, 9 H), 0.22 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.23, 140.51, 136.47, 136.19, 128.49, 128.18, 128.07, 125.73, 125.63, 125.12, 112.82, 108.84, 25.68, 25.62, 18.32, 18.21, –5.18, –5.38. MS (EI): *m*/*z* = 234

(12) The 2-bromoenol *tert*-butyldimethylsilyl ethers **1c′** and **1d′** were synthesized in a similar manner to that used for the preparation of the 2-boromoenol trimethylsilyl ethers. The crude products were purified by column chromatography [SiO_2; hexane–CH_2Cl_2, 10:0 to 8:2 (v/v)].

2-Bromo-1-*tert*-butyldimethylsilyloxy-3-phenylpropene (1c′): IR(neat): 3029, 2954, 2929, 2858, 1659, 1254, 1211, 1171, 838 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.4–7.2 (m, 5 H), 6.61 (s, 1 H), 3.64 (s, 2 H), 0.96 (s, 1 H), 0.19 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.38, 137.72, 128.63, 128.34, 126.61, 106.92, 441.42, 25.51, 18.27, –5.17. MS (EI): *m*/*z* (%) = 326 (100), 328 (100).

2-Bromo-1-*tert*-butyldimethylsilyloxy-2-phenylethene (1d′): Ratio major/minor = 65:35 (determined by ^{1}H NMR). Major isomer: IR (neat): 2954, 2929, 2858, 1635, 1261, 1168, 828 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.5–7.4 (m, 2 H), 7.4–7.2 (m, 3 H), 6.98 (s, 1 H), 0.99 (s, 1 H), 0.24 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.91, 137.11, 128.31, 127.53, 127.32, 106.74, 25.50, 18.26, –5.11. MS (EI): *m*/*z* (%) = 312(100), 314(100). Minor isomer: IR(neat): 2955, 2929, 2858, 1617, 1259, 1228, 1136, 827 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.8–7.7 (m, 2 H), 7.4–7.1 (m, 3 H), 6.91 (s, 1 H), 0.91 (s, 9 H), 0.19 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.24, 135.50, 128.99, 127.74, 127.31, 106.93, 25.44, 18.07, –5.30. MS (EI): *m*/*z* (%) = 312 (100), 314 (100)

(13) General procedure for the synthesis of 2,2-[60]fullerenoalkanals. The KF/18-crown-6 method: KF (5.8 mg, 0.10 mmol) and an 18-crown-6 solution in toluene (0.10 M, 0.20 mL, 0.020 mmol) were added to a solution of [60]fullerene (72 mg, 0.10 mmol) and 2-BrESE (0.10 mmol) in toluene (72 mL). After the mixture was stirred at r.t. for 72 h, the solvent was evaporated to dryness. The residue was purified by preparative thin layer chromatography (SiO_2, CS_2) to afford the corresponding 2,2-[60]fullerenoalkanal as a dark-brown solid.

The TBAF method: A TBAF solution (1 M in THF, 0.30 mL, 0.30 mmol) was added to a solution of [60]fullerene (72 mg, 0.10 mmol) and 2-BrESE (0.10 mmol) in toluene (72 mL). After the mixture was stirred at r.t. for 3 h, the solvent was evaporated to dryness. The residue was purified by column chromatography [SiO_2; hexane–toluene, 9:1 to 2:1 (v/v)] to afford the corresponding 2,2-[60]fullerenoalkanal as a dark-brown solid.

2,2-[60]Fullerenobutanal (2a): See ref. 5.

2,2-[60]Fullerenododecanal (2b): IR (KBr): 2921, 2849, 1719, 1461, 1428, 1186, 578, 555, 526 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.57 (s, 1 H), 2.79 (t, *J* = 8.1 Hz, 2 H), 2.02–1.85 (m, 2 H), 1.66–1.18 (m, 14 H), 0.89 (t, *J* = 6.6 Hz, 3 H). ^{13}C NMR [125 MHz, $CDCl_3$/CS_2, 1:1 (v/v)]: δ = 194.24, 146.84, 145.79, 145.26, 145.25, 145.23, 145.16, 145.13, 144.97, 144.70, 144.64, 144.62, 144.60, 144.40, 143.76, 143.69, 143.19, 143.08, 143.01, 142.94, 142.92, 142.91, 142.05, 141.98, 141.97, 141.57, 141.10, 141.04, 137.96, 137.83, 75.17, 50.23, 31.99, 30.05, 29.71, 29.69, 29.55, 29.46, 27.70, 25.87, 22.84, 14.23. MS (MALDI-TOF): *m*/*z* [M]$^{\cdot+}$ calcd for $C_{72}H_{22}O$: 902.17; found: 902.11.

2,2-[60]Fullereno-3-phenylpropanal (2c): IR (KBr): 2922, 2850, 1718, 1494, 1427, 1260, 1186, 1073, 1030, 732, 706, 576, 555, 526 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.55 (s, 1 H), 7.58 (d, *J* = 7.4 Hz, 2 H), 7.38 (dd, *J* = 7.4, 7.4 Hz, 2 H), 7.30 (d, *J* = 7.4 Hz, 1 H), 4.23 (s, 2 H). ^{13}C NMR [125 MHz, $CDCl_3$/CS_2, 1:1 (v/v)]: δ = 193.83, 146.85, 145.61, 145.38, 145.35, 145.28, 145.27, 144.98, 144.82, 144.81, 144.80, 144.78, 144.76, 144.58, 143.88, 143.78, 143.20, 143.18, 143.06, 143.01, 142.17, 142.10, 142.07, 141.62, 141.24, 138.15, 138.12, 136.77, 129.40, 128.95, 127.25, 74.98, 50.15, 31.56; three peaks are overlapped. MS (MALDI-TOF): *m*/*z* [M]$^{\cdot+}$ calcd for $C_{69}H_8O$: 852.06; found: 851.80.

2,2-[60]Fullereno-2-phenylethanal (2d): See ref. 7.

2,2-[60]Fullerenoethanal (2e): See ref. 7.

(14) [60]Fullerene derivatives having two or more alkanal moieties were obtained as by-products.

(15) Br_2 (0.40 M in CH_2Cl_2, 1.25 mL, 0.50 mmol) and Et_3N (1.5 M in CH_2Cl_2, 0.50 mL, 0.75 mmol) were successively added dropwise to a solution of 1-trimethylsilyloxy-1-butene (**4a**; 72 mg, 0.50 mmol) in CH_2Cl_2 (7.5 mL) at –78 °C, and the mixture was stirred at r.t. for 3 h. A solution of [60]fullerene (0.10 mM in toluene, 72 mL), KF (29 mg, 0.50 mmol), and 18-crown-6 (26 mg, 0.10 mmol) were successively added to the mixture. After the mixture was stirred at r.t. for 42 h, the solvent was evaporated to dryness. The residue was purified by preparative thin layer chromatography (SiO_2, CS_2) to afford 2,2-[60]fullerenobutanal **1a** (36 mg, 0.46 mmol, 46% yield) as a dark-brown solid

(16) Jung, M. E.; Nishimura, N. *Org. Lett.* **2001**, *3*, 2113.