Photoaddition of Silyl Ketene Acetal to [60]Fullerene. Synthesis of α-Fullerene-substituted Carboxylic Esters

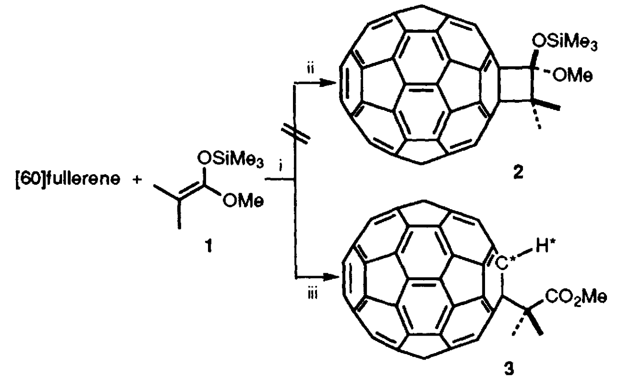
Hidetoshi Tokuyama, Hiroyuki Isobe and Eiichi Nakamura*

Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan

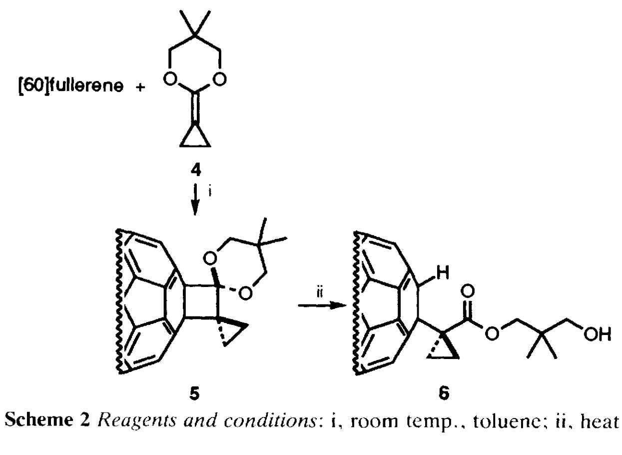
Photoaddition reaction of a silyl ketene acetal to [60]fullerene takes place at low temperature in wet toluene to afford α-fullerene-substituted carboxylic esters in good yields instead of the expected [2 + 2] cycloadduct.

Organofunctionalized [60]fullerenes play vital roles in fullerene science and technology, and there is an increasing demand for simple and practical synthetic entries to organofullerenes. Among a variety of fullerene derivatives thus far available, carboxylic acid derivatives represent an important class of compounds, for instance, in bioorganic research on fullerenes.[1,2] We report here that a carboxylic ester side chain can be introduced on to [60]fullerene by the reaction of a silyl ketene acetal (KA) under neutral photolytic conditions in wet toluene (Scheme 1). A small amount of water is indispensable and gives rise to the ester adduct **3** rather than the expected [2 + 2] cycloadduct **2**, which did not form either in the presence or absence of water.

We recently reported[3] that a highly strained KA **4** undergoes stepwise [2 + 2] cycloaddition with [60]fullerene to give **5**, whose C–C bond is cleaved upon heating in aqueous H_2SO_4 to give the ester **6** (Scheme 2). An unstrained counterpart **1** was found to be totally unreactive even under high pressure conditions.[3] Photolysis was expected[4] to facilitate the reaction. Indeed, irradiation of a dry toluene solution of [60]fullerene (0.01 mol dm^{-3}) and 2 equiv. of **1** at 0 °C for 6 h promoted consumption of the starting materials to afford the ester **3** (variable yield, trace–20%), Scheme 1. The use of 4 equiv. of **1** increased the yield to *ca.* 40%, but further increases (10 equiv.) did not improve the yield due to the formation of side products. Even in the presence of excess KA, the photoconversion stopped after some time, leaving both starting materials unreacted.



Scheme 1 *Reagents and conditions*: i, toluene; ii, thermal (9 kbar), or photo with or without H_2O; iii, H_2O, *hν*



Scheme 2 *Reagents and conditions*: i, room temp., toluene; ii, heat

In no cases could we detect the [2 + 2] cycloadduct **2** in the reaction mixture and it was most likely that **3** was formed directly in the photoreaction. Since **3** formed also in $1,2\text{-}Cl_2C_6H_4$ or CS_2, H* in **3** could not have come from the solvent (toluene), but must have come from water, which was found to be present in the reaction mixture (1.4 mmol dm^{-3} for [60]fullerene) at a 2.5–4 ppm level (0.1–0.16 H_2O : [60]fullerene). Realizing this fact, we carried out the reaction with 4 equiv. of **1** and 10 equiv. of H_2O to obtain **3** in a dramatically improved yield of 80% (Table 1, entry 1). There also formed in 14% yield a 2 : 1 adduct of C_1 symmetry, most probably due to the addition of two isobutyrate groups to the two adjacent double bonds in a six-membered ring with 1,3-disposition of two hydrogen atoms (δ 5.51 and 5.98, $J_{H\text{-}H}$ = 2 Hz; $CDCl_3$). Such double addition, however, is sluggish as supported by an experiment wherein **3** was re-exposed to the reaction conditions. With the added water, the reaction became reproducible. The following simple photolysis procedure was employed in the subsequent studies.

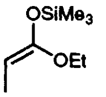
A mixture of [60]fullerene (100 mg, 0.139 mmol), **1** (114 μl, 0.555 mmol) and water (25.0 μl, 1.39 mmol) was dissolved in degassed toluene (100 ml), and irradiated for 10 h at 5 °C (internal temperature, ice cooling bath) with an immersion type 400 W high-pressure mercury lamp (Pyrex filter). The colour of the solution gradually turned from magenta to brown. Solvent and excess KA were removed *in vacuo* and the remaining solid product was chromatographed on silica gel to obtain the ester **3** in 47% yield (53.3 mg). Essentially the same experiment performed for 20 mg of [60]fullerene in 20 ml toluene using a merry-go-round setup gave **3** in 80% yield (18.3 mg).

The structural assignment of the adduct **3** rests on the spectral comparisons with related compounds.[†] The ^1H NMR spectrum of **3** displayed two singlets at δ 2.30 and 6.67 due to the α-methyl groups and H*, respectively. The assigned C_s structure was deduced from the presence of 25 sp^2 [60]ful-

Table 1 Photoaddition of silyl ketene acetal to [60]fullerene in wet toluene at 5 °C[a]

Entry	KA (equiv.)	H_2O (equiv.)	t/h	Product	Yield (%)
1	**1** (4.0)	10.0	10	**3**	80
2	**7** (4.0)	10.0	10	**13**	59
3	**8** (4.0)	*ca.* 0[b]	10	**13**	<3
4	**8** (4.0)	3.0	10	**13**	40[c]
5	**8** (4.0)	10.0	10	**13**	51[d]
6	**9** (10.0)[e]	10.0	6	**14**	62
7	**10** (10.0)	10.0	7	**14**	7[c]
8	**11** (10.0)	10.0	4	**15**	54[f]
9	**12** (4.0)	10.0	4	—	0

[a] The reaction was carried out with 20 mg of [60]fullerene in 20 ml of dry toluene as described in the text. Some recovery of [60]fullerene and the formation of multiadducts account for the material balance. [b] The reaction was carried out in the presence of 4 Å molecular sieves. [c] Yield was determined by NMR using an internal standard. [d] 72% yield based on recovered [60]fullerene. [e] A 6 : 4 mixture of *O*- and *C*-silylated ethyl acetate was used. [f] 65% yield based on recovered [60]fullerene.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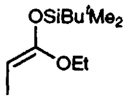
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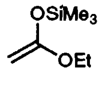
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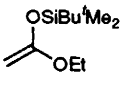
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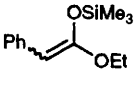
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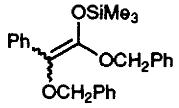
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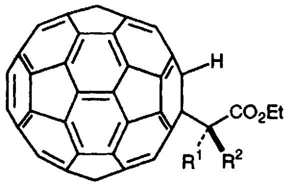
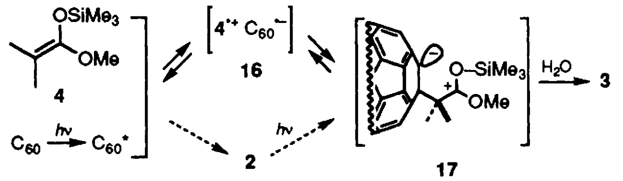

13 R^1, R^2 = Me, H
14 R^1, R^2 = H, H
15 R^1, R^2 = Ph, H



Scheme 3

lerene signals, of which three signals are due to four overlapping carbon atoms.

The effect of added water was further ascertained for the *tert*-butyldimethylsilyl (TBDMS) derivative of ethyl propionate **8** (Table 1, entries 3–5). Thus, in the presence of molecular sieves (4 Å), essentially no reaction took place and 97% of [60]fullerene was recovered, the reaction in 'dry' toluene containing 0.19 equiv. of water afforded the adduct in 20% yield, and the yield increased to 40 and 51% in the presence of 3.0 and 10.0 equiv. of water, respectively. Trimethylsilyl (TMS) KA is more reactive than TBDMS KA, as is clearly seen for **9** and **10** (entry 6 *vs.* 7), where **10** was almost inert to [60]fullerene.

The reactivity of the KA increases as the number of electron-donating substituents on the olefin increases (entries 1–7). The KAs **9** and **10** derived from ethyl acetate were less reactive than **7** and **8** derived from ethyl propionate, which in turn were less reactive than **1** and **11**. The enol TMS ethers derived from pentan-3-one, acetophenone, and 2-methylcyclohexanone ($\Delta^{1,6}$ isomer) were unreactive. The electron-rich but sterically hindered KA **12** was unreactive (entry 9).

There are *a priori* two reaction pathways possible for the present reaction (Scheme 3). One involves a [2 + 2] cycloadduct **2**, and the other a zwitterionic species **17**, which is formed through a radical ion pair **16**. The active role of water in the photoaddition combined with the TMS/TBDMS-dependent reactivity difference indicates that the oxonium intermediate **17** is the direct precursor of the photoproduct **3**, which forms by water-assisted loss of the silyl group from **17**. The radical ion pair **16** is the most plausible precursor to **17**, in light of the high electron affinity of excited [60]fullerene[5] and the excellent single-electron donating ability of silyl KA.[6] The Rehm–Weller analysis[7] of the reaction, however, suggests that **16** is formed only in minute quantities, as **16** is less stable by 10 kcal mol^{-1} (1 cal = 4.184 J) than **4** and triplet [60]fullerene. A free radical ion species is not involved in this reaction, since the photoreaction is not affected by the presence of a radical trap (6 equiv. TEMPO). The experimental facts do not exclude, however, the possibility that a minute quantity of **2** forms and undergoes photoassisted heterolytic C–C bond cleavage *via* **17**.

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Footnote

† *Physical properties* of fullerene ester **3**: R_f 0.50 (50% toluene in hexane); IR ν_{max}/cm^{-1} (CCl$_4$) 2970, 2930, 2850, 1740, 1260, 530; ^{1}H NMR (500 MHz, CS$_2$–CDCl$_3$) δ 2.32 (s, 6H, CCH$_3$), 4.10 (s, 3H, OCH$_3$), 6.68 (s, 1H, C$_{60}$H); ^{13}C NMR (125 MHz, CS$_2$–CDCl$_3$) δ 23.98 (CH$_3$, 2C), 52.48 (C$_{60}$H), 53.01 (quaternary carbon), 58.02 (OCH$_3$), 70.60 (C$_{60}$), 125.17 (C$_{60}$, 2C), 128.10 (C$_{60}$, 2C), 128.87 (C$_{60}$, 2C), 136.29 (C$_{60}$ 2C), 136.99 (C$_{60}$, 2C), 138.87 (C$_{60}$, 2C), 140.22 (C$_{60}$, 4C), 141.30 (C$_{60}$, 2C), 141.50 (C$_{60}$, 2C), 141.96 (C$_{60}$, 2C), 142.01 (C$_{60}$, 2C), 142.51 (C$_{60}$, 2C), 143.11 (C$_{60}$, 2C), 144.30 (C$_{60}$, 2C), 144.63 (C$_{60}$, 2C), 145.16 (C$_{60}$, 2C), 145.21 (C$_{60}$, 4C), 145.32 (C$_{60}$, 2C), 145.65 (C$_{60}$, 2C), 145.98 (C$_{60}$, 2C), 146.06 (C$_{60}$, 2C), 146.24 (C$_{60}$, 2C), 146.75 (C$_{60}$), 147.04 (C$_{60}$, 4C), 147.37 (C$_{60}$), 152.46 (C$_{60}$, 2C), 153.82 (C$_{60}$, 2C), 175.88 (C=O).

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