

## Reaction of Sodium Alkoxides with [60]Fullerene: Formation of a 1,3-Dioxolane Derivative and Involvement of O<sub>2</sub> in a Nucleophilic Addition Reaction of C<sub>60</sub>

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[60]Fullerene reacts with PhCH<sub>2</sub>ONa–PhCH<sub>2</sub>OH in the presence of air to afford a 1,3-dioxolane derivative of C<sub>60</sub>, which was characterized by FD-MS, FTIR, UV–VIS, <sup>1</sup>H NMR, <sup>13</sup>C NMR, HMQC and HMBC; a possible reaction mechanism is discussed.

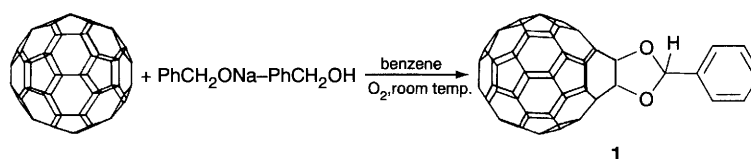
The chemistry of C<sub>60</sub> has developed very rapidly since [60]fullerene became readily available.<sup>1</sup> A number of nucleophiles, such as organolithiums, Grignard reagents,<sup>2</sup> amines<sup>3</sup> and hydroxide<sup>4</sup> are known to react with [60]fullerene. However, the alkylation of [60]fullerene has been much less intensively investigated. Olah *et al.* reported<sup>5</sup> that polymethoxylation of [60]fullerene could be achieved by treating [60]fullerene with chlorine at high temperature, followed by KOH in refluxing methanol. Recently, Wilson's group<sup>6</sup> detected a series of addition products C<sub>60</sub>O<sub>n</sub>(OMe)<sub>m</sub> (*n* = 0–3, *m* = 1,3,5) by EIMS when they studied the reaction of NaOMe–MeOH with C<sub>60</sub> in toluene. Nevertheless, until now, no pure product had been separated and characterized from reaction mixture of alkoxides with [60]fullerene. In this communication, we report the synthesis and characterization of alkoxide–C<sub>60</sub> adducts.

Compound **1** was prepared by adding 5 equiv. of PhCH<sub>2</sub>ONa in PhCH<sub>2</sub>OH to a solution of C<sub>60</sub> in benzene at room temp. in the presence of air (Scheme 1). Typically, 50.0 mg of C<sub>60</sub> was completely dissolved in 50 ml of benzene, then, 0.7 ml (5 equiv.) of PhCH<sub>2</sub>ONa–PhCH<sub>2</sub>OH (freshly prepared by treating 115 mg of sodium with 10 ml of benzyl alcohol) was added. The reaction mixture was stirred and monitored by HPLC. The product **1** reached its maximum yield after *ca.* 1.5 h. At that time, the reaction was quenched by adding excess dilute aq. HCl. Standard workup and silica gel column chromatography (20% toluene in *n*-hexane as eluent) afforded 39.0 mg of unreacted C<sub>60</sub> and 8.8 mg (68%, based on consumed C<sub>60</sub>) of compound **1**.†

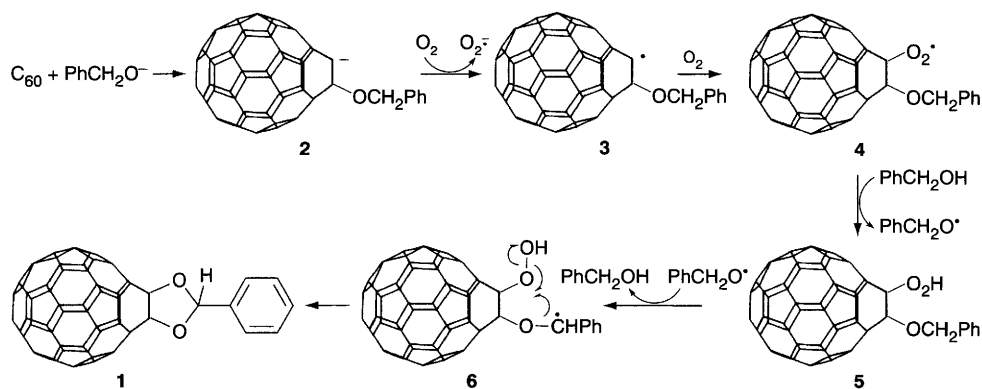
The field desorption mass spectrum (FD-MS) of **1**, which showed molecular ion peak at *m/z* 842 as base peak together with another peak at *m/z* 720 (21%) due to the fragment C<sub>60</sub>, agreed with the proposed structure. In the IR spectrum of **1**,

besides the four characteristic bands of the fullerene moiety, a number of bands due to sp<sup>3</sup> C–O and phenyl were observed. The UV–VIS spectrum of **1** showed the three absorption bands from the fullerene cage with a slight blue shift in the ultraviolet region, and was structureless in the visible region. This spectrum was similar to that of a reported 1,3-dioxolane derivative of C<sub>60</sub>.<sup>7</sup> In the <sup>1</sup>H NMR spectrum, in addition to the five phenyl protons, only one singlet acetal proton was observed. This signal shifted downfield greatly due to the influence of the fullerene ring as compared to common acetal protons. The <sup>13</sup>C NMR spectrum of **1** consisted of 36 sets of inequivalent carbons. Four peaks from δ 127 to 135 were due to those of phenyl, the peak at δ 103.25 corresponded to the acetal carbon, and the remaining 31 peaks were from the fullerene with one overlapping peak appearing at δ 146.62. The peak at δ 94.39 was originated from the sp<sup>3</sup> carbon of C<sub>60</sub>. This is consistent with the C<sub>s</sub> symmetry of **1**, which requires 32 peaks for the fullerene moiety. The proposed structure of **1** was further substantiated by HMQC (heteronuclear multiple quantum coherence) and HMBC (heteronuclear multiple bond correlation). It was found that the proton at δ 7.26 was attached to the carbon at δ 103.25 and showed a three-bond correlation with the phenyl carbon at δ 127.93. The structure of **1** was also confirmed by comparison with the reported <sup>13</sup>C chemical shifts of the ketal carbon and sp<sup>3</sup>-C of fullerene, IR and UV–VIS spectra of a 1,3-dioxolane derivative of [60]fullerene.<sup>7</sup>

It is well known that reaction of tertiary carbanion with O<sub>2</sub> affords corresponding alkyl radical, and finally hydroperoxide.<sup>8</sup> We observed that the reaction of sodium benzyloxide with C<sub>60</sub> proceeded much slower when oxygen was partially excluded from the reaction mixture. Hence, oxygen must be involved in the reaction. A possible mechanism for the reaction is outlined



Scheme 1



Scheme 2

in Scheme 2. It seems that the carbanion **2** reacts with O<sub>2</sub> much faster than it undergoes protonation. Another possible mechanism is that C<sub>60</sub> reacts with PhCH<sub>2</sub>ONa by electron transfer to give [60]fullerene radical anion and benzyloxy radical.<sup>6</sup> The benzyloxy radical then adds to C<sub>60</sub> to give the intermediate **3**.

We have also conducted the reaction of C<sub>60</sub> with NaOEt-EtOH using the same method. The reaction was faster than that with PhCH<sub>2</sub>ONa-PhCH<sub>2</sub>OH. An ethoxide-C<sub>60</sub> adduct was isolated, which was pure by TLC and HPLC. The FTIR and UV-VIS spectra of the adduct showed that the fullerene cage remained unchanged. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the ethoxide-C<sub>60</sub> adduct were complex, and its assignment is underway.

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## Footnotes

† Spectral data for **1**: *R<sub>f</sub>* = 0.28 (SiO<sub>2</sub>, n-hexane : toluene, 5 : 1). FD-MS *m/z* (%) 842 (100), 720 (21). FT-IR (KBr)  $\nu/\text{cm}^{-1}$  3033, 2918, 2853, 1625, 1459, 1425 (C<sub>60</sub>), 1400, 1219, 1181 (C<sub>60</sub>), 1153, 1401, 1081, 1059, 1050, 1034, 1025, 1003, 784, 694, 575 (C<sub>60</sub>), 562, 553, 525 (C<sub>60</sub>), 478. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\text{max}}/\text{nm}$  227, 253, 315. <sup>1</sup>H NMR (600 MHz, CS<sub>2</sub>-CDCl<sub>3</sub>, Me<sub>4</sub>Si)  $\delta$  8.00 (d, *J* 6.7 Hz, 2 H, arom. H), 7.54 (m, 3H, arom. H), 7.26 (s, 1H). <sup>13</sup>C NMR (150.9 MHz, CS<sub>2</sub>-CDCl<sub>3</sub> with Cr(acac)<sub>3</sub> as relaxation reagent)  $\delta$  (number of carbon atoms) 148.40 (2), 148.12 (2), 147.71 (2), 146.62 (4), 146.47 (2), 146.39 (2), 146.34 (2), 146.30 (2), 145.55 (1), 145.44 (2), 145.29 (2), 145.26 (2), 145.17 (1), 145.00 (2), 144.94 (2), 144.73 (2), 143.23 (1), 142.94 (2), 142.88 (2), 142.78 (1), 142.50 (2), 142.48 (2), 142.41 (2), 142.38 (2), 142.27 (2), 141.73 (2), 139.95 (2), 139.78 (2), 138.79 (2), 138.52 (2), 134.80 (1, quart. arom. C), 130.57 (1, arom. CH), 128.93 (2, arom. CH), 127.93 (2, arom. CH), 103.25 (1, acetal C), 94.39 (2, sp<sup>3</sup>-C of C<sub>60</sub>).