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# Buckminsterfullerene $C_{60}$ – *o*-Quinone Methide Cycloadduct

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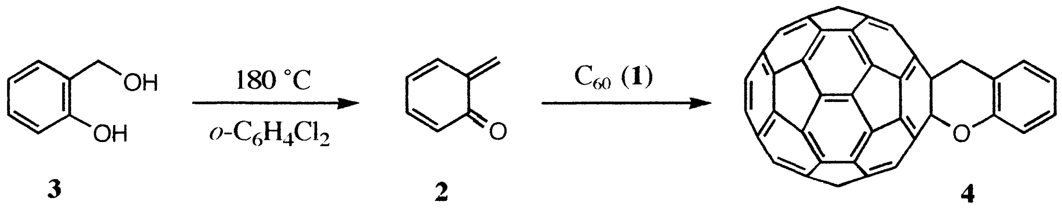
Buckminsterfullerene $C_{60}$ underwent [4+2]cycloaddition reaction across 6,6 ring junction with *o*-quinone methide generated *in situ* from *o*-hydroxybenzylalcohol in 1,2-dichlorobenzene (180 °C).

The cycloaddition reaction is one of the fascinating methods for derivatization of buckminsterfullerene $C_{60}$ (**1**) which possesses low-lying LUMO orbitals.1,2) Since initial survey by Wudl et al.2) who suggested that the Diels-Alder reaction, based on sufficient dienophilicity, is promising, some selected [4+2]cycloaddition reactions of **1** were studied with several dienes.3-9) Particularly it was demonstrated that they are fruitful in such a case that a cycloadduct can avoid cycloreversion by stabilization of the resulting double bond with aromaticity.7-9) We now wish to report our own finding on this type of reaction using *o*-quinone methide (**2**), as the first example of hetero Diels-Alder reaction of **1**.

For this aim, *o*-hydroxybenzylalcohol (**3**) was employed as a precursor of the typical *o*-quinone methide.10) While acid catalyzed conditions (*e.g.* *p*-$CH_3C_6H_4SO_2OH$, $CF_3SO_2OH$, or $BF_3Et_2O$/benzene/r.t.–80 °C) were not effective, thermolysis of **3** with **1** at 180 °C afforded the desired cycloadduct **4**. Thus, a solution of **1** (22 mg) and large excess of **2** (74 mg) in 1,2-dichlorobenzene (6 ml) was placed in a sealed glass cylinder under an atmosphere of nitrogen and heated to reflux for 30min. The solution color changed gradually from purple to dark brown. After removal of the solvent under vacuum, the residue was subjected to silica gel chromatography (Fuji-Davison BW-300) eluted with hexane and hexane-toluene (10/1) successively to give 1:1 cycloadduct **4** (8 mg; 50% yield based on consumed **1**) as a brown solid after the first elution of unreacted **1** (8 mg).11) When a toluene solution of **4** was allowed to stand at room temperature, crystalline needles were formed after vaporization of the solvent, which had mp>300 °C (Scheme 1; the structure of **4** is drawn from only front view because of convenience).



Scheme 1.

The structure was elucidated by spectral informations as follows. The IR spectrum (KBr) showed absorptions at 1591, 1483, 1460, 1426, 1236, 1188, 1022, 966, 802, 756, 575 and 527 cm$^{-1}$. The FAB-MS spectroscopy supported 1:1 cycloadduct by a parent peak at m/z 826 together with a base peak at m/z 720. Both $^1$H- and $^{13}$C-NMR spectra indicated that the addition occurred across a 6,6 ring junction; in the $^1$H-NMR spectrum (500 MHz, $CDCl_3$) the methylene signal appeared as a sharp singlet$^{12)}$ at δ 4.62 together with phenyl ring protons ( δ 7.39-7.69), implying that these two protons are environmentally equal, and accordingly, the structure has Cs-symmetry owing to the above ring fusion. This was further confirmed by the $^{13}$C-NMR spectrum (125 MHz, $CDCl_3/CS_2$), in which 36 lines expected for sp$^2$ carbons were observed [δ 157.12, 155.24, 149.18, 148.58, 147.87, 146.84, 146.64, 146.47, 146.40, 146.34, 145.66, 145.59, 145.54, 145.45, 144.91, 144.88, 144.80, 143.23, 143.00, 142.84, 142.82, 142.81, 142.50, 142.30, 142.15, 141.66, 141.62, 140.38, 139.85, 138.03, 136.15, 130.80, 129.32, 128.34, 124.85, 119.89 (The last four lines were relatively strong and assignable to CH on benzene ring) together with 96.43 and 65.75 (quaternary C adjacent to O and $CH_2$, respectively, on $C_{60}$ ring) and 41.24 (benzyl-C)]. The UV/vis spectrum (THF) showed absorptions at $\lambda_{max}$ 213 (log ε 4.68), 245 (log ε 4.54), 253 (log ε 4.54), 315 (log ε 4.08), 430 (log ε 3.33), 704 (log ε 2.84), which were characteristic of $C_{60}$-cycloadducts.$^{4,9)}$ Consequently, these data were compatible with the assigned Diels-Alder product, which, like previous cycloadducts,$^{3-10)}$ arised from cycloaddition across a 6,6 ring junction.

The present reaction demonstrated the feasibility of utilitarian extension of the cycloaddition methodology for $C_{60}$ functionalization, and thus, further studies are now in progress to prepare other $C_{60}$-fused heterocycles along this strategy.

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11) Several by-products were accompanied as a post-eluent. Although no effort was made for characterization at present, they might include a bisadduct.
12) The observed pattern of *singlet* assigned to chroman methylene protons indicates free ring inversion at room temperature in contrast to the related ring systems (Refs. 8,9).

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