J. Org. Chem. **1993**, *58*, 3613-3615 **3613**

Addition of Quadricyclane to C_{60}: Easy Access to Fullerene Derivatives Bearing a Reactive Double Bond in the Side Chain

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Received April 13, 1993

Summary: The reaction of C_{60} with quadricyclane gives a stable 6,6 adduct which has been spectroscopically characterized. The double bond of the [2.2.1]bicycloheptene moiety reacts readily with electrophiles (e.g., PhSCl).

Soon after the isolation and characterization of fullerene C_{60},[1] the electrophilic character of this carbon cluster was disclosed by both experimental[2] and theoretical[3] results. Additions of several electrophiles to C_{60} have also been reported, but the conditions necessary for these reactions to occur led often to inseparable mixtures of products of multiple addition.[4] In order to allow a controlled addition of electrophiles[5] and to enrich the chemistry of functionalization, C_{60} has to be structurally modified. Herein we report a simple cycloaddition approach to a stable and characterizable C_{60} derivative, in which the incorporated olefinic moiety shows high reactivity toward electrophiles.

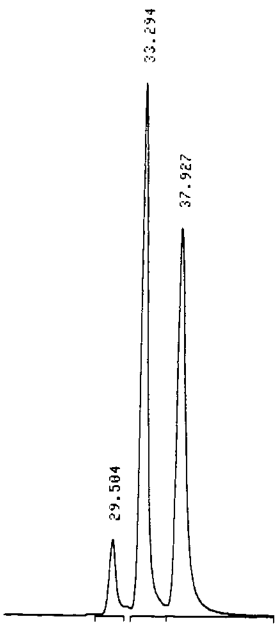

Figure 1. Gel-permeation liquid chromatography separation of 1 (33.29 min) and C_{60} (37.93 min).

The reaction between C_{60} and a 10-fold excess of quadricyclane in toluene proceeds smoothly at 80 °C in 5 h, affording a mixture of two products. Milligram quantities of the main product were isolated by means of gel permeation chromatography (GPC)[6] in 43% yield along with 46% unreacted C_{60} (Figure 1).[7] The structure 1 was assigned to this compound on the basis of spectroscopic and computational analyses (Scheme I, geometries optimized at the MNDO level).

The ^{1}H-NMR spectrum (Figure 2, bottom) of 1 is in agreement with the presence of a [2.2.1]bicycloheptene moiety.[8] The stereochemistry of the addition, *exo* with respect to the norbornene moiety and in line with the known cycloaddition behavior of quadricyclane,[9] is sug-

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(6) A PL-GEL 1210-6120 column (300 × 25 mm) filled with polystyrene–divinylbenzene gel (10 μm, 100 Å) from Polymer Laboratories Ltd. was used in the GPC separations. Isocratic elution was performed on a LC pump unit Shimadzu LC-8A at a flow rate of 8 mL min^{-1} with HPLC-grade toluene as a mobile phase. After filtration of the reaction mixture with a Teflon 0.2-μm membrane filter, 2-mL portions of the brown solution were injected. The elution was monitored with a Shimadzu SPD-6A UV spectrophotometric detector (0.65-μL cell; light path 0.5 mm) at 340 nm. For the separation of fullerene mixtures, see: Gügel, A.; Beker, M.; Hammel, D.; Mindach, L.; Rader, J.; Simon, T.; Wagner, M.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 644.

(7) The minor component (<5% by GPC), probably a product of double addition of quadricyclane to C_{60}, was not investigated.

(8) ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker spectrometers at 200 and 62.5 MHz, respectively. The UV–vis spectra were recorded with a Perkin-Elmer Lambda 5 spectrophotometer. 1: ^{1}H-NMR (CS_2/benzene-d_6 (3:1), 200 MHz) δ 6.50 (m, H-5 and H-6), 3.91 (dm, H-7′, $J_{7,7'}$ = 10.2 Hz), 3.72 (m, H-2 and H-3), 3.68 (m, H-1 and H-4), 1.89 (d quintets, H-7, $J_{7,7'}$ = 10.2 Hz, $J_{1,7} = J_{2,7} = J_{3,7} = J_{4,7}$ = 1.6 Hz); ^{13}C-NMR (CS_2/benzene-d_6 (3:1), 62.5 MHz) δ 41.82, 46.23, 48.37, 67.56, 135.77, 139.16, 140.43, 140.74, 140.91, 141.36, 142.33, 142.34, 142.37, 142.79, 143.00, 143.05, 144.63, 144.76, 145.18, 145.27, 145.44, 145.60, 145.83, 146.09, 146.13, 146.16, 146.92, 147.85, 150.61, 156.31.

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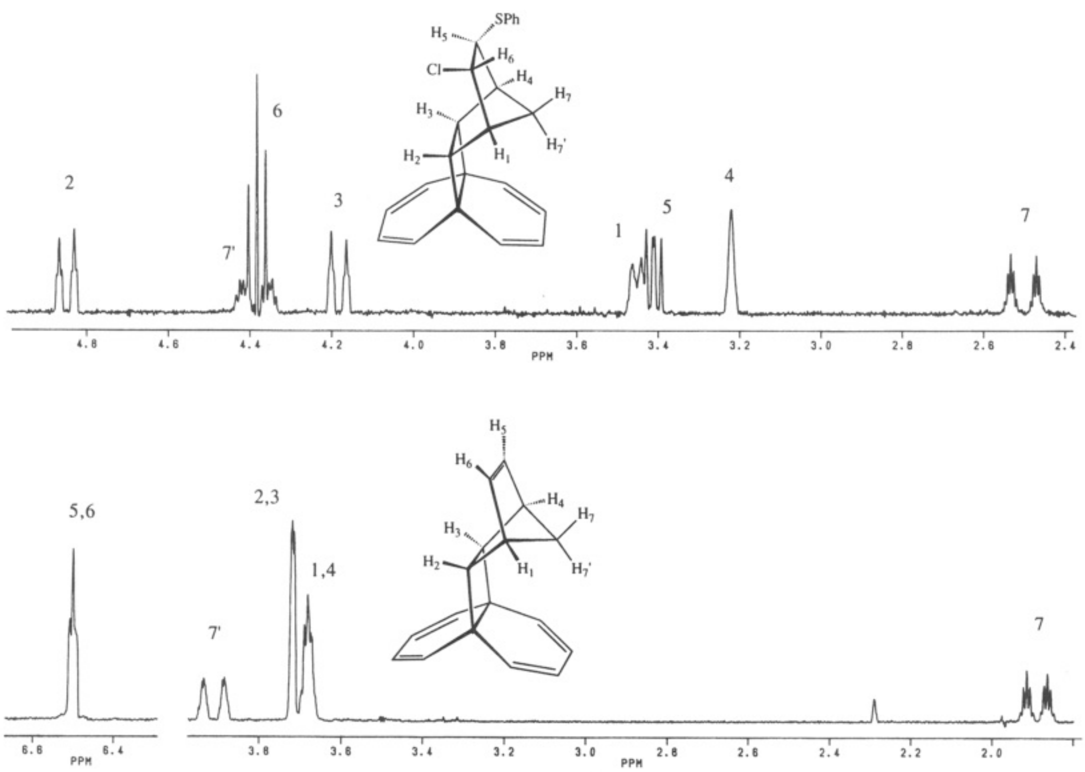
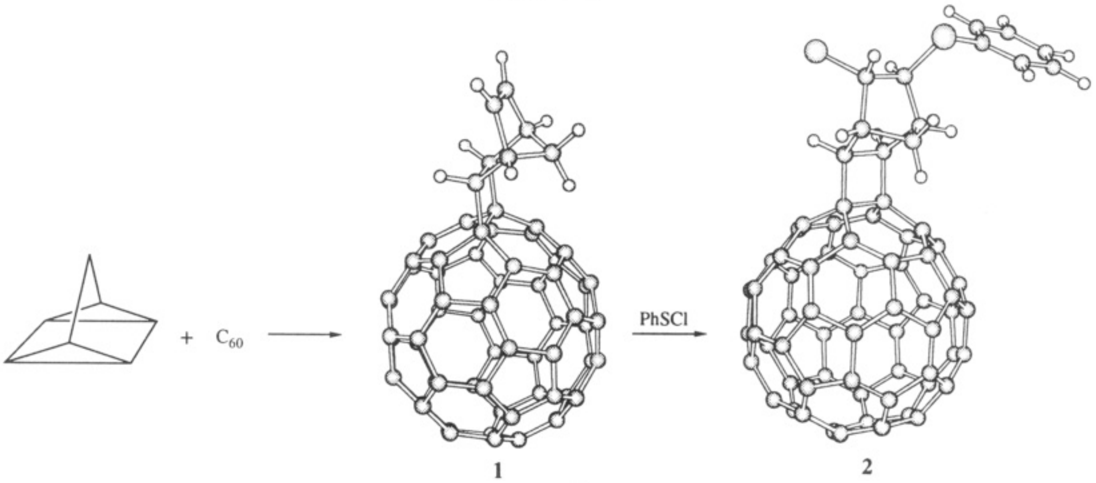


Figure 2. 200-MHz ^{1}H-NMR spectra of **1** in 3:1 CS_2/benzene-d_6 (bottom) and of **2** in $CDCl_3$ (top, aromatics not included). Some assignments are based on NOE analysis.

Scheme I



1 **2**

gested by the detection of a long-range *W* coupling constant between the high-field methano bridge proton and the cyclobutane protons. The structure is confirmed by NOE experiments, where the cyclobutane protons show relevant dipolar interactions with the vinyl protons, but none with either methano bridge proton. One relevant feature of the ^{1}H spectrum of **1** is the striking difference of chemical shift between the two methano bridge protons next to and far from the fullerene sphere (3.88 and 1.87 ppm, respectively). Together with the relatively low-field resonances of cyclobutane and bridgehead protons, these shifts are clearly dependent on the proximity to the spheroid and are to be attributed to the overall deshielding effect of the fullerene surface.[10]

The ^{13}C-NMR spectrum of **1** shows four peaks in the aliphatic region: of these, the low-field signal at 67.56 ppm is attributed to the fullerene sp^3 carbons. The resonance is at higher field than that reported (78.75 ppm) for the analogous carbons of the adduct of C_{60} with benzyne.[11] This trend parallels the ^{13}C aliphatic shifts of cyclobutane and cyclobutene.[12]

As both adducts across the 5,6 and 6,6 junction possess the same C_s symmetry, it is not possible to unambiguously assign the site of addition of quadricyclane to C_{60} from spectroscopic data (the number of the potentially distinct ^{13}C fullerene resonances would be 32 in both cases). The 6,6 adduct is here suggested on the basis of the following considerations. So far, only 6,6 additions have been

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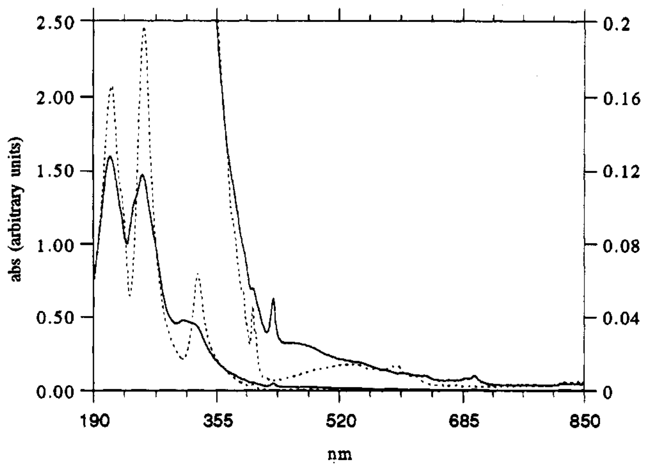

Figure 3. UV-vis spectra of 1 (solid line) and C_{60} (dotted line) in cyclohexane.

observed as primary processes; the reported 5,6 adducts are to be considered secondary rearranged products.[13] Furthermore, frontier orbital symmetry considerations strongly favor the 6,6 attack. At a local level, the 3-fold degenerate LUMO orbitals of fullerene are antisymmetric across any 6,6 junction, and symmetric across most 5,6 junctions. The opposite applies to the 5-fold degenerate HOMO orbitals.[3,14] Thus, the HOMO and LUMO of quadricyclane, which are, respectively, antisymmetric and symmetric with respect to the 1,4 addition mode, will give an in-phase two-electron interaction with the 6,6 junction, but an out-of-phase interaction with the 5,6 junction. Finally, the attack on a 5,6 junction would generate a structure containing a destabilizing endocyclic double bond in a 5-membered ring of the spheroid.[15]

The UV-vis spectrum of 1 exhibits the typical absorptions of C_{60} derivatives with one saturated double bond as in the methanofullerenes[16] (Figure 3). The FAB mass spectrum has a consistent peak at *m/e* 812 (M^+, 20; base peak at *m/e* 720), showing that the cycloadduct is stable with respect to the retro cycloaddition process.[17] This event has represented a major problem in C_{60} functionalization, except in few reported cases of irreversible additions.[18,19]

The norbornene double bond in 1 is unhindered and reacts readily with electrophiles. As an example, benzenesulfenyl chloride and 1 at room temperature afford quantitatively the product 2[20] of *anti* addition (Scheme I).[21,22] The endo and exo orientations of the chloride and sulfide moieties, determined by ^{1}H-NOE spectroscopy, are in agreement with the Alder exo rule.[23] The ^{1}H spectrum of 2 is reported in Figure 2 (top). Due to the asymmetric substitution, all carbons in the fullerene and norbornane moieties are now different. The ^{13}C spectrum of the aromatic region is very complex, and several degeneracies occur. The aliphatic signals are easily distinguished, and the fullerene sp^3 carbons resonate in the same region as in the case of 1 (68.92 and 69.66 ppm).

We have shown that the addition of quadricyclane to C_{60} is a valid pathway to functionalized fullerenes. The product is a stable compound that shows high reactivity towards electrophiles. Further elaboration of 1 and in particular the cationic copolymerization[24] with suitable partners is currently under investigation.

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(17) The loss of cyclopentadiene from 1 in FABMS, if present, is hidden under the matrix signals (NBA). The preparation of the cyclobutene–C_{60} compound via flash vacuum pyrolysis of 1 is presently pursued in our laboratory.

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(20) 2: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 7.6-7.1 (multiplets, aromatics), 4.85 (dt, H-2, $J_{2,3} = 7.3$, $J_{1,2} = J_{2,7} = 1.4$ Hz), 4.38 (ddt, H-7′, $J_{7,7'} = 12.6$, $J_{5,7'} = 3.2$, $J_{1,7'} = J_{4,7'} = 1.7$ Hz), 4.38 (dd, H-6, $J_{1,6} = 4.2$, $J_{5,6} = 4.0$ Hz), 4.18 (dt, H-3, $J_{2,3} = 7.3$, $J_{3,4} = J_{3,7} = 1.4$ Hz), 3.45 (broad d, H-1, $J_{1,6} = 4.2$ Hz), 3.41 (dd, H-5, $J_{5,7'} = 3.2$, $J_{5,6} = 4.0$ Hz), 3.22 (broad s, H-4), 2.50 (d quintets, H-7, $J_{7,7'} = 12.6$, $J_{1,7} = J_{2,7} = J_{3,7} = J_{4,7} = 1.4$ Hz); ^{13}C-NMR ($CDCl_3$, 62.5 MHz) δ 32.38, 46.82, 47.38, 51.51, 59.49, 66.09, 68.92, 69.66, 125.28, 127.53, 128.21, 129.02, 129.32, 131.62, 134.41, 135.93, 139.71, 140.17, 140.29, 140.38, 140.45, 140.61, 140.65, 141.05, 141.90, 141.92, 142.04, 142.06, 142.09, 142.11, 142.48, 142.65, 142.69, 142.76, 142.84, 142.98, 143.06, 144.44, 144.59, 144.63, 145.09, 145.29, 145.41, 145.45, 145.50, 145.93, 145.99, 146.04, 146.91, 147.39, 147.43; FAB mass spectrum *m/e* 956 (M^+, 7), 720 (C_{60}^+, 100).

(21) In a blank experiment we found that excess PhSCl does not react appreciably at room temperature with C_{60}.

(22) Molecular bromine also adds cleanly to the norbornene double bond of 1. The product, though not very soluble in organic solvents, shows a proton NMR pattern very similar to that of 2.

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(24) For C_{60}-containing polymers, see: Shi, S.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 10656.