An Unusual Addition−Rearrangement of a Dialkoxycarbene to C_{60}: Exclusion of Methanofullerene Products

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Received February 14, 1996[⊗]

The expected (dialkoxymethano)fullerene **3**, which would be generated by the addition of methoxy-[2-(trimethylsilyl)ethoxy]carbene across a carbon−carbon double bond of C_{60}, was not obtained; the 1,2- and 1,4-dihydrofullerenes **1** and **2** were isolated instead. The novel compounds **1** and **2** were characterized by ^{13}C- and ^{1}H-NMR as well as FTIR and UV-vis spectroscopies. A mechanism for their formation is suggested.

The functionalization of Buckminsterfullerene C_{60} has been an area of growing interest during the past few years.[1,2] Among the large number of functionalization reactions of C_{60}, the addition of diazoalkanes has been extensively used in our group for the preparation of fulleroids and methanofullerenes.[3−6] 2,2-Dialkoxy-Δ^3-1,3,4-oxadiazolines are convenient sources of dialkoxycarbenes, which are interesting as potential synthons of carbonyl compounds, by thermolysis at 100 °C in solution.[7,8] Recently, we reported the synthesis of (dimethoxymethano)fullerene by addition of dimethoxycarbene to C_{60} and its transformation to methyl 1,2-dihydrofullerenecarboxylate.[9] Here we report the regioselective preparation of 1,2- and 1,4-(methoxycarbonyl)-[(trimethylsilyl)ethyl]dihydrofullerenes by thermolysis of the corresponding oxadiazoline in the presence of C_{60}.

The reaction of C_{60} with methoxy-[2-(trimethylsilyl)-ethoxy]carbene, generated in situ by thermolysis of the corresponding oxadiazoline in 1,2-dichlorobenzene at 120 °C overnight led to a mixture of the 1,2- and 1,4-dihydrofullerenes **1** and **2** in a 2.5/1 ratio according to HPLC (Cosmosil Buckyprep Analytical column, 25% toluene in hexane, 1 mL/min, $\lambda = 326$ nm). The expected (dialkoxymethano)fullerene **3**, which would be generated by the addition of the carbene across a carbon−carbon double bond of C_{60}, was not obtained; instead, two dihydrofullerene adducts were isolated (see Scheme 1).

Isomers **1** and **2** were separated by HPLC on a Cosmosil Buckyprep semiprep column using 30% toluene in hexane as eluent (5 mL/min, $\lambda = 326$ nm) and were characterized as the 1,2 and 1,4 adducts by ^{1}H and ^{13}C NMR, FTIR, UV-vis, mass spectrometry, elemental analysis, and cyclic voltammetry. They are the most soluble C_{60} derivatives (ca. 50 mg/mL in ODCB) made to-date in our laboratory.

The ^{1}H NMR spectra of both compounds are consistent with their structure, showing the signals corresponding to the trimethylsilyl, methoxy, and the two methylene groups. From the number of carbon resonances in the fullerene region it is clear that the ^{13}C NMR spectrum of compound **1** corresponds to a derivative with C_s symmetry. However, the absence of symmetry for compound **2** (42 signals in the region between 158 and 138 ppm) is in agreement with the structure of a 1,4-adduct.

FTIR for both isomers shows the absorption corresponding to the ester carbonyl (1736 and 1741 cm^{-1} for compounds **1** and **2**, respectively) as well as the strong peak at 526 cm^{-1}, typical for C_{60} derivatives. The absorptions at 1429, 1246, and 1211 (1224 for the 1,4-adduct) can be assigned to $CH_3{-}Si$ and $CH_2{-}Si$ stretching.

MS confirms that compounds **1** and **2** are isomers with molecular weight 880. FABMS shows the molecular peak for the 1,2-adduct, but it failed for the other isomer. The molecular ion of the 1,4-dihydrofullerene **2** was observed in negative ion electrospray MS.

The UV-vis absorption of **1** is identical to that of other 1,2-dihydrofullerenes. However, the 1,4-dihydrofullerene **2** shows a broad band in the visible at 448 nm typical of fullerenes with a double bond endocyclic to a pentagon as recently reported for a 1,4-dialkyldihydrofullerene.[10]

One possible mechanism for this reaction is depicted in Scheme 2 and is in agreement with the nucleophilic nature of dialkoxycarbenes and the electrophilicity of C_{60}. The addition of dimethoxycarbene to olefins with one or more electron-withdrawing groups, yielding the corresponding 1,2-adducts, has been previously observed.[11] Moreover, methoxy[(trimethylsilyl)ethoxy]carbene adds to *N*-phenylmaleimide to afford **4**, which must have

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.

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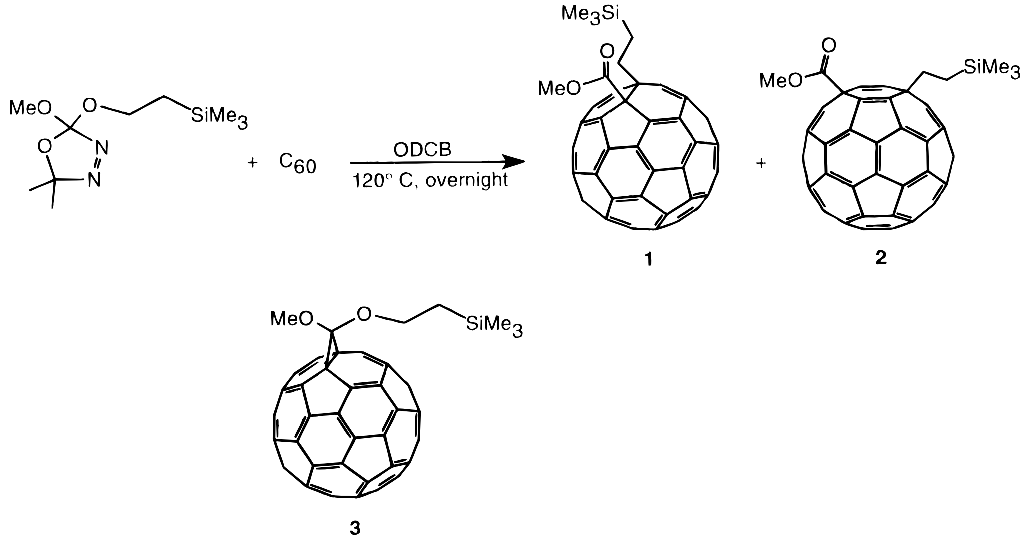
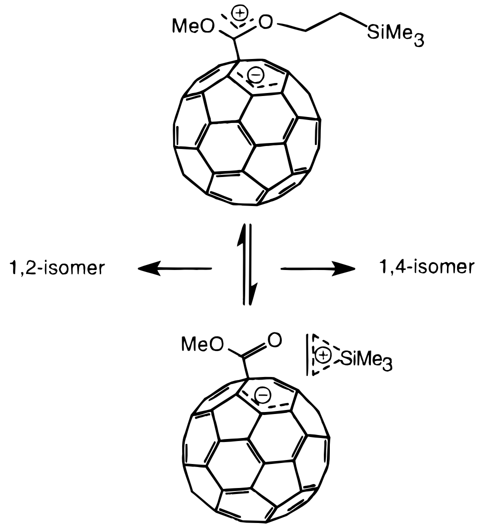
S0022-3263(96)00313-1 CCC: $12.00

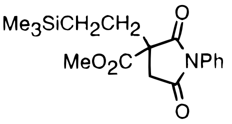
Scheme 1



Scheme 2



arisen by migration of the (trimethilsilyl)ethyl group from oxygen to carbon.[12]



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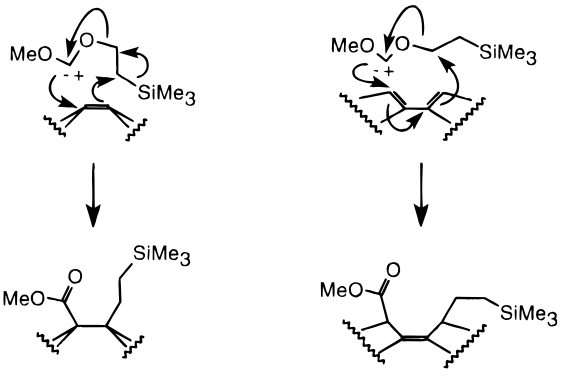
In Scheme 2, the reactions forming **1** and **2** are depicted in stepwise form, to emphasize the analogy to β-(trimethylsilyl)ethyl cation intermediates, in which the β-effect[13] of the TMS group plays an important stabilizing role.[14]

Although a stepwise mechanism is illustrated, to draw attention to the possibility that the methylene groups in the products may not have their original connections, we have no evidence that the reactions are not partially or fully concerted, as in Scheme 3.

Scheme 3



Cyclic voltammetry experiments[15] (CV) showed that **1** exhibited three reversible reductions and a fourth reduction which was irreversible. The first reduction occurred at a potential approximately 85 mV more negative than for C_{60}, as expected for a 1,2-dihydrofullerene.[16,17] The half-cell potentials (defined as $E_n = 0.5[E_{p,c} + E_{p,a}]$) for the reversible reductions of **1** relative to F_c/F_c^+ were −1141, −1520, and −2050 mV, while the peak potential of the irreversible fourth reduction occurred at −2602 mV. The corresponding E_n values for the reduction of C_{60} under the same conditions were −1056, −1451, and −1906 mV.

The CV of **2** demonstrated the relative similarity of the 1,4-isomer toward reduction. At low scan rates ($\leq$100 mV/s), the CV shows three reductions which are chemically reversible, followed by a fourth reduction which is irreversible. However, at higher scan rates (>100 mV/s) or with repeated cycling, it becomes obvious that **2** undergoes coupled chemical reactions upon the addition of one or more electrons, as an additional anodic wave became evident. An estimate of the half-cell potentials E_n for **2** gives values of −1148, −1598, and −2048 mV for the first three waves, while the peak potential of the

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(15) Cyclic voltammetry experiments were performed at 1 mM analyte concentration in 1,2-dichlorobenzene with 0.1 M Bu_4NBF_4, Ag/$AgNO_3$ (nonaqueous) reference electrode, and Pt disc working electrode. Ferrocene (0.5 mM)was added as an internal reference. The scan rate was 100 mV/s.

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fourth reduction comes at −2578 mV, indicating similar electron affinities for the two regioisomers.

Experimental Section

Addition of 2-Methoxy-2-[2-(trimethylsilyl)ethoxy]-oxadiazoline to C_{60}. To a solution of C_{60} (300 mg, 0.41 mmol) in 25 mL of anhydrous 1,2-dichlorobenzene was added 2-methoxy-2-[2-(trimethylsilyl)ethoxy]oxadiazoline (100 mg, 0.41 mmol) under nitrogen, and the mixture was heated at 120 °C overnight. The solvent was removed *in vacuo*, and the product was dissolved in a minimum amount of carbon disulfide and purified by column chromatography on silica gel using cyclohexane/toluene (95/5) as eluent. The column was first eluted with 50 mL of carbon disulfide and then with the 95/5 cyclohexane/toluene mixture. Unreacted C_{60} was collected first, and then the fraction containing a mixture of 1,2- and 1,4-isomers was recovered. Solvents were removed *in vacuo*, and the product was precipitated with methanol from a toluene solution. The precipitate was centrifuged, washed with methanol, centrifuged twice more, and finally dried *in vacuo*. The mixture of isomers (2.5:1 ratio by analytical HPLC chromatography using an analytical Cosmosil Buckyprep column, 25% toluene in hexane, 1 mL/min, UV/326 nm) was separated by preparative HPLC, using a semipreparative Cosmosil Buckyprep column (30% toluene in hexane, 5 mL/min, UV/326 nm), to afford 75 mg of **1** and 30 mg of **2**; total yield, 105 mg (29%).

1,2-isomer. ^{1}H NMR (CS_2/500 MHz): 4.18 (3H, s), 3.41 (2H, m), 1.43 (2H, m), 0.24 (9H, s) ppm. ^{13}C NMR (1,2-dichlorobenzene-d_4/125 MHz): 171.20, 155.38, 152.17, 147.67, 147.58, 146.43, 146.23, 146.11, 145.74, 145.53, 145.36, 145.21, 144.65, 144.53, 143.17, 142.64, 142.54, 142.23, 141.97, 141.43, 141.36, 139.79, 139.67, 135.88, 135.29, 72.97, 68.41, 53.66, 37.17, 15.76, −1.46 ppm. FTIR (KBr): 1736 m, 1429 w, 1246 m, 1211 m, 1195 m, 1016 w, 857 m, 834 m, 822 m, 788 w, 765 w, 745 w, 576 m, 562 w, 552 m, 531 m, 526 s cm^{-1}. FABMS (toluene/NBA): m/z 881 (M + H)$^+$, 720 (C_{60})$^+$. Anal. Calcd for $C_{67}H_{16}O_2Si$: C, 91.36; H, 1.82; Si, 3.18. Found: C, 90.71; H, 1.79; Si, 2.28. UV-vis (toluene) λ_{max} (nm): 320, 432, 472, 556, 700.

1,4-isomer. ^{1}H NMR (CS_2/500 MHz): 4.09 (3H, s), 3.10 (2H, m), 1.46 (2H, m), 0.24 (9H, s) ppm. ^{13}C NMR (1,2-dichlorobenzene-d_4/125 MHz): 168.77, 157.54, 152.05, 151.76, 149.06, 148.75, 148.55, 147.89, 147.80, 147.61, 147.21, 146.96, 146.87, 145.53, 145.45, 145.38, 144.93, 144.76, 144.71, 144.53, 144.45, 144.35, 144.25, 144.06, 143.95, 143.80, 143.23, 143.16, 143.03, 142.93, 142.59, 142.53, 142.33, 142.26, 142.18, 141.99, 141.94, 141.09, 140.53, 139.80, 138.63, 138.56, 138.16, 62.88, 62.17, 53.91, 37.56, 13.86, −1.58 ppm. FTIR (KBr): 1741 s, 1429 m, 1246 s, 1224 s, 1187, m, 1018 m, 859 m, 835 m, 531 w, 527 s cm^{-1}. ESMS (toluene): m/z 880 (M), 720 (C_{60}). Anal. Calcd for $C_{67}H_{16}O_2Si$: C, 91.36; H, 1.82; Si, 3.18. Found: C, 90.36; H, 1.79; Si, 2.20. UV-vis (toluene) λ_{max} (nm): 332, 448, 538, 618, 688.

Acknowledgment. F.W. thanks the National Science Foundation for support through Grants DMR-91-22536, DMR-9500888, and CHE 93-00954. R.G. thanks the Ministerio de Educación y Ciencia (Spain) for a postdoctoral fellowship. J.W. acknowledges the Natural Sciences and Engineering Research Council of Canada (NSERC).

JO9603136