Novel Bismethanofullerenes and Ethenofullerene from the Reaction of Propiolates with C_{60} in the Presence of Triphenylphosphine

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Methyl propiolate reacts with C_{60} in the presence of triphenylphosphine in toluene to give a bismethanofullerene **2**. Compound **2** is an adduct of two methyl propiolate units to a C_{60} moiety and consists of two methano bridges across two 6,6-ring junctions of the same six-membered ring on the fullerene moiety. Similarly, ethyl propiolate reacts with C_{60} in the presence of PPh_3 to yield bismethanofullerene **3**. Detailed analysis of the products from the reaction of methyl propiolate with C_{60} shows, in addition to **2** and C_{60}, an ethenofullerene **4** and an unidentified insoluble material were isolated. Compound **4**, which may be viewed as a [2 + 2] cycloaddition adduct of C_{60} and methyl propiolate, consists of a cyclobutene ring fused to the carbons on a 6,6-ring junction of the C_{60} moiety. On the basis of the known chemistry of phosphine with electron-withdrawing alkynes and C_{60}, mechanisms are proposed to account for the formation of the bismethanofullerenes **2** and **3** and ethenofullerene **4**.

Introduction

Multiple functionalization of C_{60} has attracted increasing attention recently.[1,2] Due to the presence of 30 identical carbon−carbon double bonds in a C_{60} moiety, multiple functionalization generally creates a complex mixture of regioisomers. Earlier investigations in this area were focused on the separation and characterization of the regioisomers and the understanding of regioselectivity.[2] The development of selective routes to multiple adducts of fullerene is not only a great challenge to synthetic chemists but also of practical utility. Recent studies in this aspect have led to significant progress.[3]

Cyclopropanation of C_{60} has led to the synthesis of various methanofullerenes and fulleroids.[4,5] For most examples, multiple cyclopropanations on C_{60} occur on different rings of the fullerene moiety, yielding various regioisomers.[2a,4] An exception is the preparation of bisfulleroid **1** from an intramolecular [4 + 4] photocyclization of a cyclohexadiene derivative of C_{60}.[6] This bisfulleroid product contains two methano bridges across two 5,6-ring junctions of the same six-membered ring on the C_{60} moiety. Other than this [4 + 4] photocyclization reaction, there is no effective method for the synthesis of bisfulleroid or bismethanofullerene with the two methano groups attached to the same ring on the C_{60} moiety. In this paper, we report an unusual route for the construction of two cyclopropane groups across two 6,6-ring junctions of the same six-membered ring on the C_{60} moiety. The formation of these bismethanofullerenes involves an interesting triphenylphosphine-mediated addition of two propiolate units to a C_{60} moiety.

Results and Discussion

Treatment of methyl propiolate with C_{60} in the presence of triphenylphosphine in toluene at ambient temperature gave a C_{60} derivative **2** in 41% yield based on the C_{60} recovered. The structure of **2**, which consists of two methano bridges across two 6,6-ring junctions of the same six-membered ring on the C_{60} moiety, was determined on the basis of the MS, NMR, and IR spectral data.

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MS analysis of **2** clearly shows the molecular ion at 888 supporting an adduct of two methyl propiolate units to a C_{60} moiety. In accordance with the proposed structure, the ^1H NMR spectrum displays four characteristic singlets at 8.51 (s), 4.28 (s), 4.09 (s) and 3.99 (s) ppm assigned to the olefin, methine, and methyl protons, respectively. The presence of two different ester groups is evidenced by the strong IR absorptions at 1745 and 1710 cm^{-1} for the C═O groups. Unlike the observed simple ^1H NMR pattern, the ^{13}C NMR spectrum of **2** is complicated, showing more than 60 signals. These ^{13}C NMR data, indicative of the lack of symmetry element, are consistent with the C_1 symmetry of the proposed structure. Characteristic ^{13}C NMR signals for the two cyclopropane rings appear at 50.69, 52.95, 64.54, 68.48, 31.82 (*C*H), and 43.06 ppm. The former four resonances are assigned to the quaternary carbons on the C_{60} moiety, while the latter two are due to the methano groups. To provide further evidence for the proposed atom connection of compound **2**, a HMBC (heteronuclear multiple-bond connectivity) spectrum of the C_{60} derivative was taken. It is known that the HMBC technique is a powerful tool for detecting the connectivity of a proton to carbons two and three bonds away via long-range H−C couplings and thus is useful in determining the skeleton of an organic molecule.[7] Key results of the HMBC experiment of compound **2** are summarized below. The olefin proton (H62) at 8.51 ppm shows connectivity to C61 (43.06 ppm), C63 (128.30 ppm) (two bonds away), C64 (31.82 ppm), C65 and C66 (165.38 and 165.64 ppm) (three bonds away), and two (52.95, 64.54 ppm) quaternary carbons on the C_{60} moiety. On the other hand, the tertiary proton (H64) on a cyclopropane ring at 4.28 ppm reveals connectivity to C63 (two bonds away), C62, C66 (three bonds away), the four quaternary sp^3 carbons (50.69, 52.95, 64.54, and 68.48 ppm), and some sp^2 carbons on the C_{60} moiety.[8] The observed connectivity of the olefin and methine protons to carbons on the substituent of **2** is in excellent agreement with the proposed head-to-tail addition mode of the two propiolate units. Other types of connection cannot lead to the results shown in the HMBC spectrum. The observed connectivity between the tertiary proton (H64) and some of the sp^2 carbons on the C_{60} moiety may be understood in view of the fact that the nearest sp^2 carbons on the C_{60} moiety are only three bonds away from the tertiary proton. In contrast, the olefin proton does not couple to any of the sp^2 carbons of the C_{60} moiety due to the longer distance of this proton to the nearest fullerene sp^2 carbons.

Under similar reaction conditions, ethyl propiolate reacts with C_{60} in the presence of PPh_3 to yield a biscyclopropane adduct **3** in 15% yield based on the C_{60} recovered. This species is also characterized by various spectral data. The ^1H NMR resonances for the olefin and methine protons appear at 8.51 and 4.29 ppm, respectively. Due to the asymmetric nature of this fullerene derivative, the methylene protons on one of the ester groups appear at 4.54 ppm as an AB-type pattern. Except for the resonances of the alkyl substituents, the ^{13}C spectrum of **3** closely resembles that of compound **2**. These results indicate that **2** and **3** are analogous in structure.

Detailed analysis of the products from the reaction of methyl propiolate with C_{60} shows, in addition to **2** and recovered C_{60} (51%), a [2 + 2] cycloaddition adduct **4** and an unidentified insoluble material. The yield of the minor product **4** increases as the relative ratio of PPh_3 to C_{60} increases. At $PPh_3/C_{60} = 20$, compound **4** was isolated in 6% yield. The relative ratio of propiolate to C_{60} also effects the yield. The optimal ratio of propiolate/PPh_3/C_{60} is ca. 4/20/1. Higher propiolate stoichiometry reduces significantly the yield of **4**, while a lower propiolate ratio (2/20/1) gives approximately the same yield but with longer reaction time. The structure of this derivative was determined on the basis of the observed MS, NMR, and IR spectral data. The mass spectrum of **4** shows clearly the molecular ion at 804, confirming a monoadduct of methyl propiolate to C_{60}. In agreement with the proposed structure, the ^1H NMR spectrum reveals two singlets at 8.31 (s), 3.91 (s) ppm for the olefin and methyl protons, respectively. The presence of an ester group is evidenced by the strong IR absorptions at 1712 (s). In the ^{13}C NMR spectrum, 36 signals were observed consisting of a C_s symmetry of the proposed structure. The signals for the two quaternary carbons appeared at remarkably low field (82.89 and 111.09 ppm) compared to those of fullerene derivatives. It is noteworthy that there are only two cyclobutene derivatives of C_{60} reported. One is from a photochemical reaction of C_{60} with *N,N*-diethylpropynylamine,[9] and the other is from the reaction of benzyne with C_{60}.[10] The former is relatively unstable, and no ^{13}C NMR data were reported. The latter exhibits a signal at 78.75 ppm for the fused carbons on a 6,6-ring junction of the fullerene moiety. Compound **4** appears to be one of the few cyclobutene derivatives of C_{60} that is thermally stable.

The reactions of C_{60} with electron-withdrawing alkynes assisted by phosphines have been studied.[11,12] We reported a PCy_3-promoted (Cy = cyclohexyl) cotrimerization of propiolates with C_{60} to give six-membered ring adducts and a codimerization of 2-butynoates with C_{60} to yield four-membered ring products. Subsequently, two independent reports showed that the butynoate adducts are five-membered ring species.[12] The reactivities of PCy_3 and PPh_3 toward alkyl propiolate and C_{60} are markedly different. In the presence of PCy_3, alkyl propiolate reacts with C_{60} instantly, but the reaction of alkyl propiolate with C_{60} in the presence of PPh_3 requires more than 10 h. Most surprisingly, the products from these two phosphine-promoted reactions are different. Although the exact cause is still unknown, the differences in nucleophilicity and steric effect of these two phosphines are likely the driving forces for the formation of these two different products.

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[8] The observed cross-peak in the HMBC spectrum of the methine proton to the sp^2 carbons on the C_{60} moiety appears at ca. 145 ppm. Since the cross-peak is broad and many resonances of compound **2** occur in this region, it is impossible to determine correctly the ^{13}C signals that couple to the methine proton.

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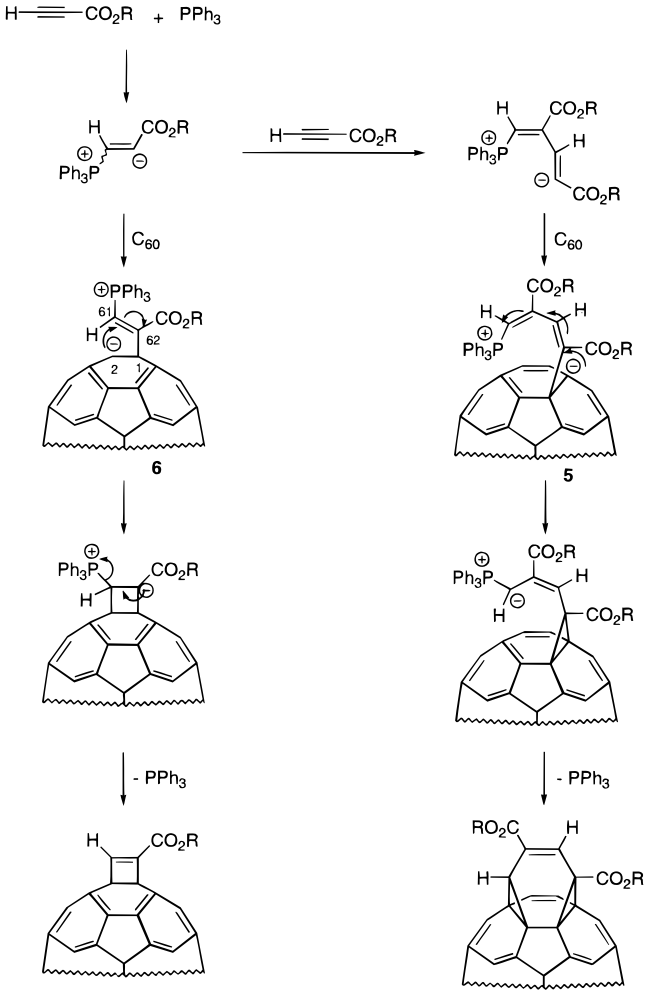
Scheme 1



On the basis of the known chemistry of phosphine with electron-withdrawing alkynes,[13] the mechanisms shown in Scheme 1 are proposed to account for the formation of the biscyclopropane and cyclobutene derivatives. In both cases, the first step involves the attack of PPh_3 at the β-carbon of a propiolate molecule. For the formation of the biscyclopropane derivatives, this is followed by another attack at a second propiolate molecule prior to addition to the fullerene moiety. Back-attack of the resulting fullerene intermediate **5** at the α-carbon gives the first cyclopropane ring and an ylide function at the terminal carbon of the substituent. Reaction of the ylide function with a neighboring carbon−carbon double bond on the fullerene moiety affords the second cyclopropane ring and completes the reaction. The reactions of phosphorus and sulfur ylides with fullerenes to give cyclopropane derivatives are known.[14] In addition, the reaction of a phosphorus ylide with a carbon−carbon double bond to form a cyclopropane ring was implicated in the reaction of $Ph_3P^+CH_2^-$ with fluorenone.[15] For the formation of the cyclobutene derivative **4**, the nucleophile produced from the addition of a PPh_3 to a propiolate molecule attacks a C_{60} instead of a second molecule of propiolate. Back-attack of the resulting intermediate **6** at the β-carbon of the substituent followed by an elimination of the phosphine group affords the final product. It should be noted that, according to Baldwin's rule,[16] a normal 4-*endo-trig* cyclization to give a cyclobutene ring is disfavored. In the present case, however, the bond angles around the C1 center of the proposed intermediate **6** are expected to be greatly different. The angle C2−C1−C62 should be much smaller than a normal sp^3 angle, while the other three surrounding the C1 center are larger than 109.5° due to the rigid structure of the fullerene moiety. The small C2−C1−C62 angle in intermediate **6** is expected to facilitate 4-*endo-trig* ring closure.

Conclusion

Regioselective synthesis of bismethanofullerenes has been achieved by the reaction of C_{60} with methyl or ethyl propiolate in the presence of triphenylphosphine. HMBC and other spectroscopic techniques unambiguously confirm that the cyclopropane rings in the bismethanofullerenes are formed across two 6,6-ring junctions of the same six-membered ring on the C_{60} moiety. An unusual [2 + 2] cycloaddition product of C_{60} and methylpropiolate has also been isolated. Mechanisms have been proposed for the formation of bismethanofullerens and ethenofullerene.

Experimental Section

All reactions were performed under an atmosphere of dry nitrogen, and all solvents were dried by standard methods. Triphenylphosphine, methyl propiolate, and ethyl propiolate (Aldrich) and C_{60} (MER) were used as purchased.

Synthesis of Compound 2. To a mixture of C_{60} (0.0360 g, 0.0500 mmol) and PPh_3 (0.0524 g, 0.200 mmol) in a round-bottom sidearm flask was added toluene (25 mL). The system was evacuated and filled with nitrogen three times and was then stirred until C_{60} was completely dissolved in the solvent. Methyl propiolate (0.0168 g, 0.200 mmol) was added to the system via a syringe. The solution was stirred at ambient temperature for 12 h. The reaction mixture was first passed through a short silica gel column to remove undissolved material and then concentrated on a rotary evaporator. The compounds in the concentrated solution were separated on a silica gel column using toluene as eluent. The fractions containing C_{60} and compound **2** were collected separately. After solvent removal, both compounds were washed with ether and acetone to afford C_{60} (0.0184 g, 0.0255 mmol, 51%) and compound **2** (0.0089 g, 0.0100 mmol). The yield of **2** based on the fullerene consumed is 41%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99 (s, 3 H, CH_3), 4.09 (s, 3 H, CH_3), 4.28 (s, 1 H, CH), 8.51 (s, 1 H, =CH). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 31.82 (CH), 43.06, 50.69, 52.95, 53.07 (CH$_3$), 53.44 (CH$_3$), 64.54, 68.48, 128.30, 133.04 (=CH), 138.05, 138.97, 141.35, 141.39, 141.49, 141.57, 141.68, 141.77, 141.85, 141.99, 142.17, 142.34, 142.53, 142.71, 142.88, 142.94, 142.99, 143.08, 143.43, 143.47, 143.51, 143.57, 143.63, 144.15, 144.16, 144.25, 144.39, 144.63, 144.67, 144.69, 144.95, 145.04, 145.07, 145.11, 145.43, 145.53, 145.55, 145.83, 145.87, 146.09, 146.22, 146.47, 146.56, 147.06, 147.15, 147.24, 147.40, 147.89, 148.55, 149,79, 151.46, 165.38, 165.64. IR (KBr): 1745, 1710, 1636, 1278, 1234, 1190, 1111, 760, 736, 563, 525 cm^{-1}. UV−vis (chloroform) λ_{max}: 257, 327, 439, 682 nm. FAB-MS m/z (rel intensity): 890 (M + 2$^+$, 30), 889 (M +

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1^+, 46), 888 (M^+, 40). HRMS: calcd for $C_{68}H_8O_4$ 888.0423, found 888.0429.

Compound **3** was prepared in 15% yield based on C_{60} consumed by following a procedure similar to that of compound **2**. C_{60} was recovered in 47% yield. Important spectral data are as follows. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (t, $J = 7.6$ Hz, 3 H, C*H*$_3$), 1.52 (t, $J = 7.2$ Hz, 3 H, C*H*$_3$), 4.29 (s, 1H, C*H*), 4.45 (q, $J = 7.6$ Hz, 2 H, C*H*$_2$), 4.54 (m, 2 H, C*H*$_2$), 8.51 (s, 1H, ═C*H*). ^{13}C {H} NMR (150 MHz, $CDCl_3$): δ 14.32 (*C*H$_3$), 14.44 (*C*H$_3$), 31.96 (*C*H), 43.29, 50.86, 53.02, 62.18 (*C*H$_2$), 62.97 (*C*H$_2$), 64.66, 68.58, 128.57, 132.90 (═*C*H), 138.07, 138.98, 141.34, 141.39, 141.51, 141.59, 141.62, 141.80, 141.83, 141.98, 142.15, 142.29, 142.50, 142.72, 142.88, 142.95, 142.99, 143.09, 143.34, 143.45, 143.49, 143.57, 143.62, 144.15, 144.23, 144.36, 144.62, 144.68, 144.98, 145.10, 145.13, 145.18, 145.43, 145.52, 145.55, 145.81, 145.88, 146.09, 146.22, 146.48, 146.49, 146.57, 147.07, 147.15, 147.36, 147.61, 147.96, 148.60, 149,85, 151.54, 165.22, 165.23. IR (KBr): 1738, 1716, 1632, 1367, 1231, 1180, 1101, 728, 563, 525 cm^{-1}. UV−vis (chloroform) λ_{max}: 259, 330, 438, 523 nm. FAB-MS *m*/*z* (rel intensity): 918 ($M + 2^+$, 18), 917 ($M + 1^+$, 30), 916 (M^+, 36). HRMS: calcd for $C_{70}H_{12}O_4$ 916.0736, found 916.0728.

Synthesis of Compound 4. To a mixture of C_{60} (0.0360 g, 0.0500 mmol) and PPh_3 (0.262 g, 1.00 mmol) in a round-bottom sidearm flask was added toluene (25 mL). The system was stirred under an atmosphere of nitrogen until C_{60} was completely dissolved. Addition of methyl propiolate (0.0168 g, 0.200 mmol) via a syringe was followed by stirring at ambient temperature for 12 h. The solvent in the reaction mixture was removed, and the residue was washed with ether to remove triphenylphosphine. The residue was separated on a silica gel column using toluene as eluent. The fractions containing compounds **2** and **4** were collected separately. After solvent removal, both compounds were washed by ether and acetone to afford compound **2** (0.0115 g, 0.0130 mmol) in 26% yield and compound **4** (0.0024 g, 0.0030 mmol) in 6% yield. Spectral data for compound **4** are as follows. ^{1}H NMR (400 MHz, $CDCl_3/CS_2 = 1/1$): δ 3.91 (s, 3 H, C*H*$_3$), 8.31 (s, 1H, ═C*H*). ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3/CS_2 = 1/1$): δ 51.49 (*C*H$_3$), 82.89, 111.09, 135.30, 137.47, 139.79, 139.87, 141.33, 141.56, 142.18, 142.22, 142.32, 142.38, 142.60, 142.67, 142.70, 142.93, 143.36, 144.04, 144.38, 144.56, 144.96, 145.10, 145.39, 145.46, 145.88, 145.92, 146.04, 146.18, 146.35, 146.79, 147.18, 147.43, 147.97, 157.34 (═*C*H), 163.80. IR (KBr): 1712, 1624, 1432, 1329, 1156, 1123, 903, 883, 728, 526 cm^{-1}. UV−vis (chloroform) λ_{max}: 255, 320, 426, 682 nm. FAB-MS *m*/*z* (rel intensity): 806 ($M + 2^+$, 11), 805 ($M + 1^+$, 16), 804 (M^+, 12).

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for compounds **2** and **4** and a HMBC spectrum for **2** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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