Fullerene Derivatives Bearing a Phosphite Ylide, Phosphonate, Phosphine Oxide, and Phosphonic Acid: Synthesis and Reactivities

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Treatment of phosphites ($P(OR)_3$) and MeO_2CCCCO_2Me with C_{60} affords the corresponding fullerene derivatives (**1**, R = Me; **2**, R = Et; **3**, R = *n*-Bu) consisting of a phosphite ylide group and a cyclopropane ring on the fullerene moiety in high yields. NMR data indicate that all phosphite ylides **1**−**3** exist as mixtures of *E* and *Z* isomers. Under similar reaction conditions, the reaction of phosphinite $PPh_2(OMe)$ and MeO_2CCCCO_2Me with C_{60} gives ylide **4**. Ylides **1**−**3** readily undergo hydrolysis with HBr to give corresponding phosphonates **5**−**7** in excellent yields, while ylide **4** reacts with hydrobromic acid to afford phosphine oxide **8**. A mechanism is proposed to account for the formation of these phosphonate derivatives. Further treatment of phosphonate derivative **5** with trimethylsilyl iodide followed by water gave phosphonic acid derivative **9** in 83% yield.

Introduction

The synthesis of fullerene derivatives with polar substituents has attracted considerable attention recently due to the potential applications of these compounds in biological systems.[1−3] Promising activities of these fullerene derivatives for HIV inhibition,[4] DNA cleavage,[5] or cytotoxicity[6] have been reported. Organic phosphorus compounds are well-known biologically active species.[7] The introduction of phosphorus substituents onto fullerene derivatives is not only synthetically challenging but also biologically interesting. Only a couple of methods for the preparation of fullerene derivatives bearing phosphorus substituents have been reported. Nakamura and coworkers reported that lithiated phosphine−borane or phosphinite−borane reacts with C_{60} to give a fullerene derivative having a phosphine or phosphonate group.[8] Recently, the reactions of electron-deficient acetylenes with C_{60} in the presence of phosphines have been studied[9−11] leading to the formation of several types of adducts. In these studies, we observed that addition of a phosphine and an electron-withdrawing acetylene to C_{60} occurred to afford adduct (**A)** bearing a cyclopropane ring and a phosphorus ylide.[10] In this paper, we wish to report that phosphites react with dimethyl acetylenedicarboxylate (DMAD) and C_{60} to give phosphite ylides. Moreover,

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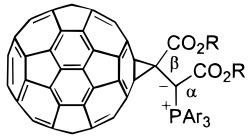
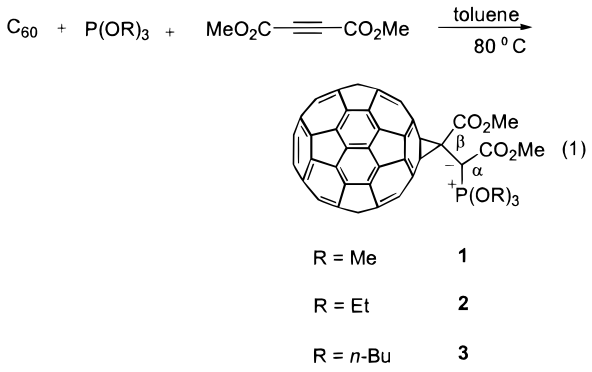
selective hydrolysis of these ylides provides a novel route to introduce various polar phosphorus substituents such as phosphonate ester and phosphine oxide and phosphonic acid to a fullerene moiety.

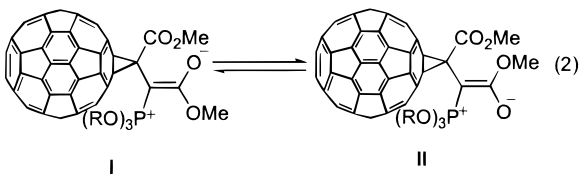


A

Results and Discussion

Synthesis of Ylide Derivatives. Treatment of phosphites $P(OR)_3$ with C_{60} and DMAD at 80 °C gave products (R = Me, **1**; Et, **2**; *n*-Bu, **3**) consisting of a phosphite ylide group and a cyclopropane ring on the fullerene moiety in 66−77% yields (eq 1). The structures of these compounds were determined on the basis of their MS, NMR, IR, and UV−vis spectral data. Compound **1** shows a molecular ion at *m*/*z* 986 in its MS spectrum strongly supporting an adduct of DMAD and $P(OMe)_3$ onto a C_{60} moiety. The IR data reveal two carbonyl absorptions at 1628 and 1734 cm^{-1}. The strong low-frequency absorption at 1628 cm^{-1} is typical for an ylide ester group.[12] In the ^1H NMR spectrum, compound **1** shows a doublet for methoxy protons connected to the phosphorus atom and two singlets for methoxy protons of the carboxylic ester groups at room temperature. The spectrum splits into two sets of resonances at 223 K. Two doublets and four singlets for the methoxy protons were observed. These observations may be rationalized based on the presence of *E*,*Z*-isomers **I** and **II** that undergo rapid interchange at room temperature on the ^1H NMR time scale (eq 2). Similar results were observed for the fullerene derivatives bearing a triarylphosphine ylide group prepared by the reaction of DMAD and $P(Ar)_3$ and C_{60}.[10] In addition, *E* and *Z* isomers of phosphorus ylides are known in the literature.[13]





I II

^{31}P and ^{13}C NMR spectra of **1** also suggest the presence of *E* and *Z* isomers. At 223 K, two ^{31}P NMR signals at 55.0 and 53.4 ppm were clearly observed. In the ^{13}C NMR spectrum at 223 K, there are two sets of signals that consist of nearly 100 resonances in total. Key signals include two sets of carbonyl resonances at 171.7 (d, $^3J_{PC}$ = 25.2 Hz), 170.1, 169.8, 169.0 (d, $^3J_{PC}$ = 21.4 Hz) ppm and the ylide carbon resonances at 44.2 (d, $^1J_{PC}$ = 239.6 Hz), 41.6 (d, $^1J_{PC}$ = 232.0 Hz) ppm. The large $^1J_{PC}$ coupling constants are typical for phosphite ylides.[14] Two sets of ^{13}C signals for the cyclopropane ring in **1** were also observed. The resonances for the two sp^3 carbons on the fullerene moiety appear at 75.8, 75.7 (d, $^3J_{PC}$ = 12.6 Hz), 75.6 (d, $^3J_{PC}$ = 17.1 Hz) ppm and for the quaternary carbon on the DMAD moiety occur at 48.4 (d, $^2J_{PC}$ = 16.4 Hz), 47.3 (d, $^2J_{PC}$ = 13.7 Hz) ppm. These chemical shifts are comparable to the values for reported fullerene derivatives of phosphine ylides[10] and methanofullerenes.[15] Similar spectral properties were observed for compounds **2** and **3**, and thus, ylide structures similar to **1** were assigned to these two compounds.

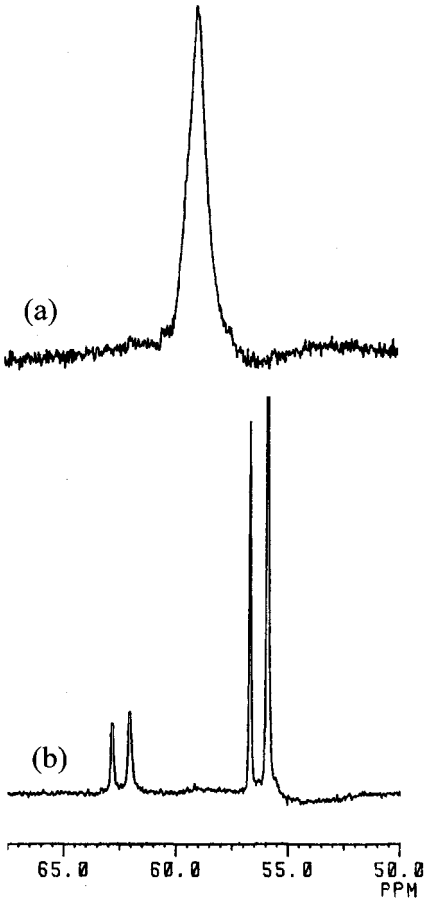


Figure 1. ^{31}P NMR spectra of compound **4** (a) at 293 K; (b) at 243 K.

The reaction of phosphinite $PPh_2(OMe)$ with C_{60} and DMAD at 80 °C gave ylide product **4**. Based on its MS and IR data, we conclude that the structure of this product is similar to compounds **1**−**3** consisting of an

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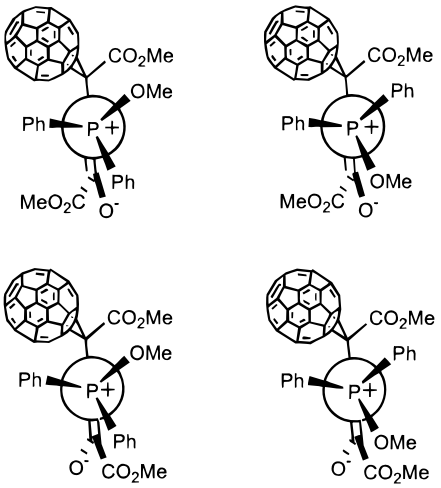
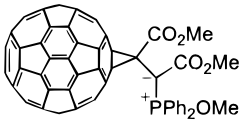
Scheme 1

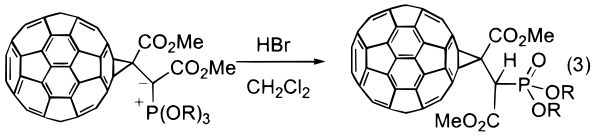


ylide group and a cyclopropane ring fused with the fullerene moiety. However, its ^{1}H, ^{13}C, and ^{31}P NMR spectra are more complicated than those for compound **1**. The ^{31}P NMR clearly shows the presence of four signals with different intensities at 223 K and one broad signal at room temperature (Figure 1). This result strongly indicates that there are four isomers for compound **4** that undergo rapid interconversion at room temperature. As shown previously, there are only two isomers for symmetrical triarylphosphine ylide **A** and trialkyl phosphite ylides **1**−**3** (eq 2). We have shown that in triarylphosphine ylides **A**, the rotation of C_{α}-PAr_3 bond is restricted at low temperature.[10] Thus, it is likely that the observed four isomers of **4** arise from *E*,*Z*-isomerism and restriction rotation of the $C_{\alpha}-PPh_2(OMe)$ bond. There are two conformers for each *E* and *Z* structure. The possible four isomers are shown in Scheme 1.



4

Synthesis of Phosphonate Esters from Phosphite Ylides. Phosphite ylides hydrolyze slowly at ambient temperature to give the corresponding phosphonates. This hydrolysis becomes much faster in the presence of an acid.[16] Thus, treatment of **1**−**3** with hydrobromic acid at ambient temperature in dichloromethane for 3 h afforded phosphonates **5**−**7** in excellent yields (eq 3).



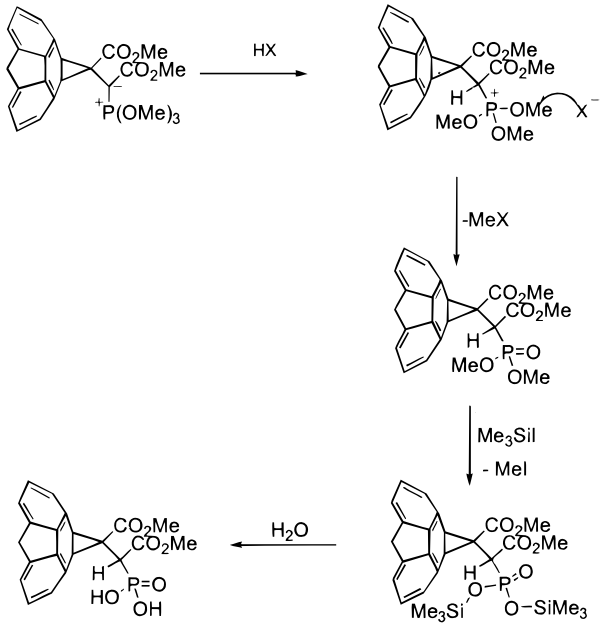
R = Me **5**

R = Et **6**

R = *n*-Bu **7**

These products are fully characterized by their spectral data. The MS spectrum of **5** displaying a molecular ion

Scheme 2



at *m*/*z* 972.6 is in agreement with the proposed molecular formula consisting of a C_{60}, $PO(OMe)_2$, and DMAD moieties. The characteristic absorption for P═O stretching appears at 1270 cm^{-1} in the IR spectrum. In accordance with the proposed structure, the ^{1}H NMR spectrum of **5** shows four resonances at 4.06 (s), 4.02 (d), 4.00 (d), 3.98 (s) ppm for the methoxy protons and a doublet at 4.58 ppm with a coupling constant of 25.6 Hz for the methine proton. The observed two different chemical shifts at 4.02 (d) and 4.00 (d) ppm for the two methoxy groups attached to the phosphorus atom may be understood on the basis of the presence of a chiral center at the methine carbon. The number of ^{13}C NMR signals for **5** is only ca. 1/2 that of the corresponding ylide derivative **1** suggesting only one isomer for **5**. Analysis of the spectral data of **6** and **7** reveals that the structures of these compounds are similar to **5** consisting of a cyclopropane ring and a phosphonate group.

Phosphinite ylide **4** reacts with hydrobromic acid to give phosphine oxide derivative **8**. Presumably, the only P−OR bond in **4** is converted to a P═O bond on reacting with an acid. Evidence for a phosphine oxide moiety is the observation of a strong IR absorption at 1256 cm^{-1} for P═O stretching and the detection of a ^{31}P NMR signal at 26.5 ppm. This ^{31}P NMR resonance is close to that of triphenylphosphine oxide at 28.9 ppm. There are four isomers of **4**, but on hydrolysis or reacting with an acid, these isomers are converted to phosphine oxide **8** that exists as a single isomer. As shown in Scheme 2, the formation of phosphonates or phosphine oxides from the corresponding ylides and hydrobromic acid is likely to occur via protonation at the α-carbon of the ylides, followed by attack of a bromide ion at a carbon attached to a phosphorus oxygen to yield the final product.

Synthesis of Phosphonic Acid 9 from Phosphonates. Attempts to further hydrolyze phosphonate derivatives of fullerene **5**−**7** by reacting with hydrobromic acid did not succeed. However, treatment of **5** with Me_3SiI at 0 °C and then with water led to further hydrolysis

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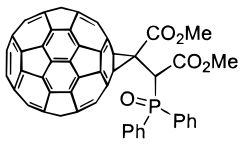
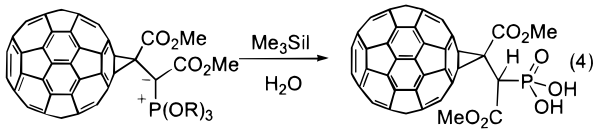


8

of **5** at the phosphonate group[17] and the formation of a new fullerene derivative **9**, which consists of a cyclopropane ring and a phosphonic acid group in good yield.



R = Me, Et, *n*-Bu **9**

Under similar reaction conditions, **6** and **7** were also converted to **9**. MS data of **9** showing a molecular ion at *m*/*z* 944 firmly support the proposed molecular formula. Its IR spectrum confirms the presence of hydroxyl groups at 3433 cm^{-1}. Strong evidence for selective hydrolysis of the ester groups in **5** is given in the ^1H NMR spectrum. Unlike phosphonate **5** that shows two doublets and two singlets for the methoxy protons, only two singlets for the methoxy protons appear in the ^1H NMR spectrum of **9**. The absence of P−H coupling for the methoxy protons of **9** undoubtedly indicates that no methoxy group is directly bound to the phosphorus atom and two -methoxy groups are attached to the carbonyl groups. The ^{13}C NMR spectrum of **9** is similar to that of **5** except for the absence of two methoxy carbons. These ^{13}C NMR data suggest that the skeleton of **9** is similar to that of **5**.

Conclusion

We have demonstrated that phosphites react with DMAD and C_{60} to give fullerene derivatives containing a cyclopropane ring and a phosphite ylide group. Selective hydrolysis of these ylides provides methods for the preparation of fullerene derivatives bearing a phosphonate ester, phosphine oxide and phosphonic acid. Temperature-dependent NMR experiments clearly show that each ylide of $P(OR)_3$ exists as a mixture of two Z and E isomers, but the ylide of $PPh_2(OR)$ exists as a mixture of four isomers including Z and E isomers and conformers. The biological activities of these highly polar fullerene derivatives are currently under investigation.[18]

Experimental Section

Reaction of C_{60}, Dimethyl Acetylenedicarboxylate and Trimethyl Phosphite: Synthesis of Compound 1. To a 100-mL sidearm flask consisting of C_{60} (0.0724 g, 0.101 mmol) and $P(OMe)_3$ (0.21 mL) in toluene (60 mL) with stirring at 80 °C was injected a solution of dimethyl acetylenedicarboxylate (0.0425 g, 0.299 mmol) in toluene (20 mL) via a syringe pump with an injection rate 1.5 mL/h. After injection, the mixture was further stirred for 3 h at the same temperature. The solution was concentrated in a vacuum system to ca. 2 mL. The mixture was separated on a silica gel column. Elution of the column with toluene led to isolation of unreacted C_{60} (0.0059 g) in 8% yield. Further elution with a mixture of hexanes, ethyl acetate and dichloromethane (2:2:1) yielded two fractions consisting of monoadduct **1** (R_f = 0.53) and bisadducts, collected separately. After solvent removal, both fractions were washed with hexane thoroughly to afford the desired pure monoadduct (0.0701 g) in 77% yield and bisadducts (0.0211 g) in 18% yield as a mixture of isomers. Spectral data for compound **1** follow. ^1H NMR (400 MHz, $CDCl_3$) 223 K: δ 4.03 (OCH_3), 4.00 (OCH_3), 3.99 (OCH_3), 3.98 (OCH_3), 3.97 (OCH_3), 3.95 (OCH_3), 3.75 (OCH_3), 3.72 (OCH_3). ^{13}C NMR (150 MHz, $CDCl_3$) 228 K: δ 171.65 (d, $^3J_{PC}$ = 25.2 Hz), 170.12, 169.84, 169.03 (d, $^3J_{PC}$ = 21.4 Hz), 150.06, 149.52, 148.87, 148.41, 147.70, 147.62, 147.05, 146.58, 145.95, 145.73, 145.56, 145.15, 145.02, 144.90, 144.84, 144.81, 144.77, 144.74, 144.69, 144.50, 144.47, 144.44, 144.42, 144.39, 144.35, 144.33, 144.31, 144.29, 144.27, 144.24, 144.21, 144.12, 144.07, 144.02, 143.99, 143.95, 143.81, 143.77, 143.76, 143.71, 143.49, 143.38, 143.35, 143.30, 142.70, 142.67, 142.65, 142.62, 142.60, 142.58, 142.54, 142.48, 142.45, 142.40, 142.37, 142.29, 142.25, 142.05, 141.96, 141.91, 141.85, 141.81, 141.77, 141.74, 141.51, 141.45, 141.06, 140.58, 140.38, 140.33, 140.28, 140.23, 139.04, 138.52, 138.04, 137.90, 137.83, 136.89, 136.30, 75.77, 75.69 (d, $^3J_{PC}$ = 12.6 Hz), 75.63 (d, $^3J_{PC}$ = 17.1 Hz), 55.52 (OCH_3), 55.49 (OCH_3), 55.35 (OCH_3), 53.39 (OCH_3), 50.74 (OCH_3), 48.36 (d, $^2J_{PC}$ = 16.4 Hz), 47.25 (d, $^2J_{PC}$ = 13.7 Hz), 44.19 (d, $^1J_{PC}$ = 239.6 Hz), 41.57 (d, $^1J_{PC}$ = 232.0 Hz). FTIR (KBr): 2952, 1734, 1628, 1434, 1315, 1263, 1183, 1050, 908, 837, 730, 575, 526 cm^{-1}. ^{31}P NMR (162 MHz, $CDCl_3$) δ 223 K: δ 55.01, 53.44. UV−vis λ_{max} (ϵ) (CH_2Cl_2): 696 (330), 470 (2003), 427 (2926), 325 (37 633), 258 (106 760), 226 (90 905) nm. DCI-MS *m*/*z*: 986.5 (100). HRMS (FAB): calcd for $C_{69}H_{15}O_7P$ ($M + H^+$) 987.0634, found 987.0642.

Similar procedures were employed for the preparation of compounds **2**−**4** from the reactions of C_{60} and DMAD with $P(OEt)_3$, $P(O\text{-}n\text{-}Bu)_3$, and $PPh_2(OMe)$, respectively. Important spectral data of these products follow.

Compound 2 from C_{60}, DMAD and $P(OEt)_3$. Yield: 68%. R_f = 0.26 (TLC, SiO_2, hexanes/ethyl acetate/dichloromethane = 2:1:1). ^1H NMR (400 MHz, $CDCl_3$): δ 4.42−4.30 (m, 6 H, OCH_2), 3.96 (s, OCH_3), 3.72 (s, OCH_3), 1.42 (t, 9 H, J = 7.0 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): 293 K δ 49.89, 48.56 ppm. ^{13}C NMR (150 MHz, $CDCl_3$) 228 K: δ 171.48, 171.30, 169.96, 169.72, 150.28, 149.77, 149.02, 148.69, 147.93, 147.80, 147.63, 147.14, 146.04, 145.83, 145.45, 145.41, 145.25, 145.24, 145.18, 145.02, 144.96, 144.91, 144.88, 144.86, 144.80, 144.79, 144.73, 144.51, 144.49, 144.42, 144.37, 144.30, 144.27, 144.10, 144.06, 144.04, 144.01, 143.98, 143.84, 143.81, 143.76, 143.53, 143.42, 143.34, 142.75, 142.72, 142.69, 142.66, 142.65, 142.62, 142.58, 142.56, 142.53, 142.51, 142.48, 142.41, 142.39, 142.34, 142.20, 142.11, 142.07, 142.03, 141.98, 141.90, 141.88, 141.86, 141.82, 141.78, 141.77, 141.56, 141.54, 141.50, 140.63, 140.54, 140.50, 140.48, 140.38, 140.28, 140.21, 140.10, 138.76, 138.28, 138.23, 138.22, 138.03, 137.65, 136.87, 136.23, 76.13 (d, $^3J_{PC}$ = 11.0 Hz), 76.05 (d, $^3J_{PC}$ = 11.8 Hz), 75.86, 75.79, 65.03 (OCH_2, br), 64.79 (OCH_2, br), 53.38 (OCH_3), 53.21 (OCH_3), 50.64 (OCH_3), 50.39 (OCH_3), 48.95, 48.89 (sb), 47.93 (sb), 44.69 (d, $^1J_{PC}$ = 235.1 Hz), 42.31 (d, $^1J_{PC}$ = 229.2 Hz), 16.33 (CH_3). FTIR (KBr): 2985, 2946, 2906, 1733, 1629, 1432, 1316, 1282, 1223, 1179, 1037, 979, 910, 730, 575, 526 cm^{-1}. UV−vis λ_{max} (ϵ) (CH_2Cl_2): 696 (255), 474 (2050), 428 (2885), 326 (34 333), 258 (116 350) nm. DCI-MS *m*/*z*: 1028 (M^-, 100), 720 (C_{60}, 4). HRMS (FAB): calcd for $C_{72}H_{22}O_7P$ ($M + H^+$) 1029.1103, found 1029.1121.

Compound 3 from C_{60}, DMAD and $P(O\text{-}n\text{-}Bu)_3$. Yield: 66%. R_f = 0.18 (TLC, SiO_2, hexanes/ethyl acetate/dichloromethane = 4:1:1). ^1H NMR (400 MHz, $CDCl_3$): δ 4.33−4.23 (m, 6 H, OCH_2), 3.94 (s, OCH_3), 3.71(s, OCH_3), 1.72 (m, 6 H, CH_2), 1.48 (m, 6 H, CH_2), 0.93 (m, 9 H, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$) 293 K, δ 50.82, 49.47 ppm. ^{13}C NMR (150 MHz, $CDCl_3$) 253 K: δ 171.30 (d, $^3J_{PC}$ = 26.7 Hz), 169.78, 169.48, 168.91 (d, $^3J_{PC}$ = 24.1 Hz), 150.67, 150.13, 149.39, 149.18, 148.11, 147.93, 147.82, 147.42, 146.20, 145.98, 145.57, 145.52, 145.26, 145.20, 145.09, 145.06, 145.03, 144.99, 144.96, 144.95, 144.92, 144.85, 144.62, 144.58, 144.57, 144.53, 144.51, 144.44, 144.43, 144.41, 144.38, 144.19, 144.17, 144.14, 144.12, 144.08,

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143.97, 143.94, 143.90, 143.65, 143.58, 143.55, 143.49, 142.84, 142.81, 142.77, 142.76, 142.73, 142.70, 142.65, 142.63, 142.59, 142.49, 142.45, 142.39, 142.32, 142.23, 142.18, 142.11, 142.03, 141.99, 141.95, 141.91, 141.67, 141.61, 141.17, 140.75, 140.53, 140.50, 140.47, 140.44, 140.27, 140.15, 138.61, 138.43, 138.27, 138.14, 137.63, 136.91, 136.26, 76.35, 76.22 (d, $^3J_{PC}$ = 13.9 Hz), 76.04 (d, $^3J_{PC}$ = 12.6 Hz), 68.58 (d, $^2J_{PC}$ = 6.7 Hz, O*C*H$_2$), 68.34 (d, $^2J_{PC}$ = 6.6 Hz, O*C*H$_2$), 53.04 (O*C*H$_3$), 52.97 (O*C*H$_3$), 50.61 (O*C*H$_3$), 50.22 (O*C*H$_3$), 48.50, 48.38, 44.98 (d, $^1J_{PC}$ = 235.4 Hz), 42.71 (d, $^1J_{PC}$ = 229.5 Hz), 32.22 (d, $^3J_{PC}$ = 7.2 Hz, *C*H$_2$), 32.13 (d, $^3J_{PC}$ = 7.3 Hz, *C*H$_2$), 18.80 (d, $^4J_{PC}$ = 4.7 Hz, *C*H$_2$), 13.73 (*C*H$_3$). FTIR (KBr): 2950. 1734, 1631, 1430, 1185, 1031, 575, 526 cm^{-1}. UV−vis (CH$_2$Cl$_2$) λ_{max}: 227, 258, 325, 428, 473, 696 nm. DCI-MS *m*/*z*: 1113.7 (M$^-$ + 1, 100).

Compound 4 from C_{60}, DMAD, and $PPh_2(OMe)$. Yield: 62%. R_f = 0.17 (TLC, SiO$_2$, hexanes/ethyl acetate/dichloromethane = 3:1:1). ^{1}H NMR (400 MHz, CDCl$_3$) 293 K: δ 7.91 (br), 7.48 (br), 4.17 (br), 4.06 (s), 3.70 (br), 3.36 (br).^{31}P NMR (162 MHz, CDCl$_3$): 293 K δ 58.76 (br). 243 K δ 62.75, 61.95, 56.62, 55.85. FTIR (KBr): 3058, 2995, 2946, 1728, 1631, 1433, 1186, 572, 526 cm^{-1}. UV−vis λ_{max} (CHCl$_3$): 240, 258, 326, 428, 475, 695 nm. FAB-MS *m*/*z*: 1079 (M + 1, 22), 720 (C_{60}, 100). HRMS (FAB): calcd for $C_{79}H_{20}O_5P$ (M + H$^+$) 1079.1048, found 1079.1042.

Reaction of Compound 1 with Hydrobromic Acid: Synthesis of Phosphonate 5. To a 50-mL flask was added phosphite ylide **1** (0.0143 g, 14.5 μmol), dichloromethane (5 mL), and concentrated hydrobromic acid (0.95 mL). The mixture was stirred at ambient temperature for 3 h. The solution was concentrated on a rotary evaporator and then separated on a silica gel column with a mixture of hexanes, ethyl acetate, and dichloromethane (1:1:1) as eluent to give product **5** (0.0134 g) in 95% yield. Important spectral data follow. ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.59 (d, $^2J_{HP}$ = 25.5 Hz, 1 H), 4.06 (s, 3 H), 4.02 (d, $^3J_{HP}$ = 3.7 Hz, 3 H), 4.00 (d, $^3J_{HP}$ = 3.9 Hz, 3 H), 3.98 (s, 3 H). ^{31}P NMR (162 MHz, CDCl$_3$): δ 20.5. DCI-MS *m*/*z*: 972.6. ^{13}C NMR (150 MHz, CDCl$_3$): δ 167.09, 166.11 (d, $^3J_{PC}$ = 2.0 Hz), 147.19, 147.07, 146.65, 146.24, 145.45, 145.37, 145.35, 145.30, 145.27, 145.24, 145.00, 144.97, 144.86, 144.83, 144.75, 144.73, 144.70, 144.59, 144.54, 144.52, 144.02, 143.75, 143.30, 143.12, 143.09, 143.00, 142.97, 142.74, 142.72, 142.22, 142.15, 142.12, 141.96, 141.94, 142.22, 142.15, 142.12, 141.96, 141.94, 141.26, 140.90, 140.88, 139.46, 139.39, 137.08, 136.87, 73.29 (d, $^3J_{PC}$ = 14.9 Hz), 72.77, 54.26 (d, $^3J_{PC}$ = 5.6 Hz, O*C*H$_3$), 54.22 (d, $^2J_{PC}$ = 5.6 Hz, O*C*H$_3$), 53.64 (O*C*H$_3$), 53.50 (O*C*H$_3$), 45.24 (d, $^2J_{PC}$ = 2.4 Hz), 45.10 (d, $^1J_{PC}$ = 145.0 Hz). FTIR (KBr): 2953, 1743, 1433, 1270, 1043, 905, 839, 730, 668, 575, 526 cm^{-1}. UV−vis λ_{max} (ϵ) (CH$_2$Cl$_2$): 686 (278), 479 (1428), 427 (2390), 325 (30 768), 257 (92 097), 227 (74 283) nm.

Similar procedures were employed for the preparation of compounds **6**−**8** from **2**−**4**, respectively, and hydrobromic acid. Important spectral data follow.

Compound 6 from Reaction of 2 with Hydrobromic Acid. Yield: 87%. R_f = 0.15 (TLC, SiO$_2$, hexanes/ethyl acetate/dichloromethane = 1:1:1). ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.57 (d, $^2J_{HP}$ = 25.3 Hz, 1 H), 4.40 (m, 4 H), 4.04 (s, 3 H), 3.97 (s, 3 H), 1.42 (td, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 2.4 Hz, 6 H). ^{31}P NMR (162 MHz, CDCl$_3$): δ 17.9. FTIR (KBr): 2927, 2854, 1745, 1439, 1265, 1050, 1023, 970, 575, 526 nm. UV−Vis λ_{max} (CH$_2$Cl$_2$): 691, 487, 427, 325, 257, 227 nm. DCI-MS *m*/*z*: 1000.6.

Compound 7 from Reaction of 3 with Hydrobromic Acid. Yield: 87%. R_f = 0.03 (TLC, SiO$_2$, hexanes/ethyl acetate/dichloromethane = 4:1:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.58 (d, $^2J_{HP}$ = 25.6 Hz, 1 H), 4.30 (m, 4 H), 4.04 (s, 3 H), 3.96 (s, 3 H), 1.73 (m, 4 H), 1.45 (m, 4 H), 0.92 (2 t, ^3J = 7.2 Hz, $^3J'$ = 7.5 Hz, 6 H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 167.20, 166.01, 147.24, 147.20, 146.83, 146.36, 145.46, 145.35, 145.33, 145.30, 145.27, 145.24, 145.17, 145.08, 145.01, 144.93, 144.84, 144.81, 144.76, 144.72, 144.70, 144.67, 144.55, 144.44, 144.00, 143.76, 143.73, 143.29, 143.22, 143.10, 143.07, 142.98, 142.95, 142.73, 142.71, 142.20, 142.15, 142.11, 141.96, 141.24, 141.00, 140.87, 140.78, 139.41, 139.34, 137.06, 137.02, 73.56 (d, $^3J_{PC}$ = 15.9 Hz), 72.94, 67.30 (d, $^2J_{PC}$ = 7.0 Hz, O*C*H$_2$), 67.22 (d, $^2J_{PC}$ = 7.0 Hz, O*C*H$_2$), 53.51 (O*C*H$_3$), 53.36 (O*C*H$_3$), 45.25 (d, $^1J_{PC}$ = 144.1 Hz), 45.48, 32.76 (d, $^3J_{PC}$ = 6.1 Hz, *C*H$_2$), 32.70 (d, $^3J_{PC}$ = 6.0 Hz, *C*H$_2$), 18.84 (d, $^4J_{PC}$ = 6.5 Hz, *C*H$_2$), 13.66 (*C*H$_3$). ^{31}P NMR (162 MHz, CDCl$_3$): δ 18.74. FTIR (KBr): 2953, 1744, 1438, 1267, 1185, 1013, 912, 730, 576, 525 cm^{-1}. UV−vis (CH$_2$Cl$_2$) λ_{max}: 226, 257, 325, 427, 484, 689 nm. DCI-MS *m*/*z*: 1056.7.

Compound 8 from Reaction of Ylide 4 with Hydrobromic Acid. Yield: 78%. R_f = 0.04 (TLC, SiO$_2$, hexanes/ethyl acetate/dichloromethane = 3:1:1). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.03 (br, 4 H), 7.61 (br, 3 H), 7.41 (br, 3 H), 5.07 (d, $^2J_{HP}$ = 13.1 Hz), 3.96 (s, 3 H), 3.78 (s, 3 H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 167.60, 166.06, 147.24, 147.19, 147.11, 146.29, 145.45, 145.41, 145.36, 145.34, 145.31, 145.25, 145.22, 145.21, 145.03, 145.00, 144.95, 144.81, 144.79, 144.63, 144.60, 144.57, 144.39, 144.04, 144.01, 143.71, 143.69, 143.67, 143.30, 143.12, 143.05, 143.04, 143.01, 142.97, 142.89, 142.53, 142.50, 142.19, 142.14, 142.12, 142.03, 141.92, 141.90, 141.73, 141.16, 140.85, 140.39, 140.32, 139.62, 139.40, 136.50, 136.19, 132.62 (d, $^1J_{PC}$ = 96.7 Hz), 132.48 (d, $^4J_{PC}$ = 2.4 Hz, CH), 132.16 (d, $^4J_{PC}$ = 2.4 Hz, *C*H), 132.08 (d, $^2J_{PC}$ = 10.0 Hz, *C*H), 131.94 (d, $^1J_{PC}$ = 98.7 Hz), 131.39 (d, $^2J_{PC}$ = 9.2 Hz, *C*H), 128.94 (d, $^2J_{PC}$ = 12.4 Hz, *C*H), 128.65 (d, $^2J_{PC}$ = 12.5 Hz, *C*H), 72.99, 72.73 (d, $^3J_{PC}$ = 11.6 Hz), 53.57 (O*C*H$_3$), 53.15 (O*C*H$_3$), 47.12 (d, $^1J_{PC}$ = 63.0 Hz, *C*H), 44.78. ^{31}P NMR (162 MHz, CDCl$_3$): δ 26.5. FTIR (KBr): 3075, 3050, 2951, 1741, 1434, 1256, 1193, 1118, 906, 729, 696, 575, 524 cm^{-1}. UV−vis (CH$_2$Cl$_2$) λ_{max}: 227, 257, 326, 427, 693 nm. DCI-MS *m*/*z*: 1065.7 (M$^-$ + 1). HRMS (FAB): calcd for $C_{78}H_{18}O_5P$ (M + H) 1065.1892, found 1065.0902.

Synthesis of Phosphonic Acid Derivative of Fullerene 9 from Phosphonate 5. To a 25-mL flask were added **5** (0.0394, 0.0410 mmol) and toluene (20 mL). The system was evacuated and flushed with nitrogen three times. To the system at 0 °C was added trimethylsilyl iodide (0.0192 mL) via a syringe. The system was then stirred at the same temperature for 1.5 h. The solvent and unreacted trimethylsilyl iodide were removed completely by vacuum. To the residue were added toluene (20 mL) and water (0.050 mL), and the mixture was stirred at ambient temperature for 30 min. The system was centrifuged, and the solution was decanted. The solid remained was washed several times by toluene until no color in the toluene solution was observed. The solid was then dried in a vacuum to give product **9** (0.0326 g) in 83% yield. ^{1}H NMR (600 MHz, THF-d_8): δ 4.51(d, $^2J_{PH}$ = 24.6 Hz, 1H), 3.91 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (150 MHz, THF-d_8): δ 169.70 (*C*=O), 167.67 (*C*=O), 151.09, 150.64, 149.91, 149.47, 147.95, 147.93, 147.85, 147.49, 147.29, 147.26, 147.24, 147.22, 147.18, 146.94, 146.87, 146.82, 146.78, 146.72, 146.66, 146.56, 146.47, 146.42, 146.30, 146.07, 146.04, 145.89, 145.80, 145.22, 145.17, 145.09, 145.04, 144.94, 144.91, 144.82, 144.76, 144.45, 144.41, 144.29, 144.23, 144.15, 144.03, 143.95, 143.01, 142.90, 142.73, 142.59, 141.69, 141.53, 139.55, 139.15, 76.26, 75.20, 54.74 (s, O*C*H$_3$), 54.10 (s, O*C*H$_3$), 49.07, 47.49 (d, $^1J_{PC}$ = 137.8 Hz, *C*H). ^{31}P NMR (162 MHz, THF-d_8): δ 15.06. UV−vis λ_{max}(ϵ) (DMSO): 681 (123), 482 (1164), 431 (1969), 328 (25623), 265 (71404), 259, 220 nm. IR (KBr): 526, 575, 712, 739, 812, 1010, 1241, 1434, 1734, 2949, 3433 cm^{-1}. HRMS (FAB): calcd for $C_{66}H_9O_7P$ (M) 944.0086, found 944.0075.

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Supporting Information Available: Copies of ^{1}H, ^{13}C, and ^{31}P NMR and mass spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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