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Synthesis of $C_{60}(O)_3$: An Open-Cage Fullerene with a Ketolactone Moiety on the Orifice

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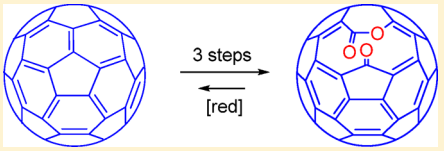
Supporting Information

ABSTRACT: Four isomers are currently known for the trioxygenated fullerene derivative $C_{60}(O)_3$, three regioisomers with all of the oxygen addends as epoxy groups and the unstable ozonide isomer with a 1,2,3-trioxolane ring. Here we report the synthesis of an open-cage isomer for $C_{60}(O)_3$ with a ketolactone moiety embedded into the fullerene skeleton through a three-step procedure mediated by fullerene peroxide chemistry. Two fullerene skeleton carbon−carbon bonds are cleaved in the process. The open-cage derivative $C_{60}(O)_3$ can be converted back to C_{60} through deoxygenation with PPh_3. Single crystal X-ray structure confirmed the open-cage structure.



INTRODUCTION

Oxygenation is one of the most intensively investigated reactions in fullerene chemistry because of their biological activity and possible applications in materials science.[1] A number of methods have been reported for the preparation of oxygenated fullerene derivatives $C_{60}(O)_n$.[2] Ozone,[3] cytochrome P450 model catalyst,[4] peracids,[5] and dimethyldioxirane[6] can generate C_{60} epoxides $C_{60}(O)_n$ with n up to 3. Highly oxygenated fullerenes, $C_{60}O_n$ with $3 \leq n \leq 9$, have been prepared by the Lewis base enhanced catalytic oxidation of C_{60} with $ReMeO_3/H_2O_2$.[7] Oxygenated fullerenes anions $C_{60}(O)_n^-$ with n up to 30 were observed by mass spectra in a corona discharge ionizer in the presence of trace amount of oxygen.[8]

Structures of $C_{60}(O)_n$ have been studied through calculations and a number of stable isomers have been predicted,[9] but it has been a challenging problem to isolate and fully characterize the structure of multioxygenated fullerenes. Most of the known reactions give a mixture of products with different numbers of oxygen addends and also various isomers for the same number of oxygen addends. Despite numerous reports about their preparation and application, there are only a few isomerically pure oxygenated fullerenes. Diederich et al. isolated $C_{70}(O)$ from a crude mixture of fullerenes by graphite arc evaporation.[10] The corresponding C_{60} epoxide $C_{60}(O)$ with the oxygen at the 6,6-junction was prepared from photooxidation of C_{60} in benzene by Smith et al.[11a] The crystal structure of its iridium complex was later obtained by Balch et al.[11b] The 5,6-open oxafulleroid $C_{60}(O)$ was produced from ozonation of C_{60} by Heymann et al.[12] For the bisepoxide $C_{60}(O)_2$ two isomers have been isolated. Balch et al. characterized a C_s isomer of the diepoxide $C_{60}O_2$.[5a] Tajima et al. isolated an equatorial isomer.[13] For the trioxygenated compound $C_{60}(O)_3$, Lebrilla et al.[5c] studied its mass spectra in detail. Curci et al.[6b] observed two epoxy isomers having C_2 and C_s symmetry, respectively, as a mixture by NMR spectra. Tajima et al. isolated the epoxy isomer of $C_{60}(O)_3$ with C_{3v} symmetry.[5b] In all of these tris-epoxides, the epoxy rings are located over 6:6 ring junctions and in close proximity to each other. Another known isomer for $C_{60}(O)_3$ is the unstable ozonide with the ozone attached to the C_{60} cage at the 6,6-junction to form a 1,2,3-trioxolane ring.[14] Recently we reported the preparation of two isomers of $C_{60}(O)_4$ both with an open-cage structure.[15] Oxygenated derivatives with more than 4 oxygen atoms are readily observed in the gas phase by mass spectra,[7,8,16] but their isolation and characterization is problematic. When the oxygen content is high, cage rupture is evident from the appearance of IR bands due to ketonic and carboxylic groups as observed from the polymeric products of ozonation of C_{60}.[14] The mechanism of the rupture is not clear. Here we report the preparation of another isomer for $C_{60}(O)_3$ with an open-cage structure. The presence of a keto and a lactone group in this open-cage isomer sheds light on the cage rupture process of fullerenes upon overoxygenation.

RESULTS AND DISCUSSION

Controlled Cleavage of Fullerene Skeleton Bonds. Compound **1** was prepared as previously reported.[17] Its reaction with triphenylphosphine and iodine was found to produce the iodo-derivative **2**.[18] When compound **2** was stored under ambient conditions, it slowly decomposed into several products including **3**, **4**, and **5**. Reexamination of the iodination reaction of **1** indicates that compounds **3**, **4**, and **5** can be formed in moderate yields directly from the reaction solution if the reaction time is extended to a few days (Scheme 1). Trace amount of **2** and the dihydroxyl analogue of **2** were also

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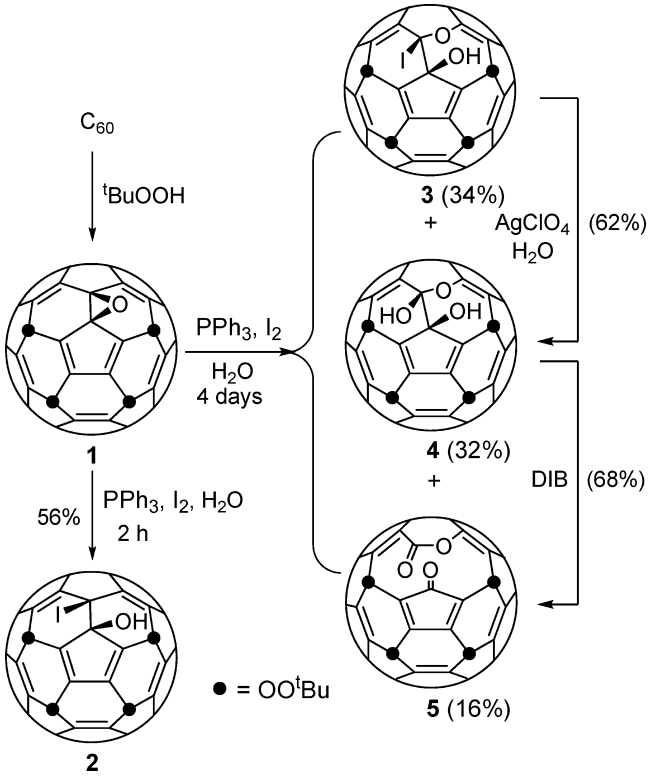
Scheme 1. Reaction of 1 with Triphenylphosphine and Iodine

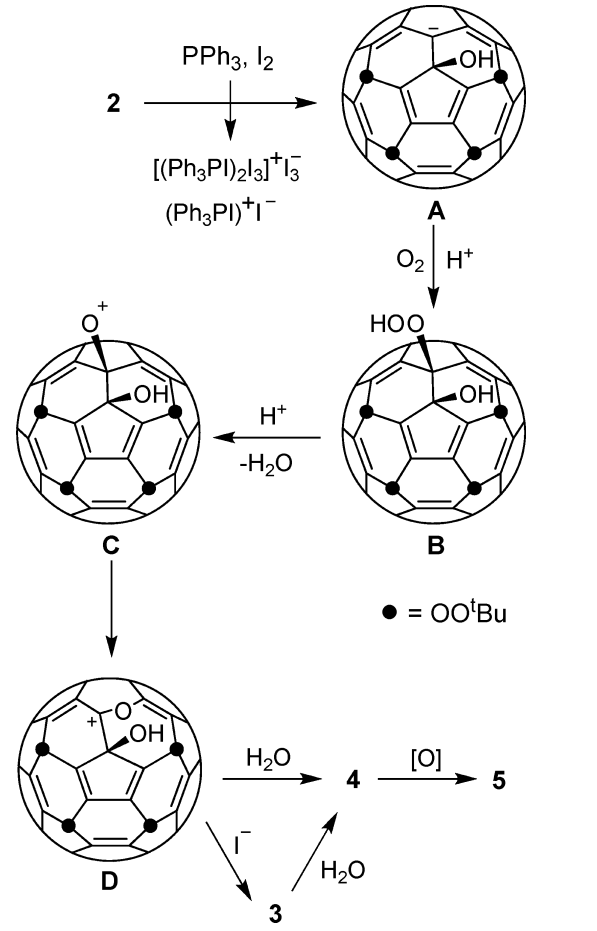


detected under this condition. The overall yield of ketolactone derivative **5** can be improved to 60% since both compounds **3** and **4** can be converted into **5** after further treatments, as shown in Scheme 1.

The formation of compounds **3**, **4**, and **5** involves fullerene skeleton bond cleavage. A possible mechanism is shown in Scheme 2. Compound **2** is the precursor since it was formed under exactly the same conditions in 2 h[18] and could slowly decompose into the present compounds as mentioned above. Formation of the anionic intermediate **A** may be due to reduction by Ph_3P or iodide ion.[19] Phosphine is known to induce reductive dehalogenation of halofullerenes.[15,20] Protonation of **A** could produce the hydroderivative $C_{60}(OOt\text{-}Bu)_4(OH)H$, which can be oxidized into intermediate **B** under the conditions since the fullerene C−H bond is relatively acidic. The regioselectivity of the oxygen insertion step, **C** to **D**, is probably mainly due to thermodynamic reason. Insertion at the alternative 6,6-junction would generate two seven-membered rings on the cage, whereas **D** has just one seven-membered ring. C_{60} has only five- and six-membered rings. Introduction of a seven-membered ring increases steric strain. The oxidant in the step from **4** to **5** could be hypervalent iodine species formed from disproportion of iodine. The iodo reagent $PhI(OAc)_2$ was shown to oxidize **4** to **5** efficiently as shown in Scheme 1.

Characterization Data for Compounds 3, 4, and 5. Their NMR spectra showed the expected pattern for these C_1 symmetric compounds. The hydroxyl groups appear at 6.33 ppm for **3** and 6.05 and 6.47 ppm for **4** on the ^1H NMR spectrum. The unique hemiketal of **4** appears at 101.4 ppm on the ^{13}C NMR spectrum. The same carbon of the iodo analogue **3** is at 92.6 ppm. The keto and the lactone carbonyl carbons of **5** are at 193.3 and 159.0 ppm. Compound **5** also showed strong IR bands at 1731 and 1796 cm^{-1} for the carbonyl groups.

Scheme 2. Proposed Mechanism for Formation of 3, 4, and 5



The structure of compound **4** was further confirmed by single crystal X-ray analysis. Various solvents and combination of solvents were tested for growing suitable crystals. The only successful solvent system was a mixture of CS_2/EtOH/CH_2Cl_2/$CHCl_3$/*c*-C_6H_{12} (cyclohexane). There is much strain around the hemiketal moiety judging from the bond distances in Figure 1. The single bond at the junction between the central pentagon and the seven-membered ring (1.622 Å) is the longest bond in the molecule. All other single bonds surrounding the two hydroxyl groups are relatively longer than those on the other parts of the cage. The double bond connected to the bridging hemiketal oxygen atom is the shortest (1.297 Å) among all of the double bonds on the cage. The torsion angle between the two hydroxyl groups is 30°.

Selective Removal of Peroxo Groups To Form $C_{60}(O)_3$ and its Diels−Alder Reaction. We have recently reported that borontribromide is an effective reagent for removal of peroxo groups in fullerene-mixed peroxides.[15] The method can also be applied to compound **5** to form **6** (Scheme 3). The solubility of **6** decreased significantly compared to **5**. A mixture of CS_2/C_6D_6 had to be used to obtain the ^{13}C NMR spectrum for **6**. The keto carbonyl signal was not observed probably due to coincidence with the CS_2 signal. The carbonyl IR stretching bands are at 1790 and 1736 cm^{-1}. Compound **6** is very stable under atmosphere and can be stored under ambient conditions for weeks without noticeable change. Heating a chlorobenzene solution of **6** for 2 days resulted in little decomposition.

Locations of the keto and lactone moieties in compound **6** are analogous to the first open-cage derivative reported by

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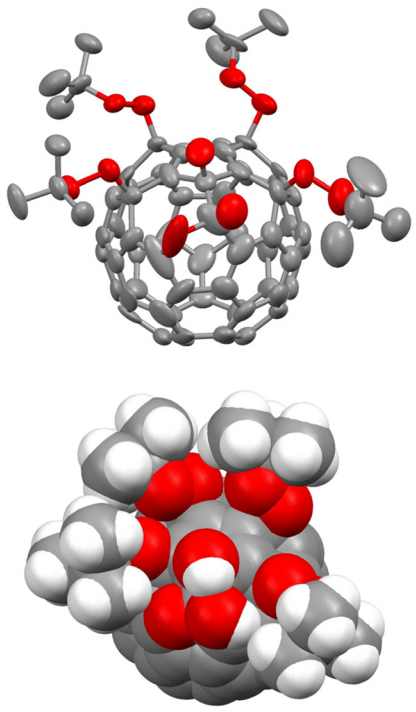
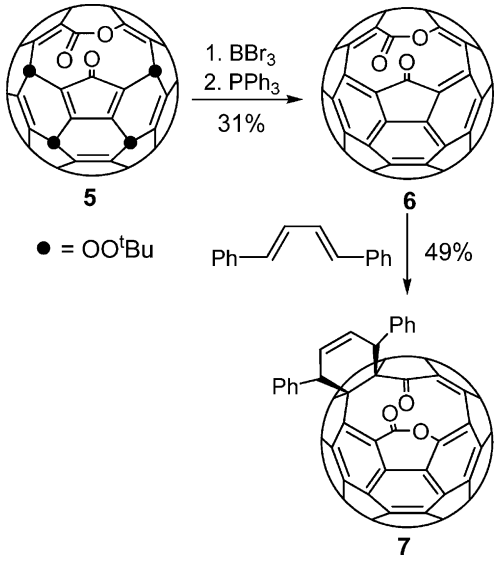


Figure 1. X-ray structure of **4**. For clarity hydrogen atoms were not shown for the ellipsoid model. Color scheme: O = red; C = gray; H = white.

Scheme 3. Formation of 6 and Its Diels–Alder Reaction



Wudl et al. in which the keto and lactam forms an 11-membered orifice.[21] To test the effect of the carbonyl groups on the fullerene cage, we treated **6** with 1,4-diphenylbutadiene to obtain the Diels–Alder adduct **7** (Scheme 3). Regioselectivity of the addition is in good agreement with the electron-withdrawing effect of the carbonyl groups. The keto and lactone carbonyl carbons of **7** appear at 196.9 and 162.0 ppm, respectively, both of which are slightly shifted downfield compared to **5**. The carbonyl stretching bands of **7** on the IR spectrum appear at 1784 and 1727 cm^{-1}, which are smaller than those of **5**.

Single crystal X-ray diffraction structure of **7** was obtained as shown in Figure 2. The fullerene-fused cyclohexene adopts a

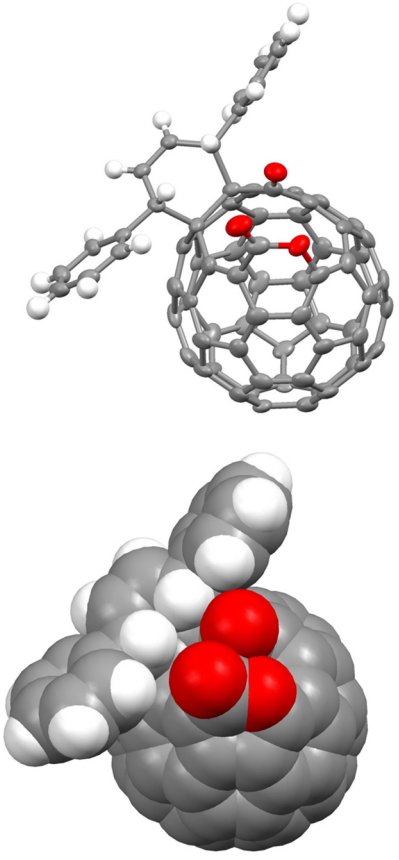


Figure 2. X-ray structure of **7**. Color scheme: O = red; C = gray; H = white.

boat conformation with the two phenyl groups in the equatorial positions. The single bond between the two sp^3 fullerene carbons is the longest at 1.639 Å. The other four single bonds connected to these two carbons on the cage range from 1.539 to 1.602 Å. The distance between the two carbonyl carbons is 2.85 Å, and the torsion angle between the two carbonyl groups is 36°, which is slightly increased compared to the dihydroxyl derivative **4** mentioned above (30°). Unlike the rather short bond distance in **4** (1.297 Å), the corresponding bond distance of the lactone oxygen-bound double bond (1.377 Å) is comparable to other double bonds on the cage.

Deoxygenation of 6 To Form C_{60}. Fullerene epoxide has been reported to react with triphenylphosphine to form C_{60}.[11b,22] The process can be used as an effective way for removing trace amount of $C_{60}(O)_n$ impurity in the production of C_{60}.[23] Heating the ketolactone **6** with PPh_3 at 100° can also remove the oxygen atoms and produce C_{60} in low yield (less than 10%). Adding strong acid such as trifluoroacetic acid or trifluoromethylsulfuric acid can lower the temperature to room temperature (Scheme 4). The identity of C_{60} was confirmed by ^{13}C NMR, MALDI-MS, and also HPLC analysis.

A possible mechanism is shown in Scheme 5 for the formation of C_{60} from **6**. The key step is the formation of the C–C bond between the two carbonyl carbons to form intermediate **C**. The attack of the hemiketal anion on the carbonyl carbon in **B** is the opposite process of oxidative C–C bond cleavage in **4** to **5** in Scheme 1. The distance between the

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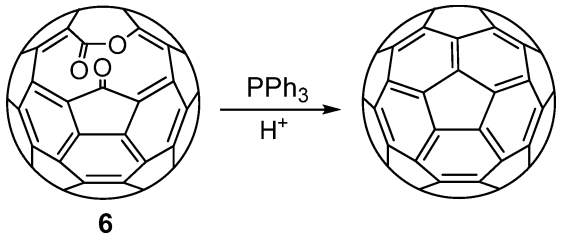
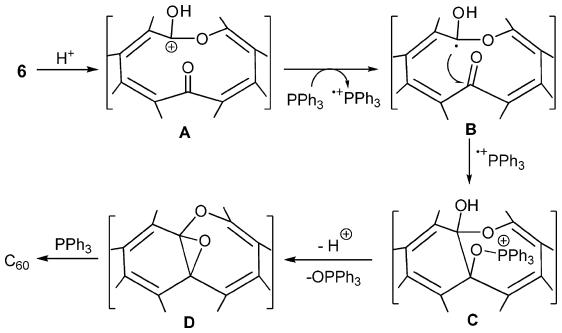
Scheme 4. Deoxygenation of 6 to form C_{60}



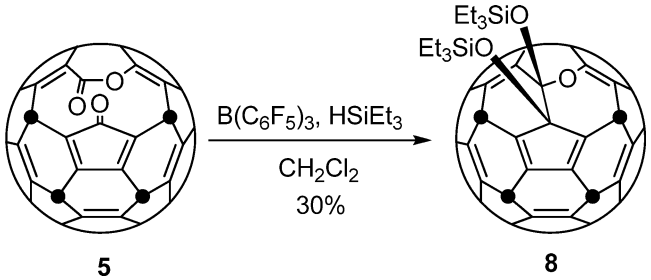
Scheme 5. Proposed Mechanism for Deoxygenation



two carbonyl groups is relatively small as shown in the above X-ray structure of **7**. Elimination of triphenylphophine oxide and proton from **C** forms the reactive dioxide **D**. Further deoxygenation of **D** by PPh_3 to form C_{60} is the same as the deoxygenation reaction between fullerene epoxide $C_{60}(O)_n$ and PPh_3.[22]

To obtain more evidence to support the above proposed mechanism, we treated the open-cage derivative **5** with Et_3SiH in the presence of $B(C_6F_5)_3$. Compound **8** was obtained, which has exactly the same skeleton structure as that of **4** (Scheme 6).

Scheme 6. Hole-Closing Reaction of 5



Besides the main product **8**, a trace amount of monosilylated product $C_{60}(OOt\text{-}Bu)_4(O)(OH)(OSiEt_3)$ was also detected from this reaction. Both the ^{13}C NMR and IR spectra clearly indicate that there is no carbonyl group in compound **8**. A unique signal at 103.1 ppm can be assigned to the ketal carbon on the ^{13}C NMR spectrum of **8**, which is very close to the hemiketal carbon of **4** at 101.4 ppm. Treating **6** with Et_3SiH in the presence of $B(C_6F_5)_3$ resulted in a complex mixture of products including C_{60}.

A similar mechanism as in Scheme 5 can explain the formation of **8**. The interaction between Et_3SiH and $B(C_6F_5)_3$ can activate the silane by forming $Et_3Si{-}H{\cdots}B(C_6F_5)_3$. The activated silane attacks the lactone in **5** to form a siloxyl ketal group -C(H)(O)($OSiEt_3$). The acidic proton on this ketal group is then reduced by silane to form hydrogen gas and a carbon anion analogous to **B** in Scheme 5. In agreement with the proposed mechanism, gas bulbs were observed upon addition of Et_3SiH and $B(C_6F_5)_3$. The formation of **8** from **5** provides strong supporting evidence for the proposed mechanism in Scheme 5 for the formation of C_{60} from **6**.

In summary, the open-cage isomer for $C_{60}(O)_3$ has been prepared in a three-step sequence through a peroxide-mediated procedure. The fullerene cage rupture process involves oxonium insertion and vicinal diol oxidation. The oxygen atoms in the ketolactone moiety of the present open-cage derivative $C_{60}(O)_3$ can be completely eliminated to reform C_{60} under reductive conditions. The transformations observed here represent a cage-open and -closing process.[24] Because the orifice is too small it is impossible to make endohedral fullerene compounds by the present process.[25] The cage cleavage and formation of carbonyl groups provide mechanistic information for carbon−carbon cleavage phenomenon in extensive oxidation of fullerenes,[26] carbon nanotubes,[27] and graphenes.[28] Further work is underway to prepare an oxafulleroid[15,29] such as $C_{59}(O)_2$ and the dioxafullerene $C_{58}(O)_2$ starting from the present compounds.

EXPERIMENTAL SECTION

All reagents were used as received. Toluene used for the reactions was distilled from potassium under nitrogen. Dichloromethane (DCM) was distilled from phosphorus pentoxide. Other solvents were used as received. All reactions were carried out in air except the preparation of **6**, which was under nitrogen atmosphere. The NMR spectra were obtained at 25 °C unless noted.

Caution: *A large amount of peroxides is involved in some of the reactions. Care must be taken to avoid possible explosion.*

Preparation of Compounds 3, 4, and 5. To a solution of compound **1** (1.30 g, 1.19 mmol) in 250 mL of CH_2Cl_2 were added 638 mg of PPh_3 (2.44 mmol) and 2.50 g of I_2 (9.84 mmol), and the resulting solution was stirred at room temperature for 4 days. Then the reaction was treated with excess $Na_2S_2O_3$ aqueous solution three times. The organic layer was separated, and the solvent was removed under vacuum. The residue was chromatographed on silica gel (5.3 cm × 10 cm) eluting with toluene/petroleum ether (1:1). trace amount of the known compound **2**[18] was eluted out first. Then a red band was collected and evaporated to give compound **3** (506 mg, 34%) as an orange solid. The eluting solvent was changed to toluene, and another red band was eluted to give compound **5** (212 mg, 16%) as an orange solid. The eluting solvent was changed to CH_2Cl_2, and a third red band was eluted to give compound **4** (431 mg, 32%) as an orange solid. Characterization data for **3**: ^1H NMR ($CDCl_3$, 400 MHz) δ 6.33 (s, 1H), 1.53 (s, 9H), 1.52 (s, 9H), 1.46 (s, 9H), 1.45 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) (all signals represent 1C except noted) δ 159.44, 153.89, 152.42, 150.57, 150.09, 150.07, 149.04, 148.90, 148.47, 148.38 (2C), 148.24, 148.21, 148.07, 147.94, 147.91, 147.85, 147.81, 147.73, 147.61, 147.52, 147.45, 147.13, 147.09, 146.92, 146.59, 145.90, 145.82, 145.79, 145.31, 145.28, 145.15, 144.99, 144.88 (2C), 144.86 (2C), 144.78, 144.45, 144.39, 144.16, 143.99, 142.46, 142.40, 141.43, 141.02; 140.90, 140.79, 139.61, 137.85, 136.93, 134.12, 130.74, 127.93, 92.63 (1C, C-OH), 88.39, 86.35, 83.81 (C-$(CH_3)_3$), 82.22, 82.14 (C-$(CH_3)_3$), 81.84 (C-$(CH_3)_3$), 81.79 (C-$(CH_3)_3$), 80.81, 80.31, 27.04 ($3CH_3$), 26.89 ($3CH_3$), 26.74 ($3CH_3$), 26.72 ($3CH_3$). FT-IR (microscope): 3457, 2977, 2928, 2870, 1473, 1460, 1387, 1364, 1261, 1243, 1193, 1167, 1092, 1042, 1024, 933, 870, 752. ESI-MS: $C_{76}H_{41}INO_{10}$ (M + NH_4^+) calcd 1254.0, found 1254.

Characterization Data for ***4****.* ^1H NMR ($CDCl_3$, 400 MHz) δ 6.47 (s, 1H), 6.05 (s, 1H), 1.52 (s, 9H), 1.50 (s, 9H), 1.46 (s, 9H), 1.39 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) (all signals represent 1C except noted) δ 157.70, 154.39, 153.42, 150.49, 150.34, 150.12, 148.97, 148.91, 148.49, 148.47, 148.44, 148.27, 148.24, 148.22, 147.94, 147.88, 147.83, 147.67, 147.54, 147.48, 147.42, 147.19, 147.13, 146.96, 146.69, 146.62, 146.13, 146.00, 145.21, 145.06, 144.99, 144.83, 144.80, 144.77,

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144.65, 144.63, 144.35, 144.30, 144.27, 144.24, 144.01, 142.22, 141.80, 141.65, 141.06, 140.75, 140.69, 139.99, 137.59, 136.22, 134.11, 131.67, 131.47, 127.93, 101.38 (1C-OH), 89.73 (1C, C−OH), 87.72, 86.84, 83.99 (*C*-$(CH_3)_3$), 81.97 (*C*-$(CH_3)_3$), 81.86 (*C*-$(CH_3)_3$), 81.70 (*C*-$(CH_3)_3$), 80.81, 80.46, 26.82 ($3CH_3$), 26.73 ($6CH_3$), 26.68 ($3CH_3$). FT-IR (microscope): 3410, 2978, 2930, 1474, 1459, 1387, 1364, 1250, 1192, 1155, 1143, 1098, 1091, 1061, 1043, 1020, 923, 907, 869, 732 assignment was obtained from HMBC spectrum. ESI-FT-ICR-HRMS: $C_{76}H_{42}NO_{11}$ (M + NH_4^+) calcd 1144.2725, found 1144.2752.Crystal data for compound **4**: $C_{76}H_{42}O_{13}$, T = 293(2) K, monolinic, space group $P2(1)/c$; unit cell dimensions a = 19.674(4) Å, b = 14.365(3) Å, c = 20.551(4) Å, β = 90.25(3)°. V = 5733 (2) Å^3. Z = 4, ρ_{calcd} = 1.348 Mg/m^3. Reflections collected/unique 23657/8739 [R(int) = 0.0763]. Final R indices [$I > 2\sigma(I)$] R_1 = 0.733, wR_2 = 0.1356. CCDC 611162.

Characterization Data for ***5***. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.46 (s, 9H), 1.43 (s, 18H), 1.42 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) (all signals represent 1C except noted) δ 193.31, 159.00, 150.77, 150.70, 150.45, 149.87, 149.81, 149.70, 149.61, 148.98, 148.90, 148.87, 148.80, 148.58, 148.56, 148.39, 148.23, 148.19, 148.13, 148.10, 148.04, 147.72, 147.65, 147.56, 147.33, 147.01, 146.73, 146.67, 146.54, 146.29, 145.86, 145.25, 145.20, 145.12, 145.10, 145.05, 144.78, 144.70, 144.55, 144.38, 144.12, 143.98, 143.86, 143.37, 143.07 (2C), 139.26, 139.19, 138.95, 138.52, 137.94, 135.92, 131.12, 126.42, 126.38, 122.38, 90.84, 90.08, 82.57 (*C*-$(CH_3)_3$), 82.36 (*C*-$(CH_3)_3$), 82.26 (*C*-$(CH_3)_3$), 82.24 (*C*-$(CH_3)_3$), 78.66, 78.49, 26.62 ($6CH_3$), 26.55 ($3CH_3$), 26.52 ($3CH_3$). FT-IR (microscope): 2979, 2929, 2869, 1796, 1731, 1570, 1515, 1459, 1423, 1388, 1365, 1331, 1263, 1244, 1192, 1155, 1099, 1055, 1026, 1012, 947, 893, 869, 755, 694 assignment was obtained from HMBC spectrum. ESI-FT-ICR-HRMS: $C_{76}H_{40}NO_{11}$ (M + NH_4^+) calcd 1142.2585, found 1142.2596.

Reaction of 3 To Form 4. To a solution of compound **3** (657 mg, 0.532 mmol) in 120 mL of CH_2Cl_2 were added 170 mg of $AgClO_4$ (0.819 mmol) and 2 drops of water. The resulting solution was stirred at room temperature for 0.5 h. The solution was chromatographed on silica gel (4.0 cm × 5.0 cm) eluting with CH_2Cl_2. The first red band was some unreacted compound **3**, and the second red band was collected and evaporated to give compound **4** (370 mg, 62%) as an orange solid.

Reaction of 4 To Form 5. To a solution of compound **4** (102 mg, 0.0906 mmol) in 20 mL of benzene was added 68.2 mg of DIB (0.212 mmol), and the resulting solution was stirred at room temperature for 20 min. The solution was chromatographed on silica gel (4.0 cm ×5.0 cm) eluting with toluene. The first red band was collected and evaporated to give compound **5** (69.2 mg, 68%) as an orange solid.

Preparation of Compound 6. To a stirred solution of compound **5** (708 mg, 0.630 mmol) in 150 mL of toluene was added BBr_3 (0.60 mL, 6 mmol) at room temperature under nitrogen atomsphere. After about 15 min, 200 mL of toluene was added, and then the reaction was quenched by adding $Na_2S_2O_3$ aqueous solution. The organic layer was separated and treated with PPh_3 (165 mg, 0.630 mmol). The solvent was removed under vacuum. The residue was chromatographed on silica gel (4.0 cm × 5.0 cm) eluting with toluene/petroleum ether (1:1). The first yellow-green band was collected and evaporated to give compound **6** (150 mg, 31%) as a brownish solid. ^{13}C NMR (125 MHz, CS_2/C_6D_6) (all signals represent 1C except noted) δ 150.71, 150.36, 149.61, 148.02, 147.48, 147.36, 147.33, 146.99, 146.72, 146.67, 146.45, 146.38, 146.21, 146.11, 146.09, 146.04, 145.75, 145.70, 145.43, 145.34, 145.32, 145.21, 145.09, 144.66, 144.50, 144.41, 144.38, 144.26, 144.12 (2C), 144.05 (2C), 143.55, 143.54, 143.40, 143.32 (2C), 142.94, 142.54, 141.54, 140.46, 140.00 (2C), 139.80, 139.74, 139.70, 138.99, 138.52, 137.47, 136.34, 136.25, 136.18, 135.88, 135.47, 133.81, 132.83, 130.49, 128.81, 119.63. FT-IR (microscope): 1790, 1736, 1563, 1510, 1427, 1368, 1270, 1249, 1191, 1154, 1131, 1115, 1049, 995, 953, 941, 899, 773, 748 cm^{-1}. MALDI-TOF: $C_{60}O_3$ calcd 768.0, found 767.8.

Preparation of Compound 7. To solution of compound **6** (25.6 mg, 0.0333 mmol) in 15 mL of toluene was added *trans,trans*-1, 4-diphenyl-1,3-butadiene (20.6 mg, 0.100 mmol), and the resulting solution was stirred at 65 °C for 2.5 h. The solution was directly chromatographed on silica gel (2.6 cm × 10 cm) eluting with toluene/petroleum ether (1:1). The first band was the product **7** (15.9 mg, 49%, light brown solid), and the second band was unreacted **6**. ^{1}H NMR (500 MHz, CS_2/C_6D_6) δ 7.26−7.25 (m, 3H), 7.10−6.97 (m, 7H), 6.74−6.72 (m, 1H), 6.65−6.63 (m, 1H), 5.46 (s, 1H), 5.40 (s, 1H) ^{13}C NMR (125 MHz, CS_2/C_6D_6) (all signals represent 1C except noted) δ 196.91, 161.96, 152.94, 151.13, 151.08, 150.38, 150.18, 149.66, 149.32, 147.95 (2C), 147.65, 147.45, 147.12, 147.04, 146.91, 146.63, 146.39, 146.01, 145.78, 145.77, 145.61, 145.57 (2C), 145.40, 145.37, 145.08, 144.35, 144.29, 144.21 (2C), 143.86, 143.77, 143.47, 143.36, 143.25, 143.17, 142.86, 142.71, 142.63, 142.06, 141.95, 141.90, 141.23, 141.17, 140.61, 139.69, 139.19, 138.83, 138.49, 136.93, 136.56 (2C) 136.42, 135.32, 135.04, 134.79 (2C), 134.17, 134.06, 132.22 (2C), 130.10, 129.71, 128.86, 128.62 (2C), 128.38 (2C), 127.65 (2C), 118.98, 82.62, 65.70, 53.74, 51.99. FT-IR (microscope): 3058, 3030, 2922, 2278, 2267, 1784, 1727, 1565, 1493, 1471, 1455, 1406, 1370, 1269, 1168, 1153, 1109, 1081, 1065, 1042, 998, 907, 854, 798, 752, 742, 704, 675 cm^{-1}. ESI-FT-ICR-HRMS: $C_{76}H_{15}O_3$ (M + H^+) calcd 975.1016, found 975.0993.

Crystal Data for Compound ***7***. $C_{83}H_{22}O_3$, T = 173(2) K, monolinic, space group $P2(1)/n$; unit cell dimensions a = 16.947(4) Å, b = 15.195(3) Å, c = 18.824(4) Å, β = 114.551(4)°. V = 4409.1 (17) Å^3. Z = 4, ρ_{calcd} = 1.607 Mg/m^3. Reflections collected/unique 28263/7749 [R(int) = 0.0771]. Final R indices [$I > 2\sigma(I)$] R_1 = 0.1158, wR_2 = 0.2707. CCDC 912220.

Reaction of Compound 7 To Form C_{60}. Excess CF_3CO_2H (0.60 mL, 8.1 mmol), CF_3SO_3H (0.80 mL, 9.1 mmol), and PPh_3 (60 mg, 0.23 mmol) were added to a solution of compound **6** (6.6 mg, 0.086 mmol) with 18 drops of chlorobenzene. After the solution was stirred at room temperature for 18 h, 5 mL of CS_2 was added, then the reaction was quenched by adding water, and the organic layer was chromatographed on silica gel eluting with toluene/petroleum ether (1:1). The first band was collected and evaporated to give a solid containing C_{60} and some unidentified impurities (which could not be separated by silica gel column). The yield of C_{60} was determined to be around 8% for several parallel samples by HPLC on a Buckyprep column using standard C_{60} sample for comparison. MALDI-TOF mass spectrum and ^{13}C NMR spectrum confirmed the presence of C_{60}.

Preparation of Compound 8. A 259 mg portion of $HSiEt_3$ (2.23 mmol) and 158 mg of $B(C_6F_5)_3$ (0.309 mmol) were added to the solution of 316 mg of compound **5** (0.281 mmol) in 50 mL of CH_2Cl_2. The resulting solution was stirred at room temperature for about 30 min. Then the solution was condensed to 5 mL and chromatographed on silica gel (4.0 cm × 8.0 cm) eluting with toluene to give compound **8** (115 mg, 30%) as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (s, 9H), 1.40 (s, 9H), 1.38 (s, 9H), 1.29 (s, 9H), 1.23−1.20 (m, 9H), 1.19−1.16 (m, 6H), 1.02−0.97 (m, 9H), 0.87−0.82 (m, 6H) ^{13}C NMR (125 MHz, $CDCl_3$) (all signals represent 1C except noted) δ 158.74, 154.66, 154.05, 150.57, 150.35, 150.19, 149.96, 149.18, 148.97, 148.42, 148.25, 148.22, 148.07, 148.01, 147.87, 147.80, 147.79, 147.58, 147.56, 147.35, 147.21, 147.17, 146.91, 146.64, 146.18, 146.07, 145.92, 145.42, 145.28, 145.25, 145.02 (2C), 144.92, 144.64, 144.47, 144.34, 144.18, 143.89, 143.62, 143.50, 142.19, 141.85, 141.51, 141.24, 141.17, 141.03, 140.57, 140.18, 136.32, 135.81, 135.60, 131.37, 131.30, 103.06, 94.93, 89.23, 87.10, 81.45, 81.39, 81.36, 81.29, 81.04, 80.69, 80.25, 26.74 (3C), 26.67 (3C), 26.66 (3C), 26.57 (3C), 7.83 (3C), 6.92 (3C), 6.13 (3C), 6.11 (3C). FT-IR (microscope): 3532, 3406, 2975, 2954, 2928, 2876, 1459, 1385, 1364, 1240, 1193, 1163, 1099, 1015, 974, 871, 823, 795, 746, 731 cm^{-1}. ESI-FT-ICR-HRMS: $C_{88}H_{70}NO_{11}Si_2$ (M + NH_4^+) calcd 1372.4482, found 1372.4513.

■ ASSOCIATED CONTENT

Supporting Information

Selected spectroscopic data for all new compounds and crystallographic data for **4** and **7** including CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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