A Methodology for the Reversible Solubilization of Fullerenes

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The poor solubility of certain fullerene derivatives, especially those bearing several fullerene moieties, has hampered the preparation of new materials. We are proposing a strategy which uses fullerenes bearing a readily removable solubilizing group to carry out reaction steps leading to a final product with intrinsic low solubility. This is now possible with the one-step conversion of the *t*-BOC derivative **8a** to C_{60} in over 95% yield. This one-pot conversion involves the *in situ* formation of diene **4** which, after [4 + 2] cycloaddition with dimethyl acetylenedicarboxylate, affords the bicyclic adduct **11** undergoing rapid cycloreversion to C_{60} and dimethyl phthalate. This method was tested with two functionalized C_{60} derivatives (**14** and **18**) as a first step toward the preparation of new nanosized molecular allotropes of carbon and rigid fullerene-rich polymers.

Introduction

There are presently a large number of functionalization reactions available for fullerenes.[1-3] We have exploited the Diels–Alder reaction between C_{60} and 1,3-dienes to obtain a variety of very stable adducts that have properties similar to those of C_{60}.[4,5] The convenient preparation, relative ease of purification, and diversity of C_{60} adducts, together with their associated photophysical and redox properties, have opened new avenues into the interesting chemistry of fullerene derivatives.[6,7] However, the intrinsically low solubility of fullerene-rich compounds and fullerene-based polymers still presents a major obstacle to their preparation and characterization. The subject of this paper is to resolve this problem through the

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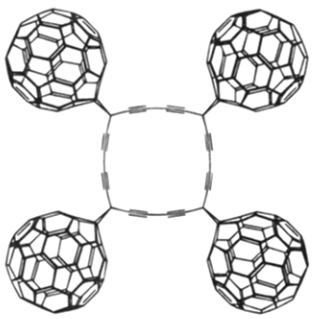
temporary addition of a solubilizing group to a fullerene framework.

We have recently reported our progress toward the preparation of large molecular allotropes of carbon (**1**) combining fullerene and cyclo[*n*]carbon frameworks.[8] Two independent syntheses of 1,2-(diethynylmethano)buckminsterfullerene (**2**) have laid down a seemingly straightforward approach to these fullerenocyclo[*n*]carbons through oxidative coupling reactions.[8,9] However, our efforts to obtain characterizable products from Eglinton–Glaser or Hay coupling of **2** were frustrated by severe solubility problems of the oligomeric intermediates or macrocyclic products.[10] The poor solubility of some symmetrical fullerene derivatives and those containing more than one fullerene unit per molecule has been reported.[4a,7a,f,11] This problem appears to be severely inhibiting efforts to build new molecular architectures based on fullerenes that could display enhanced properties related to the conductivity and superconductivity of C_{60},[12] its ferromagnetism,[13] and optical nonlinearity.[14] Solubility is also a problem in the scaled-up separation of the higher fullerenes[15] or their endohedral metal complexes.[16]

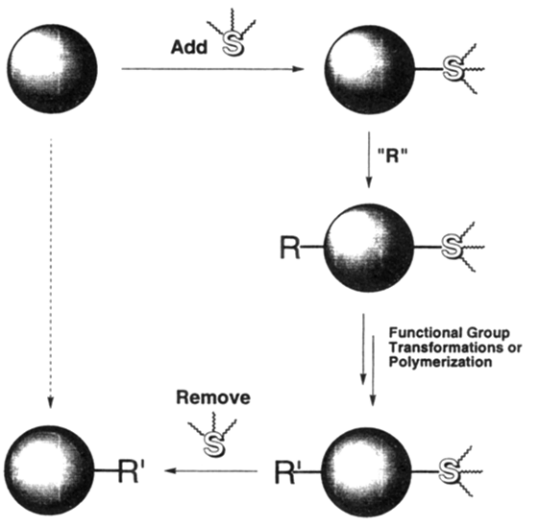


1

2

A solution to this essential problem lies in the design of a methodology which enables the straightforward attachment and removal of a highly solubilizing group to fullerenes using mild chemical methods (Scheme 1). A solubilizing "tag" S is added to C_{60} or another fullerene and the resulting solubilized fullerene, is functionalized with the desired group R. Alternatively, this sequence can be reversed by tagging an already functionalized fullerene. When the penultimate product is obtained after chemical transformations of the functional group R to R′, the solubilizing tag S is removed in a high-yielding reaction, and the final product characterized.[17] We envision X-ray crystallography to be the most suitable method for characterizing poorly soluble compounds generated in this way, provided that crystals can be obtained using slow removal conditions favoring crystallization. Other alternatives include STM, AFM, or high-resolution transmission electron microscopy, especially in the case of polymeric products.

Scheme 1



At least seven regioisomers[18] can be formed from the addition of a solubilizing group to a monoderivatized C_{60} framework. Working with such mixtures is not problematic in this application, since the solubilizing tag is removed at the end of the transformations. The use of a stereoisomerically pure solubilized fullerene derivative can also be envisaged, since methods for preparing multisubstituted fullerenes in a controlled fashion have started to appear in the literature.[10,19]

The problem of removing a carbocyclic fragment from the C_{60} surface did not appear to be trivial at the beginning of our work. The reversibility of cyclopentadiene,[20a–c] furan,[20d] anthracene,[20e–g] and iso-

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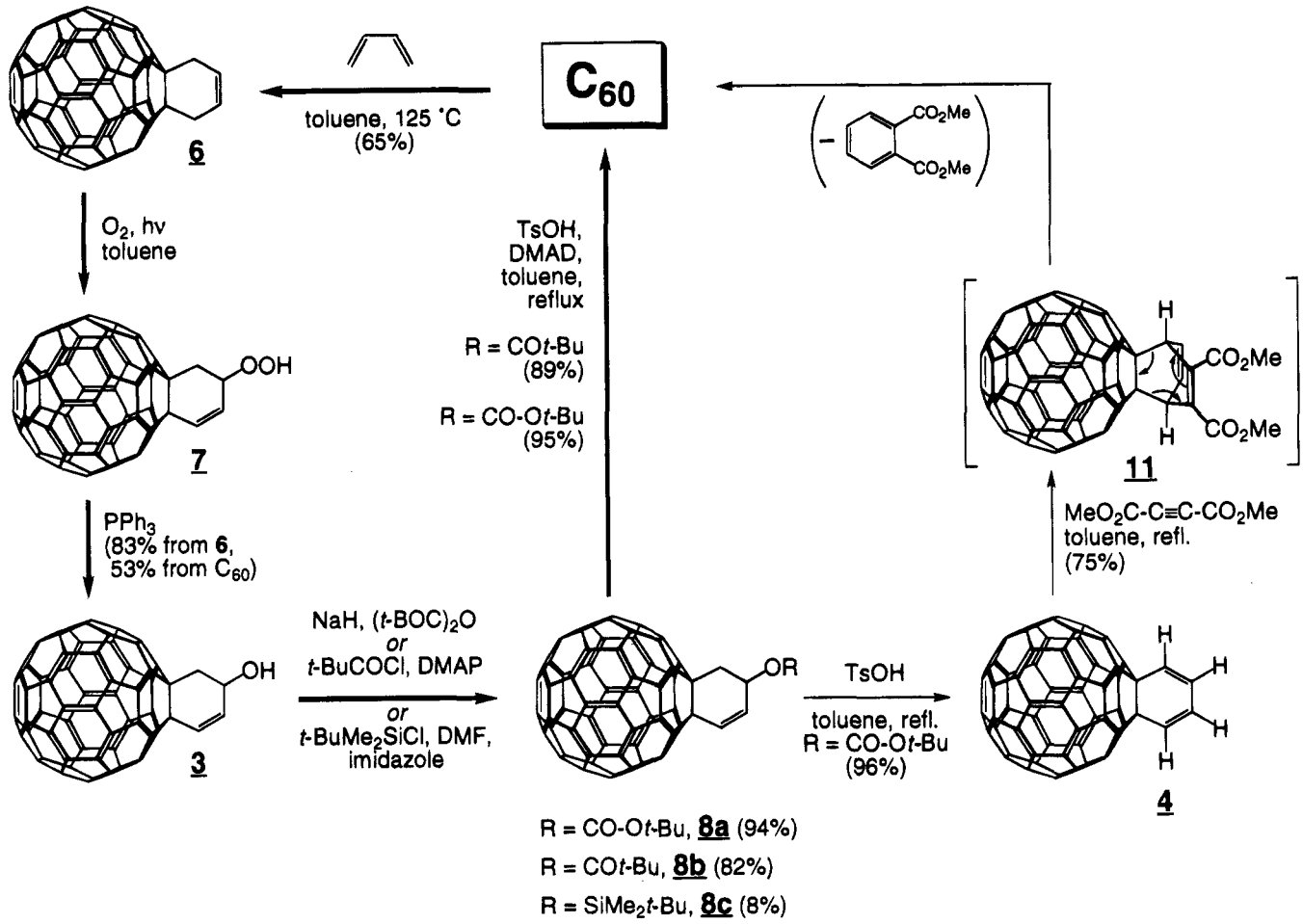
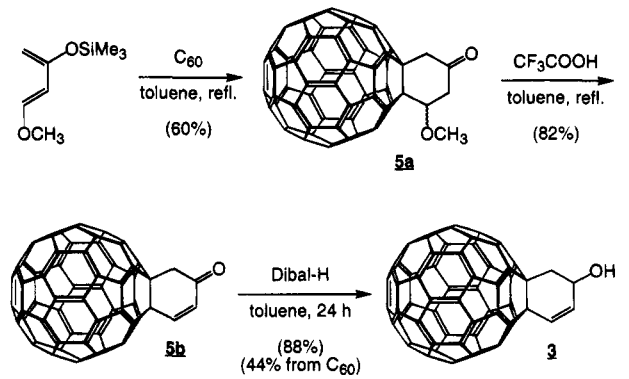
Scheme 2



münchnone[21] additions to C_{60} has been described. However, we felt that these systems would not be suitable for the purpose described above since *retro*-Diels–Alder reaction in the corresponding adducts occurs at low temperatures, for example around 80–90 °C for the cyclopentadiene adduct.[20a–c] This ease of removal would clearly be unsuitable for most organic transformations, especially where more than one step is involved. We believed that the best way to achieve clean and quantitative removal of a carbocyclic fragment attached to a fullerene moiety would be to convert the solubilizing group into a system prone to undergo *retro*-Diels–Alder reaction, while the leaving fragment would be inert toward the electrophilic fullerene system.

In our first successful step toward this goal, we found that the allylic alcohol **3** can be converted to C_{60} *via* the cyclohexadiene derivative **4** in a sequence of mild, high-yielding reactions (Scheme 2). This approach provides an answer to the conditions of our design for the *first time* by being a stable and cleanly removable solubilizing group. Allylic alcohol **3** is readily available *via* two reaction sequences described below, and the alcohol moiety in **3** can be derivatized with a variety of solubilizing/protecting groups.

Scheme 3



Results and Discussion

The allylic alcohol **3** was first prepared from C_{60} in 44% overall yield *via* Dibal-H reduction of enone **5b** (Scheme 3). Enone **5b** was obtained *via* Danishefsky's diene cycloaddition to C_{60} to give methoxy ketone **5a**, followed by acid-catalyzed methanol elimination.[22] Although this reaction sequence is easily carried out, we wished to find

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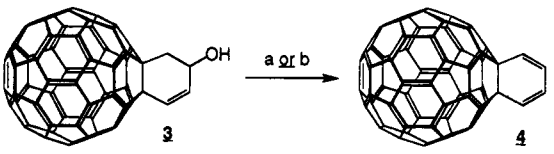
a higher yielding "one-pot" reaction sequence that would lead to alcohol **3** without several time-consuming purification steps. We found that the cyclohexene derivative **6**, prepared in 65% yield by Diels–Alder reaction of 1,3-butadiene with C_{60} in a screw-capped sealed tube (toluene, 2 h, 125 °C), can be converted to alcohol **3** in 83% yield *via* an ene reaction with singlet oxygen ($h\nu \geq 300$ nm, 5 h) and subsequent reduction of the intermediate allylic hydroperoxide **7** with PPh_3 (Scheme 2). The reaction sequence starting from C_{60} can be carried out in toluene without isolation of any intermediates in 53% overall yield. The attractive aspect of this highly efficient ene reaction is that it is *self-sensitized*;[23] the 1,2-dihydrofullerene moiety in compound **6** plays the role of $^1O_2$ sensitizer, and the cyclohexene moiety is the reaction center.[5,24,25] As a testimony to the reactive nature of this system, the isolation of pure cyclohexene **6** devoid of hydroperoxide **7** proved difficult unless strict exclusion of air and light was achieved throughout the purification steps. The efficient $^1O_2$ sensitization by C_{60} has been known since its isolation.[26] C_{60} and a few of its derivatives have been used recently as $^1O_2$ sensitizers for endoperoxide formation from dienes[27] and in the ene reaction with allylic systems.[27–29]

To obtain a highly soluble derivative of alcohol **3**, formation of *tert*-butyldimethylsilyl (TBDMS) ether **8c** was attempted first because the ease of formation and mild removal conditions for this group are well established (Scheme 2).[30] Reaction of **3** with excess TBDMS-Cl/imidazole in DMF at 20 °C afforded only 8% of the desired silyl ether **8c**, along with polymeric material. To enhance the reactivity of the silyl moiety, *tert*-butyldimethylsilyl triflate (TBDMS-OTf) was used in the presence of 4-(dimethylamino)pyridine (DMAP). Interestingly in this case, the apolar cyclohexadiene derivative **4** rather than silyl ether **8c** was isolated in 31% yield after chromatography on silica gel with cyclohexane (Scheme 4). Compound **4** must arise from an E1-type elimination promoted by the Lewis acidic *t*-$BuMe_2Si^+$ species. Compound **4** was also formed by acid-catalyzed dehydration of **3** (TsOH, toluene, reflux) in 48% yield, the low isolated yield reflecting the high reactivity of this diene toward $^1O_2$ (see below).

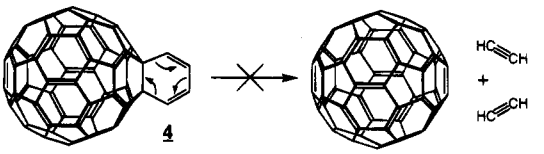
The goal of removing the attached carbocyclic fragment from diene **4** was pursued. Initially, we investigated the possibility that **4** could undergo thermal cycloreversion to C_{60} and two acetylene molecules (Scheme 5). However, we obtained no evidence to support this mechanism.

Scheme 4

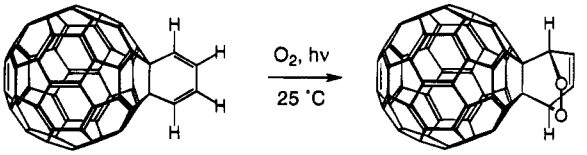


a) TBDMS-OTf, DMAP, toluene, 25 °C (31%)
b) TsOH, toluene, refl., 1/2 h (48%)

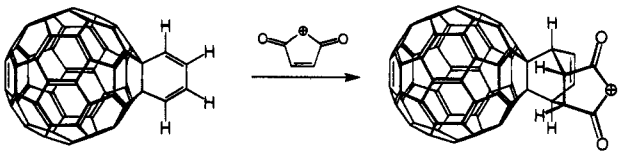
Scheme 5



Scheme 6



Scheme 7



10a, ⊕ = N-Ph (84%)
10b, ⊕ = O (29%)

Instead, self-sensitized reaction of **4** with $^1O_2$ occurred readily in the ambient light of the laboratory, as demonstrated by the formation of unstable endoperoxide **9** *via* [4 + 2] cycloaddition with $^1O_2$ (Scheme 6). Endoperoxide **9** was unstable and decomposed within a few hours at 20 °C to malealdehyde (itself unstable) and C_{60}-based polymeric material *via* a retro [4 + 2] mechanism. Similarly, the Diels–Alder reactivity of **4** was portrayed in its cycloaddition reactions with *N*-phenylmaleimide and maleic anhydride, affording bicyclic derivatives **10a** (84%) and **10b** (29%), respectively (Scheme 7).

We concluded that a similar [4 + 2] cycloaddition of diene **4** with dimethyl acetylenedicarboxylate (DMAD) would lead to the bicyclo[2.2.2]octadiene intermediate **11** *which would then collapse to unreactive dimethyl phthalate and* C_{60} (Scheme 2).[31] This was indeed the case: reaction of **4** with an excess of DMAD (toluene, reflux, 3 h) gave C_{60} in 75% yield! The identity of C_{60} thus generated was confirmed by comparison with authentic material by TLC (SiO_2, cyclohexane) and ^{13}C NMR (δ = 142.93 ppm in $CS_2/CDCl_3$, 2:1).[32]

(23) This is a general reaction of cyclohexenofullerenes which can become a significant side reaction in the preparation of such compounds. This reaction can be used preparatively, providing access to highly functionalized systems: (a) An, Y.-Z.; Rubin, Y. Presented at the 207th National Meeting of the American Chemical Society in Anaheim, California, April 2–7, 1995. (b) An, Y.-Z.; Viado, A. L.; Arce, M.-J.; Rubin, Y. *J. Org. Chem.*, submitted.

(24) Unidentifed polar compounds, presumably ene reaction products with $^1O_2$, have been reported in the Diels–Alder reaction of C_{60} with 2,3-dimethyl-1,3-butadiene and myrcene: Kräutler, B.; Puchberger, M. *Helv. Chim. Acta* **1993**, *76*, 1626–1631. See also: ref 19a.

(25) For reviews on singlet oxygen chemistry, see: (a) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359–387. (b) Foote, C. S. *Singlet Oxygen*; Academic Press: New York, 1979; pp 139–171. (c) Clennan, E. L. *Tetrahedron* **1991**, *47*, 1343–1382.

(26) Arbogast, J. W.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992**, *114*, 2277–2279.

(27) Tokuyama, H.; Nakamura, E. *J. Org. Chem.* **1994**, *59*, 1135–1138.

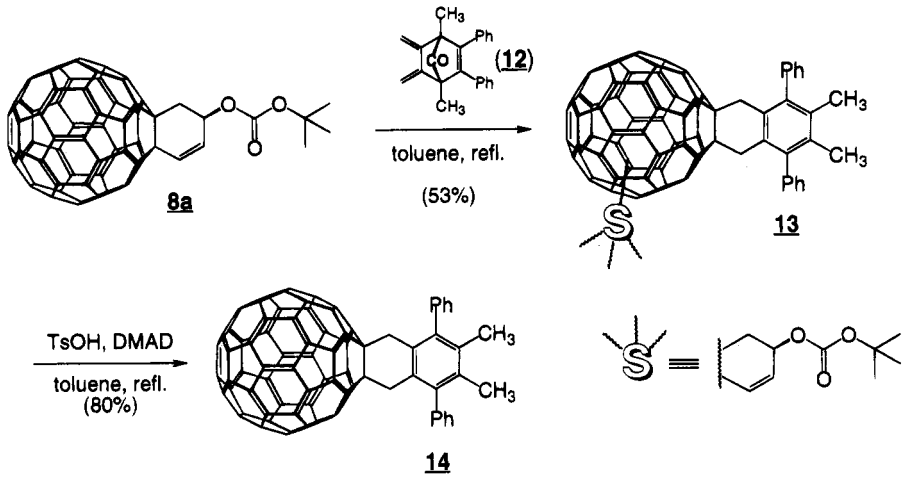
(28) (a) Orfanopoulos, M.; Kambourakis, S. *Tetrahedron Lett.* **1994**, *35*, 1945–1948. (b) Orfanopoulos, M.; Kambourakis, S. *Tetrahedron Lett.* **1995**, *36*, 435–438.

(29) For other ene reactions with C_{60}, see: (a) Wu, S. H.; Shu, L. H.; Fan, K. N. *Tetrahedron Lett.* **1994**, *35*, 919–922. (b) Komatsu, K.; Murata, Y.; Sugita, N.; Wan, T. S. M. *Chem. Lett.* **1994**, 635–636.

(30) Greene, T. W.; Wuts, P. G. M. In *Protective Groups in Organic Synthesis;* John Wiley & Sons: New York, 1991.

(31) For a similar concept in the preparation of *cis*-3,4-dichloro-1-cyclobutene from cyclooctatetraene, see: Pettit, R.; Henery, J. *Organic Syntheses;* Wiley: New York, 1988; Collect. Vol. VI, pp 422–423.

Scheme 8



Having established the feasibility of our goal, we returned to the preparation of a soluble derivative of alcohol **3** capable of affording diene **4** cleanly in a one-pot reaction. *t*-BOC-protected alcohol **8a** was prepared in excellent yield (94%) by reaction of **3** with di-*tert*-butyl dicarbonate and NaH in THF (Scheme 2). Similarly, pivalate ester **8b** was prepared in 82% yield by esterification of **3** with pivaloyl chloride/DMAP. Compounds **8a** and **8b** are both dark brown resins in the neat state. Their solubilities were tested in cyclohexane, an apolar solvent in which C_{60} itself is known to be poorly soluble (0.051 mg/mL).[33] The solubilities of **8a** and **8b** in this solvent were higher than 1 mg/mL each, more than 20 times higher than that of C_{60}. In more polar solvents such as CH_2Cl_2 or toluene, their solubilities are practically infinite.

Importantly, conversion of the *t*-BOC-protected alcohol **8a** to C_{60} was achieved *in one step* in excellent yield (95%) by heating under reflux in toluene in the presence of *p*-toluenesulfonic acid and DMAD (Scheme 2). Pivalate ester **8b** yielded 89% of C_{60} under identical conditions. Thus, the overall conversion cycle starting from C_{60} and returning to it is as high as 48%, the initial 1,3-butadiene cycloaddition to C_{60} being the low-yielding step due to the formation of variable amounts of bis- and tris-adducts (see Experimental Section). It is also noteworthy that the *t*-BOC-protected alcohol **8a** is quite stable, since it is unaffected by reflux in THF/36% HCl for several hours.

Our methodology was tested on a substituted fullerene to evaluate the effect of a second added moiety on the conditions of removal of the solubilizing group. Diene **12**[34] was reacted with carbonate **8a** to give a diastereomeric mixture of adducts **13** (Scheme 8). The solubilized adduct **13** was characterized by LD-MS. Its proton NMR shows patterns of absorptions (from the presence of several diastereomers) in the expected chemical shift regions of both **14**[4a] and **8a**. Removal of the solubilizing group from **13** under conditions used for **8a** afforded pure adduct **14** in 80% yield. Adduct **14** is very difficult to redissolve in aromatic solvents once crystalline, while its solubilized derivative **13** is a highly soluble dark brown resin.

The solubilized diethynylmethanofullerene **15a** was prepared by reaction of 3-bromo-1,5-bis(trimethylsilyl)-1,4-pentadiyne (**16a**) with **8a** (NaH, toluene/THF 3:1, 20 °C) (Scheme 9).[9a,35,36] Monoadduct **15a** was desilylated to the solubilized diethynylmethanofullerene **15b** (aqueous Borax, THF, 20 °C, 12 h). Flash chromatography with cyclohexane/toluene (1:1) afforded **15b** as a diastereomeric mixture in 66% yield. A partial separation of several distinctly colored diastereomers of **15b** occurred during chromatography. The ^1H NMR spectrum of the first main fraction is shown in Figure 1. The spectrum of **15b** diastereomers illustrates nicely the combination of resonances expected from both units of 1,2-(diethynylmethano)buckminsterfullerene (**2**) and *t*-BOC-protected alcohol **8a**.

The Hay coupling method[37] was tested on **15b** in a mixed coupling[9a] with excess phenylacetylene, affording bis(phenylbutadiynyl) derivative **17** in 74% yield (CuCl, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), O_2, PhCl, 20 °C, 2 h). The removal of the solubilizing group from **17** afforded methanofullerene **18** in 24% yield (TsOH, DMAD, toluene, reflux, 3 h). The low yield obtained in this particular removal may be due to the reactive nature of the dialkynylmethano bridge. The cationic mechanism necessary for the removal of the *t*-BOC group and the formation of the diene moiety in **17** presumably favors ring opening of the cyclopropane

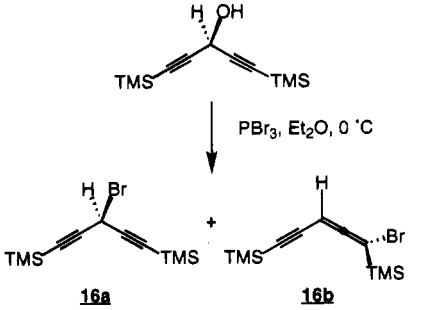
(32) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630–8633.

(33) Sivaraman, N.; Dhamodaran, R.; Kaliappan, I.; Srinivasan, T. G.; Rao, P. R. V.; Mathews, C. K. *J. Org. Chem.* **1992**, *57*, 6077–6079.

(34) Warrener, R. N.; Russell, R. A.; Pitt, I. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1675–1676.

(35) (a) Hauptmann, H. *Tetrahedron Lett.* **1974**, 3587–3588. (b) Hauptmann, H. *Tetrahedron* **1976**, *32*, 1293–1297.

(36) The conversion of 1,5-bis(trimethylsilyl)-1,4-pentadiyn-3-ol[35] to the corresponding bromide (**16a**) by reaction with PBr_3 was invariably complicated by the competing formation of the corresponding allene (**16b**), a side reaction not reported for this particular compound in refs 35 or 9a. If the mixture of diyne **16a** and allene **16b** was used in the formation of methanofullerenes (e.g. **15a**), the yields were poor compared to the use of pure diyne **16a**. See Experimental Section for the isolation of pure diyne **16a**.



(37) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320–3321.

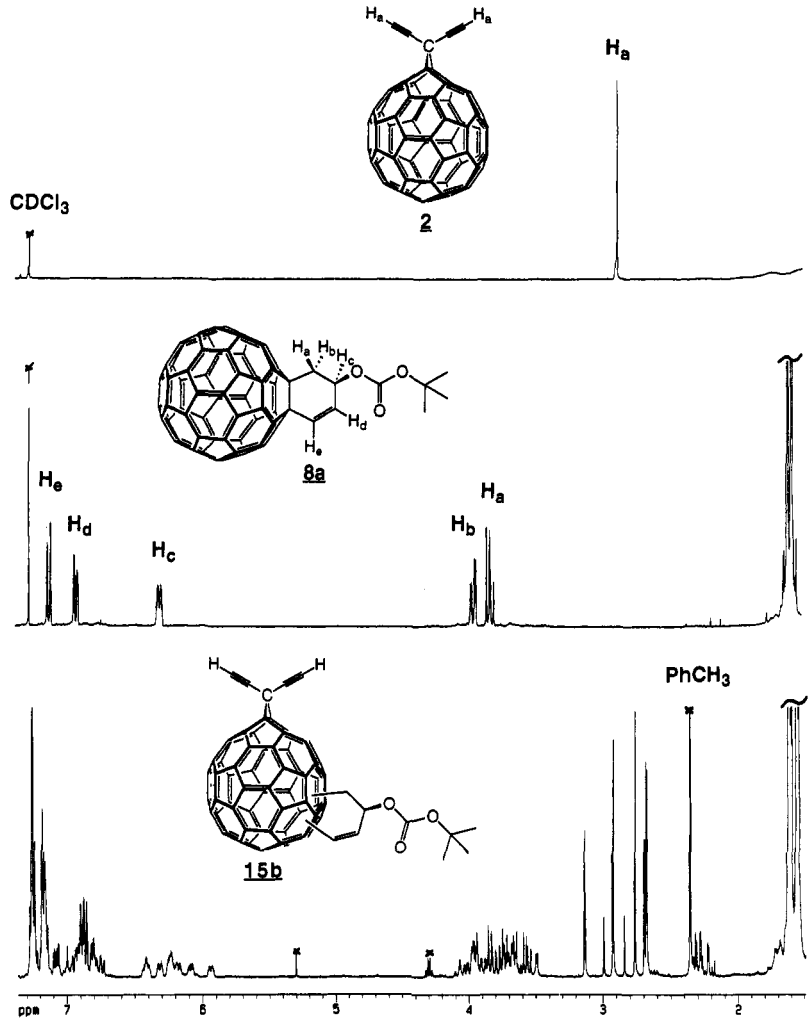
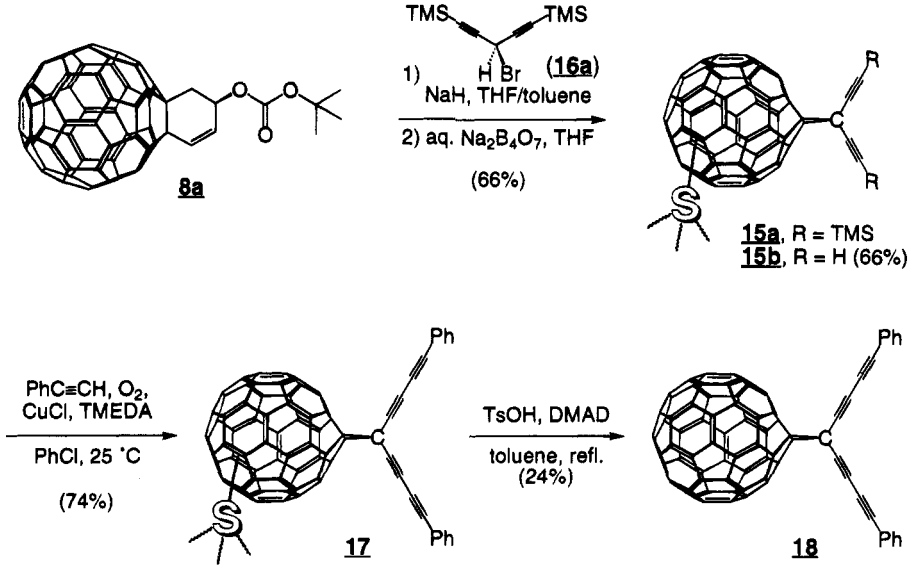


Figure 1. ^{1}H NMR spectra of the C_{60} derivatives 1,9-(diethynylmethano)buckminsterfullerene (**2**), solubilized derivative **8a**, and solubilized diethynylmethanofullerene derivative **15b** as a mixture of stereoisomers.

Scheme 9



ring leading to a highly stabilized, doubly-propargylic pentadiynyl carbocation. The potential cumulative effect of this low removal yield on cyclization products from **15b** (e.g. solubilized **1**) has led us to investigate the formation of the diene moiety from protected alcohol **3** using non-acidic reagents. The cyclization of a suitably solubilized derivative of **2** and the formation of fullerenocyclo[*n*]-carbons will be reported in due course. However, the method described in this paper is highly suitable for systems containing non-acid sensitive groups such as Diels–Alder adduct **13**. We are currently investigating the addition of a polar solubilizing group to higher fullerenes (C_{76}, C_{78}, C_{84}, and higher) which should allow their preparative separation on common supports such

as silica gel. The preparation of rigid polymers incorporating a high fullerene content should also become possible.[7f]

Experimental Section

General. All reactions were performed under argon and, for $^1O_2$ sensitive compounds, in the absence of light. The matrix used for FAB mass spectra was *m*-nitrobenzyl alcohol. Matrix-assisted laser desorption ionization time-of-flight mass spectra (MALDI-TOF-MS; matrix 9-nitroanthracene or 3,5-dihydroxybenzoic acid) were recorded in the negative ion mode with relatively low laser power on a PerSeptive Biosystems Voyager RP instrument. Column chromatography was performed on silica gel 70–230 mesh or 230–400 mesh (flash) from E. Merck or Scientific Absorbents; thin layer chromatography (TLC) was performed on glass plates coated with silica gel 60 F_{254} from E. Merck.

Materials. The C_{60}/C_{70}-soluble extract was obtained from MER Corporation, Tucson, AZ. Pure C_{60} was isolated using the convenient procedure described by Tour *et al.*[38] Reagents and solvents were purchased reagent grade. Toluene, benzene, and dichloromethane were distilled over calcium hydride prior to use. DMF was dried over CaH_2 and distilled *in vacuo*. Anhydrous $MgSO_4$ or Na_2SO_4 was used as the drying agent after workup in all the experiments. *p*-Toluenesulfonic acid monohydrate used in the deprotection experiments was dried at 70 °C *in vacuo* for several hours prior to use. Photosensitization experiments were performed either with a 300 W xenon lamp (Oriel) using a water-cooled Pyrex cell filter or with a 450 W Hanovia high-pressure mercury lamp in a Pyrex photochemical reactor.

Appreciable amounts of dialkyl *o*-phthalates were present in reagent grade solvents used for column chromatography. These and other high boiling impurities had a general tendency to contaminate C_{60} derivatives; all new compounds were therefore either reprecipitated and washed with spectrograde cyclohexane, ether, or methanol in case they had low solubility in these solvents or repurified by flash chromatography using spectrograde solvents (toluene, cyclohexane). Unless these precautions were used, substantial amounts of dialkyl phthalates were invariably present in the ^1H and ^{13}C NMR spectra of our compounds.

Synthesis.[39] **1,2-(6′-Methoxy-4′-oxocyclohexano)buckminsterfullerene (5a).** A total of 440 mg (0.61 mmol) of C_{60} in 180 mL of toluene was heated to reflux while 126.1 mg (0.73 mmol) of (*E*)-1-methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene (Danishefsky's diene) in 20 mL of toluene was added over 1.5 h *via* syringe pump. After addition, the reaction was maintained at reflux for another 3 h until completion of the reaction. After cooling, the solution was stirred with aqueous 1 M HCl and THF (100 mL each) for 4 h. After separation of the aqueous layer, the toluene solution was washed with water, dried, and evaporated to dryness. The product was redissolved in the minimum of CS_2 and purified by flash chromatography (CS_2 first, then toluene) to give 300.9 mg (60%) of pure **5a** as shiny black crystals: ^1H NMR (500 MHz, $CDCl_2CDCl_2$, 90 °C) δ (ppm) 3.70 (dd, J = 19.1, 4.9 Hz, 1H), 3.89 (dd, J = 19.1, 2.7 Hz, 1H), 3.93 (s, 3H), 4.21 (br d, J = 15.1 Hz, 1H), 5.05 (br d, J = 15.1 Hz, 1H), 5.38 (dd, J = 4.9, 2.7 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_2CDCl_2$) δ (ppm) 29.3, 44.2 (br), 52.7, 59.4 (C_{60} sp^3-*C*), 61.8 (C_{60} sp^3-*C*), 68.0, 134.8, 135.2, 136.8 (br), 140.0 (br), 140.2, 140.5, 141.5, 141.68, 141.72, 142.0, 142.1, 142.15, 142.18, 142.55, 142.61, 142.67, 142.72, 143.2, 143.3, 144.6, 144.7, 144.8, 144.9, 145.41, 145.44, 145.52, 145.60, 145.63, 145.67, 145.72, 145.83, 146.32, 146.36, 146.51, 146.55, 146.61, 147.8, 156.0, 156.5, 158.0, 158.3, 207.7 (*C*=O); FT-IR (KBr) ν (cm^{-1}) 1725 s (C=O), 527 s; HRMS calcd for $C_{65}H_8O_2$ 820.052, found 820.0547.

1,2-(5′-Oxo-3′-cyclohexeno)buckminsterfullerene (5b). A total of 106.6 mg (0.13 mmol) of 1,2-(6′-methoxy-4′-oxocyclohexano)buckminsterfullerene (**5a**) in a 1:1 mixture of toluene and CF_3CO_2H (50 mL) was heated under reflux for 4 h. After cooling to 20 °C, the reaction mixture was diluted with 100 mL of toluene, washed with 100 mL of water and then several times with brine, and dried. The solution was concentrated to ~10 mL and purified by flash chromatography on silica gel (toluene, then toluene/EtOAc 8:2) to afford 84.4 mg (82%) of pure **5b** as shiny black crystals: ^1H NMR (500 MHz, $CDCl_2CDCl_2$) δ (ppm) 4.49 (s, 2H), 6.89 (d, J = 10.2 Hz, 1H), 7.96 (d, J = 10.2 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_2CDCl_2$) δ (ppm) 50.7, 60.6 (C_{60} sp^3-*C*), 63.6 (C_{60} sp^3-*C*), 128.8 (=CH, DEPT), 134.0, 135.2, 140.4, 140.5, 141.6, 141.7, 141.9, 142.05, 142.11, 142.25, 142.66, 142.76, 143.4, 144.4, 144.6, 144.8, 145.2, 145.6, 145.7, 146.0, 146.4, 146.5, 146.6, 146.7, 148.0, 150.2 (=*C*H, DEPT), 153.4, 156.3, 196.3 (*C*=O); FT-IR (KBr) ν (cm^{-1}) 1694 s (C=O), 527 s; UV/vis (CH_2Cl_2) λ_{max} (nm) 258 (ϵ 75 500), 306 sh (27 800), 437 (4 500), 702 (470); LRMS calcd for $C_{64}H_4O$ 788.03; found 788.03.

1,2-(5′-Hydroxy-3′-cyclohexeno)buckminsterfullerene (3), Method A. A solution of 125 mg (0.173 mmol) of C_{60} in 70 mL of degassed toluene and 1.5 mL of 1,3-butadiene was heated to between 120 and 130 °C for 2.5 h in a resealable pressure tube (Ace Glass fitted with an Ace-Thread stopper; purple color of C_{60} changes to a deep brown solution) and then cooled to 20 °C. The solvent was evaporated to dryness. The residue consisting mostly of **6** (R_f = 0.94, SiO_2, cyclohexane) was redissolved in 100 mL of toluene. The solution was irradiated for 4.5 h with a 300 W xenon lamp (Pyrex filter) under O_2 bubbling. After complete conversion to hydroperoxide **7** (R_f = 0.33, SiO_2, toluene/EtOAc 95:5), 79 mg (0.30 mmol) of PPh_3 was added. The reaction mixture was stirred for 15 min at 20 °C and concentrated to ~10 mL. Flash chromatography (SiO_2, toluene) afforded 72.5 mg (53% overall) of pure **3** (R_f = 0.22, SiO_2, toluene/EtOAc 95:5) as black crystals: ^1H NMR (400 MHz, $CDCl_2CDCl_2$) δ (ppm) 2.23 (d, J = 5.6 Hz, 1H), 3.72 (dd, J = 12.4, 9.5 Hz, 1H), 3.89 (ddd, J = 12.4, 3.8, 1.1 Hz, 1H), 5.60 (m, 1H), 6.98 (ddd, J = 9.8, 2.4, 1.1 Hz, 1H), 7.11 (dd, J = 9.8, 2.0 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_2CDCl_2$) δ (ppm) 48.5, 60.9, 63.5, 66.5, 125.5, 128.4, 129.2, 132.3, 133.7, 134.1, 135.5, 135.8, 136.9, 140.29 (× 2), 140.33, 140.4, 141.53, 141.54, 141.6, 141.7, 141.9, 142.0, 142.10, 142.12, 142.13, 142.2, 142.47, 142.54, 142.55, 142.6, 142.7, 143.27, 143.31, 144.5, 144.6, 145.0, 145.05, 145.09, 145.16, 145.3, 145.4, 145.48, 145.51, 145.54, 145.55, 145.7, 145.95, 145.99, 146.1, 146.27, 146.31, 146.38, 146.4, 146.50, 146.53, 146.58, 146.6, 147.8, 147.9, 155.6, 156.5, 157.2, 158.9; FT-IR (KBr) ν (cm^{-1}) 1427 m (C=C), 527 s; UV/vis (CH_2Cl_2) λ_{max} (nm) 254 (ϵ 93 000), 304 sh (33 000), 320 sh (30 700), 436 (3230), 466 sh (1540), 708 (340); HRMS calcd for $C_{64}H_6O$ 790.0419, found 790.0437.

Method B. To a solution of 1,2-(5′-oxo-3′-cyclohexeno)-buckminsterfullerene (**5b**) (54.4 mg, 0.069 mmol) in 70 mL of toluene was added dropwise a 1.0 M solution of DIBAL-H in hexanes (1.5 mL, 1.5 mmol) at 0 °C, and the mixture was stirred at 20 °C for 24 h. The reaction mixture was poured into 50 mL of 0.1 M HCl, the organic layer was washed twice with saturated $NaHCO_3$ and dried, and the solvent was evaporated *in vacuo*. The crude product was purified by flash chromatography (SiO_2, toluene) to give 47.9 mg of **3** (88%) as a black crystalline solid, identical by ^1H NMR and TLC to product prepared as described in method A.

1,2-(5′-Hydroperoxy-3′-cyclohexeno)buckminsterfullerene (7). In one experiment repeated as above for the preparation of **3** (method A), the unstable intermediate hydroperoxide **7** was isolated by flash chromatography (SiO_2, toluene) and characterized by ^1H NMR spectroscopy: ^1H NMR (400 MHz, $CDCl_3/CS_2$ 1:1) δ (ppm) 3.90 (s, 1H, C*H*$_2$), 3.92 (d, J = 1.3 Hz, 1H, C*H*$_2$), 5.72–5.76 (m, 1H, C*H*OOH), 6.95 (dd, J = 9.8, 3.5 Hz, 1H, =C*H*), 7.19 (dd, J = 9.8, 1.5 Hz, 1H, C*H*=), 8.13 (br, 1H, OO*H*).

1,2-(4′-Cyclohexeno)buckminsterfullerene (6). The formation of **6** as described above was repeated with 64.8 mg (0.09 mmol) of C_{60} and approximately 2.5 mL of 1,3-butadiene in 35 mL of degassed toluene. The solvent was evaporated to dryness and the residue redissolved in cyclohexane. The cyclohexane was evaporated until near saturation and loaded onto a column packed with flash silica gel. Elution with

(38) (a) Scrivens, W. A.; Bedworth, P. V.; Tour, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 7917–7919. (b) Scrivens, W. A.; Tour, J. M. *J. Org. Chem.* **1992**, *57*, 6932–6936.

(39) For the IUPAC nomenclature of fullerenes, see: Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1993**, 813–824.

cyclohexane afforded 27.0 mg (39%) of pure **6** as black crystals: ^{1}H NMR (500 MHz, $CDCl_2CDCl_2$) δ (ppm) 4.06 (d, J = 3.6 Hz, 4H), 7.03 (t, J = 3.6 Hz, 2H); ^{13}C NMR (125.7 MHz, $CDCl_2CDCl_2$) δ (ppm) 39.9, 66.0 (C_{60} sp^3-*C*), 132.4, 135.8, 140.1, 141.6, 142.1, 142.4, 142.6, 143.2, 144.8, 145.4, 145.5, 145.6, 145.9, 146.3, 146.5, 147.7, 157.6 (*HC*=*CH*); FT-IR (KBr) ν (cm^{-1}) 1428 m (C=C), 527 s; UV/vis (CH_2Cl_2) λ_{max} (nm) 256 (ϵ 94 400), 308 (32 800), 324 (30 200), 436 (3740), 710 (400); FAB-MS m/z (rel intensity) 775 (MH^+, 45), 721 ($C_{60}H^+$, 100).

When a lesser excess of butadiene was used, the reaction yield was greatly improved: for example, from 20.0 mg (0.028 mmol) of C_{60} and 100 μL of butadiene in 10 mL of toluene (2 h, 125 °C), 14.1 mg (65%) of **6** was obtained after chromatography. A systematic optimization of the reaction conditions was not carried out.

1,2-(3′,5′-Cyclohexadieno)buckminsterfullerene (4), Method A. A mixture of 9.8 mg (0.0124 mmol) of 1,2-(5′-hydroxy-3′-cyclohexeno)buckminsterfullerene (**3**), 65.5 mg (0.248 mmol) of *tert*-butyldimethylsilyl trifluoromethanesulfonate, and 15.2 mg (0.124 mmol) of 4-(dimethylamino)pyridine in 10 mL of toluene was stirred at 20 °C for 20 h. The reaction was then treated with saturated $NaHCO_3$, washed with brine, and dried. Flash chromatography on silica gel with cyclohexane afforded 3.0 mg (31%) of **4** as dark brown crystals which converted rapidly to the endoperoxide **9** in solution, unless strict exclusion of air and light during reaction and purification was performed (including chromatography): ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ 2:1) δ (ppm) 6.55–6.65 (AA′BB′-m); ^{13}C NMR (125.7 MHz, $CDCl_3/CS_2$ 2:1) δ (ppm) 64.3 (C_{60} sp^3-*C*), 122.0, 126.6, 134.4, 140.6, 141.3, 142.1, 142.4, 142.5, 143.0, 144.4, 145.0, 145.3, 145.4, 146.2, 146.30, 146.32, 147.8, 150.5. FAB-MS: m/z (rel intensity) 773 (MH^+, 40), 720 (C_{60}^+, 100).

Method B. To a solution of 20 mg (0.0253 mmol) of 1,2-(5′-hydroxy-3′-cyclohexeno)buckminsterfullerene (**3**) in 40 mL of degassed toluene was added an excess of *p*-toluenesulfonic acid (80 mg), and the solution was heated under reflux for 30 min. After cooling, the crude compound was purified by flash chromatography as above to give 9.4 mg (48%) of **4**.

Method C. A solution of **8a** (3.0 mg, 0.00337 mmol) and *p*-toluenesulfonic acid monohydrate (20 mg) in 3 mL of degassed toluene was heated under reflux for 2.5 h. The product was purified by flash chromatography as above to give 2.5 mg (96%) of **4**.

1,2-(3′,5′-Cyclohexadieno)buckminsterfullerene 3′,6′-Endoperoxide (9). A solution of **4** in 0.5 mL of $CDCl_3/CS_2$ (2:1) was left in contact with air and ambient light (fluorescent tubes) for 12 h. The diene gradually transformed to endoperoxide **9** (TLC, SiO_2, cyclohexane; R_f(**4**) = 0.50, R_f(**9**) = 0.41), which decomposed more slowly to polymeric material and malealdehyde, recognizable by its ^{1}H NMR spectrum. Spectral characteristics for endoperoxide **9**: ^{1}H NMR (400 MHz, $CDCl_3/CS_2$ 2:1) δ (ppm) 6.09 (dd, J = 4.5, 3.3 Hz, 2H), 7.65 (dd, J = 4.5, 3.2 Hz, 2H).

Spectral characteristics for **malealdehyde**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.69 (dd, J = 4.1, 2.8 Hz, 2H), 10.50 (dd, J = 4.1, 2.8 Hz, 2H).

Diels–Alder Adduct of Compound 4 with *N*-Phenylmaleimide: 1,2-[*N*-Phenyl-4′-aza-3′,5′-dioxo(1′a,2′aβ,6′aβ,7′aα)tricyclo[5.2.2.0^{2,6}]undec-8′-eno]buckminsterfullerene (10a). A solution of 3.4 mg (0.0044 mmol) of 1,2-(3′,5′-cyclohexadieno)buckminsterfullerene (**4**) and 100 mg (0.58 mmol) of *N*-phenylmaleimide in 5 mL of deoxygenated toluene was stirred at 20 °C for 2 days. After evaporation *in vacuo*, the crude product was purified by flash chromatography on silica gel (TLC, SiO_2, toluene; R_f(**10a**) = 0.43, R_f(**4**) = 0.95). Elution with toluene furnished 3.5 mg of **10a** (84%) as a thermally unstable solid: ^{1}H NMR (400 MHz, $CS_2/CDCl_3$, 1:1) δ (ppm) 4.59 (dd, J = 1.6, 1.3 Hz, 2H), 4.81 (ddd, J = 6.4, 3.2, 1.6 Hz, 2H), 7.30 (apparent dd, J = 6.4, 3.2, 1.3 Hz, 2H), 7.40–7.55 (m, 5H).

Diels–Alder Adduct of Compound 4 with Maleic Anhydride: 1,2-[4′-Oxa-3′,5′-Dioxo(1′aα,2′aβ,6′aβ,7′aα)-tricyclo[5.2.2.0^{2,6}]undec-8′-eno]buckminsterfullerene (10b). A solution of 6.3 mg (0.0082 mmol) of 1,2-(3′,5′-cyclohexadieno)-buckminsterfullerene (**4**) and 300 mg (3.1 mmol) of maleic anhydride in 15 mL of deoxygenated toluene was heated under reflux for 30 min. After evaporation *in vacuo*, the crude product was submitted to flash chromatography on silica gel with toluene (TLC, SiO_2, toluene; R_f(**10b**) = 0.31, R_f(**4**) = 0.95). Partial decomposition/hydrolysis occurred during chromatography, and 2.1 mg (29%) of **10b** was obtained as a thermally unstable solid: ^{1}H NMR (360 MHz, $CS_2/CDCl_3$, 1:1) δ (ppm) 4.70 (dd, J = 1.6, 1.4 Hz, 2H), 4.78 (ddd, J = 6.4, 3.1, 1.6 Hz, 2H), 7.34 (apparent dd, J = 6.4, 3.1, 1.4 Hz, 2H).

1,2-[5′-((*tert*-Butoxycarbonyl)oxy)-3′-cyclohexeno]buckminsterfullerene (8a). A solution of 100 mg (0.126 mmol) of 1,2-(5′-hydroxy-3′-cyclohexeno)buckminsterfullerene (**3**), 700 mg (3.2 mmol) of di-*tert*-butyl dicarbonate, and 160 mg (4 mmol) of NaH (60% oil dispersion washed with dry toluene) in 60 mL of THF was stirred under reflux for 1.5 h. After cooling to 20 °C, the reaction mixture was filtered through a plug of silica gel with toluene. Evaporation of the solvents to ~3 mL and flash chromatography (SiO_2, toluene/cyclohexane 1:1; TLC, R_f = 0.75) afforded 106 mg (94%) of pure **8a** as a dark brown resin: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.60 (s, 9H), 3.81 (dd, J = 12.6, 9.5 Hz, 1H), 3.93 (ddd, J = 12.6, 3.7, 1.1 Hz, 1H), 6.29 (dddd, J = 9.5, 3.7, 2.6, 1.9 Hz, 1H), 6.91 (ddd, J = 9.9, 2.6, 1.1 Hz, 1H), 7.10 (dd, J = 9.9, 1.9 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm) 26.9, 29.7, 44.7, 60.4, 63.4, 71.0, 83.1, 132.8, 133.6, 133.8, 134.4, 135.6, 135.9, 140.21, 140.33, 140.36, 140.39, 141.53, 141.56, 141.66, 141.70, 141.91, 141.95, 142.06, 142.11, 142.12, 142.18, 142.24, 142.42, 142.57 (intensity × 2), 142.63, 142.72, 143.28, 143.31, 144.53, 144.60, 144.97, 145.01, 145.03, 145.04, 145.32, 145.47, 145.50, 145.56 (×2), 145.57, 145.65, 145.90, 145.94, 146.00, 146.29, 146.32, 146.38, 146.45, 146.54, 146.55, 146.61, 146.64, 147.86, 147.88, 153.1, 155.2, 155.9, 156.6, 158.2; FT-IR ν (cm^{-1}) 1738 (m), 1272 (m), 1251 (m), 863 (m), 767 (m), 526 (s); UV/vis (CH_2Cl_2) λ_{max} (nm) 256 (ϵ 88 200), 302 sh (32 800), 320 sh (30 700), 434 (3150), 706 (300); FAB-MS m/z (rel intensity) 890 (M^+, 100), 773 ($M^+ - t$-$BuOCO_2$, 43), 721 ($C_{60}H^+$, 91); HRMS calcd for $C_{69}H_{14}O_3$ 890.0943, found 890.0955.

1,2-[5′-(2,2-Dimethylpropanoyl)-3′-cyclohexeno]buckminsterfullerene (8b). To a solution of 23.7 mg (0.03 mmol) of 1,2-(5′-hydroxy-3′-cyclohexeno)buckminsterfullerene (**3**) and 201 mg (1.65 mmol) of DMAP in 20 mL of toluene was added dropwise 0.2 mL (1.5 mmol) of trimethylacetyl chloride at 20 °C. The solution was stirred at 20 °C for 6 h and then diluted with toluene, washed with saturated $NaHCO_3$ and water, and dried. After evaporation of the solvents to dryness, the residue was redissolved in the minimum of toluene/cyclohexane (1:1). Flash chromatography (SiO_2, toluene/cyclohexane 1:1) afforded 21.3 mg (81%) of pure **8b** as a dark brown resin: ^{1}H NMR (400 Hz, $CDCl_3$) δ (ppm) 1.37 (s, 9H), 3.78 (dd, J = 13.0, 8.2 Hz, 1H), 3.89 (ddd, J = 13.0, 3.7, 0.8 Hz, 1H), 6.38 (dddd, J = 8.2, 3.7, 3.5, 1.6 Hz, 1H), 6.87 (ddd, J = 9.8, 3.5, 0.8 Hz, 1H), 7.14 (dd, J = 9.8, 1.6 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm) 27.4, 39.1, 44.4, 60.3 (C_{60} sp^3-*C*), 63.5 (C_{60} sp^3-*C*), 67.7, 131.9, 134.3 (×2), 134.6, 135.2, 135.4, 140.25, 140.35, 140.40, 140.43, 141.58, 141.65 (×2), 141.66, 141.99, 142.05, 142.11 (×2), 142.16, 142.19, 142.21, 142.3, 142.61, 142.63, 142.65, 142.73, 143.3 (×2), 144.65, 144.75, 144.91, 144.97, 145.1, 145.3, 145.44, 145.47, 145.50, 145.54 (×2), 145.58 (×2), 145.80, 146.00, 146.04, 146.33, 146.36, 146.40, 146.47, 146.57, 146.59, 146.62, 146.68, 147.89, 147.92, 155.8, 156.5, 156.6, 158.2, 178.3 (*C*=O); FT-IR ν (cm^{-1}) 1732 s (C=O), 1145 vs (C–O), 526 vs; HRMS calcd for $C_{69}H_{14}O_2{\cdot}H^+$ 875.1072, found 875.1061.

1,2-[5′-((*tert*-Butyldimethylsilyl)oxy)-3′-cyclohexeno]-buckminsterfullerene (8c). A solution of 23.7 mg (0.03 mmol) of 1,2-(5′-hydroxy-3′-cyclohexeno)buckminsterfullerene (**3**), 112.4 mg (1.65 mmol) of imidazole, and 397 mg (2.63 mmol) of *tert*-butyldimethylsilyl chloride in 15 mL of dry DMF was stirred at 20 °C for 24 h. The solvent was evaporated *in vacuo* and the residue dissolved in cyclohexane, washed with saturated $NaHCO_3$ and brine, and dried. The solution was concentrated to ~5 mL, and flash chromatography (cyclohexane) gave 2.3 mg (8.5%) of product **8c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.31 (s, 3H), 0.34 (s, 3H), 1.06 (s, 9H), 3.66 (dd, J = 12.7, 8.7 Hz, 1H), 3.71 (ddd, J = 12.7, 4.2, 0.9 Hz, 1H), 5.48 (dddd, J = 8.7, 4.2, 2.5, 1.8 Hz, 1H), 6.83 (ddd, J = 9.8, 2.5, 0.9 Hz, 1H), 6.97 (dd, J = 9.8, 1.8 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm) −4.36, −4.34, 18.3, 25.9, 48.9, 61.0 (C_{60} sp^3-*C*), 63.5 (C_{60} sp^3-*C*), 66.8, 131.4, 133.7, 134.3, 135.6, 135.8, 137.8, 140.24, 140.30, 140.33, 140.38, 141.53,

141.57 (2C), 141.70, 141.94, 142.05, 142.12 (2C), 142.13, 142.14, 142.28, 142.52, 142.55 (2C), 142.62, 142.72, 143.30, 143.34, 144.58, 144.60, 145.02, 145.10, 145.15, 145.25, 145.30, 145.38, 145.45, 145.49, 145.50 (2C), 145.52, 145.59, 145.75, 146.00, 146.01, 146.10, 146.26, 146.32, 146.39, 146.43, 146.51, 146.54, 146.59, 146.61, 147.85, 147.88, 155.8, 156.9, 157.5, 159.2; FT-IR ν (cm^{-1}) 1427 m, 1250 s, 1109 vs, 1091 vs, 526 vs; HRMS calcd for $C_{70}H_{20}SiO{\cdot}H^+$ 905.1362, found: 905.1338.

Solubilization Group Removal. Regeneration of C_{60}: (a) From 1,2-[5′-((*tert*-Butoxycarbonyl)oxy)-3′-cyclohexeno]buckminsterfullerene (8a). A solution of 6.0 mg (0.0067 mmol) of **8a**, 25 mg of *p*-toluenesulfonic acid, and 100 mg (0.7 mmol) of DMAD in 6 mL of degassed toluene was heated under reflux for 4 h in the absence of light. TLC (SiO_2, cyclohexane) indicated the presence of C_{60} (cospotted with authentic material) and unreacted DMAD. The reaction mixture was diluted with 6 mL of cyclohexane, and flash chromatography (toluene/cyclohexane 3:7) gave 4.6 mg (95%) of pure C_{60}: ^{13}C NMR (100.6 MHz, $CS_2/CDCl_3$ 2:1) δ (ppm) 142.93.[32]

(b) From 1,2-[5′-(2,2-Dimethylpropanoyl)-3′-cyclohexeno]buckminsterfullerene (8b). A solution of 6.0 mg (0.0069 mmol) of **8b**, 25 mg of *p*-toluenesulfonic acid, and 100 mg (0.7 mmol) of DMAD in 3 mL of degassed toluene was heated under reflux for 4 h in the absence of light. Chromatography as above gave 4.4 mg (89%) of pure C_{60}: ^{13}C NMR (100.6 MHz, $CS_2/CDCl_3$ 1:1) δ (ppm) 142.86.[32]

(c) From 1,2-(3′,5′-Cyclohexadieno)buckminsterfullerene (4). A solution of 2.0 mg (0.0026 mmol) of **4** and 100 mg (0.7 mmol) of DMAD in 3 mL of degassed toluene was heated under reflux for 3 h in the absence of light. Chromatography as above gave 1.4 mg (75%) of C_{60}.

[3′,10′-Tetrahydro-5′,8′-dimethyl-6′,7′-diphenylnaphthaleno][5′-((*tert*-butoxycarbonyl)oxy)-3′-cyclohexeno]-buckminsterfullerene Stereoisomers (13) (Diels–Alder Reaction of 8a with 12). A solution of 30.0 mg (0.0337 mmol) of **8a** and 25.0 mg (0.080 mmol) of diene **12**[34] in 50 mL of dry toluene was heated under reflux for 18 h. The reaction mixture was filtered through a pad of silica gel with toluene. Evaporation of the solvent *in vacuo* and flash chromatography on silica gel (hexane/toluene 3:1) afforded 21.0 mg (53%) of stereoisomeric adducts **13** as a dark brown resin: LD-MS *m*/*z* (rel intensity) 1175 (M^-, 87), 1057 ($M^- - t$-$BuOCO_2$, 100), 891 ($M^- - (CH_2)_2C_6Me_2Ph_2$, 50), 772 (891 − *t*-$BuOCO_2$, 89), 720 ($C_{60}$, 90).

1,2-(3′,10′-Tetrahydro-5′,8′-dimethyl-6′,7′-diphenylnaphthaleno)buckminsterfullerene (14). A solution of 21.0 mg (0.018 mmol) of **13**, 40 mg of *p*-toluenesulfonic acid, and 200 mg (1.4 mmol) of DMAD in 20 mL of degassed toluene was heated under reflux for 3 h in the dark. Filtration through a pad of silica gel with toluene, evaporation of the solvent *in vacuo*, and flash chromatography on silica gel (cyclohexane/toluene 3:1) afforded 14.4 mg (80%) of pure **14** as a black crystalline powder, identical with authentic material:[4a] ^1H NMR (400 MHz, $CS_2/CDCl_3$ 5:1) 2.29 (s, 6 H), 4.7 (br d, 2H), 6.95−7.15 (m, 10H).

3-Bromo-1,5-bis(trimethylsilyl)-1,4-pentadiyne (16a) and 1-Bromo-1,5-bis(trimethylsilyl)-1,2-pentadien-4-yne (Allene 16b).[9a,35] A solution of 1.7 g (7.6 mmol) of 1,5-bis(trimethylsilyl)-1,4-pentadiyn-3-ol[35] and 0.7 mL (7.4 mmol) of PBr_3 in 30 mL of dry Et_2O was stirred at 0−10 °C for 18 h. The reaction was diluted with H_2O and extracted with ether (3×). The organic phase was dried and evaporated *in vacuo*. Flash chromatography on silica gel (cyclohexane) afforded 1.1 g (50%) of pure pentadiyne **16a** as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.19 (s, 18H, Me_3Si), 5.15 (s, 1H, C*H*Br); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) −0.51, 18.8, 92.1, 99.0; EI-MS *m*/*z* (rel intensity) 286/288 (M^+, 25), 207 (M^+ − Br, 100); HRMS calcd for $C_{11}H_{19}{}^{79}BrSi_2$ 286.0209, found 286.0210.

Further elution with cyclohexane gave 0.5 g (23%) of pure allene **16b** as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 0.19 (s, 9H), 0.21 (s, 9H), 5.40 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) −1.0, −0.1, 68.2, 93.6, 96.7, 101.6, 210.0.

[3′,3′-Bis((trimethylsilyl)ethynyl)methano][5′-((*tert*-butoxycarbonyl)oxy)-3′-cyclohexeno]buckminsterfullerene Stereoisomers (15a). A solution of 34.0 mg (0.038 mmol) of **8a**, 15.0 mg (0.052 mmol) of 3-bromo-1,5-bis(trimethylsilyl)-1,4-pentadiyne (**16a**), and 80 mg (2 mmol) of NaH (60% oil dispersion washed with dry toluene) in 15 mL of toluene and 5 mL of THF was stirred at 20 °C for 36 h. The solution was filtered through a pad of silica gel with toluene, affording crude **15a** used directly in the next step: FAB-MS *m*/*z* (rel intensity) 1097 (MH^+, 5), 979 ($M^+ - t$-$BuOCO_2$, 7), 891 ($MH^+ - C_5(TMS)_2$, 9), 834 (891 − *t*-Bu, 11), 773 (891 − *t*-$BuOCO_2H$, 32), 720 (C_{60}, 100).

[3′,3′-Diethynylmethano][5′-((*tert*-butoxycarbonyl)oxy)-3′-cyclohexeno]buckminsterfullerene Stereoisomers (15b). To a solution of crude adduct **15a** in 20 mL of THF was added 6 mL of a 0.01 M aqueous sodium tetraborate, and the reaction was stirred at 20 °C for 15 h. After dilution with toluene, aqueous workup with saturated NH_4Cl and water, drying, and evaporation, flash chromatography (SiO_2, cyclohexane/toluene 1:1) afforded 24.0 mg (66% from **8a**) of **15b** diastereomers as a dark brown resin: ^1H NMR (400 MHz, $CDCl_3$) see Figure 1; FAB-MS *m*/*z* (rel intensity) 953 (MH^+, 60), 835 ($M^+ - t$-$BuOCO_2$, 33), 720 (C_{60}, 100); HRMS calcd for $C_{74}H_{16}O_3$ 952.1099; found 952.1096.

[3′,3′-Bis(4′-phenyl-1′,3′-butadiynyl)methano][5′-((*tert*-butoxycarbonyl)oxy)-3′-cyclohexeno]buckminsterfullerene Stereoisomers (17). A solution of 7.0 mg (0.0074 mmol) of **15b**, 93.0 mg (0.91 mmol) of phenylacetylene, and 1 mL of Hay catalyst[37] (from 100 mg (1 mmol) of CuCl and 118 mg (1 mmol) of TMEDA in 10 mL of chlorobenzene) in 5 mL of chlorobenzene was stirred under O_2 at 20 °C for 2 h. Filtration through a pad of silica gel with toluene, evaporation to dryness, and flash chromatography (SiO_2, cyclohexane/toluene 1:1) afforded 6.3 mg (74%) of **17** diastereomers as a dark brown waxy solid: FAB-MS *m*/*z* (rel intensity) 1153 (MH^+, 5), 1036 ($MH^+ - t$-$BuOCO_2$, 7), 773 (1036 − H − C_9Ph_2, 20), 720 (C_{60}, 100).

1,2-[3′,3′-Bis(4′-phenyl-1′,3′-butadiynyl)methano]buckminsterfullerene (18). A solution of 5.4 mg (0.0047 mmol) of **17**, 25 mg of *p*-toluenesulfonic acid, and 100 mg (0.7 mmol) of DMAD in 6 mL of degassed toluene was heated under reflux for 3 h. The solution was filtered through a pad of silica gel with toluene. After evaporation of the solvent, the residue was dissolved in 0.1 mL of CS_2 and diluted with 1.0 mL of cyclohexane. Flash chromatography (SiO_2, cyclohexane) afforded 1.1 mg (24%) of **18** as a black crystalline solid, identical with material prepared by mixed Hay coupling of **2** and phenylacetylene: ^1H NMR (500 MHz, $CS_2/CDCl_3$ 5:1) δ (ppm) 7.35−7.45 (m), 7.55−7.6 (m); ^{13}C-NMR (125 MHz, $CS_2/CDCl_3$ 5:1) δ (ppm) 70.6, 73.8, 73.9, 74.8, 79.9, 120.9, 128.1, 129.0, 132.5, 139.0, 141.0, 141.9, 142.2, 142.6, 142.7, 142.8, 143.8, 144.4, 144.5, 144.8, 144.9, 145.0, 145.20 (×2), 145.22; signal for ≡C−*C*−C≡ (~30 ppm) too weak to be observed;[8] FAB-MS *m*/*z* (rel intensity) 983 (MH^+, 19), 720 (C_{60}, 100).

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Supporting Information Available: ^1H and/or ^{13}C NMR spectroscopic data for compounds **3**, **4**, **5b**, **6**, **8a−c**, **10a**, **17**, and **18** (17 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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