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[2 + 2] Cycloaddition of Fullerenes with Electron-Rich Alkenes and Alkynes

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Photochemical [2 + 2] cycloaddition of C_{60} with *N*,*N*-diethyl-4-methyl-3-penten-1-yn-1-amine (**1**) afforded the stable C_{60}-fused cyclobutenamine **2** which underwent self-sensitized photooxidation to dihydrofullerenone amide **4** in high yield. Fullerenes C_{60} and C_{70} react thermally with tetraalkoxyethylenes to give dihydrofullerene cyclobutanediketals, which undergo a clean cycloreversion to fullerenes on irradiation with visible or UV light. Attempted hydrolysis of the ketals was unsuccessful, but treatment of 1,2-(6161,62,62-tetraethoxycyclobutano)dihydro[60]fullerene (**8**) with TMSI gave ring-contracted product **11** (by cleavage of the C−C bond to the fullerene fragment) along with reduction product **12**.

Introduction

Many methods of functionalizing fullerenes have been reported, including many that employ cycloaddition.[1−3] Among the cycloaddition routes, Diels−Alder[4−17] and 1,3-dipolar cycloadditions[18−27] are particularly useful because they usually give good yields of characterizable monoadducts. These reactions make use of the electron deficiency of fullerenes. However, [2 + 2] cycloadditions of fullerenes are less common. Hoke reported that benzyne reacted with C_{60} to give a series of [2 + 2] adducts, from which the monoadduct was isolated and characterized.[28] We and Wilson et al. have reported photochemical [2 + 2] cycloaddition of fullerenes with *N*,*N*-diethylpropynylamine (ynamine) and cyclohexenone, respectively.[29−31] Reactions with several other ynamines have been reported, as have some of the reactions of the initial adducts.[32] The initial cycloadducts of ynamines with fullerenes are labile and are easily cleaved to dicarbonyl dihydrofullerenes (DHFs) through an interesting self-sensitized mechanism. In this paper, we report a further example of photochemical [2 + 2] cycloaddition of an enynamine to C_{60} to give a stable C_{60}-fused cyclobutenamine, and its self-sensitized photooxygenation to a fullerenyl enone. We also report that tetraalkoxyethylenes, another type of electron-rich olefin, react with fullerenes thermally to give good yields of DHF bisketals, which undergo a facile photocycloreversion on irradiation.

Results

Photochemical Reaction of C_{60} with *N*,*N*-Diethyl-4-methyl-3-penten-1-yn-1-amine (1). Mixing C_{60} and enynamine[33] **1** in deoxygenated toluene without light gave negligible reaction in 2.0 h at room temperature. However, upon irradiation >500 nm, a rapid and clean reaction was observed in 50 min by HPLC and TLC (Scheme 1). A C_{60}-fused cyclobutenamine **2** was obtained

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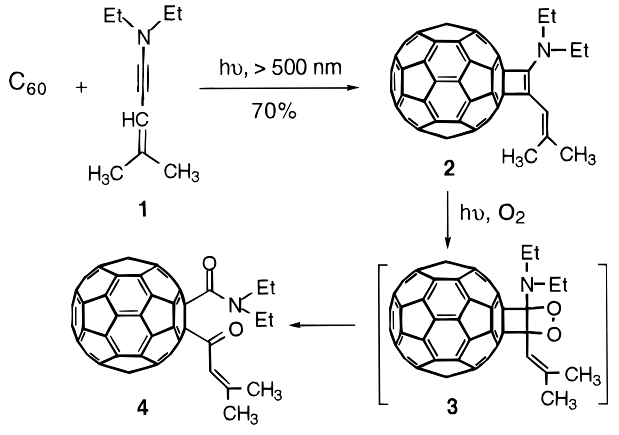
Scheme 1

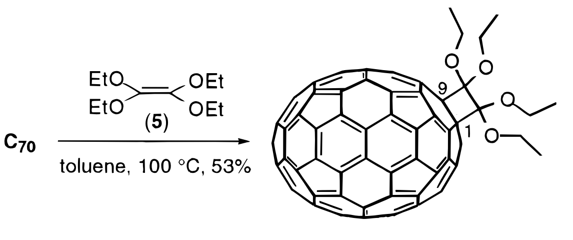


in 70% yield based on recovered C_{60}. Detailed spectroscopic studies support the structure of **2**. The ^{1}H NMR spectrum of **2** resembles that of **1**, but with significant downfield shifts: the vinyl proton singlet shifts to 6.45 ppm (5.35 ppm in **1**) because of the electron-withdrawing effect of the DHF ring. ^{13}C NMR spectra (125 MHz) resolved 34 olefinic carbon signals between 157.75 and 116.10 ppm, of which 30 belong to C_{60} and four belong to the dienamine moiety. Among the 34 olefinic carbon signals, 28 have intensity of two and 6 have intensity of one. This is the correct number and intensity for an adduct of C_s symmetry with addition occurring at the 6:6-ring junction, like other such C_{60} adducts. The two sp^{3} dihydrofullerenyl (DHF) carbons resonate at 76.10 and 75.42 ppm. Besides the characteristic stretching frequencies for DHFs,[34] FTIR spectrum of **2** showed several absorptions between 1635 and 1684 cm^{-1}, which we assign to the strained cyclobutene C=C bands. Negative FABMS gave the expected M^{-} at 871. These spectroscopic characteristics resemble similar adducts reported previously.[31,32]

Irradiation of a solution of **2** in toluene under a slow stream of oxygen cleanly produced the fullerenone amide **4** in a self-sensitized photooxygenation of the enamines like that observed previously.[31,32] Fullerenes[35,36] and dihydrofullerenes[37,38] have been shown to be excellent singlet oxygen sensitizers. 1,2-Dioxetane **3** is the most likely intermediate for the photocleavage. Such unstable dioxetanes have been characterized in photooxidation of other systems by low-temperature NMR experiments.[39] Compound **4** could also be prepared in similar yield, in one pot without isolation of **2**.

Fullerenone amide **4** was characterized by FAB-MS and ^{13}C NMR (carbonyls at 169.3 ppm for the amide and 193.4 ppm for the ketone and overall C_s symmetry for the fullerene carbons) as well as FTIR and ^{1}H NMR. It shows temperature-dependent dynamic behavior in the ^{1}H NMR from restricted rotation around the amide bond: all four methylene hydrogens are nonequivalent at −40 °C; pairwise averaging occurs at room temperature, where the two pairs are still broad and are apparently beginning to coalesce to a single group.

Scheme 2



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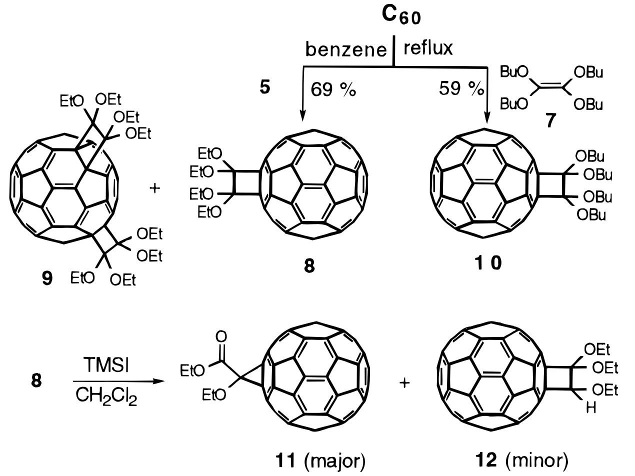
Scheme 3



[2 + 2] Cycloaddition of Tetraalkoxyethylenes to C_{60} and C_{70}. Tetraalkoxyethylenes are good π-electron donors, which are known to react with electron-deficient alkenes.[40] In view of the electron affinity of fullerenes,[41,42] we expected that adducts would be formed with these compounds. Heating a mixture of C_{70} and tetraethoxyethylene[40,43] **5** (5 mol equiv) at 100 °C in toluene for 12 h afforded a monoadduct, 1,9-(71,71,72,72-tetraethoxycyclobutano)dihydro[70]fullerene (**6**) in 53% isolated yield (Scheme 2).[44]

The ^{1}H NMR spectrum of **6** showed four sets of CH_2 protons groups (ABX_3, details in the Experimental Section). The ^{13}C NMR spectrum showed 35 sp^{2} and 2 sp^{3} fullerene carbon signals. Among the 35 sp^{2} carbon signals, 33 have double and two have single intensity. Signals at 112.35 and 111.31 ppm are assigned to the two ketal carbons. Both the ^{1}H and ^{13}C NMR data are consistent with C_s symmetry from addition at the 1,9 bond of C_{70}. The structure of **6** was also shown by FTIR, FABMS and UV−vis data.

Similarly, refluxing a mixture of C_{60} with **5** or tetrabutoxyethylene[40,43] (**7**) in benzene afforded diketal **8** (69%) or **10** (59%) respectively, after isolation (Scheme 3). These compounds were fully characterized by ^{1}H, ^{13}C

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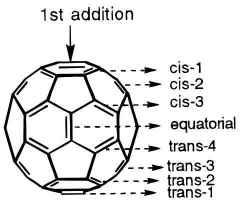


site	symmetry	no. of ^{13}C NMR resonances (relative intensity) for fullerene sp^3	sp^2
cis-1	C_s	2(2)	26(2), 4(1)
cis-2	C_s	2(2)	26(2), 4(1)
cis-3	C_2	2(1)	28(1)
equatorial	C_s	1(2), 2(1)	27(2), 2(1)
trans-4	C_2	2(2)	26(2), 4(1)
trans-3	C_s	2(1)	28(1)
trans-2	C_2	2(1)	28(1)
trans-1	D_{2h}	1(1)	14(1)

Figure 1. The eight possible regioisomers that can arise by double addition of **5** at 6:6 ring junctions in C_{60} and their symmetry.

NMR, FTIR, UV−vis, and MS data (see Experimental Section for details).

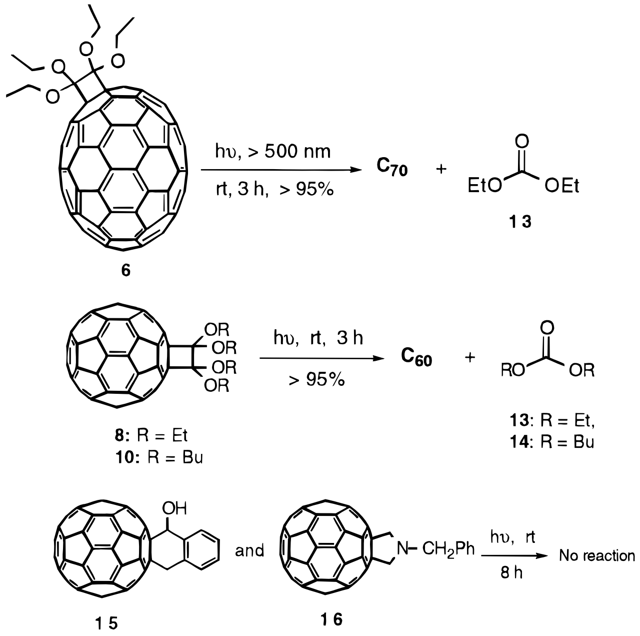
A small amount of products of multiple addition was also obtained in reaction of C_{60} with **5**; diadduct **9** was isolated after two preparative TLC separations. There are eight possible regioisomers for **9** if one assumes the second addition also occurs at 6,6-ring junctions (Figure 1). The ^{1}H NMR spectrum (500 MHz) of **9** showed a multiplet at 4.1 ppm for the methylene protons, and four sets of triplets between 1.50 and 1.35 ppm. The ^{13}C NMR of **9** showed 28 signals between 153.9 and 125.11 ppm, in which two signals have intensity of one, and 26 have intensity of two, and the remaining one has intensity of four (from two overlapping peaks of intensity two). Three sp^3 fullerenyl carbons were found; one is twice the intensity of the others. From the analysis of the symmetry of the ^{1}H and ^{13}C NMR spectra, compound **9** is probably the 1,2:18,36-diadduct.[44] The second addition occurs at the equatorial double bond (Figure 1). This is consistent with the steric effects shown for C_{60} polyadducts previously,[45,46] where attack at the octahedral sites is preferred.

Diketal **8** could not be hydrolyzed by H_2SO_4 or HCl in THF. With CF_3COOH in benzene, **8** decomposed to C_{60}. However, on treatment with trimethylsilyl iodide (TMSI) in CH_2Cl_2, **8** gave a ring-contracted product, methanofullerene **11**, and reduction product **12** in 38% total yield. Methanofullerenes of structure **11** have been reported previously by 1,3-dipolar cycloaddition of diazoacetates to C_{60} by Wudl[3] and Diederich et al.[47]

Several electron-rich alkynes, including ethyl ethynyl ether, bis(ethylthio)ethyne, and the alkene tetrakis(morpholino)ethylene did not react with C_{60} either thermally or photochemically.

Photochemical Cycloreversion of Fullerenyl Diketals 6, 8, and 10. Diketals **6**, **8**, and **10** are thermally stable compounds. However, irradiation with visible or UV light produced C_{70} and C_{60}, respectively, along with dialkyl carbonates **13** and **14** (Scheme 4). Compounds **13** and **14** are formed through singlet oxygenation of the tetraalkoxyethylenes,[48] which were produced by cycloreversion of the corresponding DHFs to the original starting materials. Preliminary studies indicate that the cycloreversion goes through the triplet excited states, because oxygen or rubrene, a well-known triplet quencher,[49] efficiently inhibits the cycloreversions. However, neither irradiation of the C_{60}-fused cyclohexane **15** (the Diels−Alder adduct of C_{60} with benzocyclobutenol[16]) nor cyclopentane **16** (the 1,3-dipolar addition product of C_{60} with the ylide[25]) gave appreciable cycloreversion or decomposition.

Scheme 4



Discussion

The photophysical properties of fullerenes have been the subject of numerous investigations,[50−52] but their photochemistry has received less attention. Most attempts to functionalize C_{60} and C_{70} have been based on thermal chemistry, especially cycloadditions. Previous results have demonstrated that the triplet excited state of C_{60} has a reduction potential near 0.98 V (36 kcal/mol triplet E) vs SCE, and is formed with a quantum yield of nearly unity.[35] Triplet C_{60} is readily photoreduced by amines and other donors to the C_{60} radical anion and donor radical cation.[51,53,54] We believe that the photoadditions of ynamines to fullerenes proceed via electron (or at least charge) transfer from the electron-rich ynamines, followed by rapid collapse of the initial ion pair or charge-transfer complex to the covalent adducts. Preliminary attempts to observe transient intermediates have not been successful.[55] It is likely that collapse of the intermediate in this case is too rapid to allow direct observation, at least on a 100 ns time scale.

Cycloadduct **2** and similar adducts from other ynamines are unique in that they have a photosensitizer (the DHF) and an easily photooxidizable group (the enamine) in the same molecule. Sensitized photooxidative cleavage of

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enamines is a well-known process and proceeds via an intermediate 1,2-dioxetane.[39,56] Recently, Wudl has reported an elegant example of this process, opening a hole in the DHF framework by self-sensitized photocleavage of a fullerene C=C bond connected to a nitrogen.[57]

It is not surprising that cycloadduct fullerenyl diketals are formed between fullerenes and tetraalkoxyethylenes, in view of the electron affinity of fullerenes and electron-donating ability of tetraalkoxyethylenes. We suspect that reactions of these very electron-rich alkenes can proceed directly to a charge-transfer state without light; similar thermal reactions were observed with the very electron-rich ynediamines and thioynamines.[32]

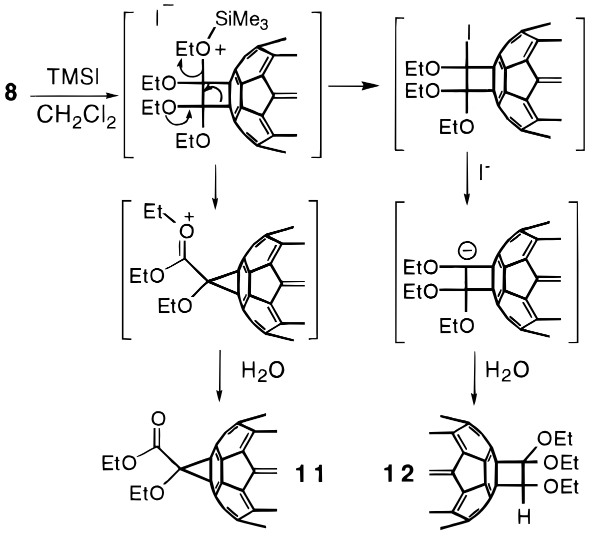
Interestingly, the cycloadducts from the tetraalkoxyethylenes undergo photocycloreversion, giving back C_{60} and C_{70} cleanly and efficiently on visible or UV light irradiation. The photocycloreversion goes through the triplet excited state, because rubrene and oxygen efficiently inhibit it. Excitation of the adducts may lead directly to a charge-transfer state that is reversibly formed from the starting materials. Further work is in progress to test these mechanistic hypotheses.

This photocycloreversion has potential applications, for example, in solubilizing fullerenes with such diketal adducts as a removable handle, or more interestingly, as a template to direct multiple additions. Examples of the use of such templates for preparation of multi-addended fullerenes in a controlled fashion have just started to appear in the literature.[58−61]

It is known that most reactions with C_{70} occur predominantly at the 1,9-bond.[32,62−65] This has been explained by the greater curvature and resulting strain at the polar region. Monitoring the reaction of C_{70} with **5** by HPLC indicated three other minor peaks at $t = 7.46$ min (3%), 5.89 min (4%), and 4.45 min (9%), besides **6** at retention time $t = 7.95$ min (84%). The peaks at 5.89 and 4.45 min were identified as a mixture of di- or polyadducts adducts by ^1H NMR after isolation. The peak at 7.46 min could not be isolated because of the small amount present in the mixture. Because its retention time is so close to that of the monoadduct **6**, it is likely that this peak corresponds to a 7,8-isomer with a similar polarity to **6**. If this is true, the ratio of 1,9 to 7,8 addition would be 28, which corresponds to a difference in free energy of activation $\Delta G^{\ddagger}$ at 293 K of 1.93 kcal/mol, with 1,9-addition more favorable. A recent study by Cahill et al. measured the equilibration of two $C_{70}H_2$ isomers, showing a $\Delta\Delta G^0$ at 295 K of 1.4 ± 0.2 kcal/mol favoring the 1,9-isomer.[63]

Hydrolysis of **8** did not produce the diketone as one would expect for hydrolysis of a diketal. The C−C bond directly connected to the DHF surface cleaves more rapidly than the C−O bond because of the strong electron-withdrawing ability of the DHFs. On treatment with the strong Lewis acid TMSI, the fullerene bond migrates to the carbocation, giving methanofullerene **11** after addition of H_2O (Scheme 5). We[31] and others[66,67] have previously observed this type of C−C bond cleavage in hydrolysis of fullerene derivatives. In a competing reaction, formation of the iodide followed by halophilic attack by iodide would give a carbanion next to the electron-withdrawing cage. Protonation of the carbanion would produce compound **12**. Nucleophilic attack on iodine in C−I bonds is precedented.[68]

Scheme 5



Conclusions

Enynamine **1** undergoes efficient photochemical [2 + 2] cycloaddition to C_{60}. The initial cycloadduct cyclobutenamine **2** is much more stable to oxygen than previously reported ones.[31,32] However, like the other adducts, **2** could also be photooxygenated to the dicarbonyl compound via self-sensitization. Since we have already demonstrated that yndiamines and thioynamines add to C_{60} and C_{70}, the reaction of fullerenes with ynamines is general and preparatively useful. Thermal cycloaddition of tetraethoxyethylene to fullerenes also gave high yields of [2 + 2] cycloadducts, which undergo efficient photochemical cycloreversion through the triplet excited state. Because these cycloadducts are very soluble in many organic solvents, this novel photochemistry should be useful for reversible solubilization of fullerenes.[61]

Experimental Section[32]

1,2-[61-(Diethylamino)-62-isopropylidenecyclobuteno]-dihydro[60]fullerene (2). A solution of C_{60} (86 mg, 0.12 mmol) in 50 mL of toluene was sonicated for 5 min and degassed by bubbling with argon for 20 min. With stirring, *N,N*-diethyl-4-methyl-3-penten-1-yn-1-amine (**1**) (20 mg, 20 μL, 0.12 mmol) was added via a syringe. The mixture was irradiated with a 300 W Xenon lamp with a $K_2Cr_2O_7$ filter (pathlength 3.5 cm, 530 nm) for 50 min. The resulting brown

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reaction mixture was condensed. Column chromatography (hexane−toluene, gradient elution) furnished unreacted C_{60}, cyclobutenamine **2** (58 mg, 70%), and enone amide **4** (6 mg). Enone amide **4** could also be prepared in a one-pot procedure using oxygen-saturated toluene in ~60% yield. Representative physical data for **2**: ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ 6.45 (s, 1 H), 3.83 (q, 4 H, $J = 7.00$ Hz), 2.25 (s, 3 H), 2.09 (s, 3 H), 1.48 (t, 6 H, $J = 7.00$ Hz); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) δ 157.74 (2 C), 155.97 (2 C), 150.09, 146.67 (2 C), 146.35, 146.21, 146.14 (2 C), 145.72 (2 C), 145.59 (2 C), 145.52 (2 C), 144.91 (2 C), 144.86 (2 C), 144.78 (2 C), 144.74 (2 C), 144.67 (2 C), 144.38 (2 C), 144.06 (2 C), 142.74 (4 C), 142.44 (2 C), 142.42 (2 C), 142.15 (4 C), 142.03 (2 C), 141.80 (2 C), 141.73 (2 C), 141.64 (2 C), 139.85 (2 C), 139.64 (2 C), 139.58 (2 C), 138.32 (2 C), 137.69, 118.44 (=CH), 116.10, 76.10 (sp^3 fullerenyl carbon), 75.42 (sp^3 fullerenyl carbon), 43.16 (2 C, CH_2N), 25.85 ($=C\mathbf{CH_3}$), 21.70 ($=C\mathbf{CH_3}$), 13.99 (2 C, $\mathbf{CH_3}CH_2$); FTIR (KBr) cm^{-1} 1671 (m), 1636 (m), 1541 (w), (w), 1094 (w), 694 (m), 527 (s); FABMS *m/z* 871 (M^-, 50), 720 (C60, 100).

1,2-[61-(Diethylamido)-62-isopropylidenecarbonyl]-dihydro[60]fullerene (4): ^{1}H NMR (360 MHz, $CS_2/CDCl_3$) at 25 °C δ 7.41 (t, 1 H, $J = 1.21$ Hz, =CH), 4.00−3.20 (b, 4 H, NCH_2), 2.46 (d, 3 H, $J = 1.07$ Hz, $=CCH_3$), 2.19 (d, 3 H, $J = 1.04$ Hz, $=CCH_3$), 1.38 (t, 6 H, $J = 7.03$ Hz); at −40 °C 7.41 (s, 1 H, =CH), 5.13 (dt, 1 H, $J = 14.6, 6.80$ Hz), 4.01 (dt, 1 H, $J = 12.41, 6.64$ Hz), 3.59 (dt, 1 H, $J = 14.7, 7.29$ Hz), 3.22 (dt, 1 H, $J = 12.40, 6.20$ Hz), 2.45 (s, 3 H, $=CCH_3$), 2.20 (s, 3 H, $=CCH_3$), 1.36 (t, 6 H, $J = 6.20$ Hz); ^{13}C NMR (90 MHz, $CS_2/CDCl_3$, 25 °C) δ 193.37 (CO), 169.31 (NCO), 160.72, 151.89, 147.30, 147.19, 146.18 (2 C), 146.10, 145.92 (2 C), 145.89 (br), 145.33, 145.16 (br, 2 C), 144.28 (br), 142.99, 142.43 (2 C), 141.98, 141.91, 141.53 (br), 141.25, 139.79 (br), 139.36 (br), 122.97 (=CH), 81.15 (sp^3 fullerenyl carbon), 75.00 (sp^3 fullerenyl carbon), 43.58 (NCH_2), 42.66 (NCH_2), 28.13 ($=C\mathbf{CH_3}$), 21.58 ($=C\mathbf{CH_3}$), 13.81 ($\mathbf{CH_3}CH_2$), 11.82 ($\mathbf{CH_3}CH_2$); FTIR (KBr) cm^{-1} 2950 (w), 1676 (m), 1636 (s), 1260 (m), 1115 (m), 770 (m), 576 (w), 527 (s); FABMS *m/z* 903 (M^-, 50), 720 (C_{60}, 100); UV−vis λ_{max} (ϵ) (CH_2Cl_2) 702 (250), 436 (2920), 312 (33 300), 256 (90 000).

1,9-(7171,72,72-Tetraethoxycyclobutano)dihydro[70]-fullerene (6). A solution of C_{70} (20 mg, 0.024 mmol) in 20 mL of toluene was degassed by bubbling with argon for 20 min. To this solution was added tetraethoxyethylene (**5**) (40 μL, 0.20 mmol). The mixture was refluxed overnight. Toluene was removed *in vacuo*. The crude product was chromatographed on SiO_2. Elution with hexane−toluene (from 10:1 to 1:5) gave **6** (13 mg, 53%): ^{1}H NMR(500 MHz, $CS_2/CDCl_3$) δ 4.36 (ABX_3, 2 H, $J_{AB} = 9.50$ Hz, $J_{AX} = 7.00$ Hz), 4.25 (ABX_3, 2 H, $J_{AB} = 9.50$ Hz, $J_{AX} = 7.00$ Hz), 4.03 (ABX_3, 2 H, $J_{AB} = 9.50$ Hz, $J_{AX} = 7.00$ Hz), 3.91 (ABX_3, 2 H, $J_{AB} = 7.00$ Hz, $J_{AX} = 7.00$ Hz), 1.57 (t, 6 H, $J = 7.00$ Hz), 1.37 (t, 6 H, $J = 7.00$ Hz); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) δ 156.40 (2 C), 151.98 (2 C), 151.71 (2 C), 151.41 (1 C), 151.28 (2 C), 150.69 (2 C), 150.51 (2 C), 150.15 (2 C), 150.01 (2 C), 149.70 (2 C), 149.64 (2 C), 149.14 (2 C), 148.99 (2 C), 148.94 (2 C), 148.64 (2 C), 147.51 (2 C), 147.36 (2 C), 147.05 (2 C), 146.87 (2 C), 146.81 (1 C), 146.11 (2 C), 145.57 (2 C), 143.41 (2 C), 143.39 (2 C), 143.33 (2 C), 142.54 (2 C), 142.22 (2 C), 141.96 (2 C), 140.71 (2 C), 139.26 (2 C), 134.04 (2 C), 133.57 (2 C), 131.36 (2 C), 131.08 (2 C), 131.03 (2 C), 112.35 (1C, $C(OEt)_2$), 111.30 (1 C, $C(OEt)_2$), 68.27 (1 C, sp^3 fullerene), 66.04 (1 C, sp^3 fullerene), 61.28 (2 C, OCH_2), 60.98 (2 C, OCH_2), 15.72 (2 C, CH_3), 15.49 (2 C, CH_3); FTIR (KBr) cm^{-1} 2975 (w), 1515 (m), 1428 (s), 1241 (s), 1088 (s), 1052 (s), 672 (m), 591 (m), 542 (m), 534 (m), 528 (m). FAB MS *m/z* 1044 (M, 6), 840 (C_{70}, 8); UV-vis λ_{max} (CH_2Cl_2) 664, 532, 460, 396, 308 (sh), 236.

1,2-(6161,62,62-Tetraethoxycyclobutano)dihydro[60]-fullerene (8). A solution of C_{60} (60 mg, 0.083 mmol) in 50 mL of dry benzene was degassed by bubbling with argon for 20 min. To this solution was added tetraethoxyethylene (**5**) (90 μL, 0.42 mmol). The mixture was refluxed overnight. Benzene was removed *in vacuo*. The crude product was chromatographed on SiO_2. Elution with petroleum ether−CS_2 (from 2:1 to 1:3) gave **8** (53 mg, 69%): ^{1}H NMR (360 MHz, CS_2/acetone-d_6) δ 4.33 (dq, ABX_3, 4 H, $J = 9.40, 7.0$ Hz), 4.20 (dq, ABX_3, 4 H, $J = 9.40, 6.99$ Hz), 1.49 (t, 12 H, $J = 7.00$ Hz); ^{13}C NMR (90 MHz, CS_2/acetone-d_6) δ 151.54 (4 C), 147.32 (2 C), 147.20 (4 C), 146.40 (4 C), 146.38 (4 C), 145.91 (2 C), 145.66 (4 C), 145.04 (4 C), 143.62 (2 C), 143.43 (4 C), 143.17 (4 C), 142.79 (4 C), 142.68 (4 C), 142.62 (4 C), 140.83 (4 C), 139.11 (4 C), 110.25 (2 C, $C(OEt)_2$), 76.10 (2 C, sp^3 fullerene), 61.63 (4 C, OCH_2), 16.10 (4 C, CH_3); FTIR (KBr) cm^{-1} 2973 (w), 2892 (w), 1429 (m), 1240 (s), 1177 (s), 1084 (s), 1073 (s), 1042 (s), 600 (m), 554 (w), 542 (w), 527 (s); FAB MS *m/z* 925 (M + H, 16), 879 (M − OCH_2CH_3, 100); UV−vis λ_{max} (CH_2Cl_2) (ϵ) 705 (400), 648 (820), 436 (3900), 312 (45 100), 256 (120 100).

1,2:18,36-Bis(tetraethoxycyclobutano)[60]dihydro-fullerene (9). This compound was obtained in a small amount by two preparative TLC separations of the multiaddition adducts in preparation of **8**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21−4.03 (m, 16 H, OCH_2), 1.48 (t, 6 H, $J = 7.64$ Hz), 1.46 (t, 6 H, $J = 7.66$ Hz), 1.44 (6 H, $J = 7.64$ Hz), 1.38 (t, 6 H, $J = 7.62$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.85 (2 C), 148.98 (2 C), 148.68, 148.32 (2 C), 148.18 (4 C), 147.51 (2 C), 147.35 (2 C), 147.21 (2 C), 146.77, 146.74 (2 C), 146.70 (2 C), 146.21 (2 C), 145.11 (2 C), 144.70 (2 C), 144.48 (2 C), 144.18 (2 C), 144.10 (2 C), 144.04 (2 C), 143.33 (2 C), 142.97 (2 C), 142.90 (2 C), 142.42 (2 C), 141.96 (2 C), 141.84 (2 C), 141.07 (4 C), 137.81 (2 C), 136.77 (2 C), 109.11, 109.08, 107.88 (2 C), 74.66 (2 C), 73.72, 73.68, 60.52, 60.47, 60.37, 60.04, 15.32 (2 C), 15.27, 15.13; FTIR (KBr) cm^{-1} 2974 (s), 1241 (s), 1179 (s), 1084 (s), 554 (w), 542 (w), 527 (s); FABMS *m/z* 1129 (M + H, 30).

1,2-(6161,62,62-Tetrabutoxycyclobutano)dihydro[60]-fullerene (10). Compound **10** was prepared from tetra-butoxyethylene (**7**) in 59% yield in a procedure similar to that for **8**. Physical data for **10**: ^{1}H NMR (360 MHz, $CS_2/CDCl_3$) δ 4.23 (dt, ABX_2, 4 H, $J = 9.28, 6.73$ Hz), 4.13 (dt, ABX_2, 4 H, $J = 9.28, 6.73$ Hz), 1.83 (m, 8 H), 1.60 (sextet, 8 H, $J = 7.30$ Hz), 1.05 (t, 12 H, $J = 7.25$ Hz); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) δ 150.55 (4 C), 146.47 (2 C), 146.25 (4 C), 145.55 (4 C), 145.02 (2 C), 144.80 (8 C), 144.19 (4 C), 142.76 (2 C), 142.59 (4 C), 142.34 (4 C), 141.92 (4 C), 141.83 (4 C), 141.77 (4 C), 139.96 (4 C), 138.17 (4 C), 109.15 (2 C, $C(OBu)_2$), 75.27 (2 C, sp^3 fullerene), 64.70 (4 C, OCH_2), 32.09 (4 C), 19.78 (4 C), 14.21 (4 C); FTIR (KBr) cm^{-1} 2955 (s), 2900 (s), 1239 (s), 1094 (s), 1076 (s), 1028 (s), 600 (w), 529 (s); FAB MS *m/z* 1038 (M + 2 , 25), 1037 (M + 1, 23), 1036 (M^-, 20), 720 (C_{60}, 100); UV−vis λ_{max} (CH_2Cl_2) (ϵ) 702 (400), 436 (4200), 312 (43 000), 256 (112 000).

61-Ethoxy-61-(ethoxycarbonyl)1,2-dihydro-1,2-methano-[60]fullerene (11) and 1,2-(61,61,62-Triethoxycyclobutano)-dihydro[60]fullerene (12). To a stirred solution of **8** (20 mg, 0.02 mmol) in dry degassed CH_2Cl_2 was added trimethylsilyl iodide (4 μL, 0.028 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h and at room temperature for 4 h. A few drops of a dilute solution of $NaHCO_3$ and $Na_2S_2O_5$ were added to quench the reaction. The aqueous solution was extracted with 15 mL of toluene. The extracts were dried with Na_2SO_4, condensed in *vacuo*, and chromatographed on SiO_2. Elution with petroleum ether−toluene (2:3) gave C_{60} (3 mg, 22%), **11** (4 mg, 25%), and **12** (2 mg, 13%, contained ca. 15% of **11**). Physical data for **11**: ^{1}H NMR (360 MHz, $CS_2/CDCl_3$) δ 4.59 (q, 2 H, $J = 7.15$ Hz), 4.34 (q, 2 H, $J = 7.00$ Hz), 1.59 (t, 3 H, $J = 7.09$ Hz), 1.50 (t, 3 H, $J = 6.99$ Hz); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) δ 165.48 (1 C, CO), 145.70 (1 C), 145.46 (2 C), 145.44 (2 C), 145.38 (2 C), 145.36 (2 C), 145.20 (2 C), 145.04 (2 C), 145.02 (2 C), 144.90 (2 C), 144.88 (2 C), 144.86 (2 C), 144.68 (2 C), 144.17 (2 C), 144.09 (2 C), 143.47 (2 C), 143.35 (1 C), 143.34 (2 C), 143.31 (2 C), 143.25 (1 C), 143.21 (2 C), 142.69 (2 C), 142.51 (2 C), 142.46 (2 C), 142.04 (2 C), 141.44 (2 C), 141.29 (1 C), 140.10 (2 C), 138.73 (2 C), 128.53 (2 C), 127.50 (2 C), 77.19 (sp^3 fullerene), 74.61 (sp^3 fullerene), 67.56 (OCH_2), 62.76 (OCH_2), 15.77, 14.78; FTIR (KBr) cm^{-1} 1740 (s), 1260 (m), 1184 (m), 1036 (m), 575 (w), 556 (w), 527 (s); FAB MS *m/z* 852 (M + 2H, 30), 720 (C_{60}, 100); UV−vis λ_{max} (CH_2Cl_2) 432, 328, 260. Physical data for **12**: ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ 5.58 (s, 1 H), 4.36 (m, 1 H), 4.24 (m, 1 H), 4.16 (m, 4 H), 1.50 (m, 9 H); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) δ 154.02, 150.93, 150.78, 149.95, 147.90, 147.13, 147.05, 147.01, 146.34, 146.32, 146.22, 146.21, 146.18, 146.10 (2 C), 146.09, 146.05, 145.73, 145.70, 145.67, 145.55, 145.46 (3 C), 145.42, 145.39, 145.27 (2 C), 144.83, 144.75, 144.72, 144.62, 143.31 (2 C), 143.25, 143.22, 143.17, 143.01, 142.95, 142.89, 142.78, 142.62, 142.54, 142.53, 142.51, 142.37 (2 C), 142.34 (2 C), 142.18, 141.06, 140.84, 140.66, 140.50, 140.20, 138.68, 138.58, 137.45, 107.75 ($OC(OEt)_2$), 89.51 (OCH), 77.22 (sp^3 fullerene), 69.37 (sp^3 fullerene), 67.96 (OCH_2), 61.22 (OCH_2), 59.96 (OCH_2), 16.14, 16.06, 15.79; FTIR (KBr) cm^{-1} 1514 (m), 1184 (m), 1120 (m), 667 (w), 575 (w), 527 (s); FAB MS *m/z* 881 (M + H, 45), 765 (M + H − 116, 100), 720 (C_{60}, 80).

Photocycloreversions of 6, 8, and 10 were achieved by irradiation of a solution of the corresponding diketal (1.0−1.2 mM) with a 300 W Xenon (Cermax) lamp ($K_2Cr_2O_7$ filter, >500 nm) at room temperature for 5.0 h under a slow stream of argon. HPLC and ^{13}C NMR spectra indicated clean formation of C_{70} from **6** and C_{60} from **8** and **10**, respectively. ^1H NMR indicated exclusive formation of the diethyl and dibutyl carbonates **13** and **14**, respectively.

Rubrene Inhibition of Photocycloreversion of 6. A solution of **6** (1.2 mM) and rubrene (3.6 mM) in toluene was deoxygenated by argon bubbling for 10 min. This solution was irradiated with a 300 W Xenon lamp (either with $K_2Cr_2O_7$ filter or without) at room temperature, under a slow stream of argon for 3.0 h. HPLC indicated less than 1% C_{70} was formed, while a similar irradiated solution without rubrene gave 61% of C_{70} at this point.

Oxygen Inhibition of Photocycloreversion of 6. A toluene solution of **6** (1.0 mM) was bubbled with oxygen for 10 min before irradiation, and a slow stream of oxygen was continued during irradiation. After 2.5 h, HPLC indicated no formation of C_{70}.

Inhibitions of photocycloreversion of compound **8** and **10** were done in a similar way, and HPLC indicated rubrene (3 −5 mol equiv) and oxygen completely stopped the reversion reactions.

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Supporting Information Available: ^1H NMR and ^{13}C NMR spectra of compounds **2, 6,** and **8−10** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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