[2 + 2] Photocycloaddition of Cyclic Enones to C_{60}

David I. Schuster,* Jingrong Cao, Nikolas Kaprinidis, Yunhui Wu, Anton W. Jensen, Qingyi Lu, Hui Wang, and Stephen R. Wilson*

Contribution from the Department of Chemistry, New York University, Washington Square, New York, New York 10003

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Abstract: The photocycloaddition of cyclic enones to C_{60} is a general reaction. The addition was initially explored using a crown ether-tagged C_{60} molecule which allows convenient monitoring of the reaction course by electrospray ionization mass spectroscopy (ESI-MS) after complexation with metal ions, usually K^+. A Hanovia 450-W lamp was used to excite a benzene solution of fullerene and enone, with the latter in large excess. A series of experiments in which the concentration of reagents and reaction time were systematically varied established that adduct formation occurs only upon light absorption by the enones. Thus, excitation at 532 nm or in the UV range using low enone: C_{60} ratios did not lead to adduct formation. ESI-MS analysis showed that monoaddition was favored at short irradiation times, and that up to seven enone units could be added to a single fullerene molecule upon longer exposure to light. Competitive experiments using 12 different enones indicated that the best product yields were obtained, in decreasing order, with 3-methyl-2-cyclohexen-1-one, isophorone, 2-cyclohepten-1-one, and 2-cyclohexen-1-one. Products isolated from reactions carried out on a larger scale were subjected to spectroscopic analysis (^1H NMR, ^{13}C NMR, IR, UV). Two monoadducts were formed from 2-cyclohexen-1-one, its 3-methyl analog, and 2-cyclohepten-1-one, which could be separated by HPLC on a Buckyclutcher column. In the first two cases, these products were unambiguously identified as *cis*- and *trans*-fused [2 + 2] cycloadducts. In the case of 2-cyclohexen-1-one, the *cis*-fused C_{60} adduct is the major product, while in the case of 3-methyl-2-cyclohexen-1-one the *trans* isomer predominates. ^{13}C NMR spectra indicated addition occurred across [6,6] pyracyclene bonds of the fullerene to give ring-closed structures with two sp^3 fullerene carbons. These racemic [2 + 2] adducts could be enantiomerically resolved on a chiral HPLC column. Much larger optical rotations were found for the *trans* than for the *cis* isomers. Additional long-wavelength bands were also found in the UV absorption and CD spectra of the *trans* isomers. These chiroptical effects are attributed to an additional chromophore in the *trans* isomers, which according to MM2 calculations is a C_2 symmetric chiral skewed fullerene moiety. ^{3}He-NMR analysis of the product mixture from photoaddition of 3-methyl-2-cyclohexen-1-one and 2-cyclohepten-1-one to C_{60} containing a ^{3}He atom ($^3He@C_{60}$) led to the appearance of two new peaks at ca. −9.3 ppm relative to gaseous ^{3}He, consistent with formation of two monoadduct diastereomers with [6,6]-closed structures. The mechanism of the reaction presumably involves addition of enone triplet excited states to ground state fullerenes, via triplet 1,4-biradical intermediates, as in typical enone−alkene photocycloadditions. The fact that enone triplets are not quenched by triplet energy transfer to the fullerenes, which would be highly favorable energetically, is rationalized by poor coupling of the chromophores and Marcus theory.

Introduction

The chemistry of C_{60} (buckminsterfullerene) encompasses a broad range of reactions.[1] The reactions of ground state C_{60} include thermal and photochemical cycloadditions, nucleophilic additions, radical additions, and dipolar cycloadditions.[2−8] C_{60} behaves generally like an electron deficient alkene rather than an aromatic compound.[1]

One of the most familiar and useful types of photochemical addition reactions involves the photoaddition of cyclic enones to alkenes.[9] The mechanism of this reaction involves stepwise addition of enone triplet excited states to ground state alkenes, via intermediate triplet 1,4-biradicals.[10] The first examples of [2 + 2] photocycloaddition of cyclic enones to C_{60} were reported by this lab using 3-methyl-2-cyclohexen-1-one and 2-cyclohexen-1-one.[11,12] Using the new technique of electrospray ionization MS (ESI-MS) for study of organic reactions in

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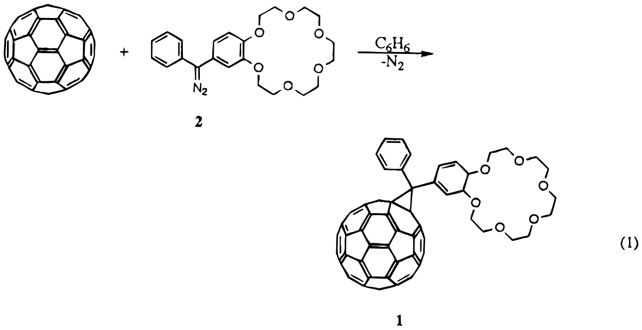
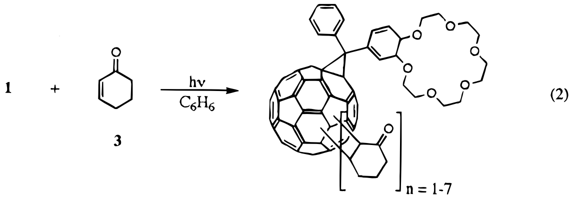
solution,[13] addition reactions to C_{60} can be conveniently followed using crown ether-tagged C_{60} methanofullerenes such as **1** complexed with metal ions, most often K^+.[14] The tagged fullerene **1** is easily prepared by cycloaddition of the crown ether diphenyl diazo compound **2** to C_{60} to give a pyrazoline, followed by loss of N_2 (see eq 1).[14,15] Photoaddition of enones to **1** gives adducts containing a crown ether moiety (see eq 2), allowing mass determination of products without fragmentation using ESI-MS techniques.[14] Alternatively, untagged C_{60} can be reacted with the reagent of interest, followed by tagging of the fullerene moiety in the adduct with **2**, and then analysis of starting material and products by ESI-MS after complexation with K^+.



2

1

(1)



(2)

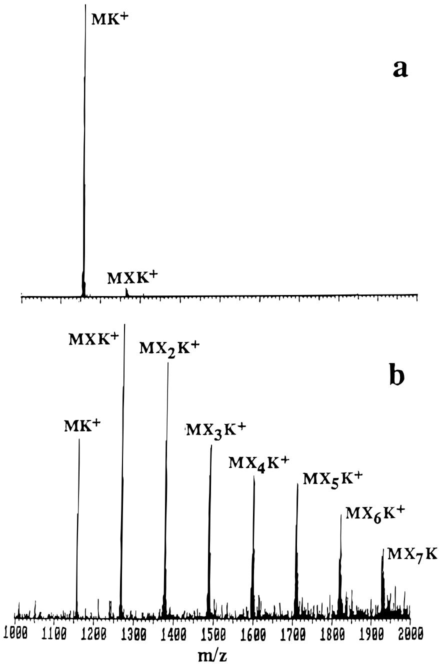


Figure 1. ESI-mass spectra of the reaction mixture from photoaddition of 3-methyl-2-cyclohexen-1-one (**4**) to crown ether-tagged C_{60} (**1**) in benzene after dilution of an aliquot with an equal volume of potassium acetate in methanol. Spectra a and b were recorded after irradiation with a Hanovia 450-W lamp through Pyrex for 2 and 12 min, respectively. M = compound **1**, and X = enone **4**. Thus, addition of one unit of **4** affords a peak at *m/z* 1269 corresponding to MXK^+.

In the present investigation, the [2 + 2] photocycloaddition of a variety of cyclic enones to C_{60} was studied using this ESI-MS methodology as well as HPLC on "Buckyclutcher" columns[16] as analytical methods. In the present paper, we present the structures of the products, the optimal reaction conditions, and the proposed reaction mechanism. We have also used the technique of ^{3}He NMR spectroscopy, recently developed by Saunders and co-workers,[17] to obtain the first ^{3}He-NMR spectra of stereoisomeric C_{60}−enone [2 + 2] photoadducts from photocycloaddition of enones to C_{60} containing an encapsulated ^{3}He atom ($^3He@C_{60}$).[18] These results provide support for the claim[18] that ^{3}He NMR is a particularly sensitive tool for studying addition reactions to fullerenes.

Results and Discussion

Photochemical Reaction of Methanofullerene 1 with Various Cyclic Enones. ESI-MS analysis of methanofullerene **1**, synthesized as shown in eq 1,[14] after complexation with K^+, gives only the molecular ion at *m/z* 1159 without any fragmentation. To explore the possibility of photoaddition of cyclic enones to fullerenes, reactions were carried out using microscale mixtures of methanofullerene **1** (0.1 mg) and a series of enones. These reactions were monitored by ESI-MS. The reactions were performed as follows. A solution of **1** and the enone (in large excess to allow preferential excitation of the enone *vis-à-vis* **1**; see the Experimental Section) in benzene was purged with Ar for 10 min, and then irradiated through Pyrex using a 450-W Hanovia lamp for 5−30 min. The reaction mixture in each case was diluted with a 1:1 ratio of 1.0×10^{-4} M KOAc in MeOH, and then analyzed by ESI-MS, which showed molecular ions corresponding to unreacted **1**, monoadduct, bisadduct, and multiple adducts. Figure 1 shows the result of typical experi-

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(15) This material (**1**) has been shown to be a mixture of a [6,6]-ring-closed methanofullerene and a [6,5]-ring-opened methanofulleroid: Arias, F.; Xie, Q.; Wu, Y.; Lu, Q.; Wilson, S. R.; Echegoyen, L. *J. Am. Chem. Soc.* **1994**, *116*, 6388. This finding in no way affects the validity of the results using **1** in [2 + 2] photoaddition reactions with cyclic enones and in other addition reactions, where determination of the mass of the adducts by ESI-MS is the experimental objective.

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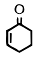
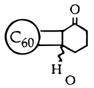
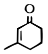
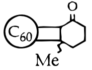
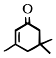
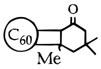
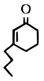
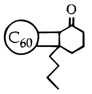
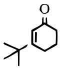
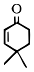
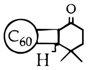
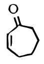
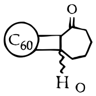
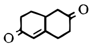
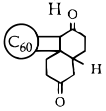
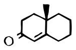
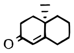
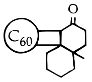
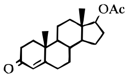
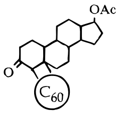
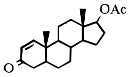
Table 1. [2 + 2] Photocycloaddition of Enones to **1** and C_{60}[b]

	Enone	Monoadduct to **1**, m/z		Product	% Yield[a]
3		1255	**15**		26.2
4		1269	**16**		55.7
5		1297			53.2
6		1321			3.3
7		N.R.			
8					10.7
9		1269	**17**		38.5
10		1323			NY
11		1323			
12		1323	**18**		1.2
13		1489			12.1
14		NR			

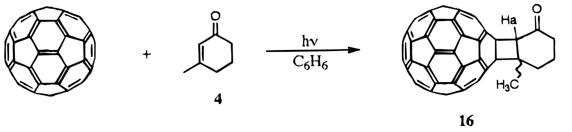
[a] Yield of photoadduct in competitive photoaddition to C_{60}. See text for details. [b] NR = no reaction under these conditions. NY = yield not reported in competitive irradiation.

ments using 3-methyl-2-cyclohexen-1-one (**4**). When limited amounts of the enone were used, ESI-MS analysis at very short reaction times showed preferential formation of monoadducts (Figure 1a). Higher adducts are clearly present when the reaction is run for a longer time using a larger excess of the enone (Figure 1b). Using this method, one can readily determine which enones undergo photoaddition to methanofullerene **1**, as well as the relative efficiency of the reaction. Table 1 gives a list of the cyclic enones which were investigated, and the *m*/*z* values of the products of monoaddition to **1** as determined by ESI-MS.

Photochemical Reaction of C_{60} with Various Cyclic Enones. Once the conditions for photoaddition of these enones to **1** were determined, the same reaction conditions were utilized for photoadditions to untagged C_{60}. Adduct formation could be followed by HPLC using a special "Buckyclutcher" column.[16] In all cases, the identity of 1:1 enone−C_{60} addition products was established by ESI-MS analysis after tagging of the fullerene moiety in the photoadducts with the crown ether derivative **2**.[14] The percent yields of monoadducts given in Table 1 were obtained from simultaneous irradiation of a series of enones and C_{60} in benzene for 2 h in a merry-go-round apparatus, followed by HPLC analysis with UV detection at 340 nm. These values are directly proportional to the relative quantum efficiencies for adduct formation, assuming the amount of light absorbed in each tube was the same, which is not strictly true because of small variations in extinction coefficients. Nonetheless, the trends in the data are meaningful. Adduct formation was most efficient using **4** and isophorone (**5**), followed by 2-cyclohepten-1-one (**9**) and 2-cyclohexen-1-one (**3**). The reaction efficiency falls off somewhat with 4,4-disubstituted and bulky 3-substituted cyclohexenones (testosterone acetate (**13**), 4,4-dimethyl-2-cyclohexen-1-one (**8**), the bicyclic octalones **11** and **12**, and 3-*tert*-butyl-2-cyclohexen-1-one (**7**)), suggesting that steric crowding may inhibit photoaddition.

The conditions for formation of photoadducts were optimized using enones **3** and **4**. A series of benzene solutions containing C_{60} and these enones in Pyrex tubes was purged with Ar, placed in a turntable (merry-go-round) surrounding a 450-W water-cooled medium-pressure Hanovia lamp, and then simultaneously irradiated for 2 h in the case of **3** and 1 h for **4**. The reaction mixtures were then analyzed by HPLC. The results in Table 2 clearly show that the efficiency of formation of enone photoadducts decreases as the C_{60} concentration is raised and increases as the enone concentration is raised. It was previously demonstrated that C_{60} photoexcited states generated by excitation at 532 nm do not undergo addition to enone ground states.[11] The present results are consistent with a competition between the enone and the fullerene for the ultraviolet excitation; i.e., adduct formation occurs only on absorption of light by the enones. Since C_{60} absorbs to some extent over almost the entire UV−vis range, the concentration of C_{60} must be kept low to allow significant absorption directly by the enones above 300 nm.

Characterization of C_{60}−Enone Photoadducts. In order to determine structures of the monomeric C_{60}−enone photoadducts, larger scale addition reactions were carried out on several of the enones listed in Table 1, typically using 100 mg of C_{60} and 64 equiv of the enone in 1 L of Ar-purged benzene. After irradiation for 12−20 h, reaction mixtures were concentrated and then subjected to flash column chromatography to separate unreacted C_{60} from the C_{60} monoadduct. In each case, a portion of the isolated product was tagged with crown ether **2** and analyzed by ESI-MS to demonstrate it was indeed a monoaddition product and not a bis- or trisadduct, etc. In the case of adduct **16**, derived from enone **4** (see eq 3), ESI-MS gave a single peak at *m*/*z* 1269, corresponding to **1** + X + K^+ where X represents the mass of the enone. ^{1}H-NMR, IR and Buckyclutcher HPLC analysis all showed that the isolated monoadduct **16** is actually a mixture of two compounds in a ratio of 57:43. ^{1}H-NMR spectra showed resonances at 4.91, 4.10, 2.00, and 1.79 ppm, corresponding to two sets of bridgehead protons and methyl groups, respectively. There are pronounced differences in deshielding of protons situated above five- as opposed to six-membered rings in fullerene adducts, due to the effects of paramagnetic ring currents.[6b,19] Accordingly, the outer (major) and inner (minor) proton resonances in **16** are due to isomeric adducts, which are proposed to be *cis*- and *trans*-fused stereoisomers arising from [2 + 2] cycloaddition across the [6,6] ring junction in C_{60}. Cycloadducts of photoexcited cyclohexenones and alkenes are generally formed with both *cis* and *trans* fusions of the four- and six-membered rings, the latter often being the major product.[9,10,20,21]



(3)

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Table 2. Percent Yield of Photoadducts as a Function of Reactant Concentrations

concn of C_{60} in benzene, mg/mL	vol of enone, mL (mol equiv)	yield of monoadduct, %	concn of C_{60} in benzene, mg/mL	vol of enone, mL (mol equiv)	yield of monoadduct, %
		Cyclohex-2-en-1-one			
0.1	1 (74)	34.6	0.5	50 (740)	16.0
0.1	10 (740)	36.1	1.0	5 (37)	0.6
0.1	100 (7400)	49.9	1.0	10 (74)	2.0
0.5	5 (74)	3.0	1.0	100 (740)	11.6
		3-Methylcyclohex-2-en-1-one			
0.1	1 (64)	7.0	0.5	50 (640)	7.3
0.1	5 (320)	18.2	0.5	100 (1280)	9.6
0.1	10 (640)	21.2	1.0	5 (32)	0.2
0.1	50 (3200)	24.8	1.0	10 (64)	0.7
0.1	100 (6400)	15.7	1.0	50 (32)	3.1
0.5	5 (64)	2.0	1.0	100 (640)	4.1

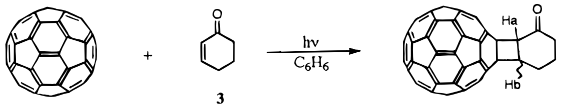
[a] See text for details on experimental procedures.

Electrocyclic additions to C_{60}, such as Diels–Alder additions of conjugated dienes and 1,3-dipolar cycloadditions of reagents such as diazomethane, generally occur across [6,6] pyracyclene ring junctions which have substantial double bond character.[1c,d,3,6a,b] Thus, it is likely that the [2 + 2] cycloadducts formed from enones also involve addition across [6,6] fullerene bonds. Support for this structure assignment comes from the ^{13}C-NMR spectra of the separated isomeric adducts **16** (natural abundance ^{13}C) derived from 3-methyl-2-cyclohexen-1-one (**4**) (the spectra are included in the supporting information). Each spectrum shows 6 distinct resonances for aliphatic carbons, resonances for 2 sp^3 carbons on the fullerene core (at 67 and 75 ppm for the *cis* isomer, and 71 and 79 ppm for the *trans* isomer), peaks for the carbonyl carbon at 208 and 201 ppm, respectively, and *ca*. 50 resolved or partially resolved peaks for sp^2 fullerene carbons between 135 and 157 ppm. These data are only consistent with closed [6,6]-bridged structures for the two adducts, and eliminate annulene-like open adduct structures from further consideration.[1a,22] Further support for these structure assignments is provided by the ^{3}He-NMR data for corresponding adducts to ^{3}He@C_{60} described below.

The IR spectrum of the mixture of isomers of **16** showed two strikingly different carbonyl stretching frequencies at 1707 (minor) and 1730 cm^{-1} (major). It is well established that carbonyl stretching frequencies are invariably larger for the more strained *trans*-fused cycloadducts of cyclohexenone and alkenes (1715–1725 cm^{-1}) than for the corresponding *cis*-fused adducts (1696–1710 cm^{-1}).[9,20,21] Thus, the major adduct in the case of **16** appears to be the *trans*-fused adduct, allowing assignment of the various ^{1}H-NMR resonances above to the individual racemic adducts. The *cis* and *trans* isomers of **16** could be separated to near homogeneity on a Buckyclutcher HPLC column.[16]

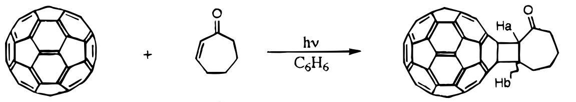
The UV absorption spectra of the diastereomers of **16** as well as of all the other [2 + 2] photoadducts isolated in this study showed sharp UV absorption at 430–435 nm, which has been proposed to be characteristic of closed [6,6]-bridged fullerenes.[23]

Photoadduct **15** derived from 2-cyclohexen-1-one (**3**) (eq 4) also consisted of two isomers which could be separated by HPLC. For the major isomer, the ^{1}H-NMR spectrum showed a doublet for the bridgehead proton adjacent to the carbonyl group at δ 4.57 ppm (J = 10.7 Hz) coupled to a second bridgehead proton appearing as a doublet of triplets centered at δ 4.45 ppm (J_{ab} = 10.7 Hz, J_{bc} = J_{bd} = 6.8 Hz). In the minor isomer, the corresponding protons appear as a doublet (J_{ab} = 14.9 Hz) centered at δ 4.76 ppm coupled to an upfield overlapping doublet of doublets at δ 4.37 ppm (J_{ab} = 14.8 Hz, J_{bc} = 11.7 Hz, J_{bd} = 4 Hz). By analogy with the literature on cyclohexenone photoadducts,[9,20,21] these NMR data indicate that for **15** the major isomer is the *cis*-fused cycloadduct. This structure assignment is supported by the IR spectrum which shows a major carbonyl stretching band at 1707 cm^{-1} and a weaker band at 1726 cm^{-1}. FAB-MS analysis of the monoadducts **15** confirmed the formula. After being tagged with crown ether **2**, **15** showed a single ESI-MS peak at m/z 1255, corresponding to **1** + X + K$^+$ where X now corresponds to cyclohexenone.



3 **15** (4)

Upon photoaddition of 2-cyclohepten-1-one (**9**) to C_{60}, two isomeric monoadducts were again observed on HPLC in a ratio of ~ 3:1 (see eq 5). After tagging of the product with the crown ether reagent **2** and complexation with K$^+$, ESI-MS showed a single peak at m/z 1269 for **1** + X + K$^+$, where X now corresponds to cycloheptenone. For the major isomer, ^{1}H NMR showed a doublet (H$_a$) centered at δ 4.99 ppm (J = 11.76 Hz) and a doublet of triplets (H$_b$) centered at δ 4.2 ppm (J = 3.09 Hz). For the minor isomer, a doublet (H$_a$) centered at δ 4.98 ppm (J = 10.92 Hz) and a doublet of triplets (H$_b$) centered at δ 4.167 ppm (J = 4.17 Hz) were observed. On the basis of the ^{1}H NMR spectra, the adducts **17** appear to be *cis*- and *trans*-fused [2 + 2] cycloadducts, analogous to **16**, but firm stereochemical assignments are not possible based on these data. Although the amounts of material precluded obtaining ^{13}C-NMR spectra, the identity of adducts **17** as [6,6]-closed cycloadducts



9 **17** (5)

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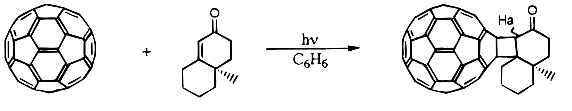
is supported by ^{3}He-NMR data on corresponding adducts to ^{3}He@C_{60} (see below).

The formation of photoadducts from 2-cyclohepten-1-one (**9**) is worthy of comment. Corey[20] reported 30 years ago that **9** does not undergo photocycloaddition to electron-rich alkenes and only undergoes photodimerization,[24] which was confirmed in our lab.[25] However, **9** indeed forms [2 + 2] cycloadducts when irradiated in the presence of electron-deficient alkenes, such as α-chloroacrylonitrile, in competition with photodimerization.[25] Since ground state *trans*-2-cyclohepten-1-one is readily formed from triplet excited states of **9**,[24] it is not possible to differentiate at this time between two mechanisms for adduct formation: (a) direct addition to C_{60} of very short-lived cycloheptenone triplet excited states[26] or (b) addition of chemically reactive relatively long-lived twisted *trans*-2-cyclohepten-1-one ground states.[24]

Photoadduct **18** (eq 6) derived from (*R*)-4,4a,5,6,7,8-hexahydro-4a-methyl-2(3*H*)-naphthalenone ((*R*)-octalone, **12**) on HPLC analysis gave three peaks in a ratio of 8:11:5 (in order of elution). The ^{1}H-NMR spectrum of **18** contained three singlets at δ 5.64, 4.98, and 4.32 ppm, respectively, which corresponds to bridgehead methyl groups for the three diastereomers. After **18** was tagged using **1**, ESI-MS analysis gave a single peak at *m/z* 1323, which corresponds to **1** + X + K$^+$, where X is the mass of the octalone, showing that the three products are indeed stereoisomers. By analogy to the stereochemistry of [2 + 2] photoaddition of conjugated steroid enones to alkenes,[21a] it is likely that these three isomers are the *cis-syn*, *cis-anti*, and *trans-anti* isomers of **18**, where the first designation refers to the 4−6 ring fusion and the second to the ring junction of the six-membered rings in the decalone moiety.[21a] A similar reaction with the enantiomeric (*S*)-octalone (**11**) also gave three monoaddition products according to HPLC analysis. By analogy with the stereochemistry of the major [2 + 2] cycloadduct formed from testosterone acetate (**13**) with cyclopentene, as determined by X-ray crystallography,[21a] it is proposed that the major [2 + 2] cycloadduct **18** has *trans-anti* stereochemistry.



(6)

12 **18**

Resolution and Properties of Enantiomeric Enone-C_{60} Photoadducts. Both *cis*- and *trans*-fused [2 + 2] photoadducts of enones and C_{60} are chiral. Thus, as previously reported,[12] upon injection of racemic *cis*- or *trans*-**16** derived from 3-methyl-2-cyclohexen-1-one on a chiral stationary phase ((*S,S*)-Whelk-O), each compound is well resolved by HPLC into its respective enantiomers, the separation factor being larger for the *cis* (1.90) than for the *trans* (1.45) diastereomer (see Figure 2). Indeed, as shown in Figure 3, the mixture of racemic *cis*- and *trans*-**16** is totally resolved into four peaks on this chiral column. As also seen in Figure 3, the polarimetric response is much greater for the enantiomers of the *trans*- than for the *cis*-fused adducts. A significant difference is also seen in the circular dichroism spectra of the *trans*- and *cis*-fused enantiomers of **16**, shown in Figure 4. While both sets of enantiomers show maxima and minima at 337 nm, the *trans*-fused isomers show intense long-wavelength bands centered at 368 nm, suggesting the presence of an additional chromophore. We propose that the long-wavelength CD bands as well as the enhanced polarimetric response are due to an induced twist in the fullerene portion of these strained *trans*-fused adducts. Molecular mechanics (MM2)[27] calculations on the *trans*-fused [2 + 2] cycloadducts indicate that the fullerene π-system in these adducts is twisted into C_2 symmetry, as shown in Figure 5. This fundamental dissymmetry is reflected, we believe, in the special chiroptical properties of these adducts. If these novel

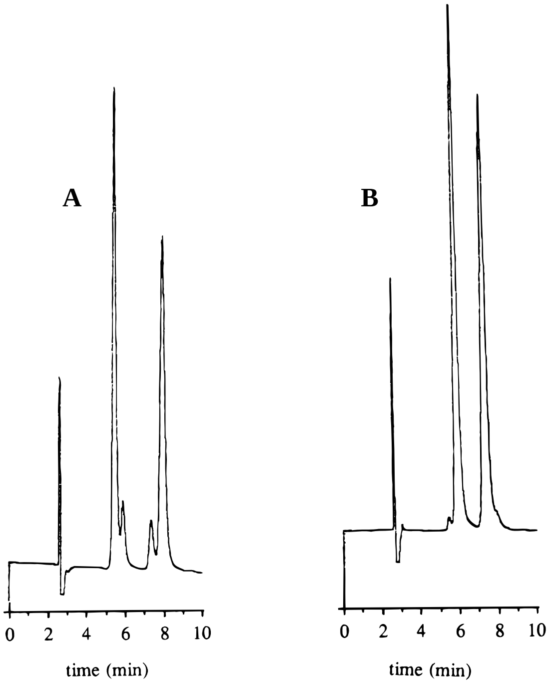


Figure 2. HPLC separation of enantiomers of chromatographically separated *cis* and *trans* photoadducts **16** using a (*S,S*)-Whelk-O column (Regis Chemical Co., Morton Grove, IL). Mobile phase = toluene; flow rate = 1 mL/min; UV detection at 300 nm.

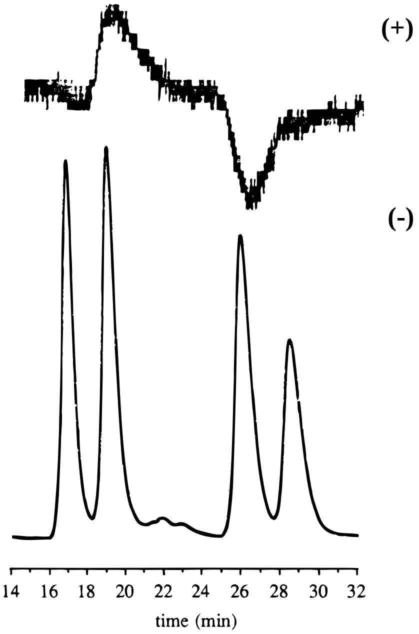


Figure 3. HPLC separation of enantiomers of unseparated mixture of *cis*- and *trans*-**16** with simultaneous UV (300 nm) and polarimetric detection (see ref 12 for details). (*S,S*)-Whelk-O column; mobile phase = 2:1 toluene/hexane; flow rate = 1 mL/min.

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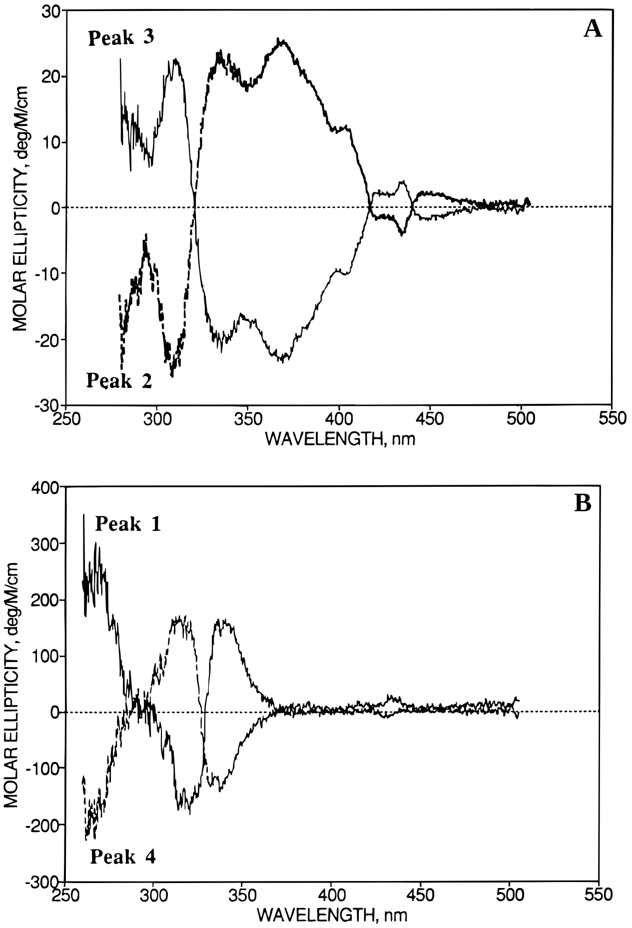

Figure 4. Circular dichroism spectra of chromatographically resolved enantiomers of photoadduct **16**. Peaks numbers correspond to Figure 3. (A) Enantiomers of *trans*-**16**; concentration 1×10^{-5} M in cyclohexane. (B) Enantiomers of *cis*-**16**; concentration 1×10^{-5} M in benzene. The CD spectra were measured in Professor N. Geacintov's lab at NYU using a 1-cm optical path length on a home-built linear CD apparatus.

structural features are confirmed by X-ray structures of these adducts, they will represent the first examples of a new chiral form of the C_{60} sphere.

HPLC separation of the racemic mixture of *cis*- and *trans*-**15** on the (*S*,*S*)-Whelk-O chiral column also gave four peaks, corresponding to the two sets of enantiomers.[12]

The CD spectra of the major monoadducts **18** from addition of the enantiomeric enones **11** and **12**, which were separated by HPLC on a Buckyclutcher column, are shown in Figure 6. The deviation of these spectra from exact mirror image symmetry is attributed to experimental errors associated with the extremely small amounts of pure compounds which were isolated. The proposed structure assignments for the major adducts of structure **18** are consistent with the sign of the long-wavelength Cotton effect near 430 nm in these CD curves using a newly-proposed octant rule for fullerene adducts.[28]

Photoaddition of Enones to $^3He@C_{60}$. In 1993, Saunders and co-workers developed a method to introduce nobel gas atoms (He, Ne, Ar, Kr, and Xe) inside the C_{60} sphere.[17] Later, they prepared $^3He@C_{60}$ and $^3He@C_{70}$ for NMR studies.[18a] Since ^3He has a spin of 1/2 and is an excellent NMR nucleus with a sensitivity ~1/2 that of ^1H, it is an excellent probe for the magnetic shielding environment inside the fullerene cavity. Using ^3He NMR, it was observed that $^3He@C_{60}$ has a very large upfield shift relative to free ^3He gas. It has been shown that ^3He-NMR chemical shifts in C_{60} derivatives are strongly affected by chemical functionalization on the fullerene surface.[18] Thus, ^3He-NMR spectrometry is a sensitive tool for studying chemical reactions with fullerenes. Indeed, each of the regioisomeric bisadducts formed in additions of bromomalonic ester (in the presence of base) and of azomethine ylides to $^3He@C_{60}$ has a distinctive ^3He-NMR chemical shift.[29]

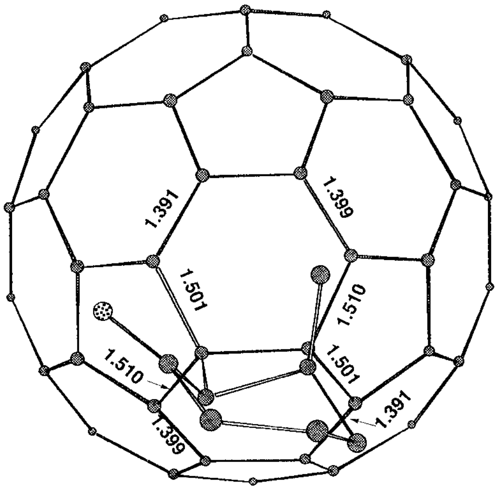

Figure 5. Structure of (2*R*,3*R*)-*trans*-**16** optimized using MM2 methodology. Selected bond distances which illustrate C_2 symmetry of the fullerene around the atoms of attachment of the enone moiety are shown. Some atoms are omitted for clarity.

Since ^3He NMR chemical shifts are sensitive to subtle structural differences in functionalized fullerenes, we reasoned that photoaddition of enones to $^3He@C_{60}$ should lend further insight into the complexity of these reactions. Photoaddition of enones **4** and **9** to $^3He@C_{60}$ in which ca. 0.1% of the fullerene contains a ^3He nucleus[18] were performed exactly as described above for additions to **1** and to untagged C_{60}. In each case, ^3He NMR spectra in 4:1 1-methylnaphthalene/CD_2Cl_2 showed two product peaks in addition to the peak due to starting material at −6.34 ppm (see parts A and B, respectively, of Figure 7). For adducts **16**, new ^3He peaks are observed at −9.28 and −9.34 ppm relative to gaseous ^3He, shifted upfield by ~3 ppm from the peak due to starting material. The product peak ratio is identical to the *cis*:*trans* ratio of 2:3 previously determined by HPLC and ^1H NMR. On the basis of the structural assignments made earlier, the larger ^3He peak at −9.28 ppm is assigned to the *trans*-fused [2 + 2] cycloadduct and the smaller peak at −9.34 ppm to the *cis*-fused [2 + 2] cycloadduct. In the case of adducts **17** from enone **9**, two peaks appear at −9.21 and −9.29 ppm in a ratio of ~1:2, comparable to the isomer ratio previously determined from HPLC and ^1H NMR analysis of the reaction mixtures, as discussed earlier. The fact that the ^3He chemical shifts of photoadducts **16** and **17** are ~ −9.3 ppm is strong supporting evidence for [6,6]-closed structures for these adducts, since in all examples to date of products of monoaddition to $^3He@C_{60}$ across [6,6] bonds, with the exception of adducts containing a three-membered ring,[18d] the ^3He resonances are found between −9.0 and −9.5 ppm.[18c,e,29] Thus, the ^3He resonances of products of bisaddition across [6,6] bonds, including $C_{60}H_4$, are shifted upfield relative to the monoadducts by up to 3 ppm,[29,30] while the resonances for methano adducts (open bridged annulenes and closed cyclopropanes) are in the

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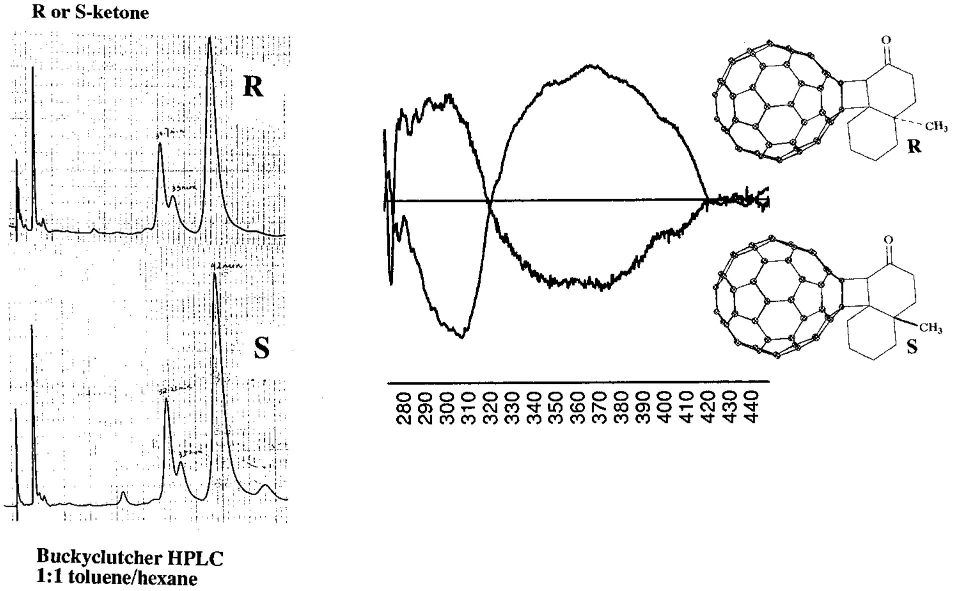

Figure 6. CD spectra of the major monoadduct enantiomers of **18**. The HPLC traces on the left show that both the *R* and *S* enantiomers have identical retention times on an achiral column while showing CD spectra which are nearly mirror images. The deviation of these spectra from exact mirror image symmetry is attributed to impurities, as seen in the HPLC traces.

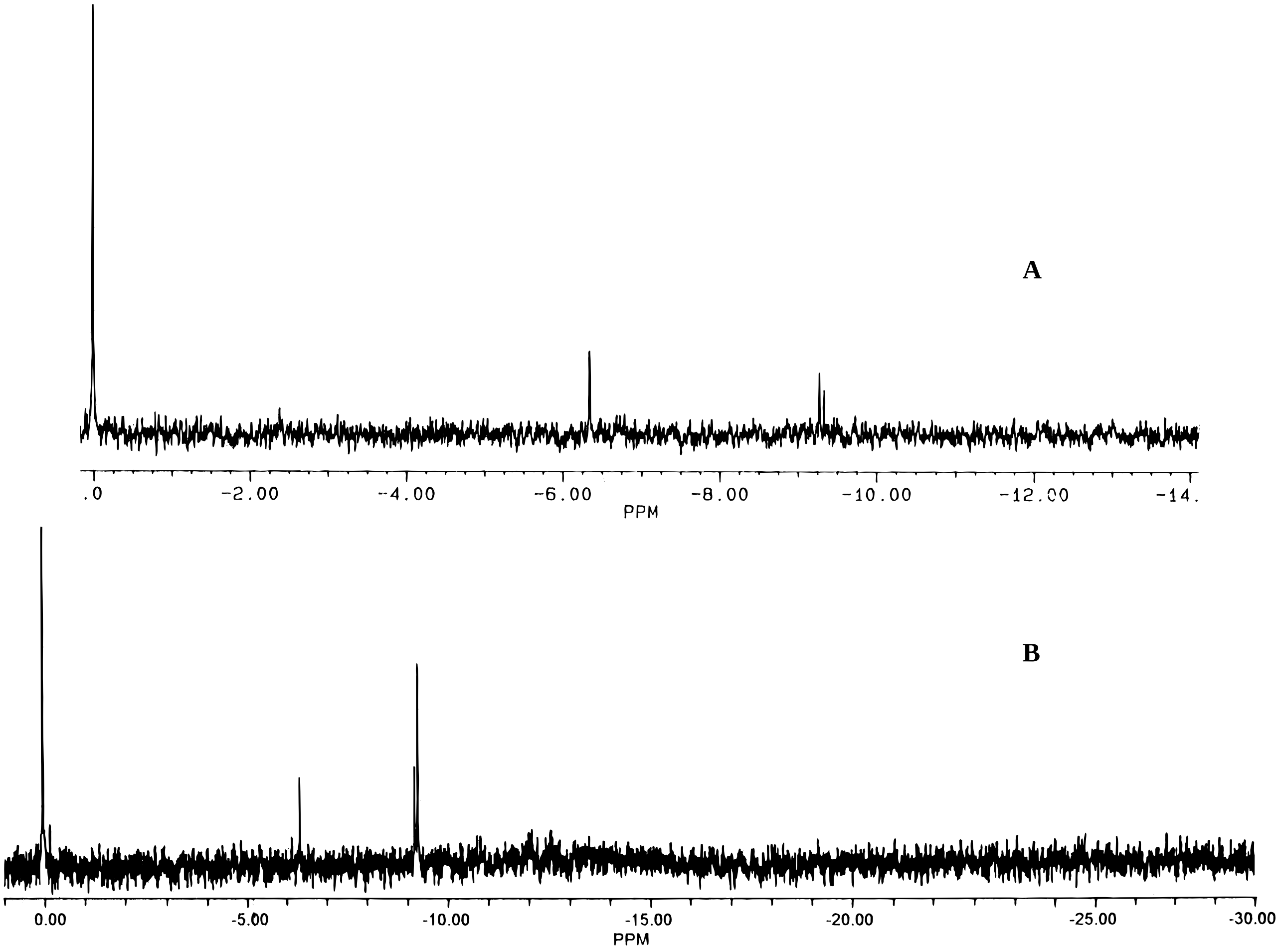

Figure 7. ^{3}He-NMR spectra in 4:1 1-methylnaphthalene/CD_2Cl_2: (A) **16**$-^3$He@C_{60}; (B) **17**$-^3$He@C_{60}. Starting material, ^{3}He@C_{60} at −6.34 ppm, is present in both (A) and (B).

range of −6.6 to −8.1 ppm.[18d] Furthermore, the very small separation, only 0.1 ppm, of the ^{3}He resonances for the *cis* and *trans* diastereomers of **16** and **17** is indicative of similar chemical structures, since the range of ^{3}He chemical shifts for regioisomeric bisadducts of C_{60} is much greater, on the order of 3 ppm.[29,30]

These results raise expectations that ^{3}He-NMR spectroscopy will prove to be an invaluable tool for determination of the number and identity of isomers formed on multiple additions of enones and other unsymmetrical reagents to fullerenes. This technique provides valuable information about the complexity of the reaction mixture before attempts are made to isolate individual products. Relative chemical shifts may also allow structure assignments. Thus, on the basis of the ^{3}He-NMR data, it is proposed that the major monoadduct from [2 + 2] photoaddition of 2-cyclohepten-1-one to C_{60} is probably the *cis*-fused [2 + 2] cycloadduct.

Mechanistic Considerations. The data in Table 2, together with the finding that enone$-C_{60}$ adducts are not formed when reaction mixtures are irradiated at 532 nm, where only the fullerene absorbs light, indicate that adduct formation occurs only when the enone component is photoexcited. To the extent that C_{60} or **1** absorbs the incident light, low-energy fullerene triplet states are formed by efficient intersystem crossing from the fullerene singlets.[31] Thus, it appears that these fullerene triplets do not react with enone ground states, but (in the absence of oxygen) slowly decay back to the ground states. The reactive intermediate derived from the photoexcited enone is presumably the enone triplet state, as in other [2 + 2] photocycloaddition reactions,[10] although this has yet to be demonstrated experimentally. Standard triplet sensitization and quenching experiments are difficult in this system because of the fact that the fullerene absorbs strongly throughout most of the UV region. A minimum in the C_{60} absorption spectrum near 308 nm allows light of this wavelength to be absorbed by other materials, such as enones. We assume that the two new σ bonds are formed sequentially via a triplet 1,4-biradical, as in other [2 + 2] photocycloadditions of enones to alkenes.[10] The formation of both *cis*- and *trans*-fused cycloadducts is consistent with this picture, although it is not in itself experimental proof.[10]

Finally, it is noteworthy that the photocycloaddition reactions occur at all in these systems. Since the lowest energy enone triplets have much higher energy (in the range 60$-$70 kcal/mol)[32] than the lowest triplet of C_{60} (<40 kcal/mol),[31] triplet energy transfer from the enone to the fullerene, which would have quenched the reaction, was a distinct possibility. The fact is that addition of enone triplets to C_{60} takes place competitively with, or perhaps even to the exclusion of, triplet energy transfer. Photophysical studies are planned to obtain rate constants to provide substantiation of this rather qualitative conclusion. It is tempting to hypothesize that there is very poor coupling of the rather localized excitation on the enone moiety with the spherical π-system of the fullerene, which inhibits triplet energy transfer. In addition, considering that the mechanism for triplet energy transfer involves an electron exchange mechanism,[33] this process may be inhibited in these systems precisely because of the excessively large negative value for ΔG. That is, triplet energy transfer in this case may be sharply inhibited because it corresponds to an inverted Marcus region for an electron exchange process.[34] Experiments to test this hypothesis are planned.

Conclusions

The [2 + 2] photocycloaddition of cyclic enones to C_{60} has been studied using ESI-MS, ^{3}He NMR, and other techniques. ESI-MS appears to be the simplest and most convenient way to assess the feasibility and efficiency of thermal and photochemical addition reactions to fullerenes. In model systems, the photoadducts were isolated and structurally characterized spectroscopically as [6,6]-closed fullerene adducts, with both *cis* and *trans* fusions of the four- and six-membered rings. It is proposed that the highly twisted fullerene moiety in the *trans*-fused adducts has local chiral C_2 symmetry. The fact that product yields are improved by decreasing the concentration of C_{60} and increasing the amount of enone is consistent with the proposed reaction mechanism which involves the addition of enone triplet excited states to fullerene ground states. Addition of fullerene triplet excited states to enone ground states is rigorously excluded by the experimental data. The lack of triplet energy transfer from the enone to C_{60} is attributed to poor coupling between the π-systems and to the very large negative value of ΔG for this process.

Experimental Section

General Considerations. ESI-MS analysis was done on a Vestec Model 201 electrospray ionization mass spectrometer. Analytical scale HPLC analysis was done on a Waters 600 E system equipped with a Lambda-Max Model 481 LC spectrophotometer and Model 745 data module, using toluene and hexane mixtures as eluents at 1 mL/min, with UV detection at 340 nm. Preparative HPLC was done with an Autochrom M500 pump equipped with a Waters loader, a Perkin-Elmer LC 90 UV spectrophotometric detector, and a semipreparative Buckyclutcher column with toluene as the eluent at 3 mL/min. The Buckyclutcher column was obtained from Regis Chemical Co.[16] ^{1}H-NMR spectra were recorded on Varian 200-MHz (NYU) and 400-MHz (Columbia) spectrometers. ^{13}C NMR spectra were recorded on General Electric 300-MHz (Rockefeller) and Varian Utility 500-MHz (NYU) spectrometers. The sample of $^3He@C_{60}$ was obtained from Professor Martin Saunders at Yale University, and ^{3}He-NMR spectra were measured on a Bruker AM-500 spectrometer at Yale.[18] All chemicals except C_{60} were purchased from either Aldrich Chemical Co. or Fischer Scientific and were used without further purification. C_{60} was obtained from TERM USA and MER Corp.

Photolysis of Methanofullerene 1 and Enones To Give the Photoadducts Shown in Table 1. To a Pyrex test tube containing a brown solution of methanofullerene **1** (0.1 mg, 8.9 × 10^{-5} mmol) in 1 mL of benzene was added 64$-$70 equiv of the enones. The solution was purged with Ar for 10 min and irradiated with a 450-W Hanovia lamp for 10 min. The resulting reaction mixtures were diluted with 1 equiv of MeOH containing 10^{-4} M KOAc and analyzed by ESI-MS, which showed a peak for **1** at *m/z* 1159 (**1** + K^+) and peaks at *m/z* (**1** + X + K^+) for the photoadducts (X = enone mass).

Microscale Irradiation of C_{60} and Enones To Give Photoadducts. A series of cyclic enones (60$-$70 equiv) was added to C_{60} (0.1 mg, 1.39 × 10^{-4} mmol) in 1 mL of benzene in a Pyrex test tube. The solutions were purged with Ar for 5 min and irradiated wth a 450-W Hanova lamp in a rotating turntable for 2 h. The conversion to the adduct was determined by HPLC analysis using the Buckyclutcher column with 7:3 toluene/hexane as eluent. The C_{60} reaction mixture was added to crown ether **2**, and the mixture was allowed to stand at 5$-$10 °C for 2 h, and then diluted with one portion of KOAc (10^{-4} M) in MeOH and analyzed by ESI-MS. The major products in all cases were 1:1 adducts of C_{60} and the enone (see Table 1).

Preparative Scale Photoaddition of 3-Methyl-2-cyclohexen-1-one to C_{60}. C_{60} (100 mg. 0.139 mmol) was dissolved in 1 L of benzene. To this solution was added 1 mL of 3-methyl-2-cyclohexen-1-one (8.83 mmol, 64 equiv). The reaction mixture was purged with Ar for 30 min and irradiated with a 450-W Hanovia lamp overnight (14 h). The solvent was removed, and the reaction mixture was purified by flash column chromatography (on silica gel) with 8:2 toluene/hexane as the eluting solvent to give first C_{60} and then adduct **16** (30 mg, 30% yield). UV$-$vis (cyclohexane, λ_{max}): 700, 433, 312, 254, and 212 nm. ^{1}H NMR (C_6D_6): δ 4.92 (s, 1H), 4.09 (s, 1H), 2.75 (m), 2.10$-$2.45 (m), 2.01 (s, 3H), 1.82$-$1.93 (m), 1.78 (s, 3H), 1.60$-$1.75 (m), 1.37 (br s). IR (KBr, cm^{-1}): 1187 (w), 1218 (w), 1382 (w), 1424 (m), 1462 (m),

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1707 (s), 1730 (s), 2867 (w), and 2935 (w). FAB-MS (3-nitrobenzyl alcohol as matrix, *m/z*, abundance): 596 (15), 648 (C_{54}, 10), 672 (C_{56}, 15), 696 (C_{58}, 20), 720 (C_{60}, 100), 737 ($C_{60}OH$, 12), 766 (10), 792 (5), 816 (5), 831 (M + H, 22). Anal. Calcd for $C_{67}H_{10}{\cdot}{}^{1}/_{4}CH_3C_6H_5$: C, 96.70; H, 1.42. Found: C, 97.04; H, 1.80. ESI-MS (KOAc in 1:1 toluene/MeOH, *m/z*): 1269.

The *cis* and *trans* isomers of **16** were further purified by preparative HPLC as described in the general experimental procedures. ^{13}C NMR of *trans*-**16** ($CS_2/CDCl_3$, 3:2): δ (ppm) 22.3 ($CH_2\mathit{C}H_2CH_2CO$), 23.9 (CH_3), 34.7 ($\mathit{C}H_2CH_2CH_2CO$), 39.5 ($CH_2CH_2\mathit{C}H_2CO$), 54 ($\mathit{C}CH_3$), 67.4 ($\mathit{C}HCO$), 71.1 (sp^3 fullerene C), 79.1 (sp^3 fullerene C), 135−157 (sp^2 fullerene C's; *ca*. 50 partially and fully resolved peaks), 201 ($\mathit{C}O$). ^{13}C NMR of *cis*-**16** ($CS_2/CDCl_3$, 3:2): δ (ppm) 20.6 ($CH_2\mathit{C}H_2CH_2CO$), 29.0 (CH_3), 35.3 ($\mathit{C}H_2CH_2CH_2CO$), 40.3 ($CH_2CH_2\mathit{C}H_2CO$), 48.3 ($\mathit{C}CH_3$), 60.7 ($\mathit{C}HCO$), 67.0 (sp^3 fullerene C), 74.9 (sp^3 fullerene C), 136−155 (sp^2 fullerene C's; *ca*. 50 partially and fully resolved peaks), 208 ($\mathit{C}O$).

Interestingly, the methyl peak in *trans*-**16** is upfield (23.9 ppm) relative to the methyl of *cis*-**16** (29.0 ppm). This is probably due to increased shielding of the *trans*-**16** methyl group, which is not only closer to the fullerene cage than the methyl in *cis*-**16** but also above a fullerene six-membered ring, while the *cis*-**16** methyl is directly above a [6,5] bond. The *trans*-**16** cyclobutyl carbons are all downfield by 4−7 ppm relative to the *cis*-**16** cyclobutyl carbons while the carbons in the trimethylene unit of the cyclohexyl rings all have essentially the same shifts.

Photoaddition of 2-Cyclohexen-1-one to C_{60}. The procedure was the same as that described above. The solvent for column chromatography was toluene/hexane (8:2). The product was **15**. UV−vis (cyclohexane, λ_{max}): 699, 433, 311, 254, and 211 nm. ^1H NMR (CS_2/C_6D_6, 4:1): δ 4.76 (d, J = 14.9 Hz), 4.57 (d, J = 10.7 Hz), 4.45 (dt, J = 10.7, 6.9 Hz), 4.37 (ddd, J = 14.9, 11.7, 4 Hz), 1.90−2.62 (m). IR (KBr, cm^{-1}): 1187 (m), 1424 (m), 1462 (m), 1511 (m), 1707 (s), 1726 (m), 2852 (w), and 2923 (s). FAB-MS (3-nitrobenzyl alcohol as matrix, *m/z*, abundance): 624 (C_{52}, 5), 648 (C_{54}, 9), 672 (C_{54}, 14), 696 (C_{58}, 18), 720 (C_{60}, 100), 736 ($C_{60}O$, 11), 744 (M − C_6, 10), 768 (M − C_4, 9), 792 (M − C_2, 5), 817 (M + H, 22), 833 (M + OH, 5). ESI-MS (KOAc in 1:1 toluene/MeOH, *m/z*): 1255.

Photoaddition of 2-Cyclohepten-1-one to C_{60}. Monoadduct **17** was prepared in the same way as described above in 30% yield. The solvent for column chromatography was toluene/hexane (8:2). UV−vis (cyclohexane, λ_{max}): 686, 432, 325, 252, and 200 nm. ^1H NMR ($CS_2/CDCl_3$, 2:1): δ 4.98 (dd, 2H, J = 11.76 Hz, 10.92 Hz), 4.2 (dt, 2H, J = 3.09 Hz, 4.17 Hz), 1.6−2.7 (m, 16H). ESI-MS (KOAc in 1:1 toluene/MeOH, *m/z*): 1269.

Photoaddition of (*S*)-(+)-4, 4a, 5, 6, 7, and 8-Hexahydro-4a-methyl-2(3*H*)-naphthalenone to C_{60}. Monoadduct **18** was prepared in the same way as described above in about 10% yield. The product was purified by flash column chromatography (toluene/hexanes, 8:2). UV−vis (cyclohexane, λ_{max}): 424, 395, 319, 247, and 202 nm. ^1H NMR ($CS_2/CDCl_3$): δ 4.32 (s, 1H), 4.98 (s 1H), 5.64 (s, 1H), 1.0−1.1 (3s, 9H), 1−3 (m, 36H). ESI-MS (KOAc in 1:1 toluene/MeOH, *m/z*): 1323.

Photoaddition of 3-Methyl-2-cyclohexen-1-one to $^3He@C_{60}$. $^3He@C_{60}$ (20 mg) was dissolved in 200 mL of benzene, to which was added 200 mL of 3-methyl-2-cyclohexen-1-one (1.76 mmol, 64 equiv). The solution was purged with Ar for 35 min and then irradiated in a Pyrex flask with a Hanovia 450-W lamp for 12 h. Most of the benzene was removed, and the remaining residue was washed several times with ethyl ether to remove the residual 3-methyl-2-cyclohexen-1-one. The liquid was decanted from the residue after centrifugation. The remaining volatile material was removed from the residue by pumping on the sample overnight under high vacuum. This material was then submitted for ^3He-NMR spectrometric analysis at Yale University. The spectrum showed two new peaks at −9.28 and −9.34 ppm in addition to the C_{60} peak at −6.3 ppm (relative to gaseous ^3He at 0.0 ppm) in a ratio of *ca*. 3:2, which was consistent with the product ratio determined by HPLC.

Photoaddition of 2-Cyclohepten-1-one to $^3He@C_{60}$. The experiment was performed under the same conditions as for **4**. ^3He NMR showed two peaks at −9.21 and −9.29 ppm in addition to the C_{60} peak at −6.3 ppm in a ratio of *ca*. 1:2, which was consistent with the ratio determined by HPLC.

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Supporting Information Available: ^1H-NMR spectra of compounds **15**−**17**, (*S*,*S*)-Welch-O HPLC separation of *cis*- and *trans*-**15**, Buckyclutcher HPLC separation of *cis*- and *trans*-**16**, ^{13}C-NMR spectra of *cis*- and *trans*-**16**, FAB-MS spectra of **15** and **16**, UV spectra of *cis*- and *trans*-**16**, and ESI mass spectra for all photoadducts (31 pages). Ordering information is given on any current masthead page.

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