J. Org. Chem. **2002,** *67,* 3284−3289

Stereochemistry of the [4 + 2] Cycloadditions of *trans,trans*- and *cis,trans*-2,4-Hexadiene to C_{60}

Nikos Chronakis, George Froudakis, and Michael Orfanopoulos*

Department of Chemistry, University of Crete, 71409 Iraklion, Crete, Greece

orfanop@chemistry.uoc.gr

Received September 27, 2001

The [4 + 2] cycloaddition of *trans,trans*-2,4-hexadiene with C_{60} proceeds via a concerted mechanism with retention of stereochemistry in the cycloadduct **1a**. However, when *cis,trans*-2,4-hexadiene reacts with C_{60}, isomerization of the cis,trans to the thermodynamically more stable trans,trans isomer occurs. Subsequently, the cis,trans diene isomerized to the trans,trans isomer and cycloadds to C_{60}, to form adduct **1a**. When the reaction is carried out at higher temperatures, the formation of cycloadduct **1b** is also obtained. This result is consistent with a concerted cycloaddition of *cis,trans*-2,4-hexadiene with C_{60}, which is more reactive at elevated temperatures and leads to the formation of the Diels−Alder adduct **1b**.

Introduction

The isolation of macroscopic amounts of C_{60} from soots[1] produced by the vaporization of graphite has precipitated a flood of research activity. Buckminsterfullerene acts as an electrophile[2] and reacts with alkenes and dienes to afford [4 + 2],[3,4] [2 + 2],[5,6] and ene[7] adducts. Among the reactions of C_{60}, the [4 + 2] cycloadditions are the most widely used, since they usually give thermally stable adducts. The mechanism of this reaction, however has received limited attention, and to our knowledge, only a few reports deal with the mechanism of the Diels−Alder reaction. Specifically, Mikami and co-workers[8] have reported a stepwise bond-forming process via an electron transfer[9] in the Diels−Alder reaction of [60]fullerene with Danishefsky's dienes. However, because of the polarized electronic structure of these dienes and their stereochemical asymmetry due to two heteroatoms, that conclusion may not be general. Recent work from our laboratory on isotope effects of the [4 + 2] cycloadditions of anthracene and rigid s-cis dienes to C_{60} supports a concerted and symmetrical transition state.[10]

We report here the experimental results and discuss the mechanistic possibilities of the [4 + 2] cycloadditions of simple acyclic 2,4-hexadienes to C_{60}. These substrates have been used often in the past to elucidate the stereochemistry of the [4 + 2] and [2 + 2] cycloadditions of a number of other electrophiles, such as singlet oxygen ($^1O_2$),[11] 4-phenyltriazoline-3,5-dione (PTAD),[12] tetracyanoethylene (TCNE),[13] and 1,1-dichloro-2,2-difluoroethylene.[14]

Results and Discussion

Thermal [4 + 2] Cycloaddition of *trans,trans*- and *cis,trans*-2,4-Hexadiene to C_{60}. After 40 h of reaction at 25 °C, a mixture of C_{60} and a 200-fold excess of *trans,trans*-2,4-hexadiene in deoxygenated benzene, in the absence of light, gave a single adduct in 50% yield (based on recovered C_{60}). The adduct was analyzed by ^1H NMR

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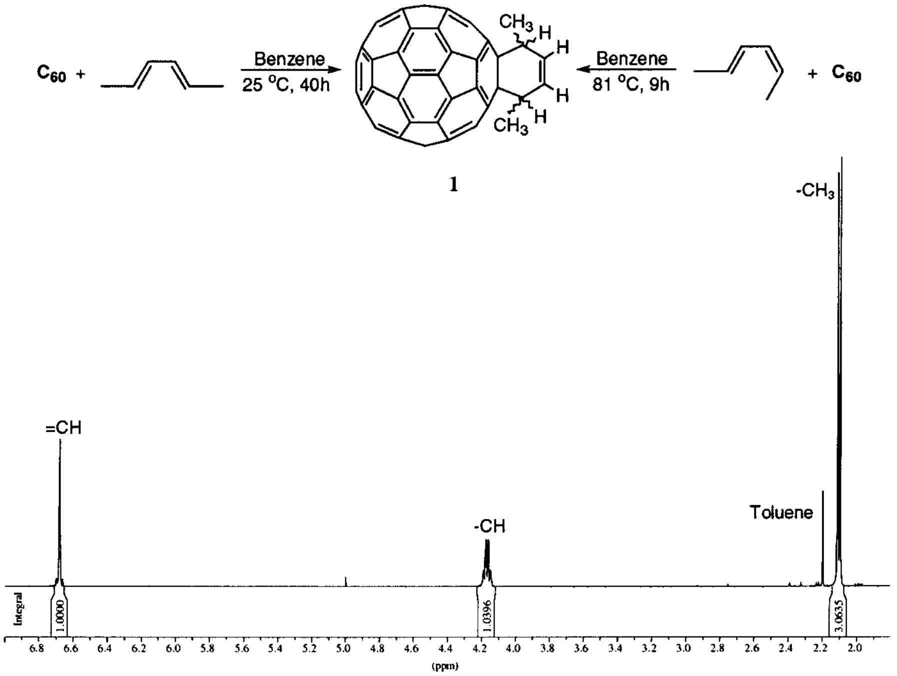
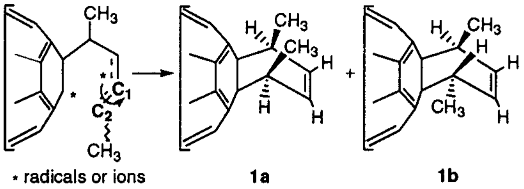


Figure 1. ^1H NMR of the adduct formed in the Diels–Alder reaction of *trans,trans*- and *cis,trans*-2,4-hexadiene with C_{60}.

spectroscopy and FAB-MS. The ^1H NMR spectrum (Figure 1), a doublet at 2.10 ppm, (two methyl groups), a doublet of quartets at 4.16 ppm (allylic hydrogens), and a downfield absorption at 6.67 ppm (vinyl hydrogens) is consonant with a [4 + 2] adduct. What the stereochemistry of the methyl groups is, however, could not be deduced from the NMR. The FAB-MS showed the M^+ ion at 802, which corresponds to the molecular formula $C_{66}H_{10}$. The UV–vis absorption spectrum showed a strong absorption at 437 nm, with a weak absorption at 709 nm. These absorptions are characteristic[15] of the dihydrofullerene structure, which is an indication that the cycloaddition took place at the junction of two six-membered rings. In addition to this major cycloadduct formed in the Diels–Alder reaction, a small amount (~5%) of a side product was detected by HPLC. This byproduct, probably a bisadduct, had a shorter retention time than the major adduct and was not characterized further.

The corresponding reaction of *cis,trans*-2,4-hexadiene with C_{60} was performed in refluxing benzene (81 °C), using a 200-fold excess of the diene in the absence of light. It is useful to note here that the cis,trans diene was unreactive toward C_{60} at room temperature, even after prolonged reaction times. The reaction was followed by HPLC equipped with a Separon C_{18} reverse-phase column. After 9 h, a 50% yield of a fullerene adduct was obtained (based on recovered C_{60}). Following chromatographic purification, the adduct was characterized by FAB-MS and ^1H NMR spectroscopy. The FAB-MS showed the M^+ ion at 802, which corresponds to the molecular formula $C_{66}H_{10}$. The ^1H NMR spectrum (Figure 1) was found to be identical with that obtained from the Diels–Alder reaction of *trans,trans*-2,4-hexadiene with C_{60}. It is important to note that the isolated cycloadduct does not cycloreverse to the starting materials even after prolonged heating in toluene at 110 °C.

Scheme 1. Stepwise Mechanism in the Diels–Alder Reaction of Isomeric Hexadienes with C_{60}



The thermal [4 + 2] cycloaddition of the two isomeric hexadienes to C_{60} could proceed through an open dipolar or diradical intermediate (Scheme 1). Had this been the case, however, rotation around the C_1–C_2 would lead to the formation of a mixture of cycloadducts **1a** and **1b**. Furthermore, efforts to trap a dipolar intermediate with methanol were unsuccessful.

During the cycloaddition of *cis,trans*-2,4-hexadiene to C_{60}, isomerization of the diene to the thermodynamically more stable trans,trans isomer was detected by capillary gas chromatography. Control experiments showed that the observed isomerization of cis,trans to trans,trans isomer is directly dependent on [60]fullerene concentration and reaction temperature. For example, no isomerization of the *cis,trans*-2,4-hexadiene was observed in the absence of C_{60} at temperatures ranging from 25 to 81 °C, in benzene solvent. When a mixture of stoichiometric amounts of C_{60} and *cis,trans*-2,4-hexadiene was heated to reflux, a 3% isomerization to the trans,trans diene was detected by capillary gas chromatography, whereas, no isomerization was observed at room temperature. The isomerization of *cis,trans*-2,4-hexadiene to the trans,trans isomer may occur via an electron-transfer process[8,9] from the diene to the ground state of C_{60}, since C_{60} is a good electron acceptor.[2c] Thus, the formation of a charge-transfer complex ($C_{60}^{\delta-}\cdots$*cis,trans*-2,4-hexadiene$^{\delta+}$) followed by isomerization and the release of the trans,trans isomer cannot be excluded. In a recent report, the calculated rate constants for thermal electron transfer

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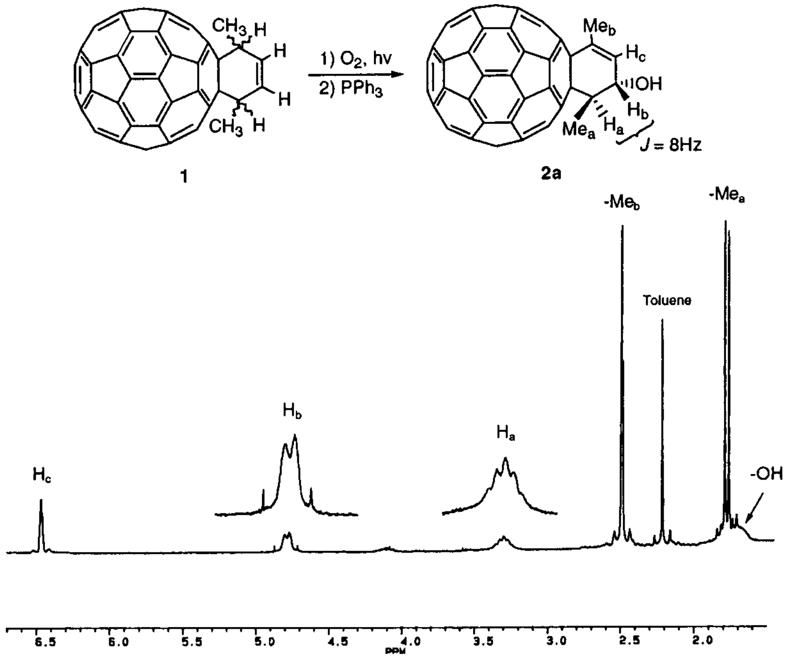

Figure 2. Self-sensitized photoxygenation of **1**.

from Danishefsky's dienes to C_{60} are reported to be very small. Thus, the isomerization process though electron transfer must be very slow compared to the reaction rate of dienes with C_{60} through orbital interaction.

To elucidate the mechanism of these reactions, it became necessary to determine the stereochemistry of the methyl groups in the Diels–Alder adducts obtained from the thermal cycloaddition reaction of *trans,trans*- and *cis,trans*-2,4-hexadiene with C_{60}.

Structural Assignment of the [4 + 2] Cycloadduct Formed in the Cycloaddition of *trans,trans*- and *cis,trans*-2,4-Hexadiene with C_{60}. Attempts to elucidate the structure of **1a** and **1b** by X-ray crystallography were unsuccessful. However, an indirect method to determine the stereochemistry of the methyl groups in the [4 + 2] cycloadducts might be the epoxidation of the double bond on the cyclohexene ring of cycloadduct **1**.[10a] Cycloadduct **1b** (Scheme 1) possesses a C_2 symmetry axis, and therefore, a single epoxide is expected to be formed, whereas in **1a** two diastereomeric epoxides could be formed. However, both *m*-CPBA (3-chloroperbenzoic acid)[16] and dimethyldioxirane[17] gave a complicated mixture of unidentified products. This result may rationalized by a multiple epoxidation process of the fullerene of the cycloadduct.

Finally, the study of the photooxygenation products of **1** may be give useful information on the stereochemistry of adducts **1a** and **1b**. It is well-established that C_{60} and its derivatives are efficient photosensitizers[5b,18] and produce singlet oxygen upon irradiation of their oxygenated solutions, with a quantum yield close to unity. When the fullerene derivative bears an oxidizable moiety, upon irradiation, a self-photooxygenation has been reported. The cycloadducts obtained from the Diels–Alder reaction of the isomeric hexadienes with C_{60} have an oxidizable group (alkene moiety) and therefore are expected to undergo facile self-sensitized photooxygenation. The self-oxidation reaction was carried out by irradiating an oxygen-saturated solution of the Diels–Alder adduct **1** in toluene, at 0 °C. After 2 h of irradiation, the cycloadduct was quantitatively transformed to the corresponding hydroperoxide, as observed from HPLC (Figure 2). Triphenylphosphine reduction of the hydroperoxide gave the corresponding allylic alcohol, which was purified by flash column chromatography (SiO_2, toluene:hexane = 3:1) and characterized by ^1H NMR spectroscopy.

Homonuclear decoupling experiments revealed that the coupling constant between H_a and H_b was 8 Hz. Upon irradiation of the doublet at 1.78 ppm, which corresponds to the methyl Me_a of **2a**, the multiplet at 3.29 ppm, which corresponds to the hydrogen H_a, collapsed to a doublet, with coupling constant $J = 8$ Hz. This value is typical of the threo configuration[19] of H_a and H_b in adduct **2a**. Similarly, in a recent report, the cycloadducts structurally similar to **1a** and **1b**, produced from the cycloaddition of Danishefsky's dienes to C_{60}, were deduced to be the threo and erythro from the coupling constants of the 1,2 neighboring hydrogens of the six-member ring ($J_{(H1,H2)} = 11.4$ and 2.7 Hz, respectively). Self-oxidation of **1b** would lead to the formation of **2b**, with an erythro configuration of H_a and H_b. In this case, the J value between H_a and H_b would be expected to be less than 8 Hz. The isolation of adduct **1b** in pure form was achieved by the self-oxidation of a mixture of **1a** and **1b**. The **1b** did not self-photooxidize and was recovered free of **1a**. Unfortunately, additional prolonged irradiation of cy-

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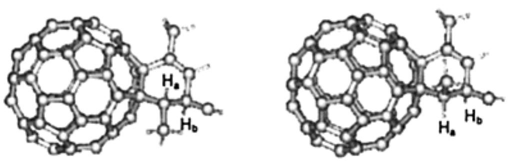
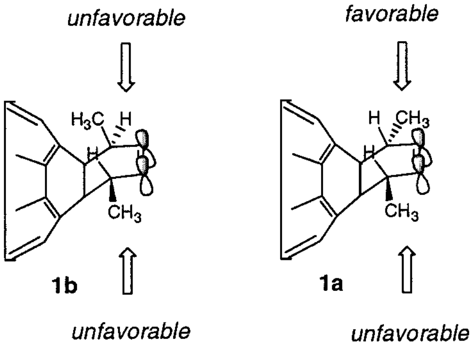


2a (*threo*): dih (H_a,H_b) = 174°

2b (*erythro*): dih (H_a,H_b) = 57°

Figure 3. Fully optimized geometries of **2a** and **2b** at the HF/3-21G level.

Scheme 2. Favorable and Unfavorable Faces in 1a and 1b, for the Ene Reaction with Singlet Oxygen



cloadduct **1b** did not give photooxygenation product. This result is not surprising, because the presence of only one allylic hydrogen in each face of the cycloalkene double bond of **1b** (compared to two allylic and cis hydrogens in **1a**) makes the ene photooxygenation[20] of **1b** very slow, if it occurs at all (Scheme 2).

To verify further the threo configuration of H_a, H_b in the adduct **1**, formed when the Diels−Alder cycloadduct was autooxidized, we used ab initio theoretical calculations. The geometries of **2a** and **2b** were fully optimized at the HF/3-21G level of theory. The dihedral angles between H_a and H_b for the two local minima that came out of the optimizations were 174° for the threo and 57° for the erythro stereoisomers (Figure 3).

All the computations were performed with the GAUSSIAN 94 program package.[21] According to the dihedral angles predicted by the theoretical calculations, the J values were calculated to be 10 and 3.6 Hz for the threo and erythro isomers, respectively. The J = 10 Hz value between H_a and H_b for the threo isomer is in good agreement with that measured by ^{1}H NMR spectroscopy (J = 8 Hz). These results support further our conclusion that the Diels−Alder reactions of the *trans,trans*- and the *cis,trans*-2,4-hexadiene with C_{60} gave cycloadduct **1a**. Taking into account the [60]fullerene-induced isomerization of cis,trans to trans,trans diene, formation of cycloadduct **1a** from the reaction of cis,trans diene with C_{60} in elevated temperature can be rationalized. These results definitely support a concerted mechanism.

Temperature Dependent Diels−Alder Reaction of *trans,trans*- and *cis,trans*-2,4-Hexadiene with C_{60}.

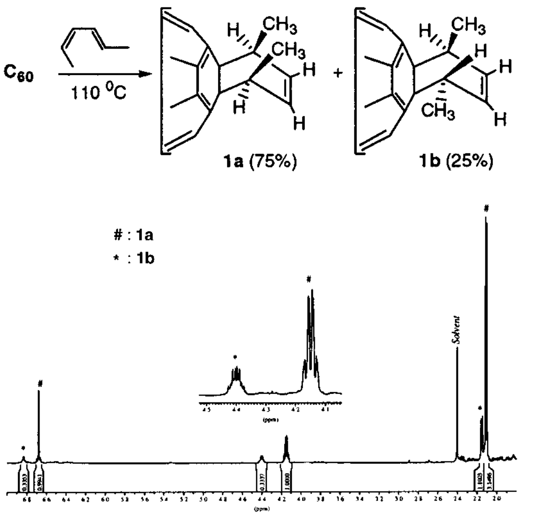


Figure 4. Diels−Alder reaction of *cis,trans*-2,4-hexadiene with C_{60} at 110 °C.

The [4 + 2] cycloaddition reactions of *trans,trans*- and *cis,trans*-2,4-hexadiene with C_{60} were carried out at higher temperatures than those in the previous experiments. When the *trans,trans*-hexadiene was reacted with C_{60} at 110 °C in toluene, (200-fold excess of the diene) a 51% yield of cycloadduct **1a**, as the only product, was obtained in 15 min.

When the *cis,trans*-2,4-hexadiene was reacted with C_{60}, at 110 °C in toluene, isomerization of the diene to the trans,trans isomer was observed (GC analysis). Along with the **1a** adduct, ^{1}H NMR spectroscopy confirmed the formation of cycloadduct **1b** (Figure 4).

It should be mentioned that the two diastereomeric adducts appear as a single peak in the HPLC chromatograph and could not be separated by either flash column chromatography or HPLC. The ratio **1a**/**1b** was measured by integrating the appropriate signals in the ^{1}H NMR spectrum and found to be 75/25. The reaction was also performed at 140 °C by using xylenes as the solvent. Isomerization of the cis,trans diene to the trans,trans was again observed, and the ratio of the **1a** and **1b** products was found to be 67/33. The results are summarized in Table 1.

From the data of Table 1, we conclude that the concerted Diels−Alder reaction (Scheme 3) of *cis,trans*-2,4-hexadiene with C_{60} at elevated temperatures (path II) competes with its isomerization to trans,trans (path I). In contrast, the reaction of the trans,trans diene with C_{60} is much faster than its isomerization to cis,trans.

The relative energies of the s-cis conformations of the isomeric dienes, which are reflected in the corresponding transition states, apparently control their relative reactivities toward C_{60} (Scheme 4). It has been reported by Foote[9b] that the energy differences between the s-trans and the s-cis conformations for the trans,trans and cis,-trans dienes, as calculated by MM2, are 2.8 and 5.9 kcal/mol, respectively.

In conclusion, the [4 + 2] cycloaddition reaction of *trans,trans*-2,4-hexadiene with C_{60} occurs by a concerted mechanism, to give cycloadduct **1a.** Self-oxidation of cycloadduct **1a** and reduction of the allylic hydroperoxide gives the allylic alcohol **2a** with threo stereochemistry, as was determined by ^{1}H NMR and theoretical calculations. In the Diels−Alder reaction of *cis,trans*-2,4-hexa-

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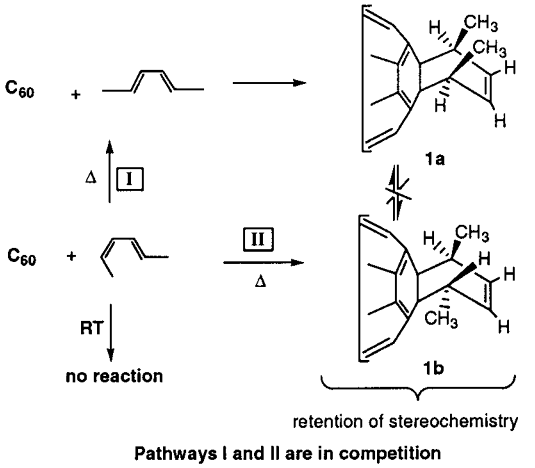
Table 1. Conditions and Experimental Results in the Diels−Alder Reaction of *trans,trans*- and *cis,trans*-2,4-Hexadiene with C_{60}

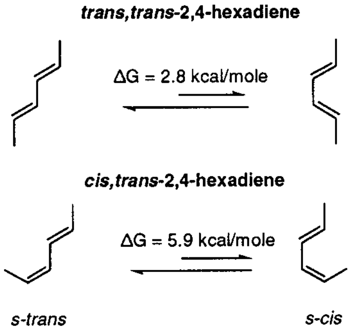
diene	solvent	*T*, °C	*t*, h	convn, %[a]	isomerization[b]	**1a**, %[c]	**1b**, %[c]
trans,trans	benzene	25	40	50	no	100	0
trans,trans	toluene	110	0.25	51	no	100	0
cis,trans	benzene	81	9	50	yes	100	0
cis,trans	toluene	110	2	66	yes	75	25
cis,trans	xylenes	140	0.5	62	yes	67	33

[a] Based on recovered C_{60}. [b] Observed by capillary gas chromatography. [c] Determined by ^{1}H NMR integration of the appropriate signals.

Scheme 3. Mechanistic Possibility of the Cycloaddition of *cis,trans*-2,4-Hexadiene to C_{60}



Scheme 4. s-Trans and s-Cis Conformations of the Isomeric Hexadienes



diene with C_{60} isomerization of the diene to the trans,-trans isomer is faster than its cycloaddition. The isomerized trans,trans diene cycloadds to C_{60} in a concerted fashion to give again adduct **1a**. At elevated temperatures the *cis,trans*-2,4-hexadiene (a) cycloadds to C_{60} to form **1b** by a concerted mechanism and (b) isomerizes to trans,trans diene, which also cycloadds to C_{60} to give **1a**. The two reaction pathways I and II are in competition.

Experimental Section.

General Considerations. ^{1}H NMR spectra were recorded on 250 and 500 MHz spectrometers, using a mixture of CS_2:C_6D_6 (4:1) as a solvent and Me_4Si as internal standard. Chemical shifts are reported in ppm downfield from Me_4Si. Isomerization of the 2,4-hexadienes during the Diels−Alder reactions was determined by gas chromatography on an HP 5890 Series II analytical gas chromatograph equipped with a 50%−50% phenyl methyl silicone capillary column and FID detector. Cycloaddition and photooxygenation reactions were monitored using a HPLC chromatograph equipped with a Separon C_{18}, 7 μm, 200 mm × 4.6 mm i.d., reversed-phase column. A mixture of toluene:acetonitrile (1:1) was used as eluent at 1 mL/min flow rate, and UV detection at 310 nm. FAB mass spectra were obtained on a VG-ZAB−SE mass spectrometer, using *m*-nitrobenzyl alcohol as a matrix. Photooxygenations were achieved with a xenon Variac Eimac Cermax 300 W lamp. Chromatography refers to flash column chromatography and was carried out on SiO_2 (silica gel 60, SDS, 230−400 mesh ASTM). Chemical reactions and flash column chromatographic purifications were performed using HPLC-grade solvents. Evaporation of solvents was accomplished with a rotatory evaporator. *trans,trans*- and *cis,trans*-2,4-hexadienes were commercially available (Wiley Organics) and their isomeric purities were 99%. The *cis,trans*-2,4-hexadiene was further purified to obtain 100% isomeric purity by Foote's method.[13]

Experimental Procedure for the Thermal [4 + 2] Cycloaddition Reactions of *trans,trans*- and *cis,trans*-2,4-Hexadiene to C_{60}. To a solution of C_{60} (25 mg, 0.0347 mmol) in deaerated benzene (25 mL) was added *trans,trans*-2,4-hexadiene (0.8 mL, 6.94 mmol, 200-fold excess), and the reaction mixture was stirred in the dark, at room temperature. The reaction was followed by HPLC and a 50% yield of the cycloadduct **1a** was obtained after 40 h, based on recovered C_{60}. Benzene solvent, along with the excess of the diene, was removed under reduced pressure, and the cycloadduct **1a** was separated from the unreacted C_{60} by flash column chromatography (SiO_2, hexane). The reaction of *trans,trans*-2,4-hexadiene was also performed at 110 °C using toluene as the appropriate solvent. After 0.25 h, a 51% yield of **1a** was obtained, based on recovered C_{60}.

The [4 + 2] cycloaddition reaction of *cis,trans*-2,4-hexadiene with C_{60} was performed in benzene, toluene, and xylenes as solvents at 81, 110, and 140 °C, respectively. In each case the diene was used in 200-fold molar excess relative to C_{60}, according to the procedure described above. The reactions were monitored by HPLC and the product(s) (see Table 1) formed were purified by flash column chromatography (SiO_2, hexane).

The ^{1}H NMR and FAB-MS spectroscopic data for **1a** and **1b** are given below.

6,6-(61,64-*cis*-Dimethylcyclohex-62-ene)dihydro[60]-fullerene (1a). ^{1}H NMR (500 MHz): δ 2.10 (d, $J = 7$ Hz, 6H), 4.15 (dq, $J_1 = 7$ Hz, $J_2 = 1.8$ Hz, 2H), 6.67 (d, $J = 1.8$ Hz, 2H). HRMS (FAB): calcd for $C_{66}H_{10}$ (M) 802.0782, found 802.0784.

6,6-(61,64-*trans*-Dimethylcyclohex-62-ene)dihydro[60]-fullerene (1b). ^{1}H NMR (500 MHz): δ 2.15 (d, $J = 7.1$ Hz, 6H), 4.39 (dq, $J_1 = 7.1$ Hz, $J_2 = 2.8$ Hz, 2H), 6.83 (br s, 2H). HRMS (FAB): calcd for $C_{66}H_{10}$ (M) 802.0782, found 802.0784.

Self-Sensitized Photooxygenation of 1a and (1a + 1b). An oxygen-saturated solution of **1a** (5 mg) in 10 mL of toluene was irradiated at 0 °C. The photooxygenation was monitored by HPLC, and after 2 h of irradiation the reaction was complete (100% conversion). Reduction of the allylic hydroperoxide with triphenylphosphine afforded the corresponding alcohol **2a**. Toluene solvent was evaporated under reduced pressure, and the solid residue was washed with diethyl ether to remove the excess of PPh_3 and the $PPh_3{=}O$ formed during the reduction of the hydroperoxide. Adduct **2a** was purified by flash column chromatography using a mixture of toluene:hexane (3:1) as eluent.

An oxygen-saturated solution of **1a**:**1b** (75:25) obtained from the Diels−Alder reaction of *cis,trans*-2,4-hexadiene with C_{60} at 110 °C was irradiated in toluene solvent, at 0 °C. The reaction was followed by HPLC, while complete disappearance of the starting material was not observed, even after prolonged irradiation. After reduction with triphenylphosphine, the fullerene adducts were separated by flash column chromatography (SiO_2, toluene:ethyl acetate = 4:1). The first adduct eluted from the column was assigned to be **2a**, derived from the self-sensitized photoxygenation of **1a**. The structure of the second adduct isolated is in agreement with that of **1b**, which is unreactive toward autoxidation and is isolated in pure form.

6,6-(63-Hydroxy-61,64-dimethylcyclohex-61-ene)-dihydro[60]fullerene (2a). ^1H NMR (250 MHz): δ 1.67 (br s, $-$OH), 1.76 (d, $J = 6.9$ Hz, 3H), 2.48 (t, due to the allylic splitting, $J = 1.5$ Hz, 3H), 3.28 (m, 1H), 4.78 (d, $J = 8.2$ Hz, 1H), 6.46 (q, due to the allylic splitting, $J = 1.5$ Hz, 1H). FAB-MS *m*/*z*: 818 (M^+, weak), 720 (C_{60}, 100).

Acknowledgment. We thank the Greek Secretariat of Research and Technology (ΠΕΝΕΔ 1999) for financial support and for a research fellowship to N.C. Dedicated to Prof. G. J. Karabatsos on the occasion of his 70th birthday.

Supporting Information Available: ^1H NMR spectra for **1a**, **1b**, **2a**, **1a** + **1b**; FAB-MS for **1a**, **1b**, **2b**; and energetics and Cartesian coordinates for **2a** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0109570