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# A New [2 + 2] Functionalization of $C_{60}$ with Alkyl-Substituted 1,3-Butadienes: A Mechanistic Approach. Stereochemistry and Isotope Effects

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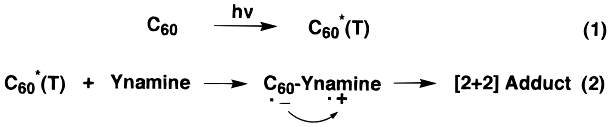
**Abstract:** The stereochemistry and secondary isotope effects of the [2 + 2] photocycloaddition of *trans,trans-* **(7)**, *cis,cis-* **(8)**, and *cis,trans*-2,4-hexadiene **(9)**, 2,5-dimethyl-2,4-hexadiene (**1**), and its deuterated analogues **1-$d_1$**, **1-$d_6$**, and ***trans*-1-$d_3$** to $C_{60}$ have been investigated. A loss of stereochemistry in the cyclobutane ring for photocycloaddition of all three 2,4-hexadiene isomers **7**, **8**, and **9** to $C_{60}$ was observed (the *trans* stereochemistry in the cyclobutane ring predominates in all cases), while the unreactive double bond retained its stereochemical integrity in the adducts. The *cis* double bond of **9** is 1.5 times more reactive than the *trans*. The [2 + 2] photocycloaddition of (*E*)-2,4-dimethyl-2,4-hexadiene **(10)** to $C_{60}$ is regiospecific, affording two diastereomeric adducts, **10a** and **10b**, by addition on the methyl monosubstituted terminal double bond. These results, when taken in conjunction with the small inverse intramolecular secondary isotope effect ($k_H/k_D$ = 0.90 ± 0.05) in the [2 + 2] photocycloaddition of **1-$d_6$** to $C_{60}$, favor the formation of an open biradical intermediate in the rate-determining step.

## Introduction

The discovery of $C_{60}$[1,2] (buckminsterfullerene) and its isolation in large quantities[3] triggered the investigation of a remarkable array of its reactions in the last seven years. Buckminsterfullerene is electrophilic,[4−6] reacts with alkenes and dienes, and affords [4 + 2],[7,8] [2 + 2],[9−12] and ene[13] adducts. Most of the work has focused on adduct isolation and characterization, with less emphasis given to reaction mechanisms. The ene, as well as the [2 + 2] additions to $C_{60}$ and $C_{70}$, are less common.

Foote and co-workers have reported [2 + 2] photocycloadditions of $C_{60}$ with electron-rich alkynes (ynamines), such as *N,N*-diethylpropynylamine[9a,b] and *N,N*-diethyl-4-methylpenten-3-yn-1-amine.[9c] They proposed the formation of the triplet excited state of $C_{60}$ as the first step in the reaction sequence (eq 1). Previous results[14] had demonstrated that the triplet excited state of $C_{60}$ has a reduction potential close to 0.98 V (36 kcal/mol triplet E) vs SCE and is formed with a quantum yield of about unity. The second step of the reaction includes the addition of ynamines to the triplet excited state of $C_{60}$ 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 [2 + 2] cycloadducts (eq 2). In contrast, with extremely electron rich substrates, such as ynediamines (e.g., *N,N,N′,N′*-tetraethylethynediamine), thioynamines (e.g., *N,N*-diethyl-2-ethylthioethyneamine),[9b] and tetraalkoxyethylenes (e.g., tetraethoxyethylene),[9c] thermal [2 + 2] cycloadditions to $C_{60}$ have been reported. It was suggested that these reactions with electron-rich alkynes and alkenes proceed through a charge-transfer mechanism in the absence of light, because of the high electron affinity of $C_{60}$ and the high electron-donating ability of these molecules. The thermal [2 + 2] cycloaddition of benzyne to $C_{60}$ has also been reported.[10]



$$C_{60} \xrightarrow{h\nu} C_{60}^{*}(T) \qquad (1)$$

$$C_{60}^{*}(T) + \text{Ynamine} \longrightarrow \underset{\cdot\,-\qquad\quad\cdot\,+}{C_{60}\text{-Ynamine}} \longrightarrow [2{+}2]\ \text{Adduct} \qquad (2)$$

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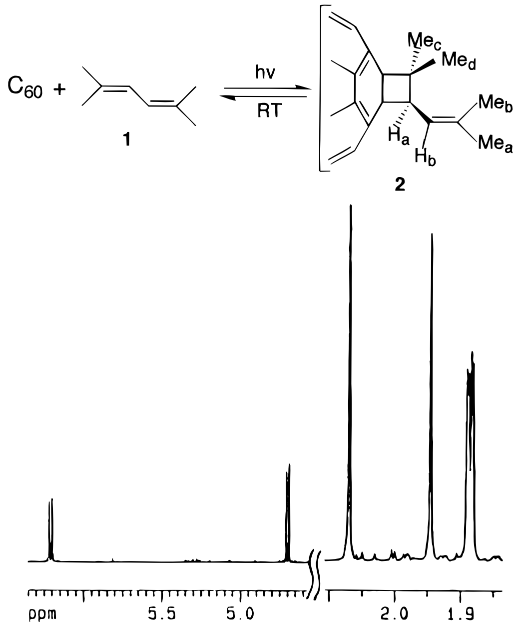


**Figure 1.** [2 + 2] photocycloaddition of DMHD to $C_{60}$.

Schuster and Wilson and co-workers recently reported a new photochemical [2 + 2] cycloaddition of cyclic enones[11a−c] and cyclic 1,3-diones[11d] to $C_{60}$. Since this type of photocycloaddition cannot be achieved by irradiation at 532 nm, where $C_{60}$ is the only light-absorbing component, this result indicates that fullerene triplets do not undergo addition to the ground state of enones. The authors proposed that the photochemical [2 + 2] cycloadditions of enones to $C_{60}$ proceed by stepwise addition of enone triplet excited states to the fullerene via a triplet 1,4-biradical intermediate. The proposed mechanism was consistent with the observation that alkenes, such as cyclopentene or cyclohexene, do not photochemically add to $C_{60}$.

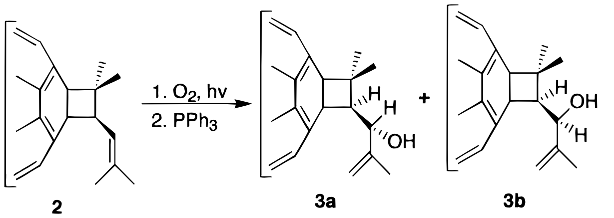
Recently, we reported a new type of [2 + 2] functionalization of $C_{60}$ with moderately electron-rich *p*-methoxyarylalkenes.[12] The stereochemistry and the secondary isotope effects of the reaction with *p*-methoxystyrene[12a] showed that the photochemical [2 + 2] cycloaddition occurs by a two-step mechanism, involving the formation of a dipolar or diradical intermediate in the rate-determining step. The stepwise mechanism was also supported by results of the [2 + 2] photochemical reaction of $C_{60}$ with *cis*/*trans*-4-propenylanisole.[12b] In this case, the thermodynamically most stable *trans* cycloadduct was formed, regardless of the geometry (*cis* or *trans*) of the propenylanisole.

In this paper, we report the stereochemistry and the secondary isotope effects of a new type of photochemical [2 + 2] cycloaddition of $C_{60}$ with the less electron-rich alkyl-substituted 1,3-butadienes.

## Results

**Addition of 2,5-Dimethyl-2,4-hexadiene and Its Deuterated Analogues to $C_{60}$.** A mixture of $C_{60}$ and 20-fold excess of 2,5-dimethyl-2,4-hexadiene (DMHD, **1)** in deoxygenated toluene, in the absence of light, did not react after 24 h at solvent reflux. However, upon irradiation with a xenon lamp (Variac Eimac Cermax 300 W), a rapid reaction was observed within 15 min (HPLC). A $C_{60}$-fused cyclobutane, 6,6-(61,61-dimethyl-62-(2′-methyl)propenylcyclobutane)dihydro[60]fullerene (**2**, Figure 1), was formed in 60% yield, based on recovered $C_{60}$. Additional irradiation did not increase the yield, even after prolonged reaction time (7 h). The yield of the reaction increased only after an increase of the diene concentration.

**Scheme 1.** Self-Sensitized Photooxygenation of **2**



Photolysis of the isolated cycloadduct **2** gave complete cycloreversion to $C_{60}$ and diene in 3 min, consistent with an equilibrium between $C_{60}$ and **2**. The $K_{eq}$ calculated from the recovered $C_{60}$ is approximately $7.7 \times 10^{-2}$. Similar [2 + 2] reversible photocyclizations were recently reported by Foote.[9c] Along with the major cycloadduct **2**, a small amount (~3%) of a side product was detected by HPLC. This byproduct, probably a bisadduct, had a shorter retention time than adduct **2** and was not further characterized. The adduct **2**, which is stable at room temperature, was purified by flash column chromatography (toluene:hexane 2:1) and characterized by mass spectrometry, by $^1$H NMR spectroscopy (Figure 1), and by its reaction with $^1O_2$. FAB-MS of **2** gave the expected M + 1 ion at 831, which corresponds to the molecular formula $C_{68}H_{14}$. The $^1$H NMR spectrum of **2** shows two signals due to the diastereotopic methyls ($Me_a$, $Me_b$) at 1.88 and 1.89 ppm with the proper allylic coupling, $J_1 = 1.3$ Hz and $J_2 = 1.2$ Hz, respectively; two downfield absorptions at 1.94 and 2.07 ppm (lower fields due to the influence of the $C_{60}$ currents) which correspond to the diastereotopic methyls on the cyclobutane ring ($Me_c$, $Me_d$); a doublet at 4.70 ppm which corresponds to the cyclobutane ring hydrogen ($H_a$); and a doublet with allylic coupling at 6.20 ppm for the vinylic hydrogen ($H_b$) (Figure 1). The UV−vis absorption spectrum of **2** in toluene shows a strong absorption at 437 nm, accompanied by a weak absorption at 709 nm. These absorptions are characteristic[15] of the dihydrofullerene structure, thus indicating that the cycloaddition took place at the junction of two six-membered rings.

It is interesting to note that, like $C_{60}$ and $C_{70}$,[16] cycloadduct **2** is also an efficient photosensitizer and produces singlet oxygen upon irradiation of its oxygenated solutions. Because adduct **2** bears an oxidizable group (alkene moiety), it undegoes facile self-sensitized photooxygenation and produces, after triphenylphosphine reduction, a mixture of the threo/erythro allylic alcohols **3a** and **3b** as the only products, in a 55/45 ratio (Scheme 1). The two stereoisomers were separated by flash column chromatography using a mixture of toluene:hexane (2:1) as eluent. The stereochemistry of adducts **3a** and **3b** (which is erythro and which is threo) was not assigned. Similar self-sensitized photooxygenated products of $C_{60}$ adducts have been recently reported.[9a,17]

The intramolecular secondary product isotope effects of the [2 + 2] photocycloadditions of $C_{60}$ with the 2-methyl-*1′,1′,1′*-$d_3$-5-methyl-2,4-hexadiene-*1,1,1*-$d_3$ (**DMHD-$d_6$, 1-$d_6$)** and the 2,5-dimethyl-2,4-hexadiene-*3*-$d_1$ (**DMHD-$d_1$, 1-$d_1$**) were measured. Substrates **1-$d_6$** and **1-$d_1$** reacted under the same conditions described above for substrate **1** to yield the [2 + 2]

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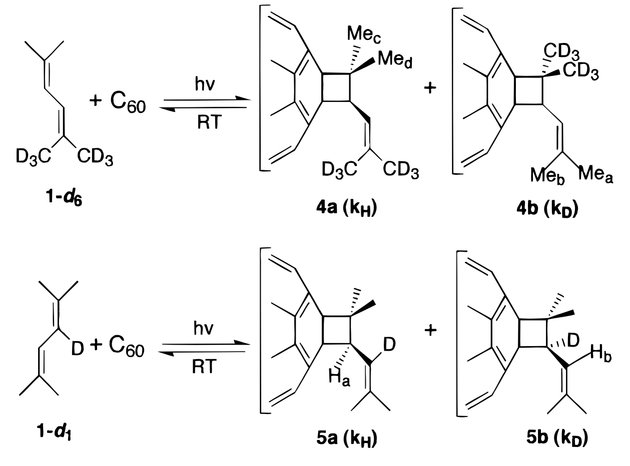


| Diene | Irradiat. time (min) | Conversion %$^a$ | $k_H/k_D$$^b$ |
|---|---|---|---|
| 1-d6 | 15 | 60 | 0.90±0.05 |
| 1-d6 | 420 | 60 | 0.89±0.05 |
| 1-d1 | 15 | 60 | 1.03±0.05 |
| 1-d1 | 420 | 60 | 1.04±0.05 |

[a] *Based on recovered C60*

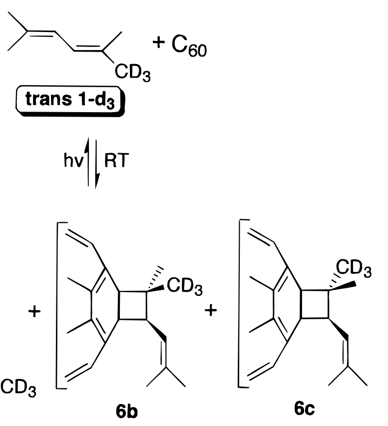
[b] *By $^1$H-NMR (500 MHz) integration of the relevant signals. The error was ± 5%*

**Figure 2.** Intramolecular secondary isotope effects in the [2 + 2] photocycloaddition of **1-*d*$_6$** and **1-*d*$_1$** to $C_{60}$.

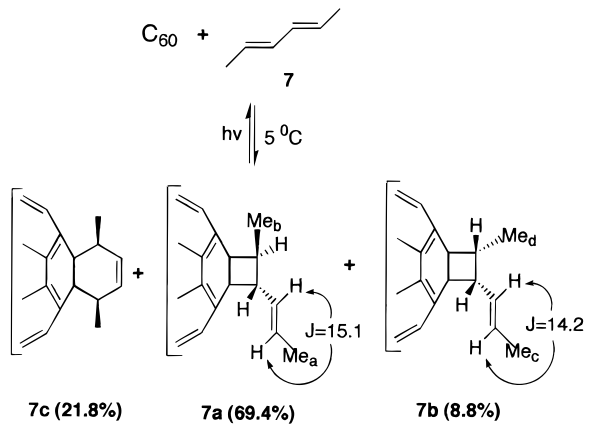
deuterated cycloadducts **4a, 4b** and **5a, 5b**, respectively (Figure 2). After flash column chromatographic purification (toluene: hexane 2:1) of the reaction products, the secondary isotope effects $k_H/k_D$, which result from the intramolecular competition between the two double bonds of **1-*d*$_6$** and **1-*d*$_1$**, were measured by integration of the relevant $^1$H NMR signals of the [2 + 2] products **4a**, **4b** and **5a**, **5b**, respectively. The product ratios **4a/4b** and **5a/5b**, which are proportional to the secondary isotope effects $k_H/k_D$, are shown in Figure 2. The ratio **4a/4b** was measured by integration of the $^1$H NMR signals at 1.94, 2.07 ppm for **4a** ($Me_c$, $Me_d$) and at 1.88, 1.89 ppm for **4b** ($Me_a$, $Me_b$). Similarly, the **5a/5b** ratio was determined by integrating the two single peaks at 4.70 and 6.17 ppm, which correspond to **5a** ($H_a$) and **5b** ($H_b$), respectively. The results are summarized in Figure 2.

To examine the stereochemistry of the [2 + 2] cycloaddition of the diene to $C_{60}$, the 2,5-dimethyl-2,4-hexadiene-*1,1,1-d*$_3$ (**DMHD-*d*$_3$, *trans*-1-*d*$_3$**) was prepared in high stereochemical purity by specific deuterium labeling of the *trans* methyl group at the diene terminal. Reaction of $C_{60}$ with ***trans*-1-*d*$_3$** under the previously described conditions gave three of the possible four [2 + 2] adducts (Scheme 2). The ratio **6a/6b/6c** was measured by $^1$H NMR integration of the signals of the four differently shifted methyl groups to be 2:1:1. Under the experimental conditions, only a small fraction (~4%) of the recovered ***trans*-1-*d*$_3$** was isomerized to the *cis* analogue.

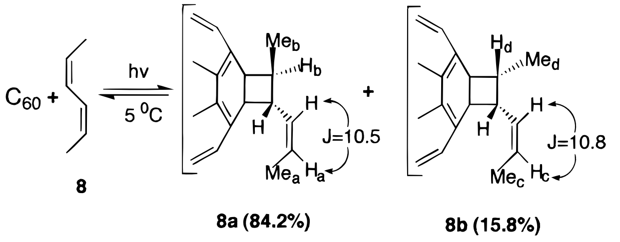
**Scheme 2.** [2 + 2] Photocycloaddition of ***trans*-1-*d*$_3$** to $C_{60}$



**Scheme 3.** Photocycloaddition of *trans,trans*-2,4-Hexadiene to $C_{60}$



**Scheme 4.** Photocycloaddition of *cis,cis*-2,4-Hexadiene to $C_{60}$



To obtain further information on the stereochemistry of the [2 + 2] photocycloaddition reaction of dienes, the addition of the three stereoisomers of 2,4-hexadiene to $C_{60}$ was studied. These substrates have been successfully used in the past to elucidate the stereochemistry of the [4 + 2] and [2 + 2] cycloadditions of a number of other electrophiles, such as $^1O_2$,[18] 4-phenyltriazoline-3,5-dione (PTAD),[19] tetracyanoethylene (TCNE),[20] and 1,1-dichloro-2,2-difluoroethylene.[21]

**Addition of the *trans,trans*-2,4-Hexadiene to $C_{60}$.** A mixture of $C_{60}$ and 80-fold excess of the *trans,trans*-2,4-hexadiene **7** in deoxygenated toluene reacted rapidly upon irradiation at 5 °C for 20 min. After solvent evaporation under reduced pressure, the products were purified by washing many times with distilled *n*-hexane. The solid was dried in a vacuum and characterized by $^1$H NMR and FAB-MS. The $^1$H NMR spectrum revealed the presence of the [2 + 2] diastereomeric adducts **7a** and **7b** (Scheme 3, Figure 3). The coupling constant between the hydrogens on the cyclobutane ring was 8.5 Hz for the major adduct and 10.3 Hz for the minor adduct. The first value is typical for a *trans*- and the second for a *cis*-substituted cyclobutane ring,[12a,b] indicating that **7a** is the major product. The stereochemistry of the unreacted double bonds of **7a** and **7b** was determined by homonuclear decoupling experiments.

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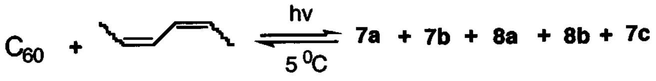

| **Diene** | **Irradiat. t (min)** | **conv %[a]** | **Products** | | | | |
|---|---|---|---|---|---|---|---|
| | | | **7a** | **7b** | **8a** | **8b** | **7c** |
| trans, trans | 20 | 33 | 69.4 | 8.8 | - | - | 21.8 |
| cis, trans | 20 | 41 | 51.9 | 7.4 | 31.7 | 7.5 | 1.5 |
| cis, cis | 20 | 43 | - | - | 84.2 | 15.8 | - |

[a] *Based on the recovered $C_{60}$*

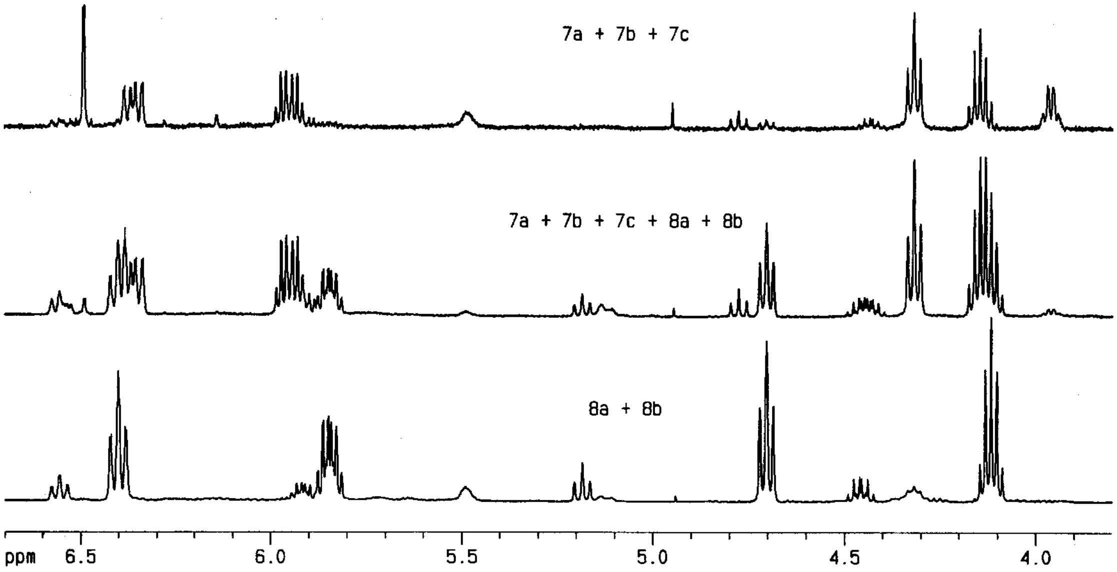

**Figure 3.** Photocycloadditions of the three 2,4-hexadienes isomers **7**, **8**, and **9** to $C_{60}$.

Upon irradiation of the doublets at 1.83 ppm, which correspond to the methyls $Me_a$, $Me_c$ of **7a** and **7b**, the multiplets at 5.96 and 5.91 ppm, which correspond to the olefinic hydrogens geminal to the $Me_a$ and $Me_c$, collapsed to doublets, with coupling constants $J = 15.1$ and 14.2 Hz, respectively. These values are typical for *trans*-alkyl-substituted double bonds.[22] The ratio **7a**/**7b** was measured by $^1H$ NMR to be 7.8:1.

Along with the [2 + 2] products **7a** and **7b**, a substantial amount (21.8%) of the *cis* [4 + 2] adduct **7c** was shown by $^1H$ NMR. The identical [4 + 2] adduct was isolated by the thermal addition of *trans,trans*-2,4-hexadiene to $C_{60}$ at room temperature. The structure of **7c** was confirmed by matching its $^1H$ NMR spectrum to that of the adduct produced separately by the thermal addition of diene **7** to $C_{60}$.[23] Efforts to separate these cycloadducts by either flash column chromatography or HPLC were unsuccessful. At the end of irradiation, a small isomerization of the recovered *trans,trans*-2,4-hexadiene to the *cis,trans*-2,4-hexadiene (~2%) was found by gas chromatography.

**Addition of the *cis,cis*-2,4-Hexadiene to $C_{60}$.** Cycloaddition of *cis,cis*-2,4-hexadiene **8** to $C_{60}$ under photochemical conditions identical to those described previously produced two diastereomeric [2 + 2] products, **8a** and **8b** (Scheme 4). $^1H$ NMR analysis of the reaction mixture **8a** and **8b** showed a spectrum remarkably different from that of **7a** and **7b** (Figure 3). In this case, the thermal [4 + 2] cycloadduct was not detected, because the thermal reaction of $C_{60}$ with **8** is very slow.[23] For example, in the absence of light (thermal conditions), the [4 + 2] adduct was not detected after 48 h of stirring at room temperature. The stereochemistry of these products was confirmed by homonuclear decoupling experiments. Decoupling of the hydrogens $H_b$ and $H_d$ of the cyclobutane rings of **8a** and **8b** by irradiation of the methyl groups $Me_b$, $Me_d$ at 1.98 ppm showed that the resulting doublet of $H_d$ at 4.46 ppm, which belongs to the less predominant isomer, had a coupling constant $J = 10.4$ Hz. This value, typical for a *cis*-substituted cyclobutane ring,[12] indicates a *cis* stereochemistry for the minor adduct on the cyclobutane ring. Moreover, the coupling constant between the hydrogens for the major adduct, $J = 8.7$ Hz, is typical of a *trans*-substituted cyclobutane ring.[12] Irradiation of the vinylic methyl groups $Me_a$, $Me_c$ at 1.88 ppm simplified the multiplet absorptions of $H_a$ and $H_c$ at 5.84 and 5.91 ppm of **8a** and **8b**, into two doublets with coupling constants $J = 10.5$ and 10.8 Hz, respectively. These values are consistent with a *cis* stereochemistry of the double bonds[22] in **8a** and **8b**. The ratio **8a**/**8b** was measured by $^1H$ NMR to be 5.3:1. Capillary column gas chromatographic analysis of the recovered *cis,cis* diene **8** showed only 4% isomerization to the *cis,trans* isomer.

**Addition of the *cis,trans*-2,4-Hexadiene to $C_{60}$.** The photochemical cycloaddition of the *cis,trans*-2,4-hexadiene **9** to $C_{60}$ was also studied under experimental conditions identical to those described. $^1H$ NMR analysis of the reaction mixture revealed the formation of the expected four [2 + 2] stereoiso-

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(23) A detailed report for the [4 + 2] cycloadditions of the isomeric 2,4-hexadienes to $C_{60}$ will appear elsewhere.

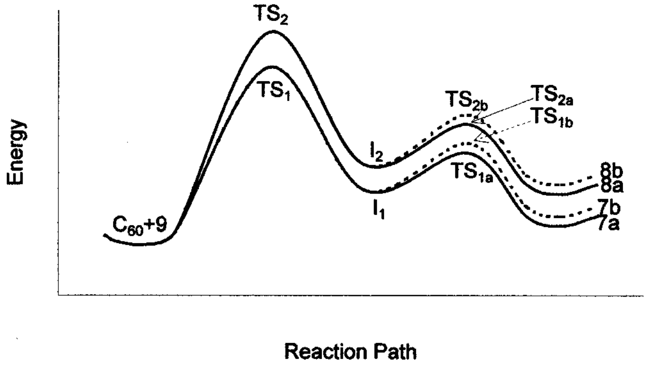


**Figure 4.** Energy profile in the [2 + 2] photocycloaddition of *cis,trans*-2,4-hexadiene to $C_{60}$.

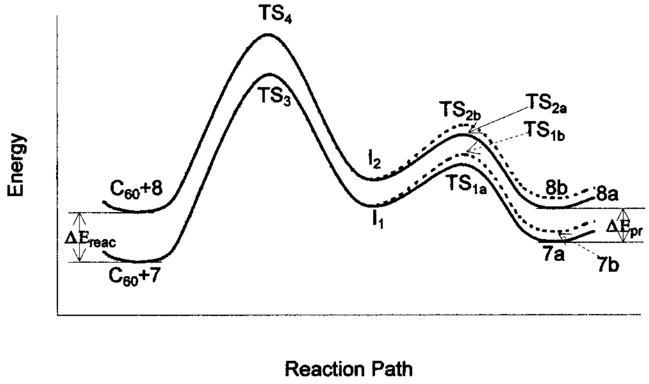
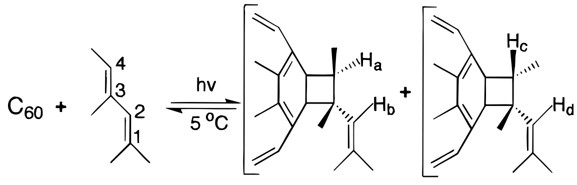


**Figure 5.** Energy profiles in the [2 + 2] photocycloadditions of *trans,trans*- and *cis,cis*-2,4-hexadienes to $C_{60}$.

**Scheme 5.** [2 + 2] Photocycloaddition of (*E*)-2,4-Dimethyl-2,4-hexadiene to $C_{60}$



**10** **10a** **10b**

mers **7a**, **7b**, **8a**, **8b**, accompanied by a negligible amount of the [4 + 2] adduct **7c** (Figure 3). A small isomerization of the recovered diene (~3% of the *trans,trans*- and 1% of the *cis,cis*-2,4-hexadiene) was detected by capillary column gas chromatography.

**Regiospecific [2 + 2] Photocycloadditions of Dienes to $C_{60}$.** To study the regioselectivity of the photochemical [2 + 2] cycloaddition of dienes to $C_{60}$, (*E*)-2,4-dimethyl-2,4-hexadiene **10** was prepared. Diene **10** is appropriate for this purpose because it bears methyl-monosubstituted and -disubstituted olefinic terminals. A mixture of $C_{60}$ and 40-fold excess of **10** in deoxygenated toluene was irradiated for 20 min. The reaction mixture was purified by flash column chromatography (toluene: hexane, 2:1) followed by hexane extractions. HPLC showed a 35% conversion based on the recovered $C_{60}$. The $^1H$ NMR analysis of **10a** and **10b** showed two quartets due to $H_a$ and $H_c$ at 4.10 and 4.53 ppm, respectively, accompanied by two singlets due to $H_b$ and $H_d$ at 6.21 and 6.29 ppm (Scheme 5). The vinylic hydrogens of similar adducts such as **2, 7a, 7b, 8a**, and **8b** absorb at lower fields than the cyclobutane ring hydrogens. The $^1H$ NMR region between 1.85 and 2.08 ppm is complicated due to the eight different methyls of **10a** and **10b**. Attempts to separate **10a** from **10b** by either flash column chromatography or HPLC were unsuccessful. The $^1H$ NMR spectrum indicates that the [2 + 2] addition takes place exclusively at the $C_3-C_4$ double bond. Had the $C_1-C_2$ double bond added to $C_{60}$, additional downfield (two quartets) and upfield (two singlets) signals would have been detected. Moreover, the addition of (*E*)-2,4-dimethyl-2,4-hexadiene to $C_{60}$ is slightly diastereoselective (~10% diastereomeric excess).

## Discussion

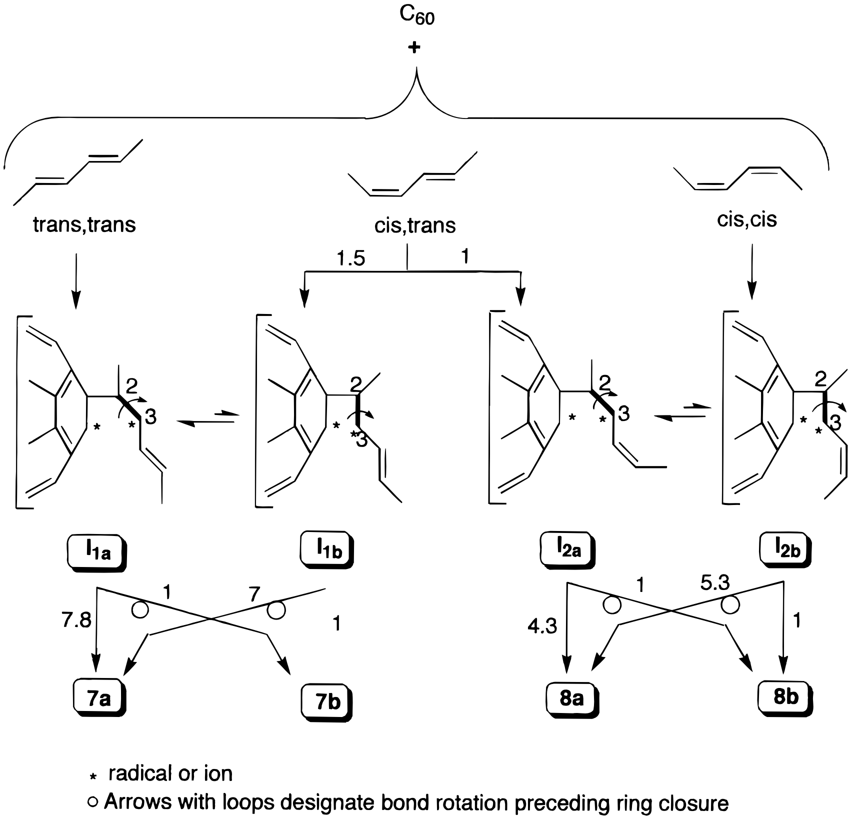
While a wide variety of dienes are well-known to react in a [4 + 2] mode with $C_{60}$, no [2 + 2] reactions involving dienes have been reported, and only a few have been reported with other electron-rich substrates. In the present work, a new class of [2 + 2] photochemical cycloadditions to $C_{60}$ is reported. Apart from the [2 + 2] addition of enones to $C_{60}$, which follows different mechanistic pathways than all the previous examples reported in the literature, this is the first example of [2 + 2] additions dealing with substrates substantialy less electron rich than the ynamines and tetraalkoxyethylenes.

These reactions reach equilibrium and, upon irradiation of the isolated fullerenyl cycloadducts, cyclorevert to $C_{60}$ and the starting dienes. The yields are low, because the equilibrium favors the reactants rather than the products. However, higher yields can be achieved (based on $C_{60}$) if excess diene is used. Similar cycloreversion reactions of $C_{60}$ [2 + 2] adducts have been reported earlier.[9c]

The $^1H$ NMR spectroscopic data of the [2 + 2] photochemical adducts formed by the cycloadditions of the three isomers of 2,4-hexadiene of known stereochemical purity to $C_{60}$ provide rich mechanistic information for this type of reaction. A remarkable result is the retention of stereochemistry of the diene double bond which has not reacted with $C_{60}$ to form the [2 + 2] cycloadducts. For example, cycloaddition of *trans,trans*-2,4-hexadiene to $C_{60}$ leads to the formation of diastereoisomers **7a**, **7b** (Scheme 3), where the unreacted double bond of the diene retains the *trans* stereochemistry in the products. Similarly, in the adducts **8a** and **8b** (Scheme 4) that are formed by cycloaddition of the *cis,cis*-2,4-hexadiene to $C_{60}$, the *cis* stereochemistry of the nonreacted double bond is completely retained.

Furthermore, the [2 + 2] cycloaddition of the hexadiene isomers is diastereoselective with respect to the stereochemistry of the formed cyclobutane ring. Regardless of the initial stereochemistry of the double bond in the hexadiene, a preference for the *trans* configuration of the cyclobutane ring of the adduct in the range of 7.8:1 to 4.2:1 (*trans:cis*) was observed (Figure 3). For example, the *trans:cis* ratio with respect to the stereochemistry of the cyclobutane ring was measured to be 7.8 in the cycloaddition of $C_{60}$ with the *trans,trans* diene. In the reaction of the *cis,trans* diene with $C_{60}$, when the addition took place on the *cis* double bond of the diene, the *trans:cis* ratio was found to be 7.0, while that for the addition of the *trans* double bond was 4.2. Finally, a ratio of 5.3 for the addition of *cis,cis* diene to $C_{60}$ was measured (Scheme 6). The loss of stereochemistry of the initial reactive diene double bond in the [2 + 2] adducts is consistent with the formation of an open, free to rotate, intermediate. These results definitely exclude the possibility of a concerted mechanism, where in all cases retention of stereochemistry in the cyclobutane ring would have been expected. The remarkable preference of the *trans* over the *cis* stereochemistry of the cyclobutane ring must be due to the difference in activation energy of the diastereomeric transition states in the second step of the reaction leading to the diastereomeric products. The *trans*-cyclobutane adduct is

**Scheme 6.** Proposed Mechanism of the [2 + 2] Photocycloaddition of $C_{60}$ to 2,4-Hexadienes



* radical or ion

○ Arrows with loops designate bond rotation preceding ring closure

favored, because each of the factors that stabilize the products also stabilizes the corresponding transition states in the second step of the reaction coordinate. Thus, **7a** is energetically favored over **7b**, and **8a** is favored over **8b** (Figure 4, 5).

Considering the retention of stereochemistry of the unreacted diene double bond, it is possible to estimate the relative reactivity of the *cis* vs the *trans* double bond in the reaction of *cis,trans*-2,4-hexadiene with $C_{60}$. When the *cis* double bond of the *cis,trans* diene **9** reacts with $C_{60}$, products **7a** and **7b** are formed. Reaction of the *trans* double bond affords adducts **8a** and **8b**. The ratio of **(7a + 7b)** versus **(8a + 8b)** reflects the relative reactivity of the *cis* and *trans* double bonds in the *cis, trans* hexadiene. This ratio was measured to be (**7a** + **7b**)/(**8a** + **8b**) = 3:2 (Figure 3, Scheme 6). This result shows that the *cis* double bond of the *cis,trans*-2,4-hexadiene **9** is 1.5 times more reactive than the *trans*. The higher reactivity of the *cis* double bond requires that the transition state $\mathbf{TS_1}$ (*cis* double bond addition) have lower energy than transition state $\mathbf{TS_2}$ (*trans* double bond addition, Figure 4, Scheme 6). Thus, $\mathbf{TS_1}$ leads to intermediate $\mathbf{I_1}$ and has a *trans* double bond, while $\mathbf{TS_2}$ leads to intermediate $\mathbf{I_2}$ and has a *cis* double bond. These intermediates, whether diradicals or dipolar, retain the stereochemistry of the unreacted double bond of the initial diene (Scheme 6).

The first step of the cycloaddition of *trans,trans*-2,4-hexadiene to $C_{60}$ involves the formation of intermediate $\mathbf{I_1}$. The lifetime of this intermediate is apparently long enough to permit rotation around the $C_2-C_3$ bond, leading to the formation of the adducts **7a** and **7b** through the diastereomeric transition states $\mathbf{TS_{1a}}$ and $\mathbf{TS_{1b}}$, respectively (Figure 5, Scheme 6). Similarly, in the case of the *cis,cis*-2,4-hexadiene, rotation around the $C_2-C_3$ bond of the intermediate $\mathbf{I_2}$ leads to **8a** and **8b** through the diastereomeric transition states $\mathbf{TS_{2a}}$ and $\mathbf{TS_{2b}}$ (Figure 5, Scheme 6).

As we mentioned, the first step of the reaction is responsible for the observed regioselectivity in the [2 + 2] reaction of *cis, trans*-2,4-hexadiene with $C_{60}$; it favors addition of the *cis* double bond of the diene over the *trans* by a factor of 1.5. The second step is the one that determines the diastereoselectivity for the thermodynamically more stable *trans*-cyclobutane products **7a** and **8a**. The low rotational barrier around the $C_2-C_3$ single bond in the open intermediate, which is expected to be around 1−2 kcal/mol (libration rather than complete rotation), leads to loss of stereochemical integrity in the cycloadducts. Thus, the reaction of *cis,trans*-2,4-hexadiene with $C_{60}$ showed a 59.4% *cis* double bond reactivity (**7a** + **7b** vs **8a** + **8b**, Figure 3) and 87.5% *trans* diastereoselectivity in the cyclobutane ring of the adducts (**7a** + **8a** vs **7b** + **8b**, Figure 3). Similarly, the reaction of *cis,cis*-2,4-hexadiene gave a 84.2% *trans* diastereoselectivity in the cyclobutane ring (Figure 3). These results indicate that the observed stereochemistry of the ring is controlled by the rate of rotation around the $C_2-C_3$ bond. Subsequent cyclization must be slower than rotation about this bond. The present results definitely exclude the two other mechanistic possibilities, namely, a synchronous reaction or formation of an open intermediate whose closure is faster than rotation.

The competition between internal rotation and ring closure in the intermediate is such that rotational equilibrium is approached but not fully attained before ring closure. This fact makes it possible to estimate quantitatively[21a] the relative rates of these competing processes. In the additions of the 2,4-hexadiene isomers to $C_{60}$, the ratio of adducts with *trans* ring configuration to those with *cis* was 7.8 in the case of the *trans, trans* diene **7** and 5.3 in the case of the *cis,cis* diene **8** (Scheme 6). From these values we estimate that rotation in the open intermediate is approximately 18 times faster than ring closure.[21a,24]

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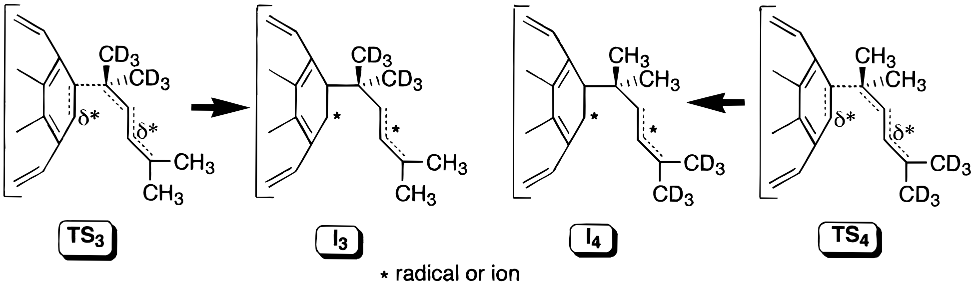
(24) Bartlett, P. D.; Walldillich, G. E. H. *J. Am. Chem. Soc.* **1969**, *91*, 409.

**Scheme 7.** Intermediates and Transition States in the [2 + 2] Photoaddition of **1-*d*$_6$** to $C_{60}$

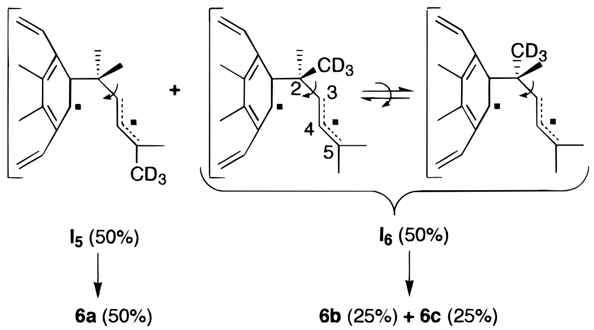


It is important to note that only in the reaction of the *trans,trans*-2,4-hexadiene (Scheme 3) is a significant amount of the [4 + 2] cycloaddition product **7c** (21.8%) formed. Control experiments showed that Diels−Alder adduct **7c** results from a thermal reaction even at ambient temperatures. Under the same thermal conditions, the *cis,trans* and *cis,cis* diene isomers were totaly unreactive. Molecular calculations have shown[19] that the cisoid conformation, required for the Diels−Alder reaction, of the *trans,trans* hexadiene has the lowest rotation barrier (2.8 kcal/mol), compared to the *cis,trans* (5.9 kcal/mol), the *cis,cis* (11.5 kcal/mol), and the DMHD (12.9 kcal/mol). Consequently, the energy difference of the *s-cis* conformation of the ground state of the diene isomers shows up in the transition states of the Diels−Alder reactions, and only the *trans,trans* diene is energetically favored to undergo this reaction.

The possibility that the [4 + 2] cycloadduct **7c** may arise photochemically from the open intermediates **I$_1$** and **I$_2$** is remote, because, in that case, the *cis,cis*-2,4-hexadiene and the 2,5-dimethyl-2,4-hexadiene would also give the corresponding [4 + 2] adducts, which were not found. Furthermore, it is unlikely that the favored transoid conformation of the open zwitterion or biradical intermediate could close in a [4 + 2] mode involving a *trans* double bond in a six-membered ring. The negligible amount (1.5%) of the [4 + 2] adduct **7c** in the reaction of $C_{60}$ with *cis,trans*-2,4-hexadiene is probably derived from a small isomerization (∼3%) of the starting diene into the *trans,trans* analogue.

To probe this mechanism further and elucidate the nature of the proposed open intermediate, the intramolecular secondary isotope effects were measured. A small inverse secondary isotope effect was found in the intramolecular competition for the [2 + 2] adducts of **1-*d*$_6$** with $C_{60}$. The new C−C bond between $C_{60}$ and **1-*d*$_6$** is preferentially formed ($k_H/k_D = 0.9$) at the carbon which bears the geminal $-CD_3$ groups. It is expected that transition state **TS$_3$**, which leads to the formation of **I$_3$**, would be energetically favored over transition state **TS$_4$**, because the developing radical or positive charge is stabilized better in **TS$_3$** by hyperconjugation from the six hydrogens of the two methyls than in **TS$_4$** by the six deuteriums of the two deuterated methyls (Scheme 7). Assuming the existence of an open intermediate, this isotope effect is nominally an $\epsilon$-secondary isotope effect, since the isotopic labeling is at the $\epsilon$ position (five chemical bonds away) with respect to the newly formed C−C bond. Because of the magnitude of the secondary product isotope effect, and on the basis of additional experimental evidence, we favor the formation of a biradical over a zwitterionic intermediate. In the case of a zwitterionic intermediate, a higher isotope effect would have been expected, because a carbocationic-type transition state is stabilized more efficiently by hyperconjucation than a radical-type transition state. For example, the ionic [2 + 2] cycloadditions of **1-*d*$_6$** to tetracyanoethylene (TCNE) gave a significant secondary isotope effect of $k_H/k_D = 0.72$.[25] It has been well established that the mechanism of this reaction involves the formation of a dipolar intermediate in the rate-determining step. Comparably large secondary isotope effects have been observed[26] in the methanol trapping experiments of 4-phenyltriazoline-3,5-dione (PTAD) with tetramethylethylene-*d*$_6$, which is a reaction that involves a zwitterionic-like transition state.

**Scheme 8.** Proposed Mechanism in the [2 + 2] Photoaddition of ***trans*-1-*d*$_3$** to $C_{60}$



Ionic intermediates are usually trapped by protic solvents, such as methanol[25,26] or water. Successful water trapping experiments reported in the [2 + 2] photochemical reaction of $C_{60}$ with silyl ketene acetals[27] led to the conclusion that the reaction proceeded via a dipolar intermediate. However, in the present work, no methanol trapping products were detected when the reaction of $C_{60}$ with hexadienes was run in the presence of significant amounts of methanol. This result also favors the involvement of a biradical rather than a dipolar intermediate. The finding that the stereochemistry of the unreacted double bond in the cycloadducts is retained is also in agreement with the known propensity of allylic radicals to resist rotation around the partial double bonds.[28]

Based on the previous discussion, it is now easy to understand why the photochemical [2 + 2] cycloaddition of $C_{60}$ to ***trans*-1-*d*$_3$** gives only three of the possible four [2 + 2] adducts in a ratio **6a/6b/6c** = 2:1:1. Disregarding a possible small secondary isotope effect (for three deuteriums), the two double bonds of ***trans*-1-*d*$_3$** must react at the same rate to give the two biradical intermediates **I$_5$** and **I$_6$** in the same ratio (Scheme 8). These biradicals permit rotation around the $C_2-C_3$ bond but resist rotation about the $C_4-C_5$ partial double bond. Thus, biradical **I$_5$** gives exclusively **6a** with retained geometry of the $C_4-C_5$

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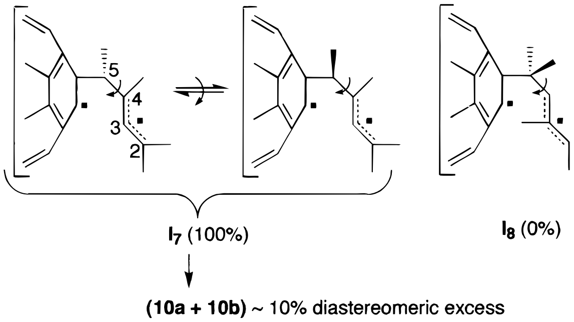
(25) Vassilikogiannakis, G.; Orfanopoulos, M. *Tetrahedron Lett.* **1996**, *37*, 3075.

(26) Elemes, Y.; Orfanopoulos, M. Unpublished results.

(27) Tokuyama, H.; Isobe, H.; Nakamura, E. *J. Chem. Soc., Chem. Commun.* **1994**, 2753.

(28) (a) Walling, C.; Thaler, W. *J. Am. Chem. Soc.* **1961**, *83*, 3877. (b) Krusic, P. J.; Meakin, P.; Smart, B. E. *J. Am. Chem. Soc.* **1974**, *96*, 6211. (c) Korth, H.-G.; Trill, H.; Sustmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4483.

**Scheme 9.** Proposed Mechanism in the [2 + 2] Photoaddition of (*E*)-2,4-Dimethyl-2,4-hexadiene to $C_{60}$



double bond. In contrast, $\mathbf{I_6}$ leads to the formation of both **6b** and **6c** in equal amounts.

In the case of the [2 + 2] reaction of $C_{60}$ with (*E*)-2,4-dimethyl-2,4-hexadiene, the addition took place exclusively at the $C_4-C_5$ double bond. This unexpected regiospecificity may be due to the cooperation of two different factors. The first one involves differences in the stereochemical hindrance of the two terminals of the dienic system ($C_2$ and $C_5$), which favor reaction at $C_5$. The second factor may be the stability of the intermediate biradicals. Thus, the reaction of the less substituted terminus ($C_5$) of the (*E*)-2,4-dimethyl-2,4-hexadiene leads to the formation of the tertiary allylic biradical $\mathbf{I_7}$, which is more stable than the secondary allylic biradical $\mathbf{I_8}$ that is formed from the addition at the more substituted terminus ($C_2$) of the diene (Scheme 9).

## Conclusion

In this paper, we have reported a new type of photochemical [2 + 2] cycloaddition of $C_{60}$ to alkyl-substituted 1,3-butadienes. These compounds are less electron rich than the reported unsaturated substrates that undergo a [2 + 2] addition to $C_{60}$. The [2 + 2] cycloadditions take place only under photochemical conditions. This observation demonstrates the strong electrophilic character of the triplet excited state of $C_{60}$. The [2 + 2] photocycloadditions are reversible and reach an equilibrium. The stereochemical studies and the secondary isotope effects show that the first step of the reaction involves the addition of the dienes to the triplet excited state of $C_{60}$ via electron transfer from the diene, followed by rapid collapse of the initial ion pair to the [2 + 2] cycloadducts. The first (rate-determining) step of the reaction, which leads to the formation of a biradical intermediate, is responsible for the observed regioselectivity and the secondary isotope effects. The second step (collapse of the initial ion pair) dictates the diastereoselectivity that favors the thermodynamically more stable *trans*-cyclobutane products. The lifetime of the biradical intermediate is long enough to permit rotation around the $C_2-C_3$ bond, thus leading to loss of stereochemical integrity of the cycloadducts. However, the stereochemistry of the unreacted double bond of the dienes is retained, and this result is consistent with the known propensity of allylic radicals to resist rotation around the partial double bond.

## Experimental Section

**General Considerations.** $^1$H NMR and $^{13}$C NMR spectra were recorded on 250 and 500 MHz spectrometers, in $CDCl_3$ solutions, by using $Me_4Si$ as internal standard, except for the $^1$H NMR spectra of the $C_{60}$ adducts, which were run in a mixture of $CS_2$:$C_6D_6$ (4:1). Chemical shifts are reported in ppm downfield from $Me_4Si$. Isomeric purities were determined by $^1$H NMR and with an analytical gas chromatograph with 50%−50% phenyl methyl silicone capillary column and a 5971A MS detector. The photochemical cycloadditions were monitored using a HPLC chromatograph equipped with a Separon $C_{18}$, 7 $\mu$m, 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 was at 310 nm. FAB mass spectra were obtained on a VG-ZAB-SE mass spectrometer by using *m*-nitrobenzyl alcohol as a matrix. Photocycloadditions and photooxygenations were achieved with a xenon Variac Eimac Cermax 300 W lamp. TLC was carried out on $SiO_2$ (silica gel $F_{254}$). Chromatography refers to flash chromatography and was carried out on $SiO_2$ (silica gel 60, SDS, 230−400 mesh ASTM). Drying of organic extracts during workup of reactions was performed over anhydrous $MgSO_4$. Evaporation of solvents was accomplished with a rotatory evaporator. $C_{60}$ was purified from soot according to a literature procedure.[3]

**General Procedure for Photocycloadditions of 1, 1-$d_6$, 1-$d_1$, *trans*-1-$d_3$, 7, 8, 9, and 10, to $C_{60}$.** The solvent used was HPLC grade toluene, sample size was 30 mL, and the concentrations of $C_{60}$ and dienes ranged between 0.7 and 0.92 mM and between 15 and 70 mM, respectively. Samples were stirred for 45 min with argon bubbling through them and subsequently irradiated for 15−20 min. Longer irradiation did not affect the reaction yields. During irradiation, the reaction mixtures were cooled with ice water and monitored by HPLC. Toluene was removed under reduced pressure. In most cases, the products were separated from the unreacted $C_{60}$ by flash column chromatography by using a mixture of toluene:hexane (2:1) as eluent. A very small amount (~3%) of a side product was detected by HPLC in the reaction of **1** and its deuterated analogues. This byproduct, probably a bisadduct, had a shorter retention time than adduct **2** and was not further characterized. Side products or higher adducts were not detected by HPLC and $^1$H NMR in the photocycloadditions of **7**, **8**, **9**, and **10** to $C_{60}$. When the solvent was removed, the products were sonicated with hexane, and then the hexane was decanted from the precipitated solid. The remaining volatile material was removed from the residue by pumping on the sample under high vacuum.

The $^1$H NMR and FAB-MS spectroscopic data for **2**, (**3a** + **3b**), (**4a** + **4b**), (**5a** + **5b** + **5c**), **7a**, **7b**, **7c**, **8a**, and **8b** are given below.

**6,6-(61,61-Dimethyl-62-(2′-methyl)propenylcyclobutane)dihydro[60]fullerene (2).** $^1$H NMR (500 MHz): $\delta$ 1.88 (d, $J$ = 1.3 Hz, 3H), 1.89 (d, $J$ = 1.2 Hz, 3H), 1.94 (s, 3H), 2.07 (s, 3H), 4.70 (d, $J$ = 9.7 Hz, 1H), 6.20 (d with allylic splitting $J_1$ = 9.7 Hz, $J_2$ = 1.2 Hz, 1H). FAB-MS for $C_{68}H_{14}$: (M + 1) 831.06.

**(4a + 4b).** $^1$H NMR (500 MHz): $\delta$ 1.88 (d, $J$ = 1.3 Hz, 3H of **4b**), 1.89 (d, $J$ = 1.2 Hz, 3H of **4b**), 1.94 (s, 3H of **4a**), 2.07 (s, 3H of **4a**), 4.70 (d, $J$ = 9.7 Hz, 1H of **4a** + 1H of **4b**), 6.20 (d with allylic splitting $J_1$ = 9.7 Hz, $J_2$ = 1.2 Hz, 1H of **4a** + 1H of **4b**). FAB-MS for $C_{68}H_8D_6$: (M + 1), 837.14.

**(5a + 5b).** $^1$H NMR (250 MHz): $\delta$ 1.88 (br s, 6H of **5a** + 6H of **5b**) 1.94 (s, 3H of **5a** + 3H of **5b**), 2.07 (s, 3H of **5a** + 3H of **5b**), 4.70 (s, 1H of **5a**), 6.17 (br s, 1H of **5b**). FAB-MS for $C_{68}H_{13}D$: (M + 1) 832.05.

**(6a + 6b + 6c).** $^1$H NMR (500 MHz): $\delta$ 1.88 (br s, 3H of **6a** + 3H of **6b** + 3H of **6c**), 1.89 (br s, 3H of **6b** + 3H of **6c**), 1.94 (s, 3H of **6a** + 3H of **6b** or **6c**), 2.07 (s, 3H of **6a** + 3H of **6c** or **6b**), 4.70 (d, $J$ = 9.7 Hz, 1H of **6a** + 1H of **6b** + 1H of **6c**), 6.20 (d, $J$ = 9.7 Hz, 1H of **6a** + 1H of **6b** + 1H of **6c**).

**6,6-(61-Methyl-62-*trans*-propenyl-*trans*-cyclobutane)dihydro[60]fullerene (7a).** $^1$H NMR (500 MHz): $\delta$ 1.83 (dd, $J_1$ = 6.4 Hz, $J_2$ = 1.3 Hz, 3H), 1.95 (d, $J$ = 7.1 Hz, 3H), 4.15 (m, 1H), 4.32 (t, $J$ = 8.5 Hz, 1H), 5.95 (m, 1H), 6.35 (dd with allylic splitting, $J_1$ = 15.1 Hz, $J_2$ = 8.7 Hz, $J_3$ = 1.5 Hz). FAB-MS for $C_{66}H_{10}$ (mixture of **7a**, **7b**, and **7c**): calcd 802.0782, found 802.0784.

**6,6-(61-Methyl-62-*trans*-propenyl-*cis*-cyclobutane)dihydro[60]fullerene (7b).** $^1$H NMR (500 MHz): $\delta$ 1.84 (dd, $J_1$ = 5.9 Hz, $J_2$ = 1.5 Hz, 3H), 1.98 (d, $J$ = 7.1 Hz, 3H), 4.43 (m, 1H), 4.77 (t, $J$ = 10.3 Hz, 1H), 5.94 (m, 1H), 6.54 (dd, $J_1$ = 14.2 Hz, $J_2$ = 10.3 Hz). FAB-MS for $C_{66}H_{10}$ (mixture of **7a**, **7b**, and **7c**): calcd 802.0782, found 802.0784.

**6,6-(61-Methyl-62-*cis*-propenyl-*trans*-cyclobutane)dihydro[60]fullerene (8a).** $^1$H NMR (500 MHz): $\delta$ 1.89 (dd, $J_1$ = 6.9 Hz, $J_2$ = 1.7 Hz, 3H), 1.98 (d, $J$ = 7.1 Hz, 3H), 4.11 (m, 1H), 4.70 (t, $J$ = 8.7

Hz, 1H), 5.85 (m, 1H), 6.40 (dd with allylic splitting but seems like a triplet with allylic splitting, $J_1 \approx 10.0$ Hz (an average), $J_2 = 1.7$ Hz). FAB-MS for $C_{66}H_{10}$ (mixture of **8a** and **8b**): calcd 802.0782, found 802.0784.

**6,6-(61-Methyl-62-*cis*-propenyl-*cis*-cyclobutane)dihydro[60]fullerene (8b).** $^1$H NMR (500 MHz): $\delta$ 1.86 (dd, $J_1 = 6.9$ Hz, $J_2 = 1.7$ Hz, 3H), 1.98 (d, $J = 7.1$ Hz, 3H), 4.46 (m, 1H), 5.18 (t, $J = 10.3$ Hz, 1H), 5.91 (m, 1H), 6.55 (t with allylic splitting, $J_1 = 10.4$ Hz, $J_2 = 1.7$ Hz). FAB-MS for $C_{66}H_{10}$ (mixture of **8a** and **8b**): calcd 802.0782, found 802.0784.

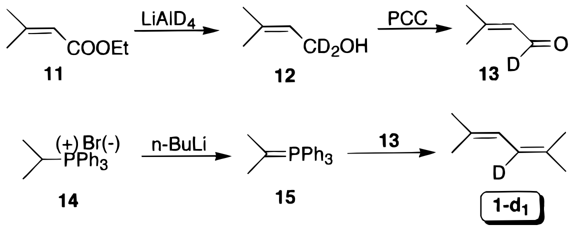
**6,6-(61,64-*cis*-Dimethylcyclohex-62-ene)dihydro[60]fullerene (7c).** $^1$H NMR (500 MHz): $\delta$ 1.92 (d, $J = 7.1$ Hz, 6H), 3.96 (dq, $J_1 = 7.1$ Hz, $J_2 = 1.7$ Hz, 2H), 6.49 (d, $J = 1.7$ Hz, 2H). FAB-MS for $C_{66}H_{10}$: calcd 802.0782, found 802.0784.

**Self-Sensitized Photooxygenation of 2 or (4a + 4b).** An oxygen-saturated solution of **2** or **(4a + 4b)** (5 mg) in a 5 mL mixture of $CS_2$:$C_6D_6$ (4:1) was irradiated. The photooxygenation was monitored by $^1$H NMR, and after 20 min of irradiation the reaction was complete (100% conversion). The diastereomeric excess of the two hydroperoxides was measured by $^1$H NMR integration of the doublets which correspond to the cyclobutane product hydrogens at 4.00 and 4.11 ppm. Subsequently, the hydroperoxides were reduced by triphenylphosphine to the corresponding alcohols **3a** and **3b**. These alcohols were separated by flash chromatography using a mixture of toluene:hexane (2:1) as eluent.

$^1$H NMR (250 MHz) for the first diastereomer: $\delta$ 1.31 (d, $J = 3.7$ Hz, −OH), 1.97 (s, 6H), 1.99 (s, 3H), 4.12 (d, $J = 11.0$ Hz, 1H), 5.04 (s, 1H), 5.05 (dd, $J_1 = 11.0$ Hz, $J_2 = 3.7$ Hz, 1H), 5.21 (s, 1H). When a drop of $D_2O$ was added, the coupling between the −OH and the hydrogen geminal to the hydroxyl group disappeared, and the doublet of doublets at 5.05 ppm was converted into a doublet.

$^1$H NMR (250 MHz) for the second diastereomer: $\delta$ 1.28 (d, $J = 3.2$ Hz, −OH), 1.89 (br s, allylic methyl, 3H), 2.09 (s, 3H), 2.18 (s, 3H), 4.02 (d, $J = 10.9$ Hz, 1H), 4.86 (t, due to the allylic splitting, $J = 1.5$ Hz, 1H), 5.05 (dd, $J_1 = 10.9$ Hz, $J_2 = 3.2$ Hz, 1H), 5.06 (s, 1H). When a drop of $D_2O$ was added, the coupling between the −OH and the hydrogen geminal to the hydroxyl group disappeared, and the doublet of doublets at 5.05 ppm was converted into a doublet.

**2,5-Dimethyl-2,4-hexadiene-*3-d*$_1$ (1-*d*$_1$).** This compound was prepared according to the procedure shown below:



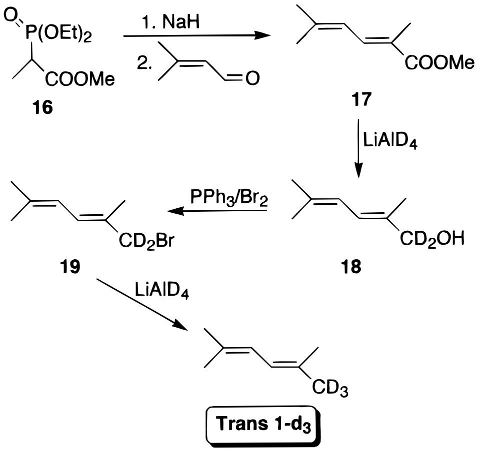
**3-Methyl-2-buten-1-ol-*1,1-d*$_2$ (12).** To a mixture of $LiAlD_4$ (0.42 g, 10 mmol) in dry ether (30 mL) under $N_2$ atmosphere at 0 °C was added dropwise a solution of ethyl 3-methylcrotonate (1.92 g, 15 mmol) in dry ether (10 mL). The mixture was heated under reflux for 1 h. The reaction was quenched at 0 °C by addition of 0.4 mL of $H_2O$, 0.4 mL of 15% NaOH, and 1.2 mL of $H_2O$, followed by filtration. The mixture was washed with 5% $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated to give the 3-methyl-2-buten-1-ol-*1,1-d*$_2$ (1.2 g, 90%). $^1$H NMR (250 MHz): $\delta$ 1.65 (d, $J = 1.2$ Hz, 3H), 1.72 (d, $J = 1.2$ Hz, 3H), 5.37 (br s, 1H).

**3-Methyl-2-butenal-*1-d*$_1$ (13).** To a cooled solution (0 °C) of pyridinium chlorochromate (3.88 g, 18 mmol) in dry $CH_2Cl_2$ (40 mL) was added dropwise a solution of 3-methyl-2-buten-1-ol-*1,1-d*$_2$ (1.2 g, 13.6 mmol) in $CH_2Cl_2$ (10 mL). The reaction mixture was stirred at room temperature for 3 h, followed by a bulb-to-bulb distillation. The solvent was evaporated without vacuum to afford 3-methyl-2-butenal-*1-d*$_1$ (0.72 g, 62%). $^1$H NMR (250 MHz): $\delta$ 1.91 (d, $J = 0.9$ Hz, 3H), 2.10 (d, $J = 0.9$ Hz, 3H), 5.80 (t, $J = 0.9$ Hz, 1H).

**2,5-Dimethyl-2,4-hexadiene-3-*d*$_1$ (1-*d*$_1$).** To a cooled mixture (0 °C) of isopropyltriphenylphosphonium bromide (3.47 g, 9 mmol) in dry THF (20 mL) was added a 5.7 mL solution of *n*-BuLi (1.6 M) in hexane under $N_2$ atmosphere. The solution was red due to the formation of triphenylphosphoranylidene isopropane (15). After the mixture was stirred for 1 h at room temperature, a solution of 3-methyl-2-butenal-*1-d*$_1$ (0.72 g, 8.4 mmol) in 5 mL of dry THF was added dropwise. The resulting mixture was stirred at room temperature for 3 h and poured into 50 mL of pentane. Triphenylphosphine oxide ($Ph_3PO$) precipitated. After filtration the solution was concentrated, and the residue was chromatographed (pentane) to give the **1-*d*$_1$** diene (0.65 g, 69%). $^1$H NMR (250 MHz): $\delta$ 1.72 (s, 6H), 1.78 (s, 6H), 5.96 (s, 1H). MS: *m*/*z* 111 ($M^+$, 100). The precursor to ylide phosphonium salt **14** was prepared by heating neat an excess of isopropyl bromide (4.92 g, 40 mmol) and triphenylphosphine (5.2 g, 20 mmol) in a sealed tube for 24 h at 140 °C. The phosphonium salt was collected as a white solid and was washed with hot toluene. $^1$H NMR (300 MHz): $\delta$ 1.29 (dd, $J_{H-P} = 19.0$ Hz, $J_{H-H} = 6.8$ Hz, 6H), 5.56 (m, 1H), 7.63−7.73 (m, 9H), 7.92−7.99 (m, 6H).

**2,5-Dimethyl-2,4-hexadiene-*1,1,1,2′,2′,2′-d*$_6$ (1-*d*$_6$).** This compound was prepared by Wittig coupling of triphenylphosphoranylidene-3-methyl-2-butene with acetone-*d*$_6$ in dry THF at 0 °C (65% yield). $^1$H NMR (250 MHz): $\delta$ 1.72 (s, 3H), 1.78 (s, 3H), 5.96 (s, 2H). Exact mass for $C_8H_8D_6$: calcd 116.1472, found 116.1452. The precursor to the ylide, the phosphonium salt, was prepared in 90% yield by heating 4-bromo-2-methyl-2-butene (Aldrich) and an equimolar amount of triphenylphosphine in a sealed tube for 12 h at 100 °C. The phosphonium salt was collected as a white solid and was washed with hot toluene. $^1$H NMR (250 MHz): $\delta$ 1.28 (d, $J = 3.9$ Hz, 3H), 1.67 (d, $J = 5.8$ Hz, 3H), 4.52 (dd, $J_{H-P} = 14.5$ Hz, $J_{H-H} = 7.7$ Hz, 2H), 5.13 (m, 1H), 7.63−7.90 (m, 15H).

**2,5-Dimethyl-2,4-hexadiene-*1,1,1-d*$_3$ (*trans*-1-*d*$_3$).** This compound was prepared according to the procedure shown below:



**(*E*)-Methyl-2,5-dimethyl-2,4-hexadienate (17).** This compound was prepared by the Wittig Horner reaction. A solution of methyl diethyl-2-phosphonopropionate (7.84 g, 35 mmol) in dry DME (20 mL) was added to a mixture of NaH (60% in paraffin oil, 1.43 g, 36 mmol) in dry DME (40 mL) under $N_2$ atmosphere at room temperature. To the resulting solution, after 1 h stirring at room temperature, was added dropwise a solution of 3-methyl-2-butenal (2.77 g, 33 mmol) in 10 mL of dry DME. After 1 h of stirring, the reaction was quenched with MeOH and washed with $H_2O$. After concentration, the resulting residue was chromatographed using a mixture of 4:1 hexanes−EtOAc as eluent and yielded exclusively *E*-ester **17** (3.85 g, 75%). $^1$H NMR (250 MHz): $\delta$ 1.84 (s, 3H), 1.85 (s, 3H), 1.87 (s, 3H), 3.70 (s, 3H), 6.07 (d with allylic splitting, $J_1 = 11.9$ Hz, $J_2 = 1.3$ Hz, 1H), 7.40 (d with allylic splitting, $J_1 = 11.9$ Hz, $J_2 = 1.0$ Hz, 1H).

**(*E*)-2,5-Dimethyl-2,4-hexadien-1-ol-*1,1-d*$_2$ (18).** To a mixture of $LiAlD_4$ (0.7 g, 16.7 mmol) in dry ether (40 mL) under $N_2$ atmosphere at 0 °C was added dropwise a solution of (*E*)-methyl-2,5-dimethyl-2,4-hexadienate (3.85 g, 25 mmol) in dry ether (10 mL). The mixture was stirred at room temperature for 3 h. The reaction was quenched at 0 °C by addition of 0.7 mL of $H_2O$, 0.7 mL of 15% NaOH, and 2.0 mL of $H_2O$ and filtered. The mixture was washed with 5% $NaHCO_3$

and brine, dried over $MgSO_4$, and concentrated to give *E*-alcohol **18** (2.55 g, 80%). $^1$H NMR (250 MHz): $\delta$ 1.62 (br s, $-$OH), 1.74 (s, 6H), 1.79 (s, 3H), 5.98 (d with allylic splitting, $J_1 = 11.2$ Hz, $J_2 = 1.3$ Hz, 1H), 6.19 (d with allylic splitting, $J_1 = 11.2$ Hz, $J_2 = 1.1$ Hz, 1H).

**(*E*)-1-Bromo-2,5-dimethyl-2,4-hexadiene-*1,1-d*$_2$ (19).** A 2 M solution of $Br_2$ (1 mL, 20 mmol) in dry $CH_2Cl_2$ was added under $N_2$ atmosphere to a solution of triphenylphosphine (5.24 g, 20 mmol) in dry $CH_2Cl_2$ at 0 °C. The $PPh_3Br_2$ complex immediately precipitated. After 1 h of stirring at room temperature, the reaction mixture was cooled at 0 °C, and a solution of (*E*)-2,5-dimethyl-2,4-hexadien-1-ol-*1,1-d*$_2$ (2.55 g, 19.9 mmol) in dry $CH_2Cl_2$ was added dropwise. The solution was concentrated, and the resulting solid residue afforded the *E*-bromide **19** (2.58 g, 68%) after vacuum distillation. $^1$H NMR (250 MHz): $\delta$ 1.75 (s, 3H), 1.80 (s, 3H), 1.84 (s, 3H), 5.94 (d, $J = 11.2$ Hz, 1H), 6.19 (d, $J_1 = 11.2$ Hz, 1H).

**2,5-Dimethyl-2,4-hexadiene-*1,1,1-d*$_3$ (*trans*-1-*d*$_3$).** To a mixture of $LiAlD_4$ (0.21 g, 5 mmol) in dry ether (15 mL) under $N_2$ atmosphere at 0 °C was added dropwise a solution of (*E*)-1-bromo-2,5-dimethyl-2,4-hexadiene-1,1-*d*$_2$ (2.58 g, 13.5 mmol) in dry ether (10 mL). The mixture was stirred at room temperature for 2 h. The reaction was quenched at 0 °C by addition of 0.2 mL of $H_2O$, 0.2 mL of 15% NaOH, and 0.6 mL of $H_2O$, followed by filtration of the inorganic salts. The mixture was washed with 5% $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated, and the residue was chromatographed (pentane) to give ***trans*-1-*d*$_3$** diene (0.95 g, 62%). $^1$H NMR (250 MHz): $\delta$ 1.72 (s, 6H), 1.78 (s, 3H), 5.96 (s, 2H). MS: *m*/*z* 113 ($M^+$, 100).

**(*E*)-2,4-Dimethyl-2,4-hexadiene (10).** This compound was prepared by Wittig coupling of triphenylphosphoranylidene isopropane with tiglic aldehyde in dry THF at 0 °C (75% yield). $^1$H NMR (500 MHz): $\delta$ 1.66 (d, $J = 6.8$ Hz, 3H), 1.70 (s, 3H), 1.74 (s, 3H), 1.75 (s, 3H), 5.3 (q, $J = 6.8$ Hz, 1H), 5.62 (s, 1H). $^{13}$C NMR (125 MHz): $\delta$ 13.57, 16.64, 19.38, 26.70, 122.79, 129.02, 131.57, 133.73. The synthesis of tisopropyltriphenylphosphonium bromide was previously described.

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**Supporting Information Available:** $^1$H NMR spectra for **1-*d*$_6$, 1-*d*$_1$, *trans*-1-*d*$_3$, (3a + 3b)** hydroperoxides, **3a, 3b, (4a + 4b), (5a + 5b), (7a + 7b + 7c), (8a + 8b), (7a + 7b + 7c + 8a + 8b), 10,** and **(10a + 10b)**; decoupled $^1$H NMR spectra of **(7a + 7b + 7c), (8a + 8b),** and **(7a + 7b + 7c + 8a + 8b)**; FAB-MS of **2, (4a + 4b), (5a + 5b),** and **(8a + 8b)**; HRMS of **1-*d*$_6$**; and GC-MS of **1-*d*$_1$** and ***trans*-1-*d*$_3$** (38 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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