

Photocycloaddition of Cyclic 1,3-Diones to C<sub>60</sub>Anton W. Jensen,<sup>#,†</sup> Anthony Khong,<sup>‡</sup> Martin Saunders,<sup>‡</sup> Steven R. Wilson,<sup>†</sup> and David I. Schuster<sup>\*,†</sup>

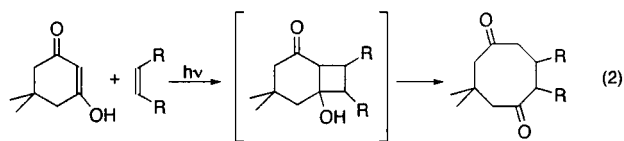
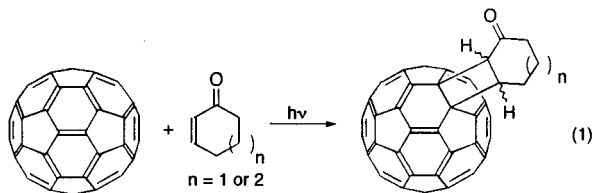
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**Abstract:** Irradiation of cyclic 1,3-diones (**1a** and **2a**) with C<sub>60</sub> in benzene leads to formation of two fused furanylfullerenes, one achiral (**3**) and the other chiral (**4**), as opposed to the expected De Mayo cyclooctane-1,3-dione addition product. The same products are obtained when 1,3-diones are replaced with trimethylsilyl-protected diones (**1b** and **2b**). The adduct structures were characterized by MS (ESI and MALDI), IR, UV, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>3</sup>He NMR spectroscopy. These fullerene adducts presumably are formed after initial [2 + 2] photocycloaddition, followed by either *intermolecular* oxidation of the cyclobutyl intermediates (**5–8**) by <sup>1</sup>O<sub>2</sub> to form **3** or *intramolecular* oxidation of the appended group by the triplet fullerene moiety of **5–8** to form **4**.

## Background

Cycloadditions constitute a convenient method for functionalization of buckminsterfullerene, C<sub>60</sub>.<sup>1</sup> Previously, we reported that enone [2 + 2] photocycloadditions with C<sub>60</sub> give rise to both *cis*- and *trans* fused [6,6] adducts (eq 1) via enone triplet excited states.<sup>2,3</sup> We wished to extend these studies by investigating De Mayo-type photoadditions to C<sub>60</sub>.<sup>4</sup> The De Mayo reaction consists of [2 + 2] photocycloaddition of the enol form of 1,3-diketones to alkenes, followed by ring opening of the resulting cyclobutanone to give cyclooctadiones (eq 2).



## Results and Discussion

It was found that irradiation of benzene solutions containing C<sub>60</sub> and either dimedone (**1a**), 1,3-cyclohexanedione (**2a**), or

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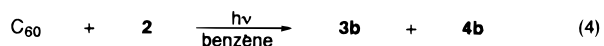
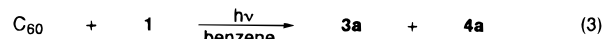
(1) Hirsch, A. *The Chemistry of Fullerenes*; Thieme Medical Publishers: New York, 1994.

(2) A [6,6] fullerene cycloadduct is one in which the adduct has added across a fullerene double bond between two six-membered rings of the fullerene sphere.

(3) (a) Wilson, S. R.; Kaprinidis, N.; Wu, Y.; Schuster, D. I. *J. Am. Chem. Soc.* **1993**, *115*, 8495. (b) Wilson, S. R.; Wu, Y.; Kaprinidis, N. A.; Schuster, D. I. *J. Org. Chem.* **1993**, *58*, 6548. (c) Schuster, D. I.; Cao, J.; Kaprinidis, N.; Wu, Y.; Jensen, A. W.; Lu, Q.; Wang, H.; Wilson, S. R. *J. Am. Chem. Soc.* **1996**, *118*, 5639.

(4) Weedon, A. C. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; [2 + 2]-Photocycloaddition Reactions of Enolized 1,3-Diketones and 1,2-Diketones with Alkenes: *The de Mayo Reaction*; CRC Press Inc.: Boca Raton, 1995; Chapter 54.

their respective trimethylsilyl enol ethers<sup>5</sup> (**1b**, **2b**) gave two products, **3a,b** and **4a,b** (see eqs 3 and 4).<sup>6</sup> These adducts were



conveniently detected by either TLC or HPLC (Buckyclutcher<sup>7</sup> column) with toluene as the eluent and are readily separable by flash chromatography on silica gel. Both **3a** and **3b** are brownish-red in dilute solutions and less polar than **4a** and **4b**, which are more yellowish. In general, irradiation gave higher conversions to **3** and **4** with **1b** or **2b** than with **1a** or **2a**. Irradiations of silylated enones gave yields of between 6% and 21% for each product at conversions between 16% and 54% (yields are not based on conversion). Mass spectral analysis (ESI and MALDI) of the adducts confirmed that both isomers are monoadducts.

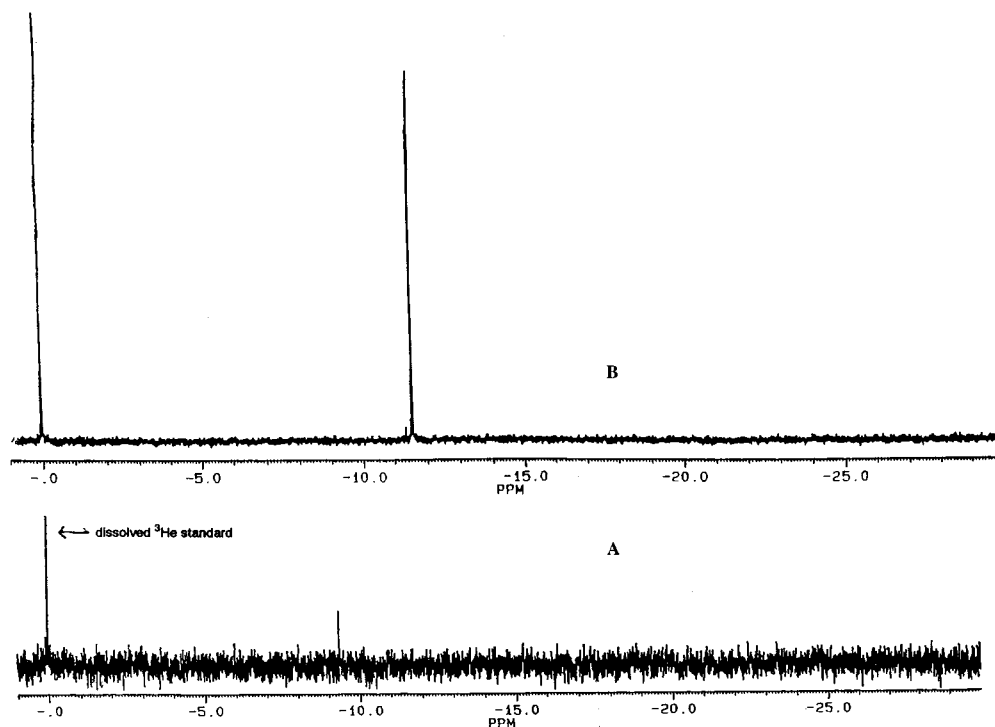
<sup>3</sup>He NMR spectroscopy on derivatives of <sup>3</sup>He@C<sub>60</sub> in which <sup>3</sup>He is trapped inside the C<sub>60</sub> cage has proven useful in probing the magnetic field inside the fullerene cage.<sup>8</sup> Thus, [6,6] monoadducts have <sup>3</sup>He resonances in a restricted range between -9.10 and -9.66 ppm relative to dissolved <sup>3</sup>He,<sup>8b</sup> excluding fused three-ring structures.<sup>8d</sup> When <sup>3</sup>He@C<sub>60</sub> was subjected to our irradiation conditions with **1b**, two products were again observed. The <sup>3</sup>He NMR spectra of the crude mixture in methylnaphthalene showed peaks at -9.37 and -11.56 ppm, apart from unreacted <sup>3</sup>He@C<sub>60</sub> (-6.35 ppm). After isolation of <sup>3</sup>He@**3a** and <sup>3</sup>He@**4a**, their individual <sup>3</sup>He NMR spectra in methylnaphthalene were recorded (Figure 1). The <sup>3</sup>He@**3a** peak is at -9.37 ppm, which is in the range of [6,6] closed

(5) Torkelson, S.; Ainsworth, C. *Synthesis* **1976**, 722. See note on synthesis in Experimental Section.

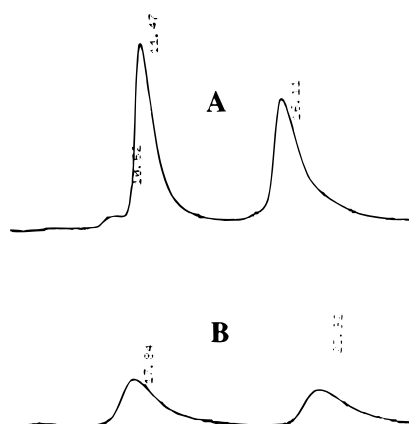
(6) Schuster, D. I.; Lem, G.; Jensen, A. W.; Hwang, E.; Safonov, I.; Courtney, S. H.; Wilson, S. R. *Proc. Electrochem. Soc.* **1996**, PV 96-10, 287.

(7) Welch, C. J.; Pirkle, W. H. *J. Chromatogr.* **1992**, 609, 89. (This column is commercially available from the Regis Chemical Company, Morton Grove, IL.)

(8) (a) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Mroczkowski, S.; Freedberg, D. I.; Anet, F. A. L. *Nature* **1994**, 367, 256. (b) Saunders, M.; Cross, R. J.; Jiménez-Vázquez, H. A.; Shimshi, R.; Khong, A. *Science* **1996**, 271, 1693. (c) Cross, J.; Jiménez-Vázquez, H. A.; Lu, Q.; Saunders, M.; Schuster, D. I.; Wilson, S. R.; Zhao, H. *J. Am. Chem. Soc.* **1996**, *118*, 11454; (d) Smith, A. B., III; Strongin, R. M.; Brard, L.; Romanow, W. J.; Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 1083.



**Figure 1.** (A)  $^3\text{He}$  NMR trace of  $\text{He}@3\mathbf{a}$  in methylnaphthalene. (B)  $^3\text{He}$  NMR trace of  $\text{He}@4\mathbf{a}$  in methylnaphthalene.



**Figure 2.** (A) HPLC separation of enantiomers of  $4\mathbf{a}$  with use of a (*S,S*)-Whelk-O column (Regis Chemical Co., Morton Grove, IL) with toluene as the eluent. (B) HPLC separation of enantiomers of  $4\mathbf{b}$  with use of a (*S,S*)-Whelk-O column (Regis Chemical Co., Morton Grove, IL) with toluene as the eluent.

adducts,<sup>3c,8b</sup> while the peak for  $^3\text{He}@4\mathbf{a}$  is at  $-11.56$  ppm, outside the range of [6,6] closed monoadducts as well as [6,5] open methylene-bridged adducts ( $-6.63$  ppm),<sup>8b</sup> suggestive of a novel structure for fullerene monoadduct  $4\mathbf{a}$ .

Samples of pure  $3\mathbf{a}$  or  $3\mathbf{b}$  dissolved in toluene showed one peak on both achiral<sup>7</sup> and chiral<sup>9</sup> HPLC columns, while samples of  $4\mathbf{a}$  and  $4\mathbf{b}$  showed one peak on the achiral column and two baseline resolved peaks (1:1 ratio) on the chiral column (Figure 2). IR spectra of both  $3$  and  $4$  show peaks at around  $1660$  and  $1640$   $\text{cm}^{-1}$ . Although this is lower than expected for 1,3-cyclooctanediones, it was initially thought that fusion to fullerenes might result in a shift to lower frequencies. UV spectra of  $3$  and  $4$  in benzene exhibit a shoulder at  $430$  nm, which is considered to be indicative of [6,6] closed structures.<sup>10</sup>

(9) Pirkle, W. H.; Welch, C. J.; Lamm, B. *J. Org. Chem.* **1992**, *57*, 3856. (This column is commercially available from the Regis Chemical Company, Morton Grove, IL.)

(10) Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231.

However, this assignment is not unequivocal in light of recent reports that compounds thought not to be [6,6] closed adducts also show a shoulder at  $430$  nm.<sup>11,12</sup>

The  $^1\text{H}$  NMR spectra of  $4\mathbf{a}$  and  $4\mathbf{b}$  in  $\text{CS}_2:\text{CDCl}_3$  (1:1) contain similar 2H doublets of doublets (dds) at  $6.3$  ppm. The spectrum of  $4\mathbf{a}$  contains two additional 2H dds centered at  $2.85$  and  $2.6$  ppm, respectively, along with nonequivalent 3H methyl signals at  $1.5$  and  $1.3$  ppm. The spectrum of  $4\mathbf{b}$  contains three complex 2H multiplets centered at  $3.0$ ,  $2.7$ , and  $2.4$  ppm. Due to the poor solubility of  $4\mathbf{a}$  and  $4\mathbf{b}$  ( $4\mathbf{b}$  being the more polar and less soluble), a  $^{13}\text{C}$  NMR spectrum was attainable only with a  $^{13}\text{C}$  enriched sample of  $4\mathbf{a}$ , prepared by irradiating a mixture of 10% and 20%  $^{13}\text{C}$ -enriched  $\text{C}_{60}$  and unenriched silylated dimerone as described above. The  $^{13}\text{C}$  NMR spectrum of  $4\mathbf{a}$  (see Supporting Information) shows 40 to 56 peaks in the fullerene  $\text{sp}^2$  region, two large peaks in the fullerene  $\text{sp}^3$  region at  $54.3$  and  $56.0$  ppm, and two smaller peaks at  $100$  and  $64$  ppm. The spectrum is indicative of an asymmetric fullerene structure with two to four fullerene  $\text{sp}^3$  carbons, which suggested initially that  $4$  might have a [6,5] closed structure.<sup>6</sup>

The  $^1\text{H}$  NMR spectrum of  $3\mathbf{a}$  in  $\text{CS}_2:\text{CDCl}_3$  (1:1) is composed of only three singlets at  $3.0$ ,  $2.6$ , and  $1.4$  ppm with a relative integration of 1:1:3, while that of  $3\mathbf{b}$  has two triplets at  $3.2$  and  $2.7$  ppm leaning toward a pentet at  $2.5$  ppm. Thus, adducts  $3\mathbf{a}$  and  $3\mathbf{b}$  are missing a methylene signal expected from the presumed [6,6]-fused cyclooctanedione structure. One possibility was that this might be due to fast conformational interconversion at room temperature, leading to broadening of the signal for the methylene group adjacent to the fullerene.<sup>13</sup> However, variable-temperature  $^1\text{H}$  NMR over a range of  $-50$

(11) (a) Hummelen, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 7003. (b) Dong, G.-X.; Li, J.-S.; Chan, T.-H. *J. Chem. Soc., Chem. Commun.* **1995**, 1725.

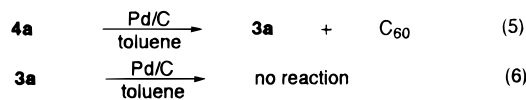
(12) (a) It was recently suggested by Wudl, Hummelen, and co-workers that a "broad, rounded band at  $442$  nm is typical of fullerenes with a double-bond endocyclic to a pentagon."<sup>12b</sup> Thus, a broad band in this region may be characteristic of a double-bond endocyclic to a pentagon, while a sharp band may correspond to something else. (b) Hummelen, J. C.; Knight, B.; Pavlovich, J.; Gonzalez, R.; Wudl, F. *Science* **1995**, *269*, 1554.

(13) For an example of such an effect, see: An, Y.-Z.; Anderson, J. L.; Rubin, Y. *J. Org. Chem.* **1993**, *58*, 4799.

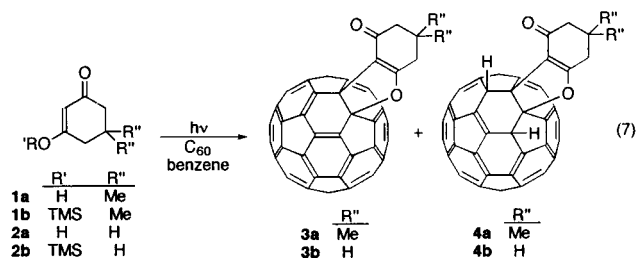
to +40 °C did not reveal any new peaks. The <sup>13</sup>C NMR spectrum of **3a** shows 30 peaks in the sp<sup>2</sup> fullerene region and 2 peaks in the sp<sup>3</sup> fullerene region. It was not possible to obtain a <sup>13</sup>C NMR spectrum of **3b** due to its poor solubility in CDCl<sub>3</sub>/CS<sub>2</sub>.

Very recently, Eguchi and co-workers reported a method for preparation of dihydrofuranylfullerenes via reaction of 1,3-diones with piperidine and C<sub>60</sub> at room temperature for 35 h in chlorobenzene.<sup>14</sup> No mechanism was proposed for this thermal addition reaction.<sup>14</sup> Indeed, dione **1a** gave adduct **3a** when subjected to the Eguchi reaction conditions. The identity of photoadduct **3a** with the Eguchi reaction product was confirmed by TLC, co-injection on the achiral HPLC column, and comparison of <sup>1</sup>H NMR spectra. The chiral photoproduct **4a** was not formed under Eguchi's conditions. The close similarity of the IR spectra of **3** and **4** suggested that **4** is structurally related to **3**. Both possess 1660- and 1640-cm<sup>-1</sup> bands characteristic of enone carbonyls and vinyl ethers, respectively.<sup>15</sup> Confirmation of this structural relationship was obtained by dehydrogenation of **4a** under conditions similar to those used by Cahill and co-workers to reform C<sub>70</sub> from C<sub>70</sub>H<sub>2</sub>.<sup>16</sup> Thus, stirring **4a** over Pd/C in toluene afforded **3a** and C<sub>60</sub> (eq 5). Adduct **3a** was unreactive under the same conditions (eq 6).<sup>17</sup>

We therefore propose that adducts **4** have the structure shown



in eq 7. The 2H dd centered at 6.3 ppm is in the range for protons bonded to fullerene carbons, while the coupling constant of ≈1.8 Hz is consistent with a 1,4 relationship of the protons



on the fullerene core.<sup>18</sup> The two large peaks in the <sup>13</sup>C NMR spectrum of **4a** may be assigned to tertiary sp<sup>3</sup> fullerene carbons, while the quaternary fullerene carbons are assigned to the smaller peaks in the same region. Peaks near 100 ppm can be assigned to sp<sup>3</sup> fullerene carbons adjacent to oxygen (100 ppm in **4a**, 95 ppm for **3a**) by analogy to the literature.<sup>14,19,20</sup> Finally, the <sup>3</sup>He@**4a** peak at -11.56 ppm is in the range of the

(14) Ohno, M.; Yashiro, A.; Eguchi, S. *J. Chem. Soc., Chem. Commun.* **1996**, 291.

(15) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; John Wiley & Sons: New York, 1991; pp 113–115.

(16) Henderson, C. C.; Rohlfling, C. M.; Gillen, K. T.; Cahill, P. A. *Science* **1994**, *264*, 397.

(17) Compounds **3a** and **4a** could not be interconverted by our standard photoreaction conditions nor could they be interconverted thermally. However, we did observe decomposition of both products photochemically and thermally. Under photochemical conditions, **4a** is more labile than **3a**. Furthermore, irradiation of a mixture of **3a** and **4a** after bubbling with O<sub>2</sub> did not cause conversion of **4a** to **3a**.

(18) From comparison of the <sup>1</sup>H NMR spectra at 200 and 500 MHz, the coupling constants could be unambiguously determined (*J* = 1.83 Hz for **4a**; *J* = 1.77 Hz for **4b**). For comparison, the AA'BB' splitting pattern of 1,2,3,4-C<sub>60</sub>H<sub>4</sub> exhibits an A–A' coupling of 1.7 Hz (see: Henderson, C. C.; Rohlfling, C. M.; Assink, R. A.; Cahill, P. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 786).

**Table 1.** Product Dependence on Dissolved O<sub>2</sub>

| product        | photoproduct yields after initial deoxygenation or oxygenation <sup>a</sup> (%) |                |                         |
|----------------|---|----------------|-------------------------|
|                | freeze/pump/thaw <sup>b</sup>   | argon bubbling | O <sub>2</sub> bubbling |
| <b>3a</b>      | 2.6   | 4.6            | 0                       |
| <b>4a</b>      | 7.1   | 4.9            | 0                       |
| <b>3a + 4a</b> | 9.7   | 9.5            | 0                       |

<sup>a</sup> Yields are based on integration of HPLC peaks. <sup>b</sup> At least three cycles with a rough pump down to pressures of about 15 Torr.

corresponding peak for <sup>3</sup>He@1,2,3,4-C<sub>60</sub>H<sub>4</sub>.<sup>21</sup> It should be noted that the bonding pattern in **4** is structurally different from that of 1,2,3,4-C<sub>60</sub>H<sub>4</sub>, in that **4** is a bis-[6,5] closed C<sub>60</sub> adduct while 1,2,3,4-C<sub>60</sub>H<sub>4</sub> has a bis-[6,6] closed structure. Furthermore, it is unlikely that compound **4** is a 1,2,3,4-C<sub>60</sub> adduct with hydrogens at C<sub>1</sub> and C<sub>4</sub>, since **3**, a [6,6] closed adduct, is formed upon treatment of **4** with Pd/C. Low yields and poor solubility prevented us from obtaining <sup>13</sup>C and <sup>3</sup>He NMR data on adduct **4b**, but the similarity of its <sup>1</sup>H NMR and IR spectral data to that of **4a** (see Supporting Information) indicates that **4b** possesses an analogous structure.

The ratio of **4a** to **3a** is dependent on the method used for removal of oxygen prior to irradiation. When argon bubbling was used for deoxygenation, the **4a/3a** ratio was approximately 1:1 (Table 1). When several freeze–pump–thaw cycles were used to outgas samples, the **4a/3a** ratio was about 3:1 while the overall conversion remained the same. Bubbling with O<sub>2</sub> prior to the photoreaction completely quenched the formation of both **3a** and **4a**.

Our suggested mechanism for formation of **3** and **4** is shown in Scheme 1. The first step involves [2 + 2] photocycloaddition<sup>3</sup> across a [6,6] bond to form cyclobutanols (**5** and **6**) or cyclobutyl TMS ethers (**7** and **8**) from **1a**, **2a**, **1b**, and **2b**, respectively. Since the photoaddition is completely quenched when oxygen is bubbled through the solution prior to irradiation (see Table 1), triplet states of the enones are implicated as reaction intermediates, consistent with the mechanism proposed previously for [2 + 2] photocycloadditions to C<sub>60</sub>.<sup>3</sup> Oxidation of the cyclobutyl intermediate by <sup>1</sup>O<sub>2</sub> (formed from C<sub>60</sub> triplets and dioxygen)<sup>22</sup> would give radical **9**. Cleavage to **10** followed by cyclization would give furanyl radical **11**,<sup>23</sup> which would give **3** after abstraction of a hydrogen atom by <sup>1</sup>O<sub>2</sub> or a peroxy radical. This mechanism is consistent with the decreased yields of **3** following initial freeze–pump–thaw outgassing of solutions prior to exposure to light. A competitive process involves formation of fullerene triplets by absorption of a second photon by **5–8**, followed by intramolecular hydrogen atom abstraction to give diradical **12**. Cleavage and cyclization as above would lead to the furanyl diradical **14**,<sup>23</sup> which could go directly to **4** via a thermodynamically driven 1,3-H atom shift.

The difference in energies between the transition states for intramolecular hydrogen abstraction upon excitation of **5** and **6** (five-membered ring) vs **7** and **8** (seven-membered ring) may account for the difference in reaction efficiency between the silylated (**1b** and **2b**) and unsilylated (**1a** and **2a**) starting materials (Figure 3).

(19) Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McCauley, J. P., Jr.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 1103.

(20) Sun, Ya-Ping, Department of Chemistry, Clemson University, unpublished results.

(21) The exact shift of 1,2,3,4-C<sub>60</sub>H<sub>4</sub> is unknown but lies between -10.30 and -12.79 ppm.<sup>8c</sup>

(22) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11.

(23) Suginome, H.; Liu, C. F.; Seko, S.; Kobayashi, K. *J. Org. Chem.* **1988**, *53*, 5952.

## Scheme 1

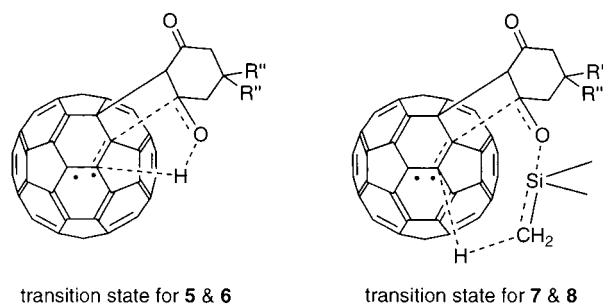
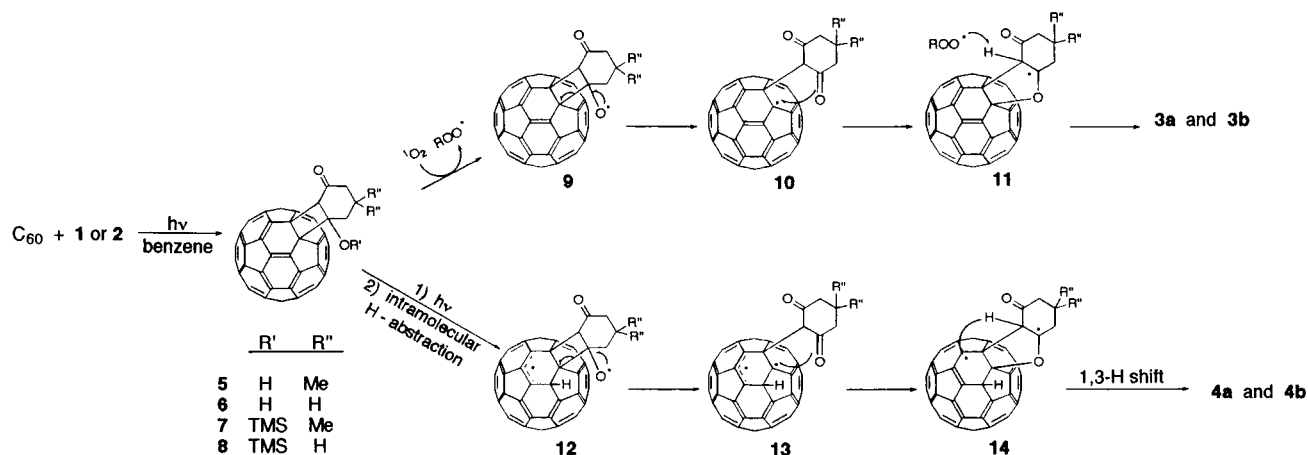
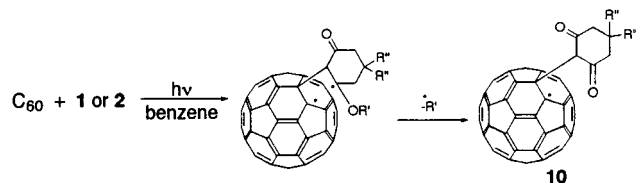


Figure 3. Transition states for H-abstraction by the fullerene moiety.

## Scheme 2



An alternative mechanism for formation of **3**, involving disproportionation of the initially formed triplet biradical to give dione intermediate **10** directly (see Scheme 2), was proposed by a reviewer, who noted that such disproportionations are common in cases where one radical site is stabilized.

Compound **4** represents a unique type of fullerene adduct in which four adjacent stereogenic centers are formed on the fullerene sphere. Only the (*S,S,R,R*)/(*R,R,S,S*) enantiomeric pair can be formed due to the nature of the reaction. The formation of **4** illustrates the need to consider the possibility of intramolecular hydrogen atom abstraction from adducted groups by a triplet excited fullerene moiety during photoreactions. This leads to the prediction that it may be possible to synthesize De Mayo-type photoadducts of fullerenes with use of enol ethers of 1,3-diones in which the protecting group lacks abstractable hydrogens.

## Experimental Section

**General Considerations.** HPLC was carried out with toluene as eluent at 1 mL/min and UV detection at 340 nm. ESI-mass spectrometry was carried out on a Vestec Model 201 ESI-mass spectrometer. UV-vis spectra were determined in benzene solution. For IR spectroscopy samples were prepared by dissolving each of the respective adducts in carbon disulfide and allowing a drop of the solution to dry on a salt plate and allowing the CS<sub>2</sub> to evaporate prior to analysis. MALDI-MS was performed on a Krato Kompact MALDI 1. <sup>1</sup>H NMR and <sup>13</sup>C NMR were carried out on Varian 200-MHz and Varian Utility 500-MHz spectrometers (NYU). <sup>3</sup>He NMR spectra were taken at Yale

University on a Bruker AM-500 spectrometer.<sup>8</sup> C<sub>60</sub> was obtained from different sources, including Terrasimco Incorporated.

**Synthesis of 1b and 2b.** In repeating this procedure from the literature,<sup>5</sup> we found that care must be taken to perform the distillation in an oxygen-free environment and at as low a pressure as possible, because the desired products tend to decompose. For the photoaddition to C<sub>60</sub>, it is not necessary to distill **1b** and **2b**, which are formed in quantitative crude yields. One only needs to evaporate off the excess HMDS. However, both **1b** and **2b** should also be used within a week of their syntheses, since they slowly decompose on standing (*t*<sub>1/2</sub> is about 2 or 3 weeks).

**General Procedures for Photoaddition of 1a, 1b, 2a, or 2b to C<sub>60</sub>** (a specific experimental protocol for the case of photoaddition of **1b** is given below). The reaction light source is a Hanovia 450-W medium-pressure Hg arc lamp cooled by a quartz jacket fitted with a Pyrex filter between the lamp and the inner wall of the jacket. The solvent was reagent grade benzene purchased from Fischer. Sample sizes were either 5, 25, or 160 mL with C<sub>60</sub> concentrations of between 0.2 and 0.4 mM and concentrations of **1** or **2** between 10.2 and 12.7 mM. Under these conditions the enone absorbs a significant portion of light in the presence of C<sub>60</sub> (still not more than 10% though). Each sample was sonicated until the desired solubility was reached. Normally samples were bubbled with argon for 1/2 h and subsequently irradiated in Pyrex test tubes of varying sizes at a distance of about 1 cm from the water-cooled lamp assembly described above. Samples were typically irradiated for 15 to 30 min. Over-irradiation led to diminished yields of **4**, which is apparently less photostable than **3**.

**Irradiation of C<sub>60</sub> and 1b.** To a Pyrex test tube was added 6.0 mg (8.3 μmol) of C<sub>60</sub>, 60.0 mg (0.283 mmol) of **1b**, and 25 mL of reagent grade benzene. The solution was sonicated until the C<sub>60</sub> completely dissolved and then bubbled with argon for 1/2 h. The test tube was positioned at a distance of about 1 cm from the water-cooled lamp assembly and irradiated for 15 min. The crude sample was concentrated on a rotovap and dissolved in just enough CS<sub>2</sub> to dissolve the colored portion of the crude mixture. The colorless solid residue contained no fullerenes. The products were then separated by flash column chromatography (Pasteur Pipet Column) with use of CS<sub>2</sub> to elute unreacted C<sub>60</sub> (purple) and toluene to separate **3a** (brownish-red) from **4a** (yellowish). After removal of toluene, the products were washed with diethyl ether to remove traces of dioctyl phthalate, dissolved by toluene from the tygon tubing during chromatography, which interfered with spectral analysis. The <sup>1</sup>H and <sup>13</sup>C NMR spectra for **3a** and **4a** in CDCl<sub>3</sub>/CS<sub>2</sub> are shown in the Supporting Information and are described above in the Results and Discussion section. Assignment of the fullerene sp<sup>3</sup> carbon adjacent to the oxygen atom is based on literature precedent.<sup>14,19,20</sup>

**Dehydrogenation of 4a.** A few milligrams of 10% Pd/C was added to a round-bottom flask which was then flushed with argon. About 5 mL of a dilute solution of **4a** in toluene was added to the flask, and the contents were stirred for 1 h at room temperature. Bubbling was observed during the course of the reaction. After separation of the catalyst by gravity filtration, the remaining solution was concentrated.

HPLC analysis indicated that **4a** was completely converted under these conditions to a mixture of **3a** and C<sub>60</sub>. Adduct **3a** was unreactive under identical reaction conditions.

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**Supporting Information Available:** UV-vis spectra for **3a**, **4a**, **3b**, and **4b**; IR spectra for **3a**, **4a**, **3b**, and **4b**; ESI-MS of tagged derivatives of **3a**, **4a**, and **3b**; MALDI-MS of **3a** and **4a**; <sup>1</sup>H NMR spectra for **3a**, **4a**, **3b**, and **4b**; <sup>13</sup>C NMR spectra of **3a** and **4a** (45 pages). See any current masthead page for ordering and Internet access instructions.

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