

Stereochemistry and Isotope Effects of the [2 + 2] Photocycloadditions of Arylalkenes to C₆₀. A Stepwise Mechanism

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Since the discovery of the C₆₀¹ (buckminsterfullerene) and its isolation in large quantities,^{2,3} a remarkable array of its reactions have been studied in the last six years. Whereas many [4 + 2]^{4–6} and [3 + 2]^{4,7–9} cycloadditions have been reported, whose monoadducts have been isolated and well characterized, only a few [2 + 2] cycloadditions to C₆₀ are known^{10–12} and, other than product isolation and characterization, little is known of their mechanism. For example, Foote and co-workers reported recently that the [2 + 2] photocycloaddition of ynamines to the triplet excited state¹³ of C₆₀ possibly proceeds through a charge transfer mechanism.^{11c} However, as they stated, attempts to observe transient intermediates have not been successful.

We report here for the first time the stereochemistry and the secondary isotope effects of a novel [2 + 2] photocycloaddition between arylalkenes and C₆₀. These results shed light on the mechanism of [2 + 2] photocycloadditions of arylalkenes to C₆₀.

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(2) Kratschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167.

(3) Scrivens, W. A.; Bedworth, P. V.; Tour, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 7917.

(4) Hirsch, A. *Synthesis* **1995**, 895–913.

(5) (a) Kräutler, B.; Puchberger, M. *Helv. Chim. Acta* **1993**, *76*, 1626. (b) Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretzyan, C. *J. Am. Chem. Soc.* **1993**, *115*, 344. (c) An, Y. Z.; Anderson, J. L.; Rubin, Y. *J. Org. Chem.* **1993**, *58*, 4799. (d) Linssen, T. G.; Dürr, K.; Hirsch, A.; Hanack, M. *J. Chem. Soc., Chem. Commun.* **1995**, 103. (e) Khan, S. I.; Oliver, A. M.; Paddon-Row, M. N.; Rubin, Y. *J. Am. Chem. Soc.* **1993**, *115*, 4919.

(6) (a) Gügel, A.; Kraus, A.; Spikermann, J.; Belik, P.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 559. (b) Iyoda, M.; Sultana, F.; Sasaki, S.; Yoshida, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1929. (c) Zhang, X.; Foote, C. S. *J. Org. Chem.* **1994**, *59*, 5235.

(7) (a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *Science* **1991**, *254*, 1186. (b) Prato, M.; Suzuki, T.; Wudl, F.; Lucchini, V.; Maggini, M. *J. Am. Chem. Soc.* **1993**, *115*, 7876. (c) Isaacs, L.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 2454. (d) Prato, M.; Bianco, A.; Maggini, M.; Scorrano, G.; Toniolo, C.; Wudl, F. *J. Org. Chem.* **1993**, *58*, 5578. (e) Diederich, F.; Isaacs, L.; Philp, D. *J. Chem. Soc., Perkin. Trans. I* **1994**, 391.

(8) (a) Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231. (b) Prato, M.; Li, Q.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148. (c) Tokuyama, H.; Nakamura, M.; Nakamura, E. *Tetrahedron Lett.* **1993**, *34*, 7429. (d) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798. (e) Maggini, M.; Scorrano, G.; Bianco, A.; Toniolo, C.; Sijbesma, R. P.; Wudl, F. *J. Chem. Soc., Chem. Commun.* **1994**, 305.

(9) (a) Vasella, A.; Uhlmann, P.; Waldraff, C. A.; Diederich, F.; Thilgen, C. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1388. (b) An, Y. Z.; Rubin, Y.; Schaller, C.; McEivany, S. W. *J. Org. Chem.* **1994**, *59*, 2927. (c) Anderson, H. L.; Faust, R.; Rubin, Y.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1366.

(10) Hoke, S. H., II; Molstad, J.; Dilattato, D.; Jay, M. J.; Carlson, D.; Kahr, B.; Cooks, R. G. *J. Org. Chem.* **1992**, *57*, 5069.

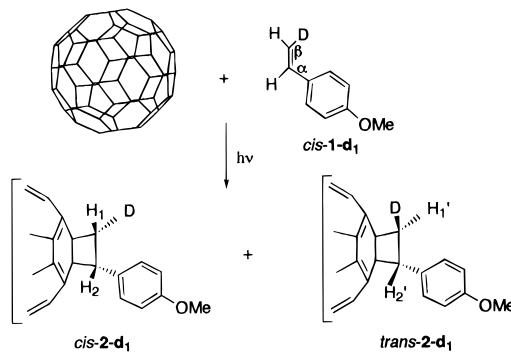
(11) (a) Zhang, X.; Romero, A.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 11024. (b) Zhang, X.; Romero, A.; Foote, C. S. *J. Am. Chem. Soc.* **1995**, *117*, 4271. (c) Zhang, X.; Fan, A.; Foote, C. S. *J. Org. Chem.* **1996**, *61*, 5456.

(12) (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.; Schuster, D. I. *J. Org. Chem.* **1993**, *58*, 6548.

(13) Previous results have demonstrated that the triplet excited state of C₆₀ has a reduction potential near 0.98 eV (36 Kcal/mol) VS SCE and is formed with a quantum yield of nearly unity: Arbogast, J. W.; Darmanyan, A. O.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11.

Although thermal [$\pi 2_s + \pi 2_a$] cycloadditions are symmetry allowed,¹⁴ they occur rarely if at all. In contrast, suprafacial [2 + 2] photochemical cycloadditions are allowed and proceed easily with retention of stereochemistry. To test the stereochemistry on the [2 + 2] cycloaddition of arylalkenes to C₆₀, *cis*-1-(*p*-methoxyphenyl)-ethylene-2-*d*₁, *cis*-1-*d*₁, was prepared in greater than 96% isomeric purity.^{15,16} This substrate is ideal for this purpose because it bears a deuterium *cis* to the aryl group, which allows elucidation of the stereospecificity on the reaction.

In the absence of light, a mixture of C₆₀ and a 200-fold excess of *cis*-1-*d*₁ did not react when heated for 12 h at reflux in deoxygenated toluene. Upon irradiation at $\lambda > 500$ nm, with a Xenon lamp Variac Eimac Cermax 300W, a 30% of the [2 + 2] adduct, as monitored by HPLC, was obtained after 30 min based on the recovered C₆₀. The adduct, which was stable at room temperature (no traces of decomposition or cycloreversion products were detected by ¹H NMR and HPLC after standing for several days), was purified by flash column chromatography (toluene/hexane 2/1) and characterized by ¹H NMR¹⁷ (Figure 1) and FAB-MS [*m/z* 856 (M + 1, 8), 720 (M - 135, 100)]. A synchronous cycloaddition is expected to give only one product, *cis*-2-*d*₁. However, two doublets of equal intensity due to H₁ and H₁' were observed in the ¹H NMR spectrum at 4.3 and 4.25 ppm, respectively ($J_{H_1H_2} = 10.4$ Hz, $J_{H_1'H_2'} = 8.3$ Hz). Therefore, the lack of any stereoselectivity mitigates against a synchronous one-step mechanism for this cycloaddition reaction.



A plausible mechanism that could account for the ¹H NMR data includes the formation of dipolar or diradical intermediate in a rate determining step (see below), followed by fast rotation of the aryl moiety around the former double bond, leading to the [2 + 2] adducts *cis*-2-*d*₁ and *trans*-2-*d*₁. This intermediate may or may not be preceded by an electron or charge transfer complex between the triplet excited state of C₆₀ and the alkene.

(14) Hoffmann, R. W.; Woodward, R. B. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

(15) Alkenes *cis*-1-*d*₁, 3-*d*₁, and 3-*d*₃ were prepared as follows: Reaction of 4'-methoxybenzaldehyde with bromomethylenetriphenylphosphorane gave *cis*-1-bromo-2-(*p*-methoxyphenyl)ethylene in >96% isomeric purity. Transmetalation of *cis*-1-bromo-2-(*p*-methoxyphenyl)ethylene with *tert*-butyllithium followed by D₂O quench gave *cis*-1-*d*₁ in >96% isomeric purity. ¹H NMR (CDCl₃) δ 3.81 (s, 3H), 5.11 (d, $J = 10.9$ Hz, 1H), 6.66 (td, $J_{HH} = 10.9$ Hz, $J_{DH} = 2.6$ Hz, 1H), 6.86 (dd, $J_1 = 6.8$ Hz, $J_2 = 2.1$ Hz, 2H), 7.35 (dd, $J_1 = 6.8$ Hz, $J_2 = 2.1$ Hz, 2H). MS *m/z* 135 (M⁺, 100). Reduction of 4'-methoxyacetophenone with LiAlD₄, followed by dehydration gave alkene 3-*d*₁. ¹H NMR (CDCl₃) δ 3.81 (s, 3H), 5.11 (d, $J = 0.9$ Hz, 1H), 5.6 (dt, $J_{DH} = 2.6$ Hz, $J_{HH} = 0.9$ Hz, 1H), 6.86 (dd, $J_1 = 6.8$ Hz, $J_2 = 2.1$ Hz, 2H), 7.35 (dd, $J_1 = 6.8$ Hz, $J_2 = 2.1$ Hz, 2H). MS *m/z* 135 (M⁺, 100). Addition of CD₃MgI to the *p*-methoxybenzaldehyde followed by PCC oxidation gave 4'-methoxyacetophenone-*d*₃ in good yield. Subsequent LiAlD₄ reduction of 4'-methoxyacetophenone-2,2,2-*d*₃, followed by dehydration gave alkene 3-*d*₃. ¹H NMR (CDCl₃) δ 3.81 (s, 3H), 6.86 (dd, $J_1 = 6.8$ Hz, $J_2 = 2.1$ Hz, 2H), 7.35 (dd, $J_1 = 6.8$ Hz, $J_2 = 2.1$ Hz, 2H), MS *m/z* 137 (M⁺, 100).

(16) Matsumoto, M.; Kuroda, K. *Tetrahedron Lett.* **1980**, *21*, 4021.

(17) ¹H NMR of the [2 + 2] adduct from 3-*d*₀ and C₆₀: (CS₂:C₆D₆ 3:1), δ 3.62 (s, 3H), 4.22 (m, 2H), 5.46 (dd, $J_1 = 10.4$ Hz, $J_2 = 8.6$ Hz, 1H), 7.29 (AA' MM', $J_1 = 8.6$ Hz, $J_2 = 3.1$ Hz, $J_3 = 2.1$ Hz, 4H).

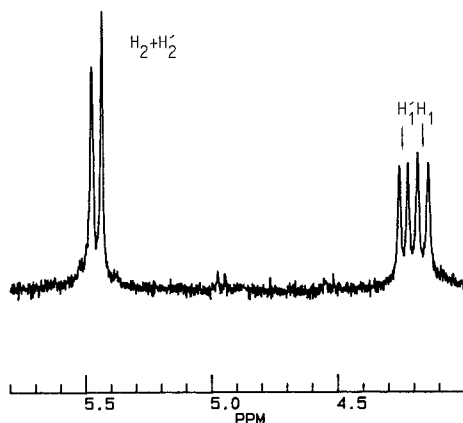
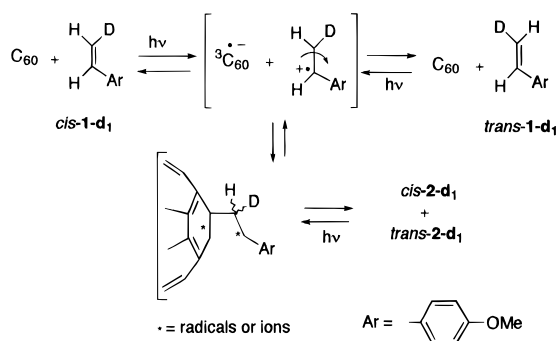
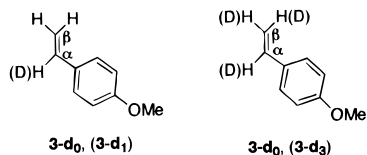


Figure 1. ^1H NMR spectrum of [2 + 2] adducts *cis-2-d*₁ and *trans-2-d*₁ from C_{60} and *cis-1-d*₁.

Interruption of the reaction after 30 min and analysis of the unreacted alkene showed the presence of about 10% of *trans-1-d*₁ in the recovered *cis-1-d*₁. Furthermore, irradiation at $\lambda > 500$ nm of the isolated products *cis-2-d*₁ and *trans-2-d*₁ gave C_{60} , *cis-1-d*₁ and *trans-1-d*₁ (cycloreversion products). These results, which eliminate a concerted photocycloaddition, are consonant with a dipolar or a diradical intermediate via an electron or charge transfer mechanism.



To probe this mechanism further and obtain information on the extent of bond making and bond breaking in the transition state, we measured the intermolecular secondary isotope effects of this [2 + 2] photocycloaddition reaction. To this end, we prepared the alkene 1-(*p*-methoxyphenyl)ethylene, **3-d**₀, and its deuterated analogs 1-(*p*-methoxyphenyl)ethylene-1-*d*₁, **3-d**₁, and 1-(*p*-methoxyphenyl)ethylene-1, 2, 2-*d*₃, **3-d**₃.^{15,16}



Equimolar ratios of **3-d**₀/**3-d**₁ as well as **3-d**₀/**3-d**₃, in 200-fold molar excess to C_{60} , were dissolved (in separate experiments) in deoxygenated toluene. Upon irradiation, 30% of the [2 + 2] adduct was obtained after 30 min, in each reaction, based on the recovered C_{60} . The reaction was monitored by HPLC on a reverse phase column. After purification of the reaction product by flash column chromatography (hexane/toluene) the secondary isotope effects $k_{\text{H}}/k_{\text{D}}$, which are the results of intermolecular competition between **3-d**₀ and **3-d**₁ as

Table 1. Intermolecular Kinetic Secondary Isotope Effects of Photocycloaddition of **3-d**₀/**3-d**₃ and **3-d**₀/**3-d**₁ to C_{60}

solvent	substrate	<i>t</i> , min	convn, ^a %	$k_{\text{H}}/k_{\text{D}}^b$
toluene	3-d ₀ / 3-d ₁	30	30	1.08 ± 0.05
toluene	3-d ₀ / 3-d ₃	30	30	0.75 ± 0.05

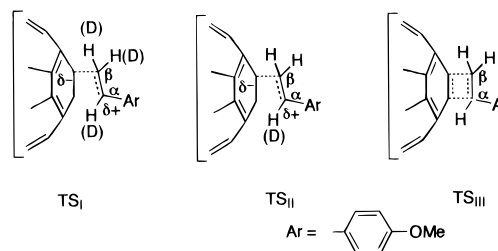
^a Based on recovered C_{60} . ^b Determined by ^1H NMR integration of the proper hydrogen signals.

well as **3-d**₀ and **3-d**₃, were measured by integrations of the proper ^1H NMR signals of the [2 + 2] products. These results are summarized in Table 1.

A small normal isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.08$) was found for deuterium substitution at the α -carbon (**3-d**₀ vs **3-d**₁). The observed inverse secondary isotope effect $k_{\text{H}}/k_{\text{D}} = 0.75$ between **3-d**₀ and **3-d**₃ can be factored into α -secondary, for deuterium substitution at the β -carbon, and β -secondary, for deuterium substitution at the α -carbon according to eq 1. Substitution of $(k_{\text{H}}/k_{\text{D}})_{\beta}$ for the value of 1.08 (Table 1) results to $(k_{\text{H}}/k_{\text{D}})_{\alpha}^2 = 0.69$ which corresponds to a $(k_{\text{H}}/k_{\text{D}})_{\alpha} = 0.83$ per deuterium.

$$(k_{\text{H}}/k_{\text{D}})_{\text{observed}} = (k_{\text{H}}/k_{\text{D}})_{\alpha}^2 (k_{\text{H}}/k_{\text{D}})_{\beta} = 0.75 \quad (1)$$

These results require the formation of a dipolar (or diradical) intermediate in a rate determining step as shown by transition states TS_{I} and TS_{II} . Substantially inverse α -secondary isotope effect $k_{\text{H}}/k_{\text{D}} = 0.83$ (normalized per deuterium) indicates extensive bond making between C_{60} and C_{β} of the alkene at the transition state (C_{β} is changing from sp^2 at the ground state to sp^3 in the transition state). Furthermore, the presence of a small normal β -secondary isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.08$) in the competition of **3-d**₀ with **3-d**₁ indicates no change in the sp^2 hybridization of the C_{α} carbon in going from the ground state (double bond) to the transition state (sp^2 carbocation or radical) and is consonant with little or no bond making at the C_{α} in the transition state. The two isotope effects, when taken in conjunction, exclude the formation of transition state TS_{III} (concerted mechanism), because in that case substitution at either C_{α} or C_{β} would have given an inverse isotope effect.



In conclusion, the photochemical [2 + 2] cycloaddition of arylalkenes to C_{60} occurs by a two-step mechanism, involving the formation of a dipolar or diradical intermediate in the rate determining step.

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Supporting Information Available: Spectra for *cis*- and *trans*-**1-d**₁, **3-d**₁, **3-d**₃, *cis*- and *trans*-**2-d**₁, **2-d**₀ and **2-d**₀ and **2-d**₂ (9 pages). See any current masthead page for ordering and Internet access instructions.

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