

# Orbital Symmetry Governed Reactions under High-Intensity Argon Laser-Jet Conditions: The Involvement of a [1,5<sub>s</sub>] Sigmatropic Shift in the Photocyclization of an *o*-Alkenylbenzaldehyde to a Benzocyclobutenone

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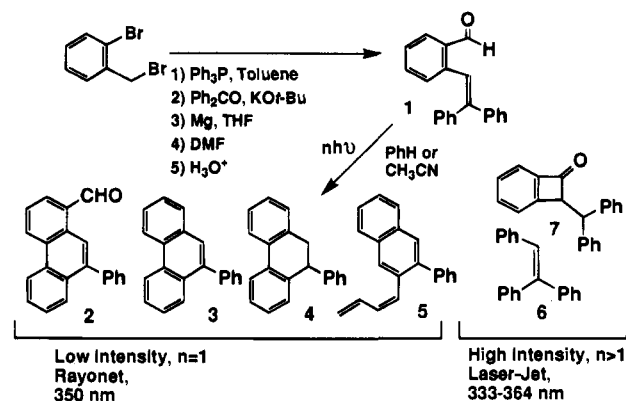
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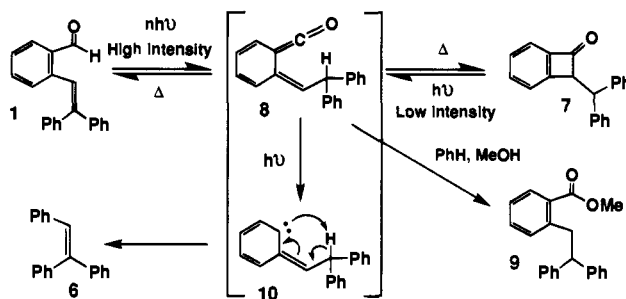
When one refers to *allowed* or *forbidden* in photochemical orbital symmetry governed reactions, one is implicitly referring to the behavior of the lowest excited states, since higher excited states are not usually accessible using conventional techniques. However, under high-intensity laser-jet conditions,<sup>1</sup> higher excited states of all possible symmetries become accessible, and reactions that are forbidden in the lowest excited state might become allowed in higher excited states of the appropriate symmetry. Our attention has been directed to this possibility during the course of the following study of a reaction which seems to constitute such an inversion of the traditional orbital symmetry rules under high-intensity conditions.

Low-intensity irradiation of aldehyde **1** (Rayonet, 350 nm, or diverged argon laser beam, all UV lines, 333, 351, and 364 nm, PhH) affords a mixture of products (**2–5** in Scheme 1) derived from combinations of phenanthrene cyclization and decarbonylation. The ratio of these low-intensity products is not changed upon high-intensity argon laser-jet irradiation (all UV lines). However, two new products are formed in laser-jet reactions (ca. 60:40 high-intensity:low-intensity products), benzocyclobutenone **7** as the major high-intensity product (12–16%, yields based on **1** consumed) and triphenylethylene (**6**) as the minor high-intensity product (1–2%). The structures of **2** and **7** have been confirmed by X-ray crystallography<sup>2</sup> and those of **3**, **4**, and **6** by comparison with authentic samples,<sup>3</sup> and the structure of **5** is tentatively assigned on the basis of its spectroscopic properties.<sup>4</sup> Transient spectroscopic studies indicated that no strongly absorbing transients were produced upon irradiation of **1**.<sup>5</sup> Deuterium labeling studies were conducted using **1** specifically labeled at the aldehyde hydrogen (**1-d<sub>1</sub>**, 96.4% deuterium incorporation).<sup>6</sup> High-intensity irradiation of **1-d<sub>1</sub>** afforded **7-d<sub>1</sub>** specifically labeled at the diphenylmethyl

Scheme 1



Scheme 2



carbon atom to the extent of 96.1%. Low-intensity irradiation of **7** produced **1** as the major product along with small amounts of products **2–5**. Under high-intensity conditions, **7** also produced **6**.

These observations are consistent with the mechanism outlined in Scheme 2. The presence of ketene methide **8** under laser-jet conditions was supported by the isolation of ester **9**, in low yield (~5–6%), from the high-intensity reaction in PhH/MeOH (40:60).<sup>7</sup> Apparently **8** either does not accumulate under these conditions, but rapidly reacts by one of the thermal or photochemical pathways shown in Scheme 2, or is relatively unreactive toward methanol.<sup>8</sup>

The hydrogen migration in carbene **10** to form **6** has direct analogy in the work of Bernard and Shechter, who generated a related carbene via photodecomposition of an azo compound.<sup>9</sup> Furthermore, it is well documented that cyclobutenones such as **7** undergo photochemical electrocyclic ring opening to ketene methides such as **8**,<sup>10</sup> and decay of **8** to **1** should occur readily via a thermally allowed [1,5<sub>s</sub>] sigmatropic shift (*vide infra*).

(1) Wilson, R. M.; Schnapp, K. A. *Chem. Rev.* **1993**, *93*, 223. Wilson, R. M.; Hannemann, K.; Schnapp, K. A.; Memarian, H. R.; Azadnia, A. *SPSE Proc.—Photochem. Imaging, Summer Symp.* **1988**, 167. Wilson, R. M.; Schnapp, K. A.; Hannemann, K.; Ho, D. M.; Memarian, H. R.; Azadnia, A.; Pinhas, A. R.; Figley, T. M. *Spectrochim. Acta* **1990**, *46A*, 551. Wilson, R. M.; Adam, W.; Schulte Oestrich, R. *Spectrum* **1991**, *4* (Fall Issue), 8.

(2) Compounds **2** and **7** had spectroscopic properties in accord with the structures proposed. **2**: mp 133–135 °C; IR (CHCl<sub>3</sub>) 1693 cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 10.53 (s, 1 H), 9.10 (s, 1 H), 9.05 (d, *J* = 7.5 Hz, 1 H), 8.81 (d, *J* = 7.50 Hz, 1 H); mp 150–152 °C; IR (CHCl<sub>3</sub>) 1762 cm<sup>-1</sup>; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 5.07 (d, *J* = 9.3 Hz, 1 H), 4.43 (d, *J* = 9.3 Hz, 1 H). The structures of these compounds were confirmed by X-ray crystallographic studies. For detailed X-ray crystallographic data, see the paragraph about supporting information at the end of this paper.

(3) The structure of **6** was confirmed by comparison with commercially available material (Aldrich), that of **3** by comparison with material prepared via the oxidative cyclization of **6** (Mallory, F. B.; Wood, C. S. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 952), and that of **4** by comparison with material prepared by the Li/NH<sub>3</sub> reduction of **3** (Harvey, R. G.; Fu, P. P.; Rabideau, P. W. *J. Org. Chem.* **1976**, *41*, 3722).

(4) The structure of **5** is based upon comparison of its <sup>1</sup>H NMR spectrum with that of 2-vinylnaphthalene, upon its <sup>1</sup>H COSY NMR spectrum, and upon mass spectral data which shows a pattern that would be expected from electrocyclic ring closure followed by aromatization: *m/e* 256 (1000, M<sup>+</sup>), 255 (354), 254 (102), 253 (183), and 252 (182).

(5) Transient spectroscopic studies were done by absorption spectroscopy (1000 W xenon arc source with an optical multichannel analyzer for signal acquisition and averaging) following irradiation of the sample with a focused XeCl excimer laser pulse (308 nm, PWHM = 20 ns): Soundararajan, N.; Platz, M. S.; Jackson, J. E.; Doyle, M. P.; Oon, S.-M.; Liu, M. T. H.; Anand, S. M. *J. Am. Chem. Soc.* **1988**, *110*, 7143. Haider, K. W.; Migirdicyan, E.; Platz, M. S.; Soundararajan, N.; Despres, A. *J. Am. Chem. Soc.* **1990**, *112*, 733.

(6) The synthesis of **1-d<sub>1</sub>** was achieved by the route outlined in Scheme 1 in which DMF was replaced by DMF-*d*<sub>7</sub> (99.5% deuterium).

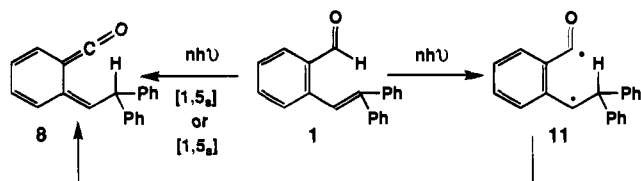
(7) Authentic **9** was synthesized from 1-(2-bromophenyl)-2,2-diphenylethane (Wilson, R. M.; Schnapp, K. A.; Patterson, W. S. *J. Am. Chem. Soc.* **1992**, *114*, 10987) via carbonylation of the Grignard reagent and esterification with diazomethane.

(8) It is interesting to note that Scaiano and coworkers have observed the parent ketene methide derived from *o*-vinylbenzaldehyde under low-intensity conditions using transient spectroscopy techniques. While this parent molecule had a lifetime in excess of 100 μs, it was not trapped efficiently by methanol (unpublished results kindly provided by J. C. Scaiano).

(9) Bernard, R. E.; Shechter, H. *Tetrahedron Lett.* **1972**, 4529.

(10) Baldwin, J. E.; McDaniel, M. C. *J. Am. Chem. Soc.* **1968**, *90*, 6118. Cava, M. P.; Spangler, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 4550. Chapman, O. L.; Lassila, J. D. *J. Am. Chem. Soc.* **1968**, *90*, 2449.

Scheme 3

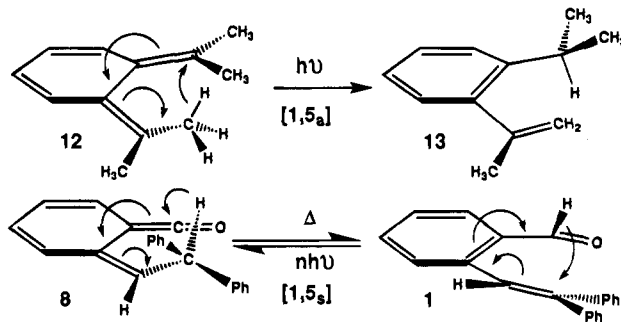


Thus, of the transformations outlined in Scheme 2, only the high-intensity conversion of **1** to **8** appears to be exceptional.<sup>11</sup>

Two fundamentally different mechanisms might be considered for this reaction: (1) stepwise mechanisms which would very likely involve biradical intermediates such as **11** (Scheme 3) or (2) concerted [1,5<sub>a</sub>] or [1,5<sub>s</sub>] sigmatropic shifts. A stepwise pathway seems unlikely, since photochemical intramolecular hydrogen abstraction by olefins that are not conjugated to heteroatoms or constrained in small rings is rarely observed.<sup>12</sup> Furthermore, excited diphenylmethyl radicals, a possible candidate for the hypothetical hydrogen-abstracting species in a twisted, excited olefin intermediate, are known to function poorly in this capacity.<sup>13</sup> Finally, failure to observe any transients associated with this reaction speaks against a stepwise process and indicates the involvement of a rapid, possibly concerted singlet pathway.

Such a pathway might be a [1,5] sigmatropic shift which would be symmetry allowed via either a [1,5<sub>a</sub>] geometry from the lowest excited state or a [1,5<sub>s</sub>] geometry from a higher excited state. McCullough<sup>14</sup> and Scaiano<sup>15</sup> have studied the decay of tetramethyl-*o*-xylylene (**12**,  $\tau = 9.1$  min., PhH, room temperature). They concluded that this process can proceed through a photochemically allowed [1,5<sub>a</sub>] geometry in the lowest excited state (Scheme 4), since excitation of **12** accelerates its conversion to **13** by at least 10 orders of magnitude relative to the equivalent reaction under thermal conditions. The thermally allowed [1,5<sub>s</sub>] geometry apparently is not readily accessible in **12** as shown in Scheme 4. Molecular modeling studies<sup>16</sup> indicate that ketene methide **8** is not nearly as sterically

Scheme 4



congested as **12** and that the analogous [1,5<sub>s</sub>] process in **8** should be a very facile process. Furthermore, if a [1,5<sub>a</sub>] process were active in the photochemical formation of **8** from **1**, one would expect formation of cyclobutenone **7** to occur under low-intensity conditions, which is not the case. Consequently, it seems most likely that the interconversion of **1** and **8** proceeds to a significant extent through the more favorable [1,5<sub>s</sub>] geometry, and that this reaction is both energetically favorable and [1,5<sub>s</sub>]-symmetry allowed only from a higher excited state.<sup>17</sup> Even though an explicit assignment of the higher excited state(s) involved in this reaction is not possible, it is clear that about half of the available higher excited states will have a symmetry suitable for an allowed [1,5<sub>s</sub>] sigmatropic shift.

On the basis of these observations, we have initiated a program to examine other "photochemically forbidden" processes under high-intensity conditions and find that this is a viable strategy for the application of the laser-jet technique.<sup>18</sup>

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**Supporting Information Available:** X-ray data for **2** and **7**, figures listing the atomic numbering scheme, and tables for each compound, including X-ray structure determination experimental details and summary, atomic positional parameters, anisotropic temperature factors, hydrogen positional parameters, bond distances and angles, and least-squares planes and selected torsion angles for **2** (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(17) The fact that Scaiano and co-workers (ref 8) have been able to observe ketene methide formation from the parent *o*-vinylbenzaldehyde under low-intensity conditions indicates either that the lowest excited state of **1** has insufficient energy to form **8** or that the bulky phenyl substituents inhibit the system from achieving the requisite geometry for a [1,5<sub>a</sub>] shift. In either case, a higher excited state would provide the only viable route to **8**.

(18) Other classes of "symmetry forbidden" photochemical reactions have also been observed under high-intensity laser-jet conditions and will be reported in due course.

(11) The loss of <sup>13</sup>CHO during photochemical cyclization to **3**, **4**, and **5** is typical behavior for *o*-aroyl-substituted stilbenes; unpublished results: Wilson, R. M.; Hannemann, K. Also, it should be mentioned that cyclobutenone **7** is the major high-intensity photochemical product formed upon argon laser-jet irradiation of 2,2-diphenylindan-1-one. However, this unprecedented ring contraction proceeds through aldehyde **1**, which is the primary photoproduct: Patterson, W. S. Ph.D. Thesis, University of Cincinnati, 1993.

(12) Hornback, J. M.; Proehl, G. S. *J. Am. Chem. Soc.* **1979**, *101*, 7367.

(13) Scaiano, J. C.; Johnston, L. J. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1989; Vol. 10, p 309. Scaiano, J. C.; Johnston, L. J.; McGimpsey, W. G.; Weir, D. *Acc. Chem. Res.* **1988**, *21*, 22. Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

(14) de Fonseca, K. K.; McCullough, J. J.; Yarwood, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 3277.

(15) Wintgens, V.; Netto-Ferreira, J. C.; Casal, H. L.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 2363. Scaiano, J. C.; Wintgens, V.; Netto-Ferreira, J. C. *Pure Appl. Chem.* **1990**, *62*, 1557.

(16) Calculations were conducted using Spartan, Version 3.0, on a Silicon Graphics Indigo XS24 4000. Minimizations and energy calculations were conducted using PM3 and RHF to gradients of <0.01 kcal/(Å·mol).