

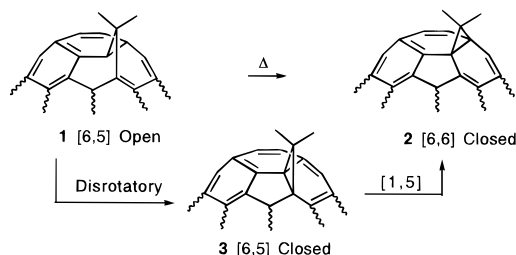
## Why Is the Rearrangement of [6,5] Open Fulleroids to [6,6] Closed Fullerenes Zero Order?

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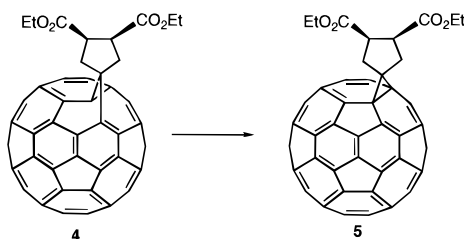
Received September 3, 1996

Addition of carbene transfer reagents such as diazo compounds to C<sub>60</sub> often generates the [6,5] open fulleroid, **1**, as the kinetically controlled product while the thermodynamically controlled product is the [6,6] closed methanofullerene, **2**.<sup>1</sup> When the [6,5] open isomers are isolated, they have been reported to rearrange to [6,6] methanofullerene thermally,<sup>2</sup> photochemically,<sup>3</sup> electrochemically,<sup>4</sup> or under acid catalysis.<sup>5</sup> The thermal conversion of **1** to **2** has been postulated to involve first an



electrocyclization to the closed [6,5] fullerene, **3**, followed by a [1,5] shift to generate **2**.<sup>6</sup> Semiempirical PM3 calculations, which indicate that **3** is energetically accessible, support such a mechanism.<sup>6</sup> However, measurements of the kinetics of the rearrangement of **1** to **2** reveal that this is a zero-order reaction,<sup>2,7</sup> implicating a more complex mechanism.<sup>8</sup>

We now report a study of the rearrangement of the conveniently prepared and purified cyclopentylidenefulleroid **4**<sup>9</sup> to the corresponding spiro[2.4]methanofullerene, **5**, in which we demonstrate that a photochemical step in the thermal rearrangement is responsible for the zero-order behavior.



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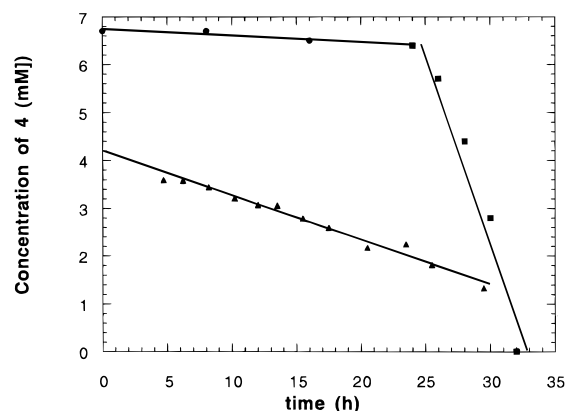
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(8) The interesting complexity in these systems was first pointed out by Prato et al.: Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479.

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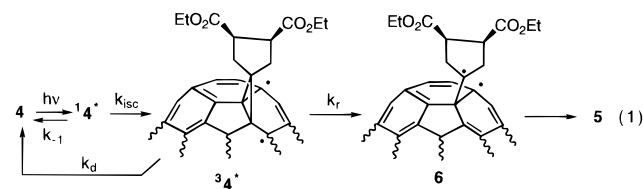
**Figure 1.** Rearrangement of **4** to **5** at 153 °C in *o*-dichlorobenzene-*d*<sub>4</sub> under various conditions: (a) (▲) nondegassed solution in ambient light; (b) (●) degassed solution in the dark; (c) (■) degassed solution in ambient light.

Heating a dichlorobenzene-*d*<sub>4</sub> solution of **4** at 153 °C and following the rearrangement to **5** by NMR result in a zero-order decay,  $K_0 = 9.07 \times 10^{-5} \text{ M h}^{-1}$ , of **4** with **5** as the only product (Figure 1a). However, when this experiment is repeated in an NMR tube which has been degassed, sealed, and rigorously protected from ambient light, there is virtually no change in the concentration of **4** after heating for 24 h at 153 °C (Figure 1b). When this same sample is exposed to ambient light, a clean zero-order rearrangement of **4** to **5** is observed in 8 h at 153 °C ( $k_0 = 7.78 \times 10^{-4} \text{ M h}^{-1}$ , Figure 1c). It thus appears that exposure to light is required for the rearrangement to proceed at an appreciable rate.

A photochemical rearrangement of a [6,5] fulleroid to a [6,6] methanofullerene has been reported by Janssen, Hummelen, and Wudl.<sup>3</sup> These workers photolyzed (488 nm, Ar ion laser for 1 h) a [6,5] fulleroid with phenyl and methyl butyrate substituents and observed quantitative conversion to the [6,6] methanofullerene. A mechanism involving a di- $\pi$ -methane rearrangement was invoked. Since intersystem crossing is efficient in C<sub>60</sub><sup>10</sup> and the reaction is strongly inhibited by O<sub>2</sub>, a triplet biradical intermediate was proposed.

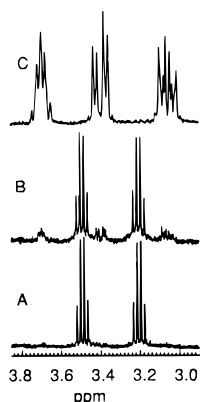
We have photolyzed a degassed solution of **4** with filtered light ( $\lambda > 500 \text{ nm}$ , 200 W Hanovia lamp) and observed quantitative conversion to **5** in 16 h. In this case, the increased light intensity is sufficient to cause the reaction to proceed at room temperature. There is also an inhibitory effect of O<sub>2</sub>. For example, the light-promoted thermal rearrangement of **4** to **5** in a degassed dichlorobenzene solution (Figure 1c) proceeds with a zero-order rate constant which is 11.6 times greater than that of the oxygen-containing solution at the same temperature (Figure 1a).

On the basis of the above facts and in analogy with the mechanism proposed by Janssen, Hummelen, and Wudl,<sup>3</sup> we propose that the light-promoted thermal rearrangement of **4** to **5** proceeds as shown in eq 1. The first step is photochemical



conversion of **4** to an electronically excited state,  $^14^*$ , which

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**Figure 2.** NMR spectra of a solution of **4** (6.7 mM) in 1,2-dichlorobenzene-*d*<sub>4</sub>: (A) before heating; (B) after heating at 180 °C in the absence of light for 24 h; (C) after heating at 180 °C in room light for an additional 3 h. Peaks at  $\delta = 3.49$  and 3.20 ppm are for the protons  $\alpha$  to the carboxy group in **4**. Peaks at  $\delta = 3.69$  ppm are for the corresponding protons in **5**. Peaks at  $\delta = 3.39$  and 3.06 ppm are for the protons  $\beta$  to the carboxy group in **5**.

undergoes intersystem crossing to a triplet ( $^3\mathbf{4}^*$ ). The step requiring thermal activation is postulated to be rearrangement of  $^3\mathbf{4}^*$  to biradical **6**, which then collapses to **5**. Assuming that  $k_{isc} \gg K_{-1}$  and using the steady state approximation for  $^1\mathbf{4}^*$ ,  $^3\mathbf{4}^*$ , and **6**, in the absence of O<sub>2</sub>, we obtain the expression for [**4**] as a function of time in eq 2, where  $I_{abs}$  is the intensity of the absorbed light. Thus a zero-order reaction with  $k_{obs} = k_r I_{abs} / (k_d + k_r)$  is predicted.

$$[\mathbf{4}] = -\frac{k_r I_{abs}}{(k_d + k_r)} + [\mathbf{4}_0] \quad (2)$$

As expected for a reaction requiring thermal activation, the ambient light-promoted rearrangement of **4** to **5** is accelerated as temperature is increased over the range 111 °C ( $k_0 = 2.78 \times 10^{-4} \text{ M h}^{-1}$ ) to 180 °C ( $k_0 = 2.08 \times 10^{-3} \text{ M h}^{-1}$ ). The NMR spectrum of a solution of **4** at 180 °C (Figure 2), which shows only 8% loss of **4** over 24 h in the dark followed by complete rearrangement in 3 h after exposure to ambient light, exemplifies this effect in a particularly dramatic fashion. If it is assumed that  $I_{abs}$  is independent of temperature and  $k_d \gg k_r$ , a four-point Arrhenius plot of  $\ln(k_{obs})$  vs  $1/T$  yields a  $\Delta H_r^\ddagger - \Delta H_d^\ddagger = 9.9 \pm 1.4 \text{ kcal/mol}$  and a  $\Delta S_r^\ddagger - \Delta S_d^\ddagger = 9.4 \pm 3.4 \text{ eu}$ . These assumptions lead to the conclusion that the barrier to rearrangement of  $^3\mathbf{4}^*$  to **6** has an upper limit of 9.9 kcal<sup>11</sup> and is entropically favored over decay of  $^3\mathbf{4}^*$  to **4**.

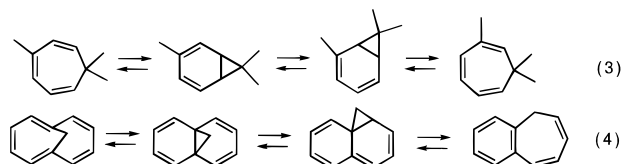
We have been able to use the fact that the rearrangement of fulleroids to cyclopentylidenefullerenes is light promoted and inhibited by O<sub>2</sub> to increase the ratio of fulleroid to fullerene in our additions of tosylhydrazone salts to C<sub>60</sub>.<sup>9</sup> For example, addition of the lithium salt of cyclopentanone tosylhydrazone to C<sub>60</sub> under conditions previously described gives a fulleroid:

(11) Although a number of assumptions are involved in determining this value, it compares favorably with a value of 10 kcal/mol reported by Zimmerman and Elser<sup>12</sup> for the rearrangement of the triplet derived from the photolysis of a diphenylcyclohexenone.

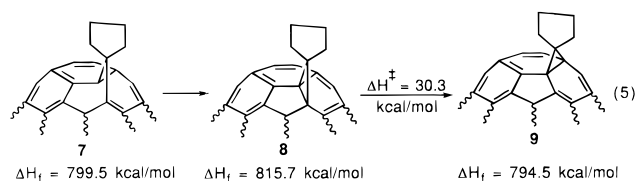
(12) Zimmerman, H. E.; Elser, W. *J. Am. Chem. Soc.* **1968**, *91*, 887.

fullerene ratio of 3:1.<sup>9</sup> However, when the reaction is carried out in the dark in an oxygenated solution, this ratio is 32:1.

These results indicate that the thermal first-order rearrangement of **4** to **5** has a sufficiently high barrier that it cannot compete with the photoassisted process even at temperatures as high as 180 °C. This is not surprising when one considers the two steps which would be involved in this process. The first is simply an example of the cycloheptatriene–norcaradiene tautomerism which would be expected to be facile.<sup>13</sup> As has been pointed out by Wudl,<sup>5</sup> the second step may be thought of as a Berson–Wilcott rearrangement, and this is the probable source of the high barrier. The original example of this rearrangement<sup>14</sup> (eq 3) requires temperatures in excess of 300 °C, while a closer analogy to the present process reported by Vogel<sup>15</sup> (eq 4) requires FVP conditions at 500 °C. A qualitative



rationalization of our results is provided by the PM3<sup>16</sup> semiempirical heats of formation in eq 5 which predict that the closure of the [6,5] cyclopentylidene-methanofulleroid, **7**, to the [6,5] cyclopentylidene-fullerene, **8**, is endothermic by 16.2 kcal/mol while rearrangement of **8** to [6,6] cyclopentylidene-methanofullerene, **9**, is exothermic by 21.2 kcal/mol but must traverse a barrier of 30.3 kcal/mol. Although computational difficulties have prevented us from locating the transition state for the rearrangement of **7** to **8**, these calculations indicate that a barrier of at least 46.5 kcal/mol must be traversed in going from **7** to **9**.



Although we have not investigated other fulleroid–fullerene rearrangements, it is expected that this light-assisted process may be a general alternative to direct first-order thermal rearrangement in systems where the corresponding Berson–Wilcott rearrangement is a high-energy process. Conversely, analogues in which this rearrangement is facile such as dicyanofulleroids should rearrange thermally.

**Acknowledgment.** We thank the National Science Foundation (CHE-9508570) for support of this research.

**Supporting Information Available:** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **4** and **5** and plots and tables for the kinetics and activation parameters in the conversion of **4** to **5** (7 pages). See any current masthead page for ordering or Internet access information.

JA963088I

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