



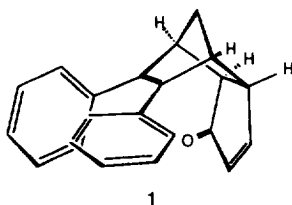
## Photochemistry of Bichromophoric Systems. Photoreactions of Cyclopentenone and Stilbene Fixed in a Rigid Molecule

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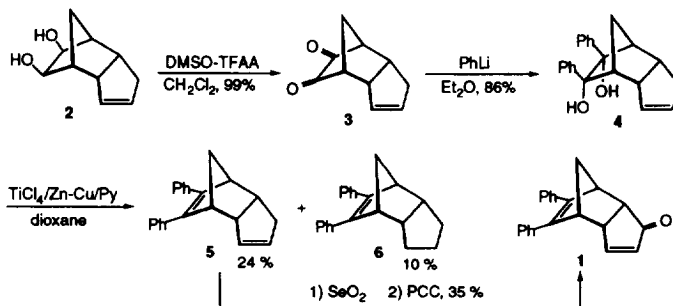
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**Abstract:** The photochemistry of newly synthesized 8,9-diphenyltricyclo[5.2.1.0<sup>2,6</sup>]deca-4,8-dien-3-one (**1**) has been explored. A novel [1, 3] sigmatropic rearrangement via a singlet excited state was observed as well as a [2 + 2] intramolecular cycloaddition via a triplet excited state. The formation of an intramolecular singlet exciplex was indicated by emission spectra. Copyright © 1996 Elsevier Science Ltd

Although cyclopentenones and stilbenes play important roles in the field of organic photochemistry, studies on molecules having these chromophores together in an interactive disposition are quite limited. In connection with our previous study on the photochemistry of cyclopentenone and styrene fixed together in a tricyclic bridged system,<sup>1</sup> our interest in the effect of orbital interaction of the two conjugated systems on photochemical reactivity and energy transfer has prompted us to synthesize 8,9-diphenyltricyclo[5.2.1.0<sup>2,6</sup>]deca-4,8-dien-3-one (**1**) and to explore its photochemical behavior.

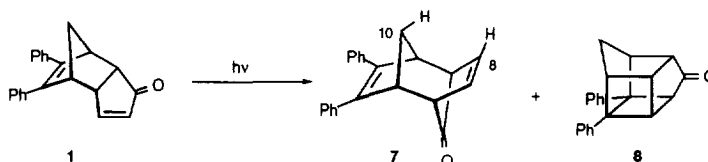


The compound **1** was synthesized starting with the diol **2**<sup>2</sup> by the procedure shown in Scheme 1.<sup>3</sup>

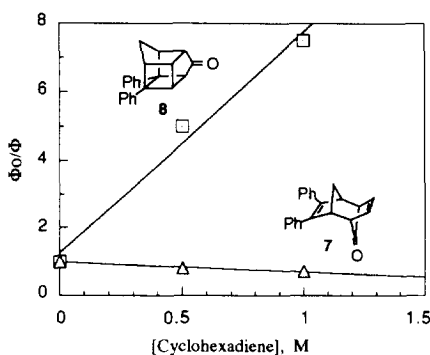


Scheme 1

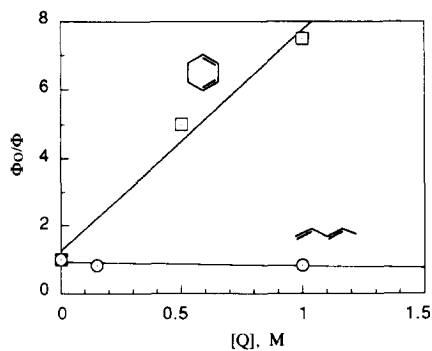
Excitation of the stilbene chromophore of **1** in benzene by the light of  $\lambda \geq 334$  nm using an uranyl glass filter yielded two products, **7** (15 %) and **8** (15 %) as well as unreacted **1** (13 %).<sup>4</sup> The structures of the products were determined by spectroscopic data.<sup>3</sup> In particular, the orientation of diphenylcyclopentene and 3-cyclopentenone in **7** was determined by NOE observed between C<sub>8</sub>-H and C<sub>10</sub>-H. Excitation of the enone chromophore of **1** by the light of  $\lambda \geq 366$  nm using a Fuji Photo Film SC-37 filter also resulted in the formation of **7** and **8** in a similar ratio.



Quenching experiments were performed in a merry-go-round using cyclohexadiene ( $E_T = 52.4$  kcal mol<sup>-1</sup>)<sup>5</sup> and *trans*-piperlylene ( $E_T = 59.2$  kcal mol<sup>-1</sup>)<sup>5</sup> and the results are shown in Figs. 1 and 2 in the form of Stern-Volmer plots. It is clearly indicated that the cage product **8** is derived from a triplet excited state while the product **7** is derived from a singlet excited state (Fig. 1). The quenching data (Fig. 2) further indicate that **8** arises from the triplet of the stilbene chromophore but not from that of the cyclopentenone chromophore since the lowest triplet of 2-cyclopentenone ( $E_T = 73.6$  kcal mol<sup>-1</sup>)<sup>6</sup> is known to be quenched by piperlylene.<sup>7</sup> Upon irradiation in the presence of thioxanthone ( $E_T = 65.5$  kcal mol<sup>-1</sup>),<sup>5</sup> under conditions where thioxanthone absorbs most of the incident light ( $\lambda \geq 366$  nm), the formation of **8** was effectively sensitized, whereas the formation of **7** was completely depressed. This agreed with the conclusion obtained from the quenching experiments.



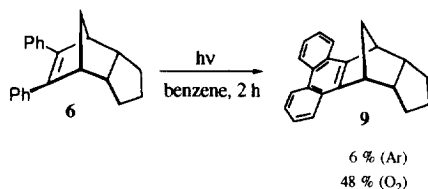
**Figure 1.** Stern-Volmer plots for the photoreaction of **1** in the presence of cyclohexadiene.



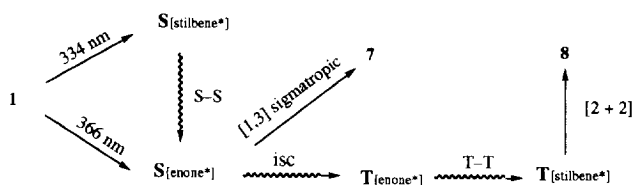
**Figure 2.** Stern-Volmer plots for the formation of **8**. Q = 1,3-cyclohexadiene or *trans*-piperlylene.

From the following observations, it is deduced that the singlet excited state of the stilbene chromophore does not seem to play an important role in the photoreaction of **1**. Irradiation of **6** ( $\lambda \geq 334$  nm) at room temperature in an Ar atmosphere leads to the development of the orange color of a dihydrophenanthrene and to the formation of a phenanthrene product **9** (6 %) upon subsequent exposure to air in the dark, and the irradiation in the presence of oxygen leads to an extensive formation of **9** (48 %). On the other hand, no phenanthrene product is detected in the reaction of **1** under similar conditions. It has been generally accepted

that *cis*-stilbenes undergo photocyclization via a singlet excited state to give dihydrophenanthrenes which subsequently give phenanthrenes by oxidation.<sup>8</sup>



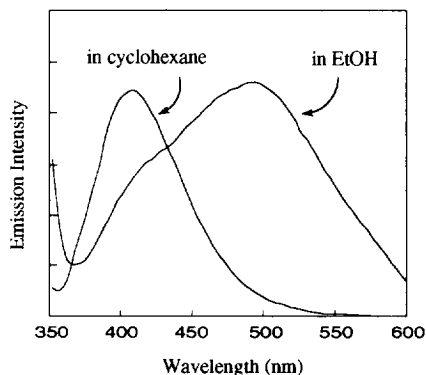
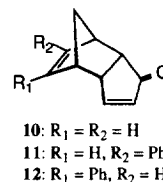
Taking into account these observations, the photochemical pathway of **1** can be outlined as shown in Scheme 2, in which the reacting excited state for the formation of **7** is a singlet of the cyclopentenone chromophore and that for the formation of **8** is a triplet of the stilbene chromophore.



**Scheme 2**

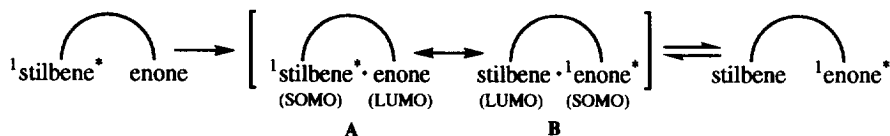
This is the first reported observation of a C<sub>10</sub> dienone of this type ring system undergoing [1, 3] sigmatropic rearrangement via a singlet excited state, while the cyclopentadienone dimer<sup>9</sup> and its substituted derivatives<sup>10</sup> are known to undergo a similar [1, 3] rearrangement via a triplet excited state. The presence of two phenyl groups at C8 and C9 is essential for the formation of **7** since the dienone **10**<sup>11</sup> and its monophenyl derivatives, **11** and **12**,<sup>1</sup> are known to afford only a cage product upon irradiation, respectively. This suggests that the stilbene chromophore plays a role in prolonging the lifetime of the enone singlet, presumably owing to SOMO-LUMO interaction between the two chromophores, so that the concerted [1, 3] rearrangement can compete with the intersystem crossing to the triplet state. The increase of the opportunity for the reaction from the singlet state may also be responsible for the decomposition occurring during the direct irradiation, because the ratio of the unrecovered products in the thioxanthone sensitized reaction is much smaller.

The compound **1** shows a weak emission band with a maximum at 408 nm in cyclohexane (Fig. 3), which is very similar (in shape but not in intensity) to those observed with **6** (412 nm, cyclohexane, r. t.) and 1,2-diphenylcyclopentene (400 nm, MCIP, 77 K).<sup>12</sup> On the other hand, a new broad band centered at 496 nm, likely attributable to an exciplex, was observed when measurement was performed in ethanol. An exciplex which is depicted as a resonance hybrid of two electronic configurations, A



**Figure 3.** Emission spectra of **1** at room temperature; 313 nm excitation; uncorrected for spectral sensitivity of spectrophotometer.

and **B**, can be assumed to form during the singlet-singlet energy transfer process as shown in Scheme 3. The contribution of **B** to the resonance is usually much dominant and the exciplex does not fluoresce in cyclohexane because of the strong ( $n, \pi^*$ ) character. On the other hand, it can be expected that in ethanol the contribution of **A** to the resonance is raised by protonation or polar solvation to the carbonyl group, so that the exciplex will acquire more ( $\pi, \pi^*$ ) character to fluoresce.



Scheme 3

### References and Notes

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- All new compounds were fully characterized. The following data are for selected compounds from this work. **1**: Amorphous; IR (KBr)  $1690\text{ cm}^{-1}$ ; UV (EtOH)  $\lambda_{\text{max}}$  227 ( $\epsilon$  25300), 292 ( $\epsilon$  8400) nm;  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.81 (dt, 1H,  $J = 8.5, 1.5$  Hz), 2.20 (dt, 1H,  $J = 8.5, 1.5$  Hz), 3.00 (t, 1H,  $J = 5$  Hz), 3.47 (dd, 1H,  $J = 4.5, 1.5$  Hz), 3.54 (dd, 1H,  $J = 4.5, 1.5$  Hz), 3.72 (m, 1H), 5.95 (dd, 1H,  $J = 6, 1.5$  Hz), 7.1–7.3 (m, 10 H, Ph), 7.34 (dd, 1H,  $J = 6, 2.5$  Hz);  $^{13}\text{C-NMR}$  (50 MHz,  $\text{CDCl}_3$ ) 849.81 (>CH-), 50.43 (>CH-), 50.56 (>CH-), 51.07 (>CH-), 52.22 (C-10), 135.65 (=C<), 136.03 (=C<), 136.42 (=CH-), 165.14 (=CH-), 209.59 (>C=O); MS  $m/z$  (% in total intensity) 218.0 ( $\text{M}^+ - \text{C}_5\text{H}_4\text{O}$ , 19 %); HRMS calcd for  $\text{C}_{22}\text{H}_{18}\text{O}$ , 298.13576; found, 298.13566. **7**: mp. 96–98 °C; IR ( $\text{CHCl}_3$ )  $1690\text{ cm}^{-1}$ ; UV (EtOH)  $\lambda_{\text{max}}$  229 ( $\epsilon$  18400), 293 ( $\epsilon$  7700) nm;  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  2.08 (d, 1H,  $J = 11$  Hz), 2.31 (dt, 1H,  $J = 11, 3.5$  Hz), 2.79 (br.dd, 2H,  $J = 6, 3.5$  Hz), 3.03 (dt, 2H,  $J = 6, 2, 2$  Hz), 6.63 (t, 2H,  $J = 2$  Hz), 7.20 (m, 10 H, Ph);  $^{13}\text{C-NMR}$  (50 MHz,  $\text{CDCl}_3$ )  $\delta$  38.58 ( $-\text{CH}_2-$ ), 43.92 (>CH-  $\times 2$ ), 51.79 (>CH-  $\times 2$ ), 134.72 (=CH-  $\times 2$ ), 136.13 (=C<  $\times 2$ ), 201.27 (>C=O); MS  $m/z$  (% in total intensity) 218.0 ( $\text{M}^+ - \text{C}_5\text{H}_4\text{O}$ , 19 %); HRMS calcd for  $\text{C}_{22}\text{H}_{18}\text{O}$ , 298.13576; found, 298.13572. **8**: mp. 165–167 °C; IR ( $\text{CHCl}_3$ )  $1750\text{ cm}^{-1}$ ;  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.94 (d, 1H,  $J = 12$  Hz), 2.36 (d, 1H,  $J = 12$  Hz), 2.49 (m, 1H), 2.95 (d, 1H,  $J = 4.5$  Hz), 3.10 (m, 1H), 3.19–3.36 (m, 2H), 3.34 (m, 1H), 6.8–7.2 (m, 10 H, Ph);  $^{13}\text{C-NMR}$  (50 MHz,  $\text{CDCl}_3$ )  $\delta$  41.25 ( $-\text{CH}_2-$ ), 32.93 (>CH-), 36.88 (>CH-), 44.56 (>CH-), 47.39 (>CH-), 50.25 (>CH-), 52.26 (>CH-), 59.28 (>C<), 63.08 (>C<), 216.07 (>C=O); MS  $m/z$  (% in total intensity) 218.0 ( $\text{M}^+ - \text{C}_5\text{H}_4\text{O}$ , 5 %), 270 ( $\text{M}^+ - \text{CO}$ , 10 %); HRMS calcd for  $\text{C}_{22}\text{H}_{18}\text{O}$ , 298.13576; found, 298.13584.
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