

Novel Photo-induced Reactions of 1,1-Dimethyl-2,5-diphenylsilacyclopentadiene with Benzophenone Derivatives

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Irradiation of 1,1-dimethyl-2,5-diphenylsilacyclopentadiene with benzophenone derivatives afforded two oxetanes *via* photo-induced electron transfer processes.

Silacyclopentadienes (siloles) have attracted wide attention because of interest in the chemistry of metalloles.¹⁻³ 1,1-Dimethyl-2,5-diphenylsilacyclopentadiene, which forms yellow crystals with strong blue fluorescence, is of particular photochemical interest, its photoreactions including dimerization⁴ and cycloaddition with 1,1-dimethoxyethene.⁵ We now report novel electron transfer reactions of the silole **1** with benzophenone and its derivatives, and demonstrate that the silole acts as an effective electron donor.

On irradiation of an acetonitrile solution of the silole **1** (0.02 mol dm⁻³) and benzophenone **2b** (0.4 mol dm⁻³) with a medium-pressure mercury lamp through a glass filter [Toshiba Y-44; $\lambda > 440$ nm (transmission 50%)], two cycloadducts **3b** and **4b** were formed along with small amounts of three photodimers **5**, **6** and **7**.^{4a,b} The structures of **3b** and **4b** were

easily determined from their ¹H and ¹³C NMR spectra.† When an acetonitrile solution of isolated **3b** or **4b** was irradiated with a medium-pressure mercury lamp through a Pyrex filter, **1** and **2b** were re-formed, together with three photodimers of **1**,

† *Spectroscopic data for (3b):* ¹H NMR (CDCl₃) δ -0.01 (s, 3H), 0.49 (s, 3H), 4.47 (d, 1H, *J* 3.7 Hz), 6.61 (d, 1H, *J* 3.7 Hz) and 7.00-7.46 (m, 20H); ¹³C NMR (CDCl₃) δ -5.8, -1.8, 61.3, 84.0, 91.6, 123.1, 124.8, 125.7, 125.9, 126.46, 126.52, 126.6, 126.8, 127.6, 127.7, 128.5, 139.7, 142.4, 143.5, 145.1, 146.8 and 147.1; *m/z* 444 (M⁺). (**4b**): ¹H NMR (CDCl₃) δ -0.29 (s, 3H), -0.21 (s, 3H), 6.11 (d, 1H, *J* 3.3 Hz), 7.18 (d, 1H, *J* 3.3 Hz) and 6.98-7.65 (m, 20H); ¹³C NMR (CDCl₃) δ -0.4, 0.1, 54.4, 85.7, 90.8, 125.1, 125.8, 126.4, 126.8, 126.9, 127.3, 127.5, 127.6, 128.0, 128.5, 138.8, 140.1, 141.1, 143.6, 145.5 and 154.3; *m/z* 444 (M⁺).

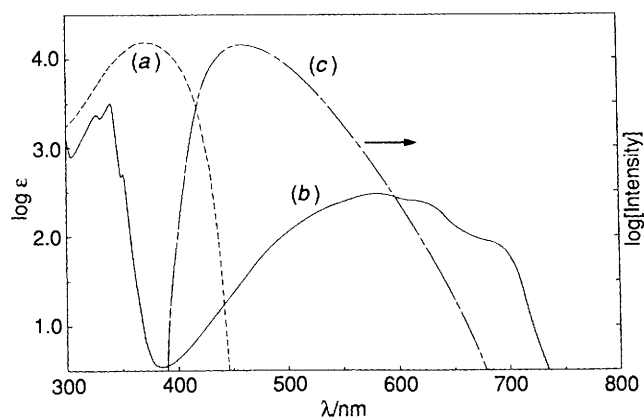
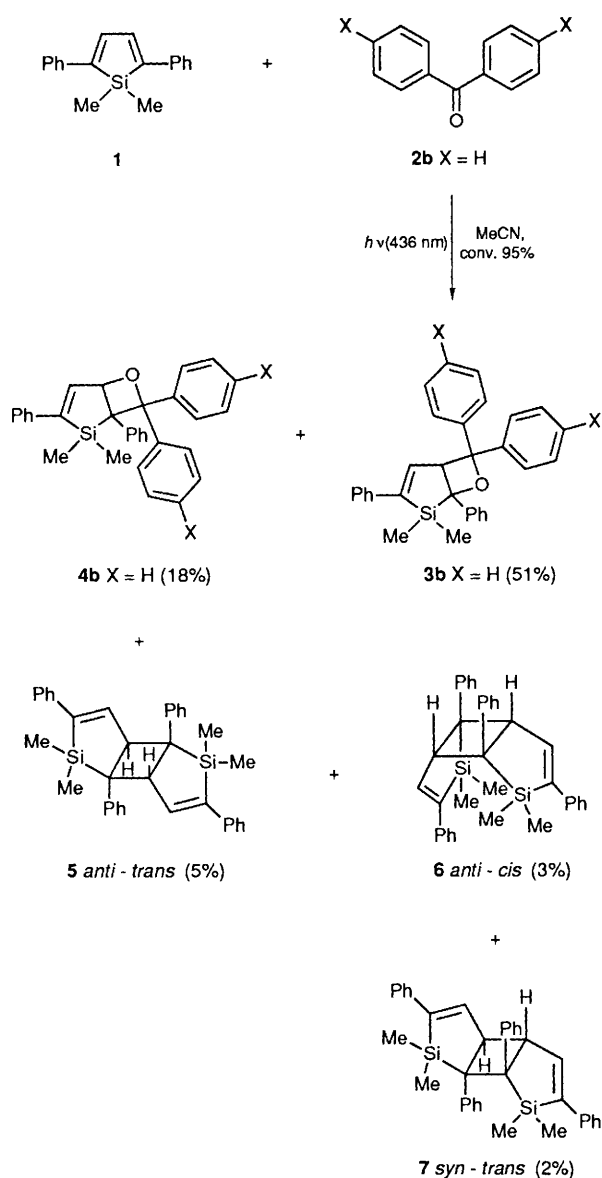


Fig. 1 UV-VIS spectra of (a) **1** and (b) azulene and (c) fluorescence spectrum of **1** in MeCN

Table 1 Fluorescence quenching constants of **1** by benzophenone derivatives **2a-d** and the calculated free-energy changes for the electron transfer processes in MeCN

Donor ^a	Acceptor ^a	ΔG / kcal mol ⁻¹	k /dm ³ mol ⁻¹ s ⁻¹
1 (-1.83)	2a X = Me (-1.84)	-1.2	— ^b
1	2b X = H (-1.77)	-2.8	1.1×10^9
1	2c X = F (-1.76)	-3.0	1.6×10^9
1	2d X = Cl (-1.58)	-7.2	1.5×10^{10}

^a $E_{\text{red}}^{\text{red}}/V$ vs. standard calomel electrode are given in parentheses.

^b This value is too small to be measured accurately by a Stern-Volmer plot.

rate constant of quenching ($5.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) is far larger than the diffusion controlled rate in acetonitrile and the value is essentially the same in liquid paraffin. These results indicate that singlet-singlet energy transfer from **1** to azulene effectively occurs *via* a long-range mechanism.⁶ In the presence of azulene, the photoaddition of **1** and **2b** was quenched under irradiation with light of 400 nm. The rate constants for quenching of the formation of **3b** and **4b** are 4.7×10^{10} and $5.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. These values are comparable with that of quenching of the fluorescence of **1**. From these results, the photoaddition of **1** and **2b** is considered to proceed *via* the excited singlet state of **1**.

Reactivity in the cycloaddition was investigated by using *p,p'*-disubstituted benzophenones **2a,c,d**. Since the rate constant for the formation of dimers of **1** can be considered to be constant in each case, the relative rate constants for the formation of **3** + **4** were determined on the basis of the concentrations of dimers **5** + **6** + **7** formed together with **3** and **4**.§ A good Hammett correlation was obtained [$\log(k_{\text{x}}/k_{\text{H}})$ vs. σ_{p}^0] with a ρ value of 0.906 ($r = 0.999$). Although [2+2] photocycloaddition *via* a short-lived excited singlet state often proceeds by a concerted mechanism,⁶ the reactivity cannot be rationalized by such a mechanism, because the reactivity increased progressively with increase in the energy gap between the LUMO of **1** and the LUMOs of **2** estimated by the reduction potentials (Table 1).¶ However, the reactivity may be explained by electron transfer from the excited singlet state of **1** to **2**. The free-energy change for the electron transfer process calculated by the Rehm-Weller equation for **2a-d** is

§ The ratios of **3** : **4** and **5** : **6** : **7** are about 4 : 1 and 3 : 1 : 1 in every case.

¶ Since the oxidation potentials of **1** and **2b** are 1.24 and >2 V, respectively, the HOMO-HOMO interaction could be neglected.

showing that the photoaddition of **1** with **2b** is reversible. On irradiation with 436 nm light, only cycloaddition occurred and cycloreversion of **3b** and **4b** was suppressed because **3b** and **4b** do not absorb at 436 nm.

In order to determine the multiplicity of the excited state of **1** participating in this cycloaddition, azulene was used as a possible singlet quencher of **1**. Since the singlet energies of **1** and azulene are 68.1 and 40.6 kcal mol⁻¹ (1 cal = 4.184 J), respectively, singlet-singlet energy transfer from **1** to azulene is an exothermic process. A Stern-Volmer plot of the fluorescence quenching of **1** by azulene was constructed by monitoring the fluorescence of **1** at 420–480 nm to give the $k_{\text{q}}\tau$ values from which the k_{q} values were obtained assuming $\tau = 1.1 \text{ ns}$.‡ Since the fluorescence of **1** overlaps the S_0 - S_1 absorption band of azulene to a considerable extent (Fig. 1), the true k_{q} value of singlet-singlet energy transfer was estimated by extrapolation of the plot of k_{q} vs. ϵ of azulene to $\epsilon = 0$, excluding the contribution of a trivial mechanism. The

‡ As the molar extinction coefficients of **1** and azulene at 400 nm are 9550 and 5 in acetonitrile, respectively, it is possible to excite **1** selectively with 400 nm light in the presence of azulene (Fig. 1).

negative in each case and decreases as the reactivity increases. Furthermore, the fluorescence of **1** is quenched by **2** and the quenching constant is the nearly diffusion controlled rate in the case of **2d**. Therefore, we conclude that an electron transfer process participates in the initial stage of these reactions.

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