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Photochemistry of Locally Excited and Intramolecular Charge Transfer States of a Disilane Bearing a Cyclic Arylethenyl Electron Acceptor Substituent

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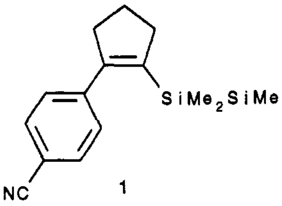
Abstract: 1-(*p*-cyanophenyl)-2-(pentamethyldisilanyl)cyclopentene (**1**) exhibits a fluorescence at $\lambda > 400$ nm, which strongly shifts to the red with increasing polarity of the solvent. The corresponding solvatochromic plot is indicative of an emissive, lowest energy charge-transfer (CT) state. Stern–Volmer quenching of the fluorescence by dilute methanol in pentane gives a linear plot with a unit intercept and a slope $k_Q\tau_{ct} = 0.70$. Quenching is accompanied by formation of (arylcyclopentenyl)dimethylsilane **7**, the major product observed upon photolysis of **1** in the presence of methanol. This is evidenced by the linear double-reciprocal plot of quantum yields of **7** versus methanol concentration, which gives a $k_Q\tau_{ct}$ value in agreement with fluorescence quenching. In addition to nucleophilic attack by methanol at the terminal trimethylsilyl group to give **7**, two minor photoproducts, (arylcyclopentenyl)trimethylsilane **6** and a tricyclic product **8** are observed, which are attributable to silylene extrusion and to homolytic Si–Si bond cleavage, the latter process giving a silyl radical pair that cyclizes onto the ortho position of the aryl group with subsequent disproportionation. The Stern–Volmer plot of Φ°/Φ versus [MeOH] for **8** is curved, suggesting that both the locally excited (LE) and CT states are involved in the formation of this product. In contrast, quantum yields of **6** do not vary with alcohol concentration, consistent with the LE state as the origin of this product.

Introduction

Certain substituted aryldisilanes exhibit, in addition to fluorescence of the π,π^* locally excited (LE) state, a longer wavelength emission ascribable to an intramolecular charge transfer (CT) excited state.[1–3] The direction of the electron transfer is from the σ Si–Si bond to the photoexcited arene, which serves as the acceptor.[2–4] Based upon stereoelectronic effects on the fluorescence intensities and wavelengths of benzosilacyclopentanes in which the Si–Si σ bond is constrained to be either orthogonal or conjugated to the arene p orbitals, Sakurai, Kira, and co-workers have proposed[2,3] that the intramolecular charge transfer state is stabilized in the orthogonal orientation and can thus be designated as a TICT state.[5]

Few reports have appeared on the actual chemistry of CT states of aryldisilanes or other p-conjugated disilane systems.[6] Until recently, none of the aryldisilanes had a strong electron acceptor aryl group. Kira, Sakurai, and co-workers addressed this aspect in their photochemical study of the *p*-trifluoromethyl-substituted derivative of phenylpentamethyldisilane.[4] The major product,



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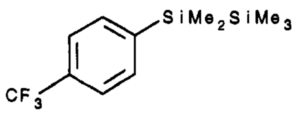

which corresponded to a 1,3-Si shift of the trimethylsilyl group to the ortho position of the aryl group, was attributed to reactivity of the ^{1}LE state of the arene. Regioselective nucleophilic attack by alcohol on the terminal trimethylsilyl group in the CT state was proposed to account for the formation of one of the minor products of the aryldisilane, an aryldimethylsilane. These assignments were based on the differing behavior of product quantum yields as the concentration of alcohol varied.

We wish to report on the photochemistry of LE and intramolecular CT states of the rigid, *p*-cyano-substituted styryldisilane **1**. Although no 1,3-Si shift is observed in this case, *p*-cyano compound **1** does afford a major product attributable to addition of alcohol across the Si–Si bond in the CT state.[8] The roles of LE and CT states in the formation of additional minor products

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(3) Sakurai, H.; Sugiyama, H.; Kira, M. *J. Phys. Chem.* **1990**, *94*, 1837 and references cited therein.

(4) (a) For intermolecular electron transfer from hexamethyldisilane to electron deficient benzenes, see: Horn, K. A.; Whitenack, A. A. *J. Phys. Chem.* **1988**, *92*, 3875. (b) For examples of intramolecular photochemical electron transfer in arylacetylenic disilanes, see: Horn, K. A.; Grossman, R. B.; Thorne, J. R. G.; Whitenack, A. A. *J. Am. Chem. Soc.* **1989**, *111*, 4809.

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(6) (a) A number of examples of intermolecular photoreactivity are available however.[6b–f] (b) Nakadaira, Y.; Sekiguchi, A.; Funada, Y.; Sakurai, H. *Chem. Lett.* **1991**, 327. (c) Watanabe, H.; Kato, M.; Tabei, E.; Kuwabara, H.; Hirai, N.; Sato, T.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1662. (d) Nakadaira, Y.; Komatsu, N.; Sakurai, H. *Chem. Lett.* **1985**, 1781. (e) Sakurai, H.; Sakamoto, K.; Kira, M. *Chem. Lett.* **1984**, 1213. (f) Fukuzumi, S.; Kitano, T.; Mochida, K. *Chem. Lett.* **1989**, 2177.

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of silylene extrusion and homolytic Si–Si bond cleavage have also been elucidated.

Results

Synthesis of 1-(*p*-cyanophenyl)-2-(pentamethyldisilanyl)cyclopentene (1). The key step in the synthesis of *p*-cyano compound **1** was the free radical cyclization reaction of iodo-1,4-diene **3** with tributylstannane (Scheme 1). Yields were low because the major products of the reduction were the acyclic 1,4-dienes **5**. Iodo-1,4-diene **3** was obtained in high yield via the addition of allylzinc bromide to (arylethynyl)disilane **2** upon quenching with iodine, following the method of Erdic[9a] and Negishi.[9b,c] Compound **1** was purified by medium-pressure liquid chromatography (MPLC) and used immediately for the spectroscopic and photochemical studies described below.

Fluorescence Studies. A single strong fluorescence was observed for *p*-cyano compound **1** in isooctane at 412 nm. Both the wavelength and intensity of the emission were sensitive to the solvent, shifting to 463 nm or more in polar solvents such as acetonitrile and trifluoroethanol, while appearing at intermediate wavelengths in medium-polarity solvents such as THF and dichloromethane (Figures 1 and 2 and Table 1). Compared to isooctane, significantly lower emission intensities were observed for all solvents except dichloromethane. Unlike phenylpentamethyldisilane,[3] a distinct dual fluorescence was not observed with any of the solvents, with the exception of trifluoroethanol (Figure 2). As expected,[1c,10] the excitation spectra in isooctane and acetonitrile resembled absorption spectra of **1** (Figure 3). From standard compounds it was established that the shift in the excitation spectra of ca. 25 nm to the red is an artifact of our instrument.

Large Stokes shifts are evident upon comparison of the absorption and emission frequencies in Table 1. The polarity dependence of the Stokes shift, $\tilde{\nu}_a - \tilde{\nu}_f$ or $\Delta\tilde{\nu}_{ct}$, is related to the square of the difference in ground- and excited-state dipole moments, $\mu_e - \mu_g$, by the Lippert–Mataga equation (eq 1),[11,12]

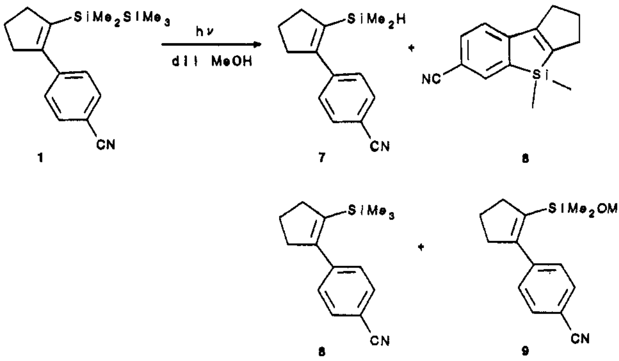
$$\Delta\tilde{\nu}_{ct} = \text{constant} + \frac{(2\Delta\mu)^2 L(\epsilon,n)}{hca^3} \qquad (1)$$

$$L(\epsilon,n) = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad (2)$$

where h is Planck's constant, c is the speed of light, and a is the Onsager radius of **1** in its CT excited state. The solvent polarity parameter $L(\epsilon,n)$ is a function of the solvent dielectric constant, ϵ, and refractive index n (eq 2). The solvatochromic plot (Figure 4) of $\Delta\tilde{\nu}_{ct}$ versus $L(\epsilon,n)$, utilizing the absorption and emission data in Table 1, gives a least squares fit to a line (correlation coefficient = 0.952) with a slope of 5600 ± 1040 (error limit of one standard deviation).

In pure methanol the long-wavelength CT emission of *p*-cyano compound **1** was quenched almost completely, leaving a residual fluorescence attributable, for the most part, to the π,π^* excited state (LE state) of the π-conjugated arene (Figure 1), as suggested by comparison to the fluorescence of 1-(*p*-cyanophenyl)-2-(trimethylsilyl)cyclopentene (Figure 5) in methanol. A plot of the relative quantum yield for fluorescence, Φ_f°/Φ_f, against [methanol] in pentane as the solvent was linear (R^2 = 0.998), with a slope ($k_Q\tau$) of 0.700 ± 0.016 σ and an intercept of 1.12 ± 0.12 σ (Figure 6). The more nucleophilic alcohol, ethanol, in pentane as the solvent, gave a lower least squares slope of 0.506 ± 0.003 σ (R^2 = 0.9998). Like methanol, the intercept of the plot was close to unity or 0.925 ± 0.023 σ.

Photoproducts. Photolysis of 10^{-2}–10^{-3} M solutions of *p*-cyano compound **1** in pure methanol at 254 nm with a Rayonet photolysis apparatus equipped with 16 low-pressure mercury lamps or at 290 or 310 nm with a high-pressure mercury lamp and monochromator gave 1-(*p*-cyanophenyl)-2-(dimethylsilyl)cyclopentene (**7**) along with methoxytrimethylsilane as the photoproducts. Product **7** was isolated from photolysates by MPLC and identified by ^{1}H and ^{13}C NMR spectroscopy, whereas the volatile methoxytrimethylsilane was characterized by GC–MS and by comparison of GC retention times to an authentic sample on three columns.



(3)

Photolyses of **1** performed with dilute solutions of methanol in pentane or hexane at 254 or 310 nm with a high-pressure mercury lamp and monochromator also gave **7**, but with accompanying formation of three minor products, whose relative yields increased with decreasing concentration of methanol. At 310 nm with 10 M methanol in pentane the yield of **7** was 42%, and each of the three minor products was present in ca. 1% yield, while the remaining mass balance was 55% of unreacted **1**.

The three minor products observed in the photolyses with dilute methanol were identified from GC–MS data and GC retention times as **6**, **8**, and **9** (eq 3). Minute amounts of **8** were also detected in photolyses conducted in pure methanol. Samples of the tricyclic photoproduct **8** were obtained from photolysis of **1** in hexane as the solvent, utilizing Vycor filtered light of a 450-W medium-pressure mercury lamp or, preferably, from 254-nm photolysis in 2,2,2-trifluoroethanol. The photolyses in hexane produced, in addition to **8**, (arylcyclopentenyl)trimethylsilane **6**, which was separated by MPLC and identified spectroscopically, whereas the 254-nm photolyses in the polar, nonnucleophilic alcohol led to pronounced decreases in yields of **6** relative to **8**. An authentic sample of **6** was synthesized according to Scheme 2. Reaction of compound **7** with methanol and catalytic Pd–C gave a sample of **9**, which was used for GC coinjection and GC–MS analyses to identify this minor product in photolysates. An attempt at trapping dimethylsilylene with 0.09 M triethylsilane gave $Et_3SiSiMe_2H$, but in substantially lower yield than its expected coproduct, trimethylsilane **6**.[13]

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(11) (a) See ref 5 and references cited therein. (b) Lippert, E. *Z. Naturforsch. A* **1955**, *10*, 541. (c) Lippert, E. *Z. Elektrochem.* **1957**, 962. (d) Mataga, N.; Kaufu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1956**, 465.

(12) Comparable solvatochromic plots have been constructed for aryldisilanes. See refs 1c and 3.

(13) (a) Photolysis of 0.012 M **1** in 29 mL of pentane containing pure 0.090 triethylsilane (distilled from CaH_2) was performed for 1 h with a medium-pressure mercury lamp equipped with a Pyrex filter. $Et_3SiSiMe_2H$ was identified by comparison of GC–MS retention times and mass spectra to an authentic sample,[13b] prepared by 254-nm photolysis of 0.05 M dodecamethylcyclohexasilane and 0.35 M triethylsilane in 20 mL of pentane.[13c] Accompanying **6**, **8**, and unreacted **1** were at least six unidentified products at similar retention times and a large amount of an unidentified, insoluble precipitate. (b) Braddock-Wilking, J.; Chiang, M. Y.; Gaspar, P. P. *Organometallics* **1993**, *12*, 197. (c) The procedure was similar to trapping with diethylmethylsilane: Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325.

Quantum Yields of Photoproducts. Quantum yields for formation of products were determined with a microoptical bench apparatus (Experimental Section). As shown in Table 2, the only two products observed in pure methanol or ethanol as solvents were dimethylsilane **7** and tricyclic product **8**, while with dilute methanol in pentane, trimethylsilane **6** and methoxydimethylsilane **9** were also formed. Compound **9** was not a factor in this study, since its quantum yields were generally too low to be determined. With pentane or hexane as the solvents in the absence of alcohol the photoproducts were exclusively trimethylsilane **6** and tricyclic product **8** (Table 2 and Experimental Section). This was also the case with 2,2,2-trifluoroethanol, although the quantum yield of **6** substantially decreased relative to **8** in this polar nonnucleophilic solvent. Use of acetonitrile as a cosolvent with 1.0 M methanol led to large decreases in the quantum efficiencies for formation of all of the products.

A plot (Figure 7) of Φ_a^{-1} (**7**) versus $[\mathrm{MeOH}]^{-1}$ for a 1.0–10 M range of concentrations of methanol in pentane as the solvent was linear (correlation coefficient of 0.995), with each point representing the average of two complete determinations (Table 3). The least squares slope was 13.14 ± 0.76 σ, and the intercept was 9.74 ± 0.29 σ. From the ratio of intercept:slope, $k_Q\tau = 0.74$, which was comparable to $k_Q\tau = 0.70$ obtained from quenching of fluorescence by methanol. Methanol in pentane was used as the solvent due to the limited solubility of methanol in hexane.

A pronounced decrease in the quantum yields of **6** relative to **8** was observed with decreasing wavelength. At 290 nm in hexane or pentane the ratio **6**:**8** was generally 1.2–1.4:1, as compared to 0.1–0.2:1 at 254 nm. No significant temperature effect on 290-nm quantum yields of **6** or **8** was observed upon photolysis at 1, 20, or 40 °C.

Deuterium Labeling. Photolyses of **1** in methanol-*O-d* at 254 nm with a Rayonet apparatus or at 290 nm with a high-pressure mercury lamp and monochromator produced dimethylsilane **7**-d_1, monodeuterated to an extent of 90% according to GC–MS analyses. No detectable SiH absorption was observed in the ^{1}H NMR spectrum, and ^{2}H NMR spectroscopy showed that the deuterium was present exclusively as Si–D. Photolysis at 254 nm with dilute 1.0 M methanol-*O-d* in pentane gave comparable results. Monodeuterated dimethylsilane **7**-d_1 was labeled exclusively at silicon and contained no detectable deuterium in the Si methyls or elsewhere in the molecule. Under these latter conditions, **6**, **8**, and **9** were additional minor products. From GC–MS data for the parent ion in the case of **8** and **9**, each was found to be >97% undeuterated; the yield of trimethylsilane **6** was too low for analysis.

Discussion

The strong bathochromic shift of the fluorescence wavelength maximum of *p*-cyano compound **1** with an increase in polarity of the solvent is consistent with an emissive, lowest energy CT excited state. The change in dipole moment upon excitation to the CT state is estimated to be roughly 5.3 D from the slope of the solvatochromic plot (Figure 4), or somewhat higher than the estimate of 4 D for phenylpentamethyldisilane.[1c,3] Our estimate is calculated from eq 1, assuming a value for the Onsager radius *a* of 5 Å, taken as 40%[14] of the 12.3-Å total length of **1**. The total length was obtained from the AM1[15]-optimized geometry of ground-state **1** in a distended conformation, which was considered a reasonable approximation of the geometry of a TICT state. The dihedral angle of the Si–Si bond and the C=C bond of the cyclopentene ring was 159° rather than 180° (within the plane of the double bond) due to steric interactions with the aryl group. From the AM1-calculated ground-state dipole moment of 3.6 D, the excited-state dipole moment would then be approximately 8.9 D.

The observed quenching of CT fluorescence by methanol and ethanol can be discussed in terms of the kinetic processes summarized in Scheme 3. The fluorescence quantum yield in the absence of alcohol, Φ_f°, is the product of the quantum yield for formation of the CT excited state, Φ°_{ct}, and the ratio of k_f to all other processes that serve to deactivate the CT excited state (eq 4). The quantum yield for fluorescence in the presence of alcohol, Φ_f, is expressed as eq 5, which incorporates the terms, $k_a[\mathrm{ROH}]$, for addition of alcohol across the Si–Si bond in the CT state to give silane **7** plus methoxytrimethylsilane, and $k_q[\mathrm{ROH}]$, for quenching by alcohol with return to ground-state **1** through back electron transfer. Product formation without participation by ROH is represented by k_r. The dependence of the relative quantum yield of fluorescence, Φ_f°/Φ_f, on [ROH] is thus given by eq 6. Although Φ_{ct}, in principle, can vary with [ROH], the linearity and near unit intercepts displayed in Figure 6 indicate that $\Phi_{ct}^\circ \approx \Phi_{ct}$ for both methanol and ethanol in pentane. For ROH = methanol, the experimental slope of 0.70 corresponds to $(k_a + k_q)\tau_{ct}$, where $\tau_{ct} = (k_d + k_f + k_r)^{-1}$.

$$\Phi_f^\circ = \Phi_{ct}^\circ\left(\frac{k_f}{k_d + k_f + k_r}\right) \tag{4}$$

$$\Phi_f = \Phi_{ct}\left(\frac{k_f}{k_d + k_f + k_r + k_a[\mathrm{ROH}] + k_q[\mathrm{ROH}]}\right) \tag{5}$$

$$\frac{\Phi_f^\circ}{\Phi_f} = \frac{\Phi_{ct}^\circ}{\Phi_{ct}}\left(1 + \frac{(k_a + k_q)}{(k_d + k_f + k_r)}[\mathrm{ROH}]\right) \tag{6}$$

The quantum yield, Φ_a, (Scheme 3) for reaction of the CT excited state with methanol to form product **7** is given by eq 7. The experimental plot of $\Phi^{-1}{}_a$ versus $[\mathrm{MeOH}]^{-1}$ (Figure 7), corresponding to eq 8,gives a ratio of intercept to slope $(k_a + k_q)\tau_{ct} = 0.74$. This value matches that obtained from the slope of Φ_f°/Φ_f versus [MeOH] of Figure 6. Thus, we conclude that **7** is formed by reaction of methanol with the singlet CT excited state of **1**. A significant increase in Φ_{ct} with increasing concentration of methanol would have been expected to have led to a nonlinear plot for Figure 7.

$$\Phi_a = \Phi_{ct}\left(\frac{k_a[\mathrm{ROH}]}{k_r + k_d + k_f + (k_a + k_q)[\mathrm{ROH}]}\right) \tag{7}$$

$$\Phi_a^{-1} = \Phi_{ct}^{-1}\left(\frac{k_a + k_q}{k_a} + \frac{k_r + k_d + k_f}{k_a[\mathrm{ROH}]}\right) \tag{8}$$

In contrast to **7**, quantum yields of tricyclic product **8** strongly decrease with increasing concentration of methanol. Although this behavior implicates reaction in the CT state, with quenching by methanol serving as a competitive photoprocess, the curved Stern–Volmer plot of Φ°/Φ versus methanol (Figure 8) is more consistent with involvement of both the CT and LE states in the formation of **8** (Φ° was obtained by extrapolating Φ^{-1} to 0 [MeOH]). If conversion of the initially populated LE state to the CT state is irreversible and not subject to a significant solvent effect as the concentration of methanol in pentane is varied, and if only the CT state is quenched by the alcohol, then the situation becomes analogous to the more general case of reaction of both a singlet and triplet excited state to form a product, with only the latter state quenched by a triplet quencher.[16]

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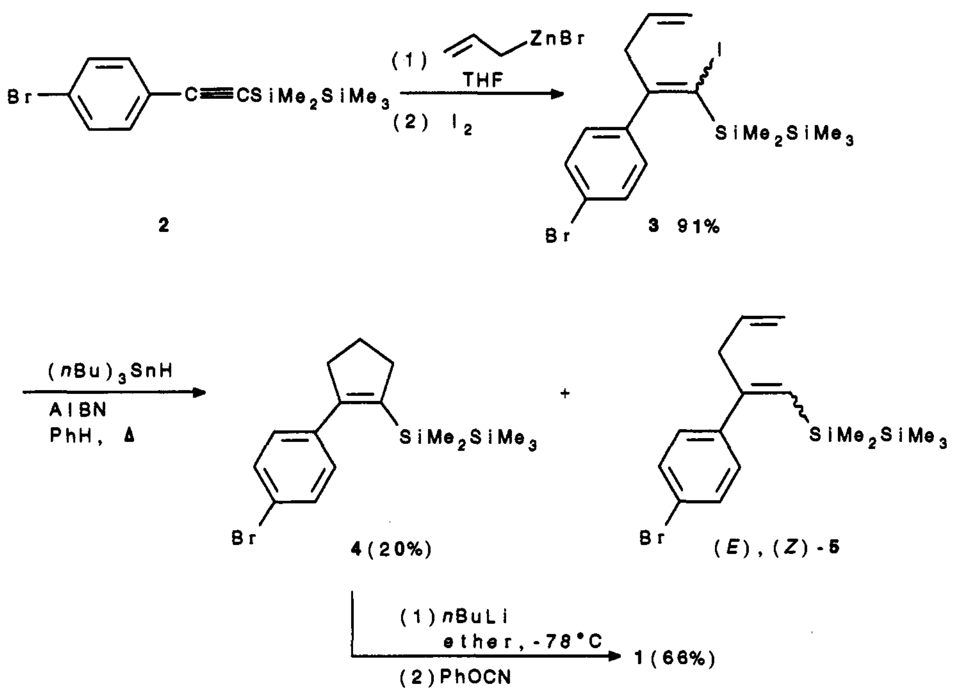
(14) Pasman, P.; Mes, G. F.; Koper, N. W.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1985**, *107*, 5839.

(15) The calculations used the AM1 method implemented in AMPAC (QCPE program no. 506). The AM1 parameters for silicon were taken from the following reference: Dewar, M. J. S.; Jie, C. *Organometallics* **1987**, *6*, 1486.

(16) (a) Wagner, P. J. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, 1989; Vol. II, Chapter 11. (b) Dalton, J. C.; Dawes, K.; Turro, N. J.; Weiss, D. S.; Barltrop, J. A.; Coyle, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 7213.

Scheme 1



Following the previous procedure,[16b] we assume that Φ°/Φ at high [MeOH] approximates the LE component of tricyclic product **8**, which in Figure 8 corresponds to the asymptotic intercept $\Phi^\circ(\mathrm{LE})/\Phi(\mathrm{LE}) \geq$ ca. 2.5. The fraction of LE component $((\Phi^\circ/\Phi)/(\Phi^\circ(\mathrm{LE})/\Phi(\mathrm{LE})))$[16b] for each relative quantum yield, Φ°/Φ, is used to calculate contributions of $\Phi(\mathrm{LE})$ and $\Phi(\mathrm{CT})$ to each Φ. A plot of $\Phi^\circ(\mathrm{CT})/\Phi(\mathrm{CT})$ versus [MeOH] then gives $(k_a + k_q)\tau_{ct}$ from the slope at low [MeOH] (<8 M). Taking $\Phi^\circ(\mathrm{LE})/\Phi(\mathrm{LE}) = 3.0$ (33% LE contribution at 0 [MeOH]) gives a near unit intercept of 0.86 ± 0.35 and a slope $(k_a + k_q)\tau_{ct} = 0.72 \pm 0.11$ ($R^2 = 0.955$) that agrees with fluorescence quenching (Figure 9). A value of $\Phi^\circ(\mathrm{LE})/\Phi(\mathrm{LE}) = 2.46$, which seems more consistent with the data in Figure 8, leads to greater deviation from a unit intercept (0.35 ± 0.68), and the slope (1.39 ± 0.22) differs significantly from $(k_a + k_q)\tau_{ct}$ obtained from fluorescence quenching by methanol. The agreement of $(k_a + k_q)\tau_{ct}$ values for fluorescence quenching and $\Phi^\circ(\mathrm{CT})/\Phi(\mathrm{CT})$ versus [MeOH], though possibly fortuitous, is better than expected, considering that the quantum yields of **8** cover a very narrow range of values for 1–10 M [MeOH].

In contrast to **8**, quantum yields for trimethylsilane **6** were essentially independent of the concentration of methanol in pentane (Table 3). Such behavior suggests that **6** derives from the LE state, since the rate of conversion from this state to the CT state is not significantly affected for the 1–10 M range of concentrations of methanol in pentane investigated, according to $\Phi_{ct} \approx \Phi_{ct}^\circ$ found for quenching of fluorescence by methanol.

The rate of intramolecular CT, k_{ct}, is not necessarily invariant with large changes in solvent polarity. Increases in k_{ct} are needed to accommodate the observed strong decrease in quantum yields of both **6** and **8** in pure methanol compared to dilute solutions of methanol in pentane and to account for the decrease in quantum yield of **6** in going from pentane to trifluoroethanol as solvents (Table 2). In contrast to **6**, a smaller decrease in quantum yields of **8** is observed for the more polar solvent, trifluoroethanol, in accord with the above conclusion, based on Stern–Volmer quenching by alcohol, that this product is formed via both the LE and CT states.

The pronounced decrease in the quantum yields of **6** relative to **8** in going from 290 to 254 nm in hexane or pentane (Results section) is possibly attributable to strong coupling of nonradiative decay to internal rotation about the C–Si bond so as to convert the initial Franck–Condon (S_2) state to the TICT state. This process, which effectively competes with internal conversion, presumably proceeds via a crossing with the lower energy S_1 (LE) potential surface. Crossing of S_1 and S_2 potential surfaces has been proposed for phenyldisilanes,[7b] reminiscent of the ^1L_a and ^1L_b state crossing of *p*-cyano-*N*,*N*-dimethylaniline.[5,17]

Conclusions

In the presence of nucleophilic alcohols such as methanol or ethanol the principal photoprocess of *p*-cyano compound **1** is cleavage of an electron deficient Si–Si bond with regioselective attack by the alcohol at the terminal trimethylsilyl group. To form the final product, (arylcyclopentenyl)dimethylsilane **7**, proton transfer to the internal silicon must occur, either concertedly during attack by the alcohol or at a later stage via an ion pair intermediate. Protic interaction of alcohol with the internal silicon or arylvinyl group in the excited state is suggested by the higher quantum yields observed for the more acidic alcohol, methanol, than for ethanol (Table 2). Methanol is also more effective as a quencher of CT fluorescence than ethanol (Figure 6). The Scheme 4 mechanism, moreover, accounts for deuterium incorporation from methanol-*O*-*d* exclusively into the SiH group of **7**.

The excited state undergoing alcohol addition must be highly polar, as evidenced by the strong bathochromic shift of the emission of **1** with increasing polarity of the solvent. Such behavior indicates a considerable degree of charge transfer. That this singlet excited state is the reactive state follows from the strong correlation of relative quantum yields for quenching of fluorescence by methanol with quantum yields for formation of product **7**.

During an initial stage in the formation of **7** nucleophilic attack by alcohol is required at an electron deficient silicon. When the alcohol is weakly nucleophilic, as in the case of trifluoroethanol, product **7** is not observed. Cleavage of the Si–Si bond still occurs, but the major product formed, tricyclic silane **8**, is consistent with involvement of a silyl radical pair (Scheme 5). Cyclization of the π-conjugated silyl radical is more rapid than dispropor-

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(17) A wavelength effect on radiationless conversion to a TICT state has been observed for a sterically hindered *p*-cyanoaniline: Rotkiewicz, K.; Rubaszewska, W. *J. Lumin.* **1982**, *27*, 221.

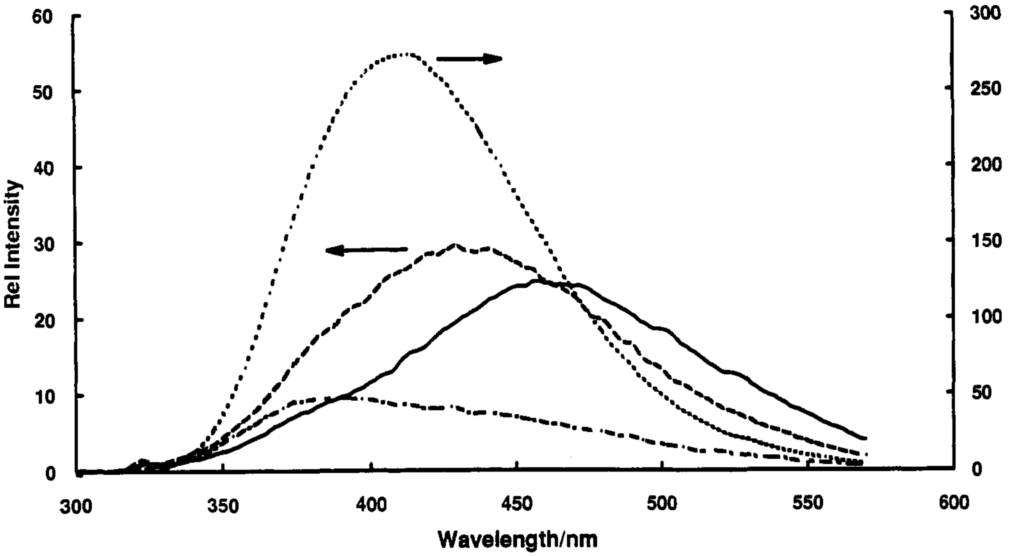

Figure 1. Fluorescence spectra of 1-(*p*-cyanophenyl)-2-(pentamethyldisilanyl)cyclopentene (**1**) in isooctane (···, 1.47 × 10^{-4} M), acetonitrile (—, 1.36 × 10^{-4} M), tetrahydrofuran (- - -, 1.46 × 10^{-4} M), and methanol (- · · -, 1.56 × 10^{-4} M). The latter three solvents use the left-hand scale.

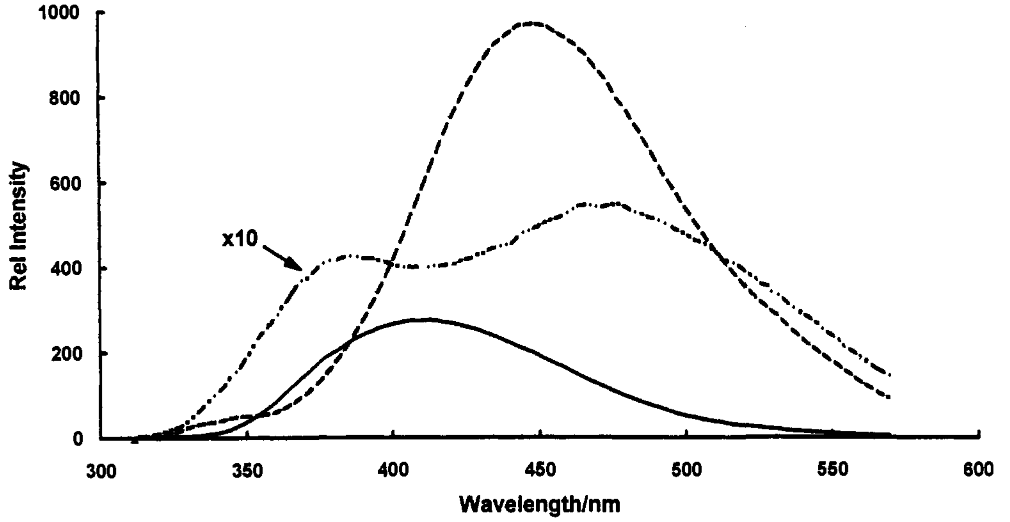

Figure 2. Fluorescence spectra of 1.14 × 10^{-4} M 1-(*p*-cyanophenyl)-2-(pentamethyldisilanyl)cyclopentene (**1**) in isooctane (—), dichloromethane (- - -), and trifluoroethanol (- ·· -).

Table 1. Absorption and Fluorescence Data for ((*p*-Cyanophenyl)cyclopentenyl)disilane **1**[a]

solvent	$\tilde{\nu}_a$/cm^{-1} × 10^3	$\tilde{\nu}_f$/cm^{-1} × 10^3	$\Delta\tilde{\nu}_{ct}$/cm^{-1} × 10^3	$\Delta L(\epsilon,n)$[b]
isooctane	35.6	24.3	11.3	0.001
THF	35.0	23.0	12.0	0.209
CH_2Cl_2	34.6	22.3	12.3	0.217
CH_3CN	35.0	21.6	13.4	0.332
CF_3CH_2OH	34.1	21.3	12.8	0.318

[a] $\tilde{\nu}_a$ is the absorption frequency, $\tilde{\nu}_f$ is the emission frequency, and $\Delta\tilde{\nu}_{ct} = \tilde{\nu}_a - \tilde{\nu}_f$. [b] Solvent polarity parameter, calculated according to ref 5a and references cited therein, using data for dielectric constants, ε, and refractive indexes, *n*, from the following reference from Scaiano: *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, 1989; Vol. II, Chapter 14.

tionation to give a silene intermediate, since the quantum yield for **9** is negligible. Additionally, the low yields of **9** that are formed do not arise from such radical pair disproportionation, because no detectable deuterium is incorporated into the silyl methyls from methanol-*O-d*, as would be the case if a silene intermediate is involved.

That both the LE and CT states are involved to a significant extent in the formation of **8** is suggested qualitatively by solvent effects on efficiencies and by the nonlinear Stern–Volmer plot of Φ°/Φ for **8** versus [MeOH]. After subtraction of the contribution to **8** made by the LE component, assuming that a dual reactive state model is operative for the kinetics of product formation, an apparent correlation is found between the Stern–Volmer slope for formation of product **8** via the CT state and quenching of CT fluorescence by methanol. In a nonpolar, nonnucleophilic solvent such as pentane, competing silylene extrusion to form trimethylsilane **6** in the LE state becomes an important photoprocess.

Experimental Section

Spectra were recorded with the following spectrometers: GE GN 300 (300 MHz, ^{1}H, 75 MHz, ^{13}C, 46 MHz, ^{2}H NMR), Mattson 4020 Galaxy Series (FTIR), Perkin-Elmer 320 (UV), Perkin-Elmer LS-5 (fluorescence). A Hewlett-Packard 5890 GC and a HP 5970 mass selective detector were used for GC–MS analysis, which were performed at 70 eV with a 0.25 mm × 30 m DB-1 capillary column programmed at 100 or 150 °C for 4 min and then 265 °C at 10 °C min^{-1}, unless noted otherwise.

Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Medium-pressure liquid chromatography (MPLC) utilized a 82 cm × 2.5 cm column of flash silica gel (0.030–0.075 mm, Janssen Chimica) with hexanes as eluant or a 52 cm × 2.5 cm column of flash silica gel with ether in hexanes as eluant; the flow rate was 13 mL min^{-1}. Columns were connected via a septum injector to a Gilson Model 302 pump equipped with a 100 mL min^{-1} capacity head, and the eluant was passed through an ISCO UA-5 detector. Silica

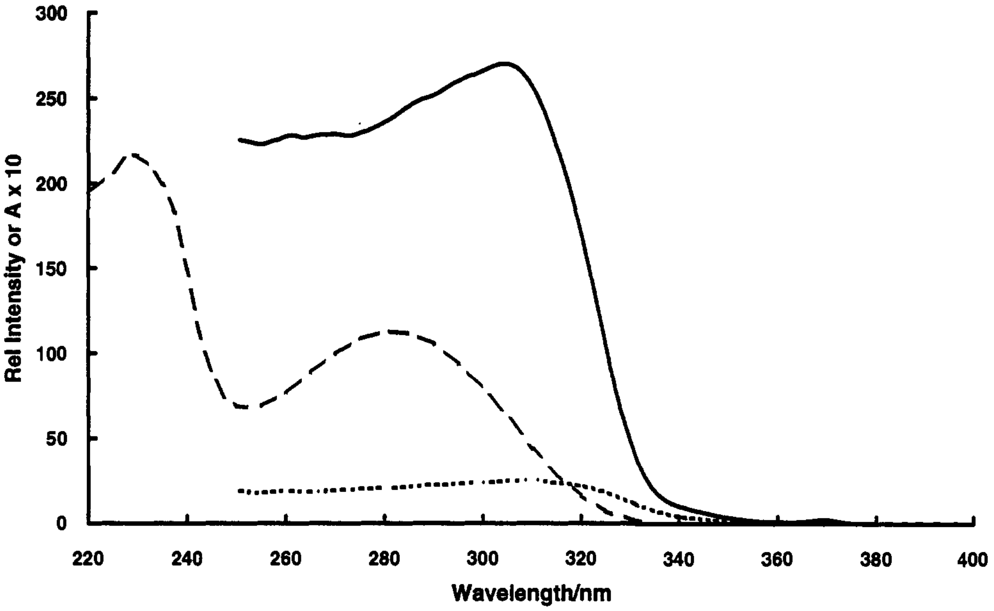

Figure 3. Excitation spectra of *p*-cyano compound **1** in acetonitrile (- - -, 1.36 × 10^{-4} M, λ_{em} = 470 nm) and isooctane (—, 1.47 × 10^{-4} M, λ_{em} = 420 nm) and corresponding absorption spectrum in isooctane (– – –).

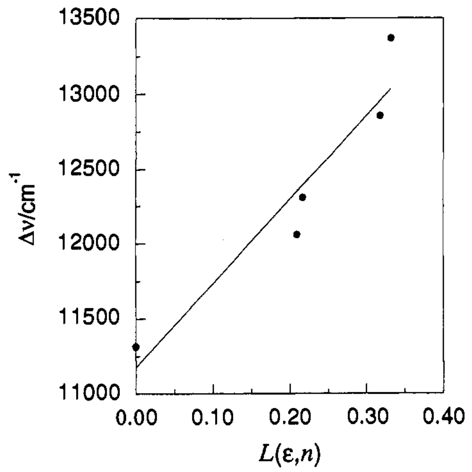

Figure 4. Solvatochromic plot of $\Delta\tilde{\nu}_{cr}$ versus solvent polarity parameter $L(\epsilon,n)$.

gel (60–200 mesh, grade 62, Mallinckrodt) was used for standard column chromatography.

Varian 1400 and HP 5710 gas chromatographs equipped with flame ionization detectors and a HP 3390 A electronic integrating recorder or a PE NELSON 1020 integrator were used for analytical separations. Nitrogen was the carrier gas. The silanized glass-lined injectors were at 250 °C. Detector response was calibrated against standard mixtures utilizing column A, 0.547 mm × 30 m Megabore DB-1 capillary, column B, 23 ft × 1/8 in. 10% OV-101 on 100/120 mesh Chromosorb W HP, and column C, 12 ft × 1/8 in. 10% QF-1 on 100/120 mesh Chromosorb W HP.

The following solvents were used: methanol (EM Omnisolv, distilled from magnesium), hexanes (Mallinckrodt, distilled from Na), THF (Milsolv, distilled from $LiAlH_4$), acetonitrile (Aldrich, HPLC grade, refluxed over CaH_2 for several days and distilled under nitrogen), 2,2,4-trimethylpentane (Aldrich, HPLC), benzene (Aldrich, HPLC), ether (Mallinckrodt, anhydrous), pentane (Aldrich, spectrophotometric grade), dichloromethane (Aldrich, distilled from CaH_2), 2,2,2-trifluoroethanol (Aldrich, refluxed with $NaHCO_3$ and $CaSO_4$ and then distilled), and ethanol (Aldrich spectrophotometric or Aaper Chemical, distilled from KOH).

((*p*-Bromophenyl)ethynyl)pentamethyldisilane (2). To a solution of 5.9 g (21 mmol) of 1-iodo-4-bromobenzene (Aldrich) and 4.4 g (28 mmol) of ethynylpentamethyldisilane (prepared following the method of Kraihanzel and Losee[18]) in 110 mL of diethylamine (Aldrich) were added 367 mg (0.521 mmol) of bis(triphenylphosphine)palladium(II) chloride (Aldrich) and 39 mg (0.20 mmol) of cuprous iodide (Aldrich). The reaction was stirred overnight under nitrogen at 23 °C. Concentration in vacuo and silica gel column chromatography (50 cm × 2.8 cm) with hexanes as eluant gave 6.2 g (95.3% yield) of NMR pure ((*p*-bromophenyl)ethynyl)pentamethyldisilane (**2**). A portion of the disilane was further purified by preparative MPLC, eluting with hexanes. The peak collected at a retention time of 46 min gave a satisfactory combustion analysis. The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.15 (s, 9H, methyl), 0.26 (s, 6H, methyl), 7.30 (B part of AA′BB′, m, 2H, aromatic), 7.42 (A part of AA′BB′, m, 2H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.17, −2.57, 94.72, 105.97, 122.38, 122.48, 131.41, 133.29; IR (CCl_4) 3.38, 3.45, 4.64, 6.73, 6.79, 8.03, 9.32, 9.89, 11.92, 12.11, 13.68 μm; GC–MS (70 eV) *m*/*z* (relative intensity) 312 (24), 310 (23), 298 (18), 297 (80), 296 (19), 295 (74), 239 (39), 237 (37), 231 (33), 209 (11), 207 (9), 143 (15), 128 (11), 73 (100), 53 (8); mp 48–48.5 °C. Anal. Calcd for $C_{13}H_{19}BrSi_2$: C, 50.15; H, 6.15. Found: C, 50.31; H, 6.17.

(*E*)-1-Iodo-1-(pentamethyldisilanyl)-2-(*p*-bromophenyl)-1,4-pentadiene (3). A mixture of 10.0 g (153 mmol) of zinc (Aldrich) and 2.6 g (14 mmol) of 1,2-dibromoethane (Aldrich) in 110 mL of dry THF were refluxed for 30 min. The reaction mixture was cooled to room temperature, and 9.0 g (29 mmol) of ((*p*-bromophenyl)ethynyl)pentamethyldisilane (**2**) and 7.0 g (58 mmol) of allyl bromide (Aldrich) were added. The reaction mixture was stirred at 60 °C for 54 h. After cooling slightly, the reaction was quenched by gradual addition of 25 g (98 mmol) of iodine. The mixture turned slightly pink. The mixture was diluted with 300 mL of ether and washed twice with 100 mL of saturated aqueous ammonium chloride and once with 100 mL of water. The ether phase was dried over anhydrous sodium sulfate. GC–MS analysis of the reaction mixture showed two isomeric products in a ratio of 81:19. After the ether was removed in vacuo, the residue was chromatographed on a 100 cm × 2.8 cm column of silica gel, eluting with hexanes, to give 12.6 g (91% yield) of NMR pure 1-iodo-1-disilanyl-2-(*p*-bromophenyl)-1,4-pentadiene **3** as a mixture of *E* and *Z* isomers. The major isomer, (*E*)-**3**, was further purified by MPLC, eluting with hexanes. NMR pure material was obtained by collecting the peak at a retention time of 48 min. The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.18 (s, 6H, methyl), 0.14 (s, 9H, methyl), 3.43 (dt, *J* = 6.6 Hz, 1.3 Hz, 2H, methylene), 4.98–5.08 (m, 2H, vinyl), 5.69 (ddt, *J* = 16.8 Hz, 10.0 Hz, 6.6 Hz, 1 H, vinyl), 6.92 (B part of AA′BB′, m, 2H, aromatic), 7.42 (A part of AA′BB′, m, 2H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.32, −0.05, 52.27, 111.83, 117.28, 121.53, 130.09, 131.01, 132.58, 140.78, 155.15; IR (CCl_4) 3.24, 3.36, 3.39, 3.45, 6.11, 6.37, 6.73, 6.99, 7.13, 8.03, 8.94, 9.32, 9.89, 10.89, 11.97, 12.26, 14.48 μm; GC–MS (70 eV) *m*/*z* (relative intensity) no parent, 407 (0.7), 406 (1.2), 405 (0.9), 353 (1.6), 351 (1.9), 279 (2), 277 (1.6), 243 (13), 239 (29), 237 (29), 199 (29), 185 (72), 131 (7), 99

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[18] Kraihanzel, C. S.; Losee, M. L. *J. Organomet. Chem.* **1967**, *10*, 427.

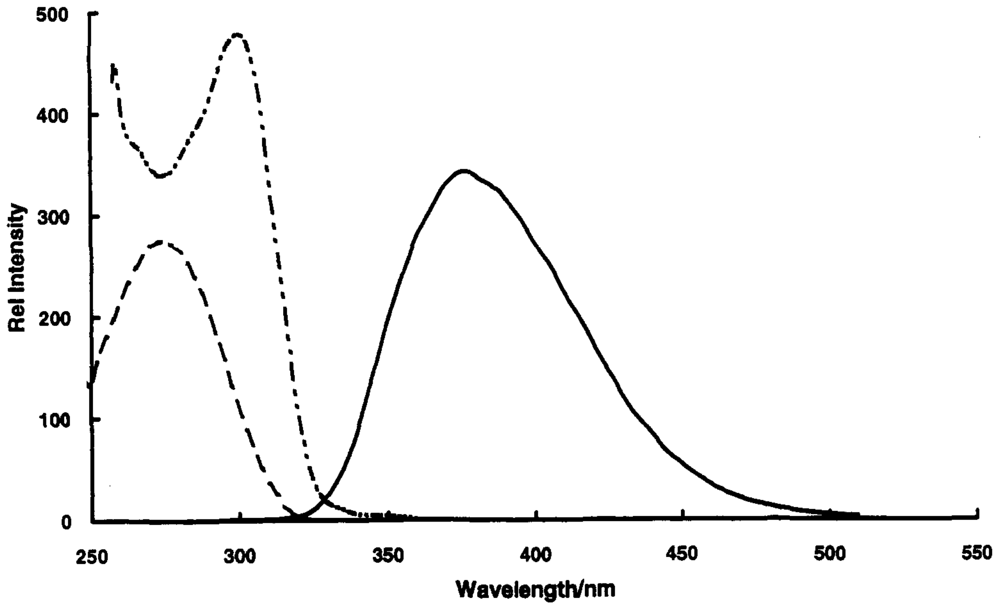

Figure 5. Fluorescence spectrum (—) of 10^{-4} M 1-(*p*-cyanophenyl)-2-(trimethylsilyl)cyclopentene (**6**) in methanol. Absorption (- - -) and excitation (- ·· -) spectra are shown for comparison.

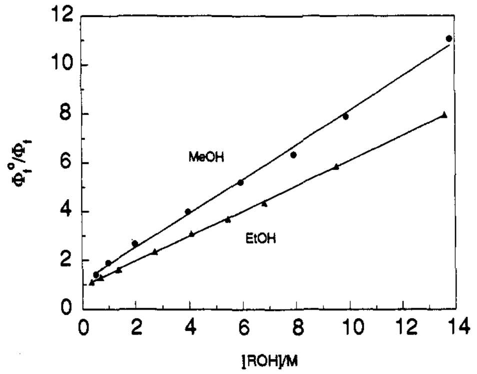

Figure 6. Fluorescence quenching by methanol and ethanol in pentane as the solvent.

(16), 73 (100), 59 (12), 45 (33), 43 (26). Anal. Calcd for $C_{16}H_{24}BrISi_2$: C, 40.09; H, 5.05. Found: C, 40.29; H, 5.16.

1-(*p*-Bromophenyl)-2-(pentamethyldisilanyl)cyclopentene (4). A mixture of 6.9 g (20.7 mmol) of tributyltin hydride (prepared by the method of Kuivia[19]) and 90 mg of AIBN in 120 mL of benzene was added dropwise to 9.9 g (20.7 mmol) of a mixture of (*E*)- and (*Z*)-1-iodo-1-(pentamethyldisilanyl)-2-(*p*-bromophenyl)penta-1,4-dienes (**3**) in 500 mL of refluxing benzene over a 3-h period, followed by an additional 30 min at reflux. The benzene was removed in vacuo. Flash chromatography of the residue on a 2.5 cm × 50 cm column of silica gel with hexanes as eluant was performed three times to remove organotin impurities. The 1-(*p*-bromophenyl)-2-(pentamethyldisilanyl)cyclopentene (**4**) was separated from two isomeric, acyclic products by MPLC, eluting with hexanes. Cuts from the leading edge of the peak at a retention time of 54 min gave 1.44 g (19.7% yield) of NMR pure product. The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ -0.04 (s, 6H, methyl), 0.03 (s, 9H, methyl), 1.91 (quintet, J = 7.5 Hz, 2H, methylene), 2.55 (tt, J = 7.5 Hz, 2.1 Hz, 2H, methylene), 2.70 (tt, J = 7.5 Hz, 2.1 Hz, 2H, methylene), 7.06 (B part of AA′BB′, m, 2H, aromatic), 7.40 (A part of AA′BB′, m, 2H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ -3.08, -1.71, 24.33, 40.29, 41.05, 120.46, 129.51, 130.75, 138.65, 139.83, 152.22; IR (CCl_4) 3.39, 3.45, 3.49, 3.52, 6.32, 6.73, 7.18, 8.03, 9.31, 9.87, 10.01, 11.55, 12.00, 12.58, 13.19, 14.52 μm; GC–MS (70 eV) *m/z* (relative intensity) 354 (3.6), 353 (1.0), 352 (3.5), 281 (30), 280 (16), 279 (28), 265 (8), 264 (2), 263 (8), 201 (19), 200 (100), 199 (23), 186 (14), 185 (84), 183 (16), 141 (13), 139 (8), 137 (7), 131 (8), 115 (10), 73 (85), 72 (18), 59 (41), 45 (39), 43 (32). Anal. Calcd for $C_{16}H_{25}BrSi_2$: C, 54.37; H, 7.13. Found: C, 54.33; H, 7.20.

1-(*p*-Cyanophenyl)-2-(pentamethyldisilanyl)cyclopentene (1). To 1.24 g (3.52 mmol) of 1-(*p*-bromophenyl)-2-(pentamethyldisilanyl)cyclopentene (**4**) in 50 mL of dry ether at -78 °C was added 2.8 mL (2.5 M, 7.0 mmol) of *n*-butyllithium in hexane dropwise via a syringe. The reaction mixture was gradually warmed to room temperature, stirred for 2 h, and then cooled to -78 °C. Addition of 0.90 g (7.6 mmol) of phenyl cyanate (prepared by the procedure of Murray and co-workers[20]), dropwise via syringe, was performed at a rate such that the temperature of the reaction remained below -60 °C. The mixture was stirred for 30 min at -60 °C and for 15 min at -40 °C and warmed to room temperature, and 50 mL of ether was added. After washing twice with 50 mL of saturated aqueous ammonium chloride, only, and drying over anhydrous sodium sulfate, the ether phase was decolorized twice with activated carbon and concentrated in vacuo. Conventional 2.8 cm × 50 cm column chromatography, eluting with 1% ether in hexanes, gave 0.70 g (66.1% yield) of NMR pure 1-(*p*-cyanophenyl)-2-(pentamethyldisilanyl)cyclopentene (**1**). A portion of product was further purified by preparative MPLC, eluting with 1% ether in hexanes, collecting the peak at a retention time of 44 min. MPLC was repeated prior to each photophysical and photochemical experiment reported below. The spectral data were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ -0.05 (s, 6H, methyl), 0.03 (s, 9H, methyl), 1.93 (quintet, J = 7.5 Hz, 2H, methylene), 2.58 (tt, J = 7.5 Hz, 2.1 Hz, 2H, methylene), 2.72 (tt, J = 7.5 Hz, 2.1 Hz, 2H, methylene), 7.29 (B part of AA′BB′, m, 2H, aromatic), 7.57 (A part of AA′BB′, m, 2H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ -3.15, -1.74, 14.11, 15.25, 24.36, 40.57, 40.88, 110.20, 119.09, 128.50, 131.54, 141.45, 145.94, 151.58; IR (CCl_4) 3.25, 3.29, 3.39, 3.45, 3.52, 4.48, 6.22, 6.66, 7.12, 8.03, 9.34, 9.80, 10.01, 11.55, 11.97, 14.48, 16.10 μm; GC–MS (70 eV) *m/z* (relative intensity) 299 (25), 298 (47), 284 (8), 226 (38), 225 (12), 210 (24), 198 (10), 184 (7), 170 (12), 85 (5), 73 (100), 59 (65), 45 (34), 43 (33); UV λ_{max} (methanol) 285 nm (ϵ 7650). Anal. Calcd for $C_{17}H_{25}NSi_2$: C, 68.16; H, 8.37. Found: C, 68.09; H, 8.37.

The long wavelength UV band of **1** also appeared at 281 nm (ϵ 7680) in isooctane, 286 (ϵ 8520) in THF, 286 nm (ϵ 7360) in acetonitrile, 289 nm (ϵ 8780) in dichloromethane, and 293 nm (ϵ 7510) in trifluoroethanol.

((*p*-Bromophenyl)ethynyl)trimethylsilane (10). To a solution of 5.0 g (18 mmol) of 1-bromo-4-iodobenzene (Aldrich) and 2.1 g (21 mmol) of ethynyltrimethylsilane (prepared following the method of Kraihanzel and Losee[18]) in 80 mL of diethylamine (Aldrich) were added 0.23 g (0.33 mmol) of bis(triphenylphosphine)palladium(II) chloride and 19 mg (0.10 mmol) of cuprous iodide (Aldrich). The reaction mixture was stirred in a room temperature water bath under nitrogen for 15 h, then diluted with benzene, washed twice with 200 mL of water, and dried over sodium sulfate. The benzene was removed in vacuo. The residue was chromatographed on a 2.8 cm × 100 cm column of silica gel to give 4.0 g (89% yield) of NMR pure ((*p*-bromophenyl)ethynyl)trimethylsilane (**10**). Crystallization from ethanol gave a product with mp 63–63.5 °C. The

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(19) Kuivia, H. G. *Synthesis* **1970**, 499.

(20) Murray, R. E.; Zweifel, G. *Synthesis* **1980**, 150.

Scheme 2

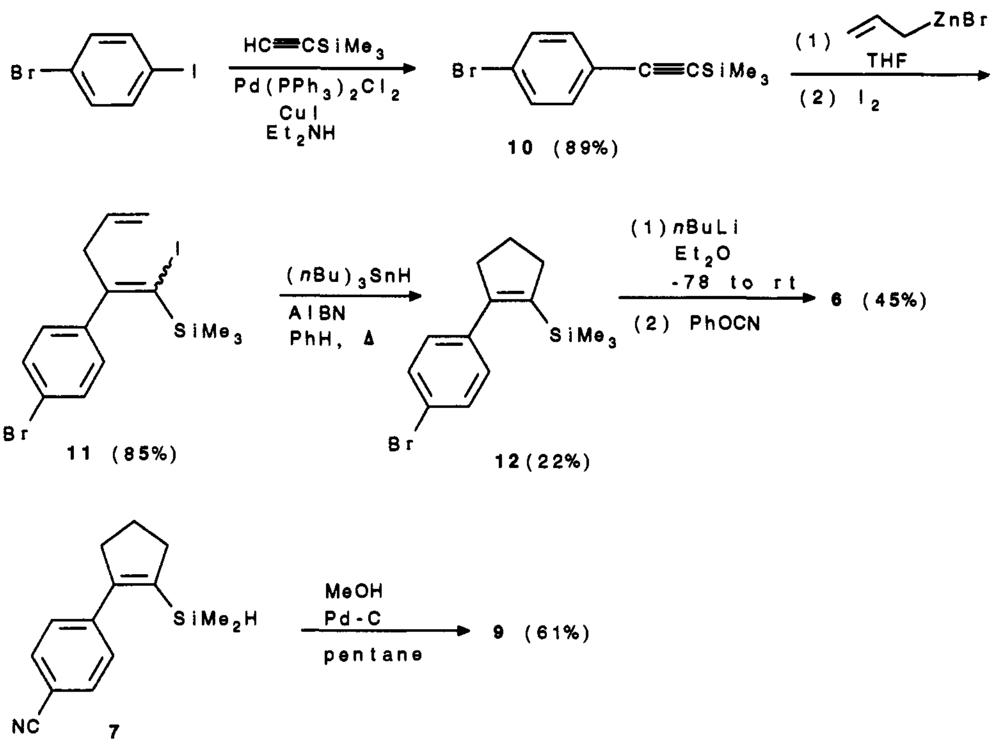


Table 2. Quantum Yields of Products in Various Solvents[a]

solvent	products 6	7	8	9
MeOH	nd[b]	0.0674	0.003 20	nd
EtOH	nd	0.0359	0.003 35	*c*
CF_3CH_2OH	0.002 74	nd	0.0118	nd
pentane	0.0134	nd	0.0168	nd
1 M MeOH in CH_3CN	0.001 79	0.006 78	0.004 57	0.000 68

[a] Determined at 290 nm (23 °C) with a microoptical bench apparatus (Experimental Section); values are the average of two independent photolyses, average deviation <4%. [b] Not detected (nd). [c] The ethoxydimethylsilane analog of **9** was not detected by GC–MS analysis.

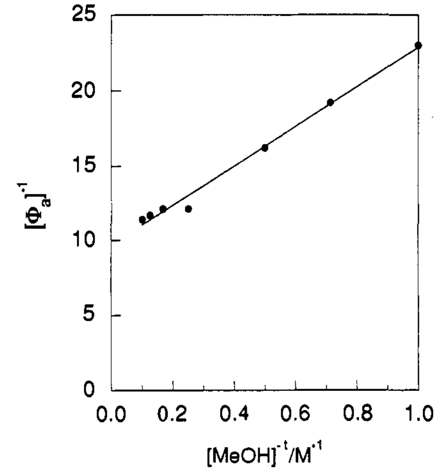


Figure 7. Dependence of quantum yields for formation of silane photoproduct **7** on the concentration of methanol in pentane.

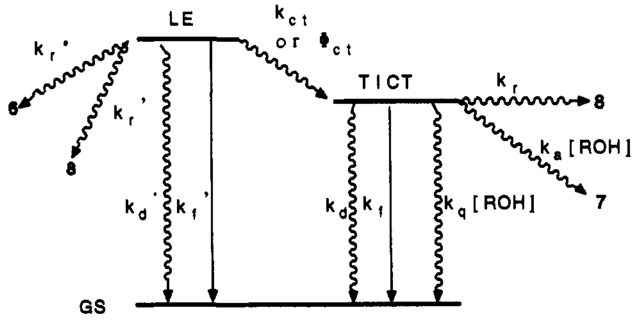
spectral data were as follows: ^1H NMR (300 MHz, $CDCl_3$) δ 0.24 (s, 9H, methyl), 7.32 (B part of AA′BB′, m, 2H, aromatic), 7.43 (A part of AA′BB′, m, 2H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.14, 95.56, 103.82, 122.06, 122.72, 131.45, 133.37; IR (CCl_4) 3.38, 3.45, 4.63, 6.72, 6.79, 7.99, 8.24, 9.32, 9.89, 11.55, 11.84, 12.43 μm; GC–MS (70 eV) *m*/*z* (relative intensity) 254 (20), 252 (19), 240 (16), 239 (100), 238 (19), 237 (98), 143 (9), 128 (8), 79 (8), 53 (9), 43 (23). Anal. Calcd for $C_{11}H_{13}BrSi$: C, 52.18; H, 5.17. Found: C, 52.28; H, 5.25.

Table 3. Quantum Yields of Products with Dilute Solutions of Methanol in Pentane[a]

[MeOH]/M	products 6	7	8	9
1.0	0.008 50	0.0435	0.0287	nq[b]
1.4	0.008 40	0.0522	0.0278	0.004 11
2.0	0.007 99	0.0616	0.0208	nq
4.0	0.008 08	0.0829	0.0165	nq
6.0	nq	0.0825	0.0163	nq
8.0	nq	0.0856	0.0141	nq
10.0	0.007 61	0.0874	0.0138	nq

[a] Performed at 290 nm (23 °C) with a microoptical bench apparatus (Experimental Section). Conversions were <10%. Each quantum yield represents the average of two independent photolyses, average deviation <6% for **6** and **8**, <2% for **7**. [b] Detected but not quantified (nq) due to a low yield.

Scheme 3



(*E*)-1-Iodo-1-(trimethylsilyl)-2-(*p*-bromophenyl)penta-1,4-diene (11). The (*p*-bromophenyl)pentadiene **11** was prepared in 85% yield from 7.4 g (29 mmol) of ((*p*-bromophenyl)ethynyl)trimethylsilane (**10**), 6.0 g (50 mmol) of allyl bromide, 6.0 g (92 mmol) of zinc, and 12 g (47 mmol) of iodine in 90 mL of dry THF, following the procedure for the synthesis of (*p*-bromophenyl)(pentamethyldisilanyl)-1,4-pentadiene **3** (vide supra). The reaction time was 30 h. Two isomeric products in the ratio 78:22 were observed by GC–MS. The major isomer, (*E*)-iodo-1-(trimethylsilyl)-2-(*p*-bromophenyl)-1,4-pentadiene (**11**), was obtained by MPLC, eluting with hexanes. The peak at a retention time of 52 min was collected. The spectral data were as follows: ^1H NMR (300 MHz, $CDCl_3$) δ −0.09 (s,

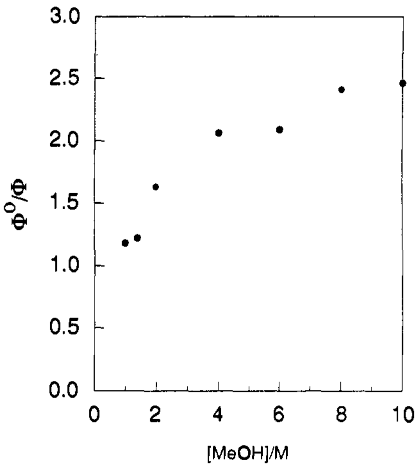


Figure 8. Dependence of relative quantum yields of **8** on the concentration of methanol in pentane.

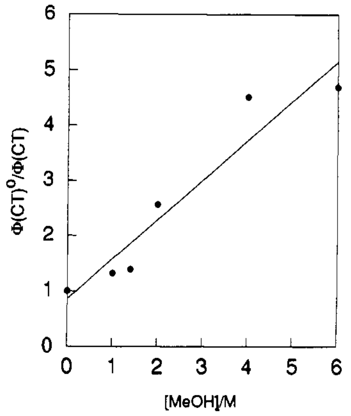


Figure 9. Dependence of relative quantum yields of **8** on methanol concentration after subtraction of the LE component.

9H, methyl), 3.44 (dt, J = 6.8 Hz, 1.3 Hz, 2H, methylene), 4.99–5.07 (m, 2H, vinyl), 5.68 (ddt, J = 16.8 Hz, 10.2 Hz, 6.6 Hz, 1H, vinyl), 6.94 (B part of AA'BB', m, 2H, aromatic), 7.43 (A part of AA'BB', m, 2H, aromatic); ^{13}C NMR (75 MHz, CDCl$_3$) δ 0.99, 52.15, 113.16, 117.37, 121.65, 130.04, 131.09, 132.46, 140.75, 155.99; IR (CCl$_4$) 3.24, 3.36, 3.38, 3.41, 3.45, 3.48, 6.11, 6.36, 6.73, 7.00, 7.11, 7.20, 8.00, 8.94, 9.32, 9.89, 10.89, 11.60, 11.86, 12.40 μm; GC–MS (70 eV) m/z (relative intensity) 422 (5.4), 420 (5.3), 295 (2.3), 293 (2.3), 239 (2.9), 237 (2.9), 215 (1.1), 213 (1.2), 185 (13.4), 141 (3.2), 115 (4.0), 74 (9.0), 73 (100), 45 (9.0). Anal. Calcd for $C_{14}H_{18}BrISi$: C, 39.92; H, 4.31. Found: C, 40.47; H, 4.44.

1-(*p*-Bromophenyl)-2-(trimethylsilyl)cyclopentene (12). A mixture of 4.8 g (17 mmol) of tributyltin hydride and 42 mg of AIBN in 120 mL of benzene was added dropwise to 6.0 g (14 mmol) of (*E*)- and (*Z*)-1-iodo-1-(trimethylsilyl)-2-(*p*-bromophenyl)-1,4-pentadiene (**11**) in 400 mL of refluxing benzene over a 2-h period, followed by an additional 30 min at reflux. The benzene was removed in vacuo. Flash chromatography of the residue on a 2.5 cm × 50 cm column of silica gel, eluting with hexanes, was performed three times to separate the organotin impurities. 1-(*p*-Bromophenyl)-2-(trimethylsilyl)cyclopentene (**12**) was then separated from two isomeric acyclic products by MPLC, eluting with hexanes. Cuts from the leading edge of the peak at a retention time of 52 min gave 0.94 g (22% yield) of NMR pure product. The spectral data were as follows: ^{1}H NMR (300 MHz, CDCl$_3$) δ –0.05 (s, 9H, methyl), 1.91 (quintet, J = 7.5 Hz, 2H, methylene), 2.58 (tt, J = 7.5 Hz, 2.4 Hz, 2H, methylene), 2.70 (tt, J = 7.5 Hz, 2.4 Hz, 2H, methylene), 7.08 (B part of AA'BB', m, 2H, aromatic), 7.41 (A part of AA'BB', m, 2H, aromatic); ^{13}C NMR (75 MHz, CDCl$_3$) δ –0.42, 24.06, 39.42, 41.23, 120.54, 129.46, 130.82, 139.62, 140.01, 152.51; IR (CCl$_4$) 3.38, 3.45, 3.49, 3.52, 6.22, 6.32, 6.73, 8.00, 9.29, 9.87, 9.97, 11.05, 11.92, 12.14 μm; GC–MS (70 eV) m/z (relative intensity) 296 (29), 294 (27), 281 (38), 279 (37), 215 (33), 201 (16), 200 (81), 199 (13), 185 (30), 183 (11), 143 (15), 142 (100), 141 (44), 139 (11), 115 (20), 74 (10), 73 (90), 72 (14), 59 (13), 45 (37), 43 (35). Anal. Calcd for $C_{14}H_{19}BrSi$: C, 56.93; H, 6.48. Found: C, 56.75; H, 6.60.

1-(*p*-Cyanophenyl)-2-(trimethylsilyl)cyclopentene (6). To 197 mg (0.667 mmol) of 1-(*p*-bromophenyl)-2-(trimethylsilyl)cyclopentene (**12**) in 40 mL of dry ether at –78 °C was added 0.6 mL (2.5 M, 1.5 mmol) of *n*-butyllithium in hexanes, dropwise via syringe. The reaction mixture was gradually warmed to room temperature and then stirred for 1 h. After cooling to –78 °C, 0.13 g (1.1 mmol) of phenyl cyanate was added via syringe, followed by stirring for 30 min. The mixture was warmed to room temperature, diluted with 50 mL of ether, washed twice with 40 mL of saturated aqueous ammonium chloride, and dried over sodium sulfate. The ether phase was decolorized once with activated carbon and concentrated in vacuo. MPLC, eluting with 1% ether in hexanes, gave 73 mg (45% yield) of NMR pure 1-(*p*-cyanophenyl)-2-(trimethylsilyl)-cyclopentene (**6**), collecting the peak at a retention time of 44 min. The spectral data were as follows: ^{1}H NMR (300 MHz, CDCl$_3$) δ –0.06 (s, 9H, methyl), 1.93 (quintet, J = 7.5 Hz, 2H, methylene), 2.61 (tt, J = 7.5 Hz, 2.4 Hz, 2H, methylene), 2.72 (tt, J = 7.5 Hz, 2.4 Hz, 2H, methylene), 7.30 (B part of AA'BB', m, 2H, aromatic), 7.58 (A part of AA'BB', m, 2H, aromatic); ^{13}C NMR (75 MHz, CDCl$_3$) δ –0.50, 24.11, 39.66, 41.05, 110.35, 119.07, 128.50, 131.59, 142.11, 146.16, 151.85; IR (CCl$_4$) 3.29, 3.38, 3.45, 3.49, 3.52, 4.48, 6.26, 6.66, 6.95, 7.12, 8.00, 9.31, 9.97, 11.05, 11.97, 12.49 μm; GC–MS (70 eV) m/z (relative intensity) 241 (55), 227 (11), 226 (55), 210 (24), 198 (14), 170 (11), 73 (100), 59 (48), 45 (29), 43 (31); UV λ_{max} (isooctane) 270 (ε 1.04 × 10^4).[21] Anal. Calcd for $C_{15}H_{19}NSi$: C, 74.63; H, 7.93. Found: C, 74.59; H, 7.90.

The position of the longest wavelength UV absorption of **6** was also observed at 275 nm (ε 9720) in acetonitrile and at 278 nm (ε 9740) in dichloromethane.

Synthesis of 1-(*p*-Cyanophenyl)-2-(dimethylmethoxysilyl)cyclopentene (9). To 5 mg of 5% Pd on C (Aldrich) under nitrogen was added 21 mg (0.090 mmol) of 1-(*p*-cyanophenyl)-2-(dimethylsilyl)cyclopentene (**7**) in 15 mL of pentane; dimethylsilane **7** was obtained from 254-nm direct photolysis of **1** (vide infra). The mixture was stirred for 1 min, and 12 mg (0.36 mmol) of methanol (distilled from Mg) was then added rapidly via syringe. After stirring 1.5 h at room temperature, the mixture was filtered through Celite and concentrated in vacuo to give 13.8 mg (60.9% yield) of NMR pure 1-(*p*-cyanophenyl)-2-(dimethylmethoxysilyl)cyclopentene (**9**). Compound **9** did not elute upon attempted MPLC and thus was not purified further. The spectral data were as follows: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.04 (s, 6H, methyl), 1.96 (quintet, J = 7.6 Hz, 2H, methylene), 2.65 (tt, J = 7.6 Hz, 2.2 Hz, 2H, methylene), 2.77 (tt, J = 7.6 Hz, 2.2 Hz, 2H, methylene), 3.26 (s, 3H, methoxy), 7.42 (B part of AA'BB', m, 2H, aromatic), 7.59 (A part of AA'BB', m, 2H, aromatic); ^{13}C NMR (75 MHz, CDCl$_3$) δ –1.63, 24.07, 39.70, 40.36, 50.17, 110.52, 119.05, 128.36, 131.57, 140.27, 144.94, 153.74; IR (CCl$_4$) 3.38, 3.41, 3.49, 3.52, 4.48, 6.22, 6.65, 7.98, 8.42, 9.19, 9.97, 11.97, 12.49, 12.99 μm; GC–MS (70 eV) m/z (relative intensity) 257 (32), 242 (24), 225 (12), 211 (14), 210 (67), 140 (10), 89 (100), 75 (14), 59 (95), 45 (14), 43 (19).

General Procedure for 254-nm Direct Photolyses. A jacketed quartz immersion well through which was circulated cold methanol in water or water (for preparative runs) was mounted in the center of a Rayonet reactor containing 16 2537-Å lamps. A Vycor tube containing 29 mL or 5 mL (only for quantum yield determinations) of photolysate was inserted into the immersion well. All photolysates were purged with nitrogen 30 min prior to and during photolyses. Photolyses were monitored by GC or GC–MS analyses of aliquots taken at time intervals. Each 0.25-0.5-mL aliquot was subjected to a standard workup involving addition of 0.5 mL of hexanes, followed by washing one to three times with 1 mL of water and drying over anhydrous sodium sulfate.

Preparative Direct Photolysis of 1-(*p*-Cyanophenyl)-2-(pentamethyldisilanyl)cyclopentene (1) in Methanol. A solution of 127 mg (0.420 mmol) of the *p*-cyano compound **1** in 29 mL of methanol (distilled from Mg) maintained at 5 °C was irradiated at 254 nm for 8 h following the general procedure. Progress of the photolysis was monitored by GC–MS. In addition to starting **1**, two major products were observed, which had retention times and mass spectra corresponding to methoxytrimethylsilane (Aldrich) and 1-(*p*-cyanophenyl)-2-(dimethylsilyl)cyclopentene (**7**). The presence of methoxytrimethylsilane was also established by comparison of GC retention times on three columns: capillary DB-1 (GC–MS at 40 °C), 1.96 min; column B (80 °C, flow rate 15 mL min^{-1}), 6.6 min; column C (60 °C, flow rate 15 min^{-1}), 2.6 min. The photolysate was diluted with 100 mL of hexanes, washed twice with water, and dried

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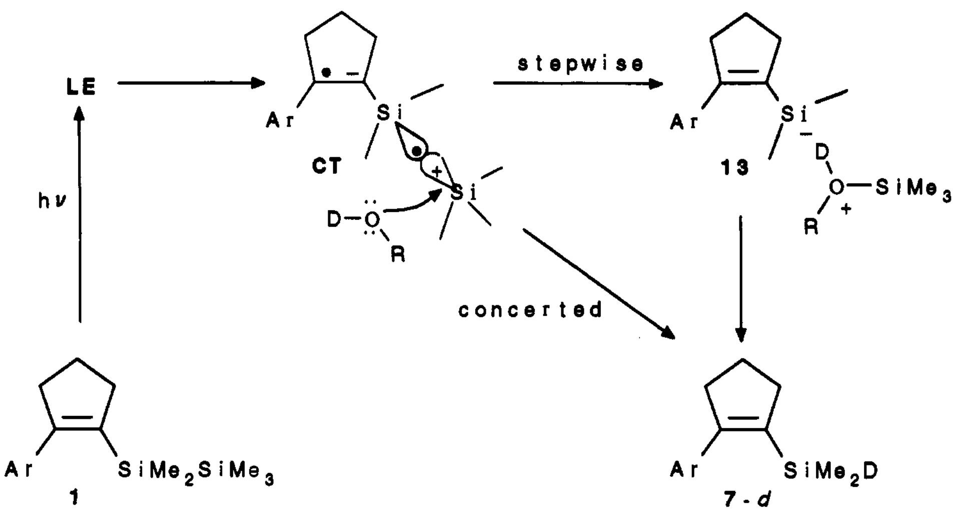
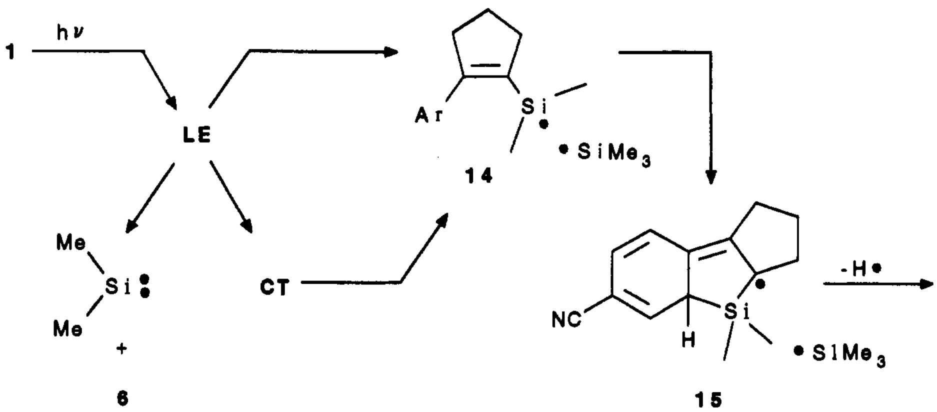
[21] (a) For comparison (*p*-cyanophenyl)cyclopentene absorbs at λ_{max} (isooctane) 280 nm (ε 21 600). (*p*-Cyanophenyl)cyclopentene[21b] was synthesized by reaction of *p*-lithiobenzonitrile with cyclopentanone at –100 °C in THF, followed by dehydration with oxalic acid in toluene. (b) Hahn, R. C.; Corbin, T. F.; Shechter, H. *J. Am. Chem. Soc.* **1968**, *90*, 3404.

Scheme 4



Scheme 5



over anhydrous sodium sulfate. After the solvent was removed in vacuo, dimethylsilane 7 was isolated by MPLC, eluting with 1% ether in hexanes. Cuts from the trailing edge of the peak at a retention time of 46 min were collected. Reactant 1 was present in the earlier eluting portion of the peak. The spectral data of dimethylsilane 7 were as follows: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.10 (d, *J* = 3.6 Hz, 6H, methyl), 1.96 (quintet, *J* = 7.5 Hz, 2H, methylene), 2.63 (tt, *J* = 7.5 Hz, 2.1 Hz, 2H, methylene), 2.78 (tt, *J* = 7.5 Hz, 2.1 Hz, 2H, methylene), 4.14 (septet, *J* = 3.6 Hz, 1H, silane), 7.37 (B part of AA'BB', m, 2H, aromatic), 7.59 (A part of AA'BB', m, 2H, aromatic); ^{13}C NMR (75 MHz, CDCl$_3$) δ -4.02, 23.98, 39.24, 39.63, 110.28, 119.07, 128.26, 131.64, 140.31, 144.55, 152.61; IR (CCl$_4$) 3.29, 3.38, 3.44, 3.49, 3.52, 4.48, 4.68, 6.22, 6.65, 6.96, 7.13, 7.99, 9.27, 9.95, 10.96, 11.17, 11.97, 13.75 μm; GC–MS (70 eV) *m*/*z* (relative intensity) 227 (74), 226 (37), 212 (45), 210 (14), 184 (24), 168 (25), 167 (29), 166 (12), 160 (11), 153 (14), 146 (14), 143 (31), 141 (11), 140 (18), 59 (100), 58 (37), 53 (13), 45 (18). Anal. Calcd for $C_{14}H_{17}NSi$: C, 73.95; H, 7.54. Found: C, 73.86; H, 7.68.

Preparative Direct Photolyses of *p*-Cyano Compound 1 in Methanol-*O*-*d* at 254 nm. A solution of 115 mg (0.380 mmol) of the *p*-cyano compound 1 in 29 mL of methanol-*O*-*d* (Aldrich, 99.5+ atom % D) was irradiated at 5 °C for 6 h following the above procedure. GC–MS analyses of aliquots after standard workup showed that product 7 was at least 90.5% monodeuterated, using the parent ion to calculate[22] the isotopic distribution. The 1-(deuteriodimethylsilyl)-2-(*p*-cyanophenyl)cyclopentene (7-*d*) was isolated as above to obtain the following data: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.10 (s, 6H, methyl), 1.96 (quintet, *J* = 7.6 Hz, 2H, methylene), 2.63 (tt, *J* = 7.6 Hz, 2.2 Hz, 2H, methylene), 2.78 (tt, *J* = 7.6 Hz, 2.2 Hz, 2H, methylene), 7.37 (B part of AA'BB', m, 2H, aromatic), 7.59 (A part of AA'BB', m, 2H, aromatic); ^{2}H NMR (46 MHz, CDCl$_3$) δ 4.20; ^{13}C NMR (75 MHz, CDCl$_3$) δ -4.10, 23.99, 39.24, 110.30, 119.09, 128.26, 131.66, 140.31, 144.56, 152.61; GC–MS (70 eV) *m*/*z* (relative intensity) 228 (100), 227 (48), 214 (11), 213 (61), 210 (14), 186 (10), 185 (22), 184 (10), 169 (14), 168 (29), 167 (18), 153 (11), 146 (13), 144 (39), 140 (15), 60 (80), 59 (47), 58 (37), 53 (11), 45 (13), 43 (51).

Photolysis of *p*-Cyano Compound 1 in Methanol-*O*-*d* at 290 nm. A solution of 44 mg (0.15 mmol) of *p*-cyano compound 1 in 41 mL of methanol-*O*-*d* (Aldrich, 99.5+ atom % D) was purged with nitrogen for 30 min and irradiated at 290 nm for 6.5 h, following the general procedure for quantum yield determinations (vide infra), but without the actinometry. GC–MS analyses of aliquots after the standard workup showed that product 7-*d* was at least 90.2% monodeuterated, as calculated[22] from the parent ion. After workup (vide supra) the residue was analyzed by ^{2}H NMR, which showed only one peak at δ 4.21, corresponding to SiD in compound 7-*d*.

Photolysis of *p*-Cyano Compound 1 in 1.0 M Methanol-*O*-*d* in Pentane at 254 nm. A solution of 110 mg (0.367 mmol) of *p*-cyano compound 1 and 1.0 g (30 mmol) of methanol-*O*-*d* (Aldrich, 99.5+ atom % D) in 29 mL of pentane was irradiated at 10 °C for 6 h, following the procedure described above for runs in pure methanol. GC–MS analyses of aliquots showed that product 7 was at least 90% monodeuterated, as calculated[22] from the parent ion. GC–MS also showed the presence of two minor products, 6-cyano-1,1-dimethyl-1-sila-2,3-cyclopentenoindene (8) (vide infra) and 1-(*p*-cyanophenyl)-2-(dimethylmethoxysilyl)cyclopentene (9), which were at least 97% undeuterated. Pure 7-*d* was isolated from the middle cut of the peak at a retention time of 50 min by MPLC, eluting with 1% ether in hexanes. GC–MS showed that compounds 8 and 9 were present in fractions collected from the tail of the peak. ^{1}H NMR spectra of 7-*d* indicated that the amount of SiH was less than 0.5%, and the ^{2}H NMR spectrum showed only one peak at δ 4.21, corresponding to SiD.

Preparative Direct Photolysis of *p*-Cyano Compound 1 in Hexanes. A solution of 275 mg (0.920 mmol) of *p*-cyano compound 1 in 290 mL of hexanes was purged with nitrogen and then irradiated through a Vycor filter with a Hanovia 450-W medium-pressure lamp for 4 h. GC–MS analyses of aliquots after workup showed peaks with retention times and mass spectra corresponding to reactant 1, authentic 6, and a product

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[22] Biemann, K. *Mass Spectrometry*; McGraw-Hill: New York, 1962; p 209.

identified (vide infra) as tricyclic 6-cyano-1,1-dimethyl-1-sila-2,3-cyclopentenoindene (**8**). After concentration in vacuo, MPLC with ca. 3% ether in hexanes as eluant gave NMR pure compound **6** in the middle cut of a peak at a retention time of 49 min, according to ^{1}H and ^{13}C NMR, IR, and GC–MS analyses. NMR pure tricyclic 6-cyano-1,1-dimethyl-1-sila-2,3-cyclopentenoindene (**8**) was isolated from cuts of the trailing edge of the peak. The spectral data of **8** were as follows: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.31 (s, 6H, methyl), 2.23 (quintet, J = 7.5 Hz, 2H, methylene), 2.54–2.66 (m, 4H, methylene), 7.14 (d, J = 7.8 Hz, 1H, aromatic), 7.58–7.67 (m, 2H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ –4.64, 26.87, 30.13, 33.15, 108.97, 120.00, 121.06, 134.06, 134.45, 144.11, 149.93, 151.35, 161.56; GC–MS (70 eV) m/z (relative intensity) 225 (88), 212 (12), 211 (21), 210 (100), 184 (21), 166 (9), 156 (8), 140 (8), 59 (15), 53 (11), 43 (25).

Preparative Direct Photolysis of *p*-Cyano Compound 1 in 2,2,2-Trifluoroethanol at 254 nm. A solution of 200 mg (0.669 mmol) of *p*-cyano compound **1** in 29 mL of 2,2,2-trifluoroethanol was irradiated at 23 °C for 24 h following the general procedure for 254-nm photolyses. GC–MS analyses of aliquots after workup showed peaks with retention times and mass spectra corresponding to reactant **1**, authentic **6**, a minor product, and tricyclic compound **8**, the major product. The photolysate was concentrated in vacuo (20 mm), and the residue was further dried at 0.5 mm. MPLC with 1.5% ether in hexane gave 12 mg, mp 100–102 °C, of **8** in the second peak eluting at a retention time of 88 min. The first peak, eluting at 58 min, was reactant **1**, containing trimethylsilane **6** in the trailing edge of the peak. Crystallization of **8** from absolute ethanol gave a product with mp 107–109 °C. The spectral data for tricyclic compound **8** was identical to that obtained from the photolysis in hexane. Additional spectral and analytical data follow: IR (CCl_4) 3.38, 3.52, 4.49, 6.29, 6.47, 6.88, 7.17, 8.00, 9.49, 12.40, 12.96, 13.40 μm. Anal. Calcd for $C_{14}H_{15}NSi$: C, 74.61; H, 6.71. Found: C, 74.30; H, 6.80.

Determination of Product Yields for Photolysis of *p*-Cyano Compound 1 in 10.0 M Methanol in Pentane at 310 nm. A solution of 45 mg (0.15 mmol) of the *p*-cyano compound **1**, 14.1 g (0.44 mol) of methanol (distilled from Mg), and 11.0 mg (0.0486 mmol) of hexadecane (Supelco) as internal standard in 26 mL of pentane was purged with nitrogen for 30 min and irradiated at 310 nm, following the procedure for quantum yield determinations. Aliquots at time intervals of 90, 180, and 300 min were analyzed by GC as described above. The results were as follows: 90 min, 12.8% conversion of **1**, 13.2% yield of **7**, 0.8% of **8**, and 0.4% of **9**, respectively; 180 min, 26.9% conversion of **1**, 26.5% yield of **7**, 1.1% of **8**, and 0.9% of **9**, respectively; 300 min, 45.4% conversion of **1**, 42.5% yield of **7**, 1.2% of **8**, and 1.0% of **9**, respectively.

Procedure for Quantum Yield Determinations of Photolyses of *p*-Cyano Compound 1. A semimicrooptical bench for quantum yield determinations was constructed along the lines specified by Zimmerman.[23a] Light from a 200-W high-pressure mercury lamp was passed through an Oriel monochromator at 270, 290, or 310 nm with entrance and exit slits set at 3 mm to give a 20-nm bandpass at half-peak height. Light was collimated through a lens and passed through a beam splitter, which diverted 13% of the light to a cell containing actinometer, perpendicular to the light path. A jacketed quartz cylindrical cell, 2.5 cm × 8 cm of 40-mL volume, which contained the photolysate, was mounted in line with the optics, monochromator, and lamp. Light output was monitored by ferrioxalate actinometry,[23b] using the splitting ratio technique.[23a]

All photolysates were purged with nitrogen for 30 min before and during the irradiations. In the cases of methanol, ethanol, and 2,2,2-trifluoroethanol as solvents, the photolysates were subjected to a standard workup involving addition of an equal volume of hexanes, followed by washing once with water and drying over sodium sulfate. GC analyses were performed on column A (140 °C for 35 min and then 160 °C). The retention times were follows: 1-(dimethylsilyl)-2-(*p*-cyanophenyl)cyclopentene (**7**), 20.4 min; 6-cyano-1,1-dimethyl-1-sila-2,3-cyclopentenoindene (**8**), 26.7 min; 1-(trimethylsilyl)-2-(*p*-cyanophenyl)cyclopentene (**6**), 22.0 min; 1-(dimethylmethoxysilyl)-2-(*p*-cyanophenyl)cyclopentene (**9**), 31.6 min. Hexadecane (Supelco) served as the internal standard.

***p*-Cyano Compound 1 in Methanol at 290 nm. Run 1**: reactant, 3.05 × 10^{-3} M, 0.111 mEinsteins, product **7**, 7.80 × 10^{-3} mmol, Φ = 0.0705; product **8**, 3.70 × 10^{-4} mmol, Φ = 0.00334, percent conversion, 6.7%. **Run 2**: reactant, 3.05 × 10^{-3} M, 0.119 mEinsteins, product **7**, 7.67 × 10^{-3} mmol, Φ = 0.0643; product **8**, 3.65 × 10^{-4} mmol, Φ = 0.00306; percent conversion, 6.6%.

***p*-Cyano Compound 1 in 1.0 M Methanol in Hexanes at 290 nm. Run 1**: reactant, 3.05 × 10^{-3} M, 0.137 mEinsteins, product **7**, 4.70 × 10^{-3} mmol, Φ = 0.0344; product **8**, 3.36 × 10^{-3} mmol, Φ = 0.0246; product **6**, 4.08 × 10^{-4} mmol, Φ = 0.00299; product **9**, 6.37 × 10^{-4} mmol, Φ = 0.00467; percent conversion, 7.5%. **Run 2**: reactant, 3.05 × 10^{-3} M, 0.114 mEinsteins, product **7**, 3.89 × 10^{-3} mmol, Φ = 0.0341; product **8**, 2.94 × 10^{-3} mmol, Φ = 0.0259; product **6**, 3.83 × 10^{-4} mmol, Φ = 0.00318; product **9**, 5.77 × 10^{-4} mmol, Φ = 0.00487; percent conversion, 6.4%.

***p*-Cyano Compound 1 in 1.0 M Methanol in Acetonitrile at 290 nm. Run 1**: 3.18 × 10^{-3} M, 0.184 mEinsteins, product **7**, 1.20 × 10^{-3} mmol, Φ = 0.00650; product **8**, 7.94 × 10^{-4} mmol, Φ = 0.00430; product **6**, 3.24 × 10^{-4} mmol, Φ = 0.00176; product **9**, 1.16 × 10^{-4} mmol, Φ = 0.00063; percent conversion, 1.9%. **Run 2**: reactant, 3.18 × 10^{-3} M, 0.201 mEinsteins, product **7**, 1.53 × 10^{-3} mmol, Φ = 0.00706; product **8**, 9.77 × 10^{-4} mmol, Φ = 0.00485; product **6**, 3.69 × 10^{-4} mmol, Φ = 0.00183; product **9**, 1.50 × 10^{-4} mmol, Φ = 0.00074; percent conversion, 2.4%.

***p*-Cyano Compound 1 in 1.0 M Methanol in Hexanes at 310 nm. Run 1**: 3.37 × 10^{-3} M, 0.229 mEinsteins, product **7**, 1.04 × 10^{-2} mmol, Φ = 0.0453; product **8**, 5.56 × 10^{-3} mmol, Φ = 0.0243; product **6**, 1.49 × 10^{-3} mmol, Φ = 0.00653; product **9**, 1.79 × 10^{-3} mmol, Φ = 0.00781; percent conversion, 13.1%. **Run 2**: reactant, 3.37 × 10^{-3} M, 0.134 mEinsteins, product **7**, 5.92 × 10^{-3} mmol, Φ = 0.0441; product **8**, 2.88 × 10^{-3} mmol, Φ = 0.0228; product **6**, 7.85 × 10^{-4} mmol, Φ = 0.00619; product **9**, 8.84 × 10^{-4} mmol, Φ = 0.00659; percent conversion, 7.0%.

***p*-Cyano Compound 1 in 1.0 M Methanol in Hexanes at 270 nm. Run 1**: reactant, 3.11 × 10^{-3} M, 0.0266 mEinsteins, product **7**, 8.70 × 10^{-4} mmol, Φ = 0.0327; product **8**, 6.78 × 10^{-4} mmol, Φ = 0.0255; product **6**, 3.70 × 10^{-4} mmol, Φ = 0.0139; percent conversion, 1.6%. **Run 2**: reactant, 3.11 × 10^{-3} M, 0.0405 mEinsteins, product **7**, 1.23 × 10^{-3} mmol, Φ = 0.0303; product **8**, 1.06 × 10^{-3} mmol, Φ = 0.0260; product **6**, 4.81 × 10^{-4} mmol, Φ = 0.0118; percent conversion, 2.4%.

***p*-Cyano Compound 1 in 1.0 M Methanol in Pentane at 290 nm. Run 1**: reactant, 3.64 × 10^{-3} M, 8.78 × 10^{-2} mEinsteins, product **7**, 3.77 × 10^{-3} mmol, Φ = 0.0429; product **8**, 2.48 × 10^{-3} mmol; Φ = 0.0283; product **6**, 7.30 × 10^{-4} mmol, Φ = 0.00831; percent conversion, 4.8%. **Run 2**: reactant, 3.64 × 10^{-3} M, 8.82 × 10^{-2} mEinsteins, product **7**, 3.89 × 10^{-3} mmol, Φ = 0.0441; product **8**, 2.57 × 10^{-3} mmol, Φ = 0.0291; product **6**, 7.65 × 10^{-4} mmol, Φ = 0.00868; percent conversion, 5.0%.

***p*-Cyano Compound 1 in 1.4 M Methanol in Pentane at 290 nm. Run 1**: reactant, 3.64 × 10^{-3} M, 8.72 × 10^{-2} mEinsteins, product **7**, 4.58 × 10^{-3} mmol, Φ = 0.0525; product **8**, 2.44 × 10^{-3} mmol, Φ = 0.0280; product **6**, 7.47 × 10^{-4} mmol, Φ = 0.00856; product **9**, 3.43 × 10^{-4} mmol, Φ = 0.00393; percent conversion, 5.6%. **Run 2**: reactant, 3.64 × 10^{-3} M, 8.95 × 10^{-2} mEinsteins, product **7**, 4.65 × 10^{-3} mmol, Φ = 0.0520; product **8**, 2.48 × 10^{-3} mmol, Φ = 0.0277; product **6**, 7.52 × 10^{-4} mmol, Φ = 0.00840; product **9**, 3.84 × 10^{-4} mmol, Φ = 0.00429; percent conversion, 5.7%.

***p*-Cyano Compound 1 in 2.0 M Methanol in Pentane at 290 nm. Run 1**: reactant, 3.64 × 10^{-3} M, 9.71 × 10^{-2} mEinsteins, product **7**, 5.86 × 10^{-3} mmol, Φ = 0.0603; product **8**, 2.05 × 10^{-3} mmol, Φ = 0.0211; product **6**, 7.65 × 10^{-4} mmol, Φ = 0.00788; percent conversion, 6.0%. **Run 2**: reactant, 3.64 × 10^{-3} M, 9.66 × 10^{-2} mEinsteins, product **7**, 6.04 × 10^{-3} mmol, Φ = 0.0625; product **8**, 1.97 × 10^{-3} mmol, Φ = 0.0204; product **6**, 7.83 × 10^{-4} mmol, Φ = 0.00811; percent conversion, 6.1%.

***p*-Cyano Compound 1 in 4.0 M Methanol in Pentane at 290 nm. Run 1**: reactant, 3.64 × 10^{-3} M, 9.82 × 10^{-2} mEinsteins, product **7**, 8.13 × 10^{-3} mmol, Φ = 0.0827; product **8**, 1.53 × 10^{-3} mmol, Φ = 0.0156; product **6**, 7.96 × 10^{-4} mmol, Φ = 0.00811; percent conversion, 7.2%. **Run 2**: reactant, 3.64 × 10^{-3} M, 9.73 × 10^{-2} mEinsteins, product **7**, 8.09 × 10^{-3} mmol, Φ = 0.0831; product **8**, 1.68 × 10^{-3} mmol, Φ = 0.0173; product **6**, 7.83 × 10^{-4} mmol, Φ = 0.00805; percent conversion, 7.3%.

***p*-Cyano Compound 1 in 6.0 M Methanol in Pentane at 290 nm. Run 1**: reactant, 2.94 × 10^{-3} M, 7.84 × 10^{-2} mEinsteins, product **7**, 6.42 × 10^{-3} mmol, Φ = 0.0819; product **8**, 1.23 × 10^{-3} mmol, Φ = 0.0157; percent conversion, 6.5%. **Run 2**: reactant, 2.94 × 10^{-3} M, 8.45 × 10^{-2} mEinsteins, product **7**, 7.03 × 10^{-3} mmol, Φ = 0.0832; product **8**, 1.42 × 10^{-3} mmol, Φ = 0.0168, percent conversion, 7.2%.

***p*-Cyano Compound 1 in 8.0 M Methanol in Pentane at 290 nm. Run 1**: reactant, 2.94 × 10^{-3} M, 8.80 × 10^{-2} mEinsteins, product **7**, 7.41 × 10^{-3} mmol, Φ = 0.0842; product **8**, 1.17 × 10^{-3} mmol, Φ = 0.0133; percent conversion, 7.3%. **Run 2**: reactant, 2.94 × 10^{-3} M, 8.75 × 10^{-2} mEinsteins, product **7**, 7.60 × 10^{-3} mmol, Φ = 0.0868; product **8**, 1.31 × 10^{-3} mmol, Φ = 0.0150; percent conversion, 7.6%.

***p*-Cyano Compound 1 in 10.0 M Methanol in Pentane at 290 nm. Run 1**: reactant, 3.64 × 10^{-3} M, 9.22 × 10^{-2} mEinsteins, product **7**, 7.94 × 10^{-3} mmol, Φ = 0.0861; product **8**, 1.22 × 10^{-3} mmol, Φ = 0.0133; product

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(23) (a) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281. (b) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London* **1956**, *235*, 518.

6, 6.85 × 10^{-4} mmol, Φ = 0.00743; percent conversion, 6.8%. **Run 2**: reactant, 3.64 × 10^{-3} M, 9.64 × 10^{-2} mEinsteins, product **7**, 8.56 × 10^{-3} mmol, Φ = 0.0888; product **8**, 1.39 × 10^{-3} mmol, Φ = 0.0144; product **6**, 7.52 × 10^{-4} mmol, Φ = 0.00780; percent conversion, 7.4%.

***p*-Cyano Compound 1 in 2,2,2-Trifluoroethanol at 290 nm. Run 1**: reactant, 2.86 × 10^{-3} M, 0.115 mEinsteins, product **8**, 1.57 × 10^{-3} mmol, Φ = 0.0113; product **6**, 3.82 × 10^{-4} mmol, Φ = 0.00275; percent conversion, 1.7%. **Run 2**: reactant, 2.86 × 10^{-3} M, 0.144 mEinsteins, product **8**, 1.79 × 10^{-3} mmol, Φ = 0.0124; product **6**, 3.92 × 10^{-4} mmol, Φ = 0.00272; percent conversion, 1.9%.

***p*-Cyano Compound 1 in Pentane at 290 nm. Run 1**: reactant, 2.83 × 10^{-3} M, 0.128 mEinsteins, product **8**, 2.13 × 10^{-3} mmol, Φ = 0.0166; product **6**, 1.74 × 10^{-3} mmol, Φ = 0.0136; percent conversion, 3.4%. **Run 2**: reactant, 2.83 × 10^{-3} M, 0.131 mEinsteins, product **8**, 2.23 × 10^{-3} mmol, Φ = 0.0171; product **6**, 1.74 × 10^{-3} mmol, Φ = 0.0133; percent conversion, 3.5%.

***p*-Cyano Compound 1 in Ethanol at 290 nm. Run 1**: reactant, 2.84 × 10^{-3} M, 8.73 × 10^{-2} mEinsteins, product **7**, 3.01 × 10^{-3} mmol, Φ = 0.0345; product **8**, 2.73 × 10^{-4} mmol, Φ = 0.00311; percent conversion, 2.9%. **Run 2**: reactant, 2.84 × 10^{-3} M, 8.97 × 10^{-2} mEinsteins, product **7**, 3.35 × 10^{-3} mmol, Φ = 0.0373; product **8**, 2.99 × 10^{-4} mmol, Φ = 0.00333; percent conversion, 3.2%.

***p*-Cyano Compound 1 in Hexane at 290 nm. Run 1 at 40 °C**: reactant, 3.26 × 10^{-3} M, 0.0935 mEinsteins, product **6**, 1.91 × 10^{-3} mmol, Φ = 0.0204; product **8**, 2.20 × 10^{-3} mmol, Φ = 0.0235; percent conversion, 2.9%. **Run 2 at 20 °C**: reactant, 3.26 × 10^{-3} M, 0.0848 mEinsteins, product **6**, 1.50 × 10^{-3} mmol, Φ = 0.0177; product **8**, 1.96 × 10^{-3} mmol, Φ = 0.0231; percent conversion, 2.4%. **Run 3 at 1 °C**: reactant, 3.26 × 10^{-3} M, 0.0819 mEinsteins, product **6**, 1.37 × 10^{-3} mmol, Φ = 0.0167; product **8**, 1.89 × 10^{-3} mmol, Φ = 0.0230, percent conversion, 2.3%.

Quantum Yields for Photolyses of *p*-Cyano Compound 1 in Pentane at 254 nm. A solution of the *p*-cyano **1** and hexadecane (Supelco) as internal standard in 5 mL of pentane or hexane in a Vycor tube was degassed with nitrogen for 30 min and irradiated at 254 nm with 16 RPR 2537-Å lamps for 30 or 50 min, following the general procedure described above. Samples were analyzed by GC. Light output was determined by ferrioxalate actinometry.

Run 1 in pentane at 6 °C: reactant (2.26 × 10^{-3} M), 0.160 mEinsteins, product **8**, 1.65 × 10^{-3} mmol, Φ = 0.0103; product **6**, 1.51 × 10^{-4} mmol, Φ = 0.00094; percent conversion, 15.8%. **Run 2 in pentane 6 °C**: reactant (2.26 × 10^{-3} M), 0.102 mEinsteins, product **8**, 1.20 × 10^{-3} mmol, Φ = 0.0118; product **6**, 1.58 × 10^{-4} mmol, Φ = 0.00156; percent conversion, 12.0%. **Run 3 in hexane at 23 °C**: reactant (3.26 × 10^{-3} M), 0.200 mEinsteins, product **8**, 1.67 × 10^{-3} mmol, Φ = 0.00832; product **6**, 4.01 × 10^{-4} mmol, Φ = 0.0020; percent conversion, 12.7%.

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