transition state by complexation. Interestingly, the 4×10^{11} factor for **6** is comparable to the $\sim 10^{11}$ factor observed when **3** was similarly compared to noncomplexing **9** as a standard in the same medium but with R_3N/R_3NHClO_4 buffer present to deprotonate the hydroxyl of **3**. The R_3N present is $>10^4$ stronger as a base than the phenylimidazole group of **5** or **6**. Thus, covalently bonding a complexing site to an imidazole as in **5** or **6** provides large kinetic transacylation factors without addition of bases stronger than those present in the transacylase enzymes.

In semiquantitative experiments, catalytic turnover was observed at 25 °C in $CDCl_3$ saturated with D_2O with **6** or **10** as catalyst.[13] Without catalyst, the hydrolysis of **8** had a 50-h half-life. With **10** present, 1.5 equiv of **8** hydrolyzed in 2 h. Host **6** produced a catalytic rate initially 3 times that of **10**, but the alanine produced acted as an inhibitor and slowed the rate until its crystallization maintained a steady state of turnover of about 1 equiv per 3-4 h. Addition of 25 equiv of **8** and 30 equiv of 2,4,6-trimethylpyridine (divided into five equal increments, one per day) to 1 equiv of **6** hydrolyzed all of the **8**, after which 63% of pure **6** was recovered. In the same medium, **5** reacted initialy faster than **10** but slower than **6** in reacting with **8**. Spectral experiments (^1H NMR) suggested that conformationally isomeric esters of **13** were produced in a 3:2 ratio at about 5-10 times the rate at which alanine was generated.

(13) The catalyst concentration was 0.01 M, that of **8** was initially 0.05 M, and 2,4,6-trimethylpyridine was 0.06 M. Liberation of *p*-nitrophenol (ArH protons give signals downfield of 8 ppm) was monitored by ^1H NMR spectra with tetrachloroethane as internal standard. The 2,4,6-trimethylpyridine was added to potentially buffer the accumulating *p*-nitrophenol as it was produced. The p*K*a values of *p*-nitrophenyl in water [Gordon, A. J., Ford, R. A., Eds. "The Chemists Companion"; Wiley: New York, 1972; p 61], protonated 2,4,6-trimethylpyridine [Pritchard, J. G., Long, F .A. *J. Am. Chem. Soc.* **1957**, *79*, 2365-2368], and protonated phenylimidazole [Potts, K. T., Ed. "Comprehensive Heterocyclic Chemistry"; 4A, Pergamon Press: Oxford, 1984: Vol, *5*, p 384] are 7.2, 7.4, and 6.1, respectively.

Trans-Cis Photoisomerization of 3-Styryl-2′,4′,6′-triisopropylstilbene: Steric Effects on Location of the Electronic Excitation

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We have recently studied the photocyclization reaction of 2,4,6-triisopropylbenzophenone and its polycarbonyl derivatives into the corresponding benzocyclobutenols in great detail.[1] Spectroscopic and photokinetic examinations of this reaction have led to the conclusion that excited states of meta-substituted aromatic polyketones can be represented by rapid intramolecular energy migration between the component carbonyl groups and, furthermore, that the electronic excitation resides predominantly at the strained carbonyl group ($K = k_{et}/k_{-et} >> 1$) (Scheme Ia).[1,2] We here present another reaction showing steric control of partitioning of the electronic excitation in polychromophoric molecules.

The trans,trans isomer (**1a**) of 3-styryl-2′,4′,6′-triisopropylstilbene was irradiated in hexane (0.01 M) under bubbling nitrogen with Pyrex-filtered light (>290 nm) and the progress of the reaction was followed by HPLC analyses. Isomerization to the trans,cis isomer **1b** (a major product) and the cis,trans isomer **1c** (a minor product) occurred immediately after exposure to light.

(1) Ito, Y.; Kawatsuki, N.; Giri, B. P.; Yoshida, M.; Matsuura, T. *J. Org. Chem.* **1985**, *50*, 283 and references cited therein.

(2) The preferential energy migration toward the strained carbonyl group ($K >> 1$) was ascribed to the entropy factor associated with the hindered rotation around bonds a and b.[1]

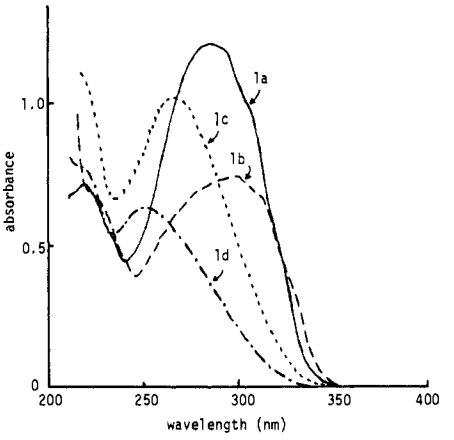
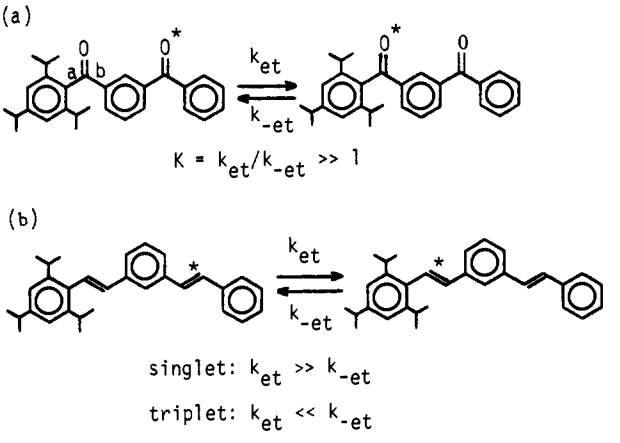
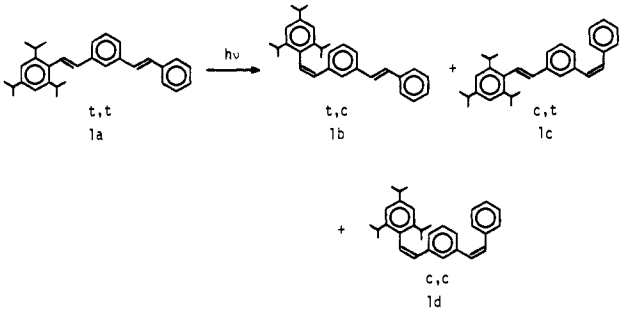


Figure 1. Absorption spectra for 3-styryl-2′,4′,6′-triisopropylstilbenes in hexane: **1a**, 3.0×10^{-5} M (—); **1b**, 2.5×10^{-5} M (---); **1c**, 3.1×10^{-5} M (···); **1d**, 2.7×10^{-5} M (·-·).

Scheme I



Accumulation of the cic,cis isomer **1d** started only after significant amounts of **1b** and **1c** were formed. This fact precludes the possibility of two-double-bond isomerization (**1a** → **1d**) by one photon. Upon extended irradiation a photostationary mixture of the four isomers was reached (**1a**, 8%; **1b**, 20%; **1c**, 31%; **1d**, 41%), but several uncharacterized byproducts were slowly formed.



The four isomers were separated by column chromatography on silica gel using hexane as eluent. Their structures could be unequivocally determined by analyzing their 400-MHz NMR spectra. The signals for olefinic protons and ortho isopropyl methyls were as follows: **1a**, δ 7.16 (2 H, s), 7.23 and 6.51 (2 H, AB, J = 16.4 Hz), 1 22 (12 H, d, J = 7.0 Hz); **1b**, δ 6.85 and 6.70 (2 H, AB, J = 16.4 Hz), 6.69 and 6.67 (2 H, AB, J = 12.3 Hz), 1.16 (6 H, d, J = 6.8 Hz), 0.99 (6 H, d, J = 6.8 Hz); **1c**, δ 6.95 and 6.35 (2 H, AB, J = 16.5 Hz), 6.66 and 6.62 (2 H, AB, J = 12.3 Hz), 1.17 (12 H, d, J = 6.8 Hz); **1d**, δ 6.62 and 6.54 (2 H, AB, J = 12.4 Hz), 6.50 and 6.38 (2 H, AB, J = 12.2 Hz), 1.14 (6H, d, J = 6.8 Hz), 0.97 (6H, d, J = 6.8 Hz). The methyl signal of the ortho isopropyl group in **1b** and **1d** appeared as two doublets owing to slow rotation of the triisopropylphenyl ring on the NMR time scale, supporting the cis configuration of the

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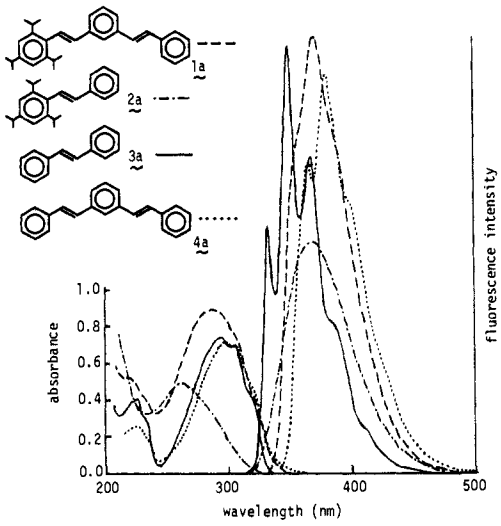

Figure 2. Absorption (at room temperature) and fluorescence spectra (at 77 K) for **1a**, **2a**, **3a**, and **4a** in methylcyclohexane: **1a**, 2.3×10^{-5} (---); **2a**, 2.9×10^{-5} M (·–·); **3a**, 2.9×10^{-5} M (—); **4a**, 1.5×10^{-5} M (···).

2,4,6-triisopropylstyryl unit.[3] The absorption spectra of the four isomers are displayed in Figure 1. The isomers **1c** and **1d**, which lack the unsubstituted *trans*-styryl unit, underwent a significant blue shift.

The quantum yield for trans–cis isomerization was measured in degassed hexane at 25 °C, by irradiation at 313 nm (K_2CrO_4, 0.6 g, and Na_2CO_3, 2.1 g, in water, 1 L).[4] The trans to cis isomerizations of *trans*-2,4,6-triisopropylstilbene (**2a**) and *trans*-stilbene (**3a**) were found to proceed in comparable efficiencies: $\Phi_{trans \rightarrow cis} = 0.35$ and 0.50, respectively. By contrast, the trans to cis isomerization of **1a** occurred in high selectivity at the hindered olefinic double bond: $\Phi_{1a \rightarrow 1b} = 0.34$, $\Phi_{1a \rightarrow 1c} = 0.026$ and $\Phi_{1a \rightarrow 1d} = 0.00$.

The absorption spectra of **1a**, **2a**, **3a**, and **4a** are summarized in Figure 2. Comparison of the spectra of **2a** and **3a** demonstrates that 2,4,6-triisopropyl substitution produces a considerable hypsochromic and hypochromic shift (**2a**, λ_{max} 262 nm (ϵ 18 000); **3a**, λ_{max} 294 (26 000), 307 (24 000), 320 sh (14 000)). The spectrum for **1a** (λ_{max} 285 nm (ϵ 39 000), 307 sh (32 000), 323 sh (17 000)) is approximately the sum of the spectra for **2a** and **3a**, indicating that the two olefinic moieties in the **1a** molecule are relatively independent because of their cross-conjugation. Similarly the absorption maxima of *trans*-stilbene (**3a**) and *trans,trans-m*-distyrylbenzene (**4a**) are nearly at the same position because of the cross-conjugation that **4a** has. These results reveal that, although the incident light is absorbed mainly by the unhindered stilbene side of **1a**, it is the hindered stilbene moiety that photoisomerizes. It is noticeable that steric hindrance apparently functions to collect the excitation energy, as in the meta-substituted aromatic polyketones.[1]

Very interestingly, benzophenone (BP)-sensitized photolysis of **1a** in degassed hexane ([**1a**] = 0.01 M, [BP] = 0.1 M, $h\nu > 350$ nm (phenanthrene in methanol, 5 g/L)[4]) produced almost exclusively the cis,trans isomer **1c**, i.e., $\Phi_{1a \rightarrow 1b} = 0.026$, $\Phi_{1a \rightarrow 1c} = 0.49$, and $\Phi_{1a \rightarrow 1d} = 0.00$.[6] The BP-sensitized trans–cis isomerization of **2a** and **3a** proceeded with the almost same efficiency: $\Phi_{trans \rightarrow cis} = 0.47$ and 0.50, respectively. Quenching studies of BP phosphorescence by **1a**, **2a**, and **3a** in degassed benzene at room temperature afforded $k_q\tau$ values of 17 000, 12 000, and 27 000 M^{-1}, respectively. On the basis of reported triplet lifetime of BP (τ = 6.5 μs),[7] the triplet quenching rate by **1a**, **2a**, and **3a** was estimated to be 2.6×10^9, 1.8×10^9, and 4.1×10^9 M^{-1} s^{-1}, respectively. While this result suggests an existence of appreciable steric hindrance to the triplet energy transfer (the k_q ratio of **3a** to **2a** = 2.3), the effect is not sufficiently large to explain the high reaction selectivity ($\Phi_{1a \rightarrow 1c}/\Phi_{1a \rightarrow 1b} = 19$).

As a result, if the excited state of **1a** can be formulated by intramolecular energy migration (Scheme Ib), it may be concluded that $k_{et} >> k_{-et}$ for direct excitation and $k_{et} << k_{-et}$ for benzophenone sensitization. Since the transients of *trans*-stilbene photoisomerization are very short-lived ($^1t^*$, 10^{-10} s; $^1p^*$, 10^{-9} s; $^3t^*$, 10^{-7} s; $^3p^*$, 10^{-7} s),[8] the rate for the intramolecular energy migration must be very rapid. However, the origin of the observed highly regioselective photoisomerization of **1a** in both the singlet and triplet excited states is not yet clear. The fluorescence spectra of **1a**–**4a** are shown in Figure 2. The distilbenes **1a** and **4a** emit quite different fluorescence from *trans*-stilbene (**3a**), contrary to the analogous absorption spectra of these compounds (vide supra). Therefore, the two olefinic moieties of **1a** and **4a** will have a significant intramolecular interaction in the excited singlet state and hence a straightforward rationalization of the high regioselectivity of the present photoreaction appears unlikely.[9] We are continuing further effort to reach the solution.

(3) Ito, Y.; Umehara, Y.; Nakamura, K.; Yamada, Y.; Matsuura, T.; Imashiro, F. *J. Org. Chem.* **1981**, *46*, 4359. The ortho isopropyl methyls of *cis*-2,4,6-triisopropylstilbene (**2b**) also exhibited magnetic nonequivalence, while those of the trans isomer **2a** did not.

(4) The trans–cis photoisomerization of *trans*-stilbene (**3a**)[5] was used as a standard.

(5) Malkin, S.; Fischer, E. *J. Phys. Chem.* **1964**, *68*, 1153.

(6) Upon continued irradiation a quasiphotostationary mixture consisting of **1a** (39%), **1b** (8%), **1c** (44%), and **1d** (9%) was obtained.

(7) Clark, W. D. K.; Litt, A. D.; Steel, C. *J. Am. Chem. Soc.* **1969**, *91*, 5413.

(8) Saltiel, J.; Charlton, J. L. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1981; Vol. 3, p 25.

(9) A large fluorescence Stokes shift for **2a** compared with that for *trans*-stilbene (**3a**) suggests a large change in geometry upon excitation of **2a**.[10] The positions of their fluorescence maximum (**2a**, 369 nm; **3a**, 350 nm) seem to indicate that the relaxed excited singlet state of **2a** is lower in energy than *trans*-stilbene singlet. However, the slightly structured fluorescence for **1a** is shifted to somewhat shorter wavelenths than that for **4a** (**1a**, 370 nm; **4a**, 380 nm). Thus, the highly regioselective isomerization of **1a** in the excited singlet state cannot be interpreted simply in terms of the fluorescence maxima.

(10) Bush, T. E.; Scott, G. W. *J. Phys. Chem.* **1981**, *85*, 144.

γ-Silicon Stabilization of Carbonium Ions in Solvolysis. 1. Solvolysis of *cis*- and *trans*-3-(Trimethylsilyl)cyclohexyl *p*-Bromobenzenesulfonates

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We wish to report the first conclusive evidence for the stabilization of a carbonium ion center by a γ-situated silyl group. We believe that the intramolecular mode of electronic interaction involved is of general significance but not generally recognized. The effects of the trimethylsilyl substituent (Me_3Si) on carbonium ion reactions have been examined previously by several authors.[1-4] Relative to carbon, an α-silyl group retards[1] but a β-silyl group strongly accelerates[2,3] solvolysis. Lambert[3] found *cis*-2-(trimethylsilyl)cyclohexyl trifluoroacetate to solvolyze 33 500 times

(1) (a) Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 481. (b) Stang, P. J.; Ladika, M.; Apeloig, Y.; Stanger, A.; Schiavelli, M. D.; Hughey, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 6852. (c) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806.

(2) Jarvie, A. W. P. *Organomet. Chem. Rev. A* **1970**, *6*, 153.

(3) Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 2020.

(4) Fessenden, R. J.; Seeler, K.; Dagani, M. *J. Org. Chem.* **1966**, *31*, 2483.

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