of acetonide **44** (0.20 g, 0.96 mmol) in 3 mL of THF under nitrogen. The orange reaction solution was allowed to warm to room temperature and, after 12 h, poured into 20 mL of ice-cold 1 M H_3PO_4 and extracted with 2 × 20 mL of ether. The combined organic extracts were washed sequentially with saturated $NaHCO_3$ and brine, dried over sodium sulfate, filtered, and concentrated in vacuo to afford 0.15 g of an orange oil, which contained 38% of the adduct **45** (GLC). Purification of this residue by repeated flash chromatography with 50% ether/hexane as eluent, followed by HPLC with 15% ethyl acetate/hexane, furnished an analytically pure sample of diol **45**: IR (CCl_4) 3580 cm^{-1} (OH); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.58 (ddd, *J* = 17.0, 10.9, 1.8 Hz, 1 H, C(*H*)=CH$_2$), 6.05 (m, 3 H), 5.74 (m, 1 H), 5.34 (dd, *J* = 17.0, 2.0 Hz, 1 H, C(H)=C(*H*)H), 4.95 (dd, *J* = 10.9, 2.0 Hz, 1 H, C(H)=C(H)*H*), 4.59 (d, *J* = 6.8 Hz, 1 H, OC(H)=), 4.33 (d, *J* = 6.8 Hz, 1 H, OC′(H)), 3.92 (s, 1 H), 2.92 (d, *J* = 7.6 Hz, 1 H, C(OH)C(*H*)), 2.77 (d, *J* = 1.8 Hz, 1 H), 1.61 (s, 3 H, CH$_3$), 1.48 (s, 3 H, C′H$_3$), 1.27 (s, 6 H, C(OH)(C*H*$_3$)$_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 132.0, 131.6, 126.5, 123.8, 107.2, 89.0, 85.5, 83.3, 82.1, 67.0, 49.9, 29.6, 28.1, 25.6, 23.8, 23.0, 14.7; MS, *m/z* (relative intensity) 274 (M$^+$ − H_2O, 3). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.82; H, 8.29. Found: C, 69.38; H, 8.34.

Aldol Condensation of Trienone 43. A THF solution of potassium hexamethyldisilazide (0.8 mL of a 1.5 M solution, 1.2 mmol) was added dropwise with stirring to a solution of trienone **43** (0.12 g, 0.9 mmol) in 4 mL of THF under an argon atmosphere at −78 °C. The dark brown reaction solution was warmed to 0 °C, poured into 5 mL of ice-cold 1 M H_3PO_4, and extracted with 3 × 20 mL of ether. The combined ether extracts were washed with brine, dried with sodium sulfate, filtered, and concentrated in vacuo. The residue was purified by flash chromatography using 20% ether/hexane as eluent to afford 27 mg (23%) of aldol product **46** as a pale yellow oil: IR (CCl_4) 3510 (OH), 1745 (C=O) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.27–5.8 (m, 8 H), 5.68 (dd, *J* = 7.0, 0.7 Hz, 1 H, C(*H*)=C(H)), 5.53 (dd, *J* = 7.0, 2.3 Hz, 1 H, C(H)=C(*H*)), 5.23 (dd, *J* = 6.1, 2.7 Hz, 1 H, C′(*H*)=C′(H)), 5.14 (ddd, *J* = 6.2, 2.7, 0.4 Hz, 1 H, =C′(H)), 3.38 (dd, *J* = 7.7, 2.7 Hz, 1 H, C(*H*)C(OH)), 3.34 (s, 1 H, OH), 3.20 (dd, *J* = 7.8, 2.0 Hz, 1 H, COC(*H*)), 2.82 (dd, *J* = 7.5, 2.7 Hz, 1 H, C′(*H*)C(OH)); MS, *m/z* (relative intensity (CI)), 265 (M$^+$ + 1, 45), 264 (M$^+$, 15), 247 (M$^+$ − OH, 100).

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Steric Inhibition of Photochemical Reactions: The [2 + 2]-Cycloaddition Reaction

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Photochemical [2 + 2]-cycloaddition reactions of a number of diphenylcycloalkenes to tetrachloroethylene (TCE) have been examined. 1,2-Diphenylcyclobutene (**1**) reacts efficiently with TCE to yield the cyclobutane anticipated for a [2 + 2]-photocycloaddition reaction. In contrast, 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (**1TM**), 1,2-diphenylcyclopentene (**2**), and 1,2-diphenylcyclohexene (**3**) yield only phenanthrene products. Photochemical quantum yields have been determined for all four reactions. For **1** and **1TM**, excited-state lifetimes have been measured as a function of the concentration of added TCE and 2,5-dimethyl-2,4-hexadiene (DMHD). The observed data indicate that the methyl groups in **1TM** effectively inhibit the interaction of possible [2 + 2]-reactants with the **1TM*** excited state.

Steric effects are a well-known and widely investigated phenomenon in ground-state chemistry. Unequivocal observations of the same effects in excited-state chemistry are, however, rare.[1] This is mainly due to the large number of mechanisms by which excited-state energy can be dissipated. In our current investigation of the photochemical and photophysical properties of sterically modified stilbenes,[2,3] we have now found an example that clearly demonstrates steric hindrance in photochemical [2 + 2]-cycloaddition reactions of olefins.

1,2-Diphenylcyclobutene (**1**) is a model *cis*-stilbene where the four-membered ring strongly limits twisting of the central double bond. Contrary to sterically less constrained stilbenes, the first excited singlet state of **1** cannot relax into a "perpendicular" geometry where the p orbitals of the central double bond form an angle of about 90°.[4-12] The stabilization of the "planar" excited state through the steric constraint of the cyclobutene ring leads to unusual photochemical behavior for **1**. Irradiation under high dilution conditions in solvents like hexane[13] or acetonitrile[14] leads to a ring cleavage reaction (eq 1). In the presence of appropriate substrates, however, **1** undergoes efficient photoinduced [2 + 2]-cycloaddition reactions as shown in eq 2.[3,13-15] The first step of this reaction is most likely

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(1) (a) Turro, N. J.; Farrington, G. *J. Am. Chem. Soc.* **1980**, *102*, 6051. (b) Froelich, P. M.; Morrison, H. A. *J. Am. Chem. Soc.* **1974**, *96*, 332. (c) Wamser, C. C.; Lou, L.; Mendoza, J.; Olson, E. *J. Am.* Chem. *Soc.* **1981**, *103*, 7228.

(2) Hohlneicher, G.; Mueller, M.; Demmer, M.; Lex, J.; Penn, J. H.; Gan, L.-X.; Loesel, P. D. *J. Am. Chem. Soc.* **1988**, *110*, 4483.

(3) Penn, J. H.; Gan, L.-X.; Chan, E. Y.; Eaton, T. A.; Lin, Z. *J. Org. Chem.* **1988**, *53*, 1519.

(4) (a) Mulliken, R. S. *J. Chem. Phys.* **1977**, *66*, 2448. (b) Johnson, R. P.; Schmidt, M. W. *J. Am. Chem. Soc.* **1981**, *103*, 3244.

(5) Kropp, P. J. *Org. Photochem.* **1979**, *4*, 1.

(6) Schulte-Frohlinde, D.; Gainer, H. *Pure Appl. Chem.* **1979**, *59*, 279.

(7) Bonneau, R. *J. Photochem.* **1979**, *10*, 439.

(8) Saltiel, J.; Charlton, J. L. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed., Academic Press: New York, 1980; Vol. 3, p 25.

(9) Goerner, H.; Eaker, D. W.; Saltiel, J. *J. Am. Chem. Soc.* **1981**, *103*, 7164.

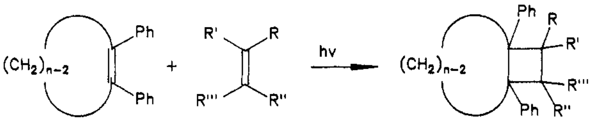
(10) Caldwell, R. A.; Cao, D. V. *J. Am. Chem. Soc.* **1982**, *104*, 6174.

(11) Saltiel, J.; Rousseau, A. D.; Thomas, B. *J. Am. Chem. Soc.* **1983**, *105*, 7631.

(12) Lewis, F. D. *Adv. Photochem.* **1986**, *13*, 165.

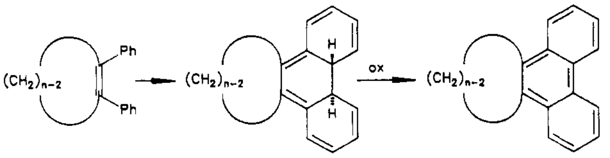
0022-3263/89/1954-0601$01.50/0

(1)



(2)

the formation of an exciplex.[16-18] The tendency to participate in [2 + 2]-cycloaddition reactions distinguishes 1 from larger 1,2-diphenylcycloalkenes like 1,2-diphenylcyclopentene (**2**) and 1,2-diphenylcyclohexene (**3**). These compounds undergo photochemical transformations into the corresponding phenanthrene derivatives, most likely via an unstable dihydrophenanthrene intermediate as shown in eq 3.



(3)

Contrary to **1**, 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (**1TM**) does not undergo [2 + 2]-cycloadditions. The corresponding phenanthrene **4** is formed.[14] This is true even when substrates such as 2,5-dimethyl-2,4-hexadiene (DMHD) or tetrachloroethylene (TCE) are used as the solvent for the reaction. In the present study, we present quantum yield and lifetime measurements that clearly indicate that the differing photochemical behavior of **1** and **1TM** is due to steric hindrance preventing efficient formation of the exciplex in the case of **1TM**.

Results

Product Elucidation. Preparative irradiations in neat TCE as a solvent were performed at 350 nm with a Rayonet reactor in order to minimize secondary photoreactions (see Experimental Section for details). For **1**, the main product is the expected [2 + 2]-cycloadduct, i.e., 1,4-diphenyl-2,2,3,3-tetrachlorobicyclo[2.2.0]hexane (**5**). The structural assignment is based on the ^{1}H NMR that shows only multiplets at δ 3.16 and 2.53 and on ^{13}C NMR that, in accord with the anticipated symmetry of the molecule, shows only three nonaromatic carbons. A second product was observed by GCMS with a yield of ca. 2% of **5**. The GCMS peak had the proper retention time and the proper molecular weight for the second product being 9,10-cyclobutenophenanthrene (**8**), the product expected from eq 3. Because of the very low yield, we were unable to confirm this assignment by product isolation. Thus, the chemistry of **1** and TCE are given by eq 2.

As mentioned in the introduction, irradiation of **1** under high dilution conditions in solvents like hexane or acetonitrile[13,14] leads to cleavage of the four-membered ring, yielding ethylene and diphenylacetylene (**9**), as first observed by White and Anhalt.[19] In our experiments, we were not able to detect any traces of **9**. Even when we apply very conservative estimates of our detection limits, the amount of **9** that is formed must be considerably less than 10% of the amount of **5** that is formed. Thus, at room temperature in neat TCE, neither the formation of **8** nor of **9** can efficiently compete with the [2 + 2]-cycloaddition.

Table I. Quantitative Photophysical Data

starting material	τ′, ps	Φ_d	product	Φ_a	k_{Ex},^{d} s^{-1}	k_{DH}^{LL},^{d} s^{-1}
1	1900^a	0.15^c	5	0.13^c	3×10^9	1×10^7
1TM	2100^b	0.05^c	4	0.03^c		1.4×10^7
2	≤20^a	0.06^c	6	0.03^c		1.5×10^9
3	≤20^a	0.06^c	7	0.03^c		1.5×10^9

^{a} Reference 3. ^{b} This work. ^{c} Measured in neat TCE. ^{d} See text.

In contrast to **1**, irradiation of **1TM** in neat TCE yields only 9,10-(3′,3′,4′,4′-tetramethylcyclobuteno)phenanthrene (**4**) in accord with eq 3. The same photoreaction has been previously observed in acetonitrile under high dilution conditions.[14] A full set of spectroscopic data is given in the Experimental Section to confirm the structure and to supplement the data given in ref 14. The same product is obtained when DMHD is used as the solvent. This is extremely surprising, since DMHD quenches the fluorescence of ^{1}1* at a rate which is near the diffusion controlled limit.[3]

Similar to **1TM**, **2** and **3** yield only 9,10-cyclopentenophenanthrene (**6**) and 9,10-cyclohexenophenanthrene (**7**), respectively, when irradiated in neat TCE at 350 nm as shown in eq 3. These products, too, have been previously described in the literature.[20] Again, a full set of analytical and spectroscopic data is given to supplement the previously unavailable data.

Quantum Yield Determinations. Quantum yields were determined at 300 nm by using valerophenone actinometry. The optical densities of the samples were carefully adjusted to ensure that actinometer and substrate absorbed an equal amount of light. Quantum yields of disappearance (Φ_d) were measured directly through the use of appropriate internal standards. Quantum yields of appearance (Φ_a) were measured by calibration of the photoproduct's relative GC response to that of the internal standard. Details are given in the Experimental Section.

Special care was taken in the quantum yield determination for the photoreaction of **1** in TCE. Two highly conflicting values have been reported in the literature for the cleavage reaction of **1** under high dilution conditions. DeBoer and Schlessinger[13] conclude that in the solvent hexane, Φ_a(**9**) cannot be larger than 0.01. Kaupp and Stark,[14] however, found Φ_a(**9**) of 0.18 in acetonitrile. Since we were not able to detect any trace of **9** as a reaction product, the cleavage reaction of **1** under our conditions must be as inefficient as the cleavage reaction of **1** under the conditions of DeBoer and Schlessinger. The observed quantum yields are collected in Table I. The values of Φ_d and Φ_a agree within the experimental limit of our quantum yield determinations (ca. ±0.02).

A much longer time was required for the preparative irradiation of **3** to form phenanthrene **7** than for the preparative irradiation of **2** to form **6**. Typically, such apparent efficiency differences arise from differing excited-state lifetimes or reaction rates. However, measurement of Φ_{Phen} at low conversions for this reaction shows similar

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(13) DeBoer, C. D.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 803.

(14) Kaupp, G.; Stark, M. *Chem. Ber.* **1978**, *111*, 3608.

(15) For a recent review of photochemical cycloaddition reactions, see: McCullough, J. J. *Chem. Rev.* **1987**, *87*, 811.

(16) Chapman, O. L.; Lura, R. D. *J. Am. Chem. Soc.* **1970**, *92*, 6352.

(17) Saltiel, J.; D'Agostino, J. T.; Chapman, O. L.; Lura, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 2804.

(18) Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45.

(19) White, E. H.; Anhalt, J. P. *Tetrahedron Lett.* **1965**, 3937.

(20) (a) Mallory, F. B.; Mallory, C. W. *Org. React.* **1984**, *30*, 1. (b) Wood, C. S.; Mallory, F. B. *J. Org. Chem.* **1964**, *29*, 3373.

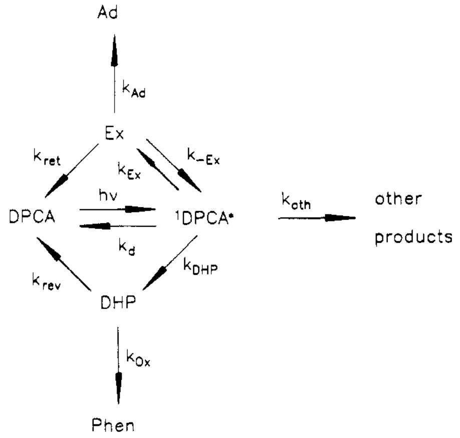

Figure 1. General reaction rate scheme for the photochemistry of 1,2-diphenylcycloalkenes.

values for 2 and for 3. The explanation for this reactivity difference is found in the irradiation wavelength and the absorption spectrum of these two compounds;[2] 350-nm light is used for the preparative irradiations of 2 and 3. We have previously shown that the $\epsilon_{350}(3)$ is ca. 2 orders of magnitude lower than $\epsilon_{350}(2)$. Thus, 3 absorbs less light per unit time than 2 and undergoes a slower overall apparent rate of reaction.

Photochemical Reaction Rates. A general scheme for the possible photoreactions of 1,2-diphenylcycloalkenes (DPCA) is shown in Figure 1. ^{1}DPCA* represents the lowest excited singlet state of the corresponding DPCA. A triplet pathway for the [2 + 2]-cycloaddition can be ruled out, at least for 1, by the work of DeBoer and Schlessinger.[13] Since the photoisomerization of the cycloalkene rings is not possible in small ring size systems, we only consider the following possibilities for the deactivation of five-membered or smaller ^{1}DPCA*: (i) direct return to the ground-state DPCA by fluorescence (k_F), radiationless decay (k_{RD}), and intersystem crossing (k_{IC}); (ii) formation of an exciplex with a suitable substrate (k_{Ex}) and adiabatic reversion to excited state DPCA (k_{-Ex}); (iii) ring closure to the corresponding dihydrophenanthrene (k_{DHP}); (iv) other reaction channels (k_{oth}) (e.g., the ring fission observed for 1 under high dilution conditions).

If an exciplex is formed as an intermediate as in the case of the stilbenes,[16-18] the exciplex can either decay back to DPCA and substrate (k_{ret}) or the reaction proceeds to yield the [2 + 2]-cycloaddition adduct (k_{Ad}). The dihydrophenanthrene, too, can revert thermally to starting material (k_{rev}) or it can be oxidized to the corresponding phenanthrene (k_{ox}).[20,21] Using this notation, the total decay rate (k_{tot}) for ^{1}DPCA* is expressed by eq 4, which

$$k_{tot} = k_f + k_{RD} + k_{IC} + k_{Ex} - k_{-Ex} + k_{DHP} + k_{oth} \quad (4)$$

$$= k_d + k_{Ex} - k_{-Ex} + k_{DHP} + k_{oth} \quad (5)$$

reduces to eq 5 if $k_d = k_f + k_{RD} + k_{IC}$. The quantum yields for adduct and phenanthrene formation are given by

$$\Phi_{Ad} = \left(\frac{k_{Ex}}{k_{tot}}\right)\left(\frac{k_{Ad}}{k_{ret} + k_{Ad} + k_{-Ex}}\right) \quad (6)$$

$$\Phi_{phen} = \left(\frac{k_{DHP}}{k_{tot}}\right)\left(\frac{k_{ox}}{k_{rev} + k_{ox}}\right) \quad (7)$$

The fact that we have found no products other than adduct or phenanthrene in our careful product analysis clearly shows that k_{oth} is much smaller than the other rate constants in eq 5. k_{oth} is therefore neglected from now on. With no substrate available ($k_{Ex} = 0$), the total decay rate (k'_{tot}) can thus be expressed by eq 8.

$$k'_{tot} = \frac{1}{\tau'} = k_d + k_{DHP} \quad (8)$$

Table II. Excited State Quenching Data

compd	reactant	concentration, M	τ, ns	χ^2
4	TCE		1.91	0.99
		0.10	1.78	1.25
		0.20	1.69	1.18
		0.40	1.54	1.13
		0.60	1.43	1.05
4TM	DHMD		2.09	1.22
		0.10	2.08	1.06
		0.20	2.10	1.42
		0.40	2.15	1.25
		0.60	2.16	1.11
	TCE		2.05	1.11
		0.10	2.11	1.16
		0.20	2.10	1.22
		0.40	2.05	1.06
		0.60	2.12	1.03

The excited-state lifetimes in nonpolar solvents (e.g., hexane) were recently measured for 1, 2, and 3 by single photon counting techniques.[3] For **1TM**, the lifetime was determined in connection with the present study. The lifetimes for all four compounds are given in Table I. The lifetimes for ^{1}1* and ^{1}**1TM*** are strikingly similar. This is in accord with our previous observation that the ground-state geometries of 1 and **1TM** as measured by a variety of spectroscopic methods do not differ significantly.[2] The lifetimes of ^{1}2* and ^{1}3* are much shorter. Only an upper limit of 20 ps could be measured, due to experimental limitations.[3] Most likely, the five- and six-membered rings have enough flexibility to allow the excited state to approach, at least in part, a "perpendicular" geometry.[22,23] This interpretation is also in accord with the fact that 1 and **1TM** exhibit much stronger fluorescence than 2 and 3.

In spite of the fact that ^{1}1* and ^{1}**1TM*** have comparable excited-state lifetimes, ^{1}**1TM*** does not undergo a photoinduced [2 + 2]-cycloaddition reaction with either TCE or DMHD as does ^{1}1*. Instead, ^{1}**1TM*** yields only phenanthrene 4 and thereby reacts in a similar fashion to ^{1}**2*** and ^{1}**3*** with their much shorter excited-state lifetimes. To verify that this drastic change in photochemical reactivity is due to a change in the rate of exciplex formation (k_{Ex}) and not due to different behavior of the initially formed exciplex, we studied the fluorescence quenching rates of ^{1}1* and ^{1}**1TM*** with both TCE and DMHD as quenchers. It is known from earlier work that all substrates that yield [2 + 2]-cycloadducts act as quenchers.[3,13,24] For example, the quenching rate constant of ^{1}1* by 2,5-dimethyl-2,4-hexadiene (k_q(DMHD)) is 4.9 × 10^9 M^{-1} s^{-1},[3,24] a value that is close to the diffusion-controlled limit. The results of our quenching experiments are given in Table II. Within experimental error, neither DMHD nor TCE have any measurable effect on the lifetime of ^{1}**1TM***. If k_q for ^{1}**1TM*** and DMHD was >4.9 × 10^7 M^{-1} s^{-1}, τ_{1TM} would be <1.97 ns, which would have been easily measurable by our equipment. Therefore, the quenching rate constant for

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(21) Laarhoven, W. H. *Pure Appl. Chem.* **1984**, *56*, 1225.

(22) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718.

(23) Caldwell, R. A.; Cao, D. V. *J. Am. Chem. Soc.* **1982**, *104*, 6174.

(24) Lewis, F. D.; Hoyle, C. E. *J. Am. Chem. Soc.* **1977**, *99*, 3779.

$^{1}\mathbf{1TM}^*$ must be at least 2 orders of magnitude less than the quenching rate constant for 1. As expected for a substrate that leads to [2 + 2]-photocycloaddition, ^{1}1* is quenched efficiently by TCE ($k_q = 2.9 \times 10^8$ M^{-1} s^{-1}) but with a lower rate than that observed for DMHD.

The knowledge that k_{Ex} is much smaller than k_d and k_{DHP} in **1TM** enables us to derive lower and upper limits for the rate of dihydrophenanthrene formation (k_{DHP}). The independence of the lifetime of $^{1}\mathbf{1TM}^*$ with added TCE up to concentrations of about 0.6 M indicates that k_d and k_{DHP} do not change too much when we go from hexane to TCE as solvent. Thus, we can use the lifetimes measured in hexane (Table I) as an estimate for τ'. By rewriting eq 7, we obtain

$$k_{\text{DHP}} = \left(\frac{\Phi_{\text{phen}}}{\tau'}\right)\left(\frac{k_{\text{rev}} + k_{\text{ox}}}{k_{\text{ox}}}\right) \qquad (9)$$

The second factor on the right hand side of eq 9 must be ≥1. Neglecting this factor (i.e., all dihydrophenanthrene is converted to phenanthrene) yields a lower limit for the rate of DHP formation as shown in eq 10.

$$k_{\text{DHP}}^{\text{LL}} = \frac{\Phi_{\text{phen}}}{\tau'} \qquad (10)$$

From the data shown in Table I, a value of 1.4×10^7 s^{-1} can be derived for $k_{\text{DHP}}^{\text{LL}}$ of **1TM**. When the same procedure is applied to **2** and **3**, a $k_{\text{DHP}}^{\text{LL}}$ is obtained for the reaction rate of DHP formation that is ca. 2 orders of magnitude larger than for **1TM**. For 1 and **1TM**, the observed lifetimes also provide an estimate for the upper limit of k_{DHP}. A lifetime of ca. 2 ns is exactly what one would expect for the pure radiative lifetime. The minimum reported[14] $\Phi_F(1)$ is 0.6. From this value and τ' (Table I), k_F must be $\geq 3.2 \times 10^8$ s^{-1}, which yields $k_{\text{DHP}}(1) \leq 2 \times 10^8$ s^{-1}. Since τ'(**1TM**) is larger than $\tau'(1)$, k_{DHP}(**1TM**) must be $< 2 \times 10^8$ s^{-1}. Thus, the value of k_{DHP} for 1 and **1TM** must be between 1×10^7 and 2×10^8 s^{-1}.

We now turn to the cycloaddition reaction of 1. If the total decay rate (k_{tot}) of ^{1}1* is dominated by the rate of exciplex formation (k_{Ex}) (note eq 4), the first factor on the right hand side of eq 6 becomes one and the quantum yield of adduct formation (Φ_{Ad}) is determined completely by the second factor. This factor represents the probability of getting a [2 + 2]-cycloadduct from the initially formed exciplex. The quenching data (Table II) indicate that 1 is close to this limit in neat TCE as solvent. If the quenching is due to exciplex formation, we can write

$$k_{\text{Ex}} = k_q[\text{TCE}] \qquad (11)$$

Extrapolating this relationship to neat TCE yields a rate for exciplex formation of ca. 3×10^9 s^{-1} compared to the total decay rate in the absence of adduct (k'_{tot}) of 5.3×10^8 s^{-1}. Even if this linear extrapolation of neat TCE is fairly crude, the total decay rate of ^{1}1* must be dominated by the quenching process under these conditions. Therefore, Φ_{Ad} is mainly a measure of the branching in the exciplex decay. The observed value of $\Phi_{\text{Ad}} = 0.13$ signifies that only one out of every seven exciplexes is finally transformed into a [2 + 2]-cycloadduct. From the above estimate of k_{Ex} and from the fact that only 1–2% of phenanthrene **8** was formed as a second product in the photoreaction of ^{1}1*, a value of about 1×10^7 s^{-1} is derived for the lower limit of k_{DHP}. This value is similar to the one obtained for **1TM**. This similarity is not surprising since we have previously shown a marked similarity in the ground-state geometries of 1 and **1TM**.[2]

Table III. Phenyl-Phenyl Interactions in 1,2-Diphenylcycloalkenes

compd	UPS ionization potentials,[a] eV π_4	π_6	π_7	$\Delta E_{\pi_4-\pi_6}$, eV
1	9.36	8.96	7.71	0.40
1TM	9.25	8.91	7.67	0.34
2	9.57	8.83	7.77	0.74
3	9.45	8.83	7.87	0.62

[a] From ref 2.

Discussion

Contrasting Photochemical Reactivity of 1 and 1TM. A striking difference in the photochemical reactivity of 1 and **1TM** has already been observed under high dilution conditions where 1 yields only diphenylacetylene and ethylene[13,19] while **1TM** yields only phenanthrene **4**.[14] We have now found that an even more striking difference exists in the reactivity of 1 and **1TM** with respect to photoinduced [2 + 2]-cycloaddition reactions. ^{1}1* undergoes efficient [2 + 2]-photocycloadditions with TCE as it does with a variety of different substrates.[3] $^{1}\mathbf{1TM}^*$, however, reacts only according to eq 3 even when a possible substrate like DMHD or TCE is present in large abundance. The observed difference in the reactivity of $^{1}\mathbf{1TM}^*$ cannot be explained by large differences in molecular structure. The differences in the geometric and electronic structure of the stilbene portion of 1 and **1TM** are only minor.[2] The lack of [2 + 2]-cycloaddition reactions in $^{1}\mathbf{1TM}^*$ must be caused by the steric hindrance that results from the methyl groups. This steric hindrance is clearly revealed from our quenching experiments. Neither TCE nor DMHD has any influence on the excited-state lifetime of $^{1}\mathbf{1TM}^*$. This is particularly striking in the case of DMHD that interacts near the diffusion-controlled limit with ^{1}1*[3] and must be diminished by 2 orders of magnitude for $^{1}\mathbf{1TM}^*$ (vide supra). This steric effect must reflect either an enhanced return of the initially formed exciplex to form the initial excited state (i.e., $^{1}\mathbf{1TM}^*$) or it reflects that the exciplex is not formed at all. Since it is only the double bond of the stilbene chromophore that is shielded effectively by the four methyl groups in **1TM**, the excited-state interaction of the stilbene with an olefin in the exciplex must have a well-defined locus that is located close to the central double bond. For other arrangements, the steric constraints differ little between 1 and **1TM**. Further investigations are in progress to find out what electronic and geometric factors govern the formation and reactions of the exciplexes that lead to adduct.

Relative Rates of Dihydrophenanthrene Formation. The pronounced differences in the rates of dihydrophenanthrene formation (k_{DHP}) are also noteworthy. For 1 and **1TM**, the upper limit for k_{DHP} is ca. 1×10^8 s^{-1} whereas for **2** and **3**, the lower limit is ca. 1×10^9 s^{-1}. A possible rationale for this marked difference is found in the ground-state geometries of the 1,2-diphenylcycloalkenes. In these compounds, the aromatic p orbitals at atoms 2′ and 2″ interact in a σ-fashion. The interaction is antibonding in the HOMO and bonding in the LUMO. Excitation from the ground state to the first excited state increases the bonding interaction between 2′ and 2″. The magnitude of this increase is proportional to the corresponding overlap and this in turn is a function of the 2′,2″ distance. In our recent spectroscopic studies,[2] we showed that an increasing 2′,2″ overlap results in an increasing splitting of the orbitals π_4 and π_6 of the stilbene-type π-system. Without a 2′,2″ overlap as in *trans*-stilbene, π_4 and π_6 are degenerate. The orbital energies derived from

Table IV. MMP2 Calculated Enthalpies (kcal/mol)

DPCA	DPCA $\Delta H°$	DHP $\Delta H°$	ΔH_r
1	79.72	129.68	49.96
1TM	52.77	100.64	47.87
2	51.87	95.54	43.67
3	44.97	83.19	38.22

UPS by application of Koopman's theorem are shown in Table III. The splitting observed for **2** and **3** is similar and nearly twice as large as the splitting observed for **1** and **1TM**. The trend in the observed splitting correlates quite well with the trend in the reaction rates.

An alternative rationale for explaining these reaction rate differences arises from consideration of the relative strain energies of the dihydrophenanthrenes that are formed in the reaction.[21] This would be a reflection of the fact that the phenanthrenes derived from **2** and **3** would contain much less strain energy than would the phenanthrenes derived from **1** and **1TM**. MMP2 calculations confirm that the ΔH_r's for these compounds are in qualitative agreement with the observed rates as can be seen in Table IV.

Summary

The behavior of two photoexcited 1,2-diphenylcyclobutenes has been found to differ greatly. **1TM** was found to have a significant steric interaction prohibiting fluorescence quenching due to the additional methyl groups. In contrast, **1** undergoes efficient [2 + 2]-cycloadditions.

Experimental Section

Melting points were determined on a Laboratory Devices Mel-temp apparatus and are uncorrected. Both ^1H and ^{13}C NMR spectra (δ (ppm) and J (hertz)) were measured in the indicated solvent with TMS as an internal standard on a Varian EM-360 or a JEOL GX-270 spectrometer. GCMS were recorded on a Finnigan Model 4021 mass spectrometer. IR spectra were recorded on a Perkin-Elmer Model 1310 IR spectrophotometer. GLC was performed on a Hewlett-Packard 5890A GLC equipped with a Hewlett-Packard 3390A or 3392A reporting integrator. HPLC was performed on a Waters Associates Protein Peptides I system capable of gradient elution and using UV detection at 254 nm. Photolysis samples in quartz tubes were degassed by bubbling with N_2 for 15 min prior to irradiation, sealed with latex septa, and irradiated at 300 or 350 nm in a Southern New England Ultraviolet RPR-100 Rayonet reactor equipped with a merry-go-round apparatus.

Solvents and chemicals were reagent grade and used without purification unless otherwise noted. **1** was synthesized by the McMurray coupling method[3,25] and **1TM** was synthesized by cycloaddition of *trans*-stilbene with tetramethylethylene followed by NBS oxidation.[26]

Quantum Yield Determinations. Valerophenone actinometry was used.[27] The optical densities of the valerophenone samples and the olefin samples were carefully adjusted to be the same value within 5%. Irradiations were performed in the merry-go-round apparatus using 300-nm light. The quantum yields of disappearance (Φ_d) were measured directly in each experiment through the use of nonanenitrile or hexanenitrile as an internal standard. The quantum yields of appearance for each product (Φ_a) were measured by using the response factor for each product relative to the internal standard.

1,4-Diphenyl-2,2,3,3-tetrachlorobicyclo[2.2.0]hexane (5). A degassed solution of **1** (100 mg, 0.485 mmol) in TCE (10 mL) was irradiated for 16 h at 350 nm. The reaction was monitored by GC analysis and ended when the starting material disappeared entirely. The TCE was removed in vacuo. Crystallization from acetone/CH_3OH yielded colorless needles of **5** (109 mg, 60% yield): mp 139–140 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 7.20 (s, 10 H), 3.16 (m, 2 H), and 2.53 (m, 2 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 138.9, 128.0, 127.7, 127.5, 98.7, 65.3 and 30.8; IR (KBr) 3080, 3060, 3030, 2980, 2940, 1605, 1560, 1495, 1445, 1280, 1235, 1180, 1140, 1090, 1035, 985, 945, 880, 860, 790, 765, 735, and 705 cm^{-1}; UV (CH_3OH) λ_{max} (ϵ) 363 (362), 203 (14600); MS, *m/e* (relative intensity) 374 ($M^+ + 4$, 0.6), 372 ($M^+ + 2$, 1.3), 370 (M^+, 0.9), 149 (100), 115 (35.5), 101 (4.8), 91 (5.6), and 77 (6.0).

Anal. Calcd for $C_{18}H_{14}Cl_4$: C, 58.10; H, 3.79; Cl, 38.11. Found: C, 57.99; H, 3.80; Cl, 38.00.

(b) A degassed solution of **1** (100 mg, 0.485 mmol) and benzophenone (20 mg, 0.109 mmol) in TCE (5 mL) was irradiated for 48 h at 350 nm. The TCE was removed in vacuo to give a brown oil (367 mg), which was developed on two thick-layer plates with $CHCl_3$/hexane (2:1). The silica gel containing the adduct was extracted with $CHCl_3$ (50 mL). The solvent was removed in vacuo to give a light yellow oil (139 mg), which crystallized from hexane (5 mL). This material was found to have an identical melting point and spectral data with material prepared in part a above.

9,10-(3′,3′,4′,4′-Tetramethylcyclobuteno)phenanthrene (4). A degassed solution of **1TM** (81 mg, 0.309 mmol) in 8 mL of TCE was irradiated for 190 h at 350 nm. After solvent removal in vacuo, the crude product was purified by column chromatography on silica gel with hexane to afford **4** (34.6 mg, 43% yield) as colorless flakes (hexane/CH_3OH): mp 183–184 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 8.74 (m, 2 H), 7.65 (m, 6 H), and 1.58 (s, 12 H); IR (KBr) 3080, 3050, 3020, 2980, 2960, 2920, 2870, 1630, 1620, 1610, 1480, 1450, 1430, 1390, 1370, 1235, 1200, 1130, 1040, 1000, 770, and 735 cm^{-1}; UV (hexane) λ_{max} (ϵ) 356 (460), 339 (240), 301 (2890), 289 (2290), 278 (2560), 270 (3700), 254 (12100), 221 (5750), and 207 (8920) nm; MS, *m/e* (relative intensity) 260 (M^+, 24.4), 245 (8.9), 230 (12.0), 217 (100), 203 (28.2), 120 (7.8), 114 (20.5), 107 (11.2), 101 (16.2), 91 (0.2), and 77 (0.5).

Anal. Calcd for $C_{20}H_{20}$: C, 92.25; H, 7.74. Found: C, 92.22; H, 7.89.

9,10-Cyclopentenophenanthrene (6). A degassed solution of **2** (55 mg, 0.25 mmol) in TCE (5.5 mL) was irradiated for 108 h at 350 nm. The reaction mixture was worked up as described for **5**. The crude product was subjected to column chromatography with hexane to give **6** (25.2 mg, 46% yield) as colorless needles (from acetone/CH_3OH): mp 147–148 °C (lit.[20b] mp 147.3–150 °C).

9,10-Cyclohexenophenanthrene (7). A degassed solution of **3** (100.0 mg, 0.427 mmol) in TCE (10.0 mL) was irradiated for 14 days at 350 nm. The reaction mixture was worked up as described for **5**. The crude product was subjected to column chromatography with hexane to give **7** (49.0 mg, 0.143 mmol, 34%) as colorless needles (from acetone/CH_3OH): mp 121–122 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 8.7 (m, 2 H), 8.1 (m, 2 H), 7.6 (m, 4 H), 3.19 (s, 2 H), 2.01 (s, 2 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 137.0, 130.4, 129.3, 126.8, 125.8, 123.4, 122.8, 27.0, 23.0; IR (KBr) 3050, 2900, 2830, 1580, 1480, 1420, 1235, 935, 740, and 710 cm^{-1}; UV (CH_3OH) λ_{max} (ϵ) 350 (710), 298 (6100), 253 (33000), and 213 (19060) nm; MS, *m/e* (relative intensity) 232 (M^+, 100), 215 (19.0), 204 (57.1), 191 (26.9), 176 (3.5), 165 (6.8), 116 (4.3), 115 (3.1), 101 (22.0), 95 (6.3), 89 (6.9), and 76 (3.1).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.82; H, 6.99.

Excited-State Lifetime Determinations. The time-correlated single photon counting unit of the Regional Laser and Biotechnology Laboratory (RLBL) at the University of Pennsylvania was used to evaluate the fluorescence lifetimes. The emission was monitored at 380 nm. Pulses from a synchronously mode-locked dye laser, driven by a CR-18 argon ion laser, were cavity-dumped into a KDP crystal to provide 286-nm excitation pulses. The electronics were run in the reverse TAC configuration. Stop pulses were provided to an Ortec 457 TAC by an HP4220 photodiode driving an Ortec 436 discriminator. Start pulses were provided from the output of a Hammamatsu R1645U-07 microchannel plate photomultiplier driving an Ortec 583 constant fraction discriminator. The output of the TAC was digitized in an Ortec 918 multichannel analyzer and transferred to an IBM

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(25) (a) Baumstark, A. L.; McCloskey, C. J.; Witt, K. E. *J. Org. Chem.* **1978**, *43*, 3609. (b) Baumstark, A. L.; Bechara, E. J. H.; Semigran, M. J. *Tetrahedron Lett.* **1976**, 3265.

(26) Chapman, O. L.; Adams, W. R. *J. Am. Chem. Soc.* **1968**, *90*, 2333.

(27) (a) Wagner, P. J.; Kemppainer, A. E. *J. Am. Soc.* **1968**, *90*, 5896. (b) Wagner, P. J. *Tetrahedron Lett.* **1968**, 5385.

Personal Computer for data storage and manipulation. The quality of the data fit was judged by the χ^2 value.[28] The data are shown in Table II.

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(28) O'Connor, D. V.; Phillips, D. *Time-correlated Single Photon Counting*; Academic Press: New York, 1984; p 171.

Isolation of Acetylenic Sterols from a Higher Plant. Further Evidence That Marine Sterols Are Not Unique

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(24*R*)-5α-Stigmast-7-en-22-yn-3β-ol, 24,24-dimethyl-5α-cholest-7-en-22-yn-3β-ol, and 24,24-dimethyl-5α-cholesta-7,25-dien-22-yn-3β-ol were isolated from *Gynostemma pentaphyllum* (Cucurbitaceae). Their structures were determined by chemical and spectroscopic methods. They are the first acetylenic sterols isolated from a nonmarine organism. It is predicted that most of the sterols, which are now considered typical marine, will eventually also be found in freshwater organisms and terrestrial plants.

The isolation and structure of two sterols with a cyclopropyl group in the side chain, gorgosterol and 23-demethylgorgosterol, were reported in 1970.[4] Approximately 200 previously unknown sterols have since been isolated from marine organisms.[5] Sponges were the most interesting source of new compounds, which included classes of sterols that have not been found in marine organisms belonging to other phyla, viz. sterols with quaternary sp^3 carbons at C24, C25, or C26,[6] with methyl groups at C26 or C27 or both, and acetylenic sterols.[7]

It has been stated in several papers that marine sterols are unusual or unique.[5] However, this ignores the fact that until recently only sterol mixtures from marine sources have been carefully investigated by using modern separation techniques and analytical instruments.

Many phyla, such as Porifera[8] and Pyrrophyta, are not exclusively marine. The only known C$_{28}$ sterol alkylated at C22 has actually been isolated from a freshwater or brackish water sponge (phylum Porifera).[9,10] Dinoflagellates (unicellular algae, phylum Pyrrophyta) have been shown to be primary producers of sterols with the gorgosterol side chain.[11,12] It will be only a matter of time before such cyclopropyl sterols are detected in freshwater algae belonging to the same phylum.

In the last 2 decades research on lipids from terrestrial plants has resulted in several papers on steroidal triterpenoids with a quaternary sp^3 carbon in the side chain[16] or a methyl group at C26 or both.[17] This strongly suggested that regular sterols with the same side chains would also be present in plants.[18] Such side chains were sup-

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(1) Nihon University.

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(4) Hale, R. L.; Leclercq, J.; Tursch, B.; Gross, R. A., Jr.; Weinheimer, A. J.; Gupta, K.; Scheurer, P. J. *J. Am. Chem. Soc.* **1970**, *92*, 2179. Ling, N. C.; Hale, R. L.; Djerassi, C. *Ibid.* **1970**, *92*, 5281. Schmitz, F. J.; Pattabhiraman, T. *J. Am. Chem. Soc.* **1970**, *92*, 6073.

(5) For references, see the following review articles: Djerassi, C. *Proceedings of the Alfred Benzon Symposium 20*; Krogsgaard-Larsen, P., Christensen, S. B., Kofod, H., Eds., Munksgaard: Copenhagen, 1984; pp 164–176. Djerassi, C. *Pure Appl. Chem.* **1981**, *53*, 873. Djerassi, C.; Theobald, N.; Kokke, W. C. M. C.; Pak, C. S.; Carlson, R. M. K. *Pure Appl. Chem.* **1979**, *51*, 1815.

(6) Makarieva, N. T.; Shubina, L. K.; Kalinovski, A. I.; Stonik, V. A.; Elyakov, G. B. *Steroids* **1983**, *42*, 267.

(7) Steiner, E.; Djerassi, C.; Fattorusso, E.; Magno, S.; Mayol, L.; Santacroce, C.; Sica, D. *Helv. Chim. Acta* **1977**, *60*, 475.

(8) Bergquist, P. R. *Sponges*; University of California Press: Berkeley, 1978.

(9) It was found in a sponge from the Black Sea. The top 100-m layer of this sea consists of fresh or brackish water depending on depth and location. See: Anikouchne, W. A.; Sternberg, R. W. *The World Ocean. An Introduction to Oceanography*; Prentice Hall-Ink: Inglewood Cliffs, NJ, 1973.

(10) Zielinski, J.; Li, H.-t.; Milkova, T. S.; Popov, S.; Marekov, N. L.; Djerassi, C. *Tetrahedron Lett.* **1981**, *22*, 2345.

(11) For a review on dinoflagellate sterols, see: Withers, N. W. *The Biology of the Dinoflagellates*; Taylor, F. J. R., Ed.; Blackwell: London, 1987; pp 316–355.

(12) The gorgosterol side chain is a marker of dinoflagellate symbiosis.[13] In most cases the host is an invertebrate. However, 4α-methylgorgostanol is a major sterol of *Kryptoperidinium foliaceum* and *K. balticum* in which the partner is another alga.[14] There are several known associations between freshwater algae[15] that have not been investigated for natural products. They are likely sources of cyclopropyl sterols.

(13) Withers, N. W.; Kokke, W. C. M. C.; Fenical, W.; Djerassi, C. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3764, 6390.

(14) Alam, M.; Martin, G. E.; Ray, S. M. *J. Org. Chem.* **1979**, *44*, 4466. Withers, N. W.; Kokke, W. C. M. C.; Rohmer, M.; Fenical, W.; Djerassi, C. *Tetrahedron Lett.* **1979**, 3601.

(15) Wilcox, L. W.; Wedemayer, G. J. *J. Phycol.* **1984**, *20*, 263; *J. Protozool.* **1984**, *31*, 444; *Science (Washington, D.C.)* **1985**, *227*, 192.

(16) Ritchie, E.; Senior, R. G.; Taylor, W. C. *Aust. J. Chem.* **1969**, *22*, 2371. Sunder, R.; Rangaswami, S. *Ind. J. Chem.* **1977**, *15B*, 541. Sunder, R.; Ayengar, K. N. N.; Rangaswami, S. *J. Chem. Soc., Perkin Trans. I* **1976**, 117. Tachi, Y.; Kamano, Y.; Sawada, J.; Tanaka, I.; Itokawa, H. *J. Pharm. Soc. Jpn.* **1976**, *96*, 1213. Hui, W. H.; Luk, K.; Arthur, R. H.; Loo, N. S. *J. Chem. Soc. C* **1971**, 2826. Chan, W.-S.; Hui, W.-H. *J. Chem. Soc., Perkin Trans. I* **1973**, *490*. Hui, W.-H.; Li, M.-M. *J. Chem. Soc., Perkin Trans. I* **1977**, 897. Manandhar, M. D.; Shoeb, A.; Kapil, R. S.; Popli, S. P. *Experientia* **1977**, *33*, 153. Ray, T. K.; Dasgupta, A.; Goswami, A.; Mishra, D. R.; Khastgir, H. N.; Shoolery, J. N. *J. Ind. Chem. Soc.* **1978**, *55*, 415. Schun, Y.; Cordell, G. A.; Cox, P. J.; Howie, R. A. *Phytochemistry* **1986**, *25*, 753.

(17) Nagai, M.; Nagumo, S.; Izawa, K. *Tetrahedron Lett.* **1975**, 3655. Croft, J. A.; Ritchie, E.; Taylor, W. C. *Aust. J. Chem.* **1975**, *28*, 2019.

0022-3263/89/1954-0606$01.50/0