for a generous gift of 19-hydroxyandrost-4-ene-3,17-dione. We are grateful for financial assistance from the Natural Sciences and Engineering Research Council of Canada and for a 1967 Science and Engineering Scholarship (S.H.).

Registry No. 2, 510-64-5; 4, 53875-00-6; 5, 113055-68-8; 6, 113055-69-9; 9, 113035-98-6; 10, 113035-99-7; 11, 113055-70-2; 12, 113055-71-3; 16, 113036-00-3.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for compound 5 (18 pages). Ordering information is given on any current masthead page.

Photochemical Reactions of Model *cis*-Stilbenes: The [2 + 2]-Cycloaddition Reaction

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Received June 8, 1987

The photochemical [2 + 2]-reactions of three model *cis*-stilbenes have been examined. 1,2-Diphenylcyclobutene was found to undergo photochemical [2 + 2]-cycloaddition reactions with 2,5-dimethyl-2,4-hexadiene and with itself but did not undergo reaction with tetramethylethylene. 1,2-Diphenylcyclopentene and 1,2-diphenylcyclohexene were unreactive in photochemical [2 + 2]-cycloaddition reactions. The singlet excited-state lifetimes of these compounds were measured. The results show that the observation of the *cis*-stilbene [2 + 2]-reaction is dependent upon the rate of deactivation of the excited state.

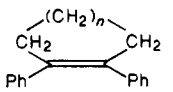
Introduction

The [2 + 2]-photocycloaddition reaction is a very well-known reaction.[1] The generality of this reaction is attested to by the fact that a recent review deals with the utility of this reaction in the synthesis of natural products.[1b] Although the reaction has achieved general usage, the mechanism is still incompletely understood. Caldwell has recently developed a method for predicting relative reactivity in [2 + 2]-reactions.[2] Although this method has achieved success in predicting reactivity in a large number of reactions,[3] a recent report shows a reactivity pattern other than would be predicted by Caldwell's method.[4] We reasoned that further examples of [2 + 2]-reactivity would serve to provide further constraints upon the limits of [2 + 2]-reactivity and lead to a more generally useful reaction.

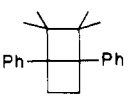
Our approach to defining the boundary conditions of this reaction was to employ the *cis*-stilbene chromophore. To date, only a few unequivocal examples[5] of the [2 + 2]-cycloaddition reaction of an excited *cis*-stilbene chromophore have been reported.[6] Yet, several examples of *trans*-stilbene intermolecular [2 + 2]-reactions abound in the literature.[7-9] One would anticipate that the reactivity of this chromophore would be similar to the reactivity of *trans*-stilbene. In one school of photochemical thought, a higher excited-state energy would result in a faster and more efficient reaction, since the energy of the excited state is closer to the transition-state energy.[10] Thus, based on the similar singlet excited-state energies of *cis*- and *trans*-stilbene and the higher triplet excited-state energy of *cis*-stilbene as compared to the trans isomer, a similar rate of [2 + 2]-cycloaddition would be predicted for these compounds. Caldwell's method for predicting [2 + 2]-reactivity predicts that *cis*-stilbene should have a slower rate of reaction than *trans*-stilbene due to the higher triplet excited-state energy of *cis*-stilbene. In order to test which of these hypotheses were correct, or if another intervening factor (such as steric hindrance of the phenyl groups) was operative, we undertook a systematic study of the [2 + 2]-cycloaddition reactions of a series of *cis*-stilbenes. These stilbenes vary only in the size of the ring in which the *cis*-stilbene chromophore is constrained. This systematic variation of size may be expected to yield effects related to the lifetime of the excited state.

Results

The compounds 1,2-diphenylcyclobutene (4), 1,2-diphenylcyclopentene (5), and 1,2-diphenylcyclohexene (6), were synthesized by the literature methods.[11] Using tetramethylethylene (TME) as a solvent, we irradiated a 0.2 M solution of 4. To our surprise, no 8 was formed!



4: $n = 0$
5: $n = 1$
6: $n = 2$



8

Only the previously known dimeric product was isolated from the reaction mixture.[12] Even when the concentration of 4 was lowered to 0.01 M, dimer 7 was still the predominant product.[5] This result is made even more startling when the strain energy of these two potential products are

(1) (a) Trecker, D. J. *Org. Photochem.* **1969**, *2*, 63–116. (b) Schreiber, S. L. *Science (Washington, D.C.)* **1985**, *227*, 857–863.
(2) Caldwell, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 4004.
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(6) Chapman[7] has reported that irradiation of *cis*-stilbene in TME produces *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane. It is not clear whether this reaction proceeds directly from the *cis*-stilbene or results from the photochemical isomerization of *cis*-stilbene to *trans*-stilbene, followed by cycloaddition.
(7) Chapman, O. L.; Adams, W. R. *J. Am. Chem. Soc.* **1968**, *90*, 2333.
(8) Chapman, O. L.; Lura, R. D. *J. Am. Chem. Soc.* **1970**, *92*, 6352–6354.
(9) Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152.
(10) Zimmerman, H. E.; Welter, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 4131.
(11) (a) Baumstark, A. L.; Bechara, E. J. H.; Semigran, M. J. *Tetrahedron Lett.* **1976**, 3265. (b) Baumstark, A. L.; McCloskey, C. J.; Witt, K. E. *J. Org. Chem.* **1978**, *43*, 3609–3611.
(12) This product was characterized by its melting point, NMR, and GCMS data to be the product previously obtained in the irradiation of 4 in hexane.[5]

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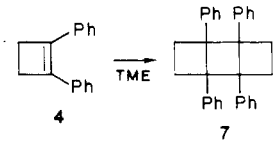
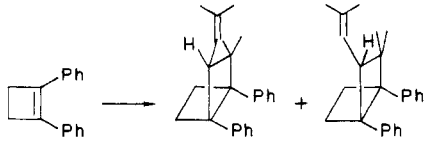
considered. The observed dimeric product 7 has the secocubane structure which has 28.8 kcal/mol more strain energy than the anticipated adduct 8 which contains a bicyclo[2.2.0]hexane structure.[13] This result is shown in eq 1.



4 7 (1)

Further information concerning the reactivity of *cis*-stilbenes in [2 + 2]-cycloaddition reactions is obtained through the reaction of 4 with 2,5-dimethyl-2,4-hexadiene (DMHD). In this case, irradiation produces only the expected [2 + 2]-cycloaddition products. Within the limits of GC detection (ca. 10%) and the product isolation studies, no dimer of 4 is formed.

The [2 + 2]-isomers were formed in a ca. 1.2:1 ratio as determined by GC analysis and confirmed by subsequent separation and purification studies. The separation of these two isomers was achieved only with great difficulty, requiring repeated chromatography on silica gel to effect a separation. Tentative identification as simple cycloaddition products was provided in both cases by MS parent ion peaks of 316. ^{1}H NMR was used to assign the product structures. For both isomers, four distinctly different CH_3 groups were observed. The product of a [4 + 2]-cycloaddition reaction would be expected to exhibit at most two different methyl groups, while the product of an ene reaction would exhibit only three CH_3 groups. Further support for this structural assignment comes from the observation of a vinyl proton and an allylic proton for both compounds, neither showing a significant coupling constant to any other protons. The final basis for a structural assignment was based on the observed NOE effects. NOE enhancements have frequently been shown to correspond to geometric proximity, even when no formal coupling constant between the hydrogens occurs.[14] This effect seemed ideally suited to application in such a compact and strained system. For the major isomer, irradiation of the vinyl proton gives a negligible effect on the cyclobutyl hydrogen intensities, while a large enhancement (ca. 25%) on one of the cyclobutyl hydrogens was observed when the allylic proton was irradiated. Thus, we have assigned the major isomer to be the exo isomer. This assignment is supported by similar NOE experiments on the minor isomer. Irradiation of the cyclobutyl protons gives a large signal enhancement to the vinyl proton (ca. 20%), but only a small enhancement of the allylic proton. Thus, the photochemical reaction of 4 with DMHD is shown in eq 2.



4 9a 9b (2)

The other *cis*-stilbenes used in this study are much less efficient in intermolecular [2 + 2]-reactions but instead undergo an intramolecular electrocyclic reaction. Irradiation of 5 (0.2 M) in TME or in DMHD yields the known

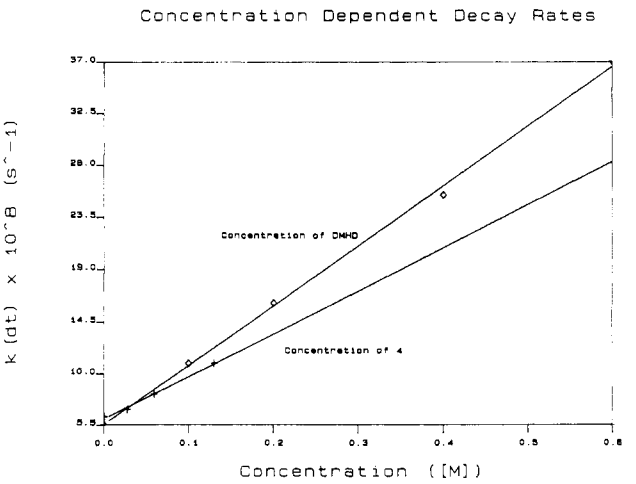


Figure 1. Concentration dependences of the excited-state lifetime of 4.

Table I. Luminescent Lifetimes of 4

solvent	conc, M: 4	conc, M: DMHD	lifetime, ns	decay rate, $\times 10^{-8}$ s^{-1}
TME	5×10^{-4}		1.87	5.34
hexane	5×10^{-4}		1.91	5.23
hexane	0.028		1.46	6.85
hexane	0.060		1.22	8.20
hexane	0.13		0.92	10.9
pentane	5×10^{-4}	0.10	0.968	10.3
pentane	5×10^{-4}	0.20	0.645	15.5
pentane	5×10^{-4}	0.40	0.398	25.1
pentane	5×10^{-4}	0.60	0.290	34.5

phenanthrene-type cyclization product[15] as the only product. The photoreactivity of 6 is similar, except that a longer irradiation time is required. These products presumably arise from a dihydrophenanthrene intermediate which is then oxidized by residual oxygen in the solution.

Excited-State Lifetime Determinations. One potential factor for the greater reactivity of 4 in intermolecular [2 + 2]-cycloadditions as compared to 5 and 6 would be a longer singlet excited-state lifetime. Thus, we attempted measurements of the fluorescent lifetimes of these compounds.

The singlet excited-state lifetime of compound 4 was determined in both hexane and TME. Within experimental error, the lifetimes are the same, indicating little excited-state interaction of 4 with TME. The concentration dependence of the lifetime of 4 in hexane was examined and the results are plotted in Figure 1. A least-squares analysis of the data yields $k_o = 5.47 \times 10^8$ s^{-1} and $k_q = 4.2 \times 10^9$ s^{-1} from a least-squares analysis of the data presented in Table I (correlation coefficient of 0.999), where k_{dt} is the total rate of decay of the excited state, k_o is the unperturbed rate of decay, and k_q is the rate of interaction of 4 with a quencher.

$$k_{dt} = k_o + k_q[4] \quad (3)$$

In order to obtain information relating to the relative reaction rates of the excited state of 4 toward other olefins, singlet excited-state lifetimes of 4 as a function of the concentration of DMHD were obtained. These data are presented in Table I and are also plotted in Figure 1. A least-squares analysis of the data yields $k_o = 5.45 \times 10^8$ s^{-1} and $k_q = 4.87 \times 10^9$ s^{-1} from a least-squares analysis. Thus, these data are also described by eq 3.

(13) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005–8025.

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Table II. $\gamma(r_c)$ Values for the [2 + 2]-Cycloaddition Reactions of *cis*-Stilbene with Various Alkenes

alkene	E_T	c^2	$\gamma(r_c)$
tetramethylethylene	78	2.48	19.0
cis-stilbene	57	1.54	16.9
2,5-dimethyl-2,4-hexadiene	53	1.71	12.9

Attempts were made to measure the fluorescent lifetimes of **5** and **6**. However, these compounds had extremely shoft lifetimes. We estimate that the lifetimes of these compounds are ≤20 ps.

Discussion

Source of the Preference in [2 + 2]-Cycloadditions. The results above describe a marked preference and selectivity of the *cis*-stilbene excited state of **4** for a reacting partner in the [2 + 2]-cycloaddition reaction. Note that while TME is unreactive toward this excited state, DMHD is very reactive. In addition, the efficient reaction of *trans*-stilbene (TS) with TME is instructive. It is tempting to suggest that the tetrasubstituted olefin (TME) encounters too much steric hindrance in the transition state for the cycloaddition reaction of **4** and TME, while the trisubstituted olefin (DMHD) encounters less steric repulsion in the encounter of **4** and DMHD and is therefore able to react. However, the facile reaction of singlet excited **4** with another ground-state **4** would also be expected to have the same amount of steric interaction in its approach, since it is also a tetrasubstituted olefin. The dimerization of **4** demonstrates that the failure of the singlet excited state of **4** to add TME does not arise from steric effects. Thus, the evidence presented in this paper suggests that the origin of the selectivity effects in these compounds results from electronic rather than steric effects. Support for this hypothesis comes from the work of Chapman.[8] In that work, the reactivity of the singlet excited state of TS was shown to fall off rapidly with decreasing substitution on the olefin in the series TME, 1-methylcyclohexene, and cyclohexene.

As noted earlier, an electronic basis for the reactivity in photochemical [2 + 2]-reactions has been developed by Caldwell.[2] In Caldwell's approach (eq 4), a $\gamma(r_c)$ value is calculated from the triplet energies (E_T) of the reacting partners, the singlet energy (E_S) of the initially excited chromophore, and the magnitude of the coefficients on the relevant orbitals (c^2). This $\gamma(r_c)$ value is thought to be

$$\gamma(r_c) = (E_T^A + E_T^B - E_S^A)/c^2 \qquad (4)$$

related to the transition-state energy, with smaller $\gamma(r_c)$ values predicting faster reaction rates. When $\gamma(r_c)$ is ≤22 kcal/mol, the [2 + 2]-cycloaddition is thought to be diffusion controlled. $\gamma(r_c)$ values are tabulated in Table II for a series of model reactions relevant to the present research. *cis*-Stilbene has been used as a model for the excited-state chromophore of **4**. The $\gamma(r_c)$ values obtained for the reaction of *cis*-stilbene with TME, *cis*-stilbene, and DMHD are in complete accord with our present results. The largest $\gamma(r_c)$ is obtained for *cis*-stilbene and TME for which we obtain no reaction of **4** and TME. The lower values for *cis*-stilbene reacting with *cis*-stilbene and DMHD would predict a faster reaction rate. This rate could compete more effectively with the overall excited-state decay.

A further check on the validity of Caldwell's method to predict relative reaction rates of [2 + 2]-cycloaddition reactions arises from the reaction of TS and TME. Caldwell has calculated a $\gamma(r_c)$ value of 16.7 for this reaction.[2] Since the $\gamma(r_c)$ for the reaction of *cis*-stilbene with *cis*-stilbene is 16.9, one might expect that the reaction rate of excited **4** with **4** would be of the same order of magnitude as the reaction rate of TS with TME. The minimum rate of exciplex formation[16] for TS and TME has been determined to be 1.2×10^9 s^{-1}, while we have determined that the minimum rate of excimer formation for excited **4** with **4** is 3.8×10^9 s^{-1}. Given the differences in the chromophores of **4** and TS and the approximations used to obtain the $\gamma(r_c)$ value, we believe that the agreement of the reaction rates is excellent. In further support of this rationale is the fact that the singlet excited state of **4** is quenched at a faster rate by DMHD than by **4**. This is in accord with the diminished value of $\gamma(r_c)$ for the [2 + 2]-cycloaddition reaction of *cis*-stilbene and DMHD (note Table II). Thus, Caldwell's method seems to rationalize these results fairly well.

Table III. Vertical Ionization Potentials of the Compounds Used in This Study

alkene	IP, eV
tetramethylethylene	8.27[a]
cis-stilbene	8.17[b]
trans-stilbene	7.87[c]
1,2-diphenylcyclobutene	7.71[c]
2,5-dimethyl-2,4-hexadiene	7.84[d]

[a] Heilbronner, et al. *Helv. Chim. Acta* **1977**, *60*, 2213. [b] Kobayashi, T.; Yokuta, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 412. [c] Hohlneicher, G.; Müller, M.; Demmer, M.; Lex, J.; Penn, J. H.; Gan, L.-X.; Loesel, P. D. *J. Am. Chem. Soc.*, in press. [d] Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

An alternative explanation for the reactivity trends seen in these compounds derives from the rate of exciplex formation. If *trans*-stilbene had a greater excited-state electron affinity than **4**, the rate of formation of an excited-state complex would be greater for TS than for **4**. Thus, the ionization potential of the reacting ground-state alkene would be the determining factor of the reaction with TS having a faster reaction rate for all reacting olefins. Table III shows the measured ionization potential data for the relevant olefins used in this study. Since TME has the highest ionization potential, it would not be surprising that it borders on the verge of reactivity with these stilbenes. However, the faster quenching of the singlet excited state of **4** is not in agreement with the ionization potential data shown in Table III. Thus, the method of Caldwell seems to adequately explain the observed reactivity trends.

Quenching of the Singlet Excited State of 4. A critical question concerns the relative quenching rates of the singlet excited state of **4** by various olefins. DeBoer and Schlessinger[5b] have reported that a plot of $1/\Phi_f$ vs [**4**] has a slope of 12. Additionally, they[5b] reported that $\Phi_f^o = 1.0$. If $\Phi_f^o = 1.0$, then $k_f = k_{dt}$ for the singlet excited state of **4**. Thus, $k_f = 5.5 \times 10^8$ s^{-1}, yielding a bimolecular rate constant for the quenching interaction (k_q) of 6.6×10^9 M^{-1} s^{-1}. It should be emphasized that these experiments are steady-state experiments in which the total emission is integrated as a function of the concentration of **4**.

An alternative determination of this value arises from the increase in the total decay rate (k_{dt}) of the singlet excited state of **4** as a function of the concentration of **4**. We have previously shown (Figure 1 and eq 3) that our measured value is 4.2×10^9 M^{-1} s^{-1}.

A potential rationale for these different k_q values arises in self-absorption effects in the determination of the steady-state fluorescence quantum yields. It may be ex-

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Table IV. Excited-State Lifetimes of Phenyl-Substituted Cyclic Olefins

	monophenyl		diphenyl	
ring size	compound	τ, ns	compound	τ, ns
4	1-phenylcyclobutene	15.89	1,2-diphenylcyclobutene	1.65
5	1-phenylcyclopentene	14.01	1,2-diphenylcyclopentene	<0.02
6	1-phenylcyclohexene	1.44	1,2-diphenylcyclohexene	<0.02

pected that at infinitely dilute solution, no self-absorption will take place. However, as the concentration of **4** increases, the self-absorption may be expected to increase in a linear fashion. DeBoer and Schlessinger have reported that the shape of the fluorescence curve and λ_{max} for the absorption do not change with [**4**]. However, a 10% decrease in Φ_f through self-absorption effects (in addition to the normal quenchers) at a concentration of 0.1 M leads to a k_q value of 5.9×10^9 s^{-1} if we assume that no self-absorption occurs at infinitely dilute solution. Thus, it is hard to envision that a ca. 30% decrease in Φ_f through self-absorption effects would not be readily apparent in the shape of the fluorescence or absorption spectra as measured previously.[5b]

An alternative rationale comes from the fact that our measurement of the fluorescent lifetime was performed in aerated solutions, while the Φ_f data were gathered in deoxygenated solutions. This would influence the slope of the k_q data as determined by transient measurements. This follows from the fact that oxygen quenching of the singlet excited state of **4** at low concentrations of **4** would be maximal. However, at high concentrations of **4**, the rate of excited-state quenching by **4** would be much greater than the quenching by oxygen. Thus, a smaller value of k_q would be obtained in aerated solutions than in degassed solutions. An estimate of this deviation can be obtained from consideration of $[O_2] = 2 \times 10^{-3}$ M and diffusion controlled quenching of the singlet excited state by $[O_2]$ ($k_{diff} \approx 3 \times 10^{10}$ M^{-1} s^{-1}).[17] Thus, the corrected k_{dt}^{o} (4.9×10^{-8} s^{-1}) would yield k_q from our transient measurements of ca. 4.5×10^9 M^{-1} s^{-1}.

Even with conservative error limits, and assuming that both effects mentioned above are operative, a considerable difference for k_q obtained by the contrasting techniques is obtained (k_q(steady state) $\approx 5.9 \times 10^9$ M^{-1} s^{-1} and k_q(transient) $\approx 4.5 \times 10^9$ M^{-1} s^{-1}). This difference may be due to the formation of a reversibly formed excimer whose decay is coupled with the decay of the singlet excited state of **4**. Experiments are currently in progress in our laboratory to verify and define the generality of this effect.

Singlet Excited-State Lifetimes of the Diphenylcycloalkenes. We had originally expected the singlet excited-state lifetimes of **4–6** to mimic the lifetimes of the monophenylcycloalkenes measured first by Zimmerman.[18] However, as seen in Table IV, these lifetimes show a dramatic decrease between a ring size of 4 and 5 for the diphenyl series and between 5 and 6 for the monophenyl series. Although this is surprising at first glance, the rapid excited-state decay of **5** and **6** likely results from the existence of a readily accessible pericyclic potential energy minimum in **5** and **6**, which arises through interaction of the phenyl groups. Construction of molecular models show that the p-orbitals of the two phenyl groups are within reasonable bonding distances. Such pericyclic potential energy minima have previously been shown to lead to excited-state energy funnels.[19] Alternatively, increased steric problems in the excited states of **5** and **6** may lead to easier and faster excited-state twisting. Thus, the rapid rate of excited-state decay of **5** is due to the additional phenyl group when compared to phenylcyclopentene.

A further comment is needed concerning the lack of [2 + 2]-cycloaddition reactivity of **5** and **6**. Both **5** and **6** have extremely rapid excited-state decay rates. A very fast reaction rate is required to compete with the overall decay of the excited state in order to yield a reaction with a reasonable quantum efficiency. Thus, [2 + 2]-cycloadditions can yield efficient and synthetically useful reactions when the excited-state lifetime is sufficiently long.

Conclusions

In this paper, we have described our results pertaining to the cycloaddition reactions of cis-substituted stilbenes. Electronic factors seem to dominate the reaction dynamics of cycloaddition reactions. It is noted that the addition of phenyl groups to an olefin shortens the excited-state lifetime. The results show that the [2 + 2]-cycloaddition reactions of *cis*-stilbenes are relatively slow. The observation of [2 + 2]-reactivity is highly dependent on the rate of deactivation of the excited state.

Experimental Section

Melting points were determined on a Laboratory Devices Mel-Temp apparatus and are uncorrected. Proton NMR spectra were measured in the indicated solvent with tetramethylsilane as the internal standard on either a Varian Anaspect EM360 or a JEOL GX-270 NMR spectrometer. Gas chromatography was performed on a Hewlett-Packard 5890A GC equipped with a Hewlett-Packard 3390A reporting integrator. High-pressure liquid chromatography was performed on a Waters Associates Protein Peptide I isolation system. Gas chromatographic mass spectra were recorded on a Finnigan Model 4021 mass spectrometer, using a 30-m, fused silica DB-5 capillary column. Photolysis samples in quartz tubes were degassed by bubbling with N_2 for 10 min prior to irradiation, sealed with latex septa, and irradiated at 300 nm in a Southern New England Ultraviolet RPR-100 Rayonet reactor, equipped with a carousel motor assembly.

Solvents and chemicals were reagent grade and used without purification, unless otherwise noted. **4–6** were synthesized by the literature methods.[11]

Photolysis of 1,2-Diphenylcyclobutene in TME. A degassed solution of **4** (0.20 g, 0.97 mmol) in TME (5 mL, 0.19 M) was irradiated for 24 h at 300 nm. A clear solid precipitated upon the walls of the reaction tube during the course of the reaction. The precipitate was recrystallized from chloroform/pentane and was identified as 1,2,5,6-tetraphenyltricyclo[4.2.0.$0^{2,5}$]octane: ^{1}NMR ($CDCl_3$) δ 2.56 (s, 8 H), 7.38 (m, 20 H); MS, *m/e* 412 (M^+). No other products were detected. Heating a solution of this solid resulted in the isolation of 1,2,5,6-tetraphenyl-1,5-cyclooctadiene, mp 222–225 °C (lit. 223–224 °C).[5]

Photolysis of 1,2-Diphenylcyclopentene in TME. A degassed solution of **5** (0.078 g, 0.35 mmol) in TME (5 mL, 0.07 M) was irradiated for 20 h at 300 nm, resulting in a bright orange solution. The only product in the resulting solution was identified as 9,10-cyclopentanophenanthrene [mp 147–148 °C (lit. 147.3–150.0 °C);[15] MS, *m/e* 218 (M^+)], which resulted from air oxidation of the initially formed dihydrophenanthrene. No evidence of dimerization or a [2 + 2]-reaction was obtained by GC, GCMS, or HPLC analyses.

Photolysis of 1,2-Diphenylcyclohexene in TME. A degassed solution of **6** (0.23 g, 0.98 mmol) in TME (5 mL, 0.20 M) was irradiated for 1 month at 300 nm. The only product in the resulting solution was identified as 9,10-cyclohexanophenanthrene [MS, 232 (M^+)], which resulted from air oxidation of the initially

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formed dihydrophenanthrene.[15] No evidence of dimerization or a [2 + 2]-reaction was obtained by GC, GCMS, or HPLC analyses.

Photolysis of 1,2-Diphenylcyclobutene in DMHD. A degassed solution of 4 (400 mg, 1.94 mmol) in 2,5-dimethyl-2,4-hexadiene (DMHD, 20 mL) was irradiated for 15 h at 300 nm. The DMHD was removed in vacuo to give a mixture of *exo*-2,2-dimethyl-1,4-diphenyl-3-(2-methyl-1-propenyl)bicyclo[2.2.0]hexane (**9a**) and *endo*-2,2-dimethyl-1,4-diphenyl-3-(2-methyl-1-propenyl)bicyclo[2.2.0]hexane (**9b**) (1.13:1, GC) as a yellow sticky oil. The crude oil was repeatedly chromatographed on silica gel with pentane to give 86 mg of **9b** and 113 mg of **9a**.

9a: colorless flake (Me_2CO–MeOH), mp 70–71 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.01–7.24 (10 H, m, Ar), 4.62 (1 H, d, J = 9.8 Hz, C=C*H*), 3.40 (1 H, d, J = 9.8 Hz, C=CHC*H*), 3.05 (1 H, ddd, J = 8.0, 8.0, 12.0 Hz, C*H*HCHH), 2.62 (1 H, ddd, J = 8.0, 12.0, 12.0 Hz, one of C*H*HCHH), 2.46 (1 H, ddd, J = 4.0, 12.0, 12.0 Hz, C*H*HCHH), 2.03 (1 H, ddd, J = 4.0, 12.0, 12.0 Hz, C*H*HCHH), 1.65 (3 H, s, CH_3), 1.51 (3 H, s, CH_3), 1.42 (3 H, s, CH_3), 1.05 (3 H, s, CH_3); IR (KBr) 3090, 3050, 3030, 2980, 2960, 2920, 2850, 1665, 1600, 1575, 1480, 1440, 1385, 1365, 1220, 1130, 1080, 1070, 1040, 860, 760, 710, and 640 cm^{-1}; GCMS, m/e (relative intensity) 316 (M^+, 12.0), 199 (1.3), 183 (0.3), 171 (100), 156 (8.5), 143 (29.5), 129 (23.6), 115 (12.5), 91 (43.1), 77 (9.4), 65 (4.3), and 55 (3.5).

Anal. Calcd for $C_{24}H_{38}$: C, 91.08; H, 8.92. Found: C, 90.93; H, 9.14.

9b: Colorless oil at room temperature, >99% pure by ^1H NMR; ^1H NMR (270 MHz, $CDCl_3$) δ 7.02–7.25 (8 H, m, Ar), 6.69 (2 H, m, Ar), 5.64 (1 H, d, J = 9.8 Hz, C=C*H*), 3.56 (1 H, d, J = 9.8 Hz, C=CHC*H*), 2.93 (1 H, ddd, J = 8.0, 8.0, 12.0 Hz, C*H*HCHH), 2.75 (1 H, ddd, J = 4.0, 8.0, 12.0 Hz, C*H*HCHH), 2.60 (1 H, ddd, J = 8.0, 12.0, 12.0 Hz, C*H*HCHH), 2.14 (1 H, ddd, J = 4.0, 12.0, 12.0 Hz, C*H*HCHH), 1.84 (3 H, s, CH_3), 1.79 (3 H, s, CH_3), 1.26 (3 H, s, CH_3), 0.71 (3 H, s, CH_3); IR (film) 3100, 3080, 3050, 2960, 2910, 1670, 1620, 1580, 1510, 1465, 1455, 1390, 1370, 1050, 870, 775, and 725 cm^{-1}; GCMS, m/e (relative intensity) 316 (M^+, 11.4), 199 (1.2), 183 (0.3), 171 (100), 156 (8.5), 143 (30.1), 129 (24.0), 115 (13.0), 105 (6.0), 91 (43.1), 77 (9.7), 65 (4.4), 55 (3.4).

Photolysis of 1,2-Diphenylcyclopentene in 2,5-Dimethyl-2,4-hexadiene. A degassed solution of **5** (0.066 g, 0.30 mmol) in DMHD (3 mL, 0.10 M) was irradiated for 20 h at 300 nm. The only product in the resulting solution was identified as 9,10-cyclopentanophenanthrene by GC and GCMS analysis.

Acknowledgment. Support of this research by the Committee to Stimulate Competitive Research in the State of West Virginia is gratefully acknowledged. We are deeply indebted to Professor Robin M. Hochstrasser and the staff at the Regional Laser and Biotechnology Laboratory Located at the University of Pennsylvania for the use of their single photon counting apparatus. Particular thanks are due to Dr. Gary Holtom for his technical assistance in the determination of the excited-state lifetimes.

Registry No. **4**, 3306-02-3; **5**, 1485-98-9; **6**, 41317-87-7; **7**, 4759-04-0; **9a**, 113036-77-4; **9b**, 113085-40-8; DMHD, 764-13-6; TME, 563-79-1; 9,10-cyclopentanophenanthrene, 723-98-8; 9,10-cyclohexanophenanthrene, 5981-10-2.

Preparation of Difluorophosphonoacetic Acid and Its Derivatives

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Received September 15, 1987

The preparation of ethyl difluoro(diethoxyphosphinyl)acetate (**1**) has been effected by the acylation of [(diethoxyphosphinyl)difluoromethyl]zinc bromide with ethyl chloroformate in the presence of a catalytic amount of cuprous bromide. Similarly prepared were ethyl difluoro(diethoxyphosphinyl)pyruvate (**2**) and *N,N*-diethyldifluoro(diethoxyphosphinyl)acetamide (**3**). Bromotrimethylsilane selectively reacted with **1** to yield ethyl difluoro[bis(trimethylsiloxy)phosphinyl]acetate (**9**). The remaining ethyl carboxylic ester of **9** reacted with iodotrimethylsilane to produce trimethylsilyl difluoro[bis(trimethylsiloxy)phosphinyl]acetate (**10**), which was subsequently hydrolyzed to yield difluorophosphonoacetic acid (**8**). The phosphonate **9** was gently chlorinated to yield ethyl difluoro(dichlorophosphinyl)acetate (**11**).

Phosphonic acids often exhibit important biological properties by virtue of their similarity to phosphates,[2] while substitution of a fluorine atom in a biologically active molecule often leads to pronounced activity enhancement.[3] Some α-fluorinated alkanephosphonic acids such as difluoromethanediphosphonic acid[4-8] have already been the subject of interest as analogues of biological phosphoryl species. However there is generally a conspicuous lack of methods for the preparation of other difluoromethanephosphonates. Such compounds have been postulated to possess biologically superior properties to those of analogous nonhalogenated phosphonates.[9] However, there are generally few synthetic methods available which lead to other difluoromethanephosphonates.

The phosphonic acids of some common carboxylic acids often have a biological origin and exhibit metabolic activity. Phosphonopyruvic acid occurs naturally[10] and was synthesized several years ago.[11] A structurally similar compound, phosphonoacetic acid, has been shown to inhibit effectively the replication of Herpes viruses[12] as well as suppress the replication of DNA tumor viruses[13] and

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