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Photodimerization of 1-Phenylcyclohexene. A Novel Transient−Transient Component

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Abstract: Low-temperature irradiations of 1-phenylcyclohexene (PC6) yield two singlet state 2 + 2 photodimers and two 4 + 2 cycloadducts. The 4 + 2 adducts are not observed in low intensity lamp irradiations at room temperature but are produced in significant quantities when PC6 solutions are subjected to higher intensity laser irradiation. The results indicate a reaction mechanism involving two *trans*-PC6 molecules. The findings are consistent with earlier kinetic observations that the decay of *trans*-PC6 adopts a significant second-order component at lower temperatures. The transient−transient reaction also occurs under triplet-sensitized low-temperature/low-intensity or room temperature/high-intensity irradiation conditions. Triplet-sensitized irradiations also yield significant amounts of the 2 + 2 photodimers produced by attack of the PC6 triplet on its ground state. Quantum yield studies reveal that the rate of addition of ^{3}PC6* to its ground state is in the range 0.28 to 4.0 × 10^5 L mol^{-1} s^{-1} consistent with the 1,2-biradical model for alkene triplet reactivity.

Photosensitized *cis*−*trans* isomerization of alkenes represents probably the most thoroughly documented organic photochemical reaction. The process is not confined to acyclic alkenes. Irradiation of even small ring cycloalkenes, either direct or sensitized, leads to the production of *trans* isomers which become increasingly strained as the ring size is decreased.[1] While *trans*-cyclooctenes have been demonstrated to be stable at ambient temperatures,[2,3] *trans*-cycloheptenes and cyclohexenes are transient species with lifetimes for the latter generally in the microsecond time regime.[4−9] The high degree of strain within a *trans*-cyclohexene structure represents a strong potential driving force for novel chemical reactivity and *trans*-cyclohexenes and cyclohexenones have been discussed as possible intermediates in numerous chemical reactions,[8,10−26] particularly those where ring formation occurs with the production of *trans* stereochemistry at the original location of the cyclohexene double bond.

trans-Phenylcyclohexene (*trans*-PC6) is by far the most widely studied example of a *trans*-cyclohexene in the literature to date. In particular, the phenyl substituent on the double bond allows for laser excitation of the *cis* isomer and spectroscopic detection of the *trans* isomer in flash photolysis studies. *trans*-PC6 was first characterized by Bonneau *et al.*,[4] who reported an absorption maximum around 380 nm and a transient lifetime of 9 μs in methanol at room temperature. The authors also reported that the species was quenched by the hydrogen ion with a rate of 7.6 × 10^6 L mol^{-1} s^{-1}. Photoacoustic studies of the triplet-sensitized production of *trans*-PC6[7] reveal a lifetime for the PC6 triplet of 65 ns and a relaxed triplet energy of 56.4 ± 0.7 kcal mol^{-1} compared to the spectroscopic triplet energy of 60.8 kcal mol^{-1}. The quantum yield for the production of *trans*-PC6 via this route is 0.36 and the energy of the *trans* isomer was found to be 44.7 ± 5 or 47.0 ± 3 kcal mol^{-1},[27] relative to the ground state *cis* isomer. Varible-temperature studies[9] reveal an activation energy for *trans*−*cis* isomerization of 12.1 ± 0.12 kcal mol^{-1}. The isomerization transition state is therefore 59.1 ± 3 kcal mol^{-1} above the *cis* isomer, demonstrating a close approach of the ground and excited triplet state potential energy surfaces at an approximately perpendicular geometry.

The first stereochemical evidence for the existence of *trans*-cyclohexenes was provided by Dauben *et al.* in a study of PC6 photochemistry.[28,29] Prolonged irradiation of PC6 in methanol generates the singlet state 2 + 2 photodimers (**1** and **2**) and a

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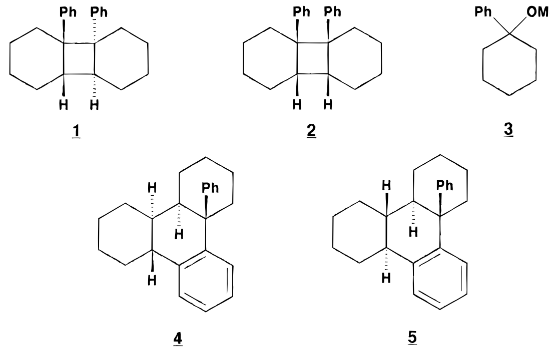
Chart 1



methanol addition product (**3**) resulting from protonation of the *trans*-PC6 isomer either by the solvent or traces of acid. The yield of this product is increased upon addition of sulfuric acid to the reaction mixtures. In addition, the authors were able to isolate and characterize a new dimer (**4**) resulting from a 4 + 2 cycloaddition reaction. The product retained a *trans* ring junction at the site of one of the original cyclohexene double bonds and was assigned to the Woodward–Hoffmann allowed concerted [π4s + π2s] addition of ground state *cis*-PC6 across the strained double bond of a *trans*-PC6 molecule. Rearomatization via a 1,3-hydrogen shift affords the isolated product. The new 4 + 2 adduct was isolated only from irradiations conducted at low temperatures in which the lifetime of the *trans*-PC6 was expected to be dramatically lengthened.

During our Arrhenius studies[9] of *trans*-PC6 isomerization, we noted that the transient decay of the *trans* isomer adopted a significant second-order component even at temperatures as high as 10 °C and speculated that we might be observing a reaction in which the 4 + 2 adduct was generated. A second-order component in the transient decay obviously suggested a process involving reaction between two *trans* isomers and not *trans* + *cis* as previously assumed. We have therefore conducted a detailed investigation of the origin of the unusual 4 + 2 adduct and find that it is indeed generated, along with a second, previously unreported stereoisomer (**5**), in a reaction involving two *trans*-cyclohexene molecules. In addition, we have been able to study the triplet-sensitized photolysis of PC6 in greater detail and find that the reported 2 + 2 photodimers (**1** and **2**) are also produced via the photoaddition of the excited PC6 triplet to a ground state PC6 molecule. This reaction is discussed in the context of the 1,2-biradical model for alkene triplets[27,30–32] with reference to a number of other recently published results reported by our group.

Experimental Section

General. 1-Phenylcyclohexene was obtained from Aldrich and purified by column chromatography (silica/hexane) and kugelrohr distillation prior to use. Spectroscopic grade solvents were used as received. Sensitizers were purified previously in our laboratories by recrystallization. ^{13}C NMR spectra were run on a JOEL-FX200 (200 MHz) for solutions in $CDCl_3$ containing tetramethylsilane as internal standard. Gas chromatography was performed on a Shimadzu GC-14A gas chromatograph using a Restek Rtx-20 (crossbonded 80% dimethyl 20% diphenyl polysiloxane) megabore capillary column (0.53 mm i.d. × 30 m) with flame ionization detection. Reported product distributions are GC peak areas normalized to 100% for the four major products under investigation unless otherwise stated.

Laser flash photolysis experiments were performed as previously described[30] with a Q-switched Continuum model YG671C-10 Nd:YAG laser, pulse width fwhm = 5 ns after the doubling crystal, using a repetition rate of 10 Hz. An Osram model XBO 150 W/I high-pressure xenon lamp and CVI Digikrom 240 monochromator and photomultiplier provided detection. Data were collected using a Tektronix DSA 602 digitizing signal analyzer and transferred to a DTK 486DX personal computer for analysis. Laser and flash lamp control and kinetic analyses were performed with the PC RAD and KS-01 software packages from Kinetic Instruments (P.O. Box 49434, Austin, TX 78765).

Preparative irradiations were performed in a standard quartz immersion well photochemical reactor with a Hanovia 679A 450W medium-pressure mercury arc lamp. A Pyrex filter was added for triplet-sensitized irradiations. Low-temperature irradiations were performed at −78 °C and required the use of a triple-walled low-temperature immersion well. The 2 + 2 photodimers were readily prepared by room temperature irradiation of a 20 mM solution of PC6 in either cyclohexane or methanol. Use of cyclohexane avoids the unwanted *trans*-PC6–methanol addition side reaction forming 1-methoxy-1-phenylcyclohexane. The reaction was monitored by GC using a tetradecane internal standard. Irradiations were generally run to >90% conversion of starting material. The two 2 + 2 dimers were produced in a 3:1 ratio determined by GC analysis of the final reaction mixture. The two 4 + 2 adducts were isolated from a low-temperature irradiation of PC6 (20 mM) in methanol. The final product distribution was **1** (20%), **2** (16.5%), **4** (26.5%), **5** (37%). The reaction was accompanied by significant quantities of 1-methoxy-1-phenylcyclohexane (**3**). The exact yield of this product was sensitive to the acidity of the solvent. The GC peak areas of the four PC6 dimers, the methanol addition product (**3**), and unreacted PC6 accounted for >90% of the total peak area.

Isolation and Characterization of Photoproducts. Solvent was removed from the irradiated mixtures which were then subjected to repeated column chromatography on silica with hexane as the eluting solvent. The R_f values for the 2 + 2 dimers were close and large quantities of mixed fractions had to be discarded in order to obtain enriched samples of each isomer. Final purification was effected by multiple recrystallizations from hexane/ethyl acetate mixtures. The 4 + 2 dimers were more difficult to isolate. Separation of **4** and **5** proved impossible on silica gel. Little resolution was achieved even under analytical HPLC conditions. A mixture of the two 4 + 2 adducts was obtained free of other contaminants via column chromatography. Recrystallizations employing a range of solvents eventually yielded a pure sample of **4**. Dimer **5** has a significantly lower melting point and was eventually isolated, through numerous recrystallization procedures, from the combined mother liquors from the **4** recrystallizations. This process eventually yielded a crystal free from contamination by **4** and suitable for X-ray analysis.

Melting points and ^{13}C NMR data for the 2 + 2 dimers were identical to literature values.[29] Dimer **4** was recrystallized many times and an eventual melting point of 207–208.5 °C was obtained. This is higher than the previously reported value[28,29] (198–201 °C) but was reproducible. Single-crystal X-ray analysis of this sample, as described below, revealed unit cell dimensions identical to those reported by Dauben *et al.*[28] Dimer **5** has a significantly lower melting point at 131–3 °C. A full single-crystal X-ray analysis was performed on this sample.

Laser synthesis of PC6 photodimers was conducted in a 5 × 10 mm quartz cuvette placed at the exit of the Nd:YAG laser described above. The laser output was controlled by variations in the oscillator and/or amplifier flash lamp voltages. Irradiations were performed at 266 nm (10 Hz) for direct excitation of PC6 or 355 nm for sensitized experiments. The laser beam impinged on the 10 mm face of the cuvette and the irradiated sample was subjected to a continuous nitrogen sparge. The laser power was monitored periodically during irradiations, which generally took 30 min to 1 h to perform. The diameter of the laser beam for all irradiations was 10 mm. Product distributions were again monitored by gas chromatography.

For variable-temperature work, the 5 × 10 mm cuvette was replaced by a 10 × 10 mm jacketed quartz cuvette. The sample path length of the cuvette was approximately 4 mm. Heating and cooling of the

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Table 1. Summary of the Crystallographic Data for the Structure of Dimer **5**

compd	$C_{24}H_{28}$
mol wt	316.49
space group	$P1$ (No. 2)
cell constants	
a, Å	10.070(2)
b, Å	14.180(4)
c, Å	6.715(2)
α, deg	94.35(3)
β, deg	107.93(2)
γ, deg	75.41(2)
cell vol, Å^3	887.6(7.9)
Z	2
density (calcd), g/cm^3	1.184
radiation (λ, Å)	Mo Kα (0.71073)
no. of reflcns obs	3094
no. of params refined	328
R	0.0467
R_w	0.0463

sample was effected by continuous circulation of water through the cell jacket from a thermostatically controlled bath. The temperature of the sample was monitored directly using a thermocouple.

X-ray Structure Determination of the Second 4 + 2 Adduct (5). Preliminary examination and data collection were accomplished using an Enraf-Nonius CAD4 diffractometer. Crystallographic and data collection parameters are given in Table 1. The space group of the cell was determined to be $P1$ (No. 2). The structure was solved by direct methods and refined on the basis of 3094 observed reflections. Hydrogen atoms were calculated at idealized positions and included in the calculations but not refined. Least-squares refinement based upon 3094 reflections converged at $R = 0.0467$ and $R_w = 0.0463$.

Quantum yields for the triplet-sensitized production of dimer **1** were determined by comparison with the rate of isomerization of *trans*-β-methylstyrene, which is known to have a *trans*−*cis* isomerization quantum yield of 0.5.[33] Dimer **1** was chosen over dimer **2** as its yield is greater by a factor of 5 under these conditions. Irradiations were performed in 10-mm jacketed quartz cuvettes arranged to be equidistant from the light source, a medium pressure mercury arc lamp. The cells were constructed with a path length of approximately 4 mm while the path length of the jacket is approximately 2 mm. Solutions of the two alkenes of identical concentration (either 0.1 or 1.0 M) were made up in the same stock solution of benzophenone ($OD_{366} = 1.0$) in methanol containing a known concentration of tetradecane as an internal standard. The cell jackets were filled with 1.0 M solutions of the appropriate alkene in methanol. The lamp was allowed to warm up for 30 min before irradiation of the samples to ensure a uniform irradiation intensity for the duration of the experiment. Samples were subjected to a continuous gentle nitrogen sparge and sampled at time intervals appropriate to the rate of product formation. Product concentrations were determined relative to the internal standard following determination of their relative GC detector response factors. Plots of concentration versus time give the relative quantum yields for product formation. The reaction was performed in the absence and presence of sulfuric acid (50 mM).

Results

Preparation and Characterization of Photodimers. The 2 + 2 photodimers **1** and **2** were isolated from room temperature irradiations of PC6 in either methanol or cyclohexane. The 4 + 2 photodimers were isolated and characterized from a reaction performed in a low-temperature quartz irradiation vessel at −78 °C. The reaction solvent was methanol. In our hands, the low-temperature reaction yielded four major photodimers. Two of these (**1** and **2**) were the 2 + 2 dimers resulting from the excited singlet state photocycloaddition reaction reported by Dauben *et al.*[29] We were also able to isolate the reported 4 + 2 adduct (**4**) which has been shown to arise from chemistry involving the *trans* isomer of PC6. Melting points and ^{13}C NMR data for **1** and **2** were identical to those previously reported. The melting point of **4** was slightly higher (*vide infra*) than expected but was sharp and reproducible. The unit cell dimensions of a crystalline sample of **4** determined by a preliminary X-ray analysis were found to be identical to literature values.[29]

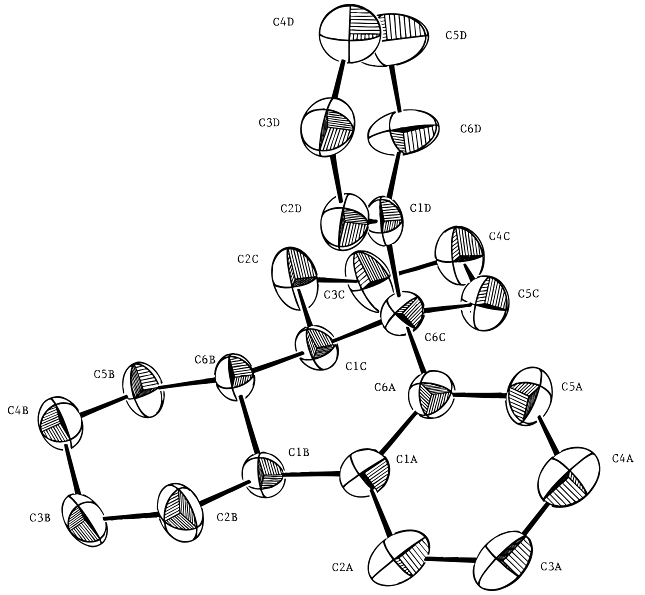

Figure 1. Thermal ellipsoid plot of dimer **5**, showing the atom-labeling scheme. The *trans* configuration across the original double bond of the dienophile (C1C−C6C) is retained.

In addition we were able to isolate and characterize a second 4 + 2 adduct (**5**), a diastereomer of **4**. This new dimer is generally produced in slightly higher yields than **4** but proved much more difficult to isolate in pure form. Repeated recrystallization of mixtures of **4** and **5** isolated by column chromatography yielded relatively pure samples of **4**. Careful GC analysis revealed traces of **5** in these crystals and multiple recrystallizations were required to produce a pure sample. This may account for the slightly higher melting point for **4** reported here. Dimer **5** possesses a melting point some 76 degrees below its stereoisomer and tends to co-crystallize with dimer **4**. These dimers were also inseparable by HPLC. Exhaustive recrystallization efforts did eventually provide a pure sample, the structure of which was obtained crystallographically (Figure 1).

Low-Intensity (Lamp) Irradiations. The product distribution upon irradiation of PC6 in solution is known to be temperature dependent, favoring the formation of 4 + 2 adducts at lower temperatures. In our hands, irradiation of a 0.1 M solution of PC6 in either methanol or cyclohexane at room temperature yielded exclusively the 2 + 2 singlet state photoadducts **1** and **2**. An upper limit for the formation of the 4 + 2 products is set at 0.1% based on the sensitivity of our GC analysis conditions and the ratio of 2 + 2 products **1**:**2** was 3:1. Irradiations in methanol also yielded significant quantities of the *trans*-PC6 methanol addition product 1-methoxy-1-phenylcyclohexane.

Lamp irradiation of PC6 in methanol was also performed at −78 °C. The concentration of the starting material was lowered somewhat to 0.02 M due to solubility problems at lower temperatures. The expected change in product distribution was observed with 4 + 2 adducts accounting for 63.5% of the total dimer yield. The relative product yields for all the irradiations performed here, determined by GC, are given in Table 2.

The irradiation was performed under triplet-sensitized conditions. Irradiation, at room temperature, of a 0.1 M cyclohexane

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Table 2. Experimental Conditions, PC6 Concentrations, and Normalized Product Distributions for Irradiations of PC6[a]

irradiation conditions	[1-PC6] (M)	% **1**	% **2**	% **4**	% **5**
RT,[b] lamp	0.1	76	24	<0.1	<0.1
LT,[c] lamp	0.02	20	16.5	26.5	37
RT, laser (266 nm)	0.1	60	25	7	8
RT, sens,[d] lamp	0.1	80	20	<0.5	<0.5
LT, sens, lamp	0.02	2	2	43	53
RT, sens, laser (355 nm)	0.1	23	10	36	32

[a] For full experimental conditions, refer to text. [b] Room temperature. [c] Low temperature (−78 °C). [d] Triplet sensitized.

solution of PC6 containing *p*-methoxyacetophenone (OD_{366} = 0.3), was performed through a Pyrex filter. The reaction, somewhat surprisingly, yielded large quantities of 2 + 2 photoadducts with a **1**:**2** ratio of 4:1 (Table 2, entry 4). The 4 + 2 adducts were not detected in the reaction mixture and a reasonable upper limit for their formation would be 0.5% for the particular GC analysis conditions employed here.

The sensitized reaction was also studied at −78 °C. The PC6 concentration was again lowered to 0.02 M and the reaction was run in toluene due to additional solubility problems encountered with the sensitizer at low temperatures. The effect of temperature upon the triplet-sensitized reaction is dramatic and 4 + 2 adducts are almost the exclusive products. In this respect, low-temperature sensitized irradiations appear to be the preferred method for the synthesis of 4 + 2 photoadducts. The 2 + 2 dimers were each present at the 2% level. The observed **4**:**5** ratio of 1:1.23 was essentially within experimental error of the value 1:1.40 noted for direct irradiation at low temperatures.

High-Intensity (Laser) Irradiations. Irradiation of a 0.1 M solution of PC6 in cyclohexane with the 266-nm output from a Nd:YAG laser (8 mJ/pulse), operated at a repetition rate of 10 Hz, for 15 min, led to the production of easily detectable concentrations of photodimers. Although, under these conditions, 2 + 2 photodimers are the dominant product, significant quantities of the 4 + 2 addition products were present.

The triplet-sensitized reaction was performed under laser irradiation conditions. Laser irradiation (10 mJ/pulse, 15 min, 355 nm) of a solution of PC6 (0.1 M) in cyclohexane containing *p*-methoxyacetophenone (OD_{355} = 1.0) produced large quantities of 4 + 2 dimers (Table 2, entry 6). The 2 + 2 dimers were also present as a significant minor component. We had initially been concerned that the formation of 2 + 2 adducts in the triplet-sensitized lamp irradiation might be due to incomplete filtering of the shorter wavelength emissions from the mercury lamp. Clearly, under 355 nm laser irradiation, these dimers do not result from direct photon absorption by PC6. Having established that, in addition to their appearance in low-temperature lamp irradiations, 4 + 2 adducts are present as a significant component of reaction mixtures resulting from higher intensity laser irradiations, we sought to illustrate this variation in the product distribution more clearly. Irradiations of 0.1 M solutions of PC6 in cyclohexane were performed with the 266-nm output from a Nd:YAG laser in the 2-30 mJ/pulse range. We observe a smooth change in the product distribution upon changes in laser power (Figure 2) with the formation of 4 + 2 adducts favored at higher irradiation intensities. At 2 mJ/pulse the concentrations of 4 + 2 dimers dropped below the sensitivity of the GC analysis (<0.1% of the dimer mixture).

A power dependence study was also performed for the sensitized reaction (benzophenone OD_{355} = 1.5, PC6 (0.2 M), laser power 5−20 mJ/pulse, in benzene). The product distribution (Figure 3) again shows a smooth change to favor the formation of 4 + 2 adducts at higher irradiation intensities. GC analysis suggested photoreduction of PC6 in this system was negligible.

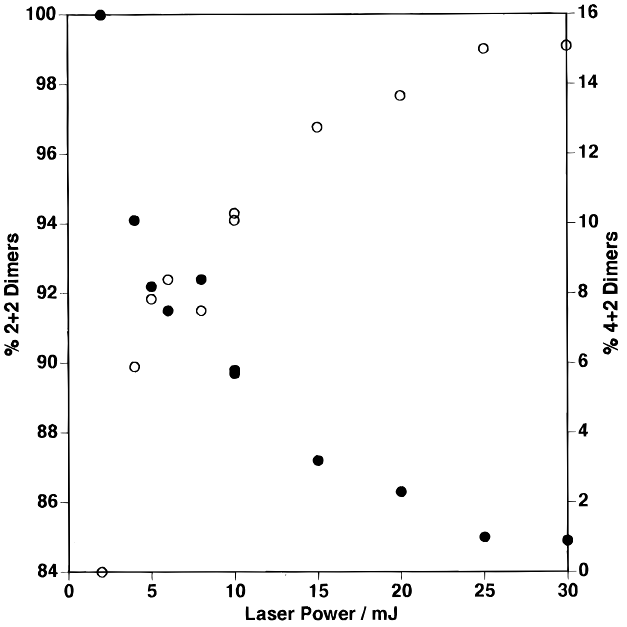

Figure 2. Plot of normalized total dimer percentages as a function of incident laser power for 266 nm laser irradiation of a solution of PC6 (0.1 M) in cyclohexane. Key: 2 + 2 dimers (●), 4 + 2 dimers (○).

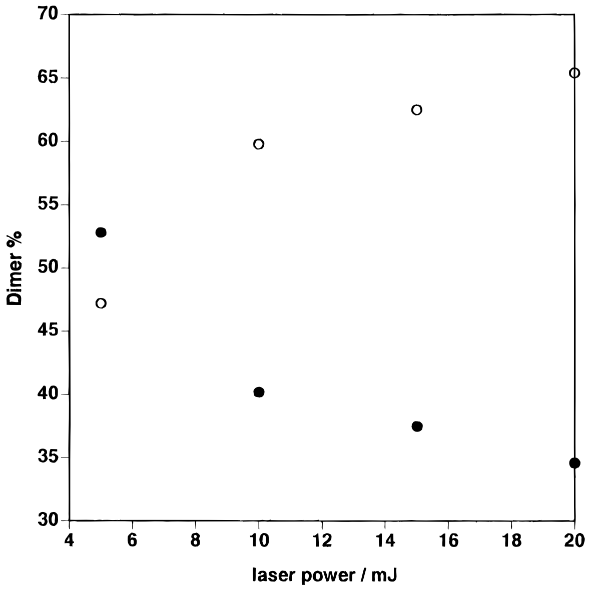

Figure 3. Plot of normalized total dimer percentages as a function of incident laser power for 355 nm laser irradiation of a solution of PC6 (0.2 M) in benzene containing benzophenone (OD_{355} = 1.5). Key: 2 + 2 dimers (●), 4 + 2 dimers (○).

The reaction temperature was also varied under 266 nm direct laser irradiation conditions (8 mJ/pulse, 15 min) between 5 and 50 °C for a solution of PC6 (0.1 M) in cyclohexane. The expected change in product distribution to favor the 4 + 2 dimers at lower temperatures was observed (Figure 4).

Triplet-Sensitized Photoadditions. The appearance of 2 + 2 photoadducts during triplet-sensitized irradiations might at first seem surprising. Dauben *et al.*[29] reported trace quantities of these products in their sensitized experiments but their presence was simply assigned to a possible residual absorbance by PC6 at longer wavelengths. We had initially considered that incomplete screening of the shorter-wavelength emissions from the mercury lamp used in our experiments might be a factor. However, sensitized experiments performed under 355 nm laser irradiation also yield 2 + 2 adducts. It is highly improbable

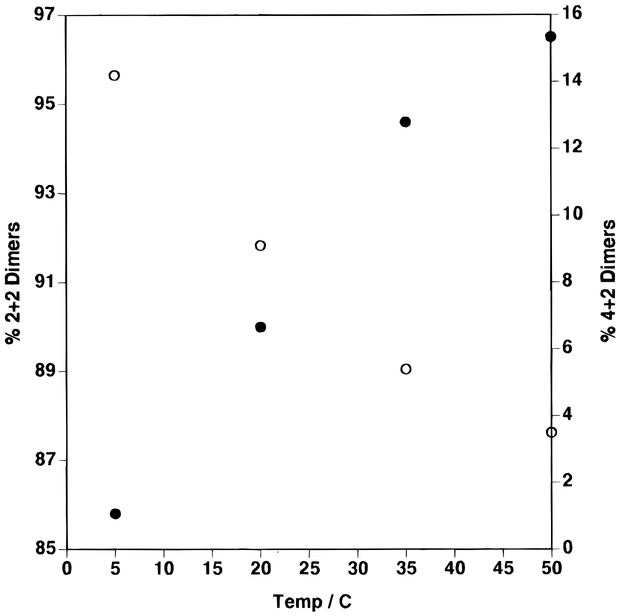

Figure 4. Plot of normalized total dimer percentages as a function of temperature for 266 nm laser irradiation of PC6 (0.1 M) in cyclohexane. Key: 2 + 2 dimers (●), 4 + 2 dimers (○).

that there is any residual absorption by PC6 at such long wavelengths.

The formation of cyclobutanes via a triplet state mechanism is not so surprising in the light of recent work published by Caldwell *et al.*[31] in which the photoaddition of *p*-acetylstyrene triplets to styrene was documented. In addition, the change in the **1**:**2** ratio from 3:1 for direct irradiations to 4:1 for the triplet-sensitized reaction may be indicative of a different reaction mechanism under sensitized conditions. With this in mind, further investigation of the mechanism of this reaction was warranted.

In order to further rule out the possibility of residual long-wavelength absorptions by PC6, an irradiation was performed using a PC6 filter solution. Irradiation of a 0.1 M solution of PC6 in cyclohexane containing *p*-MAP (OD_{366} = 1.0) was performed in a jacketed quartz cuvette. The lamp emissions were filtered through Pyrex and the cell jacket was filled with a 0.5 M solution of PC6. The effective path length of the cell jacket was approximately 2 mm. Good yields of 2 + 2 adducts were again obtained.

Having established that 2 + 2 dimers are indeed produced when the photolysis is triplet sensitized, one must now consider the mechanism of this new reaction. 2 + 2 dimer formation could, in principle, result from either a triplet state addition reaction or possibly the addition of *trans*-PC6 to a ground state *cis*-PC6 molecule. Since the lifetime of *trans*-PC6 is known to be extremely sensitive to the presence of acids,[4,29] a simple test for the intermediacy of this species is to measure the quantum yield for dimer formation in both the presence and absence of acid.

trans-PC6 is quenched by sulfuric acid with a rate constant of 9×10^6 L mol^{-1} s^{-1}. The lifetime of *trans*-PC6 at room temperature in methanol is 9 μs.[4] The addition of 50 mM sulfuric acid to a sensitized photolysis reaction should therefore result in the interception of 78% of any *trans*-PC6 molecules formed and the quantum yield for any process involving this intermediate should decrease accordingly.

The quantum yield for 2 + 2 dimer formation was determined by comparison with the rate of isomerization of *trans*-β-methylstyrene.[33] Solutions of the two alkenes in methanol containing benzophenone (OD_{366} = 1.0) were irradiated simultaneously. Benzophenone triplet is also quenched by sulfuric acid with a rate constant of 1.7×10^6 L mol^{-1} s^{-1}. The alkene concentration of 1.0 M ensured efficient quenching of the sensitizer even in the presence of 50 mM acid. The irradiations were sampled at regular intervals and the concentrations of *cis*-β-methylstyrene and **1** obtained by GC analysis against a tetradecane internal standard. Though not investigated in detail, solutions appeared to be stable in the dark on the time scale of our experiments. There was no evidence for styryl radical cation mediated dimerization.[34,35] Plots of product concentration versus time were constructed (Figure 5a,b). The relative gradients lead to Φ_1^T, the quantum yield for triplet sensitized formation of **1**. The results (Table 3) clearly demonstrate that Φ_1^T is independent of the presence of acid. We therefore conclude that the 2 + 2 dimers are formed via a triplet state addition reaction. The quantum yield, Φ_1^T, was also determined for a PC6 concentration of 0.1 M and, as expected for a reaction which is first order in [PC6], the value of Φ_1^T was lower by a factor of 10.

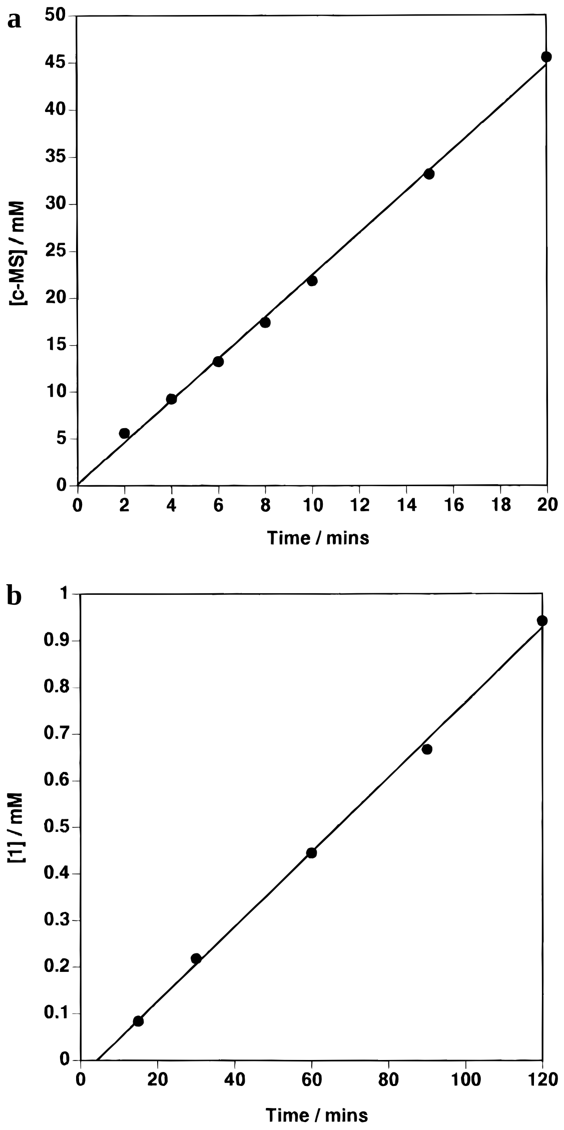

Figure 5. (a) Concentration of *cis*-β-methylstyrene as a function of time upon irradiation of *trans*-β-methylstyrene (1.0 M) in methanol containing benzophenone (OD_{366} = 1.0). (Curve fit: $f(x) = (2.23 \times 10^{-3})x + 1.89 \times 10^{-4}$; $R^2 = 0.9978$.) (b) Concentration of dimer **1** as a function of time upon irradiation of PC6 (1.0 M) in methanol containing benzophenone (OD_{366} = 1.0). (Curve fit: $f(x) = (8.01 \times 10^{-6})x - 3.35 \times 10^{-5}$; $R^2 = 0.9984$.)

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(35) Schepp, N. P.; Johnson, L. J. *J. Am. Chem. Soc.* **1994**, *116*, 6895.

Table 3. Quantum yields for the triplet-sensitized production of dimer **1** (Φ_1^T)

[PC6]/M	[H_2SO_4]/mM	ϕ_1^T
1.0	0	1.80×10^{-3}
1.0	50	1.95×10^{-3}
0.1	0	2.00×10^{-4}

Discussion

The [4 + 2] Dimerization. We have been able to isolate and characterize two 4 + 2 cycloaddition products from low-temperature irradiations of phenylcyclohexene in solution. One of these products was previously unknown and is a diastereoisomer of the 4 + 2 adduct originally characterized by Dauben *et al.*[28,29] Both products appear to arise from cycloadditions involving transition states in which π-interactions between the two phenyl groups are maximized. GC analyses of the reaction mixtures suggest that other possible isomers, if present at all, are produced in yields not exceeding a few percent of those observed for the four characterized photodimers.

The formation of a 4 + 2 cycloaddition product of PC6 (**4**) in which one ring junction retains a *trans* configuration has been presented as strong evidence for the involvement of *trans*-PC6 as the dienophile in this reaction. The configuration of the new 4 + 2 adduct (**5**) is in agreement with this conclusion. The conformation of the cyclohexene double bond in the PC6 diene moiety prior to the cycloaddition step is chemically ambiguous as a result of the 1,3-hydrogen shift, leading to rearomatization, which is expected to follow the initial cycloaddition event. The reaction was at first presumed to proceed via the addition of a *trans* dienophile to a ground state *cis*-PC6 diene.[28,29] The possibility that formation of the 4 + 2 adducts might arise from a 2-photon reaction in which *trans*-PC6 behaves as both diene and dienophile was raised in our laboratory during variable-temperature studies of *trans*-PC6 isomerization.[9] The lifetimes of *trans*-cyclohexenes have long been known to be strongly temperature dependent. At room temperature, the decay of *trans*-PC6 is almost cleanly first order, although a small second-order component is sometimes observed possibly as a result of high laser intensities and/or higher PC6 concentrations. Its lifetime is in the 10-μs range depending on the solvent. The decay of *trans*-PC6 at lower temperatures was found to include a significant second-order component (Figure 6) and we speculated at the time that this might be a manifestation of the reaction forming the 4 + 2 dimer isolated by Dauben *et al.* only at low temperatures.

The four possible triene intermediates which may result from 4 + 2 cycloadditions involving a *trans* dienophile and both *trans* and *cis* dienes are shown in Scheme 1. The "*trans* + *cis*" adducts (**6** and **7**) will lead to the two isolated 4 + 2 dimers following a 1,3-antarafacial hydrogen shift. Though theoretically predicted, 1,3-antarafacial hydrogen shifts remain experimentally undocumented. In this particular instance, the rigid carbon framework of the reaction intermediate suggests attainment of the highly strained transition state geometry required for a concerted 1,3-antarafacial shift would be impossible. Rearomatization of these intermediates would therefore almost certainly have to be a non-concerted process. The corresponding hydrogen shift required for rearomatization of the "*trans* + *trans*" reaction intermediates (**8** and **9**) to yield the observed products would be 1,3-suprafacial. While a non-concerted process may again be involved, the requirement for a 1,3-suprafacial hydrogen shift also raises the possibility that rearomatization might occur photochemically, although, to date, we have not been able to establish this experimentally.

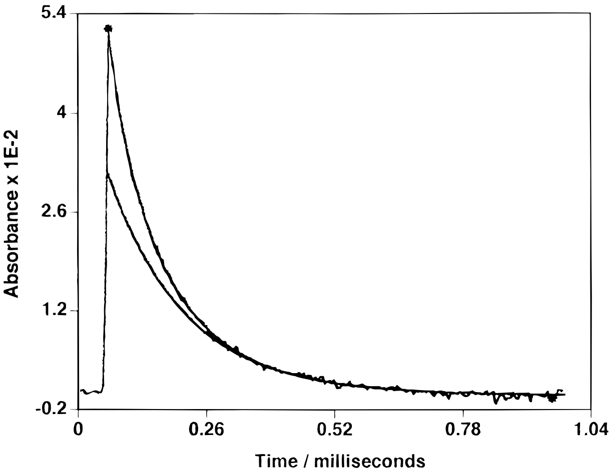
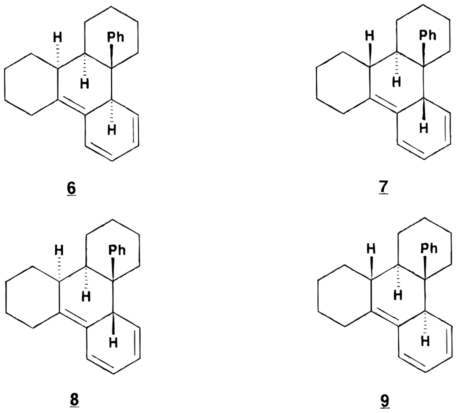


Figure 6. Transient decay of *trans*-1-phenylcyclohexene, with a competing first- and second-order kinetic fit, monitored at 370 nm at a temperature of −16.2 °C. The second-order fit overlays the raw data while the first-order component lies below it. *trans*-Phenylcyclohexene was generated by 266 nm laser excitation of a heptane solution of the *cis* isomer ($OD_{266} = 5$).

Scheme 1

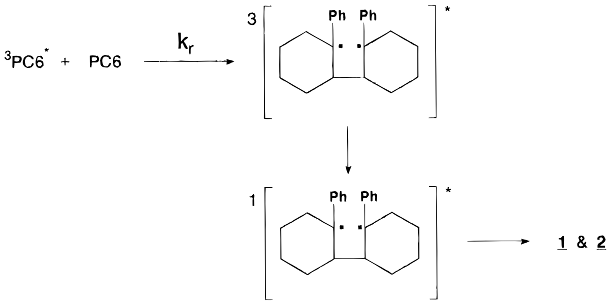


The original observation that the product distribution upon irradiation of PC6 in solution is strongly temperature dependent, favoring the production of 4 + 2 adducts at lower temperatures, is clearly consistent with both a "*trans* + *cis*" and a "*trans* + *trans*" cycloaddition mechanism. In both cases, lengthening of the *trans*-PC6 lifetime at lower temperatures favors any reaction involving this intermediate.

The crucial observation made in this study is that the product distribution is also strongly dependent on the intensity of the irradiating light source and therefore the concentration of transient intermediates in solution. An intensity-dependent product distribution is not consistent with a reaction scheme in which all products are dependent upon the transient concentration in a first-order manner. One would expect that the quantum yield for production of *trans*-PC6 upon irradiation of a solution of *cis*-PC6 of fixed concentration at room temperature would be independent of light intensity. The resulting product distribution should therefore also remain independent of this variable. The results presented in Table 2 and Figures 2 and 3 clearly demonstrate that this is not the case.

Although observed 4 + 2 dimer yields under direct laser irradiation conditions are not as high as those observed in the low-temperature irradiation, the data clearly demonstrate that significant quantities of these products are available through high-intensity irradiations. The power dependence experiments were ultimately limited to powers below 30 mJ cm^{-2} per pulse. At higher powers, a solid deposit was observed on the front

Scheme 2



face of the cuvette. This deposit eventually carbonized and prevented further irradiation. However, one would expect the proportion of 4 + 2 adducts would continue to increase at even higher light intensities.

In an effort to extend these studies to higher laser powers, preliminary experiments have been performed using a laser-drop apparatus similar to that developed by Scaiano *et al.*[36] 4 + 2 photodimers were again detected in these experiments but the reaction mixtures proved more difficult to analyze. The low overall quantum yield for dimer formation required multiple passes through the apparatus and significant decomposition of the starting material appeared to occur.

We had initially hoped to obtain more quantitative data from our laser photolysis studies which would discriminate between single- and multi-photon processes. To date this has proven difficult. The relatively complex distribution of excited states in the irradiated sample, both in terms of the depth of penetration of the exciting laser pulse and as a function of time following the pulse, added to the competing photoreactions in the system of interest, have so far led to rather complex behavior as variables such as laser power and temperature are changed. The data presented in Figure 2 appear to suggest that the proportion of 4 + 2 photodimers in the reaction mixture may level off to a constant value as the laser power is increased. Ultimately, the product distribution in the power dependence experiments will reach a limiting value at the point at which complete bleaching of the reaction sample occurs. This process is unlikely to occur in our experiments. The apparent leveling off of the distribution is an experimental artifact. Future investigations may encompass studies of excitation in optically thin samples where complete bleaching may be possible. In this case the limiting value of the product distribution should be obtained.

Triplet-sensitized experiments have proven extremely useful in the synthesis of the 4 + 2 photodimers. These dimers account for almost 70% of the characterized products under laser irradiation at 355 nm in comparison to only 15% under direct irradiation at 266 nm. Low-temperature sensitized irradiations, in our hands, gave 4 + 2 photodimers almost exclusively.

Triplet State Photoadditions. The quantum yield studies of the triplet-sensitized formation of dimer **1** provide strong evidence that the formation of 2 + 2 adducts under these conditions is a result of a triplet state addition process analogous to that outlined by Caldwell *et al.*[31] for the addition of *p*-acetylstyrene triplets to ground state styrene. The reaction is expected to proceed via a 1,4-biradical as depicted in Scheme 2. The quantum yield for the reaction is given by

$$\Phi_1^{\mathrm{T}} = k_r[\mathrm{PC6}]\alpha(k_r[\mathrm{PC6}] + \tau^{-1})^{-1}$$

where k_r is the rate of addition of the PC6 triplet to a ground state PC6 molecule to form the 1,4-biradical intermediate, α is the fraction of 1,4-biradicals which undergoes ring closure to give the final 2 + 2 adduct cyclobutane, and τ is the PC6 triplet lifetime, known to be 65 ns at infinite dilution. For high concentrations of PC6, energy transfer from the sensitizer is expected to occur with unit efficiency. One can now estimate k_r from the measured value of Φ_1^{T} by substituting reasonable values of α. The absolute lower limit for k_r in this work is obtained by substituting $\alpha = 1$ and leads to $k_r = 2.8 \times 10^4$ L mol^{-1} s^{-1}.

We attempted to measure the rate of quenching of the PC6 triplet by its ground state using laser flash photolysis. PC6 was sensitized by benzophenone ($\mathrm{OD}_{355} = 1.2$) in cyclohexane. The lifetime of the PC6 triplet was slightly longer than the previously published value at 71 ns and was insensitive to the ground state concentration up to 1.68 M. Given that we routinely expect to be able to detect 5% changes in triplet lifetimes, we estimate a maximum value for k_r of 4.0×10^5 L mol^{-1} s^{-1} which, using the above equation, corresponds to $\alpha = 0.07$.

Recently published studies[27,31,32] have demonstrated that the thermochemical and kinetic behavior of alkene triplets may be predicted with good accuracy by consideration of the relaxed perpendicular triplet as a 1,2-biradical in which there is little or no interaction between the two radical termini. The study most relevant to the present investigation is that in which the addition of the *p*-acetylstyrene triplet to styrene was monitored.[31] We reported a rate of addition in this process of 3.2×10^6 L mol^{-1} s^{-1} and a 1,4-biradical ring closure efficiency of 0.38. The results were compared to the published rate of addition of the 5-hexenyl radical to styrene[37] of 1.4×10^5 L mol^{-1} s^{-1}. We concluded that the order of magnitude discrepancy between the two rates was due to the involvement of an exciplex intermediate evidenced by the order of magnitude increase in the rate of addition when styrene is replaced by its *p*-methoxy derivative.

The present study has revealed an order of magnitude range of possible rate constants for the photoaddition of the PC6 triplet to its ground state. Published values for rates of radical addition to ethylene,[38] including methyl, isopropyl, and *tert*-butyl, are essentially independent of the primary, secondary, or tertiary nature of the attacking radical. One would expect steric factors for additions to ethylene to be relatively low. The rate of addition of the *tert*-butyl radical to styrene,[37] at 1.3×10^5 L mol^{-1} s^{-1}, is essentially identical to that for primary radical addition. Steric factors for addition to the styrene methylene group again appear to be negligible. Our upper limit for the rate of attack of the PC6 triplet on its ground state at 4×10^5 L mol^{-1} s^{-1} is therefore entirely in line with what one would expect for an unhindered alkyl radical addition process while the possible lowering of the rate constant by up to an order of magnitude would be indicative of some degree of steric hindrance for the addition of a secondary alkyl radical to the methine group of a more highly substituted styrene derivative.

It is also interesting to consider the stereochemistry of the 2 + 2 adducts arising from triplet-sensitized photoreactions.[39] It is, at first, surprising to note that the triplet-sensitized reaction yields only the *cis*-fused 2 + 2 adducts previously isolated from direct irradiations of PC6. One might imagine that the involvement of rotationally equilibrated triplet 1,4-biradicals might result in the production of *trans*-fused adducts as is often the

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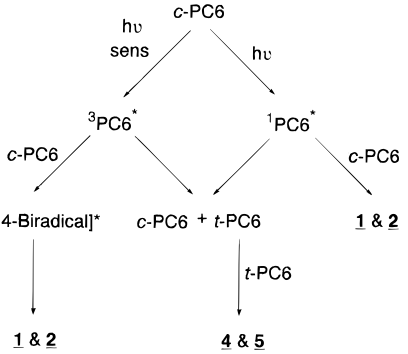
case in enone−alkene photoannelations.[20] Molecular modeling of the biradicals, however, clearly demonstrates that orbital overlap leading to cyclobutane ring-closure and a *trans*-fused adduct is severely inhibited unless significant pyramidalization of one or both phenyl-substituted radical centers is invoked. In contrast, ring closure to afford *cis*-fused adducts involves biradical conformations in which orbital overlap is easily attained and steric interactions between the two phenyl groups appear to be minimized.

It appears that orbital overlap leading to *cis*-fused adducts takes place only from 1,4-biradicals in which the initially formed linkage between the cyclohexane rings is diaxial. When this bond is formed in an equatorial−axial or diequatorial manner, orbital overlap is difficult to obtain and the two orbitals generally lie perpendicular to each other. There are two distinct diaxially linked 1,4-biradicals. Ring closure of one of these biradicals leads to the isolated *cis-anti-cis* cyclobutane **1**. Ring closure of the alternative diaxially linked biradical leads to the *cis-syn-cis* cyclobutane **2**. However, orbital overlap in the latter case involves significant steric interactions between the axial hydrogens on the two cyclohexane rings. This may account for the observation that formation of **1** over **2** in the triplet-sensitized system is favored in a 4:1 ratio.

How Reactive Are *trans*-Cyclohexenes? Our original overarching objective was to evaluate the reactivity of *trans*-cyclohexenes and their potential for providing novel chemistry. The present case has, alas, afforded a novel mechanism but not new reaction. The [4 + 2] dimerization of styrene under thermal conditions is well-known.[40] Of course, the obvious manifestation of the enorous strain (94 ± 6 kcal mol^{-1}) in two molecules of *trans*-PC6 is a far higher rate. Without further work we cannot provide a rate constant but it clearly is very high. The strong temperature dependence of the 4 + 2 dimerization reaction requires that the activation energy for dimerization be much lower than the 12.1 kcal mol^{-1} observed for *trans*-PC6 to *cis*-PC6 isomerization.[9] A photochemical 4 + 2 cycloaddition between two styrene chromophores has been outlined by Hart *et al.*[41] in a study of benzocycloheptadienone photochemistry. The dimerization mechanism was suggested to involve attack of a photogenerated *trans* double bond on a ground state *cis* styrene moiety. Hart has also raised the possibility that the observed 2 + 2 cycloaddition reactions of these and other cycloheptenones might originate from either a *trans* + *cis* interaction or one involving two *trans* intermediates.[41,42] Bonneau[43] has also suggested that the dimerization of cycloheptenones might involve two *trans* intermediates based on kinetic studies.

That the 47 ± 3 kcal mol^{-1} present in one *trans*-PC6 molecule is insufficient to allow an observable *trans* + *cis* 4 + 2 dimerization process is interesting. Presumably, the loss of aromaticity in one ring, which would be mechanistically required from either configuration of reactant, significantly counterbalances the strain of the reactant and the thermodynamic driving force is lost. An alternative possibility is that a *trans* + *cis* 4 + 2 cycloaddition occurs but the resulting triene intermediate is unable to undergo the required 1,3-antarafacial shift to afford the Diels−Alder products and therefore fragments to yield starting materials. This hypothesis is, however, inconsistent with our previous observation[9] that the lifetime of *trans*-PC6 is essentially independent of the concentration of the ground state *cis* compound. Studies of the chemistry of strained cyclohexenes performed by House *et al.*[44,45] reveal that steric interactions may also be a factor in the observed reactivity. Phenyl substitution at the 2-position of a bicyclo[3.3.1]non-1-en-3-one effectively blocks the rapid 2 + 2 dimerization reaction encountered for the parent molecule. That the only observed dimerization process involving *trans*-PC6 appears to be the 4 + 2 cycloaddition involving two *trans* intermediates may therefore reflect a complex balance of both thermodynamic and steric factors.

Scheme 3



Summary

The photoreactions of PC6 as revealed in this study are summarized in Scheme 3. Direct irradiation of PC6 leads to 2 + 2 singlet state photodimers and the generation of *trans*-PC6. Under conditions where transient−transient reactions are likely, i.e., low reaction temperatures or high irradiation intensities, reaction between two *trans*-PC6 molecules occurs giving rise to two isomeric 4 + 2 adducts. When the reaction is performed in methanol, these dimers are accompanied by significant amounts of the *trans*-PC6 methanol addition product. Under triplet-sensitized conditions *trans*-PC6 is again generated and the above arguments apply. In addition, a triplet state photodimerization occurs to produce the same pair of 2 + 2 adducts but in a ratio which increasingly favors formation of dimer **1** over dimer **2**. The rate of addition of the PC6 triplet to its ground state is in the range (0.28−4.0) × 10^5 L mol^{-1} s^{-1}, consistent with the modeling of alkene triplets as 1,2-biradicals.

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Supporting Information Available: Tables of positional and thermal parameters and complete bond distances and angles (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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