

Alkene Triplets as 1,2-Biradicals: The Photoaddition of *p*-Acetylstyrene to Styrene[†]

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Abstract: The photoaddition of *p*-acetylstyrene (PAS) triplet to styrene (STY) has been studied. Direct irradiation of PAS in the presence of styrene yielded *trans*-1-(4-acetylphenyl)-2-phenylcyclobutane, an expected addition product, its *cis* isomer, and 1-(4-acetylphenyl)-1,2,3,4-tetrahydronaphthalene. The rate of addition of ³PAS to styrene was determined by laser flash photolysis to be $3.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, and by quantum yield measurements as $2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. The rate is 1 order of magnitude greater than that of addition of a primary alkyl radical to styrene and thus in only fair agreement with the 1,2-biradical model. The reaction of ³PAS with *p*-methoxystyrene is even faster. A rough estimate of the rate constant for ³STY + STY is in better agreement with expectation. The possible involvement of a weak exciplex between the perpendicular PAS triplet and the styrene ground state is suggested to rationalize the rate enhancement. The validity of the 1,2-biradical representation of alkene triplets is discussed.

Olefin triplets are the product of sensitized or, in some cases, direct excitation of the corresponding alkene. Study of their chemistry and properties is an ongoing effort in our laboratories.¹ Many simple alkene triplets are twisted at equilibrium to the well-known perpendicular structure which is shown in Figure 1. Thermochemical studies of perpendicular alkene triplets² demonstrate that their energies are almost exactly those expected from Benson estimations³ using group equivalents for appropriate free radicals as models for the termini (the two essential carbons of the alkene triplet). This suggests that the perpendicular orbitals interact negligibly, leading to description as a "1,2-biradical". For perpendicular triplets, free radical-like chemistry and reactivity might thus be observed. Reactivities in reactions for which the termini act independently, though of course not rates of processes such as intersystem crossing (isc) which involve consideration of total spin, should be similar to corresponding reactivities for appropriate free radical models.

The "cyclopropylcarbinyl clock", i.e. the rearrangement of the cyclopropylcarbinyl radical to the corresponding homoallyl radical,^{4–7} was used to evaluate the 1,2-biradical model in cyclopropylstyrene derivatives.^{8,9} The estimated rate for ring opening of β -cyclopropylstyrene, for example, was close to the rate for ring opening of α -cyclopropylethyl radical.^{4,10} The reactivity of α -cyclopropylstyrene triplet was negligible, consistent with the reactivity predicted by the model. It was concluded that the 1,2-biradical model explained the observations and that the model was verified, at least regarding that particular molecular rearrangement.

Further validation of the model's ability to predict the kinetic

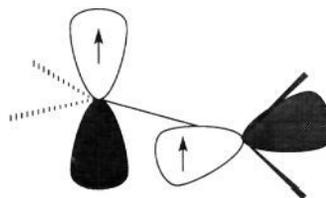


Figure 1. Perpendicular triplet or 1,2-biradical conformation.

behavior of twisted alkene triplets from free radical chemistry is required. Other characteristic reactions of free radicals, such as substitution, transfer, and addition to multiple bonds, have been well described,⁶ and kinetic information is readily available.^{11–25} Rate constant values between 10^5 and $10^7 \text{ M}^{-1} \text{ s}^{-1}$ would be advantageous when selecting a monoradical reaction for kinetic comparison with its olefin triplet homologue. Slower reactions, i.e., below $10^4 \text{ M}^{-1} \text{ s}^{-1}$, would lead to product formation insufficient for an effective product analysis. Higher rates, near the diffusion limit, would minimize the sensitivity of the reaction to reactant structure.

[†] Adapted from the M.S. Thesis of J. F. Díaz, The University of Texas at Dallas, October 1993.

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We report here addition to styrene (STY) by *p*-acetylstyrene (PAS), for which primary alkyl radical addition to styrene is the relevant model. The reported rate constant for the model reaction is within the desired range.^{26–30} The use of an acetylated arylalkene allows irradiation in the carbonyl $n-\pi^*$ band at wavelengths above 300 nm, where styrene itself is transparent. The acetyl group leads to efficient and fast intersystem crossing (ISC) without requiring a sensitizer. We find that 1:1 adducts of PAS and styrene are formed. Quantum yields and laser flash photolysis establish the rate constant for the reaction of ³PAS with styrene. We compare the measured rate to the reported rate for the addition of 5-hexenyl radical to styrene.^{21,29,30} We further report results involving variation of substituents, which suggest a role for charge transfer.

Experimental Section

General. ¹H and ¹³C NMR spectra were collected using JEOL-FX200 (200 MHz) and General Electric GN-500-51 (500 MHz) spectrometers for CDCl₃ solutions containing tetramethylsilane and chloroform as internal standards, respectively. Infrared spectra were recorded on a Matteson 2025 FT-IR spectrometer. UV/vis spectra were obtained with an HP 8450A spectrophotometer. Elemental analyses were performed by Galbraith Laboratories (P.O. Box 51610, Knoxville, TN 37950). Melting points were obtained with a Hoover capillary melting point apparatus. Both analytical and semipreparative HPLC separations were performed on an HP 1090 liquid chromatograph with diode array detector and an HP 85B data processor, using Lichrosphere (Merck) Si100, 5 μm (4.0-mm o.d. × 250 mm), and Selectosil (Phenomenex) Si100, 5 μm (10.0-mm o.d. × 250 mm), columns, respectively. 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). Light (313 and 366 nm) was provided by a Bausch & Lomb 33-86-01 monochromator with a 1.50-mm exit slit and an SP-200 mercury light source.

Materials. Polystyrene of average MW 280 000 and aluminum chloride were obtained from Aldrich Chemical Co. and used without further purification. Acetyl chloride was distilled under nitrogen prior to use. Spectroscopic grade solvents were used as provided by the supplier. HPLC solvents were filtered through 0.22 μm pore nylon membrane filters. Styrene (Aldrich) was vacuum distilled before use.

Preparation of poly(*p*-acetylstyrene)^{31,32} from aluminum chloride and freshly distilled acetyl chloride followed literature procedures. Filtration and drying *in vacuo* afforded the desired polymer in a 90% yield: ¹H NMR (200 MHz, CDCl₃) δ 1.10–1.80 (3H), 2.51 (3H), 6.44 (2H), 7.54 (2H); IR (neat) 3028, 2926, 2853, 1680, 1415, 1360, 1289, 833 cm⁻¹.

Preparation of *p*-Acetylstyrene^{31,32} (PAS). Poly(*p*-acetylstyrene) (3.0 g, 0.02 mol) was placed in a vacuum distillation apparatus and pyrolyzed by heating over an open flame for 30 min under reduced pressure (<100 μm of Hg). A nitrogen trap placed between the distillation system and the vacuum line collected small quantities of pyrolyzed material. The pyrolysis distillate, a clear yellow oil obtained in 50–70% yield, was redistilled under reduced pressure. The distilled product was dissolved in methanol, filtered through a microporous filter, and cooled to -15 °C. Upon appearance of first crystals the solution was allowed to stand at -15 °C for several hours until no further growth was observed. The methanol layer was removed and the crystals were washed with cold methanol followed by a cold water rinse. The crystals, obtained in 79% yield, were then filtered and dried *in vacuo*. A second recrystallization afforded the desired product: mp 35–35.5 °C (reported³² 35.5–36 °C); 99% GC peak area; ¹H NMR (200 MHz, CDCl₃) δ 2.59 (3H, s), 5.40 (1H, d, *J* = 11 Hz), 5.88 (1H, d, *J* = 18 Hz), 6.76 (1H, dd), 7.70 (4H, ABq, *J* = 8.5 Hz).

Preparative photoaddition of PAS and styrene was performed by irradiation of a 500-mL cyclohexane solution of PAS (1.43 g, 9.8 mmol) and styrene (95 mL, 0.83 mol), in an irradiation well. The solution was degassed with nitrogen sparging for 30 min and irradiated for 24 h through a Corning 3320 uranyl glass filter using a Hanovia medium-pressure mercury vapor lamp.

Separation of Photoaddition Products. Cyclohexane and styrene were removed from the irradiated solution through vacuum distillation. The remaining residue was dissolved in tetrahydrofuran and poured into methanol to precipitate polystyrene. Column chromatography of the concentrated filtrate on silica gel, using a 5% ethyl acetate/isooctane solution, was monitored by GC and ¹H NMR. Fractions exhibiting ¹H NMR evidence of acetylated products were combined and then rechromatographed on silica gel. Gradient elution with ethyl acetate/hexane yielded a crude mixture of photoaddition products (1.07 g). GC analysis indicated the following composition as percentage of total peak area: 73% TCB, 15% THN, 6% PAS, 2% CCA (the acronyms TCB, THN, and CCA are defined immediately below). Isocratic elution of 0.43 g of this sample, using semipreparative HPLC, with 1% ethyl acetate/hexane at 4 mL/min, yielded the photoaddition isomers: (Numbers in brackets indicate isolated quantity (*Q*) and overall yield, respectively. Overall yield calculated from (*Q* × 1.07/0.43) × (100/MW × initial PAS moles). MW = 250 g/mol).

trans-1-(4-Acetylphenyl)-2-phenylcyclobutane (TCB): {0.29 g, 29%} oil; ¹H NMR (200 MHz, CDCl₃) δ 2.10–2.50 (4H, m), 2.58 (3H, s), 3.60 (2H, m), 7.15–7.35 (7H, m), 7.89 (2H, d, *J* = 8.6 Hz); ¹³C NMR (50 MHz, CDCl₃) δ 25.6, 25.8, 26.4, 47.9, 126.3, 126.5, 126.7, 128.5, 135.3, 144.0, 150.1, 197.6; IR (neat) 3027, 2974, 2942, 2870, 1682, 1616, 1358, 1269, 1182, 956, 831, 750, 701 cm⁻¹. Anal. Calcd for C₁₈H₁₈O: C, 86.36; H, 7.25. Found: C, 85.76, 87.07; H, 7.17, 7.34.

1-(4-Acetylphenyl)-1,2,3,4-tetrahydronaphthalene (THN): {0.04 g, 4%} mp 53–54 °C; ¹H NMR (200 MHz, CDCl₃) δ 1.70–2.00 (3H, m), 2.10–2.30 (1H, m), 2.58 (3H, s), 2.80–3.00 (2H, m), 4.19 (1H, m), 6.78 (1H, d, *J* = 7.3 Hz), 6.98–7.23 (5H, m), 7.88 (2H, d, *J* = 8.6 Hz); IR (neat) 3016, 2932, 2860, 1684, 1617, 1358, 1268, 1181, 957, 823, 744 cm⁻¹; MS (EI, 70 eV) *m/z* 250 (M⁺, 100), 207 (83), 179 (78), 131 (27), 91 (25), 43 (45). Anal. Calcd for C₁₈H₁₈O: C, 86.36; H, 7.25. Found: C, 86.06; H, 7.32.

cis-1-(4-Acetylphenyl)-2-phenylcyclobutane Adduct (CCA): {0.007 g, 0.7%} mp 50–53 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.40–2.60 (4H, m), 2.49 (3H, s), 4.07 (2H, m), 6.90–7.20 (7H, m), 7.68 (2H, d, *J* = 8.6 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 24.2, 26.5, 45.4, 125.8, 127.8, 128.1, 134.8, 141.0, 147.6, 197.8.

Further purification of TCB was achieved by distillation under reduced pressure and of THN by recrystallization from hexane at -10 °C.

Photolysis of TCB and THN. A 1.0-mL cyclohexane solution of 0.76 mmol/L TCB, containing 0.96 mmol/L octadecane as internal standard, was placed in a 13 mm o.d. Pyrex tube, degassed with nitrogen sparging, and irradiated for 5 h at 313 nm using a Bausch & Lomb monochromator (described above). Styrene and PAS formation were monitored using gas chromatography. The procedure was repeated for a 0.24 mmol/L cyclohexane solution of THN.

Quantum yields were determined according to literature procedures^{33–36} using potassium ferrioxalate actinometry. A cyclohexane solution (3.00 mL) containing PAS (0.13 mol/L), styrene (1.03 mol/L), and octadecane (0.001 02 mmol/L) as internal standard was placed into each of three 13 mm o.d. Pyrex irradiation ampoules. The solutions were degassed through freeze-pump-thaw cycles to less than 10⁻⁴ Torr. The ampoules were sealed and irradiated at 366 nm for different lengths of time, after which gas chromatographic analysis was performed. The procedure was repeated for similar solutions containing other styrene concentrations (2.01 and 3.65 mol/L).

Laser flash photolysis¹ experiments were performed with a Q-switched Continuum model YG671C-10 Nd:YAG laser, pulse width fwhm = 5 ns after the doubling crystal, using energies between 2.0 and 6.0 mJ/pulse (except where noted) and a repetition rate of 10 Hz. Analyzing light was supplied by an Osram model XBO 150 W/I high pressure xenon lamp, detected with a CVI Digikrom 240 monochromator and photomultiplier. Data were collected using a Tektronix DSA 602 digitizing signal analyzer. An AST Premium 386 computer equipped

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Table 1. Summary of Crystallographic Data for the Structure of THN

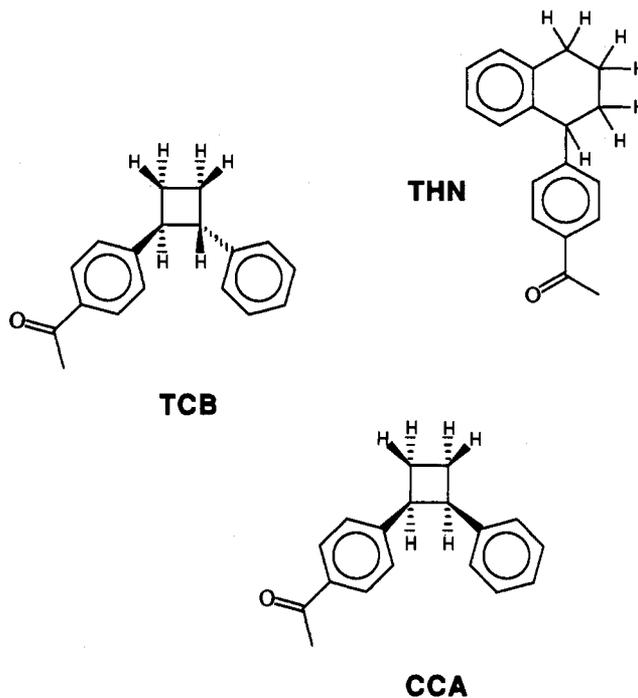
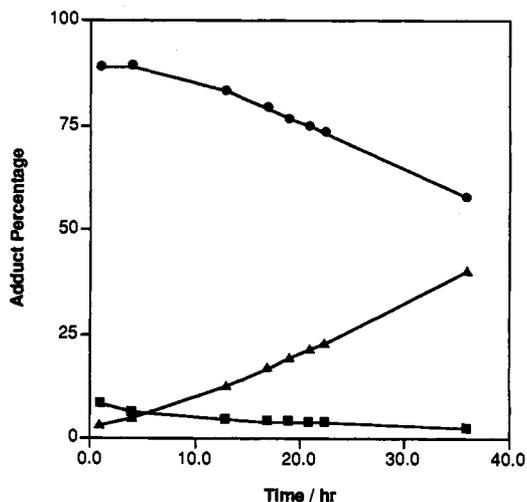
compound	C ₁₈ H ₁₈ O
mol wt	250.32 g/mol
space group	P2 ₁ /C
cell constants	
<i>a</i> , Å	11.400(4)
<i>b</i> , Å	05.545(7)
<i>c</i> , Å	22.207(3)
β , deg	99.42(3)
cell vol, Å ³	1385(1)
molec/cell	4
radiation	MoK α
scan width, deg	0.8 + 0.4 tan θ
std refl	4 1 4, -3 2 -1, 1 2 6
decay of stnds	1.5%
2(θ) range	4–50
refl meas	2833
refl obs	1255
no. params varied	172
<i>R</i>	0.044
<i>R</i> _w	0.043

with PC RAD and KS-01 software packages from Kinetic Instruments (P.O. Box 49434, Austin, TX 78765) provided laser and lamp control as well as kinetic analysis. Time-resolved spectroscopy was conducted on cyclohexane solutions of 0.041 and 0.0012 mol/L PAS with laser excitation at 355 and 266 nm, respectively, and 0.001 mol/L TCB at 266 nm. Samples were degassed through nitrogen sparging. Quenching of ³PAS by styrene was performed with 355-nm excitation using cyclohexane and benzene solutions of PAS (0.04 mol/L). Sequential 100- μ L additions of styrene were syringed into the sample cell and degassed before each measurement. Excitation was performed at 355 nm. A sensitized study of styrene self-quenching in benzene was carried out under similar conditions using a thioxanthone solution (1.0 \times 10⁻³ mol/L) and 20 mJ/pulse. In quenching experiments the molarities of styrene were determined from the amount of styrene added and the total sample volume as measured (\pm 3–4%) with a millimeter ruler or a Swiss army knife. It was necessary to measure the volume (0.8–1.5 mL) for each measurement due to the slow evaporation of solvent. Pseudo-first-order decay rate constants were readily reproducible to \pm 10% and, with more care, to \pm 5%.

X-ray Structure Determination of THN. A clear crystal was mounted in a 1.0-mm glass capillary. Preliminary examination and data collection were accomplished using an Enraf-Nonius CAD4 diffractometer. Cell constants were obtained by a least-squares fit of 25 accurately centered reflections. Crystallographic and data collection parameters are given in Table 1. The space group of the monoclinic cell was determined to be P2₁/C (no. 14). The structure was solved by direct methods and refined on the basis of 1255 observed reflections. Hydrogen atoms were calculated at idealized positions and included in the calculations but not refined. Least-squares refinement based upon 1255 observed reflections in the range 4.00° < 2 θ < 50.0° converged at *R* = 0.044 and *R*_w = 0.043. Selected bond distances, bond angles, and dihedral angles are given in Table 2.

Results

Preparative photoaddition of PAS to styrene upon 24 h of irradiation yielded three main products in a 20:6:1 GC area ratio, corresponding to the *trans*-diarylcyclobutane, TCB, the phenyltetrahydronaphthalene, THN, and the *cis*-diarylcyclobutane adduct, CCA, respectively (Figure 2). GC analysis of the irradiated solution indicated that these adducts account for 85% by peak area of the volatile products formed. Three other signals with lower retention times accounted for another 14% (5:22:1 ratio, respectively). ¹H NMR of isolated fractions suggested that these signals can be attributed to styrene dimers. This agrees with reported formation of phenyl-1,2,3,4-tetrahydronaphthalene and diphenylcyclobutane adducts from the photodimerization of styrene.^{37–39} Polystyrene accounted for 7–11% of the initial styrene. The absence of a carbonyl band in the IR spectrum of the precipitated polymer indicated no observable copolymerization with PAS.

**Figure 2.** 1:1 adducts from the photoaddition of ³PAS to styrene.**Figure 3.** Product distribution of preparative photoaddition mixture (●●) % TCB + (▲) % THN + (■) % CCA = 100.

At 12 h of irradiation the TCB:CCA ratio was 20:1, and their ratio thereafter remained constant. The concentration of THN, however, continued to increase with time over a 36-h irradiation period. The product distribution by GC area for the 1:1 adduct mixture is depicted in Figure 3 as a function of time. Irradiation of the preparative PAS/styrene solution was carried out for 24 h in order to produce sufficient quantities of the three adducts. The isolated material was richer in TCB than GC of reaction mixtures would suggest, indicating greater losses for the other components in workup. The low yield of isolated and purified CCA prevented its full characterization.

It is possible that THN is a secondary product. THN formation is not detected at the low conversions used for quantum yield determinations. The 1,4-biradical could undergo an α to ortho coupling followed by a 1,3-hydrogen shift to yield THN as a primary product, or if it is a secondary process, THN formation could be the result of a rearrangement of an excited TCB or CCA

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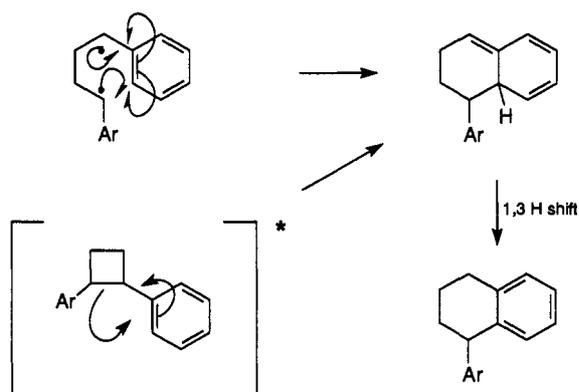
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Table 2. Selected Structural Data for DHN^a

Dihedral Angles in Degrees															
atom 1		atom 2		atom 3		atom 4		dihedral angle							
C13		C14		C17		C18		3.40 ± 9.90							
C1		C10		C11		C12		71.69 ± 0.61							
Bond Distances in Angstroms															
atom 1		atom 2		distance		atom 1		atom 2		distance					
O1	C17	1.22(1)	C14	C13	1.40(1)	C2	C1	1.41(1)	C2	C3	1.42(1)				
C17	C14	1.51(1)	C11	C12	1.39(1)	C6	C1	1.40(1)	C6	C7	1.53(1)				
C17	C18	1.52(1)	C11	C16	1.40(1)	C9	C8	1.56(1)	C7	C8	1.53(1)				
C10	C11	1.53(1)	C15	C16	1.41(1)	C7	C8	1.53(1)	C4	C3	1.39(1)				
C10	C1	1.54(1)	C12	C13	1.40(1)										
C10	C9	1.55(1)	C5	C6	1.42(1)										
C14	C15	1.40(1)	C5	C4	1.41(1)										
Bond Angles in Degrees															
atom 1		atom 2		atom 3		angle		atom 1		atom 2		atom 3		angle	
O1	C17	C14	118.7(7)	C10	C11	C16	120.3(7)	C10	C1	C2	118.4(7)	C10	C1	C6	121.0(7)
O1	C17	C18	121.5(7)	C12	C11	C16	120.4(7)	C10	C1	C6	121.0(7)	C10	C1	C6	120.4(7)
C14	C17	C18	119.8(7)	C14	C15	C16	120.5(7)	C2	C1	C6	120.4(7)	C11	C16	C15	119.2(7)
C11	C10	C1	111.4(6)	C11	C12	C13	120.2(7)	C11	C16	C15	119.2(7)	C10	C9	C8	108.6(6)
C11	C10	C9	110.2(6)	C6	C5	C4	120.0(8)	C10	C9	C8	108.6(6)	C10	C7	C8	110.0(7)
C1	C10	C9	113.0(7)	C14	C13	C12	120.0(8)	C6	C7	C8	110.0(7)	C17	C14	C15	119.3(7)
C17	C14	C15	119.3(7)	C1	C2	C3	119.8(8)	C5	C4	C3	120.4(8)	C17	C14	C13	120.9(7)
C17	C14	C13	120.9(7)	C5	C6	C1	119.5(7)	C9	C8	C7	110.2(7)	C15	C14	C13	119.7(7)
C15	C14	C13	119.7(7)	C5	C6	C7	117.1(7)	C2	C3	C4	120.0(8)	C10	C11	C12	119.2(7)
C10	C11	C12	119.2(7)	C1	C6	C7	123.4(7)								

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

Scheme 1



molecule. Scheme 1 depicts the possibilities, but the data do not permit their distinction. If a primary product, THN must be formed with very low probability from the biradical.

Structure Assignments. ¹H NMR and ¹³C NMR chemical shifts of CCA and TCB agree with values calculated from functional group shift tables.⁴⁰ Spectroscopic data reported for *cis*- and *trans*-1,2-bis(4-acetylphenyl)cyclobutanes,⁴¹ as well as for the nonacetylated homologues,^{37,38} reinforce the chemical shift assignments. Figure 4 is a ¹H NMR spectrum of TCB. Evidence for mono and *para* substitution is also observed in the IR spectrum of TCB.⁴² Further (*vide infra*), photolysis of TCB affords both the expected styrenes by GC analysis and the expected 1,4-biradical transient in flash photolysis. The ¹H NMR spectrum of THN is consistent with those reported for other *para*-substituted 1-phenyl-1,2,3,4-tetrahydronaphthalenes.^{43,44} X-ray crystallog

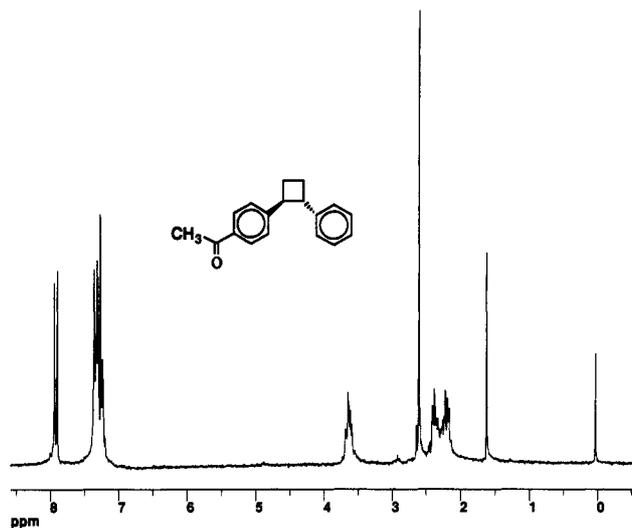


Figure 4. 200-MHz ¹H NMR of TCB in CDCl₃ (0.03% TMS). 1.5 δ signal is H₂O.

raphy of a THN crystal yielded the structure shown in Figure 5. A summary of crystal data is given by Table 1.

Photolysis of TCB (0.76 mmol/L) at 313 nm yielded styrene and PAS in a 1:1 ratio, as shown by the product distribution curves in Figure 6. Quantitative decomposition of TCB was achieved after 5 h. Observations on the photolysis of other diarylcyclobutanes are consistent with this result.⁴¹ GC monitoring of the irradiation suggests the formation of CCA and THN in less than 4% quantities. CCA disappears during the first 2 h, while THN tends to a maximum over the irradiation period. Irradiation of THN (0.24 mmol/L) under similar conditions did not produce detectable amounts of styrene and only marginal quantities of PAS. Only an 11% decrease in the initial amount of THN was observed after 5 h.

Laser flash photolysis of TCB at 266-nm excitation produced a transient (λ_{max} at 315 nm) which decayed by first-order kinetics with a lifetime of 199 ± 4 ns in cyclohexane. This is consistent with the absorption properties and values of 190 and 205 ns

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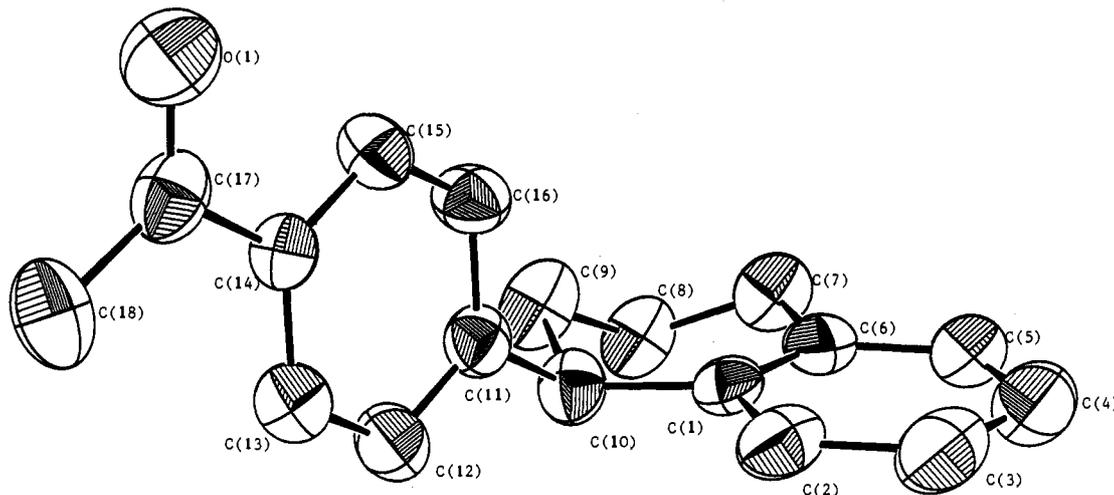


Figure 5. Thermal ellipsoid plot (50% probability surfaces) of THN, showing the atom-labeling scheme.

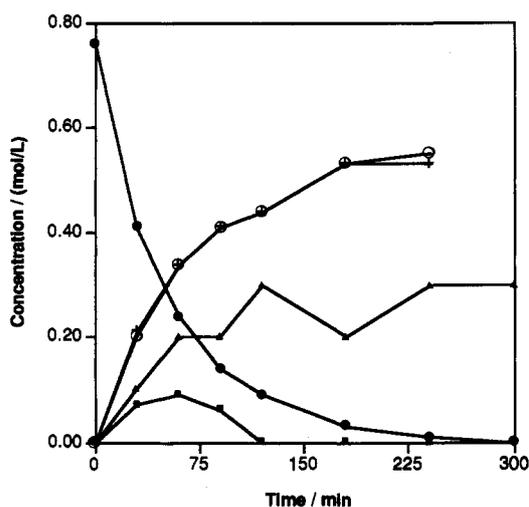


Figure 6. Product distribution for the photolysis of TCB at 313 nm (●) TCB; (+) PAS; (○) STY; (▲) THN; (■) CCA) $\times 10$.

reported for the 1,4-diphenyl-1,4-butanediyl biradical⁴⁵ and the bis(*p*-acetyl) analogue,¹ respectively. Figure 7 displays both the absorption spectrum and a decay curve of the TCB transient. The lifetime and absorption properties of the transient are consistent with its assignment as the 1,4-biradical.⁴¹

Quantum yields for the photoaddition of ³PAS to styrene in cyclohexane correspond to the average of three independent determinations made at different irradiation times. All measurements were made within a 0.2–1.5% conversion range for which TCB formation showed linear behavior, as illustrated by Figure 8. A constant TCB:CCA ratio of 11:1 was observed for all runs. The quantum yields measured were 0.021 ± 0.001 , 0.048 ± 0.002 , and 0.073 ± 0.001 for 1.03, 2.01, and 3.65 mol/L styrene, respectively, for $\Phi(\text{TCB}) + \Phi(\text{CCA})$.

Laser flash photolysis of PAS yields a transient signal between 305 and 370 nm, which exhibits first-order decay. Kinetic analysis at 320 and 365 nm determined its lifetime to be 22 ± 1 ns in cyclohexane and 21 ± 1 ns in benzene. The least-squares fit superimposed on the transient decay and the transient absorption spectrum are displayed in Figure 9. The absorption of the ground state prevented absorption measurements below 305 nm. The lifetime of the transient is consistent with triplet lifetimes reported for styrene (22 ns) and styrene derivatives (22–31 ns).^{2,46,47} Quenching of the transient by styrene was monitored at 365 nm.

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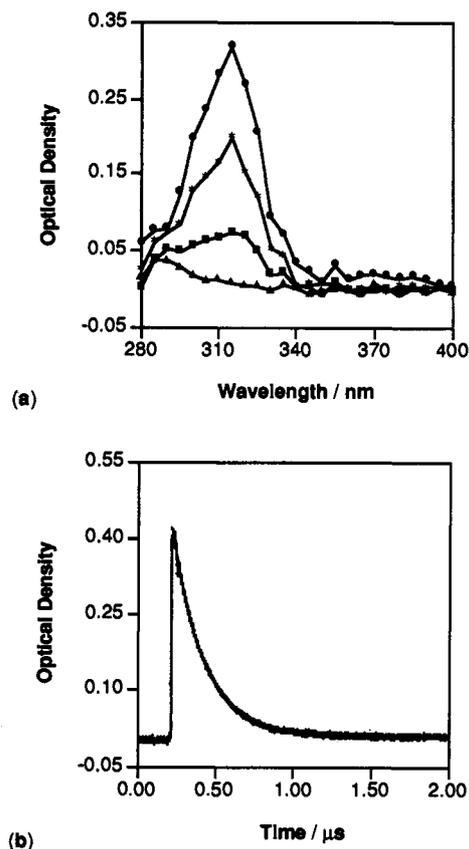


Figure 7. Transient absorption spectrum (at $t =$ (●) 0.024, (*) 0.116, (■) 0.308, and (▲) 1.052 μs) (a) and first order decay at 320 nm (b) of the transient from TCB in cyclohexane.

The quenching rate was obtained from the slope of the plot of styrene concentration vs rate constant of transient decay. Figure 10 displays one such curve. Values of the first-order decay rate constant ($\pm 5\%$) for ³PAS in cyclohexane at various styrene molarities were 0 M, $4.6 \times 10^7 \text{ s}^{-1}$; 1.03 M, $4.7 \times 10^7 \text{ s}^{-1}$; 1.89 M, $5.3 \times 10^7 \text{ s}^{-1}$; 2.62 M, $5.2 \times 10^7 \text{ s}^{-1}$; 3.17 M, $5.8 \times 10^7 \text{ s}^{-1}$; 3.71 M, $5.6 \times 10^7 \text{ s}^{-1}$; 4.19 M, $5.9 \times 10^7 \text{ s}^{-1}$. The rate constant k_Q for styrene quenching of PAS triplet was thus $3.2 \times 10^6 \pm 0.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ in cyclohexane: the value in benzene was nearly identical. The quenching rate showed minimal variation (*vide infra*) whether styrene was used with or without distillation.

Laser flash photolysis of styrene (0.35 mol/L) sensitized by thioxanthone in benzene produced a transient with a lifetime of

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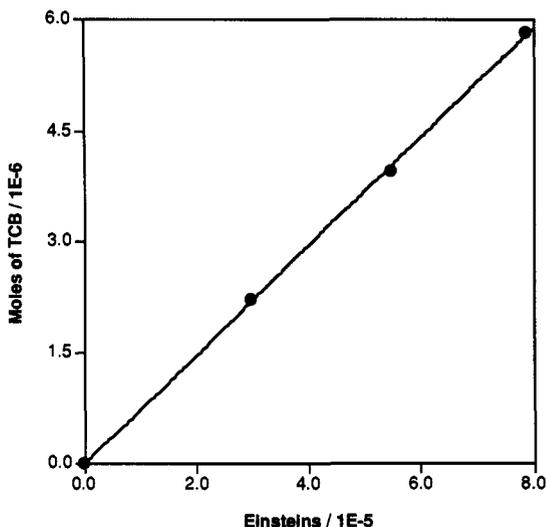


Figure 8. TCB formation at 366 nm from quantum yield measurements (curve fit: $f(x) = 7.34 \times 10^{-2}(x) - 4.14 \times 10^{-10}$; $R^2 = 0.9998$).

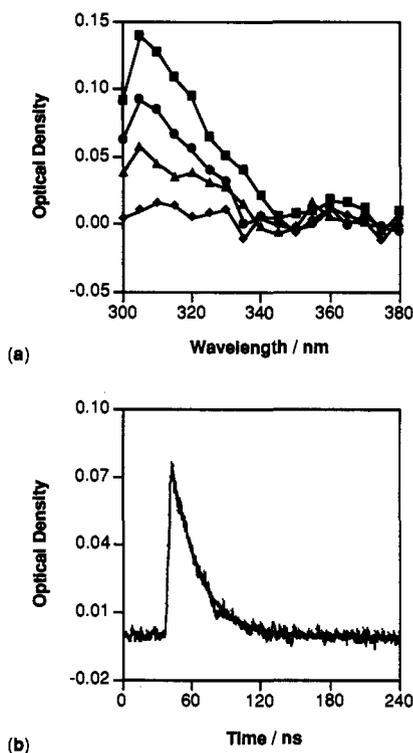


Figure 9. Time-resolved absorption spectrum (at $t =$ (■) 2.00, (●) 11.5, (▲) 125.5, and (◆) 135.5 ns) (a) and first-order decay and fit at 320 nm (b) of 3 PAS in cyclohexane.

22.7 ± 0.3 ns, the styrene triplet. Upon addition of more styrene a second transient with a longer lifetime was observed between 305 and 325 nm. Kinetic analysis as two first-order decays, as shown in Figure 11, revealed a lifetime of 195 ± 14 ns for the slow component and no systematic variation in the lifetime of either component over the styrene concentration range 0.35–5.08 mol/L. An increase in the intensity of the slow component followed the increase of styrene concentration. The new transient agrees with the expected lifetime and absorption behavior of the 1,4-diphenyl-1,4-butanediyl biradical.⁴⁵ Values of the first-order decay rate constant for styrene triplet in benzene at various styrene molarities were 0.35 M, 4.4×10^7 s⁻¹; 0.97 M, 4.5×10^7 s⁻¹; 1.87 M, 4.6×10^7 s⁻¹; 2.05 M, 4.6×10^7 s⁻¹; 3.67 M, 4.5×10^7 s⁻¹; 5.08 M, 4.2×10^7 s⁻¹. The 5.08 M experiment was contaminated by a small cable ring, and when it was removed and the decay curve interpolated over the range of the ring, the decay rate was

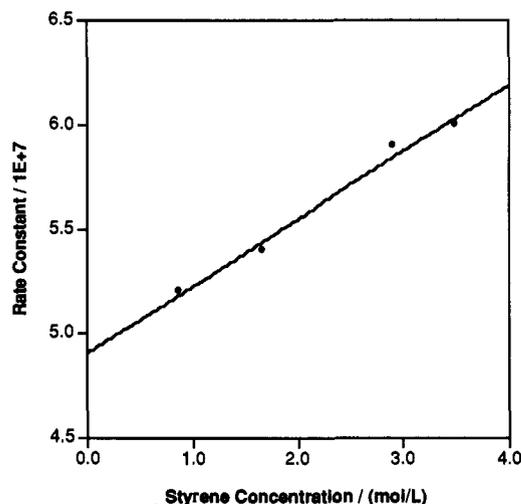


Figure 10. Quenching curve for 3 PAS by styrene in cyclohexane at 365 nm.

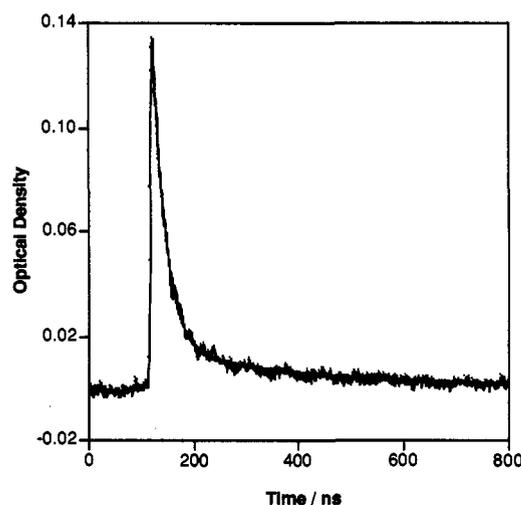


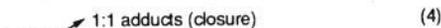
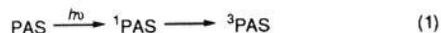
Figure 11. First-order decays for 3 STY (fast component) and longer lived transient in benzene.

5.1×10^7 s⁻¹. We thus find no significant variation in the lifetime of styrene triplet for the range of concentration used. We thus estimate the upper limit of the self-quenching rate to be *ca.* 1×10^6 M⁻¹ s⁻¹. A lower limit may be estimated crudely by a guess that the extinction coefficient of the biradical is no more than 1 order of magnitude more than that of the styrene triplet. The ratio of 3 STY absorbance to that of the biradical is *ca.* 7 from 300 to 335 nm with 4.36 M styrene. Use of this ratio and the stated assumption yields a lower limit of *ca.* 1×10^5 M⁻¹ s⁻¹. We believe that the extinction coefficients are unlikely to differ so greatly and consequently believe that the self-quenching rate is not quite that low.

Discussion

The main objectives of this work were the demonstration that styrene type triplets could undergo addition to ground-state styrene, analogous to the addition of primary alkyl radicals to styrene, and the determination of the rate constant for the reaction. The observation of TCB and CCA as primary photoproducts shows that this occurs and suggests the mechanism given in eqs 1–5. In the absence of any triplet quencher the rate of triplet decay corresponds to the rate of intersystem crossing, k_{isc} (eq 2). Addition of the alkene triplet to ground-state styrene would yield the 1-(4-acetylphenyl)-4-phenyl-1,4-butanediyl biradical (BRD). The formation of this 1,4-biradical (eq 3) is analogous to the above mentioned primary radical addition. Formation of *cis*-

and *trans*-1,2-diarylcyclobutanes is expected from a 1,4-biradical intermediate (eq 4).^{37,38}



Unfortunately, operational reasons precluded observation of BRD directly by irradiation of PAS in the presence of styrene. Using 355-nm excitation required a concentration of PAS too high to permit analyzing light to pass through the sample in the 300–340-nm range where BRD absorption occurs; 266-nm excitation was absorbed too strongly by styrene to allow either excitation of PAS or penetration of the exciting light adequately deeply into the sample for observation. However, the existence of BRD follows from its observation as a transient in the time-resolved photolysis of TCB, with a lifetime and absorption spectrum comparable to other 1,4-diaryl-1,4-butanediyl radicals.¹ Further evidence for eq 3 follows from direct observation of 1,4-diphenyl-1,4-butanediyl, analogous to BRD, in thioxanthone sensitized photolysis of styrene. Observation in this case is permitted by the window at 290–330 nm in the ground-state absorption of thioxanthone and by the relative transparency of unsubstituted styrene above 295 nm even at the high concentrations required to observe eq 6:



Quenching of ³PAS by Styrene. With the demonstration that products from eqs 1–5 are formed and that an analogue (eq 6) to eq 3 occurs, we determined the rate of triplet addition of eq 3 by observation of the attenuation of ³PAS lifetime in the presence of high styrene concentrations. PAS/styrene solutions in both cyclohexane and benzene afforded $k_{\text{Q}} = 3.2 \times 10^6 \pm 0.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. A small increase in the rate constant was noticed when nondistilled styrene was used. A diffusion controlled quenching impurity, i.e. $k_{\text{Q}}^{\text{impurity}} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, present in 0.06% would account for the observation. It is possible that such a quencher could not be removed by distillation. Thus, kinetic observation alone cannot rule out the involvement of low concentration impurities in the styrene, to which the ³PAS quenching could be attributed, i.e. that $k_{\text{Q}} > k_{\text{B}}$ of eq 3.

Quantum Yields for the Formation of Cyclobutanes. The determination of the rate constant k_{B} (eq 3) can also be done from the quantum yields of formation of the primary photo-products TCB and CCA. The kinetic analysis of eqs 1–5 leads to eq 7.

$$\Phi = \frac{k_{\text{B}}[\text{STY}]}{k_{\text{B}}[\text{STY}] + k_{\text{isc}}} \alpha \quad (7)$$

In eq 7, k_{isc} is known to be $4.6 \times 10^7 \text{ s}^{-1}$, the inverse of the ³PAS lifetime (Figure 9). The parameter α is a measure of the 1,4-biradical efficiency toward undergoing closure to yield the cyclobutane adducts, eq 4, as compared to cleavage, which leads to the generation of ground-state reactants, eq 5. Rearrangement of eq 7 results in eq 8.

$$\frac{1}{\Phi} = \frac{1}{\alpha} + \frac{k_{\text{isc}}}{k_{\text{B}}\alpha[\text{STY}]} \quad (8)$$

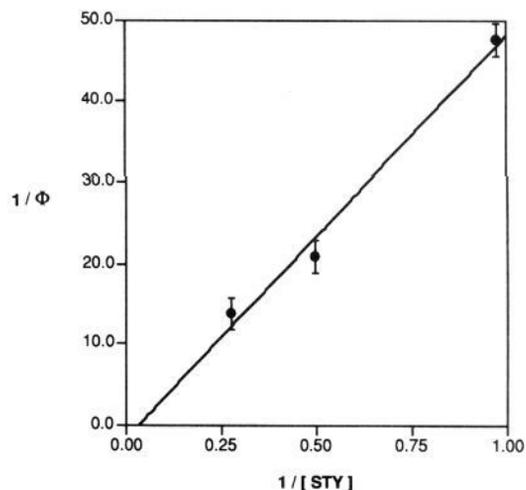


Figure 12. Least-squares fit for the determination of $k_{\text{B}}\alpha$ from eq 8 (curve fit: $f(x) = 49.8(x) - 1.56$; $R^2 = 0.99$).

Figure 12 combines eq 8 with the quantum yields for TCB formation from the PAS photoaddition to styrene. The slope of the curve affords $k_{\text{B}}\alpha = 7.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. The range of concentration used for this experiment does not give a meaningful intercept from which α can be assessed. However, a reasonable estimate of α is available⁴⁸ from the quantum yield of PAS formation from the photolysis of *trans*-1,2-bis(4-acetylphenyl)cyclobutane. The closure efficiency, α , for this system is 0.38. Using this value for the ³PAS/styrene system affords $k_{\text{B}} = 2.0 \times 10^6 \pm 0.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, which is in good agreement with the quenching rate $k_{\text{Q}} = 3.2 \times 10^6 \pm 0.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ obtained above for the quenching of ³PAS decay by styrene. If k_{B} is assumed equal to k_{Q} , a closure efficiency α of 0.39 ± 0.1 is obtained from Figure 12, which value is almost identical to that for the bis-acetylated homologue. The agreement of the two different values of α suggests that quenching of ³PAS by STY is not substantially affected by an adventitious impurity in the styrene.

The agreement between the two independent methods of obtaining k_{B} is strong evidence both for the value of k_{B} and for the validity of the mechanism we propose. It allows us to rule out reaction *via* a preformed ground-state complex or a ¹PAS addition. Prior results on dimerization of perpendicular triplets are consistent with the present results.^{49,50} Special attention must be given to the rate of isoprene dimerization,⁴⁹ $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. Isoprene forms a perpendicular triplet, as can be inferred from its 27-ns lifetime. Its dimerization rate should resemble that of the ³PAS to styrene addition, as it does.

Radical Modeling of ³PAS/³STY Additions to Styrene. The 1,2-biradical model for alkene triplets would suggest that the rate of eq 3 be similar to the rate of primary alkyl radical addition to styrene. In reality k_{B} is a bit more than 1 order of magnitude faster than the $1.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ observed for the rate of addition of 5-hexenyl radical to styrene.²¹ This could be considered to be fair agreement. However, the self-quenching rate for styrene triplet, estimated above as *ca.* 1×10^5 to $1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, is in fact in still better agreement with the 5-hexenyl-styrene rate. We consider below possible reasons for enhancement of k_{B} . We believe that the best explanation is that the monoradical model reaction satisfactorily (within a factor of 7) predicts the ³STY-STY addition rate because of the absence of polar substituents, but that polar substituent effects play some role.

The model reaction was done in acetonitrile/acetic acid,²¹ but we do not believe the solvent difference can explain an effect this large. Alternatively, reactivity at the β position might have been

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enhanced by the fact that any reaction at this position will relieve the repulsion between the unpaired electrons. Such an effect may contribute to the enhanced reactivity of indene and dihydronaphthalene triplets in dimerizations.² However, if such an effect accelerated addition in the present case, it would also have been expected to accelerate cyclopropylcarbinyl ring opening in β -cyclopropylstyrene,^{8,9} where the radical model leads instead to an accurate prediction of the reaction rate.

The Paterno-Büchi reaction, the formation of oxetanes from excited carbonyl compounds and alkenes, occurs readily for a number of triplet n,π^* aromatic ketones.^{51,52} One might have assigned the enhanced reactivity of 3 PAS to a Paterno-Büchi reaction through its $^3n,\pi^*$ state, but we observe no such products. Also, the perpendicular alkene triplet of PAS would have an energy of *ca.* 52 kcal/mol,² far below the $n-\pi^*$ state, and, as shown by the lifetime and spectrum observed, is indeed the state quenched by styrene. There is thus presumptive evidence against this hypothesis.

We suggest that the 15-fold-enhanced rate observed for the triplet addition (eq 3), and the ≥ 2 -3-fold rate increase for 3 PAS over 3 STY, might be the effects of a triplet exciplex intermediate stabilized by some degree of charge transfer. The exciplex would be the product of the 3 PAS interaction with ground-state styrene and would be the precursor of the 1,4-biradical. On this basis the best agreement between the present styrene triplet quenching results and the monoradical model would be expected to be the 3 STY + STY reaction, i.e. the case without polar substituents. Indeed, the crude rate range we estimate for this reaction (*vide supra*) includes the model rate.

This mechanism would be analogous to those proposed for the Paterno-Büchi reaction of $^3n,\pi^*$ aryl ketones with simple alkenes^{51,52} and the reaction of phenanthrene triplets with dimethyl fumarate and dimethyl maleate.⁵³⁻⁵⁵ In each of those cases important components of the evidence for exciplex involvement were rate enhancements analogous to what we here report, in particular by substituents which would stabilize charge separation. Although in those cases the enhancements were far greater than for the present case, we find the similarity suggestive. This mechanism has been mentioned in the literature for sensitized dimerization of styrene,³⁷ although with no experimental evidence. The mechanism of addition outlined above thus might be modified to include eqs 3a and 3b.



In further support of this mechanism, we have recently measured the rate constant for the quenching of 3 PAS by *p*-methoxystyrene, a case with an electron-attracting group in one quenching partner and an electron donor in the other, to be $1.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. This is a 5-fold increase over the 3 PAS + STY rate, more than 1 order of magnitude over the 3 STY + STY rate, and 2 orders of magnitude above the monoradical model. Whatever explanation is to be given clearly must consider polar substituent effects. The weak exciplex hypothesis in our opinion follows well from the precedent cited.

Conclusions. The addition of *p*-acetylstyrene triplets to styrene affords products as predicted by the 1,2-biradical model for alkene triplets, and the rate constant for the reaction is near to, but somewhat larger than, that for the free radical model reaction.

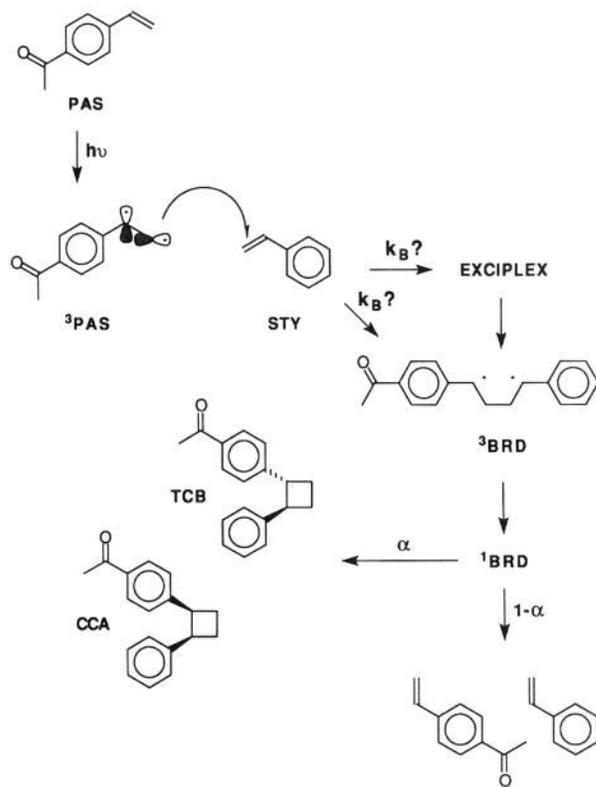


Figure 13. Schematic representation of the 3 PAS addition to styrene.

The validity of the 1,2-biradical model is reinforced. The only modification suggested by the present experiments is a possibly general modest reactivity enhancement of alkene triplets toward addition to double bonds by polar substituents. The scheme in Figure 13 depicts the overall mechanism including a possible exciplex. However, further experimental evidence is required to substantiate exciplex involvement, particularly to examine the alternate possibility that an unexpectedly large polar effect of remote substituents on the radical-like processes of alkene triplets exists. As both absolute^{56,57} and relative⁵⁸⁻⁶⁰ rates of abstraction of hydrogens by $^3\text{Ph}_2\text{CO}$ are well modeled by *tert*-butoxy radical, we expect that atom abstractions by alkyl radicals will be good models for abstractions by analogously substituted alkene triplets. Abstraction reactions should not involve exciplexes. We are thus planning experiments with atom abstractions by alkene triplets as a further test of the 1,2-biradical model.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-9121313) and the Robert A. Welch Foundation (Grant AT-0532). We thank Dr. Wayne E. Britton for the mass spectrum.

Supplementary Material Available: Tables of positional and thermal parameters, complete bond distances, and angles (5 pages); table of observed and calculated structure factors (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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