

Photochemistry of Organic Molecules Entwined in Spiderwebs; The Use of Poly(methyl methacrylate) Glass for Restricting Excited-State Motion^{1,2}

Howard E. Zimmerman* and Michael E. O'Brien

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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A study of several unimolecular photochemical rearrangements in poly(methyl methacrylate) glass was carried out with the intent of comparing the behavior of excited-state species trapped in a polymer matrix with both the corresponding solution photochemistry and that in crystal lattices. Three reactants were studied: (a) 4,5,5-triphenylcyclohex-2-en-1-one, (b) 1,1-dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene, and (c) 2,2-dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane. The solution photochemistry of the three compounds had previously been studied in our laboratory, and the photochemistry in the crystal lattice had been similarly investigated for the first two. The crystal lattice photochemistry of the last of the three was investigated in the present study. For each of the three reactants, different photochemical behavior was observed depending on the environment—polymer glass, solution, or crystal lattice. The experimental behavior correlated nicely with theoretical assessment of molecular motion of the component atoms in proceeding onward from that point along the reaction coordinate where multiple reaction pathways are available. The preferred reaction pathway proved consistently to require the least motion and the minimum molecular volume displacement. A concept of least motion dependent on its application to the “branch point” rather than the entire conversion of reactant to product was established.

Introduction

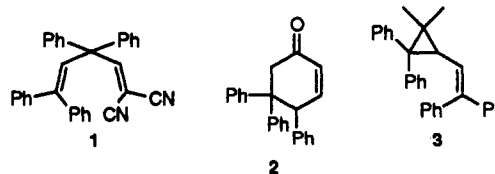
One area of interest in our previous research has been the behavior of excited-state molecules in constrained media. Thus, we have reported on the effect of crystal lattice confinement on reactivity.^{3,4} In the present study, we investigated the photochemistry of molecules entrapped in polymer matrices with the idea of restricting the molecular motion of the excited-state reactants. Confinement control in photochemistry has been investigated in a number of individual examples in previous literature.³⁻⁷ Except for the elegant work of Scheffer,^{6f-h,j} efforts have been largely focused on assessment of the polymer

environment rather than the entrapped molecule. Our efforts have been directed toward study of a series of reactants and a search for a general theory of reactivity in restrictive environments. For photochemistry in crystal lattices we have reported success in correlating molecular fit and molecular motion to observed reactivity. We now turn to consideration of photochemistry in a polymer matrix.

The effect of a polymer matrix can be viewed in two ways. One might just consider the polymer matrix to provide a viscous medium. Alternatively, on a molecular level one might envisage the polymer strands as providing a “molecular spiderweb” inhibiting molecular motion. For the study described in this report, we decided to use poly(methyl methacrylate) as the polymeric medium.

Results

Choice of Reactants. Three photochemical systems were of particular interest for the present study, since their solution photochemistry was known⁸⁻¹⁰ and the excited-state behavior of two of these, compounds 1 and 2, had been studied in a crystal lattice.⁴ For completeness we needed to study the crystal lattice photochemistry of



the third reactant (i.e., 3) as well as investigate the behavior of all three in poly(methyl methacrylate).

* Abstract published in *Advance ACS Abstracts*, March 1, 1994.

(1) Part 166 of our photochemical series and part 230 of our general sequence.

(2) For our previous paper see: Zimmerman, H. E.; Sulzbach, H. M.; Tollefson, M. B. *J. Am. Chem. Soc.*, **1993**, *115*, 6548–6556.

(3) Zimmerman, H. E.; Zuraw, M. J. *J. Am. Chem. Soc.*, **1989**, *111*, 2358–2361.

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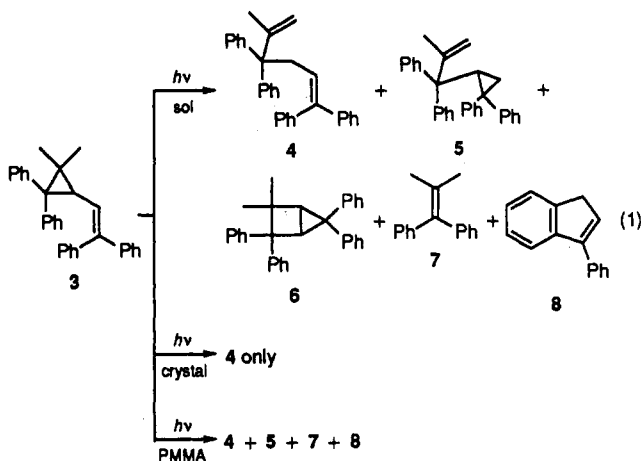
(7) (a) Cowell, G. W.; Pitts, J. N. *J. Am. Chem. Soc.* **1968**, *90*, 1106–1110. (b) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, England, Chapter 12. (c) Photopolymerizations; see ref 6e and: Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, England, Chapter 11.

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Crystal Lattice Photochemistry of 2,2-Dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (3). Irradiation of crystalline vinylcyclopropane **3** led to a single photoproduct, in contrast to the solution photochemistry. This photoproduct proved to be 5-methyl-1,1,4,4-tetraphenyl-1,5-hexadiene (**4**), which was one of the products encountered in our earlier study¹⁰ of the solution photochemistry of cyclopropane **3**. Note eq 1 below. This



reaction condns	product ratio ^a				
	4	5	6	7	8
solution (<i>t</i> -BuOH)	13	17	8	13	1
crystal lattice (10% convn)	only	-	-	-	-
polymer matrix ^b (21% convn ^c)	4.8	1.1	-	1.0	trace
(53% convn ^d)	4.0	1.6	2.8	1.3	1.0
(60% convn ^e)	5.2	1.5	1.3	1.0	1.6

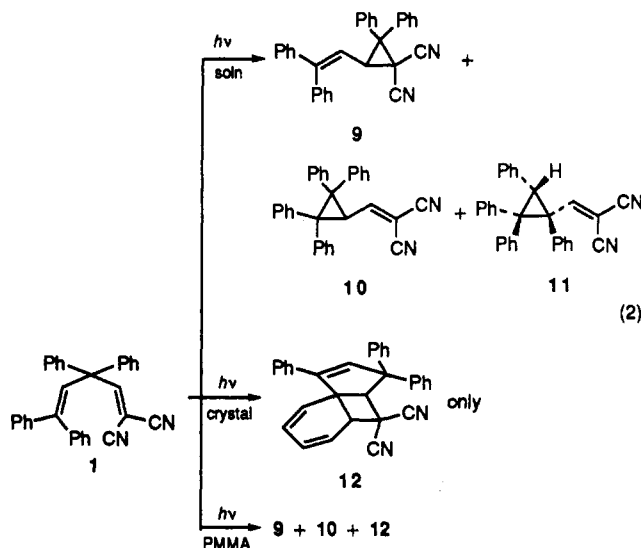
^a All PMMA photolysis ratios were determined by ¹H-NMR. ^b All experiments done at 0 °C. ^c 30 wt % of vinylcyclopropane **3** in PMMA. ^d 25 wt % of vinylcyclopropane **3** in PMMA.

modification of photoreactivity was reminiscent of our earlier crystal lattice studies where in the solid state the formation of photoproducts resulting from minimal molecular motion proved general. However, the present example is discussed in detail below.

Polymer Photochemistry of 2,2-Dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (3). Irradiation of the known vinylcyclopropane **3** in a poly(methyl methacrylate) glass was carried out at 0 °C. Note eq 1. The photochemistry was carried out at different conversions with the finding that the major product at low conversion (21%) was the same diene **4** observed in the crystal lattice study. In addition, allylcyclopropane **5** was found as a more minor product. However, no tetraphenylhousane **6** was detectible. Interestingly, at higher conversions, both the allylcyclopropane **5** and the tetraphenylhousane **6** were observed in increasing relative amounts. Again, refer to eq 1 for details on the dependence on the conversion extent as well as for comparison with the solution and crystal lattice behavior.

Polymer Photochemistry of 1,1,3,3-Tetraphenyl-5,5-dicyano-1,4-pentadiene (1). Previously, the solution and the crystal lattice photochemistry of tetraphenyl diene **1** was studied.^{4,8} With direct irradiation the solution chemistry afforded the three vinylcyclopropanes resulting from different di- π -methane rearrangements as depicted in eq 2. Sensitized photolysis in solution led only to the dicyanovinyl photoproduct **10**. In contrast, photochemistry of the crystal afforded a single 2 + 2 photoproduct, a triphenyltricyclic triene **12**. Finally, irradiation in the

polymer web led at low conversion to two of the three photoproducts observed in the solution photochemistry, namely the diphenylvinylcyclopropane **9** and the dicyanovinylcyclopropane **10**. These various results are summarized in eq 2. However, at higher conversions (ca. 26%),



reaction condns	product ratio ^a			
	9	10	11	12
solution, direct (Benzene)	1.1	1.2	1.3	-
solution, sensitized (Benzene)	-	only	-	-
crystal lattice	-	-	-	only
matrix ^b polymer (10% convn)	1.0	1.0	-	trace
(26% convn)	1.2	1.0	-	<0.5
(40% convn)	3.0	1.0	-	0.5

^a All PMMA photolysis ratios were determined by ¹H-NMR. ^b All experiments were done at room temperature using 25 wt % of tetraphenyl diene **1** in PMMA.

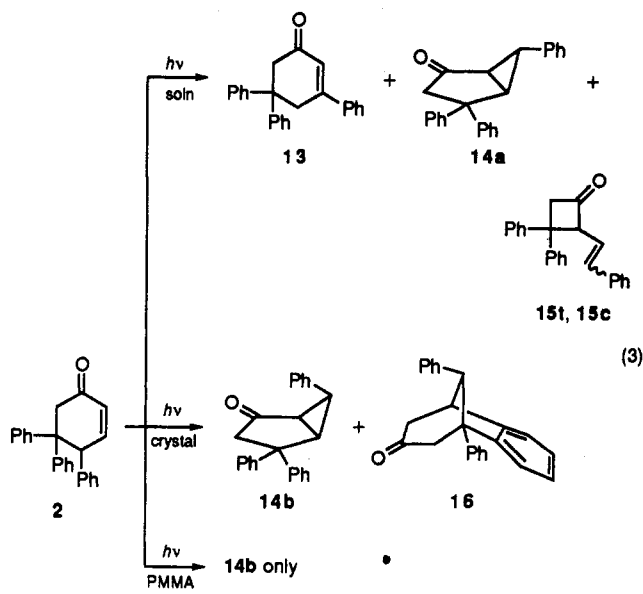
the triphenyltriene **12** became detectible.

Polymer Photochemistry of 4,5,5-Triphenylcyclohex-2-en-1-one (2). The solution photochemistry led to three photoproducts, the triphenylcyclohexenone **13**, the exo stereoisomer of 4,4,6-triphenylbicyclo[3.1.0]hexanone (i.e., **14a**), and the cyclobutanone **15**.⁹ Note eq 3. Crystal lattice photolysis led, instead, to the endo stereoisomer (**14b**) of the 4,4,6-bicyclic ketone and the benzobicyclic ketone **16** (cf. eq 3 again).⁴ Interestingly, in the case of photolysis in the polymer web, we observed the endo-triphenylbicyclic ketone **14b** as the sole photoproduct. This, too, is outlined in eq 3.

Interpretative Discussion

Factors Controlling the Polymer Web Photochemistry. In our previous studies of the photochemistry of molecular systems confined by a restrictive medium, we found that the reaction course was limited to reaction geometries permitted by the crystal lattice. Minimum molecular motion was one characteristic which we explored quantitatively and generally for a series of reactions.^{3,4} A second controlling factor we found was minimization of overlap of the reacting molecule with the surrounding crystal lattice. Minimum molecular volume displacement did correlate weakly with observation.

Interestingly, photochemical reactivity in the polymer webs, although not the same as in solution, was different from that which we previously encountered in the crystalline state. Hence, the web photochemistry cannot be



reaction condns	product ratio ^a					
	13	14a	14b	15t	15c	16
solution, direct (Benzene)	16	4	-	4	1	-
crystal lattice	-	-	4	-	-	1
matrix ^a polymer (<1% convn)	-	-	only	-	-	-
0 °C, (10% convn)	-	-	only	-	-	-
(20% convn)	-	-	only	-	-	-
25 °C, (1% convn)	-	-	only	-	-	-
(10% convn)	-	-	only	-	-	-
(40% convn)	-	-	only	-	-	-

^a All experiments used 30 wt % cyclohexenone 2 in PMMA.

considered to be controlled in the same way as crystal photochemistry.

Nevertheless, least motion seemed most likely to be involved in understanding the web reactivity. This concept has been proposed to account for some solution ground-state chemistry, however, in a form different from that which seemed most likely applicable to crystal lattice and polymer web confinement control. The original idea of minimization of molecular motion seems to be due to Rice and Teller.^{11a} The idea was quantified by Hine^{11b,c} by comparing the coordinates of the reactant versus product for an elimination reaction. A similar treatment is due to Tee^{11d} who developed a "rigid superposition" treatment in which the product molecule was superimposed on the reactant, and the root mean square (rms) displacement of atomic coordinates was then determined. This method was applied by Tee and Yates^{11e} to a number of ground-state transformations.

For our situation in which an excited state is surrounded by the polymer web, a different approach was required. Thus, in the photochemistry of the vinylcyclopropane 3, the partition among potential pathways is not determined at the excited-state reactant stage (i.e., with geometry of 3), but rather only after three-ring opening to give diradical 17. Thus, we needed to compare motion from that point along the reaction coordinate where a mechanistic partition among pathways takes place. We term this the "branch point" (B). Hence, for each reaction pathway, we need to select two points along the reaction coordinate for deter-

mination of extent of molecular motion: (a) the branch point where the molecule can select two or more pathways and (b) the very next species one can write, the "target species" (T). In some cases, the branch point is the reactant excited state while in other examples it is some (e.g., diradical) species further along the reaction hypersurface.

Secondly, in contrast to the literature which employed ordinary geometries of reactants and products, we needed to consider that conformation of the target species which is closest to that of the branch-point structure, since it is this target conformation that emerges from transformation of the branch point species. Flexible superpositions of the target species to give the best rms fit to the branch point molecule were used with variation of dihedral angles but fixed bond lengths and valence angles.

Where the branch-point species was a diradical intermediate, that conformation of the diradical most resembling its geometry-optimized precursor was employed. Nondiradical branch-point species were themselves geometry optimized. The philosophy here was that diradical branch-point species would be formed in the conformation closest to its predecessor. Without this assumption, poor correlations were observed. This differs from our solid-state studies where the reactant conformation is rigidly controlled by crystal lattice forces.

For determination of molecular change during conversion of the branch-point (B) to the target species (T), we have determined the rms displacement of the various atoms in species B necessary to arrive at the geometry of species T. For each reactant the rms motion for the various B to T conversions is listed in Table 1. A more simple index is the one we utilized in our previous report,⁴ namely the sum of atomic coordinate changes in proceeding from B to T. This index, termed ΔM , is also included in Table 1. Displaced volume, ΔDV , is another measure of the extent of molecular movement. It is defined as the new volume in space occupied by the target molecule which is not already occupied by the branch-point species. This may also be found in Table 1. Finally, total change in molecular volume, ΔV , in proceeding from branch-point to target species was considered as possibly controlling. This index correlated with observation except in the case of diradical 26 leading to cyclobutanone 15.

Schemes 1-3 outline the reaction mechanisms for the three reactants we have investigated. The branch points and target species are specified in the schemes. Thus, for example, in Scheme 1, the initial 1,3-diradical 17, in principle, has the choice of forming any of the three products outlined above in eq 1 in addition to 7 and 8 deriving from carbene (i.e., $\text{Ph}_2\text{C}=\text{CHCH}$: 18) fragmentation. The three major solution products result from the three transformations outlined in Scheme 1. Simple visual inspection of the scheme does not reveal that any one involves less motion than the others. However, reference to Table 1 indicates that intramolecular hydrogen transfer to afford tetraphenyldiene 4 requires less molecular motion as measured by all indices: rms motion, ΔM , ΔDV and ΔV .

In the case of the reaction of tetraphenyldiene 1 we refer to Scheme 2. In this case, at low conversion both di- π -methane photoproducts resulting from vinyl-vinyl bridging are formed in the polymer web while the di- π -methane product 11 resulting from phenyl-vinyl bridging is absent as is the crystal lattice photoproduct 12. It is clear that this is not a consequence of web sensitization,

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Table 1. Correlation of Calculated Reactivity Parameters^a with Observation for Reaction in the Polymeric Web Matrix

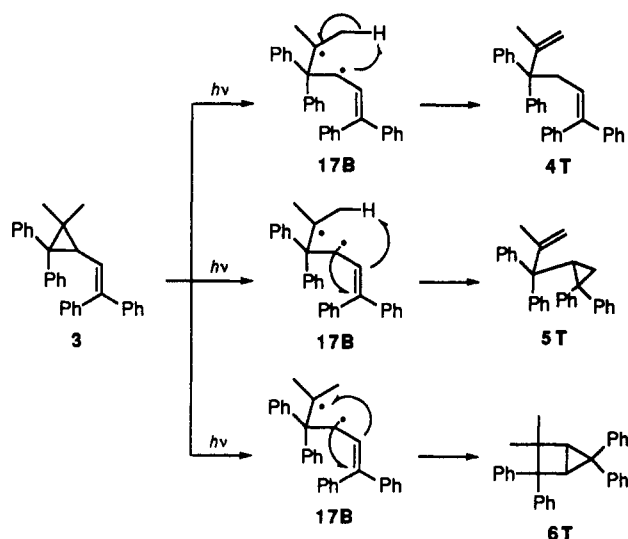
reactant ^b	branch-point species ^{b,c}	target species	rms (Å)	ΔM (Å/atom)	ΔDV (%)	ΔV (Å ³)		
tetraphenyl diene 1	tetraphenyl diene 1	phenyl-bridged diradical 19	3.01	2.69	25.8	8.10		
		triphenyltricyclic triene 12	2.15	1.92	23.6	35.4		
		cyclopropyl carbinyl diradical 20	1.66	1.76	24.6	1.57 ^e		
			1.58	1.56	22.4	9.24 ^d		
		1,4-diradical 20	diphenylvinyl 1,3-diradical 21		1.18	1.28	22.1	-4.24 ^d
					1.86	1.83	26.1	-3.41 ^e
					0.51	0.55	12.0	2.01 ^d
					1.71	2.23	24.4	-1.28 ^e
					2.34	3.13	30.1	-1.04
		enone 2	phenyl-bridged/ diradical 19 enone triplet 2*	phenyl-migrated cyclopropane 11	1.24	2.79	19.4	1.57
half-migrated phenyl diradical 23	2.76			3.42	34.7	-7.46		
cyclobutane precursor diradical 26	2.52			3.39	26.0	6.02		
benzobicyclic diradical 27	1.79			2.02	23.7	1.94		
diene 4	1.91			2.23	27.4	6.37		
vinylcyclopropane 3	1,3-diradical 17	tetraphenylhousane 6	2.38	2.60	26.7	21.6		

^a See text for definitions. ^b All reactants and diradicals were optimized with MM3 molecular mechanics calculations.¹⁶ ^c Branch-point radical geometries used were derived from the geometries that were superimposed on the optimized reactants. ^d *trans*-Cyclopropyldicarbonyl. ^e *cis*-Cyclopropyldicarbonyl. ^f Not a true branch point since only one product.

Table 2. Correlation of Calculated Reactivity Parameters^a with Observation for Crystal Photochemistry of Vinylcyclopropane 3

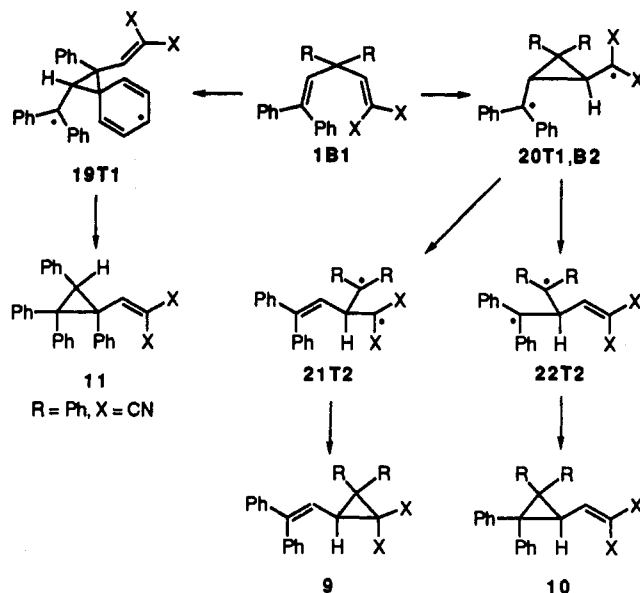
reactant	branch-point species	photoproduct	rms (Å)	ΔM (Å/atom)	ΔDV (%)	ΔV (Å ³)
vinylcyclopropane 3	vinylcyclopropane 3	diene 4	0.47	0.64	13.2	-20.8
		allylcyclopropane 5	2.14	3.18	31.0	-13.3
		tetraphenylhousane 6	2.31	2.44	26.0	3.65
		1,3-diradical 17 ^b	1.35	1.99	24.9	18.5

^a See text for definitions. ^b The optimized geometry of the 1,3 diradical was used.

Scheme 1. Rearrangement Mechanism of Vinylcyclopropane 3

since the solution triplet chemistry leads selectively to dicyanophenylvinylcyclopropane 10 and the singlet reaction affords the formation of 9 and 10. The observed selectivity is nicely predicted by their lesser motion indices as in Table 1.

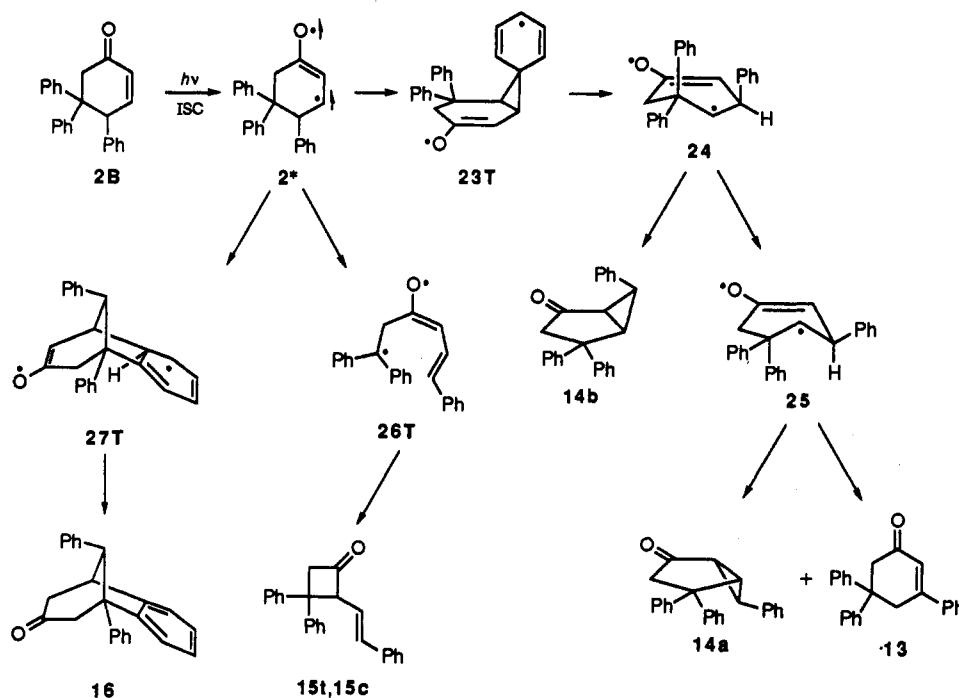
Finally, for the case of the triphenylcyclohexenone 2 the observed reaction mechanisms are outlined in Scheme 3. The most striking feature is the formation of a single photoproduct, the endo stereoisomer of 4,4,6-triphenylbicyclo[3.1.0]hexanone (14b). In solution, the corresponding exo stereoisomer 14a was formed to the exclusion of this endo isomer, with *endo*-phenyl to *endo*-phenyl steric repulsions accounting for the stereochemistry. However, in the polymer photochemistry, the same endo isomer 14b was formed as in the crystal. The formation of the endo stereoisomer, despite intramolecular van der Waals repulsions, makes sense in view of the more compact nature of the endo product and the transition

Scheme 2. Reaction Mechanisms in the Photochemistry of Tetraphenylidene 1

state leading to it. Thus, intermolecular forces have dominated the intramolecular ones. The vinylcyclobutanone 15 was shown in our earlier study⁹ to result from an open-chain diradical intermediate 26. It is not too surprising that this space-demanding mechanism was not seen either in the crystal lattice or in the polymer web. Finally, we note that the web chemistry was even simpler than the crystal lattice behavior in affording only one photoproduct. Superficially, one might think of the polymer web as being relatively more free. However, a crystal lattice environment is irregular and permits selective motions in a way to be discussed in some of our forthcoming publications.

One further item needs consideration, namely the dependence of the product distribution on the extent of conversion. It is known that there is heterogeneity in

Scheme 3. Reaction Mechanisms in the Photochemistry of the Triphenylenone 2



polymer matrices, and, therefore, one might think that some sites would be used first. However, were this the case, the larger cavities would permit more facile reaction and exhibit lower selectivity early in the reaction. Since the converse is observed, this seems unlikely. Another thought is that there might be some crystallinity. However, the differing photoproduct distribution compared with the crystal lattice studies belies this possibility. A likely rationale is that lowered selectivity at higher conversions results from polymer matrix distortion as the reaction proceeds, thus providing a less constraining medium.

Conclusion

The results for the three systems studied are thus seen to correlate nicely with restriction of motion as measured by rms displacements, ΔM (i.e., motion) measurement, ΔDV (displaced volume), and to a lesser extent by minimization of molecular volume (i.e., ΔV). This can be understood in a variety of ways. One can argue that the polymeric environment merely imposes a very high viscosity medium, inhibiting molecular motion. However, this is tantamount to a direct molecular interpretation wherein the reacting species is considered to be entrapped by one or more web polymeric strands.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of anhydrous nitrogen. Melting points were determined with a calibrated Mel-Temp apparatus. Column chromatography was performed on silica gel (J. T. Baker, Inc. 60–200 mesh) mixed with 0.1% (v/v) Silvania 2282 green phosphor and slurry-packed into Vycor quartz columns which were monitored by a hand-held UV lamp. Plates (20 × 20 cm) for preparative thick-layer chromatography were prepared with MN-Kieselgel G/UV 254 silica gel. High-pressure liquid chromatography (HPLC) was performed on a system incorporating a LDC 5000-psi minipump and a LDC 254-nm detector. A 0.46-

× 50-cm polished stainless steel column packed with silica beads¹² was employed with 1 mg of sample separated at a time. Hexane used for HPLC elution was purified by stirring a 1:1 mixture of concentrated nitric acid and sulfuric acid, followed by repeated washing with water until the hexane remained colorless. This was followed by washing with saturated aqueous sodium bicarbonate and saturated sodium chloride, drying over anhydrous calcium chloride, filtration through alumina, and distillation over calcium hydride. Acetonitrile used for HPLC was distilled over calcium hydride. All exploratory irradiations were performed with an immersion well apparatus and a 450-W Hanovia medium-pressure mercury lamp equipped with either a Pyrex ($\lambda > 280$ nm) or a Correx ($\lambda > 260$ nm) 2-mm filter. All photolysis experiments were purged with deoxygenated and dried nitrogen¹³ for 1 h before and during photolysis.

Poly(methyl methacrylate) (PMMA, Aldrich) had a molecular weight of approximately 350 000. It was purified by dissolving the PMMA in chloroform and precipitating the polymer with diethyl ether.^{9c} This precipitation process was repeated three times. After suction filtration, the PMMA was dried under vacuum.

General Procedure for the Preparation and Workup of Thin-Film Photolysis Experiments. The films were prepared by dissolving the appropriate amount of poly(methyl methacrylate) (PMMA) and substrate in chloroform. The chloroform solution was used to coat a 1-L photolytic cell or glass slides. The chloroform was removed in vacuo, leaving a thin film on the inside of the cell or on the glass slide. The slides were suspended 5 cm from the lamp. The polymer films were irradiated for the specified time using the appropriate filter at room temperature or 0 °C. The irradiated film was dissolved in chloroform, the solution concentrated, the residue dissolved in a minimum amount of chloroform, the PMMA precipitated with either hexane or ether, and the filtrate concentrated. The precipitation procedure was repeated three times. The mass balances refer to the photoproducts and starting material isolated and characterized.

Exploratory Photolysis of 4,5,5-Triphenylcyclohex-2-en-1-one (2) in a PMMA Matrix: 1.5-h Photolysis at 0 °C. The polymer film was prepared as described using 225 mg (0.69 mmol) of 4,5,5-triphenylcyclohex-2-en-1-one⁹ (2) and 750 mg of PMMA.

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The film was irradiated for 1.5 h using a Pyrex filter at 0 °C, and the standard workup using hexane yielded 234.7 mg of crude material. The total conversion was approximately 20% as determined by ¹H NMR. The product mixture was seen to be reactant 2 plus endo product 14b with polymer. This crude material was chromatographed on a 63- × 2.5-cm column of silica gel and eluted with 5% diethyl ether in hexane. Fractions were collected in 200-mL increments. Fractions 1–3 (22.1 mg) contained polymer. Fractions 4–7 (16.3 mg, 7.4%) contained polymer with traces of photoproducts. Fractions 8 and 9 (22.3 mg, 9.9%) contained *endo*-4,4,6-triphenylbicyclo[3.1.0]hexan-2-one (14b). Recrystallization from a mixture of ethyl acetate in hexane gave 13.1 mg (5.8%) of the endo product as a white solid, mp 161–162 °C (lit.⁴ mp 145.0–145.5 °C). Fractions 10–12 gave 165 mg (73%) of 4,5,5-triphenylcyclohex-2-en-1-one (2). Recrystallization from ethyl acetate in hexane gave 137.4 mg (61%) of the enone as a white solid, mp 216.0–217.5 °C (lit.⁹ mp 216.5–217.5 °C). NMR analysis provided an upper limit of 3% of isomeric products. The mass balance was 67%.

The spectral data for *endo*-4,4,6-triphenylbicyclo[3.1.0]hexan-2-one (14b) were the following: IR (KBr) 3055, 3050, 1725, 1490, 1445, 1415, 1185, 1015, 775, 715, 700 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.33–6.92 (m, 13 H), 6.70 (d, 2 H, *J* = 7.1 Hz), 3.20 (dd, 1 H, *J* = 5.1, 8.2 Hz), 3.03 (t, 1 H, *J* = 8.7 Hz), 2.75 (dd, 1 H, *J* = 5.0, 8.9 Hz), 2.41 (d, 1 H, *J* = 17.8 Hz), 2.16 (d, 1 H, *J* = 17.6 Hz); MS *m/e* 324.1514 (calcd for C₂₄H₂₀O, *m/e* 324.1485).

Exploratory Photolysis of 4,5,5-Triphenylcyclohex-2-en-1-one (2) in a PMMA Matrix: 30-min Photolysis at 0 °C. The polymer film was prepared as described using 225 mg (0.69 mmol) of 4,5,5-triphenylcyclohex-2-en-1-one (2) and 750 mg of PMMA. The polymer film was irradiated for 30 min at 0 °C using a Pyrex filter. The standard workup using hexane yielded 232.2 mg of crude material. The total conversion was approximately 10% as determined by ¹H NMR. This material was recrystallized from ethyl acetate in hexane yielding 157.7 mg (70%) of 4,5,5-triphenylcyclohex-2-en-1-one (2) as a white solid, mp 215–216 °C (lit.⁹ mp 216.5–217.5 °C). The filtrate was concentrated (74.4 mg) and chromatographed on a 32- × 1.5-cm column of silica gel. The column was eluted with 5% ether in hexane. Fraction 1 (400 mL, 9.3 mg, 4.1%) contained a mixture of 2-(*trans*-2'-phenylvinyl)-3,3-diphenylcyclobutanone (15t) and polymer. Fraction 2 (150 mL, 6.4 mg, 2.8%) contained *endo*-4,4,6-triphenylbicyclo[3.1.0]hexan-2-one (14b) and polymer. Recrystallization with ethyl acetate in hexane gave 2.0 mg (0.8%) of the endo product as a white solid, mp 159–160 °C (lit.⁴ mp 145.0–145.5 °C). Fraction 3 (40 mL, 3.6 mg, 1.6%) contained the endo photoproduct. Recrystallization from ethyl acetate in hexane gave 2.2 mg (0.8%) of the endo product. Fraction 4 (40 mL, 15.6 mg, 6.9%) contained a mixture of the endo product, a small amount of 4,5,5-triphenylcyclohex-2-en-1-one (2), and polymer. Recrystallization from ethyl acetate in hexane gave 1.1 mg (0.5%) of the endo product as a white solid, mp 159–160 °C (lit.⁴ mp 145.0–145.5 °C). Fraction 5 (40 mL, 29 mg, 12.9%) contained 4,5,5-triphenylcyclohex-2-en-1-one (2), a trace amount of the endo photoproduct, and polymer. Recrystallization from ethyl acetate in hexane gave 15.5 mg (6.9%) of the starting enone as a white solid, mp 214–216 °C (lit.⁹ mp 216.5–217.5 °C). NMR analysis provided an upper limit of 3% of isomeric products. The mass balance was 79%.

Exploratory Photolysis of 4,5,5-Triphenylcyclohex-2-en-1-one (2) in a PMMA Matrix: 15-min Photolysis at 0 °C. The polymer film was prepared as described using 225 mg (0.69 mmol) of 4,5,5-triphenylcyclohex-2-en-1-one (2) and 750 mg of PMMA. The polymeric film was irradiated for 15 min at 0 °C using a Pyrex filter. The standard workup using hexane yielded 226.3 mg of crude material. The total conversion was less than 1% as determined by ¹H NMR. Recrystallization from diethyl ether in hexane gave 174.6 mg (78%) of 4,5,5-triphenylcyclohex-2-en-1-one (2) as a white solid, mp 216–217 °C (lit.⁹ mp 216.5–217.5 °C). The filtrate was concentrated (51.4 mg) and chromatographed on a 32- × 1.5-cm column of silica gel. The column was eluted with 5% diethyl ether in hexane. Fraction 1 (550 mL, 7.7 mg, 3.4%) contained an inseparable mixture of *endo*-4,4,6-triphenylbicyclo[3.1.0]hexan-2-one (14b), a trace of an unidentified photoproduct, and polymer. Fraction 2 (40 mL, 5.3 mg, 2.4%) contained an inseparable mixture of the endo photoproduct,

starting enone, and polymer. Fraction 3 contained (40 mL, 4.8 mg, 2.1%) the starting enone. Fractions 4 and 5 (40 mL each) contained 5.7 mg (2.5%) and 3.9 mg (1.7%) of starting enone, respectively. Fractions 3–5 were combined and recrystallized from diethyl ether in hexane to yield 7.8 mg (3.5%) of the starting enone as a white solid, mp 216–217 °C (lit.⁹ mp 216.5–217.5 °C). NMR analysis provided an upper limit of 3% of isomeric products. The mass balance was 82% (starting material only).

Exploratory Photolysis of 4,5,5-Triphenylcyclohex-2-en-1-one (2) in a PMMA Matrix: 3-h Photolysis at Room Temperature. The polymer film was prepared as described using 225 mg (0.69 mmol) of 4,5,5-triphenylcyclohex-2-en-1-one (2) and 750 mg of PMMA. The polymeric film was irradiated for 3 h at room temperature using a Pyrex filter. The standard workup using hexane yielded 263.7 mg of crude material. The total conversion was approximately 40% as determined by ¹H NMR. This material was chromatographed on a 75- × 3-cm column of silica gel and eluted with 5% ether in hexane. Fractions were collected in 200-mL increments. Fractions 1 and 2 nil. Fractions 3–5 (27.2 mg, 12.1%) contained an unidentified photoproduct mixture with traces of 2-(*trans*-2'-phenylvinyl)-3,4-diphenylcyclobutanone. Fractions 6 and 7 (16.7 mg, 7.4%) contained polymeric residue and a trace of an unidentified photoproduct mixture. Fractions 8–11 (52.7 mg, 23.4%) contained *endo*-4,4,6-triphenylbicyclo[3.1.0]hexan-2-one (14b) along with a trace of unidentified photoproducts. Recrystallization from ethyl acetate in hexane gave 37.5 mg (16.7%) of the endo isomer as a white solid, mp 157–158 °C (lit.⁴ mp 145.0–145.5 °C). Fractions 12–17 contained 149.5 mg (66.4%) of 4,5,5-triphenylcyclohex-2-en-1-one (2) as a white solid, mp 218–219 °C (lit.⁹ mp 216.5–217.5 °C). NMR analysis provided an upper limit of 3% of isomeric products. The mass balance was 83%.

Exploratory Photolysis of 4,5,5-Triphenylcyclohex-2-en-1-one (2) in a PMMA Matrix: 30-min Photolysis at Room Temperature. The polymer film was prepared as described using 225 mg (0.69 mmol) of 4,5,5-triphenylcyclohex-2-en-1-one (2) and 750 mg of PMMA. The polymeric film was irradiated for 30 min at room temperature using a Pyrex filter. The standard workup using hexane yielded 232.5 mg of crude material. The total conversion was approximately 10% as determined by ¹H NMR. The yellow solid was recrystallized with ethyl acetate in hexane to give 163.8 mg (73%) of 4,5,5-triphenylcyclohex-2-en-1-one (2), mp 217–218 °C (lit.⁹ mp 216.5–217.5 °C), as a white solid. The filtrate was concentrated and chromatographed on a column of silica gel (64 × 3 cm) and eluted with 5% diethyl ether in hexane. Fractions were collected in 300-mL increments. Fractions 1–4 (60.2 mg) contained polymer. Fraction 5 (18.1 mg, 8.0%) contained *endo*-4,4,6-triphenylbicyclo[3.1.0]hexan-2-one (14b). Recrystallization from ethyl acetate in hexane gave 7.9 mg (3.5%) of the endo isomer as a white solid, mp 161–162 °C (lit.⁴ mp 145.0–145.5 °C). Fraction 6 (20.0 mg, 8.9%) contained a mixture of endo photoproduct and starting material. Recrystallization with ethyl acetate in hexane gave 12.4 mg (5.5%) of the starting enone as a white solid, mp 214–216 °C (lit.⁹ mp 216.5–217.5 °C). NMR analysis provided an upper limit of 3% of isomeric products. The mass balance was 82%.

Exploratory Photolysis of 4,5,5-Triphenylcyclohex-2-en-1-one (2) in a PMMA Matrix: 15-min Photolysis at Room Temperature. The polymer film was prepared as described using 225 mg (0.69 mmol) of 4,5,5-triphenylcyclohex-2-en-1-one (2) and 750 mg of PMMA. The polymeric film was irradiated for 15 min at room temperature using a Pyrex filter. The standard workup using hexane yielded 236.4 mg of crude material. The total conversion was approximately 1% as determined by ¹H NMR. The solid was recrystallized in ethyl acetate in hexane to yield 206.9 mg (92%) of 4,5,5-triphenylcyclohex-2-en-1-one (2), mp 217–218 °C (lit.⁹ mp 216.5–217.5 °C), as a white solid. The residue was chromatographed on a 10- × 20-cm preparative TLC plate and eluted with 1% diethyl ether in hexane twice and 3% diethyl ether in hexane twice. Band 1 (8.6 mg, 3.8%) contained polymer. Band 2 (18.7 mg, 8.3%) contained a mixture of starting enone, *endo*-4,4,6-triphenylbicyclo[3.1.0]hexan-2-one (14b), and polymer. Recrystallization from ethyl acetate in hexane gave 16.2 mg (7.2%) of starting enone, mp 216–217 °C (lit.⁹ mp 216.5–217.5 °C). The filtrate (2.0 mg, 0.9%) contained an inseparable mixture of starting enone, endo photoproduct, and polymer. No

isomeric photoproducts were detected throughout. NMR analysis provided an upper limit of 3% of isomeric products. The mass balance was 99% (starting material only).

Exploratory Photolysis of 2,2-Dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (3) in a PMMA Matrix. A variety of separation methods such as column chromatography, preparative chromatography, and HPLC were used to separate the mixtures of photoproducts. However, none of these methods proved successful in separating the photoproduct mixtures. Therefore, the ^1H NMR data for the known photoproducts¹⁰ were used to identify the products that were produced. The ^1H NMR spectral data used for identification of the photoproducts are presented below. NMR analysis provided an upper limit of 3% of isomeric products.

5-Methyl-1,1,4,4-tetraphenyl-1,5-hexadiene (4):¹⁰ ^1H NMR (200 MHz, CDCl_3) δ 7.39–6.82 (m, 20 H), 5.97 (t, 1 H, $J = 6.7$ Hz), 5.08 (s, 1 H), 4.93 (s, 1 H), 3.13 (d, 2 H, $J = 6.7$ Hz), 1.60 (s, 3 H).

2-(2-Methyl-1,1-diphenyl-2-propenyl)-1,1-diphenylcyclopropane (5):¹⁰ ^1H NMR (200 MHz, CDCl_3) δ 7.32–6.67 (m, 20 H), 5.48 (s, 1 H), 5.15 (s, 1 H), 2.99 (dd, 1 H, $J = 7.4, 9.5$ Hz), 1.55 (s, 3 H), 1.40 (dd, 1 H, $J = 5.1, 7.4$ Hz), 1.27 (d, 1 H, $J = 5.1, 9.5$ Hz).

3,3-Dimethyl-2,2,5,5-tetraphenylbicyclo[2.1.0]pentane (6):¹⁰ ^1H NMR (270 MHz, CDCl_3) δ 7.48–6.74 (m, 20 H), 3.10 (d, 1 H, $J = 6.0$ Hz), 2.30 (d, 1 H, $J = 6.0$ Hz), 1.04 (s, 3 H), 0.83 (s, 3 H).

2-Methyl-1,1-diphenylpropene (7):¹⁰ ^1H NMR (200 MHz, CDCl_3) δ 7.31–7.11 (m, 10 H), 1.80 (s, 6 H).

3-Phenylindene (8):¹⁰ ^1H NMR (200 MHz, CDCl_3) δ 7.63–7.26 (m, 9H), 6.59 (t, 1 H, $J = 2.2$ Hz), 3.51 (d, 2 H, $J = 2.0$ Hz).

Exploratory Photolysis of 2,2-Dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (3) in a PMMA Matrix: 5-min Photolysis at 0 °C. The polymer film was prepared as described using 61.7 mg (0.1 mmol) of 2,2-dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane¹⁰ and 205.6 mg of PMMA. The polymer film was irradiated for 5 min at 0 °C using a Corex filter. The standard workup using ether yielded 81.7 mg of crude material. The total conversion was approximately 21% as determined by ^1H NMR. The distribution of photoproducts was 4.8:1.1:0:1.0:trace 5-methyl-1,1,4,4-tetraphenyl-1,5-hexadiene (4)/2-(2-methyl-1,1-diphenyl-2-propenyl)-1,1-diphenylcyclopropane (5)/3,3-dimethyl-2,2,5,5-tetraphenylbicyclo[2.1.0]pentane (6)/2-methyl-1,1-diphenylpropene (7)/3-phenylindene (8).

Exploratory Photolysis of 2,2-Dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (3) in a PMMA Matrix: 30-min Photolysis at 0 °C. The polymer film was prepared as described using 100 mg (0.25 mmol) of 2,2-dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane and 400 mg of PMMA. The polymer film was irradiated for 30 min at 0 °C using a Corex filter. The standard workup using ether yielded 130.7 mg of crude material. The total conversion was approximately 53% as determined by ^1H NMR. The distribution of photoproducts was 4.0:1.6:2.8:1.3:1.0 5-methyl-1,1,4,4-tetraphenyl-1,5-hexadiene (4)/2-(2-methyl-1,1-diphenyl-2-propenyl)-1,1-diphenylcyclopropane (5)/3,3-dimethyl-2,2,5,5-tetraphenylbicyclo[2.1.0]pentane (6)/2-methyl-1,1-diphenylpropene (7)/3-phenylindene (8).

Exploratory Photolysis of 2,2-Dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (3) in a PMMA Matrix: 2-h Photolysis at 0 °C. The polymer film was prepared as described using 225 mg (0.25 mmol) of 2,2-dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane and 750 mg of PMMA. The polymer film was irradiated for 2 h at 0 °C using a Corex filter. The standard workup using ether yielded 254.6 mg of crude material. The total conversion was approximately 60% as determined by ^1H NMR. The distribution of photoproducts was 5.2:1.5:1.3:1.0:1.6 5-methyl-1,1,4,4-tetraphenyl-1,5-hexadiene (4)/2-(2-methyl-1,1-diphenyl-2-propenyl)-1,1-diphenylcyclopropane (5)/3,3-dimethyl-2,2,5,5-tetraphenylbicyclo[2.1.0]pentane (6)/2-methyl-1,1-diphenylpropene (7)/3-phenylindene (8).

Exploratory Photolysis of 1,1-Dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene (1) in a PMMA Matrix. These experiments used 25 wt % of 1,1-dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene⁸ in PMMA. The solution was prepared by dissolving 1,1-dicyano-3,3,5,5-tetraphenyl-1,4-pentadiene (32.6 mg) and PMMA (130.4 mg) in 2–3 mL of chloroform and coating three slides with the solution. The films were irradiated using a Pyrex filter. The polymer films were dissolved in chloroform and precipitated with hexane (20 mL). The solution was filtered and concentrated.

The ^1H NMR spectra were used to identify the mixture of photoproducts.^{4,8} In all extracted samples, polymeric residue was present. NMR analysis provided an upper limit of 3% of isomeric products. The ^1H NMR spectral data used to identify the photoproducts in the mixture were the following:

1,1-Dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (9):⁸ ^1H NMR (200 MHz, CDCl_3) δ 7.60–7.15 (m, 20 H) 5.75 (d, 1 H, $J = 10$ Hz), 3.46 (d, 1 H, $J = 10$ Hz).

1,1,2,2-Tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane (10):⁸ ^1H NMR (270 MHz, CDCl_3) δ 7.68–6.98 (m, 21 H), 4.13 (d, 1 H, $J = 6.0$ Hz).

1,1,2,3-Tetraphenyl-2-(2,2-dicyanovinyl)cyclopropane (11):⁸ ^1H NMR (270 MHz, CDCl_3) δ 7.60–7.00 (m, 21 H), 5.47 (s, 1 H).

7,7-Dicyano-9,9,11-triphenyltricyclo[6.3.0.0^{1,6}]undeca-2,4,10-triene (12):⁴ ^1H NMR (200 MHz, CDCl_3) δ 7.82–7.10 (m, 16 H), 6.28 (m, 1 H), 5.93 (m, 2 H), 5.45 (d, 1 H, $J = 10.0$ Hz), 4.60 (s, 1 H), 3.80 (br s, 1 H).

20-min Photolysis at Room Temperature. The slide was irradiated for 20 min at room temperature. After the standard workup using hexane, the ^1H NMR revealed approximately 10% conversion to photoproducts. The distribution of 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (9) and 1,1,2,2-tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane (10) was approximately 1:1 with a trace of 7,7-dicyano-9,9,11-triphenyltricyclo[6.3.0.0^{1,6}]undeca-2,4,10-triene (12) present based on the ^1H NMR spectrum.

One-Hour Photolysis at Room Temperature. The slide was irradiated for 1 h at room temperature. After the standard workup using hexane, the ^1H NMR revealed approximately 26% conversion to photoproducts. The distribution of 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (9) and 1,1,2,2-tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane (10) was approximately 1.2:1 with a trace of 7,7-dicyano-9,9,11-triphenyltricyclo[6.3.0.0^{1,6}]undeca-2,4,10-triene (12) present based on the ^1H NMR spectrum.

Three-Hour Photolysis at Room Temperature. The slide was irradiated for 3 h at room temperature. After the standard workup using hexane, the ^1H NMR revealed approximately 40% conversion to photoproducts. The distribution of 1,1-dicyano-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (9), 1,1,2,2-tetraphenyl-3-(2,2-dicyanovinyl)cyclopropane (10), and 7,7-dicyano-9,9,11-triphenyltricyclo[6.3.0.0^{1,6}]undeca-2,4,10-triene (12) was approximately 3:1:0.5 based on the ^1H NMR spectrum.

Exploratory Solid-State Photolysis of 2,2-Dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (3). In an NMR tube, 2,2-dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (31.1 mg, 0.08 mmol) crystals (needles from ethanol) were irradiated using a Corex filter for 14.5 h. The crystals were dissolved in chloroform- d_3 , and the ^1H NMR spectrum was obtained. The crude spectrum showed a 10% conversion to a single photoproduct based on the ^1H NMR. This photoproduct was identified as 5-methyl-1,1,4,4-tetraphenyl-1,5-hexadiene (4) based on the ^1H NMR spectral data.

Single-Crystal X-ray Structure of 2,2-Dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (3). Single crystals of 2,2-dimethyl-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane were prepared by slow evaporation of ethanol. X-ray data were collected with Cu K α radiation on a Siemens P4 diffractometer from a prism-shaped crystal of dimensions $0.3 \times 0.4 \times 0.6$ mm. Unit cell parameters were obtained by least-squares refinement of 25 reflections. Data were collected with three reflections monitored every 50 reflections. A total of 2814 unique reflections were collected with 2475 of $F > 4\sigma(F)$. Lorentz and polarization corrections were applied, and the structure was solved under $P2_1c$ symmetry by direct methods using SHELXTL PLUS (VMS).¹⁷ A full matrix least-squares refinement was carried out with anisotropic thermal parameters for all carbon atoms and

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isotropic thermal parameters for all hydrogen atoms. Refinement of 281 parameters converged to $R(F) = 8.81$ and $R_w(F) = 14.16$.²⁰

Molecular Mechanics Calculations. Molecular mechanics calculations were performed with MM3.¹⁶ For diradical species in which an aryl group is half migrated, the spiro system is treated as a cyclopropyl ring, and the odd-electron centers are treated as sp^2 carbons.

General Procedure for Geometric Analysis. Geometry analyses were performed with MACROMODEL.^{14,15} Superimpositions were accomplished with the flexible superimpositions routine. Volumes were calculated with the use of a modified version of VOLUME from the TRIBBLE package.¹⁸ The volume program calculates the volume of a molecule by placing the molecule in a three-dimensional box of known volume and generating a large number of random points within the box. The fraction of the points that were within the van der Waals radii of any atom in the molecule is the fraction of volume of the box displaced by the molecule. The program was modified to allow

a variable-point density and averaging of a series of volume calculations. The point density used and the number of averaged calculations gave a reproducibility better than $\pm 1\%$. The van der Waals radii used were those reported¹⁹ in the literature.

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Supplementary Material Available: Complete proton NMR data, with peak assignments (2 pages). This material is contained in 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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