JOC Article

Regioselectivity of the Tri-π-methane Rearrangement: Mechanistic and Exploratory Organic Photochemistry[1,2]

Howard E. Zimmerman* and Tibor Novak

Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706

zimmerman@chem.wisc.edu

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The di-π-methane rearrangement with two π-groups attached to the central "methane carbon" of the reactant and which leads to a π-substituted cyclopropane has been studied intensively. Our present research had the goal of elucidating the regioselectivity of the tri-π-methane counterpart. The reactants with three π groups attached to the central carbon mechanistically are capable of affording both di-π-methane and tri-π-methane photoproducts. In common with the di-π-methane system, bridging of two of the π-systems affords a cyclopropyldicarbinyl diradical intermediate that opens to an allyl carbinyl diradical. This diradical has the option of closing to a three-membered or a five-membered ring. It was found that the regioselectivity of the initial π−π-bridging step and the three-ring opening of the cyclopropyldicarbinyl diradical exhibit regioselectivity parallel to that of the di-π counterpart. Both three-ring and five-ring photoproducts were formed with the ratio varying with conversion. Since the three-ring (i.e. di-π-methane) photoproducts were found to ring expand to the five-ring (i.e. tri-π-methane) products, kinetics were employed to determine to what extent the reaction proceeds in a two-step versus direct formation of the five-ring product. It was found that the direct route was the major one.

Introduction

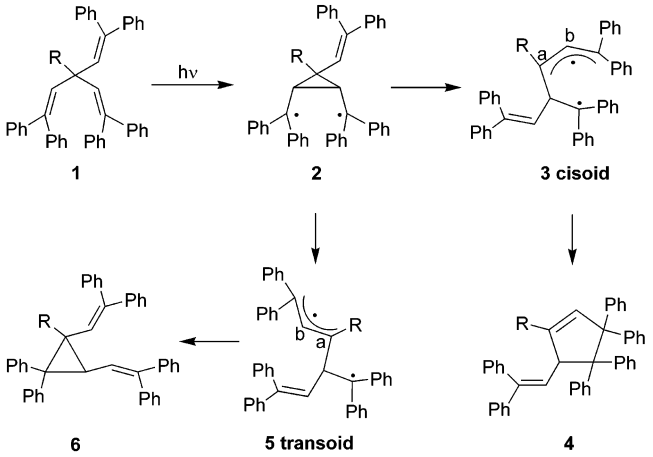
Recently we reported the tri-π-methane rearrangement,[3,4] which is related to the well-known di-π-methane counterpart.[5] As with the di-π-methane reaction, the mechanism (note Scheme 1) begins with π−π bridging to afford a cyclopropyldicarbinyl diradical. However, on three-ring opening, the diradical produced is allylic and may close to either a three-membered or five-membered ring.

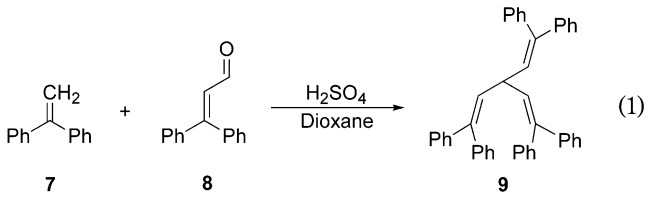
In the case of the di-π-methane rearrangement,[5] investigations of the effect of para substituents on regioselectivity,[6] as well as in other unsymmetrical systems,[5c] afforded insight into mechanistic details. Thus it was of special interest in the present study to investigate the tri-π-methane rearrangement regioselectivity.

Results

Synthetic Aspects. In our previous study[3] a very simple approach to the trivinylmethane structure was developed by using the Prins reaction as shown in eq 1.

SCHEME 1. The Di-π-methane and Tri-π-methane Rearrangements





(1)

However, with para substitution in the diphenylacrolein reactant (i.e. **8**) anticipated to afford substitution in one of the three vinyl moieties, an unanticipated but rather interesting reaction occurred. In each case the unsubsti-

(1) This is paper 271 of our general series.

(2) For paper 270 see: Zimmerman, H. E.; Nesterov, E. E. *J. Am. Chem. Soc.* **2003**, *125*, 5422−5430.

(3) Zimmerman, H. E.; Cirkva V. *J. Org. Chem.* **2001**, *66*, 1839−1851.

(4) One early example of the tri-π-methane rearrangement occurred only in a solid-state photolysis; note: Zimmerman, H. E.; Zuraw, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 7974−7989.

(5) (a) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718−1727. (b) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281−292. (c) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6259−6267.

(6) (a) Zimmerman, H. E.; Gruenbaum, W. T. *J. Org. Chem.* **1978**, *43*, 1997−2005. (b) Zimmerman, H. E.; Welter, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 4131−4145.

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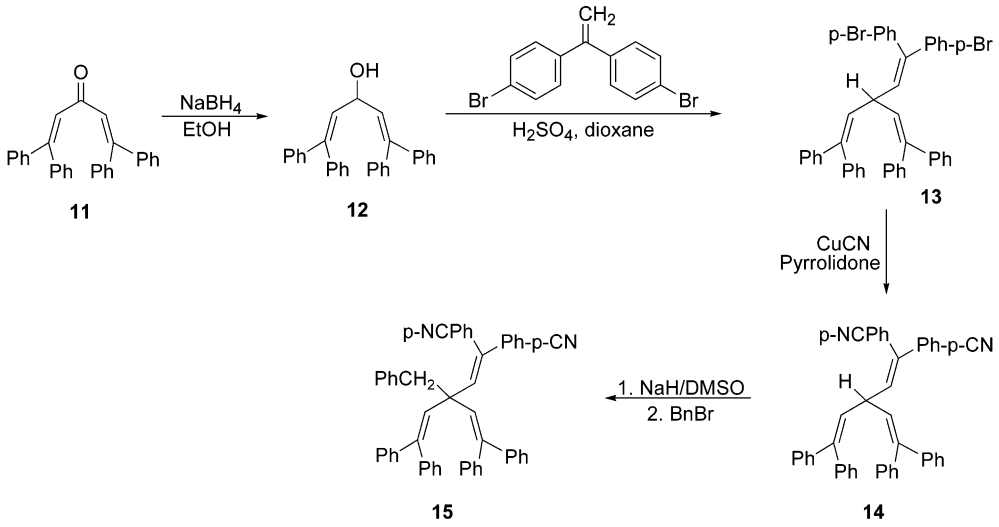
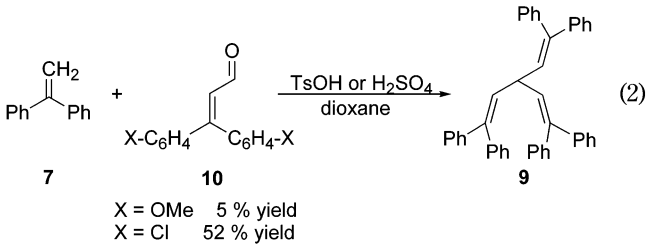
SCHEME 2. Synthesis of the Dicyanophenyl Triene



tuted hexaphenyl product **9** resulted. Note eq 2. The

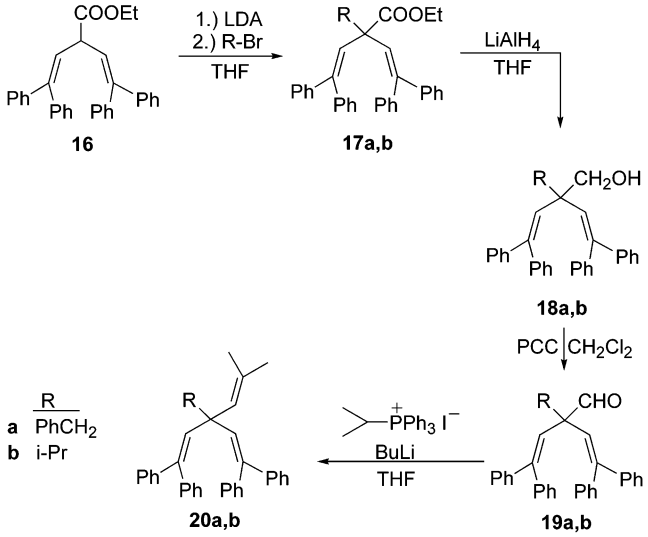


(2)

reaction results from the reversibility of the Prins reaction and also the low reactivity of di-*p*-chlorophenylethylene;[7] however, consideration of the mechanism is delayed to the Discussion section (vide infra).

Thus different approaches were needed. These are as outlined in Schemes 2 and 3. The synthesis in Scheme 2, beginning with the known[14] tetraphenyldienone **11**, is basically a modified Prins sequence wherein the dienol **12** employed is the first intermediate of a more typical Prins reaction. This synthesis afforded a 53% yield of tri-π-methane **13**. Also, this result confirms that the problem in the original approach (note eq 2) was with formation of diphenylacrolein **8** as a consequence of the Prins reversibility, and in the present synthesis **8** is not formed.

SCHEME 3. Synthesis of the Isopropylidene Tri-π-methane Systems



Scheme 3 outlines the approach employed where one isopropylidene moiety was desired. This approach, starting with the known[3] carbethoxydiene **16**, was employed since the Prins approach was unsuccessful with dimethylacrolein and diphenylethylene as reactants.

Another interesting facet was the observation that the trienyl carbanions derived from trienes **9** and **14** were uniquely deep blue. The alkylation of these anions went regioselectively at the center carbon. Similarly, protonation of the delocalized species occurred at the central carbon. This regioselectivity is considered in the Discussion section.

The structures of the tri-π-methane species (**15**, **20a**, and **20b**) were confirmed by NMR, mass spectral analysis, and X-ray in the case of the di-*p*-cyano-triene **15**.

Exploratory Photochemistry. (a) Reactivity of the Isopropylidene Tri-π-methane Reactants. Equation 3 outlines the course of the direct and sensitized photolyses of the isopropylidene tri-π-methane reactants. Both on direct and acetophenone-sensitized irradiation photoproducts **21**, **22**, and **23** were observed. In addition, photoproduct **24b** was encountered in sensitized runs of

(7) (a) Zimmerman, H. E.; English, J., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 2285−2290. (b) Zimmerman, H. E.; English, J., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 2291−2294. (c) Zimmerman, H. E.; English, J., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 2294−2300.

(8) *Quantum Mechanics for Organic Chemists*; Zimmerman, H. E., Ed.; Academic Press, New York, 1975; pp 153−155.

(9) Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. *J. Am. Chem. Soc.* **1973**, *95*, 5094−5095.

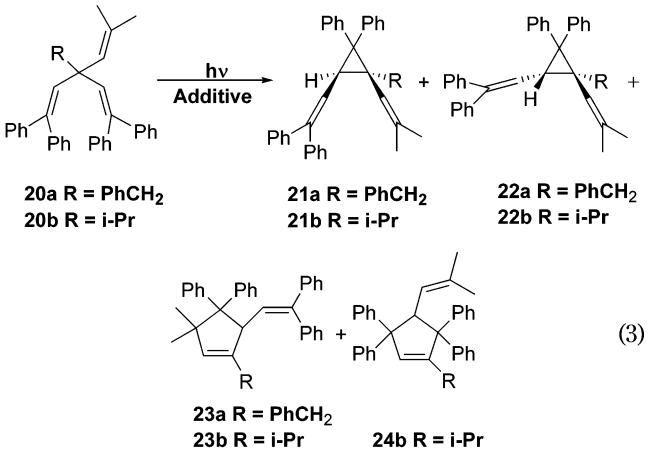
(10) (a) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6267−6271. (b) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531−551. (c) Zimmerman, H. E.; Schissel, D. N. *J. Org. Chem.* **1986**, *51*, 196−207.

(11) (a) Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367−6383. (b) Zimmerman, H. E.; Factor, R. E. *Tetrahedron*, **1981**, *37*, Suppl. 1, 125−141. (c) Zimmerman, H. E.; Penn, J. H.; Johnson, M. R. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2021−2025.

(12) (a) Sheldrick, G. M. *SHELXTL*, Version 5.1; Bruker AXS, Inc.: Madison, WI, 1997. (b) Obtained from Prof. G. Sheldrick, Göttingen.

(13) Corey, E. J.; Suggs, J. W. *Terahedront. Lett.* **1975**, *31*, 2647−2650.

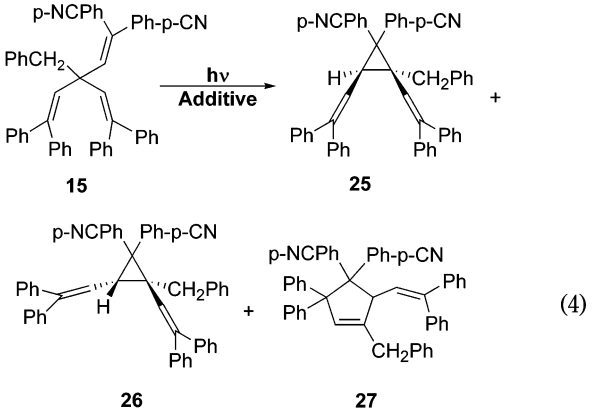
(14) Marin, G.; Chodkiewicz, W.; Cadiot, P.; Willemart, A. *Bull. Soc. Chim. Fr.* **1958**, 1594−1597.



(3)

20b. Table 1 summarizes the product distributions from both the benzyl reactant **20a** and the isopropyl reactant **20b** in high conversion runs. The product distribution varied with the extent of conversion; and product distributions as a function of conversion are given below in connection with the reaction kinetics. One other point is that photoproduct **23** was a very minor product in the acetophenone-sensitized runs while **24b** was encountered only in the sensitized photolysis of **20b**.

(i) Reactivity of the Tris-diarylvinyl Tri-π-methane Reactants. In the case of the cyano-substituted triene **15**, the direct and sensitized photochemistry, again, proceeded to afford both di-π-methane and tri-π-methane products. As with the isopropylidene reactions, acetophenone sensitization did not lead to the tri-π-methane product. These runs are described in eq 4. Table 2 summarizes typical photochemical product distributions.



(4)

(ii) Assay of Photoproducts for Kinetic and Identification Purposes. In the reactions described above, the photoproducts were separated by column chromatography and crystallization as described in the Experimental Section. The mass balances were generally close to 80%. However, for kinetic purposes, NMR analysis proved most helpful. Thus, the di-π-methane and tri-π-methane photoproducts were easily identified as a consequence of their characteristic NMR spectra. For example, the AB quartet of the di-π-methane products (**21**, **22**, and **25**, **26**) derived from the vicinal cyclopropyl methine and diphenylvinyl hydrogen. Cyclopentenes (**23** and **27**) have a very typical broad doublet, a broad triplet, and a sharp doublet coupling pattern as a consequence of allylic coupling. The structures of all products were similar to those reported earlier.[3] The structures of **21a** and **25** were established by X-ray and thus confirmed the validity of the NMR spectral assignment methodology.

(b) Kinetic Aspects. In our previous study[3] of the tri-π-methane rearrangement we encountered two routes to the five-membered-ring products: a direct route and an indirect route proceeding via the three-ring photoproduct as outlined in Scheme 4 for the present cases. Using the kinetic approach of our previous study, the partition between these routes was determined. For this it was necessary to obtain the product distributions as a function of extent of conversion. The detailed data are given in the Supporting Information but examples are plotted in Scheme 5.

Direct irradiations were used for the kinetic runs. In addition, runs were made with a naphthalene sensitizer under concentration conditions where naphthalene absorbs minimally 99% of the light and with reactant concentrations high enough to permit singlet energy transfer. The purpose of the naphthalene was to have constant light absorption as the reaction proceeded and the distribution of compounds, with slightly different absorbtivities, varied.

In Scheme 4a,b, the reactants are labeled "A", the di-π-methane products are labeled "B", and the tri-π-methane products are labeled "C". We note here that the cis and trans stereoisomers of the di-π-methane products are taken as one kinetic entity, since they are rapidly equilibrated. The analytic expressions for an A−B−C sequence in which "A" may also proceed directly to "C" had not been solved, but were derived in our earlier publication.[3] Equation 5 gives the relative concentration of species "B" as a function of time. Then eq 6a gives the deviation of B from experiment at a single time corresponding to variations of k_1, k_2, and k_3. For measurements at a series of times, we obtain eqs 6b, giving ΔB_1, ΔB_2, ΔB_3, etc., as deviations from the theoretical B as given in eq 5 and at times t_1, t_2, t_3, etc. The partial derivatives in 6 are obtained from derivatization of eq 5 and thus are known. Hence we have a large series of simultaneous eqs 6b with deviations of B as a function of variations in the three rate constants. It is necessary to adjust the Δk values to minimize the ΔB_t values. The problem is overdetermined and one can solve for the deviations of the rate constants.

$$B = (k_1A_0)[e^{-(k_1+k_2)t} - e^{-k_3t}]/(k_3 - k_1 - k_2) \qquad (5)$$

$$\Delta B_t = (\partial B_t/\partial k_1)\Delta k_1 + (\partial B_t/\partial k_2)\Delta k_2 + (\partial B_t/\partial k_3)\Delta k_3 \qquad (6)$$

These equations can be formulated more neatly in matrix form as in eqs 7a and 7b. Then, solving for the unknown deviations of the rate constants needed to minimize error in the calculated B versus time, we obtain eq 8.

$$\begin{bmatrix}\Delta B_1\\ \Delta B_2\\ \Delta B_3\\ \vdots\end{bmatrix} = \begin{bmatrix}(\partial B_1/\partial k_1) & (\partial B_1/\partial k_2) & (\partial B_1/\partial k_3)\\ (\partial B_2/\partial k_1) & (\partial B_2/\partial k_2) & (\partial B_2/\partial k_3)\\ (\partial B_3/\partial k_1) & (\partial B_3/\partial k_2) & (\partial B_3/\partial k_3)\\ \vdots & \vdots & \vdots\end{bmatrix}\begin{bmatrix}\Delta k_1\\ \Delta k_2\\ \Delta k_3\end{bmatrix} \qquad (7a)$$

$$\mathbf{\Delta B} = \mathbf{F}\ \mathbf{\Delta k} \qquad (7b)$$

$$\mathbf{\Delta k} = (\mathbf{F^tF})^{-1}\mathbf{F^t\Delta B} \qquad (8)$$

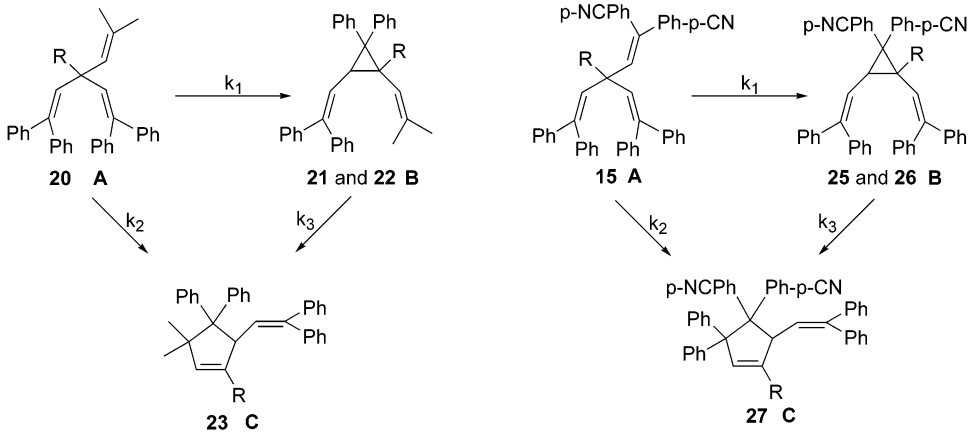
TABLE 1. Photoproducts Obtained on Direct and Sensitized Irradiation of 20a and 20b

reactant	additive	irrad. time (min)	conv (%)	cis-di-π-photoproduct **21**	trans-di-π-photoproduct **22**	tri-π-photoproduct **23**	secondary photoproduct **24b**
20a	none	12	66	24	19	23	0
20a	none	50	100	35	23	42	0
20b	none	9	75	21	20	34	0
20b	none	35	100	20	17	63	0
20a	acetophenone	18	100	67	28	5	0
20b	acetophenone	8	100	45	10	trace	45

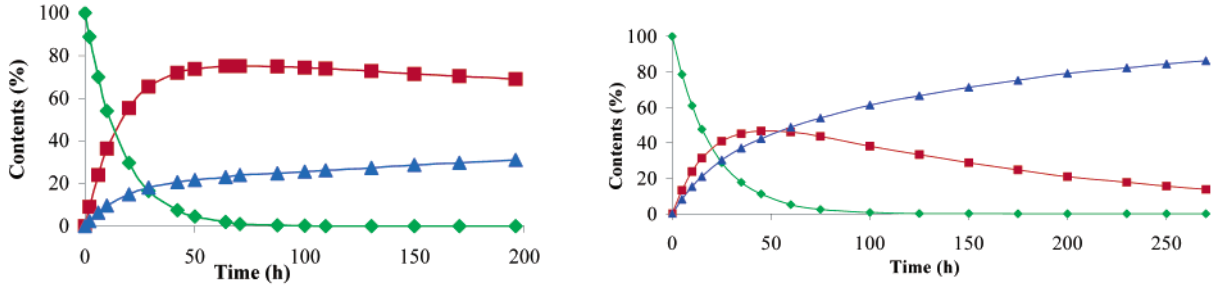
TABLE 2. Photoproducts Obtained on Direct and Sensitized Irradiation of 15

reactant	additive	irrad. time (min)	conv. (%)	cis-di-π-photoproduct **25**	trans-di-π-photoproduct **26**	tri-π-photoproduct **27**
15	none	25	82	32	32	18
15	none	50	100	34	27	39
15	acetophenone	20	100	53	47	0

SCHEME 4. Alternative Reaction Pathways Leading to Tri-π-methane Products



SCHEME 5. Kinetics of Direct Solution Photolysis of Tri-π-methane Reactants (15 and 20b)[a]



[a] Diamonds are for the tri-π-methane reactant, squares are for di-π-methane, and triangles are for the tri-π-methane photoproducts: left, **15**; right, **20b**.

Further details of the derivation are given in our previous publication[3] and there is a description of our program "ABC_kinetics", which obtains the rate constants iteratively. Thus one starts with a set of assumed rate constants and the vector of eq 7 listing the differences in experimental and theoretical concentrations of B as a function of time. Equation 8 solves for the errors in the three rate constants corresponding to these errors. Then the program "ABC_kinetics" in each step calculates the change in the correction in each rate constant to diminish the error in the concentration of B. Table 3 gives the rate constants obtained in this way.

Interpretative Discussion

General. Having dealt with the experimental observations, we now need to interpret these results. Thus, one aspect of the synthesis is of particular interest, namely the regioselectivity of electrophilic attack on a delocalized trivinyl methane system. However, most of our efforts have been photochemical and are to be interpreted.

Hence, we note that in the direct irradiations the tri-π-methane and di-π-methane rearrangements occur competitively and that the ratio of the two types of photoproducts is dependent on the extent of conversion. At higher conversions, we find an increasing amount of five-

TABLE 3. Representative Relative Rate Constants

tri-π-methane reactant	sensitizer	obsd relative rate constants k_1	k_2	k_3
3-benzyl tri-π-methane (**20a**)	none	0.02396	0.01117	0.00149
	naphthalene	0.02658	0.00365	0.00160
3-isopropyl tri-π-methane (**20b**)	none	0.03109	0.01851	0.00609
	naphthalene	0.04271	0.01399	0.00592
3-benzyl dicyano-π-methane (**15**)	none	0.04850	0.01236	0.00081
	naphthalene	0.04677	0.01197	0.00096

FIGURE 1. Bond orders of type 1,2 are larger than those of type 2,3.

membered-ring formation. Thus there are two modes of formation of the vinylcyclopentenes: a direct formation and a secondary reaction of the vinylcyclopropanes. The sensitized reactions lead to little or none of the tri-π-methane products.

Synthetic: Regioselectivity of Alkylation and Protonation. It was noted in the Results section that both alkylation and protonation of the trivinylmethyl carbanions proceeded regioselectivity at the central carbon. This phenomenon has been encountered previously in the case of pentadienyl-type systems where, again, protonation occurs at the central carbon. The effect results from the highest electron density being at the central carbon. The same effect is now seen in the trivinylmethyl carbanions. Interestingly, simple Hückel computations of these odd-alternant systems predict equal density at the central and allylic carbons. However, as has been noted,[8] even Hückel theory is not naïve regarding the bond orders of such systems. The bond orders of the bonds allylic to the central carbon (type 1,2 in Figure 1) are larger than those of type 2,3.

With the pentadienyl 1,2-bond orders in these systems compared with the 2,3-bond orders, the corresponding 1,2-resonance integrals (and the Fock Matrix elements in SCF theory) become larger than the 2,3-counterparts. This then leads to concentration of the electron density at the central carbon.

Regioselectivity of the Isopropylidene Tri-π-Methane Reaction. Several aspects are of special interest in the reactions of the isopropylidene reactants **20a** and **20b**. The first is the partition between Paths A and B as outlined in Scheme 6. In the direct irradiation there is a preference for bridging between the two diphenylvinyl groups to afford diradical **28** compared with bridging between one diphenylvinyl and one isopropylidene to give diradical **30.** This is readily understood on consideration of the greater odd-electron delocalization of diradical **28** in Path A compared to diradical **30** in path B; the preferred diradical **28** has benzhydryl delocalization for both odd-electron centers while species **30** has only one benzhydryl group.

Additionally, the S_1 rates for di-π-methane reactants **35**[5a] and **37**[5c] (Scheme 7) are known.[9] That for S_1 of the "Mariano compound" **35** is 1.4×10^{11} while that for S_1 of the "Pratt compound" **37** is 6.9×10^9; note Scheme 7, thus illustrating the effect of extra delocalization.

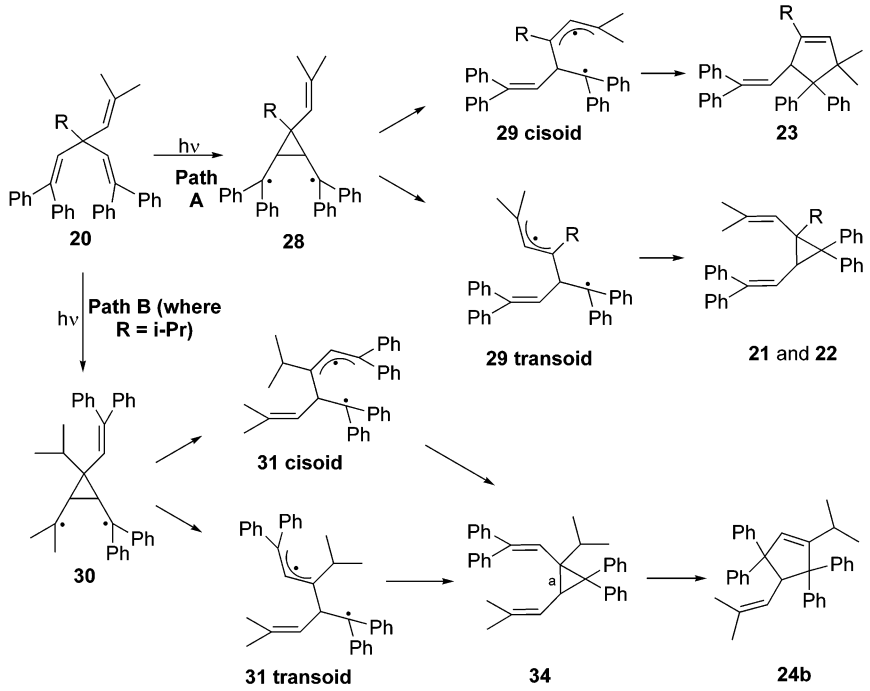
In the case of the triplet of **20** with R = i-Pr it appears that steric congestion inhibits bonding of the two diphenylvinyl moieties to the extent that Path B becomes accessible. Another point is that the triplet of **20** is reactive only where the central substituent is isopropyl but not benzyl. In the simpler di-π-methane systems the triplets of acyclic dienes generally are either nonreactive or minimally so. One exception is those with bulky substituents, as isopropyl, on the central (i.e. "methane") carbon.[10c] The lack of reactivity has been attributed to a "free-rotor effect",[9,10] wherein triplet excited π-bonds tend to dissipate energy by rotation with concomitant intersystem crossing to the ground state. However, in the case of the tri-π-methane system presently studied with isopropyl central substitution (i.e. **30**), the bulky nature of the groups bonded to the "methane carbon" inhibits free-rotor energy dissipation. With the benzyl group at the central carbon, the triplet is unreactive. This is not unexpected, since the bulky phenyl part of this group is more remote.

The mechanism of formation of vinylcyclopentene **24b** is relevant to the triplet reactivity. This product appears to be formed via the di-π-methane precursor **34**, which is seen in the NMR spectrum of the reaction mixture at lower conversion but is not formed in sufficient quantities to permit isolation (note the Experimental Section).

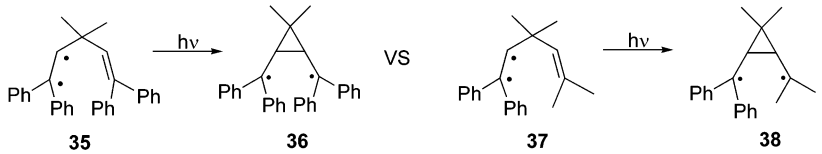
Regioselectivity of the Bis-*p*-Cyanophenylvinyl Tri-π-methane Reactant. Turning next to consideration of the reactivity of the cyanophenyl tri-π-methane reactant, we find in Scheme 8 that the regioselectivity, again, is definitive with preferential bridging to give that diradical which has the greater odd-electron delocalization (i.e. **39** rather than **41**). Both the di-π-methane (**25** and **26**) and tri-π-methane (**27**) photoproducts are formed with the former being preferred. Again, the amount of five-membered-ring product increased with the extent of conversion suggesting a contribution from a secondary reaction of the initial di-π-methane product. This point is considered further in connection with discussion of the reaction kinetics. As in the case of the isopropylidene reactant, the triplet led only to the di-π-methane photoproducts.

Di-π-methane Versus Tri-π-methane Photoproduct Formation. We have seen that the tri-π-methane photoproducts are formed only in the direct (i.e. S_1) irradiations. This is understood when one considers that triplet diradicals prefer to have their odd-electron centers as remote as possible. The effect relates to our "large K − small K" exchange integral postulate,[11] which suggested that in general singlets prefer "small K" transition

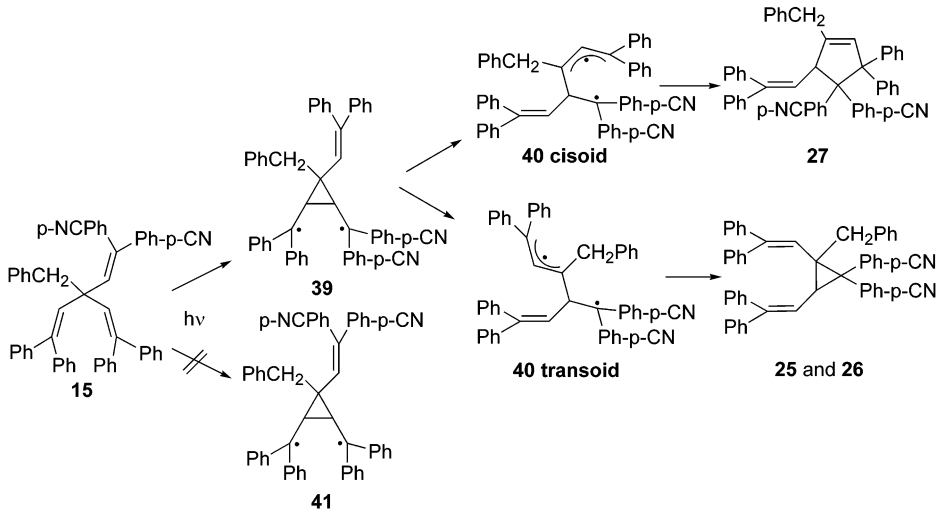
SCHEME 6. Mechanism of the Tri-π-methane Rearrangement in Competition with the Di-π-methane Process in the Case of 20



SCHEME 7. Comparison of Two Singlets Processes



SCHEME 8. Mechanism of the Tri-π-methane Rearrangement in Competition with the Di-π-methane Process in the Case of 15



structures while triplets prefer "large *K*" reaction routes. Note Figure 2. The quantum mechanical exchange integral, 2*K*, increases with odd-electron separation. Thus, the transoid open diradicals **29** and **40** have larger *K* values than the cisoid counterparts and are preferentially formed from triplet precursors. However, these transoid allylic systems cannot close to five-membered-ring products. Conversely, the cisoid allylic diradicals **29** and **40**, with lesser odd-electron separations, are preferentially formed from the singlet (i.e. S_1) precursors. These can close to the five-membered-ring products.

Discussion of the Kinetic Results

Experimentally, the three-membered-ring photoproducts (**21**, **22**, **25**, and **26**) dominate, and reference to Table 3 reveals that in general the rate constant k_1 for direct formation of the di-π-methane product is the largest of

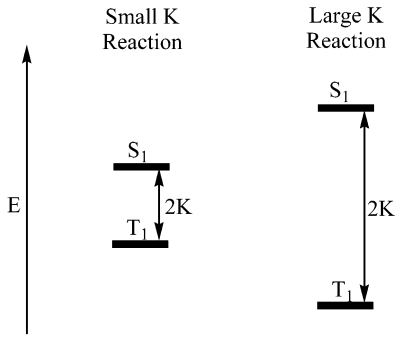
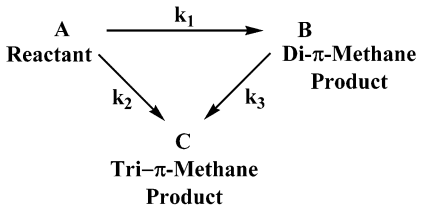


FIGURE 2. Energy levels as a function of singlet−triplet separation and the exchange integral.

SCHEME 9. Alternative Reaction Pathways Leading to Tri-π-methane Products



the three involved (note Scheme 9) in both the direct and the naphthalene-sensitized runs. However, the question was whether there is a direct route for formation of the tri-π-methane photoproduct rather than merely a route proceeding via initial formation of the di-π-methane product. Comparison in Table 3 of k_2 with k_3 shows that the direct route has an effective rate constant k_2 that is from 2.3- to 15-fold larger than k_3, the rate constant for the secondary process. We need to recognize that these rate constants are "operational" and include effects due to differential light absorption in the direct irradiation runs and effects due to differential energy transfer in the naphthalene singlet-sensitized runs. In both the direct and naphthalene sensitized S_1 reactions we can conclude that the direct route for formation of the tri-π-methane photoproduct is the dominant one.

Conclusion

Three new examples of the tri-π-methane rearrangement have been found and their regioselectivity studied. There is a parallelism with the di-π-methane rearrangement in the initial $\pi-\pi$-bridging step with a preference for the more delocalized cyclopropyldicarbinyl diradical. The dependence on multiplicity appears to result from the tendency of triplets to afford the transoid conformer of the allylic-carbinyl diradical resulting from three-ring opening of the cyclopropyldicarbinyl diradical. Finally, the tri-π-methane product is shown to arise by two routes, a direct one and a two-step one that proceeds via a di-π-methane product initially formed. A kinetic treatment shows that the direct route is the predominant one.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of dry nitrogen. Melting points were determined in open capillaries with a Meltemp heating block. Column chromatography was performed on silica gel (Aldrich, 60 Å, 200−400 mesh) mixed with 1% (v/v) of fluorescent indicator (Sylvania 2282 green phosphor, UV_{254}) and slurry packed into quartz columns to allow monitoring with a hand-held UV lamp. Tetrahydrofuran, diethyl ether, and 1,4-dioxane were purified by storage over potassium hydroxide, followed by successive distillation under a nitrogen atmosphere from calcium hydride and sodium benzophenone ketyl. Dimethyl sulfoxide was distilled from calcium hydride prior to use. Photograde benzene (1 L) was prepared by washing two times with a mixture of 100 mL of saturated potassium permanganate and 10 mL of sulfuric acid, water, saturated sodium bicarbonate, and brine, drying over calcium chloride, and distilling from calcium hydride.

^{1}H NMR spectra were recorded at 300 MHz and are reported in ppm downfield from tetramethylsilane. UV spectra were measured at 25 °C in hexane. The high-resolution electron impact mass spectra were run at 150 °C source temperature on a MS50TC ultra-high-resolution mass spectrometer manufactured by Kratos, Inc. (Manchester, England). The samples were run via direct insertion probe and the data collected via a Kratos DS-55 data acquisition system.

General Procedure for Kinetic Photolyses. Kinetic solution photolyses were carried out in sealed NMR tubes (17 cm × 0.5 cm o.d.) in d_6-benzene under nitrogen at 25 °C. The tube was irradiated in a Black-box apparatus.[5b] Three filter cells were used (2.0 M $NiSO_4$ in 5% H_2SO_4, 0.004 M $SnCl_2$ in 15% HCl, and 0.8 M $CoSO_4$ in 5% H_2SO_4) providing a 300−350-nm band-pass.

General Procedure for Preparative Solution Photolyses. Preparative photolyses were carried out with an immersion well apparatus and a Hanovia 450 W medium-pressure mercury lamp equipped with a 5-mm recirculating filter solution of 0.020 M copper sulfate. The solution was purged with deoxygenated and dried nitrogen for 1 h prior to and during photolysis.

General Procedure for X-ray Crystallography Analysis. X-ray diffraction data were collected on a Bruker-AXS P4 diffractometer with a Smart 1000 CCD area detector for single crystals of each compound. Lorentz and polarization correction were applied, and each structure was solved with the appropriate space group symmetry by direct methods with use of SHELXTL[12a] and SHELXS.[12b] Hydrogen atom positions were calculated at idealized positions and included in the structure factor calculation with fixed isotropic displacement parameters. Full-matrix least-squares refinement on F^2 was carried out employing anisotropic displacement parameters for all non-hydrogen atoms. The Crystallographic Information Files (cif files) for all compounds studied by X-ray crystallography are provided as Supporting Information.

Ethyl 2-Alkyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenoate (17). To a solution of 3.2 mL (22.8 mmol, 2 equiv) of diisopropylamine in 90 mL of anhydrous THF at −10 °C was added dropwise 10.6 mL (15.77 mmol, *c* 1.49, 1.4 equiv) of butyllithium in hexane. After the mixture was stirred for 30 min, a solution of 5.0 g (11.25 mmol) of ethyl 2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenoate[3] (**16**) in 30 mL of anhydrous THF was added dropwise. The solution was allowed to warm to 10 °C, when 3.0 equiv of alkyl bromide was added. The resulting solution was stirred 2 h at room temperature before being quenched with addition of 10% hydrochloric acid. The mixture was diluted with ethyl ether, successively washed with saturated $NaHCO_3$, water, and brine, and dried over anhydrous magnesium sulfate. Concentration in vacuo afforded a brown-yellow oil, which was crystallized from ethanol.

Ethyl 2-benzyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenoate (**17a**): 85.6%; mp 118−119 °C (lit.[3] mp 117−119 °C) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.96 (t, J = 7.2 Hz, 3H), 3.22 (s, 2H), 3.42 (q, J = 7.1 Hz, 2H), 6.18 (s, 2H), 7.12−7.27 (m, 25H).

Ethyl 2-isopropyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenoate (**17b**): 83%; mp 121 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.99 (d, J = 6.9 Hz, 6H), 1.03 (t, J = 7.2 Hz, 3H), 1.23 (heptet, J = 6.8 Hz, 1H), 3.48 (q, J = 7.1 Hz, 2H), 6.29 (s, 2H), 7.15−

7.26 (m, 20H); MS-EI 486 (2), 443 (12), 291 (12), 263 (100), 167 (15); HRMS (ESI) ($M + Na^+_{calc}$) 509.2457, ($M + Na^+_{found}$) 509.2433.

2-Alkyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenol (18). To the suspension of 2.5 g (67 mmol, 4.27 equiv) of lithium aluminum hydride in 100 mL of anhydrous THF was added 15.7 mmol of ethyl 2-alkyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenoate (17) in 50 mL of anhydrous THF. The reaction mixture immediately turned blue-green and was stirred for 2−5 h at 25 °C (described bellow). The excess lithium aluminum hydride was quenched by cautious addition of 3.0 mL of water and 5.0 mL of 1.0 M NaOH. The gray solid was filtered and washed with 100 mL of ether. The filtrate was dried and concentrated in vacuo to afford a clear oil, which was crystallized from ethanol.

2-Benzyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenol (**18a**): 2 h at 25 °C; 81.2%; mp 137−139 °C (lit.[3] mp 137−139 °C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27 (t, J = 6.0 Hz, 1H), 2.98 (s, 2H), 3.12 (d, J = 6.6 Hz, 2H), 5.80 (s, 2H), 6.92−7.33 (m, 25H).

2-Isopropyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenol (**18b**): 5 h at 25 °C; 88%; oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.07 (d, J = 7.2 Hz, 6H), 1.27 (t, J = 6.0 Hz, 1H), 2.13 (heptet, J = 6.9 Hz, 1H), 3.29 (d, J = 6.6 Hz, 2H), 5.92 (s, 2H), 6.95−7.33 (m, 20H); MS-EI 444 (1), 401 (100), 305 (76), 191 (57), 167 (85); HRMS (EI) [$(M - {}^iPr)^+_{calc}$] 401.1905, [$(M - {}^iPr)^+_{found}$] 401.1899.

2-Alkyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenal (19). To the suspension of 4.62 g (21.4 mmol) of pyridinium chlorochromate[13] in 60 mL of anhydrous CH_2Cl_2 was added 10.72 mmol of 2-alkyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenol (**18**) in one portion. After 2 h 60 mL of ether was added and the supernatant decanted from the black gum. The insoluble residue was washed thoroughly 3 times with 30-mL portions of ether whereupon it became a black granular solid. The combined organic solution was passed through a short pad of silica gel. Concentration in vacuo afforded a green-yellow solid, which was recrystallized from hexane.

2-Benzyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenal (**19a**): 92.2%; mp 139−140 °C (lit.[3] mp 139−141 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.15 (s, 2H), 6.03 (s, 2H), 6.97−7.33 (m, 25H), 8.98 (s, 1H).

2-Isopropyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenal (**19b**): 88.6%; mp 144 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.00 (d, J = 7.5 Hz, 6H), 2.24 (heptet, J = 7.1 Hz, 1H), 6.17 (s, 2H), 7.10−7.27 (m, 20H), 9.09 (s, 1H); MS-EI 442 (38), 413 (50), 360 (60), 323 (73), 233 (94), 167 (100); HRMS (EI) (M^+_{calc}) 442.2297, (M^+_{found}) 442.2306.

3-Alkyl-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (20). To the suspension of 5.34 g (12.36 mmol, 1.25 equiv) of triphenylisopropyl phosphonium iodide in 90 mL of anhydrous THF at −10 °C was added 7.7 mL (11.5 mmol, c 1.448, 1.125 equiv) of butyllithium dropwise. The resulting red solution was allowed to stir for 30 min and then 9.89 mmol of 2-alkyl-2-(2,2-diphenylvinyl)-4,4-diphenyl-3-butenal (**19**) in 40 mL of anhydrous THF was quickly added. The solution immediately turned blue and was stirred for 3 h at room temperature. After the reaction was completed, 1.0 mL of acetone was added, and the solvent was removed in vacuo. The resulted mixture was filtered through a short plug of silica gel (2 × 2 cm) with 20% ether in hexane as eluent. Evaporation of the solvents in vacuo resulted yellow oil, which was crystallized from hexane.

3-Benzyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**20a**): 60%; mp 110 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.25(d, J = 1.2 Hz, 3H), 1.58 (d, J = 1.2 Hz, 3H), 2.99 (s, 2H), 4.81 (m,1H), 6.02 (s, 2H), 6.90−7.26 (m, 25H); ^{1}H NMR (C_6D_6, 300 MHz) δ 1.27 (d, J = 1.5 Hz, 3H), 1.59 (d, J = 1.5 Hz, 3H), 3.10 (s, 2H), 4.96 (t, J = 1.4 Hz, 1H), 6.22 (s, 2H), 6.80−7.36 (m, 25H); UV (hexane) λ(max) 254 (ϵ 31 720), λ 218 (ϵ 31 600), λ(shoulder) 232 (ϵ 29 300); MS-EI 516 (3), 425 (100), 291 (16), 167 (52); HRMS (EI) (M^+_{calc}) 516.2817, (M^+_{found}) 516.2822.

3-Isopropyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**20b**): 45%; mp 91 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.93 (d, J = 6.6 Hz, 6H), 1.31 (d, J = 1.5 Hz, 3H), 1.64 (d, J = 1.5 Hz, 3H), 1.87 (h, J = 6.6 Hz, 1H), 4.89 (t, J = 1.2 Hz, 1H), 6.17 (s, 2H), 6.88−7.28 (m, 20H); ^{1}H NMR (C_6D_6, 300 MHz) δ 1.01 (d, J = 6.6 Hz, 6H), 1.37 (d, J = 1.5 Hz, 3H), 1.70 (d, J = 1.5 Hz, 3H), 2.03 (h, J = 6.6 Hz, 1H), 5.09 (t, J = 1.2 Hz, 1H), 6.42 (s, 2H), 7.00−7.26 (m, 20H); UV (hexane) λ(max) 246 (ϵ 32 867), λ 278 (ϵ 16 667); MS-EI 468 (8), 425 (100), 291 (18), 167 (56); HRMS (EI) (M^+_{calc}) 468.2817, (M^+_{found}) 468.2829.

Synthesis of 1,1,5,5-Tetraphenyl-1,4-pentadien-3-ol (12). To the cooled (0 °C) slurry of 11 g (28.5 mmol) of 1,1,5,5-tetraphenyl-1,4-pentadien-3-one[14] (**11**) in 100 mL of ethanol was added 1.14 g (30 mmol) of $NaBH_4$ in portions. The mixture was kept at reflux for an hour. The resulting solution was poured into 300 mL of 1 M NaOH solution. The phases were separated and the water phase was washed by ether. The combined organic phases were washed with water and dried over $MgSO_4$. Concentration in vacuo gave 10.3 g of slightly yellow oil. ^{1}H NMR spectroscopy showed the oil was 95% pure. The product was not purified further because of the decomposition on column or during crystallization.

1,1,5,5-Tetraphenyl-1,4-pentadien-3-ol (**12**): 89%; ^{1}H NMR ($CDCl_3$) δ 1.62 (d, J = 3.0 Hz, 1H), 4.88 (dt, J_1 = 9.3 Hz, J_2 = 3.3 Hz, 1H), 6.18 (d, J = 9.0 Hz, 2H), 7.36−6.95 (m, 20H).

Ethyl-3-(1,1,5,5-tetraphenyl-1,4-pentadienyl) ether (**12a**) was formed during recrystallization from ethanol. The saturated solution of 1,1,5,5-tetraphenyl-1,4-pentadien-3-ol in ethanol was cooled to −20 °C. After weeks yellow crystals precipitated: mp 112 °C; ^{1}H NMR ($CDCl_3$) δ 1.10 (t, J = 7.2 Hz, 3H), 3.31 (q, J = 7.2 Hz, 2H), 4.50 (t, J = 9.3 Hz, 1H), 6.14 (d, J = 9.3 Hz, 2H), 7.36−6.93 (m, 20H); HRMS (ESI) ($M + Na^+_{calc}$) 439.2038, ($M + Na^+_{found}$) 439.2038.

Synthesis of 3-(2,2-Bis(4-bromophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (13). To the solution of 7.76 g (0.02 mol) of 1,1,5,5-tetraphenyl-1,4-pentadien-3-ol (**12**) and 0.02 mol of 1,1-bis(4-bromophenyl)ethylene[15] in 50 mL of anhydrous dioxane was added 0.50 mL of concentrated sulfuric acid. The solution turned blue and then was heated to reflux for 5 h. The mixture was cooled, successively washed with saturated $NaHCO_3$, water, and brine, and dried over anhydrous magnesium sulfate. The dioxane was removed at reduced pressure to afford oil. Chromatography on silica gel column eluted with hexane gave white crystals.

3-(2,2-Bis(4-bromophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (**13**): 53%; mp 193 °C; ^{1}H NMR ($CDCl_3$) δ 4.24 (q, 1H, J = 9.8 Hz), 6.03 (d, 2H, J = 9.9 Hz), 6.04 (d, 1H, J = 10.2 Hz), 6.40−6.49 (m, 2H), 6.65−6.72 (m, 4H), 6.97−7.40 (m, 22H); HRMS (EI) ($[M - H]^-_{calc}$) 705.0793, ($[M - H]^-_{found}$) 705.0800.

Synthesis of 3-(2,2-Bis(4-cyanophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (14). A mixture of 11 g (15.5 mmol) of 3-(2,2-bis(4-bromophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (**13**), 20 g (15 equiv) of cuprous cyanide, and 100 mL of *N*-methyl-2-pyrrolidinone was heated to reflux for 5.5 h. After cooling, the mixture was shaken with a solution of 8.0 g of sodium cyanide in 200 mL of water. This was benzene extracted, washed with 10% sodium cyanide and then water, dried over anhydrous sodium sulfate, and concentrated in vacuo to give oil. Chromatography on silica gel column eluted with hexane and dichloromethane gave white crystals.

3-(2,2-Bis(4-cyanophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (**14**): 77.4%; mp 206 °C; ^{1}H NMR ($CDCl_3$) δ 4.11 (q, 1H, J = 9.8 Hz), 6.05 (d, 2H, J = 9.6 Hz), 6.22 (d, 1H, J = 10.2 Hz), 6.65−6.75 (m, 6H), 6.95−7.15 (m, 4H), 7.15−7.30 (m, 16H), 7.53−7.60 (m, 2H); HRMS (EI) (M^+_{calc}) 600.2565, (M^+_{found}) 600.2569.

Synthesis of 3-Benzyl-3-(2,2-bis(4-cyanophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (15). To a suspen-

(15) Matsumoto, T.; Ishida, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114* (25), 9952−9959.

sion of 0.42 g (17.5 mmol, 1.5 equiv) of sodium hydride in 150 mL of DMSO was added 7.11 g (11.8 mmol) of 3-(2,2-bis(4-cyanophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (**14**) in 50 mL of a mixture of anhydrous DMSO−THF (1:1). After the deep blue solution was stirred for 6 h at room temperature, 4.0 mL (34 mmol, 3 equiv) of benzyl bromide was added quickly. The mixture was diluted with water and extracted with ether. Concentration of the extract in vacuo afforded brown oil, which was purified on a silica gel column with hexane−dichloromethane eluent.

3-Benzyl-3-(2,2-bis(4-cyanophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (**15**): 30.5%; mp 178 °C; ^{1}H NMR ($CDCl_3$) δ 3.04 (s, 2H), 5.76 (s, 2H), 6.12 (s, 1H), 6.54−6.66 (m, 6H), 6.84−6.90 (m, 2H), 7.00−7.40 (m, 20H); ^{1}H NMR (C_6D_6) δ 2.96 (s, 2H), 5.80 (s, 2H), 6.04 (s, 1H), 6.24−6.28 (m, 2H), 6.40−6.51 (m, 2H), 6.72−7.20 (m, 24H); UV (hexane) λ(max) 204 (ϵ 91 736), λ 262 (ϵ 32 500); MS (EI) 599 (11), 382 (20), 197 (68), 181 (100); MS (MALDI, Ag^+, anthracene) 972 (4, M + Ag^+ + anthracene-5H), 970 (5, M + Ag^+ + anthracene-5H), 799 (1, M + Ag^+), 797 (1, M + Ag^+), 109 (88, Ag^+), 107 (100, Ag^+); HRMS (EI) ([M − CH_2Ph]$_{calc}$) 599.2487, ([M − CH_2Ph]$_{found}$) 599.2489. The structure assignment was confirmed by X-ray crystallography (see Supporting Information).

Prins Reaction of 1,1-Diphenylethylene (7) with 3,3-Bis(4-chlorophenyl)-2-proprenal (10-Cl). To the solution of 1.0 g (5.56 mmol) of 1,1-diphenylethylene[16a,b] (**7**) and 1.54 g (5.56 mmol) of 3,3-bis(4-chlorophenyl)-2-proprenal[16a] (**10-Cl**) in 10 mL of dry 1,4-dioxane was added 0.025 g (0.13 mmol) of *p*-toluenesulfonic acid monohydrate. The solution was heated to reflux for 30 h in N_2 atmosphere. The solvent was evaporated in vacuo and the oil was filtered through a short plug of Florisil (3 × 1) and then through a plug of Alumina (3 × 1) with dichloromethane as eluent. The solvent was evaporated in vacuo. The mixture was purified by column chromatography (5% ethyl acetate in hexane, silica gel). The concentration in vacuo afforded crystals, which were recrystallized from ethanol to yield 52% of 3-(2,2-diphenylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**9**): mp 226−228 °C (lit.[17] mp 228−230 °C (*n*-BuOH)); ^{1}H NMR ($CDCl_3$) δ 4.33 (q, J = 10 Hz, 1H), 6.05 (d, J = 10 Hz, 3H), 6.70−7.40 (m, 30H).

Direct Solution Photolysis of 3-Benzyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (20a). A solution of 150 mg (0.29 mmol) of 3-benzyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**20a**) in 200 mL of benzene was irradiated. Concentration in vacuo yielded yellow oil. Conversion and the composition of the reaction mixture were determined by ^{1}H NMR spectroscopic analysis. The mixtures at 66% conversion (12 min of irradiation) contained 34% of starting material (20a), 19% of *trans*-2-benzyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**22a**), 24% of *cis*-2-benzyl-2-(2-methyl-propenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**21a**), and 23% of 1-benzyl-3,3-dimethyl-4,4-diphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**23a**). The mixtures at 100% conversion (50 min of irradiation) contained 23% of *trans*-2-benzyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**22a**), 35% of *cis*-2-benzyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)-cyclopropane (**21a**), and 42% of 1-benzyl-3,3-dimethyl-4,4-diphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**23a**). The compounds were purified by column chromatography (silica gel, hexane as eluent) and by crystallization from ethanol.

cis-2-Benzyl-2-(2-methyl-propenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**21a**): 30% after 50 min of irradiation; mp 178−179 °C from ethanol; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.36 (s, 3H), 1.63 (s, 3H), 2.14 (d, J = 14.1 Hz, 1H), 2.66 (d, J = 10.8 Hz, 1H), 2.78 (d, J = 14.1 Hz, 1H), 5.51 (m, 1H), 5.59 (d, J = 10.8 Hz, 1H), 6.83−7.56 (m, 25H); ^{1}H NMR (C_6D_6, 300 MHz) δ 1.37 (d, J = 0.9 Hz, 3H), 1.50 (d, J = 0.9 Hz, 3H), 2.32 (d, J = 13.8 Hz, 1H), 2.82 (d, J = 13.8 Hz, 1H), 2.98 (d, J = 11.1 Hz, 1H), 5.71 (m, 1H), 5.95 (d, J = 11.1 Hz, 1H), 6.86−7.62 (m, 25H); MS-EI 516 (7), 425 (100), 291 (15), 167 (15); HRMS (EI) (M^+_{calc}) 516.2817, (M^+_{found}) 516.2811. The structure assignment was conformed by X-ray crystallography (see Supporting Information).

trans-2-Benzyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**22a**): 18% after 50 min of irradiation; mp 162−163 °C from ethanol; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.00 (s, 3H), 1.25 (s, 3H), 2.59 (d, J = 10.8 Hz, 1H), 2.88 (d, J = 14.7 Hz, 1H), 3.25 (d, J = 14.4 Hz, 1H), 4.95 (m, 1H), 6.02 (d, J = 11.1 Hz, 1H), 6.95−7.63 (m, 25H); ^{1}H NMR (C_6D_6, 300 MHz) 1.08 (d, J = 0.9 Hz, 3H), 1.20 (d, J = 0.9 Hz, 3H), 2.93 (d, J = 10.8 Hz, 1H), 3.05 (d, J = 14.4 Hz, 1H), 3.31 (d, J = 14.7 Hz, 1H), 5.15 (m, 1H), 6.33 (d, J = 11.1 Hz, 1H), 6.85−7.65 (m, 25H); MS-EI 516 (8), 425 (100), 291 (15), 167 (64); HRMS (EI) (M^+_{calc}) 516.2817, (M^+_{found}) 516.2819.

1-Benzyl-3,3-dimethyl-4,4-diphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**23a**): 31% after 50 min of irradiation; mp 107 °C from ethanol; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.97 (d, J = 1.5 Hz, 3H), 1.57 (d, J = 0.9 Hz, 3H), 3.62 (d, J = 15.3 Hz, 1H), 3.82 (d, J = 15.3 Hz, 1H), 4.31 (t, J = 9.6 Hz, 1H), 5.18 (dm, J = 9.6 Hz, 1H), 5.92 (d, J = 10.2 Hz, 1H), 6.75−7.35 (m, 25H); ^{1}H NMR (C_6D_6, 300 MHz) δ 1.14 (d, J = 1.2 Hz, 3H), 1.63 (d, J = 1.2 Hz, 3H), 3.68 (d, J = 15.6 Hz, 1H), 3.93 (d, J = 15.3 Hz, 1H), 4.63 (t, J = 9.6 Hz, 1H), 5.39 (dm, J = 9.3 Hz, 1H), 6.18 (d, J = 9.9 Hz, 1H), 6.85−7.40 (m, 25H); MS-EI 516 (26), 425 (64), 181 (80), 119 (100); HRMS (EI) (M^+_{calc}) 516.2817, (M^+_{found}) 516.2816.

Kinetics: Direct Solution Photolysis of 3-Benzyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (20a). A solution of 10 mg (0.019 mmol) of 3-benzyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**20a**) in 2.5 mL of d_6-benzene in a NMR tube was irradiated for varying times (see Supporting Information). The course of the reaction was monitored by ^{1}H NMR spectroscopy. The spectral characteristics of **21a**, **22a**, and **23a** were the same as before (see above).

Kinetics: Sensitized (Naphthalene) Solution Photolysis of 3-Benzyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (20a). A solution of 10 mg (0.019 mmol) of 3-benzyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**20a**) and 90 mg (0.71 mmol) of naphthalene in 2.5 mL of d_6-benzene in a NMR tube was irradiated for varying times (see Supporting Information). The course of the reaction was monitored by ^{1}H NMR spectroscopy. The spectral characteristics of **21a**, **22a**, and **23a** were the same as before (see above).

Sensitized (Acetophenone) Solution Photolysis of 3-Benzyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (20a). A solution of 150 mg (0.29 mmol) of 3-benzyl-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**20a**) and 5.0 mL (43 mmol) of acetophenone in 200 mL of benzene was irradiated for 18 min. Concentration in vacuo yielded 180 mg of yellow oil. ^{1}H NMR spectroscopic analysis showed 100% conversion and the composition of the reaction mixture was 28% of *trans*-2-benzyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**22a**), 67% of *cis*-2-benzyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)-cyclopropane (**21a**), and 5% of 1-benzyl-3,3-dimethyl-4,4-diphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**23a**). The compounds were purified by column chromatography (silica gel, hexane as eluent) and by crystallization from ethanol. The spectral characteristics of **21a**, **22a**, and **23a** were the same as before (see above), and the yields were 58%, 19%, and 2%, respectively.

Direct Solution Photolysis of 3-Isopropyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (20b). A solution of 150 mg (0.32 mmol) of 3-isopropyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**20b**) in 200 mL of benzene was irradiated. Concentration in vacuo yielded yellow oil. Conversion and the composition of the reaction mixture

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were determined by ^{1}H NMR spectroscopic analysis. The mixtures at 75% conversion (9 min of irradiation) contained 25% of starting material, 20% of *trans*-2-isopropyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**22b**), 21% of *cis*-2-isopropyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**21b**), and 34% of 1-isopropyl-3,3-dimethyl-4,4-diphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**23b**). The mixtures at 100% conversion (35 min of irradiation) contained 17% of *trans*-2-isopropyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (22b), 20% of *cis*-2-isopropyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**21b**), and 63% of 1-isopropyl-3,3-dimethyl-4,4-diphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**23b**). The compounds were purified by column chromatography (silica gel, hexane as eluent) and by crystallization from ethanol.

cis-2-Isopropyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**21b**): 9% after 35 min of irradiation; mp 161−162 °C from ethanol; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.79 (s, 3H), 0.86 (m, 1H), 0.89 (s, 3H), 1.64 (d, J = 1.2 Hz, 3H), 1.70 (d, J = 1.2 Hz, 3H), 2.46 (d, J = 13.2 Hz, 1H), 5.65 (d, J = 12.9 Hz, 1H), 5.67 (m, 1H), 6.97−7.58 (m, 20H); ^{1}H NMR (C_6D_6, 300 MHz) δ 0.86 (d, J = 6.6 Hz, 3H), 1.01 (d, J = 6.3 Hz, 3H), 1.12 (m, 1H), 1.56 (d, J = 1.2 Hz, 3H), 1.71 (d, J = 0.9 Hz, 3H), 2.82 (d, J = 11.1 Hz, 1H), 5.85 (m, 1H), 6.05 (d, J = 11.1 Hz, 1H), 6.85−7.63 (m, 20H); MS-EI 468 (25), 425 (100), 167 (74); HRMS (EI) (M^+_{calc}) 468.2817, (M^+_{found}) 468.2822.

trans-2-Isopropyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**22b**): 10% after 35 min of irradiation; mp 147−148 °C from ethanol; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.77 (s, 3H), 0.85 (m, 1H), 0.91 (s, 3H), 1.29 (d, J = 1.2 Hz, 3H), 1.35 (d, J = 1.5 Hz, 3H), 2.51 (d, J = 11.4 Hz, 1H), 5.08 (m, 1H), 5.84 (d, J = 11.4 Hz, 1H), 7.00−7.59 (m, 20H); ^{1}H NMR (C_6D_6, 300 MHz) δ 0.86 (d, J = 6.6 Hz, 3H), 1.03 (d, J = 6.6 Hz, 3H), 1.08 (m, 1H), 1.26 (d, J = 1.2 Hz, 3H), 1.36 (d, J = 1.2 Hz, 3H), 2.83 (d, J = 11.4 Hz, 1H), 5.29 (m, 1H), 6.12 (d, J = 11.4 Hz, 1H), 6.85−7.66 (m, 20H); MS-EI 468 (20), 425 (100), 167 (85); HRMS (EI) (M^+_{calc})468.2817, (M^+_{found}) 468.2809.

1-Isopropyl-3,3-dimethyl-4,4-diphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**23b**): 52% after 35 min of irradiation; oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.98 (t (dd), J = 7.05 Hz, 6H), 1.11 (d, J = 0.9 Hz, 3H), 1.61 (d, J = 0.9 Hz, 3H), 2.77 (h, J = 7.2 Hz, 1H), 4.05 (t, J = 9.3 Hz, 1H), 5.25 (d of m, J = 9.3 Hz, 1H), 6.13 (d, J = 9.6 Hz, 1H), 6.87−7.45 (m, 20H); ^{1}H NMR (C_6D_6, 300 MHz) δ 1.08 (d, J = 2.7 Hz, 3H), 1.10 (d, J = 2.7 Hz, 3H), 1.24 (d, J = 1.2 Hz, 3H), 1.65 (d, J = 1.2 Hz, 3H), 2.93 (h, J = 7.05 Hz, 1H), 4.34 (t, J = 9.2 Hz, 1H), 5.46 (d of m, J = 9.3 Hz, 1H), 6.36 (d, J = 9.9 Hz, 1H), 6.83−7.47 (m, 20H); MS-EI 468 (31), 425 (100), 167 (90); HRMS (EI) (M^+_{calc}) 468.2817, (M^+_{found}) 468.2828.

Sensitized (Acetophenone) Solution Photolysis of 3-Isopropyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (20b). A solution of 150 mg (0.32 mmol) of 3-isopropyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**20b**) and 5.0 mL (43 mmol) of acetophenone in 200 mL of benzene was irradiated for 8 min. Concentration in vacuo yielded 167 mg of yellow oil. ^{1}H NMR spectroscopic analysis showed 100% conversion and the composition of the reaction mixture was 10% of *trans*-2-isopropyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**22b**), 45% of *cis*-2-isopropyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**21b**), 45% of 4-(2-methylpropenyl)-1-isopropyl-3,3,5,5-tetraphenyl-1-cyclopentene (**24b**), and a trace of 1-isopropyl-3,3-dimethyl-4,4-diphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**23b**). The compounds were purified by column chromatography (silica gel, hexane as eluent) and by crystallization from ethanol. The spectral characteristics of **21b** and **22b** were the same as before (see above), and the yields were 33% and 5%, respectively.

4-(2-Methylpropenyl)-1-isopropyl-3,3,5,5-tetraphenyl-1-cyclopentene (**24b**): 36%; mp 164 °C from ethanol; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.65 (d, J = 6.6 Hz, 3H), 1.04 (d, J = 6.6 Hz, 3H), 1.28 (d, J = 0.9 Hz, 3H), 1.50 (d, J = 0.9 Hz, 3H), 2.20 (heptett, J = 6.6 Hz, 1H), 4.57 (d, J = 11.1 Hz, 1H), 4.69 (d of m, J = 11.1 Hz, 1H), 6.29 (s, 1H), 6.90−7.86 (m, 20H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 18.40 (=C-*C*H$_3$), 24.30 (CH-*C*H$_3$), 24.41 (CH-*C*H$_3$), 25.88 (=C-*C*H$_3$), 28.15 (*C*-CH$_3$), 59.86 (*C*-H), 62.61 (*C*Ph$_2$), 76.56 ((^{i}Pr)C-*C*Ph$_2$), 125.33 (*C*H=), 131.92 (Ph$_2$C-*C*H=), 132.40 ((CH$_3$)$_2$*C*=), 155.72 ((^{i}Pr)*C*=); HRMS (EI) (M^+_{calc}) 468.2817, (M^+_{found}) 468.2814.

Sensitized (Acetophenone) Solution Photolysis of 3-Isopropyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (20b). A solution of 10 mg (0.021 mmol) of 3-isopropyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**20b**) and 90 mg (0.75 mmol) of acetophenone in 2.5 mL of d_6-benzene in a NMR tube was irradiated for 4 min. Concentration in vacuo yielded 17 mg of yellow oil. The mixture was purified by flash column chromatography (silica gel, hexane as eluent). ^{1}H NMR spectroscopic analysis showed 45% conversion and the composition of the mixture was 4% of *trans*-2-isopropyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**22b**), 21% of *cis*-2-isopropyl-2-(2-methylpropenyl)-1,1-diphenyl-3-(2,2-diphenylvinyl)cyclopropane (**21b**), 16% of 4-(2-methylpropenyl)-1-isopropyl-3,3,5,5-tetraphenyl-1-cyclopentene (**24b**), a trace of 1-isopropyl-3,3-dimethyl-4,4-diphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**23b**), and 4% of *cis*-2-isopropyl-2-(2,2-diphenylvinyl)-1,1-diphenyl-3-(2-methylpropenyl)cyclopropane (*cis*-**34**) (^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.49 (d, J = 11.4 Hz, 1H, *CH*=C(CH$_3$)), 5.55 (s, 1H, CH=C*H*Ph$_2$); *cis*-**34** did not form in sufficient quantities to permit isolation and its assignment was based on NMR).

Kinetics: Direct Solution Photolysis of 3-Isopropyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (20b). A solution of 10 mg (0.021 mmol) of 3-isopropyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**20b**) in 2.5 mL of d_6-benzene in a NMR tube was irradiated for varying times (see Supporting Information). The course of the reaction was monitored by ^{1}H NMR spectroscopy. The spectral characteristics of **21b**, **22b**, and **23b** were the same as before (see above).

Kinetics: Sensitized (Naphthalene) Solution Photolysis of 3-Isopropyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (20b). A solution of 10 mg (0.021 mmol) of 3-isopropyl-3-(2,2-dimethylvinyl)-1,1,5,5-tetraphenyl-1,4-pentadiene (**20b**) and 90 mg (0.71 mmol) of naphthalene in 2.5 mL of d_6-benzene in a NMR tube was irradiated for varying times (see Supporting Information). The course of the reaction was monitored by ^{1}H NMR spectroscopy. The spectral characteristics of **21b**, **22b**, and **23b** were the same as before (see above).

Direct Solution Photolysis of 3-Benzyl-3-(2,2-bis(4-cyanophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (15). A solution of 150 mg (0.22 mmol) of 3-benzyl-3-(2,2-bis(4-cyanophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (**15**) in 200 mL of benzene was irradiated for 50 min. Concentration in vacuo yielded yellow oil. Conversion and the composition of the reaction mixture were determined by ^{1}H NMR spectroscopic analysis. The mixtures contained 27% of *trans*-2-benzyl-1,1-bis(4-cyanophenyl)-2,3-bis(2,2-diphenylethenyl)cyclopropane (**26**), 34% of *cis*-2-benzyl-1,1-bis(4-cyanophenyl)-2,3-bis(2,2-diphenylethenyl)cyclopropane (**25**), and 39% of 1-benzyl-4,4-bis(4-cyanophenyl)-3,3-diphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**27**). The compounds were purified by column chromatography (silica gel, hexane−dichloromethane 100:10 as eluent) and by crystallization from ethanol to a constant mp of 170−171 °C.

trans-2-Benzyl-1,1-bis(4-cyanophenyl)-2,3-bis(2,2-diphenylethenyl)cyclopropane (**26**): 23%; mp 190 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.75 (d, J = 15.3 Hz, 1H), 2.76 (d, J = 9.9 Hz, 1H), 3.26 (d, J = 15.3 Hz, 1H), 5.70 (d, J = 9.0 Hz, 1H), 5.71 (s, 1H), 6.30−6.36 (br d, J = 8.1 Hz, 2H), 6.48−6.55 (br d, J = 6.6 Hz, 2H), 6.91−7.65 (m, 29H); ^{1}H NMR (C_6D_6, 300 MHz) δ 2.69 (d, J = 14.1 Hz, 1H), 2.73 (d, J = 7.4 Hz, 1H), 3.11 (d, J

= 14.7 Hz, 1H), 5.62 (s, 1H), 5.86 (d, J = 9.9 Hz, 1H), 6.25−6.31 (br d, J = 7.2 Hz, 2H), 6.49−6.56 (br d, J = 8.4 Hz, 4H), 6.85−7.28 (m, 27H); MS (MALDI, Ag^+, anthracene) 972 (4, M + Ag^+ + anthracene-5H), 970 (4, M + Ag^+ + Anthracene-5H), 799 (1, M + Ag^+), 797 (1, M + Ag^+), 109 (98, Ag^+), 107 (100, Ag^+). Anal. Calcd for $C_{52}H_{38}N_2$: C, 90.40; H, 5.54; N, 4.05. Found: C, 90.32; H, 5.55; N, 4.12.

cis-2-Benzyl-1,1-bis(4-cyanophenyl)-2,3-bis(2,2-diphenylethenyl)cyclopropane (**25**): 28%; mp 233−234 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.21 (d, J = 5.5 Hz, 2H), 2.72 (d, J = 10.7 Hz, 1H), 5.72 (d, J = 10.7 Hz, 1H), 6.18 (s, 1H), 6.76−6.82 (m, 2H), 6.97−7.56 (m, 27H), 7.65 (s, 4H); ^{1}H NMR (C_6D_6, 300 MHz) δ 2.20 (br s, 2H), 2.79 (d, J = 10.7 Hz, 1H), 5.86 (d, J = 10.7 Hz, 1H), 6.37 (s, 1H), 6.72−7.45 (m, 33H); MS (MALDI, Ag^+, anthracene) 972 (13, M + Ag^+ + anthracene-5H), 970 (14, M + Ag^+ + anthracene-5H), 799 (3, M + Ag^+), 797 (3, M + Ag^+), 109 (99, Ag^+), 107 (100, Ag^+). Anal. Calcd for $C_{52}H_{38}N_2$: C, 90.40; H, 5.54; N, 4.05. Found: C, 90.42; H, 5.49; N, 4.08. The structure assignment was confirmed by X-ray crystallography (see Supporting Information).

1-Benzyl-4,4-bis(4-cyanophenyl)-3,3-diphenyl-5-(2,2-diphenylvinyl)-1-cyclopentene (**27**): 30%; mp 170−171 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.57 (br d, J = 3.7 Hz, 2H), 4.79−4.88 (m, 2H), 6.29 (br d, J = 3.6 Hz, 1H), 6.43−6.47 (m, 2H), 6.72−7.56 (m, 31H); ^{1}H NMR (C_6D_6, 300 MHz) 4.30 (br s, 2H), 4.75−4.84 (m, 2H), 6.15 (br s,1H), 6.50−6.57 (m, 2H), 6.59−7.70 (m, 4H), 6.82−7.17 (m, 27H); MS (MALDI, Ag^+, anthracene) 972 (17, M + Ag^+ + anthracene-5H), 970 (18, M + Ag^+ + anthracene-5H), 799 (5, M + Ag^+), 797 (6, M + Ag^+), 109 (97, Ag^+), 107 (100, Ag^+). Anal. Calcd for $C_{52}H_{38}N_2$: C, 90.40; H, 5.54; N, 4.05. Found: C, 90.52; H, 5.41; N, 4.06.

Kinetics: Direct Solution Photolysis of 3-Benzyl-3-(2,2-bis(4-cyanophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (15). A solution of 10 mg (0.015 mmol) of 3-benzyl-3-(2,2-bis(4-cyanophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (**15**) in 2.5 mL of d_6-benzene in a NMR tube was irradiated for varying times (see Supporting Information). The course of the reaction was monitored by ^{1}H NMR spectroscopy. The spectral characteristics of **25**, **26**, and **27** were the same as before (see above).

Kinetics: Sensitized (Naphthalene) Solution Photolysis of 3-Benzyl-3-(2,2-bis(4-cyanophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (15). A solution of 10 mg (0.015 mmol) of 3-benzyl-3-(2,2-bis(4-cyanophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (**15**) and 90 mg (0.71 mmol) of naphthalene in 2.5 mL of d_6-benzene in a NMR tube was irradiated for varying times (see Supporting Information). The course of the reaction was monitored by ^{1}H NMR spectroscopy. The spectral characteristics of **25**, **26**, and **27** were the same as before (see above).

Sensitized (Acetophenone) Solution Photolysis of 3-Benzyl-3-(2,2-bis(4-cyanophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (15). A solution of 150 mg (0.22 mmol) of 3-benzyl-3-(2,2-bis(4-cyanophenyl)ethenyl)-1,1,5,5-tetraphenylpenta-1,4-diene (**15**) and 5.0 mL (43 mmol) of acetophenone in 200 mL of benzene was irradiated for 20 min. Concentration in vacuo yielded 175 mg of yellow oil. ^{1}H NMR spectroscopic analysis showed 100% conversion and the composition of the reaction mixture was 47% of *trans*-2-benzyl-1,1-bis(4-cyanophenyl)-2,3-bis(2,2-diphenylethenyl)cyclopropane (**26**) and 53% of *cis*-2-benzyl-1,1-bis(4-cyanophenyl)-2,3-bis(2,2-diphenylethenyl)cyclopropane (**25**). The compounds were purified by column chromatography (silica gel, hexane−dichloromethane 100:10 as eluent) and by crystallization from ethanol. The spectral characteristics of **26** and **25** were the same as before (see above), and the yields were 41% and 43%, respectively.

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Supporting Information Available: Kinetic data, X-ray coordinates for three compounds (**15**, **21a**, and **25**) and CIF files, ABC kinetic iterative details for two typical runs. This material is available free of charge via the Internet at http://pubs.acs.org.

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